Mon. Mar 18, 2024

Academic Program [Poster] | 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry：Poster

Mon. Mar 18, 2024 10:00 AM - 11:30 AM JST | Mon. Mar 18, 2024 1:00 AM - 2:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-1am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Japanese

[P1-1am-01]

Theoretical Study of Metal-Supported Catalyst Conversion of Cellulose to Sugar Alcohols

○Yuto Nakata[1,2], Takehiko Sasaki[1], Motoyuki Shiga[2] (1. The Univ. of Tokyo, 2. Japan Atomic Energy Agency)

Japanese

[P1-1am-02]

Considering the role and application of large-scale generative AI in promoting "Autonomous Chemical Research" in the information age

○Kohtaro Yuta[1] (1. In Silico Data, Ltd.)

Japanese

[P1-1am-03]

Prediction of bond dissociation free energy using SQM-ML model

○Miki Kaneko[1], Toru Saito[1] (1. Hiroshima City University)

English

[P1-1am-04]

Designing Novel Organoselenium Derivatives as SARS-CoV-2 Main Protease Inhibitors by Integrating QSAR and LB-PaCS-MD Techniques

○Thanyada Rungrotmongkol[1,4], Borwornlak Toopradab[1], Wanting Xie[2], Kowit Hengphasatporn[3], Phornphimon Maitarad[2], Athina Geronikaki[5] (1. Center of Excellence in Structural and Computational Biology Research Unit, Department of Biochemistry, Faculty of Science, Bangkok 10330, Thailand, 2. Research Center of Nano Science and Technology, Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, China, 3. Center for Computational Sciences, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan, 4. Program in Bioinformatics and Computational Biology, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand, 5. Department of Pharmaceutical Chemistry, School of Pharmacy, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece)

English

[P1-1am-05]

Improved photocatalytic performance of eosin Y-sensitized anatase by anchoring group modification. A DFT/TDDFT insight

○Juan Shang[1], Aleksandar Staykov[1], Tatsumi Ishihara[1] (1. International Institute for Carbon-Neutral Energy Research I2CNER, Kyushu University)

Japanese

[P1-1am-06]

Chemoinformatics study on the evaluation of binding free energies of IDO1 inhibitors

○Tatsuya Fujiwara[1], Toru Saito[1] (1. Hiroshima City University)

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Japanese

[P1-1am-07]

Topological Interpretation of the Stability of Polycyclic Conjugated Systems

○Rika Sekine[1], Kei Saito[1], Mizuki Nakamura[1] (1. Shizuoka Univ.)

Japanese

[P1-1am-08]

Automated Prediction of NMR Chemical Shift of Aromatic Compounds Using SQM-ML Approach

○Yuto Shiotake[1], Toru Saito[1] (1. The Univ. of Hiroshima City)

Japanese

[P1-1am-09]

Prediction of pH dependence of peptides containing acidic residues by the configuration-selection constant pH (CS-CpH) method

Fuka Inagaki[1], ○Yukichi Kitamura[2], Haruka Yotsuya[1], Masataka Nagaoka[1,3] (1. Grad. of Info., Nagoya Univ., 2. Engin., Shizuoka Univ., 3. FVC Research Center, Nagoya Univ.)

Japanese

[P1-1am-10]

Analysis of solvent electrostatic potential described by solvation models in charged systems

○Yuki Kanamaru[1], Norio Yoshida[2], Toru Matsui[1] (1. Univ. of Tsukuba, 2. Nagoya University)

Japanese

[P1-1am-11]

A regression study for odor character prediction based on molecular structural representation by machine learning

○Yuki Harada[1], Shuichi Maeda[1], Junwei Shen[1], Taku Misonou[2], Hirokazu Hori[2], Shinichiro Nakamura[1] (1. Kumamoto University, 2. University of Yamanashi)

Japanese

[P1-1am-12]

Development of FMO-CDFT method by Integrating FMO method and Constrained Density Functional Theory

○Shohei Osaki[1], Masato Kobayashi[2], Tetsuya Taketsugu[2], Toru Matsui[1] (1. Univ. of Tsukuba, 2. Univ. of Hokkaido)

Japanese

[P1-1am-13]

Crystal structure prediction using generalized hypersphere search method focusing on packing fraction

○Yoshiki Ueda[1], Takuto Oki[2], Yuuki Midoro[2], Hideo Yamakado[1,2] (1. Faculty of Systems Engineering, Wakayama Univ., 2. Graduate School of Systems Engineering, Wakayama Univ.)

Japanese

[P1-1am-14]

Multi-Objective Generative Adversarial Network for Inorganic Chemical Compositions

○Tomiya Yamamoto[1], Mamoru Nishijo[1], Yosuke Harashima[1,2], Shogo Takasuka[1], Tomoaki Takayama[1,2], Yoshihide Sawada[4], Mikiya Fujii[1,2,3] (1. Nara Institute of Science and Technology, Japan, 2. DSC, Nara Institute of Science and Technology, Japan, 3. CMP, Nara Institute of Science and Technology, Japan, 4. Aichi Sangyo University ,Japan)

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Japanese

[P1-1am-15]

How Precisely Can Semiempirical Molecular Orbital Calculations Reproduce Electronic State Fluctuations of Biomolecules? Comparison with high-precision methods toward bio-system analysis.

○Nichika Ozawa[1], Nahoko Kuroki[1,2], Hirotoshi Mori[1] (1. Chuo University, 2. JST ACT-X)

Japanese

[P1-1am-16]

Theoretical analysis of nucleophilic addition reaction of 1,3,5-trimethoxybenzene to *N*-methylmaleimide in 1,4-dioxane

○Chizuru Muguruma[1], Nobuaki Koga[2] (1. Chukyo University, 2. Nagoya University)

Japanese

[P1-1am-17]

Theoretical study of hydrogen diffusion in Pd and AgRh nanoclusters

○Manaka Kimura[1], Koji Ando[1] (1. Tokyo Woman's Christian University)

Japanese

[P1-1am-18]

Structure and dynamics of water molecular clusters in the ligand binding pocket of taste receptor proteins

○Kie Araki[1], Koji Ando[1] (1. Tokyo Woman's Christian University)

Japanese

[P1-1am-19]

Analysis of photophysical properties of naphthalimide derivatives and carboxylic acid clusters

○Natsumi Watanabe[1], Yuki Kanamaru[1], Toru Matsui[1], Masato Sumita[2], Hironori Izawa[3], Kenji Morihashi[1] (1. University of Tsukuba, 2. RIKEN AIP, 3. University of Miyazaki)

English

[P1-1am-20]

Molecular Dynamics Study of Rhamnose-Conjugated Antimicrobial Cyclotetrapeptides for Developing Novel Antibody Recruiting Molecule

○Jelang Muhammad Dirgantara[1], Regaputra Satria Janitra[2], Rani Maharani[2], Ari Hardianto[2], Yoshiyuki Manabe[2], Koichi Fukase[2] (1. Osaka University, 2. Universitas Padjadjaran)

Japanese

[P1-1am-21]

Study of the structure of ferrocene using the GRRM

○Yosuke Tokuda[1], Yoshiki Ueda[2], Hideo Yamakado[1,2] (1. Graduate School of Systems Engineering, Wakayama Univ., 2. Faculty of Systems Engineering, Wakayama Univ.)

Japanese

[P1-1am-22]

Nonadiabatic *ab initio* dynamics study of the photoisomerization process for 3,5-dimethylisoxazole via S_1 electronic state

○Mizuki Kimura[1], Shinkoh Nanbu[1] (1. Sophia University)

Japanese

[P1-1am-23]

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Theoretical study on tne cyclization reaction of allene type zerumbone under acidic condition

○Noriko Tsuchida[1], Gengo Kashiwazaki[2], Aoi Nakamura[3], Takashi Kitayama[2,3] (1. Saitama Med. Univ., 2. Graduate School of Agriculture, Kindai Univ., 3. Faculty of Agriculture, Kindai Univ.)

Japanese

[P1-1am-24]

Mechanistic analysis of double proton transfer in DNA base pairs by QM and QM/MM-MD

○Urabe Takayuki[1], Toru Saito[1] (1. Hiroshima City University)

Japanese

[P1-1am-25]

Exploration of reaction pathways for hydrogen addition to ethylene using Global Reaction Route Mapping (GRRM).

○Hiroki Shimizu[1], Yoshiki Ueda[1], Hideo Yamakado[1,2] (1. Faculty of Systems Engineering, Wakayama University, 2. Graduate School of Systems Engineering, Wakayama University)

Japanese

[P1-1am-26]

Theoreticall study on enantioselectivity of catalytic propargyl substitution reaction using chiral ion pair

○Takeshi Yoshikawa[1], Ken Sakata[1], Yuya Nakajima[2] (1. Toho University, 2. ENEOS Corporation)

Japanese

[P1-1am-27]

Quantum Chemical Solvent Effects Evaluation for Improving Amine-based CO2 Chemical Absorbents

○Haruka Nobuoka[1], Nahoko Kuroki[1], Hirotoshi Mori[1] (1. huo University)

Japanese

[P1-1am-28]

Beyond-Born-Oppenheimer analysis of chemical reactions exhibiting secondary kinetic isotope effects: nucleophile dependence of S_N2 reactions

○Kohei Motoki[1], Hirotoshi Mori[1] (1. The Univ. of Chuo)

Japanese

[P1-1am-29]

Density functional theory study on the formation of inclusion complexes of (-)-epigallocatechin-3-*O*-gallate derivatives with β-cyclodextrin

○Hirohito Ikeda[1], Tomonori Ohata[1], Rie Nakashima[1], Hiroyuki Tsutsumi[1], Masao Fujisawa[2] (1. Fukuoka University, 2. Kindai University)

Japanese

[P1-1am-30]

Quantum chemical Investigation of substituent effects in the initial reaction step of Hypergolic Bipropellant

○Miori Nogamida[1], Nahoko Kuroki[1], Hirotoshi Mori[1] (1. Chuo university)

Japanese

[P1-1am-31]

Quantum Chemical Calculations of Intermolecular Complexes of Fullerenes with Oligoethylene Glycol and Oligo Propylene Glycol

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○Sota Arima[1], Shin-ichiro Sato[2] (1. Hokkaido University Graduate School of Engineering Course of Applied Chemistry, 2. Hokkaido University Faculty of Engineering)

Japanese

[P1-1am-32]

Theoretical study on the hydrogen bond between ligand water and water in the hydrated sodium and magnesium ion clusters

○Ryu Kato[1], Chisa Furukawa[1], Yuuna Mikami[1], Yasuhiro Sunaga[1], Shoji Kudo[1], Hidenori Matsuzawa[1] (1. Chiba Institute of Technology)

English

[P1-1am-33]

Effect of anchoring group on electron transfer in hybrid dye-sensitized photocatalyst. DFT and TD-DFT study.

○Yasuhiro Kayo[1], Alexander Staykov[2], Motonori Watanabe[2] (1. Graduate School of Integrated Frontier Sciences, Kyushu University, 2. International Institute for carbon-Neutral Energy Research, Kyushu University)

Japanese

[P1-1am-34]

Molecular dynamics simulation of topology-induced changes in surface physisorption dynamics of cyclic polymers

○Tsuyoshi Nakai[1], Shin-ichiro Sato[1] (1. Hokkaido Univ.)

Japanese

[P1-1am-35]

Analyses of protein-glycan multivalent interaction in bacterial infection

○Kaori Ueno Noto[1] (1. Kitasato University)

Japanese

[P1-1am-36]

Creating a prediction model for activation barriers for cycloreversion of diarylethenes by using machine learning

○Kousei Yamanaka[1], Staykov Aleksandar[1] (1. The Univ. of Kyushu)

Japanese

[P1-1am-37]

Reconsideration of the internal protonation mechanism of the [1.1.1] cryptand

○Shigeru Ishikawa[1] (1. Tokai University)

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Academic Program [Poster] | 06. Analytical Chemistry：Poster

Mon. Mar 18, 2024 3:45 PM - 5:15 PM JST | Mon. Mar 18, 2024 6:45 AM - 8:15 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-1vn] 06. Analytical Chemistry

Japanese

[P1-1vn-01]

Analysis of natural Amber

○Sachi Miyamoto[1], Jiro Tanaka[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

Japanese

[P1-1vn-02]

Concentration of trace components in environmental water by freezing and melting

○Itsuki Murakami[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

Japanese

[P1-1vn-03]

Adsorption of tantalum ions on silica gel under strong acidic condition

○Ayaka Saito[1], Kayo Yanagisawa[1], Makoto Matueda[1], Yoshitaka Takagai[1] (1. Fukushima University)

Japanese

[P1-1vn-04]

Degradation analysis of cellulose polymers - Effects of light and moisture

○Yushiaki Akutsu[1], Fujio Ooishi[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

Japanese

[P1-1vn-05]

Study of the cross-linked structure of bridged poly(methyl methacrylate) using gel-state NMR spectroscopy

○Koyuki Takahashi[1], Yasuko Saitou[2], Yoshiharu Mitoma[1], Keita Sakakibara[2] (1. Prefectural University of Hiroshima, 2. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese

[P1-1vn-06]

Development of auto-analyzing tool for huge numbers of single-molecule fluorescence images.

○Satoshi Kayano[1], Syoji Ito[1,2] (1. Osaka University, 2. RILACS, Osaka Metropolitan University)

Japanese

[P1-1vn-07]

Utilization of cesium ion for the mass axis calibration of atom probe

○Kenji Yoshikawa[1], Masahiro Taniguchi[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-1vn-08]

Study on Dissolved Carbon Dioxide Detection Using Infrared Optical Waveguide

○Masayuki Taniarashi[1], Guangji Meng[1], Ryuhei Nakano[2], Hiroki Hotta[1,2,3], Kin-ichi Tsunoda[3], Takashi Kimoto[4] (1. Graduate School of Maritime Sciences, Kobe University, 2. Maritime Sciences, Kobe University, 3. International Maritime Research Center, 4. Kimoto Electric Co, ltd.)

Japanese

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[P1-1vn-09]

Gap distance dependence of infrared absorption enhancement on line and space nanostructures of silicon

○Shiori Sato[1], Toru Shimada[1] (1. Hirosaki Univ.)

Japanese

[P1-1vn-10]

Study on skin persistence of nonwoven fabric of a new face mask containing silkworm droppings extract(SDE)

○Yukio Watanabe[1], Tadanobu Sawada[1], Yasuhito Kondo[2], Mayu Akai[1], Hanaka Kajiwara[1], Hisao Ito[3], Naoyuki Higashi[4], Masato Yoshida[5] (1. Meisei University, 2. Gunma Industrial Technology Center Textile Research Institute of Gunma, 3. Art Co. Ltd., 4. Hanakoganei Higashi Skin Clinic, 5. Nippon Medical School Tama Nagayama Hospital)

Japanese

[P1-1vn-11]

Measurement of deteriorate over time in milk using ATR - infrared spectroscopy

○TAIYO YAKUSHI[1], KOKI JODOI[1], YUKO HAMEBE[1], YOSHISUKE FUTAMI[1] (1. National Institute of Technology, Kumamoto College)

Japanese

[P1-1vn-12]

Evaluation of real sample measurements in BCAA analysis using aminoacyl-tRNA synthetases

○Akimitsu Kugimiya[1], Akari Kawamura[1] (1. Hiroshima City University)

Japanese

[P1-1vn-13]

Development of a High-Precision Single-Molecule Identification Method for Fluorouracil for Genome Editing

○Akari Okada[1], Takahiro Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2] (1. Osaka Kyoiku University Tennoji HighSchool, 2. Osaka University,ISIR)

Japanese

[P1-1vn-14]

Development of a Rapid Single-Molecule Detection Method for Cancer Marker Molecules Using Nano-Gap Devices Towards Diagnosis of Pancreatic Cancer

○Yui Yamane[1], Takahito Ohshiro[2], Yuki Komoto [2], Masamitsu Konno[3], Masateru Taniguchi[2] (1. Tokushima Municipal High School, 2. Osaka University, SANKEN, 3. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-1vn-15]

Development of a Single-Molecule Identification Method for 8-Oxoguanosine, a Marker of Aging

○Ryo Kokubu[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguti[2] (1. Osaka Meisei Senior High School, 2. Osaka University, ISIR)

Japanese

[P1-1vn-16]

Multi-component analysis in saliva using a paper-based analytical device

○Hitoshi Asano[1] (1. Sanyo-Onoda City Univ.)

Japanese

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[P1-1vn-17]

Development of a Single-Molecule Identification Method for N4-Acetylcytosine (ac4C) in Cancer Suppression

○Nakamura Misaki[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguti[2] (1. Kyoto Prefectural Rakuhoku High School, 2. Osaka University, ISIR)

Japanese

[P1-1vn-18]

Anion Response of a Fluorescent Probe Based on Zwitterionic Indium(III) Complex

○Koji Kubono[1], Arisa Ishihara[1], Yukiyasu Kashiwagi[2], Keita Tani[1], Kunihiko Yokoi[1] (1. Osaka Kyoiku University, 2. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P1-1vn-19]

Simultaneous Characterization and Prediction Modeling of Reaction Kinetics and Enthalpy from Spatially Resolved Temperature Profiles in a Flow Reactor

○Jun-ichi Ogawa[1], Yuuka Manabe[1], Ryosuke Nakamura[1], Yuma Otake[1], Kazuhiko Inamura[1], Daisuke Kubo[1] (1. Yokogawa Electric Corporation)

Japanese

[P1-1vn-20]

Synthesis of a novel diol having pyrene moiety and its fluorescence behavior in the presence of 2-formylphenylboronic acid and polyamine

○Kisara Murakami[1], Naoto Hamaguchi[1], Tetsuo Ohta[1], Yohei Oe[1] (1. Doshisha University)

Japanese

[P1-1vn-21]

Paper-based analytical devices for semi-quantitative analysis of copper and aluminum ions

○Satoko Takeuchi[1], Aya Katoh[1], Ryuichi Matsubara[2], Tetsuya Sawatsubashi[2], Yuki Hiruta[1], Daniel Citterio[1] (1. Keio University , 2. Mitsubishi Heavy Industries, Ltd.)

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Academic Program [Poster] | 11. Organic Chemistry -Structural Organic Chemistry-：Poster

Mon. Mar 18, 2024 10:00 AM - 11:30 AM JST | Mon. Mar 18, 2024 1:00 AM - 2:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-1am] 11. Organic Chemistry -Structural Organic Chemistry-

Japanese

[P2-1am-01]

Synthesis of Macrocyclic Compounds of Anthracenes with Electron-donating Substituents and Formation of Saturn-shaped Complex with C_{60}

○Yuki Shigihara[1], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Institute of Technology)

Japanese

[P2-1am-02]

Synthesis and Properties of Dithiazolopyrrolo[3,2-*b*]pyrrole

○Akihiro Goto[1], Junichi Usuba[2], Aiko Fukazawa[2] (1. Graduate School of Engineering, Kyoto University, 2. Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University)

Japanese

[P2-1am-03]

Synthetic study of molecular valve-pillar[6]arene conjugates

○Oubu Noguchi[1], Tomoki Katayama[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho univ., 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-04]

Peripheral Protection of [7]Helicene and its effects on the Photophysical Properties

○Reo Shimura[1], Zhibo Liu[1], Takashi Hirose[1] (1. Kyoto Univ.)

Japanese

[P2-1am-05]

Synthesis and Properties of Carbazole Dimers Annulated with a Benzene in Various Manners

○Masaki Maeda[1], Yuya Domoto[1], Yosuke Nakamura[1] (1. Gunma Univ.)

Japanese

[P2-1am-06]

Synthesis and properties of novel aza[5]helicene with acridine backbone

○Moeko Chujo[1], Satoru Hiroto[1] (1. Kyoto Univ.)

English

[P2-1am-07]

Synthesis of large macrocylces based on the functionalization of azabora[6]helicene

○Yuchuan Jiang[1], soji shimizu[1] (1. Kyushu University)

Japanese

[P2-1am-08]

Structural property of aromatic squaramides with chiral side chains

○Kazusa Kuyama[1], Kosuke Katagiri[2], Masatoshi Kawahata[3], Hiroyuki Kagechika[4], Aya Tanatani[1] (1. Ochanomizu Univ., 2. Konan Univ., 3. Showa Pharmaceutical Univ., 4. Tokyo Medical and Dental Univ.)

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Japanese

[P2-1am-09]

Development of efficient synthesis method of Pentapyrrins

○Yuki Nishimura[1], Takuya Kurahashi[1] (1. Grad. Sch. of Sci. and Tech., Kwansei Gakuin Univ.)

Japanese

[P2-1am-10]

Temperature-tunable inversion of chirality in *m*-quarterphenyl derivatives

○Yoshino Kaneko[1], Yuka Takeuchi, Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ., 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-11]

Single-molecule electron transfer properties of fluorinated cubanes

○Keima Higashio[1], Midori Akiyama[1], Ryo Yamada[2], Tatsuhiko Ohto[3], Hirokazu Tada[2], Hiroshi Imahori[1] (1. Kyoto Univ., 2. Osaka Univ., 3. Nagoya Univ.)

Japanese

[P2-1am-12]

Studies on the selectivity in glycosylation reaction using azobiphenyl-thioglycoside conjugates

○hidenori wakui[1], mari ikeda[2], yuta shinozuka[1], kaname sasaki[1], yoichi habata[1], syunsuke kuwahara[1] (1. toho-udai, 2. tibakoudai)

Japanese

[P2-1am-13]

Oxindole-type chiral derivatizing reagents for stereochemical assignments of primary amines

○Ryosuke Kimura[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ., 2. Chiba Institute of Technology)

Japanese

[P2-1am-14]

Coupling reaction between bromopropynylbenzene derivatives and tertiary alcohols

○Masaaki Matsumoto[1], Mari Ikeda[2], Yoichi Habata[1], Syunsuke kuwahara[1] (1. Toho University, 2. Chiba Institute of Technology)

Japanese

[P2-1am-15]

6-(Diethylboryl)-1-(4-pyridyl)azulene: Flow Synthesis and Reaction with DMAP

○Shigeharu Wakabayashi[1], Tatsuya Higaki[2], Masayuki Wakioka[3], Masahiro Takumi[4], Hikari Nakanishi[1], Yasuhiro Ohki[2], Aiichiro Nagaki[5] (1. Faculty of Health Science, Suzuka Univ. of Medical Science, 2. Institute for Chemical Research, Kyoto Univ., 3. Sagami Chemical Research Institute, 4. Graduate School of Engineering, Kyoto Univ., 5. Graduate School of Science, Hokkaido Univ.)

Japanese

[P2-1am-16]

Self-organization and aggregation properties of ion-responsive unilamellar large vesicles derived from squalene

○Linh Ngoc Tran[1], Kenichi Tominaga[1,2], Hiroko Isoda[2], Sosaku Ichikawa[2], Takashi Arimura[1,2] (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba)

English

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[P2-1am-17]

Synthesis and Properties of Tripodal Molecules Integrating Carbazoles Substituted with Ethynyl-Pyridine Groups

○Masamune Fujikawa[1], Yuya Domoto[1], Yosuke Nakamura[1] (1. Gunma University)

Japanese

[P2-1am-18]

Influence of Varying Oxyethylene Chain Length on the Allosteric Properties of Cylindrical Cryptand/Silver Complexes

○Haruki Kumagai[1], Yutaro Nihei[1], Shinji Kamo[1], Akihiro Otsuka[1], Masaki Fujisawa[1], Mari Ikeda[2], Shunsuke Kuwahara[1], Yoichi Habata[1] (1. Toho University, 2. Chiba Institute of Technology)

Japanese

[P2-1am-19]

Cross-Coupling of Fluorenones for Metal-Free Polyarene Synthesis

○Rion Noda[1], Tetsuo Iwasawa[1] (1. Graduate School of Ryukoku University)

Japanese

[P2-1am-20]

A New Synthetic Route to Tetrabenzo[*b*,*g*,*k*,*p*]chrysene

○Takumi Ikenaga[1], Tetsuo Iwasawa[1] (1. Ryukoku university)

Japanese

[P2-1am-21]

Synthesis and properties of 9-azadibenzo[a.f]pentalenyl cations exhibiting asymmetric ring current effect due to mesoionic TMM substructure

○Koki Yamamoto[1], Daiki Shimizu[1], Kenji Matsuda[1,2] (1. Kyoto University, 2. Fukui Institute for Fundamental Chemistry, Kyoto University,)

Japanese

[P2-1am-22]

Scholl reaction of V-shaped aromatic compounds with fused anthracene: structure and properties of intramolecular cyclization products

○Moe Kobayashi[2], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Tech, 2. Kitasato)

Japanese

[P2-1am-23]

Synthetic study of a *meta*-phenylene-bridged trimer of tetraphenylhexaazaanthracene (TPHA)

○Sokan Shiomi[1], Daiki Shimizu[1], Kenji Matsuda[1,2] (1. Graduate School of Engineering Kyoto University, 2. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese

[P2-1am-24]

Synthesis of novel hetero [8]circulenes and hetero[10]circulenes

○Aoi Nakagawa[1], Yusuke Matsuo[1], Shu Seki[1], Takayuki Tanaka[1] (1. Graduate School of Engineering, Kyoto University)

Japanese

[P2-1am-25]

Synthesis of Azuleno[1,2-*c*]pyran-1-ones

○Taku Shoji[1], Nichika Sasahara[2], Ryuta Sekiguchi[3], Shunji Ito[3] (1. Nihon University, 2. Shinshu University, 3. Hirosaki University)

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Japanese

[P2-1am-26]

Synthesis of molecular tweezers bridged with diethanotetracene moiety

○Aoki Moe[1], Mori Shigeki[2], Takehana Ryosuke, Takase Masayoshi[3], Okujima Tetsuo[3], Uno Hidemitsu[3] (1. Faculty of Science,Ehime University, 2. Advanced Research Support Center(ADRES),Ehime University, 3. Graduate School of Science and Engineering,Ehime University)

Japanese

[P2-1am-27]

Synthesis and optical properties of π-electron systems with propeller chirality

○Yumi Sugano[1], Shigeki Mori[3], Tetsuo Okujima[2], Hidemitsu Uno[2], Masayoshi Takase[2] (1. Faculty of Science of Ehime University, 2. Graduate school of Science and Engeneering, Ehime University, 3. Advanced Reserch Center (ADRES), Ehime University)

Japanese

[P2-1am-28]

Synthesis and Reaction of Thiophene-fused Tetracene

○Yoshiki Dodo[1], Yui Tsuboi[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese

[P2-1am-29]

Synthesis and reactivity of indeno[2,1-a]azulenes

○Masayuki Iwabuchi[1], Taku Shoji[1] (1. Nihon University)

Japanese

[P2-1am-30]

Synthetic study of azulene -fused phenalenons bearing the arly substituent.

○Ryunosuke Ishikawa[1], taku shoji[1] (1. Nihon University)

Japanese

[P2-1am-31]

Synthesis and photo-functional properties of tetraarylphenanthrene derivatives having aryl groups at 9,10-positions

○Takuro Wataru[1], Takeshi Kawase[1], Jun-ichi Nishida[1] (1. Graduate School of Engineering, University of Hyogo, Department of Applied Chemistry)

English

[P2-1am-32]

Intramolecular Bi/Sb/As-O Noncovalent Interaction for Enhanced Planarity of Bibenzofurans

○Conghuan Wang[1], Yohei Adachi[1], Joji Ohshita[1], Akifumi Sumida[2], Hiroaki Imoto[2], Kensuke Naka[2] (1. Hiroshima University, 2. Kyoto Institute of Technology)

Japanese

[P2-1am-33]

Expansion of a σ-Delocalized Systems Using a Diselenide Bond

○Konishi Kyosuke[1], Furukawa Syunsuke[1], Saito Masaichi[1] (1. Graduate School of Science and Engineering, Saitama University)

Japanese

[P2-1am-34]

Single-Molecule Conductances of Compounds Bearing σ-Delocalized Systems

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○Saya Seko[1], Shintaro Fujii[2], Masaichi Saito[1] (1. Graduate School of Science and Engineering, Saitama University, 2. Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology University)

Japanese

[P2-1am-35]

A triplet/singlet ground-state switch due to pai-conjugation prohibition triggered by hydrogen bonding

○Takayuki Ishida[1], Nagito Haga[1] (1. The University of Electro-Communications)

Japanese

[P2-1am-36]

Synthesis and Properties of 2, 5, 8-Tribromophenalenyl Radical

○Masaya Kishimoto[1], Kei Sugita, Tomohiko Nishiuchi[1], Takashi Kubo[1] (1. Osaka University)

Japanese

[P2-1am-37]

Solubilization of Trioxotriangulene Macrocyclic Oligomer by Dialkylamido Groups

○Shinji Hayasaki[1], Tsuyoshi Murata[1], Yasushi Morita[1] (1. Aichi Institute of Technology)

Japanese

[P2-1am-38]

Synthesis, Structure and Halochromism of Galvinol-Substituted Thiophene Compounds

○Yuki Wakabayashi[1], Motoko Akita[1] (1. Josai University)

Japanese

[P2-1am-39]

Studies on the Reaction between Tetracene Imide with Lawesson's Reagent

○Shingo Hirai[1], Takumu Ito[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese

[P2-1am-40]

Development of Non-Fullerene Acceptors Containing Dithienothiaborin

○Makoto Kimura[1], Wataru Suzuki[1], Tomohiro Agou[1], Tomokazu Umeyama[1] (1. University of Hyogo)

English

[P2-1am-41]

Synthesis of Three-Dimensional Organic Boron Compounds with Unique Structure

○Kenshin Nakano[1], Katsuhiko Ono[1] (1. Nagoya Institute of Technology)

Japanese

[P2-1am-42]

Productive Synthesis of a C_{60} fragmentary octacycle, Metelykene

○Yuki Ueda[1], Tetsuo Iwasawa[1] (1. Ryukoku University)

Japanese

[P2-1am-43]

Synthetic investigation of mechanopolymers using π-cluster as a mechanophore

○Shoichi Hasegawa[1], Tomohiko Nishiuchi[1], Takashi Kubo[1] (1. Osaka Univ.)

Japanese

[P2-1am-44]

Different emission colors of optical active and racemic pyridinium salt-linked phenanthroimidazoles

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○NGUYEN QUANG DUY[1] (1. Osaka Kyoiku Univ.)

Japanese

[P2-1am-45]

Synthesis and Photophysical Properties of Carbazolophane Derivatives by Sonogashira Cross Coupling Reaction

○Hiroaki Chihara[1], Miyuki Masaki[1], Kazushige Hori[1], Koji Kubono[1], Masatsugu Taneda[1], Masayoshi Bando[2], Tamaki Nakano[2], Takunori Harada[3], Yuji Kinose[4], Yoshinobu Tsujii[4], Keita Tani[1] (1. Osaka Kyoiku Univ., 2. ICAT, Hokkaido Univ., 3. Faculty of Science and Engineering, Oita Univ., 4. ICR, Kyoto Univ.)

Japanese

[P2-1am-46]

Solid State Molecular Arrangements and Optical Properties of 2,5-Di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione Derivatives

○Kazumasa Ueda[1], Ryoya Hayashi[1], Misaki Kinoshita[1], Tsunayoshi Takehara[2], Takeyuki Suzuki[2] (1. Shizuoka Univ., 2. Osaka Univ.)

Japanese

[P2-1am-47]

[Withdraw] Synthesis of Adamantane Derivatives with Plasticity

○Moe Kusumoto[1] (1. Kwansei Gakuin University)

English

[P2-1am-48]

Solar-driven steam generation properties of donor-acceptor molecules functionalized by [2+2] cycloaddition- retroelectrocyclization reactions

○CHIA-YANG LIN[1], Tsuyoshi Michinobu[1] (1. Tokyo Institute of Technology)

Japanese

[P2-1am-49]

Syntheses and Fluorescence Properties of Imidazodiazaborole Derivatives with D-π-A Structure

Youhei Miura[1], ○Ryoka Tsukimoto[1], Kosuke Mohri[1], Naoki Yosioka[1] (1. Keio University)

Japanese

[P2-1am-50]

Development of Non-Fused Non-Fullerene Acceptors with 1,4-Naphthoquinone Units as Terminal Groups

○Kae Oshitani[1], Wataru Suzuki[1], Jun-ichi Nisida[1], Takeshi Kawase[1], Tomokazu Umeyama[1] (1. University of Hyogo)

Japanese

[P2-1am-51]

Emission Enhancement of Near-infrared Phosphorescence Found in Structurally Similar Host-Guest System

○Misuzu Nakaya[1], Taisuke Matsumoto[2], Tsutomu Ishi-i[1] (1. National Institute of Technology, Kurume College, 2. IMCE, Kyushu Univ.)

Japanese

[P2-1am-52]

Regulation of Fluorescence and Phosphorescence Emission in Benzothiadiazole-based Dyes

○Eri Hirata[1], Tsutomu Ishi-i[1] (1. National Institute of Technology, Kurume College)

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Japanese

[P2-1am-53]

Synthesis of new coumarin probes for determination of the absolute configuration of chiral amines

○Yuuka Gotoh[1], Ryoto Araki[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ. , 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-54]

Synthesis and photoisomerization of new molecular switches with spiro skeleton

○Moeka Notake[1], Karina Nakanishi[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ., 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-55]

Development of Fluorescent Agent Inhibiting Lateral Root Growth in *Arabidopsis*

○Koyo shibasaki[1], Takeshi Yamada, Kazuki Arai, Kazuki Arai, Sentaro Okamoto[1] (1. Kanagawa University)

Japanese

[P2-1am-56]

A Water-Soluble Helicene: Hydrostatic Pressure Effects and Cellular Uptake

○Iori Okamura[1], Keiichi Nakagawa[2], Shinji Toyota[1], Gaku Fukuhara[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Bioengineering, The University of Tokyo)

Japanese

[P2-1am-57]

Singlet Fission in Pentacene Dimers Controlled by Addition of Alkali Metal Ions

○Tomoya Kuwabara[1], Gaku Fukuhara[1] (1. Tokyo Institute of Technology)

Japanese

[P2-1am-58]

Chemical Modification Using Coupling Reaction of 2-Benzoylimidazole Based Organoboron Complexes and Emission Property

Youhei Miura[1], ○Kanta Kato[1], Naoyuki Ando[1], Kohsuke Mohri[1], Naoki Yoshioka[1] (1. Keio University)

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Academic Program [Poster] | 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-：Poster

Mon. Mar 18, 2024 1:00 PM - 2:30 PM JST | Mon. Mar 18, 2024 4:00 AM - 5:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

English

[P1-1pm-01]

Halogenation of aromatic compounds catalyzed by camphorsulfonic acid-$BiCl_3$

○Kiyoshi Tanemura[1] (1. The Nippon Dental University)

Japanese

[P1-1pm-02]

Synthesis of Aryl Enol Ethers from Phenols and Ketals

○Kwihwan Kobayashi[1], Shun-ya Onozawa[1], Koichiro Masuda[1] (1. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-1pm-03]

Synthetic Study of Diaporisoindole A Using Chiral Selenium-catalyzed Lactamization

○Daiki Yamamoto[1,2], Takuya Hashimoto[1,2] (1. Chiba Univ., 2. RIKEN)

Japanese

[P1-1pm-04]

Synthesis and properties of [7] helicenes with a dimethoxy group at the symmetrical position

○Masato Yada[1], Makoto Miyasaka[1] (1. Tokyo Denki University)

Japanese

[P1-1pm-05]

2-Iodobenzoyl Group as a Protecting Group for Alcohols Deprotected under Mild Oxidative Conditions

Jin Nakamura[1], Yuta Mori[2], Tatsuya Oda[2], Takumi Masuhara[2], Yuna Yamada[2], ○Atsuhito Kuboki[1,2], Masayuki Haramura[1,2] (1. Graduate School of Science, Okayama Univesity of Science, 2. Okayama Univesity of Science)

Japanese

[P1-1pm-06]

Synthesis of 2-Vinylnapthalenes via Gold(I)-Catalyzed Cyclopropanation of Indenes

○Shota Nakagawa[1], Yoshikazu Horino[1] (1. Chitose Inst. Sci. Tech.)

Japanese

[P1-1pm-07]

Synthesis of Phenylpropanoids in *Coreopsis lanceolata* L. Petals

○Takuma Matsunaga[1], Yosiharu Okada[1] (1. Kinki Univ.)

Japanese

[P1-1pm-08]

Reductive multiple propargylation of corannulene

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○Kaiki Nishi[1], Shinobu Aoyagi[1], Kazuhira Miwa[2], Toru Amaya[1], Takahiro Sasamori[3], Takashi Kurogi[4], Hideki Yorimitsu[4] (1. Nagoya City University, 2. Nagoya University, 3. University of Tsukuba, 4. Kyoto University)

Japanese

[P1-1pm-09]

Ir-Catalyzed C-H borylation of benzyl position; substrate scope and effects of multidentate ligands.

○Kou Kagawa[1], Tatsuya Nonaka[1], Ryuto Horikoshi[1], Natsumi Naito[1], Noriyuki Suzuki[1] (1. Sophia University)

Japanese

[P1-1pm-10]

Ir-Catalyzed C-H borylation of benzyl position; study on catalytically active species

○Kentaro Kasai[1], Hiroshi Araki[1], Keigo Sakurai[1], Noriyuki Suzuki[1] (1. Sophia Univ.)

Japanese

[P1-1pm-11]

Synthesis of Bis(1-indanyl)amine Quaternary Ammonium Salts and Their Phase Transfer Catalysis

○Aoi Sugiyama[1], Nobuhiro Kanomata[1] (1. Waseda University)

Japanese

[P1-1pm-12]

Reaction of N-sulfonyl-1,2,3-triazole with β-Diketone

○Takuya Koizumi[1], Yuto Yabuchi[1], Yuki Sakai[1], Taiga Fujimoto[1], Ryoto Itani[1], Naoki Michihiro[1], Takuto Kamio[1] (1. Kobe City College of Technology)

English

[P1-1pm-13]

Push-pull chromophores with different heterocyclic donor moieties synthesized by [2+2] cycloaddition-retroelectrocyclization reaction

○Xu Chen[1], Tsuyoshi Michinobu[1] (1. Tokyo Institute of Technology)

Japanese

[P1-1pm-14]

Color Changes of Naphthalenetetracarboxylic Acid Diimide Derivatives by Odor Substances

○Reiko Yamashita[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P1-1pm-15]

Regioselective condensation of 3,5-dimethylisoxazole with aldehydes not using strong bases

○Aki Tanaka[1], Kyosuke Sugihara[1], Hitoshi Abe[1] (1. Graduate School of Science and Engineering, The Univ. of Toyama)

Japanese

[P1-1pm-16]

Synthesis of 4-Alkynyl-2-pyrones Using Conjugate Addition Reaction of Diethyl Malonate Derivatives to Dialkynyl Ketones and Its Application

Kotaro Hirano[1], ○Kosuke Sakurai[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-17]

Synthesis of β-Carbolin-1-ones by Intramolecular C-H Amination of 3-Amino-2-pyridones

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Rikuto Sasaki[1], ○Akihiko Matsuo[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-18]

Synthesis of 4-Ethoxycarbonyl-β-carbolin-1-ones via C-H/N-H Cyclization of 3-Amino-2-pyridones as a Key Reaction

Honoka Mori[1], ○Maho Morimura[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-19]

Synthesis of Pyrroles by Intramolecular Cyclization of β-Cyanocarbonyl Compounds Using Titanium Tetraiodide

Shunya Tochigi[1], ○Taichi Uemura[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-20]

The effect of intramolecular hydrogen bond on fluorescence of C4N4

○Mao Niimura[1], Miki Kohei[1], Ryosuke Tsutsumi[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

Japanese

[P1-1pm-21]

Synthesis of Fluorinated Isocoumarins by Copper-Catalyzed Coupling Reaction

○Haruki Sakagami[1], Akira Tsubouchi[1], Akio Saito[1] (1. Grad. Sch. Eng., Tokyo Univ. Agric. Tech.)

Japanese

[P1-1pm-22]

Synthesis and properties of 6,9-bis(diphenylaminobiphenyl)-substituted phenanthroimidazoles

○Riku Taniguchi[1], Keiji Mizuki[1], Taizo Hatta[1] (1. Sojo University)

Japanese

[P1-1pm-23]

Reaction Mechanism of Hexaazatrinaphthylene Reductant Synthesis

○Takahiro Oshima[1], Kan Wakamatsu[1], Kiyoshi Fujisawa[2], Hideyuki Higashimura[1] (1. Grad. Sch. of Sci. and Eng., Okayama Univ. of Sci., 2. Col. of Sci., Ibaraki Univ.)

Japanese

[P1-1pm-24]

Design and Synthesis of Enlarged TriQuinoline

○Mai Yamashita[1], Ryosuke Tsutsumi[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

Japanese

[P1-1pm-25]

Synthetic studies of alkaloid skeletons for development in biocatalytic reactions

○Yunosuke Adachi[1], Hiroaki Inaba[1], Fumiyuki Uchida[1], Keita Isaka[1], Ken-ichi Fushuku[1] (1. Meisei University)

Japanese

[P1-1pm-26]

One-pot Synthesis of Chromans in the presence of $NaHSO_4/SiO_2$ using 2-(1-hydroxyalkyl)phenols

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○Eri Kurosawa[1], Mamiko Hayakawa[1], Takuya Furukawa[1], Tadashi Aoyama[1] (1. College of Science and Technology, Nihon University)

Japanese

[P1-1pm-27]

Synthesis of benzoselenotetramisole using isothiocyanates derived from amino alcohols with an isopropyl group.

○Rika SAITO[1], Hayato ICHIKAWA[1] (1. Nihon University)

Japanese

[P1-1pm-28]

Preparation of Dibenzoxanthene Derivatives by Bismuth Triflate-catalyzed Reaction of 2-Naphthols with an Allylic Alcohol

○Maki Minakawa[1], Syuya Sato (1. Yamagata University)

Japanese

[P1-1pm-29]

Cyclization of 4-pyrazolyl esters of propiolate with iodine

○Ayana Sato[1], Furuya Yashuaki[2], Ichikawa Hayato[1] (1. Nihon University, 2. Graduate School of Nagasaki University)

Japanese

[P1-1pm-30]

Solvent effects on asymmetric cyclopropanation with tertiary pyridylalkanol catalysis

○Narumi Shimizu[1], Yuki Kamata[1], Nobuhiro Kanomata[1] (1. Department of Chemistry and Biochemistry, Waseda University)

Japanese

[P1-1pm-31]

Synthesis of various diselenides with urea skeleton and Baeyer-Villiger oxidation with hydrogen peroxide

○Kai Machiyama[1], Hayato Ichikawa[1] (1. Nihon University)

Japanese

[P1-1pm-32]

Synthesis of Azulene Ester Derivatives and Their Pharmacological Activities

○Hiyuto Furuichi[1], Miura Wataru[1], Hiroshi Sakagami[2], Hidetugu Wakabayashi[1] (1. Josai University, 2. Meikai University)

Japanese

[P1-1pm-33]

Carbon-sulfur bond cleavage with Hantzsch ester anion under blue-light irradiation

○Koki Matsune[1], Takuma Shimotori[1], Nagisa Kikuchi[1], Haruto Hijikata[2], Tetsuya Sengoku[1] (1. Shizuoka University Graduate School of Integrated Science and Technology, 2. Department of Applied Chemistry and Biochemical Engineering, Faculty of Engineering, Shizuoka University)

Japanese

[P1-1pm-34]

Development of stereoselective decarboxylative aldol reaction of α-amido malonic acid half esters to isatins

○Kazuki Fujita[1], Ibuki Kumazawa[1], Jyunpei Yokoi[1], Kazuki Abe[1], Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

Japanese

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[P1-1pm-35]

Development of Conjugate Addition Reaction of Ketene Silyl Acetals to Terminal Alkynyl Imines

Ryo Sakai[1], ○Hitoshi Nishimura[1], Iwao Hachiya[1] (1. Mie University)

English

[P1-1pm-36]

Multicomponent Synthesis of 4-Iminoimidazolidines and their Bioactivities

○Komoreng Oriel Hlokoane[1], Raku Irie[1], Masato Oikawa[1] (1. Yokohama City University)

Japanese

[P1-1pm-37]

Rearrangement Reactions of Helical Quinone Derivatives to Various Oxygen-Containing Heterocyclic Derivatives

○Satoshi Joken[1], Nanami Kimura[1], Michinori Karikomi[1] (1. Utsunomiya Univercity)

Japanese

[P1-1pm-38]

Baeyer-Villiger Oxidation with the Diselenide Bearing Trifluoromethoxy group and Hydrogen Peroxide

○Riku Sakamoto[1], Hayato Ichikawa[1] (1. Nihon University)

Japanese

[P1-1pm-39]

Synthetic Studies of New Bicyclic Pipecolic Acid Derivatives

○Yuu Tamura[1], Masahiko Yamamoto[1], Takesi noda[1] (1. Kanagawa Institute of Technology)

Japanese

[P1-1pm-40]

Metal-free dibenzoxazepinone synthesis from salicylamides mediated by hypervalent iodine reagent

○Naoki Miyamoto[1], Arisu Kasai[1], Kotaro Kikushima[1], Toshifumi Dohi[1] (1. Ritsumeikan University)

Japanese

[P1-1pm-41]

[Withdraw] Synthesis of chiral oxazolines from the reaction of α–isocyanoacetonitriles with ketones

○Tatsuya Kato[1], Shuichi Nakamura[1], Naoki Yasukawa[1] (1. Nagoya Institute of Technology)

Japanese

[P1-1pm-42]

Cyclization for construction of bicyclic hydantoin derivatives

○Yuki Fuzisawa[1], Tomoya Katakura, Jun-ichi Yamaguchi[1] (1. Kanagawa institute of technology)

Japanese

[P1-1pm-43]

Design, synthesis and evaluation of photoresponsive properties of chiral macro cyclic compounds containing an azobenzene-unit.

○Shotaro Otaki[1], Ryota Shibauchi[1], Toshifumi Tojo[1], Norio Tanada[3], Yoshiyuki Kageyama[3], Shin Aoki[1,2] (1. Grad. Sch. Pharm. Sci., Tokyo Univ. of Science., 2. Res. Inst. for Sci., Tokyo Univ. of Science., 3. Grad. Sch. Sci., Hokkaido Univ.)

Japanese

[P1-1pm-44]

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Study of electrophilic chlorination reactions using sodium hypochlorite pentahydrate

○Reo Shimada[1], Michio Iwaoka[1] (1. Tokai University)

Japanese

[P1-1pm-45]

Synthesis of a bis(ferrocenyl)bromostibine bearing an intramolecularly coordinating phosphine moiety and its attempted debromination reaction

○Shinya Kawamoto[1], Koichiro Masada[2], Takahiro Sasamori[2,3] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-46]

Nickel Bromide-DBU-Catalyzed Synthesis of Cyclic Carbonates from Diols and CO_2 Using 2-Cyanopyridine

○Masatoshi Mihara[1], Yoshinobu Esaki[2], Kengo Hyodo[2], Shuichi Nakao[1], Takeo Nakai[1], Takatoshi Ito[1] (1. Osaka Research Institute of Industrial Science and Technology, 2. Faculty of Science and Engineering, Kindai University)

Japanese

[P1-1pm-47]

Synthesis and Reactivities of *N*-(9-Anthryl)thiazolium Salts

○Takahide Nishikawa[1], Yosuke Uchiyama[1,2], Hideyo Matsuzawa[1], Anthony J. Arduengo III[2,3] (1. Kitasato University, 2. The University of Alabama, 3. Georgia Institute of Technology)

Japanese

[P1-1pm-48]

Attempted Synthesis of a Novel Oligosila-cage Compound bearing Phenyl Groups

○Koichi Sato[1], Takahiro Sasamori[1] (1. University of tsukuba)

Japanese

[P1-1pm-49]

Synthesis of a new bulky ferrocenyl group bearing an intramolecularly coordinating selenium moiety.

○Ryusei Hamano[1], Takahiro Sasamori[2,3] (1. School of Science and Engineering, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-50]

Generation of a bissilylcarbenoid and its reaction with phosphine trichloride

○Akihiro Nomoto[1], Koh Sugamata[2], Takahiro Sasamori[3] (1. Graduate School of Science and Engineering, Univ. of Tsukuba, 2. Department of Chemistry, College of Science, Rikkyo University, 3. Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-51]

Synthesis of Mercaptoundecahydrododecaborate/Fucose Conjugate

○Taiga Fujita[1], Akira Morihara[2], Tomoyuki Tajima[3] (1. The Univ. of Okayama, 2. Graduate school of environmental, life, natural science and technology, Okayama University, 3. Graduate school of environmental, life, natural science and technology, Okayama University)

Japanese

[P1-1pm-52]

Synthesis of diferrocenyldimethylstannane for encapsulation in single walled carbon nanotubes

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○Taichi Kamiya[1], Yusuke Kondo[2], Tomoyuki Tajima[3] (1. Faculty of environmental science and technology, Okayama University , 2. Graduate school of environmental, life, natural science and technology, Okayama University , 3. Graduate school of environmental, life, natural science and technology, Okayama University)

Japanese

[P1-1pm-53]

Attempted synthesis of a binaphthyl substituted silylene

○Masaru Kanaoka[1], Shogo Morisako[2], Takahiro Sasamori[2] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-54]

Attempted Synthesis of Cyclic Phoshine-Alane bridged by a biphenyl unit

○Takanori Iwasaki[1], Takahiro Sasamori[2,3] (1. Graduate School of Science and Technology, University of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-55]

Syntheses and properties of donor-acceptor type fused polycyclic compounds with a triphenylamine skeleton as a donor unit

○Katsutaka Nishiyama[1], Yoshimitsu Tachi[1], Masatoshi Kozaki[1] (1. Osaka Metropolitan University)

Japanese

[P1-1pm-56]

Synthesis of an *o*-dibromobenzene derivative toward the synthesis of a 9,10-distibaanthracene

○Shunsuke Otsuji[1], Koichiro Masada[2], Takahiro Sasamori[2,3] (1. School of Science and Technology, University of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-57]

Insertion reactions of chlorogermylene bearing a bulky ferrocenyl group into dihaloalkanes

○Hiroto Chida[1], Takahiro Sasamori[2] (1. College of Chemistry, School of Science and Engineering, University of tsukuba, 2. Department of Chemistry, Institute of Pure and Applied Sciences, University of Tsukuba)

Japanese

[P1-1pm-58]

Development and application of reduction reaction of unsaturated carbon- carbon bond via α-iodotoluene structure

○Chika Ishizumi[1], Shota Amamoto[1], Rumi Kawatani[1], Nobuhiro Kotoda[1], Akiya Ogawa[2], Shin-ichi Kawaguchi[1] (1. Saga University, 2. Osaka Metropolitan University)

Japanese

[P1-1pm-59]

Enantioselective Addition of Thiols to α–Ketiminoesters using Cinchona Alkaloid Amide/Zinc(II) Catalysts

○Obata Kouki[1], Iizuka Yuka[1], Nakamura Shuichi[1] (1. Nagoya Institute of Technology)

Japanese

[P1-1pm-60]

Synthesis and properties of benzene and naphthalene derivatives having sulfide and sulfonium groups

○Kazunori Hirabayashi[1], Ren Takahashi[1], Naoya Kitamura[1], Toshio Shimizu[1] (1. Tokyo Metropolitan University)

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Japanese

[P1-1pm-61]

A study on preparation of a common precursor for *α*-difluoromethyl amino acids.

○Masaya Shiraishi[1], Toshimasa Katagiri[1], Shinji Hiramatsu[2] (1. Tokyo University of Technology, 2. Okayama University)

Japanese

[P1-1pm-62]

Synthesis of a bis(phosphide) ligand bearing sterically demanding substituents

○Riko Kato[1], Takahiro Sasamori[2] (1. Graduate School of Science and Tchnology, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-63]

Attempt to Synthesis of Complex with Selanyl Sulfanyl Imidazo[1,5-*a*]pyridine Ligands

○Akito Tanaka[1], Osamu Niyomura[1] (1. Chubu University)

Japanese

[P1-1pm-64]

Synthesis and structure of hexanuclear silver complex ($[Ag_6(f\text{-}BiSC)_4]$ $(TfO)_2$) with bisimmnosulfancarbone(0) ligand bearing free imino nitrogen.

○Keiko Noguchi[1], Takayoshi Fujii[1] (1. Nihon University)

Japanese

[P1-1pm-65]

Synthesis of silanes bearing a bulky ferrocenyl group and their reactivity with aryl lithium

○Ryuju Iwasaki[1], Koichiro Masada[2], Takahiro Sasamori[2,3] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Institute of Pure and Applied Science, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-66]

Attempted Synthesis of a 1,6,2,5-dioxadisilocine derivative

○Shiryu Nakamura[1], Takahiro Sasamori[2] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Department of Chemistry, Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-67]

Generation of a 2,3-Digerma-1,4-Dihydronaphthalene

○Miwako Kawai[1], Takahiro Sasamori[2] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Department of Chemistry, Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-68]

Synthesis and Optical Properties of Selenium- or Tellurium-containing 1,6-Di-*t*-butyl-substituted 1,3,5-Hexatriene Derivatives Incorporated with a Dibenzobarrelene Skeleton

○Koki Oshima[1], Jun Naito[2], Norio Nakata[2], Akihiko Ishii[2] (1. Faculty of Science, Saitama University, 2. Graduate School of Science and Engineering, Saitama University)

Japanese

[P1-1pm-69]

Synthesis and Application of Tris[1-(diphenylphosphino)isoquinolin-3-yl]phosphine Ligand

○Ryuki Kano[1], Hidetoshi Ohta[1], Minoru Hayashi[1] (1. Grad. Sch. Sci., Eng., Ehime Univ.)

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Japanese

[P1-1pm-70]

Design and Synthesis of Substituted Isoindoro[2,1-*a*]quinolines:Substituent effects at positions 5 and 11

○shimoguri reiji[1], isii hirokazu[2], sako makoto[1], murai keniti[1], nemoto tomomi[2], arisawa mituhiro[1] (1. osaka university, 2. institute of physiology)

Japanese

[P1-1pm-71]

The Synthesis and Properties of Group 14 Element Compounds Bearing Four Phenylethynyl Groups

○Junji Kobayashi[1], Rika Watanabe[1] (1. International Christian University)

Japanese

[P1-1pm-72]

Synthesis, structures and CH···O hydrogen bonding of dioxytetrylene dimers derived from 2,2′-methylenediphenols

Asuka Sugihara[2], Rise Shimogaito[1], Yoichi Ishii[2], ○Takuya Kuwabara[1] (1. Ochanomizu University, 2. Chuo University)

Japanese

[P1-1pm-73]

Preparation of derivatives bearing an azaazzulene-2-yl group and their characters

○Yuya Onishi[1], Jun-ichi Yamaguchi[1] (1. Kanagawa institute of technology)

Japanese

[P1-1pm-74]

Preparation of 2,6-ziazulenylpyridines and their coloration

○Hiro Watanabe[1], Rina sato[1], Yuya Onishi[1], Jun-ichi Yamaguchi[1] (1. kanagawa institute of technology)

Japanese

[P1-1pm-75]

Structure and Functions of Quinoline-Based Amide Oligomers

○Ayami Takeda[1], Wei Xu[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

Japanese

[P1-1pm-76]

Enantioselective synthesis of tetrasubstituted 2,3-dihydro-4-quinolones using chiral phosphoric acid catalysts

○Yuto Terashima[1], Rio Kawamura[1], Yoichiro Matsuda, Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

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Academic Program [Poster] | 23. CIP Poster：Poster

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[P2-1vn] 23. CIP Poster

Japanese P1. Energy

[P2-1vn-01]

Observation of Water Behavior Inside Polymer Electrolyte Fuel Cells by Complementary Use of Synchrotron X-ray and Neutron Sources

○Wataru Yoshimune[1], Yuki Higuchi[1], Akihiko Kato[1], Shogo Hibi[1], Satoshi Yamaguchi[1], Yoshihiro Matsumoto[2], Hirotoshi Hayashida[2], Hiroshi Nozaki[1], Takenao Shinohara[3], Satoru Kato[1] (1. Toyota Central R&D Labs., Inc., 2. Comprehensive Research Organization for Science and Society, 3. Japan Atomic Energy Agency)

Japanese P1. Energy

[P2-1vn-02]

Orientation analysis for proton-conducting covalent organic framework (COF) membranes

○Koki Fujiu[1], Masane Kin[1], Takahiro Nishio[1], Hiroki Watanabe[1], Hiroyasu Tabe[2], Ryota Shinozaki[1], Satoshi Horike[2], Takumi Okamoto[1] (1. DENSO CORPORATION , 2. Kyoto University)

Japanese P1. Energy

[P2-1vn-03]

Development of Sulfur-Based Materials “SPAN” and Battery Creations to Realize a World's Lightest Secondary Battery and Demonstration of Long Drone Flight Time

○Kenji Kakiage[1], Shunsuke Saito[2], Masaki Kakiage[3], Toru Yano[1] (1. ADEKA CORPORATION, 2. URUTAMA.INC, 3. Gunma University)

Japanese P1. Energy

[P2-1vn-04]

Development of High-Capacity Cathode Active Materials for All-Solid-State Batteries using Organosulfur Compounds

○Takeshi Shimizu[1], Kazuki Shinoda[1], Yusei Noda[1], Kosei Nawa[1], Naoki Tanifuji[1], Hirofumi Yoshikawa[2], Mari Yamamoto[3], Atsutaka Kato[3], Masanari Takahashi[3] (1. National Institute of Technology, Yonago College, 2. Kwansei Gakuin University, 3. Osaka Research Institute of Industrial Science and Technology)

Japanese P1. Energy

[P2-1vn-05]

Improving the performance of hematite photoelectrodes for solar water splitting

○Yoshitaka Kumabe[1], Takashi Tachikawa[1,2] (1. Mol. Photosci. Res. Center, Kobe Univ., 2. Grad. Sch. of Sci., Kobe Univ.)

Japanese P1. Energy

[P2-1vn-06]

Ultra-low Excitation Intensity Visible-to-UV Photon Upconversion with High Spin Statistical Probability Factor

○Kiichi Mizukami[1], Yuya Watanabe[1], Minlang Yang[1], Nobuhiro Yanai[1,2], Takuma Yasuda[1,3], Nobuo Kimiuzka[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. IAS, Kyushu Univ.)

Japanese P1. Energy

[P2-1vn-07]

Charge Separation Kinetics in non-fullerene acceptors by femtosecond time-resolved infrared spectroscopy

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○Rintaro Adachi[1], Tomokazu Umeyama[2], Hiroshi Imahori[3], Akira Yamakata[1] (1. Okayama University, 2. University of Hyogo, 3. Kyoto University)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-08]

Highly Efficient Solar CO_2 Conversion by Coupling Silicon Solar cells with Gas Diffusion Electrolyzer using Mn(I) Complex and β-FeOOH Catalysts

○Keita Sekizawa[1], Shunsuke Sato[1], Naonari Sakamoto[1], Tomiko M Suzuki[1], Takeshi Morikawa[1] (1. Toyota Central Research and Development Laboratories)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-09]

Continuous flow synthesis / oxidation and reduction case studies using the Microscale CSTR®

○Nobuyuki Nakayama[1], Isao Kotani[2], Kentaro Kotani[2], Hiroshi Haji[2], Sadayoshi Nakatsukasa[2] (1. Rigaku Kobo, LLC, 2. MAK Engineering Corporation)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-10]

Investigation of reaction mechanism of CO_2 to C_3H_7OH electrochemical conversion dinuclear Cu molecular catalysis

○Naonari Sakamoto[1], Keita Sekizawa[1], Soichi Shirai[1], Takamasa Nonaka[1], Takeo Arai[1], Shunsuke Sato[1], Takeshi Morikawa[1] (1. Toyota Central R&D Labs., Inc.)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-11]

Development of microbeads concentration method using phase separation phenomenon with temperature-responsive polymer PNIPAM

○Yui Yamashita[1], Atsushi Manaka[1,2], Mitsuhiro Ebara[2] (1. National Institute of Technology, Toyama College, 2. National Institute for Materials Science(NIMS))

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-12]

Reducion of Trace PCBs in Whale Oil by Steam Thin Film Distillation

○Arihiro Iwata[1], Tomoki Ogawa[1], Haruka Ino[1], Misato Miyamoto[1], Mitsuhiro Kishimoto[2], Kouji Yoshida[3], Takahiro Yoshida[3], Genta Yasunaga[4], Yoshihiro Fujise[4] (1. Yamaguchi Pref. Industrial Technology Institite, 2. Shimonoseki City Univ., 3. Yoshida Sogo Techno, 4. The Institute of Cetacean Research)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-13]

Complete defluorination of fluoroelastomer FKMs using subcritical water with alkaline reagents

○Jin Hamaura[1], Hisao Hori[1], Hirofumi Mukae[2], Ayane Fujishima[2] (1. Kanagawa University, 2. Daikin Industries, Ltd.)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-14]

Carboxylic Acid-Catalyzed Peptide Synthesis Using Diketopiperazine

○Kazumasa Kon[1], Hisashi Yamamoto[1] (1. Peptide Research Centre, Chubu University)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-15]

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Pd/CHA as a NOx Adsorber
-The Effect of Pd Loading methods on NOx Desorption Temperature-

○Takeshi OHTSU[1], Washiyama Shohei[1], Usami Tomoya[1], Tsunoji Nao[2], Oda Akira[1], Satsuma Atsushi[1] (1. Nagoya University, 2. Hiroshima University)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-16]

Preparation of gold nanoparticle electrocatalysts supported by single-walled CNTs and their application to aerobic oxidation of alcohols under electrochemical conditions

○Yuta Uetake[1,2,3], Honoka Nakamura[1], Rento Yabuki[1], Taiyo Shimizu[3], Ken Kokubo[3], Hidehiro Sakurai[1,2] (1. Osaka Univ., 2. ICS-OTRI, 3. AIST)

English P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-17]

Introduction to the Chemical Substances Control Act in South Korea

○YOON JIN CHO[1], YOUNGWOO CHON[1] (1. The Univ. of Inha)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-18]

Adsorption of polycyclic aromatic hydrocarbons(PAHs) on biodegradable plastics and its effect on biodegradability

○Shodai Hino[1], Naoko Yamano[1], Norioki Kawasaki[1], Atsuyoshi Nakayama[1] (1. AIST)

Japanese P6. Featured topic: Biomass-related technologies

[P2-1vn-19]

Aliphatic Polyesters with Ester-Functionalized Side Chains Synthesized from Methacrylates

○Shin-nosuke Nishimura[1], Ryosuke Kanai[1], Tomoyuki Koga[1] (1. Doshisha Univ.)

Japanese P6. Featured topic: Biomass-related technologies

[P2-1vn-20]

Hagfish Intermediate Filament Protein LLPS-Mediated Preparation of Bioinspired Hydrogels

○Ryuki Kobayashi[1], Syunsuke Kondo[2], Jin Gong[2], Hideki Nabika[1] (1. Faculty of Science, Yamagata University, 2. Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University)

Japanese P6. Featured topic: Biomass-related technologies

[P2-1vn-21]

In silico design of the active site of chitosanase catalyzing β-1,4-glycosylation between GlcN and GlcNAc

○Mariko Kojima[1], Mehdi Davari[2], Akira Onoda[1] (1. Hokkaido University, 2. Leibniz Institute of Plant Biochemistry)

Japanese P3. New materials

[P2-1vn-22]

Development of high-speed organic crystal photoactuators toward application to soft robotics

○Yuki Hagiwara[1], Shodai Hasebe[1], Toru Asahi[1], Hideko Koshima[1] (1. Waseda University)

Japanese P3. New materials

[P2-1vn-23]

Analysis of micro amount of CWO particles in resin

○Saihei Fujimoto[1], Katsushi Ono[1], Masaki Yano[1], Takehide Morimoto[1], Naoki Hashimoto[1] (1. Sumitomo Metal Mining Co., Ltd.)

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Japanese P3. New materials

[P2-1vn-24]

Effect of electrolyte on Au anode dissolution reaction

○Shinichiro Ozawa[1], Moe Hokugo[1], Riki Yamakawa[1], Yoichi Okamoto[1] (1. National Defense Academy)

Japanese P3. New materials

[P2-1vn-25]

Modification of cationic chlorophyll derivatives to polymers containing pyridine residues and their physical properties

○Shin Ogasawara[1], Hiroaki Marumoto[1], Hitoshi Tamiaki[1] (1. Ritsumeikan University)

Japanese P3. New materials

[P2-1vn-26]

C(sp^3)–H bond functionalization promoted by a semiconductor photocatalyst and water aiming at polymer modification

○Yuji Sakai[1], Shogo Mori[2], Mineto Uchiyama[3], Masami Kamigaito[3], Susumu Saito[2,4] (1. Sch. Sci., Nagoya Univ., 2. IRCCS, Nagoya Univ., 3. Grad. Sch. Eng., Nagoya Univ., 4. Grad. Sch. Sci., Nagoya Univ.)

Japanese P3. New materials

[P2-1vn-27]

Influence of Post Annealing on Crystal Growth in Liquid Crystalline Organic Semiconductor Thin Films

○Takayuki Oka[1], Nobutaka Shioya[1], Taizo Mori[1], Takeshi Hasegawa[1] (1. Kyoto Univ. ICR)

Japanese P3. New materials

[P2-1vn-28]

Development of Triazine Derivatives Bearing Electron-Withdrawing Substituent and Their Application to TADF Emitter with Near-Infrared Two-Photon Absorption Character

○Youhei Chitose[1,2,3], Youichi Tsuchiya[3], Chihaya Adachi[1,3,4] (1. Grad. Sch. of Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. OPERA, Kyushu Univ., 4. WPI-I2CNER)

Japanese P3. New materials

[P2-1vn-29]

Novel Ethylene-based Polymers as Sustainable Elastomers

○Shigenaga Takano[1], Chikako Kuroiwa[1], Jyunichi Ishigami[1], Tomoko Kamata[1], Shojiro Kaita[1] (1. Bridgestone Corporation)

English P4. DX-related technologies

[P2-1vn-30]

Verification of required ventilation amount for evaporated gas after inflammable liquid leakage through CFD program

○YOUN HO LEE[1], Youngwoo Chon[1] (1. The Univ. of Inha)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-31]

Thermo-switchable adhesive hydrogel inspired by mussel

○Hiroya Abe Abe[1], Yoshihara Daichi[1], Daigo Terutsuki[1], Matsuhiko Nishizawa[1] (1. Tohoku University)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-32]

Effects of plant polysaccharides on skin barrier function

○Ai Sugita[1], Yuki Takeuchi[1] (1. KYOWA PHARMA CHEMICAL CO.,LTD.)

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Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-33]

Small-Molecule Aptamer for Regulating RNA Functions in Mammalian Cells and Animals

○Keisuke Fukunaga[1,3], Dhamodharan Venugopal[1], Nao Miyahira[1], Yoko Nomura[1], Mustafina Kamila[1,4], Yasuaki Oosumi[2], Kosuke Takayama[2], Akira Kanai[2], Yohei Yokobayashi[1] (1. OIST, 2. Astellas Pharma Inc., 3. Tokyo Tech, 4. MIT)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-34]

Molecular structure and biocompatibility of star polymer at water interface

○Masayasu TOTANI[1,2], Hiroharu AJIRO[2], Jun-ichi KADOKAWA[1], Tsuyoshi ANDO[2], Masao TANIHARA[2] (1. Kagoshima University, 2. Nara Institute of Science and Technology)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-35]

Membrane-deforming liposomes for highly efficient encapsulation and detoxification of huge biomacromolecules such as viruses.

○Noriyuki Uchida[1], Yunosuke Ryu[1], Teruhiko Matsubara[2], Toshinori Sato[2], Yasutaka Anraku[3], Takahiro Muraoka[1,4] (1. Tokyo Univ. Agri. Tech., 2. Keio Univ., 3. Tokyo Institute. Tech., 4. KISTEC)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-36]

Design and Synthesis of a Body Fluid-Responsive Instantly Solidifying Liquid and Dedicated Macroporous Sponges: Realizing Simple but High-Performance Hemostatic Materials

○Hiroyuki Kamata[1], Shohei Ishikawa[1], Ayano Fujisawa[1], Yuki Yoshikawa[1], Kazuyoshi Matsubara[2], Katsuyuki Hoshina[2], Takamasa Sakai[1] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. Grad. Sch. Med., The Univ. of Tokyo)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-37]

Effect of ganglioside GM1 on amyloid fibrillogenesis in the coexistence of amyloid β 40 and 42

○Kiyo Fukase[1], Hideki Nabika[2] (1. Graduate School of Sci. and Eng, Yamagata Univ., 2. Faculty of Sci, Yamagata Univ.)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-38]

Effect of cholesterol / lanosterol on DOPC membrane properties and amyloid β aggregation

○Kyohei Akiho[1], Hideki Nabika[2] (1. Graduate School of Science and Engineering, Yamagata University, 2. Faculty of Science, Yamagata University)

English P5. Medical care/Health care/Biotechnology

[P2-1vn-39]

Contribution of Sebum and Sweat Condition to Men’s Daytime Skin Appearance and Feel

○Songjie Zhang[1], Mamiko Kikuchi[1], Ai Terai[1], Jicheng Zhang[1], Shinichi Ikegaki[1], Satoru Naitou[1] (1. Kao Corporation)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-40]

Development of supramolecular gelling peptides for *in-vitro* three-dimensional tissue culture and stable collection of the tissue

○Atsuya Yaguchi Yaguchi[1], Itsuki Ajioka[2,3], Takahiro Muraoka[1,3] (1. Tokyo Univ. of Agri. and Tech., 2. Tokyo Med. and Dent. University, 3. KISTEC)

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Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-41]

Development of polysaccharide modified photo cross-linked gelatin hydrogel cell scaffolds

○Hiroki Miyajima[1], Kodai Onodera[1], Yuki Hatta[1], Kaori Kojima[1], Masaru Mukai[1], Shoji Maruo[1], Kazutoshi Iijima[1]
(1. Yokohama National Univ.)

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Academic Program [Poster] | 03. Physical Chemistry -Structure-：Poster

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[P1-2vn] 03. Physical Chemistry -Structure-

Japanese

[P1-2vn-01]

A study on the electric dipole moment and molecular structure of the Kr-OCS cluster by microwave double resonance spectroscopy

○Yutaro Osawa[1], Yoshihiro Sumiyoshi[1] (1. Gunma University)

English

[P1-2vn-02]

Paramagnetic ion doping in MOFs to accelerate solid-state NMR measurements

○Henric Mezzomo[1], Takuya Kurihara[1], Yasuhiro Shigeta[1], Shogo Amemori[1], Tomonori Ida[1], Motohiro Mizuno[1] (1. Kanazawa University)

Japanese

[P1-2vn-03]

Exact Analyses of ESR Spectra of Cobalt Complexes with Sizable Zero-Field Splitting Tensors

○Takeshi Yamane[1], Kenji Sugisaki[1,2,3], Kazunobu Sato[1], Kazuo Toyota[1], Daisuke Shiomi[1], Takeji Takui[1] (1. Osaka Metropolitan Univ., 2. Keio Univ., 3. JST PRESTO)

Japanese

[P1-2vn-04]

Characterization of self-assembled monolayers consisting of helical polymers: Topography modification depending on applied electric field

○Nano Kobayakawa[1], Naoya Kanbayashi[1], Taka-aki Okamura[1], Kiyotaka Onitsuka[1], Seiya Watanabe[1], Megumi Akai-Kasaya[1], Hiroyuki S. Kato[1] (1. Osaka University)

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Academic Program [Poster] | 04. Physical Chemistry -Properties-：Poster

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[P2-2vn] 04. Physical Chemistry -Properties-

Japanese

[P2-2vn-01]

Solvation Gibbs energies of natural cyclodextrins

○Masao Fujisawa[1], Tomonori Ohata[2], Hiroyuki Tsutsumi[2], Hirohito Ikeda[2] (1. Dept. of Biotechnological Science, Kindai Univ., 2. Fac. of Pharmaceutical Science, Fukuoka Univ.)

Japanese

[P2-2vn-02]

Solubilization of Heated Egg White Aggregates by Direct Addition of Alkali Halides

○Takahiro Takekiyo[1], Yurina Emori[2], Kou Kato[2], Suzu Kondo[2], Taichi Matsuda[2], Rikuto Nozawa[2], Miyuu Tsumuraya[2], Atsushi Yamada[1], Yukihiro Yoshimura[1] (1. National Defense Academy, 2. Yokosuka High Scool)

Japanese

[P2-2vn-03]

High Electrically Conductive Deep Eutectic Solvents Using Organic Halides and Iodine

○Junpei Sato[1], Maharoof Koyakkat[2], Satoshi Asakura[3], Hiroyuki Kawamoto[3,4], Katsuhiko Moriyama[2], Hideaki Shirota[2] (1. Faculty of Science, Chiba University, 2. Graduate School of Science, Chiba University, 3. Ise Chemicals Corporation, 4. Chiba Iodine Resource Innovation Center)

Japanese

[P2-2vn-04]

Enhancement of hydrophobicity in oxicam group of acidic drugs by pH-induced conformational change

○Kota Moritake[1], Kanji Hasegawa[1], Tomohiro Tsuchida[1], Satoru Goto[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-05]

Distinguishing the transitions of fluorescence spectra of tryptophan-134 and 213 in BSA induced by bindings of UV filters, oxybenzone-3, and avobenzone

○Horizumi Yusuke[1], Minamide Megumi[1], Tsurushima Minori[1], Kurosawa Yuya[1], Koga Ryotaro[1], Hasegawa Kanji[1], Tsuchida Tomohiro[1], Goto Satoru[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-06]

XAS measurements for aqueous solutions of nitrogen-containing organic compounds

Haoran Xu[1], ○Takehiko Sasaki[1] (1. The University of Tokyo)

English

[P2-2vn-07]

Plasmon-influenced photoluminescence blinking behavior of lead halide perovskite quantum dots

○Tianci Wang[1], Lei Duan[1], Takuya Okamoto[1], Vasudevan pillai Biju[1] (1. Hokkaido University)

Japanese

[P2-2vn-08]

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Auger Recombination-Assisted Photoisomerization of Diarylethene Derivatives with Semiconductor Quantum Dots

○Moe Yamamoto[1], Daichi Eguchi[1], Naoto Tamai[1] (1. The Univ. of Kwansei Gakuin)

Japanese

[P2-2vn-09]

Synthesis of new magnetic acetylides containing ethynyl-substituted TTF-based derivatives

○Sodai Sasaki[1], Junichi Nishijo[1], Masaya Enomoto[2], Motoko Akita[3] (1. Meisei University, 2. Tokyo University of Science, 3. Josai University)

Japanese

[P2-2vn-10]

Crystal structures, magnetic properties, and their deuterium substitution effects of hydrogen-bonded dinuclear copper complexs, $[Cu(Eta)(Heta)(NO_3)]_2$

Tasuku Murai[1], Shinobu Aoyagi[2], ○Wataru Fujita[1] (1. Tokyo University of Marine Science and Technology, 2. Nagoya City University)

Japanese

[P2-2vn-11]

Proton Conductivity of Alginic Acid-Polyacrylic Acid-Triazole Composites

○Genta Yamamoto[1], Yasuhiro Shigeta[1], Takuya Kurihara[1], Shogo Amemori[1], Tomonori Ida[1], Motohiro Mizuno[1] (1. Kanazawa University)

Japanese

[P2-2vn-12]

Structure and properties of BEDT-TTF-based salt with indigodisulfonate, (BEDT-TTF)$_3$(indigodisulfonate) • H_2O

○Kento Yamanobe[1], Hiroki Akutsu[1], Yasuhiro Nakazawa[1] (1. Osaka University)

Japanese

[P2-2vn-13]

Electronic Properties of Azachrysene Compounds

○Nobutsugu Hamamoto[1], Makoto Inokuchi[1] (1. Sanyo-Onoda City University)

Japanese

[P2-2vn-14]

Mixed-Sequence Oligomer Salt $4P^HS$–*X* for High Conductivity

○Takeshi Nishida[1] (1. The University of Tokyo)

Japanese

[P2-2vn-15]

Relationship between polar structure and g-tensor for (BEDT-TTF)$_2$(PO-CONHC$_2$H$_4$SO$_3$)

Sato Shiori[1], ○Ko Furukawa[1,2], Hiroki Akutsu[3], Tasuhiro Nakazawa[3] (1. Niigata Univ., 2. CCRF, Niigata Univ., 3. Osaka Univ.)

Japanese

[P2-2vn-16]

Synthesis and physical properties of fluorine-substituted TMTTF derivatives

○Shuya Goto[1], Tatsuro Imakubo[1] (1. Nagaoka University of Technology)

Japanese

[P2-2vn-17]

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Synthesis of TTF Derivatives with Hydrogen Bonding and Chiral Moieties and Characterization of One-dimensional Helical Structures Composed of TTF Derivative and F_4TCNQ Complexes.

○Fumiya Hirose[1], Sadafumi Nishihara[2,3], Tsuyoshi Minami[4], Tomoyuki Akutagawa[5], Takayoshi Nakamura[6], Yoko Tatewaki[1] (1. Tokyo Univ. of Agri. and Tech., 2. Hiroshima Univ., 3. JST PRESTO, 4. Univ. of Tokyo, 5. Tohoku Univ., 6. Hokkaido Univ.)

Japanese

[P2-2vn-18]

Preparation of Scaffolds Composed of Molecular Nanocoils and Application to Saos-2 Cell Culture

○Aoba Sasaki[1], Noritaka Maezono[1], Akira Matsumoto[2], Sadafumi Nishihara[3,4], Tomoyuki Akutagawa[5], Takayoshi Nakamura[6], Tsuyoshi Minami[2], Yoko Tatewaki[1] (1. Tokyo Univ. of Agri. and Tech, 2. Univ. of Tokyo, 3. Hiroshima Univ., 4. JST PRESTO, 5. Tohoku Univ., 6. Hokkaido Univ.)

Japanese

[P2-2vn-19]

Theoretical studies on electronic properties in iron-oxo porphyrin model complex and reaction process in P450

○Mizuki Otsuka[1], Takashi Kawakami[2,1], Marie Tsuchikawa[1], Shusuke Yamanaka[1], Mitsutaka Okumura[1], Kizashi Yamaguchi[2,1] (1. Osaka University, 2. RIKEN)

Japanese

[P2-2vn-20]

Development of a hydrogen-bonding cobalt(II)-organic framework bridged by a dicarboxylic acid linker

○Tomohiro Okano[1], Takuya Kanetomo[1], Masaya Enomoto[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-21]

Effects of desymmetrization on structures and physical properties in canted antiferromagnetic single-component molecular conductors

○shota arai[1], So Yokomori[1], Nobuyuki Matsushita[1] (1. The College of Science,Rikkyo University)

Japanese

[P2-2vn-22]

Electrical and Magnetic Properties of Axially Ligated Manganese Benzoporphyrin-based Conducting Crystals

○Kosuke Mine[1], Noriaki Hanasaki[3], Hiroshi Murakawa[3], Masaki Matsuda[2] (1. Graduate School of Science and Technology, Kumamoto University, 2. Faculty of Advanced Science and Technology, Kumamoto University, 3. Department of Physics, Osaka University)

English

[P2-2vn-23]

Magnetic monitoring electrochemical properties in strongly correlated Cu3BHT

○Yigang Jin[1] (1. Nagoya University, Graduate School of Science)

Japanese

[P2-2vn-24]

On energy transfer to added fluorescence dopant in the solid system of near-infrared triplet-triplet annihilation photon upconversion by using quantum dot

Neeti Tripathi[1], ○Kenji Kamada[1] (1. National Institute of Advanced Industrial Science and Technology (AIST))

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Japanese

[P2-2vn-25]

Fabrication and characterization of sensitized dye solar cells with energy transfer in the presence of spiropyran derivative and cyclodextrin -SQ2/$SPNO_2$ system-

○Ryuhei Ejima[1], Michihiro Hara[1] (1. Fukui University of Technology)

Japanese

[P2-2vn-26]

Aggregate formation and multicolor fluorescence emission shown by dye blocking ESIPT sites

○Yuma Hirose[1], ken-ichi Sakai[1], Tomoyuki Akutagawa[2] (1. Chitose Inst. Sci. Tech., 2. IMRAM, Tohoku Univ.)

Japanese

[P2-2vn-27]

Creation of optical properties by controlling axial rotation in *p*-terphenyl derivatives

○Kei Kobayashi[1], Ken-ichi Sakai[1], Tomoyuki Akutagawa[2] (1. Chitose Institute of Science and Technology, 2. IMRAM)

Japanese

[P2-2vn-28]

Calculation and analysis of absorption and fluorescence spectra, and radiative and non-radiative rate constants of rubrene based on the theory of vibronic coupling

○Motoyuki Uejima[1], Hiroo Fukunaga[1], Wataru Ota[2,3], Tohru Sato[2,3] (1. MOLFEX Inc., 2. FIFC, Kyoto Univ. , 3. Graduate School of Technology, Kyoto Univ.)

Japanese

[P2-2vn-29]

Luminescent Chiral Binaphthalimide as Liquid Crystal Dopant for Enhance CPL Emission

○Yuki Yamashita[1], Chigusa Goto[1], Yugo Tsuji[1], Tsuyoshi Kawai[1], Yo Shimizu[1], Marine Louis[1] (1. Nara Institute of Science and Technology)

Japanese

[P2-2vn-30]

Synthesis of diarylethene-fused metal dithiolene complexes for the development of novel photoresponsive molecular conductors

○Kaito Wakao[1], So Yokomori[1], Ryo Nishimura[1], Masakazu Morimoto[1], Nobuyuki Matsushita[1] (1. The College of Science, Rikkyo University)

Japanese

[P2-2vn-31]

Analysis Stabilization Mechanism of Avobenzone and β-Cyclodextrin complex

○Ryotaro Koga[1], Chihiro Kuroda[1], Ryosuke Hiroshige[1], Megumi Minamide[1], Kanji Hasegawa[1], Tomohiro Tsuchida[1], Satoru Goto[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-32]

Synthesis of N-Methylcarbazole - FTCNQ

○Kota Tsuchiaki[1], Yosuke Tokuda[2], Hideo Yamakado[1,2] (1. Wakayama University, 2. Wakayama University Graduate School)

Japanese

[P2-2vn-33]

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Effect of Introducing Substitutions into Anthraquinone-Based Compounds as Organic Anolytes for Aqueous Redox Flow Batteries

○Momoka Kawgauchi[1], Atsushi Okazawa[1], Kosuke Kawai[1], Masashi Okubo[1] (1. Waseda University)

Japanese

[P2-2vn-34]

Synthesis and physical properties of complexs of Methoxyphenazine and TCNQ compounds

○Kodai Ichinose[1], Yosuke Tokuda[2], Hideo Yamakado[1,2] (1. Faculty of Systems Engineering, Wakayama Univ., 2. Graduate School of Systems Engineering, Wakayama Univ.)

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Academic Program [Poster] | 05. Physical Chemistry -Chemical Kinetics and Dynamics-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 3(理工スポーツホール [1階] アリーナ)

[P3-2vn] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Japanese

[P3-2vn-01]

Effect of intramolecular hydrogen bond on photoisomerization of hemiindigo

○Reona Yoshida[1], Takayuki Murai[1], Sora Ishikawa[1], Yu Matsunaka[1], Yuki Shimizu[1], Yugo Isawa[1], Risa Kojima[1], Yutaka Nagasawa[1] (1. Ritsumeikan Univ.)

Japanese

[P3-2vn-02]

Size-Dependent Single-photon Emission of Cesium Lead Iodide Perovskite Nanocrystals

○Nicholas Huang[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

Japanese

[P3-2vn-03]

Photoisomerization dynamics of *N*,*N*'-substituted indigo derivatives with aromatic substituents

○Yuki Shimizu[1], Takayuki Murai[1], Sora Ishikawa[1], Yu Matsunaka[1], Yugo Isawa[1], Reona Katayama[1], Risa Kojima[1], Yutaka Nagasawa[1] (1. The Univ. of Ritsumeikan)

Japanese

[P3-2vn-04]

Construction of Photoresponsive Quantum Dot Assemblies Using Azobenzene Derivatives

○Manato Kiriyama[1], Naoki Kubo[1], Sadahiro Masuo[1] (1. Kwansei gakuin university)

Japanese

[P3-2vn-05]

Photocleavage reaction of asymmetric spiropyran SBP-β-AP with a large aromatic substituent on one side

○Yugo Isawa[1], Yu Matsunaka[1], Takayuki Murai[1], Sora Ishikawa[1], Yutaka Nagasawa[1] (1. Ritsumeikan University)

Japanese

[P3-2vn-06]

Energy transfer in $CsPbBr_3$ perovskite nanocrystals – pentacene system

○Seiju Koyama[1], Miyu Yoshioka[1], Sadahiro Masuo[1] (1. kwansei gakuin university)

Japanese

[P3-2vn-07]

Development of transient grating method for studies on biomolecular reactions in microenvironments

○Akito Nishino[1], Yusuke Nakasone[1], Kosuke Nishitani[1], Moeto Nagai[2], Masahide Terazima[1] (1. Kyoto University, 2. Toyohashi University of Technology)

Japanese

[P3-2vn-08]

Energy transfer in a CdZnS/ZnS quantum dot – perylene bisimide system

○Ami Goto[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

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Japanese

[P3-2vn-09]

Development of nanoscopic photoexcitation method by using triplet-triplet annihilation up-conversion emission

○Makoto Yamada[1], Hirotaka Kageyama[1], Haruki Nagae[1], Hayato Tsurugi[1], Syoji Ito[1,2], Hiroshi Miyasaka[1] (1. The Univ. of Osaka, 2. RILACS, Osaka Metropolitan Univ.)

Japanese

[P3-2vn-10]

Constructing One-Dimensional Arrangements of Heterogenous Quantum Dots using Molecular Assemblies

○Megumi Tomonaga[1], Naoki Kubo[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

English

[P3-2vn-11]

Understanding the DNA hybridisation kinetics under optical condensation with simultaneous single particle detection

○Bhagya Lakshmi Sankaramangalam Balachandran[1], Shuichi Toyouchi[2,4], Syoji Ito[1,4], Shiho Tokonami[3,4], Takuya Iida[2,4] (1. Graduate School of Engineering Science, Osaka University, 2. Graduate School of Science, Osaka Metropolitan University, 3. Graduate School of Engineering, Osaka Metropolitan University, 4. Research Institute for Light-induced Acceleration System (RILACS), Osaka Metropolitan University)

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Academic Program [Poster] | 07. Inorganic Chemistry：Poster

Tue. Mar 19, 2024 1:00 PM - 2:30 PM JST | Tue. Mar 19, 2024 4:00 AM - 5:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-2pm] 07. Inorganic Chemistry

Japanese

[P1-2pm-01]

Synthesis of metal oxide nanoparticles employing amino acid hydrochloride as a structure-directing agent and their dispersion control

○Yuto Hibi[1], Nagisa Hattori[1], Takashi Sugiura[1], Kazuhiro Manseki[1] (1. Gifu University)

Japanese

[P1-2pm-02]

Synthesis of magnesium ionic conductive solid electrolite and composition dependence of crystal structure and electric propert

○Shota Tange[1], Naoya Kinokiri[1], Rie Shimanouchi[1] (1. Kochi University)

Japanese

[P1-2pm-03]

Immobilization of molybdate ion in inorganic amorphous materials by vacuum freeze drying method

○HUIXIN LIU[1], Akihiko Kajinami[1] (1. Kobe University)

Japanese

[P1-2pm-04]

Synthesis of Lambda-phase Trititanium Pentoxide by Block Copolymer Method

○Kazuya Yamaguchi[1] (1. University of Tsukuba)

Japanese

[P1-2pm-05]

Immobilization of Cesium Ion in Inorganic Amorphous Materials by Vacuum Freeze-Drying Method

○Naoki Hamada[1], Akihiko Kajinami[1], HUIXIN LIU[1] (1. Kobe University)

Japanese

[P1-2pm-06]

Study of the synthesis conditions for tetragonal zirconium dioxide

○Yuki Konno[1], Natsuki Asano[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. University of Tokyo)

Japanese

[P1-2pm-07]

Synthesis method of zirconium dioxide

○Natsuki Asano[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. University of Tokyo)

Japanese

[P1-2pm-08]

Synthesis method for gallium-substituted tetratitanium heptoxide ($Ti_{4-x}Ga_xO_7$) and evaluation of its magnetic properties

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○Tomoko Kubota[1], Riku Seiki[1], Akito Fujisawa[1], Akhmad Fadel Fadilla[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. The Univ. of Tsukuba, 2. The Univ. of Tokyo)

Japanese

[P1-2pm-09]

Flow-type LP-ALD process for the preparation of α-Fe_2O_3 thin films

○Mitsuki Takayanagi[1], Yohei Yamane[1], Naoki Osaka[1], Kentarou Mori[1] (1. College of Industrial Technology, Nihon University)

Japanese

[P1-2pm-10]

Examination of crystal structure control by elements substutution in cyclosilicate compounds

○Rie Futagami Shimanouchi[1], Hayato Osawa[1], Takuro Ikeda[1] (1. Kochi University)

Japanese

[P1-2pm-11]

Luminescence property of lead halide perovskite single crystals controlled by lanthnide ions

○Mizuki Noto[1], Tomohide Yamada[2], Ayumi Ishii[2] (1. Teikyo University of Science, 2. Waseda University)

Japanese

[P1-2pm-12]

Development of lanthanide based up-conversion materials with multicolor luminescence

○Ryusuke Mizoguchi[1], Truptimayee Behera[2], Ryota Komatsuzaki[2], Ayumi Ishii[2] (1. Teikyo Univ. of Sci., 2. Waseda Univ.)

Japanese

[P1-2pm-13]

Synthesis and luminescent copper(I) carbene complexes

○Kanta Nakamura[1], Taro Tsubomura[1] (1. Seikei University)

Japanese

[P1-2pm-14]

Electrochemical Ag nanoparticles synthesis inside MOF

○Junya Kato[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-15]

Pb nanoparticle synthesis within COF by electrochemical reduction method

○Weihua Wang[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-16]

Synthesis and evaluation of Cu(BDC-NH_2) MOF oriented film by casting method

○Takumi Nishigaki[1], Qiyuan ZHANG[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-17]

Fabrication of oriented crystalline thin film of cationic MOF by casting method

○Taisei Sato[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

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Japanese

[P1-2pm-18]

Construction of oriented COF film by casting method

○Koichi Takano[1], Tomoyuki Haraguchi[1] (1. Tokyo University Of Science)

Japanese

[P1-2pm-19]

Construction and evaluation of MOF oriented films with three-dimensional framework by casting method

○Yusuke Fujii[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1] (1. Tokyo University of Science)

Japanese

[P1-2pm-20]

Fabrication and Evaluation of Oriented Crystalline Zn_3(TCPP)(DABCO) MOF Thin Film by Casting Method

○Jiahao Zhang[1], Qiyuan Zhang[1], tomoyuki haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-21]

Construction of Aluminosilicate Frameworks from Double-Four-Ring-Type Molecular Precursor

○Yurika Ohnishi[1], Akira Imaizumi[2], Akinori Honda[1], Ho-Chol Chang[1] (1. Faculty of Science and Engineering, Chuo Univ., 2. Graduate School of Science and Engineering , Chuo Univ.)

Japanese

[P1-2pm-22]

Creation of molecular-sized electride compounds by using tin oxide cluster as a base material

○Takamasa Tsukamoto[1,2], Mayumi Otake[1], Nozomi Yoshida[3], Tatsuya Moriai[3,4], Kimihisa Yamamoto[3,4] (1. IIS, The Univ. of Tokyo, 2. JST-PRESTO, 3. Lab. for Chemistry and Life Science, Tokyo Tech, 4. JST-ERATO)

Japanese

[P1-2pm-23]

Efficient reducibility of layered polysilane (LpSi) for selective recovery of platinum ions from aqueous media

○Masataka Ohashi[1], Goto Yasutomo[1], Nakano Hideyuki[1] (1. TOYOTA CENTRAL R&D LABS., INC.)

Japanese

[P1-2pm-24]

Does the origin of montmorillonite affect cesium ion exchange behavior?

○Noriko Suzuki[1], Masato Sawada[1], Reishi Moriya[1] (1. Showa Pharmaceutical University)

Japanese

[P1-2pm-25]

Organically modified layered silicates dispersing in a polyurethane foam

○Haruna Sasaki[1], Tomonori Watanabe[1], Tomohiko Okada[1] (1. Shinshu University)

Japanese

[P1-2pm-26]

Development of microporosity by the selective leaching of fluorine muscovite mica ceramics

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○Daichi Aoyagi[1], Tomohiro Yamaguchi[1], Seiichi Taruta[1] (1. Shinshu University)

Japanese

[P1-2pm-27]

Formation of Zn-Al LDHs as coating on a Zn plate by the homogeneous precipitation method using a polyhydroxoaluminum complex solution

○Issei Kokubo[1], Tomohiro Yamaguchi[1], Seiichi Taruta[1] (1. Shinshu University)

Japanese

[P1-2pm-28]

Synthesis and Evaluation of Sodium-doped Hydrogen Boride Sheets with controlling dopant amount

○Shohei Shimozato[1], Miwa Hikichi[1], Shinichi Ito[1], Natsumi Noguchi[1], Kosuke Takeshita[1], Takahiro Kondo[1] (1. The Univ. of Tsukuba)

Japanese

[P1-2pm-29]

^{1}H solid state NMR spectra of lanthanoid nitrate hydrate

○Mineyuki Hattori[1], Emiko Oonuma[1] (1. NMIJ, AIST)

Japanese

[P1-2pm-30]

Catalytic activity of water-soluble fluorinated chlorin iron(III) complexes

○Shino Nakashima[1], Reina Ishikawa[1], Haruo Akashi[1] (1. Okayama University of Science)

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Academic Program [Poster] | 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 4(理工スポーツホール [1階] アリーナ)

[P4-2vn] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Japanese

[P4-2vn-01]

Development of the electrochemical methylation reaction of organic molecules.

○Shoya Banzawa[1], Yuma Morii[1], Yutaka Saga[1], Tetuya Kambe[1], Mio Kondo[1,2,3], Shigeyuki Masaoka[1] (1. Osaka University, 2. Tokyo Tech., 3. JST PRESTO)

Japanese

[P4-2vn-02]

Study on energy conversion via quantum tunneling of proton-coupled electron transfer

○Tatsushi Nakayama[1], Bunji Uno[2] (1. Gifu Pharmaceutical University, 2. Gifu University of Medical Science)

Japanese

[P4-2vn-03]

π-Facial Selectivity and Reaction Mechanism of the Hydroboration of Allylic Substituted Alkenes

○Shotaro Ogawa[1], Kaname Takaoka[1], Daisuke Kaneno[1] (1. Kochi Univ.)

Japanese

[P4-2vn-04]

Regioselectivity and Reaction Mechanism on Tricyanovinylation Reaction of *N*-Substituted Pyrroles

○Ayako Hidaka[1], Yoshiaki Sasaki[1], Sora Takahashi[1], Saori Arisawa[1], Ryota Tani[1], Daisuke Kaneno[1] (1. Kochi Univ.)

Japanese

[P4-2vn-05]

Development of dicyanomethylation of styrene derivatives over Platium-loaded TiO_2

○Ryo Takeda[1] (1. National Institute of Technology, Miyakonojo College)

Japanese

[P4-2vn-06]

Development of molecules exhibiting circularly polarized luminescence based on cyclodextrins as a chiral source

○Kentaro Takaji[1], Hajime Shigemitsu[1], Toshiyuki Kida[1] (1. Osaka University)

Japanese

[P4-2vn-07]

Suppression of Quinine, an Antimalarial Drug, Photosensitized Singlet Oxygen Generation by Catechol Related Molecules

○Yuto Yoshimoto[1], Mikio Yagi[2], Azusa kikuchi[2] (1. Yokohama national university engineering, 2. Yokohama national university)

Japanese

[P4-2vn-08]

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New Phosphate Protecting Group Deprotected by PET Using Visible LED

○Aoi Murakami[1], Mugen Yamawaki[1] (1. National Institute of Technology, Fukui College)

Japanese

[P4-2vn-09]

Synthesis of diarylethene-subporphyrazine hybrids and their photochemical properties

○Nanari Tamiya[1], Taichi Muto[2], Mihoko Yamada[2], Tsuyoshi Kawai[2], Akuto Takagi[1], Tadashi Mizutani[1] (1. Doshisha University, 2. Nara Institute of Science and Technology)

Japanese

[P4-2vn-10]

Investigation of fluorescence properties and the emission mechanism of mesoionic 1,3-diaryltetrazolium compounds

○Yuta MATSUKAWA[1], Hitoshi TAMIAKI[1] (1. Ritsumeikan University)

Japanese

[P4-2vn-11]

Synthesis and Circularly Polarized Emission Properties of Bis-1,8-Naphthalimide Derivatives and Their Analogues

○Mami Naoe[1], Shiori Eguchi[1], Hiroshi Takashima[1], Yoshitane Imai[2], Norimitsu Tohnai[3], Shoko Yamazaki[4], Eiji Nakata[5] (1. Nara Women's University, 2. Kindai University, 3. Osaka University, 4. Nara University of Education, 5. Kyoto University)

Japanese

[P4-2vn-12]

Development of Visible-light-induced π-Extension of Perylene Diimide Derivatives and its Regioselectivity

○Shingo Miyano[1], Kenshin Norizuki[1], Keisuke Fujimoto[1], Tetsuya Sengoku[1], Masaki Takahashi[1] (1. Shizuoka University)

Japanese

[P4-2vn-13]

1,10-Phenanthroline-Based Octahedra Induced by Protonation of a Nitrogen Atom: Structures and Emission Properties

○Hiroshi Takashima[1], Naokazu Yoshikawa[1], Shoko Yamazaki[2], Norimitsu Tohnai[3], Eiji Nakata[4] (1. Nara Women's University, 2. Nara University of Education, 3. Osaka University, 4. Kyoto University)

Japanese

[P4-2vn-14]

Chiroptical properties of difluoroboron complexes with optically-active-7-iminomethylindole ligands

○Ryosuke Horio[1], Masahiro Ikesita[2], Yoshitane Imai[3], Takashi Tsuno[2], Seika Suzuki[3] (1. Graduate School of Industrial Technology, Nihon University, 2. College of Industrial Technology, Nihon University, 3. Graduate School of Science and Engineering, Kindai University)

Japanese

[P4-2vn-15]

Synthesis and Characterization of BODIPY with Phosphorus-based Substituents

○Daiki Ito[1], Shota Yamagishi[1], Keisuke Fujimoto[1], Masaki Takahashi[1] (1. Shizuoka University)

Japanese

[P4-2vn-16]

A Singlet Oxygen Sensor bearing Triphenylimidazole

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○Yuna Fukuoka[1], Takato Kurashina[1], Mikio Yagi[1], Azusa Kikuchi[1] (1. Yokohama National University)

Japanese

[P4-2vn-17]

Development of new photoswitches by modifying thermally stable stiff-stilbene skeleton

○Soseki Kurokawa[1], Keiichi Imato[1], Naoki Kaneda[1], Ichiro Imae[1], Yousuke Ooyama[1] (1. The Univ. of Hiroshima)

Japanese

[P4-2vn-18]

Persistent Room-Temperature Phosphorescence exhibited by organic compounds with triazine skeleton.

○Masaya Sugimoto[1], Daisuke Aoki[1], Tatsuo Taniguchi[1], Takashi Karatsu[1] (1. Chiba University)

Japanese

[P4-2vn-19]

Effect of crystals forming conglomerates on Persistent Room-Temperature Phosphorescence

○Kyoshiro Tanno[1], Daisuke Aoki[1], Tatsuo Taniguchi[1], Masami Sakamoto[1], Takashi Karatsu[1] (1. Chiba University)

Japanese

[P4-2vn-20]

Synthesis of Heterocyclic Compounds by Photocyclization of *N*-Substituted-*o*-alkynylaniline Derivatives

○Kan Wakamatsu[1], Risa Shirahama[1], Teruaki Nakamura[1], Yotaro Omae[1] (1. Okayama University of Science)

Japanese

[P4-2vn-21]

Internal Conversion as a Phonon-Emission/Absorption Process: Role of Vibronic Couplings and Energy Gap

○Tohru Sato[1,2], Wataru Ota[1,2], Motoyuki Uejima[3] (1. Fukui Institute for Fundamental Chemistry, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. MOLFEX, Inc.)

Japanese

[P4-2vn-22]

Oxidation reactions of phenanthrene derivatives using organic acridinium-type photo-redox catalyst

○Shou Yasui[1], Takeshi Kawase[1], Jun-ichi Nishida[1] (1. Grad. School. of Engi., Univ. of Hyogo)

Japanese

[P4-2vn-23]

Transient and Persistent One-electron σ-Bonded Radical Cations Generated by Photoinduced Electron Transfer

○Kanata Wada[1], Ryohei Takayasu[1], Takuya Ogaki[1], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ.)

Japanese

[P4-2vn-24]

Sodium salt of terphenyl caboxylate as an anode for Na-ion batteries were synthesized and investigated

○YUUKI KAMOCHI[1], Kanata Takahashi[1], Naoaki Yabuuchi[2], Makoto Miyasaka[1] (1. Tokyo Denki University, 2. Yokohama National University)

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Academic Program [Poster] | 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 5(理工スポーツホール [1階] アリーナ)

[P5-2vn] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Japanese

[P5-2vn-01]

Development of novel synthetic method for chiral phosphine-containing β-amino acid precursors through asymmetric conjugate addition reaction

○Kosei Miyake[1], Kazuki Fujita[1], Akane Iwamura[1], Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

Japanese

[P5-2vn-02]

Asymmetric Aza-Friedel-Crafts Reaction of 2-Naphthols and Imines Using Chiral Phosphoric Acid Ctalysts

○Tomoki Marui[1], Akira Yanagisawa[1] (1. Chiba University)

Japanese

[P5-2vn-03]

Highly Chemoselective Triflation of Phenols Using *N*-Trifluoromethanesulfonylimidazole

○Momoko Ishikawa[1], Ranmaru Terasawa[1], Honoka Jinda[1], Emi Ikebe[1], Yukiko Fujiyama[1], Tsubasa Hirata[1], Manabu Hatano[1], Junki Nitta[2], Takako Yamazaki[2], Ren Tomita[2], Katsuhiro Akiyama[2] (1. Kobe Pharmaceutical University, 2. Central Glass Co., Ltd.)

Japanese

[P5-2vn-04]

Development of stereoselective reactions using tertiary alkyl halides

○Naoki Tsuchiya[1], Takashi Nishikata[1] (1. The Univ. of Yamaguchi)

Japanese

[P5-2vn-05]

Study on Efficient Introduction of Silyl Protecting Groups into Borneol and Isoborneol as Secondary Alcohols

○Yoshikazu Hiraga[1,2], Koya Tayama[2], Mio Sugiura[2], Yuki Takahashi[2], Baohe Lyu[1], Ryukichi Takagi[3] (1. Graduate School of Science and Technology, Hiroshima Institute of Technology, 2. Hiroshima Institute of Technology, 3. Graduate School of Science, Hiroshima University)

English

[P5-2vn-06]

Selective Monooxidation of Symmetric Dialdehydes in Aqueous Media

Pullaiah Kattanguru[1], Ren Ogawa[1], Yutaro Suzuki[1], ○Satomi Niwayama[1] (1. Muroran Institute of Technology)

Japanese

[P5-2vn-07]

Gold-Catalyzed Tandem Allylation/Enyne Cycloisomerization of Propargyl Acetate with Allylsilanes

○Yoshikazu Horino[1], Shota Nakagawa[1], Nene Murata[1], Sota Akima[1] (1. Chitose Inst. Sci. Tech.)

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Japanese

[P5-2vn-08]

Transformation focused on the carbonyl groups of fluorinated benzocyclobutenones

○Jo Kashiwabuchi[1] (1. Gunma university)

Japanese

[P5-2vn-09]

Stereoselective Synthesis of (*Z*)-*anti*-Homoallylic Alcohols Using Palladium-Catalyzed Three-Component Reaction

○Ayumu Natsubori[1], Mizuki Akagawa[1], Yoshikazu Horino[1] (1. Chitose Inst. Sci. Tech.)

Japanese

[P5-2vn-10]

O-Alkylation of α-Ketoamides Suppressing the Hydride Reduction

○Maika Yasue[1], Ayaki Yamamoto[1], Isao Mizota[1] (1. Mie University)

Japanese

[P5-2vn-11]

Thiazolidine Amide Synthesis Utilizing Umpolung of α-Imino Amide

○Kotomi Kanda[1], Takehiro Shimizu[1], Isao Mizota[1] (1. Mie University)

English

[P5-2vn-12]

Synthesis of 5-spiroproline derivatives by organocatalytic enantioselective [3+2] cycloaddition between enals and isatinimines

○Qian Liu[1], Kazuaki Kudo[1] (1. The University of Tokyo)

Japanese

[P5-2vn-13]

Development of 1,4-oxazin-2-one Synthesis Utilizing Umpolung Reaction to α-Hydrazonoketone

○Nozomi Hoshiai[1], Keiji Oshima[1], Isao Mizota[1] (1. Mie University)

English

[P5-2vn-14]

Dynamic kinetic resolution of axially chiral heterobiaryl N-oxides via peptide catalyzed aldol reaction

○JIAQI TIAN[1], Kazuaki Kudo[1] (1. The University of Tokyo)

Japanese

[P5-2vn-15]

Quaternary Amino Ester Synthesis Utilizing Tandem Umpolung/Radical AdditionReaction of α-Iminoester

○Yuki Ito[1], Isao Mizota[1] (1. Mie University)

English

[P5-2vn-16]

Synthesis of α-chloro-β-ketoesters and chlorine-containing polyketides via decarboxylative condensation of chloromalonic acid half-esters

○Yihao Shi[1], Kazuaki Kudo[1] (1. The University of Tokyo)

Japanese

[P5-2vn-17]

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[Withdraw] Synthesis of Functionalized C_2 Symmetric Compounds with Dibenzosuberane Skeleton and Their Use in Organic Synthesis

○Yusei Minagawa[1], Takanori Shibata[1] (1. Waseda University)

Japanese

[P5-2vn-18]

Study on Alkoxylation of Alkyl Halide under External Electric Field

○Asato Gake[1], Gen Onodera[1], Hironobu Tahara[1], Taichi Otsuji[1], Tsutomu Fukuda[1], Masanari Kimura[1] (1. Nagasaki University)

Japanese

[P5-2vn-19]

Direct Synthesis of Thioamide from Ketones

○Ishin Tomiya[1], Kengo Hyodo[1] (1. Kindai University)

Japanese

[P5-2vn-20]

Synthesis of substituted cyclobutanones and application to *y*-aminobutyric acid esters.

○Yuhao Wu[1], Issin Tomiya[1], Kengo Hyodo[1] (1. Kindai University)

Japanese

[P5-2vn-21]

Development of rapid electrochemical thiol-ene click reaction in a microfluidic reactor

○Kakeru Yamamoto[1], Kenta Arai[1] (1. Tokai Univ.)

Japanese

[P5-2vn-22]

Green Manufacturing: Reaction Condition Optimization for the Pseudo-Steady Flow Synthesis of the Functional Group Evaluation Kit

○Tomoki Sugimura[1], Kohei Sato[1], Tetsuo Narumi[1], Nobuyuki Mase[1] (1. Shizuoka University)

Japanese

[P5-2vn-23]

Fine Bubble Organic Chemistry: Development of Atmospheric Pressure Gas-Liquid Phase Reactions of Highly Viscous Liquids Using a Microporous Method

○Houto MORITA[1], Hiroto SAKURAI[2], Kohei SATO[1], Tetsuo NARUMI[1], Nobuyuki MASE[1] (1. Shizuoka University, 2. Shizuoka University Graduate School of Integrated Science and Technology)

English

[P5-2vn-24]

Microwave Flow Chemistry: Estimation Dielectric Loss Tangent Using Machine Learning

○Azmi Aisi[1], Kohei Sato[1], Tetsuo Narumi[1], Nobuyuki Mase[1] (1. Shizuoka Univ.)

Japanese

[P5-2vn-25]

Hydrogen/deuterium exchange of acyl hydrogens in cyclodextrin D_2O solutions

○Takatoshi Kawaji[1], Yuua Nishikawa[1] (1. NIT, Wakayama College)

Japanese

[P5-2vn-26]

Single-process desalting of pyridine hydrochloride derivatives and water forbidden reactions using integrated flow reactors

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○Hiroki Soutome[1,2], Yusuke Kimuro[3], Yosuke Ashikari[2], Aiichiro Nagaki[2] (1. AGC Inc., 2. Hokkaido University, 3. Juzen Chemical Corp.)

Japanese

[P5-2vn-27]

PCBM Synthesis by using Flow Photoreactor

○Shuhei Sumino[1], Yuya Tanaka[2], Michihisa Murata[2], Fukashi Matsumoto[1], Toshiyuki Iwai[1], Takatoshi Ito[1] (1. ORIST, 2. Osaka Institute of Technology)

Japanese

[P5-2vn-28]

Exploring the application of Highly volatile organic compounds in flow reactions

○Kensuke Muta[1,2], Kazuhiro Okamoto[2], Aiichiro Nagaki[2] (1. Central Glass Co., Ltd., 2. The Univ. of Hokkaido)

Japanese

[P5-2vn-29]

Alkylation of β-dicarbonyl compounds by microwave irradiation in the presence of $NaHSO_4/SiO_2$

○Keisuke Kumada[1], Mamiko Hayakawa[1], Shinpei Suzuki[1], Tadashi Aoyama[1] (1. College of Science and Technonology, Nihon University)

Japanese

[P5-2vn-30]

Synthesis of Esters and Amids under Microwave Irradiation and Investigation of Their Reaction-Promoting Effects

○Riko Arai[1], Hirokazu Iida[1] (1. Kanto Gakuin University)

Japanese

[P5-2vn-31]

A simple synthesis of 4-phenylbutanoic acid and related compounds using microwave irradiation

○Akane Takahashi[1], Mika Sakai[1], Ai Tsudo[1], Hirokazu Iida[1] (1. Kanto Gakuin Univ.)

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Academic Program [Poster] | 17. Biofunctional Chemistry, Biotechnology：Poster

Tue. Mar 19, 2024 1:00 PM - 2:30 PM JST | Tue. Mar 19, 2024 4:00 AM - 5:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-2pm] 17. Biofunctional Chemistry, Biotechnology

Japanese

[P2-2pm-01]

Study on optimization of synthesis of a cyclodextrin dimer for the practical application of dual antidote against carbon monoxide and cyanide poisoning.

○Takashi Onishi[1], Atsuki Nakagami[1], Kitagishi Hiroaki[1] (1. Doshisha university)

Japanese

[P2-2pm-02]

Coordination behavior of sulfide ions to porphyrin iron complexes in aqueous solution and cellular environment

○Riria Honda[1], Atsuki Nakagami[1], Hiroaki Kitagishi[1] (1. Doshisha University)

Japanese

[P2-2pm-03]

Synthesis and secondary Structure of collagen model peptides incorporating N-terminal His-tag

○Raraho Kanda[1] (1. Ryukoku University)

Japanese

[P2-2pm-04]

Development of a calcium ion concetration-resposive imaging probe for intracellular redox behavior

○Yuhei Sato[1], Rumi Mikami[1], Kenta Arai[1] (1. Tokai Univ.)

Japanese

[P2-2pm-05]

Modification of golg nanorods with peptides containing cell recognition sequence and evaluation of their anti-cancer drug loading performance

○Conoha Yamaoka[1], Takahito imai[1], Masahiro asano[1], Kin-ya Tomizaki[1] (1. Ryukoku University Faculty of Advanced and Technology)

Japanese

[P2-2pm-06]

Indole-3-butyric Acid Derivative (JAX-44) Promoting Lateral Root Elongation

○Ami Watanabe[1], Kazuki Arai, Haruka Yamamoto, Takeshi Yamada[2], Kota Ibe[1], Sentaro Okamoto[1] (1. Kanagawa University , 2. Kobe Pharmaceutical University)

Japanese

[P2-2pm-07]

Development of novel fluorescent DNA probes containing bis-pyrene unit

○Yuta Kanezawa[1], Saika Kobayashi, Katsuhiko Matsumoto, Yoshio Saito[1] (1. Nihon University)

Japanese

[P2-2pm-08]

Design and studies of o-keto benzaldehyde derivatives as a probe for efficient fluorescent lysine modification

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○Guosheng Gao[1], Mariko Aso[1] (1. Kyushu University)

Japanese

[P2-2pm-09]

Fluorescence properties and excited-state calculations of amino group-modified GFP dyes

○Takashi Kanamori[1], Yuki Sadai[1], Kenji Hida[1], Hiroya Asami[2], Hideya Yuasa[1] (1. Tokyo Institute of Technology, 2. Gakushuin University)

English

[P2-2pm-10]

Toward the measurement of micellar dipole potentials by voltage sensitive dyes

○Minami Nakada[1], Makoto Roppongi[2], Toru Oba[3] (1. Department of Material and Environmental Chemistry, Utsunomiya University, 2. Center for Instrumental Analysis, Utsunomiya University, 3. Department of Materials and Environmental Chemistry, Graduate School of Utsunomiya University)

Japanese

[P2-2pm-11]

Discovery and utilization of pseudo-luciferase activities in non-luminescent proteins

○Ryo Nishihara[1,2], Ryoji Kurita[1,3] (1. National Institute of Advanced Industrial Science and Technology, 2. JST PREST, 3. University of Tsukuba)

English

[P2-2pm-12]

Synthesis and photophysical properties of novel solvatochromic fluorescent dyes with quinolone-based molecular wires

○Satoshi Saito[1], Makoto Roppongi[1], Toru Oba[1] (1. The Univ. of Utsunomiya)

Japanese

[P2-2pm-13]

Control of molecular assembly of platinum(II) complex bearing thymine subsitutents by selective hydrogen bonding with adenine oligomer

○Shun Fujii[1], Manabu Nakaya[1] (1. Graduate school of Science Josai University)

Japanese

[P2-2pm-14]

Synthesis and characterization of a mitochondria transfer signal peptide derivative.

○Soshin Saita[1], Kin-ya Tomizaki[1] (1. Ryukoku University Faculty of Advanced Science and Technology)

Japanese

[P2-2pm-15]

Synthesis and Properties of Schiff Base-Modified Chlorophyll Derivatives

○Hodaka Imose[1], Tomohiro Miyatake[1] (1. Ryukoku University)

Japanese

[P2-2pm-16]

Synthesis and evaluation of membrane-localizable gefitinib ligands targeting the epidermal growth factor receptor

○Keishi Mitamura[1], Keita Tsutsui[2], Masaru Yoshikawa[2], Shinya Tsukiji[2] (1. Fac. of Eng., Nagoya Inst. of Tech., 2. Grad. Sch. of Eng. Nagoya Inst. of Tech.)

Japanese

[P2-2pm-17]

Development of a novel environmentally responsive pterin-type fluorescent probes

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○Saki Nakai[1], Yasushi Kawai[1], Tetsuya Takemoto[1], Muyon Asami[1] (1. Nagahama Institute of Bio-Science and Technology)

Japanese

[P2-2pm-18]

Photodynamic effect of coumaryl alcohol derivative-modified 5-aminolevulinic acid

○Hideki Azuma[1], Kosuke Morita[1], Rin Fukushima[1], Takeshi Nagasaki[1] (1. Osaka Metropolitan Univ.)

Japanese

[P2-2pm-19]

Preparation of plasmonic chip sensor chip by visible light of photo-responsible molecule

○Kyohei Asano[1], Syohei Horio[1], Yasunori Nawa[1], Mutsuo Tanaka[2], Keiko Twa[1] (1. Kwansei Gakuin University, 2. Saitama Institute of Technology)

Japanese

[P2-2pm-20]

Effect of linker length on conjugation-extended pterin-type fluorescence probes

○Haruka Nishitani[1], Yasushi Kawai[1] (1. Nagahama Institute of Bio-Science and Technology)

English

[P2-2pm-21]

Development of photo-triggered DNA double-strand invasion method targeting long chain oligonucleotides oriented to genome manipulation

○ZUMILA HAILILI[1], JUNLING MO[1], Fujimoto Kenzo[1] (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-22]

Development of crosslinking to purine bases in DNA accelerated by reversible DNA photo-crosslinking

○Junling Mo[1], Rei Hirahara[1], kenzo Fujimoto[1] (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-23]

Synthesis and properties of oligonucleotides conjugated with sugar ligands for selective cell delivery

○Daiki Shimamura[1], Remi Arie[1], Shuri Kaneyama[2], Aya Miyauchi[2], Koji Seio[1], Yoshiaki Masaki[1] (1. Sch. Life Sci. Tech., Tokyo Tech., 2. Showa Univ.)

Japanese

[P2-2pm-24]

Photo-control of intracellular RNA behavior using artificial nucleic acids with photo-crosslinking

○QINGYUAN HUANG[1] (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-25]

Development of novel DNA photo-crosslinking that enables switching of crosslink sites by peripheral sequences.

○touya odai[1], junling MO, kenzo fujimoto (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-26]

Effect of polyvinyl alcohol on G-quadruplex formation

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○Takahiro Nakamura[1], Ryoko Uda[1] (1. National Institute of Technology (KOSEN), Nara College)

Japanese

[P2-2pm-27]

Synthesis of guanosine tetra phosphate analogue has photoreactive biotinylation linker.

○Yudai Suzuki[1], Yukine Suda[1], Ayano Iwake[1], Yoshiaki Masaki[1], Kohji Seio[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese

[P2-2pm-28]

Structures of DNAs having diphenylanthracene- or pyrene-modified deoxycytidine

○Ryosuke Izumi[1], Aoi Okamoto[1], Mitsunobu Nakamura[1], Tadao Takada[1] (1. University of Hyogo)

Japanese

[P2-2pm-29]

Structures of DNAs having pyrene-modified deoxyguanosine and deoxyadenosine

○yuto nakajima[1], yojiro takiguti[1], mitunobu nakamura[1], tadao takada[1] (1. University of Hyogo)

Japanese

[P2-2pm-30]

Fluorescence properties of C5-heteroaryl-pyrimidine nucleosides and post-synthetic modification of DNA

Miu Hara[1], Keita Kudo[1], Kie Sakurai[2], Wakaba Yoshizawa[2], ○Hiroaki Ozaki[1] (1. Graduate School of Science and Technology, Gunma University, 2. School of Science and Technology, Gunma University)

Japanese

[P2-2pm-31]

Development of RNA-binding small molecules that recognize specific nucleobase based on hydrogen bonding

○Kosuke Tsuzuki[1,2], Kazumitsu Onizuka[1,2], Ryosuke Nagasawa[1,2], Emi Miyashita[3], Kaoru Richard Komatsu[3], Hirohide Saito[3], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku University, 2. Department of Chemistry, Tohoku University, 3. CiRA, Kyoto University)

Japanese

[P2-2pm-32]

Increased sensitivity of HCR-based nucleic acid detection using the concentration effect of microbeads

Yu Yasuhara[1], ○Takashi Sakamoto[1] (1. Wakayama Univ.)

Japanese

[P2-2pm-33]

Synthesis of novel nucleopeptides with oxime bonds

○Yukino Fukushima[1], Toda Hiroki[1], Moriguchi tomohisa[1] (1. Gunm University)

Japanese

[P2-2pm-34]

Development of a photothermal-induced drug release system using DNA-modified gold nanoparticles

○Kento Noguchi[1], Takuya Yui[1], Mitsunobu Nakamura[1], Tadao Takada[1] (1. University of Hyogo)

Japanese

[P2-2pm-35]

Synthesis and properties of oligonucleotides having 7-pyridyl-7-deazadeoxyguanosine

Kento Miyaji[1], ○Narumi Habu[1], Kohji Seio[1], Yoshiaki Masaki[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

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Japanese

[P2-2pm-36]

Synthesis of novel diphenylsilylpyrene derivatives directed to fluorescent labeling of DNA

○Mayuko Hoshiba[1], Tomohisa Moriguchi[1] (1. The Univ. of Gunma)

Japanese

[P2-2pm-37]

Effect of introduction of guanidino group on complex formation of G-quadruplex and thioflavin T derivative

○Yuuka Shiratori[1], Tomoaki Nakamura[2], Tomoko Wariishi[2], Yuka Kataoka[2], Masayasu Kuwahara[2] (1. Nihon University, 2. Grad. Sch. Integrated Basic Sci, Nihon Univ.)

Japanese

[P2-2pm-38]

Effect of tetraphenylethylene derivative-modified DNA on the stability of G-quadruplexes

○MAAYA KIYOSE[1] (1. TOKYO UNIVERSITY OF TECHNOLOGY GRADUATE SCHOOL)

Japanese

[P2-2pm-39]

Molecular Dynamics Study on the Difference in Molecular Fluctuations between Wild Type and G93A Mutant of Superoxide Dismutase 1

○Kazuaki Fukushima[1], Noriko Fujiwara[1] (1. Hyogo Medical University)

Japanese

[P2-2pm-40]

Development of Oxidative Protein Folding Catalysts Involving Chaperone-like Activity

○Yuki Iwata[1], Yuya Nishizawa[1], Kenta Arai[1] (1. Tokai Univ.)

Japanese

[P2-2pm-41]

Chemical synthesis of new long-acting insulin via an easily modifiable insulin as a key precursor.

○Rikana Takahashi[1], Kenta Arai[1] (1. Tokai Univ.)

English

[P2-2pm-42]

The effect of sorbitol addition on the asymmetric reduction of ketones using cyanobacterium *Synechocystis* sp. PCC 6803

○Satsuki Fukui[1], Hideo Kojima[1], Satomi Takeda[1], Rio Yamanaka[2] (1. Osaka Metropolitan University, 2. Himeji Dokkyo University)

English

[P2-2pm-43]

Lipase-catalyzed alkoxycarbonylation in the presence of a solid acid catalyst

○Yuto Yamamoto[1], Hideo Kojima[1] (1. Osaka Metropolitan University)

English

[P2-2pm-44]

Lipase-catalyzed alkoxycarbonylation in the deep eutectic solvent/water system

○Taito Nagamoto[1], Yuto Yamamoto[1], Hideo Kojima[1] (1. Osaka Metropolitan Univercity)

English

[P2-2pm-45]

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Asymmetric reduction of keto esters using *Pisum sativum* as a whole-cell biocatalyst

○Ryota Shimamoto[1], Yuya Machi[1], Hideo Kojima[1], Satomi Takeda[1] (1. Osaka Metropolitan University)

English

[P2-2pm-46]

Biotransformation of cyclohexane to ε-caprolactone using *Arabidopsis thaliana* as a whole-cell biocatalyst

○Yuya Machi[1], Jina Yoshida[1], Hideo Kojima[1], Satomi Takeda[1] (1. Osaka Metropolitan University)

Japanese

[P2-2pm-47]

In vitro selection of streptavidin-binding cyclic peptide aptamers by cDNA display

○Daiki Katakura[1] (1. Saitama University)

Japanese

[P2-2pm-48]

Enzymatic metabolic reactions compartmentalized in a liposome with a skeletal DNA nanostructure

○Futa Komatsubara[1,2], Eiji Nakata[1], Lin Peng[1], Hiroaki Konishi[1,2], Takashi Morii[1] (1. Institute of Advanced Energy, Kyoto University, 2. Graduate School of Energy Science, Kyoto University)

Japanese

[P2-2pm-49]

Prediction and Validation of Proline-containing Tripeptides with Angiotensin I-converting Enzyme Inhibitory Activity

○Mizuho Tanaka[1], Yuki Fujimoto[1], Toshiya Hatakenaka[1,2], Tamaki Kato[1] (1. Kyushu Institute of Technology, 2. Vital Resources Applied Laboratory)

Japanese

[P2-2pm-50]

Functional Regulation of Oxidative Enzymes Through On/Off Switching of Electron Transfer Chain

○Satoshi Hasegawa[1], Ryota Kato[1], Daisuke Umeno[1] (1. Waseda University)

Japanese

[P2-2pm-51]

Protein Folding Promotion Using Redox-Active Liquid-Liquid Phase Separation Materials

○Yukino Yamashita[1], Takahiro Muraoka[1,2] (1. Grad. Sch. of Eng. Tokyo Univ. of Agri. and Tech., 2. KISTEC)

English

[P2-2pm-52]

Improved Degradation of Polyethylene Terephthalate Film by Cutinase Using 1-Dodecyl-1*H*-1,2,3-Triazole-4-Carbaldehyde Surfactant.

○JOEL MUYOMBA[1], MD SADIKUR RAHMAN SHUVO[1], AKIRA ONODA[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

Japanese

[P2-2pm-53]

Preparation and properties of chymotrypsin chemically modified with benzoxaborole

○Ryoga Tsuchiya[1], Yamato Yoshida[1], Shin Ono[1] (1. Kanazawa Institute of Technology)

Japanese

[P2-2pm-54]

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Detection of TEV protease by pore blockage in Outer Membrane Protein-G Nanopore mutation

○Haruka Suzuki[1], Tosiyuki Tosaka[1], Kouki Kamiya[1] (1. Grad. Sch. Sci. Tec., Gunma Univ.)

Japanese

[P2-2pm-55]

Enzyme integration by YK peptide tag fusion in E. coli and its effect on 3-hydroxybutyrate synthesis.

○Bungo Kozasa[1], Nakayama Sae[1], Masahiro Hashimoto[1], Takayuki Miki[1,2], Hisakazu Mihara[1] (1. School of Life Science and Technology, Tokyo Institute of Technology , 2. School of Engineering,The University of Tokyo)

Japanese

[P2-2pm-56]

Examination of proximity and reaction efficiency of enzymes by external stimulation

○Momoka Takazawa[1], Koki Kamiya[2] (1. School of Science and Technology, Gunma Univ., 2. Graduate School of Science and Technology, Gunma Univ.)

Japanese

[P2-2pm-57]

Investigation of crystallization of crystallized protein expressed using cell-free protein synthesis

○Yume Kosuge[1], Koki Kamiya[2] (1. School of Science and Technology, Gunma Univ., 2. Graduate School of Science and Rechnology, Gunma Univ.)

English

[P2-2pm-58]

Synthesis of self-assembling peptides conjugated with integrin-targeting peptides as biomaterials for cancer cell culture.

○MAN LI[1], Hisakazu Mihara[1], Hiroshi Tsutsumi[1] (1. Tokyo Institute of Technology, School of Life Science and Technology)

English

[P2-2pm-59]

Enhancing antitumor efficacy by glutathione-depleted nanophotosensitizers with photo-triggered strong hyperthermia and ROS generation

○Wen-Hsuan Chiang[1], Yu-Hsin Chen[1], I-Ju Liu[1] (1. National Chung Hsing University)

Japanese

[P2-2pm-60]

Synthesis of Gold Nanorods Modified with Hepatocellular Carcinoma Targeting Sequence Peptides and Verification of Their Photothermal Effects

○Shoya Fujimoto[1], Takahito Imai[1], Masahiro Asano[1], Masayuki Yamazaki[1], Kin-ya Tomizaki[1] (1. Ryukoku University)

English

[P2-2pm-61]

Wireless charging-mediated angiogenesis and nerve repair by adaptable microporous hydrogels

○Shang-Hsiu Hu[1] (1. National Tsing Hua University)

Japanese

[P2-2pm-62]

Intracellular behavior of peptide heterodimers labeled with FRET probes

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○Karen Tanaka[1], Masayuki Yamasaki[1], Kin-ya Tomizaki[1] (1. Ryukoku University)

Japanese

[P2-2pm-63]

RNA encapsulation and photo-responsive release by caged coacervates based on liquid-liquid phase separation

○Akinari Bando[1], Kazunori Watanabe[1], Takashi Ohtsuki[1], Mizuki Kitamatsu[2], Yuuki Kanazaki[2] (1. Okayama University, 2. Kindai University)

Japanese

[P2-2pm-64]

Synthesis of Amphiphilic Imidazolyl Porphyrinatozinc Having a Fatty Amide Group, and Their Introduction to Lipid Bilayer Membrane.

○Miki Oono[1], Kazuma Yasuhara[2], Akiharu Satake[1] (1. Tokyo University of Science, 2. NARA INSITUTE of SCIENCE and TECHNOLOGY)

Japanese

[P2-2pm-65]

Synthesis of Imidazolyl Porphyrinatozinc Having a Maleimide Group Linked with Different Methylene Groups, and Their Self-organization in Lipid Bilayer Membrane.

○Yohei Yanase[1], Kazuma Yasuhara[2], Akiharu Satake[1] (1. Tokyo University of Science, 2. NNARA INSTITUTE of SCIENCE and TECKNOLOGY)

Japanese

[P2-2pm-66]

Monitoring ERK activity in cancer cells following photothermal stimulation

○Kenji Omori[1] (1. Graduate School / Faculty of Information Science and Technology, Hokkaido University)

Japanese

[P2-2pm-67]

Photoinduced cytotoxicity of diarylethene based on photoswitching isomerization

○Norikazu Maruyama[1], Kimio Sumaru[2], Kana Morishita[2], Kingo Uchida[1] (1. Ryukoku University, 2. National Institute of Advanced Industrial Science and Technology)

Japanese

[P2-2pm-68]

A microbail BOD biosensor by a FRET based intercellular ATP measurment

○Yuto Kanno[1], Yuta Tateno[1], Takuo Akimoto[1] (1. Tokyo University of Technology)

Japanese

[P2-2pm-69]

Detection of landmines using FRET based Microbial biosensor

○Taiga Yoshizawa[1], Kai Nishimura[1], Suzuna Nakajima[1], Takuo Akimoto[1] (1. Tokyo University of Technology)

Japanese

[P2-2pm-70]

Bacterial cellulose-based hydrogels carrying sulfated galactosides as naked-eye monitoring systems of carbohydrate-carbohydrate interactions

○Jiayu Dong[1], Teruaki Hasegawa[1] (1. Toyo Univ.)

Japanese

[P2-2pm-71]

Synthetic studies of lipid-peptide antigen conjugation for targeting multiple factors on antigen-presenting cells

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○Shunya Kikuchi[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Keio University)

Japanese

[P2-2pm-72]

Fusogenic liposomes containing pH-responsive malachite green

○Kaede Nikaido[1], Ryoko Uda[1] (1. National Institute of Technology (KOSEN), Nara College)

Japanese

[P2-2pm-73]

Protein pairs which change FRET based fluorescent color for an intercellular pH indicator.

○Shuzo Homma[1], Sohki Miyazaki[1], Takuo Akimoto[1] (1. Tokyo University of Technology)

Japanese

[P2-2pm-74]

Synthesis and molecular properties of gossypols having multiple carbohydrates

○Kotomi Ishikawa[1], Teruaki Hasegawa[1] (1. Toyo Univ.)

Japanese

[P2-2pm-75]

Luminescence of a Firefly luciferin on the plasmonic chip

○Hitomi Yamanaka[1], Yasunori Nawa[1], Keiko Tawa[1] (1. Kwansei Gakuin University)

Japanese

[P2-2pm-76]

Development of polymeric micelles containing photosensitizer for deep tissue photodynamic therapy

○Hayato Yao[1], Yohiyuki Uruma[1], Batbayar Altannavch[1], Kunishige Onuma[2], Masahiro Inoue[2], Chung Yu Lin[3], Ping Shan Lai[3] (1. NIT(KOSEN), Yonago College, 2. The Univ. of Kyoto, 3. NCHU)

Japanese

[P2-2pm-77]

Microbial degradation process of biodegradable polymer directly monitored by QCM andElectrochemistry

○Maika Yoshimura[1], Takuma Otsuki[1], Yasumasa Takenaka[2], Tomohiro Hiraishi[2], Hideki Abe[2], Noriyuki Asakura[1,2] (1. Tokyo Institute of Technology, 2. RIKEN)

Japanese

[P2-2pm-78]

Fundamental investigation and understanding of characteristics from engineering aspects relating to the production of valuable material through plants

Akito Matsushima[1], ○Tsubasa Hirabayashi[1], Mizuki Saegusa[1], Hiroki Muramatsu[1], Sho Yoshida[1], Naoko Nishida[1] (1. Chiyoda Corporation)

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Academic Program [Poster] | 20. Materials Chemistry -Basic and Application-：Poster

Tue. Mar 19, 2024 10:00 AM - 11:30 AM JST | Tue. Mar 19, 2024 1:00 AM - 2:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-2am] 20. Materials Chemistry -Basic and Application-

Japanese

[P1-2am-01]

Heterogeneous photoreaction in photomechanical crystals: evaluation of a cooperative effect by simultaneous tracking of reaction progress and crystal shape

○Shin Ozamoto[1], Hikaru Sotome[1], Daichi Kitagawa[2], Seiya Kobatake[2], Hiroshi Miyasaka[1] (1. Graduate School of Engineering Science, Osaka University, 2. Grad. Sch. of Eng., Osaka Metropolitan Univ.)

English

[P1-2am-02]

Luminescent Properties of Room-Temperature Liquid-Crystalline Trinuclear Gold(I) Complex

○Abhilash Sahu[1], Tamon Nakao[1], Kohsuke Matsumoto[1], Ganesan Prabusankar[2], Osamu Tsutsumi[1] (1. Ritsumeikan University , 2. Indian Institute of Technology Hyderabad)

Japanese

[P1-2am-03]

Synthesis of a methacryl monomer having a 2-aminopyridyl group and its application to photo-adhesive materials

○Hinata Okada[1], Masahiro Furutani[1] (1. Natioal Institute of Technology, Fukui College)

Japanese

[P1-2am-04]

Chemical analysis of solid components separated from mucilage of roots of Tororo-aoi

Makoto Kono[1], ○Masahiro Furutani[1], Chika Shimada[1] (1. Natioal Institute of Technology, Fukui College)

Japanese

[P1-2am-05]

Synthesis of a methacryl monomer having a hydroxypyridyl group and its application to photo-adhesive materials

○Miku Matsui[1], Masahiro Furutani[1] (1. Natioal Institute of Technology, Fukui College)

Japanese

[P1-2am-06]

Development of dissimilar bonding technology using sheet material.

○Yuya Nakazawa[1], Kenji Harada[1], Masaki Ozaki[1], Atsushi Fumikura[1] (1. Sumitomo Osaka Cement Co.,Ltd.)

Japanese

[P1-2am-07]

Preparation and Characterization of Transparent Alicyclic Polyimide Aerogel

○Masaki Negoro[1], Kazuyoshi Kanamori[1] (1. Kyoto University)

Japanese

[P1-2am-08]

Degradation factors due to environmental conditions of giant surface potential of vacuum-deposited diarylethene films

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○Tsuyoshi Tsujioka[1], Junwei Shen[2], Shinichiro Nakamura[2] (1. Osaka Kyoiku University, 2. Kumamoto University)

Japanese

[P1-2am-09]

Development of Molecular Crystals of Platinum Complexes Equipped with Substituted Heteroaromatic Groups

○Rintaro Ishikawa[1], Tomohiro Seki[1] (1. Department of Chemistry, Faculty of Science, Shizuoka University)

Japanese

[P1-2am-10]

Synthesis and Aggregation-Induced Emission Properties of Dibenzoylmethanato Boron Difluoride Complexes with an Alkyl Group at the α-position

○Kazunori Ichihara[1], Haruto Koide[1], Naoto Miyasaka[1], Keita Makabe[1], Kotaro Moriya[1], Kazumitsu Minemura[1], yushi Fujimoto[3], Fuyuki Ito[2,3] (1. Suwaseiryo High school, 2. Inst. of Edu., Shinshu Univ, 3. Grad. Sch. of Sci. and Tech., Shinshu Univ)

Japanese

[P1-2am-11]

Development of Stimuli-Responsive Molecular Crystals of Benzoselenophene Platinum Complex

○Akihito Yano[1], Tomohiro Seki[1] (1. Department of Chemistry, Faculty of Science, Shizuoka University)

Japanese

[P1-2am-12]

Fabrication of Thermoelectric Films Containing π-Conjugated Nickel Complexes with Vinylthiophene Units

○Iku Miyatake[1], Tomoya Yaoita[1], Devon Aditya Jobs[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese

[P1-2am-13]

Synthesis and Properties of Novel D–π–A Type Molecules Bearing Bridged Bithiophene π-Spacers

○Miyu Ueda[1], Ryo Nagayama[2], Naoya Suzuki[1,2], Shintaro Kodama[1,2], Takeshi Maeda[1,2], Shigeyuki Yagi[1,2] (1. Graduate School of Engineering, Osaka Metropolitan University, 2. College of Engineering, Osaka Prefecture University)

Japanese

[P1-2am-14]

Evaluation of film materials using TEMPO oxidized CNF

○Yusaku Koitabashi[1], Yuji Kimura[1] (1. Nihon University)

Japanese

[P1-2am-15]

Synthesis and Photo-degradation behavior of polyphthalaldehydes with oxime ether terminals

○Hirokazu Hayashi[1], Hideki Tachi[1], Kanji Suyama[2] (1. Osaka Research Institute of industrial Science and technology, 2. Osaka Metropolitan University)

Japanese

[P1-2am-16]

Gas separation property of MOF801-PDMS composite membranes fabricated by in situ synthesis of MOF in gel under various condition.

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○Takara Nishikawa[1], Takuya Kurihara[1], Yasuhiro Shigeta[1], Shogo Amemori[1], Tomonori Ida[1], Motohiro Mizuno[1] (1. Kanazawa Universuty)

Japanese

[P1-2am-17]

Imaging X-ray photoelectron analysis of polyelectrolyte multilayers deposited on polyethylene terephthalate filaments

○Ginga Watanabe[1], Aoi Yoshimitsu[1], Shota Yasuda[1], Toyoaki Hirata[1], Kenji Hisada[1] (1. University of Fukui)

Japanese

[P1-2am-18]

Synthesis and characterization of PAMAM dendrimer/water-soluble polymer membranes for CO_2 separation

○Keisuke Serizawa[1], Yuji Kimura[1] (1. Nihon University)

Japanese

[P1-2am-19]

Accelerated aging test of polypropylene material used in ankle-foot orthosis

○Yoshihiro Mihara[1], Shin Murahara[1], Toshiaki Horiuchi[1] (1. Hokkaido Univ. of Science)

Japanese

[P1-2am-20]

Preparation and properties evaluation of solid acid catalyst on cedar

○Yui Igaki[1], Takumi Akinaga[1], Ryuki Ikeda[1], Yuko Shikami[2], Toshiyuki Miyauchi[2] (1. Gradute of Chubu University, 2. Chubu University)

Japanese

[P1-2am-21]

Evaluation of Optical Properties in Water Soluble Lanthanide Complex Nanoparticles

○Shunsuke Kobashi[1], Yoshinori Okayasu[1], Yuki Nagai[1], Yoichi Kobayshi[1] (1. Ritsumeikan University)

Japanese

[P1-2am-22]

Investigation of chromism and molecular orientation of aromatic amine intercalated between layers of tetrasilicicfluormica

○Reira Kinoshita[1], Shin'ichi Ishimaru[1] (1. Tokyo Denki University)

Japanese

[P1-2am-23]

Fabrication of Yellow Luminescent Dy Hydroxide Nanoparticle-Based Composite Films

○Hidetoshi Miyazaki[1], Wataru Kato[1] (1. Shimane University)

Japanese

[P1-2am-24]

Development of slow-release material of corrosion inhibitor for plating film by the intercalation into layered double hydroxide

○Junna Taki[1], Daiyu Kodama[2], Yoshiumi Kohno[3] (1. Graduate School of Engineering, Shizuoka University , 2. Kamiya Riken Co., 3. School of Engineering, Shizuoka University)

Japanese

[P1-2am-25]

Chlorophyll/organo-modified clay composites as a stable green colorant

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○Asuka Ueda[1], Yoshiumi Kohno[2], Masashi Shibata[3], Ryo Watanabe[2], Choji Fukuhara[2] (1. Graduate School of Engineering, Shizuoka University , 2. School of Engineering, Shizuoka University, 3. School of Biotechnology, Tokyo University of Technology)

Japanese

[P1-2am-26]

Introduction of carboxyl group to single-molecule magnets and construction of thin film using air-liquid interface

○Miki Yamada[1], Akane Mizoguchi, Yoji Horii, Takashi Kajiwara (1. Nara Women's University)

Japanese

[P1-2am-27]

Preparation of Au nanocubes supported on magnetic Fe_3O_4 and its catalytic performance of alcohol oxidation reaction

○Mutsumi Nagafune[1], Riko Kawahara[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P1-2am-28]

Preparation of hemispherical gold nanoflowers supported on cerium oxide for alcohol oxidation reaction

○Yuta Jino[1], Asuka Kasuga[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P1-2am-29]

Improved Electrochromic Properties and Addition of Layered Inorganic-imidazoline Covalently Bonded Hybrid for Ru(II)-based Metallo-supramolecular Polymer

○Kazuko Fujii[1], Dines Chandra Santra[1], Manas Kumar Bera[1], Kazuhiko Sakata[1], Takatsugu Wakahara[1], Ritsuko Nagahata[2], Masayoshi Higuchi[1] (1. National Institute for Materials Science, 2. National Institute for Advanced Industrial Science and Technology)

Japanese

[P1-2am-30]

Intercalation of gemini quaternary ammonium into zirconium phosphate

○Hiroaki Katsuzaki[1], Takeru Kasuga[1], Takayuki Tsukegi[1], Osamu Yoshimura[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-2am-31]

Preparation of concave gold nanorods supported alumina for alcohol oxidation reaction

○Kousuke Kinoshita[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P1-2am-32]

Formation of Metal Oxide Multilayer for Optic Materials by Electrochemical Depositions

○Mitsuru Watanabe[1], Yuro Saegusa[2], Naoaki Ito[2], Hiroyuki Enomoto[2,3], Seiji Watase[1] (1. Osaka Research Institute of Industrial Science and Technology, 2. Osaka Electro-Commun. Univ., 3. Grad. Sch. of Eng., Osaka Electro-Commun. Univ.)

Japanese

[P1-2am-33]

Study of evaluation method for the mechano-bactericidal effect in water

○Satoshi Toba[1,2], Ryo Yamano[1,2], Yukari Miyazaki[2], Nobuaki Negishi[2], Naoko Kurosaki[1] (1. Chiba Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology)

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Japanese

[P1-2am-34]

Dynamic deformation of three-dimensionally microfabricated temperature-responsive hydrogels

○Shunsuke Nagahama[1,2] (1. Kyoto University of Advanced Science, 2. Waseda University)

Japanese

[P1-2am-35]

Separation and analysis of volatile sulfur compounds using disulfide compounds

○Shuta Miura[1], Yasuko Yamada Maruo[1] (1. Grad. Sch. Eng, Tohoku. Inst. Tech.)

Japanese

[P1-2am-36]

Effect of substrates on an acetone detection using porous material-substrate sensors

○Kaito Murayama[1], Yasuko Yamada Maruo[1], Sei Sakano[2] (1. Grad.Sch.Eng Tohoku Inst Tech, 2. Tohoku Inst Tech)

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Academic Program [Poster] | 22. Resources Utilization Chemistry, Environmental and Green Chemistry：Poster

Tue. Mar 19, 2024 10:00 AM - 11:30 AM JST | Tue. Mar 19, 2024 1:00 AM - 2:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-2am] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Japanese

[P2-2am-01]

Synthesis of sulfated cellulose pulp with a swollen fiber structure and application to completely dispersed cellulose nanofibers

○Ayato Nishimura[1], Sonoka Otsuka[1] (1. Marusumi Paper Co., Ltd.)

Japanese

[P2-2am-02]

Development and evaluation of water-based paint for wood using cellulose nano fiber and ultraviolet absorber

○Shunpei Kuma[1], Yuki Taguri[1], Keiji Hoaki[1], Masayuki Yano[1] (1. Industrial Technology Center of Saga)

Japanese

[P2-2am-03]

Effect of calcium salt additives on the crystal phase of calcined calcium phytate

○Kazuki Maeda[1], Yoshiki Aoto[1], Satoru Dohshi[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P2-2am-04]

Preparation of transparent sulfated pulp desperation

○Sakura Morimitsu[1], Ayato Nishimura[1] (1. Marusumi Paper Co., Ltd.)

Japanese

[P2-2am-05]

Research on the development of an efficient degradation method for lignin and its application

○Tsubasa Kojima[1], Yoshiyuki Uruma[1], Tomohiro Yamada[2], Hirofumi Maekawa[2], Matsumi Doe[3], Kan Wakamatsu[4] (1. National Institute of Technology, Yonago College., 2. Nagaoka University of Technology, 3. Osaka Metropolitan University., 4. Okayama University of Science)

Japanese

[P2-2am-06]

Antibacterial activity of Polyethylene Glycol (PEG)-Modified Lignin

○Akane Sakaguchi-Mikami[1], Miku Takagi[1], Nagisa Hara[1], Takashi Yamashita[1] (1. Tokyo Univ. of Technology)

Japanese

[P2-2am-07]

Mechanical properties of network polymers based on epoxidized marine oils and preparation of bio-based composite

○Yohtaro Inoue[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P2-2am-08]

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Synthesis of MOFs using various metal ions with Azobenzene-4,4'-dicarboxylic acid ligands.

○Teppei Kagaya[1], Shigeki Furukawa[1] (1. College of Industrial Technology, Nihon University)

Japanese

[P2-2am-09]

Development of the detection method of pathogenic viruses in the environment water and its application

○Yuzu Ueki[1], Takeji Takamura[1] (1. Kanagawa Institute of Technology)

Japanese

[P2-2am-10]

Preparation of supported Ni catalysts using carbon nanotubes as supports and the investigation of their permanence in reduction reactions

○Yuika Aoki[1], Naoki Toyama[1], Hiroe Kimura[2], Norifumi Terui[2], Shigeki Furukawa[1] (1. Nihon University, 2. National Institute of Technology, Ichinoseki College)

Japanese

[P2-2am-11]

Synthesis of silica hollow spheres supported on transition metal catalysts and their reduction of *p*-nitrophenol

○Maki Ueshima[1], Kenzo Deguchi[2], Shinobu Ohki[2], Yuuki Mogami[2], Naoki Toyama[1], Shigeki Furukawa[1] (1. Nihon University, 2. National Institute for Materials Science)

Japanese

[P2-2am-12]

Capture of low concentration CO2 by using silica with amino groups

○Liao Hansheng[1], YAMAZOE SEIJI[1], KIKKAWA SOUICHI[1] (1. Tokyo Metropolitan University)

Japanese

[P2-2am-13]

Highly efficient capture and release system of low-concentration carbon dioxide using solid-liquid phase separation.

○Li Xuanbing[1], CAO FURONG[1], Souichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P2-2am-14]

Analyses of extracted compounds from bottle caps with organic solvents

○Keisuke Nakagawa[1], Yukimi Iwamoto[1], Masahiro Furutani[1], Tomoya Kataoka[2] (1. Natioal Institute of Technology, Fukui College, 2. Ehime University)

Japanese

[P2-2am-15]

Research in the cause of abnormal daily variation of ozone concentration in Ho Chi Minh City, Vietnam

○Norimichi Takenaka[1], Yusuke Fujii[1], Hien Thi To[2] (1. Osaka Metropolitan University, 2. Vietnam National University Ho Chi Minh)

Japanese

[P2-2am-16]

Nitrite production from carbon dioxide on snow and ice surfaces in nature

○Arisa Hinoshita[1], Ayane Yamamura[1], Yusuke Fuji[1], Izumi Noguchi[2], Hiroki Motomichi[3], Keiichi Sato[4], Norimichi Takenaka[1] (1. Osaka Metropolitan University, 2. Hokkaido Research Organization Industrial Technology and

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Environment Research Headquarters Institute of Energy, Environment and Geology, 3. National Institute for Disaster Prevention Science and Technology Snow and Ice Disaster Prevention Research Center, 4. Asian Air Pollution Research Center Atmospheric Research Department)

Japanese

[P2-2am-17]

Synthesis of mesoporous silica-titania hollow spheres and their methylene blue decomposition and hydrogen generation reactions

○Naoki Toyama[1], Kouki Mizumura[1], Asa Hayashi[1], Shigeki Furukawa[1] (1. Nihon University)

Japanese

[P2-2am-18]

Studies on oil and fat accumulation and Triglyceride lipase gene expression in *Microchloropsis gaditana*

○Ayumu Watanabe[1], Tomoe Komoriya[1], Shigeki Furukawa[1] (1. Nihon University)

Japanese

[P2-2am-19]

Copper free Sonogashira coupling reaction catalyzed by a complex of palladium-bistheophyllines

○Katsuya Kaikake[1], Asuma Shingo[1], Ren-Hua Jin[1] (1. Kanagawa University)

Japanese

[P2-2am-20]

Effect of plasticisers, additives and stabilisers on the dechlorination reaction of polyvinyl chloride under hydrothermal conditions

○Satomi Hosokawa[1], Douglas Hungwe[1], Kenji Sugiyama[1], Yuki Yamasaki[1] (1. Hosei University)

Japanese

[P2-2am-21]

Preparation of a cation exchanger based on some biomass and adsorption characteristics of metal ions

○Takumi Akinaga[1], Yui Igaki[1], Ryuki Ikwda[1], Toshiyuki Miyauchi[2], Yuko Shikami[2] (1. Gradute of Chubu University, 2. Chubu University)

Japanese

[P2-2am-22]

Investigation of flow synthesis conditions utilizing Bayesian optimization of antimicrobial spike particles

○Takahiro Nakae[1], So Ito[1] (1. KRI, Inc.)

Japanese

[P2-2am-23]

Fabrication and Evaluation of Dye-sensitized Solar Cells Using Extracts from Aquatic Organisms

○Masaharu Komatsu[1] (1. Tokai University)

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Wed. Mar 20, 2024

Academic Program [Poster] | 01. Education and History of Chemistry：Poster

Wed. Mar 20, 2024 10:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:00 AM - 2:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-3am] 01. Education and History of Chemistry

Japanese

[P1-3am-01]

Alkaline Hydrolysis Reaction of Prussian Blue Suspension in the Presence of Alkaline Earth Metal Ions

○Tadatsugu Yamaguchi[1] (1. Hyogo University of Teacher Education)

Japanese

[P1-3am-02]

Development of teaching materials using a decomposition reaction on aspartame

○Akino Uchiyama[1], Shizuka Takami[2], Tadatsugu Yamaguchi[1] (1. Hyogo University of Teacher Education, 2. National Institute of Technology, Niihama College)

Japanese

[P1-3am-03]

Estimation of the Stokes Radius for Transition Metal Ions and Complexes by Electrophoresis on Filter

○Syusuke Koizumi[1], Hidekazu Arii[1] (1. University of Miyazaki)

Japanese

[P1-3am-04]

Aerobic oxidation of oils accelerated by iron compounds of animal origin in foods

○Kiko Takenouchi[1], Masayuki Inoue[1] (1. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-05]

Suppression effect of amino acids on air oxidation of lipids plant oils catalyzed by iron (III) salts

○Yukino Tanigawa[1], Masayuki Inoue[2] (1. Graduate School of Science, Tokyo University of Science, 2. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-06]

Hydration of alkynes with sulfuric acid silica gel

○Kohei Yamada[1], Masayuki Inoue[2] (1. Graduate School of Science, Tokyo University of Science, 2. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-07]

Mechanism of oxidation of sugars by copper (II) compounds in alkaline aqueous solutions

○Akari Matsubara[1], Masayuki Inoue[2] (1. Graduate School of Science, Tokyo University of Science, 2. Faculty of Science, Tokyo University of Science)

Japanese

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[P1-3am-08]

Development of microscale experimental teaching materials to distinguish aromatic carboxylic acid through neutralization reactions.

○Ueda Tatsuya[1], Masatada Matsuoka[1] (1. Fukuoka Univ.)

Japanese

[P1-3am-09]

Development of Quantitative Experiments Using Iodine Clock Reaction -Experiments to estimate the concentration of an unknown sample from the reaction time-

○Sanefuji Shota[1], Masatada Matsuoka[1] (1. Fukuoka Univ.)

Japanese

[P1-3am-10]

Formation of a Pd catalyst layer using an Anionic Surfactant and Subsequent Fabrication of a Glucose Fuel Cell

○Takahiro Suzuki[1] (1. Otsuma Ranzan Junior and Senior High School)

Japanese

[P1-3am-11]

New Development of Microscale Experiments: Science exhibitions after Covid-19

○Marina Kawata[1], Yuna Moriwaki[1], Reina Ono[1], Chika Takahashi[1], Yumiko Takagi[1], Kazuko Ogino[2] (1. Kagawa University, 2. Tohoku University)

Japanese

[P1-3am-12]

Consideration of Methods for Shape Control and Comparison of Physical Properties in Vinylon Synthesis Using Acetaldehyde

○Kotone Ai[1], Mio Watanabe[2], Izumi Imai[1] (1. Toho University, 2. Fuzikawaguchiko High School)

Japanese

[P1-3am-13]

Development of an evaluation method to visualize the environmental load and safety of chemical experiments in secondary education

○Moeka Kudo[1], Masashi Yamada[2], Izumi Imai[1] (1. Toho university, 2. Graduate school of science, Toho University)

Japanese

[P1-3am-14]

PuzMol: Molecule-building Puzzle

○Norifumi Yamamoto[1] (1. Chiba Tech)

Japanese

[P1-3am-15]

BasePairPuzzle: An experiential molecular model that reproduces hydrogen bonds with magnetic force

○Jiro Kondo[1], Shota Nakamura[2] (1. Sophia University, 2. StudioMIDAS Inc.)

Japanese

[P1-3am-16]

Developing Human Resources for Women in Science with Sechi Kato as a Role Model

○YASUNAO KURIYAMA[1], Mizue Kissho[1,2] (1. Yamagata University, 2. Science Studio Marie)

Japanese

[P1-3am-17]

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Development of a simple and highly precise visual type polarimeter equipped with a constant temperature bath

○Tetsumaru Uzawa[1], Izumi Imai[1] (1. The Univ. of Toho)

Japanese

[P1-3am-18]

Development of a Simple Colorimeter using a White-color LED and a Color sensor IC

○Yasutada Suzuki[1], Natsumi Sakai[1], Syunichi Oshima[1], Mune-aki Sakamoto[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-3am-19]

Introduction to chemical experiments in class using hydrophilic polymer

○Masayuki Toyoshima[1], Tatsuya Takahashi[1] (1. Tokyo Metropolitan College of Industrial Technology)

Japanese

[P1-3am-20]

Color reaction of pH change using anthocyanin of rough extract via Butterfly pea

Ken Nozawa[1], Masahide Niboshi[1], Nagi Itou[1], Hiroki Oka[1], Shiho Goto[1], ○Tatsuya Takahashi[1], Masayuki Toyoshima[1] (1. Tokyo Metropolitan College of Industrial Technology)

Japanese

[P1-3am-21]

Chem Tube: A group of students for producing video teaching materials for chemistry experiments (4)

○Saki Takanashi[1], Sona Okamoto[1], Jiro Ito[1], Junya Ataka[1], Ryota Inomata[1], Yutaro Ogawa[1], Akinari Futamura[1], Ikuhiro Tanida[1], Shin Ono[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-3am-22]

Chem Tube: A group of students for producing video teaching materials for chemistry experiments (5)

○Shin Ono[1], Ikuhiro Tanida[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-3am-23]

New Development of Microscale Experiments: Experimental Classes after Covid-19

○Reina Ono[1], Yuna Moriwaki[1], Marina Kawata[1], Chika Takahashi[1], Yumiko Takagi[1], Kazuko Ogino[2] (1. Kagawa University, 2. Tohoku University)

Japanese

[P1-3am-24]

Development of Multi Sided Liberal Arts Educaion Based on Historical Peppermint Industry of Kitami, Hokkaido
- An attempt to create an educational material which incorporate feelings of people

○Mitsunori Izumi[1] (1. Tokai Univ.)

Japanese

[P1-3am-25]

Application of Generative AI to Inquiry Based Experiments at College of Technology

○Hirotoshi Sato[1], Kozo Fukumoto[2], Aiko Oshio[1] (1. Kobe City College of Technology, 2. University of the Ryukyus)

Japanese

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[P1-3am-26]

Development of teaching materials for chemical experimentation using quantum chemical simulations: An estimate of XPS spectra of organic compounds

○Tsugiko Takase[1], Fuga Miyazawa[1], Katsuhiko Yamaguchi[1] (1. Fukushima University)

Japanese

[P1-3am-27]

Attempts to develop chemistry-based liberal arts for students who are not good at chemistry

○Tamotsu Sugimori[1] (1. University of Toyama)

Japanese

[P1-3am-28]

Current State and Challenges in General Chemistry Education within the Model Core Curriculum of the National Institute of Technology

○Junko Ninomiya[1] (1. National Institute of Technology, Oita College)

Japanese

[P1-3am-29]

Educational Effectiveness of Face-to-Face and On-Demand Practice in Chemistry Experiments

○Toshiyuki Katsumata[1] (1. Tokyo Medical and Dental University)

Japanese

[P1-3am-30]

Designing of Organic Chemistry Experiment Classes for University Students Using Aromatic Compounds

○AKIKO KIDO[1], Naoya Iwasaki[1], Takayuki Suzuki[1] (1. Tokyo Denki University)

Japanese

[P1-3am-31]

Chemistry-based Approach to High School Biology in Closer Connection with University Education

○Yuriko Kai[1], Hiroyuki Oshikane[2] (1. Kanagawa Institute of Technology, 2. Osaka University)

Japanese

[P1-3am-32]

From "resonance" to "delocalization": The Terms and Usages on Electron Delocalization in Conjugate Systems for Organic Chemistry in University Fundamental Education

○Masato M. Ito[1] (1. Soka Univ.)

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Academic Program [Poster] | 08. Catalysts and Catalysis：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-3vn] 08. Catalysts and Catalysis

Japanese

[P1-3vn-01]

Degradation mechanism of ruthenium oxide electrocatalysts during oxygen evolution reaction

○Kazuki Obigane[1], Kosuke Beppu[1], Fumiaki Amano[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-02]

Utilization of low-energy electron beam for the immobilization of Pd nanoparticle catalyst on polymer substrate by radiation irradiation method

○Ryohei Iwano[1], Satoshi Seino[1], Naoto Uegaki[1], Fumiyasu Ishiguro[1], Yuji Ohkubo[1], Takashi Nakagawa[1] (1. Osaka Univ.)

Japanese

[P1-3vn-03]

Greenhouse gas conversion reaction catalyzed by precise nickel clusters

○Tatsuya Moriai[1,2], Takamasa Tsukamoto[2,3,4], Makoto Tanabe[2,5], Tetsuya Kambe[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. for Chemistry and Life Science, Tokyo Tech, 2. JST-ERATO, 3. Inst. of Industrial Science, The Univ. of Tokyo, 4. JST-PRESTO, 5. Ctr. for Integrated Sciences and Humanities, Fukushima Medical Univ.)

English

[P1-3vn-04]

Size effect of V group metal oxide clusters on base catalytic property

○Supisara Hongpuek[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

English

[P1-3vn-05]

Precise separation of mixed metal oxide clusters by HPLC

○Nattamon Panichakul[1], Tomoki Matsuyama[1], Soichi Kikkawa[1], Koichi Kikuchi[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-06]

Study on the correlation between photoelectrochemical properties and photocatalytic activities of various GaN:ZnO powders

○Shuji Sekimori[1], Hiroka Sandaiji[1], Shintaro Abe[1], Natsudogi Iwasa[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Graduate School of Science and Technology, Shinshu University, 2. Graduate School of MedicineScience and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4. PRESTO, Japan Science and Technology Agency)

Japanese

[P1-3vn-07]

Optimization of the synthesis conditions for GaN:ZnO solid solution depending on water content of starting materials

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○Hiroka Sandaiji[1], Natsutogi Iwasa[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Graduate School of Science and Technology, Shinshu University, 2. Graduate School of Medicine, Science and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4. PRESTO, Japan Science and Technology Agency)

Japanese

[P1-3vn-08]

Effects of temperature near the photocatalyst under light illumination in aqueous suspension on hydrogen evolution rate

○Mika Hirata[1], Hiroto Inuduka[1], Yosuke Kageshima[1,2], Katsuya Teshima[1,2], Hiromasa Nishikiori[1,2] (1. Shinshu University, 2. RISM)

Japanese

[P1-3vn-09]

Modification of polymer layer containing phosphate functional groups to surface of hydrogen-evolving photocatalytic particles

○Kiyoharu Yamamura[1], Masataka Yamamoto[1], Yousuke Kageshima[1,3], Katsuya Teshima[1,3], Kazunari Domen[2], Hiromasa Nishikiori[1,3] (1. Shinshu University, 2. The Univ. of Tokyo, 3. RISM)

Japanese

[P1-3vn-10]

Water Splitting under Visible Light Irradiation over a Tiny Amount of Ru-Doped $SrTiO_3$ Photocatalyst Prepared by Various Synthesis Methods

○Chisato Hanafusa[1], Yoshiya Ueki[1], Motonori Ando[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese

[P1-3vn-11]

Hydrogen production by photoreforming of organic waste using CdS/ZnS composite photocatalyst via MOF precursor.

○Yusei Kumai[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese

[P1-3vn-12]

Hydrogen production by water splitting using carbon-based metal-free photocatalyst

○Eitaro Nishimura[1], Morio Nagata[1] (1. Tokyo University of Science)

English

[P1-3vn-13]

Pelletized photoelectrodes for photoelectrochemical water splitting

○Surya Pratap Singh[1], Kosuke Beppu[1], Fumiaki Amano[1] (1. Tokyo Metropolitan University, Faculty & Graduate School of Urban Environmental Sciences)

Japanese

[P1-3vn-14]

Development of Visible-Light Photocatalyst for the Conversion of Glucose to Fungicide

○Mana Akita[1], Sho Usuki[1], Kazuya Nakata[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P1-3vn-15]

Synthesis of aragonite immobilized photocatalysts exhibiting mechano-bactericidal effects and its evaluation of bactericidal performance

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○Ayako Gomi[1,2], Kaoru Igarashi[1], Yukari Miyazaki[2], Nobuaki Negishi[2], Ryo Yamano[1,2], Satoshi Toba[1,2] (1. Chiba Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-3vn-16]

Photocatalytic nitrate generation from water and air on tungsten oxide loaded with noble metal

○Kazuki Miyata[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Osaka University)

Japanese

[P1-3vn-17]

Photocatalytic hydrogen peroxide generation on ion-exchange resin-incorporated resorcinol-formaldehyde semiconducting resins

○Yoshihiro Nishiyama[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Graduate School of Osaka University)

Japanese

[P1-3vn-18]

Infrared-responsive covalent organic framework (COF) photocatalysts with metal ions atomically immobilized with hydrogen peroxide generation ability

○Kei Oyama[1] (1. Kyushu Institute Technology)

Japanese

[P1-3vn-19]

Development of g-C_3N_4 with high degradation activity for phenol

○Naoko Taki[1], Sho Usuki[1], Kazuya Nakata[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P1-3vn-20]

Visible light responsive photocatalytic methane production using graphite-type carbon nitride (PCN)

○Tatsuki Kanazawa[1], Teruhisa Ohno[1] (1. Kyushu Institute of Technology)

Japanese

[P1-3vn-21]

Photocatalytic hydrogen production and selective CO_2 reduction using nitrogen-rich carbon nitride (C_3N_5)

○Kosei Ito[1], Kei Noda[1] (1. Keio Univercity)

Japanese

[P1-3vn-22]

Photocatalytic Roles of Vacancy Sites on Iron nanoparticle supported Zirconium oxide for CO_2 photoconversion

○Ayana Omata[1], Keisuke Hara[1], Tomoki Oyumi[1], Kaori Niki[1], Yasuo Izumi[1] (1. Chiba University)

Japanese

[P1-3vn-23]

Production of Rare Sugars by Electrochemical Oxidation of Monosaccharide

○Kio Kawakatsu[1], Sho Usuki[1], Yasuaki Einaga[2], Kazuya Nakata[1] (1. Tokyo University of Agriculture and Technology, 2. Keio University)

Japanese

[P1-3vn-24]

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Development of Pt/C-based electrocatalysts intended for direct oxidation of cellulose dissolved in a strong alkaline aqueous solution

○Kenta Maeda[1], Yosuke Kageshima[1], Katsuya Teshima[1], Hiromasa Nishikiori[1] (1. Shinshu University)

Japanese

[P1-3vn-25]

Development of Helical Organocatalyst Based on (*cis*, *cis*)-Diphenylurea

○Fumi Takeda[1], Mayumi Kudo[2], Mamika Ogura[1], Yayoi Orihara[3], Minami Odagi[3], Kazuo Nagasawa[3], Aya Tanatani[1] (1. Ochanomizu University, 2. National Institute of Technology, Gunma College, 3. Tokyo University of Agriculture and Technology)

Japanese

[P1-3vn-26]

Mechanism of organic dye decomposition using persulfate activated by carbon catalysts with varied surface oxidation states

○Urushidate Ryusuke[1], Shimoda Syuhei[2], Suzuki Keita[3], Fukuoka Atsushi[2], Takada Tomoya[1] (1. Chitose Institute of Science and Technology, 2. Institute for Catalysis, Hokkaido University, 3. Faculty of engineering, Hokkaido University)

Japanese

[P1-3vn-27]

Development of catalytic reaction system utilizing vibration energy

○Ryuichi Fujikake[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-28]

Dehydrogenation of ammonia on the $CoAl_n$(n=10-13) cation clusters

○Kazuki Kodaira[1], Shoji Kudo[1], Hidenori Matsuzawa[1] (1. Chiba Institute of Technology)

Japanese

[P1-3vn-29]

Catalytic reaction and the mechanism over vibro-catalyst using low-frequency vibration

○Yuto Oba[1], Taiki Uno[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-30]

Effect of reaction temperature on gas phase decomposition of dibromomethane using iron-supported alumina

○Daisuke Fujimoto[1], Liu Dan[1] (1. National Institute of Technology, Ariake College)

Japanese

[P1-3vn-31]

Effect of sodium chloride on the asymmetric ring-opening reaction of epoxides by Plant-based Organic Molecular Catalyst

○Koichi Wada[1], Yasuo Kato[2], Makoto Hibi[2], Yuki Takeuchi[1], Tatsuhiro Asano[1] (1. Kyowa Pharma Chemical Co., Ltd, 2. Toyama Prefectural University)

Japanese

[P1-3vn-32]

Fabrication of metal nanoparticles by electrolytic reduction of composite metal oxides

○Toshiaki Oka[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

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Academic Program [Poster] | 09. Coordination Chemistry, Organometallic Chemistry：Poster

Wed. Mar 20, 2024 1:00 PM - 2:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Japanese

[P1-3pm-01]

Synthesis and Reactions of Mononuclear Vanadium(II) Phenoxide Complexes

○Toyama Yudai[1], Ishida Yutaka[1], Kawaguchi Hiroyuki[1] (1. Tokyo Institute of Technology)

Japanese

[P1-3pm-02]

Synthesis of Titanium and Zirconium Complexes Having Sterically Hindered Tripodal Tetradentate [O_3C] Ligands

○Masato Komura[1], Yutaka Ishida[1], Hiroyuki Kawaguchi[1] (1. Tokyo institute of technology)

Japanese

[P1-3pm-03]

Catalytic primary alcohol oxidation by copper(II)-phenoxyl radical complexes under aerobic condition

○Marina Yoshii[1], Yuichi Shimazaki[1] (1. College of Science, Ibaraki University)

Japanese

[P1-3pm-04]

Syntheses and crystal structures of novel Cu(I)-C_2H_4 coordination polymers bridged by 2,2':4',4''-terpyridine

○Sho Yoshimura[1], Masahiko Maekawa[1], Kunihisa Sugimoto[1], Takayoshi Kuroda[1] (1. Kindai university)

Japanese

[P1-3pm-05]

Construction of Six-membered Silacycle Frameworks by Barbier Reaction

○Kaori Noguchi[1], Mai Tsugaya[1], Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

Japanese

[P1-3pm-06]

Introduction of Alkynyl Groups to the Ends of Oligosilanes

○Mizuki Wamme[1], Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

Japanese

[P1-3pm-07]

Introduction of thiolate into silylene bridged palladium hexanuclear clusterand functional development

○Suda Tetsuro[1], Sunada Yusuke[2,3,4] (1. Faculty of Science and Engineering, Chuo University, 2. Graduate School of Engineering, The University of Tokyo, 3. Institute of Industrial Science, The University of Tokyo, 4. JST PRESTO)

English

[P1-3pm-08]

Substitution reactions of cobalt cubane complexes by bridging bis-pyridine molecules

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○Wataru Ishikawa[1], Toshi Nagata[1] (1. Meijo University)

Japanese

[P1-3pm-09]

Synthetic Study of Silyllithium Bearing Benzodiazaborolanyl Group

○Gai Kadoishi[1], Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

English

[P1-3pm-10]

Synthesis of Copper Complexes of Dipicolylamines with Various Degrees of Steric Hindrance and Their Electrochemical Behaviors

○Yumiko Kitamura[1], Toshi Nagata[1] (1. Meijo University)

Japanese

[P1-3pm-11]

Synthesis and Intramolecular C-H Bond Activation of Low-valent Cobalt Complexes Supported by Electron-Donating Diamide Ligands

○Suiho Kobayashi[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

Japanese

[P1-3pm-12]

Silylation of an oxo-molybdenum dimeric complex $(^{t}BuC_5H_4)_2Mo_2Se_2O_2$

○Takeru Hayakawa[1], Shinji Inomata[1] (1. Fukushima University)

English

[P1-3pm-13]

Redox Properties of a Composite Material of Boron-oxide Layers and a Pentanuclear Cluster

○Nicole Sallier de la Tour[1,2], Maho Imai[1], Tetsuya Kambe[1], Yutaka Saga[1], Mio Kondo[1,3,4], Shigeyuki Masaoka[1] (1. Osaka University, 2. Heidelberg University, 3. Tokyo Institute of Technology, 4. JST PRESTO)

Japanese

[P1-3pm-14]

Synthesis and properties of heterometallic multinuclear complexes with an intense electronic interaction among metal centers

○Akira Hasegawa[1], Masaya Sakamoto[1], Misa Tomoda[1,2,3], Yutaka Saga[1], Tetsuya Kambe[1], Mio Kondo[4,1,5], Shigeyuki Masaoka[1] (1. Osaka University, 2. Institute for Molecular Science, 3. The Graduate University for Advanced Studies, 4. Tokyo Institute of Technology, 5. JST PRESTO)

Japanese

[P1-3pm-15]

Synthesis of a novel metal–organic framework consisting of tetravalent metal cation and tetracarboxylate ligand

○Haruka Kusumi[1], Masaaki Sadakiyo[1] (1. Tokyo Univ. of Sci.)

Japanese

[P1-3pm-16]

Synthesis, structure, and multinuclear reactivities of unsymmetrical dinuclear platinum complex containing diethyl sulfides as co-ligands

○Junnosuke Miyamura[1], Shota Knamori[2], Kzuhiro Uemura[1] (1. Faculty of Engineering, Gifu Univ., 2. Graduate School of Natural Science and Technology, Gifu Univ.)

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Japanese

[P1-3pm-17]

Synthesis of Cu9 Hydride Clusters Supported by Linear Tetraphosphine Ligand

○Madoka Shimada[1], Yurika Komura[1], Seina Sakabe[1], Takayuki Nakajima[1], Tomoaki Tanase[1] (1. Nara Women's University)

Japanese

[P1-3pm-18]

Synthesis and Evaluation as Metal Fluorescent Sensor of Novel Schiff Base [2+2] Macrocycles

○Michiru Matsuoka[1], Yuki Yamaguchi[1], Makoto Miyasaka[1] (1. Tokyo Denki University)

Japanese

[P1-3pm-19]

Synthesis and Structure iron(II) complex of $[Fe(tppz)_2]^{2+}$ constructed by terpyridine moiety

○Mao Kihara[1], Zi Lang Goo[1], Masahiko Maekawa[1], Takayoshi Kuroda-Sowa[1], Kunihisa Sugimoto[1] (1. Kindai University)

English

[P1-3pm-20]

Syntheses and Structures of Aminoalcohol-ligated Mononuclear and Dinuclear Samarium Complexes

○Kulsum Bano[1], Tetsuro Kusamoto[1], Hayato Tsurugi[1] (1. Osaka University)

Japanese

[P1-3pm-21]

Synthesis of Tetranuclear Iron-oxo Complexes Having Bipyridonate Ligands

○Aina Sakamoto[1], Yasuyuki Ura[1] (1. Nara Women's University)

Japanese

[P1-3pm-22]

Synthesis on dinuclear cobalt complexes with the triply bridge structures by the oxygen- or nitrogen- donor ligands.

○Ryosei Ito[1], Tomoyo Misawa[1], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

Japanese

[P1-3pm-23]

Syntheses and characterization of Tridentate Abnormal NHC Pd(II) Complexes

○Ai Watanabe[1], Takeyoshi Yagyu[1] (1. Nagoya Institute of Technology)

Japanese

[P1-3pm-24]

Syntheses of ruthenium complexes bearing a macrocyclic ligand consisting of two bis(imino)pyrrole units

○Karin Yasue[1], Tomoyo Misawa[1], Yasuhiro Funahashi[2], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ., 2. Osaka Univ.)

Japanese

[P1-3pm-25]

Effect of multinuclear structures on the selective formation of heterometallic cycliccomplexes using flexible tripeptides

○Haruka Hasegawa[1], Ryosuke Miyake[1] (1. Ochanomizu University)

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Japanese

[P1-3pm-26]

Synthesis of metal-organic rhombic dodecahedra with trimesic acid derivatives

○Ryohei Yoshida[1], Ayana Miyata[1], Shun Tokuda[1], Shuhei Furukawa[1] (1. Kyoto University)

Japanese

[P1-3pm-27]

Effects of axial ligand on Ru(II) complexes with both hydrogenated metal and organic ligands

○Asato Morihara[1], Dai Oyama[1], Tsugiko Takase[1], Ito Keiya (1. Fukushima University)

Japanese

[P1-3pm-28]

Development of ternary metallic MOFs incorporating multiple luminescent centers

○ZHOU YAO[1] (1. Kyushu University)

Japanese

[P1-3pm-29]

Structures and Solid-State Photoluminescence of Novel Polymorphic Platinum(II) Complexes Containing a Pyridylthiazole Ligand

○Ren Hashimoto[1], Ryota Nakamura[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo)

Japanese

[P1-3pm-30]

Structures and Reativity of Heterogeneous Dinuclear Dinitrogen Complexes using Vanadium and Chromium Ions

○Yuji Kajita[1], Yoshiaki Kokubo[2] (1. Aichi Institute of Technology, 2. Tokyo Institute of Technology)

Japanese

[P1-3pm-31]

Effect of Highly-Coordinated Iron Complex on Redox Flow Battery Performance

○Soshi Kodama[1], Atsushi Okazawa[1], Kosuke Kawai[1], Masashi Okubo[1] (1. Waseda University)

Japanese

[P1-3pm-32]

Fabrication of two-dimensional oriented thin film $[NPr_4][MnCr(C_2O_4)_3]$ by casting method

○Yuki Funahashi[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-3pm-33]

Synthesis and magnetic properties of cyano-bridged Fe^{II}-W^{IV} complex incorporated three-types of organic ligands

○Daiki Kobayashi[1], nagashima syuntarou[1], Wang Junhao[1], Ohkoshi Shinichi[2], Tokoro hiroko[1] (1. The Univ. of Tsukuba, 2. The Univ. of Tokyo)

Japanese

[P1-3pm-34]

Control of Emission States of Mixed Crystals of Platinum(II)/Palladium(II) Complexes by Mixing Ratio

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○Kaito Segawa[1], Masaki Yoshida[2], Masako Kato[2] (1. Kwansei Gakuin Univ. Graduate school of Science and Technology., 2. Kwansei Gakuin Univ. School of Biological and Environmental Sciences.)

Japanese

[P1-3pm-35]

Synthesis and Properties of Platinum Complexes with 2,3'-Bipyridine

○Masashi HASHIMOTO[1], Kazushi Takemoto[1], Hideo Konno[2] (1. Josai Univ., 2. AIST)

Japanese

[P1-3pm-36]

Creation of a Novel Calcium Ion Conductor Using a Metal–Organic Framework

○Takahiro Erikawa[1], Masaaki Sadakiyo[1] (1. Tokyo Univ. of Sci.)

Japanese

[P1-3pm-37]

Dependence of Guest-Induced Ionic Conductivity on Cationic Species in Divalent Ion-Containing Metal–Organic Frameworks

○Kaori Taniguchi[1], Sadakiyo Masaaki[1] (1. Tokyo Univ. of Sci.)

English

[P1-3pm-38]

Self-assembly behavior of porphyrins having terpyridine sites by metal ions

○Tomoya Abe[1], Joe Otsuki[1], Kosuke Sugawa[1] (1. Nihon Univ.)

Japanese

[P1-3pm-39]

Synthesis and gas adsorption properties of the fluorinated three-dimensional porous coordination polymer

○Yuki Saito[1], Xin Zheng[1], Shin-ichiro Noro[1,2] (1. Fac. of Env.Earth Sci., Hokkaido Univ., 2. Grad. Sch. of Env. Sci., Hokkaido Univ.)

Japanese

[P1-3pm-40]

Fabrication of Oriented Crystalline Pillared-Layer-Type MOF Thin Film Using the Casting Method and Analysis of the Spin-Crossover Phenomena

○QIYUAN ZHANG[1], TOMOYUKI HARAGUCHI[1] (1. Tokyo University of Science)

English

[P1-3pm-41]

The complex formation behavior of porphyrins with phenylbisbipyridine introduced at positions 5 and 15

○Aguri Akitomi[1], Joe Otsuki[1], Sugawa Kosuke[1] (1. Nihon Univ.)

Japanese

[P1-3pm-42]

Electrochemical Properties of *C*3-Symmetric Schiff Base Nickel Complexes with Thienyl Groups

Yuri Oshima[1], Teturo Furukawa[1], ○Naoto Kuwamura[2], Noriko Chikaraishi[1], Masakazu Hirotsu[1] (1. Graduate School of Science, Kanagawa University, 2. Kogakuin University)

Japanese

[P1-3pm-43]

The π-electronic system-dependence on the energy relaxation process of triboluminescence of the chiral lanthanide complexes

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○Daisuke Hayauchi[1], Reo Ohno[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

English

[P1-3pm-44]

Ligand- and aggregation-dependent photoluminescence in nitrogen-centered pentagold(I) clusters protected by *N*-heterocyclic carbenes

○Leonado Hayato Takeshige[1], Xiao-Li Pei[1], Pei Zhao[2], Koichi Nagata[1], Hitoshi Ube[1], Zhen Lei[1], Masahiro Ehara[2], Mitsuhiko Shionoya[1] (1. The University of Tokyo, 2. Institute for Molecular Science)

Japanese

[P1-3pm-45]

Investigation of protonation-deprotonation behavior of azophenines as ligands for metal complexes in solution

○Noriya Nakamaru[1], Yuka Inagaki[1], Keiji Ohno[2], Takashi Fujihara[3] (1. Grad. Sch. Sci., Eng., Saitama Univ, 2. Jpn. Women's Univ, 3. CACS, Saitama Univ)

Japanese

[P1-3pm-46]

Synthesis and Properties of Tris(salen)-Type Macrocyclic Ligands with *N*-Heterocyclic Building Blocks Introduced onto the Outer Periphery

○Takumi Kitajima[1], Shohei Tashiro[1], Mitsuhiko Shionoya[1] (1. Grad. Sch. of Sci.; The Univ. of Tokyo)

Japanese

[P1-3pm-47]

Magnetic properties of a one-dimensional copper(II) compound bridged by a terpyridine-based biradical ligand

○Kazuki Ochiai[1], Takuya Kanetomo[1], Masaya Enomoto[1] (1. Tokyo University of Science)

Japanese

[P1-3pm-48]

The phase transition behavior of fatty acids in metal–organic frameworks

○Rei Yoshii[1], Genki Hatakeyama[1], Kunyi Leng[1], Teppei Yamada[1] (1. The University of Tokyo)

Japanese

[P1-3pm-49]

Structural and Physical Properties of Dto-bridged Iron Mixed Valence Complexes with Intercalation of Polarizable Cations

○Takashi Oba[1], Masaya Enomoto[1], Takuya Kanetomo[1] (1. Tokyo University of Science)

English

[P1-3pm-50]

Synthesis and Photochemical Properties of Phthalocyanine Complexes Bearing Fluorine and Alkyl Groups

○HongFeng Liu[1], Kei Murata[1], Kazuyuki Ishii [1] (1. IIS, The Univ. of Tokyo)

Japanese

[P1-3pm-51]

Luminescence spectra of glassy europium complexes with linolic acid and phenanthroline derivative

○Kota Chikaraishi[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

Japanese

[P1-3pm-52]

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Identification of luminescent species contributing to induced CPL of a Eu(III) complex with Δ(Λ)-Co(III) complexes by time-resolved CPL spectroscopy

○Juri Yamashita[1], Munetaka Iwamura[1], Koichi Nozaki[1], Taro Tsubomura[2] (1. Grad. Sch. Sci. Eng., Univ. Toyama, 2. Seikei Univ.)

English

[P1-3pm-53]

Spin state changes of luminescent cobalt(II) complexes bearing bulky substituent in the solid state and solution

○Manabu Nakaya[1], Naoki Izumiyama[1] (1. Josai University)

Japanese

[P1-3pm-54]

Luminescence spectra of valinamide-bipyridine lanthanide complexes with a series of alkyl groups

○Reo Ohno[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

Japanese

[P1-3pm-55]

Design, Synthesis, and Complexation Behavior of Sulfur-Embedded TriQuinoline (t-TQ)

○Ryo Otani[1], Toi Kobayashi[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

English

[P1-3pm-56]

Synthesis and Characterization of Iron (II) Complex with an Unsymmetrical Heterocyclic Multidentate Azine Ligands, (2-Pyridyl)(4-imidazolyl)azine

○Kennedy Mawunya Hayibor[1], Yukinari Sunatsuki [2], Takayoshi Suzuki[1,3] (1. Graduate School of Natural Science and Technology, Okayama University, 2. Advanced Science Research Center, Okayama University, Okayama , 3. Research Institute for Interdisciplinary Science, Okayama University, Okayama)

Japanese

[P1-3pm-57]

Development of LB films of lanthanide complexes with photochromic and polarized luminescence properties

○Junya Kondo[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

English

[P1-3pm-58]

Mechanism of water molecule adsorption/desorption and phase transition in cobalt terpyridine complex crystals

○Yusaku Kobayashi[1], Otsuki Joe[1], K Sugawa[1] (1. The Univ. of NIhon)

Japanese

[P1-3pm-59]

Development and chromism control of visible-transparent and UV/NIR-absorbing dyes based on mixed-valence clusters

○Tomoki Kamada[1], Takashi Morino[1], Naoki Shimomoto[1], Yasuko Osakada[2], Mamoru Fujitsuka[2], Yoshiki Ozawa[1], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo, 2. SANKEN, Osaka University)

Japanese

[P1-3pm-60]

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Synthesis of Rare-Earth Phthalocyanine Double-Decker Complexes and Their Chiral Induction

○Tomohito Mori[1], Kei Murata[1], Kazuyuki Ishii[1] (1. IIS, The Univ. of Tokyo)

Japanese

[P1-3pm-61]

Synthesis and phase transition behavior of Fe(III) ion-based plastic crystal aimed at endowing vapor response

○Yasuhiro Shigeta[1], Motohiro Mizuno[1] (1. Nanomaterials Research Institute, Kanazawa University)

Japanese

[P1-3pm-62]

Synthesis of a novel donor-acceptor molecular assembly composed by Rh binuclear unit with a bulky dicarboxylic acid ligand and an electron acceptor molecule

○Fuminori Kimura[1], Kazuya Otsubo[1] (1. Tokyo University of Science)

Japanese

[P1-3pm-63]

Chiral induced spin selectivity of magnetic coordination molecular chain

○Kubo Karin[1], Zhongyue ZHANG[1], Sekine Yoshihiro[1], Hayami Shinya[1] (1. Kumamoto University)

Japanese

[P1-3pm-64]

Synthesis of Pd_6L_8 and Pd_6L_4 cages from triptycene-based tripodal shaped ligands

○Hiromu Yamamoto[1], Masahiro Yamashina[1], Shinji Toyota[1] (1. Tokyo Tech.)

Japanese

[P1-3pm-65]

Effects of cationic surfactants on the emission properties of $[Au(CN)_2]^-$ oligomers

○Ryo Okada[1], Daichi Inoue[1], Koichi Nozaki[1], Munetaka Iwamura[1] (1. Sch. of Sci., Univ. of Toyama)

English

[P1-3pm-66]

Optical and Magnetic Properties of Octacyanidemetalate Ionic Crystals with Alkali Cations and Glycine

○Tatsuya Konishi[1], Kunal Kumar[1], Kazuki Nakamura[1], Yuuki Mineo[1], Taiki Sakaguchi[1], Koji Nakabayashi[1], Shin-ichi Ohkoshi[1] (1. The University of Tokyo)

Japanese

[P1-3pm-67]

Formation of porphyrin dimer by coordination bonding and supramolecular host function

○Shigeki Miyazaki[1], Ken Sato[1], Kosuke Sugawa[2], Joe Otsuki[2] (1. Graduate School of Science and Technology, Nihon University, 2. College of Science and Technology, Nihon University)

Japanese

[P1-3pm-68]

Rapid CO_2 Fixation Using a Trinuclear Zn(II) Cryptate Complex and Analysis of its Structure State

○Masakazu Murase[1], Yoshifumi Maegawa[1], Masataka Ohashi[1], Yasutomo Goto[1], Naonari Sakamoto[1], Takamasa Nonaka[1], Takeshi Uyama[1], Takeo Arai[1] (1. Toyota Central R&D Labs., Inc.)

English

[P1-3pm-69]

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Heterogenized Cationic Ru(II) Polypyridine Complexes for Visible-Light Photoredox Catalysis

○Seong Huh[1], Jongseo Kim[1] (1. Hankuk University of Foreign Studies)

Japanese

[P1-3pm-70]

Synthesis and Reaction of the anionic vanadium thionitrosyl complex with an [ONO] ligand

○Daichi Sugawara[1], Yutaka Ishida[1], Hiroyuki Kawaguchi[1] (1. Tokyo Institute of Technology)

Japanese

[P1-3pm-71]

Electrochemical CO_2 reduction using a Re(I) complex catalyst and carbamate as a CO_2 source

○Kenshu Nemoto[1], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

English

[P1-3pm-72]

Mechanisms of hydrosilylation of carbonyl compounds catalyzed by rhodium-phosphine complexes: The rate enhancement by proximate two Si-H groups

○Hideo Nagashima[1], Yoshihito Shiota, Kazunari Yoshizawa (1. Kyushu University)

Japanese

[P1-3pm-73]

Development of the dehydrogenation coupling reactions of group 14 hydrides mediated by iron catalyst

○TAEWOO KIM[1], Yusuke Sunada[1,2,3] (1. Graduate School of Engineering, The University of Tokyo, 2. Institute of Industrial Science, The University of Tokyo, 3. JST PRESTO)

Japanese

[P1-3pm-74]

Development of the Asymmetric Friedel-Crafts Alkylation Using the Chiral Rare Earth Organophosphate

○Shoko Suzuki[1], Yudai Tsukada[1], Natsumi Oyama[1], Misaki Sogen[1], Yasuo Yokoyama[2] (1. The Kyoto University of Education, 2. National Institute of Technology, Akita College)

Japanese

[P1-3pm-75]

CO_2 Hydrosilylation Catalyzed by Tetranuclear Copper Hydride Complex Supported by Tridentate Phosphine Ligand

○Konoka Baba[1], Takayuki Nakajima[1], Tomoaki Tanase[1] (1. Nara Women's University)

Japanese

[P1-3pm-76]

Photo and electrochemical properties of Ru complexes immobilized on Al-containing mesoporous silica thin films on ITO electrodes.

○Narumi Nakano[1], Shunpei Harada[1], Ayano Yamada[1], Masaya Okamura[1], Shiro Hikichi[1] (1. Kanagawa University)

Japanese

[P1-3pm-77]

Synthesis of Hydrogels with Thermoresponsive Crosslinked Domains Containing Iridium Complex for Ammonia Sensing and Selective Catalytic Reaction

○Shohichi Furukawa[1], Ida Shohei[2], Fujita Ken-ichi[1] (1. Kyoto university, 2. The University of Shiga prefecture)

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English

[P1-3pm-78]

Photoinduced Carbon-Heteroatom Cross-Coupling Catalyzed by Nickel Naphthyridine Complexes

○PAVAN KUMAR VARDHANAPU[1], Janet Bahri[1], Julia Khusnutdinova[1] (1. Okinawa Institute of Science and Technology Graduate University)

Japanese

[P1-3pm-79]

Pd/Fe-catalyzed Synthesis of Terminal Acetals from Terminal Alkenes

○Nanako Fukui[1] (1. nara women's university)

Japanese

[P1-3pm-80]

Catalytic hydrogenation of CO_2 at mild conditions using a photo-activated (PNNP)Ir complex

○Koki Taga[1], Bendik Grømer[1], Jieun Jung[1], Susumu Saito[1,2] (1. Graduate School of Science, 2. Integrated Research Consortium on Chemical Sciences)

Japanese

[P1-3pm-81]

Photocatalytic Reduction of Carbon Dioxide using β-Ketoimine Boron Complexes

○Riku Urita[1], Yuma Hisata[2], Tatsuki Morimoto[1] (1. Tokyo University of Technology Graduate School, 2. Tokyo University of Technology)

Japanese

[P1-3pm-82]

Expression of the Reaction Selectivity and the Substituent Effect in Coupling Reactions by Reducing the Catalyst Loading

Tomohiro Shibata[1], ○Hiroto Saga[1], Hana Kimura[1], Misa Kawase[1], Yoshimasa Matsumura[1], Osamu Shimomura[1], Atsushi Ohtaka[1] (1. Osaka Institute of Technology)

English

[P1-3pm-83]

Synthesis and Characterization of Uio-67 MOFs Incorporated with Photocatalytic Components for Solar Energy Conversion

○Qingen Zheng[1], Kosei Yamauchi[1], Ken Sakai[1] (1. Kyushu Univ.)

Japanese

[P1-3pm-84]

Theoretical study of reduction of nitrite into NO by copper(II) complexes

○Yoshihito Shiota[1], yohei Kametani[1], Kazunari Yoshizawa[1] (1. Kyushu University)

Japanese

[P1-3pm-85]

Reactivity of Nickel Complexes bearing Two α-Cyanocarboanion Ligands

○Natsuki Nogaki[1], Hajime Kameo[1], Hiroyuki Matsuzaka[1] (1. Osaka Metropolitan University)

Japanese

[P1-3pm-86]

Catalytic Reactions with Monodentate Phosphine-Based Cu-MOF

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○Shouki Yui[1], Marina Koga[1], Hiroyuki Arafune[2], Takahiro Sawano[3], Ryo Takeuchi[1] (1. Aoyama Gakuin University, 2. National Institute of Technology, Tsuruoka College, 3. Shimane University)

English

[P1-3pm-87]

Photo-accelerated decomposition of ammonia borane with phosphine-ligated gold clusters

○Shaojing Yan[1], Tomotaka Nakajima[1], Yukatsu Shichibu[1,2], Haru Hirai[3], Tatsuya Tsukuda[3], Katsuaki Konishi[1,2] (1. Grad. Sch. of Env. Sci., Hokkaido Univ., 2. Fac. of Env. Earth Sci., Hokkaido Univ., 3. Sch. of Sci., Tokyo Univ.)

Japanese

[P1-3pm-88]

DFT study on a reaction mechanism of nitric oxide reduction by copper complex with in-built proton-donating functional group

○Yohei Kametani[1], Ryoga Toyoshima[1], Yoshihito Shiota[1], Kazunari Yoshizawa[1] (1. IMCE, Kyushu Univ.)

Japanese

[P1-3pm-89]

Antimicrobial properties of metal complexes bearing salicylideneaniline ligand

○Arisa Niinobe[1], Satoshi D. Ohmura[1] (1. National Institute of Technology, Niihama College)

Japanese

[P1-3pm-90]

Development of Pd(II) complex catalyst with tridentate *N*-heterocyclic carbene ligand immobilized on reduced graphene oxide

○Hina Yamada[1], Yagyu Takeyoshi[1] (1. Nagoya Institute of Technology)

Japanese

[P1-3pm-91]

Polarized light induced optical anisotropy PMMA films of containing [Ni(dmit)$_2$] complexes and azobenzene compound

○Taiga Imae[1], Akinori Honda[2], Daisuke Nakane[1], Takashiro Akitsu[1], Kazuo Miyamura[1] (1. Tokyo University of Science, 2. Chou University)

Japanese

[P1-3pm-92]

Synthesis and Cation Recognition Capacity of Novel Redox-Active Platinum Complexes with Oligoethylene Glycoxy Chains

○Sota Inoue[1], Akinori Honda[2], Akinobu Nakada[2,3], Ho-Chol Chang[2] (1. Graduate School of Science and Engineering, Chuo Univ., 2. Faculty of Science and Engineering, Chuo Univ., 3. Graduate School of Engineering, Kyoto Univ.)

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Academic Program [Poster] | 10. Organic Chemistry -Organometallic Compounds-：Poster

Wed. Mar 20, 2024 1:00 PM - 2:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-3pm] 10. Organic Chemistry -Organometallic Compounds-

Japanese

[P2-3pm-01]

Synthesis of NHC-Ru and NHC-Pd Complexes form Hydroxyalkyl-substituted Azolium Salts

○Ryota Usui[1], Satoshi Sakaguchi[1] (1. Kansai Univ.)

Japanese

[P2-3pm-02]

Ruthenium Hydride-Catalyzed Oxidative Dehydrogenation of Primary and Secondary Alcohols Using Hydrogen Acceptor

○Masaki Ochi[1], Yutaro Komiya[1], Aina Fujii[1], Kosho Makino[1,2], Shunsuke Sueki[1,2], Masahiro Anada[1,2] (1. Fac. Pharm., Musashino Univ., 2. Res. Inst. Pharm. Sci., Musashino Univ.)

Japanese

[P2-3pm-03]

Enantioselective Silane Reduction of Ketones Catalyzed by Polymer-supported NHC-Ir Complex

○Masamune Koyabu[1], Satoshi Sakaguchi[1] (1. Kansai Univ.)

Japanese

[P2-3pm-04]

Synthesis of NHC-Rh Complexes from Hydroxyamide- or Hydroxyalkyl-substituted Azolium Salts and Its Application for Catalytic Reactions

○Shogo Matsuo[1], Satoshi Sakaguchi[1] (1. Kansai Univ.)

Japanese

[P2-3pm-05]

Selective Synthesis of Secondary Amines from Aqueous Ammonia and Alcohols Catalyzed by Iridium Complexes

○Ryo Sei[1], Ken-ichi Fujita[1] (1. Kyoto University)

Japanese

[P2-3pm-06]

Dehydrogenation of Alcohols Catalyzed by Iridium Complexes Bearing Functional Polymer Ligands

○Hiroki Maeda[1], Taiki Kuno[1], Jaeyoung Jeong[1], Yasuhiro Morisaki[2], Ken-ichi Fujita[1] (1. The Univ. of Kyoto, 2. The Univ. of Kwansei Gakuin)

Japanese

[P2-3pm-07]

Iridium Complex-Catalyzed Methylamination of Alcohols in Aqueous Media

○Maimi Kubo[1], Nanase Yoshida[1], Ken-ichi Fujita[1] (1. Graduate School of Human and Environmental Studies, Kyoto University)

Japanese

[P2-3pm-08]

Platinum-Catalyzed Hydroiodination of Alkynes Using Phosphoric Acid and Sodium Iodide

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○Moeka Yanagisawa[1], Hidenori Kinoshita[1], Katsukiyo Miura[1] (1. The Univ. of Saitama)

Japanese

[P2-3pm-09]

Platinum-Catalyzed anti-Markovnikov Hydrochlorination of Alkynes: Effects of Neighboring Functional Groups

○Takaki Ikeshima[1], Katsukiyo Miura[1], Hidenori Kinoshita[1] (1. Saitama University)

Japanese

[P2-3pm-10]

Platinum-Catalyzed Hydrative Dimerization of Alkynylsilanes and Its Application to Arene Synthesis

○Chinatsu Ambe[1], Katsukiyo Miura[1], Hidenori Kinoshita[1] (1. Saitama University)

Japanese

[P2-3pm-11]

Research of regioselectivity and reactivity in cross-dehydrogenative coupling reaction of disubstituted benzene with polyfluoroarene

○Tianya Xiong[1], Tomoki Iida[1], Takaki Kanbara[1], Junpei Kuwabara[1] (1. Univ. of Tsukuba)

Japanese

[P2-3pm-12]

Reactivity of Tetranuclear Nickel Sheet Sandwich Clusters Bearing Cyclooctatetraene Ligands.

○Yuji Nemoto[1], Genki Sakai[1], Tsubasa Omoda[1], Koji Yamamoto[2], Tetsuro Murahashi[1] (1. Tokyo Tech, 2. Natioal Defense Academy)

Japanese

[P2-3pm-13]

Palladium-catalyzed asymmetric allylic amination using a cinnamamide-type chiral ligand with axial chirality

○Natsume Akimoto[1], Hiroto Mizuno[1], Kaho Takaya[1], Yasushi Yoshida[1], Takashi Mino[1] (1. Chiba University)

Japanese

[P2-3pm-14]

Synthesis of Novel Phosphine Ligands Bearing Three 1-Tetralone Imine Moieties and Their Palladium(II) Complexes

○Yukiko Wakimoto[1], Hidetoshi Ohta[1], Minoru Hayashi[1] (1. Grad. Sch. Sci., Eng., Ehime Univ.)

Japanese

[P2-3pm-15]

Pd-catalyzed asymmetric allylic amination using chiral P,olefin ligand with cinnamyl group

○Hiroto Mizuno[1], Kaho Takaya[1], Yuto Toba[1], Yasushi Yoshida[1], Takashi Mino[1] (1. Chiba University)

Japanese

[P2-3pm-16]

[Withdraw] Synthesis and optical analysisof unique silver nanoparticle composites

○KAZUKI MATSUO[1], KENGO ITO[2] (1. Premier Anti-Aging Co., Ltd., 2. Ito Research Institute Co.,Ltd.)

Japanese

[P2-3pm-17]

Benzylation of Isatinimines Using Metallic Barium

○Hiroto Sone[1], Akira Yanagisawa[1] (1. Chiba University)

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Japanese

[P2-3pm-18]

Synthesis, structures and reactivity of (chloro)tetraphenylgallacyclopentadienes

Ayaka Yamauchi[1], ○Takako Muraoka[1], Haruka Katayama[1] (1. Gunma University)

Japanese

[P2-3pm-19]

Ring-opneing Reaction of Epoxide Catalyzed by Hydorosilane

○Toru Hashimoto[1], Kohei Nishikimura[1], Makoto Hojo[1] (1. Sanyo-Onoda City University)

Japanese

[P2-3pm-20]

Stereoselective Addition Reaction of Allenyl Titaniums to Nitroalkenes

○Riku Okawa[1], Sentaro Okamoto[1], Kota Ibe[1] (1. Kanagawa University)

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Academic Program [Poster] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Poster

Wed. Mar 20, 2024 10:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:00 AM - 2:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-3am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Japanese

[P2-3am-01]

Elucidation of a formation mechanism of hollow structures on spherulites in photochromic diarylethene thin films

○Mami Isobe[1], Daichi Kitagawa[1,2], Seiya Kobatake[1,2] (1. Grad. Sch. of Eng., Osaka Metropolitan Univ., 2. Grad. Sch. of Eng., Osaka City Univ.)

Japanese

[P2-3am-02]

Construction and structural analysis of a heterocycle containing benzene-1,3-disulfonamide using double Mitsunobu annulation

○Kyosuke Kaneda[1,2], Takato Koideya[1], Ryuji Toshima[1], Yoshiki Konno[1], Takehiro Yamagishi[1,2] (1. Hokkaido University of Science, 2. CRILS)

Japanese

[P2-3am-03]

Synthesis of trispap, a macrocyclic ligand with three *N*,*N*,*O* tridentate chelating units in close proximity

○Jia Chen Zhao[1], Nadiia Varzhel[2], Yuya Hokimoto[1], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Taras Shevchenko Natl. Univ. of Kyiv)

Japanese

[P2-3am-04]

Construction of electroconductive elastic crystal based on phthalocyanine

○Chiharu Watanabe[1], Yoji Horii[1], Takashi Kajiwara[1] (1. Nara Women's University)

Japanese

[P2-3am-05]

Mechanofluorochromic properties of boronic acid derivatives having anthracene unit

○Natsuki Kataoka[1], Manato Nishimura[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

[P2-3am-06]

Synthesis of multinuclear lanthanoid complexes with structural changes in salen macrocyclic ligand

○Yi-Fu Liu[1], Guzman Gil-Ramirez[2], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Univ. of Lincoln)

Japanese

[P2-3am-07]

Synthesis of a luminescent chiral bis(oxazoline) ligand

○Kei Shimada[1], Junpei Yuasa[1] (1. Tokyo University of Science)

Japanese

[P2-3am-08]

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Molecular design of pyrene derivatives to make microcrystalline films with silver luster effect using drop-casting method

○Tatsuya Maeda[1], Yuuma Nakagawa[2], Ryou Nshimura[3], Masakazu Morimoto[3], Satoshi Yokojima[4], Nakamura Shinitirou[5], Kingo Uchida[1] (1. Ryukoku University, 2. Molecular Engineering Institute, Shiga University of Medical Science, 3. Rikkyo University, 4. Tokyo University of Pharmacy and Life Sciences, 5. Kumamoto University)

English

[P2-3am-09]

Synthesis of azobenzene-containing salen-based macrocycle

○Mads Nybo Sørensen[1], Masaru Kondo[2], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Univ. of Shizuoka)

Japanese

[P2-3am-10]

Crystal Structures of Quinophthalone Compounds with an Ether Bond at 8 Position

○Kento Nakamura[1], Reo Hasegawa[2], Motohiro Akazome[2], Rihito Ito[3], Joji Mikami[3], Hiroyuki Yanai[3], Shoji Matsumoto[2] (1. Faculty of Engineering, Chiba University, 2. Graduate School of Engineering, Chiba University, 3. TOYOCOLOR CO., LTD.)

Japanese

[P2-3am-11]

Synthesis of Cyclic Composites of Nickel Porphyrins and Bipyridines Having Hydrophylic Groups, and Their Conformational Changes in Solution.

○Kenta Suzuki[1], Yusuke KuramochiKuramochi[1], Akiharu Satake[1] (1. Tokyo University of Science)

Japanese

[P2-3am-12]

Phase transition and changes in chromism of halosalicylidene alkylamine crystals

○Shunji Miyazato[1], Ryo Koibuchi[1], Isao Yoshikawa[1], Hirohiko Houjou[1] (1. The University of Tokyo)

Japanese

[P2-3am-13]

Synthesis of Azaylide-Based Amphiphile with a Phosphine Coordination Site and Evaluation of its Assembling Behaviors

○Sho Naito[1], Yoshimori Akiyama[2], Masahiro Yamashina[2], Shinji Toyota[2], Tomohito Ide[1] (1. National Institute of Technology, Tokyo College, 2. Tokyo Institute of Technology)

Japanese

[P2-3am-14]

Synthesis of macrocyclic ligand hexasap that assembles *O*,*N*,*O* tridentate chelating units in the cavity

○Mamoru Kamisaka[1], Sara Machleit[1,2], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Free Univ. of Berlin)

Japanese

[P2-3am-15]

Variety and Systematics in Crystal Structure of Organic Semiconductors with Substituents

○Hiromi Minemawari[1] (1. AIST)

Japanese

[P2-3am-16]

Synthesis and solvent adsorption/desorption behavior of porous coordination polymers with heterocycles inside one-dimensional channels

○Tatsuya Okuyama[1], motoko akita[1] (1. Josai University)

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Japanese

[P2-3am-17]

X-ray structure study of co-crystals with tropolone and hydrogen-bond donor and acceptor molecules

○Hiromu Nomura[1], Hideki Saitoh[1] (1. Saitama University)

Japanese

[P2-3am-18]

Evaluation of inclusion behavior and optical properties of a host-guest conjugate with an environmentally responsive fluorescent dye

○Taiyou Tsutsumi[1], Takaaki Miyazaki[1], Osamu Hayashida[1] (1. Graduate School of Science, Fukuoka University)

Japanese

[P2-3am-19]

Synthesis of Dihydrophenazine Cationic Radical Derivative Fused by Spin Localized Nitroxyl Radical Unit and Their Physicochemical Properties

○Ryo Ohtaka[1], Shigeyuki Oba[1], Yohei Miura[1], Naoki Yoshioka[1] (1. Keio University)

Japanese

[P2-3am-20]

Synthesis of Benzodithiophenone and its Application to Stimuli Responsive Molecular Crystals

○Masahiro Ikeda[1], Tomohiro Seki[1] (1. Department of Chemistry, Faculty of Science, Shizuoka University)

Japanese

[P2-3am-21]

Complexation behavior of metalloporphyrins with bipyridyl-type ligand

○Ken Sato[1], Shigeki Miyazaki[1], Kosuke Sugawa[1], Joe Otsuki[1] (1. Nihon Univ.)

English

[P2-3am-22]

PEGylated porphyrin without phenyl groups

○Yuri Oie[1], Daiki Hirota[1], Kosuke Sugawa[1], Joe Otsuki[1] (1. Nihon Univ.)

Japanese

[P2-3am-23]

Construction of Cationic Molecular Cages Composed of Tetra(N-alkylpyridinium)porphyrins and Their Two-dimensional Assembly

○Daisuke Hayashi[1], Toshio Nishino[1], Gwénaël Rapenne[1,2] (1. Nara Institute of Science and Technology, 2. University of Toulouse)

Japanese

[P2-3am-24]

Inclusion of Iodine and halide ions in hydrogen-bonded organic frameworks composed of fused-ring pyrazine derivatives

○Moka Tabata[1], Yuto Suzuki[2], Ryusei Oketani[2], Ichiro Hisaki[2] (1. School of Engineering Science, Osaka University, 2. Graduate School of Engineering Science, Osaka University)

Japanese

[P2-3am-25]

Crystal Structures and Fluorescence Properties of Methyl-substituted Organoboron Complexes

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○Fuko Matsumoto[1], Takuya Ogaki[1], Shiori Miyazaki[2], Kiyoshi Miyata[2], Ken Onda[2], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ., 2. Kyushu Univ.)

Japanese

[P2-3am-26]

Cocrystallization of hinokitiol with hydroquinone and its physical properties

Kanji Takeuchi[1], Kyoka Taketazu[1], Junki Tomita[2], Yutaka Inoue[3], ○Mitsuaki Suzuki[1] (1. Faculty of Science, Josai University, 2. Instrumental Analysis Center, Josai University, 3. Faculty of Pharmacy and Pharmaceutical Sciences, Josai University)

Japanese

[P2-3am-27]

Synthesis, crystal structure and luminescence behavior of chrysene derivatives with butadiyne

○Ryoya Kamiyama[1], Ryusei Oketani[1], Ichiro Hisaki[1] (1. The Univ. of Osaka)

Japanese

[P2-3am-28]

Carboxylic acid recognition of a diamidine having a tetraarylethylene unit with an extended π-conjugation

○Suzu Uetani[1], Akane NAKAJIMA[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

[P2-3am-29]

Carboxylic Acid Recognition of a Diamidine Having a Tetraphenylethylene Unit

○Ryo Watanabe[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

[P2-3am-30]

Synthesis of water-soluble cyclophanes having multiple cationic side chains and a pyrene moiety

○Haruna Okuma[1], Takaaki Miyazaki[1], Osamu Hayashida[1] (1. Fukuoka University)

Japanese

[P2-3am-31]

Synthetic Study of Amide Cyclodextrin Oligomers Utilizing Imine Bonds

○Tomoya Endo[1], Takashi Nakamura[1] (1. Univ. of Tsukuba)

Japanese

[P2-3am-32]

Synthesis and STM Observation of Dissymmetric Star-shaped Molecules

○Sota Seki[1], Gwenael Rapenne[1,4], Shigeki Kawai[2], Kenichiro Omoto[3] (1. Nara Institute of Science and Technology, 2. National Institute for Materials Science, 3. Nagasaki University, 4. University of Toulouse)

Japanese

[P2-3am-33]

Self-Assembled Structures Formed by Triphenylene Derivatives with the Different Substitution Patterns of Alkoxy and Hydroxy Groups at the Liquid/Solid Interfaces.

○Wangjie Pan[1], Matsuhiro Maeda[1], Kazukuni Tahara[2] (1. Graduate School of Science and Technology, Meiji University , 2. School of Science and Technology, Meiji University)

Japanese

[P2-3am-34]

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Preparation and applications of supramolecular structures from dimethylated α-cyclodextrin

○Momoka Miyasaka[1], Haruya Isida[1], Hajime Shigemitsu[1], Toshiyuki Kida[1] (1. Osaka University)

Japanese

[P2-3am-35]

Stimuli-responsive solid-state chlorophyll derivatives possessing esterified alkyl chains at the 3- and 17-positions

○Koki Yamada[1], Tomohiro Miyatake[1] (1. Faculty of Advanced Science and Technology, Ryukoku Univ.)

Japanese

[P2-3am-36]

Coordination Self-Assembly of Triarylmethanes Modified with Their Arm Moieties

○Masaya Kobayashi[1], Yosuke Nakamura[1], Domoto Yuya[1] (1. Gunma Univ.)

Japanese

[P2-3am-37]

Steric Control over Self-Assembly of Highly Entangled Polyhedral Complexes via Acetylene Coordination

○Ren Nakabayashi[1], Yosuke Nakamura[1], Yuya Domoto[1] (1. The Univ. of Gunma)

Japanese

[P2-3am-38]

Synthesis and Properties of a Rotaxane Composed of a Redox-responsive Macrocyclic Crown Ether and a Diammonium Cation

Kabeya Natsuki[1], ○Akira Ohta[1] (1. Shinshu Univ.)

Japanese

[P2-3am-39]

Development and functions of supramolecular photocatalyst formed by self-assembly of stable carbocation molecules

○Yuya Imuro[1], Hajime Shigemitsu[1], Sakura Yamamoto[1], Toshiyuki Kida[1] (1. Osaka University)

Japanese

[P2-3am-40]

Mechanochromic Luminescence Properties of Benzothienylbenzothiadiazole Derivatives

○Haruto Furukawa[1], Suguru Ito[1,2] (1. Yokohama Natl. Univ., 2. PRESTO, JST)

Japanese

[P2-3am-41]

Crystal Structure and Luminescence Properties of Perylene-Substituted Binaphthol Derivatives

○Riko Yano[1], Suguru Ito[1,2] (1. Yokohama Natl. Univ., 2. PRESTO, JST)

Japanese

[P2-3am-42]

Circularly polarized electroluminescence (CPEL) from phthalocyanine and porphyrin luminescent materials

Seika Suzuki[1], Yuta Yamamoto[1], Shikura Ryuta[2], Satoko Suzuki[3], Shigeyuki Yagi[2], ○Yoshitane Imai[1] (1. Kindai University, 2. Osaka metropolitan University, 3. JASCO)

Japanese

[P2-3am-43]

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Synthesis and Photophysical Properties of Diarylethene containing Thienothiophene Rings with Extended π-Conjugation.

○Manami Furusen[1], Hibiki Naneko[1], Ryo Nishimura[1], Masakazu Morimoto[1] (1. Rikkyo university)

Japanese

[P2-3am-44]

Synthetic Study of a Cage-Type Molecule Undergoing Fluid Bond Shifting

○Hiromichi Yokoyama[1], Reo Kayama[1], Atsuko Kosaka[1], Yoshiaki Shoji[1], Takanori Fukushima[1] (1. CLS, Tokyo Tech.)

Japanese

[P2-3am-45]

stimuli responsive properties of rotaxane-based supramolecular mechanophores having a long rod molecule

○Riku Yamamoto[1], Yoshimitsu Sagara[1] (1. Tokyo institute of technology)

Japanese

[P2-3am-46]

Mechanism of Photo-Induced Crawling Motion of Azobenzene Crystals

○Makoto Saikawa[1,2], Keegan McGehee[1,2], Kengo Manabe[2], Koichiro Saito[2], Yoshihiro Kikkawa[2], Yasuo Norikane[2,1] (1. Univ. of Tsukuba, 2. AIST)

Japanese

[P2-3am-47]

Acridine-based 1D double-wall nanotubes as a scaffold for solid-state electron transfer

○Hiroyuki Kishi[1], Daiji Ogata[1], Junpei Yuasa[1] (1. Tokyo University of Science)

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Academic Program [Poster] | 16. Natural Products Chemistry, Chemical Biology：Poster

Wed. Mar 20, 2024 10:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:00 AM - 2:30 AM UTC Poster Site 3(理工スポーツホール [1階] アリーナ)

[P3-3am] 16. Natural Products Chemistry, Chemical Biology

Japanese

[P3-3am-01]

Chemical degradation of poecillastrins for structural analysis

Raku Irie[1], Zian Han[1], ○Masato Oikawa[1] (1. Yokohama City University)

Japanese

[P3-3am-02]

Functional analysis of putative isomerases in the biosynthesis of macrolactam antibiotic hitachimycin

○Kazuma Tsuboi[1], Ikezaki Mutsumi[1], Koichi Kawamura[1], Tadashi Eguchi[1], Fumitaka Kudo[1] (1. Tokyo Institute of Technology)

Japanese

[P3-3am-03]

Directed Evolution of Product Specificity of 4-hydroxy-3-methyl-2-butenyl diphosphate reductase IspH Using Novel Screening Method for Cellular IPP/DMAPP Ratio

○Aya Nagashima[1], Daichi Ishihara[1], Daisuke Umeno[1] (1. Waseda University)

Japanese

[P3-3am-04]

Effect of various aroma glycosides on glycosidase activity

○Shiori Miyako[1], Yasushi Kawai[1] (1. Nagahama Institute of Bio-Science and Technology)

Japanese

[P3-3am-05]

Synthetic Studies of Interleukin-8 Analog Having High Mannose-type N-glycan

○Taito Akayama[1], Haruna Kanno[1], Masayuki Izumi[1] (1. Kochi University)

Japanese

[P3-3am-06]

Preparation of desmosine-carrier protein conjugated antigen

○Mika Ryu[1], Toyonobu Usuki[1], Mayu Kodaka[1], Reiko Yoko (1. Sophia Univ)

Japanese

[P3-3am-07]

Synthesis of desmosine/isodesmosine-$^{13}C_3$,$^{15}N_1$

○Saki Kondo[1], Mika Hirose, Takahiro Tanigawa, Toyonobu Usuki[1] (1. Sophia University)

Japanese

[P3-3am-08]

Construction of β-hairpin peptides based on dynamic imine bonds

○Harunori Honda[1], Takahiro Nakama[1], Makoto Fujita[1,2,3] (1. Grad. School of Engineering, The Univ. of Tokyo, 2. UTIAS, The Univ. of Tokyo, 3. IMS)

Japanese

[P3-3am-09]

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One-pot Synthesis of Peptide Thiolactone from Hydrazide via Peptide Thioester or Selenoester

○Yuki Funyu[1], Sayaka Sasaki[1], Masayuki Izumi[1] (1. Kochi University)

Japanese

[P3-3am-10]

Fabrication of beta-barrel peptide nanopores using peptide-immobilized beads with photocleavable linkers

○Takuto Kariya[1], Fumihiro Kayamori[1], Ryuji Kawano[2], Kenji Usui[1] (1. Konan University, 2. Tokyo University of Agriculture and technology)

Japanese

[P3-3am-11]

Synthetic Studies on Cyclic Oligosaccharides Using Multivalent Linkers

○Hikari Nishida[1], Tohru Taniguchi[2], Kenji Monde[2] (1. Grad. School of Life Sci., Hokkaido Univ., 2. Grad. School of Advanced Life Sci., Hokkaido Univ.)

Japanese

[P3-3am-12]

Analysis of the main component in the periostracum of the green mussel (*Perna viridis* L.)

○Rena Ikeya[1] (1. Keio University)

Japanese

[P3-3am-13]

Development of a near-infrared fluorescence probe for hROS based on the TICT mechanism.

○Hisashi Ohno[1], Takuya Myochin[2], Shun Sumitani[3], Kenjiro Hanaoka[1,3] (1. Grad. Sch. Pharm. Sci. Keio Univ., 2. Grad. Sch. Pharm. Sci. The Univ. of Tokyo, 3. Fac. Pharm. Keio Univ.)

English

[P3-3am-14]

Development of a natural product-functionalized gold-nanoparticle photoaffinity probe for target analysis

○Masaki ONO[1], Koutharou Abe[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P3-3am-15]

In vivo synthesis of anticancer compounds from acetaldehyde

○Koichi Ishida[1], Ren Kumakura[1], Yudai Ode[1], Ambara Rachmat Pradipta[1], Tsung-che Chang[1], Katsunori Tanaka[1,2] (1. Tokyo Institute of Technology, School of Materials and Chemical Technology, Department of Chemical Science and Engineering, 2. RIKEN Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory)

Japanese

[P3-3am-16]

Photo-chemical control of anticancer activity by novel photo-triggered cyclization reaction

○Hidenori Okamura[1,2], Arisa Kawamori[1,2], Momoka Iida[1,2], Yui Kaneyama[1,2], Mamiko Ozawa[1], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku Univ., 2. Grad. Sch. Sci., Tohoku Univ.)

Japanese

[P3-3am-17]

Synthesis and biological functions of microbial 6-position-modified glucosyl acylglycerols and their analogues

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○Shingo Mochizuki[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Fac. Sci. Tech., Keio Univ.)

Japanese

[P3-3am-18]

Synthetic studies of GlcNCer derivatives with modifying acyl groups

○Ken Shirasaka[1], Kodai Sueyoshi[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Fac. Sci. Tech., Keio Univ.)

Japanese

[P3-3am-19]

Synthesis of novel glycolipids containing cyclopentanetetraol structure for immunomodulatory molecules

○Yuto Aoki[1], Hiroki Sekita[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Fac. Sci. Tech., Keio Univ.)

English

[P3-3am-20]

Improvement of a direct response version of near-infrared genetically encoded Ca^{2+} indicator, dNIR-GECO

○Takumi Kobayashi[1], Rina Hashizume[1], Yong Qian[2], Yusuke Nasu[1], Takuya Terai[1], Robert E. Campbell[1,2] (1. Sch. of Science, The Univ. of Tokyo, 2. Dept. of Chemistry, The Univ. of Alberta)

Japanese

[P3-3am-21]

Unique NMR sampling method controlling water amounts in organic solvent

○Yasuhiro Kajihara[1,2], Tatsuya Moriguchi[1], Yuta Maki[1,2], Ryo Okamoto[1,2] (1. Schl. Sci. Osaka University,, 2. FRC, Grad. Schl. Sci. Osaka university)

Japanese

[P3-3am-22]

Antimutagenic Activity of Fatty Acid Esters from *Pyrus communis*

○Yuki Kakinuma[1], Nozomi Tomaru[1], Atsushi Ogashiwa[1], Kairi Miyashita[1], Hideyuki Tomosaka[1] (1. Nat Inst Tech (KOSEN), Gunma Coll)

Japanese

[P3-3am-23]

Investigation of the photolysis reaction of pyridinium salts

○Kazuma Hiasa[1], Tomohiro Sugiyama[1], Rintaro Gemma[1], Hajime Sato[1,2,3] (1. The Univ. of Yamanashi, 2. Precursory Research for Embryonic Science and Technology, 3. Leading Initiative for Excellent Young Researchers)

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Academic Program [Poster] | 18. Polymer：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-3vn] 18. Polymer

Japanese

[P2-3vn-01]

Synthesis and properties of copolymers of trimethylene carbonate and 4-substituted trimethylene carbonate derivatives

○Ai Teranishi[1], Koji Nakano[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P2-3vn-02]

Oxidatively degradable polyesters using diol with thioacetal structure

○Miho Homma[1], Nobuhiro Kihara[1] (1. The Univ. of Kanagawa)

Japanese

[P2-3vn-03]

Identification of impure structure in the polymer obtained by oxidative polymerization of 5-cyano -2-methoxyphenol oxidizing polymer

○Shimon Takechi Takechi[1], Akiyuki Nakano[1], Takahiro Oshima[2], Hideyuki Higashimura[1,2] (1. Grad. Sch. of Sci., Okayama Univ. of Sci., 2. Grad. Sch. of Sci and Eng., Okayama Univ. of Sci.)

Japanese

[P2-3vn-04]

Synthesis and depolymerization of recyclable polymers using bifunctional aromatic molecular LEGO blocks having lophine moiety

○Wataru Morishita[1], Ryuhei Taguchi[2], Kaoru Adachi[3], Masashi Shiotsuki[1,2], Takeru Iwamura[1,2] (1. Graduate School of Integrative Science and Engineering, Tokyo City University, 2. Faculty of Science and Technology, Tokyo City University, 3. Faculty of Molecular Applied Chemistry and Engineering, Kyoto Institute of Technology)

Japanese

[P2-3vn-05]

Chain end modification of polylactide copolymers and homopolymers by isocyanates and their stereocomplex formation

○Jaeyeong Choi[1], Hiroharu Ajiro[2] (1. Sangpaedong Community Service Center, 2. NAIST)

Japanese

[P2-3vn-06]

Machine Learning-assisted Prediction of Chemical Resistance of Resin Materials for Semiconductor Manufacturing Equipment

○Shogo Kunieda[1], Mitsuru Yambe[1], Yosuke Hanawa[1], Hitoshi Kamijima[2], Toshiaki Shintani[2], Takuo Okude[2], Yoshihiro Hayashi[3], Ryo Yoshida[3] (1. SCREEN Holdings Co., Ltd., 2. Research Institute of Systems Planning, Inc., 3. The Institute of Statistical Mathematics)

Japanese

[P2-3vn-07]

The effect of side chains terminal functional group on physical properties of functional polymer hydrogels

○Riku Fukuoka[1], Yuka Wakayama[1], Takuma Kureha[1] (1. The Univ of Hirosaki)

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Japanese

[P2-3vn-08]

Structural changes of water in hydrogels of carboxymethyl cellulose nanofiber during vapor swelling and drying

○Yuta Takahara[1], Yurina Sekine[2], Takuya Nankawa[2], Tomoko Ikeda-Fukazawa[1] (1. Department of Applied Chemistry, Meiji University, 2. Materials Sciences Research Center, Japan Atomic Energy Agency)

Japanese

[P2-3vn-09]

The effect of different lengths of cross-linkers in hydrogels

○Yuki Hatakeyama[1], Takuto Hirayama[1], Takuma Kureha[1] (1. The Univ. of Hirosaki)

Japanese

[P2-3vn-10]

Effects of block copolymers on properties of aliphatic polycarbonate/vinyl polymer blends

○Mai Nakamura[1], Kousuke Sugeno[1], Hiromu Saito[1], Koji Nakano[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P2-3vn-11]

Unique temperature dependence of aqueous solutions of lactic acid oligomers

○KATSUYUKI NAMAI[1], SHIN-ICHIRO SATO[1] (1. The Univ. of Hokkaido)

Japanese

[P2-3vn-12]

Structure of water in carboxymethyl cellulose nanofiber hydrogel

○Yusuke Beni[1], Yurina Sekine[2], Takuya Nankawa[2], Tomoko Ikeda-Fukazawa[1] (1. Meiji University, 2. Materials Sciences Research Center, Japan Atomic Energy Agency (JAEA))

Japanese

[P2-3vn-13]

Effect of Carbonyl Groups in aromatic Polyimides on Optical Properties.

○Taichi Hirasima[1], Tomoyuki Hirayama[1], Hiroki Miyauchi[1] (1. Graduate School of Engineering Kyushu Sangyo University)

Japanese

[P2-3vn-14]

Ordered Structures of Liquid Crystalline Polyurethanes with Bis (benzylidene) phenylenediamine Group in the Skeletal Main-Chain

○Aya Seike[1], Ryoga Nishimura[2], Masanori Nata[3], Seiji Ujiie[3] (1. Division of Applied Chemistry, Faculty of Science and Technology, Oita University, 2. Division of Applied Chemistry,Graduate School of Engineering, Oita University, 3. Biological and Material Chemistry Program, Faculty of Science and Technology, Oita University)

Japanese

[P2-3vn-15]

Liquid Crystalline and Orientational Properties of Mesogenic Diol Compounds and Their Polyaddition Polymers

○Kanoko Miyawaki[1], Masanori Nata[2], Seiji Ujiie[2] (1. Division of Applied Chemistry, Faculty of Science and Technology, Oita University, 2. Biological and Material Chemistry Program, Faculty of Science and Technology, Oita University)

Japanese

[P2-3vn-16]

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Properties and Cross-Linked Structure of Allyl-Containing Benzoxazine–Maleimide Thermosetting Resins

○Shuichi Nakao[1], Toshiyuki Iwai[1], Masatoshi Mihara[1], Keiko Ohtsuka[1], Junichi Takashiro[2], Shimpei Obata[2], Hirosuke Saito[2] (1. Osaka Research Institute of Industrial Science and Technology, 2. Panasonic Industry Co., Ltd.)

Japanese

[P2-3vn-17]

Improvement of gel-state NMR spectroscopy to investigate the adsorption property of π-conjugated molecules onto cellulose nanofiber

○Mashu Hirogari[1], Yasuko Saito[2], Yoshiharu Mitoma[1], Keita Sakakibara[2] (1. Prefectural University of Hiroshima, 2. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese

[P2-3vn-18]

Development and biodegradability of wood adhesive polyesters composed of lignin-derived 2-pyrone-4,6-dicarboxylic acid (PDC)

○Yijie Jin[1], Takuma Araki[2], Naofumi Kamimura[3], Eiji Masai[3], Masaya Nakamura[3], Tsuyoshi Michinobu[1] (1. Tokyo Institute of Technology, 2. Forestry and Forest Products Research Institute, 3. Nagaoka University of Technology)

English

[P2-3vn-19]

Obtain thermal responsive star-shaped copolymer gel with homogeneous network containing gold nanoparticles

○YIAN WANG[1], Yukikazu Takeoka[1] (1. The Univ. of Nagoya)

Japanese

[P2-3vn-20]

Preparation and properties of indroquinoxailine-containing polymer

○Hideki Hayashi[1], Oda Mitsuo[1], Take-aki Koizumi[2] (1. Nagoya Municipal Industrial Research Institute, 2. Advanced Instrumental Analysis Center, Shizuoka Institute of Science and Technology)

Japanese

[P2-3vn-21]

Design of wireless electrochemical gel actuators

○Soma Hodono[1], Keiichi Imato[1], Taichi Hino[1], Ichiro Imae[1], Yousuke Ooyama[1] (1. Hiroshima university)

English

[P2-3vn-22]

Supramolecular Assembly of Biodegradable Amphiphilic Block Copolymers Built through Biomolecule Folic Acid as a Hydrogen Bonding Moiety

○Rongjian Lang[1], Yusuke Miyazaki[1], Masaki Nakahata[2], Kazuki Fukushima[1], Takashi Kato[1] (1. The University of Tokyo, 2. Osaka University)

Japanese

[P2-3vn-23]

Polymer matrix effects on photoinduced electron transfer

Yilin Cao[1], Hikaru Soutome[2], Syoji Ito[2], ○Hiroyasu Yamaguchi[1] (1. Graduate School of Science, Osaka Univ., 2. Graduate School of Engineering Science, Osaka Univ.)

Japanese

[P2-3vn-24]

Polymerization of 3,5-dihydroxymethylphenylacetylene with oligophenylene at position 4 and properties of the resulting polymer

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○Yuki Taguchi[1], Toshiki aoki[1], Takashi Kaneko[1], Masahiro Teraguchi[1] (1. The Univ. of Niigata)

Japanese

[P2-3vn-25]

A design of lithium-ion conductive electrolytes based on alignment of zwitterions

○Satomi Yokoyama[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P2-3vn-26]

Synthesis of silicone-based multiblock copolymers and additive effects on epoxy resins

○Hirokazu Iwata[1], Itaru Asano[1] (1. Toray Industries, Inc.)

Japanese

[P2-3vn-27]

Triple helix formation and properties of modified ß-glucan derivatives

○masami okue[1] (1. Graduate school of Engineering, Sojo University)

Japanese

[P2-3vn-28]

Preparation of polyion complex microparticles composed of salmon milt DNA and cationic lipids having a disulfide bond

○Kota Ohmukai[1], Mituhiro Shibata[1], Naozumi Teramoto[1] (1. Chiba Inst. Technol)

Japanese

[P2-3vn-29]

Effect of degree of acetylation and molecular weight on solubility of chitosans

○Miho Araki[1], Hironori Izawa[1] (1. University of Miyazaki)

Japanese

[P2-3vn-30]

Development of casein-based materials

○Hirotaka Nakashima[1], Hironori Izawa[1] (1. University of Miyazaki)

Japanese

[P2-3vn-31]

Synthesis and characterization of surface-modified nanofibrillated bacterial cellulose by EDTA for the adsorption of heavy metal ions

○Ryosui Sasa[1], Nanami Kinoshita[1], Ryota Kishimoto[1], Sayaka Fujita[1], Hiroyuki Kono[1], Kenji Tajima[2] (1. Natl. of Tech, Tomakomai Col., 2. Hokkaido Univ.)

Japanese

[P2-3vn-32]

Thermal degradation behavior of polystyrene confined in MOF pores

○Haruma Tatsumi[1], Ami Nishijima[2], Yuki Kametani[2], Takashi Uemura[2] (1. School of Engineering, The Univ. of Tokyo, 2. Graduate School of Engineering, The Univ. of Tokyo)

Japanese

[P2-3vn-33]

Aggregation behavior and molecular recognition by the thermoresponsive block polymers having optically active acrylamide units in the presence of organic substrates.

○Keisuke Takamure[1], Manabu Ishihune[1] (1. Kindaiuniversity)

English

[P2-3vn-34]

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Non-catalytic Hydrothermal Dechlorination Kinetics of Polyvinyl chloride

○Douglas Hungwe[1], Satomi Hosokawa[1], Yuki Yamasaki[1] (1. Hosei University)

Japanese

[P2-3vn-35]

Aldol reactions in water by using optically active thermoresponsive polymers having glutamic acid derived side chains – Sc (III) complexes

○Hikaru Aoyagi[1], Manabu Ishifune[1] (1. Kindai University)

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Academic Program [Poster] | 19. Colloid and Interface Chemistry：Poster

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[P3-3vn] 19. Colloid and Interface Chemistry

English

[P3-3vn-01]

Circularly polarized luminescence chiral inversion of monodisperse structural colored particles

○Jialei He[1], Yukikazu Takeoka[1] (1. Nagoya University)

Japanese

[P3-3vn-02]

Synthesis and localized surface plasmon resonance properties of PtSn nanoparticles

○HYUNJI LEE[1], Haruka TAKEKUMA[1,2], Ryota SATO[2], Kenji IIDA[3], Toshiharu TERANISHI[1,2] (1. Grad. Sch. of Fac. of Sci., Kyoto Univ., 2. ICR, Kyoto Univ., 3. ICAT, Hokkaido Univ.)

Japanese

[P3-3vn-03]

Preparation and catalytic performance of supported gold nanoflowers prepared by 3-morpholinopropanesulfonic Acid

○Yuki Ishii[1], Yshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-04]

Changing color of gold nanoflower supported on alumina by addition of solvent

○Minoru Kuge[1], Asuka Kasuga[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-05]

Improving catalytic activity of supported small-size gold nanoflower by UV-ozone treatment

○Shogo Sasaki[1], Asuka Kasuga[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-06]

Water and organic solvent dispersible gold and silver nanoparticles capped with long-chain amine

○Koshi Okada[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-07]

Effective Drying Methods for Colloidal Magnetic Iron Oxide Nanoparticles Utilizing Micro Powder Drying Technique

○Satoshi Seino Seino[1], Kota Nishigaki[1], Takashi Nakagawa[1] (1. Osaka University)

Japanese

[P3-3vn-08]

Supported anisotropic Au nanocrystals prepared by seed growth method using gold nanoparticles supported on modified silica

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○Riko Kawahara[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-09]

Synthesis of poly(*N*-isopropylacrylamide-*co*-2-carboxyisopropylacrylamide) gel particles for tumor-selective delivery of cisplatin

○Yoshiki Tajima[1], Yukiya Kitayama[1], Eiji Yuba[1], Atsushi Harada[1] (1. Osaka Metropolitan University Graduate School)

Japanese

[P3-3vn-10]

Stability of three-phase emulsion under hydrothermal conditions

○Masashi Takahashi[1], Riina Kimura[1], Kazuki Imaida[1], Koshiro Toyokawa[1], Kana Miyasaka[2], Yoko Imai[2], Kazuo Tajima[2] (1. Tokyo City University, 2. Kanagawa University)

Japanese

[P3-3vn-11]

Adsorption of Neutral Compounds on Clay Nanosheet

○Yuki Fukasawa[1], Nanako Nishida[2], Tetsuya Shimada[2], Tamao Ishida[2,3], Shinsuke Takagi[2,3] (1. Fac. of Urb. Env. Sci., Tokyo Metropolitan Univ., 2. Grad. Sch. of Urb. Env. Sci., Tokyo Metropolitan Univ., 3. ReHES, Tokyo Metropolitan Univ.)

Japanese

[P3-3vn-12]

Structural Analysis of Aggregates Formed by Cationic Gemini Surfactants Using Small-Angle X-ray Scattering and Rheology

○Tsukasa Morita[1], Shiho Yada[2], Tomokazu Yoshimura[1] (1. Nara Women's Univ., 2. Tokyo University of Science)

Japanese

[P3-3vn-13]

Wettability of Solid Surface and Antibacterial Properties of Cationic Gemini and Trimeric Surfactants

○Risa Kawai[1,2], Hideyuki Kanematsu[1], Shiho Yada[3], Tomokazu Yoshimura[2] (1. National Institute of Technology, Suzuka College, 2. Nara Women's University, 3. Tokyo University of Science)

Japanese

[P3-3vn-14]

Foam characteristics in mixed aqueous solutions of homogeneous polyoxyethylene alkyl ether sulfate-type anionic and acetic acid betaine-type zwitterionic surfactants.

○Yuta Matsumoto[1], Yukishige Kondo[1], Shiho Yada[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-15]

Organic dye-induced sol-gel transition of zwitterionic surfactants

○Nozomi Katsurai[1], Clara Imura[1] (1. Ochanomizu University)

Japanese

[P3-3vn-16]

Effect of amino acid addition on the gelation of amidoamine-derivative surfactant

○Haruka Tsurui[1], Clara Imura[1] (1. Ochanomizu University)

Japanese

[P3-3vn-17]

Gelation property of Rice Bran Wax and the aplication as a separation agent

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○Kazuaki Ito[1], Asuka Takahashi[1], Sayaka Yamada[1], Takanori Inoue[2] (1. Yamagata University, 2. Sanwa Yushi Co. Ltd.)

Japanese

[P3-3vn-18]

Effect for Thermodynamic Behaviors of Organogels with the Terminal Alkyl Chain Length in Phenyl 4-(Tridecafluorohexyl)ethylthiobenzoates

○Soma Mutaguchi[1], Junya Yamaguchi[1], Takumi Sugiura[1], Kenta Matsumoto[1], Yuki Morita[1], Hiroaki Okamoto[1] (1. Yamaguchi University)

Japanese

[P3-3vn-19]

Correlation between Thermal Properties and A Terminal Alkyl Chain Length of Organogels Formed by 4-(Semi-fluoroalkyl)thiophenyl 4-Alkoxybenzoates

○Yosei Suzuki[1], Kotaro Kanatada[1], Daiki Kajiyama[1], Kenta Matumoto[1], Yuki Morita[1], Hiroaki Okamoto[1] (1. Yamaguchi University)

Japanese

[P3-3vn-20]

Thermal and Rheological Properties of Organogels Formed by Benzoate and Biphenylcarboxylate Derivatives Having Fluoroalkyl Groups at Both Terminal Positions

○Atsuki Kojo[1], Ryotaro Takenaka[1], Sota Kanemitsu[1], Kenta Matsumoto[1], Yuki Morita[1], Hiroaki Okamoto[1] (1. Yamaguchi University)

Japanese

[P3-3vn-21]

Monolayer Formation of Quaternary-Ammonium-Salt-Type Amphiphilic Gemini Ionic Liquids at Air/Water Interface

○Yasuharu Domoto[1], Risa Kawai[1,2], Shiho Yada[3], Tomokazu Yoshimura[2] (1. National Institute of Technology, Suzuka College, 2. Nara Women's University, 3. Tokyo University of Science)

Japanese

[P3-3vn-22]

Localized formation of MOFs induced by near-infrared light irradiation on plasmonic metal nanoparticles

○Ritsurai Tomii[1], Kosuke Sugawa[1], Joe Otsuki[1] (1. Nihon University)

Japanese

[P3-3vn-23]

Preparation and Morphology Control of Silver Nanoparticles via Electrochemical Deposition on a Transparent Electrode

○Hiroyasu Nishi[1], Nozomi Yamamoto[1] (1. Univ. of Toyama)

Japanese

[P3-3vn-24]

Singlet oxygen generation by near-infrared light for metal nanoparticle/metal porphyrin MOF hybrids

○Keiichi Yamanaka[1], Kosuke Sugawa[1], Joe Otsuki[1] (1. Nihon University)

Japanese

[P3-3vn-25]

Effect of liposome and solute composition on the kinetics of insulin amyloid fibrillation

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○Satoru Goto[1], Shingo Tsurumoto[1], Yusuke Horizumi[1], Tomohiro Tsuchida[1], Kanji Hasegawa[1], Ryotaro Koga[1], Yuta Okumura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-26]

In situ microscopic measurements of stability of surfactin emulsion

○Chisato Kondo[1,2], Satoshi Tsukahara[3] (1. Osaka Prefectural Toyonaka High School, 2. Osaka Univ. SEEDS program, 3. Graduate School of Science, Osaka Univ.)

Japanese

[P3-3vn-27]

Microcontact Printing of Semiconductor Nanocrystals by Chemical Functionalization

○Takuya Okamoto[1], Vasudevanpillai Biju[1] (1. Hokkaido University)

Japanese

[P3-3vn-28]

Observation of structure formation process via structural color in spherical colloidal clusters

○Ryosuke Ohnuki[1], Yukikazu Takeoka[2], Shinya Yoshioka[1] (1. Tokyo University of Science, 2. Nagoya University)

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Academic Program [Poster] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 4(理工スポーツホール [1階] アリーナ)

[P4-3vn] 21. Energy and Related Chemistry, Geo and Space Chemistry

Japanese

[P4-3vn-01]

Electrochemical Insertion/Deinsertion of Carbonate ions into/form Layered Double Hydroxide

○Soma Sato[1], Susumu Arai[1], Masahiro Shimizu[1] (1. Shinshu University)

Japanese

[P4-3vn-02]

Electrochemical Protonation/Deprotonation of Olivine-type $FePO_4$ in Metal-Free Aqueous Electrolytes

○Tomonori Ichikawa[1], Susumu Arai[1], Masahoro Shimizu[1] (1. Shinshu University)

Japanese

[P4-3vn-03]

Synthesis and proton conductivity of Benitoite-type phosphate, $KCa_{1-x}H_{2x}(PO_3)_3 \cdot yH_2O$

○Kou Yuuka[1], Hirose Kazuhiko[1], Matsuda Yasuaki[1] (1. Chiba Institute of Technology)

Japanese

[P4-3vn-04]

Synthesis, crystal structure and proton conductivity of the Benitoite-type phosphate, $KMg_{1-x}Li_xH_x(PO_3)_3 \cdot yH_2O$

○Kazuhiko Hirose[1], Yuuka Kou [1], Yasuaki Matsuda[1] (1. Chiba Institute of Technology)

Japanese

[P4-3vn-05]

Battery Performance of Inverse Vulcanized and Sulfurized Alcohol Composites

○Ryo matushima[1], Katsuhiro Wakamatsu[1], Hirofumi Yoshikawa[1] (1. Kwanseigakuinn university)

Japanese

[P4-3vn-06]

Effects of Structural Isomers in Hydrogen-Bonded Organic Frameworks on Battery Performance

○Soichiro Furuno[1], Katsuhiro Wakamatsu[1], Yoshihiko Yamaguchi[1], Hosei Oshima[1], Hirofumi Yoshikawa[1] (1. Kwansei Gakuin University)

Japanese

[P4-3vn-07]

Battery Performance of Two-Dimensional Layered Metal−Organic Frameworks

○Shunsuke Okata[1], Katsuhiro Wakamatsu[1], Tomoki Koyanagi[1], Takeshi Shimizu[2], Hirofumi Yoshikawa[1] (1. Kwansei Gakuin University, 2. Yonago College)

Japanese

[P4-3vn-08]

Relationship between film thickness of organic p-n bilayer and its photocathodic activity for producing hydrogen peroxide in an acidic medium

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○Yuika Sakaguchi[1], Toshiyuki Abe[1] (1. Graduate School of Science and Technology, Hirosaki University)

Japanese

[P4-3vn-09]

Synthesis of Sb_2Se_3 colloidal quantum dot and film formation using salting out for the colloidal quantum dot solar cell

○Rie Kobayashi[1], Taiga Shimizu, Toshihito Ohtake[1] (1. Prefectural University of Hiroshima)

English

[P4-3vn-10]

Short-Step Synthesized Dopant-Free Spiro-Type Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells

○Nobuko ONOZAWA-KOMATSUZAKI[1], Daisuke Tsuchiya[2], Inoue Shinichi[2], Atsushi Kogo[1], Takurou N. Murakami[1] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Nippon Fine Chemical Co., Ltd.)

Japanese

[P4-3vn-11]

Evaluation of perovskite solar cells with potassium and thiocyanate ion.

○Hiroki Nagata[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese

[P4-3vn-12]

Fabrication and Evaluation of Dye-Sensitized Solar Cells Using Reduced Graphene Oxide as Redox material

○Mondo Nijuri[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese

[P4-3vn-13]

Development of solid-state dye-sensitized solar cells with a double-layered anatase TiO_2 electrode: effects of the sintering strategies on the electrode performance

○Satoka Wada[1], Mei Matsui[1], Shinapol Toranathumkul[1], Takashi Sugiura[1], Kazuhiro Manseki[1] (1. Gifu University)

Japanese

[P4-3vn-14]

Artificial Photosynthesis System Producing Formic Acid - Isolation of Pure Formic Acid from a Potassium Phosphate Electrolyte -

○Masahito Shiozawa[1], Yoshihiro Kikuzawa[1], Naohiko Kato[1], Yasuhiko Takeda[1] (1. Toyota Central R&D Labs., Inc.)

Japanese

[P4-3vn-15]

Emission wavelength control in dual annihilator-based triplet annihilation upconversion systems and plasmon-induced effects

○Toukichi Kusumikawa[1] (1. Nihon University)

Japanese

[P4-3vn-16]

Trend analysis of the technologies for environment and energy by using the data of papers and patents in e-CSTI (Evidence data platform constructed by Council for Science, Technology and Innovation)

○Naoki Mimura[1], Kazumasa Omote[1], Torazo Ikeda[1], Eiko Kono[1], Hiroaki Nagai[1], Naoaki Kashiwabara[1] (1. Cabinet Office)

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Academic Program [Poster] | 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry：Poster

Mon. Mar 18, 2024 10:00 AM - 11:30 AM JST | Mon. Mar 18, 2024 1:00 AM - 2:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-1am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Japanese

[P1-1am-01]

Theoretical Study of Metal-Supported Catalyst Conversion of Cellulose to Sugar Alcohols

○Yuto Nakata[1,2], Takehiko Sasaki[1], Motoyuki Shiga[2] (1. The Univ. of Tokyo, 2. Japan Atomic Energy Agency)

Japanese

[P1-1am-02]

Considering the role and application of large-scale generative AI in promoting "Autonomous Chemical Research" in the information age

○Kohtaro Yuta[1] (1. In Silico Data, Ltd.)

Japanese

[P1-1am-03]

Prediction of bond dissociation free energy using SQM-ML model

○Miki Kaneko[1], Toru Saito[1] (1. Hiroshima City University)

English

[P1-1am-04]

Designing Novel Organoselenium Derivatives as SARS-CoV-2 Main Protease Inhibitors by Integrating QSAR and LB-PaCS-MD Techniques

○Thanyada Rungrotmongkol[1,4], Borwornlak Toopradab[1], Wanting Xie[2], Kowit Hengphasatporn[3], Phornphimon Maitarad[2], Athina Geronikaki[5] (1. Center of Excellence in Structural and Computational Biology Research Unit, Department of Biochemistry, Faculty of Science, Bangkok 10330, Thailand, 2. Research Center of Nano Science and Technology, Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, China, 3. Center for Computational Sciences, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan, 4. Program in Bioinformatics and Computational Biology, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand, 5. Department of Pharmaceutical Chemistry, School of Pharmacy, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece)

English

[P1-1am-05]

Improved photocatalytic performance of eosin Y-sensitized anatase by anchoring group modification. A DFT/TDDFT insight

○Juan Shang[1], Aleksandar Staykov[1], Tatsumi Ishihara[1] (1. International Institute for Carbon-Neutral Energy Research I2CNER, Kyushu University)

Japanese

[P1-1am-06]

Chemoinformatics study on the evaluation of binding free energies of IDO1 inhibitors

○Tatsuya Fujiwara[1], Toru Saito[1] (1. Hiroshima City University)

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Japanese

[P1-1am-07]

Topological Interpretation of the Stability of Polycyclic Conjugated Systems

○Rika Sekine[1], Kei Saito[1], Mizuki Nakamura[1] (1. Shizuoka Univ.)

Japanese

[P1-1am-08]

Automated Prediction of NMR Chemical Shift of Aromatic Compounds Using SQM-ML Approach

○Yuto Shiotake[1], Toru Saito[1] (1. The Univ. of Hiroshima City)

Japanese

[P1-1am-09]

Prediction of pH dependence of peptides containing acidic residues by the configuration-selection constant pH (CS-CpH) method

Fuka Inagaki[1], ○Yukichi Kitamura[2], Haruka Yotsuya[1], Masataka Nagaoka[1,3] (1. Grad. of Info., Nagoya Univ., 2. Engin., Shizuoka Univ., 3. FVC Research Center, Nagoya Univ.)

Japanese

[P1-1am-10]

Analysis of solvent electrostatic potential described by solvation models in charged systems

○Yuki Kanamaru[1], Norio Yoshida[2], Toru Matsui[1] (1. Univ. of Tsukuba, 2. Nagoya University)

Japanese

[P1-1am-11]

A regression study for odor character prediction based on molecular structural representation by machine learning

○Yuki Harada[1], Shuichi Maeda[1], Junwei Shen[1], Taku Misonou[2], Hirokazu Hori[2], Shinichiro Nakamura[1] (1. Kumamoto University, 2. University of Yamanashi)

Japanese

[P1-1am-12]

Development of FMO-CDFT method by Integrating FMO method and Constrained Density Functional Theory

○Shohei Osaki[1], Masato Kobayashi[2], Tetsuya Taketsugu[2], Toru Matsui[1] (1. Univ. of Tsukuba, 2. Univ. of Hokkaido)

Japanese

[P1-1am-13]

Crystal structure prediction using generalized hypersphere search method focusing on packing fraction

○Yoshiki Ueda[1], Takuto Oki[2], Yuuki Midoro[2], Hideo Yamakado[1,2] (1. Faculty of Systems Engineering, Wakayama Univ., 2. Graduate School of Systems Engineering, Wakayama Univ.)

Japanese

[P1-1am-14]

Multi-Objective Generative Adversarial Network for Inorganic Chemical Compositions

○Tomiya Yamamoto[1], Mamoru Nishijo[1], Yosuke Harashima[1,2], Shogo Takasuka[1], Tomoaki Takayama[1,2], Yoshihide Sawada[4], Mikiya Fujii[1,2,3] (1. Nara Institute of Science and Technology, Japan, 2. DSC, Nara Institute of Science and Technology, Japan, 3. CMP, Nara Institute of Science and Technology, Japan, 4. Aichi Sangyo University ,Japan)

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Japanese

[P1-1am-15]

How Precisely Can Semiempirical Molecular Orbital Calculations Reproduce Electronic State Fluctuations of Biomolecules? Comparison with high-precision methods toward bio-system analysis.

○Nichika Ozawa[1], Nahoko Kuroki[1,2], Hirotoshi Mori[1] (1. Chuo University, 2. JST ACT-X)

Japanese

[P1-1am-16]

Theoretical analysis of nucleophilic addition reaction of 1,3,5-trimethoxybenzene to *N*-methylmaleimide in 1,4-dioxane

○Chizuru Muguruma[1], Nobuaki Koga[2] (1. Chukyo University, 2. Nagoya University)

Japanese

[P1-1am-17]

Theoretical study of hydrogen diffusion in Pd and AgRh nanoclusters

○Manaka Kimura[1], Koji Ando[1] (1. Tokyo Woman's Christian University)

Japanese

[P1-1am-18]

Structure and dynamics of water molecular clusters in the ligand binding pocket of taste receptor proteins

○Kie Araki[1], Koji Ando[1] (1. Tokyo Woman's Christian University)

Japanese

[P1-1am-19]

Analysis of photophysical properties of naphthalimide derivatives and carboxylic acid clusters

○Natsumi Watanabe[1], Yuki Kanamaru[1], Toru Matsui[1], Masato Sumita[2], Hironori Izawa[3], Kenji Morihashi[1] (1. University of Tsukuba, 2. RIKEN AIP, 3. University of Miyazaki)

English

[P1-1am-20]

Molecular Dynamics Study of Rhamnose-Conjugated Antimicrobial Cyclotetrapeptides for Developing Novel Antibody Recruiting Molecule

○Jelang Muhammad Dirgantara[1], Regaputra Satria Janitra[2], Rani Maharani[2], Ari Hardianto[2], Yoshiyuki Manabe[2], Koichi Fukase[2] (1. Osaka University, 2. Universitas Padjadjaran)

Japanese

[P1-1am-21]

Study of the structure of ferrocene using the GRRM

○Yosuke Tokuda[1], Yoshiki Ueda[2], Hideo Yamakado[1,2] (1. Graduate School of Systems Engineering, Wakayama Univ., 2. Faculty of Systems Engineering, Wakayama Univ.)

Japanese

[P1-1am-22]

Nonadiabatic *ab initio* dynamics study of the photoisomerization process for 3,5-dimethylisoxazole via S_1 electronic state

○Mizuki Kimura[1], Shinkoh Nanbu[1] (1. Sophia University)

Japanese

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[P1-1am-23]

Theoretical study on tne cyclization reaction of allene type zerumbone under acidic condition

○Noriko Tsuchida[1], Gengo Kashiwazaki[2], Aoi Nakamura[3], Takashi Kitayama[2,3] (1. Saitama Med. Univ., 2. Graduate School of Agriculture, Kindai Univ., 3. Faculty of Agriculture, Kindai Univ.)

Japanese

[P1-1am-24]

Mechanistic analysis of double proton transfer in DNA base pairs by QM and QM/MM-MD

○Urabe Takayuki[1], Toru Saito[1] (1. Hiroshima City University)

Japanese

[P1-1am-25]

Exploration of reaction pathways for hydrogen addition to ethylene using Global Reaction Route Mapping (GRRM).

○Hiroki Shimizu[1], Yoshiki Ueda[1], Hideo Yamakado[1,2] (1. Faculty of Systems Engineering, Wakayama University, 2. Graduate School of Systems Engineering, Wakayama University)

Japanese

[P1-1am-26]

Theoreticall study on enantioselectivity of catalytic propargyl substitution reaction using chiral ion pair

○Takeshi Yoshikawa[1], Ken Sakata[1], Yuya Nakajima[2] (1. Toho University, 2. ENEOS Corporation)

Japanese

[P1-1am-27]

Quantum Chemical Solvent Effects Evaluation for Improving Amine-based CO2 Chemical Absorbents

○Haruka Nobuoka[1], Nahoko Kuroki[1], Hirotoshi Mori[1] (1. huo University)

Japanese

[P1-1am-28]

Beyond-Born-Oppenheimer analysis of chemical reactions exhibiting secondary kinetic isotope effects: nucleophile dependence of S_N2 reactions

○Kohei Motoki[1], Hirotoshi Mori[1] (1. The Univ. of Chuo)

Japanese

[P1-1am-29]

Density functional theory study on the formation of inclusion complexes of (-)-epigallocatechin-3-*O*-gallate derivatives with β-cyclodextrin

○Hirohito Ikeda[1], Tomonori Ohata[1], Rie Nakashima[1], Hiroyuki Tsutsumi[1], Masao Fujisawa[2] (1. Fukuoka University, 2. Kindai University)

Japanese

[P1-1am-30]

Quantum chemical Investigation of substituent effects in the initial reaction step of Hypergolic Bipropellant

○Miori Nogamida[1], Nahoko Kuroki[1], Hirotoshi Mori[1] (1. Chuo university)

Japanese

[P1-1am-31]

Quantum Chemical Calculations of Intermolecular Complexes of Fullerenes with Oligoethylene Glycol and Oligo Propylene Glycol

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○Sota Arima[1], Shin-ichiro Sato[2] (1. Hokkaido University Graduate School of Engineering Course of Applied Chemistry, 2. Hokkaido University Faculty of Engineering)

Japanese

[P1-1am-32]

Theoretical study on the hydrogen bond between ligand water and water in the hydrated sodium and magnesium ion clusters

○Ryu Kato[1], Chisa Furukawa[1], Yuuna Mikami[1], Yasuhiro Sunaga[1], Shoji Kudo[1], Hidenori Matsuzawa[1] (1. Chiba Institute of Technology)

English

[P1-1am-33]

Effect of anchoring group on electron transfer in hybrid dye-sensitized photocatalyst. DFT and TD-DFT study.

○Yasuhiro Kayo[1], Alexander Staykov[2], Motonori Watanabe[2] (1. Graduate School of Integrated Frontier Sciences, Kyushu University, 2. International Institute for carbon-Neutral Energy Research, Kyushu University)

Japanese

[P1-1am-34]

Molecular dynamics simulation of topology-induced changes in surface physisorption dynamics of cyclic polymers

○Tsuyoshi Nakai[1], Shin-ichiro Sato[1] (1. Hokkaido Univ.)

Japanese

[P1-1am-35]

Analyses of protein-glycan multivalent interaction in bacterial infection

○Kaori Ueno Noto[1] (1. Kitasato University)

Japanese

[P1-1am-36]

Creating a prediction model for activation barriers for cycloreversion of diarylethenes by using machine learning

○Kousei Yamanaka[1], Staykov Aleksandar[1] (1. The Univ. of Kyushu)

Japanese

[P1-1am-37]

Reconsideration of the internal protonation mechanism of the [1.1.1] cryptand

○Shigeru Ishikawa[1] (1. Tokai University)

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担持金属触媒によるセルロースの糖アルコール変換反応の理論的研究

（東大院新領域創成科学研究科[1]・日本原子力研究開発機構[2]）○中田 悠人[1,2]・佐々木 岳彦[1]・志賀 基之[2]

Theoretical Study of Metal-Supported Catalyst Conversion of Cellulose of Sugar Alcohols

([1]*Graduate School of Frontier Sciences, Tokyo University*, [2]Japan Atomic Energy Agency)
○Yuto Nakata,[1,2] Takehiko Sasaki,[1] Motoyuki Shiga,[2]

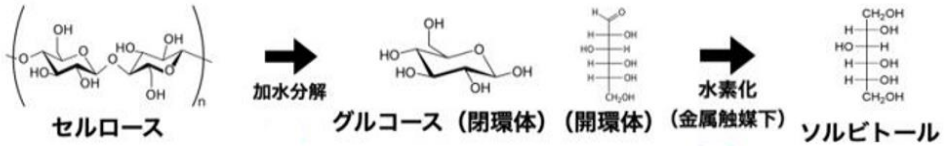
The reuse of cellulose, which is disposed of in large quantities as non-food biomass in green chemistry, is an important issue. Experimental studies have been conducted on routes to hydrolyze and hydrogenate cellulose using metal catalysts in high-temperature aqueous solutions and convert it into sugar alcohols that can be used as raw materials for fuels and chemicals. In this study, first-principles calculations using a water continuum model and metadynamics calculations explicitly including water were performed for the conversion of cellobiose to sorbitol, as a typical example, to evaluate the free energy barriers in the hydrolysis and hydrogenation processes.

The calculations show that the cellobiose hydrolysis reaction can occur by hydrogen addition over a metal catalyst, but the addition of spillover atomic hydrogen to the supported metal is more likely to occur. In addition, platinum was found to have a larger adsorption energy and a lower reaction barrier than palladium in the hydrogenation reaction.

Keywords : First-principles Calculations; Metadynamics Calculation; Green Chemistry

グリーンケミストリーにおいて非食料バイオマスとして大量に廃棄されるセルロースの再利用が重要課題である。高温水溶液中で金属触媒を用いてセルロースを加水分解・水素化し、燃料・化学品原料となる糖アルコールへの変換ルートに関して、実験的研究がおこなわれてきた。本研究では、その典型例であるセロビオースからソルビトールへの変換について、水を連続体モデルとした第一原理計算と、水を明示的に含めたメタダイナミクス計算を行い、その加水分解・水素化過程における自由エネルギー障壁を評価した。

計算の結果、セロビオース加水分解反応は金属触媒中の水素付加で起こりうるが、担持金属触媒へスピルオーバーした原子状水素の付加はさらに起こりやすいことが分かった。また、水素化反応では白金がパラジウムに比べて吸着エネルギーが大きく、反応障壁が低いことが分かった。



1) A. Fukuoka, P. L. Dhepe, Angew. Chem. Int. Ed. 45, 5161 (2006).

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情報時代の「自律型化学研究」における、大規模生成 AI の役割と適用に関する考察

（インシリコデータ）○湯田　浩太郎

Considering the role and application of large-scale generative AI in promoting "Autonomous Chemical Research" in the information age

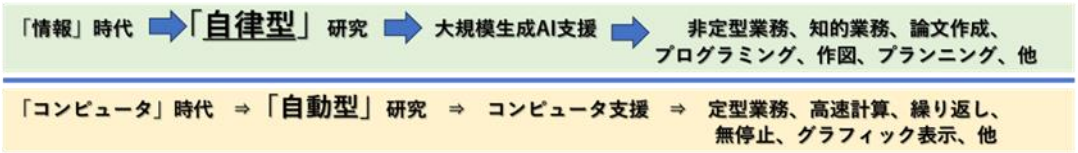
(In Silico Data, Ltd.) ○Kohtaro Yuta

Research work is classified into ``automatic research" and ``autonomous research." The former focuses on computer functions, and is characterized by fixed forms, repetition, and high-speed calculations. The latter was work that involved intellectual content such as atypical, irregular, creative work, various judgments, and planning, and was the exclusive domain of researchers. Recently deployed large-scale generative AI can directly support "autonomous chemical research". We considered the possibility of making conventional chemical research work and research methods more sophisticated and intelligent.

Keywords : Large-scale generative AI; Information age; Autonomous chemical research; Artificial Intelligence

1. はじめに

時代は常に進歩し、時代ごとに基本となる技術は変化する。本発表では現在から未来への時代の移行に伴って変化する化学関連研究の内容や形式について論じる。同時に、新時代の化学研究の基本技術となる大規模生成 AI の関与について議論する。



2. 研究業務の「自動型化学研究」と「自律型化学研究」について

湯田は、研究業務はその内容的に「自動型研究」と「自律型研究」の二種類に分類されると提唱(1)した。自動型研究は、定形、繰り返し、高速計算等が特徴でコンピュータの機能が中心の研究業務となる。自律型研究は、非定型、不規則、創造、種々判断、プランニング等の知的な内容を伴う業務である。自動型研究業務の実施や支援はコンピュータが行う。しかし、自律型研究のような知的活動を支援できる手段は存在しなかったため、自律型研究事項は研究者の専任事項となっていた。

3. 「自律型化学研究」を実施、支援する大規模生成 AI

自動型と異なり自律型は非定型、且つより高度な知的、複雑な業務が中心であり、このような業務を支援する技術は存在しなかった。大規模生成 AI は人間の知的業務の殆どを実施可能である。この技術は「自律型化学研究」を直接支援可能であり、従来の化学研究業務や研究手段を、より高度なものとする可能性を秘めている。

1) Proposal and Outline of the “Autonomous Chemistry” Research. K.Yuta, Chem-Bio Informatics Society(CBI) Annual Meeting 2022, P03-11.

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SQM-ML モデルによる結合解離自由エネルギーの予測

（広市大情報）○金子 未来・齋藤 徹
Prediction of bond dissociation free energy using SQM-ML model ([1]*Faculty of Information Sciences, Hiroshima City University*) ○Miki Kaneko[1], Toru Saito[1]

C-H bond activation reactions are an important process involved in drug metabolism and lipid oxidation, and their likelihood can be quantitatively evaluated by means of the bond dissociation free energy (BDFE) of a target site. Since BDFEs are difficult to be observed experimentally except for small compounds, we proposed a combined semiempirical quantum mechanical (SQM) and machine learning (ML) model, referred to as SQM-ML. The descriptors used are (i) the calculated BDE, (ii) HOMO energy, and (iii) the type of a C-H bond (e.g., saturated or unsaturated). We adopted the support vector regression (SVR) model implemented in scikit-learn with the features (i)–(iii). The rPM6 and GFN2-xTB methods were used for SQM calculations and density functional theory (DFT) calculations were also performed for comparison. Tests on 50 molecules (Figure 1) revealed that the BDFEs obtained from the GFN2-xTB/ML model show a strong correlation (R^2 = 0.90 and MAE=1.14 kcal/mol) with those from the high accurate (RO)CBS-QB3 approach. In particular, the contribution of (i) and (iii) was found to be remarkable.
Keywords :　Machine Learning; Oxidation reaction; Chemoinfomatics

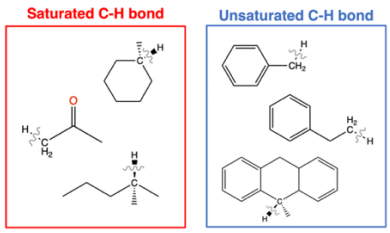

Figure 1. Part of 50 compounds used in this study

薬物代謝や脂質酸化などの酸化反応において C-H 活性化は重要な反応過程であり、その起こりやすさは結合解離自由エネルギー(BDFE)に対応している。BDFE を実験的に決定することは小分子を除いて困難である。本研究では、半経験的量子化学計算と機械学習を組み合わせた SQM-ML 法に基づく BDFE 予測モデルの構築を目的とした。SQM により得られる(i) BDE、(ii) HOMO のエネルギー、および(iii)C-H 結合の種類(飽和 or 不飽和)を説明変数とし、サポートベクター回帰を行った。SQM には rPM6 と GFN2-xTB を用いた。密度汎関数理論(DFT)による計算も比較のため実施した。50 個の分子(Figure 1)に対して本手法を適用したところ、GFN2-xTB/ML モデルが高精度計算手法である(RO)CBS-QB3 の結果と非常に良い一致（R^2 = 0.90、MAE = 1.14 kcal/mol）を示した。特に、(i)と(iii)の寄与率が高いことが分かった。

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2) M. Salamone et al. *J. Am. Chem. Soc*. **2021**, *143*, 11759.

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Designing Novel Organoselenium Derivatives as SARS-CoV-2 Main Protease Inhibitors by Integrating QSAR and LB-PaCS-MD Techniques

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Keywords: Organoselenium; SARS-CoV-2; Main Protease; QSAR; LB-PaCS-MD

The occurrence of COVID-19 pandemic caused by the SARS-CoV-2 virus; this virus had a severe negative impact on the respiratory system. We have targeted the Main protease (Mpro) in this study to design SARS-CoV-2 inhibitors. Quantitative Structure-Activity Relationship (QSAR) was used to find out the relationship between the structural properties of Organoselenium derivatives and the inhibitory activity of the Mpro enzyme using the genetic function approximation (GFA), random forest (RF), and artificial neural network (ANN). The ANN model shows results in good statistical values; the R2 of training set is above 0.9 and RMSE test was 0.209. We have determined all the possible paths and conformations of E01 (ebselen) at the Mpro catalytic site via Ligand binding path sampling based on parallel cascade selection molecular dynamics (LB-PaCS-MD). Ebselen is predicted to bind in close proximity to His41 and Cys145 of catalytic dyad, with the benzoisoselenazole ring forming π-π T-shaped and π-Sulfur with His41 and Cys145, respectively. From the ANN model and the LB-PaCS-MD technique led to the design of new compounds based on the primary structure. The structures with good predictive pIC_{50} (Cpd. T13, T29, T35 and T41) were designed so that the Ar position; C1 was added, and the halogen/OH group was added to the ring at the ortho/meta (or both ortho and meta) positions, the part of R1 filled with halogen/OH. Moreover, these compounds were predicted ADMET properties, the server predicts that Cpd. T29 and T35 do not cause any toxicity.

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Improved photocatalytic performance of eosin Y-sensitized anatase by anchoring group modification. A DFT/TDDFT insight

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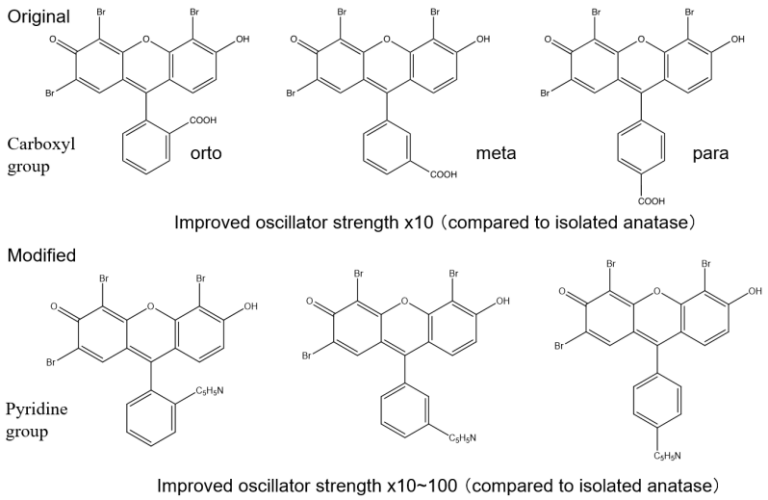
○ Juan Shang,[1] Aleksandar Staykov,[1] Tatsumi Ishihara[1]
Keywords: Photocatalysis; Visible light; Anatase; Eosin Y; Anchoring group

A great number of attempts on H_2 production from water using photocatalyst have been made to construct solar energy conversion systems to chemical energy. Eosin Y-sensitized anatase has been identified as an efficient photocatalyst because of its activity in visible light.[1] However, the hydrogen evolution rate was not stable over long-time irradiation.[2] Though eosin Y having carboxyl groups could be fixed by ester-like linkage on anatase in the organic solvent, the linkage was not stable in water because of hydrolysis.[3] In order to overcome the unstableness of the eosin Y-sensitized anatase in water, we attempted a strong chemical fixation of dye on anatase particles. We proposed the use of a pyridine ring as an anchoring group in place of a conventional carboxyl group.

Comparative study on the hybrid interface of anatase and eosin Y with the different anchoring groups were performed by density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations. The geometries, binding interaction between dye and anatase, electronic structures and transfer as well as the effect of isomers (orto-, meta, para-) on the dye-anatase systems were investigated and discussed. Theoretical results indicated that eosin Y with carboxyl and pyridine anchors had visible adsorption and electron transfer from the dye to the particle. Eosin Y with pyridine anchor had weaker binding but higher oscillator strength. The oscillator strength of para-pyridine is highest (0.20×10^{-2}), which was 10 times higher than that of carboxyl anchors.



1) T. Sreethawong, *J. Power Sources.* **2009**, 190,513. 2) M. Hiroaki, *Chem. Lett.* **1983**, 12, 1021. 3) R. Abe, *J. Photochem. Photobiol. A.* **2000**, *137*, 63.

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ケモインフォマティクスによる IDO1 阻害剤の結合自由エネルギーの評価

（広市大院情報）○藤原 竜也・齋藤 徹
Chemoinformatics Study on the Evaluation of Binding Free Energies of IDO1 Inhibitors
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Indoleamine-2,3-dioxygenase (IDO1) is the rate-limiting enzyme that metabolizes L-Trp to Kynurenine, causing immune tolerance and the development of cancer cells. Röhrig et al. found that triazole-based heterocyclic compounds exhibit high 50% inhibitory concentration (IC_{50}) values ranging from mM to nM. In this study, we proposed an AI model that can predicts the IC_{50} value of a series of heterocyclic compounds. The objective variables were the available experimental IC_{50} values were converted to the corresponding binding free energies based on the following relation: Act = RT ln(IC_{50}). Quantum chemical descriptors including Mulliken charge and frontier molecular orbital energies and structural descriptors of a ligand were used. PBE0/def2-SVP model was exploited to collect quantum chemical descriptors, while the Lasso regression model was used for multiple regression analysis. Our proposed model showed good performance, providing the R^2 value of 0.94.

Keywords : IDO1; Inbibitor design; Machine Learning

インドールアミン-2,3-ジオキシゲナーゼ(IDO1)は、L-Trp を Kynurenine に代謝する律速酵素であり、免疫寛容を引き起こし、がん細胞を発現させる。Röhrig らは、トリアゾール系の複素環式化合物が mM から nM オーダーの 50%阻害濃度(IC_{50}) 、すなわち IDO1 阻害活性を有することを見出した(図 1)。本研究では、阻害剤候補物質の IC_{50} を予測する AI モデルを提案した。実験から得られた阻害剤化合物の IC_{50} を Act = RT ln(IC_{50}) によって結合自由エネルギーに変換したものを目的変数とした。Mulliken 電荷やフロンティア分子軌道エネルギーなどの計算値と分子構造の情報を記述子とした。量子化学計算には PBE0/def2-SVP モデルを用い、重回帰分析には Lasso 回帰モデルを使用した。提案モデルの決定係数は $R^2 = 0.94$ と良好な値を示した。

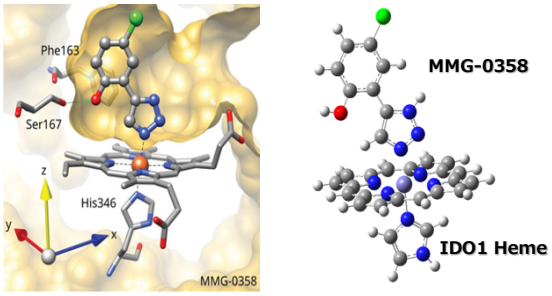

図 1： IDO1-MMG-0358複合体のX線結晶構造（左図）と活性部位モデル−MMG-0358複合体（右図）

1) U. F. Röhrig et al. *J. Med. Chem.*, **64**, 2205 (2021).
2) U. F. Röhrig et al. *J Enzyme Inhib.Med. Chem.*, **37**, 1773 (2022).

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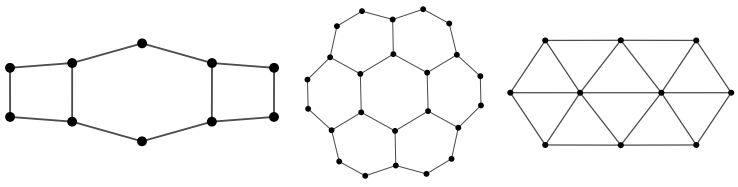
多環式共役系の安定性のトポロジー的解釈

（静岡大理[1]）○関根 理香[1]・齊藤 慧[1]・中村 瑞希[1]
Topological Interpretation of the Stability of Polycyclic Conjugated Systems ([1]*Faculty of Science, Shizuoka University*) ○Rika Sekine,[1] Kei Saito,[1] Mizuki Nakamura[1]

The Hückel Molecular Orbital method, a graph theory-based technique, evaluates molecular stability by determining eigenvalues from graphs' adjacency matrices, indicative of stability through Hückel Energy. This study explores the relationship between ring sizes in polycyclic molecules and eigenvalue distribution, with findings displayed in Fig. 1. Eigenvalues showed symmetric distribution in structures with repeating even-membered rings [(a) and (b)], a pattern persisting in less symmetric cases. Contrarily, graphs comprising odd-membered rings (c) or a mix lacked this symmetry. These properties apply to both planar structures and non-planar configurations like hexagonal close packing.
Keywords : Graph Theory, Hückel Method, Eigenvalues, Topological Indices

Hückel 分子軌道(HMO)法はグラフ理論に基づいて分子の安定性を評価する代表的な手法である。HMO 法によりグラフの隣接行列から MO 準位に対応する固有値を求め、分子の安定性の指標となる Hückel エネルギー(HE)を計算することができる。ここで HE や固有値の分布をトポロジカルインデックスとしてとらえることもできる。

本研究では、様々な多環式分子構造をグラフ理論的に取り扱って固有値を調べることにより、環の員数と固有値の分布に関連があることを発見した。いくつかの多環グラフを Fig. 1 に示す。固有値(Eigenvalues)は(a) 2.48 , 2 , 1.17 , 0.689 , 0, 0 , -0.689 , -1.17 , -2 , -2.48, (b) 2.68 , 2.21 , 2.21 , 1.68 , 1.68 , 1.54 , 1.21 , 1, 1 , 1 , 0.539 , 0.539 , -0.539 , -0.539 , -1 , -1 , -1, -1.21 , -1.54 , -1.68 , -1.68 , -2.21 , -2.21, -2.68, (c) 4.11 , 2.30 , 1.41 , 0.196 , 0 , -1.14 , -1.30 , -1.41 , -2 , -2.17 であった。(a)及び(b)のグラフは偶数員環の繰り返し構造となっており、この場合の固有値は正負対称的に分布することが分かった。Fig.1 に示したような構造よりも対称性が低い場合でも成立した。一方で、奇数員環から構成されるグラフ(c)やフラーレンのように偶数員環と奇数員環の両方が含まれるグラフでは固有値の分布に対称性はみられなかった。以上の性質は、Fig.1 に示したような平面構造（平面グラフ）だけではなく、六方最密構造(hcp)のような立体構造（非平面グラフ）においても成り立つことが確かめられた。



(a) (b) (c)

Fig. 1: Illustrative Graph featuring (a) an alternating pattern of four-membered and six-membered rings, (b) a planar structure composed exclusively of six--membered rings, resembling coronene, and (c) an arrangement of three-membered rings.

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SQM-ML による芳香族化合物の NMR 化学シフトの自動予測

（広市大院情報 [1]）○塩竹 悠人 [1]・齋藤 徹 [1]

Automated Prediction of NMR Chemical Shift of Aromatic Compounds Using SQM-ML Approach ([1] *Graduate School of Information Sciences, Hiroshima City University*)

[1]○Yuto Shiotake,[1] Toru Saito

Drug metabolism by Aldehyde Oxidase and its inhibition development have recently been of great importance in pharmaceutical area. The previous study by Montefiori and co-workers revealed that their proposed method based on ChemDraw-calculated ^{13}C-NMR chemical shifts can be useful for the prediction of site of metabolism. Despite its simplicity, drawing chemical structures and outputting chemical shifts cannot be automated. Instead, we have developed a fast, accurate, and fully automated prediction of chemical shifts quantitatively by combining semi-empirical quantum mechanical and machine learning methods. In logistic regression analysis, the cutoff value of ChemDraw-estimated chemical shifts was set to 140.0 ppm. The descriptors were five physico-chemical parameters that can be easily obtained, and descriptors were computed at the PM7 and GFN-xTB2 (xTB2) levels of theory using the Gaussian 16 and ORCA program packages. The Acc values listed in Table 1 (0.96–0.98) corroborate the high applicability of both the xTB2- and PM7-based models.

Keywords : Semiempirical Quantum Mechanical Method; Chemoinformatics; Drug Metabolism

アルデヒドオキシダーゼによる薬物代謝とその阻害剤の開発は医薬分野において重要視されている。Montefiori らによる先行研究では、ChemDraw で計算された ^{13}C-NMR 化学シフトに基づく代謝部位予測法の有効性が明らかにされた。この方法は非常に簡便であるが、描画と操作の自動化を行うことが困難という問題があった。[1)] そこで我々は、半経験的手法と機械学習を組み合わせ、化学シフトを定量的に高速・高精度・全自動で予測する手法を開発した。機械学習にはロジスティック回帰分析を使用し、記述子は簡便に求まる 5 つの物理化学パラメータを用いた。Gaussian16 と ORCA プログラムを使用して PM7 と GFN-xTB2 (xTB2)計算により記述子を算出した。Table 1 に示す混同行列に基づく解析により、PM7、xTB2 ともに 0.96–0.98 と高い Acc 値を示すことがわかった。[2)] したがって、本提案手法の有用性が示された。

Table 1. xTB2, PM7 に基づく Aldehyde Oxidase 代謝部位予測モデルの比較

		TP	FP	FN	Sens	Spec	Prec	Acc
case A	DFT	159	10	10	0.941	0.987	0.941	0.979
	ChemDraw	159	10	10	0.941	0.987	0.941	0.979
	xTB2-ER	158	11	11	0.935	0.986	0.935	0.977
	PM7-ER	155	14	14	0.923	0.979	0.901	0.968
case B	xTB2-ER	160	15	9	0.947	0.981	0.914	0.975
	PM7-ER	157	22	12	0.929	0.972	0.877	0.964

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2) Y. Shiotake *et al*. *Chem. Phys. Lett*. **2023**, 833, 140942.

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配置選択定 pH(CS-CpH)法による酸性残基を含むペプチドの pH 依存性予測

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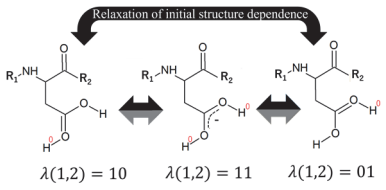
Prediction of pH dependence of peptides containing acidic residues by the configuration-selection constant pH (CS-CpH) method ([1]*Graduate School of Informatics, Nagoya University*, [2]*Faculty of Engineering, Shizuoka University*, [3]*FVC Research Center, Nagoya University*) Fuka Inagaki,[1] ○Yukichi Kitamura,[2] Haruka Yotsuya,[1] Masataka Nagaoka[1,3]

Certain peptides containing acidic residues (aspartic acid and glutamic acid) are known to self-assemble and form pores that penetrate lipid membranes even under low concentration conditions under certain pH conditions. This property is expected to be applied to drug delivery technology (DDS), in which drugs such as anticancer agents are transported directly to cancer cells. In the present study, we have developed a constant pH (CpH) method (CS-CpH method) [1,2)] that incorporates our previously developed configuration selection (CS) scheme to study the pKa reproducibility of small peptides consisting of acidic residues in transmembrane peptides. The study investigated the behavior of the solvent structure and conformational changes associated with changes in the protonation state (PS) of small peptides consisting of acidic residues in transmembrane peptides. We proposed a PS transition protocol that considers the equivalence of the oxygen in the COOH group (carboxy group) to improve the accuracy of the conventional method[1)].
Keywords : Configuration-selection Constant pH (CS-CpH) method; peptide; protonation state (PS) transition model; aspartic acid; Molecular Dynamics (MD) simulation

酸性残基(アスパラギン酸・グルタミン酸)を含むある種のペプチドは、特定の pH 条件下で低濃度条件下においても自己集合して脂質膜を貫通する細孔を形成することが知られている。この性質を利用して、抗がん剤などの薬剤をがん細胞に直接輸送する薬物送達技術(DDS)への展開が期待されている。本研究では、これまでに我々が開発してきた配置選択(CS)スキームを導入した定 pH（CpH）法（CS-CpH 法）[1,2)]を用いて、膜貫通ペプチドに含まれる酸性残基から成る小ペプチドの pK_a の再現性を調査した。本研究では、従来法 [1)]の高精度化を目指し、COOH 基(カルボキシ基)に含まれる酸素の等価性を考慮したプロトン化状態遷移プロトコルを提案した。



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荷電系において溶媒和モデルが記述する溶媒静電ポテンシャルの解析

(筑波大院数理[1]・名大院情[2]) ○金丸 雄基[1]・吉田 紀生[2]・松井 亨[1]
Analysis of solvent electrostatic potential described by solvation models in charged systems
([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*Graduate School of Informatics, Nagoya University*) ○Yuki Kanamaru,[1] Norio Yoshida,[2] Toru Matsui[1]

Conductor-like polarizable continuum model (C-PCM) is one of low-cost solvation models used in quantum chemical calculations. However, many studies have pointed out that the C-PCM overestimates solvation energy of a charged organic molecule. We considered that main cause of the overestimation is a solute-solvent electrostatic interaction, and focused on reaction field, i.e., electrostatic potential which solvent molecules form around a solute. Figure 1 shows the reaction fields around a phenol cation in water solvent, described by C-PCM, molecular dynamics (MD) and 3D-RISM. Although the overall trends are similar, the peak around the OH group are significantly gradual in C-PCM.

Keywords : Solvation Model; Polarizable Continuum Model; 3D-RISM; Molecular Dynamics

量子化学計算に用いられる代表的な溶媒和モデルの一つとして C-PCM が存在する。C-PCM は溶媒を連続体近似するために非常に軽量である。一方でカチオンの溶媒和エネルギーを 7 kcal/mol ほど過大評価する[1]。従前の改善研究では、実験値との差を埋めるためにパラメータを大量に追加して一旦の解決を図っており、物理・化学的な議論は乏しかった。我々はこの誤差要因として溶質溶媒間の静電相互作用を適切に記述できていない可能性を検討した。そこで他の溶媒和モデルと反応場を比較し、C-PCM の静電相互作用の記述に対して必要な修正を示すことを図った。

Fig. 1 に各溶媒和モデルが記述する、フェノールカチオン周りに水溶媒が形成する反応場分布を示した。この図からヒドロキシ基周りでは反応場分布が負のピークをもつなど互いに似た傾向を示すものの、MD、3D-RISM-SCF、C-PCM の順にピークが緩やかであることが分かる。溶質中央付近の反応場は上から −4.2 V、−3.9 V、−7.2 V 程度であり、3D-RISM のみ著しく外れている。この原因については現在調査中である。

他の溶質や溶媒等の結果については当日追加で報告する。

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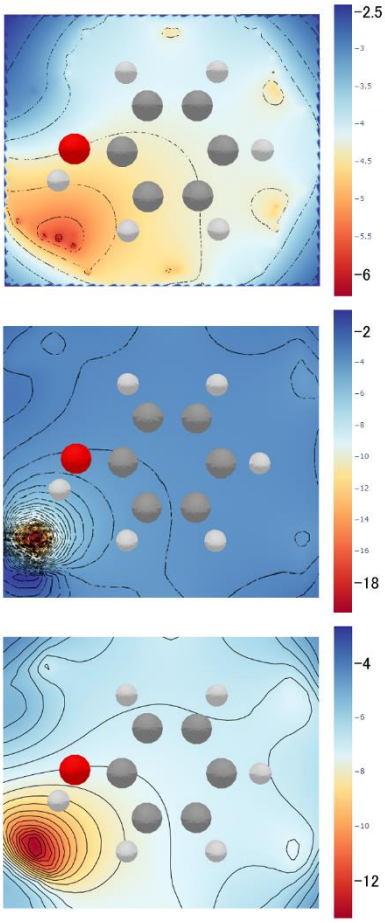

Fig. 1 フェノールカチオン周りの水溶媒による反応場分布。上から C-PCM, MD, 3D-RISM-SCF。単位は V。

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機械学習を応用した分子構造表現の検証、匂い評価の予測

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A regression study for odor character prediction based on molecular structural representation by machine learning (Kumamoto University[1], University of Yamanashi[2]) ○Yuki Harada[1], Shuichi Maeda[1], Junwei Shen[1], Taku Misonou[2], Hirokazu Hori[2], Shinichiro Nakamura[1]

The molecular representation is essential for the explanatory variables in the molecular property prediction. The chemical space potentially has an enormous amount of information. There are many ways to measure, vectorize and/or embed for molecular structure in recent studies. Some of these progress were accelerated by the machine learning.Chemical VAE is a promising approach proposed recently. This machine learning provides molecular generation from smiles input. It also provides vector representation which enable to explore chemical space.

In this study, we discuss the regression study between the odor descriptor and representation of molecular structure based on machine learning. The performance of molecular representation was evaluated by iterative cross-validation of the regression model for each odor descriptor. The further machine learning, such as CNN, GNN etc, were recently applied to pattern recognition, social networks analysis, recommendation systems, and semantic analysis. Thus, we also discuss their possibility for this problem.
Keywords : Odor, Regression, Machine learning, odor sensing space

分子の記述子は物性予測の問題において、分子構造に基づく説明変数となる可能性を持つ。分子構造から潜在的に得られる情報は大規模であり、機械学習の充実を背景に新しい分子記述子が提案されている。Chemical VAE は RNN および VAE から構成される化学情報の機械学習である。分子構造を SMILES 文字列として入力しオートエンコーダーを経て SMILES 様の文字列の出力、同時にオートエンコーダーの内部では分子構造の圧縮された表現を連続的な数値情報として、圧縮された分子表現をもとした物性予測が、この機械学習により可能である[1]。

本検討では 700 種類の単品ケミカルについて 196 の評価用語による官能評価が収載されている公開データをもとに、学習済みの Chemical-VAE を使用して得た分子構造に基づくベクトル表現と各匂い記述について回帰分析を行った。トレーニングに用いなかった化合物が匂い記述子に該当するかを予測し、汎用フィンガープリントの予測能と比較しながら、本手法の有用性を評価した。加えて本報告では、分子科学計算の結果ないし線形表記方法以外の機械学習を適用したケミカルスペース解析の有効性について考察した。

1) ACS omega 7.10 (2022): 8581-8590

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フラグメント分子軌道法と制約密度汎関数理論を組み合わせた FMO-CDFT 法の開発

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Development of FMO-CDFT method by Integrating FMO method and Constrained Density Functional Theory ([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, [2]*Faculty of Science, Hokkaido University*, [3]*WPI-ICReDD, Hokkaido University*) ○Shohei Osaki,[1] Masato Kobayashi,[2,3] Tetsuya Taketsugu,[2,3] Toru Matsui[1]

Constrained density functional theory (CDFT) is used to calculate charge-separated states because it can compute charge-localized states at a computational cost of ordinary DFT. However, due to its high computational cost, CDFT is difficult to apply directly to large-scale systems, such as solutions and amorphous systems, as well as ordinary DFT.

In this study, we focused on the fragment molecular orbital (FMO) method, one of the large-scale quantum chemistry calculation approaches. We developed FMO-CDFT by integrating the FMO method and CDFT. The developed FMO-CDFT was assessed for its accuracy through calculations on decamers of naphthalene and anthracene. Constraints based on Mulliken and Löwdin populations are applied to each decamer in four different schemes. Table 1 shows the error in total energy for FMO-CDFT with respect to conventional CDFT. The results indicate that FMO-CDFT reproduces the total energies with an error of approximately 3 mHartree.

Keywords：Constrained Density Functional Theory; Fragment Molecular Orbital Theory

制約密度汎関数理論(CDFT)は通常の DFT と同程度の計算コストで電荷が局在化した状態を計算できることから、電荷分離状態の計算に利用されている。しかし、CDFT はその計算コストのため、通常の DFT と同様に溶液やアモルファスなどの大規模系に直接適用するのは困難である。そこで本研究では、大規模系の量子化学計算手法の一つであるフラグメント分子軌道法(FMO 法)に注目した。我々は FMO 法に CDFT を組み込むこんだ FMO-CDFT を開発し、GAMESS に実装してその精度の検証を行った。

計算対象にはナフタレン及びアントラセンのそれぞれの十量体を使用した。制約には Mulliken 電荷及び Löwdin 電荷を使用し、各十量体に対して 4 通りの制約をかけた。表 1 に、通常の CDFT を参照にした FMO-CDFT の全エネルギーの誤差を示す。これより、FMO-CDFT は全エネルギーを 3 mHartree 程度の誤差で全エネルギーを再現することが確認できた。

表 1 それぞれの制約における CDFT と FMO-CDFT の全エネルギーの誤差 (mHartree)

	MSE	MAE	RMSE
Mulliken	−2.96	2.96	3.04
Löwdin	−2.62	2.62	2.81

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充填率に着目した一般化超球面探索法を適用しての結晶構造予測

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Crystal structure prediction using generalized scaled hypersphere search method focusing on packing fraction ([1]*Faculty of Systems Engineering, Wakayama University*, [2]*Graduate School of Systems Engineering, Wakayama University*) ○ Yoshiki Ueda,[1] Takuto Oki,[2] Yuuki Midoro,[2] Hideo Yamakado[1,2]

In crystal structure prediction, it is important to quickly find an initial structure for structural refinement using quantum chemical calculations. Although the Scaled Hypersphere Search method is a useful method, the quantum chemical calculations required to construct the potential energy surface are computationally expensive and a full search takes time. Therefore, we focused on the fact that in the nature, atoms and molecules are often arranged in such a way that the crystal packing fraction is high. We attempted to search for initial structure candidates at highspeed using the Generalized Scaled Hypersphere Search (GSHS) method by using the packing fraction as the objective function used in the search. This time, we searched for several 2-atom/unit ionic crystals.
Keywords : crystal structure prediction; packing fraction; Scaled Hypersphere Search method

結晶構造予測において量子化学計算による構造精密化の初期構造を迅速に探し出す事は重要である。超球面探索法[1)]は有用な方法であるが、ポテンシャルエネルギー面の構築のために必要な量子化学計算は計算コストが高く全面探索に時間がかかる。そこで、自然界では結晶の充填率が高くなるように原子や分子が配列される場合が多い事に着目し、充填率を探索に用いる目的関数にする事で初期構造候補を一般化超球面探索法(GSHS 法)[2)]により高速で探索する事を試みている[3)]。

今回はいくつかの 2 原子/unit のイオン結晶において探索を行った。NaCl ではランダムに発生させた構造から充填率関数を用いて最適化を行い、求まった構造から出発して一般化超球面探索法により探索を行った。探索で見つかった構造について Spglib[4)]を用いて空間群を分析した所、Fig.1 のように 5 種類の空間群に分類された。また、CsCl で探索を行い分子においても探索を始めているため、詳しくはポスターにて発表する。

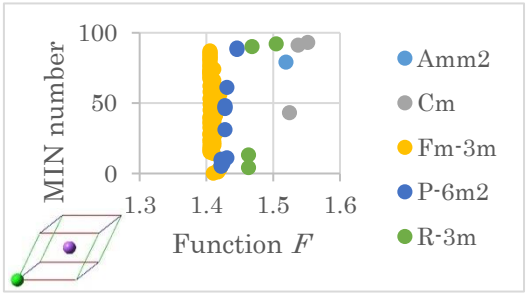

Fig.1 Distribution trend for minima value of objective function and a searched minimum structure of NaCl($Fm\bar{3}m$) by using the GSHS method.

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3) Y. Midoro, T. Oki, Y. Kodaya and H. Yamakado, Chem. Lett. 2021, Vol.50, No.8, 1559-1561.
4) https://spglib.readthedocs.io/en/latest/index.html

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無機化合物組成生成のための多目的条件付き敵対的生成ネットワークの開発

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Multi-Objective Generative Adversarial Network for Inorganic Chemical Compositions (*[1]Nara Institute of Science and Technology, [2]DSC, Nara Institute of Science and Technology, [3]CMP, Nara Institute of Science and Technology, [4]Aichi Sangyo University*) ○Tomiya Yamamoto[1], Mamoru Nishijo[1], Yosuke Harashima[1,2], Shogo Takasuka[1], Tomoaki Takayama[1,2], Yoshihide Sawada[4], Mikiya Fujii[1,2,3]

In general, solving the inverse problem of developing materials with desired physical properties is a challenging and time-consuming task. However, applying machine learning (ML) can facilitate efficient exploration. In practical material development, proposing materials that have multiple desired properties is essential. Therefore, this study aims to propose novel inorganic chemical compositions that satisfy multiple desired properties by developing a multi-objective conditional Generative Adversarial Network (GAN).

Conventional GAN consists of two components: a generator that creates the target object from random vector (noise) and a discriminator that determines whether the generated object is real. In this research, we enhanced the conventional GAN by incorporating multiple desired properties along with noise as inputs to the generator and adding a predictor that predicts the multiple properties of the generated composition. This modification enabled the generation of novel inorganic compositions that satisfy multiple desired properties. To verify the accuracy of the generation process, we utilized an ML model called CrystaLLM, which can predict crystal structures from compositions, to obtain the crystal structures. By conducting Density Functional Theory (DFT) calculations, we computed the properties of the generated compositions.
Keywords : Materials Informatics, Machine Learning, Inorganic Materials, Multi-Objective GAN

一般的に所望物性を持つ材料を開発する逆問題の解決は難しく、機械学習による効率的な探索が期待されている。また、実際の材料開発においては、複数の物性値を満たす材料提案が必要不可欠である。そのため、本研究では複数の所望物性を満たす新規無機材料の組成を提案することを目的とし、多目的条件付き敵対的生成ネットワーク(Generative Adversarial Network, GAN)の開発を行った。

従来の GAN はランダムなベクトル(ノイズ)から対象物を生成する生成器と、生成器が生成したものが本物かどうか判別する識別器の２つの学習器から構成される生成モデルである[1]。本研究では従来の GAN に対し、生成器の入力をノイズと複数の物性値とし、生成した組成の複数の物性値を予測する予測器を追加することにより複数の所望物性を満たす新規無機材料の生成を可能にした。生成精度を検証するために、組成から結晶構造を予測することができる機械学習モデルである CrystaLLM を用いて結晶構造を取得し、DFT 計算を行うことにより生成組成の物性を計算した。

[1] Y. Sawada, K. Morikawa and M. Fujii, *Chem. Lett.* **50**, 623(2021); arXiv:1910.11499

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生体分子の電子状態揺らぎは半経験分子軌道計算でどこまで正確に追えるか？ 生体機能解析を志向した高精度法との比較検討

（中央大学[1]・JST ACT-X[2]）○小澤 二千夏[1]・黒木 菜保子[1,2]・森 寛敏[1]

How Precisely Can Semiempirical Molecular Orbital Calculations Reproduce Electronic State Fluctuations of Biomolecules? Comparison with High-precision Methods toward Bio-system Analysis ([1]*Chuo University*, [2]*JST ACT-X*) ○Nichika Ozawa,[1] Nahoko Kuroki,[1,2] Hirotoshi Mori[1]

A physicochemical understanding of intermolecular interactions is essential for controlling biological functions and drug discovery. Accurately evaluating electronic state fluctuations requires calculating the whole system with quantum chemical calculations while considering structural changes and cooperative effects in dilute aqueous solutions. However, due to the high computational costs, only solutes have been evaluated by quantum chemical methods, while implicit solvent models or classical force fields have been applied to the surrounding water and ions. Toward establishing a fast analytical method for electronic state fluctuations in biological systems, this study examined the accuracy of describing semi-empirical molecular orbital methods for hydrated ion clusters.

Keywords : Semi-empirical Molecular Orbital Calculations; Intermolecular Interactions; Biomolecules; Electronic State Fluctuations; Assessment

生体機能制御や新薬開発には、分子間相互作用の理解が不可欠である。生体（希薄イオン水溶液）内で生じる構造揺らぎやシナジー効果を加味した正確な電子状態評価には、系全体をバランス良く記述可能な量子力学的手法を適用することが求められる。だが従来、計算コストの観点から、薬とタンパク質のみが量子力学で、水やイオンは陰溶媒または古典力場で評価されてきた。生体内電子状態揺らぎを高速に解析可能な手法の確立を目指して、本研究では、水分子および水和イオンクラスターを対象に半経験的分子軌道法（DFTB, PM6-D3H4, PM7 等）の記述精度を検討した。

まず、気相中における水分子の幾何構造・電荷分布を、MP2/Sapporo-dzp の結果と比較した（表 1）。検討した半経験法はいずれも、実測および MP2 レベルの結合長を化学精度で再現した。一方、結合角・双極子モーメントについては、実測を過大評価することがわかった。当日は、構造形成イオンである Na^+ の水和クラスターをはじめとして、単原子イオンに対する水和構造変化が、系の電子状態揺らぎに与える影響の定量評価結果も報告する。

表 1. 各手法で算出した H_2O の分子構造パラメーターと双極子モーメント

	Exp.	MP2	DFTB	PM6-D3H4	PM7
r(O-H) [Å]	0.957	0.964	0.957	0.963	0.955
∠(H-O-H) [º]	104.5	102.3	110.5	111.5	105.3
μ [Debye]	1.85	1.95	2.04	2.05	2.13

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1,4-ジオキサン溶液中での 1,3,5-トリメトキシベンゼンの *N*-メチルマレイミドへの求核付加反応の理論的解析

（中京大教養教育研究院[1]・名大院情報[2]）○六車千鶴[1]・古賀伸明[2]

Theoretical analysis of nucleophilic addition reaction of 1,3,5-trimethoxybenzene to *N*-methylmaleimide in 1,4-dioxane ([1] *Faculty of Liberal Arts and Sciences, Chukyo University*, [2] *Graduate School of Informatics, Nagoya University*) Chizuru Muguruma,[1] Nobuaki Koga[2]

As one of synthetic methods of 3-aryl succinimide, 1,4-addition of maleimide catalyzed by Brønsted acid has been reported by Hor et al. We previously reported with the density functional theory (DFT) method calculations that 1,4-addition of 1,3,5-trimethoxybenzene (**R1**) to *N*-methylmaleimide (**R2**) consists of three elementary reactions such as nucleophilic attack of **R1** to protonated **R2** (**R2H**), deprotonation from the nucleophilic adduct, and keto-enol tautomerization. In the present research, possible reaction pathways were investigated for nucleophilic addition of **R1** to **R2H** in 1,4-dioxane. Geometry optimization of reactant, intermediates, possible transition states, and nucleophilic adducts was carried out by using DFT method at the B3LYP+D3/6-31+G(d,p) level, taking into account the solvent effects with the PCM method. The structures obtained were characterized by vibrational frequency calculations as well as IRC calculations. We did not consider reactions of **R1** and **R2** since the contribution must be small. The most favorable reaction pathways and experimental conditions will be discussed in detail based on the calculated results.

Keywords : 1,3,5-trimethoxybenzene; N-methylmaleimide; nucleophilic addition; density functional theory method; PCM method

Horらによりブレンステッド酸を触媒としたマレイミドへの1,4-付加が3-アリールスクシンイミドの合成法の１つとして報告されている[1)]。前回、我々は密度汎関数法（DFT）計算により、1,3,5-トリメトキシベンゼン(**R1**)の*N*-メチルマレイミド(**R2**)への1,4-付加が、**R1**のプロトン化された**R2**(**R2H**)への求核攻撃、求核付加体からの脱プロトン化、keto-enol互変異性化の3つの素反応からなることを報告した[2)]。今回は、1,4-ジオキサン溶液中での**R1**と**R2H**の求核付加の可能な反応経路を、溶媒効果をPCM法により考慮したB3LYP+D3/6-31+G(d,p)レベルのDFT計算を行い調べた。寄与が小さいと予想される**R1**と**R2**の反応は考慮しなかった。反応物、中間体、可能な遷移状態、求核付加体の構造を求め、反応経路はIRC計算により確認した。当日は、得られた計算結果をもとに最も起こりやすい反応経路とより適した実験条件について検討した結果を報告する。

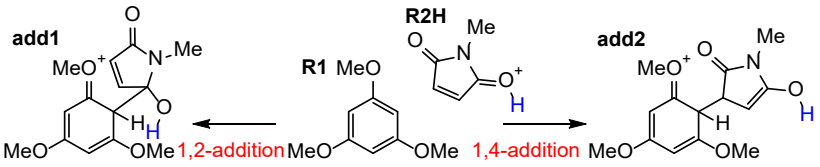

Fig. 1 Nucleophilic addition of 1,3,5-trimethoxybenzene to protonated *N*-methylmaleimide

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2) 六車千鶴、古賀伸明　日本化学会第 103 春季年会、2023、P1-2am-23.

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Pd および AgRh 合金ナノクラスター中の水素拡散に関する理論的研究

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Theoretical study of hydrogen diffusion in Pd and AgRh nanoclusters ([1]*Graduate School, Tokyo Woman's Christian University*) ○Manaka Kimura,[1] Koji Ando[1]

Pd has the property of absorbing hydrogen. Although Rh and Ag, which are next to Pd on the periodic table, do not absorb hydrogen, they have been experimentally found to absorb hydrogen when they become alloy nanoparticles, suggesting that AgRh alloy nanoparticles have an electronic structure similar to that of Pd nanoparticles[1)]. The purpose of this study is to perform molecular dynamics simulation analysis of hydrogen diffusion in Pd clusters and AgRh alloy clusters using the semiquantum time-dependent Hartree method[2)]. In this study, relativistic quantum chemical calculations were performed to determine a potential function that effectively incorporates many-body effects, and molecular dynamics simulations were performed to analyze hydrogen diffusion in Pd and AgRh alloy nanoclusters. Double-well potential energy curves describing hydrogen tunneling were obtained for Pd_3H, $AgRh_2H$, and Ag_2RhH, and the interatomic effective interaction potential functions for Pd-H, Rh-H, and Ag-H were determined from these curves. The binding energies were -119.9 kJ/mol, -104.2 kJ/mol, and -52.1 kJ/mol for Pd-H, Rh-H, and Ag-H. The results of the molecular dynamics simulation will be presented on the day.

Keywords : Molecular Dynamics Simulation; Hydrogen Diffusion; Metal Nanocluster

Pd は水素を吸蔵する能力を持っている。周期表中で Pd の両隣にある Rh と Ag は、ともに水素を吸蔵しないが、合金ナノ粒子になると水素を吸蔵することが実験的に見出され、AgRh 合金ナノ粒子は Pd ナノ粒子に類似した電子状態を持つことが示唆されている [1)]。本研究では、Pd クラスターおよび AgRh 合金クラスター中の水素拡散について、準量子的時間依存ハートリー法による分子動力学シミュレーション [2)]を実行・解析することを目的とする。今回は多体効果を有効的に取り入れたポテンシャル関数を決定するために相対論的量子化学計算を実行し、Pd および AgRh 合金ナノクラスター中の水素拡散について分子動力学シミュレーションによる解析を行なった。Pd_3H、$AgRh_2H$、Ag_2RhH について、水素トンネリングを記述する二重井戸ポテンシャルエネルギー曲線を求め、その結果から Pd-H、Rh-H、Ag-H の原子間有効相互作用ポテンシャル関数を決定した。結合エネルギーは Pd-H、Rh-H、Ag-H の順で-119.9 kJ/mol、-104.2 kJ/mol、-52.1 kJ/mol となった。分子動力学シミュレーションの結果は当日発表する。

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味覚受容体タンパク質のリガンド結合ポケット内水分子クラスター構造とダイナミクスの解析

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Structure and dynamics of water molecular clusters in the ligand binding pocket of taste receptor proteins ([1]*Graduate School, Tokyo Woman's Christian University*) ○Kie Araki,[1] Koji Ando[1]

The T1r family of taste receptor proteins are class C G protein-coupled receptors that form two heterodimers, T1r1-T1r3 and T1r2-T1r3. The former is known as a receptor for umami substances and the latter as a receptor for sweet-tasting substances, but the process of taste recognition is still largely unknown. In this study, molecular dynamics simulations were performed on the medaka fish taste receptor proteins T1r2a-T1r3 and the four ligands L-glutamine, L-glutamic acid, L-alanine, and glycine, whose structures are already known. The structure and dynamics of water molecules in the ligand binding pocket were then analyzed. Glutamine and alanine, which are considered to have high affinity to the ligand, showed similar results in the O-atom distance and angular distributions of water molecule clusters. On the other hand, glutamic acid and glycine, which are considered to have low affinity, showed different results. The time correlation function of the number of hydrogen bonds also showed results suggesting a relationship with the ligand affinity.

Keywords : Molecular Dynamics Simulation, Taste Receptor, Water Molecule Cluster

味覚受容体タンパク質 T1r ファミリーはクラス C 型 G タンパク質共役型受容体であり、T1r1-T1r3 と T1r2-T1r3 という２つのヘテロ二量体を形成する。前者はうま味物質の受容体、後者は甘味物質の受容体として知られているが、その味認識の過程には未だ不明なことが多い。本研究では、既に構造がわかっているメダカの味覚受容体タンパク質 T1r2a-T1r3[1)]と 4 種のリガンド L-グルタミン・L-グルタミン酸・L-アラニン・グリシンに関して、分子動力学シミュレーションを行った。続いて、リガンドポケット内の水分子を取り出し、構造とダイナミクスについて解析を行った。

リガンドとの親和性が高いとされるグルタミンとアラニンは、水分子クラスターの O 原子間距離分布や角度分布で、似た結果を示した。一方、親和性が低いとされるグルタミン酸とグリシンは異なる結果を示した。また、水素結合数の時間相関関数でも、リガンド親和性との関連を示唆する結果が得られた。

1) Nuemket, N., Yasui, N., Kusakabe, Y. *et al*. Structural basis for perception of diverse chemical substances by T1r taste receptors. Nat Commun 8, 15530 (2017).

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ナフタルイミド誘導体とカルボン酸クラスタの光物性の解析

（筑波大理工[1]・筑波大院数理物質[2]・理研 AIP[3]・宮崎大院工[4]）○渡邉 夏実[1]・金丸 雄基[2]・松井 亨[2]・隅田 真人[3]・井澤 浩則[4]・守橋 健二[2]
Analysis of photophysical properties of naphthalimide derivatives and carboxylic acid clusters ([1]*School of Science and Engineering, University of Tsukuba*, [2]*Degree Programs in Pure and Applied Sciences, University of Tsukuba,* [3]*RIKEN AIP,* [4]*Faculty of Engineering, University of Miyazaki*) ○Natsumi Watanabe,[1] Yuki Kanamaru,[2] Toru Matsui,[2] Masato Sumita,[3] Hironori Izawa,[4] Kenji Morihashi[2]

N-[2-(trimethylammonium)ethyl]-1,8-naphthalimide (TENI) is an effective anion sensor because of changes in fluorescence intensity and chromism depending on carboxylic anions. In this study, we investigated the fluorescence and chromism of TENI depending on carboxylic anion species through the computational analysis of TENI interacting with three distinct carboxylic acids (acetate ion, benzoate ion, phenylacetate anion). We determined the structure of the clusters of TENI interacting the several carboxylic acids, counting the structures obtained by molecular dynamics of TENI/carboxylic acids in explicit water. According to our computation, the structures depend on the density of the clusters, and various cluster structures that would not be found through the manual search were found. At higher solution concentrations, clusters comprising multiple acids and TENI were observed. Computational ultraviolet-visible spectra using time-dependent density functional theory were compared with experimental spectra. These computations were also performed assuming that both TENI and the carboxylic acid are in the excited state. The details will be presented in the poster session.

Keywords : Molecular Dynamics, Naphthalimide Derivatives, Photophysical Properties

N-[2-(trimethylammonium)ethyl]-1,8-naphthalimide (TENI)はアニオンの種類によって蛍光強度や呈色反応の有無が変わる為，アニオンの検出が可能なアニオンセンサーとして機能する[1)]．本研究では計算化学の観点から,TENI と 3 種類のカルボン酸(酢酸イオン，安息香酸イオン，フェニル酢酸イオン)が作るクラスタによる蛍光及び呈色反応について解析を行った．本研究ではまず Amber 20 を用いて分子動力学計算を実行し，TENI と酸が作るクラスタの構造を計算し，クラスタの数を数えることでクラスタ形成の頻度を調べた．また，水分子の数を変えて計算することで形成頻度の濃度依存性を調べた．その結果，単純な量子化学計算では得られない様々な配座のクラスタが得られた．加えて，溶液の濃度が高いと複数の酸と TENI からなるクラスタが形成することが分かった．次に Gaussian 16 で時間依存密度汎関数理論による計算を実行し，得られた紫外可視吸収スペクトルを実験値と比較した．この一連の計算を，TENI 及びカルボン酸が励起状態である場合を想定した計算も行った．なお，研究結果の発表は当日行う予定である．

1) Hironori Izawa, Fumika Yasufuku, Toshiki Nokami, Shinsuke Ifuku, Hiroyuki Saimoto, Toru Matsui, Kenji Morihashi, and Masato Sumita, *ACS. Omega.* **2021**, 6, 13456.

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Molecular Dynamics Study of Rhamnose-Conjugated Antimicrobial Cyclotetrapeptides for Developing Novel Antibody Recruiting Molecule

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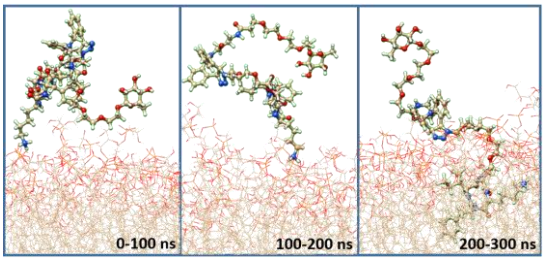
Keywords: Antimicrobial peptides; Antibody-recruiting molecules; molecular dynamics

This study presents a novel antibacterial strategy that synergistically combines the mechanism of action of Antimicrobial Peptides (AMPs) with the immune-recruiting potential of rhamnose (Rha). AMPs, known for their ability to disrupt bacterial cell membranes, form the foundation of our approach, aiming to enhance bacterial susceptibility. Furthermore, by introducing Rhamnose as a labeling agent, we exploit its capacity to recruit antibodies specifically targeting Rha. The confluence of these mechanisms is investigated through comprehensive molecular dynamics (MD) simulations, exploring the cooperative action of AMP-induced membrane disruption and the immune response triggered by Rhamnose-mediated antibody recruitment. This integrated strategy holds promise as a multifaceted approach for precise and potent antibacterial interventions, tapping into both the direct antimicrobial effect of AMPs and the immune-mediated bacterial elimination facilitated by Rhamnose. In this study, we conducted MD simulations of six rhamnose-conjugated molecules with PEG length variations, based on previously reported AMPs, c-PKAI and c-PKFI, with bacterial-mimicking membrane, palmitoyl-oleoyl-phosphatidylglycerol (POPG). The aim is to find the molecules that can disrupt the POPG membrane, while still presenting the rhamnose part in the water environment. We found that **5-6**, the molecule with based on c-PKFI, with the proline as the conjugation site are the best candidates for applying this novel antimicrobial strategy.



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GRRM を用いたフェロセンの構造の検討

（和歌山大院システム工[1]・和歌山大システム工[2]）○徳田 遥祐[1]・上田 祥輝[2]・山門 英雄[1,2]
Study of the structure of ferrocene using the GRRM ([1]*Graduate School of Systems Engineering, Wakayama Univ.*, [2]*Faculty of Systems Engineering, Wakayama Univ.*) ○Yosuke Tokuda,[1] Yoshiki Ueda,[2] Hideo Yamakado[1,2]

Ferrocene is an organometallic compound with a structure in which two cyclopentadienyl rings sandwich an iron atom. Ferrocene is experimentally known to has an eclipsed structure with D5h symmetry in the gas phase and several crystalline polymorphs, including a staggered with D5d symmetry in the solid phase. In this study, we study the difference between the equilibrium structure of ferrocene in the gas phase and in the solid phase using GRRM. An automatic search using GRRM has resulted in the D5d and D5h symmetries of ferrocene as the equilibrium structure optimized by the structure optimization. The monoclinic crystal with D5d symmetry and the triclinic crystal with D5h symmetry of ferrocene in the cell were also structure-optimized by solid-state calculations using Quantum Espresso and Gaussian09.
Keywords : ferrocene; GRRM; rotational isomer; gas phase; solid phase

フェロセンは、シクロペンタジエニル環 2 つが鉄原子を挟んだ構造の有機金属化合物である。シクロペンタジエニル環の中央部が鉄に配位しており、特殊な結合をもつ。フェロセンは、気相中では D5h 対称である重なり型、固相中では D5d 対称であるねじれ型の構造のものを含む複数の結晶多形をとることが実験的に知られている [1)]。室温で安定な結晶は monoclinic の結晶であり、セル内のフェロセンは D5d 対称である。一方低温域では、164K 以下で準安定な triclinic の結晶 [2)]と 242K 以下で安定な orthorhombic の結晶 [3)]が実験的に発見されており、orthorhombic の結晶のセル内ではフェロセンは D5h 対称であることが知られている。

本研究では、GRRM[4)]を用いて気相中と固相中の平衡構造との差異について検討する。Gaussian09 によるエネルギー計算を用いた GRRM による自動探索で、フェロセンの D5d 対称と D5h 対称が平衡構造として構造最適化された(Fig.1)。また、Quantum Espresso と Gaussian09 による固体計算によって、セル内のフェロセンが D5d 対称な monoclinic の結晶(Fig.2)と、D5h 対称な triclinic の結晶に構造最適化された。

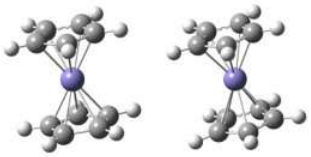

Fig.1 Ferrocene, D5d and D5h symmetry.

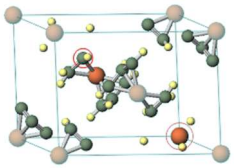

Fig.2 Monoclinic ferrocene crystal.

1) J. D. Dunitz, L. E. Orgel and A. Rich, Acta Cryst. **1956**, 9, 373-375.
2) K. Ogasahara, M. Sorai and H. Suga, Chem. Phys. Lett. **1979**, Vol. 68, Issues 2–3, 457-460.
3) P. Seiler and J. D. Dunitz, Acta Cryst. **1979**, B35, 2020-2032.
4) S. Maeda, K. Ohno, K. Morokuma, Phys. Chem. Chem. Phys., 2013, 15, 3683-3701.

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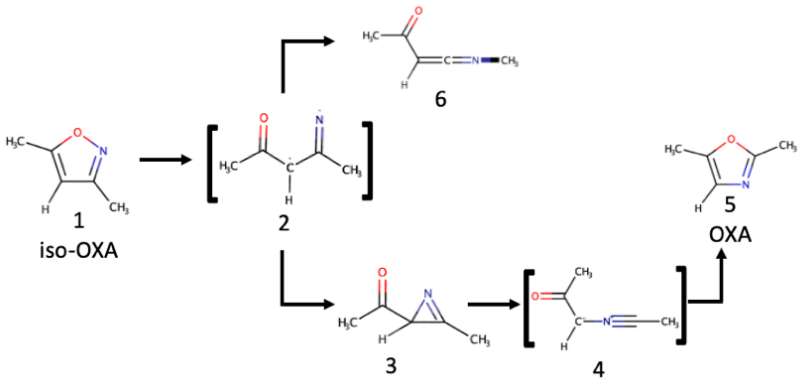
S_1 電子状態を介した 3,5-dimethylisoxazole の光異性化過程に関する非断熱 *ab initio* 動力学研究

（上智大院理工[1]・上智大理工[2]）○木村 美都稀[1]・南部 伸孝[2]
Nonadiabatic *ab initio* Dynamics for the Photoisomerization process of 3,5-dimethylisoxazole via the S_1 Electronic state ([1]*Graduate School of Science and technology, Sophia University*, [2]*Faculty of Science and Technology, Sophia University*) ○Mizuki Kimura[1], Shinkoh Nanbu[2]

To explore the photoisomerization pathway of isoxazole (iso-OXA) to oxazole (OXA), a non-adiabatic *ab initio* molecular dynamics (MD) simulation was performed; we focused on the first excited state (S_1) of 3,5-dimethylisoxazole which could produce 2,5-dimethyloxazole. However, since three electronic excited states (S_1, S_2, S_3) were found to be lying closely together around Franck-Condon region, totally 4 electronic states were considered to simulate the photoisomerization. The VDZ + *sp* gaussian functions were used as the basis-set and the 12-electron, 11-orbital CAS-PT2 method and CAS-SCF method were employed. The *sp* functions are extracted from Dunning's aug-cc-pVDZ function. The potential energy and its gradient at each time-step were obtained with this *ab initio* CAS-PT2/CAS-SCF calculation following time-evolution of the classical trajectory, and if the two electronic states were lying closely to each other, the surface-hopping judgment between these two states was performed by the anteater-procedure based on the Zhu-Nakamura formula.
Keywords : Isoxazole; Photoisomerization; Nonadiabatic ab initio Dynamics

isoxazole は 5 員環からなる分子であり，製薬，農芸化学，防錆剤などの分野で応用されている。isoxazole は光により異性化することが知られている。Nunes ら[1]は，Ar matrix 上で 3,5-dimethylisoxazole への光照射実験を行った。彼らの提案した反応機構を Fig.1 に示す。化合物 1 に光を照射すると，化合物 3, 5, 6 が観測された。本研究では非断熱遷移を考慮した全自由度 *ab initio* 分子動力学計算により，3,5-dimethylisoxazole の S_1 状態への光励起による異性化反応を解明することを目的とした。

基底関数を VDZ + *sp* を用い，12 電子 11 軌道の CAS-PT2 法を 52 軌道，CAS-SCF 法を 200 軌道，500 fs 間計算を実施した。結果，化合物 3 に異性化する収率はそれぞれ，0.54, 0.48 であった。さらに，CASPT 2 では化合物 4, 5 への異性化も確認された。



1) C.M. Nunes *et al*. *J.Org. Chem.* **78**, 10657-10665 (2013)

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酸性条件下におけるアレン型ゼルンボンの環化反応に関する量子化学的研究

（埼玉医大[1]・近大院農[2]・近大農[3]）○土田　敦子[1]・柏崎　玄伍[2]・中村蒼[3]・北山　隆[2,3]

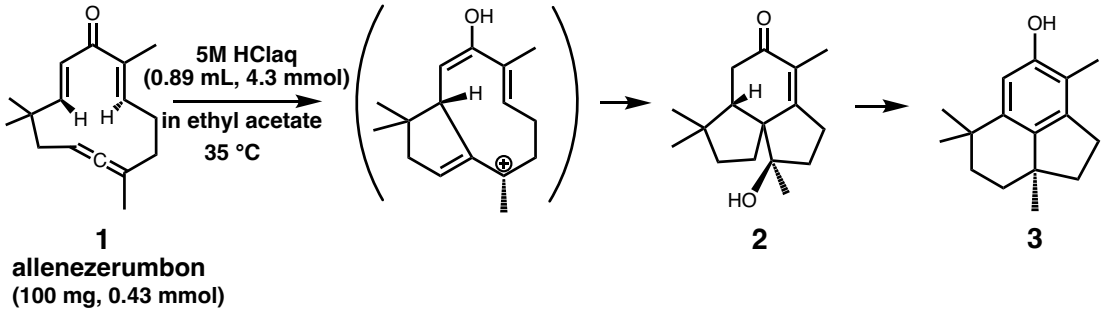
Theoretical study on tne cyclization reaction of allene type zerumbone under acidic condition

([1]*Saitama Med. Univ.*, [2]*Graduate School of Agriculture, Kindai Univ.*, [3]*Faculty of Agriculture, Kindai Univ.*) ○ Noriko Tsuchida,[1] Gengo Kashiwazaki[2], Aoi Nakamura[3] and Takashi Kitayama[2,3]

The sesquiterpene zerumbone, obtained from wild ginger, has a unique structure and is expected to be a lead compound producing a variety of carbon skeletons.[1)] We have succeeded in synthesizing several new compounds from allene-type zerumbone in ethyl acetate under hydrochloric acidic conditions by one-step process. However, the carbon skeleton changes from reactant to products are significant, and the reaction mechanisms have not yet been elucidated in detail. In this study, DFT (B3LYP/6-311G* SCRF=ethyl acetate) calculations were performed for the synthetic route of the tricyclic compound **3**. It was been found that Brønsted acidic proton play a crucial role in the formation of CC bonds.

Keywords:*DFT, allene type zerumbone, polycyclic compound, synthesis pathway, acidic condition*

南洋ハナショウガから得られるゼルンボンはユニークな構造をもち，多彩な炭素骨格を生み出すリード化合物として期待されている。塩酸酸性条件下において，アレン型ゼルンボンからワンステップで数種類の三環式化合物が生成される。元の構造から劇的に骨格が変化するため，反応機構の詳細はわかっていない。三環式化合物 **3** の生成経路について，HCl のほか，水分子を顕に加え DFT 計算を用いて追跡を行った。アレン型ゼルンボン **1** から化合物 **3** へ至るまでに複数回の CC 結合の組み換えが生じる。その全てにおいて HCl の存在が重要な役割を担うことを明らかにした。当日，前回発表の水分子を含まない経路との比較も報告する。



1) Y. Utaka et al., *J. Org. Chem.,* **2020**, *85*, 8371.

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QM 計算と QM/MM-MD 計算による DNA 塩基対の二重プロトン移動の機構解析

（広市大院情報）○卜部　孝幸・齋藤　徹
Mechanistic analysis of double proton transfer in DNA base pairs by QM and QM/MM-MD
(*Graduate School of Information Sciences, Hiroshima City University*) ○Takayuki Urabe, Toru Saito

Double proton transfer tautomerization between GC and AT base pairs in DNA can lead to errors in genetic information and can thus be used to treat cancers. Since there have been no theoretical studies that have systematically investigated these tautomerization processes, in this study, we constructed a QM-cluster model consisting of only GC and AT pairs and a QM/MM model including the B-DNA environment and bulk water molecules. Calculated results show that the B-DNA environment contributes to the formation of charge-separating intermediates and plays a role in preventing tautomerization. Details of the calculated results will be presented in the poster.
Keywords: DNA; DFT; QM/MM-MD

GC および AT 塩基対の互変異性化は遺伝情報のエラーを引き起こしうるため、がん治療に活用できる可能性がある。DNA 中の GC、AT ペアの二重プロトン移動を系統的に調べた理論研究はないため[1, 2]、本研究では、図 1 に示すように(i)GC、AT ペアのみからなる QM クラスターモデル、および(ii)B-DNA 環境とバルクの水分子を考慮した QM/MM モデルを構築した。両者を比較することで、DNA 環境が互変異性化反応に及ぼす影響を調べた。モデル(i), (ii)ともに QM 計算には半経験的手法の GFN2-xTB と密度汎関数理論（B3LYP/def2-SVP）を用い、モデル(ii)には QM/MM メタダイナミクス計算を実施した。計算結果から、DNA 環境が電荷分離中間体の生成に寄与しており、互変異性化を防ぐ役割を果たしていることがわかった。計算結果の詳細は当日発表する。

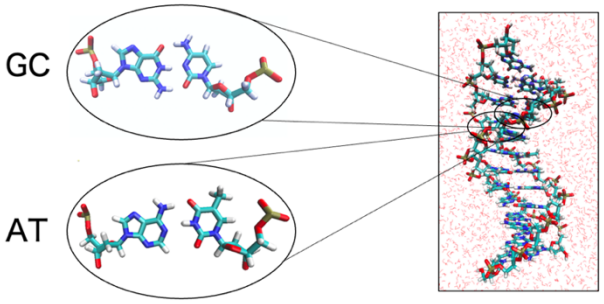

図 1　　(i) QM モデル　　(ii) QM/MM モデル

[1] D. Soler-Polo et al., *J. Chem. Theory Comput*. **2019**, *15*, 6984-6991.
[2] K. Odai et al., *J. Phys. Chem. B*. **2020**, *124*, 9, 1715-1722.

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エチレンへの水素付加反応の GRRM を用いた反応経路探索

(和歌山大システム工[1]・和歌山大院システム工[2])
○清水 宏樹[1]・上田 祥輝[1]・山門 英雄[1,2] Exploration of reaction pathways for hydrogen addition to ethylene using Global Reaction Route Mapping (GRRM).([1]Faculty of Systems Engineering, Wakayama University, [2]Graduate School of Systems)○Hiroki Shimizu[1], Yoshiki Ueda[1], Hideo Yamakado[1,2]

Ethylene (CH2=CH2) hydrogenation is fundamental in organic chemistry and industrial processes. Understanding its mechanism is vital for developing efficient catalysts and processes. This study used GRRM17 [1)] to investigate ethylene's hydrogen addition pathways, employing Artificial Force Induced Reaction (AFIR) and Anharmonic Downward Distortion Following (ADDF) within the GRRM framework. ADDF results revealed decomposition pathways (DDC0, DDC1) (see Fig.1) consistent with previous studies [2)]. Prior research [3)] discusses the reaction from ethane to ethylene, starting with C-C bond homolysis, forming methyl radicals, and involving steps like hydrogen abstraction and transfer. Our findings align with these studies. *Keywords : Reaction route search; GRRM; AFIR; ADDF*

エチレン(CH2=CH2)の水素化は、有機化学および工業プロセスにおける基本的な反応である。この反応のメカニズムの詳細を理解することは、より効率的な触媒やプロセスの開発に不可欠である。本研究では、GRRM17 [1)]を利用して、エチレンへの水素付加反応の経路を調査した。GRRM の枠組み内で Artificial Force Induced Reaction(AFIR)法と Anharmonic Downward Distortion Following(ADDF)法を用いた。ADDF 計算結果から明らかになった解離経路(DDC0(Downward Dissociation Channel0)、DDC1)（Fig.1 参照）は先行研究 [2)]と同様の内容を示した。また、先行研究 [3)]によるとエタンからエチレンへの反応は、C-C 結合のホモリシスによって開始され、メチルラジカルの形成を引き起こし、水素引き抜き、水素移動といったステップを含む複雑な過程であると議論されている。本研究で得られた結果も、この先行研究の内容と整合している。

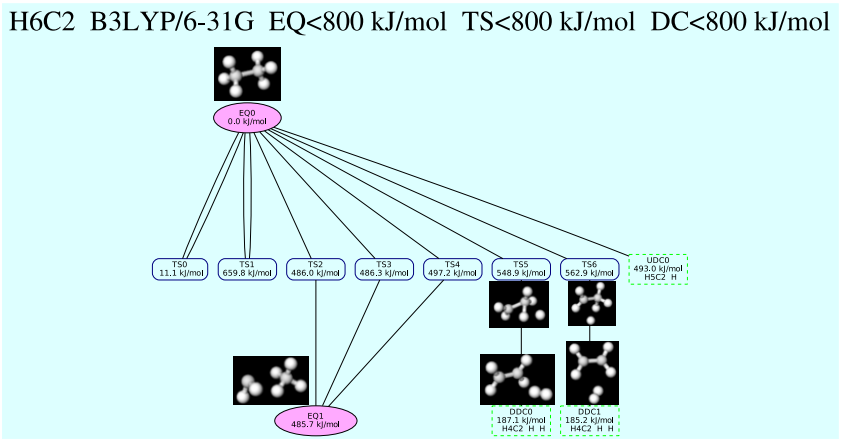

Fig.1: Reaction Routes of H6C2 to H4C2

1) S. Maeda, Y. Harabuchi, Y. Sumiya, M. Takagi, K. Suzuki, M. Hatanaka, Y. Osada, T. Taketsugu, K. Morokuma, K. Ohno, GRRM17, see http://iqce.jp/GRRM/index_e.shtml (accessed date 3 March, 2020).
2) https://iqce.jp/GRRM/GDSP/H6C2/GDSP.HTM (accessed date 8 Jan, 2024).
3) Hikaru Saito and Yasushi Sekine, RSC Adv. , 2020, 10, 21427-21453.

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Chiral ion pair を用いた触媒的プロパルギル位置換反応のエナンチオ選択性に関する理論的研究

（東邦大薬[1]・ENEOS 株式会社[2]）○吉川 武司[1]・坂田 健[1]・中嶋 裕也[2]

Theoretical study on enantioselectivity of catalytic propargyl substitution reaction using chiral ion pair ([1]*Faculty of Pharmaceutical Sciences, Toho University*, [2]ENEOS Corporation)
○Takeshi Yoshikawa,[1] Ken Sakata,[1] Yuya Nakajima[2]

A catalytic asymmetric propargylic substitution reaction of propargylic alcohols or their derivatives is an efficient tool for constructing a stereocenter at the propargylic position. Since Nishibayashi et al. reported the asymmetric propargylic alkylation reaction of propargylic alcohols with acetone in the presence of an optically active thiolate-bridged diruthenium complex, transition metal-catalyzed enantioselective propargylic substitution reactions have been gradually developed. In our previous study, we performed DFT calculations to clarify the origin of the enantioselectivity in the reaction based on the optically active ligands. On the other hand, efficient asymmetric synthesis has been developed by using ion pairs, that is relatively easy to synthesize, with noncovalent interactions instead of the optically active ligands. Recently, Jacobsen et al. have succeeded in the synthesis of asymmetric propargylic substitution reaction using chiral ion pairs. In this presentation, we used quantum chemical calculations to elucidate the asymmetric mechanism.

Keywords : Chiral ion pair; Asymmetric propargyl substitution reaction*;* Sulfur-bridged di-ruthenium catalyst*;* Density functional theory*;* Matlantis

遷移金属錯体を用いた触媒的プロパルギル位置換反応は、反応中間体の制御が困難なことからその開発が遅れており、比較的最近まで一般性の高い触媒系は報告されていなかった。西林らは、硫黄架橋二核ルテニウム錯体を触媒として用いることで、様々な求核剤による触媒的プロパルギル位置換反応を達成した[1]。さらに、配位子の硫黄架橋部位に光学活性置換基を導入することで、不斉反応への展開もしている[2]。本研究室では、量子化学計算を用いて不斉化発現機構の解明を行ってきた[3, 4]。一方、光学活性配位子の代わりに、イオン対を用いることで、一般性の高い不斉合成反応の開発も行われており[5]、最近では、Jacobsen らが光学活性なイオン対を作成することで、プロパルギル位置換反応の不斉化[6]に成功しているものの、その反応メカニズムはいまだ詳細には解明されていない。本研究では、量子化学計算を用いて不斉発現メカニズム解明を行った。不斉イオン対の構造は複雑であり、平衡構造が多数考えられたため、汎用原子レベルシミュレータ Matlantis[7]を用いて考慮すべき安定な構造を選別した。その後、密度汎関数理論を用いて、反応機構の検証を行った。

[1] Y. Nishibayashi, I. Wakiji, M. Hidai, *J. Am. Chem. Soc.*, **122**, 11019-11020 (2000). [2] Y. Inada, Y. Nishibayashi, S. Uemura, *Angew. Chem. Int. Ed.*, **44**, 7715-7717 (2005). [3] K. Sakata, Y. Goto, T. Yoshikawa, Y. Nishibayashi, *Chem. An Asian. J.*, **16**, 3760-3766 (2021). [4] K. Sakata, Y. Uehara, S. Kohara, T. Yoshikawa, Y. Nishibayashi, *ACS Omega*, **41**, 36634-36642 (2022). [5] S. Satake, T. Kurihara, K. Nishikawa, T. Mochizuki, M. Hatano, K. Ishihara, T. Yoshino, S. Matsunaga, *Nature Cat.*, **1**, 585-591 (2018). [6] J. M. Ovian, P. Vojáčková, E. N. Jacobsen, *Nature*, **616**, 84-89 (2023). [7] Matlantis (https://matlantis.com/), software as a service style material discovery tool.

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アミンの CO_2 化学吸収能改善を狙った量子化学計算による溶媒効果の検討

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Quantum Chemical Solvent Effects Evaluation for Improving Amine-based CO_2 Chemical Absorbents

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Aqueous amine absorbents to capture atmospheric CO_2 have been proposed to achieve carbon neutrality. However, aqueous amine solutions have the drawback that the carbamate ion obtained as a product of CO_2 capture is excessively stable, resulting in a high energy cost for regeneration of the absorbent solution. This study performed a set of quantum chemical calculations of non-aqueous amine solutions as more realistic amine-based CO_2 chemical absorbents, targeting ten types of primary and secondary amines with systematically varied substituents. Correlation of the amine structures and the solvents' dielectric constants to Δ_rG of the CO_2 absorption reaction was investigated by B3LYP-D3/6-31G(d'). It was found that Δ_rG well correlates with the number of occupied N-atom lone electron pairs determined by NBO analysis for the primary amines, regardless of the solvent (Figure 1).

Keywords ;CO2 chemical absorption, Carbamate reaction ; Solvent effect

カーボンニュートラル実現に向けて、大気中の CO_2 を分離回収するアミン水溶液による化学吸収を用いる方法が提案されている。しかし、アミン水溶液を用いた場合、CO_2 の固定生成物として得られるカルバメートイオンが過度に安定であるため、吸収液の再生エネルギーコストが大きい。そこで、より現実的なアミン系 CO_2 化学吸収液として、非水アミン溶液の量子化学的設計に取り組んだ。置換基を系統的に変化させたアミンを対象とし、CO_2 吸収反応の反応ギブズエネルギー（Δ_rG）について、溶媒の誘電率との相関を、B3LYP-D3/6-31G(d') で調査した。その結果、1 級アミンにおいて、NBO 解析で求めた N 原子孤立電子対の占有数と Δ_rG は溶媒によらず相関を持つことが示された（図 1）。

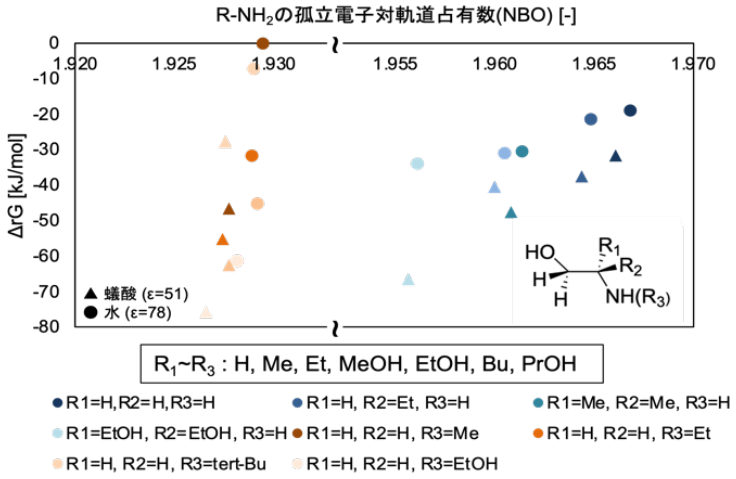

図 1. 反応 $2R\text{-}NH_2 + CO_2 \rightleftarrows R\text{-}NH\text{-}COO^- + R\text{-}NH_3^+$ のギブズエネルギーと $R\text{-}NH_2$ の孤立電子対軌道占有数（NBO）の関係

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2 次速度論的同位体効果を示す化学反応の Beyond-Born-Oppenheimer 量子化学計算 : S_N2 反応における求核剤依存性解析を例として

（中央大理工）○元木 康平・森 寛敏

Beyond-Born-Oppenheimer analysis of chemical reactions exhibiting secondary kinetic isotope effects: nucleophile dependence of S_N2 reactions

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○Kohei Motoki・Hirotoshi Mori

Deuterium science has recently attracted research interests in drug and material discovery.[1-3] With the background, this study focuses on simple S_N2 reactions, including deuterium, ($CH_3Cl/CD_3Cl + X^- \rightarrow Cl^- + CH_3X/CD_3X$; X={F,Cl}) for evaluating kinetic isotope effects as rate constant ratios (k_H/k_D). The ratios evaluated by cNEO (Constrained Nuclear-Electronic Orbital), [4] a beyond Born-Oppenheimer calculation, qualitatively reproduced the experimental trends (Table 1).

Keywords : Nuclear-Electronic Orbital; Deuterium; Chemical Reactions; Kinetic Isotope Effect; Density Functional Theory

重水素（D）置換による微小な構造と電子状態の変化を利用した分子設計が、創薬・材料開発分野で求められている。[1-3]当該分野では、D 置換が物性に与える影響は勿論、化学反応に与える影響も興味の対象となる。本研究では、シンプルな S_N2 反応に注目し、Beyond-Born-Oppenheimer 量子化学計算（cNEO-CAM-B3LYP(noepc)/aug-cc-pVDZ:PB4-D）[4] で、D 置換が反応速度に与える影響を評価した。

表 1 に、求電子剤及び求核剤として CH_3Cl/CD_3Cl と F^-/Cl^- を用いた S_N2 反応の速度定数比（k_H/k_D）を示す。我々の計算値は実験値の傾向を定性的に再現した。一般に D 置換は、ゼロ点振動エネルギーを減少させるため、反応の活性化障壁は上昇し、反応速度定数は低くなる。一方で、非調和性により CD_3 基の嵩高さが減少し、求電子剤が CD_3Cl の場合の方が CH_3Cl の場合に比べて僅かに求核剤は近付くことが可能になる。そのため、活性化障壁に至るまでの反応経路が短く活性化障壁が小さくなる効果があることが分かった。これにより求核剤が F^- の場合、D 置換が反応速度を向上させる結果に繋がると説明される。

表 1 重水素化前後の速度定数比 と 反応物の構造パラメータ

求電子剤+求核剤 (X^-)	$CH_3Cl + F^-$	$CD_3Cl + F^-$	$CH_3Cl + Cl^-$	$CD_3Cl + Cl^-$
k_H/k_D (cNEO)	0.56		1.08	
k_H/k_D (Exp.)	0.90±0.02 [5]		1.2±0.1 [6]	
C...X^- [Å]	2.494	2.486	3.182	3.180
C-H or C-D [Å]	1.107	1.101	1.110	1.104

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(-)-エピガロカテキン-3-*O*-ガレート誘導体と β-シクロデキストリンによる包接複合体形成に関する密度汎関数法を用いた検討

（福岡大薬[1]・近畿大生物理工[2]）○池田 浩人[1]・大波多 友規[1]・中島 梨恵[1]・堤 広之[1]・藤澤 雅夫[2]

Density functional theory study on the formation of inclusion complexes of (-)-epigallocatechin-3-*O*-gallate derivatives with β-cyclodextrin

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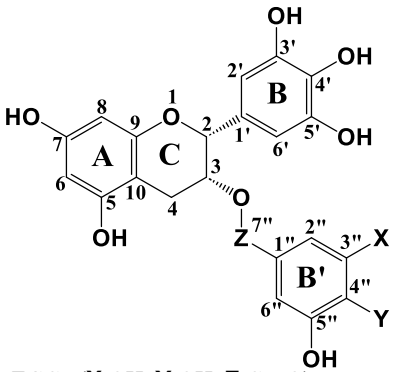
In the inclusion complexation of (-)-epigallocatechin-3-*O*-gallate (EGCg) with β-cyclodextrin (βCD) in water, the B' ring of EGCg is deeply encapsulated into the cavity of βCD, forming an energetically stable complex. To confirm the role of the hydroxy group of the B' ring and the carbonyl oxygen of EGCg, which are thought to be important in the formation of this inclusion complex, the formation of inclusion complex between each derivatives of EGCg, in which the hydroxyl group at position 3" or 4" of the B' ring is changed to hydrogen or the carbonyl group of EGCg to a methylene group, and βCD in water was investigated using density functional theory.

Keywords : Density Functional Theory; Green Tea Catechin; Inclusion Complex; Cyclodextrin

【目的】(-)-エピガロカテキン-3-*O*-ガレート(図 ; EGCg)の β-シクロデキストリン(βCD)による水中での包接化において、EGCg の B'環が βCD の空洞内に深く包接された複合体がエネルギー的に最も有利に生成することを既に報告した。上記複合体形成において、重要と考えられる EGCg の B'環の水酸基およびカルボニル酸素の役割を確認するため、密度汎関数法(B3PW91/cc-pVDZ)による検討を行った。

【方法】EGCg の B'環の 3"位または 4"位の水酸基を水素に、あるいはカルボニル基をメチレン基に変更した EGCg の各誘導体(図 ; EGCgD1～D3)の水中(PCM 法)における最安定構造を求めた。得られた各誘導体の最安定構造について、誘導体の各環に設定した基準原子と βCD の空洞内に設定した分子平面との距離を 100 pm 毎に接近させた初期構造を作成した。作成した各初期構造を水中で最適化し、各誘導体と βCD による複合体の構造ならびに全エネルギーを求めた。複合体形成エネルギー(Δ*E*)を(複合体の全エネルギー)－(各誘導体の全エネルギー＋βCD の全エネルギー)から算出し、最も小さな Δ*E* を示す複合体を選び出した。



EGCg (**X**:OH, **Y**:OH, **Z**:C＝O)
EGCgD1 (**X**: H, **Y**: OH, **Z**: C＝O)
EGCgD2 (**X**: OH, **Y**: H, **Z**: C＝O)
EGCgD3 (**X**: OH, **Y**: OH, **Z**: CH_2)

図 EGCg および各誘導体の化学構造

【結果・考察】EGCgD1 の各環は、いずれも βCD の空洞内に包接されにくく、EGCgD2 も同様であった。一方、EGCgD3 の B 環または B'環は、βCD の空洞内に深く包接されることが分かった。以上の結果より、EGCg の βCD による包接化における B'環の 3"位または 4"位の水酸基の重要性が示唆された。

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量子化学計算による 2 液系自己着火推進剤の初期反応段階における置換基効果の検討

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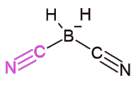
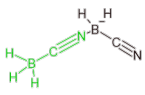
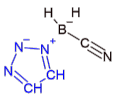
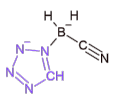
Quantum chemical investigation of substituent effects in the initial reaction step of Hypergolic Bipropellant ([1]*Faculty of Science and Engineering, Chuo University*, [2]*JST ACT-X*)
○Miori Nogamida,[1] Nahoko Kuroki,[1,2] Hirotoshi Mori[2]

N_2H_4, which generates massive heat upon contact with an oxidizer, has been used as a hypergolic bipropellant for rockets. However, N_2H_4 is highly volatile and toxic. Therefore, non-volatile and designable ionic liquids are attracting attention as new fuels[1]. With the background, we have studied reactions of $X(CN)_2^-$ {X=N,B} including ionic liquids and HNO_3 as an oxidizer[2] . Here, we discuss substituent effects on reactions between R-BH_2CN^- (Table 1) and HNO_3, of which ignition time are short[3]. With UB3LYP/6-31G(d) level quantum chemical calculations, the first step of the reaction was confirmed to be proton transfer from HNO_3 to the terminal N of $X(CN)_2^-$. It was found that introducing electron-withdrawing substituents can control the amount of exotherm in the first step of the reaction (Table 1).
Keywords : Hypergolic Ionic Liquids; Chemical Reaction; Energy density analysis; Natural Bond Orbital; Natural Resonance Theory Analysis

ロケットの 2 液系自己着火推進剤には、燃料と酸化剤の接触後、直ちに発熱し、着火までの時間が短い N_2H_4 が用いられている。だが、N_2H_4 は高い揮発毒性を持つ。そこで新燃料に、不揮発性でデザイン性のあるイオン液体が注目されている[1]。この背景下、我々は、アニオン種として $X(CN)_2^-$ {X=N,B} をもつイオン液体と HNO_3 の反応を対象として、X の違いが、初期反応経路を変化させることを示してきた[2]。本研究では、着火時間短縮の実例がある R-BH_2CN^-（表 1）と HNO_3 の初期反応について、置換基効果の解析を行った[3]。UB3LYP/6-31G(d) レベルの量子化学計算から、反応第一段階は、全ての場合において、末端 N へのプロトン移動と予測された。この際の ΔH と末端 CN 基の N 原子電荷の関係を表 1 に示す。電子吸引性置換基の導入で、反応初期の発熱量を制御可能だとわかった。更なる詳細については当日議論する。

表 1. R-BH_2CN^- + HNO_3 → R-BH_2CNH + NO_3^- の反応エンタルピー ΔH と末端 CN 基の N 原子電荷の関係

アニオン					
charge	-0.60	-0.48	-0.45	-0.47	-0.46
Δ H [kcal/mol]	-28.2	-23.1	-20.6	-22.6	-21.6

1) S. Schneider, *et al, Energy Fuels* **2008**, *22*, 2871. 2) 野上田光織, 黒木菜保子, 森寛敏, 第 61 回燃焼シンポジウム, **2023**, C315. 3) Z. Zhang, *et al, Green Energy & Environment* **2021**, *6*, 794.

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フラーレンとオリゴエチレングリコール・オリゴプロピレングリコール分子間錯体の量子化学計算

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Quantum Chemical Calculations of Intermolecular Complexes of Fullerene and Oligoethylene Glycol

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Fullerenes are spherically bonded molecules of carbon atoms, and are expected to find applications in the medical and materials fields. Fullerenes are highly electron-accepting and form charge-transfer complexes. In this study, we investigated the structure and properties of two types of complexes, fullerene-oligoethylene glycol (OEG) and fullerene-oligopropylene glycol (OPG), using DFT calculations. Intermolecular distances were calculated from structural optimization. IR spectra were obtained from DFT calculations. A peak that was not seen for the molecule alone appeared at 1500 cm^{-1} for the complex. Similar peaks were observed for the radical cations of OEG and OPG, respectively, confirming intermolecular interactions by charge transfer. In the complexes, the sum of the charges of each molecule was calculated, which also confirmed the charge transfer. OEG showed a larger charge transfer than OPG, suggesting a stronger interaction.

Keywords : Fullerene; Polyethylene glycol; Polypropylene glycol; Charge-transfer complex; Quantum chemical calculations

フラーレンは炭素原子が球状に結合した分子であり、医療分野や材料分野への応用が期待されている。フラーレンは電子受容性に優れており、電荷移動錯体を形成する。今回は DFT 計算を用いて、フラーレン-オリゴエチレングリコール(OEG)、フラーレン-オリゴプロピレングリコール(OPG)の 2 種類の錯体の構造と物性を調べた。最適化構造(図 1、図 2)から分子間距離をそれぞれ算出した。基準振動計算から IR スペクトルを得た。分子単体では見られなかったピークが、錯体では 1500 cm^{-1} に現れた。同様のピークは OEG、OPG それぞれのラジカルカチオンでも見られ、電荷移動による分子間の相互作用が確認された。また錯体において、それぞれの分子の電荷の総和を算出し、ここからも電荷の移動を確認した。OEG の方が OPG よりも大きく電荷が移動しており、より強く相互作用をしていると考えられた。

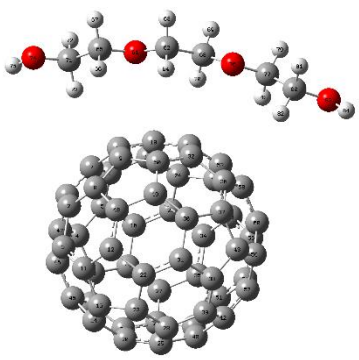

図 1 : C_{60}-OEG 錯体の最適化構造

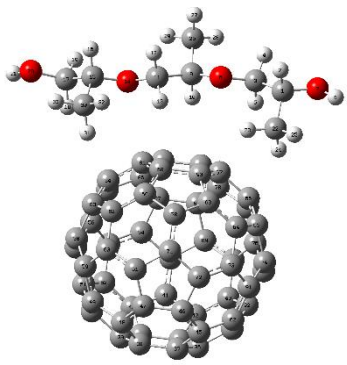

図 2 : C_{60}-OPG 錯体の最適化構造

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ナトリウムイオン及びマグネシウムイオンの水和クラスターにおける配位水−水間の水素結合に関する理論研究

(千葉工大院工) ○加藤 立・古川 千紗・三上 優菜・須長 靖博・工藤 翔慈・松澤 秀則

Theoretical Study on the Hydrogen Bond Between Ligand Water and Water in the Hydrated Sodium and Magnesium Ion Clusters (*Graduate School of Engineering, Chiba Institute of Technology*) ○Ryu Kato, Chisa Furukawa, Yuuna Mikami, Yasuhiro Sunaga, Shoji Kudo, Hidenori Matsuzawa

The hydrogen bond between ligand water and water in the hydrated sodium and magnesium ion clusters were examined using the Local Projection Molecular Orbital-based Perturbation Expansion Theory (LPMO PT) method. The hydrogen bond strength of the water-water is related with the CT term between hydrogen donor and acceptor. We examined the effects of the CT term between cation (M^{n+}) and ligand water (L), and between first adjacent water (W_1) and second adjacent water (W_2) on the hydrogen bond between L and W_1 ($L \rightarrow W_1$). As a result, there are few relationships between the CT term of $L \rightarrow W_1$ and that of M^{n+}–L. In the many cases, the large correlation between the CT term of $L \rightarrow W_1$ and that of W_1–W_2 is found.

Keywords : Hydrogen Bond ; Cation Water Cluster ; Ab Initio Calculation

我々は局所射影分子軌道法(LPMO PT)[1]を用いて、イオン−水クラスター内の水素結合(HB)1 本 1 本の結合の強さを決める要因が電荷移動(CT)項であることを見いだした。水素供与体を d、水素受容体を a とする d→a の水素結合は、相対的に d が電子不足、a が電子過剰のとき、水素移動にともなう a からdへの電子移動量が増え、CT 項が大きくなり、水素結合が強くなる。今回は Fig.1 のような陽イオン(M^{n+}; Na^+, Mg^+, Mg^{2+})の配位水(L)と第一隣接水(W_1)の水素結合 $L \rightarrow W_1$ の CT 項に対する、M^{n+}–L と W_1–W_2(第二隣接水)の CT 項の影響を調べた。Table 1 の HB type の [ ]内の数値は、L–W_1 以外の [水素供与数, 水素受容数, イオン配位数]を示し、表は L が M^{n+}とのみ相互作用する[0,0,1]の例であり、$L \rightarrow W_1$ の CT 項はタイプによって、-6.56 ～ -25.02 kJ/mol の値をとる。各 HB type の M^{n+}–L では、負の値が L から M^{n+}への電子移動を示し、Na^+は Mg^+や Mg^{2+}の約 1/10 の CT 項で、同一イオン種の中では、タイプごとの差は小さく、$L \rightarrow W_1$ の CT 項との相関も小さい。一方 W_1–W_2 の CT 項は正の場合、W_1 が電子過剰であり、その値が大きいと、$L \rightarrow W_1$ の CT 項も大きくなる傾向にある。また L が[0,0,1]以外のケースでも、同様の傾向が見られており、M^{n+}–L の CT 項よりも W_1–W_2 の CT 項の方が、$L \rightarrow W_1$ の水素結合の強さに対する影響が大きいことがわかった。

1) S.Iwata *et al. Phys. Chem. Chem. Phys.* **2016**,18, 19746.

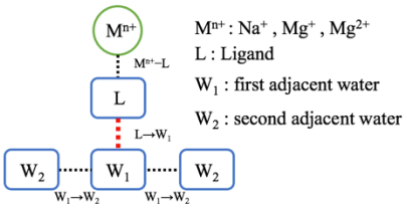

Fig.1 HB and interactions in cation-water cluster.

Table 1 CT terms [kJ/mol] for the bond types in each L-W_1 HB type.

L-W_1 HB type	Bond type	Mg^+	Mg^{2+}	Na^+
$L \rightarrow W_1$				
[0,0,1]→[0,0,0]	M^{n+}–L	-4.83	-3.85	-0.63
	L–W_1	-12.50	-22.45	-8.63
[0,0,1]→[0,1,0]	M^{n+}–L	-5.23	-3.90	-0.58
	L–W_1	-6.56	-10.49	-4.97
	W_1–W_2	-5.75	-7.73	-4.33
[0,0,1]→[1,0,0]	M^{n+}–L	-5.04		-0.63
	L–W_1	-15.85		-8.78
	W_1–W_2	5.01		5.16
[0,0,1]→[1,1,0]	M^{n+}–L	-5.74	-4.79	-0.64
	L–W_1	-10.50	-16.20	-6.42
	W_1–W_2	3.03	3.76	1.91
[0,0,1]→[2,0,0]	M^{n+}–L	-7.56		
	L–W_1	-25.02		
	W_1–W_2	10.92		
[0,0,1]→[2,1,0]	M^{n+}–L	-6.51		-0.69
	L–W_1	-14.40		-8.49
	W_1–W_2	6.20		5.03

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DFT、TD-DFT を用いた、色素増感光触媒中の電子輸送にアンカー基が及ぼす影響の調査

（九州大学　統合新領域学府[1]・九州大学　カーボンニュートラル・エネルギー国際研究所[2]）○嘉陽 安胤[1]・Aleksandar Staykov[2]・渡邊 源規[2]

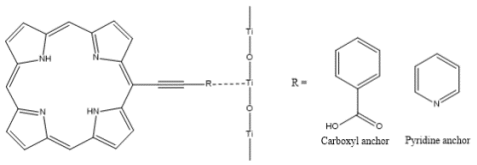
Effect of anchoring group on electron transfer in hybrid dye-sensitized photocatalyst. DFT and TD-DFT study.

([1]*Graduate School of Integrated Frontier Sciences, Kyushu University*, [2]*International Institute for carbon-Neutral Energy Research, Kyushu University*) ○Yasuhiro Kayo[1], Aleksandar Staykov[2], Motonori Watanabe[1,2]

To curb CO_2 emissions into the atmosphere, green hydrogen, produced by a CO_2 emission-free production method, is attracting attention as a new energy carrier that can replace electricity derived from fossil fuels. Water splitting is considered the ideal method to produce hydrogen without CO_2 emissions. TiO_2 has been investigated as a photocatalyst to improve the photoexcitation efficiency in water splitting, and dye-sensitized TiO_2 is one of them. Previous studies of dye-sensitized TiO_2 have shown that the anchoring group between the chromophore and the semiconductor affects the photoexcitation efficiency.[1] In this study, we investigate how the anchor group that binds the porphyrin to the TiO_2 anatase nanoparticle model affects the photocatalytic photoconversion efficiency using density functional theory (DFT) and time dependent (TD)-DFT computational methods. After obtaining the optimized structure of dye-sensitized TiO_2 with pyridine and carboxyl groups as anchor groups, we found through UV calculations that the pyridine group has a stronger absorption wavelength peak than the carboxyl group.

Keywords : Computational Chemistry; Anchoring group; Dye-sensitized photocatalyst; Density functional theory.

大気への CO_2 排出を抑制するため、原油由来の電気に代わる新たなエネルギーキャリアとして、CO_2 を排出しない製造方法によるグリーン水素が注目されているが、その方法の一つが水分解による水素製造である。TiO_2 は水分解における光励起効率を向上させる光触媒として研究されており、色素増感 TiO_2 もその 1 つである。色素増感 TiO_2 のこれまでの研究では、発色団と半導体の間のアンカー基が光励起効率に影響を与えることが示されている。[1] 本研究では、ポルフィリンと酸化チタンアナターゼ微粒子モデルを結合するアンカー基が光触媒の光変換効率にどのような影響を与えるのか、DFT、TD-DFT の計算手法を用いて調査した。アンカー基としてピリジル基、カルボキシ基を持つ色素増感 TiO_2 の最適化構造を得たのち、UV 計算を通して、ピリジル基がカルボキシ基より強い吸収波長ピークを持つことが分かった。



1) Y. Ooyama, T. Nagano, I, Imae. K. Komaguchi, J. Ohshita, and Y, Harima. *Chem. Eur. J.* **2011,** *17*, 14842.

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環状高分子のトポロジーがもたらす表面物理吸着ダイナミクスの変化についての分子動力学シミュレーション

(北大院総合化学[1]・北大院工[2])○中井 剛志[1]、佐藤 信一郎[2]
Molecular dynamics simulation of topology-induced changes in surface physisorption dynamics of cyclic polymers (*[1]Graduate School of Chemical Sciences and Engineering, Hokkaido University, [2]Graduate School of Engineering, Hokkaido University*) ○Tsuyoshi Nakai[1], Shin-ichiro Sato[2]

It was recently reported that modification of the surface of gold nanoparticles with cyclized polyethylene glycol (PEG) exhibits excellent dispersion stability. In this study, molecular dynamics simulations were used to investigate the physisorption dynamics. In particular, we focus on the free energy change during the adsorption process.
Simulations were performed on all atoms, and the CHARMM36m force field and the BAR (Bennett Acceptance Ratio) method were used to derive the free energy. The free energy changes during the adsorption process were -146 kJ/mol (cyclic PEG) and -105 kJ/mol (linear PEG), indicating cyclic PEG is energetically favorable . The main reason for this difference is expected to be the solvated water molecules released during adsorption.

Keywords：Molecular Dynamics, Cyclic Polymer, Free Energy, Adsorption

環化したポリエチレングリコール (PEG) で金ナノ粒子の表面を修飾すると、優れた分散安定性を示すことが近年報告された。本研究ではこの物理吸着ダイナミクスを検討するため、分子動力学シミュレーションを用いた。特に吸着過程の自由エネルギー変化に注目する。
シミュレーションは全原子で行い、力場には CHARMM36m、自由エネルギーの導出には BAR (Bennett Acceptance Ratio) 法を用いた。吸着過程の自由エネルギー変化は -146 kJ/mol (環状 PEG), -105 kJ/mol (直鎖状 PEG) となり環状優位であった。この差異の主要因は、吸着過程で放出される溶媒和水分子であると予想している。

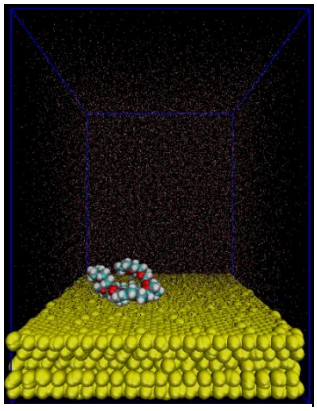
図 1）自由エネルギー計算の初期構造（環状 PEG）

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細菌感染におけるタンパク質—糖鎖間多価相互作用解析

（北里大一般教育）○能登　香
Analyses of protein-glycan multivalent interaction in bacterial infection (*College of Liberal Arts and Sciences, Kitasato University*) ○Kaori Ueno-Noto

Multivalent binding of glycans to proteins plays a central role in many important biological events, including the early stages of infection by verotoxins, such as Shiga toxin (STEC). STEC produced by enterohemorrhagic Escherichia coli specifically binds to glycosphingolipids on the surface of target cells via its B-subunit pentamer. To elucidate the mechanisms underlying the multivalent interaction between glycans and proteins, the interaction between the B-subunit pentamer of STEC and multiple glycans were analyzed in detail by MD simulations and quantum chemical calculations. Significant differences were observed between the monomer and the pentamer of STEC in structural stability and glycan-protein interactions. Interaction analyses by QM calculations showed several cooperative glycan-protein interactions, suggesting a role in protein-glycan multivalent recognition.
Keywords :Glycan recognition, Multivalent interaction, Molecular Dynamics, Quantum chemical calculation, Bacterial infection

ウィルスや細菌等の感染初段階では，生体内糖鎖とタンパク質間の結合が宿主免疫応答調節等の役割を担う．しかし，糖鎖とタンパク質間の親和性自体は強くない．腸管出血性大腸菌によって産生されるベロ毒素（志賀毒素）による感染の初段階では，ベロ毒素の B サブユニット五量体と，標的細胞表面のスフィンゴ糖脂質が，特異的かつ多価で結合することで，その親和性を高めていることが示唆されている．本研究は，タンパク質と糖鎖間の多価相互作用におけるメカニズムの解明を目的として，ベロ毒素と糖鎖間の相互作用を計算化学の手法によって解析した．

ベロ毒素の B サブユニット五量体に，複数のグロボトリオシルセラミド（Gb3）の糖鎖部分（Galα1-4Galβ1-4Glc（が多重結合する結晶構造が報告されており，単量体あたり三個の糖鎖と結合している（Fig. 1）．これを出発構造として，分子動力学シミュレーションを行い，複合体構造のダイナミクスや溶媒分布の変化を解析した．単量体で複数の糖鎖を認識する場合と，五量体全体で複数の糖鎖を認識する場合では，構造安定性および相互作用に大きな違いが見られた．シミュレーションのスナップショット構造におけるベロ毒素と糖鎖間の相互作用エネルギーを，溶媒効果を考慮した量子化学計算により算出した．各単量体間にまたがる糖鎖—タンパク質相互作用が存在し，タンパク質—糖鎖多価認識において協同的に相互作用していることが明らかになった．結果の詳細は当日報告する．

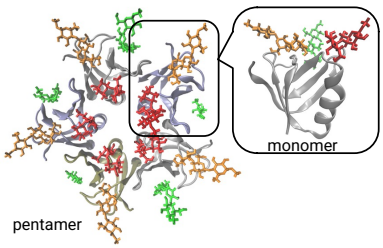

Fig.1 The crystal structure of a B-subunit pentamer bound to multiple Gb3 glycans (PDB ID: 1bos).

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ジアリールエテンの開環反応に要する活性化エネルギーの値の予測モデルの作成

（九大院工）　○山中 康生・Aleksandar Staykov

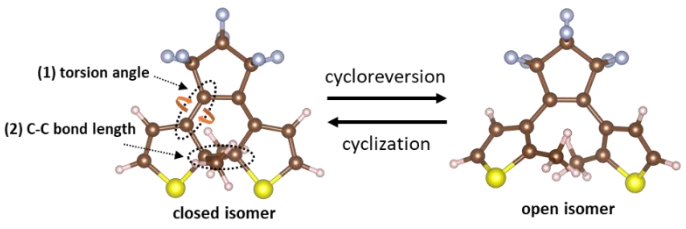
Designing a ML predictive model for activation barriers of diarylethenes cycloreversion

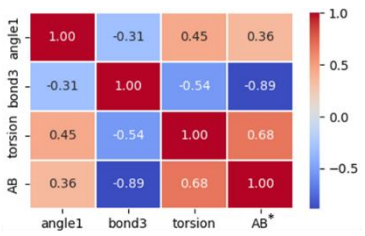
(Graduate School of Engineering, Kyushu-u University)　○Kousei Yamanaka, Aleksandar Staykov,

Diarylethene, known as a photochromic molecules, isomerize photochemically and electrochemically. While it is important to know the activation barriers for isomerization to evaluate the reaction rate and stability of the molecules, it is unclear which diarylethenes would have large activation barriers in grond or elctrochemically and photochemically exicited states. We perform theoretical calculations based on DFT to investigate the activation barriers, and apply Machine Learning to our study to design a predictive model which evaluates the activation barriers.
We have performed geometry optimizations and PES (potential energy surface) scans for 40 diarylethene derivatives. We investigated the Pearson correlation between the activation barriers and bond lengths or torsion angles in diaryethenes and it was found that in anion (1) torsion angle and (2) bond length between two carbon atoms showed relatively stronger correlation to the activation barriers for isomerization.
Keyword : Diarylethene; Electrochemical Switching; Frontier Orbital; Machine Learning

フォトクロミック分子として知られるジアリールエテンは、光化学的、電気化学的に異性化を起こす。異性化の反応速度・安定性を評価するために、異性化に要する活性化エネルギーの値を知ることは重要であるが、どのような構造を持つジアリールエテンがどの程度の活性化エネルギーを持つのか明らかにされていない。本研究では、DFT に基づいた理論化学計算によって、ジアリールエテン誘導体らの異性化に必要な活性化エネルギーについて調べ、機械学習を用いて異性化に必要な活性化エネルギーの値を予測する「予測モデル」を作成する。

これまでに、約 40 種のジアリールエテン誘導体に対し構造最適化、PES (ポテンシャルエネルギー曲線) scans を行った。結合長や二面角の大きさ、活性化エネルギーの値に対しピアソンの相関係数を調べたところ、アニオンにおいて、(1)二面角の大きさ、(2)炭素原子間距離が、活性化エネルギーに対し比較的強い相関を示していることが分かった。





*AB is the activation barrier for cycloreversion

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Reconsideration of the Internal Protonation Mechanism of the [1.1.1] Cryptand

([1]*School of Science, Tokai University*) ○Shigeru Ishikawa[1]
Keywords: [1.1.1] Cryptand; Internal Protonation; Nitrogen Inversion; Direct Protonation

The [1.1.1] cryptand $N(C_2H_4OC_2H_4)_3N$ is a bicyclic molecule consisting of two amines bridged by three diethyl ether groups. Each amine can direct its lone pair toward the inside (*i*) or outside (*o*) of the cryptand by the umbrella inversion, resulting an internally or externally protonated cryptand with one or two protons in acidic solution. The rate constant of the internal protonation (k_{AP}^{obs}) of the cryptand (*ii*) was determined by assuming an apparent first-order reaction with respect to [*ii*].[1] A plausible mechanism of the internal protonation is a unimolecular process called nitrogen inversion (NI).[1,2] The NI generates an internally monoprotonated cryptand (i^+i) via an externally monoprotonated cryptand (io^+) under weakly acidic conditions and via an externally diprotonated cryptand (o^+o^+) under strongly acidic conditions. The disadvantage of this mechanism that the rate of the former is less than 1/5 of that of the latter, even though they proceed through the same mechanism.

Another mechanism of the internal protonation is a bimolecular process called direct protonation (DP), in which a proton carrier (a^+) directly protonates the inside of *ii* via the intermediate (ia^+i) that places a^+ between the two amines. This study revisits the DP mechanism. The DP under weakly and strongly acidic conditions are denoted by DP_w and DP_s, respectively. We assume that io^+ and H_3O^+ function as the proton carriers for DP_w and DP_s, respectively. The apparent DP rate constant is given by $k_{AP}^{DP}=k_{AP}^{DPw}+k_{AP}^{DPs}$. Since DP_w is second order with respect to [*ii*], we fitted k_{AP}^{DP} to k_{AP}^{obs} by replacing [*ii*] in k_{AP}^{DPw} by the averaged value of [*ii*] over the reaction time. Fig.1 shows the fitted curves by the least-squares method. The k_{AP}^{DP} reproduced k_{AP}^{obs}. The height of k_{AP}^{DPw} is lower than that of k_{AP}^{DPs} because DP_w is originally a second-order reaction with respect to [*ii*], or autocatalytic process. Molecular orbital calculations revealed that DP_w and DP_s have almost the same activation energy.

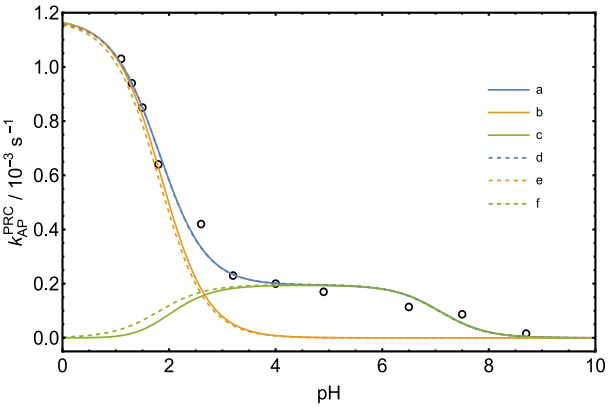

Fig.1 Rate constant for $ii+a^+ \rightarrow i^+i+a$: open circles, k_{AP}^{obs}; **a**, k_{AP}^{DP}; **b**, k_{AP}^{DPs} ; **c**, k_{AP}^{DPw}; **d**, k_{AP}^{NI}; **e**, k_{AP}^{NIs} ; **f**, k_{AP}^{NIw}.

1) P. B. Smith, J. L. Dye, J. Cheney J. M. Lehn, *J. Am. Chem. Soc*., **1981**, *103*, 6044–6048. 2) G. Alibrandi, D. G. Lister, C. L. Vecchioa, M. Maederc, *New J. Chem*., **2014**,*38*, 561-567.

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Academic Program [Poster] | 06. Analytical Chemistry：Poster

Mon. Mar 18, 2024 3:45 PM - 5:15 PM JST | Mon. Mar 18, 2024 6:45 AM - 8:15 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-1vn] 06. Analytical Chemistry

Japanese

[P1-1vn-01]

Analysis of natural Amber

○Sachi Miyamoto[1], Jiro Tanaka[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

Japanese

[P1-1vn-02]

Concentration of trace components in environmental water by freezing and melting

○Itsuki Murakami[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

Japanese

[P1-1vn-03]

Adsorption of tantalum ions on silica gel under strong acidic condition

○Ayaka Saito[1], Kayo Yanagisawa[1], Makoto Matueda[1], Yoshitaka Takagai[1] (1. Fukushima University)

Japanese

[P1-1vn-04]

Degradation analysis of cellulose polymers - Effects of light and moisture

○Yushiaki Akutsu[1], Fujio Ooishi[1], Yuko Nishimoto[1] (1. Kanagawa Univ.)

Japanese

[P1-1vn-05]

Study of the cross-linked structure of bridged poly(methyl methacrylate) using gel-state NMR spectroscopy

○Koyuki Takahashi[1], Yasuko Saitou[2], Yoshiharu Mitoma[1], Keita Sakakibara[2] (1. Prefectural University of Hiroshima, 2. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese

[P1-1vn-06]

Development of auto-analyzing tool for huge numbers of single-molecule fluorescence images.

○Satoshi Kayano[1], Syoji Ito[1,2] (1. Osaka University, 2. RILACS, Osaka Metropolitan University)

Japanese

[P1-1vn-07]

Utilization of cesium ion for the mass axis calibration of atom probe

○Kenji Yoshikawa[1], Masahiro Taniguchi[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-1vn-08]

Study on Dissolved Carbon Dioxide Detection Using Infrared Optical Waveguide

○Masayuki Taniarashi[1], Guangji Meng[1], Ryuhei Nakano[2], Hiroki Hotta[1,2,3], Kin-ichi Tsunoda[3], Takashi Kimoto[4] (1. Graduate School of Maritime Sciences, Kobe University, 2. Maritime

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Sciences, Kobe University, 3. International Maritime Research Center, 4. Kimoto Electric Co, ltd.)

Japanese

[P1-1vn-09]

Gap distance dependence of infrared absorption enhancement on line and space nanostructures of silicon

○Shiori Sato[1], Toru Shimada[1] (1. Hirosaki Univ.)

Japanese

[P1-1vn-10]

Study on skin persistence of nonwoven fabric of a new face mask containing silkworm droppings extract(SDE)

○Yukio Watanabe[1], Tadanobu Sawada[1], Yasuhito Kondo[2], Mayu Akai[1], Hanaka Kajiwara[1], Hisao Ito[3], Naoyuki Higashi[4], Masato Yoshida[5] (1. Meisei University, 2. Gunma Industrial Technology Center Textile Research Institute of Gunma, 3. Art Co. Ltd., 4. Hanakoganei Higashi Skin Clinic, 5. Nippon Medical School Tama Nagayama Hospital)

Japanese

[P1-1vn-11]

Measurement of deteriorate over time in milk using ATR - infrared spectroscopy

○TAIYO YAKUSHI[1], KOKI JODOI[1], YUKO HAMEBE[1], YOSHISUKE FUTAMI[1] (1. National Institute of Technology, Kumamoto College)

Japanese

[P1-1vn-12]

Evaluation of real sample measurements in BCAA analysis using aminoacyl-tRNA synthetases

○Akimitsu Kugimiya[1], Akari Kawamura[1] (1. Hiroshima City University)

Japanese

[P1-1vn-13]

Development of a High-Precision Single-Molecule Identification Method for Fluorouracil for Genome Editing

○Akari Okada[1], Takahiro Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2] (1. Osaka Kyoiku University Tennoji HighSchool, 2. Osaka University,ISIR)

Japanese

[P1-1vn-14]

Development of a Rapid Single-Molecule Detection Method for Cancer Marker Molecules Using Nano-Gap Devices Towards Diagnosis of Pancreatic Cancer

○Yui Yamane[1], Takahito Ohshiro[2], Yuki Komoto [2], Masamitsu Konno[3], Masateru Taniguchi[2] (1. Tokushima Municipal High School, 2. Osaka University, SANKEN, 3. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-1vn-15]

Development of a Single-Molecule Identification Method for 8-Oxoguanosine, a Marker of Aging

○Ryo Kokubu[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguti[2] (1. Osaka Meisei Senior High School, 2. Osaka University, ISIR)

Japanese

[P1-1vn-16]

Multi-component analysis in saliva using a paper-based analytical device

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○Hitoshi Asano[1] (1. Sanyo-Onoda City Univ.)

Japanese

[P1-1vn-17]

Development of a Single-Molecule Identification Method for N4-Acetylcytosine (ac4C) in Cancer Suppression

○Nakamura Misaki[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguti[2] (1. Kyoto Prefectural Rakuhoku High School, 2. Osaka University, ISIR)

Japanese

[P1-1vn-18]

Anion Response of a Fluorescent Probe Based on Zwitterionic Indium(III) Complex

○Koji Kubono[1], Arisa Ishihara[1], Yukiyasu Kashiwagi[2], Keita Tani[1], Kunihiko Yokoi[1] (1. Osaka Kyoiku University, 2. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P1-1vn-19]

Simultaneous Characterization and Prediction Modeling of Reaction Kinetics and Enthalpy from Spatially Resolved Temperature Profiles in a Flow Reactor

○Jun-ichi Ogawa[1], Yuuka Manabe[1], Ryosuke Nakamura[1], Yuma Otake[1], Kazuhiko Inamura[1], Daisuke Kubo[1] (1. Yokogawa Electric Corporation)

Japanese

[P1-1vn-20]

Synthesis of a novel diol having pyrene moiety and its fluorescence behavior in the presence of 2-formylphenylboronic acid and polyamine

○Kisara Murakami[1], Naoto Hamaguchi[1], Tetsuo Ohta[1], Yohei Oe[1] (1. Doshisha University)

Japanese

[P1-1vn-21]

Paper-based analytical devices for semi-quantitative analysis of copper and aluminum ions

○Satoko Takeuchi[1], Aya Katoh[1], Ryuichi Matsubara[2], Tetsuya Sawatsubashi[2], Yuki Hiruta[1], Daniel Citterio[1] (1. Keio University , 2. Mitsubishi Heavy Industries, Ltd.)

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天然琥珀の分析

（神奈川大理[1]、総理研[2]）宮本沙知 1、田仲二朗 2、西本右子 1，2
Analysis of natural Amber ([1] *Faculty of Science, [2]Research Institute for Integrated Science, Kanagawa Univ.*)　○Sachi Miyamoto1, Jiro Tanaka2, Yuko Nishimoto1，2

Natural amber has been used as jewelry since ancient times, and many artifacts have been excavated from ruins. The main production area for amber in Japan is the Kuji region of Iwate Prefecture, and scientific analysis is also conducted. Natural amber is mainly yellow to red, and the color of amber is affected by the oxygen, pressure, and temperature that the sap receives as it moves underground, as well as the components contained in the sap and the surrounding environment. As a result, even amber mined from the same rock layer can have completely different colors, making it difficult to identify the source through color analysis. In this study, we mainly focused on the color and origin of amber, and measured it mainly through component analysis and thermal analysis, and compared amber from Kuji with amber from the Baltic Sea coast and amber from Lithuania.

Keywords : Natural amber; Elemental analysis; Thermal analysis; FT-IR, SEM

天然琥珀は古代から装身具として用いられ、遺跡出土物も多い。我が国の琥珀の産地は岩手県久慈地方が主流であり、科学分析も行われている。天然琥珀は主に黄～赤色が多く、琥珀の色は、樹液が地中を移動する間に受けた酸素、圧力、温度の影響及び樹液に含まれる成分、周辺の環境の影響を受ける。そのため、同じ岩層から採石した琥珀でも全く異なる色を示す場合もあり、色彩分析からの産地同定は困難である。本研究では主に琥珀の色及び産地に注目し、成分分析及び熱分析を中心に測定を行い、久慈産の琥珀とバルト海沿岸産の琥珀、リトアニア産の琥珀を比較した。

検討した琥珀には微量元素として、Al, Si, S, Fe, Ni が含まれるが、黄色の琥珀で比較すると、久慈産の琥珀は S の含有量がバルト海産に比べて多く、黒色の琥珀でも同様であった。リトアニア産のグリーン琥珀では S の含有量が低く、あらかじめ加熱処理された可能性が示された。

また TG 測定から、熱分解開始温度は黄色、黒色共に久慈産の方が低く、TG 測定から得られた熱分解の活性化エネルギーも久慈産の方が低くなった。

ヘッドスペース GC-MS 及び SEM 観察の結果についても報告する。

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凍結融解過程に注目した環境水中の微量成分濃縮

（神奈川大理 [1]）村上　樹 1、西本右子 1

Concentration of trace components in environmental water by freezing and melting

([1] *Faculty of Science, Kanagawa Univ.*)
○Itsuki Murakami[1], Yuko Nishimoto[1]

An aqueous alkali halide solution forms a salt-water eutectic at low temperatures. By maintaining the temperature at around 0 to -20°C, where only the eutectic of salt and water melts, trace components in water can be concentrated in the eutectic mixture. In the temperature range above the eutectic point and below the melting point of ice, only the eutectic mixture exists as a liquid phase, so we believe that a new separation and concentration method at low temperatures can be constructed. So far, we have focused on boron in river water and hot spring water, and have conducted experiments with the aim of constructing and optimizing an experimental system. As a result, it was found that boron was concentrated in the early stages of thawing of frozen samples. In this study, we focused on organic components in environmental water, using amino acids as a model system and comparing the results with boron.

Keywords : Eutectic mixture; Freezing and melting; Environmental water;

ハロゲン化アルカリ水溶液は低温で塩と水の共晶を形成する。0～-20℃付近に保持することで、共融混合物中に水中の微量成分を濃縮することができる。低温域での新しい分離濃縮法が構築できる。河川水や温泉水中のホウ素に着目し、実験系の構築と最適化を目指して実験してきた。凍結試料の融解初期にホウ素が濃縮することが分かった。本研究では環境水中の有機成分に着目し、モデル系としてアミノ酸を取り上げ、結果を比較した。

共存塩（NaCl）濃度 100mmol/L 以下では L-Thr、L-Ala、L-Met では塩濃度によらず融解初期に濃縮するが、L-Ser では塩濃度に伴って融解初期の回収率が低下すること、L-His では逆に塩濃度に伴って融解初期の回収率が上昇した。L-Ser 及び L-His の分別の可能性が示された。他のアミノ酸についても検討を進めている。

1) 荒井健, 西本右子, *分析化学*, **69**, 673-678, 2020

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強酸性条件におけるタンタルイオンのシリカゲルへの吸着挙動

（福島大[1]）○齋藤 文加[1]・柳澤 華代[1]・松枝 誠[1]・高貝 慶隆[1]
Adsorption Behavior of Tantalum Ions on Silica Gel Under Strong Acidic Condition ([1]*Fukushima University*) ○Ayaka Saito[1], Kayo Yanagisawa[1], Makoto Matsueda[1], Yoshitaka Takagai[1]

Tantalum (Ta) has unique chemical properties such as high dielectric constant, excellent corrosion resistance and ductility, and low toxicity to the human body; therefore, it is suitable for many applications to industrial materials such as capacitors device, aircraft engine blades, and artificial tooth roots. Particularly, the recovery systems of Ta are attracting attention, because Ta is essential element using in information communication apparatus and it is also disposed of in large quantities of waste. This presentation shows various type of silica gels work as unique absorbent of Ta in the presence of 68 element in strong acidic solutions. Regardless of the type of strong acid, high adsorption percentages were shown with 100% in the concentration range from 0.01 to 8 M (HCl: 5.7 mg/g, HNO_3: 5.8 mg/g, H_2SO_4: 5.8 mg/g). Almost completes adsorption was reached in only a few minute (98.7 ± 0.5%). Kinetic analysis was investigated; thus, it was a quasi-secondary reaction. In addition, Raman spectroscopic measurements were also conducted to elucidate the state of adsorption between silica gel and Ta. This study has elucidated that kinetics and adsorption mechanisms with optimum conditions of adsorption.

Keywords：tantalum ion, adsorption, silica gel, strong acidic condition

タンタル(Ta)は誘電率が高く，耐食性および展延性に優れ，人体に無害な特徴から，電子機器のコンデンサーや航空機のエンジンブレード，人工歯根など幅広い用途で利用されている。また，情報通信機器に欠かせない元素であるがその廃棄量も多いため，電気電子廃棄物からの回収が注目を浴びている。本研究では，シリカゲルを利用して強酸性条件下における Ta の吸着を検討した。様々な種類のシリカゲルに強酸性条件下で 68 元素を作用させると，Ta およびいくつかの元素が酸性条件下で高い吸着率を示すことがわかった。強酸の種類に関わらず高い吸着率を示し，0.01～8 M の濃度範囲において吸着率 100%を示した(HCl: 5.7 mg/g，HNO_3: 5.8 mg/g，H_2SO_4: 5.8 mg/g)。また，わずかな時間で高い吸着率(98.7 ± 0.5%)を示した。反応速度論的な解析を行い，擬二次反応であることを確認した。また，吸着状態を明らかにするためラマン分光による測定を行った。

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セルロース系ポリマーの劣化解析－光及び水分の影響－

（神奈川大理[1]、総理研[2]）阿久津芳顕[1]、大石不二夫[2]、西本右子[1, 2]
Degradation analysis of cellulose polymers - Effects of light and moisture
([1] *Faculty of Science, [2]Research Institute for Integrated Science, Kanagawa Univ.*)
○Yoshiaki Akutsu[1],Fujio Ohishi[2], Yuko Nishimoto[1, 2]

As basic research on the durability of celluloid, we investigated the effects of UV irradiation using FT-IR and TG/DTA, and compared the results with cellulose acetate and ethyl cellulose. A decrease in the thermal decomposition onset temperature was observed for celluloid, and an increase in the thermal decomposition onset temperature for cellulose acetate. Information regarding the deterioration of the sample surface was obtained from the thermal decomposition onset temperature of the surface and the IR spectrum, and information regarding the deterioration of the entire sample was obtained from the DTG peak temperature. We will also report on the effects of humidity.

Keywords : Degradation analysis; Celluloid; Cellulose Polymer; Thermal analysis; FT-IR

セルロイドの耐久性の基礎研究として、紫外線照射の影響を FT-IR および TG/DTA によって検討し、結果を酢酸セルロース及びエチルセルロースと比較した。熱分解開始温度及び表面の IR スペクトルから試料表面の劣化が、DTG のピーク温度から試料全体の劣化の情報が得られた。

セルロイド試料では 254 nm の照射（光源からの距離 5 cm で 1013 μW/cm^2）では、照射によって熱分解開始温度が低下するが、12 時間以上でほぼ一定となった。 365 nm の照射（光源からの距離 5 cm で 1407 μW/cm^2）では同じく照射によって低下するが、低下の程度はゆるやかで、24 時間以上でほぼ一定となった。一方酢酸セルロースでは 2 段目の熱分解開始温度が 254 nm の照射に伴って上昇したが、365 nm では 48 時間までの照射では目立った変化は見られなかった。セルロイド試料は 254nm, 365 nm 共に影響が観測されることがわかった。

劣化試料への水分の影響についても報告する。

1）大城てつや、青柳佑希、山田絵里加、大石不二夫、西本右子，分析化学,**71**, 523-527 (2022).

謝辞　本研究の一部はセルロイドハウス横濱館の研究助成によって実施した。深謝いたします

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Gel-state NMR 法を用いた架橋 poly(methyl methacrylate)の架橋構造の推定

（県立広島大学 [1]・国立研究開発法人産業技術総合研究所 [2]）○髙橋小幸 [1]・齋藤靖子 [2]・三苫好治 [1]・榊原圭太 [2]

Study of the cross-linked structure of bridged poly(methyl methacrylate) using gel-state NMR spectroscopy ([1]*Prefectural University of Hiroshima,* [2] *National Institute of Advanced Industrial Science and Technology*) Koyuki Takahashi,[1] Yasuko Saito,[2] Yoshiharu Mitoma,[1] Keita Sakakibara[2]

In recent years, the investigation for the chemical structure-function relationships has been important in the development of synthetic resins. However, the analysis of cross-linked polymers is currently limited due to their poor solubility in common solvents. In such a context, solution-state NMR is vital for precise structural analysis, but incomplete sample dissolution reduces spectrum sensitivity and resolution. On the other hand, Gel-state NMR spectroscopy achieved precise analysis of insoluble plant samples. In this study, we apply gel-state NMR spectroscopy for the first time to investigate the precise chemical structure of bridged poly(methyl methacrylate) (PMMA). We conducted emulsion polymerization using 36.00 mmol of methyl MMA and 2.02 mmol of ethylene glycol dimethacrylate (EGDM) as an initiator, and succeeded in attributing EGDM, which exists in a small proportion (Fig.1). In this poster presentation, we will report on sample preparation conditions and future efforts.
Keywords : Gel-state NMR; crosslinked polymer; Structure analysis

高機能性樹脂の開発のためには構造-機能相関の解明が重要であるが、架橋高分子は汎用溶媒に対して難溶であるために分析手法が限られている。そのようななか、Gel-state NMR 法は不溶性試料の高分解能のスペクトル取得を達成する手法として期待されている。この方法は元来、植物の細胞壁を分析する方法として提唱されたものであるが、サンプルの調製方法と測定条件を工夫することで精密構造解析を可能にした [1]。しかしながら、その活用事例はセルロース試料に限られていた。そこで本研究では、Gel-state NMR 法の合成高分子への応用を試みた。ペルオキソ二硫酸カリウムを開始剤にメタクリル酸メチル（MMA）36.00 mmol とエチレングリコールジメタクリラート（EGDM）2.02 mmol を乳化重合し、存在割合が少ない EGDM ユニットの帰属に成功した（Fig.1）。本ポスター発表では、試料の調製条件とその解析結果について報告する。

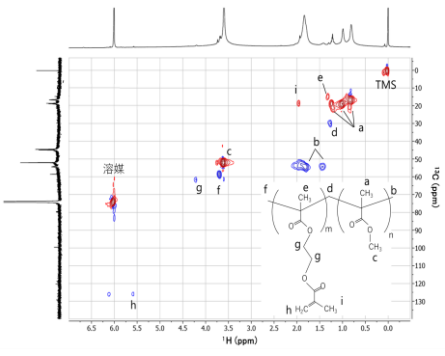

Fig.1 PMMA-EGDM (18:1) 共重合体の HSQC-NMR スペクトル
(In CD_2Cl_2, 600MHz)

1)Role of moisture in esterification of wood and stability of ulstathin lignocellulose nanofibers. S. Iwamoto, Y. Saito, Yagishita, T, Kumagai, A, T. Endo, *Cellulose*, **2019**, *26*, 4721.

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極めて多数個の単一分子に対する蛍光イメージの自動解析ツール開発

（大阪大学[1]・大阪公立大学　LAC-SYS 研究所[2]）○栢野　智[1]・伊都　将司[1,2]
Development of auto-analyzing tool for huge numbers of single-molecule fluorescence images.
([1]*Osaka University*, [2]*RILACS, Osaka Metropolitan University*) ○Satoshi Kayano,[1] Syoji Ito,[1,2]

Single molecule tracking (SMT) enables to track the lateral diffusion of molecules with a high accuracy (< 10 nm). Detailed tracking of guest molecules in host materials and successive analysis provide the information on the internal structure of the host materials and the spatial distribution of translational diffusion coefficient. In this material evaluation, the increase in the number of observed molecules leads to the improvement of the spatial accuracy of evaluation. Recently, we have developed a SMT method using fluorescence-switchable dyes and successfully observed > 10000 of single molecules for several hours[1)]. We applied this approach to a polymer alloy and, visualized the microscopic phase-separation structure and translational diffusion coefficient distributions[2)]. To advance this method as a widely applicable evaluation technique, reducing the time for data analysis is a key challenge. In this study, we addressed this challenge by developing a Python-based analysis code. This code automates the determination of molecular positions in each frame of a fluorescence movie and tracks their temporal evolutions. Our approach includes a molecule discriminant method taking into account the variations molecule by molecule in signal-to-noise ratio, size, and shape of fluorescence spot, ensuring highly accurate molecule detection. Additionally, we improved processing speed through parallelization and optimization of calls for image-processing libraries.

Keywords : single-molecule fluorescence image, auto-analysis, single-molecule tracking

単一分子追跡法は，高精度（< 10 nm）に分子追跡が可能な手法であり，材料中の蛍光分子の追跡から，材料のナノ構造や，材料中の並進拡散係数の空間分布などの情報取得が可能である。この材料評価において，観測分子数の増加は構造・物性評価の空間精度向上につながるため非常に重要である。近年我々は，蛍光スイッチング分子を用いて数千〜数万個以上の単一分子を顕微鏡視野内で数時間にわたり観察することに成功し[1)]，それを応用し高分子固体のミクロ相分離構造と相界面に特異的な並進拡散係数分布の超解像可視化に成功した[2)]。この手法を一般的な評価手法にする上で，データ解析時間の短縮が重要な課題である。そこで本研究では，蛍光動画の各フレーム中の分子位置決定とその経時変化追跡の自動化を主眼に Python を用いた解析コードを開発した。蛍光の SN 比や形状・サイズ等，分子ごとに異なる蛍光強度の空間分布を考慮した判別手法を構築し精度の高い分子検出を実現し，さらに並列化，画像処理呼出の適切化により速度向上に成功した。

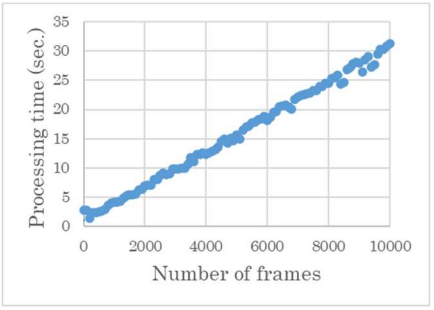

Fig. 1. Processing time as a function of the number of video frames analyzed.

1) Arai, Y. et al, Chem. Commun. 2017, 53, 4066.
2) Ito, S. et al, Polym. Chem. 2022, 13, 736.

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セシウムイオンを用いたアトムプローブの質量校正

（金工大院工[1]・金工大[2]）○吉川 兼史[1]・谷口 昌宏[2]
Utilization of cesium ion for the mass axis calibration of atom probe ([1]*Graduate School of Engineering, Kanazawa Inst Technol.*, [2]*Kanazawa Inst Technol.*) ○ Kenji Yoshikawa[1] Masahiro Taniguchi[2]

The atom probe utilizes the strong electric field around the sample tip's apex to emit the sample material's surface ion by field evaporation. There has been a problem that there are no reasonable metallic materials available as mass markers in the region of mass-to-charge ratio larger than 100 Da.[1)] This study investigated a sample preparation method for obtaining cesium ions (Cs^+) as mass markers. Three alkali metal ions were successfully obtained from the mixture of three carbonates (Cs_2CO_3, Na_2CO_3, and K_2CO_3) and polyethylene glycol 1000 (PEG) matrix together with fragment ions of PEG. The calibration was performed based on these results and is reported here.
Keywords : Atom Probe, Mass Spectrometry, Mass Calibration, Cesium

アトムプローブ（Atom Probe : AP）とは先鋭に加工した試料に電圧を印加して先端付近に強力な電界を生じさせ、電界蒸発したイオンを飛行時間法で逐一分析する装置である。AP において金属の標準試料を用いると質量価数比が 100 以上の領域のマーカーがないことが問題であった。本研究ではセシウムイオン（Cs^+）を質量マーカーとして用いるための試料作製方法を先行研究 [1)]とは異なる手法で検討した。Figure 1 に示すように、3 種類の炭酸塩（Cs_2CO_3、Na_2CO_3、K_2CO_3）とポリエチレングリコール 1000（PEG）の混合試料からセシウムを含む 3 種類の金属イオンおよび PEG のフラグメントイオンが検出することができた。この結果をもとに校正を行ったので報告する。

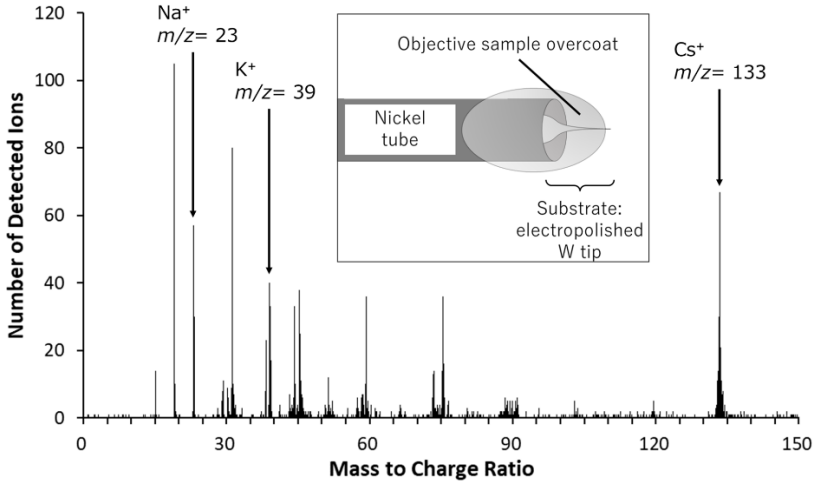

Fig.1 Mass spectrum of carbonates－PEG1000 /W and Schematic drawing of the W tip carrying the sample

1) “Mass axis calibration procedure of atom probe” M. Taniguchi, SISS-18, P-7 (2016).

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赤外光導波路を用いた溶存二酸化炭素の検出の試み

（神戸大院海事[1]・神戸大海事[2]・神戸大院国際海事セ[3]・紀本電子工業[4]）○谷嵐 正之[1]・孟 広治[1]・中野 竜平[2]・堀田 弘樹[1,2,3]・角田 欣一[3]・紀本 岳志[4]
Study on Dissolved Carbon Dioxide Detection Using Infrared Optical Waveguide ([1]Graduate School of Maritime Sciences, Kobe University, [2]Faculty of Maritime Sciences, Kobe University, [3]International Maritime Research Center, Kobe University, [4]Kimoto Electric Co., Ltd.) ○Masayuki Taniarashi[1], Guangzhi Meng[1], Ryuhei Nakano[2], Hiroki Hotta[1,2,3], Kin-ichi Tsunoda[3], Takashi Kimoto[4]

Infrared absorption measurements of aqueous solution samples are difficult due to the high absorption by water. Generally, the concentration of dissolved carbon dioxide in an aqueous solution is calculated theoretically after measuring total carbon dioxide using non-dispersive infrared spectroscopy. We have realized an infrared absorption measurement of dissolved carbon dioxide in water by a multiple total reflection method (infrared optical waveguide) using a sapphire rod in the optical path. A hydrophobic porous polymer film on the sapphire rod surface reduced the effect of background absorption by water to a negligible extent [1)]. Dissolved carbon dioxide in the sample penetrated into the hydrophobic polymer membrane and absorbed infrared light propagating through the optical path, making direct measurement of dissolved carbon dioxide possible. Furthermore, since the substance permeating into the membrane was the object of measurement, it was possible to quantify not only gas components but also organic substances such as ethanol and acetonitrile dissolved in water. The feature of this method is that it is possible to measure such aqueous samples without pretreatment.
Keyword: *Infrared Optical Waveguide*; *Dissolved Carbon Dioxide*; *Porous Polymer Membrane*; *Evanescent Wave*; *Lambert-Beer's Law*

水溶液試料の赤外吸収測定は水による吸収が大きいため困難である。一般的に、水溶液中の溶存二酸化炭素濃度は、平衡器を用いた非分散型赤外分光法により測定された全炭酸から理論計算により求められる。我々は光路にサファイアロッドを用いた多重全反射法（赤外光導波路）により、水中の溶存二酸化炭素の赤外吸収測定を実現した。サファイアロッド表面に疎水性の多孔質高分子膜を張ることで、水によるバックグラウンド吸収の影響が無視できる程度に緩和された[1)]。それにより試料中の溶存二酸化炭素が疎水性の高分子膜に浸透し、光路を伝播する赤外光を吸収するため、直接的な溶存二酸化炭素の測定が可能であった。さらに、膜内に浸透している物質が測定対象となるため、ガス成分のみならず、水中に溶解したエタノールやアセトニトリルなどの有機物質の定量も可能であった。これらの水溶液試料を前処理を行わずに測定可能であることが本法の特徴である。

1) H. Hotta, Y. Miki, Y. Kawaguchi, K. Tsunoda, A. Nakaoka, S. Ko, T. Kimoto, *Anal. Sci.*, 2017, 33, 477.

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シリコン表面ナノ溝構造における赤外吸収増強の溝幅依存性

（弘大教育）○佐藤栞・島田透

Line space dependence of infrared absorption enhancement on line and space nanostructures of silicon (*Faculty of Education*, *Hirosaki University*) ○Shiori Sato, Toru Shimada

A recent study has revealed that surface enhanced infrared absorption (SEIRA), which has been thought to occur on metal nanostructured surfaces, also occurs on non-metallic nanostructured surfaces[1]. However, the reason why surface enhanced infrared absorption occurs on non-metallic nanostructures has not been elucidated yet. The objective of this study is to clarify the relationship between the enhancement factor of the phenomenon and nonmetallic nanostructures. Infrared absorption spectroscopy was performed on line and space (L/S) structures with line spaces of 75 nm, 100 nm, 125 nm, 150 nm, 200 nm, 250 nm, and 300 nm and with a line width of 500 nm. Polyacrylic acid (PAA) thin films were fabricated on these substrates at various film thicknesses, and their spectra were measured using p-polarized multi-angle incidence resolved spectroscopy (pMAIRS). Infrared absorption was enhanced in all seven types of substrates with different line spaces of the L/S nonmetallic nano structures. Narrower line space gives larger enhancement factor.

Keywords : Surface Enhancement Infrared Absorption; Polyacrylic acid; Nanostructure

近年の研究により、金属ナノ構造表面で起こると考えられてきた表面増強赤外吸収（SEIRA）が、非金属ナノ構造表面においても起こることが明らかとなった[1]。しかし、この現象とナノ構造にどのような関係があるかはまだ解明されていない。本研究の目的は、非金属ナノ構造表面で起こる赤外吸収の増強度の溝幅による違いを明らかにすることである。シリコン基板上にさまざまな溝幅のナノ溝構造を作製し、増強度の見積もりを行った。作製したナノ構造の溝幅は 75 nm、100 nm、125 nm、150 nm、200 nm、250 nm、300 nm の 7 種類であり、溝間隔は 500 nm に固定した。これらの基板にポリアクリル酸（PAA）薄膜をさまざまな膜厚で作成し、p 偏光多角入射分解分光法（pMAIRS）によりスペクトルを測定した。解析の結果、非金属ナノ溝構造をもつ 7 種類の基板の全てで赤外吸収の増強が起き、増強度は溝幅が狭いときに大きくなることが明らかとなった。

1) What is the Key Structural Parameter for Infrared Absorption Enhancement. T. Shimada, H. Nagashima, Y. Kumagai, Y. Ishigo, M. Tsushima, A. Ikari, Y. Suzuki, *J. Phys. Chem.* **2016**, *120*, 534.

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蚕糞抽出液を利用した抗ウイルス性保湿機能をもつマスクの開発と皮膚残留性に関する研究

明星大学[1]・群馬産業技術センター繊維工業試験場[2]・株式会社アート(群馬)[3]・花小金井ひがし皮ふ科[4]・日本医科大学多摩永山病院[5] ○渡邉幸夫[1]・澤田忠信[1]・近藤康人[2]・赤井真優[1]・梶原英香[1]・伊藤久夫[3]・東 直行[4]・吉田真人[5]

Study on skin persistence of nonwoven fabric of face mask containing silkworm droppings extract(SDE) ([1]*Meisei University,* [2]*Gunma Industrial Technology Center Textile Research Institute of Gunma,* [3]*Art Co. Ltd.,* [4]*Hanakoganei Higashi Skin Clinic,* [5]*Nippon Medical School Tama Nagayama Hospital*)○Yukio Watanabe[1], Tadanobu Sawada[1], Yasuhito Kondo[2], Mayu Akai[1], Hanaka, Kajiwara[1], Hisao Ito[3], Naoyuki Higashi[4] and Masato Yoshida[5]

Keywords: Silkworm droppings extract; Faces mask(non-woven fabric);Skin Persistence; Antiviral, Antiallergic and Skin moisturizing ingredients

In a pandemic society, using face masks effectively prevents coronavirus and influenza infections caused by human droplets. However, if you use it for a long time, the temperature inside the mask will reach 28℃ and the humidity will reach over 60% due to body temperature changes by exhalation and skin blood flow, then there is concern that sweat accumulates, worsening acne, seborrheic dermatitis, etc. due to the harmful effects of sebum, and causing itching and rough skin. This scientific research focused on the application of silkworm feces extract to a new face mask, which is rich in antiviral, antiallergic, and skin moisturizing ingredients. First, 1.0 g of silkworm feces was extracted into 50 mL of water, and 10, 50, 100, 150 and 200 μL of the silkworm feces extract component solution was added to a nonwoven fabric (30 ㎜ ^{2}), and ATR measurements were performed by placing this in close contact with the upper arm. We investigated the optimal amount of silkworm feces extract component solution that would not adhere to the skin on the nonwoven fabric in the face mask. Difference spectrum analysis of ATR measurements revealed that the optimal amount of nonwoven fabric (30 ㎜ ^{2}) to add was below 10 μL.

[背景・目的] パンデミック社会の中において人の飛沫からコロナウイルス・インフルエンザ等の感染を未然に防ぐためにフェイスマスクの使用は有効であり不可欠である[1-3]。しかし長時間使用していると、呼気や皮膚血流による体温変化の影響によりフェイスマスク内の温湿度は 28℃、60%以上にも達し、口腔内の乾きがさらにウイルスの感染を増長し、皮脂の悪影響によりニキビや脂漏性皮膚炎等の悪化が認められ、肌荒れの発症が懸念される。本研究は抗ウイルス性・皮膚保湿性成分等が豊富に含まれている蚕糞の抽出成分に注目し、これをフェイスマスクの不織布に添加することにより蚕糞抽出成分液が皮膚に付着(残留)しない最適添加量について皮膚残留性試験法[4]より検証した。

[実験] 蚕糞 1.0g を水 50mL に高圧高温(120℃)下で抽出した蚕糞抽出成分液を 5, 10, 50, 100, 150, 200μL それぞれ不織布(30 ㎜×30 ㎜)シート上に添加し、これを 10 分間保持させた後、上腕部皮膚に 2 分間貼布させ、0, 5, 10, 15, 20 分毎に ATR 測定を行った。ATR 測定は Jasco(FTIR-4200)製&新潟県素材応用技術支援センターの Perkin Elmer(Spectrum Two)製測定装置をそれぞれ使用した。

[結果] ATR 測定による差スペクトル解析の結果、不織布(30 ㎜×30 ㎜)に蚕糞抽出成分液を 50,100, 150μL それぞれ添加した場合、定量バンド 1400cm^{-1} 付近の吸光度(Abs)値は直線的に上昇し、200μL では不織布から抽出液が流出し、Abs 値は減少した。次に 5～10μL の場合、抽出成分の皮膚残留性は拮抗し、抽出液の最適添加量は10μL 以下であることがわかった。また、皮膚保湿度が貼布0分後、5 分後で著しく上昇することから、蚕糞抽出液の皮膚保湿性効果は期待できると考えられる。

(1) C. Hayashi et al., *International Archives of Occupational and Environmental Health*, **2004**, 77, 73-78; Mingqian Li, et al., *Evid.-Based Complement. Alternat. Med.,* **2021**, 29:8819538. **(2)** Dae Woon Choia, et al., *Bioscience, Biotechnology Biochemistry*, **2018**, 82, 1531–1538. **(3)** Sun Young Jung, et al., *J. Sci. Food. Agric.,* **2019**, 99, 7008-7015. **(4)** Yukio Watanabe, et al., *66th J. Silk Sci. Tech. Jpn*, **2019**, O-009; *Pacifichem2021*, Poster,#3412981, #3413456, #3575291, Dec. 20, **2021**.

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ATR-赤外分光法による牛乳の経時変化の測定

(熊本高等専門学校 [1]) ○薬師 大耀 [1]・上土井 幸喜 [1]・浜辺 裕子 [1]・二見 能資 [1]

Measurement of deteriorate over time in milk using ATR - infrared spectroscopy ([1]*National Institute of Technology, Kumamoto College*) ○Taiyo Yakushi,[1] Kouki Jodoi,[1] Yuko Hamabe,[1] Yoshisuke Futami[1]

Milk has high nutritional value, so it is difficult to store it at home for a long time. Many products have a best-before date of about two weeks. Because milk is highly nutritious, it is known that bacteria can easily grow there. So-called fermentation causes changes in the constituent components. Milk stored under various temperature conditions was used to measure changes in its constituent components over time using ATR-infrared spectroscopy. Fig. 1 shows the time course of the infrared absorption spectrum of milk stored at 20 °C. Absorption attributed to fat was confirmed at approximately 1748 cm^{-1}, protein at approximately 1545 cm^{-1}, and lactose at approximately 1053 cm^{-1}.Fig. 2 shows the changes in absorbance over time. Each component tends to decrease with time. However, the decreasing trend was not uniform. It is expected that acid coagulation accompanying fermentation is the main cause of changes in milk components, however this is uncertain.

Keywords : Milk; Infrared Spectroscopy; ATR

牛乳は，栄養価が高い反面，一般家庭での長期保存が難しい食品である．多くの製品の賞味期限には, 2 週間程度が表示されている. 牛乳は, その栄養価の高さもあり, 細菌が増殖しやすいことが知られている．いわゆる，牛乳の発酵過程を含めて，保存状況によって成分に変化が生じる．本研究では，ATR-赤外分光法によって，様々な温度条件下で保存された牛乳の構成成分の経時変化を計測した．Fig.1 に，20 ℃で保存された牛乳の赤外吸収スペクトルの経時変化を示した．約 1748 cm^{-1} に脂肪、約 1545 cm^{-1} に蛋白質、約 1053 cm^{-1} には乳糖に帰属される吸収が確認された．これらの吸光度の経時変化を，Fig.2 に示した．各成分は経時変化に伴い減少傾向である．しかしながら，その減少傾向は一様ではなかった．牛乳の構成成分の変化は，発酵に伴う酸凝固が主要因であると予想されるが不確かである．他の保存条件とも比較して，食品の品質と安定性について検討中である．

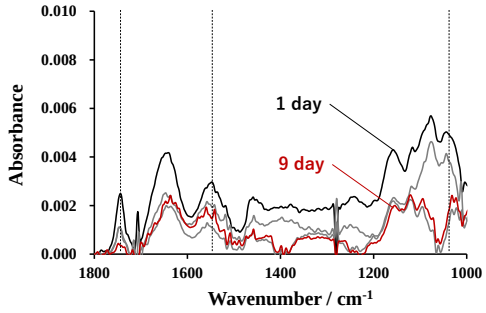

Fig.1 ATR-IR spectra of milk.

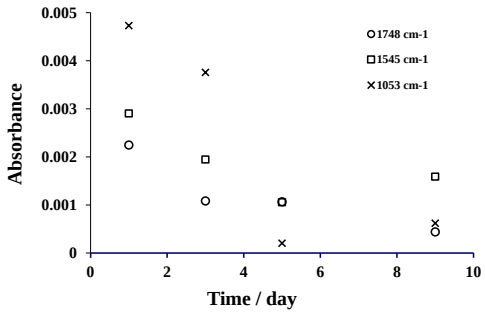

Fig.2 Time change in absorbance of milk.

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アミノアシル tRNA 合成酵素を用いる BCAA 分析における実サンプル計測評価

（広島市大院情報）○釘宮 章光・河村 星
Evaluation of real sample measurements in BCAA analysis using aminoacyl-tRNA synthetases (*Graduate School of Information Sciences, Hiroshima City University*) ○Akimitsu Kugimiya, Akari Kawamura

A novel enzymatic analysis method for each valine, leucine, and isoleucine was developed using valyl-tRNA synthetase, leucyl-tRNA synthetase, and isoleucyl-tRNA synthetase, respectively and binding abilities and specificities of each enzyme were evaluated. The analysis of each valine, leucine, and isoleucine concentration in real food sample was also examined with the aim of demonstrating the reliability of the system. The absorbances at 560 nm changes with varying initial valine, leucine, and isoleucine concentrations and the absorbance increased in proportion to the corresponding amino acid concentration, and a linear relationship was obtained from 2 to 75 μM each amino acid selectively.
Keywords : Amino acid; Aminoacyl-tRNA synthetase; BCAA; Biosensing

血液中の 20 種類のアミノ酸濃度を計測することで各種病態の診断が可能なことが知られている [1]。我々は 20 種類の各アミノ酸濃度を、アミノアシル tRNA 合成酵素(aaRS)を分子認識材料に用いて検出する方法について研究を行っている [2, 3]。本研究では分岐鎖アミノ酸のバリン、ロイシン、イソロイシンそれぞれを aaRS 酵素を用いて選択的に計測する方法について検討し、また実サンプルを用いる評価についても行った。

大腸菌由来のバリン結合性 aaRS である ValRS、0～200 μM バリン、2 mM アデノシン三リン酸、2 mM 塩化マグネシウムを 200 mM HEPES 緩衝液（pH 8.0）に溶解し、40℃で 30 分間反応させた。この反応液にトリンダー試薬を添加して呈色反応させ、マイクロプレートリーダーで 560 nm の吸光度を測定することで反応性の評価を行った。大腸菌由来のロイシン結合性 aaRS、イソロイシン結合性 aaRS についても同様に評価を行った。

その結果、2～75 μM バリン、2～50 μM ロイシン、1～150 μM イソロイシンに対してそれぞれ選択的に定量可能であることを示した。これにより、これまで酵素法では困難であった BCAA それぞれの選択的な濃度の計測が aaRS 酵素を用いることで可能であることを示した。また、実サンプルを用いる評価についても行い、夾雑物質の影響を受けることなく目的の BCAA が計測可能であることを示した。

[1] Y. Miyagi et al., *PLoS ONE*, **2011**, 6, 1.
[2] A. Kugimiya et al., *Sci. Rep*., **2022**, 12:3427.
[3] A. Kugimiya et al., *Biomed. Mater. Dev*., **2023**, 10th, Apr.

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ゲノム編集に向けたフッ化ウラシルの高精度一分子識別法の開発

（大阪教育大学附属高等学校天王寺校舎 [1], 大阪大学 [2]）○岡田あかり [1], 大城 敬人 [2]、小本 祐貴 [2]、谷口 正輝 [2]

Development of a High-Precision Single-Molecule Identification Method for Fluorouracil for Genome Editing ([1]Osaka Kyoiku University Tennoji High School, [2] Osaka University, ISIR)
○Akari, Okada[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

This study developed a new method for identifying 2'-fluorouracil (2'FU) and modified RNA molecules, potential editing sites in genome editing, at the single-molecule level. Experiments involved identifying RNA molecules containing the modified nucleotide 2'FU using a nano-gap device. The single-molecule signals obtained were analyzed using machine learning, achieving high discrimination ability with an F-measure over 0.9 between 2'FU and unmodified uracil. This advancement is expected to enhance the precision of gene therapies and reduce side effects.

Keywords : Single-Molecule Detection; Nucleotide; Epigenetic modification; Nano-device

遺伝子導入は、生物の中に新しい遺伝子を入れることで、その生物に新しい能力や特性を持たすことができる技術である。この際、遺伝子導入を正確に行い、正しく評価する手法が望まれている。本研究では、1 分子検出法によるゲノム編集の評価法を提案する。これまで、ナノギャップ電極デバイスによる高速電気計測技術を利用し、核酸塩基・アミノ酸などの生体分子の 1 分子識別に成功している [1)-4)]。一分子検出法は個別の分子を検出できるため、オフターゲット効果や予期せぬ変異を検出可能で、ゲノム編集の精度や特異性を高く評価することが可能である。また、低頻度で発生する変異や編集イベントを高い感度で検出することも可能で、従来の解析では見逃されるような希少な変異も捉えることができる。

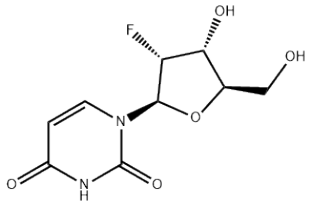

Fig.1 Structure of 2’FU

本研究では、具体的にはゲノム編集の編集点候補である 2'フッ化ウラシル（2'FU：図）に着目し、修飾 RNA の識別方法を確立することを試みた。ナノギャップ電極を用いて、2'FU と未修飾のウラシル（U）分子の高速電気計測技術を行った。実験は以下のようにして行った。まず、測定溶液として、2'FU および対照分子である U の水溶液に対して、ナノギャップ電極を用いた高速電流計測を行った。その結果、1 分子ごとの電流シグナルを得ることに成功した。これらのシグナルから特徴量を抽出し、機械学習による 1 分子の識別を試みた。2'FU と U のシグナルデータの八割をもちいて学習した分類器を、残りのデータでテストし、F1 値で評価した。その結果 精度 0.9 以上で識別することに成功した。この技術は遺伝子治療の精度向上と副作用減少に寄与する可能性がある。

引用: 1) Sci. Rep. 2021、 11, 19304, 2) Sci.Rep., 2019, 9, 3886，3）Nat. Nanotech. 2014, 9,835-840
4) J. Phys. Chem. C, 2019, 123, 15867−15873

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膵がん診断にむけたナノギャップデバイスを用いたがんマーカー分子の高速１分子検出法開発

（徳島市高[1]・阪大産研[2]・産総研[3]）○山根 由衣[1]・**大城 敬人**[2]・**小本 祐貴**[2]・**今野 雅允**[3]・**谷口 正輝**[2]

Development of a Rapid Single-Molecule Detection Method for Cancer Marker Molecules Using Nano-Gap Devices Towards Diagnosis of Pancreatic Cancer ([1]*Tokushima Municipal High School,* [2]*Osaka University, SANKEN,* [3]*National Institute of Advanced Industrial Science and Technology*) ○Yui Yamane,[1] Takahito Ohshiro,[2] Yuki Komoto,[2] Masamitsu Konno,[3] Masateru Taniguchi[2]

Pancreatic cancer is the poorest prognosis cancer, with a 5-year survival rate of about 5%. It is desirable to develop a quick, low-cost, and minimally invasive detection method for the early detection of pancreatic cancer. In this study, we aimed to develop a detection method for hydroxymethyladenosine (AOMe), a chemically modified nucleotide of adenosine (AMP), which increases with the incidence of pancreatic cancer. We focused on the Mechanically Controllable Break Junction (MCBJ) method, which measures the conductance of a single molecule using a metal nanogap electrodes. [1)]

The MCBJ measurement reveals AOMe has higher single-molecule conductance than AMP. Furthermore, we utilized machine learning to discriminate AOMe. The discrimination results are shown in Fig. 1. The discrimination accuracy was 0.70. We succeeded in detecting and identifying AOMe with MCBJ method. This study suggests the possibility of minimally invasive detection of pancreatic cancer markers in bio-samples.

Keywords : Single-Molecule Detection; Nucleotide; Epigenetic modification; Nano-device

最も予後の悪い癌が膵癌であり、5 年生存率は 5%程度である。膵癌の早期発見のための、短時間、低コスト、低侵襲性の検出手法の開発が望まれる。そこで、本研究では、膵癌の罹患に伴い増加するアデノシン（AMP）の後天的修飾分子のヒドロキシメチルアデノシン（AOMe）の検出手法の開発を目的とした。検出手法として、Mechanically Controllable Break Junction (MCBJ)法に着目した。MCBJ 法は金属ナノギャップ電極により、単一分子の伝導度を計測する手法であり、修飾塩基の検出にも適用可能である。[1)]

それぞれの核酸塩基を計測した結果、AOMe は AMP よりも電気伝導度が高いことを見出した。さらにシグナルの波形全体の特徴を学習する機械学習を活用して識別を行った。識別結果を図 1 に示す。識別精度は 0.70 であり、膵癌診断に重要な AOMe の 1 分子検出と識別に成功した。本研究はバイオ試料中の癌マーカーを低侵襲に検出できる可能性を示し、膵癌早期発見手法の開発に寄与することが期待される。

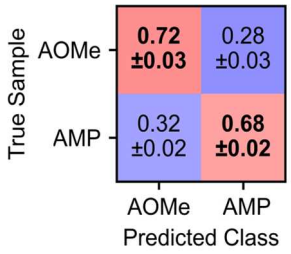

図 1　AOMe と AMP の識別結果

1)　Single-molecule RNA sequencing for simultaneous detection of m6A and 5mC. T. Ohshiro *et al.*, **2021**, *Sci. Rep.*, 11, 19304

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老化原因 8-オキソグアノシンの１分子識別法の開発

（明星高等学校 [1]，大阪大学 [2]）○國分亮 [1]，大城敬人 [2]、小本祐貴 [2]、谷口正輝 [2]
Development of a Single-Molecule Identification Method for 8-Oxoguanosine, a Marker of Aging ([1] Meisei High School, [2] Osaka University, ISIR) ○Ryo Kokubu[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

This study developed a highly sensitive and rapid detection method for 8-oxoguanosine(8-oxoG), an oxidative DNA damage marker. Produced by oxidative stress and a key factor in carcinogenesis, 8-oxoG's quantification faced sensitivity challenges. Using a nano-gap electrode device, we electrically detected 8-oxoG in DNA and distinguished it from unoxidized guanosine using machine learning, enabling significant discrimination. This technique promises efficient monitoring of 8-oxoG in pathological cells, offering potential as a biomarker for oxidative stress in cancer and aging.
Keywords：Single-Molecule Detection; Nucleotide; Epigenetic modification; Nano-device

超高齢化社会に突入した日本において，老化の影響をおさえて健康寿命を延ばすことは喫緊の課題である．そのために，分子レベルで老化を理解することは重要であり，老化の原因や指標となるマーカー分子の高感度で簡便な識別法の確立も重要である。これまで老化の原因の一つは，生体分子の酸化にあり，遺伝子の本体である DNA で最も酸化されやすいグアノシンは，8-オキソグアノシン(oxoG)となることが知られている(Fig.1).

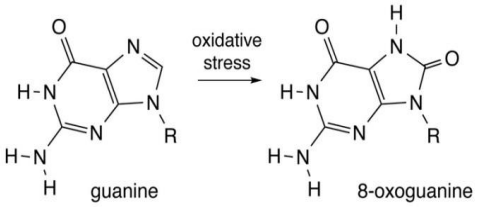

Fig.1 scheme of oxidization of guanine

本研究では DNA のグアノシンの酸化状態をモニタリングできる oxoG に注目し，この修飾分子の検出法として 1 分子検出法を用いることとした。これまで，ナノギャップ電極デバイスによる高感度・高速の電気計測技術を利用し、核酸塩基・アミノ酸などの生体分子の１分子識別に成功している [1)-4)]．測定溶液として，8-オキソグアノシン(oxoG)および対照分子であるグアニンの水溶液を濃度 1μM に調製しこれを用いた．この溶液を，ナノギャップ電極により高速電流計測を行った．その結果、１分子ごとの電流シグナルを得ることに成功した．このシグナルから特徴量を抽出し，機械学習による１分子の識別を試みた。その結果，グアニンと oxoG との識別能が F1 値としては 0.8 以上とする学習器を作成することに成功した．この技術は病態細胞内の 8-oxoG の迅速なモニタリングと癌や加齢に伴う酸化ストレス評価の新たなバイオマーカーとしての応用が期待される。

引用: 1) Sci. Rep. 2021, 11, 19304, 2) Sci.Rep., 2019, 9, 3886，3）Nat. Nanotech. 2014, 9,835-840 4) J. Phys. Chem. C, 2019, 123, 15867−15873

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紙基板分析デバイスによる唾液中マルチ成分分析

（公立大学法人山陽小野田市立山口東京理科大学）○浅野 比
Multi-component analysis in saliva using a paper-based analytical device (*Sanyo-Onoda City Univ.*)○Hitoshi Asano

Point-of-care testing (POCT) in health management is extremely important for early detection and prevention of diseases. When conducting such tests on an individual basis, it would be extremely useful if they could be carried out simply and inexpensively without the need for experts or the use of analytical equipment. Paper-based analytical devices, or PADs, are one tool that enables these objectives. In this study, we investigated the analysis of saliva components using a paper-based analysis device.
Keywords : Paper-based Analytical Device; saliva; nitrite; uric acid; pH

健康管理における臨床現場即時検査（POCT）は、病気の早期発見や病気を未然に防ぐ上で極めて重要である。このような検査を個人で行う場合、専門家を必要とせず、分析装置を使用することなく、簡便で安価に実施できれば非常に有用である。紙を基板とした分析デバイス（Paper-based Analytical Device）、すなわち PAD は、これらの目的を可能にするツールの一つである。本研究では紙基板分析デバイスによる唾液中の成分分析について検討した。

ここでは PAD を用い、発がんとの関連が指摘されている亜硝酸塩、痛風などの原因となる尿酸、基本機能をチェックする pH をターゲットとした。亜硝酸塩の定量には、スルファニルアミドと *N*-(1-ナフチル)エチレンジアミンとのジアゾカップリング反応を利用した比色法を採用した。尿酸の測定には、Cu(I)-2,2’-ビキノリン-4,4’-ジカルボン酸複合体の形成反応を用いた。pH 測定には、チモールブルー、メチルレッド、ブロモチモールブルー、フェノールフタレインの指示薬を混合したものを使用した。Fig. 1 に多成分（亜硝酸塩、尿酸、pH）分析用の PAD の一例を示す。

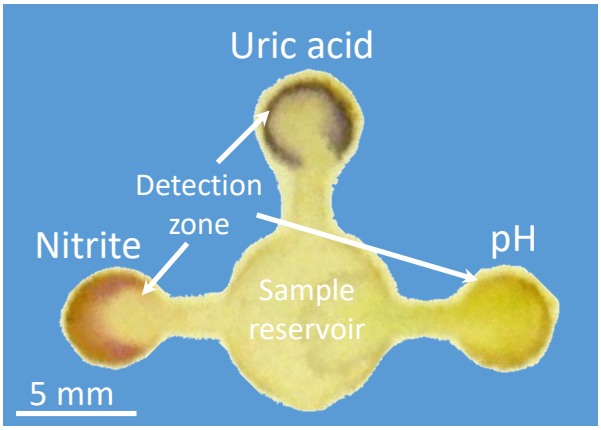

Fig. 1 PAD for analysis pf nitrite, uric acid, and pH.
1. Sample wicks into the detection zones. 2. A digital camera digitizes the results. 3. An image editing software analyzes images.

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がん化抑制にかかわる N4-アセチルシトシン(ac4C)の１分子識別法の開発

（京都府立洛北高等学校 [1]，大阪大学 [2]）○中村美咲 [1]，大城 敬人 [2]、小本 祐貴 [2]、谷口 正輝 [2]
Development of a Single-Molecule Identification Method for N4-Acetylcytosine (ac4C) in Cancer Suppression ([1] *Kyoto Prefectural Rakuhoku High School*, [2] *Osaka University*) ○ Misaki Nakamura [1] ,Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

We developed a method to identify N4-acetylcytosine (ac4C) in RNA, a modification critical for cancer suppression, at the single-molecule level. Utilizing a nano-gap device crafted through precision microfabrication, we measured the electrical conductivity changes of individual molecules. The technique revealed a high discrimination ability between ac4C and unmodified cytosine, offering insights into the epigenetic changes and potential in cancer mechanism elucidation and therapeutic development. This advancement in single-molecule detection paves the way for deeper understanding of RNA modifications and their roles in cancer biology.
Keywords : RNA; Single-Molecule Detection;Tunnel-Current; Epigentics

N4-アセチルシトシン（Fig.1）のアセチル化は、染色体を構造緩和させることで，遺伝子のオン状態の維持に関与することが知られており，遺伝子発現において重要な役割を果たしている． 本研究では N4-アセチルシトシンを検出する方法に注目した．これまでに，質量分析法、NMR、HPLC を用いてアセチル基を反応して別の塩基に変換してシーケンシングする方法があるが，この方法では酵素反応を 100%させる必要がある．

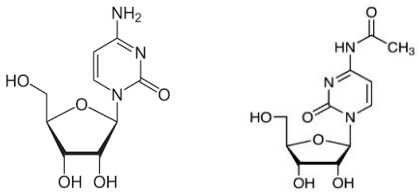

Fig.1 Molecular structures of cytidine (left) and N4 acetylcytidine (right)

本研究では，N4 アセチルシトシン(ac4C)を１分子量子計測法 [1-4] により，高感度検出を目指した．実験は以下のようにして行った．まず，測定溶液として，ac4C および対照分子である C の水溶液を濃度 1 μ M に調製した．この溶液を，ナノギャップ電極により高速電流計測を行った．その結果、ac4C と C の１分子ごとの電流シグナルを得ることに成功した．これらのシグナルを，機械学習を用いて１分子の識別を試みた。ac4C と C のシグナルデータを学習し，テストデータの識別結果を F1 値で評価した．その結果 F1 値 0.8 以上の学習器を作成することに成功した．この技術は N4-アセチルシトシンの変化を調べることで、疾患の発生や進行に関与するエピジェネティックなメカニズムを解明し、新たな治療法や予防法の開発に寄与することが期待される．

引用: 1) Sci. Rep. 2021, 11, 19304, 2) Sci.Rep., 2019, 9, 3886，3）Nat. Nanotech. 2014, 9,835-840 4) J. Phys. Chem. C, 2019, 123, 15867−15873

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双性イオン型蛍光性インジウム(Ⅲ)錯体おけるアニオン応答

(阪教大[1]・阪技術研[2]) ○久保埜 公二[1]・石原 有彩[1]・柏木 行康[2]・谷 敬太[1]・横井 邦彦[1]

Anion Response of a Fluorescent Probe Based on Zwitterionic Indium(III) Complex

([1]*Osaka Kyoiku University*, [2] *Osaka Research Institute of Industrial Science and Technology*)
○Koji Kubono[1], Arisa Ishihara[1], Yukiyasu Kashiwagi[2], Keita Tani[1], Kunihiko Yokoi[1]

A newly fluorescent probe based on zwitterionic indium(III) complex with 8-quinolinol derivative has been characterized by UV-Vis and fluorescence spectroscopy to research anion response of the complex. The probe solution of zwitterionic indium(III) complex in water/methanol displayed fluorescence. In the addition of diphosphate to the probe solution, fluorescence spectra showed selective decrease of emission intensity. The probe complex was more sensitive than other previously reported probe ones. The mechanism of the turn-off sensing in the probe complex was discussed from the changes of absorption spectra in the titration of diphosphate.

Keywords : Fluorescent Probe; Anion Response; Qinoninol Derivative; Indium Complex; Zwitterion

アニオンは環境水中や生体内に微量ながら存在しており、生命活動において重要な役割を果たしている。当研究室ではアニオン分析試薬を合成し、蛍光分析法による微量定量の開発を行っており、これまで 8-キノリノール類にジピコジルアミンを導入した配位子と亜鉛(II)やインジウム(III)との金属錯体型蛍光アニオンプローブについて検討を行ってきた。しかし、これまでのプローブ錯体は水への溶解度がそれほど高くないものや、水溶液中での蛍光強度が低いものがある。そこで、水溶性で且つ蛍光強度の高い配位子 NaHL を開発し、この配位子と塩化インジウム(III)との錯体結晶を合成・単離した。X 線構造解析の結果、この錯体結晶は HL^- と 2 つの塩化物イオンが配位し、5 分子の結晶水を含む $InCl_2(HL)\cdot 5H_2O$ であった。なお、配位子のキノリノールの OH プロトンは解離しているが、窒素原子に付加していることから、この錯体は双性イオン型であった。このプローブ錯体の水/メタノール溶液を調整して各種アニオン応答について調べたところ、二リン酸イオン (PPi) に対して高選択的な蛍光強度の減少が見られた（図 1)。PPi 添加した溶液の吸収スペクトルが配位子のみの溶液のスペクトルへと戻らないことから、水/メタノール溶液中ではこの錯体分子は少なくとも 1 つの塩化物イオンが解離し、これに PPi が配位することによって消光していると考えられる。

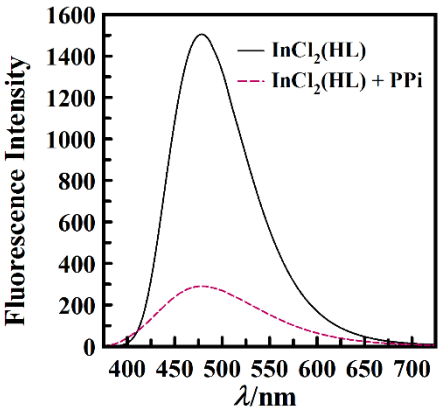

図１．蛍光スペクトル

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フローリアクター内の反応温度分布からの速度論と反応熱の同時測定と予測モデルの構築

（横河電機株式会社）○小川 潤一・眞鍋 優佳・中村 亮介・小竹 佑磨・稲村 一彦・久保 大輔
Simultaneous Characterization and Prediction Modeling of Reaction Kinetics and Enthalpy from Spatially Resolved Temperature Profiles in a Flow Reactor (*Yokogawa Electric Corporation*) ○Jun-ichi Ogawa, Yuuka Manabe, Ryosuke Nakamura, Yuma Otake, Kazuhiko Inamura, Daisuke Kubo

In process development, a quantitative understanding of reaction kinetics and reaction heat is important for optimal operation under safe conditions. Kinetics can be measured using methods based on the rate equation, and reaction heat can be measured using reaction calorimeters. However, the measurement of reaction rate constants involves laborious operations such as the preparation and the quantification of calibration curves. Therefore, we proposed a high-throughput measurement method to simultaneously determine the activation free energy ($\Delta G^{\ddagger}$) as a kinetic parameter and the reaction heat (ΔH) by using a flow reactor to measure temperature distribution in a flow channel[1)]. In this study, we utilized this simultaneous measurement method to measure $\Delta G^{\ddagger}$ with multiple substrate combinations, taking the amidation reaction in peptide synthesis, and discussed the effect of substrate on the reaction rate. We also constructed a prediction model of $\Delta G^{\ddagger}$ based on the measured data using materials informatics, and demonstrated its potential for predicting the reaction rate with unknown substrate combinations.
Keywords : Kinetics, Heat of Reaction, Flow Reactor, Materials Informatics

プロセス開発において、反応の速度論と反応熱を定量的に理解することは、安全な条件下での最適操業に有用である。速度論は速度式に基づいた手法、反応熱は反応熱量計を用いることで測定できる。しかし速度論解析としての反応速度定数の測定では、検量線の作成と定量といった煩雑な操作が伴う。そこで、フローリアクターを用いて流路内の温度分布を測定することにより、反応速度定数を決定づける活性化自由エネルギー（$\Delta G^{\ddagger}$）と反応熱（ΔH）を同時に求めるハイスループットな測定法を提案している[1)]。本研究では、この同時測定法を活用し、ペプチド合成におけるアミド化反応を例に、$\Delta G^{\ddagger}$を複数の基質の組合せで測定し、基質が反応速度に与える影響について考察した。また、測定されたデータからマテリアルズインフォマティクスを活用し、$\Delta G^{\ddagger}$の予測モデルを構築し、未知の基質の組み合わせに対する反応速度予測の可能性を示した。

1) Imamura, Y.; Ogawa, J.; Otake, Y.; Itoh, H. Simultaneous Characterization of Reaction Kinetics and Enthalpy by Calorimetry Based on Spatially Resolved Temperature Profile in Flow Reactors. *Org. Process Res. Dev.* **2023**, *27* (3), 470.
謝辞：測定データのモデル化には，MI-6 株式会社への業務委託契約による成果を含みます。ここに感謝の意を表します。

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ピレンを有した新規ジオール合成と 2-formylphenylboronic acid およびポリアミン存在下での蛍光挙動の検討

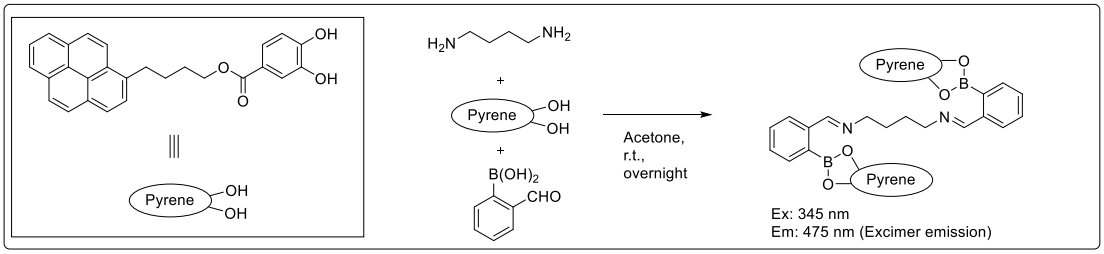
（同志社大学 [1]）○村上 綺更 [1]・濵口 尚斗 [1]・太田 哲男 [1]・大江 洋平 [1]
Synthesis of a novel diol having pyrene moiety and its fluorescence behavior in the presence of 2-formylphenylboronic acid and polyamine ([1]*Doshisha University*) ○Kisara Murakami,[1] Naoto Hamaguchi,[1] Tetsuo Ohta,[1] Yohei Oe[1]

Synthesis of a novel diol having pyrene moiety and its fluorescence behavior in the presence of 2-formylphenylboronic acid and polyamine were investigated. Thus, pyrene-tethered diol was prepared by the condensation reaction of 1-pyrenebutanol with 3,4-dihydroxybenzoic acid. 1,4-Diaminobutane was treated with the prepared diol and 2-formylphenylboronic acid in acetone to form the complex, which showed the expected excimer fluorescence at 475 nm.

Keywords : Fluorescence; Polyamine; Excimer; Pyrene

ポリアミン類の検出法として、ピレン誘導体によるエキシマー蛍光を利用した手法がある。蛍光体の一種であるピレンは、分子が互いに近接しても二量体を形成しないが、ピレン分子が光を吸収し励起状態となると、近接する他の基底状態のピレン分子と会合してエキシマーを形成する。このエキシマーからの発光現象をエキシマー蛍光と呼ぶ。このエキシマーの蛍光極大波長は 475 nm 付近であり、ピレンのモノマーが発する蛍光波長の 375 nm から大きく長波長にシフトする。本研究では、1-pyrenebutanol を基とした化合物と 2-formylphenylboronic acid、ポリアミンの三成分を用いた系において、蛍光波長が長波長シフトすることを明らかにした。

すなわち、1-pyrenebutanol と 3,4-dihydroxybenzoic acid の縮合反応にて, ピレンを有した新規ジオールを合成した。この化合物それ自体は 378 nm、398 nm の蛍光を示した。アセトン溶媒中、この化合物と 2-formylphenylboronic acid および 1,4-diaminobutane 存在下、室温で一晩攪拌した溶液は 475 nm の蛍光を示し、蛍光波長のシフトが確認された。この挙動は 1,5-diaminopentane、1,8-octanediamine、diethylenetriamine でも同様に観測された。



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アルミニウムイオンと銅イオン濃度測定のための紙製デバイスの開発

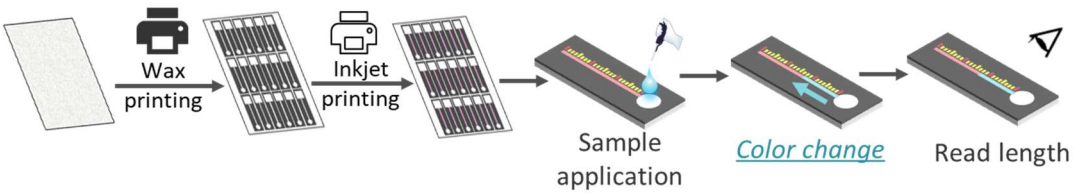
(慶応義塾大学[1]・三菱重工業株式会社[2]) ○竹内 聡子[1]、加登 絢[1]、松原 龍一[2]、澤津橋 徹哉[2]、蛭田 勇樹[1]、チッテリオ ダニエル[1]

Paper-based analytical devices for semi-quantitative analysis of copper and aluminum ions ([1]*Keio University,* [2]*Mitsubishi Heavy Industries, Ltd.*) ○Satoko Takeuchi[1], Aya Katoh[1], Ryuichi Matsubara[2], Tetsuya Sawatsubashi[2], Yuki Hiruta[1], Daniel Citterio[1]

Currently, stationary analytical instruments are used to detect heavy metal concentrations. However, this method takes several days to obtain the results, because samples must be transported from the sampling site to the laboratory. In order to achieve rapid in-situ analysis, a distance-based analytical device was developed using paper, which has the advantage of being inexpensive and easy to obtain and transport. Hydrophobic channels were formed on filter paper using a wax printer for the devices. Indicators were then placed in the flow paths using an inkjet printer to enable semiquantitative copper and aluminum ion detection. We selected Zincon for copper ion detection and a mixture of CAS and CTAB for aluminium ion detection as the indicators. The concentration response was successfully obtained by actually printing these indicators on paper, applying the sample solution and reading the color-changed length.

Keywords：Colorimetric analysis, Microfluidic paper-based analytical device , heavy metals

現在、重金属の濃度測定には定置型の大型分析機器が広く用いられている。しかし、この方法は金属イオンのサンプリング場所から分析場所にサンプルを輸送する必要があり、コストと時間を要する点が課題である。そこで、迅速なその場分析を達成するため、安価で入手が容易、かつ運搬がしやすいという利点がある紙を基板として用いた距離型の分析デバイスを開発した。本デバイスには、濾紙にワックスプリンターを用いて疎水性の流路を形成した。その後、流路上に指示薬をインクジェットプリンターで印刷し、配置した。ターゲットイオンと指示薬との反応により、色変化した距離を測定することで半定量的な銅イオン及びアルミニウムイオンの検出を可能にした。指示薬は、銅イオンの検出には、Zincon 溶液を、アルミニウムイオンの検出には CAS と CTAB の混合溶液を用いた。実際に紙上にこれらの指示薬を印刷し、ターゲットを滴下し、変色長を読み取ることで濃度応答を得ることに成功した。



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Academic Program [Poster] | 11. Organic Chemistry -Structural Organic Chemistry-：Poster

Mon. Mar 18, 2024 10:00 AM - 11:30 AM JST | Mon. Mar 18, 2024 1:00 AM - 2:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-1am] 11. Organic Chemistry -Structural Organic Chemistry-

Japanese

[P2-1am-01]

Synthesis of Macrocyclic Compounds of Anthracenes with Electron-donating Substituents and Formation of Saturn-shaped Complex with C_{60}

○Yuki Shigihara[1], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Institute of Technology)

Japanese

[P2-1am-02]

Synthesis and Properties of Dithiazolopyrrolo[3,2-*b*]pyrrole

○Akihiro Goto[1], Junichi Usuba[2], Aiko Fukazawa[2] (1. Graduate School of Engineering, Kyoto University, 2. Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University)

Japanese

[P2-1am-03]

Synthetic study of molecular valve-pillar[6]arene conjugates

○Oubu Noguchi[1], Tomoki Katayama[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho univ., 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-04]

Peripheral Protection of [7]Helicene and its effects on the Photophysical Properties

○Reo Shimura[1], Zhibo Liu[1], Takashi Hirose[1] (1. Kyoto Univ.)

Japanese

[P2-1am-05]

Synthesis and Properties of Carbazole Dimers Annulated with a Benzene in Various Manners

○Masaki Maeda[1], Yuya Domoto[1], Yosuke Nakamura[1] (1. Gunma Univ.)

Japanese

[P2-1am-06]

Synthesis and properties of novel aza[5]helicene with acridine backbone

○Moeko Chujo[1], Satoru Hiroto[1] (1. Kyoto Univ.)

English

[P2-1am-07]

Synthesis of large macrocylces based on the functionalization of azabora[6]helicene

○Yuchuan Jiang[1], soji shimizu[1] (1. Kyushu University)

Japanese

[P2-1am-08]

Structural property of aromatic squaramides with chiral side chains

○Kazusa Kuyama[1], Kosuke Katagiri[2], Masatoshi Kawahata[3], Hiroyuki Kagechika[4], Aya Tanatani[1] (1. Ochanomizu Univ., 2. Konan Univ., 3. Showa Pharmaceutical Univ., 4. Tokyo Medical and Dental Univ.)

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Japanese

[P2-1am-09]

Development of efficient synthesis method of Pentapyrrins

○Yuki Nishimura[1], Takuya Kurahashi[1] (1. Grad. Sch. of Sci. and Tech., Kwansei Gakuin Univ.)

Japanese

[P2-1am-10]

Temperature-tunable inversion of chirality in *m*-quarterphenyl derivatives

○Yoshino Kaneko[1], Yuka Takeuchi, Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ., 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-11]

Single-molecule electron transfer properties of fluorinated cubanes

○Keima Higashio[1], Midori Akiyama[1], Ryo Yamada[2], Tatsuhiko Ohto[3], Hirokazu Tada[2], Hiroshi Imahori[1] (1. Kyoto Univ., 2. Osaka Univ., 3. Nagoya Univ.)

Japanese

[P2-1am-12]

Studies on the selectivity in glycosylation reaction using azobiphenyl-thioglycoside conjugates

○hidenori wakui[1], mari ikeda[2], yuta shinozuka[1], kaname sasaki[1], yoichi habata[1], syunsuke kuwahara[1] (1. toho-udai, 2. tibakoudai)

Japanese

[P2-1am-13]

Oxindole-type chiral derivatizing reagents for stereochemical assignments of primary amines

○Ryosuke Kimura[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ., 2. Chiba Institute of Technology)

Japanese

[P2-1am-14]

Coupling reaction between bromopropynylbenzene derivatives and tertiary alcohols

○Masaaki Matsumoto[1], Mari Ikeda[2], Yoichi Habata[1], Syunsuke kuwahara[1] (1. Toho University, 2. Chiba Institute of Technology)

Japanese

[P2-1am-15]

6-(Diethylboryl)-1-(4-pyridyl)azulene: Flow Synthesis and Reaction with DMAP

○Shigeharu Wakabayashi[1], Tatsuya Higaki[2], Masayuki Wakioka[3], Masahiro Takumi[4], Hikari Nakanishi[1], Yasuhiro Ohki[2], Aiichiro Nagaki[5] (1. Faculty of Health Science, Suzuka Univ. of Medical Science, 2. Institute for Chemical Research, Kyoto Univ., 3. Sagami Chemical Research Institute, 4. Graduate School of Engineering, Kyoto Univ., 5. Graduate School of Science, Hokkaido Univ.)

Japanese

[P2-1am-16]

Self-organization and aggregation properties of ion-responsive unilamellar large vesicles derived from squalene

○Linh Ngoc Tran[1], Kenichi Tominaga[1,2], Hiroko Isoda[2], Sosaku Ichikawa[2], Takashi Arimura[1,2] (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba)

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English

[P2-1am-17]

Synthesis and Properties of Tripodal Molecules Integrating Carbazoles Substituted with Ethynyl-Pyridine Groups

○Masamune Fujikawa[1], Yuya Domoto[1], Yosuke Nakamura[1] (1. Gunma University)

Japanese

[P2-1am-18]

Influence of Varying Oxyethylene Chain Length on the Allosteric Properties of Cylindrical Cryptand/Silver Complexes

○Haruki Kumagai[1], Yutaro Nihei[1], Shinji Kamo[1], Akihiro Otsuka[1], Masaki Fujisawa[1], Mari Ikeda[2], Shunsuke Kuwahara[1], Yoichi Habata[1] (1. Toho University, 2. Chiba Institute of Technology)

Japanese

[P2-1am-19]

Cross-Coupling of Fluorenones for Metal-Free Polyarene Synthesis

○Rion Noda[1], Tetsuo Iwasawa[1] (1. Graduate School of Ryukoku University)

Japanese

[P2-1am-20]

A New Synthetic Route to Tetrabenzo[*b*,*g*,*k*,*p*]chrysene

○Takumi Ikenaga[1], Tetsuo Iwasawa[1] (1. Ryukoku university)

Japanese

[P2-1am-21]

Synthesis and properties of 9-azadibenzo[a.f]pentalenyl cations exhibiting asymmetric ring current effect due to mesoionic TMM substructure

○Koki Yamamoto[1], Daiki Shimizu[1], Kenji Matsuda[1,2] (1. Kyoto University, 2. Fukui Institute for Fundamental Chemistry, Kyoto University,)

Japanese

[P2-1am-22]

Scholl reaction of V-shaped aromatic compounds with fused anthracene: structure and properties of intramolecular cyclization products

○Moe Kobayashi[2], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Tech, 2. Kitasato)

Japanese

[P2-1am-23]

Synthetic study of a *meta*-phenylene-bridged trimer of tetraphenylhexaazaanthracene (TPHA)

○Sokan Shiomi[1], Daiki Shimizu[1], Kenji Matsuda[1,2] (1. Graduate School of Engineering Kyoto University, 2. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese

[P2-1am-24]

Synthesis of novel hetero [8]circulenes and hetero[10]circulenes

○Aoi Nakagawa[1], Yusuke Matsuo[1], Shu Seki[1], Takayuki Tanaka[1] (1. Graduate School of Engineering, Kyoto University)

Japanese

[P2-1am-25]

Synthesis of Azuleno[1,2-*c*]pyran-1-ones

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○Taku Shoji[1], Nichika Sasahara[2], Ryuta Sekiguchi[3], Shunji Ito[3] (1. Nihon University, 2. Shinshu University, 3. Hirosaki University)

Japanese

[P2-1am-26]

Synthesis of molecular tweezers bridged with diethanotetracene moiety

○Aoki Moe[1], Mori Shigeki[2], Takehana Ryosuke, Takase Masayoshi[3], Okujima Tetsuo[3], Uno Hidemitsu[3] (1. Faculty of Science,Ehime University, 2. Advanced Research Support Center(ADRES),Ehime University, 3. Graduate School of Science and Engineering,Ehime University)

Japanese

[P2-1am-27]

Synthesis and optical properties of π-electron systems with propeller chirality

○Yumi Sugano[1], Shigeki Mori[3], Tetsuo Okujima[2], Hidemitsu Uno[2], Masayoshi Takase[2] (1. Faculty of Science of Ehime University, 2. Graduate school of Science and Engeneering, Ehime University, 3. Advanced Reserch Center (ADRES), Ehime University)

Japanese

[P2-1am-28]

Synthesis and Reaction of Thiophene-fused Tetracene

○Yoshiki Dodo[1], Yui Tsuboi[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese

[P2-1am-29]

Synthesis and reactivity of indeno[2,1-a]azulenes

○Masayuki Iwabuchi[1], Taku Shoji[1] (1. Nihon University)

Japanese

[P2-1am-30]

Synthetic study of azulene -fused phenalenons bearing the arly substituent.

○Ryunosuke Ishikawa[1], taku shoji[1] (1. Nihon University)

Japanese

[P2-1am-31]

Synthesis and photo-functional properties of tetraarylphenanthrene derivatives having aryl groups at 9,10-positions

○Takuro Wataru[1], Takeshi Kawase[1], Jun-ichi Nishida[1] (1. Graduate School of Engineering, University of Hyogo, Department of Applied Chemistry)

English

[P2-1am-32]

Intramolecular Bi/Sb/As-O Noncovalent Interaction for Enhanced Planarity of Bibenzofurans

○Conghuan Wang[1], Yohei Adachi[1], Joji Ohshita[1], Akifumi Sumida[2], Hiroaki Imoto[2], Kensuke Naka[2] (1. Hiroshima University, 2. Kyoto Institute of Technology)

Japanese

[P2-1am-33]

Expansion of a σ-Delocalized Systems Using a Diselenide Bond

○Konishi Kyosuke[1], Furukawa Syunsuke[1], Saito Masaichi[1] (1. Graduate School of Science and Engineering, Saitama University)

Japanese

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[P2-1am-34]

Single-Molecule Conductances of Compounds Bearing σ-Delocalized Systems

○Saya Seko[1], Shintaro Fujii[2], Masaichi Saito[1] (1. Graduate School of Science and Engineering, Saitama University, 2. Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology University)

Japanese

[P2-1am-35]

A triplet/singlet ground-state switch due to pai-conjugation prohibition triggered by hydrogen bonding

○Takayuki Ishida[1], Nagito Haga[1] (1. The University of Electro-Communications)

Japanese

[P2-1am-36]

Synthesis and Properties of 2, 5, 8-Tribromophenalenyl Radical

○Masaya Kishimoto[1], Kei Sugita, Tomohiko Nishiuchi[1], Takashi Kubo[1] (1. Osaka University)

Japanese

[P2-1am-37]

Solubilization of Trioxotriangulene Macrocyclic Oligomer by Dialkylamido Groups

○Shinji Hayasaki[1], Tsuyoshi Murata[1], Yasushi Morita[1] (1. Aichi Institute of Technology)

Japanese

[P2-1am-38]

Synthesis, Structure and Halochromism of Galvinol-Substituted Thiophene Compounds

○Yuki Wakabayashi[1], Motoko Akita[1] (1. Josai University)

Japanese

[P2-1am-39]

Studies on the Reaction between Tetracene Imide with Lawesson's Reagent

○Shingo Hirai[1], Takumu Ito[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese

[P2-1am-40]

Development of Non-Fullerene Acceptors Containing Dithienothiaborin

○Makoto Kimura[1], Wataru Suzuki[1], Tomohiro Agou[1], Tomokazu Umeyama[1] (1. University of Hyogo)

English

[P2-1am-41]

Synthesis of Three-Dimensional Organic Boron Compounds with Unique Structure

○Kenshin Nakano[1], Katsuhiko Ono[1] (1. Nagoya Institute of Technology)

Japanese

[P2-1am-42]

Productive Synthesis of a C_{60} fragmentary octacycle, Metelykene

○Yuki Ueda[1], Tetsuo Iwasawa[1] (1. Ryukoku University)

Japanese

[P2-1am-43]

Synthetic investigation of mechanopolymers using π-cluster as a mechanophore

○Shoichi Hasegawa[1], Tomohiko Nishiuchi[1], Takashi Kubo[1] (1. Osaka Univ.)

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Japanese

[P2-1am-44]

Different emission colors of optical active and racemic pyridinium salt-linked phenanthroimidazoles

○NGUYEN QUANG DUY[1] (1. Osaka Kyoiku Univ.)

Japanese

[P2-1am-45]

Synthesis and Photophysical Properties of Carbazolophane Derivatives by Sonogashira Cross Coupling Reaction

○Hiroaki Chihara[1], Miyuki Masaki[1], Kazushige Hori[1], Koji Kubono[1], Masatsugu Taneda[1], Masayoshi Bando[2], Tamaki Nakano[2], Takunori Harada[3], Yuji Kinose[4], Yoshinobu Tsujii[4], Keita Tani[1] (1. Osaka Kyoiku Univ., 2. ICAT, Hokkaido Univ., 3. Faculty of Science and Engineering, Oita Univ., 4. ICR, Kyoto Univ.)

Japanese

[P2-1am-46]

Solid State Molecular Arrangements and Optical Properties of 2,5-Di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione Derivatives

○Kazumasa Ueda[1], Ryoya Hayashi[1], Misaki Kinoshita[1], Tsunayoshi Takehara[2], Takeyuki Suzuki[2] (1. Shizuoka Univ., 2. Osaka Univ.)

Japanese

[P2-1am-47]

[Withdraw] Synthesis of Adamantane Derivatives with Plasticity

○Moe Kusumoto[1] (1. Kwansei Gakuin University)

English

[P2-1am-48]

Solar-driven steam generation properties of donor-acceptor molecules functionalized by [2+2] cycloaddition- retroelectrocyclization reactions

○CHIA-YANG LIN[1], Tsuyoshi Michinobu[1] (1. Tokyo Institute of Technology)

Japanese

[P2-1am-49]

Syntheses and Fluorescence Properties of Imidazodiazaborole Derivatives with D-π-A Structure

Youhei Miura[1], ○Ryoka Tsukimoto[1], Kosuke Mohri[1], Naoki Yosioka[1] (1. Keio University)

Japanese

[P2-1am-50]

Development of Non-Fused Non-Fullerene Acceptors with 1,4-Naphthoquinone Units as Terminal Groups

○Kae Oshitani[1], Wataru Suzuki[1], Jun-ichi Nisida[1], Takeshi Kawase[1], Tomokazu Umeyama[1] (1. University of Hyogo)

Japanese

[P2-1am-51]

Emission Enhancement of Near-infrared Phosphorescence Found in Structurally Similar Host-Guest System

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○Misuzu Nakaya[1], Taisuke Matsumoto[2], Tsutomu Ishi-i[1] (1. National Institute of Technology, Kurume College, 2. IMCE, Kyushu Univ.)

Japanese

[P2-1am-52]

Regulation of Fluorescence and Phosphorescence Emission in Benzothiadiazole-based Dyes

○Eri Hirata[1], Tsutomu Ishi-i[1] (1. National Institute of Technology, Kurume College)

Japanese

[P2-1am-53]

Synthesis of new coumarin probes for determination of the absolute configuration of chiral amines

○Yuuka Gotoh[1], Ryoto Araki[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ. , 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-54]

Synthesis and photoisomerization of new molecular switches with spiro skeleton

○Moeka Notake[1], Karina Nakanishi[1], Mari Ikeda[2], Yoichi Habata[1], Shunsuke Kuwahara[1] (1. Toho Univ., 2. Chiba Inst. of Tech.)

Japanese

[P2-1am-55]

Development of Fluorescent Agent Inhibiting Lateral Root Growth in *Arabidopsis*

○Koyo shibasaki[1], Takeshi Yamada, Kazuki Arai, Kazuki Arai, Sentaro Okamoto[1] (1. Kanagawa University)

Japanese

[P2-1am-56]

A Water-Soluble Helicene: Hydrostatic Pressure Effects and Cellular Uptake

○Iori Okamura[1], Keiichi Nakagawa[2], Shinji Toyota[1], Gaku Fukuhara[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Bioengineering, The University of Tokyo)

Japanese

[P2-1am-57]

Singlet Fission in Pentacene Dimers Controlled by Addition of Alkali Metal Ions

○Tomoya Kuwabara[1], Gaku Fukuhara[1] (1. Tokyo Institute of Technology)

Japanese

[P2-1am-58]

Chemical Modification Using Coupling Reaction of 2-Benzoylimidazole Based Organoboron Complexes and Emission Property

Youhei Miura[1], ○Kanta Kato[1], Naoyuki Ando[1], Kohsuke Mohri[1], Naoki Yoshioka[1] (1. Keio University)

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電子供与基をもつアントラセン大環状化合物の合成とフラーレン C_{60} との土星形錯体の形成

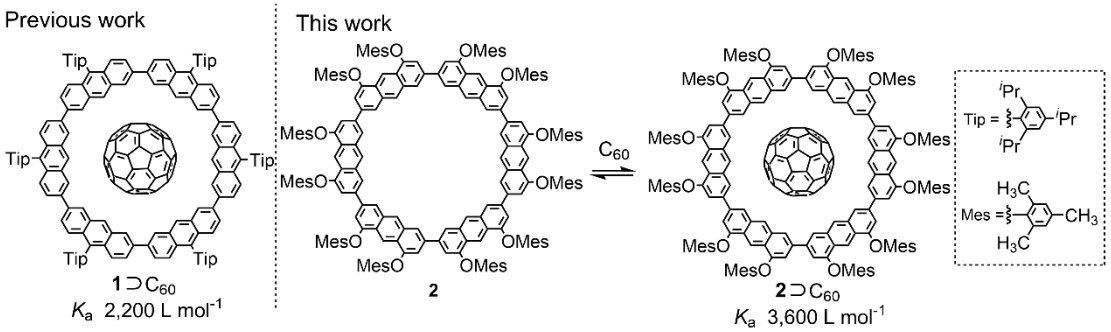
（東工大理）○鴫原 勇希・鶴巻 英治・豊田 真司

Synthesis of Macrocyclic Compounds of Anthracenes with Electron-donating Substituents and Formation of Saturn-shaped Complex with C_{60} (*School of Science, Tokyo Institute of Technology*) ○Yuki Shigihara, Eiji Tsurumaki, Shinji Toyota

We reported the synthesis of 2,7-anthrylene cyclic hexamer **1** and its formation of Saturn-shaped complex with fullerene C_{60} stabilized by multipoint C–H•••π interactions[1]. We here synthesized cyclic hexamer **2** with two electron-donating mesityloxy groups in each anthracene unit to investigate the substituent effect. Cyclic hexamer **2** was synthesized by Yamamoto coupling of the corresponding 2,7-dibromoanthracene in 16% yield. Formation of a Saturn-shaped complex with C_{60} was confirmed by ^{1}H NMR and fluorescence quenching titration experiments. The association constant K_a was determined to be 3,600 L mol^{-1} in toluene at 296 K, which was larger than that of **1**. This result suggests that the electron-donating substituents enhance the association with the guest molecules. The association constants were also determined for C_{70} and other guests.

Keywords: Macrocyclic compounds; Yamamoto coupling; Saturn-shaped complex; Anthracenes; Fullerene

我々は，10 位に 2,4,6-トリイソプロピルフェニル基（Tip 基）を持つアントラセンユニットを 2,7 位で直接連結した大環状六量体 **1** が，多点 C–H••• π 相互作用によりフラーレン C_{60} を包接した土星形錯体を形成することを報告した[1]。本研究では、ホスト分子の電子状態が錯形成に及ぼす影響を調べる目的で、電子供与性のメシチルオキシ基 (OMes 基) を 4,5 位に導入したアントラセンユニットを用いて大環状化合物を合成し，C_{60} 錯体の形成を調べた。目的の環状六量体 **2** は、対応する 2,7-ジブロモアントラセン誘導体の Yamamoto カップリングにより、収率 16%で合成した。^{1}H NMR および蛍光消光滴定により、**2** と C_{60} の錯体形成を確認し、トルエン中 296 K での会合定数を K_a 3,600 L mol^{-1} と決定した。この値は、**1** の場合比べて大きく、電子供与性の置換基が錯形成を促進することが示唆された。また、C_{70} など他のゲストとの錯体についても会合定数を決定し、結果を比較した。



[1] Y. Yamamoto, E. Tsurumaki, K. Wakamatsu, S. Toyota, *Angew. Chem., Int. Ed.* **2020**, *57*, 8199.

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ジチアゾロピロロ[3,2-*b*]ピロールの合成と物性

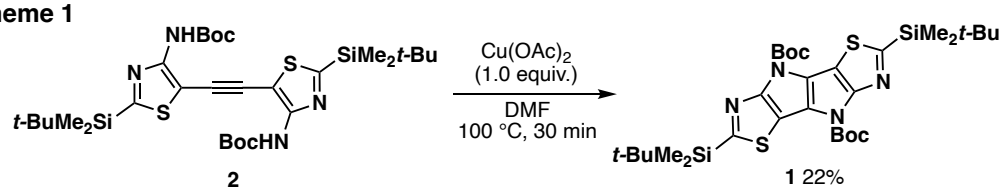
（京大院工[1]・京大 WPI-iCeMS[2]）○後藤 章浩[1]，薄葉 純一[2]，深澤 愛子[2]
Synthesis and Properties of Dithiazolopyrrolo[3,2-*b*]pyrrole ([1]*Graduate School of Engineering, Kyoto University*, [2]*Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University*) ○Akihiro Goto,[1] Junichi Usuba,[2] Aiko Fukazawa[2]

In this study, we successfully synthesized dithiazolopyrrolo[3,2-*b*]pyrrole **1**, an A–D–A type π-conjugated system with a fully fused structure, during our studies on the synthesis of novel nitrogen-containing antiaromatic π-conjugated systems. Quadrupolar-type π-conjugated systems in which electron donors (D) and acceptors (A) are linked in an A–D–A fashion are valuable as fundamental structures for various types of applications such as highly luminescent dyes, narrow-bandgap polymers, and non-fullerene acceptors, with various basic frameworks being investigated. However, it remains challenging to incorporate an A–D–A structure into a fully fused system. Based on the previously reported synthesis of indoloindole,[1] we thoroughly investigated the conditions for the intramolecular oxidative cyclization of di(4-amino-5-thiazolyl)acetylene **2** as a substrate leading to the successful synthesis of **1** in a moderate yield. The synthesis and properties of dithiazolopyrrolo[3,2-*b*]pyrrole derivatives with various substituents at both ends will also be reported.
Keywords： double cyclization, thiazole, pyrrole, polycyclic π-conjugated skeleton

電子供与体 (D) と電子受容体 (A) が A–D–A 型に連結した四重極子型の拡張 π 共役系は，高発光性色素や狭バンドギャップ半導体ポリマー，非フラーレンアクセプター材料の基本構造として有用であり，多様な基本骨格の組み合わせが研究されている．しかしながら，A–D–A 型構造を完全に縮環した構造の中に組み込むことは依然として容易ではない．このような背景のもと本研究では，新奇な含窒素反芳香族 π 共役系の合成研究の過程で，完全縮環構造をもつ A–D–A 型 π 共役系であるジチアゾロピロロ[3,2-*b*]ピロール **1** の合成に成功した．

既報のインドロインドールの合成反応[1] を参考に，ジ(4-アミノ-5-チアゾリル)アセチレン **2** を基質とする分子内酸化的環化反応の条件を徹底的に検討した結果，ジチアゾロピロロ[3,2-*b*]ピロール **1** を中程度の収率で得ることに成功し (Scheme 1)，**1** が青色の蛍光発光を示すことを明らかにした (λ_{em} = 403 nm, Φ_F = 0.20 in CH_2Cl_2)．本発表では，両端に種々の置換基をもつ誘導体の合成および物性についても報告する．

Scheme 1



2 **1** 22%

1) J. Yu, Du. Zhang-Negrerie, Y. Du, *Org. Lett*. **2016**, *18*, 3322.

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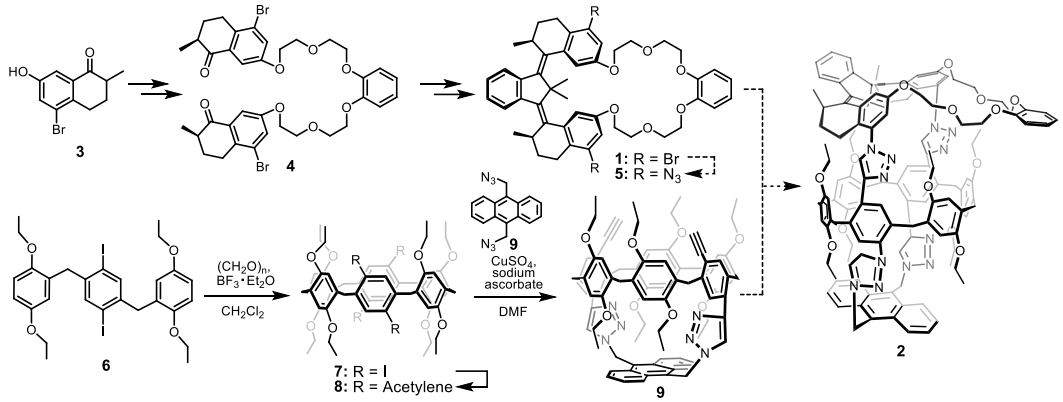
新規分子バルブとピラー[6]アレーン連結体の合成研究

（東邦大理[1]・東邦大複合物性研究セ[2]・千葉工大工[3]）○野口 桜生[1]・片山 知季[1]・池田 茉莉[3]・幅田 揚一[1,2]・桑原 俊介[1,2]
Synthetic study of molecular valve-pillar[6]arene conjugates (*[1]Department of Chemistry and [2]Research Center for Materials with Integrated Properties, Toho University, [3]Department of Chemistry, Education Center, Chiba Institute of Technology*)○Oubu Noguchi,[1] Tomoki Katayama,[1] Mari Ikeda,[3] Shunsuke Kuwahara,[1,2] Yoichi Habata[1,2]

Recently several groups have demonstrated artificial molecular machines, showing switches, gears, brakes, shuttles, and motors. We have reported a new molecular valve (**1**), which are expected to work as the one-directional molecular transport system by photo-irradiation. In this study, we designed a new molecular valve (**2**) in which the pillar[6]arene derivative is linked as a pocket. Since **2** can rotate the valve part in one direction by light, it is expected to transport the cationic molecule at the crown ether site to pillar[6]arene site by photo-irradiation. Here we will report the synthesis of pillar[6]arene derivative (**9**). Pillar[6]arene derivative (**7**) was synthesized from iodobenzene (**6**) with paraformaldehyde and BF_3. After introducing acetylenes into **7**, **9** was obtained by Huisgen cyclization using one equivalent of diazide **9**.
Keywords: Molecular machine; Pillar[6]arene; Molecular valve; Huisgen cycloaddition

近年，熱や光などの外部刺激に応答して機械的な動作を行う分子マシンの開発が行われている．われわれはこれまでに光照射によって中心のインダン部位が一方向に回転する分子バルブ **1** を報告した．本研究では，**1** とピラーアレーン誘導体との連結体 **2** を設計した．クラウンエーテル部位にカチオン分子を配位させた後，光照射によってインダン部位を回転させ，カチオン分子をピラーアレーン部位へ移動させることができるのではないかと考えた．

ヨードベンゼン誘導体(**6**)にパラホルムアルデヒドと BF_3 を作用させ，ピラー[6]アレーン誘導体(**7**)を得た．**7** に 4 つのアセチレンを導入した後，1 等量のジアジド **9** を用いた Huisgen 環化によりピラー[6]アレーン-アントラセン連結体(**9**)を得た．現在，**1** をアジド化した **5** と **9** の連結反応を検討中である．



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外周部位を環状アルキル骨格で保護したヘリセン誘導体の合成と光物性

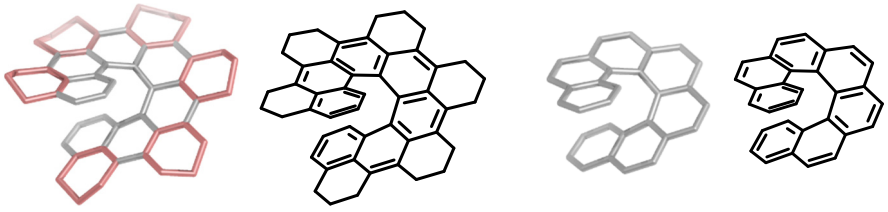
（京大化研[1]・JST さきがけ[2]）○志村 怜雄[1]・劉 之博[1]・廣瀬 崇至[1,2]

Peripheral Protection of [7]Helicene and its effects on the Photophysical Properties ([1]*Institute for Chemical Research, Kyoto University,* [2]*PRESTO, Japan Science and Technology Agency*)
○Reo Shimura,[1] Zhibo Liu,[1] Takashi Hirose[1,2]

Helical polycyclic aromatic hydrocarbons (HPAHs) are expected to exhibit strong circular dichroism (CD) and circularly polarized luminescence (CPL) because of their helically-twisted electronic structures.[1] In terms of the application of chiral emitters, chemically stable chiral luminophores are required to create circularly-polarized organic light-emitting devices (CP-OLEDs).[2] In order to develop the molecular structure of chiral emitters that exhibit good luminescence properties in the solid state, it is necessary to elucidate the excited state dynamics in the solid state and their electronic interactions between the chiral emitter and the solid matrix. In this work, we focused on a [7]helicene derivative with partially saturated six-membered rings consisting of propylene group fused to the outer moiety of the helically twisted π-conjugated core, which was prepared according to the previously reported synthetic method.[3] In this presentation, the effect of protecting the helical π-conjugated core with a cyclic alkyl skeleton on the luminescence properties will be discussed in detail.

Keywords : Emission Properties; Chirality; Cyclic Alkyl Flamework; Helicenes

らせん状の歪みを持つ多環芳香族炭化水素 (HPAHs) は、らせん状に捻じれた分子軌道に由来して、良好な円二色性 (CD) および円偏光発光 (CPL) 特性を示すことが期待される [1,2]。固体状態で良好な発光特性を示すキラル発光体の分子構造を開拓するためには、固体状態におけるキラル発光色素の電子状態と励起状態ダイナミクスを解明する必要がある。本研究では、外周部位に部分的に飽和した六員環を縮環した[7]ヘリセン誘導体 (**1**) のユニークな分子構造に着目し [3]、その光物性を調査することを目的とした。本発表では、らせん状の π 共役コアを環状アルキル骨格で保護した場合の発光特性への影響について量子化学計算の結果を踏まえて詳細に議論する。



1) Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, *112*, 1463. 2) D.-W. Zhang, M. Li, C.-F. Chen, *Chem. Soc. Rev.* **2020**, *49*, 1331. 3) Y. Nakakuki, T. Hirose, H. Sotome, H. Miyasaka, K. Matsuda, *J. Am. Chem. Soc.* **2018**, *140*, 4317.

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ベンゼンに種々の様式で縮環したカルバゾール二量体の合成と物性

（群馬大院理工）○前田 真輝・堂本 悠也・中村 洋介

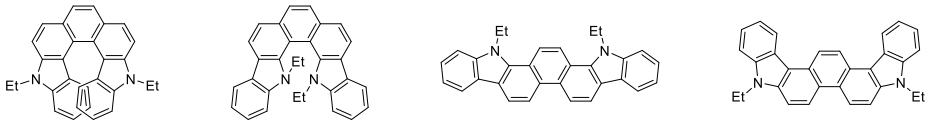
Synthesis and Properties of Carbazole Dimers Annulated with a Benzene in Various Manners

(*Graduate School of Science and Engineering, Gunma University*) ○Masaki Maeda, Yuya Domoto, Yosuke Nakamura

Carbazole dimer **2** with helical structure in which two carbazole moieties are annulated with a benzene was synthesized by Migita–Kosugi–Stille coupling using dibromide **8** and bis(trimethyltin), in order to compare its photophysical and electrochemical properties with those of **1** and clarify the effects of difference in the annulation manners on their properties.

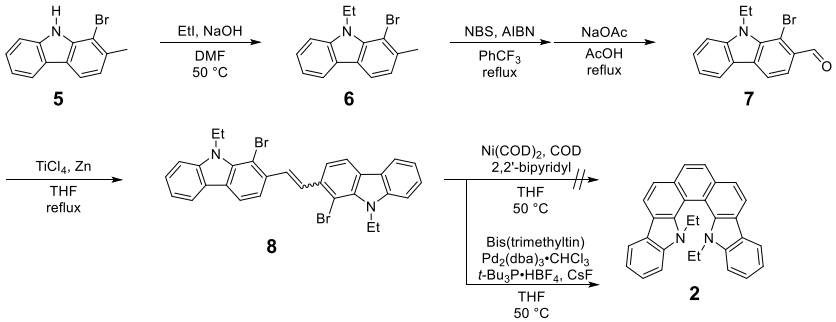
Keywords : Carbazole, Fused Polycyclic Aromatic Compound, Photophysical Properties, Electrochemical Properties, Chiroptical properties

最近、当研究室ではベンゼン環に 2 つのカルバゾールが縮環し、らせん構造を有する **1** を合成し、光物理的特性、キロプティカル特性や電気化学的特性を明らかにした。本研究では、**1** と同様にらせん構造を有し、カルバゾールとベンゼン環の縮環様式が異なる化合物 **2** を合成し、縮環様式の違いが諸物性に及ぼす効果を明らかにすることとした。さらに、縮環様式の異なる **3**, **4** についても合成することとした。



1 **2** **3** **4**

まず、**2** の合成に着手した（Scheme 1）。文献に従って合成した **5** のエチル化により **6** とした後、種々の酸化剤を用いてホルミル体 **7** の合成を試みたが、**7** は得られなかった。そこで NBS と AIBN を用いて **6** のメチル基をジブロモメチル基に変換した後、加水分解を行ったところ、**7** を得ることに成功した。**7** の McMurry 反応により **8** を得た後、**8** の $Ni(COD)_2$ を用いた Ullmann 反応によって **2** の合成を検討したが、**2** は得られなかった。次に **8** とビス（トリメチルスズ）との Migita–Kosugi–Stille 反応を検討したところ、^{1}H NMR と GC-MS により **2** の生成が示唆された。現在 **2** の単離を検討している。



Scheme 1

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アクリジン骨格を持つ新規アザヘリセンの合成とその物性解析

（京大院人環 [1]）○中條 萌絵子 [1]・廣戸 聡 [1]

Synthesis and properties of novel aza[5]helicene with acridine backbone ([1]*Graduate School of Human and Environmental Studies, Kyoto University*) ○Moeko Chujo,[1] Satoru Hiroto[1]

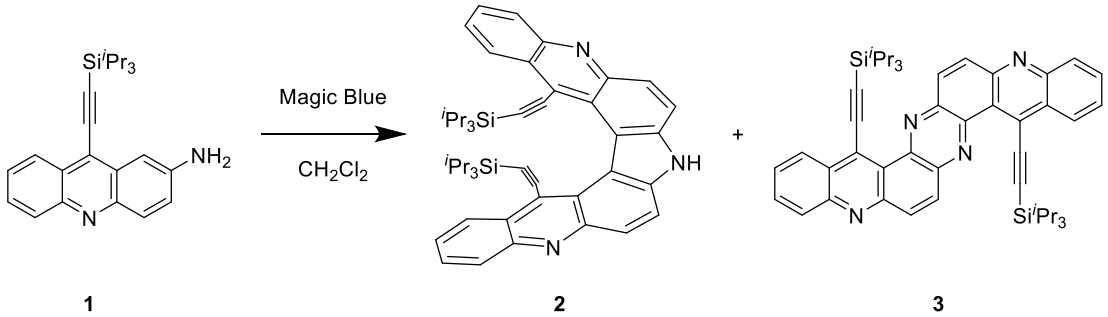
Helicenes are widely investigated π-conjugated molecules that have helical structures and excellent optical properties. Previously, we found a simple method for synthesizing π-extended azahelicenes with oligoacene backbone that exhibit excellent luminescence and chiral luminescence properties. Dye emitting and absorbing in the near-infrared region has been actively studied as a bioprobe, but there are few reports on helicene-based near-infrared dyes.

In this study, we synthesized novel helicene **2** with pyridine-type nitrogen for the purpose of exhibiting bathochromic shift, adding water solubility, and increasing molecular stability. Acridine **1** with an amino group and a triisopropylsilylethynyl group was prepared. In the oxidation of compound **1**, target compound **2** and compound **3** were successfully synthesized by using Magic Blue which is stronger oxidizing reagent than DDQ. Both compounds showed luminescence, and the luminescence showed interesting behavior in methylene chloride, changing upon addition of acid or light irradiation.

Keywords : Azahelicene; Acridine; Photochromism

ヘリセンは螺旋構造をもつπ共役化合物であり、近年様々な類縁体が合成されている。当研究室ではこれまでにオリゴアセンを骨格としたπ拡張アザヘリセンの簡便な合成法を見出し、優れた発光およびキラル発光特性を示すことを報告している[1)]。また、近赤外領域に発光および吸収を示す色素は、生体プローブとして盛んに研究されているが、ヘリセンをベースとした近赤外色素の報告は限られている。

本研究では長波長領域への吸収・発光の発現や水溶性の付与、化合物の安定性の増大を目的としてピリジン型の窒素原子を導入した新規ヘリセン **2** の合成を行った。具体的には、まず 2 位にアミノ基、9 位にトリイソプロピルシリルエチニル基を持つアクリジン **1** を合成した。化合物 **1** を DDQ で酸化したところ目的化合物は得られず、より酸化力の強い Magic Blue を用いることで目的化合物 **2** および化合物 **3** の合成に成功した(Scheme 1)。化合物 **2** および **3** は発光を示し、その発光は塩化メチレン中で酸の添加や光照射によって変化するという興味深い挙動を示した。



1 **2** **3**

Scheme 1. Oxidation of 2-amino-9-TIPSethynylacridine with Magic Blue.

1) Hiroto, S. *et al*. *Angew. Chem. Int. Ed.* **2012**, *51*, 10333.

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Synthesis of Large Macrocycles based on the Functionalization of Azabora[6]helicene

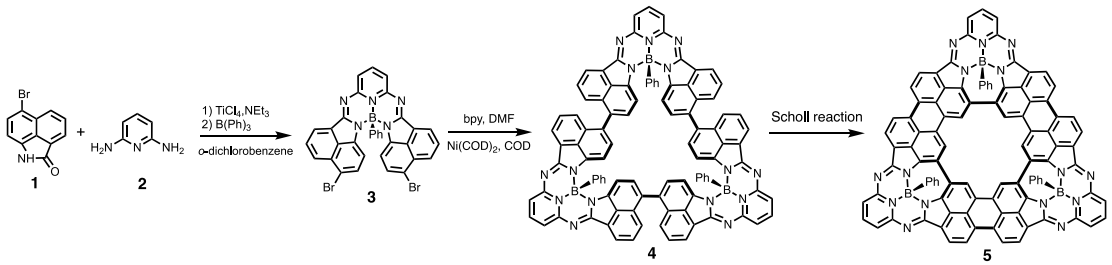
(*Graduate School of Engineering, Kyushu University*) ○Yuchuan Jiang, Soji Shimizu

Keywords: Helicene; Polyaromatic Hydrocarbon; Helicity; Macrocycle

Recently, heterohelicenes have attracted much attention because of their prominent chiroptical properties. In our previous study, a new synthetic method of heterohelicene was developed based on a Schiff base forming reaction.[1] Azabora[6]helicenes was successfully synthesized from commercially available 2,6-diaminopyridine and 6-bromobenzo[*c,d*]indole-2(1*H*)-one. Although its helical structure was elucidated by single-crystal X-ray diffraction analysis, we failed the chiral resolution due to the fast helical inversion in solution.

In this study, to further extend the synthetic chemistry of azabora[6]helicene, its peripheral functionalization and macrocyclization were investigated. The precursory azabora[6]helicene bearing bromine substituents was synthesized from 6-bromobenzo[*cd*]indol-2(1*H*)-one **1** and 2,6-diaminopyridine **2** under similar reaction conditions using *o*-dichlorobenzene as a solvent instead of toluene in the previous study. As a boron reagent, BPh_3•PPh_3 was used, and the target dibromo-substituted azabora[6]helicene (**3**) was obtained as an axially-phenyl-substituted form. Trimerization of **3** was conducted by Yamamoto coupling reaction using $Ni(COD)_2$ as a catalyst. The MALDI-TOF mass analysis revealed the formation of the trimer species (**4**). The compound was purified by silica gel and gel permeation chromatography for further characterization. Preliminarily, the ^{1}H NMR spectrum of **4** showed several signals probably due to the presence of structural isomers. Currently, the final Scholl reaction of **4** to obtain **5** is undertaken.

In this poster presentation, the synthesis and characterization of **3** and **4** and the progress in synthesizing **5** will be reported.



1) S. Shimizu, *Chem. Commun.* **2019**, *55*, 8722.

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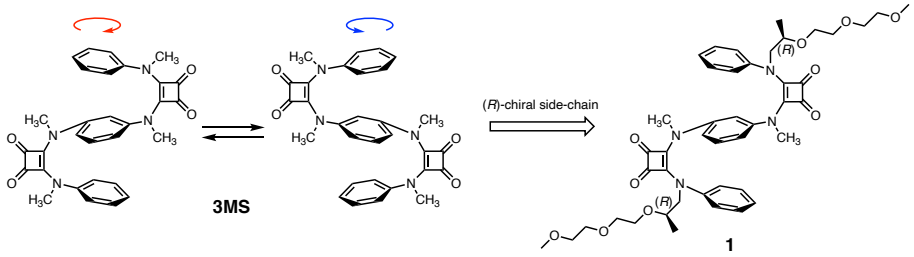
キラル側鎖をもつ芳香族スクアルアミドの立体構造解析

（お茶大院理[1]・甲南大理工[2]・昭和薬科大[3]・医科歯科大生材研[4]）○久山 和紗[1]・片桐 幸輔[2]・川幡 正俊[3]・影近 弘之[4]・棚谷 綾[1]
Structural property of aromatic squaramides with chiral side chains ([1]*Department of Chemistry, Faculty of Science, Ochanomizu University*, [2]*Department of Chemistry of Functional Molecules, Faculty of Science and Engineering, Konan University*, [3]*Faculty of Pharmaceutical Science, Showa Pharmaceutical University*, [4]*Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University*) ○Kazusa Kuyama[1], Kousuke Katagiri[2], Masatoshi Kawahata[3], Hiroyuki Kagechika[4], Aya Tanatani[1]

Squaramide is a diamino derivative of squaric acid, a four-membered cyclic dibasic acid, and has cis/trans isomer depending on the partial double-bond character of the C–N bond. *N,N'*-Diphenylsquaramide exists in (trans, trans) from, while its *N,N'*-dimethylated compound existed in (cis, cis) form, in which two benzene rings locate at face-to-face position. Previously, we reported that an aromatic squaramide **3MS** consisting of three benzene rings linked by *N,N'*-dimethylsquaramide formed the helical and aromatic layered structure. In this study, to clarify the helical properties of aromatic squaramide, we synthesized compound **1** with optically active *N*-substituents. ^{1}H NMR study indicated that compound **1** has the aromatic layered structure in solution. CD spectra of **1** showed cotton effect and molecular ellipticity decreased as temperature rose in various solvents, which indicated that compound **1** adopt a dynamic helical structure with one-handed helical bias.
Keywords : *Squaramide; Aromatic layers; Dynamic helical structure*

スクアルアミドは、四員環構造を有するスクアリン酸のジアミノ誘導体であり、C–N 結合の部分二重結合性により cis, trans 異性体が存在する。*N,N'*-ジフェニルスクアルアミドは(trans, trans)型で存在し、*N,N'*-ジメチル化によって、2 つの芳香環が向かい合った(cis, cis)型へと立体転換する[1)]。演者らは、本性質を利用して、３つのベンゼン環を *N,N'*-ジメチルスクアルアミドで連結した化合物 **3MS** がらせん状の芳香族層状構造を形成することを報告した[2)]。本研究では、本化合物のらせん分子としての性質を明らかとすることを目的に、光学活性なエチレングリコール鎖を導入した化合物 **1** を合成し、立体構造および不斉誘導の有無を解析した。^{1}H NMR スペクトル測定より、**1** は溶液中で芳香族層状構造をとることがわかった。また、UV/CD スペクトル測定より、種々の溶媒中でコットン効果が見られ、**1** が一方向巻きに偏った動的らせん構造をとることが示された。



1) Muthyala, R. S. et al. *Org. Lett*. **2004**, *6*, 4663-4665.
2) Arimura, M. et al. *ChemPlusChem*. **2021**, *86*, 198-205.

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ペンタピリンの効率的合成法の開発

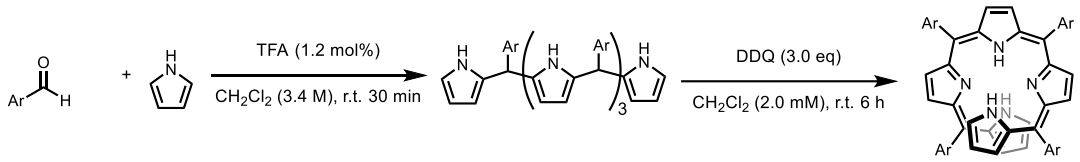
（関西学院大院理工）○西村 優輝・倉橋 拓也

Development of efficient synthesis method of Pentapyrrins (*Graduate School of Science and Technology, Kwansei Gakuin*) ○Yuki Nishimura, Takuya Kurahashi

meso-substituted oligopyrromethanes are important precursors for the synthesis of substituent-converted and isomeric porphyrins. And the oxidized oligopyrromethane is known as oligopyrrins. Recently, the synthesis of a double helical structure using tripyrrin has reported, but there are only a few synthetic examples of pentapyrrin, the smallest helical construct as a single oligopyrrin. The synthesis of pentapyrrin has been reported by the solvent-free and catalyst-free condensation reaction of pyrrole with pentafluorobenzaldehyde, followed by oxidation with DDQ, but this reaction does not proceed with any aldehyde other than pentafluorobenzaldehyde This reaction does not proceed with aldehydes other than pentafluorobenzaldehyde. [2] In this study, I attempted to develop a precise and efficient synthetic method of π-conjugated helical pentapyrrins. I achieved the synthesis of pentapyrrins in high yield and stable reproducibility.

Keywords : Helical structure; Oligopyrrin; Pyrrole; Oligomer; Multimer

meso-置換オリゴピロメタンは、置換基の変換や異性化ポルフィリンを合成するための重要な前駆体である。そして、オリゴピロメタンが酸化したものはオリゴピリンとして知られている。近年、トリピリンを用いた二重らせん構造体の合成が報告されているが、単一オリゴピリンとしての最小らせん構築体である、ペンタピリンについての合成例は数少ない [1]。ピロールとペンタフルオロベンズアルデヒドの無溶媒・無触媒下縮合反応、続く DDQ による酸化によるペンタピリンの合成が報告されているが、この反応はペンタフルオロベンズアルデヒド以外のアルデヒドでは進行しない [2]。そこで本研究では、ペンタピリンの精密かつ効率的合成法の開発を検討し、高い収率および安定した再現性を示すことを新たに見出した。



1) Y. Fukuda, Y. Akamatsu, M. Umetani, K. Kise, K. Kato, A. Osuka, T. Tanaka, *Org. Biomol. Chem.*, **2023**, *21*, 1158-1162. K.Ueta, M. Umetani, A. Osuka, G. Dan Pantos, T. Tanaka *Chem. Commun*., **2021**, *57*, 2617-2620.

2) Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Bläser, R. Boese, I. Goldberg *Org. Lett*., **1999**, *1*, 599-602.

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m-クォーターフェニル誘導体の温度制御によるキラリティー反転

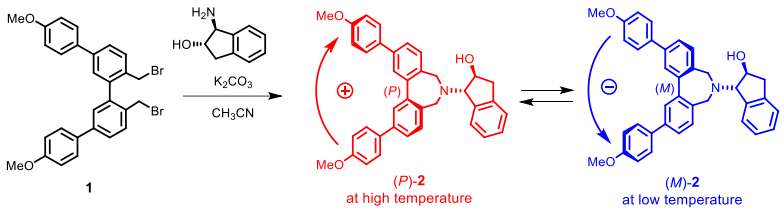
（東邦大理[1]・東邦大複合物性研究セ[2]・千葉工大工[3]）○金子 祥乃[1]・武内 悠花[1]・池田 茉莉[3]・幅田 揚一[1,2]・桑原 俊介[1,2]
Temperature-tunable inversion of chirality in *m*-quarterphenyl derivatives (*[1]Faculty of Science and [2]Research Center for Materials with Integrated Properties, Toho University, [3]Faculty of Engineering, Chiba Institute of Technology*) ○Yoshino Kaneko,[1] Yuka Takeuchi,[1] Mari Ikeda,[3] Yoichi Habata,[1,2] Shunsuke Kuwahara[1,2]

Recently, research on controlling the chirality of molecules using external stimuli, such as light and heat, has attracted attention. We have previously reported a quaterphenyl derivative (**1**) to determine the absolute configurations of acyclic primary amines[1]. We also reported the chirality inversion of (1*R*,2*R*)-**2** depending on the solvents.

We report here that the similar chirality inversion of (1*R*,2*R*)-**2** can be controlled by changing the temperature of the solvents. The CD spectra of (1*R*,2*R*)-**2** in 1,1,1,3-tetrachloropropane/1-propanol (99/1) at 323 K exhibits Cotton effects due to the exciton coupling between the two biphenyl chromophores; λ = 300 nm (Δε = +3.0) and λ = 270 nm (Δε = –5.5). The positive exciton chirality indicates that the two long axes in the biphenyl chromophores constitute an *P* twist. The CD intensity decreased as the measurement temperature was lowered, and the sign of the Cotton effects reversed below 273 K (Fig. 1).

Keywords：*Chirality inversion; Chiral Amine; CD Spectrum; m-Quarterphenyl derivative*

近年，光や熱などの外部刺激により分子のキラリティーを制御する研究が盛んに行われている．我々はこれまでにキラル 1 級アミンの絶対配置決定に有効な *m*-クォーターフェニル誘導体 **1** を報告した[1]．また，**1** と(1*R*,2*R*)-1-アミノ-2-インダノールを反応させた連結体(1*R*,2*R*)-**2** は，溶媒の種類によって 2 つのビフェニル発色団間のねじれが反転することを報告した．今回，測定温度を変えるだけでねじれが反転する現象を見出したので報告する．(1*R*,2*R*)-**2** を 1,1,1,3-テトラクロロプロパン/1-プロパノール（=99/1）混合溶媒に溶解させ 323 K で CD スペクトルを測定した結果，300 nm に正，270 nm に負の励起子型の Cotton の効果が観測された．測定温度を下げていくに従い CD の強度は減少し，273 K 以下で正負の符号が逆転した．このねじれの反転挙動の詳細について報告する予定である．



Scheme 1

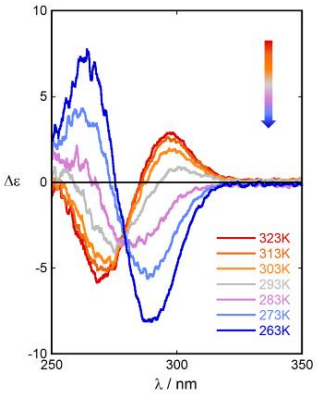


Fig.1. CD spectra of (1*R*,2*R*)-**2**. [**2**] = 2 x 10^{-4} M in 1,1,1,3-tetrachloropropane and 1-propanol (99/1).

[1] Kuwahara, S.; Nakamura, M.; Yamaguchi, A.; Ikeda, M.; Habata, Y. *Org. Lett.* **2013**, *15*, 5738–5741.

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フッ素化キュバンの単分子電子輸送特性の解明

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Single-molecule electron transfer properties of fluorinated cubanes([1]*Graduate School of Engineering, Kyoto University*, [2]*Graduate School of Engineering Science, Osaka University,* [3]*Graduate School of Engineering, Nagoya University,* [4]*iCeMS, Kyoto University,* [5]*ILAS, Kyoto University*) ○Keima Higashio,[1] Midori Akiyama,[1] Ryo Yamada,[2] Tatsuhiko Ohto,[3] Hirokazu Tada,[2] Hiroshi Imahori[1,4,5]

We investigate the electrical conductance (*G*) of fluorinated cubanes, with a particular focus on the potential contribution of the LUMO within the cube to electrical conduction.[1] We employed the scanning tunneling microscopy-break junction (STM-BJ) method to measure the *G* of individual molecules. The conductivities of both fluorinated cubane derivatives (**CubF**) and their non-fluorinated counterparts (**CubH**) were measured using the STM-BJ method, yielding the results of $10^{-3.1}$ G_0 and $10^{-4.1}$ G_0, respectively (where $G_0 = e^2/h$ represents quantized conductance). These results clearly demonstrated the impact of fluorination on *G*. In the presentation, the conduction mechanism will also be discussed.

Keywords : Fluorine; Cubane; Single-Molecule; Electron Transfer; STM-BJ

2022 年に全フッ素化キュバン（C_8F_8）が合成され、その電子受容性が証明された[1]。C_8F_8 では、フッ素原子の高い電気陰性度と立方体型構造のために、８本の C–F 結合のσ^*軌道が骨格内部で効果的に重なる。生成した低エネルギー準位の LUMO を利用して、立方体内部に電子を受容できる。今回我々は、この LUMO を介した電気伝導に着目した。立方体骨格内部に局在した LUMO は三次元井戸型ポテンシャルと類似しており、この軌道を介した電荷輸送のメカニズムは特異なものとなると考えた。

単分子電気伝導度は走査型トンネル顕微鏡ブレークジャンクション（STM-BJ）法を用いて測定した。この方法では、一定電圧を印加した Au の探針と基板の間に分子を架橋させた際に流れる電流を測定することで電気伝導度を測定する[2]。Au への配位部位としてシアノ基を導入した 1,4-ジシアノ-2,3,5,6,7,8-ヘキサフルオロキュバン（**CubF**）を設計した。**CubF** と 1,4-ジシアノキュバン（**CubH**）の単分子電気伝導度を測定し、比較した。**CubF** は $10^{-3.1}$ G_0（G_0＝e^2/h は量子化コンダクタンスという定数）、**CubH** は $10^{-4.1}$ G_0 の電気伝導度を示し、キュバン骨格をフッ素化すると電気伝導度が 1 桁向上することが分かった。発表では、伝導機構に関しても論じる。

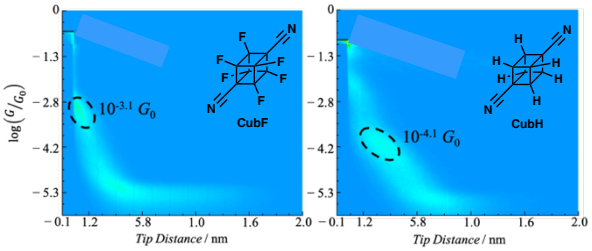

Figure 1. Two-dimensional conductance vs distance histograms for **CubF** (left) and **CubH** (right).

[1] M. Sugiyama, M. Akiyama, Y. Yonezawa, K. Komaguchi, M. Higashi, K. Nozaki, T. Okazoe, *Science* **2022**, *377*, 756
[2] D. Xiang, X. Wang, C. Jia, T. Lee, X. Guo, *Chem. Rev.* **2016**, *116*, 4318

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アゾビフェニル–チオグリコシド連結体を用いたグリコシル化反応における選択性

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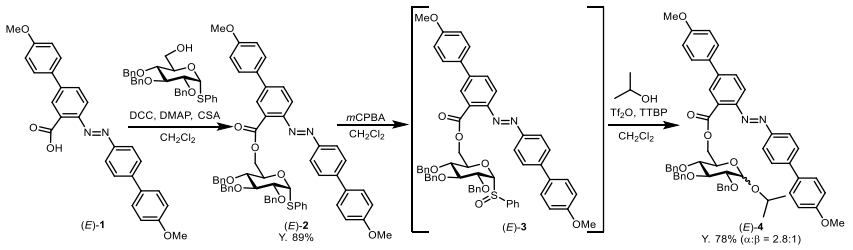
Synthesis and Conformational Analysis of Azobiphenyl-glycoside Conjugates（[1]*Faculty of Science and* [2]*Research Center for Materials with Integrated Properties, Toho University,* [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*）○Hidenori Wakui,[1] Yuta Shinozuka[1], Mari Ikeda[3], Kaname Sasaki[1], Yoichi Habata[1,2], Shunsuke Kuwahara[1,2]

Glycoside side chain conformation is an important factor in the control of the reactivity at the anomeric center. we designed a new azobiphenyl derivative (*E*)-**1** to control the side chain conformation in the glycosides by *E-Z* photoisomerization of the azobenzene unit. Previously, we synthesized an azobiphenyl-glycoside linkage and reported that the conformation of the 6-position of the glycoside changed before and after *E-Z* photoisomerization. Here, we report the synthesis and the glycosylation of azobiphenyl-thioglycoside linkage (*E*)-**2**. (*E*)-**1** was condensed with thioglycosides using DCC, DMAP, and CSA to obtain (*E*)-**2** in 89% yield. After oxidation of (*E*)-**2** by *m*CPBA, (*E*)-**4** was obtained in 89% yield (α:β = 2.8:1) by glycosylation with isopropanol. We will also report the α/β stereoselectivity in the glycosylation using (*Z*)-**2**.
Keywords : Azobiphenyl; *Photoisomerization*; *Glycosylation*; *Conformational analysis*

近年，グリコシド側鎖の配座を制御することで，アノマー位におけるグリコシル化反応の反応性を制御する研究が行われている．我々は，アゾベンゼン部位の *E-Z* 光異性化によりグリコシドのヒドロキシメチル基側鎖の配座を制御することを目的として，アゾビフェニル誘導体(**1**)を設計した．これまでにアゾビフェニル-グリコシド連結体を合成し，光異性化前後でグリコシドの 6 位部分の立体配座が変化したことを報告した．今回，チオグリコシドと **1** を連結し，*E-Z* 光異性化によるグリコシル化反応の立体選択性の検討を行った．**1** とチオグリコシドを DCC, DMAP, CSA 条件下で縮合し，アゾビフェニル-チオグリコシド連結体(*E*)-**2** を 89%の収率で得た．*m*CPBA を用いて(*E*)-**2** のスルフィドを酸化した後，イソプロパノールを糖受容体としてグリコシル化反応を行った結果，α:β = 2.8:1 の選択性で(*E*)-**4** が得られた．(*Z*)-**4** のグリコシル化反応についても報告する予定である．



Scheme 1

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オキシインドール型磁気異方性試薬によるキラル 1 級アミンの絶対配置決定

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Oxindole-type chiral derivatizing reagents for stereochemical assignments of primary amines

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○Ryosuke Kimura,[1] Mari Ikeda,[3] Yoichi Habata[1,2], Shunsuke Kuwahara[1,2]

A convenient method for determining the absolute configuration of chiral alcohols is to use a chiral derivatizing agent (CDA)[1]. Usually, a chiral alcohol is converted into diastereomers by the CDA, and the differences in the chemical shifts (ΔδRS) of the diastereomers in ^{1}H NMR are compared. However, when this method is applied to chiral amines, the $\Delta\delta_{RS}$ value becomes small due to the presence of conformers, and the absolute configuration determination may become a problem. Recently, we designed new oxyindole derivatives, (*S*)- and (*R*)-**1**, for the absolute configuration determination of chiral amines. (*S*)- and (*R*)-**1** were connected with (*R*)-**2** to yield the conjugates (*S*,*R*)-**3** and (*R*,*R*)-**3** in quantitative yield, respectively. ^{1}H NMR measurements of (*S*,*R*)-**3** and (*R*,*R*)-**3** showed that the ethyl group in (*R*,*R*)-**3** and the methyl group in (*S*,*R*)-**3** were high field shifted due to anisotropy effects by the indole ring. Application to various primary amines will also be reported.

Keywords *: Chiral derivatizing agent; Determination of the absolute configuration; Chiral primary amine; Oxindole*

キラルアルコールの簡便な絶対配置の決定法として，磁気異方性試薬を用いる方法がある[1]．これはアルコールに磁気異方性試薬を連結させ，生成した 2 種類のジアステレオマーの ^{1}H NMR スペクトルを解析することにより絶対配置を決定する方法である．しかしこの方法をキラルアミンに適用した場合，配座異性体の存在により化学シフト差が小さくなり，絶対配置決定の問題になることがある．本研究ではキラルアミンの簡便な絶対配置決定を目指し，新規オキシインドール誘導体(*S*)-, (*R*)-**1** を合成した（図 1）．キラルアミン(*R*)-**2** と(*S*)-**1** および(*R*)-**1** を炭酸カリウム存在下 THF 中で混合し，連結体(*S*,*R*)-**3** と(*R*,*R*)-**3** を定量的に得た．(*S*,*R*)-**3**，(*R*,*R*)-**3** の ^{1}H NMR を測定したところ，インドール環に由来する磁気異方性効果で(*R*,*R*)-**3** ではエチル基が，(*S*,*R*)-**3** ではメチル基が大きく高磁場シフトした．種々のキラル 1 級アミンへの適用も報告する．

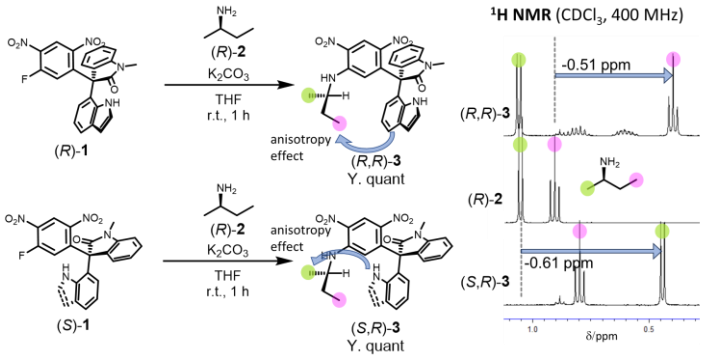

図 1. オキシインドール誘導体(**1**)によるキラルアミン類の絶対配置決定

1）Seco, J. M.; Quinoa, E.; Riguera, R. *Chem. Rev*. **2004**, *104*, 17.

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ブロモプロピニルベンゼン誘導体と３級アルコールの連結反応の検討

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Coupling reaction between bromopropynylbenzene derivatives and tertiary alcohols

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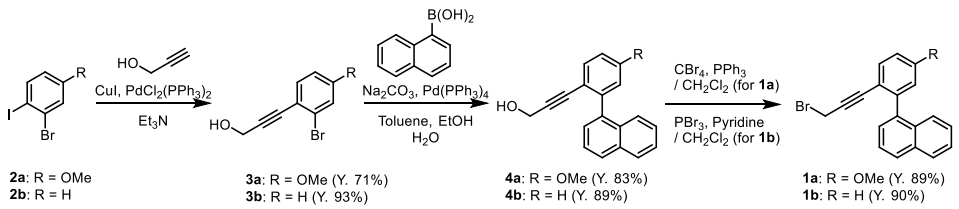
The development of practical methods to determine the absolute configuration of chiral compounds is important in the fields of chemistry and pharmacology. In some cases, derivatization methods may be employed for this purpose. However, tertiary alcohols often pose a significant challenge for the derivatization due to their steric hindrance.

We design a novel bromopropynylbenzene derivative (**1a**). We expected that (i) **1a** would couple readily with chiral tertiary alcohols, (ii) information on the absolute configurations of the alcohols would be transcribed into a spatial arrangement of propynylbenzene and naphthalene units which is detected directly by the CD method. We synthesized **1a** from methoxybenzene derivative (**2a**). The coupling reaction of **1a** with tertiary alcohols will also be reported.

Keywords : Chiral tertiary alcohols; *Determionation of absolute configuration*; *CD spectrum*

三級アルコールは立体障害が大きいため，絶対配置決定のための誘導体化が困難である場合が多い．例えば，キラル二級アルコールの絶対配置決定で汎用される絶対配置決定試薬をキラル三級アルコールへ適用した報告があるが，連結反応の収率が 10%程度と低いことに課題が残っている[1]．そこで本研究ではキラル三級アルコールと容易に反応すると考えられる新規ブロモプロピニルベンゼン誘導体（**1a**）を設計した．**1a** を三級アルコールに連結することにより，キラリティーの情報がオルト位のナフチル基のねじれに伝播する．そのねじれを CD スペクトルで検出することで絶対配置を決定できると考えた．**1a** の合成はスキーム 1 に従って行った．メトキシベンゼン誘導体（**2a**）とプロパルギルアルコールの薗頭カップリングの後，1-ナフチルボロン酸との鈴木-宮浦カップリング反応によりアルコール（**4a**）を合成した．**4a** の構造は X 線結晶構造解析から確認した．**4a** を臭素化し，目的の **1a** を合成した．**1a** および同様の方法で合成した **1b** と三級アルコールとの連結反応についても報告する．



スキーム 1.

[1] Takahashi, H.; Kato, N.; Iwashima, M.; Iguchi, K. *Chem. Lett*., **1999**, *28*, 1181-1182.

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6-(ジエチルボリル)-1-(4-ピリジル)アズレン：フロー合成と DMAP との反応

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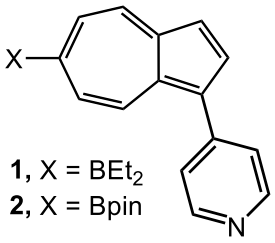
○若林 成知[1]・檜垣 達也[2]・脇岡 正幸[3]・宅見 正浩[4]・中西 ひかり[1]・大木 靖弘[2]・永木 愛一郎[5]

6-(Diethylboryl)-1-(4-pyridyl)azulene: Flow Synthesis and Reaction with DMAP ([1]*Faculty of Health Science, Suzuka University of Medical Science,* [2]*Institute for Chemical Research, Kyoto University,* [3]*Sagami Chemical Research Institute,* [4]*Graduate School of Engineering, Kyoto University,* [5]*Graduate School of Science, Hokkaido University*) ○ Shigeharu Wakabayashi,[1] Tatsuya Higaki,[2] Masayuki Wakioka,[3] Masahiro Takumi,[4] Hikari Nakanishi,[1] Yasuhiro Ohki,[2] Aiichiro Nagaki[5]

The title compound is of great interest from the viewpoint of the chirality and solvatochromism in the self-assembled oligomer. The flow microreactor systems improved the synthesis significantly and we clarified the formation of the cyclic trimer. Addition of DMAP to the solution of **1** in chloroform produced the color change from red to violet. The color change due to self-assembly and DMAP complexation are supported by DFT calculations.

Keywords: Borylpyridine; Azulene; Flow Synthesis; Color Change; DFT Calculation

表題化合物**1**が形成する会合体は、キラリティーやソルバトクロミズムなどの観点から興味がもたれる。合成は相当する臭素体に、*n*-ブチルリチウムとジエチルメトキシボランをフローマイクロ法により反応させ行った。得られた**1**は^{11}B NMR、ESIMSスペクトルなどから、環状3量体を形成していると考えられる。吸収波長は532 nm（赤色）で、非会合性のピナコラトボリル体**2**（λ_{max}: 588 nm, 青色）に比べ、約50 nm短波長に観測された。



1 のクロロホルム溶液に DMAP のクロロホルム濃厚溶液を加えると、吸収波長は 549 nm（紫色）と長波長シフトし、等吸収点が 587 nm に観測された（**Figure 1**）。得られた生成物の NMR、ESIMS スペクトルから、環状 3 量体は崩れ **1**・DMAP 錯体が生じたと考えられる。**1** の自己集合による短波長シフトおよび DMAP 配位による長波長シフトは、DFT 計算によっても支持された。

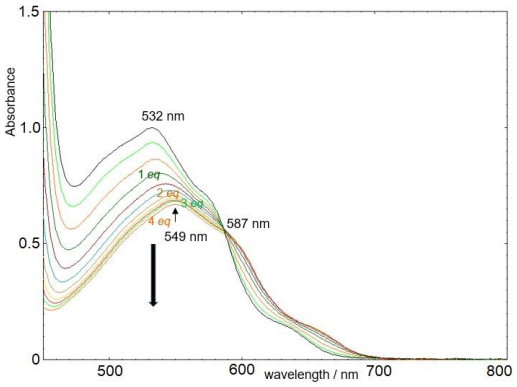


Figure 1 Color Change of **1** upon the addition of DMAP.

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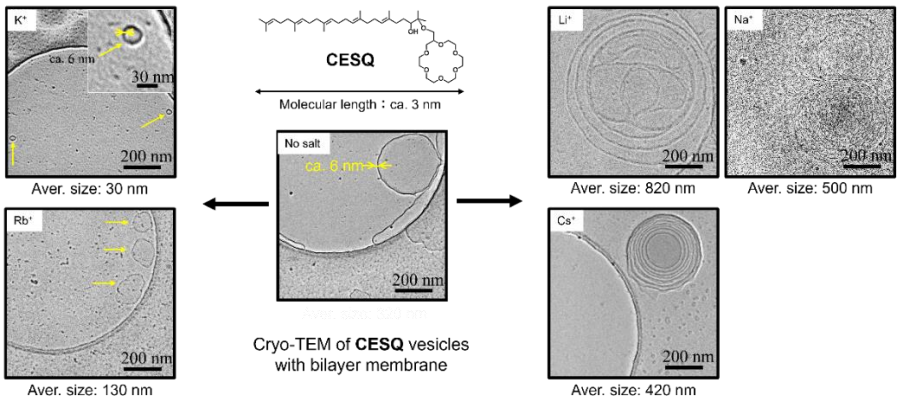
スクアレンを用いたイオン応答性ユニラメラ・ラージベシクルの自己組織化及び会合特性

（産業技術総合研究所[1]・筑波大学[2]）○Ngoc Linh Tran[1]・富永 健一[1,2]・礒田 博子[2]・市川 創作[2]・有村 隆志[1,2]
Self-organization and aggregation properties of ion-responsive unilamellar large vesicles derived from squalene ([1]*National Institute of Advanced Industrial Science and Technology*, [2]*University of Tsukuba*)○Linh Ngoc Tran,[1] Kenichi Tominaga,[1,2] Hiroko Isoda,[2] Sosaku Ichikawa,[2] Takashi Arimura[1,2]

Squalene is an edible triterpene that is highly hydrophobic and insoluble in water. We have successfully introduced 18-crown-6, which exhibits ion recognition ability, into squalene (**CESQ**). Association constants (logK_a) of **CESQ** towards alkali metal cations in acetonitrile were in order of K^+ (6.10) > Rb^+ (5.52) > Cs^+ (4.94) > Na^+ (4.86) > Li^+ (3.16). **CESQ** formed unilamellar vesicles with a diameter of ca. 320 nm and a membrane thickness of ca. 6 nm. The vesicles selectively changed size and showed metal ion responsiveness, reflecting the association constant with alkali metal ions. When the association constant was small, the vesicles became multi lamellar and showed size-increasing behavior. When the association constant was large, the vesicles remained unilamellar but showed size-decreasing behavior.
Keywords : Squalene; crown ether; unilamellar vesicle; large vesicle; self-organization

スクアレンは可食のトリテルペンであり、疎水性が強く、水に不溶である。イオン認識能を示す 18-クラウン-6-エーテルをスクアレン（**CESQ**）に導入することに成功した[1]。**CESQ** は、アルカリ金属イオンに対して 1:1 で会合し、会合定数（logK_a）は K^+ (6.10) > Rb^+ (5.52) > Cs^+ (4.94) > Na^+ (4.86) > Li^+ (3.16)の順であった。**CESQ** が、水中で、ミセルではなくユニラメラベシクル（直径：約 320 nm、膜厚：約 6nm）を形成することを Cryo-TEM で確認した。このベシクルはアルカリ金属イオンとの会合定数の大きさを反映して、選択的にサイズが変化し金属イオン応答性を示した。会合定数が小さい場合、マルチラメラベシクルとなりサイズが大きくなり、会合定数が大きい場合、ユニラメラベシクルの構造を保ったまま、サイズが小さくなる挙動を示した。



1) N. L. Tran; T. Arimura; K. Tominaga; H. Isoda; M. Kawasaki; N. Adachi, *ACS Omega* **2023**, 8, 11583.

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エチニルピリジン置換型カルバゾールを集積した三脚型分子の合成と性質

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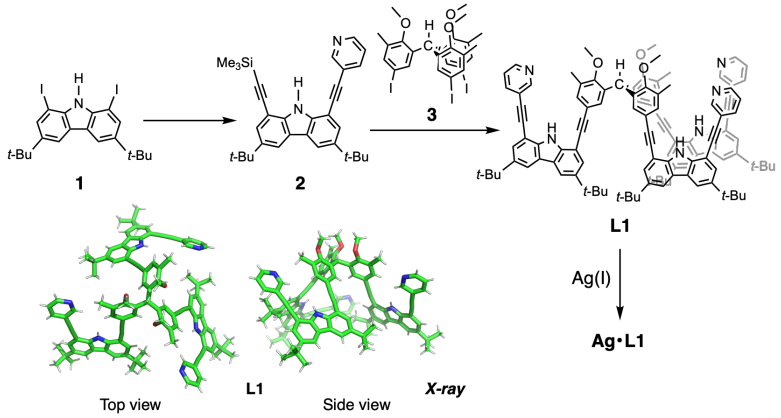
Synthesis and Properties of Tripodal Molecules Integrating Carbazoles Substituted with Ethynyl-Pyridine Groups ([1]*School of Science and Technology, Gunma University*, [2]*Graduate School of Science and Technology, Gunma University*) ○ Masamune Fujikawa,[1] Yuya Domoto,[2] Yosuke Nakamura[2]

We have investigated the syntheses of molecules composed of more than two carbazole rings via bond connection or annulation. Recently, we have also started to explore the spatial integration of carbazoles. We will present our recent results of the synthesis of triarylmethanes equipped with three carbazole units bearing pyridyl-ethynyl group, and their coordination self-assembly with Ag(I) ion.

Keywords : Carbazole; Supramolecule; Self-assembly; Heterocyclic compound

我々はこれまで、複数のカルバゾールを連結[1)]や縮環により結合経由で集積した分子群を合成してきた。一方で最近、カルバゾール環を空間的に多数集積する試みについても検討している。一義的な 3 次元構造において特異な集積配置を実現できれば、カルバゾールの光学特性や電子的性質を活かした分子マテリアルの構築が可能となると期待される。本研究ではまず、三脚型トリアリールメタンの 3 つの腕に配位性の 3-ピリジルエチニル基で修飾したカルバゾール環を導入した配位子 **L1** を合成した。この際、アセチレン協働配位[2)]に基づく 3 次元構造構築を期待し、アセチレンスペーサーによりカルバゾールを連結することとした。1,8-ジヨードカルバゾール **1** の両端に 3-ピリジルエチニル基およびトリメチルシリルエチニル基をそれぞれ導入した **2** を合成し、さらにトリヨードトリアリールメタン **3** との 3 点薗頭カップリング反応を行うことで **L1** を得た。**L1** は単結晶 X 線解析より、プロペラ型構造をとることが確認された。配位子 **L1** に対して適当な溶媒中、銀(I)塩を作用させ錯形成を行ったところ、^{1}H NMR による観察から錯形成の進行が示唆された。配位部位を 4-ピリジルに置換した配位子 **L2** についても検討を行っており、併せて議論する。



1) S.-i. Kato, H. Noguchi, A. Kobayashi, T. Yoshihara, S. Tobita, Y. Nakamura, *J. Org. Chem.* **2012**, *77*, 9120.
2) Y. Domoto, M. Fujita, *Coord. Chem. Rev.* **2022**, *466*, 214605.

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オキシエチレン長の変化が円筒状クリプタンド/銀錯体のアロステリック特性に与える影響

（東邦大理[1]・東邦大複合物性研究セ[2]・千葉工大工[3]）○熊谷　春希[1]・二瓶　祐太郎[1]・加茂 慎治[1]・大塚 晃弘[1]・藤澤 将暉[1]・池田 茉莉[3]・桑原 俊介[1,2]・幅田 揚一[1,2]

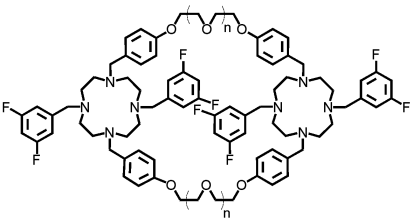
Influence of Varying Oxyethylene Chain Length on the Allosteric Properties of Cylindrical Cryptand/Silver Complexes ([1]*Department of Chemistry and* [2]*Research Center for Materials with Integrated Properties, Toho University,* [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*) ○Haruki Kumagai,[1] Yutaro Nihei,[1] Shinji Kamo,[1] Akihiro Otsuka,[1] Masaki Fujisawa,[1] Mari Ikeda,[3] Shunsuke Kuwahara,[1,2] Yoichi Habata[1,2]

When tetra-armed cyclens with aromatic side arms form complexes with Ag^+ ions, the aromatic side arms envelop the Ag^+ ions. In this study, two tetra-armed cyclens were interconnected by oxyethylene chains to create molecules with allosteric properties, where the formation of an Ag^+ complex in the first cyclen promotes the formation of a silver complex in the second cyclen. Cylindrical cryptands (**1a**–**1c**), bridging two cyclens with oxyethylene chains of varying lengths (n=1–3), were prepared and evaluated for allosteric properties using UV-vis spectra. All ligands were synthesized in 12 steps, respectively. UV-vis titration of each ligand with silver ions revealed an increase in absorption around 252 nm for all ligands, but only **1a** (n=1) exhibited a sigmoidal titration curve. As indicated by the Hill plot, it was revealed that only **1a** possesses allosteric properties.

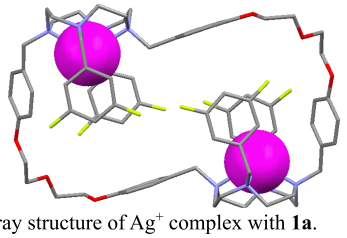
Keywords **:** *Cyclen; Silver(I) complex; Allosteric effect; Cryptand; Ag-π interaction*

サイクレンに芳香環側鎖を結合させたテトラアームドサイクレンは，Ag^+との錯形成時に芳香環側鎖が銀イオンを包み込むように立ち上がる [1]．本研究では，オキシエチレン鎖で架橋された2つのテトラアームドサイクレンから成る円筒状クリプタンド（1a–1c: n = 1–3）を合成し，それらのAg^+イオンとの錯形成挙動を検討した．

合成はそれぞれ12段階で行った．これらの合成物にAg^+を添加し，^{1}H-NMR，cold ESI-MS，およびUV-visスペクトルを用いて滴定実験を行った．それらの結果，**1a**–**1c**は最初に1:1の錯体（配位子:Ag^+）を形成し，その後に1:2の錯体（配位子:Ag^+）を形成することが確認され，また芳香環側鎖がAg+を包み込んでいることも示唆された．UV-Vis滴定実験において，**1a**のみが滴定曲線がS字曲線となる特異な挙動を示しました．Hillプロットから，**1a**がAg^+との錯体形成時に，1:1錯体を形成した後に急速に1:2錯体が形成されるアロステリック効果が示唆された．



1a (n = 1)
1b (n = 2)
1c (n = 3)



X-ray structure of Ag^+ complex with **1a**.

[1] Y. Habata *et al. Org. Lett.*, **2012**, *14*, 4576–4579.

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金属試薬を使わないクロスカップリングを用いた六環性縮環分子の合成

（龍大院理工）○野田 理温・岩澤 哲郎
Cross-Coupling of Fluorenones for Metal-Free Polyarene Synthesis (*Graduate School of Science and Technology, Department of Materials Chemistry, Ryukoku University*) ○Rion Noda, Tetsuo Iwasawa

Dibenzo[*g*,*p*]chrysene (DBC, $C_{26}H_{16}$) is known as one of the polyaromatic hydrocarbons that are attracting attention. Herein we present *cross*-dimerization reactions that employ nonequivalent 9-fluorenones have been accomplished for selective synthesis of spiroketones. Two different 9-fluorenones are predominantly *cross*-coupled, and the corresponding spiroketones are singly formed with suppression of *homo*-adducts. The *cross*-adducts are followed by conventional reduction and migration reactions, which enables high-yielding transformation into a dibenzo[*g*,*p*]chrysene core bearing two *tert*-butyl groups and two halogen atoms. The resulting hexa-cycle fused-rings are so processable in organic solvents that the two bromines readily undertake substitution reactions. Thus, this solution-compatible process is operationally simple and productively efficient for general access to non-planar polyarenes from the viewpoint of diversity-oriented synthesis. *Keywords : Dibenzo[g,p]chrysene; Metal-free cross-coupling; Selective synthesis; Polyarenes; Solution-phase synthesis*

ジベンゾ[*g*,*p*]クリセン（DBC, $C_{26}H_{16}$）は六環性のコンパクトな形状の多環芳香族炭化水素である。元来高い屈折率を有するため、その類縁体も含めて、企業研究者を中心に注目を集めている。当研究室では過去、フルオレノンの同種二量化を礎としたDBC 合成を報告してきた。今回、異なる２種類のフルオレノンの反応性の違いを利用した交差二量化を礎とした DBC 合成を見出した（Figure 1）[1]。この方法は金属試薬等を用いることなく、反応溶媒中加熱するだけで進行する。誘導される DBC は液相下での多様性指向型合成に適しており、高屈折率素材として期待される。

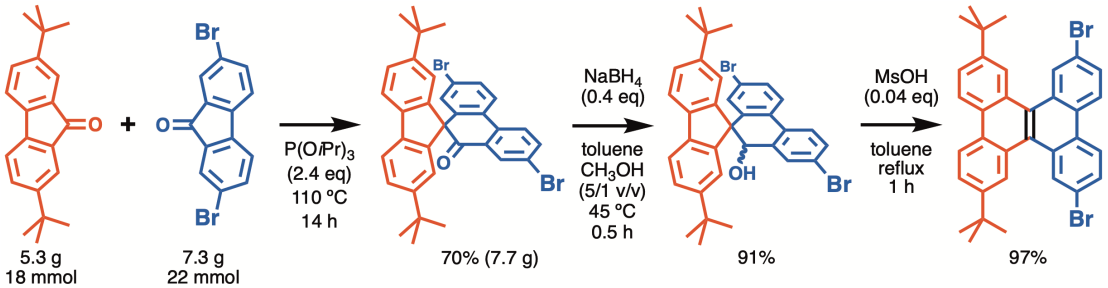

Figure 1. Metal-free cross-coupling to synthesize a dibenzo[*g*,*p*]chrysene core.

1) N. Yoshida, R. Akasaka, Y. Yamaoka, T. Yashima, Y. Tokunaga, T. Iwasawa, *Tetrahedron* **2023**, *143*, 133549. Doi: 10.1016/j.tet.2023.133549

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テトラベンゾクリセンの新しい合成経路

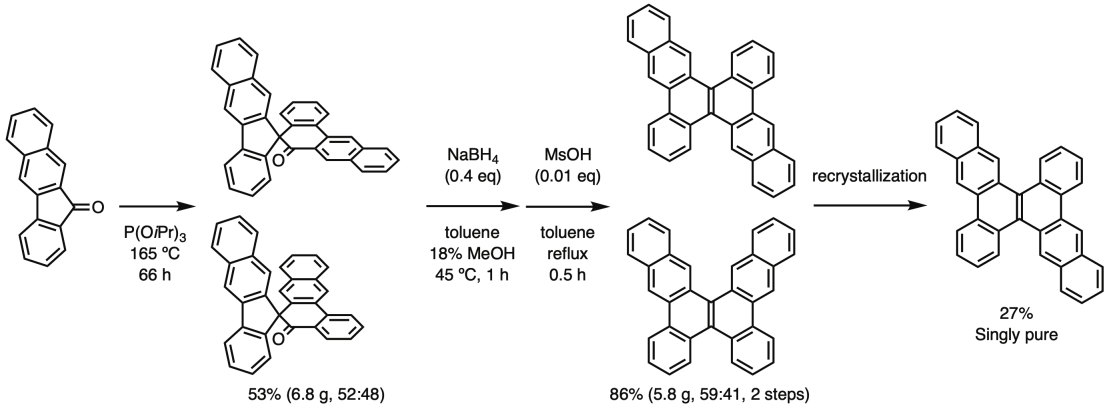
（龍大先端理工）○池永 拓実・岩澤 哲郎
A New Synthetic Route to Tetrabenzo[*b*,*g*,*k*,*p*]chrysene (*Department of Materials Chemistry, Ryukoku University*) ○Takumi Ikenaga, Tetsuo Iwasawa

Polyaromatic hydrocarbons are attractive compounds, because they are promising materials that underpin future technologies. From the industrial point of view, their productive methods are strongly demanded. So far, the predominant ways involved the use of transition metals and reactive oxidants: Undoubtedly, such reagents have been at the forefront of polyarene synthesis. However, they provide us continuing challenges wherein the reagents require sensitive conditions and remain in the products. Thus, alternative methodology for increasing rings in polyarenes is preferable. Herein we present metal-free three-step-synthesis of tetrabenzo[*b*,*g*,*k*,*p*]chrysene (TBC) that has been underrepresented despite the expectation of highly refractive index: Structural search in SciFinder disclosed only 14 hits (Oct./2023).

Keywords : Tetrabenzochrysene; Dibenzo[g,p]chrysene; Polycycles; Pi-extension; Functional organic materials

多環芳香族炭化水素は材料化学の観点から注目を集め、未来の科学技術を下支えすると期待されている。量的供給を要するため、製造に耐え得るプロセス化学を満足する高生産性スキームが求められる [1)]。一方、これまでの合成においては、Scholl 反応や金属試薬を用いた手法が主流となってきた。しかし、製造段階でこれらの方法を多用して増環すると、繊細な反応条件や残留金属の問題が無視できなくなる。

今回我々は、SciFinder の構造検索において僅少な例数しかないテトラベンゾクリセンの合成に臨んだ（Scheme 1）。市販のケトンを用いて、同種二量化・還元反応・転位反応の三工程を行い、八環性の多環芳香族炭化水素の単離を達成した。



Scheme 1. Synthetic outline of tetrabenzochrysenes.

1) Y. Fujii, Y. Taguchi, S. Tokai, Y. Matsumoto, N. Yoshida, T. Iwasawa, *Tetrahedron* **2021**, *95*, 132353. Doi: 10.1016/j.tet.2021.132353

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日本化学会 第104春季年会 (2024)

9-アザジベンゾ[a,f]ペンタレニルカチオンの合成と双性イオン TMM 型構造に由来する非対称な環電流効果の発現

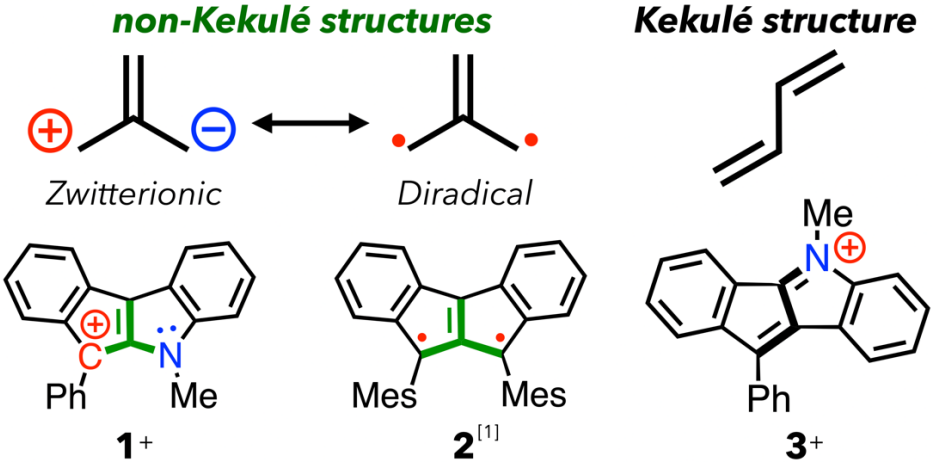
（京大院工）○山本 康貴・清水 大貴・松田建児

Synthesis and properties of azadibenzo[a,f]pentalenes towards TMM derivatives with mesoionic electronic structure (*Graduate School of Engineering, Kyoto University*) ○Koki Yamamoto, Daiki Shimizu, Kenji Matsuda

π-Conjugated hydrocarbons exhibit unique properties depending on their Kekulé/non-Kekulé-type structural topology. Non-Kekulé molecules can be classified into those with diradical electronic structure and those with zwitterionic electronic structure. Non-Kekulé molecules with zwitterionic electronic structures have not been explored well. To investigate the influence of zwitterionic non-Kekulé structure on π-conjugated systems, we designed and synthesized 9-azadibenzo[a.f]pentalenyl cation **1**$^+$ containing an isoelectronic structure of zwitterionic trimethylenemthaene (TMM). Compared to **2**$^+$ containing a diradical TMM structure and Kekulé-type isomer **3**$^+$, **1**$^+$ exhibited a larger paratropic ring current effect at the five-membered ring containing cationic carbon, as well as a suppressed diatropic ring current effect at the indole moiety.

Keywords: open-shell character; non-Kekulé molecule; isoelectronic species; mesoionic compounds; heteroaromatic compounds

π 共役系炭化水素はケクレ/非ケクレ型の構造トポロジーに由来して大きく異なる物性を示すことが知られている。非 Kekulé 分子はジラジカル型の電子構造を持つものと双性イオン型の電子構造を持つものに分類することができるが、このうち双性イオン型電子構造を持つ分子についてはその構造トポロジーと物性の相関は未開拓である。本研究では双性イオン型非 Kekulé 構造が π 共役系に与える影響を調査するため、代表的な非 Kekulé 分子であるトリメチレンメタン(TMM)の双性イオン型等電子構造を有する 9-アザジベンゾ[a.f]ペンタレニルカチオン **1**$^+$を設計・合成した。得られた **1**$^+$は、ジラジカル型等電子体である **2**[1]および Kekulé 型異性体である **3**$^+$と比較して、カチオンを含む 5 員環に強い常磁性環電流効果が見られたほか、インドール部分の芳香族性も大きく低下していることが分かった。



1. A. Konishi, M. Yasuda *et al. J. Am. Chem. Soc.* **2017**, *139*, 15284.

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アントラセン縮合 V 字形芳香族化合物の Scholl 反応：分子内環化生成物の構造と性質

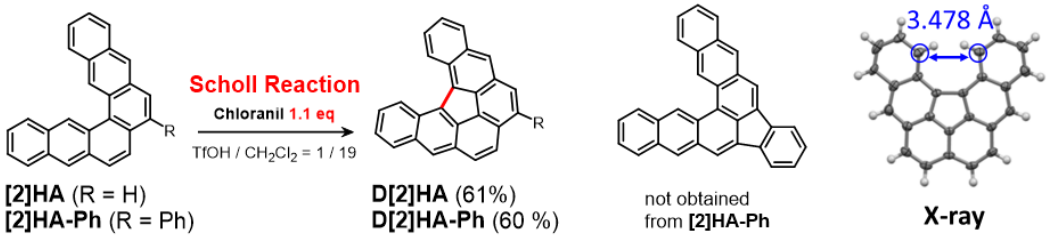
（東工大理[1]・北里大理[2]）○小林萌[2]・鶴巻 英治[1]・豊田 真司[1]

Scholl reaction of V-shaped aromatic compounds with fused anthracene: structure and properties of intramolecular cyclization products ([1]*School of Science, Tokyo Institute of Technology*, [2]*School of Science, Kitasato University*)○Moe Kobayashi,[2] Eiji Tsurumaki,[1] Shinji Toyota[1]

We reported the synthesis of π-expanded helicenes **[n]HA** consisting of helically fused multiple anthracenes. In this work, we performed the Scholl reaction of **[2]HA** and its derivative to investigate reactivities of the π-expanded helicenes. The reaction of **[2]HA** with 1.1 equiv. of *p*-chloranil in the presence of trifluoromethanesulfonic acid gave cyclized product **D[2]HA** as a red solid in good yield. The single crystal X-ray analysis revealed a highly planar structure despite the closely contacting H atoms. Phenyl derivative **[2]HA-Ph** similarly gave a cyclized product without affecting the Ph group. Structures and properties of these products will be discussed based on spectroscopic data and DFT calculations.

Keywords : Anthracene; Scholl reaction; Intramolecular oxidative cyclization; Aromatic compound

我々はこれまでに、複数のアントラセンをらせん形に縮合したπ拡張ヘリセン **[n]HA** の合成を報告した。本研究では、π拡張ヘリセンの研究の一環として、2 つのアントラセンが縮合した**[2]HA** および誘導体に対して Scholl 反応を行い、生成物の構造と性質を明らかにした。**[2]HA** に対して 1.1 当量の *p*-クロラニルをトリフルオロメタンスルホン酸存在下で作用させると、らせん内部で酸化的環化が進行したデヒドロ環化体 **D[2]HA** が赤色固体として収率 61%で得られた。この生成物の構造は単結晶 X 線解析で確認し、非常に接近した水素原子があるにも関わらず平面性の高い構造をもつことが明らかになった。周辺部にフェニル基をもつ**[2]HA-Ph** でも同様の環化生成物が得られ、Ph 基の縮合は進行しなかった。これらの生成物の構造と性質を、分光学的データおよび量子化学計算の結果から考察する。



1) K. Fujise, E. Tsurumaki, K. Wakamatsu, S. Toyota. *Chem. Eur. J.* **2021**, *27*, 4548.
2) K. Fujise, E. Tsurumaki, G. Fukuhara, N. Hara, Y. Imai, S. Toyota, *Chem. Asian J.* **2020**, *15*, 2456.

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テトラフェニルヘキサアザアントラセン (TPHA) のメタフェニレン架橋環状三量体の合成研究

(1 京大院工,2 京大福井セ) ○塩見 綜環 1 ・清水 大貴 1・松田 建児 1,2

Synthetic study of a *meta*-phenylene-bridged trimer of tetraphenylhexaazaanthracene (TPHA)

([1]*Graduate School of Engineering, Kyoto University*, [2]*FIFC, Kyoto University*)
Sokan Shiomi,[1] Daiki Shimizu,[1] Kenji Matsuda[1,2]

Tetraphenylhexaazaazaanthracene (**TPHA**) is a biscyanine-type zwitterionic compound in which a cationic 6π-conjugated system and an anionic 10π-conjugated system coexist, and the whole conjugated system shows 16π anti-aromaticity. A dimer of **TPHA** (**DI-TPHA**) has been reported as a non-luminescent species, presumably due to efficient singlet fission occurring in the excited state. In this study, we have designed a metaphenylene-bridged cyclic trimer of **TPHA** with a cationic outer side and an anionic inner side for exploring its photophysical properties and host-guest chemistry. We report the details of our synthetic efforts towards the trimer.

Keywords: Zwitterion, Macrocyclic Compound, Stable Radical, Anti-Aromatic, Singlet Ground State

Tetraphenylhexaazaanthracene (**TPHA**) はカチオン性 6π 共役系とアニオン性 10π 共役系が共存したビスシアニン型の双性イオンであり、共役系全体としては 16π 反芳香族性を示す。[1] **TPHA** の基底状態は閉殻一重項であり効率的な蛍光を示す一方、その二量体 (**DI-TPHA**) は非発光性であることが知られており、励起状態で効率的な一重項分裂の進行が示唆されている。[2] 本研究では励起状態挙動やホスト-ゲスト化学に興味を持ち、外側がカチオン性、内側がアニオン性を有する TPHA のメタフェニレン架橋環状三量体（**TRI-TPHA**）を設計した。本発表では具体的な合成への取り組みについて報告する。

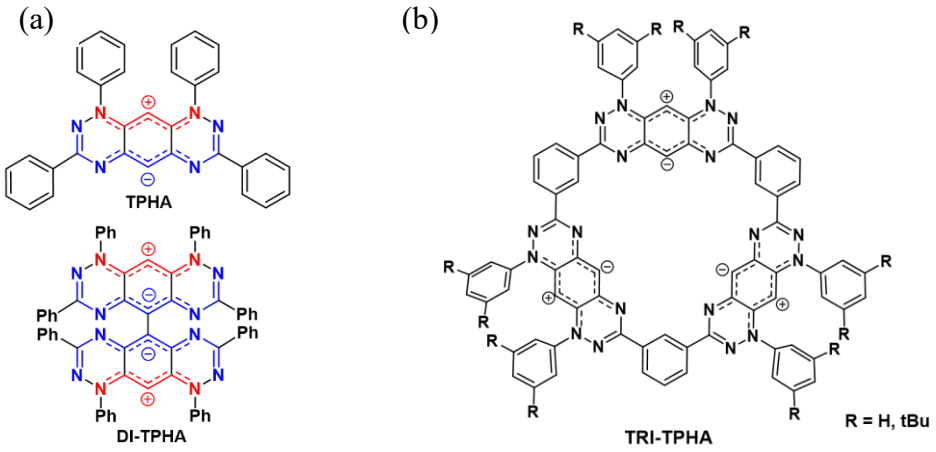

Figure 1. a) Structures of **TPHA** and **DI-TPHA**. b) Structures of the target **TRI-TPHA**.

[1] C. P. Constantinides, P. A. Koutentis, *et al*., *Org. Lett.* **2015**, *17*, 4026–4029.

[2] G. A. Zissimou, P. A. Koutentis, *et al*., *Org. Lett.* **2016**, *18*, 1116–1119.

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新規ヘテロ[8]サーキュレンやヘテロ[10]サーキュレンの合成

（京大院工[1]）○中川 蒼[1]・松尾 悠佑[1]・関 修平[1]・田中 隆行[1]

Synthesis of novel hetero[8]circulenes and hetero[10]circulenes

([1]*Graduate School of Engineering, Kyoto University*) ○Aoi Nakagawa,[1] Yusuke Matsuo,[1] Shu Seki[1], Takayuki Tanaka[1]

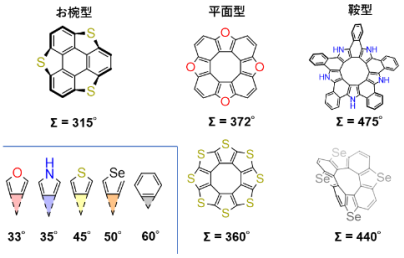
Heterocirculenes, which consist of circularly fused aromatic and/or heteroaromatic rings, have attracted much attention as heteroatom-doped nanographenes due to their optical and electronic properties. The structure of heterocirculene varies in bawl-, planar- and saddle-shaped depending on the sum of wedge angles (*Σ*) of the aromatic rings. We are challenging to synthesize new planar heterocirculenes, for example, tetraaza[8]circulene (**1**) and pentaoxapentaaza[10]circuelene (**2**). The former is expected to be applied for organic electronics due to the electron rich nature originating from the four pyrrole units and highly symmetric structure. The latter consists of pyrrole and furan, whose wedge angles are small, and thereby is expected to be planar by DFT calculation. The aromaticity of the central ten-membered ring is of particular interest. Albeit their expected planar structures, these circulenes should be soluble in THF by hydrogen bond between solvent molecules and NH site of pyrrole rings.

Keywords : Circulene; Hetero-nanographene

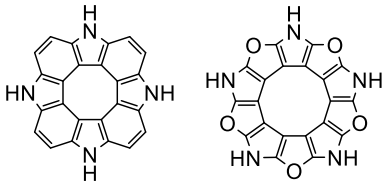
ヘテロールを含む複数の芳香環が環状に縮環した化合物はヘテロサーキュレンと呼ばれ，ヘテロ元素特有の性質を付与したナノグラフェン化合物として注目を集めている。その構造は構成する芳香環のくさび角の総和（Σ）よってお椀型，平面型，鞍型といった多様な形状へと変化する。我々は新たな平面型サーキュレンとしてテトラアザ[8]サーキュレン (**1**)とペンタオキサペンタアザ[10]サーキュレン (**2**) の合成を試みている。

テトラアザ[8]サーキュレンは，４つのピロール環によって電子豊富な化合物であり，対称性と平面性が高いことから，有機エレクトロニクスの優秀な素材となることが期待できる。

ペンタオキサペンタアザ[10]サーキュレンは，くさび角の小さいピロールとフランから構成されており，中心に十員環を持っているにもかかわらず平面構造をとると DFT 計算から予想され，平面十員環の芳香族性に関する実験的な検証が可能となる。また、外周部を向いた NH サイトが溶媒分子と水素結合することにより溶解性の向上が見込まれる。これらの目的分子の合成検討の結果について報告する。



既知のヘテロサーキュレンと構造



(1)　(2)

目的のヘテロサーキュレン
左）テトラアザ[8]サーキュレン(**1**)
右）ペンタオキサペンタアザ[10]サーキュレン(**2**)

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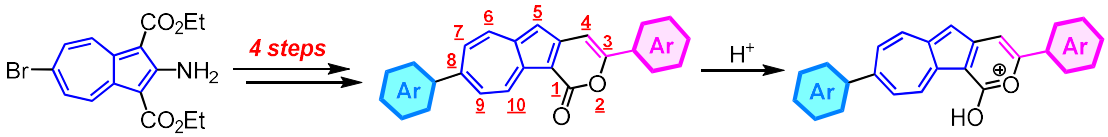
アズレノ[1,2-*c*]ピラン-1-オン類の合成と性質

(日大工[1]・信州大院総合理工[2]・弘前大院理工[3]) ○庄子 卓[1]・笹原 二千花[2]・関口 龍太[3]・伊東 俊司[3]
Synthesis and Properties of Azuleno[1,2-*c*]pyran-1-ones ([1] *College of Engineering, Nihon University*, [2]*Graduate School of Science and Technology, Shinshu University,* [3]*Graduate School of Science and Technology, Hirosaki University*) ○Taku Shoji,[1] Nichika Sasahara,[2] Ryuta Sekiguchi,[3] Shunji Ito[3]

Pyrones and their aromatic ring-fused derivatives have attracted considerable attention due to their biological activities and potential as advanced organic materials. However, effective synthesis of pyrone-fused azulene derivatives has not been reported. Recently, we have reported an efficient method for the preparation of pyrone-fused azulenes, i.e., azuleno[1,2-*c*]pyran-1-ones, by Brønsted acid-mediated intramolecular cyclization of 2-(arylethynyl)azulenes. The optical properties of azuleno[1,2-*c*]pyran-1-ones were investigated to found that azuleno[1,2-c]pyran-1-ones show remarkable spectral changes and fluorescence under acidic conditions, although they do not exhibit luminescence in neutral medium. We have developed a new synthetic method for azuleno[1,2-c]pyran-1-ones having aryl groups at the both 3- and 8-positions, as well as their optical properties.
Keywords : Azulene; Pyrone; Intramolecular cyclization; Cross-coupling; Fluorescence

ピロンやその芳香環縮合誘導体は、その多様な生物活性や先端有機材料の基礎骨格としての可能性から、大きな注目を集めている。しかしながら、アズレン環にピロンが縮環した誘導体の効率的合成法は報告されていなかった。近年、我々は Brønsted 酸をもちいた2-(アリールエチニル)アズレン類の分子内環化反応によるピロン縮環アズレン類、すなわちアズレノ[1,2-*c*]ピラン-1-オン類の効率的な合成法を報告した。さらにアズレノ[1,2-*c*]ピラン-1-オン類の光学的性質を検討したところ、中性溶液中では発光を示さないにもかかわらず、酸性条件下では顕著なスペクトルの変化と発光を示すことを明らかにした。[1]
アズレノ[1,2-*c*]ピラン-1-オン類の 3 位および 8 位にアリール基を有するアズレノ[1,2-*c*]ピラン-1-オン類の合成法を新たに開発し、それらの光学特性について検討した結果、興味ある知見が得られたため報告する。



Scheme. Synthesis of 3,8-Diarylazuleno[1,2-*c*]pyran-1-ones.

[1] T. Shoji, N. Sasahara, A. Hamasaki, S. Mori, T. Okujima, R. Sekiguchi, S. Ito, *J. Org. Chem.* **2023**, *88*, 15739–15749.

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ジエタノテトラセン部分を組み込んだピンセット型分子の合成

(愛媛大理[1]・愛媛大 ADRES[2]・愛媛大院理工[3]) ○青木　もえ[1]・竹花　諒介[1]・森　重樹[2]・髙瀬　雅祥[3]・奥島　鉄雄[3]・宇野　英満[3]
Synthesis of molecular tweezers bridged with diethanotetracene moiety (*[1]Faculty of Science, Ehime University,[2]Advanced Research Support Center (ADRES), Ehime University, [3]Graduate School of Science and Engineering, Ehime University*) ○Moe Aoki,[1] Ryosuke Takehana[1], Shigeki Mori,[2] Masayoshi Takase,[3] Tetsuo Okujima,[3] Hidemitsu Uno[3]

Molecular recognition is an ability to recognize specific molecule(s) through non-covalent interaction between host and guest molecule(s). It has been applied to solubilization and separation of poorly soluble molecules such as fullerenes and carbon nanotubes, and their optical resolution, and so on.

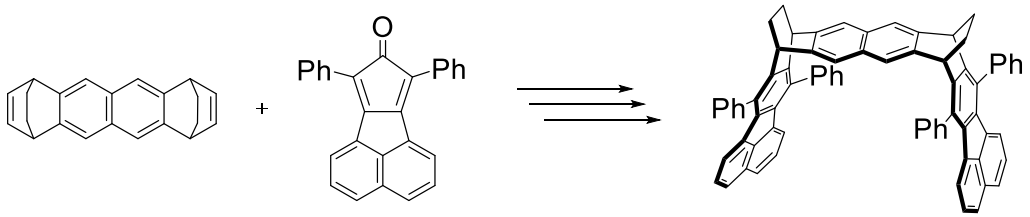
In our laboratory, we have developed π -conjugated compounds with bicyclo[2.2.2]octadiene (BCOD) moieties. Diporphyrins connected with two BCOD units were synthesized and their complexation behavior toward C_{60} and C_{70} were investigated.[1] The purpose of this study is to examine the effect of different angles formed by the bicyclic skeleton of tweezers-type molecules on their inclusion behavior. In this study, Diels-Alder reaction between diethanotetracene and cyclopentadienone compounds was carried out to construct molecule tweezers with BCOD moieties. Details of the synthesis will be presented.

Key Words ：molecular tweezers , molecular recognition, Diels-Alder reaction

分子認識とは、ホスト分子とゲスト分子の間で、非共有結合的な相互作用が働くことによってある特定の分子を認識する機能のことである。フラーレンやカーボンナノチューブなどの溶解性が低い分子の可溶化や分離、光学分割などに応用されている。

当研究室では、これまでビシクロ[2.2.2]オクタジエン(BCOD)部位を持つ二環性化合物の合成および物性調査を行ってきた。２つの BCOD ユニットをスペーサーとして連結したポルフィリン二量体の合成を報告しており、フラーレン類(C_{60},C_{70})と 1:1 で錯形成することを明らかとしている。[1] 本研究では二環性骨格の成す角度の違いによる包摂化挙動への影響を調査することを目的とした。今回は BCOD 骨格を組み込んだピンセット型分子を構築するため、ジエタノテトラセンとシクロペンタジエノン化合物との Diels-Alder 反応を行った。当日は合成の詳細を発表する。

[1] (a) H. Uno *et al*., *J. Porphyrin. Phthalocyanine.*, **2011**, *15*, 951-963. (b) S. Mori, N. Kawamoto, H. Uno, *ChemPlusChem*, **2019**, *84*, 686-693.



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プロペラキラリティーを有するπ電子系の合成と光学特性

（愛媛大理[1]・愛媛大院理工[2]・愛媛大 ADRES[3]）○菅野優海[1]・森 重樹[3]・奥島鉄雄[2]・宇野英満[2]・髙瀬雅祥[2]
Synthesis and optical properties of π-electron systems with propeller chirality (*[1]Faculty of Science, [2]Graduate School of Science and Engineering, [3]Advanced Research Support Center (ADRES), Ehime University*) ○Yumi Sugano,[1] Shigeki Mori,[3] Tetsuo Okujima,[2] Hidemitsu Uno,[2] and Masayoshi Takase[2]

Due to the applications in 3D displays, optical communications, etc., synthesis of circularly polarized luminescent (CPL) molecules with high luminescence and high anisotropy has been explored. Hexacarbazolylbenzene **1** (Figure 1a), composed of luminescent carbazoles, has a propeller structure but does not exhibit propeller chirality due to equilibrium between right-handed and left-handed conformation.[1,2] In this study, we synthesized carbazole oligomers with point or plane chiral sources and evaluated their chiral optical properties.

Synthesis of the target compounds **2** was performed using a stepwise aromatic nucleophilic substitution (S_NAr) reaction for hexafluorobenzene (Figure 1b). The synthesized **2** gave circular dichroism (CD) and circular polarized luminescence (CPL) with reversed positive and negative values depending on the chirality introduced.

Keywords : Hexaarylbenzene; Propeller chirality; S_NAr reaction; Circular dichroism; Circularly polarized luminescence

3D ディスプレイ、光通信などへの応用が期待されることから、高発光かつ高異方性を示す円偏光発光 (CPL) 物質が模索されている。発光性のカルバゾールから構成されるヘキサカルバゾリルベンゼン **1** (Figure 1a) は、プロペラ構造を有するが、右巻きと左巻きの平衡状態にあるため、プロペラキラリティーを示さない[1,2]。そこで本研究では、点不斉ならびに面不斉源を導入したカルバゾールオリゴマーを合成し、そのキラル光学特性について評価した。

目的化合物 **2** の合成は、ヘキサフルオロベンゼンに対する段階的な芳香族求核置換 (S_NAr) 反応を用いて行った。まず不斉源を有する置換基を導入し、その後カルバゾールを導入した (Figure 1b)。合成した **2** は不斉源のキラリティーに応じて正負が逆転した円二色性 (CD) ならびに円偏光発光 (CPL) を与えた。発表では **2** の合成、キラル光学特性について報告する。

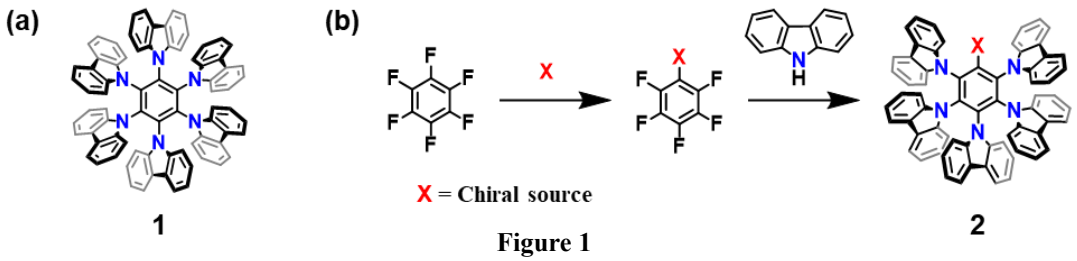

Figure 1

[1] J. J. Piet *et al.*, *Chem. Phys. Lett.* **1998**, *289*, 13-18.
[2] T. Kosaka *et al.*, *J. Phys. Chem. A.*, **2018**, *122*, 7455-7463.

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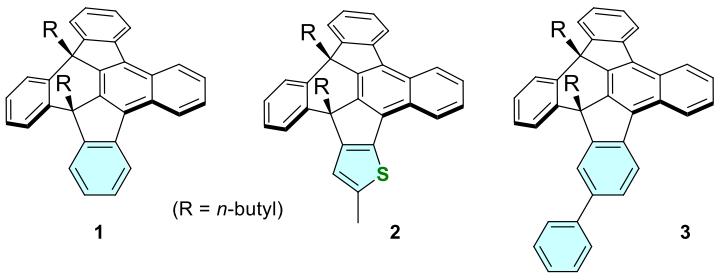
チオフェン縮環テトラセンの合成と反応

（阪工大工）○百々 佳輝・坪井 由衣・村田 理尚
Synthesis and Reaction of Thiophene-fused Tetracene (*Faculty of Engineering, Osaka Institute of Technology*) ○Dodo Yoshiki, Yui Tsuboi, Michihisa Murata

We have recently reported that a polycyclic aromatic hydrocarbon, which contains fully unsaturated five-membered rings, possesses high electron affinity and was found to undergo addition reaction with *n*-butyllithium. This reaction led to the formation of 1,4-addition compound with strong emission behavior attributable to the excimer in the solid state. We have also reported that a domino Scholl reaction occurs between tetracene and six molecules of benzene in one pot to furnish an aromatic compound with a curved π-system. Herein, we studied concise synthesis of the curved π-systems with thiophene or biphenyl moieties and examined their photophysical properties in the solid-state.
Keywords : Tetracene, Scholl Reaction, Dehydrogenative Coupling, Polycyclic Aromatic Hydrocarbon, Direct Functionalization

5 員環を含む多環芳香族炭化水素は，高い電子受容性に基づく特異な反応を示し，湾曲したπ共役系をもつ固体発光性分子に変換することができる [1-4]。化合物 **1** はエキシマー形成に基づく高効率な黄色の固体発光を示すことを先に報告した [1]。本研究では固体発光特性に関するさらなる知見を得るために，**1** のベンゼン環部位をチオフェン環またはビフェニル構造に変換した化合物 **2** および **3** をそれぞれ合成し，蛍光特性を検討した。



得られた化合物 **2** および **3** はトルエン溶液中において青色の類似した蛍光を示したのに対し，固体状態ではそれぞれ橙色および青色の異なる蛍光を示した。この結果は，**3** が粉末状態において主としてモノマーからの発光を示すことを示唆している。さらに，粉末状態の **3** の蛍光はボールミルを使用した機械的刺激により黄色に変化することを見出した。

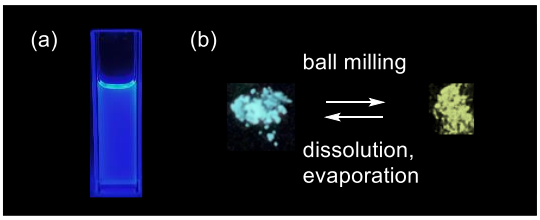


Figure 1. The pictures of (a) the toluene solution and (b) powders of **3** with irradiation at 365 nm bofore and after the ball milling.

1) Chaolumen, M. Murata, Y. Sugano, A. Wakamiya, Y. Murata, *Angew. Chem. Int. Ed.* **2015**, *54*, 9308.
2) M. Murata, M. Togo, D. Mishima, A. Harada, M. Muraoka, *Org. Lett.* **2020**, *22*, 4162.
3) D. Mishima, H. Nakanishi, Y. Tsuboi, Y. Kishimoto, Y. Yamanaka, A. Harada, M. Togo, Y. Yamada, M. Muraoka, M. Murata, *Org. Lett.* **2021**, *23*, 7921.
4) K. Ueda, H. Nakanishi, Y. Tsuboi, M. Murata, *J. Synth. Org. Chem. Jpn.* **2022**, *80*, 930.

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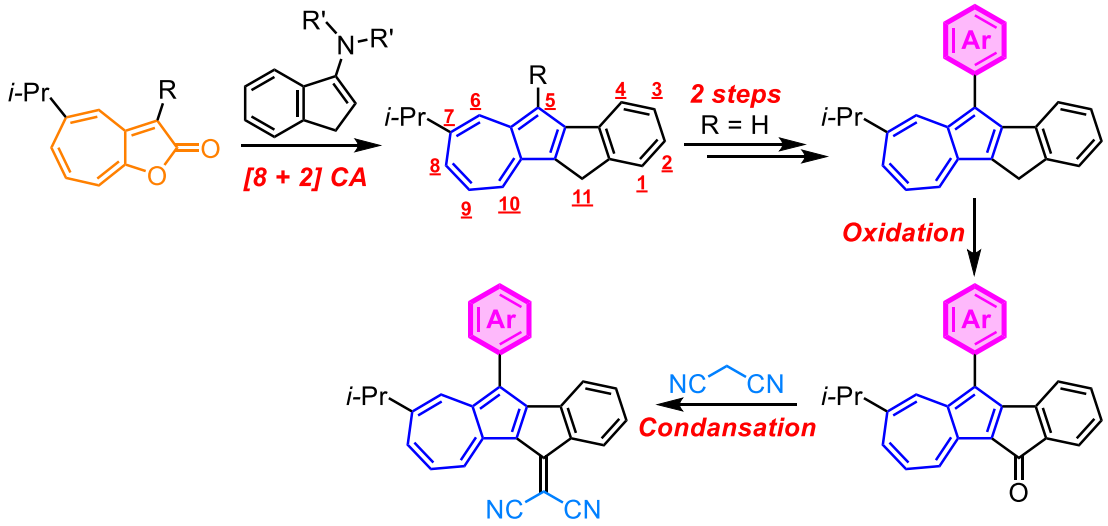
アズレノ[2,1-a]アズレン類の合成と反応性

(日大工) ○岩渕　正恭・庄子 卓
Synthesis and reactivity of indeno[2,1-a] azulenes (*College of Engineering, Nihon University*)
○ Masayuki Iwabuchi, Taku Shoji

Indenes, fluorenes, and their derivatives have attracted much attention as advanced organic materials. In this study, we have accomplished the synthesis of novel fused azulenes, in which indene and indenone are fused to the azulene ring. Indeno[2,1-*a*]azulenes were prepared by [8 + 2] cycloaddition reaction of 2*H*-cyclohepta[*b*]furan-2-ones with enamines prepared from 1-indenone. Various aryl groups were introduced into the 5-position of these derivatives, and then the 11-position was oxidized to obtain indenone-fused azulene derivatives. These were converted to dicyanofulvene derivatives by condensation reaction with malononitrile. The optical and electrochemical properties of these novel compounds were also evaluated.
Keywords : Azulene; Indene; Fluorenes; Fulvene; Electrochemistry

インデンやフルオレンおよびそれらの誘導体は、先端有機材料の骨格として大きな注目を集めている。本研究では、アズレン環にインデン、インデノン、ジシアノフルベンが縮環した新規な縮環アズレン類を合成し、それらの反応性、光学特性および電気化学特性について検討を行った。2*H*-シクロヘプタ[*b*]フラン-2-オン類と 1-インデノンから調製したエナミンとの[8 + 2]環化付加反応 ([8 + 2] CA)により、インデノ[2,1-*a*]アズレン類を合成した。さらに 2 段階を経て 5 位へ種々のアリール基を導入したのち、11 位を酸化することでインデノン縮環アズレン誘導体を得た。これらはマロノニトリルとの縮合反応によってジシアノフルベン誘導体に変換することができた。これらの新規化合物について光学特性および電気化学特性の評価を行った結果、興味ある地検が得られたため報告する。



Scheme. Synthesis and Reactivity of Indeno[2,1-*a*]azulenes.

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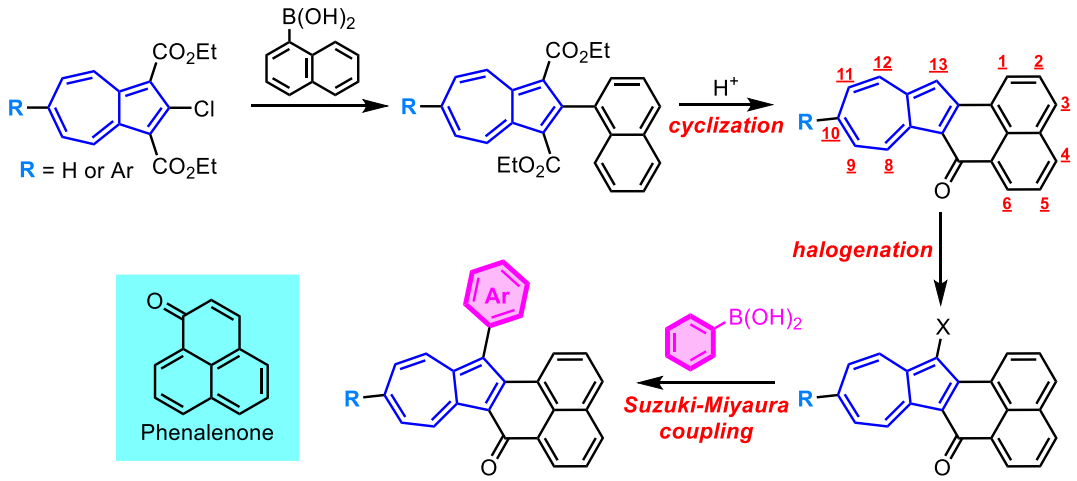
アリール基が置換したアズレン縮環フェナレノン類の合成研究

(日大工) ○石川　龍之介・庄子　卓
Synthetic study of azulene -fused phenalenons bearing the arly substituent (*College of Engineering, Nihon University*) ○Ryunosuke Ishikawa, Taku Shoji

Polycyclic aromatic compounds (PAHs) have attracted much attention as the advanced organic materials. In this study, synthesis of azulene-fused phenalenones with an aryl goup were investigated, as well as their reactivity, optical and electrochemical properties. 2-Naphthylazulene derivatives were prepared by Suzuki-Miyaura coupling reaction of 2-chloroazulene derivatives bearing two ester functions with 1-naphthaleneboronic acid. Intramolecular cyclization reactions of these derivatives with Brønsted acids gave azulene-fused phenalenones. Furthermore, these halogenation reactions of the compounds at the 13-position, followed by Suzuki-Miyaura coupling reactions with various arylboronic acids, afforded corresponding coupling products. Azulene-fused phenalenones with an aryl group at the 10-position were also synthesized. The optical and electrochemical properties of these novel compounds were investigated.
Keywords : Azulene; Phenalenone; Fluorescence; Electrochemistry

多環式芳香族化合物 (PAHs)は、先端有機材料の骨格として大きな注目を集めている。本研究では、アリール基を有するアズレン環にフェナレノンが縮環した新奇な縮環アズレン類を合成し、それらの反応性、光学特性および電気化学特性について検討を行った。エステル基を有する 2-クロロアズレン誘導体と 1-ナフタレンボロン酸との鈴木-宮浦カップリング反応により、2-ナフチルアズレン誘導体を合成した。これらのブレンステッド酸を用いた分子内環化反応により、アズレン縮環フェナレノン類を得た。さらにハロゲン化反応と続く種々のアリールボロン酸との鈴木-宮浦カップリング反応により 13 位のアリール化を行った。10 位にアリール基を有するアズレン縮環フェナレノン類についても同様に合成した。これらの新奇化合物について光学特性および電気化学特性の評価を行った結果、興味ある知見が得られたため報告する。



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9，10 位にアリール基を有するテトラアリールフェナントレン誘導体の合成と光機能特性

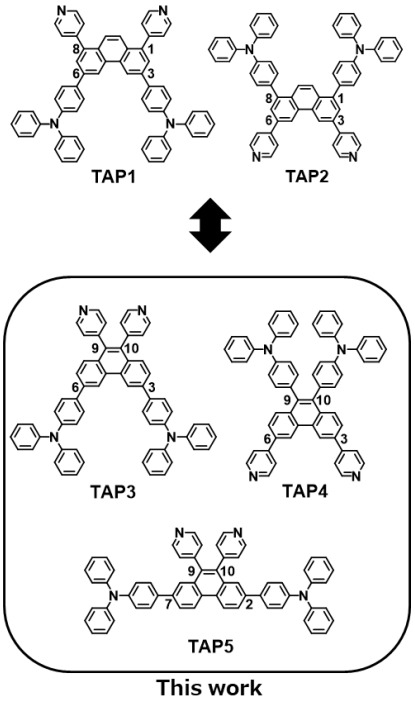
（兵庫県立大院工）○渡 琢朗・川瀬 毅・西田 純一

Synthesis and photo-functional properties of tetraarylphenanthrene derivatives having aryl groups at 9,10-positions (*Graduate School Of Engineering, University of Hyogo*) ○Takuro Wataru, Takeshi Kawase, Jun-ichi Nishida

Phenanthrene is a π-conjugated unit having two different environments on its concave and convex sides, and it can be converted into various compounds for using in organic electronics. So far, we have prepared phenanthrene derivatives with bromo and chloro groups at 1,3,6,8-positions, and synthesized tetraarylphenanthrene (TAP) derivatives (**TAP1** and **TAP2**) by stepwise introduction of aminophenyl or pyridyl groups.[1] In this study, at first, we prepared phenanthrene derivatives with aryl groups at the 9,10-positions, and then introduced next aryl groups at 3,6- or 2,7- positions to give TAP derivatives (**TAP3**, **TAP4**, and **TAP5**). We have investigated the difference of their photoluminescent and electrochemical properties depending on the different aryl substitution patterns.

Keywords: phenanthrene; fluorescence molecule; donor-acceptor compound; mechanochromic luminescence; electrochromism

フェナントレンは、凹側と凸側で異なる環境を持つ π 電子ユニットであり、π 拡張させることで有機エレクトロニクスに利用可能な様々な化合物に変換できる。これまでに 1,3,6,8 位にブロモ基やクロロ基を導入したフェナントレンを基に、アミノフェニル系電子ドナー基やピリジル基を段階的に導入したテトラアリールフェナントレン（TAP）誘導体（**TAP1**, **TAP2**）を得ている。[1] 本研究では、9,10 位にアリール基を最初に導入し、続けて 3,6 位や 2,7 位を修飾した化合物（**TAP3**, **TAP4**, **TAP5**）の合成を行った。導入するアリール基の違いや置換位置の違いにより、それぞれの化合物が示す発光特性、電気化学的特性について比較検討を行った。



1） *Asian J. Org. Chem.*, **2022**, *11*, e202100789.

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Intramolecular Bi/Sb/As-O Noncovalent Interaction for Enhanced Planarity of Bibenzofurans

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Keywords: Bismuth; Noncovalent Interaction; Conformational Lock

Intramolecular noncovalent interactions are of interest as a convenient method to enhance the molecular planarity via conformational locks, which can readily reduce the band gaps. Recently, it was demonstrated that a P-substituted bibenzofuran showed enhanced planarity via noncovalent P···O interactions.[1] However, the introduction of heavier elements may result in stronger noncovalent interactions.

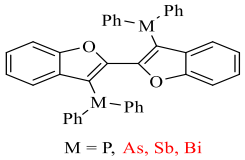

Figure 1 Structure of Group 15 element substituted bibenzofurans.

In this presentation, we report the synthesis of Bi-, Sb-, and As-substituted bibenzofurans. The single crystal X-ray diffraction study revealed the presence of attractive intramolecular noncovalent Bi···O, Sb···O, and As···O interactions, which enhanced the self-planarization and rigidification of the π-conjugated systems. Computer simulation was also performed to support the noncovalent interactions. The experimental data and the DFT calculations revealed the stronger noncovalent interactions of bismuth- and antimony-substituted bibenzofurans than those reported previously for BFP. In addition, the absorption spectra were red-shifted as a result of enhanced conjugation due to the higher planarity owing to these interactions. It is noteworthy that bismuth, antimony, and arsenic atoms may provide both intermolecular and intramolecular interactions in the solid state, likely leading to, ultimately, improved device performance. In contrast, no evident interactions were observed in the bibenzothiophene congemers

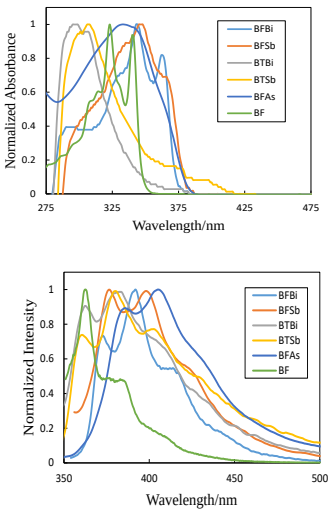

Figure 2 Absorption (top) and PL spectra (bottom) of Group 15 element substituted bibenzofurans and bibenzothiophenes in dichloromethane. Ref.2. *Copyright © 2023, American Chemical Society*

1) C. Wang, Z. Gao, W. Sun, X. Guo, F. Zhang, *Dyes and Pigments*. **2021**, *184*, 108820. 2) C. Wang, A. Sumida, Y. Adachi, H. Imoto, K. Naka, J. Ohshita, *Organometallics*. **2023**, *42*, 3397.

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ジセレニド結合を利用したσ非局在電子系の拡張

（埼玉大院理工[1]）○小西 恭輔[1]・古川 俊輔[1]・斎藤 雅一[1]
Expansion of a σ-Delocalized System Using a Diselenide Bond ([1]*Department of Chemistry, Graduate School of Science and Engineering, Saitama University*,) ○Kyosuke Konishi,[1] Shunsuke Furukawa,[1] Masaichi Saito[1]

Electron delocalization is one of the most important fundamental phenomena in chemistry, and π-delocalization, in which electrons are delocalized on a bond axis, has mainly been studied. On the other hand, the use of σ-symmetry orbitals enables electronic delocalization (σ-delocalization) between non-bonded atoms. We have found that six selenyl groups on the periphery of a benzene ring produce σ-symmetric delocalized orbitals (Figure 1).[1)] Considering the history of the expansion of π-delocalization, expansion of σ-delocalization is of considerable importance. In this work, we have designed and synthesized compound **2** bearing two σ-delocalized systems connected by a diselenide bond (Scheme 1). Further expansion of the σ-delocalization in compound **2** is also reported.
Keywords : σ delocalization; π delocalization; diselenide; chalcogen

電子の非局在化は化学において重要な現象の一つであり、これまで主に結合軸上で電子が非局在化する π 非局在化が研究されてきた。一方、結合をもたない原子上で可能になる電子の非局在化（σ 非局在化）に関する研究例は限られている。当研究室は、ベンゼン環周縁部に 6 個のセレニル基を有する化合物 **1** において結合をもたないセレン原子上に σ 対称性の軌道が広がり、σ 非局在化が可能であることを見いだしている（**Figure 1**）[1)]。π 非局在系を拡張する研究に対応して、σ 非局在系を拡張する試みは基礎化学的に重要である。そこで本研究では、6 個のセラニル基を有するベンゼンどうしをジセレニド結合で連結させた分子 **2** を設計・合成した（**Scheme 1**）。また化合物 **2** を鍵分子としてさらなる σ 非局在電子系の拡張を検討したので、併せて報告する。

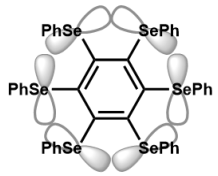
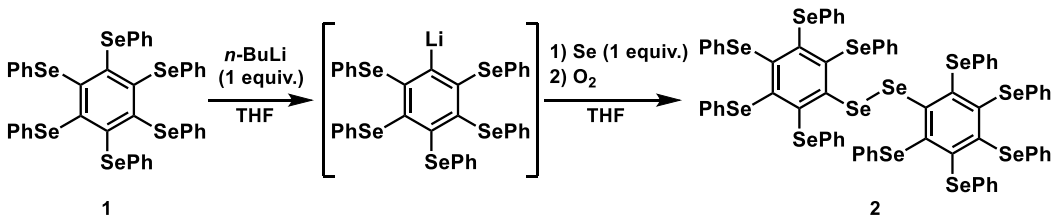


Figure 1 σ-Delocalized system developed by our group.

Scheme 1 Synthesis of expanded σ-delocalized diselenide **2**.



1 2

1) (a) Saito, M.; Kanatomi, Y. *J. Sulfur Chem.* **2009**, *30*, 469; (b) Hatanaka, M.; Saito, M.: Fujita, M.; Morokuma, K. *J. Org. Chem.* **2014**, *79*, 2640; (c) Furukawa, S.; Fujita, M.; Kanatomi, Y.; Minoura, M.; Hatanaka, M.; Morokuma, K. Ishimura, K.; Saito, M. *Commun. Chem.* **2018**, *1*, 60; (d) Saito, M.; Suzuki, T.; Takahashi, K.; Seko, S.; Furukawa, S.; Ishimura, K. *Chem. Lett.* **2023**, *52*, 97.

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σ非局在電子系を有する分子の単分子電気伝導度

(埼玉大院理工[1]・東工大理学院[2]) ○瀬古 紗弥[1]・藤井 慎太郎[2]・斎藤 雅一[1]

Single-Molecule Conductances of Compounds Bearing σ-Delocalized Systems

([1]*Department of Chemistry, Graduate School of Science and Engineering, Saitama University*, [2]*Department of Chemistry, Graduate School of Science, Tokyo Institute of Technology*) ○Saya Seko,[1] Shintaro Fujii,[2] Masaichi Saito[1]

We have fabricated a single-molecule junction composed of a benzene derivative, the carbon atoms of which are substituted by selenium functionalities, and succeeded for the first time in the measurement of a single-molecule conductance arising from a conduction path composed of σ-delocalized orbitals on non-bonded selenium atoms.

Keywords : σ-delocalized system; selenium; single-molecule conductance; benzene skeleton

金属電極間を一分子で架橋した単一分子接合は、その架橋分子の電子状態に応じて電流が変化する究極に小さい電子デバイスとして興味深い。これまで架橋分子としては、主に結合軸方向に広がるπ非局在電子系が用いられているが、結合のない原子間上に広がるσ非局在電子系を用いた例はなく、その効果を評価することは基礎化学的に興味深い。これまで当研究室は、ベンゼン環に 6 個のセレン原子官能基が導入された化合物がベンゼン環周縁部に σ 非局在電子系を有することを明らかにしている（Fig. 1）。そこで今回、結合をもたないセレン原子どうしの相互作用によって構築されるσ非局在軌道による電気伝導パスを評価する目的で、この分子を架橋分子とする単一分子接合を作製し、その電気伝導度を測定した（Fig. 2）。

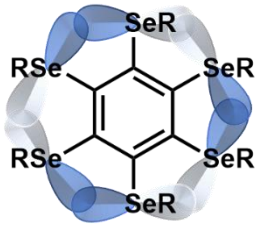
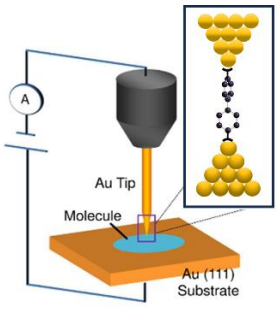
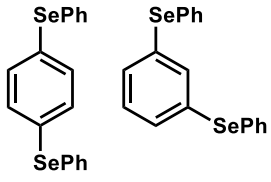


Figure 1. Compounds bearing σ delocalized systems (R = Ph (**1**); Me (**2**)).

まず、セレン上の置換基が Ph 基の化合物 **1** を架橋分子とすることを試みたところ、セレン原子は電極に接合せず、換わりにフェニル基が接合した。セレン原子が電極に接合しなかったのはフェニル基の立体障害のためであると考えられる。そこで、置換基をメチル基に換えた化合物 **2** を架橋分子としたところ電極とセレン原子が観測され、そのコンダクタンスは $1.4\times10^{-2}\ G_0$（$G_0 = 2e^2/h$）であった。一方参照化合物として σ 非局在電子系をもたない PhSe 二置換ベンゼンのコンダクタンスを測定したところ、パラ置換体 **3** では $7\times10^{-3}\ G_0$、メタ置換体 **4** では $2\times10^{-3}\ G_0$ であった。つまり σ 非局在軌道を電気伝導パスとすることにより、分子の電気伝導度が向上することを明らかにした。





3 **4**

Figure 2. Single-molecule junction between Au electrodes and reference compounds **3** and **4**.

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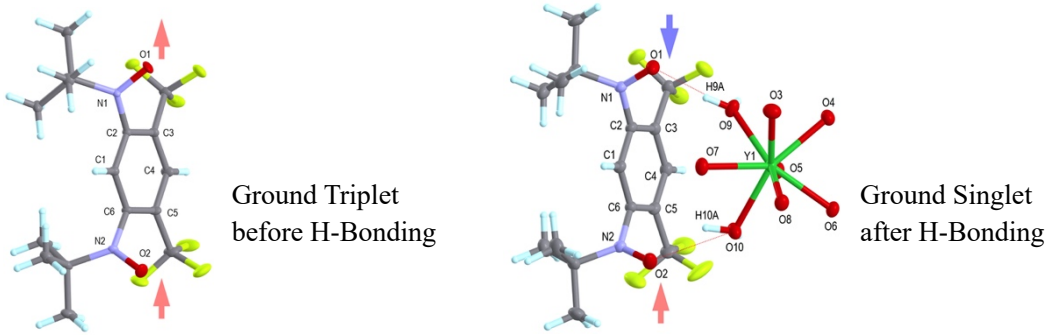
水素結合を利用した共鳴の立体禁止によるビラジカルの三重項/一重項基底状態のスイッチング

（電通大[1]）○石田　尚行[1]・芳賀　凪斗[1]
A triplet/signlet ground-state switch due to π-conjugation prohibition triggered by hydrogen bonding ([1]*The University of Electro-Communications*) ○Takayuki Ishida,[1] Nagito Haga[1]

Ground triplet 4,6-bis(trifluoromethyl)-1,3-phenylene bis(*tert*-butyl nitroxide) (TF2PBN) reacted with $[Y(hfac)_3(H_2O)_2]$, affording a doubly hydrogen-bonded adduct $[Y(hfac)_3(H_2O)_2$-(TF2PBN)]. Crystallographic analysis clarified that the torsion angle between the benzene ring and nitroxide groups was 79.9° in the adduct, which is larger than that of intact TF2PBN (59.3°). Susceptometry of the adduct indicated a ground singlet state with $2J/k_B = -128(2)$ K. DFT calculations (UB3LYP/6-311+G(2d,p)) gave $2J/k_B = -162.3$ K for the adduct and +87.2 K for intact TF2PBN. The relationship between the ground spin state and torsion angle will be discussed after comparison among a few known *m*-phenylene bisnitroxides.
Keywords: diradical; singlet-triplet equilibrium; aminoxyl; π conjugation; exchange interaction

基底三重項の 4,6-bis(trifluoromethyl)-1,3-phenylene bis(*tert*-butyl nitroxide) (TF2PBN; 下図左) と反磁性の $[Y(hfac)_3(H_2O)_2]$ から，ラジカル酸素原子と配位水が水素結合した $[Y(hfac)_3(H_2O)_2(TF2PBN)]$ を得た（下図右）．エタノールを用いた再結晶によりこの付加体から TF2PBN を回収できた．結晶構造解析によると TF2PBN のベンゼン環とニトロキシド基間のねじれ角（$|\theta| \leq 90°$）は，水素結合後では平均 79.9°であり，未反応の TF2PBN の 59.3°よりも大きく，非平面性が顕著になっていた．２つの水素結合による変形がπ共役性を低下させている．磁気解析は水素結合後の TF2PBN が $2J/k_B = -128(2)$ K の基底一重項であることを示した．この傾向は Rajca らの先行研究と定性的に一致している [1]．付加体の DFT 計算 (UB3LYP/6-311+G(2d,p)) は $2J/k_B = -162.3$ K を与えたが、対応する未反応 TF2PBN の計算結果は $2J/k_B = +87.2$ K であった. いくつかの既知の化合物と比較した結果, $2J$ とねじれ角 $|\theta|$ の間に相関が見られ，強磁性／反強磁性的相互作用を決する臨界角は 65(3)°と見積もられた．TF2PBN では J に対する強磁性的と反強磁性的な相互作用の寄与が均衡しており，水素結合のような小さな構造摂動によって基底状態のスイッチングが可能になったと考えられる [2].



Ground Triplet before H-Bonding　　Ground Singlet after H-Bonding

1) Rajca, A. et al. *Polyhedron* **2001**, *20*, 1669. 2) Haga, N. et al. *Molecules* **2024**, *29*, 70.

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2, 5, 8-トリブロモフェナレニルラジカルの合成と物性

（阪大院理）○岸本昌也・杉田圭・西内智彦・久保孝史

Synthesis and Properties of 2, 5, 8-tribromophenalenyl radical

(*Graduate School of Science, Department of Chemistry, Osaka University,*) ○Masaya Kishimoto, Kei Sugita, Tomohiko Nishiuchi, Takashi Kubo

One-dimensional chains of organic radical species have been theoretically predicted and studied to exhibit metallic behavior due to the appearance of half-filled bands. In this study, we designed Br-PLY, in which a polarizing substituent, bromo group, is introduced into the phenalenyl (PLY) skeleton to construct a one-dimensional organic radical aggregate (Figure 1). The aim is to achieve infinite stacking of molecules (Figure 2). Halogen-halogen interactions of Br groups between different one-dimensional chains may also contribute to control the integrated structure (Figure 2). X-ray crystallography of black crystals obtained by recrystallization from toluene-benzene solution showed that Br-PLY has a π-dimer structure, but no interaction between one-dimensional chains or Br groups was confirmed.

We are currently investigating recrystallization methods and attempting to obtain crystals of one-dimensional chains.

Keywords : radical, phenalenyl skeleton, 1D-chain, spin-spin interaction

有機ラジカル種が一次元的に積層した集積体は、半充填バンドの出現により金属的な挙動を示すことが理論的に予測され、研究されてきた。本研究では、有機ラジカル一次元集積体構築を目的として、フェナレニル(PLY)骨格に分極性の置換基であるブロモ基を導入した **Br-PLY** を設計し、目的分子とした(図 1)。Br 基が負に、PLY 環上の水素が正に帯電し、π ダイマー間に静電引力が生じることを利用して分子を無限積層させることを狙いとした(図 2)。また、異なる一次元鎖間における Br 基同士のハロゲン―ハロゲン相互作用により、集積化構造の制御に寄与することが考えられる(図 2)。既知化合物であるフェナラノンを出発物質として 4 ステップの合成経路を経て **Br-PLY** の合成及び単離に成功し、ESR 測定によってラジカル種であることが確認できた。トルエン-ベンゼン溶液から再結晶することで得た黒色の結晶の X 線結晶構造解析によって **Br-PLY** は π ダイマーの構造をとっていたことがわかった。

現在、再結晶の方法について検討を行い、一次元鎖の結晶を得ることを試みている。

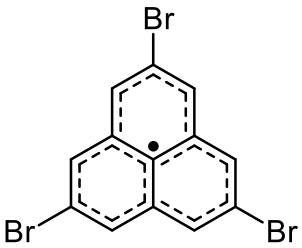
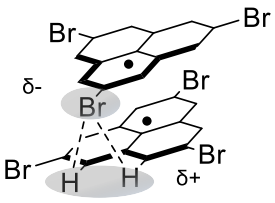


図 1.**Br-PLY**



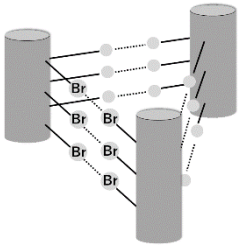


図 2.静電相互作用を利用した **Br-PLY** の重なりとハロゲン―ハロゲン相互作用による集積化

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ジアルキルアミド基の導入によるトリオキソトリアンギュレン大環状オリゴマーの可溶化

（愛工大院工[1]・愛工大工[2]）○早崎 真治[1]・村田 剛志[2]・森田 靖[2]
Solubilization of Trioxotriangulene Macrocyclic Oligomer by Dialkylamido Groups
([1]*Graduate School of Engineering, Aichi Institute of Technology*, [2]*Faculty of Engineering, Aichi Institute of Technology*) ○Shinji Hayasaki,[1] Tsuyoshi Murata,[2] Yasushi Morita[2]

Trioxotriangulene (**TOT**) neutral radical is a fused polycyclic air-stable neutral radical, having a highly delocalized electronic-spin structure on the 25π-electronic system. Recently we synthesized π-conjugated macrocyclic oligomers of **TOT** having a large cavity. However, these compounds have a poor solubility toward common organic solvents. In order to improve their solubility, we have newly designed and synthesized macrocyclic **TOT** oligomer having dialkylamido groups and succeeded in improvement of the solubility. Here, we will report on the solution-state physical properties of the dialkylamino-substituted macrocyclic **TOT** pentamer pentaanion.

トリオキソトリアンギュレン (**TOT**, 図 1) は、我々が独自に開発した縮合多環型の安定有機中性ラジカルであり、25π 電子系に広く非局在化した電子スピン構造を有している[1]。我々はこれまでに **TOT** 骨格を直接連結した巨大空孔をもつπ共役型大環状オリゴマーを合成した[2]。しかし、この化合物は難溶性であり溶液状態での物性測定が困難であった。そこで本研究では、**TOT** 大環状オリゴマー周辺にアルキル側鎖を導入することで可溶化させる手法を考えた。今回は、骨格周辺部にジアルキルアミド基で修飾した **TOT** 大環状五量体のペンタアニオン体 (図 2) について各種溶液物性を調べたので報告する。

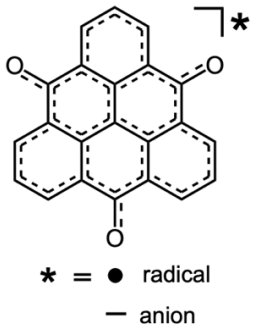

図1. トリオキソトリアンギュレン (TOT)

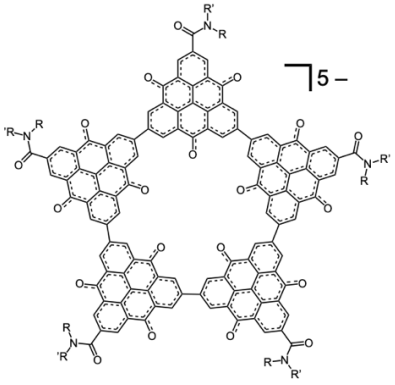

図2. ジアルキルアミド基を導入した TOT 環状五量体ペンタアニオン体

[1] Y. Morita, T. Murata, A. Ueda, T. Takui, et al. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 922, 他
[2] a) 鵜飼修作・村田剛志・森田 靖, *第 49 回中部化学関連学協会支部連合秋季大会*, 2018 年, b) 村田剛志・鵜飼修作・奥田裕貴・森田 靖, *第 52 回 中部化学関係学協会支部連合秋季大会*, 2021 年, c) 早崎真治・村田 剛志・森田 靖, *第 33 回基礎有機化学討論会*, 2023 年

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日本化学会 第104春季年会 (2024)

ガルビノール置換チオフェン化合物の合成・構造とハロクロミズム

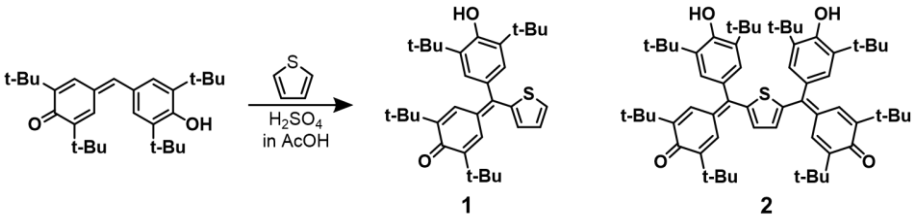
（城西大院理）　若林 勇希・秋田 素子

Synthesis, Structure and Halochromism of Galvinol-Substituted Thiophene Compounds (*Graduate School of Science, Josai University*) Yuki Wakabayashi and Motoko Akita

Stable organic radicals are of great interested in not only fundamental chemistry but also material science. The highly reversible redox properties of organic radicals are due to the formation of closed-shell species when they are oxidized or reduced. As compared with closed-shell molecules, longer-wavelength absorptions and emissions based on SOMO/HUMO or LUMO/SOMO transition are also typical properties of organic radicals. For these reasons, organic radicals are candidates for fundamental materials for electronic devices. We present here the synthesis, structure and halochromism of new galvinol derivertives that serve as precursors for the generation of galvinoxyl radicals. Reaction of galvinol and thiophene in acetic acid with catalytic amount of sulfric acid gave five components. Three compounds were identified by MS and/or NMR spectra in which the 2 or 2,5- or 2,3,5- positions of the thiophene ring were substituted with galvinol. The structure of mono and di substituted compounds were also determined by single crystal X-ray structure analysis. Halochromism of **1** and **2** was confirmed.

Keywords : Galvinol, Thiophene, Precursors of Galvinoxyl, Halochromism

有機ラジカルは酸化・還元において比較的安定な一重項閉殻種であるカチオンやアニオンを生成するため、酸化還元の可逆性が高い。また、吸収・発光に伴う電子遷移はLUMO-SOMO/SOMO-HOMO 遷移であるため吸収・発光波長は閉殻種に比べ超波長にシフトする。これらの特徴を活かし二次電池や半導体、有機 EL 素子、有機太陽電池などの材料に有機ラジカルを活用する研究が近年盛んに行われている。本研究ではラジカルの前駆体であるガルビノールをチオフェンに複数置換させた化合物を合成し、その構造、物性を検討した。酢酸中硫酸触媒を用いてガルビノールとチオフェンと縮合させることにより一置換体 **1**、二置換体 **2** が得られた。これらの構造を MS, NMR スペクトル及び単結晶 X 線構造解析により決定した。中性及び塩基性条件下での UV-Vis 測定により、**1**, **2** のハロクロミズムを示すこと確認した。



Scheme 1

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テトラセンイミドとローソン試薬との反応に関する研究

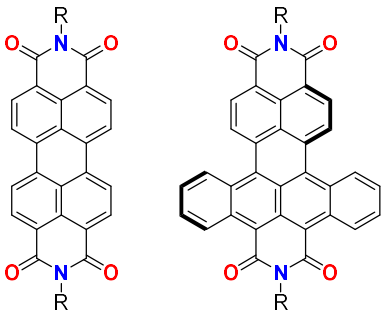
（阪工大工）○平井 慎剛・伊藤 巧夢・村田 理尚

Studies on the Reaction between Tetracene Imide with Lawesson's Reagent ([1]*Osaka Institute of Technology*) ○Shingo Hirai, Takumu Ito, Michihisa Murata

Perylene bisimides (PBIs) have been extensively investigated in the past several decades as fascinating dyes with great potentials for various applications. We have previously synthesized electron deficient π-systems based on the dimerization of tetracene imide derivatives. In this work, the reaction of a tetracene imide derivative with Lawesson's reagent was studied. The structure of the obtained product was unambiguously characterized by single crystal X-ray analysis. The mechanism of the reaction as well as the electronic structure of the product will be discussed.

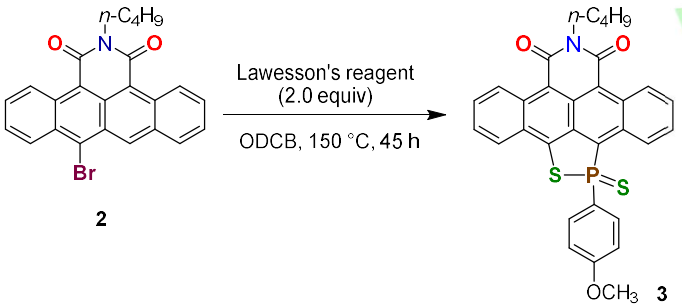
Keywords : Perylene Bisimide; n-Type Semiconductor; Tetracene; Lawesson's Reagent; X-ray Analysis

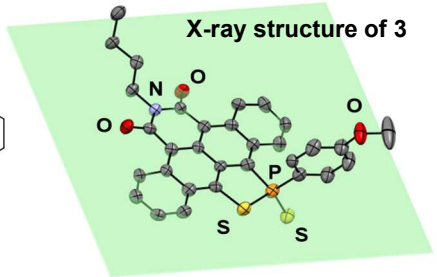
ペリレンビスイミド（PBI）は、優れた電子受容性を示す平面π共役化合物であり、n 型有機半導体材料として知られている。PBI に二つのベンゾ縮環構造を導入してテトラセン骨格を構築した化合物 **1** は、長波長領域に吸収帯を示すことが報告されている [1]。また、PBI やその類縁体のカルボニル基をチオカルボニル基に変換することにより、優れた電子受容性や長波長領域の吸収特性を示すことが報告されている [2]。本研究では、テトラセンイミドとローソン試薬との反応を検討し、得られた化合物の構造と性質を明らかにした。



まず、以前に報告された手法 [1]を用いてテトラセンイミドのブロモ体 **2** を合成した。次に、**2** とローソン試薬との反応を検討したところ，加熱条件下において、化合物 **3** が生成することを見出し，チオカルボニル化された生成物は観測されなかった。化合物 **3** の構造は単結晶 X 線構造解析により確認した。UV-vis スペクトル測定の結果、化合物 **3** の吸収帯 (λ_{abs} = 668 nm) はテトラセンイミド (λ_{abs} = 613 nm) と比較して 55 nm レッドシフトしていることがわかった。反応のメカニズムについても発表する。

Scheme 1





1. Chaolumen, H. Enno, M. Murata, A. Wakamiya, Y. Murata, *Chem. Asian J.* **2014**, *9*, 3136.
2. C. P. Yu, A. Yamamoto, S. Kumagai, J. Takeya, T. Okamoto, *Angew. Chem. Int. Ed.* **2023**, *62*, e202206417.

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ジチエノチアボリン骨格含有非フラーレンアクセプターの開発

（兵庫県大院工[1]・兵庫県大院理[2]）○木村 誠[1]・鈴木 航[1]・吾郷 友宏[2]・梅山 有和[1]

Development of Non-Fullerene Acceptors Containing Dithienothiaborin ([1]*Graduate School of Engineering, University of Hyogo*, [2]*Graduate School of Science, University of Hyogo*)

○Makoto Kimura,[1] Wataru Suzuki,[1] Tomohiro Agou,[2] Tomokazu Umeyama[1]

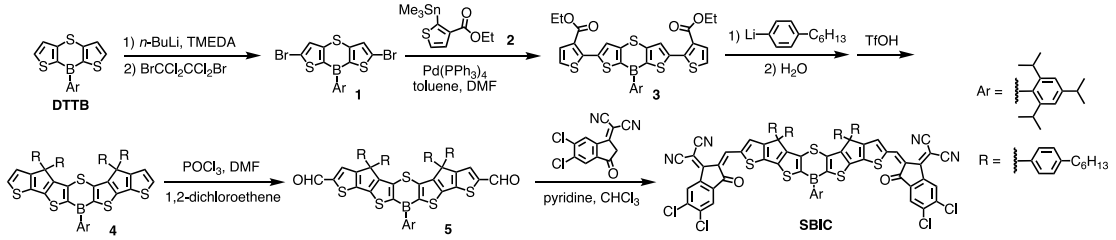
As a novel acceptor-donor-acceptor'-donor-acceptor (A-D-A'-D-A) type non-fullerene acceptor (NFA), we synthesized a novel NFA, SBIC, which has a dithienothiaborin (DTTB) as the central A' unit, thiophene units as the D units, and dichlorinated 1,1-dicyanomethylene-3-indanone as the terminal A units. The absorption and photoluminescence (PL) spectra of SBIC in chloroform showed peaks at 650 and 677 nm, respectively. The SBIC film exhibited red-shifted absorption and PL maxima at 688 and 790 nm, respectively. The optical bandgap estimated from the intersection of normalized absorption and PL spectra of the SBIC film was 1.74 eV. The LUMO energy level estimated by the differential pulse voltammetry measurement of the SBIC in chloroform was −3.91 eV.

Keywords : Nonfullerene Acceptor; Dithienothiaborin; Organic Photovoltaics; Conjugated Polymers

新規アクセプター(A)-ドナー(D)-アクセプター(A')-ドナー(D)-アクセプター(A)型非フラーレンアクセプターとして、A'骨格としてホウ素上にトリピル基を導入したジチエノチアボリン（DTTB）ユニット[1]、D 骨格にチオフェンユニット、A 骨格に塩素置換 1,1-ジシアノメチレン-3-インダノン（IC-Cl）を有する SBIC を設計し、合成を行った（Scheme 1）。まず DTTB をジブロモ化した化合物 **1** と化合物 **2** との Stille カップリングにより化合物 **3** を合成し、4-ヘキシルフェニルリチウムの求核付加反応と脱水縮環により化合物 **4** を合成した。さらに、Vilsmeier-Haack 反応によるビスホルミル化と、Knoevenagel 縮合による IC-Cl の導入により、SBIC を得た。

SBIC の希薄クロロホルム溶液の吸収および発光の極大波長は 650 nm および 677 nm であったが、薄膜化するとそれぞれ 688 nm および 790 nm まで長波長シフトした。薄膜での吸収と発光スペクトルの交点から見積もられるバンドギャップは 1.74 eV となった。また、微分パルスボルタンメトリー測定から見積もられた SBIC クロロホルム溶液中の LUMO 準位は−3.91 eV であった。

Scheme 1. Synthetic route for SBIC.



1) Yan, Y.; Sun, Z.; Li, C.; Zhang, J.; Lv, L.; Liu, X. Liu, X. *Asian J. Org. Chem.* **2017**, *6*, 496.

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Synthesis of Three-Dimensional Organic Boron Compounds with Unique Structure

(*Graduate School of Engineering, Nagoya Institute of Technology*) ○Kenshin Nakano, Katsuhiko Ono

Keywords: Organoboron Compound; *β*-Diketone; Three-Dimensional Structure; J-Aggregation; Organic Photovoltaics

Organoboron compounds have attracted attention as semiconductor materials that can be applied to organic photovoltaics (OPV) because of their excellent light absorption and electron transport capabilities. While semiconductor materials with planar structures have been extensively studied, there have been few studies on semiconductor materials with three-dimensional (3D) structures. In this study, we synthesized two types of 3D organoboron compounds, **3CB-ph** and **3CB-carph**, in which three boron *β*-diketonate moieties are bonded to a triphenylene moiety. Their photophysical and electrochemical properties were investigated in comparison to those of simple boron *β*-diketonate compounds.[1]

The UV/Vis spectra of **3CB-ph** and **3CB-carph** are shown in Fig. 1. The maximum absorption wavelength and molar absorption coefficient in solution were 610 nm and 298,000 M^{-1} cm^{-1} for **3CB-ph** and 523 nm and 184,000 M^{-1} cm^{-1} for **3CB-carph**, respectively. For both compounds, the corresponding absorption bands were redshifted in the thin films, suggesting the formation of J-aggregate films. Compared to the simple boron compounds, the absorption coefficients were about three times higher, and the redshifts were larger. The HOMO/LUMO energies determined by cyclic voltammetry were −5.40/−3.95 eV for **3CB-ph** and −5.63/−3.88 eV for **3CB-carph**. These values were lower than those of the simple boron compounds, with particularly large decreases at the LUMO levels (0.35 eV for **3CB-ph**, 0.17 eV for **3CB-carph**). In the presentation, the OPV properties of **3CB-ph** and **3CB-carph** will be reported.

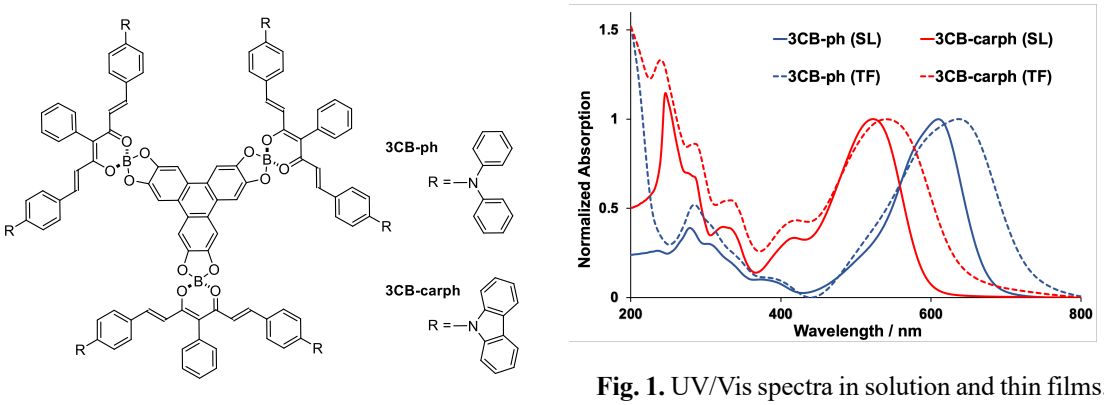

Fig. 1. UV/Vis spectra in solution and thin films.

1) H. Kobayashi, S. Izawa, C. Kitamura, M. Hiramoto, K. Ono, *Asian J. Org. Chem.* **2023**, *12*, e202300377.

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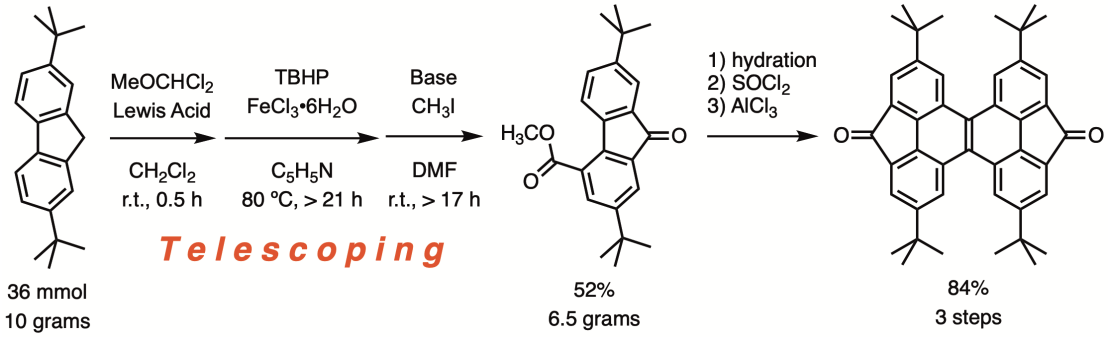
C_{60} 断片メテリケン骨格の量的供給経路の開発

（龍大先端理工）○植田 友規・岩澤 哲郎
Productive Synthesis of a C_{60} Fragmentary Octacycle, Metelykene (*Department of Materials Chemistry, Ryukoku University*) ○Yuki Ueda, Tetsuo Iwasawa

In 1985, Kroto *et al*. reported the C_{60} molecule, sparking significant interest across scientific disciplines. Organic chemistry research on C_{60} has expanded structural possibilities, particularly focusing on its fragment that allows for various cutting approaches. However, synthesis of these fragments faced inherent challenges in carbon-rich molecules: low solubility prevents us from synthesizing them productively in solution-phase. Herein we report development of productive scheme for *metelykene* that is a C_{60} fragmentary octacycle of $C_{28}H_{16}$ we achieved the first time[1]. The key to success locates on scalable synthesis of methyl 2,7-di-*tert*-butyl-9-oxo-9*H*-fluorene-4-carboxylate, that has not been reported heretofore (Scheme 1).

Keywords : Metelykene; C_{60}fragments; Buckybowls; Buckminsterfullerene; Polycycles

1985 年にクロトーらが C_{60} 分子を発見し、現在まで C_{60} は幅広い学問分野で研究されている。有機化学分野においては、新たな立体化学の可能性が拓かれ、C_{60} 断片構造に焦点が当てられてきた。断片体には新機能が宿るのではないかと目されたからである。しかし、炭素密度が高いため溶媒に溶けにくく、そもそも合成が難しい。これに対し当研究室は、新規な八環性 C_{60} 断片であるメテリケン（$C_{28}H_{16}$）の液相合成を達成し報告した [1]。ただし、画期的な材料へ進展させるためには、初報で示した経路よりも桁違いに生産性の高いスキームが求められる。今回我々は、メテリケン合成をプロセス化学に見合う形で作ることを目指し、フルオレノンの４位にメチルエステルを導入した化合物の新規合成を達成した（Scheme 1）。



Scheme 1. Synthesis of methyl 2,7-di-*tert*-butyl-9-oxo-9*H*-fluorene-4-carboxylate for manufacturing *metelykenone* that has skeletal octacycle *metelykene*.

1) N. Yoshida, R. Akasaka, T. Imai, M. P. Schramm, Y. Yamaoka, T. Amaya, T. Iwasawa, *Eur. J. Org. Chem.* **2023**, *26*, e202300407. Doi: 10.1002/ejoc.202300407

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πクラスター分子をメカノフォアとしたメカノポリマーの合成検討

（阪大理[1]・阪大院理[2]）○長谷川 翔一[1]・西内 智彦[2]・久保 孝史[2]

Synthetic investigation of mechanopolymers using π-cluster as a mechanophore

([1]*School of science, Osaka University,* [2]*Graduate School of Science, Osaka University*)
○Shoichi Hasegawa[1], Tomohiko Nishiuchi[2], Takashi Kubo[2]

Various mechanopolymers have been synthesized by incorporating mechanophores into the polymer chain, in which the absorption and emission colors change significantly due to changes in molecular structure and the breaking of chemical bonds in response to mechanical stimuli.

In this study, we used dianthrylbenzene **1** as a mechanophore. Dianthrylbenzene can form excimer between intramolecular anthracene in the excited state. Therefore, we aimed to create mechanopolymers that can control excimer formation between anthracenes in the excited state, i.e., localization and delocalization of excitons, by changing the distance between anthracenes through polymer stretching.

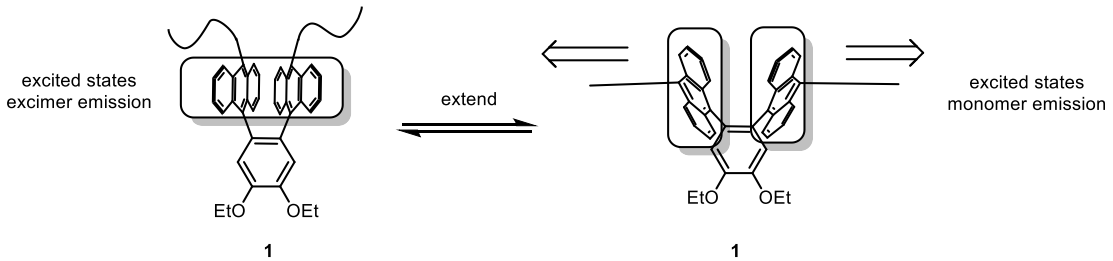
In the presentation, the synthesis, structure and properties of the mechanopolymers will be reported.

Keywords : mechanophor, π - π interaction, mechanopolymer

機械的刺激に応答して分子構造の変化や化学結合の切断が生じることで吸収・発光色が大きく変化する分子をメカノフォアとしてポリマー鎖に組み込むことで、様々なメカノポリマーが合成されている[1)]。

本研究では、メカノフォアとして以下に示すようなジアントリルベンゼン **1** を利用した。ジアントリルベンゼンは光励起状態において分子内のアントラセン間でエキシマーを形成することができる。そこで、アントラセン間の距離をポリマーの延伸により変化させることで、光励起状態におけるアントラセン間のエキシマー形成、すなわち励起子の局在化・非局在化をコントロールできるメカノポリマーの創出を目的とした。

発表ではこのメカノポリマー**1** の合成、構造と物性について報告する。



1 1

1) Keiichi Imato et al., *ACS Macro Lett.*, **2015**, *4*, 1307-1311

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光学活性体とラセミ体で異なる発光色を示すピリジニウム塩連結型フェナントロイミダゾール

（阪教育大）○グエン クアン ユイ・掛村 直樹・堀 一繁・谷 敬太
Different emission colors of optical active and racemic pyridinium salt-linked phenanthroimidazoles (*Osaka-Kyoiku University*) ○Nguyen Quang Duy, Naoki Kakemura, Kazushige Hori, Keita Tani

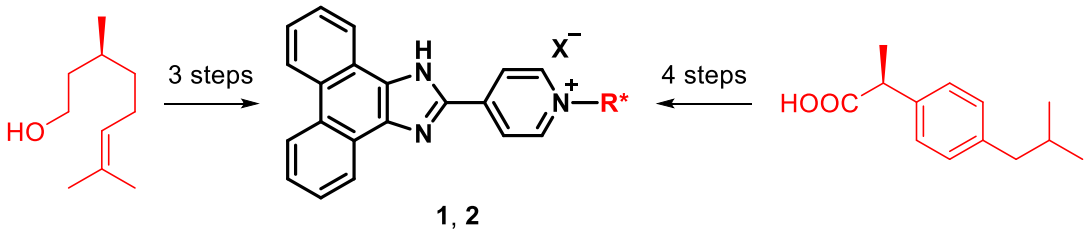
Many donor-acceptor linked molecules (D-A molecules) have been reported to exhibit mechanofluorochromism (MFC), which is phenomenon of fluorescence wavelength change in response to external mechanical stimuli such as grinding in a solid-state. For the control of MFC behavior and emission color between chiral and racemic D-A molecules, we have investigated chiral pyridinium salt-linked phenanthroimidazoles derived from commercially available β-citronellol and ibuprofen.

As a result, it was found that ibuprofen derived chiral phenanthroimidazole **2** with PF_6^- anion exhibited the maximum emission wavelength of 549 nm before grinding, while the racemic **2** showed the emission wavelength of 540 nm. After grinding, both their chiral and racemate showed the same orange emission with maximum emission wavelength of approximately 565 nm.

Keywords : Pyridinium salt; Phenanthroimidazole; Optically active form; Solid emission

ドナー・アクセプター連結型分子には、摩擦など外部からの機械的刺激に応答し、蛍光波長が変化するメカノフルオロクロミズム（MFC）を示す分子が多く報告されている。我々は MFC が分子配列の変化によるものであることから、MFC を示すドナー・アクセプター連結型分子であるピリジニウム塩連結型フェナントロイミダゾールに光学活性置換基を導入することで、分子間パッキングを調節し MFC 挙動や発光色を制御できないかと考え、光学活性化合物として入手が容易なβ-シトロネロールやイブプロフェン由来のピリジニウム塩連結型フェナントロイミダゾール **1**, **2** を合成した。

その結果、アニオンに PF_6^-を持つイブプロフェン由来の **2**･**PF$_6$** は、摩砕前、光学活性体は極大発光波長が 549 nm、ラセミ体は 540 nm で、光学活性体とラセミ体で異なる発光波長を示すことが分かった。しかし、摩砕後の光学活性体とラセミ体の極大蛍光波長は、いずれも約 565 nm の橙色蛍光を示した。



1, **2**

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薗頭クロスカップリング反応を用いたカルバゾロファン誘導体の合成とその光物性

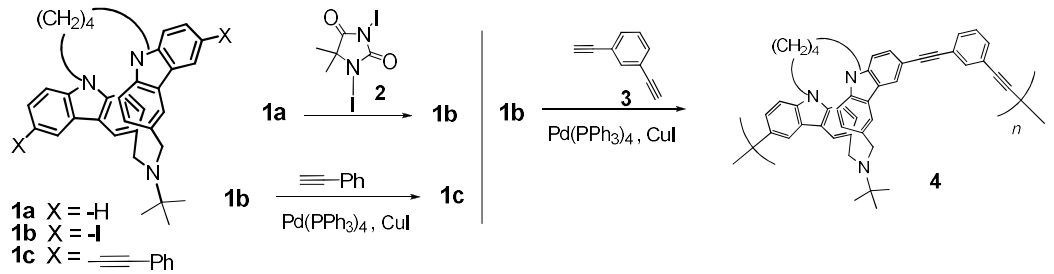
(阪教育大[1]・北大触媒研[2]・大分大理工[3]・京大化研[4]) ○千原 大明[1]・正木 深雪[1]・堀 一繁[1]・久保埜 公二[1]・種田 将嗣[1]・坂東 正佳[2]・中野 環[2]・原田 拓典[3]・黄瀬 雄司[4]・辻井 敬亘[4]・谷 敬太[1]

Synthesis and Photophysical Properties of Carbazolophane Derivatives by Sonogashira Cross Coupling Reaction ([1]*Osaka Kyoiku University.*, [2]*ICAT, Hokkaido University.*, [3]*Faculty of Science and Engineering, Oita University.*, [4]*ICR, Kyoto University.*) ○Hiroaki Chihara[1], Miyuki Masaki[1], Kazushige Hori[1], Koji Kubono[1], Masatsugu Taneda[1], Masayoshi Bando[2], Tamaki Nakano[2], Takunori Harada[3], Yuji Kinose[4], Yoshinobu Tsujii[4], Keita Tani[1]

Various carbazolophane derivatives have been synthesized as model compounds for the excimer in poly(*N*-vinylcarbazole). Among these, partially overlapped (PO) carbazolophanes, in which two carbazole moieties are helically stacked, possess planar chiral. We found out that the *g* value of carbazolophanes in circularly polarized luminescence (CPL) were as large as the order of 10^{-2}. In order to investigate the correlation between CPL properties and molecular structure, we plan to synthesize macrocyclic compounds and/or polymers containing carbazolophane units. In this study, 6,6'-diiodocarbazolophane derivatives **1b** is prepared from **1a** and is supplied to Sonogashira cross-coupling reaction to give **1c**. Sonogashira reaction between **1b** and **3** is in progress.

Keywords : Carbazole; Cyclophane; Circularly Polarized Luminescence; g valu; Sonogashira cross-coupling reaction

当研究室では、ポリ（*N*-ビニルカルバゾール）中のエキシマー構造のモデル化合物として種々のカルバゾロファン誘導体を合成してきた。このうちカルバゾール環部位がらせん状に重なった部分重なり型(PO)カルバゾロファンは、面不斉を有しており、円偏光発光(CPL)における異方性因子 *g* 値が 10^{-2} オーダーと大きな値を示すことを報告した。そこで CPL 特性と分子構造との相関を調べるために、カルバゾロファン単位を含む大環状化合物ならびにポリマー体の合成を計画した。ラセミ体の[3.4]系 PO 型カルバゾロファン **1a** をヨード体 **1b** に導き、フェニルアセチレンとの薗頭クロスカップリング反応により **1b** が合成できることがわかった。今後、**1b** と **3** との薗頭反応により、ポリマー体 **4** や大環状化合物の合成を行う予定である。



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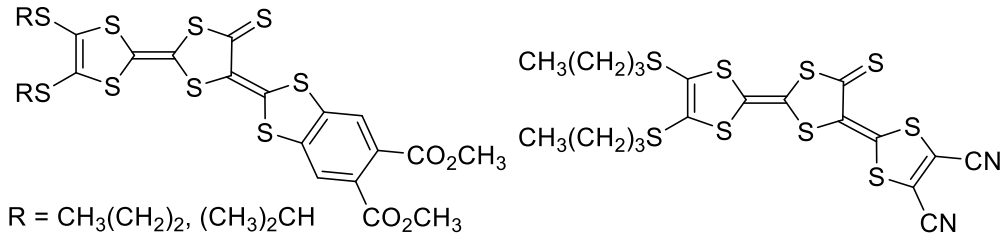
2,5-ジ(1,3-ジチオール-2-イリデン)-1,3-ジチオラン-4-チオン誘導体の固体中での分子配列とその光物性

（静大工[1]・阪大産研[2]）○植田 一正[1]・林 稜也[1]・木下 実咲[1]・嵩原 綱吉[2]・鈴木 健之[2]

2,5-Di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione Derivatives ([1]*Facalty of Engineering, Shizuoka University*, [2]*SANKEN, Osaka University*) ○Kazumasa Ueda,[1] Ryoya Hayashi,[1] Misaki Kinoshita,[1] Tsunayoshi Takehara,[2] Takeyuki Suzuki[2]

Tuning of solid-state colors of redox active molecules is one of the current issues for an application of functional dyes to the light absorbing system. We have synthesized methyl phthalate and phthalonitrile fuzed 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione derivatives and investigated their optical properties. Recently we succeeded in molecular structure analyses of the phthalonitrile fuzed derivatives and the nitrile substituted derivative, and examined correlation their molecular arrangements in solid state and the optical properties. Single crystal Xray structure analyses revealed that molecules are stacked one dimensionally in crystals. Furthermore, the derivatives which absorb almost all near-infrared region light are stacked in the same orientation in the columns. On the other hand, the derivatives which merely absorb near-infrared region light are alternatively stacked in opposite orientation in the columns. We will also discuss some details on the inter columnar arrangements.
Keywords : Functional Dyes; Molecular Arrangement; Optical Properties

酸化還元能を有する分子の希薄溶液中および固体状態での色調制御法の確立は、機能性色素の光吸収材料への応用の際の重要な要素技術の一つである。これまでに、フタル酸ジメチルやフタロニトリルの縮環した表題のπ共役骨格の誘導体の末端のアルキル基の長さを変えることによる、固体の光吸収を検討してきた。今回、フタル酸ジメチルの縮環した誘導体とニトリルの置換した誘導体の分子配列と光物性の相関を検討した。単結晶 X 線構造解析に成功した誘導体は、1 次元カラム構造を形成していることが明らかとなった。近赤外光領域に大きな吸収を持つ誘導体は、カラム内で、並進対称性を保ちながら積層していた。一方、近赤外光領域に吸収をほとんど持たない誘導体は、カラム内で、反転対称性を保ちながら積層していた。隣接カラム間の位置関係の詳細な説明は発表当日に行う。



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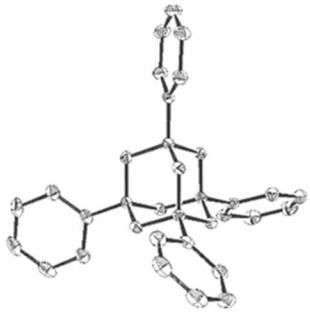
柔粘性を有するアダマンタン誘導体の合成

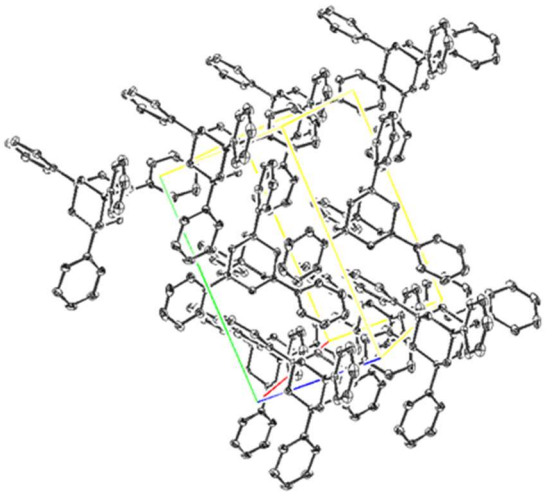
（関西学院大院理工）〇楠本もえ
Synthesis of Adamantane Derivatives with Plasticity (*Graduate School of Engineering, Kwansei Gakuin University*) 〇Moe Kusumoto

Adamantane is known to form plastic crystals. In general crystals, the position and orientation of the particles are regularly aligned, but in the case of a plastic crystal, the position of the particles remains regular because melting occurs first with respect to the orientation from the crystalline state. In this study, we synthesized adamantane derivatives and investigated the effects on thermophysical properties when substituents are introduced into the adamantane skeleton. We investigated the use of machine learning to determine the correlation between thermophysical properties measured by differential scanning calorimetry (DSC) and dipole moments calculated by quantum chemical calculations for various substituted adamantane derivatives as an index for designing substituents.

Keywords：Adamantane derivative; Plastic crystal; Glass transition temperature

アダマンタンは柔粘性結晶を形成することが知られている。一般的な結晶では粒子の位置と配向が規則的に並んでいるが、結晶状態から配向について先に融解が起こって位置は規則的なままである状態のことを柔粘性結晶と呼ぶ。本研究ではアダマンタン誘導体を合成し、アダマンタン骨格に置換基を導入した場合の熱物性への影響を調べた。種々の置換アダマンタン誘導体の示差走査熱量（DSC）測定などによる熱物性測定値と量子化学計算によって求めた双極子モーメントなどの相関関係を機械学習により求めて、置換基設計の指標に活用することを検討した。また、単結晶X線構造解析を行い、置換基ならびに原子間の距離を測ることで、置換基による結晶性ならびに融点の差異を調査した。





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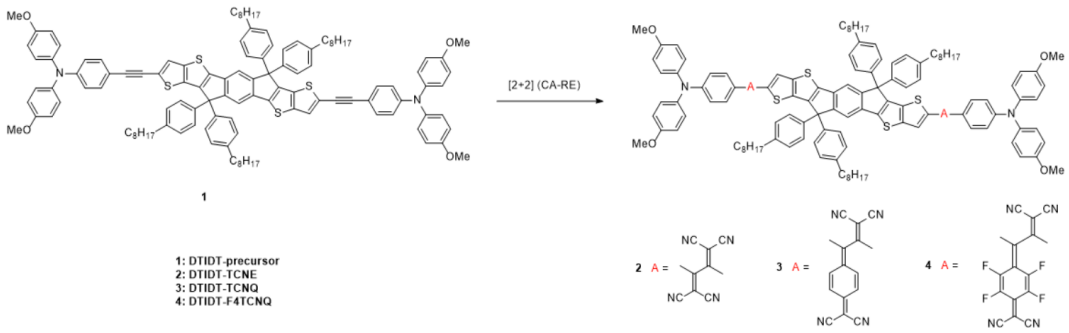
[2+2]付加環化反応によって機能化されたドナーアクセプター分子の太陽光蒸気発生特性

（東工大物質理工[1]）○林 佳揚[1]・道信 剛志[1]
Solar-driven steam generation properties of donor-acceptor molecules functionalized by [2+2] cycloaddition-retroelectrocyclization reactions ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Chia-Yang Lin[1], Tsuyoshi Michinobu[1]

With the rapid development of the world economy, global water shortages are occurring. Solar steam generation (SSG) technology is a promising approach to solve water shortages while minimizing the environmental impact.[1] The purpose of this study is to synthesize donor-acceptor molecules by applying the [2+2] cycloaddition-retroelectrocyclization (CA-RE) click reaction and to develop highly efficient photothermal materials (PTMs). By tuning the building block structures and band gaps, solar absorption and light-to-heat conversion efficiency can be altered. In this research, several PTMs were synthesized by the [2+2] CA-RE reactions between the alkyne-containing DTIDT precursor molecule and different olefinic acceptors. The resulting PTMs were loaded on filter paper by casting the chloroform solutions. Temperature changes of the PTMs under simulated sunlight were evaluated by thermal images of an infrared camera. In addition, the evaporation efficiency exceeded 70%.

Keywords : [2+2] Cycloaddition, Donor-Acceptor Molecules, Photothermal Materials, Solar Steam Generation

太陽光蒸気発生技術は、環境への影響を最小限に抑えつつ水不足を解決する有望な手段である。本研究の目的は、[2+2]付加環化（CA-RE）クリック反応を適用してドナーアクセプター分子を合成し、高効率な光熱変換材料を創製することである。DTIDT前駆体と異なるオレフィン受容体の[2+2] CA-RE反応によりドナーアクセプター分子を合成した。ろ紙の上にドナーアクセプター分子のクロロホルム溶液をキャストした後、疑似太陽光を照射した。表面の温度変化は、赤外線カメラの熱画像によって評価し、化学構造と光熱変換効率の相関を明らかにした。さらに、疑似太陽光を用いて効率よく蒸気発生できることを実証した。



1) C.-Y. Lin, T. Michinobu, *Beilstein J. Nanotechnol.* **2023**, *14*, 454.

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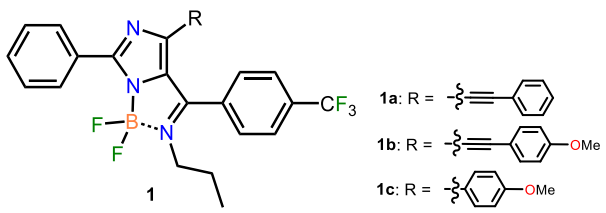
D-π-A 構造を持つイミダゾジアザボロール誘導体の合成と蛍光特性

(慶大理工) 三浦 洋平、○築本 涼花、毛利 匡佑、吉岡 直樹
Syntheses and Fluorescence Properties of Imidazodiazaborole Derivatives with D-π-A Structure (*Faculty of Science and Technology*, *Keio University*) Youhei Miura, ○Ryoka Tsukimoto, Kosuke Mohri, Naoki Yoshioka

Fluorescent molecules generally have a wide π-conjugated system and exhibit self-quenching due to π-stacking in the solid state. We have reported that imidazo[1,5-c][1,3,2] diazaborole skeleton can be chemically modified by cross coupling reactions and exhibits excellent fluorescent properties in both solution and solid states. In this study, we have synthesized three derivatives (**1a-c**) with electron-donor/accepter at appropriate positions to investigated the effect of the D-π-A structure on the fluorescent properties of imidazo-diazaborole skeleton. We obtained **1a-c** in good yields by the Sonogashira/Suzuki-Miyaura coupling reaction, and all showed fluorescence both in solution and solid states. Also, **1a-c** had a larger Stokes shift more than 100 nm (**1a**:127 nm in MeCN). These were clearly larger than those of the derivatives without the CF_3 group (82 nm). the detailed optical properties will be discussed in connection with their structures.
Keywords : Imidazole; D- π -A structure; Organic fluorescence molecule; Mechanofluorochromism

蛍光分子は一般的に広いπ共役系を持つため、固体状態ではスタッキングし自己消光する傾向がある。我々は、溶液のみならず固体状態においても良好な蛍光特性を示す分子の設計・開発を目指している。具体的には、イミダゾ[1,5-*c*][1,3,2]ジアザボロール骨格がカップリング反応による化学修飾が可能で、溶液/固体状態で良好な蛍光特性を示すことを報告している。本研究では、イミダゾジアザボロール骨格に対するD-π-A構造の効果を検討するため、適切な位置に電子供与/求引性置換基を導入した3種の誘導体(**1a-c**, **Scheme 1**)を合成し、その蛍光特性について報告する。

誘導体 **1a-c** は薗頭/鈴木−宮浦カップリング反応を用いることで良好な収率で得られ、いずれも溶液/固体状態で蛍光を示した。また UV−Vis・蛍光測定(**Fig. 1**)より、**1a-c** は 100 nm を超すストークスシフトを示し(**1a**:127nm, MeCN 中)、これは CF_3 基のない誘導体(82 nm)に比べ明らかに大きい。当日は詳しい光学特性をその構造と交えて議論する。



Scheme 1

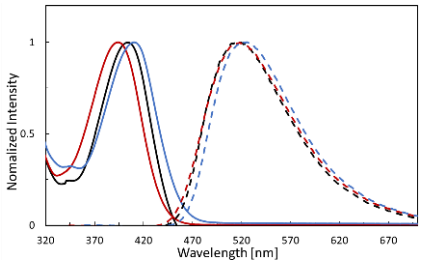


Fig. 1 UV-Vis (solid line) and fluorescence (dashed line) spectra of **1a** in selected solvents (red: MeCN, black: DCM, blue: toluene).

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ナフトキノンを末端基とした非縮環型非フラーレンアクセプターの開発

（兵庫県大院工）○押谷 花衣・鈴木 航・西田 純一・川瀬 毅・梅山 有和

Development of Non-Fused Non-Fullerene Acceptors with 1,4-Naphthoquinone Units as Terminal Groups (*Graduate School of Engineering, University of Hyogo*)

○Kae Oshitani, Wataru Suzuki, Jun-ichi Nishida, Takeshi Kawase, Tomokazu Umeyama

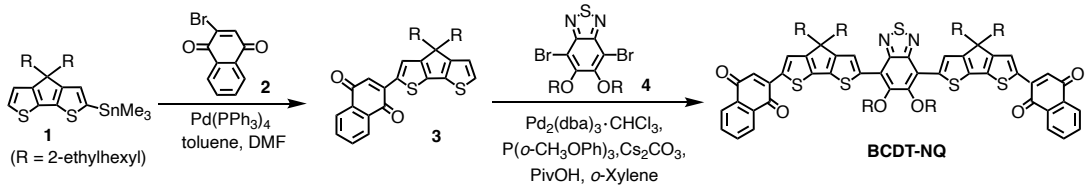
As a novel acceptor-donor-acceptor'-donor-acceptor (A-D-A'-D-A) type non-fused non-fullerene acceptor (NFA), we synthesized BCDT-NQ, which has 1,4-naphthoquinone as the terminal A units, dithienocyclopentadiene as the D units, and 2,1,3-benzothiadiazole as the central A' unit. The structure of BCDT-NQ was characterized by ^{1}H NMR spectrum and mass spectrometry. The chloroform solution of BCDT-NQ showed broad absorption bands in the visible and near infrared regions with a peak at 691 nm ($\varepsilon_{max} = 3.5 \times 10^4$ M^{-1} cm^{-1}). The BCDT-NQ film exhibited a red-shifted absorption maximum at 768 nm. The HOMO and LUMO energy levels estimated by the cyclic voltammetry measurement of the BCDT-NQ solution in dichloromethane were −5.13 and −3.73 eV, respectively.

Keywords：Nonfullerene Acceptor; 1,4-Naphthoquinone; Organic Photovoltaics; Conjugated Polymers; Non-fused

末端アクセプター（A）ユニットにナフトキノンを初めて用い、ドナー（D）ユニットにジチエノシクロペンタジエン、中心アクセプター（A'）ユニットに 2,1,3-ベンゾチアジアゾールを有する新規 A-D-A'-D-A 型非縮環非フラーレンアクセプター BCDT-NQ を設計し、合成を行った（Scheme 1）。まず、α 位がモノスタニル化されたジチエノシクロペンタジエン **1** と 2-ブロモ-1,4-ナフトキノン **2** との Stille カップリング反応により中間化合物 **3** を合成し、それを用いてジブロモ化されたベンゾチアジアゾール **4** の直接アリール化を行うことで BCDT-NQ を得た。BCDT-NQ の構造は、^{1}H NMR やマススペクトルにより確認した。

BCDT-NQ のクロロホルム溶液は、可視から近赤外領域に強く幅広い吸収帯を示し、吸収極大波長は 691 nm、モル吸光係数は 3.5×10^4 M^{-1} cm^{-1} であった。また、BCDT-NQ を薄膜化すると吸収極大は 768 nm まで長波長シフトした。さらに、サイクリックボルタンメトリー測定により、ジクロロメタン中での BCDT-NQ の HOMO および LUMO のエネルギー準位を見積もると、それぞれ−5.13 eV および −3.73 eV であり、HOMO-LUMO ギャップは 1.40 eV であった。

Scheme 1. Synthetic route for BCDT-NQ.



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構造類似性ホスト・ゲスト系における近赤外リン光の発光増強

(久留米高専[1]・九大先導研[2]) ○仲矢 美涼[1]・松本 泰昌[2]・石井 努[1]

Emission Enhancement of Near-infrared Phosphorescence Found in Structurally Similar Host-Guest System ([1]*National Institute of Technology, Kurume College*, [2]*Institute for Materials and Chemistry and Engineering, Kyushu University*) ○Misuzu Nakaya,[1] Taisuke Matsumoto,[2] Tsutomu Ishi-i[1]

An emission enhancement of near-infrared phosphorescence was studied in a host-guest doped system with structural similarity. An efficient energy-transfer was proceeded from red-emitting benzothiadiazole dye host to near-infrared-emitting benzoselenodiazole dye guest, resulting in the enhancement of near-infrared phosphorescence.

Keywords : Phosphorescence; Near-infrared Emission; Host-guest; Benzoselenodiazoles; Energy-transfer

リン光は長寿命特性より、生体イメージングの分野で注目されている。特に赤色～近赤外領域のリン光は組織透過性の観点より重要性が高い。先に当研究室では、ベンゾチアジアゾール色素 **1** が赤色リン光を示すことを見出している[1]。更に最近、**1** の硫黄原子をセレン原子に置換したベンゾセレノジアゾール色素 **2** が類似の結晶構造を維持したまま長波長側の近赤外リン光を与えることを見出したが、量子収率は顕著な低下を示した。本研究では、結晶構造類似性に着目し、赤色リン光色素 **1** をホスト、近赤外リン光色素 **2** をゲストとする二成分系に展開することで、エネルギー移動による近赤外リン光の発光増強を目的とした。

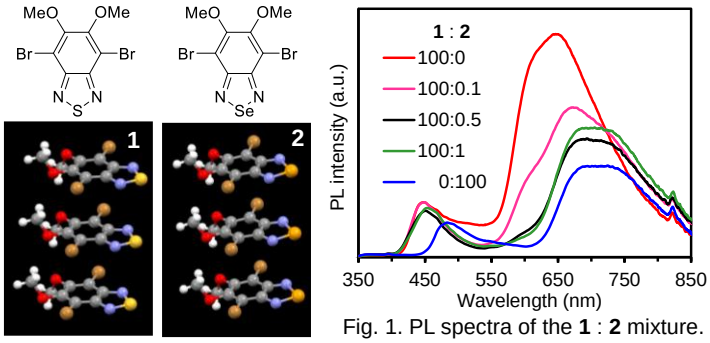

Fig. 1. PL spectra of the **1** : **2** mixture.

ホスト **1** 中にゲスト **2** を混合した系で、650 nm 付近の **1** の赤色リン光が消光し、720 nm 付近の **2** の近赤外リン光が発現した (Fig. 1)。その強度は **2** 単体より向上し、モル比から算出すると 200 倍以上のリン光強度の増強が認められた。本二成分系の結晶構造がホスト **1** と一致した知見より、**1** の結晶構造内への **2** の取込みが示された。秩序性の高い結晶構造内で **1** から **2** への効率的なエネルギー移動が進行することで、近赤外リン光が与えられている。本エネルギー移動は、励起スペクトル及びリン光寿命からも支持される。本二成分系で **1** 由来の蛍光のみが認められた知見より、本エネルギー移動がホスト **1** とゲスト **2** の励起三重項間の Dexter 型で進行していることが示唆された。以上の結果より、結晶構造類似性の二成分系で効率的なエネルギー移動が進行することで、近赤外リン光の発光増強に成功した。

1) T. Ishi-i, R. Kichise, I. S. Park, T. Yasuda, T. Matsumoto, *J. Mater. Chem. C*, **2023**, *11*, 3003.

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ベンゾチアジアゾール発光色素における蛍光・リン光制御

（久留米高専 [1]）○平田 衣麗 [1]・石井 努 [1]

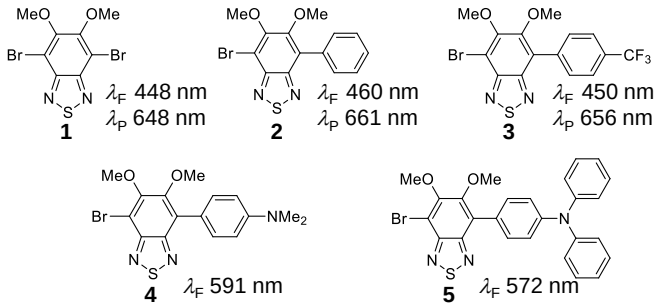
Regulation of Fluorescence and Phosphorescence Emission in Benzothiadiazole-based Dyes

([1]*National Institute of Technology, Kurume College*) ○Eri Hirata,[1] Tsutomu Ishi-i[1]

A regulation of fluorescence and phosphorescence emission was studied in a series of benzothiadiazole-based dyes in the solid state. The inherent phosphorescence was maintained by introducing elector-accepting substituents into the parent dye. In contrast, the introducing of elector-donating substituents resulted in the phosphorescence quenching together with the fluorescence enhancement.

Keywords : Fluorescence, Phosphorescence, Benzothiadiazole, Solid Emission

近年、発光材料が生体イメージング等のバイオ分野や有機電界発光素子などの材料分野への応用で注目されている。当研究室では、ベンゾチアジアゾール色素を基盤とした蛍光発光の研究を遂行してきた。最近、本色素への２個の臭素原子とメトキシ基の導入によりリン光が出現することを見出している [1]。本研究では、色素 **1** に対し１個の臭素原子を芳香環で置換した **2-5** を設計・合成し、リン光及び蛍光発光特性に与える置換基効果について検討した。



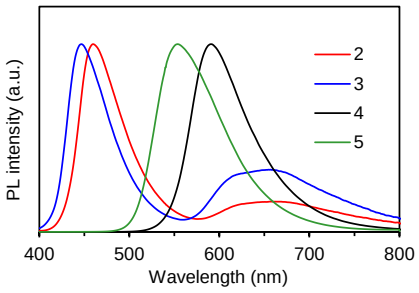


Fig. 1 PL spectra of **2-5**.

フェニル体 **2** は、固体状態で 660 nm にリン光を与えたが、母体色素 **1** と比較してリン光量子収率は 6.9% から 1.9% へ低下した。フェニル基上に電子吸引性トリフルオロメチル基を導入した **3** でも 656 nm に低強度のリン光が認められた。一方、電子供与性ジメチルアミノ基を導入した **4** では、リン光が消光すると共に、長波長側の 591 nm に強蛍光が認められた (Fig. 1)。蛍光量子収率は 37% であり **1** と比較して著しく向上した。ジフェニルアミノ体 **5** では蛍光特性が更に向上し、蛍光量子収率は 50% に達した。色素 **4** 及び **5** が 77 K の極低温条件下でもリン光不活性のため、項間交差が進行していないと判断できる。

以上の結果より、１個の臭素原子をフェニル基で置換しても、低強度ではあるがリン光特性を維持できることが判明した。一方、フェニル基上への電子供与性置換基の導入により、リン光性から強蛍光性に発光変換できる知見を見出すことができた。

1) T. Ishi-i, R. Kichise, I. S. Park, T. Yasuda, T. Matsumoto, *J. Mater. Chem. C*, **2023**, *11*, 3003.

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キラルアミンの絶対配置決定を目指した新規クマリンプローブの合成

(東邦大理[1]・東邦大複合物性研究セ[2]・千葉工大工[3]) ○後藤 優歌[1]・荒木 玲人[1]・池田 茉莉[3]・幅田 揚一[1,2]・桑原 俊介[1,2]

Synthesis of new coumarin probes for determination of the absolute configuration of chiral amines ([1]*Department of Chemistry and* [2]*Research Center for Materials with Integrated Properties, Toho University*, [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*) ○ Yuuka Gotoh,[1] Ryoto Araki,[1] Mari Ikeda,[3] Yoichi Habata,[1,2] Shunsuke Kuwahara[1,2]

The development of simple absolute configuration determination methods for chiral compounds is important in chemistry and pharmacology. Wolf et al. developed a coumarin probe that reacts with chiral amines, and succeeded in amplifying the chirality of amines by CD spectroscopy. In this study, we designed novel coumarin probes (**1**, **2**). **1** and **2** will be easily coupled with chiral amines by Michael reaction. The chirality of the amine controls the twist of the two coumarin chromophores, and the twist is detected by the exciton-splitting Cotton effect of CD.

Carboxylic acid **6** was synthesized from malonic acid **5**. After converting **5** to the acid chloride, it was reacted with amines **7** and **8** to obtain **1** and **2** in 80% and 69% yields, respectively. Coupling reaction of **1** and **2** with chiral amines are also reported.

Keywords : chiral sensing, chiral amine, CD spectrum, coumarin, determination of absolute configuration

キラル化合物の簡便な絶対配置決定法の開発は化学や薬学の分野において重要である．Wolf らはクマリン型マイケル受容体とキラルアミンを連結することでキラリティー増幅に成功しているが，絶対配置決定には至っていない[1]．本研究では，2 つのクマリン発色団を連結した新規プローブ（**1**, **2**）を設計した．**1** または **2** とキラルアミンを連結することで 2 つのクマリン発色団間にねじれが生じ，そのねじれを CD スペクトルで検出することによってキラルアミンの絶対配置を決定できると考えた（図 1）．

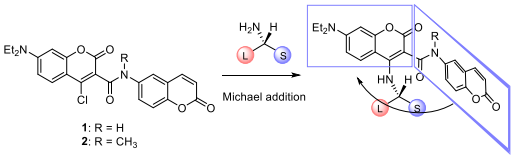
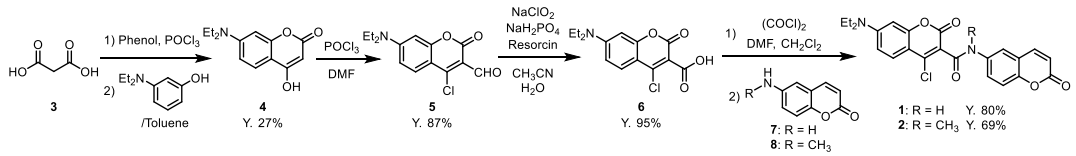


図 1．新規クマリンプローブのねじれ配座

マロン酸 3 から 4 段階の反応でカルボン酸 **6** を得た．**6** を酸塩化物に変換後，アミン **7** および **8** と反応させ，**1** および **2** をそれぞれ 80%および 69%の収率で得た（スキーム 1）．**1** および **2** とキラルアミンとの連結反応についても併せて報告する．



スキーム 1

1) Thanzeel, F. Y.; Balaraman, K.; Wolf, C. *Nat. Commun.* **2018**, *9*, 5323.

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スピロ骨格をもつ新規分子スイッチの合成と光異性化反応

（東邦大理[1]・東邦大複合物性研究セ[2]・千葉工大工[3]）○野竹 萌加[1]・中西 佳里奈[1]・池田 茉莉[3]・幅田 揚一[1,2]・桑原 俊介[1,2]
Synthesis and photoisomerization of a new molecular switch with spiro skeleton ([1]*Department of Chemistry and* [2]*Research Center for Materials with Integrated Properties, Toho University*, [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*) ○Moeka Notake,[1] Karina Nakanishi,[1] Mari Ikeda,[3]Yoichi Habata,[1,2] Shunsuke Kuwahara[1,2]

Photoresponsive crown ethers have attracted much attention as a part of molecular machines since the pioneering research on azobenzene-based photoresponsive crown ethers by Shinkai et al. 1) We have previously reported a new molecular switch *trans*-**1** with a spiro skeleton. When *trans*-**1** was irradiated at 338 nm light, photocyclization product **2** was obtained instead of isomer *cis*-**1**.

In this study, we designed new molecular switches *trans*-**4** and *cis*-**4** with fluorine to prevent the formation of cyclized products. *trans*-**4** and *cis*-**4** were synthesized by McMurry coupling of spiro ketone **9**. The structures of *trans*-**4** and *cis*-**4** were determined by X-ray crystallography. We also report on the photoisomerization of *trans*-**4** and *trans*-**3**.

Keywords：*molecular switch; spiro skeleton, photoisomerization; photocyclization*

新海らによる先駆的な研究に代表される光応答性クラウンエーテルは，分子マシンとしての応用が期待され，注目を集めている．我々はこれまでに，光異性化によるカチオン分子の選択的な包接を期待し，剛直なスピロ骨格にクラウンエーテルを導入した分子スイッチ *trans*-**1** を合成したが，異性化させた際に望まない環化体 **2** が生成してしまうことに問題があった（Figure 1）．

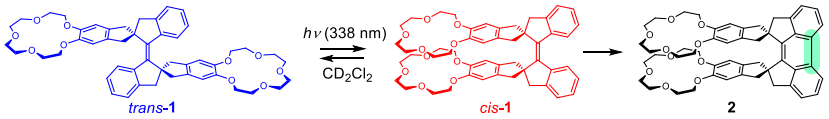

Figure 1. Photoisomerization of **1** and byproduct **2**.

本研究では，環化反応を防ぐためフッ素を導入した誘導体 *trans*-**4** および *cis*-**4** を設計した．*trans*-**4** および *cis*-**4** はスピロケトン **9** の McMurry 反応により合成し，その構造は X 線結晶構造解析により決定した．同様に合成した *trans*-**3** と *trans*-**4** の光異性化挙動の詳細についても報告する予定である．

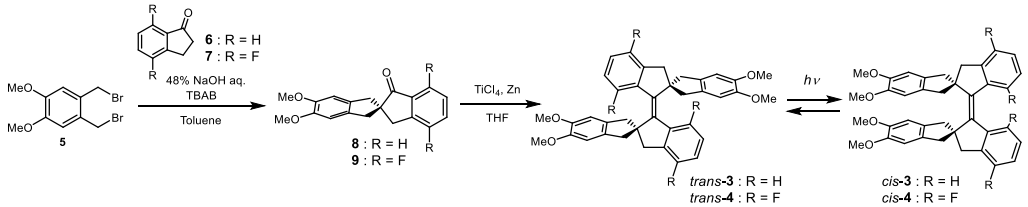

Figure 2. Synthesis of *trans*-**3** and *trans*-**4**.

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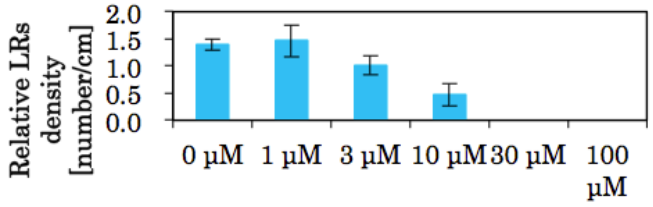
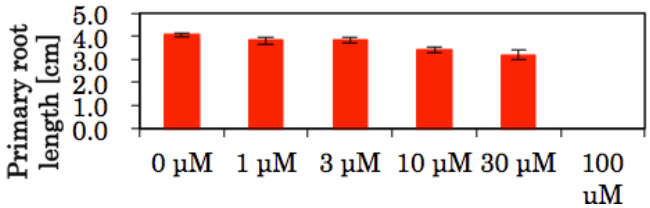
シロイヌナズナの側根伸長を阻害する蛍光発光性分子の開発

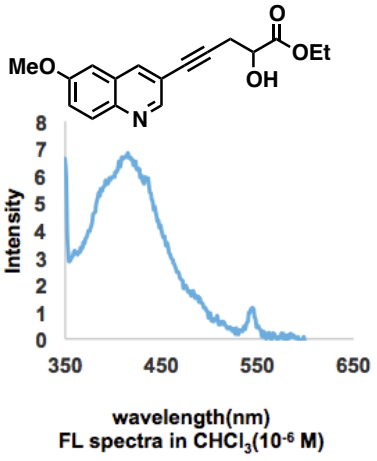
（神奈川大院工[1]）○柴﨑光陽[1]・酒井一樹[1]・荒井一輝[1]・山田健[1]・岡本専太郎[1]
Development of Fluorescent Agent Inhibiting Lateral Root Growth in Arabidopsis
([1]Graduate School of Engineering, Kanagawa University)
○Koyo Shibasaki,[1] Kazuki Sakai,[1] Kazuki Arai,[1] Takeshi Yamada,[1] and Sentaro Okamoto[1]

We have discovered a series of IBA derivatives that selectively inhibit lateral root elongation in *Arabidopsis*. However, mechanism of the inhibition is still unclear. Among these derivatives, those having a quinoline skeleton exhibit high activity and high selectivity for inhibiting lateral root growth. In this study, we designed a derivative having 6-methoxy quinoline structure that can show the inhibition activity and emits itself fluorescence under UV. The synthesized derivative showed selective inhibiiton of lateral root elongation in *Arabidopsis* under agar culture conditions and emitted the visible light under UV irradiation. We will also report on the development of molecular probes with additional functional tags. In the future, we will proceed with imaging using these derivatives and identifying proteins to be evaluated.
Keywords : inhibition of lateral root growth ; IBA derivatives ; fluorescence emission

当研究室では、シロイヌナズナの側根伸長を選択的に阻害する IBA 誘導体群を見いだしている。しかしばがら，これら誘導体の作用機序は未だ不明である。これらの誘導体の中でキノリン骨格を有する誘導体は，活性強度，選択性が高い。そこで，本研究では、このキノリン型誘導体の 6 位にメトキシ基を導入し、阻害剤それ自身が可視光領域で蛍光発光を示す誘導体の開発を企画した。合成した誘導体のシロイヌナズナでの根成長阻害活性を行った結果，寒天培地育成条件下，側根伸長阻害を示した。この誘導体は UV 照射下，可視光領域で発光した。また、さらなる機能性タグを付与した分子プローブの開発について報告する。今後，これら誘導体を用いるイメージングや評定タンパクの特定を進めて行く。







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円偏光発光を示す水溶性ヘリセンの静水圧効果および細胞導入

（東工大理[1]・東大院工[2]）○岡村 伊織[1]・中川 桂一[2]・豊田 真司[1]・福原 学[1]
A Water-Soluble Helicene: Hydrostatic Pressure Effects and Cellular Uptake ([1]*Department of Chemistry, Tokyo Institute of Technology*, [2]*School of Engineering, The University of Tokyo*) ○ Iori Okamura,[1] Keiichi Nakagawa,[2] Shinji Toyota,[1] Gaku Fukuhara[1]

Mechanical properties in living systems have attracted much attention as a biomarker. In the present study, to develop a new pressure-responsive chemosensor that emits circularly polarized luminescence, we focused on an anthracene-fused helicene skeleton as a fluorophore that was further modified by hydrophilic side chains. In this presentation, the cellular uptake experiments of the hydrophobic helicene counterparts and the (chir)optical properties of the newly synthesized hydrophilic helicene in aqueous solutions under hydrostatic pressure.
Keywords : Chemosensor; Helicene; Circularly Polarized Luminescence; Hydrostatic Pressure

がん細胞のヤング率は正常細胞よりも小さいことから、細胞の力学的性質はバイオマーカーとして利用できる[1]。当研究室では、溶液中における静水圧下のコンフォメーション変化や発色団の分子間相互作用の変化に着目し、感圧化学センサーの開発を行ってきた[2]。このような背景のもと、本研究では円偏光発光を用いた新たな感圧化学センサーの構築を目的として、アントラセンがらせん状に縮合した構造をもつヘリセンに着目し、ヘリセン骨格の末端に親水基として Triethylene glycol（TEG）を有する親水性ヘリセン（**Fig.1**）を設計した。はじめに細胞内のリアルタイムな圧力（動圧や衝撃波）伝播イメージングに向けて、親水基のないヘリセン（R=Ph）を細胞に導入できるか、またその細胞毒性を調査した。本発表では、細胞導入可能と考えられる水溶性ヘリセンの合成を行ったので報告する。

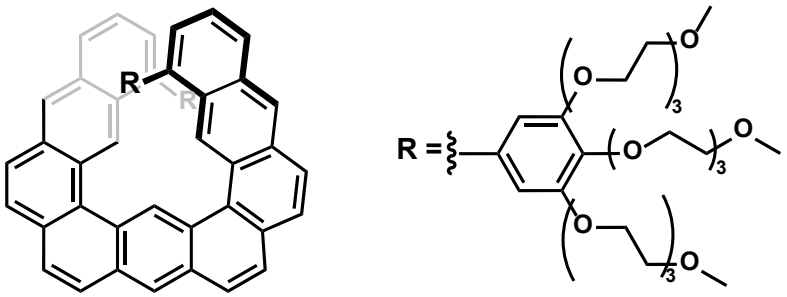

Fig.1 Chemical structure of **[3]HA($C_6H_2TEG_3$)$_2$**.

1) Cross, S. E.; Jin, Y. S.; Rao, J.; Gimzewski, J. K. *Nat. Nanotech.* **2007**, *2*, 780–783.
2) Mizuno, H.; Fukuhara, G. *Acc. Chem. Res.* **2022**, *55*, 1748–1762.

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ペンタセン二量体の一重項分裂におけるアルカリ金属イオン添加による動的制御

（東工大理[1]）○桑原 知也[1]・福原 学[1]

Singlet Fission in Pentacene Dimers Controlled by Addition of Alkali Metal Ions ([1]*Department of Chemistry, Tokyo Institute of Technology*) ○Tomoya Kuwabara,[1] Gaku Fukuhara[1]

In this study, a series of pentacene dimers through oxyethylene linkers were synthesized for dynamically controlling singlet fission (SF) by the addition of alkali metal ions. In this presentation, we report the photophysical properties of the dimers in the absence and presence of alkali metal ions and the factors that control the SF properties upon the addition of the ions and also upon hydrostatic pressurization as an external stimulus.

Keywords：Singlet Fission；Pentacene；Hydrostatic Pressure

クラウンエーテルを足場としたペンタセン二量体(Figure. 1 (a))において、アルカリ金属イオン添加により、一重項分裂（SF）速度と三重項量子収率の上昇が報告された[1)]。

本研究では、オキシエチレン鎖をリンカーとしたペンタセン二量体におけるアルカリ金属イオン添加による分子内 SF の制御を目的とした。溶液中での分子内 SF の速度は、発色団間の距離が短いほど高速になることが知られている[2)]。アルカリ金属イオン添加により、この発色団間の距離を制御することを目的に、オキシエチレン鎖をリンカー構造にもつ複数のペンタセン二量体（Figure 1. (b)）を合成した。本発表では、アルカリ金属イオン非添加・添加時の分光特性の差異について報告する。

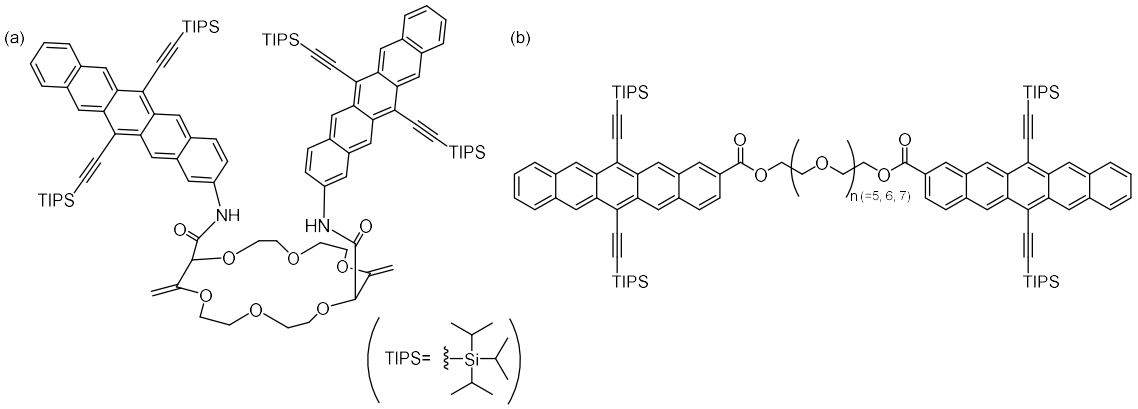

Figure 1. Chemical structures of pentacene dimers linked with (a) crown ether and (b) oxyethylenes.

(1) Aster, A.; Zinna, F.; Rumble, C.; Lacour, J.; Vauthey, E. *J. Am. Chem. Soc.* **2021**, *143*, 2361.
(2) Hasobe, T.; Nakamura, S.; Tkachenko, N. V.; Kobori, Y. *ACS Energy Lett.* **2022**, *7*, 390.

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2-ベンゾイルイミダゾール誘導体を配位子とした有機ホウ素錯体のカップリング反応を用いた化学修飾と蛍光特性

（慶大理工）三浦洋平、○加藤幹太、安藤直行、毛利匡佑、吉岡直樹

Chemical Modification Using Coupling Reaction of 2-Benzoylimidazole Based Organoboron Complexes and Emission Property (*Faculty of Science and Technology, Keio University*)

Youhei Miura, ○Kanta Kato, Naoyuki Ando, Kohsuke Mohri, Naoki Yoshioka

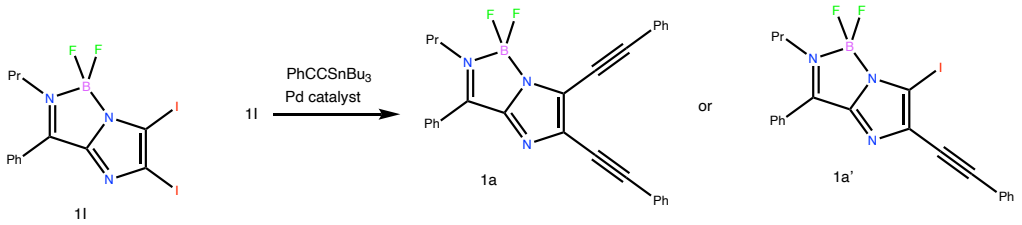
We have reported that imidazo[1,2-*c*][1,3,2]diazaborole-based organoboron complexes have fluorescent properties regardless of the state, such as solution, solid, and glass, because of their rigid and non-planar twisted moieties in the molecular structure. However, there are restrictions on the molecular structure due to synthetic routes that include severe basic and acidic conditions. In this study, we report the synthesis of the organoboron complexes having substituent groups that are difficult to be introduced by previous procedures using coupling reactions to **1I**.

When **1I** was subjected to the conditions of the Sonogashira coupling, the decomposition reaction proceeded by the organic base. After optimization of the reaction condition, the coupling reaction proceeded under the Stille coupling, in which the reaction proceeds under neutral conditions.

Keywords : Mechanofluorochromism; Organic fluorescent molecules; Imidazole; Boron Complex

我々は、イミダゾ[1,2-*c*][1,3,2]ジアザボロール骨格を持つ有機ホウ素錯体が、骨格の剛直性とアリール基同士の立体反発による立体的に特異な構造を有するため、溶液、固体、ガラスなど状態を問わない優れた蛍光特性を持つことを報告している。しかし、合成段階で厳しい反応条件を必要とするため、導入できる置換基の種類が大きく制約されるなど解消すべき問題点がある。本研究では、これまで導入が困難であった置換基の導入を目指し、**1I** に対する温和な条件で進行するカップリング反応について条件検討を行った。

化合物 **1I** を薗頭カップリングの条件に付すと、有機塩基による分解反応が確認された。そこで中性条件で反応が進行する Stille カップリングの条件を用いて反応を行ったところ、カップリング反応の進行が確認された。(Scheme 1) 当日はカップリング反応の条件や光学特性について議論する。



Scheme 1. Molecular structure and synthetic procedure of **1a** and **1a'**.

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Academic Program [Poster] | 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-：Poster

Mon. Mar 18, 2024 1:00 PM - 2:30 PM JST | Mon. Mar 18, 2024 4:00 AM - 5:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

English

[P1-1pm-01]

Halogenation of aromatic compounds catalyzed by camphorsulfonic acid-$BiCl_3$

○Kiyoshi Tanemura[1] (1. The Nippon Dental University)

Japanese

[P1-1pm-02]

Synthesis of Aryl Enol Ethers from Phenols and Ketals

○Kwihwan Kobayashi[1], Shun-ya Onozawa[1], Koichiro Masuda[1] (1. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-1pm-03]

Synthetic Study of Diaporisoindole A Using Chiral Selenium-catalyzed Lactamization

○Daiki Yamamoto[1,2], Takuya Hashimoto[1,2] (1. Chiba Univ., 2. RIKEN)

Japanese

[P1-1pm-04]

Synthesis and properties of [7] helicenes with a dimethoxy group at the symmetrical position

○Masato Yada[1], Makoto Miyasaka[1] (1. Tokyo Denki University)

Japanese

[P1-1pm-05]

2-Iodobenzoyl Group as a Protecting Group for Alcohols Deprotected under Mild Oxidative Conditions

Jin Nakamura[1], Yuta Mori[2], Tatsuya Oda[2], Takumi Masuhara[2], Yuna Yamada[2], ○Atsuhito Kuboki[1,2], Masayuki Haramura[1,2] (1. Graduate School of Science, Okayama Univesity of Science, 2. Okayama Univesity of Science)

Japanese

[P1-1pm-06]

Synthesis of 2-Vinylnapthalenes via Gold(I)-Catalyzed Cyclopropanation of Indenes

○Shota Nakagawa[1], Yoshikazu Horino[1] (1. Chitose Inst. Sci. Tech.)

Japanese

[P1-1pm-07]

Synthesis of Phenylpropanoids in *Coreopsis lanceolata* L. Petals

○Takuma Matsunaga[1], Yosiharu Okada[1] (1. Kinki Univ.)

Japanese

[P1-1pm-08]

Reductive multiple propargylation of corannulene

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○Kaiki Nishi[1], Shinobu Aoyagi[1], Kazuhira Miwa[2], Toru Amaya[1], Takahiro Sasamori[3], Takashi Kurogi[4], Hideki Yorimitsu[4] (1. Nagoya City University, 2. Nagoya University, 3. University of Tsukuba, 4. Kyoto University)

Japanese

[P1-1pm-09]

Ir-Catalyzed C-H borylation of benzyl position; substrate scope and effects of multidentate ligands.

○Kou Kagawa[1], Tatsuya Nonaka[1], Ryuto Horikoshi[1], Natsumi Naito[1], Noriyuki Suzuki[1] (1. Sophia University)

Japanese

[P1-1pm-10]

Ir-Catalyzed C-H borylation of benzyl position; study on catalytically active species

○Kentaro Kasai[1], Hiroshi Araki[1], Keigo Sakurai[1], Noriyuki Suzuki[1] (1. Sophia Univ.)

Japanese

[P1-1pm-11]

Synthesis of Bis(1-indanyl)amine Quaternary Ammonium Salts and Their Phase Transfer Catalysis

○Aoi Sugiyama[1], Nobuhiro Kanomata[1] (1. Waseda University)

Japanese

[P1-1pm-12]

Reaction of N-sulfonyl-1,2,3-triazole with β-Diketone

○Takuya Koizumi[1], Yuto Yabuchi[1], Yuki Sakai[1], Taiga Fujimoto[1], Ryoto Itani[1], Naoki Michihiro[1], Takuto Kamio[1] (1. Kobe City College of Technology)

English

[P1-1pm-13]

Push-pull chromophores with different heterocyclic donor moieties synthesized by [2+2] cycloaddition-retroelectrocyclization reaction

○Xu Chen[1], Tsuyoshi Michinobu[1] (1. Tokyo Institute of Technology)

Japanese

[P1-1pm-14]

Color Changes of Naphthalenetetracarboxylic Acid Diimide Derivatives by Odor Substances

○Reiko Yamashita[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P1-1pm-15]

Regioselective condensation of 3,5-dimethylisoxazole with aldehydes not using strong bases

○Aki Tanaka[1], Kyosuke Sugihara[1], Hitoshi Abe[1] (1. Graduate School of Science and Engineering, The Univ. of Toyama)

Japanese

[P1-1pm-16]

Synthesis of 4-Alkynyl-2-pyrones Using Conjugate Addition Reaction of Diethyl Malonate Derivatives to Dialkynyl Ketones and Its Application

Kotaro Hirano[1], ○Kosuke Sakurai[1], Iwao Hachiya[1] (1. Mie University)

Japanese

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[P1-1pm-17]

Synthesis of β-Carbolin-1-ones by Intramolecular C-H Amination of 3-Amino-2-pyridones

Rikuto Sasaki[1], ○Akihiko Matsuo[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-18]

Synthesis of 4-Ethoxycarbonyl-β-carbolin-1-ones via C-H/N-H Cyclization of 3-Amino-2-pyridones as a Key Reaction

Honoka Mori[1], ○Maho Morimura[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-19]

Synthesis of Pyrroles by Intramolecular Cyclization of β-Cyanocarbonyl Compounds Using Titanium Tetraiodide

Shunya Tochigi[1], ○Taichi Uemura[1], Iwao Hachiya[1] (1. Mie University)

Japanese

[P1-1pm-20]

The effect of intramolecular hydrogen bond on fluorescence of C4N4

○Mao Niimura[1], Miki Kohei[1], Ryosuke Tsutsumi[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

Japanese

[P1-1pm-21]

Synthesis of Fluorinated Isocoumarins by Copper-Catalyzed Coupling Reaction

○Haruki Sakagami[1], Akira Tsubouchi[1], Akio Saito[1] (1. Grad. Sch. Eng., Tokyo Univ. Agric. Tech.)

Japanese

[P1-1pm-22]

Synthesis and properties of 6,9-bis(diphenylaminobiphenyl)-substituted phenanthroimidazoles

○Riku Taniguchi[1], Keiji Mizuki[1], Taizo Hatta[1] (1. Sojo University)

Japanese

[P1-1pm-23]

Reaction Mechanism of Hexaazatrinaphthylene Reductant Synthesis

○Takahiro Oshima[1], Kan Wakamatsu[1], Kiyoshi Fujisawa[2], Hideyuki Higashimura[1] (1. Grad. Sch. of Sci. and Eng., Okayama Univ. of Sci., 2. Col. of Sci., Ibaraki Univ.)

Japanese

[P1-1pm-24]

Design and Synthesis of Enlarged TriQuinoline

○Mai Yamashita[1], Ryosuke Tsutsumi[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

Japanese

[P1-1pm-25]

Synthetic studies of alkaloid skeletons for development in biocatalytic reactions

○Yunosuke Adachi[1], Hiroaki Inaba[1], Fumiyuki Uchida[1], Keita Isaka[1], Ken-ichi Fushuku[1] (1. Meisei University)

Japanese

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[P1-1pm-26]

One-pot Synthesis of Chromans in the presence of $NaHSO_4/SiO_2$ using 2-(1-hydroxyalkyl)phenols

○Eri Kurosawa[1], Mamiko Hayakawa[1], Takuya Furukawa[1], Tadashi Aoyama[1] (1. College of Science and Technology, Nihon University)

Japanese

[P1-1pm-27]

Synthesis of benzoselenotetramisole using isothiocyanates derived from amino alcohols with an isopropyl group.

○Rika SAITO[1], Hayato ICHIKAWA[1] (1. Nihon University)

Japanese

[P1-1pm-28]

Preparation of Dibenzoxanthene Derivatives by Bismuth Triflate-catalyzed Reaction of 2-Naphthols with an Allylic Alcohol

○Maki Minakawa[1], Syuya Sato (1. Yamagata University)

Japanese

[P1-1pm-29]

Cyclization of 4-pyrazolyl esters of propiolate with iodine

○Ayana Sato[1], Furuya Yashuaki[2], Ichikawa Hayato[1] (1. Nihon University, 2. Graduate School of Nagasaki University)

Japanese

[P1-1pm-30]

Solvent effects on asymmetric cyclopropanation with tertiary pyridylalkanol catalysis

○Narumi Shimizu[1], Yuki Kamata[1], Nobuhiro Kanomata[1] (1. Department of Chemistry and Biochemistry, Waseda University)

Japanese

[P1-1pm-31]

Synthesis of various diselenides with urea skeleton and Baeyer-Villiger oxidation with hydrogen peroxide

○Kai Machiyama[1], Hayato Ichikawa[1] (1. Nihon University)

Japanese

[P1-1pm-32]

Synthesis of Azulene Ester Derivatives and Their Pharmacological Activities

○Hiyuto Furuichi[1], Miura Wataru[1], Hiroshi Sakagami[2], Hidetugu Wakabayashi[1] (1. Josai University, 2. Meikai University)

Japanese

[P1-1pm-33]

Carbon-sulfur bond cleavage with Hantzsch ester anion under blue-light irradiation

○Koki Matsune[1], Takuma Shimotori[1], Nagisa Kikuchi[1], Haruto Hijikata[2], Tetsuya Sengoku[1] (1. Shizuoka University Graduate School of Integrated Science and Technology, 2. Department of Applied Chemistry and Biochemical Engineering, Faculty of Engineering, Shizuoka University)

Japanese

[P1-1pm-34]

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Development of stereoselective decarboxylative aldol reaction of α-amido malonic acid half esters to isatins

○Kazuki Fujita[1], Ibuki Kumazawa[1], Jyunpei Yokoi[1], Kazuki Abe[1], Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

Japanese

[P1-1pm-35]

Development of Conjugate Addition Reaction of Ketene Silyl Acetals to Terminal Alkynyl Imines

Ryo Sakai[1], ○Hitoshi Nishimura[1], Iwao Hachiya[1] (1. Mie University)

English

[P1-1pm-36]

Multicomponent Synthesis of 4-Iminoimidazolidines and their Bioactivities

○Komoreng Oriel Hlokoane[1], Raku Irie[1], Masato Oikawa[1] (1. Yokohama City University)

Japanese

[P1-1pm-37]

Rearrangement Reactions of Helical Quinone Derivatives to Various Oxygen-Containing Heterocyclic Derivatives

○Satoshi Joken[1], Nanami Kimura[1], Michinori Karikomi[1] (1. Utsunomiya Univercity)

Japanese

[P1-1pm-38]

Baeyer-Villiger Oxidation with the Diselenide Bearing Trifluoromethoxy group and Hydrogen Peroxide

○Riku Sakamoto[1], Hayato Ichikawa[1] (1. Nihon University)

Japanese

[P1-1pm-39]

Synthetic Studies of New Bicyclic Pipecolic Acid Derivatives

○Yuu Tamura[1], Masahiko Yamamoto[1], Takesi noda[1] (1. Kanagawa Institute of Technology)

Japanese

[P1-1pm-40]

Metal-free dibenzoxazepinone synthesis from salicylamides mediated by hypervalent iodine reagent

○Naoki Miyamoto[1], Arisu Kasai[1], Kotaro Kikushima[1], Toshifumi Dohi[1] (1. Ritsumeikan University)

Japanese

[P1-1pm-41]

[Withdraw] Synthesis of chiral oxazolines from the reaction of α–isocyanoacetonitriles with ketones

○Tatsuya Kato[1], Shuichi Nakamura[1], Naoki Yasukawa[1] (1. Nagoya Institute of Technology)

Japanese

[P1-1pm-42]

Cyclization for construction of bicyclic hydantoin derivatives

○Yuki Fuzisawa[1], Tomoya Katakura, Jun-ichi Yamaguchi[1] (1. Kanagawa institute of technology)

Japanese

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[P1-1pm-43]

Design, synthesis and evaluation of photoresponsive properties of chiral macro cyclic compounds containing an azobenzene-unit.

○Shotaro Otaki[1], Ryota Shibauchi[1], Toshifumi Tojo[1], Norio Tanada[3], Yoshiyuki Kageyama[3], Shin Aoki[1,2] (1. Grad. Sch. Pharm. Sci., Tokyo Univ. of Science., 2. Res. Inst. for Sci., Tokyo Univ. of Science., 3. Grad. Sch. Sci., Hokkaido Univ.)

Japanese

[P1-1pm-44]

Study of electrophilic chlorination reactions using sodium hypochlorite pentahydrate

○Reo Shimada[1], Michio Iwaoka[1] (1. Tokai University)

Japanese

[P1-1pm-45]

Synthesis of a bis(ferrocenyl)bromostibine bearing an intramolecularly coordinating phosphine moiety and its attempted debromination reaction

○Shinya Kawamoto[1], Koichiro Masada[2], Takahiro Sasamori[2,3] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-46]

Nickel Bromide-DBU-Catalyzed Synthesis of Cyclic Carbonates from Diols and CO_2 Using 2-Cyanopyridine

○Masatoshi Mihara[1], Yoshinobu Esaki[2], Kengo Hyodo[2], Shuichi Nakao[1], Takeo Nakai[1], Takatoshi Ito[1] (1. Osaka Research Institute of Industrial Science and Technology, 2. Faculty of Science and Engineering, Kindai University)

Japanese

[P1-1pm-47]

Synthesis and Reactivities of *N*-(9-Anthryl)thiazolium Salts

○Takahide Nishikawa[1], Yosuke Uchiyama[1,2], Hideyo Matsuzawa[1], Anthony J. Arduengo III[2,3] (1. Kitasato University, 2. The University of Alabama, 3. Georgia Institute of Technology)

Japanese

[P1-1pm-48]

Attempted Synthesis of a Novel Oligosila-cage Compound bearing Phenyl Groups

○Koichi Sato[1], Takahiro Sasamori[1] (1. University of tsukuba)

Japanese

[P1-1pm-49]

Synthesis of a new bulky ferrocenyl group bearing an intramolecularly coordinating selenium moiety.

○Ryusei Hamano[1], Takahiro Sasamori[2,3] (1. School of Science and Engineering, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-50]

Generation of a bissilylcarbenoid and its reaction with phosphine trichloride

○Akihiro Nomoto[1], Koh Sugamata[2], Takahiro Sasamori[3] (1. Graduate School of Science and Engineering, Univ. of Tsukuba, 2. Department of Chemistry, College of Science, Rikkyo

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University, 3. Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-51]

Synthesis of Mercaptoundecahydrododecaborate/Fucose Conjugate

○Taiga Fujita[1], Akira Morihara[2], Tomoyuki Tajima[3] (1. The Univ. of Okayama, 2. Graduate school of environmental, life, natural science and technology, Okayama University, 3. Graduate school of environmental, life, natural science and technology, Okayama University)

Japanese

[P1-1pm-52]

Synthesis of diferrocenyldimethylstannane for encapsulation in single walled carbon nanotubes

○Taichi Kamiya[1], Yusuke Kondo[2], Tomoyuki Tajima[3] (1. Faculty of environmental science and technology, Okayama University , 2. Graduate school of environmental, life, natural science and technology, Okayama University , 3. Graduate school of environmental, life, natural science and technology, Okayama University)

Japanese

[P1-1pm-53]

Attempted synthesis of a binaphthyl substituted silylene

○Masaru Kanaoka[1], Shogo Morisako[2], Takahiro Sasamori[2] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-54]

Attempted Synthesis of Cyclic Phoshine-Alane bridged by a biphenyl unit

○Takanori Iwasaki[1], Takahiro Sasamori[2,3] (1. Graduate School of Science and Technology, University of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-55]

Syntheses and properties of donor-acceptor type fused polycyclic compounds with a triphenylamine skeleton as a donor unit

○Katsutaka Nishiyama[1], Yoshimitsu Tachi[1], Masatoshi Kozaki[1] (1. Osaka Metropolitan University)

Japanese

[P1-1pm-56]

Synthesis of an *o*-dibromobenzene derivative toward the synthesis of a 9,10-distibaanthracene

○Shunsuke Otsuji[1], Koichiro Masada[2], Takahiro Sasamori[2,3] (1. School of Science and Technology, University of Tsukuba, 2. Institute of Pure and Applied Sciences, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-57]

Insertion reactions of chlorogermylene bearing a bulky ferrocenyl group into dihaloalkanes

○Hiroto Chida[1], Takahiro Sasamori[2] (1. College of Chemistry, School of Science and Engineering, University of tsukuba, 2. Department of Chemistry, Institute of Pure and Applied Sciences, University of Tsukuba)

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Japanese

[P1-1pm-58]

Development and application of reduction reaction of unsaturated carbon- carbon bond via α-iodotoluene structure

○Chika Ishizumi[1], Shota Amamoto[1], Rumi Kawatani[1], Nobuhiro Kotoda[1], Akiya Ogawa[2], Shin-ichi Kawaguchi[1] (1. Saga University, 2. Osaka Metropolitan University)

Japanese

[P1-1pm-59]

Enantioselective Addition of Thiols to *α*–Ketiminoesters using Cinchona Alkaloid Amide/Zinc(II) Catalysts

○Obata Kouki[1], Iizuka Yuka[1], Nakamura Shuichi[1] (1. Nagoya Institute of Technology)

Japanese

[P1-1pm-60]

Synthesis and properties of benzene and naphthalene derivatives having sulfide and sulfonium groups

○Kazunori Hirabayashi[1], Ren Takahashi[1], Naoya Kitamura[1], Toshio Shimizu[1] (1. Tokyo Metropolitan University)

Japanese

[P1-1pm-61]

A study on preparation of a common precursor for *α*-difluoromethyl amino acids.

○Masaya Shiraishi[1], Toshimasa Katagiri[1], Shinji Hiramatsu[2] (1. Tokyo University of Technology, 2. Okayama University)

Japanese

[P1-1pm-62]

Synthesis of a bis(phosphide) ligand bearing sterically demanding substituents

○Riko Kato[1], Takahiro Sasamori[2] (1. Graduate School of Science and Tchnology, Univ. of Tsukuba, 2. Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-63]

Attempt to Synthesis of Complex with Selanyl Sulfanyl Imidazo[1,5-*α*]pyridine Ligands

○Akito Tanaka[1], Osamu Niyomura[1] (1. Chubu University)

Japanese

[P1-1pm-64]

Synthesis and structure of hexanuclear silver complex ($[Ag_6(f\text{-}BiSC)_4]$ $(TfO)_2$) with bisimmnosulfancarbone(0) ligand bearing free imino nitrogen.

○Keiko Noguchi[1], Takayoshi Fujii[1] (1. Nihon University)

Japanese

[P1-1pm-65]

Synthesis of silanes bearing a bulky ferrocenyl group and their reactivity with aryl lithium

○Ryuju Iwasaki[1], Koichiro Masada[2], Takahiro Sasamori[2,3] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Institute of Pure and Applied Science, Univ. of Tsukuba, 3. TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-66]

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Attempted Synthesis of a 1,6,2,5-dioxadisilocine derivative

○Shiryu Nakamura[1], Takahiro Sasamori[2] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Department of Chemistry, Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-67]

Generation of a 2,3-Digerma-1,4-Dihydronaphthalene

○Miwako Kawai[1], Takahiro Sasamori[2] (1. Graduate School of Science and Technology, Univ. of Tsukuba, 2. Department of Chemistry, Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba)

Japanese

[P1-1pm-68]

Synthesis and Optical Properties of Selenium- or Tellurium-containing 1,6-Di-*t*-butyl-substituted 1,3,5-Hexatriene Derivatives Incorporated with a Dibenzobarrelene Skeleton

○Koki Oshima[1], Jun Naito[2], Norio Nakata[2], Akihiko Ishii[2] (1. Faculty of Science, Saitama University, 2. Graduate School of Science and Engineering, Saitama University)

Japanese

[P1-1pm-69]

Synthesis and Application of Tris[1-(diphenylphosphino)isoquinolin-3-yl]phosphine Ligand

○Ryuki Kano[1], Hidetoshi Ohta[1], Minoru Hayashi[1] (1. Grad. Sch. Sci., Eng., Ehime Univ.)

Japanese

[P1-1pm-70]

Design and Synthesis of Substituted Isoindoro[2,1-*a*]quinolines:Substituent effects at positions 5 and 11

○shimoguri reiji[1], isii hirokazu[2], sako makoto[1], murai keniti[1], nemoto tomomi[2], arisawa mituhiro[1] (1. osaka university, 2. institute of physiology)

Japanese

[P1-1pm-71]

The Synthesis and Properties of Group 14 Element Compounds Bearing Four Phenylethynyl Groups

○Junji Kobayashi[1], Rika Watanabe[1] (1. International Christian University)

Japanese

[P1-1pm-72]

Synthesis, structures and CH···O hydrogen bonding of dioxytetrylene dimers derived from 2,2′-methylenediphenols

Asuka Sugihara[2], Rise Shimogaito[1], Yoichi Ishii[2], ○Takuya Kuwabara[1] (1. Ochanomizu University, 2. Chuo University)

Japanese

[P1-1pm-73]

Preparation of derivatives bearing an azaazzulene-2-yl group and their characters

○Yuya Onishi[1], Jun-ichi Yamaguchi[1] (1. Kanagawa institute of technology)

Japanese

[P1-1pm-74]

Preparation of 2,6-ziazulenylpyridines and their coloration

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○Hiro Watanabe[1], Rina sato[1], Yuya Onishi[1], Jun-ichi Yamaguchi[1] (1. kanagawa institute of technology)

Japanese

[P1-1pm-75]

Structure and Functions of Quinoline-Based Amide Oligomers

○Ayami Takeda[1], Wei Xu[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

Japanese

[P1-1pm-76]

Enantioselective synthesis of tetrasubstituted 2,3-dihydro-4-quinolones using chiral phosphoric acid catalysts

○Yuto Terashima[1], Rio Kawamura[1], Yoichiro Matsuda, Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

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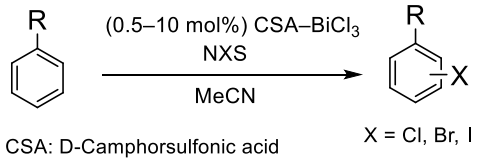
Halogenation of aromatic compounds catalyzed by camphorsulfonic acid-$BiCl_3$

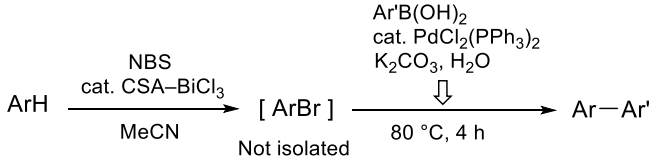
(*School of Life Dentistry at Niigata, The Nippon Dental University*) ○Kiyoshi Tanemura
Keywords: Halogenation; Aromatic Compounds; $BiCl_3$; NBS; Suzuki-Miyaura Cross-Coupling

Halogenation of aromatic compounds is one of the widely used reactions in organic chemistry. Aromatic halides are important intermediates which were employed in metal-catalyzed cross-coupling reactions such as Suzuki-Miyaura cross-coupling, Grignard reactions, substitution reactions, the preparation of natural products, pharmaceuticals, and materials science. *N*-Bromo-, *N*-chloro-, and *N*-iodosuccinimides (NBS, NCS, and NIS, respectively) are superior halogenating reagents in terms of ease of handling. We have previously reported that $FeCl_3$ is an efficient catalyst for the halogenation of aromatic compounds with NBS, NCS, and NIS in MeCN.[1] However, this method required large amounts (10-100 mol%) of $FeCl_3$. In this report, we describe the efficient and practical procedure for the halogenation of aromatic compounds with NXS catalyzed by 0.5-10 mol% of D-camphorsulfonic acid (CSA)–$BiCl_3$ in MeCN. CSA and $BiCl_3$ are not expensive reagents. The reactions can be conducted under an atmosphere of air. Furthermore, we report one-pot bromination followed by Suzuki-Miyaura cross-coupling reactions.

Aromatic bromination catalyzed by 0.5–10 mol% of D-camphorsulfonic acid–$BiCl_3$ with *N*-bromosuccinimides (NBS) was carried out in MeCN under air conditions. The procedure was extended to the reactions with *N*-chlorosuccinimides (NCS) and *N*-iodosuccinimides (NIS). In all cases, the corresponding halides were obtained in good to excellent yields. One-pot bromination / Suzuki-Miyaura cross-coupling reactions were achieved without the removal of the solvent.



Scheme 1. Halogenation of aromatic compounds.



Scheme 2. One-pot bromination / Suzuki-Miyaura cross-coupling reactions.

1) K. Tanemura, T. Suzuki, Y. Nishida, K. Satsumabayashi, T. Horaguchi, *Chem. Lett.*, **2003**, *32*, 932.

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フェノール類とケタールからのアリールエノールエーテル合成法の開発

（産総研）○小林 貴範・小野澤 俊也・増田 光一郎

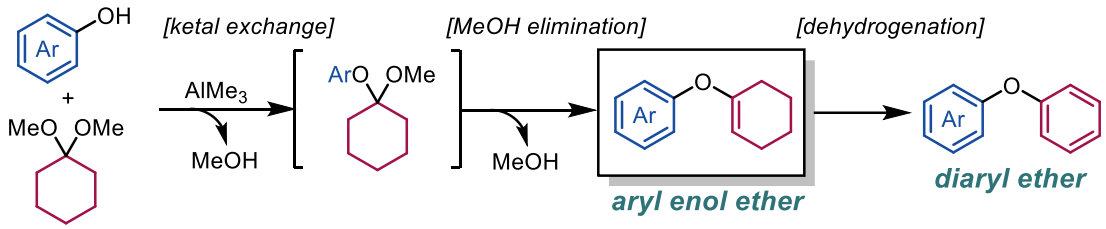
Synthesis of Aryl Enol Ethers from Phenols and Ketals (*National Institute of Advanced Industrial Science and Technology*) ○Kwihwan Kobayashi, Shun-ya Onozawa, Koichirio Masuda

Aryl enol ethers are used as organic synthesis and polymer chemistry intermediates are less explored to them because of its synthetic difficulty. Synthetic methods for aryl enol ethers from phenols are limited to Buchwald-Hartwig alkoxylation and Ulmann-type etherification with vinyl halides or vinyl triflates, which are required halogenated substrates, transition metals, and equimolar bases. We developed a halogen- and transition metal-free synthetic method of aryl enol ethers from phenols and ketals via an acid-catalyzed ketal-exchange and methanol elimination step. Aryl enol ether was obtained from 2-naphthol and cyclohexanone dimethyl ketals with trimethylaluminum as a pre-catalyst in 86% yield. Obtained aryl enol ether was also transformed into diaryl ether via dehydrogenation.

Keywords : Aryl enol ether; Phenol; Ketal; Aluminum

アリールエノールエーテルは、有機合成やポリマー合成の中間体として用いられるが、その合成の難しさから研究例は少ない。フェノール類を原料としたアリールエノールエーテルの合成法としては、Buchwald-Hartwig アルコキシ化や Ulmann タイプのエーテル化があるが、いずれもビニルハライドまたはビニルトリフレートをカップリングパートナーとする必要があるだけでなく、遷移金属や過剰量の塩基を用いる必要があった。今回我々は、フェノール類とケタール類を原料としたアリールエノールエーテルの合成法を確立し、これは酸触媒によるケタール交換反応と脱メタノール反応を経由することで達成される。

実際に 2-ナフトールとシクロヘキサノンジメチルケタールを原料とし、トリメチルアルミニウムを触媒として反応させることで、目的のアリールエノールエーテルを86%の収率で得ることができた。さらに、得られたアリールエノールエーテルは脱水素反応を経由することで、任意のジアリールエーテルへと変換できる



ref) *Org. Biomol. Chem.* **2023**, *21*, 8259–8262.

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キラルセレン触媒ラクタム化反応を利用した Diaporisoindole A の合成研究

（千葉大 [1]・理研 [2]）○山本 大貴 [1,2]・橋本 卓也 [1,2]

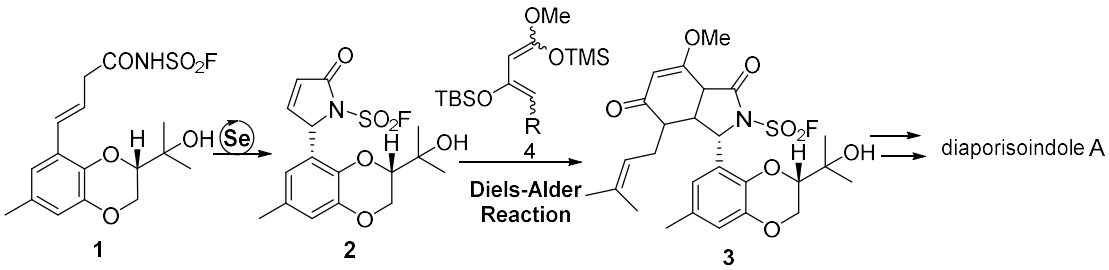
A Synthetic Study of Diaporisoindole A Using Chiral Selenium-catalyzed Lactamization

([1]*Chiba University*, [2]*RIKEN*) ○Daiki Yamamoto,[1,2] Takuya Hashimoto,[1,2]

In our research group, successful enantioselective lactamization reactions of N-fluorosulfonyl-β,γ-unsaturated amides using selenium catalysts have been achieved. In this presentation, we report on the asymmetric total synthesis of diaporisoindole A, a novel isoprenylisoindole alkaloid derived from mangrove endophytic fungi, employing selenium-catalyzed lactamization as a key step, followed by a Diels-Alder reaction utilizing the electron-deficient alkene moiety of the subsequent lactam. Initially, *p*-cresol was employed as the starting material, and through multiple steps, lactamization precursor **1** was synthesized. Subsequently, lactam **2** was synthesized through a lactamization reaction using a chiral selenium catalyst. For the subsequent Diels-Alder reaction, diene **4**, synthesized in three steps from methyl acetoacetate, was employed to generate compound **3**. Ongoing investigations focus on the de-fluorosulfonylation and aromaticization steps.

Keywords : Selenium, Lactam, Alkaloid, Diaporisoindole A

当研究室では、セレン触媒を用いた N-フルオロスルホニル-β,γ-不飽和アミドのエナンチオ選択的ラクタム化反応に成功している [1)]。本発表では、マングローブ内生菌由来の新規イソプレニルイソインドールアルカロイドである diaporisoindole A のセレン触媒ラクタム化反応と、続くラクタムの電子不足性アルケン部位を利用した Diels-Alder 反応を鍵反応とする不斉全合成研究について報告する [2)]。まず、出発物質として *p*-クレゾールを用い、複数の段階を経てラクタム化反応前駆体 **1** を合成した。その後、キラルセレン触媒を用いたラクタム化反応によりラクタム **2** を合成した。続く Diels-Alder 反応ではアセト酢酸メチルから 3 段階で合成されるジエン **4** を用いて **3** を合成した。その後の脱フルオロスルホニル化、芳香族化については引き続き検討を行っている。



1) 山本 大貴、山﨑 駿、橋本 卓也 日本化学会第 103 回春季年会 K703-3am-04
2) H. Cui, Y. Lin, M. Luo, Y. Lu, X. Huang, Z. She, *Org. Lett*. **2017**, *19, 20*, 5621–5624.

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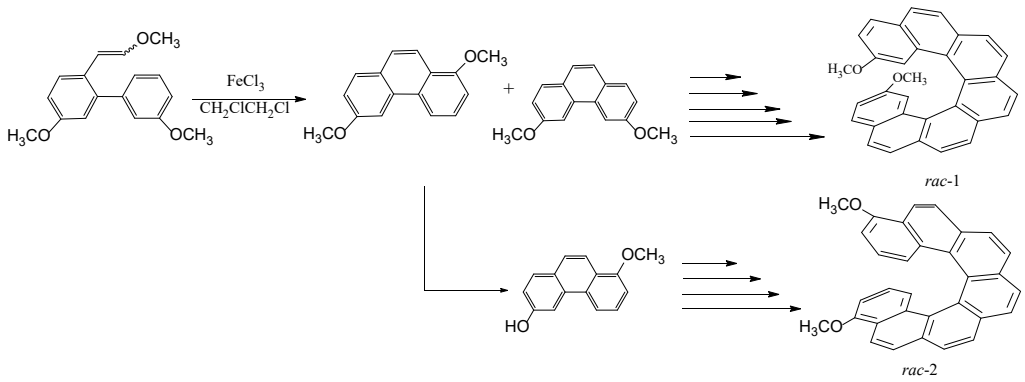
対称位にジメトキシ基を有する[7]ヘリセンの合成とその特性評価

（東電大工）○矢田　聖斗・宮坂　誠
Synthesis and characterization of [7] helicenes with a dimethoxy group at the symmetry position ([1]*Graduate School of Engineering, Tokyo Denki University*)○Masato Yada, Makoto Miyasaka

Helicenes, polycyclic aromatic hydrocarbons with a nonplanar helical structure formed by ortho-fused aromatic rings such as benzene, have no chiral carbon but exist as right-handed (*P*-form) and left-handed (*M*-form) mirror-image isomers[1)]. These compounds have a helical delocalized π-electron system and are characterized by semiconductivity, photoconductivity, conformational stability, circularly polarized emission properties, and optical absorption in the visible range[2)]. Carbohelicenes without substituents have the problem of low fluorescence quantum yields, and the introduction of substituents has been reported as a method to improve fluorescence quantum yields. In our laboratory, we have reported the synthesis of unsubstituted or halogen-substituted [7]helicenes. In this study, we report the synthesis of chiral helicene derivatives in which methoxy groups are introduced at 2,17- and 4,15-positions, which are the terminal symmetry positions of the [7]helicene skeleton.

Keywords : Helicene; Chiral; Circular polarized luminescence

ベンゼンなどの芳香環がオルト縮合してできた非平面の螺旋構造を有する多環芳香族炭化水素のヘリセンは、不斉炭素を持たないが右巻き（*P* 体）と左巻き（*M* 体）の鏡像異性体が存在する [1)]。これらの化合物は、らせん状の非局在π電子系を持ち、半導電性、光伝導性、配座安定性、円偏光発光特性、可視域での光吸収などの特徴を持つ [2)]。置換基を持たないカルボヘリセンには蛍光量子収率が低いという問題点があり、蛍光量子収率を改善する方法として置換基の導入が報告されている。当研究室では、今までに無置換またはハロゲン置換[7]ヘリセンの合成を報告してきた。本研究では、[7]ヘリセン骨格の末端側の対称位である 2,17-位および 4,15-位にメトキシ基を導入したキラルヘリセン誘導体の合成を報告する。



1) C. Chen, *et al*., *Chem. Rev*. **2012**, *112*, 1463-1535.
2) S. Raouafi, *et al.*, *J. Mol. Struct*. **2022**, *1268,133680*

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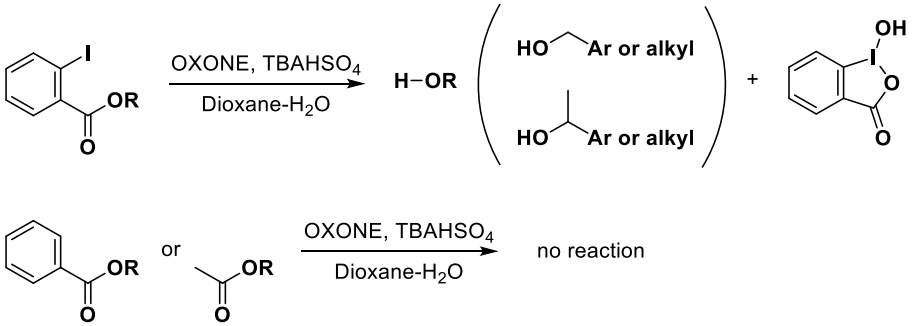
2-ヨードベンゾイル基の保護基としての利用

（岡山理大院理[1]・岡山理大理[2]）中村 仁[1]・森 祐太[2]・尾田 達哉[2]・増原 拓海[2]・山田 侑那[2]・○窪木 厚人[1,2]・原村 昌幸[1,2]
2-Iodobenzoyl Group as a Protecting Group for Alcohols Deprotected Under Mild Oxidation Conditions ([1]*Graduate School of Science, Okayama University of Science*, [2]*Faculty of Science, Okayama University of Science*) Jin Nakamura[1], Yuta Mori[2], Tatsuya Oda[2], Takumi Masuhara[2], Yuna Yamada[2], ○Atsuhito Kuboki[1,2], Masayuki Haramura[1,2]

Acyl protecting groups are generally stable under oxidative conditions. 2-Iodobenzoyl group has been reported as an acyl protecting group deprotected under oxidative conditions, however, there is concern about side reactions caused by highly reactive oxidizing agent and saponification of other acyl groups. We would describe an improved deprotection procedure of 2-iodobenzoyl group to afford various alcohols using OXONE as a weak oxidizing agent and $TBAHSO_4$ as an additive under neutral conditions. Other acyl protecting groups such as acetyl and benzoyl groups were stable under the conditions.
Keywords： Acyl Protecting Group; Deprotection; 2-Iodobenzoyl Group

アシル系保護基は一般に酸性条件下や酸化に安定であり、その脱保護は塩基性条件下や還元によって行われる。したがって、酸化によって脱保護可能なアシル基があれば、有機合成の経路に新たな選択肢を与えることができる。そのような保護基として、2-ヨードベンゾイル基が報告されている[1]が、脱保護に用いる高反応性の酸化剤による副反応、塩基性条件による他のアシル基のけん化の併発が実用上の問題となる。そこで本研究では、弱い酸化剤を中性～弱酸性で作用させる反応条件による、2-ヨードベンゾイル基の脱保護について検討した。

検討の結果、酸化剤として OXONE を、添加剤として $TBAHSO_4$ を 1,4-ジオキサン - 水の溶媒系中で作用させることによって、1 級および 2 級のベンジルアルコールまたはアルキルアルコールの 2-ヨードベンゾイル保護体の脱保護が円滑に進行することを見出した。また、この条件では対応するベンゾイル保護体およびアセチル保護体は反応しなかった。



1) R. A. Moss, P. Scrimin, S. Bhattacharya, S. Chatterjee, *Tetrahedron Lett.*, **1987**, *28*, 5005.

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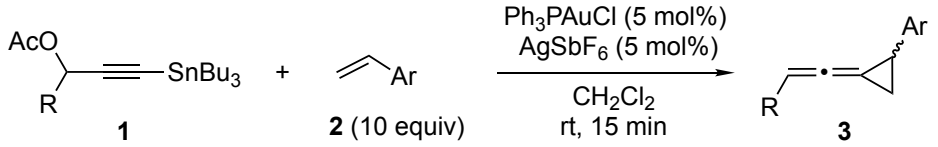
金触媒によるインデンのシクロプロパン化反応を経る 2-ビニル置換ナフタレン誘導体の合成

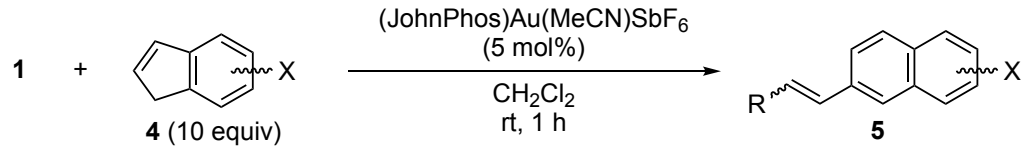
（公立千歳科技大[1]）○中川　翔太[1]・堀野 良和[1]
Synthesis of 2-Vinylnapthalenes via Gold(I)-Catalyzed Cyclopropanation of Indenes
([1]*Department of Applied Chemistry and Bioscience, Chitose Institute of Science and Technology*) ○Shota Nakagawa[1] and Yoshikazu Horino[1]

We previously developed a mild and general method for the synthesis of vinylidenecyclopropanes (VDCPs) via gold(I)-coordinated allenylidene species (eqn 1). VDCPs are synthetically valuable molecules due to their extraordinary properties. In this study, we found that the reaction of indene **4** with tributylstannylated propargylic acetates **1** in the presence of gold(I) catalyst yielded 2-vinyl-substituted naphthalene derivatives **5** (eqn 2). This reaction is considered to proceed via a rarely reported allenylidene-gold(I)-mediated cyclopropanation and ring-expansion reaction. Interestingly, the tandem reaction proceeded when JohnPhos or IPr ligands were used. On the other hand, the use of phosphine ligands other than JohnPhos or IPr provided cyclopropanation reaction products.
Keywords : Gold; Cyclopropanation; Ring Expansion; Indene; Naphthalene

当研究室では、一価のカチオン性金触媒存在下、トリブチルスタンニル基が置換したプロパルギルアセテート **1** とスチレン誘導体 **2** との反応を行うと、ビニリデンシクロプロパン誘導体 **3** が得られることを見出した（式 1)。ビニリデンシクロプロパン誘導体 **3** は、反応性の高いアレン結合部位と環歪みを有するシクロプロパン環部位を併せ持つため多様な反応性を示す高反応性活性種として興味深い。今回、(JohnPhos)Au(MeCN)SbF_6 触媒存在下、**1** とインデン誘導体 **4** との反応を行うと、2−ビニル置換ナフタレン誘導体 **5** が得られることを見出した（式 2)。

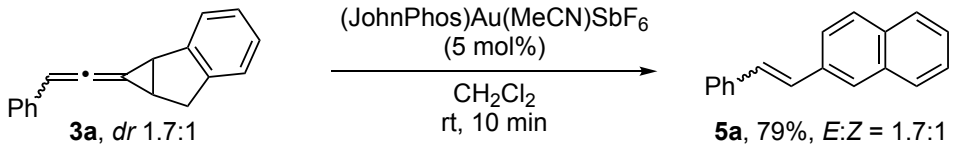


(1)



(2)

本反応がビニリデンシクロプロパン誘導体 **3** を経由して進行しているのかを確かめる目的で **3a** の環拡大反応を検討したところ、**5a** が 79%の収率で得られた（式 3)。



(3)

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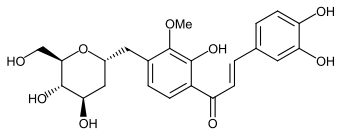
Synthesis of Phenylpropanoids in *Coreopsis lanceolata* L. Petals

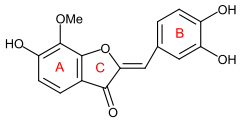
(Graduate school of systems engineering, Kinki University) ○Matsunaga Takuma, Okada Yoshiharu

Keyword: *Coreopsis lanceolata* L.; Phenylpropanoid; β-Keto Phosphonate; Antioxidant

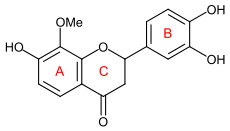
Previously, we have reported the isolation of 7,3',4'-trihydroxy-8-methoxy-flavanone, 2',3,4,4'-tetrahydroxy-3'-methoxychalcone-4'-glucoside, (Z)-3',4',6-trihydroxy-7-methoxyaurone from *Coreopsis lanceolata* L. petals and the synthesis of their analogues. We reported herein the synthesis flavanones and flavonols from chalcones prepared with β-Keto phosphonates and aromatic aldehydes.



(2',3,4,4'-tetrahydroxy-3'-methoxychalcone-4'-glucoside)
(lanceolin)



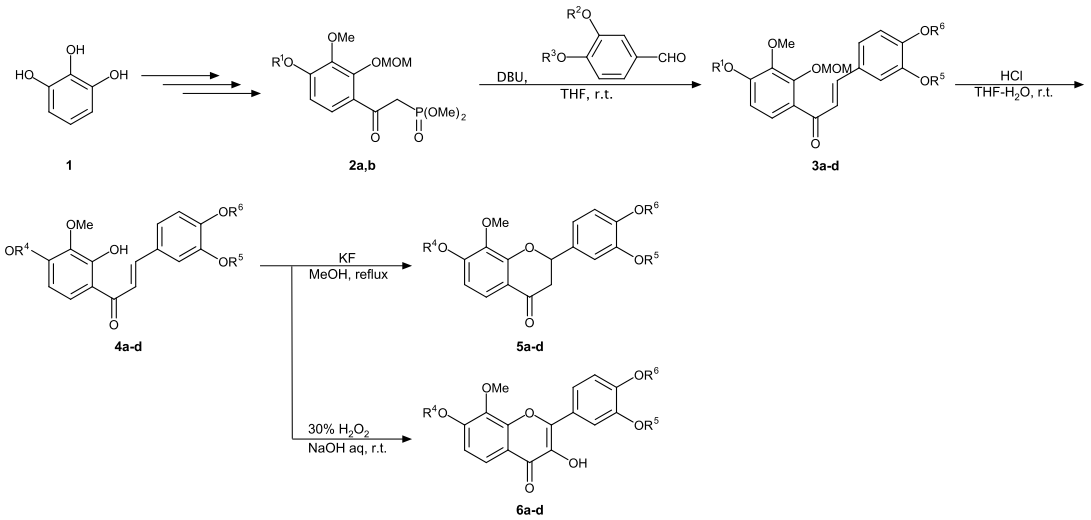
((Z)-3',4',6-trihydroxy-7-methoxyaurone)
(leptosidin)



(3',4',7-trihydroxy-8-methoxyflavanone)

α-(dimethylphosphono)-2-methoxy-3-methylacetophenones were readily prepared from pyrogallol in 7-26% yields with four steps. Reaction of the acetophenones with aromatic aldehydes in THF included DBU as base gave the corresponding chalcones in 85-98% yields. Treatment of the chalcones in boiling methanol with potassium fluoride gave flavanones in 22-51% yields. On the other hand, treatment of the chalcones with hydrogen peroxide in sodium oxide solution gave flavonols in 34-43% yields.

Scheme 1. synthesis of chalcones **4a-d**, flavanone **5a-d**, and flavonol **6a-d.**



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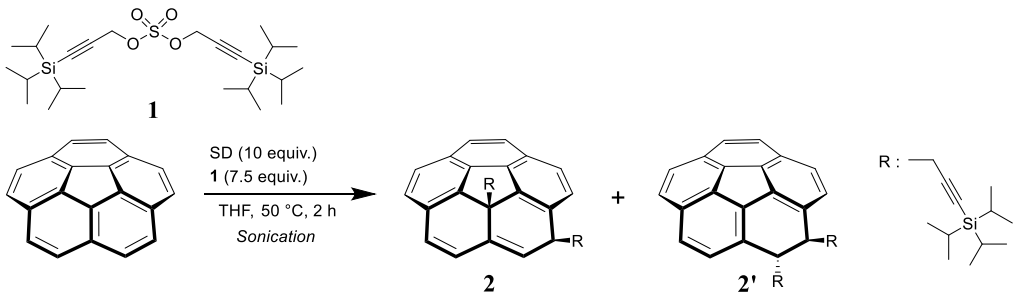
コランニュレンの還元的多重プロパルギル化

(名市大理[1]・名大院工[2]・筑波大院理[3]・京大院理[4]) ○西 海輝[1]・青柳 忍[1]・三輪 和平[2]・雨夜 徹[1]・笹森 貴裕[3]・黒木 尭[4]・依光 英樹[4]
Reductive multiple propargylation of corannulene ([1]*School of Biology and Integrated Sciences, Nagoya City University,* [2]*Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University,* [3]*Division of Chemistry, Faculty of Pure and Applied Sciences and Tsukuba Research Center for Energy Materials Sciences (TREMS), University of Tsukuba,* [4]*Department of Chemistry, Graduate School of Science, Kyoto University*)
○Kaiki Nishi,[1] Shinobu Aoyagi,[1] Kazuhira Miwa,[2] Toru Amaya,[1] Takahiro Sasamori,[3] Takashi Kurogi,[4] Hideki Yorimitsu[4]

We had achieved multiple propylation of C_{60}[1], multiple methylation[2] and allylation[3] of corannulene ($C_{20}H_{10}$) using reduction with sodium dispersion (SD) and the following electrophilic reaction with dialkyl sulfate. To apply this reaction to multiple propargylation of C_{60} and corannulene, we have designed and synthesized a novel reduction-resistant electrophile **1** with propargylic groups protected with triisopropylsilyl (TIPS) groups. We reacted **1** with corannulene in the presence of excess SD in THF at 50 °C for 2 h under sonication, and consequently obtained two kinds of bis-TIPS propargylic corannulenes **2** and **2'**. The differences in positions of TIPS propargylic groups between **2** and **2'** were revealed using NMR and X-ray crystallography. This reaction would be potentially applicable to multiple propargylation of C_{60} and to advanced functionalization using Huisgen cycloaddition reaction.
Keyword: Corannulene; Sodium Dispersion; Propargylation

これまでに我々はナトリウム分散体 (SD) による還元と硫酸ジアルキルによる求電子反応を用いることでC_{60}の多重プロピル化[1]とコランニュレン ($C_{20}H_{10}$) の多重メチル化[2]および多重アリル化[3]を達成してきた。この反応を C_{60} とコランニュレンの多重プロパルギル化に応用するために、本研究ではトリイソプロピルシリル (TIPS) 基で保護されたプロパルギル基を持つ耐還元性求電子剤 **1** を新規に設計・合成した。得られた **1** を過剰の SD 存在下でコランニュレンと THF 中、超音波照射下で 50 °C で 2 時間反応させた結果、2 種類のビス TIPS プロパルギルコランニュレン **2** および **2'** を得た。NMR と X 線結晶構造解析により、両者の TIPS プロパルギル基の付加位置の違いを明らかにした。この反応は、C_{60} の多重プロパルギル化と、ヒュスゲン環化付加反応を利用した高度官能基化への応用展開が期待できる。



1) K. Miwa, S. Aoyagi, T. Sasamori, S. Morisako, H. Ueno, Y. Matsuo, H. Yorimitsu, *Molecules.* **2022**, *27*, 450.
2) K. Miwa, S. Aoyagi, T. Amaya, T. Sasamori, S. Morisako, T. Kurogi, H. Yorimitsu, *Chem. Eur. J.* **2023**, 29, e202301557.
3) K. Ohtake, K. Miwa, S. Aoyagi, S. Morisako, T. Sasamori, H. Yorimitsu, The 103rd CSJ Annual Meeting (2023) [P3-2vn-06]

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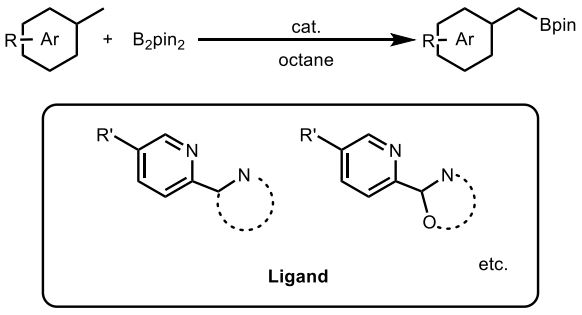
イリジウム触媒によるベンジル位 C-H ホウ素化反応；基質と多座配位子に関する検討

（上智大理工）○香川 滉・野中 達也・堀越 竜翔・内藤 夏海・鈴木 教之
Ir-Catalyzed C-H borylation of benzyl position; substrate scope and effects of multidentate ligands (*Sophia University*) ○Kou Kagawa, Tatsuya Nonaka, Ryuto Horikoshi, Natsumi Naito, Noriyuki Suzuki

There have been many reports on metal-catalyzed site-selective C-H borylation reactions, while examples of selective borylation of the benzyl position are still rare.[1)] We recently reported Ir-catalyzed borylation of a benzyl position using N,N-multidentate ligands.[2)] In this study, we investigated scope of substrates, as well as steric and electronic effects of ligands. Borylation reaction of 4-methylbenzoate ester using iridium complex and bidentate ligands as a catalyst system revealed that pyridyl-triazole ligands gave the benzyl-borylated product in good yield and selectivity. Attempts with varied substrates indicated that toluene derivatives bearing electron-withdrawing groups on para-position prone to afford the benzyl-borylated products.
Keywords : Borylation, C-H Activation, Iridium, N,N-Bidentate ligand

触媒による C-H 活性化による選択的なホウ素化は多く報告されているが、ベンジル位への選択的ホウ素化は報告例が少ない[1)]。当研究室では、二つの窒素原子を配位部位に持つ多座配位子を用いたイリジウム触媒によるベンジル位への位置選択的な C-H ホウ素化反応を報告した[2)]。本研究では、ベンジル位ホウ素化反応における基質適用範囲と多座配位子の立体・電子的効果について検討を行った。

合成した配位子とイリジウム触媒を用いて、オクタン溶媒中で 4-メチル安息香酸エチルを基質としてホウ素化反応を行ったところ、ピリジル部位とトリアゾール部位を併せ持つ配位子が良好な収率で、ベンジル位ホウ素化体を優先的に与えることが分かった。次に様々な基質を用いてホウ素化反応を試みたところ、メチル基のパラ位に電子吸引基を有する基質において特にベンジル位ホウ素化が進行しやすいことが分かった。



1) M. A. Larsen, C. V. Wilson, J. F. Hartwig, *J. Am. Chem. Soc.* **2015**, *137*, 8633.
2) M. Asoma, N. Suzuki et al. 日本化学会第 103 春季年会 P1-1am-97 (2023).

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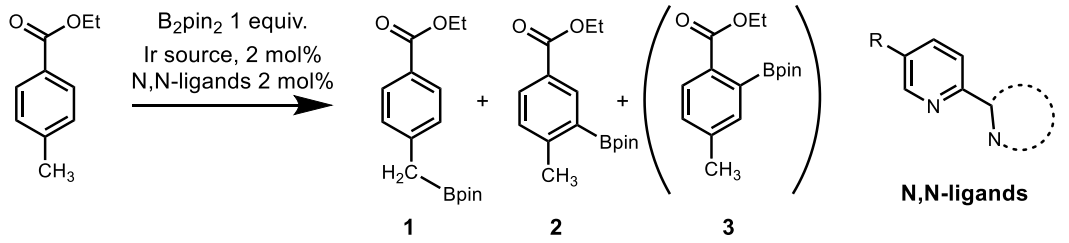
イリジウム触媒によるベンジル位 C-H ホウ素化反応；触媒種に関する検討

（上智大理工）○笠井 健太郎・荒木 啓次・櫻井 啓吾・鈴木 教之
Ir-Catalyzed C-H borylation of benzyl position; study on catalytically active species (*Sophia University*) ○Kentaro Kasai, Hiroshi Araki, Keigo Sakurai, Noriyuki Suzuki

Iridium-catalyzed aromatic C-H borylation has attracted much attention. Reports on borylation of benzyl position, on the other hand, has been still rare.[1)] In this study, we employed a few N,N-bidentate ligands for Ir-catalyzed borylation. Various N,N-ligands and $[Ir(OCH_3)(cod)]_2$ were used for borylation of ethyl 4-methylbenzoate with an equimolar amount of B_2pin_2. Product **1** was obtained selectively, of which the benzyl position was borylated. Reactions with substituted ligands resulted in similar yields and selectivity, indicating that no significant electronic effects of the ligands. The ligand bearing bulky substituents gave **1** with higher selectivity. The attempt with a ligand bearing oxazole gave an ortho-borylated product **3** selectively. Kinetic isotope effects of the selective formation of **1** and **3** were investigated; k_H/k_D were 1.11 and 1.95, respectively.
Keywords: Borylation, C-H Activation, Iridium, N,N-bidentate ligand

近年イリジウム錯体触媒を用いた芳香環上の位置選択的な C-H ホウ素化反応は注目を集めている。一方、ベンジル位のホウ素化反応については報告例が少ない[1)]。本研究では数種の N,N-二座配位子を用いて Ir 触媒による C-H ホウ素化反応を試み、反応における触媒種について検討した。ピリジル基をもつ N,N-二座配位子と $[Ir(OCH_3)(cod)]_2$ から触媒種を調製し、等量のピナコラートジボロン(B_2pin_2)を用いて 4-メチル安息香酸エチルのホウ素化を行ったところ、ベンジル位がホウ素化された生成物 **1** が優先的に得られた。配位子の電子的効果を調べるために様々な置換基 R を有する配位子で反応を試みたが著しい差異は見られなかった。嵩高い置換基を持つを用いたところ **1** が高い選択性で得られた。またオキサゾリン部位を持つ配位子を用いたところ選択的にオルト位で反応が進行した **3** が優先的に得られた。**1** と **3** の選択的な生成について速度論的同位体効果を観測したところ、k_H/k_D がそれぞれ 1.11 と 1.95 であった。



1) M. A. Larsen, C. V. Wilson, J. F. Hartwig, *J. Am. Chem. Soc.* **2015**, *137*, 8633.

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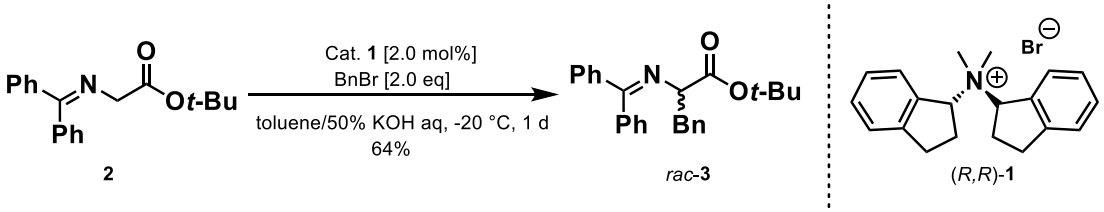
Bis(1-indanyl)amine 四級アンモニウム塩の合成とその相間移動触媒機能

（早大先進理工）○杉山 蒼・鹿又 宣弘
Synthesis of Bis(1-indanyl)amine Quaternary Ammonium Salts and Their Phase Transfer Catalysis (*Department of Chemistry and Biochemistry, Waseda University*) ○Aoi Sugiyama, Nobuhiro Kanomata

We have developed chiral pyridinophane-based phase-transfer catalysts (PTCs) and evaluated their catalytic functionality in asymmetric alkylation, achieving high enantioselectivities in C-C bond formation. However, the lengthy syntheses of these catalysts lead to difficulty in their availability. In this study, we designed a novel, more accessible quaternary ammonium salt **1**, synthesized via reductive amination of 1-indanone with (1*R*)-aminoindane followed by methylation of the resulting bis(1R-indanyl)amine. Their PTC activities in the asymmetric benzylation of glycine derivatives were also evaluated. An asymmetric benzylation reaction was performed using PTC **1** in toluene/50% KOH solution to give the desired but racemic product *rac*-**3** in 64% yield. Although PTC **1** demonstrated the catalytic activity, no significant enantioselectivity was observed in such reactions.
Keywords : Phase-transfer catalysis; Quaternary ammonium salts; C-C bond formation; Bis(1-indanyl)amine

我々はこれまでに面不斉ピリジノファン部位を有する相間移動触媒を合成し，不斉アルキル化反応の機能評価を行ってきた．所望の生成物が良好な化学収率および不斉収率で得られる一方，触媒合成には長い工程を必要とするため触媒調達の点で課題であった．そこで本研究では，より簡便に合成可能なインダン骨格を有する第四級アンモニウム塩を設計・合成し，グリシン誘導体の不斉ベンジル化[1]における相間移動触媒活性を評価した．

触媒として用いる N,N-dimethyl-bis(1R-indanyl)amine **1** は，1-indanone と (1R)-aminoindane の還元的アミノ化で得られる bis(1R-indanyl)amine をジメチル化して合成した．得られた触媒 **1** を用いてトルエン/50% KOH 水溶液の混合溶媒中，glycine 誘導体 **2** の不斉ベンジル化反応を行った．その結果，**1** は相間移動触媒としての活性を示して所望の phenylalanine 誘導体 **3** を収率 64%で与えたものの，**3** はラセミ体であり，顕著なエナンチオ選択性は確認されなかった．詳細については本発表にて報告する．



2 *rac*-**3** (*R*,*R*)-**1**

1) O'Donnell, M. J.; Benett, W. D.; Wu. S. *J. Am. Chem. Soc*. **1989**, *111*, 2353-2355.

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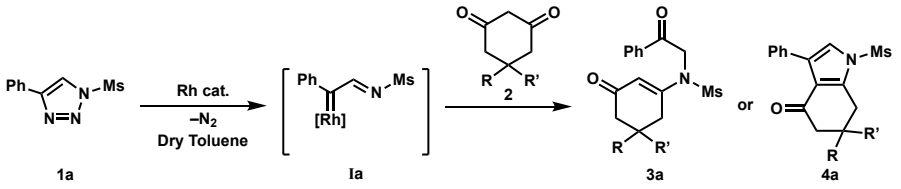
Reaction of *N*-Sulfonyl-1,2,3-Triazole with *β*-Diketone

([1]*Department of Applied Chemistry, Kobe City College of Technology*, [2]*Advanced Course of Applied Chemistry, Kobe City College of Technology*) ○Takuya Koizumi,[1] Yuto Yabuuchi,[2] Yuki Sakai,[1] Taiga Fujimoto,[1] Ryoto Itani,[1] Naoki Michihira[1] and Takuto Kamio[1]
Keywords: *N*-Sulfonyl-1,2,3-Triazole; Imino Carbenoid; 1,3-Diketone; Ligand Effect

Imino carbenoids **I** derived from *N*-sulfonyl-1,2,3-triazoles **1** can undergo useful tandem reactions, because they have a nucleophilic imino group in addition to an electrophilic carbenoid moiety.[1,2] In the present study, we investigated that Rh(II)-catalyzed reaction of *N*-mesyl-1,2,3-triazole (**1a**) with cyclic *β*-diketones **2**.

Enaminones **3a** were formed as a major product by the 2 mol% $Rh_2(piv)_4$-catalyzed reactions of **1a** with 3 equiv. of **2a–c** (Scheme 1, Table 1, Entries 1, 2, and 4). Furthermore, 2,3-fused pyrrole **4ac** was obtained in moderate yield by the 2 mol% Rh(II)-catalyzed reactions of **1a** with 3 equiv. of dimedone (**2c**) (Table 1, Entries 3, and 4).

On the other hand, in the case of the 2 mol% Rh(II)-catalyzed reactions of **1a** with 3 equiv. of 5-phenyl-1,3-cyclohexanedione (**2d**), the imino carbenoid **Ia**-participated products **3ad** and **4ad** were not observed, and the triazole skeleton-remained products **5ad** and **6ad** were obtained as a major product (Scheme 2).

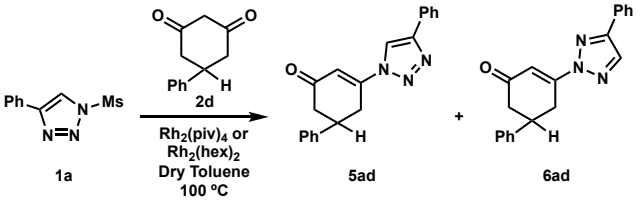


Scheme 1

Table 1. Reaction of triazole 1a with cyclic *β*-diketones 2 under various conditions[a]

Entry	2	R	R'	Rh cat.	Temp.	Yield[b] (%)	
						3a	4a
1	2a	H	H	$Rh_2(piv)_4$	100 °C	42	–
2	2b	CH_3	H	$Rh_2(piv)_4$	100 °C	58	–
3	2c	CH_3	CH_3	$Rh_2(hex)_4$	100 °C	23	22
4	2c	CH_3	CH_3	$Rh_2(piv)_4$	100 °C	33	12

[a]Conditions: 1 (1.0 mmol), 2 (3.0 mmol), 4 Å MS (400 mg), and Rh(II) catalyst (2 mol%) were combined in solvent (5 ml) and stirred under an argon atmosphere. [b]Isolated yield.



Scheme 2

1) a) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *143*, 5151. b) Gevorgyan, V.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2012**, *51*, 862. 2) a) Cheng, W.; Tang, Y.; Xu, Z.-F.; Li, C.-Y. *Org. Lett.* **2016**, *18*, 6168. b) Mi, P.; Yuan, H.; Wang, H.; Liao, P.; Zhang, J.; Bi, X. *Eur. J. Org. Chem.* **2017**, 1289.

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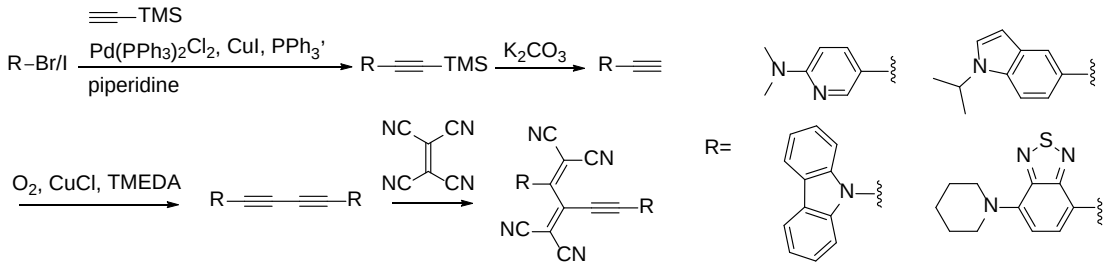
Push-pull chromophores with different heterocyclic donor moieties synthesized by [2+2] cycloaddition-retroelectrocyclization reaction

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*)
○Xu Chen,[1] Tsuyoshi Michinobu[1]

Keywords: Push-Pull Chromophores; Heterocyclic Donors; Nonplanar Structure; [2+2] Cycloaddition-Retroelectrocyclization Reaction

The [2+2] cycloaddition-retroelectrocyclization (CA-RE) reaction is an effective method for synthesizing push-pull chromophores with the advantages of the click reaction.[1] 2-[4-(Dimethylamino)phenyl]-3-([4(dimethylamino)phenyl]-ethynyl)-buta-1,3-diene-1,1,4,4-tetracarbonitrile (DDMEBT), obtained by the [2+2] CA-RE reaction, is a promising nonlinear optical (NLO) material.[2] DDMEBT can form a homogenous film with high-optical quality due to the nonplanar structure, leading to further advanced applications in all-optical switching.[3]

NLO properties of organic molecules can be tuned by molecular design. In this study, we designed and synthesized various donor-substituted 1,1,4,4-tetracyanobutadienes (TCBDs), in which the donor moiety is substituted with different heterocyclic substituents, including pyridine, carbazole, indole, and benzothiadiazole, referring to the structure of DDMEBT. These new TCBDs were characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR, and MALDI-TOF MS. Optical properties, electrochemical properties, and thermal stability of these chromophores were investigated by UV-Vis spectroscopy, cyclic voltammetry, TGA and DSC. Single crystal XRD data were employed to estimate the bond length alternation of the donor cyclic unit, which is a good indication of the efficiency of intramolecular charge transfer from donor to acceptor moieties.



1) T. Michinobu, F. Diederich, *Angew. Chem. Int. Ed.* **2018**, *57*, 3552. 2) T. Michinobu, J. C. May, J. H. Lin, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun*. **2005**, 737. 3) a) B. Esembeson, M. L. Scimeca, T. Michinobu, F. Diederich, I. Biaggio, *Adv. Mater.* **2008**, *20*, 4584. b) L. Dallachiesa, I. Biaggio, *Opt. Lett.* **2022**, *47*, 1924.

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ナフタレンテトラカルボン酸ジイミド誘導体のにおい物質による色彩変化

（大阪技術研）○山下 怜子
Color Changes of Naphthalenetetracarboxylic Acid Diimide Derivatives by Odor Substances
(*Osaka Research Institute of Industrial Science and Technology*) ○Reiko Yamashita

Naphthalenetetracarboxylic acid diimide derivatives with different functional groups were synthesized as pigments that allow easy visual recognition for the presence of odor substances in living spaces. In this presentation, we will report the synthesis of the derivatives and the color changes of derivatives obtained by exposing these derivatives to various odor substances such as acetaldehyde, hydrogen sulfide, and acetic acid.
Keywords : Odor Substances; Naphthalenetetracarboxylic Acid Derivatives; Color Change

生活空間におけるにおい物質（臭気ガス）の存在を、視覚で簡便に認識するための色素として、これまでに複数のナフタレンテトラカルボン酸ジイミド誘導体(NTADD)を合成してきた[1)]。本研究では、従来とは異なる 2 種類の置換基を導入した NTADD-c および NTADD-d (Fig. 1) を合成した。合成した NTADD-c と NTADD-d は、異なる色を示した。さらに NTADD-c と NTADD-d は、アセトアルデヒドおよび硫化水素の各臭気ガスとの接触に伴い色彩が変化した(Table 1)。一方、酢酸ガスに接触させても、NTADD-c および NTADD-d に色彩変化は認められなかった。

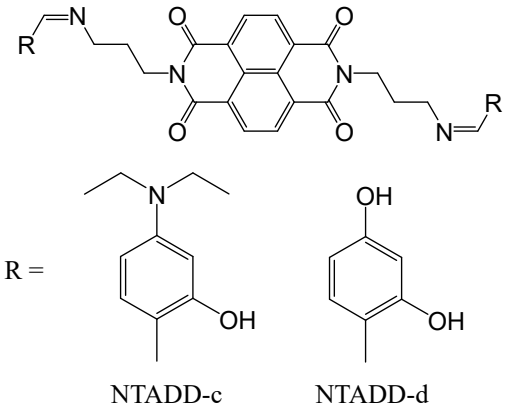

Fig. 1　NTADDs-c および NTADDs-d

ポスターでは、NTADD-c および NTADD-d の合成経路、それらを臭気ガスに曝した際の吸光度の経時変化についても報告する。

Gas	CH_3CHO	H_2S	CH_3COOH
NTADD-c			
NTADD-d			

Table 1　NTADD-c および NTADD-d の
ニオイ物質に対する色彩変化

1) 山下怜子, 喜多幸司：日本化学会第 96 春季年会(2016)講演予稿集, 公益社団法人日本化学会, 2016, 2PA-162

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強塩基を必要としない 3,5-ジメチルイソオキサゾールとアルデヒドの位置選択的縮合反応

（富山大院理工 [1]）○田中 亜希 [1]・杉原 匡祐 [1]・阿部 仁 [1]

Regioselective condensation of 3,5-dimethylisoxazole with aldehydes not using strong bases

([1]Graduate School of Science and Engineering, University of Toyama) ○Aki Tanaka,[1] Kyosuke Sugihara,[1] Hitoshi Abe [1]

The α-proton which is adjacent to two carbonyl groups in β-diketone, referred as to active methylene, has high acidity, and can be easily deprotonated by weak bases. Then, the resulting anion reacts with electrophiles affording α-substituted products. On the other hand, the γ-proton of β-diketones is less acidic, therefore, when two equivalents of a strong base such as LDA are used, the dianion species will be formed and reacts with electrophiles only at the γ-position. However, this method is not suitable for industrial use because of employing the strong base. In this study, we converted acetylacetone into isoxazole followed by condensation with various aldehydes. Then, the condensation product was reductively transformed into β-diketone. Consequently, we obtained γ-substituted β-diketone using milder reaction conditions than the conventional method.

Keywords : 3,5-dimethylisoxazole, aldehyde, condensation, regioselective, milder condition

β-ジケトン化合物の α 位のプロトンは酸性度が高く、比較的弱い塩基で容易に脱プロトン化が進行する。この際、生じたエノラートが求電子剤と反応することで α 位へ置換基導入が行える。一方、LDA などの強塩基を 2 等量用いるとジアニオンを形成し、γ 位へ置換基導入を行うことができる [1]。しかしながら強塩基を用いるこの方法は低温条件を必要とするなど工業利用には適していない。そこで我々は、強塩基を必要としない温和な条件下で γ 位に置換基が導入された β-ジケトン化合物の合成を試みた。

本研究ではアセチルアセトンから容易に誘導できるイソオキサゾールに対してアルドール型反応を検討した。その結果、強塩基を用いることなく様々なアルデヒドとの脱水縮合反応が位置選択的に進行した。その後、再びイソオキサゾール部を還元的に開裂することで最終的に γ 位に置換基が導入された β-ジケトン化合物が得られた (Figure 1)。

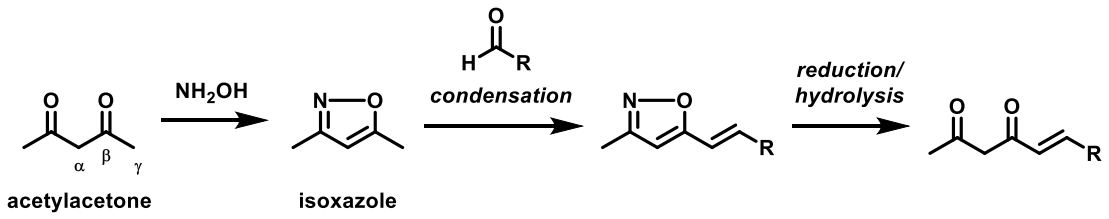

Figure 1. Regioselective condensation of β-diketones

1) Kel'in, A. V.; Mioli, A. *Curr. Chem. Org.* **2003**, *7*, 1855.

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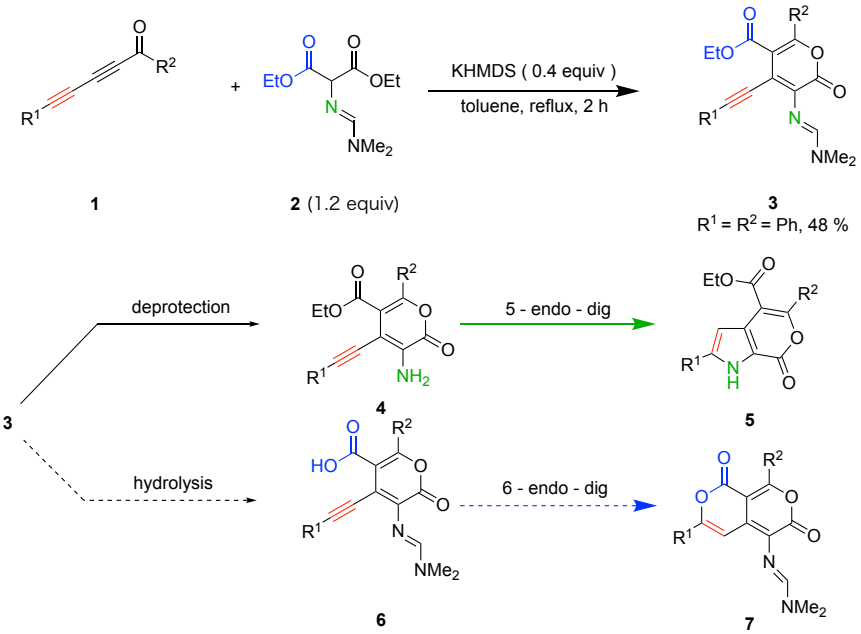
マロン酸ジエチル誘導体のジアルキニルケトンへの共役付加反応を用いた 4-アルキニル-2-ピロン合成とその応用

（三重大院工）平野 航太郎・○櫻井康佑・八谷 巖
Synthesis of 4-Alkynyl-2-pyrones using Conjugate Addition Reaction of Diethyl Malonate Derivatives to Dialkynyl Ketones and Its Application (*Graduate School of Engineering, Mie University*) Kotaro Hirano, ○Kosuke Sakurai, Iwao Hachiya

The pyrone skeleton is an important structure found in many natural products. Recently, we have reported the synthesis of pyranoindoles via intramolecular amination of 3-amino-2-pyrones.[1)] In this study, we have succeeded in synthesizing 4-Alkynyl-2-pyrones **3** with multisubstituted groups such as internal alkynes, ethoxycarbony and amino groups by conjugate addition of 2-aminomalonate **2** to dialkynyl ketones **1**. In this poster presentation, we report on the substrate scope and synthetic study of pyranopyrrol-7-one **5** and pyranopyran-1,6-dione **7** by subsequent functional group transformations.
Keywords : Alkynyl Ketone; Conjugate Addition Reaction; 2-Pyrone

ピロン骨格は多くの天然物に見られる重要な骨格である。近年当研究室では、3-アミノ-2-ピロンの分子内アミノ化反応によるピラノインドール合成を報告している。[1)] 今回、ジアルキニルケトン **1** と 2-アミノマロン酸ジエチル **2** の共役付加反応により、内部アルキン・エトキシカルボニル基・アミノ基といった官能基を有する多置換 4-アルキニル-2-ピロン **3** の合成を達成した。本ポスター発表では、基質適用範囲とその後の官能基変換によるピラノピロール-7-オン **5** およびピラノピラン-1, 6-ジオン **7** の合成を検討したので報告する。



1) K. Fukuoka, K. Imai, K. Hirano, S. Goto, R. Miura, I. Hachiya, *Asian J. Org. Chem.* **2022**, *11*, 2e202200110.

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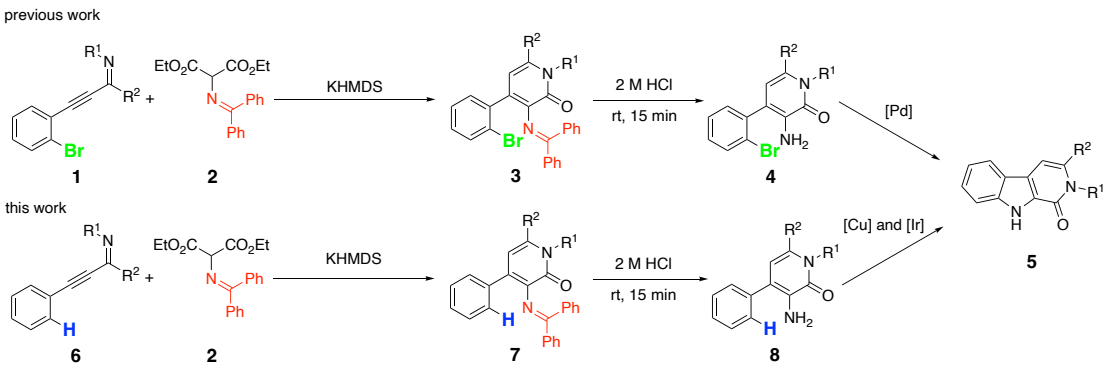
3-アミノ-2-ピリドンの分子内 C-H アミノ化反応による β-カルボリン-1-オンの合成

（三重大院工）佐々木 陸斗・○松尾 明彦・八谷 巖
Synthesis of β-Carboline-1-one by Intramolecular C-H Amination of 3-Amino-2-pyridone (*Graduate School of Engineering, Mie University*) Rikuto Sasaki, ○Akihiko Matsuo, Iwao Hachiya

Synthesis of 2,3-disubstituted β-carbolin-1-ones is disclosed using copper and iridium-catalyzed intramolecular amination of 3-amino-4-phenyl-2-pyridones prepared by the conjugate addition reaction of diethyl 2-aminomalonate having a bulkier ketimine moiety to alkynyl imines. The transformation of the synthesized 3-amino-4-phenyl-2-pyridones using copper and iridium-catalyzed intramolecular amination produced 2,3-disubstituted β-carbolin-1-ones in good yields.
Keywords : C-H Amination; 2-Pyridone; β-Carboline-1-one

β−カルボリン−1−オン骨格を有する化合物は、医薬品としての効果が期待されている。最近我々は、2-アミノマロン酸ジエチル **2** のアルキニルイミン **1** への共役付加反応および脱保護により合成した 3-アミノ-2-ピリドン **4** の Pd 触媒を用いた分子内アミノ化による基質適用範囲の広い、2,3-二置換-β-カルボリン-1-オン **5** の新規合成法を報告している。[1]しかし、この合成法では、分子内アミノ化を適用するためにカップリングの手がかりとなるブロモ基を事前に導入しておく必要があるため、出発物質のアルキニルイミンの合成ステップ数が多い欠点がある。そこで今回我々は、ブロモ基を有さないアルキニルイミン **6** への 2-アミノマロン酸ジエチルの共役付加反応および脱保護により合成した 3-アミノ-2-ピリドン **8** を銅およびイリジウム触媒を用いた分子内 C-H アミノ化反応により、2,3-二置換-β-カルボリン-1-オン **5** を合成できることを見出した。本ポスター発表では、反応条件および基質適用範囲について報告する。



1) Masuda, H.; Morishita, H.; Sasaki, R.; Takahata, K.; Uemura, K.; Hachiya, I. *ChemistrySelect*, **2022**, *7*, e202201737.

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3-アミノ-2-ピリドンの C-H/N-H 環化反応を鍵反応とする 4-エトキシカルボニル-β-カルボリン-1-オンの合成

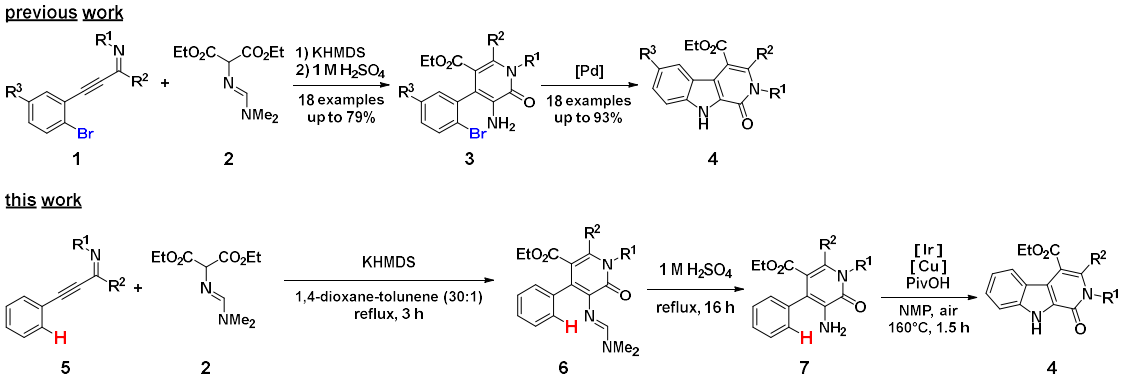
（三重大院工）森 保乃華・○森村 真帆・八谷 巖

Synthesis of 4-Ethoxycarbonyl-β-carbolin-1-ones via C-H/N-H Cyclization of 3-Amino-2-pyridones as a Key Reaction (*Graduate School of Engineering, Mie University*) Honoka Mori, ○Maho Morimura, Iwao Hachiya

β-Carbolin-1-ones are found in various alkaloids, and in particular, substrates with a carbonyl group at the 4-position are known to possess biological activity. We have previously reported the synthesis of 4-ethoxycarbonyl-β-carbolin-1-ones **4** by intramolecular Buchwald-Hartwig amination of 3-amino-4-(2-bromophenyl)-2-pyridones **3**, which was synthesized by conjugate addition of diethyl 2-aminomalonate to alkynylimines having a bromo group.[1] However, this method requires the prior introduction of a bromo group as a coupling clue, which is a disadvantage in terms of the large number of steps and atom economy. In this work, we have found that 4-ethoxycarbonyl β-carboline-1-ones **4** can be synthesized by intramolecular C-H amination of 3-amino-2-pyridones **7** via iridium-catalyzed carbon-hydrogen bond activation. In this presentation, we report on the scope of substrate and reaction conditions.

Keywords：Intramolecular C-H Amination; 2-Pyridone; β-Carbolin-1-one

β-カルボリン-1-オンは、様々なアルカロイドに含まれており、特に 4 位にカルボニル基を有する基質は生物活性を有することで知られている。当研究室は過去にブロモ基を持つアルキニルイミン **1** への 2-アミノマロン酸ジエチル **2** の共役付加反応によって合成した 3-アミノ-4-(2-ブロモフェニル)-2-ピリドン **3** の、分子内 Buchwald-Hartwig アミノ化反応による 4-エトキシカルボニル-β-カルボリン-1-オン **4** の合成法を報告した。[1] しかし、この合成法において、カップリングの手がかりとなるブロモ基を事前に導入しておく必要があり、ステップ数が多いことや、アトムエコノミーの観点において欠点がある。今回、我々はブロモ基を有さない 3-アミノ-2-ピリドン **7** の、イリジウム触媒を用いた炭素-水素結合活性化を経る分子内 C-H アミノ化反応により、4-エトキシカルボニル-β-カルボリン-1-オン **4** を合成できることを見出した。本ポスター発表では基質適用範囲および反応条件について報告する。



1) Miura, R.; Goto, S.; Hashimoto, T.; Hachiya, I. *ACS Omega.* **2020**, *5*, 15631.

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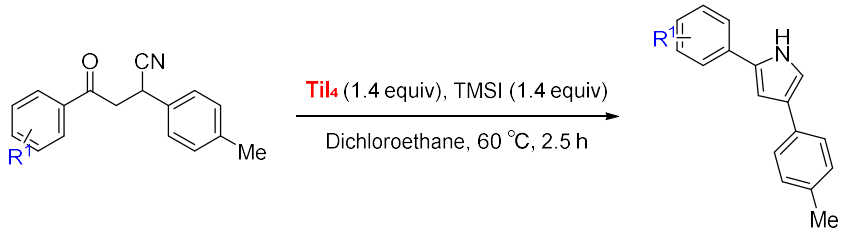
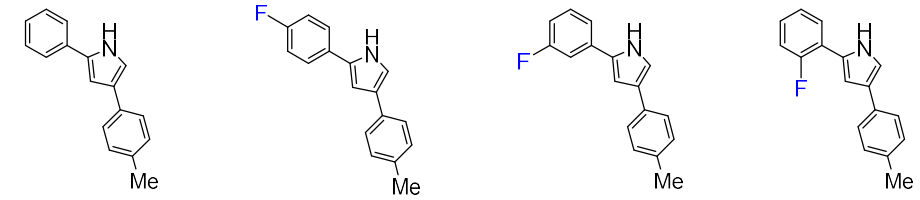
四ヨウ化チタンを用いたβ−シアノカルボニル化合物の分子内環化によるピロールの合成

（三重大院工）栃木 駿哉・○上村 太一・八谷 巖
Synthesis of Pyrroles by Intramolecular Cyclization of β-Cyanocarbonyl Compounds Using Titanium Tetraiodide (*Graduate School of Engineering, Mie University*) Shunya Tochigi, ○ Taichi Uemura, Iwao Hachiya

Pyrrole, a nitrogen-containing hetero 5-membered ring compound, is often found in natural products and bioactive substances, and the development of efficient synthetic methods is highly desired. The intramolecular cyclization of β-cyanocarbonyl compounds using titanium tetraiodide proceeded to produce pyrroles. In the presentation, we report on the scope of substrate in detail.
Keywords : Titanium Tetraiodide; Pyrrole; Intramolecular cyclization;

ピロール構造は、生理活性物質に多く含まれる含窒素ヘテロ環化合物の一つであり、効率的な合成法の開発が望まれている。当研究室では、四ヨウ化チタンの中程度のルイス酸性、ヨウ素化能力、還元能力および環化能力を活用した合成反応を報告している。[1] ヨウ素化ー環化反応の例として、2-ヨードピリジン、ヨードイソキノリン、2-アリール-4-ヨードキナゾリンの合成法を見出し報告している。[2-4] 今回、β-シアノカルボニル化合物の四ヨウ化チタンを用いた分子内環化反応により、ピロールを合成できることを見出した。本発表では、基質適用範囲について詳細を述べる。





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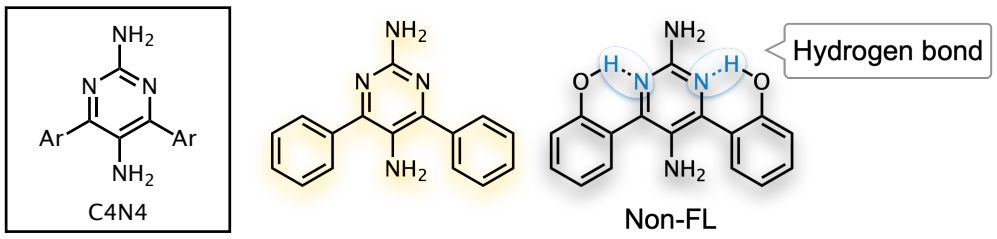
C4N4 化合物の蛍光発光における分子内水素結合の影響

（慶應院薬[1]・微化研[2]）○新村 万緒[1]・公平 実希[1]・堤 亮祐[1]・熊谷 直哉[1,2]
The effect of intramolecular hydrogen bond on fluorescence of C4N4 ([1]*Graduate School of Pharmaceutical Science, Keio University*, [2]*Institute of Microbial Chemistry*) ○Mao Niimura,[1] Miki Kohei,[1] Ryosuke Tsutsumi,[1] Naoya Kumagai[1,2]

C4N4, a new scaffold for fluorescent material based on a 2,5-diaminopyrimidine core, features a single-step modular synthesis, high quantum yield, and large Stokes shift, anticipating a broad range of fluorometric applications. Recently, we found that the C4N4 compounds with a hydrogen-bonding functional group proximal to the central pyrimidine core prefer non-radiative decay. In this study, we performed systematic investigation to elucidate the effect of steric and electronic properties of neighboring hydrogen-bonding units on the physicochemical behavior of C4N4. C4N4 compounds with various substituents bearing hydroxy and amino groups were examined. Most of the C4N4 compounds capable to form intramoleculrar hydrogen bonds were non-fluorescent, while some compounds bearing specific functional groups (e.g. amide groups) retained fluorescence.
Keywords : C4N4; Fluorescence; Probe; Quenching

当研究室は，2,5-ジアミノピリミジンを母骨格とする C4N4 化合物が強蛍光性を示すことを見出し，報告している[1)]。C4N4 化合物は市販試薬より 1 工程で合成可能で，一般に高い量子収率と大きなストークスシフトを示し，汎用型蛍光化合物としての応用が期待される。今回，4,6 位アリール基のオルト位にピリミジン窒素と水素結合を形成可能な官能基を導入することで，蛍光性が消失することを見出した。本研究では，水素結合供与能や構造的特徴の異なる様々な置換基を導入し，分子内水素結合による蛍光性への影響を系統的に精査した。

ヒドロキシ基およびアミノ基を基軸とする種々の水素結合性官能基を導入した C4N4 化合物を合成し、蛍光特性を調査した。分子内水素結合を形成し得るほとんどの化合物は無蛍光性であったが，アミド基などを有する一部の C4N4 化合物は，蛍光性を維持した。



1) H. Noda, Y. Asada, T. Maruyama, Takizawa, Naoki, N. Noda, M. Shibasaki, N. Kumagai, *Chem. Eur. J.* **2019**, *25*, 4299–4304.

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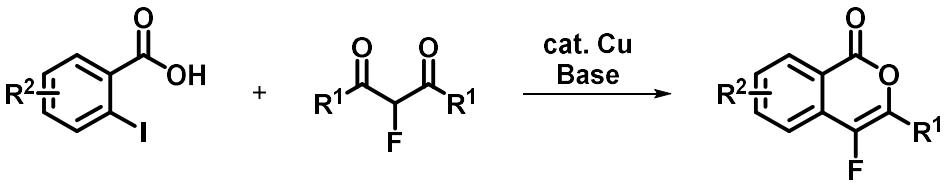
銅触媒によるカップリング反応を利用した含フッ素イソクマリンの合成

（東農工大院工 [1]）○坂上晴紀 [1]・坪内 彰 [1]・齊藤亜紀夫 [1]
Synthesis of Fluorinated Isocoumarins by Copper-Catalyzed Coupling Reaction ([1]*Grad. Sch. Eng., Tokyo Univ. Agric. Tech.*) ○Haruki Sakagami,[1] Akira Tsubouchi,[1] Akio Saito[1]

Since organofluorine compounds have been widely applied in the fields of medicinal, agrochemical, and material chemistry due to their unique properties, the development of their synthetic methods is an important research theme. However, synthetic methods of fluorinated isocoumarins are limited to methods based on intramolecular cyclization and carbon monoxide insertion reactions and the number and positions of fluorine substitutions are restricted. Therefore, on the basis of Xi's isocoumarin synthesis, we investigated the synthesis of fluorinated isocoumarins by tandem coupling-cyclization-deacylation reaction of 2-halobenzoic acids and 2-fluoro-1,3-diketones. As a result, it was found that the desired 4-fluoroisocoumarins were obtained in good yield from 2-iodobenzoic acids and 2-fluoro-1,3-diketones using a copper catalyst and a base. The synthesized 4-fluoroisocoumarin is also useful as a synthetic intermediate and can be derived into other organofluorine compounds.
Keywords : Fluorinated Heterocycles; Isocoumarins; Copper; Coupling Reaction

有機フッ素化合物はユニークな性質を有することから、医農薬化学や材料科学の分野で幅広く応用されているため、その合成法の開発は重要な研究課題である。しかし、含フッ素イソクマリンの合成法は、分子内環化反応や一酸化炭素挿入反応を基盤とする手法に限られており、フッ素の置換位置や数は制限されている [1)]。そこで我々は、Xi らによるカップリング反応を基盤とするイソクマリン合成法 [2)]の知見を基に、2-ハロ安息香酸と 2-フルオロ-1,3-ジケトンのカップリングー環化ー脱アシル化反応による含フッ素イソクマリンの合成について検討した。

その結果、2-ヨード安息香酸と 2-フルオロ-1,3-ジケトンとの混合物を、銅触媒存在下、塩基で処理することで、目的の 4-フルオロイソクマリンが良好な収率で得られることが明らかとなった。また、合成した 4-フルオロイソクマリンは合成中間体としても有用であり、他の有機フッ素化合物に誘導できた。詳細な検討結果については本年会で述べる。



1) (a) Y. V. Zonov, V. M. Karpov, T. V. Mezhenkova, *Russ. J. Org. Chem.* **2019**, *55*, 1103; (b) T. Yata, Y. Nishimoto, K. Chiba, M. Yasuda, *Chem. Eur. J.* **2021**, *27*, 8288; (c) 坂上晴紀, 坪内 彰, 齊藤亜紀夫, 第 46 回フッ素化学討論会, **2023**, O-12.
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6,9-ビス（ジフェニルアミノビフェニル）置換フェナントロイミダゾールの合成と物性

（崇城大院工 [1]）○谷口 莉玖 [1]・水城 圭司 [1]・八田 泰三 [1]

Synthesis and properties of 6,9-bis(diphenylaminobiphenyl)-substituted phenanthroimidazoles

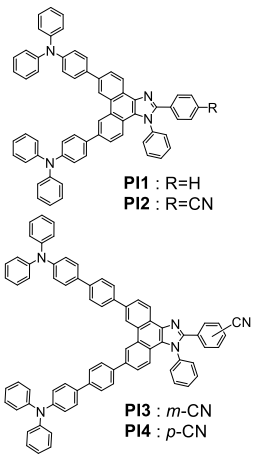
([1]*Graduate School of Engineering, Sojo University*) ○Riku Taniguchi,[1] Keiji Mizuki,[1] Taizo Hatta[1]

Organic light-emitting diodes (OLEDs) are attracting much attention as a light source for the next generation flat panel displays and flat plane lightings. In general, practical OLEDs have complicated multi-layered structures, which have increased the cost of OLED devices and have hindered their widespread use. In recent years, solution-coatable bipolar non-doped emitters have attracted attention as materials that can reduce the cost of OLED devices.[1)] We have previously synthesized 6,9-disubstituted phenanthroimidazoles **PI1** and **PI2** with triphenylamino groups and have found them to be solution-coatable bipolar materials with strong deep blue fluorescence[2)].

In this study, 6,9-disubstituted phenanthroimidazole derivatives **PI3** and **PI4** having diphenylaminobiphenyl groups were synthesized to improve luminescent properties of **PI1** and **PI2**. It was revealed that both **PI3** and **PI4** were solution-coatable bipolar deep blue fluorescent materials, and showed higher thermal stability and fluorescence intensity, and better carrier balance compared to **PI1** and **PI2**.

Keywords : Organic light-emitting diodes; Phenanthroimidazole; Deep blue fluorescent material; Bipolar property; Solution-coatable property

次世代フラットパネルディスプレイ・平面照明の光源として、Organic light-emitting diodes (OLEDs) が注目されている。しかし、実用的な OLED は、一般的に複雑な多層構造をしているためデバイスのコストが高く、普及の妨げとなっている。近年、OLED デバイスの低コスト化を可能とする材料として、溶液塗布可能なバイポーラ性ノンドープエミッターに関心がもたれている [1)]。先に我々は、トリフェニルアミノ基を持つ 6,9-ジ置換フェナントロイミダゾール **PI1**, **PI2** を合成し、これらが溶液塗布可能なバイポーラ性深青色強蛍光材料であり、ノンドープエミッターとしての期待が持たれることを明らかにした [2)]。



本研究では、**PI1**, **PI2** の発光特性の向上を目指してジフェニルアミノビフェニル基を持つ 6,9-ジ置換フェナントロイミダゾール誘導体 **PI3**, **PI4** を合成した。**PI3**, **PI4** はいずれも溶液塗布可能なバイポーラ性深青色強蛍光材料であり、**PI1**, **PI2** と比較して熱安定性および蛍光強度、キャリアバランスの向上がみられた。

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ヘキサアザトリナフチレン還元体合成の反応機構

（岡理大院理工[1]・茨城大理[2]）○大島 貴宏[1]・若松 寛[1]・藤澤 清史[2]・東村 秀之[1]
Reaction Mechanism of Hexaazatrinaphthylene Reductant Synthesis ([1]*Graduate School of Science and Engineering, Okayama University of Science*, [2]*College of Science, Ibaraki University*) ○ Takahiro Oshima,[1] Kan Wakamatsu,[1] Kiyoshi Fujisawa,[2] Hideyuki Higashimura[1]

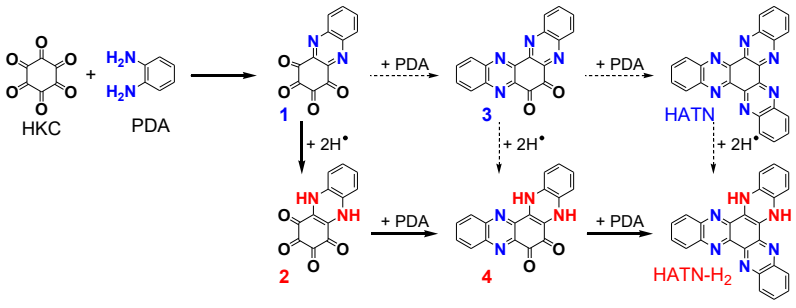
Although hexaazatrinaphthylene (HATN) was obtained by the reaction of hexaketocyclohexane (HKC) with 1,2-phenylenediamine (PDA), we have found that the HATN reductant (HATN-H_2) with long wavelength absorption can be synthesized by the reaction at a higher temperature.[1)] In this report, we examined the reaction mechanism by experiment and calculation.

First, the reaction of HKC with PDA only gave HATN-H_2, showing that the reducing agent was PDA. In addition, no reduction of HATN occurred even with excess PDA, indicating that the reaction intermediate was reduced by PDA. Next, the LUMO and electronic energy of each compound in the following scheme were calculated by DFT method. The LUMO levels were in the order of HATN > **3** > **1**, meaning that **1** is the easiest to reduce. The energy changes in reduction steps of **1** → **2**, **3** → **4**, and HATN → HATN-H2 were compared, and hence, **1** → **2** was the most favorable. From these results, the most likely pathway could be the formation of **1** from HKC and PDA, followed by reduction by PDA to form **2**, which reacts with two molecules of PDA to produce HATN-H_2.
Keywords Hexaazatrinaphtylene Reductant; Hexaketocyclohexane; 1,2-Phenylenediamine; Long wavelength absorption; DFT calculation

ヘキサアザトリナフチレン (HATN) はヘキサケトシクロヘキサン (HKC) と 1,2-フェニレンジアミン (PDA) の反応で得られていたが、当研究室では本反応をより高温で行うことで HATN 還元体 (HATN-H_2) を合成できることを見出している。4 つのイミノ基と 2 つのアミノ基が集積されることで 667 nm の長波長吸収を持つことが特徴である [1)]。この反応機構の解明のため、実験と計算の両面から検討を行った。

まず、HKCとPDAのみで反応してもHATN-H_2が得られたことから、還元剤はPDAと考えられる。またHATNに過剰のPDAを反応させても、還元体は全く得られなかったことから、反応中間体が還元されていると思われる。

次に、下式に示す **1**、**3**、HATN の LUMO 準位と電子エネルギーを DFT 計算で求めた。LUMO 準位は HATN> **3**> **1** の順に低くなり、**1** が最も還元されやすくなることが分かった。また **1→2**、**3→4**、HATN→HATN-H_2 のエネルギー変化を比較したところ、**1→2** が最も有利なことが判明した。以上から、HKC と PDA から **1** を形成し、PDA で還元されて **2** が得られ、PDA と反応して **4** そして HATN-H_2 が生成する経路が最も有力であると考えられる。



1) 大島貴宏、若松寛、藤澤清史、東村秀之、日本化学会第 102 春季年会，P3-2vn-49 (2023).

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環拡大型キノリン 3 量体 Enlarged TriQuinoline の創製

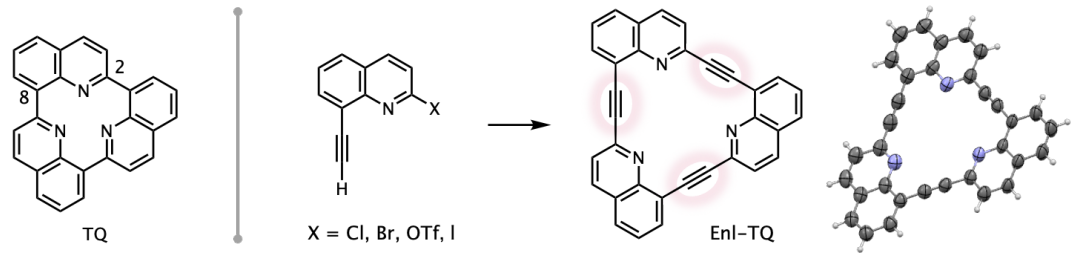
（慶大院薬[1]・微化研[2]）○山下 舞[1]・堤 亮祐[1]・熊谷 直哉[1,2]
Design and Synthesis of Enlarged TriQuinoline ([1]*Graduate School of Pharmaceutical Sciences, Keio University*, [2]*Institute of Microbial Chemistry*) ○Mai Yamashita,[1] Ryosuke Tsutsumi,[1] Naoya Kumagai[1,2]

TriQuinoline (TQ), a quinoline trimer concatenated at the 2- and 8-positions in a head-to-tail fashion, strongly binds a proton in the central atomic-sized cavity and exhibits various unique physicochemical properties. We newly designed a ring-expanded congener, Enlarged TriQuinoline (Enl-TQ), by inserting three acetylene linkers between the quinoline units. Enl-TQ is expected to accommodate larger guests other than a proton in the central enlarged cavity surrounded by three sp^2-hybridized N atoms and acetylene π orbitals.

Herein, we report the synthesis of Enl-TQ via a single step trimerization of 8-ethynyl-2-haloquinoline as the precursor. While Sonogashira coupling reactions were unsuccessful in obtaining cyclized products, the desired Enl-TQ was synthesized under Castro–Stephens coupling conditions utilizing copper(I) acetylide prepared from 8-ethynyl-2-iodoquinoline in refluxing pyridine.
Keywords :　Quinoline; Acetylene; Macrocycle; Supramolecular Chemistry

キノリン 3 分子が 2,8 位で逐次環状連結した TriQuinoline（TQ）は，中心に位置する 1 原子サイズの空隙に強固にプロトンを包摂し，水溶性や超分子会合等の様々な特異物性を発現する [1)]。本研究では，TQ の環拡大型類縁体として，キノリン連結部位に直線型トポロジーを有するアセチレンユニットを挿入した Enlarged TriQuinoline（Enl-TQ）をデザインした。本新奇分子はそれぞれ 3 つの窒素 sp^2 軌道·配位性 π 軌道を同一平面内に擁する特異な中心空隙を有しており，プロトン以外のゲストの捕捉が期待される。

8-エチニル-2-ハロキノリンを環化前駆体とした一挙 3 量化による合成を試みた。合成した環化前駆体を薗頭カップリング反応に付したところ，Enl-TQ は全く得られなかった。一方，8-エチニル-2-ヨードキノリンから化学量論量の銅アセチリドを調製しピリジン中で加熱還流する Castro–Stephens カップリング反応を用いたところ，Enl-TQ の合成に成功した。



1) S. Adachi, M. Shibasaki, and N. Kumagai, *Nat. Commun.* **2019**, *10*, 3820

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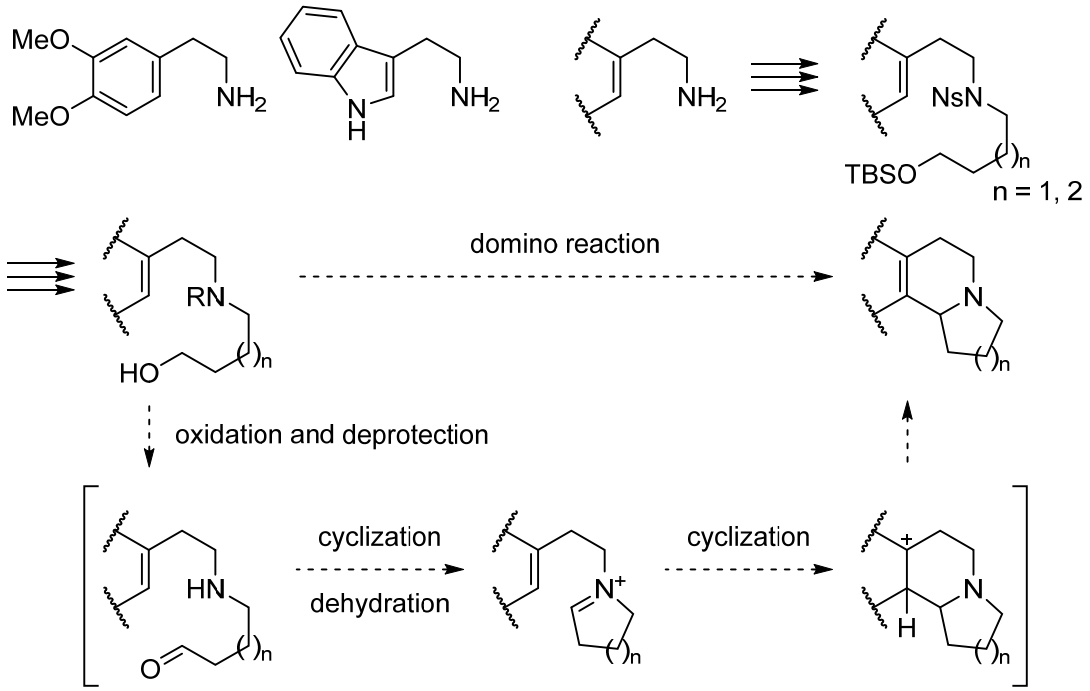
生体触媒反応での展開を志向するアルカロイド骨格の合成研究

（明星大理工）○安達 悠之介・稲葉 浩晃・内田 郁之・井坂 圭汰・冨宿 賢一
Synthetic Studies of Alkaloid Skeletons for Development in Biocatalytic Reactions (*Department of Interdisciplinary Science and Engineering, Meisei University*) ○Yunosuke Adachi, Hiroaki Inaba, Fumiyuki Uchida, Keita Isaka, Ken-ichi Fuhshuku

Domino-type reactions that progress continuously from functional group transformations such as hydrolysis or oxidation-reduction were investigated. The reactions are those in which bond formation or skeletal construction proceed continuously from the intermediates produced by functional group transformation to construct the skeletons of isoquinoline alkaloids and indole alkaloids. We believe that these reactions can be developed into biocatalytic reactions and used as asymmetric synthesis. Starting from commercially available amines, the corresponding amino alcohol derivatives were synthesized, and various functional group transformations were investigated.
Keywords : Alkaloid; Domino Reaction; Hydrolysis; Oxidation-Reduction; Intramolecular Cyclization

加水分解や酸化還元による官能基変換から連続的に進行するドミノ型合成反応の研究を進めている。官能基変換により生じる中間体から連続的に結合形成や骨格構築が進行し、イソキノリンアルカロイドやインドールアルカロイドの基本骨格を構築する反応である。生体触媒反応に展開し、不斉合成として利用することができると考えている。市販のアミンから対応するアミノアルコール誘導体に変換後、各種の官能基変換を検討している。



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$NaHSO_4/SiO_2$ 存在下 2-(1-ヒドロキシアルキル)フェノール類を用いたクロマン類のワンポット合成

（日大理工）○黒澤 恵里・早川 麻美子・古川 拓哉・青山 忠
One-pot Synthesis of Chromans in the presence of $NaHSO_4/SiO_2$ using 2-(1-hydroxyalkyl)phenols (*College of Science and Technology, Nihon University*) Eri Kurosawa, Mamiko Hayakawa, Takuya Furukawa, Tadashi Aoyama

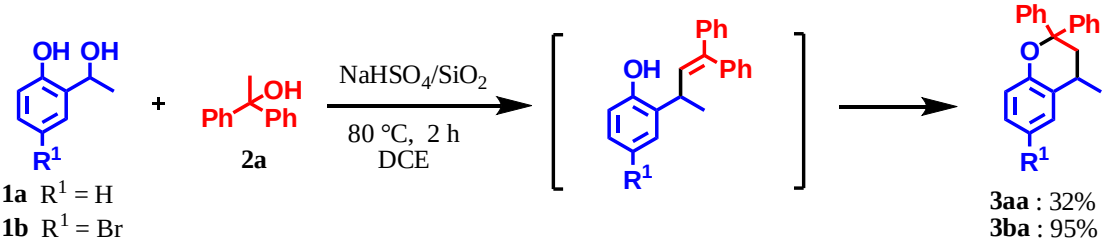
We have previously developed a simple one-pot method for the synthesis of chromans from two alcohols in the presence of $NaHSO_4/SiO_2$. It is attempts to synthesize 4-alkylchromanes using 2-(1-hydroxyethyl)phenol (**1a**) and 1,1-diphenylethanol (**2a**). However, the desired products could only be obtained 32% yields [1]. Whereas a similar reaction was performed using 2-(1-hydoroxyethyl)4-bromophnol(**1b**) instead of **1a** in the presence of $NaHSO_4/SiO_2$ (2.1mmol/g), and the corresponding chroman was obtained with a yield of 95% (**Scheme**).

In this study, we investigated the synthesis of 4-alkylchromanes using various 2-(1-hydoroxyalkyl)4-bromophnol, which was difficult by the previous method.

Keywords : Chroman, One-pot Synthesis, supported reagents, Copling

先に我々は $NaHSO_4/SiO_2$ 存在下、2 種のアルコールからクロマン類をワンポットで合成する簡便な手法を開発した。しかし、2-(1-ヒドロキシエチル)フェノール (**1a**)と 1,1-ジフェニルエタノール(**2a**)を用いて、4-アルキルクロマン類の合成を試みたが、目的物は 32%の収率でしか得られなかった [1]。一方、**1a** の代わりに 2-(1-ヒドロキシエチル)4-ブロモフェノール(**1b**)を用いて反応を行ったところ、**3ba** は 95%の収率で得られた(**Scheme**)。

本研究では種々の 2-(1-ヒドロキシアルキル) 4-ブロモフェノール類を用いて、先の手法では困難であった 4-アルキルクロマン類の合成の検討を行った。



1a R^1 = H
1b R^1 = Br

3aa : 32%
3ba : 95%

1) T. Aoyama, *et al., Synlett,* **2015**, 1875

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イソプロピル基を有するアミノアルコールから誘導したイソチオシアネートを用いるベンゾセレノテトラミソールの合成

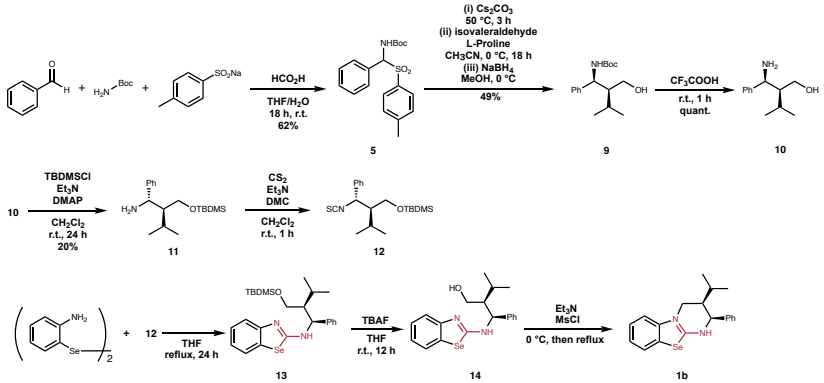
（日大生産工 [1]）○齋藤 梨花 [1]・市川 隼人 [1]

Synthesis of benzoselenotetramisole using isothiocyanates derived from amino alcohols with an isopropyl group. ([1]*College of Industrial Technology, Nihon University.*) ○Rika Saito,[1] Hayato Ichikawa[1]

Isothiourea compounds containing sulphur, are Lewis bases and have been actively investigated as organocatalysts. However, there are a few reports on isoselenourea catalysts, which is the homologue of selenium. Among these reports, isoselenourea-catalyzed kinetic resolution of tertiary alcohols showed reactivity comparable to or better than that of isothiourea catalysts[1]. On the other hand, we have previously synthesised 2-amino-1,3-benzoselenazoles without transition metal elements, using diselenides and commercial amino alcohols as starting materials[2]. Using that method, we investigated the synthesis of chiral benzoselenotetramisoles from isothiocyanates derived from the synthesised amino alcohols[3] with an isopropyl group.

Keywords : Selenium; Isoselenourea catalyst; Benzoselenotetramisole

イソチオ尿素化合物はルイス塩基であり，有機触媒として盛んに研究されている．一方で, 同族元素であるセレンを含むイソセレノ尿素触媒に関する報告は非常に少ない．この報告の中で，イソセレノ尿素触媒を用いた第 3 級アルコールの速度論的光学分割では, イソチオ尿素触媒を用いた場合と比較して同等またはそれ以上の反応性を示したことが報告された [1]．この報告例から，イソセレノ尿素が別の不斉合成反応においても高い反応性を示すことが期待できる．当研究室では，過去にジセレニドと市販のアミノアルコールを出発原料とした 2-アミノ-1,3-ベンゾセレナゾールの合成法を報告した [2]．そこで本研究では，はじめにイソプロピル基を有するアミノアルコールを合成 [3,4] し，環化反応の原料であるイソチオシアネートに官能基変換するための前段階としてヒドロキシ基のシリル保護を行った．



1) McLaughlin, C.; Smith, A. D. *Chem. Eur. J.* **2021**, *27*, 1533-1555.
2) Ichikawa, H.; Miyashi, N.; Ishigaki, Y.; Mitsuhashi, M. *Heterocycles*, **2020**, *101*, 444.
3) Yang, J. W.; Pan, S. C.; List, B. *Org. Synth*. **2009**, *86*, 11.
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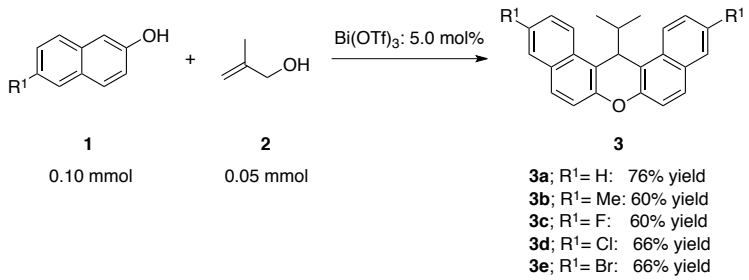
Bismuth Triflate 触媒を用いた 2-Naphthol 類と Allyl Alcohol の反応による Dibenzoxanthene 誘導体合成

（山形大院理工）○皆川 真規・佐藤 秀哉
Preparation of Dibenzoxanthene Derivatives from 2-Naphthols and an Allylic Alcohol by Bismuth Triflate Catalyst (*Graduate School of Science and Engineering, Yamagata University*)
○Maki Minakawa, Syuya Sato

O-Containing heterocyclic compounds are significant chemical structures due to their biological activities and photochromic properties. Previously, we described the bismuth triflate-catalyzed intermolecular cyclization of phenols with diols[1] and the bismuth triflate-catalyzed intermolecular cyclization of phenols with allylic alcohols.[2] This time, a bismuth triflate-catalyzed reaction of 2-naphthols (**1a**–**e**) with an allylic alcohol **2** to give the corresponding dibenzoxanthene derivatives **3a**–**e** is reported. The reaction of 2-naphthol (**1a**: 0.10 mmol) with 2-methylprop-2-en-1-ol (**2**: 0.05 mmol) in the presence of bismuth triflate (5.0 mol% based on **1a**) as a catalyst in toluene at 60 °C for 17 hours afforded dibenzoxanthene **3a** (R^1=H) in 76% isolated yield. Under similar reaction conditions, dibenzoxanthene derivatives **3b**–**e** were obtained in 60–66% isolated yield.

Keywords : Bismuth Triflate; Catalyst; Dibenzoxanthene; Allylic Alcohol

含酸素ヘテロ環化合物は, 生体活性や光機能性特性を有する需要な化学構造である. 当研究室では, ビスマストリフラート触媒を用い, フェノール類とジオールを原料とした含酸素ヘテロ環骨格の構築,[1] およびフェノール類とアリルアルコールを原料とした含酸素ヘテロ環化合物の合成を達成した.[2] 今回, ビスマストリフラート触媒を用いた 2-ナフトール類 **1a–e** とアリルアルコール **2** を原料とした dibenzoxanthene **3a–e** の合成を報告する. すなわち, 2-naphthol (**1a**: 0.10 mmol)と 2-methylprop-2-en-1-ol (**2**: 0.05 mmol) をビスマストリフラート(5.0 mol% based on **1a**) 存在下, toluene 溶媒中, 60 °C, 17 時間で加熱攪拌した場合, dibenzoxanthene **3a** (R^1=H)を 76%収率で得た (Scheme 1). 同様の触媒反応条件下, dibenzoxanthene 誘導体 **3b**–**e** を 60–66%の収率で得ることができた.



Scheme 1. 2-Naphthol 類 とアリルアルコールからの dibenzoxanthene 合成

1) Minakawa, M.; Sakurai, Y. *Synlett,* **2022**, *33*, 694–698.
2) Minakawa, M.; Sato, S. *Asian J. Org. Chem.* **2023**, e202300446.

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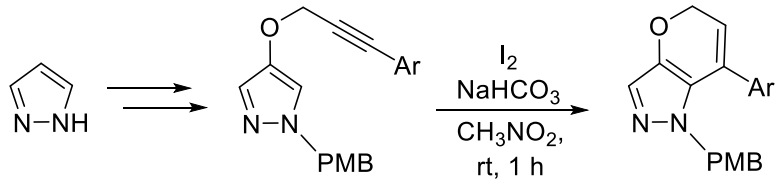
ヨウ素を用いるプロピオール酸 4-ピラゾリルエステルの環化反応

（日大生産工[1]・長崎大院水産環境[2]）○佐藤 礼菜[1]・古家 康明[2]・市川 隼人[1]
Cyclization of 4-pyrazolyl esters of propiolate with iodine ([1]*Graduate School of Industrial Technology, Nihon University,* [2]*Graduate School of Aquatic Environment, Nagasaki University*) ○Ayana Sato,[1] Yasukaki Furuya[2] ,Hayato Ichikawa,[1]

Many pyrazole derivatives exhibit biological activity. Therefore, the development of synthetic methods for new pyrazole derivatives has attracted huge attention[1)]. Pyranopyrazole, a fused six-membered ring ether with an oxygen atom at the 4 position of pyrazole, has attracted huge attention as an M4-positive allosteric modifier, but there are few synthetic reports. In our laboratory, to form the ring structure, 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylenediene (acetonitrile) gold(I) tetrafluoroborate was added to propargyloxy pyrazoles at 12 mol% and heated in an oil bath dissolved in chlorobenzene at 60 °C for 6 to 24 hours. As a result, the cyclized product was obtained in excellent yields. Herein, we report the synthesis of new pyrazole derivatives by cyclization reaction using iodine instead of gold catalyst[2)]. Iodine sodium bicarbonate and substrates were dissolved in nitromethane, and the reaction mixture was stirred at room temperature for 1 h. The target product, 6-iodo-7-aryldihydropyrano[3,2-*c*]pyrazole, was synthesized in 42% yield.

Keywords : Iodine, Pyrazole, Cyclization

ピラゾールから誘導される多くの物質は生理活性を示す。そのため、新規ピラゾール誘導体の合成方法の開発が盛んに行われている [1)]。ピラゾールの 4 位の炭素に酸素原子を持つ 6 員環エーテルが縮環したピラノピラゾールは、M4 陽性アロステリック修飾薬として注目されているが合成報告がほとんどない。当研究室では、環構造を形成するために、プロパルギルオキシピラゾールに 1,3-ビス(2,6-ジイソプロピルフェニル)イミダゾール-2-イルジエン(アセトニトリル)金(I)テトラフルオロボレートを 12 mol% 加え、クロロベンゼン中、 60 ℃で 6～24 時間加熱することで反応させた。その結果、90%以上の非常に良い収率で環化体を得た。そこで今回は、金触媒の代わりにヨウ素を用いて環化反応を行い [2)]、新規ピラゾール誘導体の合成を検討したため報告する。原料にヨウ素と炭酸水素ナトリウムをニトロメタンに溶解させ、室温で 1 時間反応させたところ、42%の収率で目的物である 6-ヨード-7-アリールジヒドロピラノ[3,2-*c*]ピラゾールを合成した。



1) H.Ichikawa,; H. Takashima,; S. Shimizu, *Heterocycles*, **2021**, *103*, 980.
2) N. Mukherjee, *et.al*. *Green Chemistry*, **2022**, *24*, 7029.

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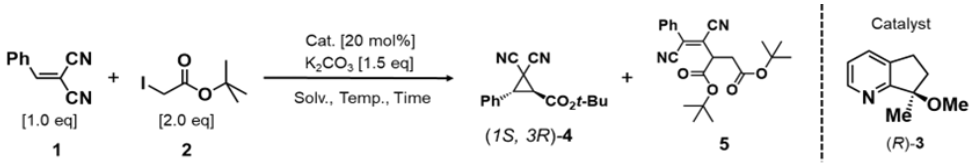
第三級ピリジルアルカノール触媒の不斉シクロプロパン化反応における溶媒効果

（早大先進理工）○清水 成巳・鎌田 祐輝・鹿又 宣弘
Solvent effects on asymmetric cyclopropanation with tertiary pyridylalkanol catalysis (*Department of Chemistry and Biochemistry, Waseda University*) ○Narumi Shimizu, Yuki Kamata, Nobuhiro Kanomata

We previously reported asymmetric cyclopropanation reactions employing tertiary pyridylalkanols as organocatalysts, yielding *trans*-cyclopropane derivatives with good enantioselectivity (83% *ee*) [1]. In this study, our focus was on optimizing various reaction parameters, including the base and solvent particularly using (*R*)-**3** as the catalyst. Notably, the solvent plays a crucial role in reactivity: the use of polar aprotic solvents resulted in a significant decrease in the yield of cyclopropane **3**, leading to the formation of **5** characterized by a rearrangement of the CN groups and the addition of two equivalent of iodoacetate **2** with malononitrile **1**. However, employing DCE as the solvent led to an improved chemical yield of **3** (85%). This outcome underscores the substantial impact of solvent choice on chemical reactivity in such cyclopropanation reactions.
Keywords : Pyridylalkanol; Asymmetric cyclopropanation; Organocatalysis; Pyridinium ylide; Solvent effects

我々は第三級ピリジルアルカノール触媒を用いたイリド型不斉シクロプロパン化反応において，*trans*-シクロプロパン誘導体を良好なエナンチオ選択性（83% *ee*）で与えることを報告している [1]．今回，触媒に(*R*)-**3** を用いて新たに塩基や溶媒等の反応条件を詳細に検討した．

溶媒として THF や 1,4-Dioxane，DMF などの非プロトン性極性溶媒を用いた場合，シアノ基の転位を伴い，マロノニトリル **1** とヨード酢酸エステル **2** が 1 : 2 で付加した **5** の生成が確認され，シクロプロパン **4** の収率は大幅に低下した．一方，DCE 溶媒では良好な収率（85%）で **4** が得られたことから，本シクロプロパン化反応を選択的に進行させるためには溶媒の選択が極めて重要であることが明らかとなった．



Entry	Solv.	Temp. [°C]	Time [h]	Yield of **4** [a] [%]	Ee of **4** [% *ee*]	Yield of **5** [%]
1	DCE	reflux	43	85	83	0
2	THF	reflux	51	41	85	7
3	1,4-Dioxane	85	20	11	82	21
4	DMF	85	3	0	-	11

a) ^{1}H NMR yield after chromatography separation (1,3,5-trimethoxybenzene used as an internal standard).

1) 清水成巳，鎌田祐樹，鹿又宣弘，日本化学会第103回春季年会, 2023, K702-3pn-12.

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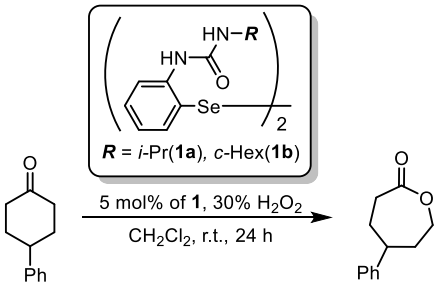
尿素骨格を有する各種ジセレニドの合成および過酸化水素を用いた Baeyer-Villiger 酸化

（日大生産工 [1]）○町山 快 [1]・市川 隼人 [1]
Synthesis of various diselenides with urea skeleton and Baeyer-Villiger oxidation with hydrogen peroxide ([1]*College of Industrial Technology, Nihon University*)○Kai Machiyama,[1] Hayato Ichikawa[1]

Baeyer-Villiger (BV) oxidation with hydrogen peroxide has attracted attention as an environmentally friendly oxidant, but its oxidising power is lower than that of organic peroxides, and a development of the catalysts is actively progressing. Our laboratory has reported the synthesis and reaction of diselenide as a homogeneous catalyst for BV oxidation. However, there are few reports on the use of diselenides as catalysts, and the development of new diselenide catalysts is required to elucidate the more detailed catalytic chemistry of selenium. Based on the finding that organocatalysts with a urea moiety activate the reaction substrates via hydrogen bonding, in this study, new diselenide compounds with isopropyl and cyclohexyl groups were synthesised and investigated for catalysis of BV oxidation with hydrogen peroxide.
Keywords : Catalyst ; Selenium ; Baeyer-Villiger oxidation ; Urea

Baeyer-Villiger (BV) 酸化は医薬品の合成中間体に使われるラクトンの合成に有効な反応として工業的利用が期待されている [1)]。近年環境に優しい酸化として過酸化水素を利用する BV 酸化が注目されており，その触媒の開発が盛んに行われている。当研究室では BV 酸化の均一性触媒としてジセレニドの合成および反応を報告している [2)]。しかし触媒にジセレニドを用いた報告例は少なく，セレンのより詳細な触媒化学の解明を目指して，新規ジセレニド触媒の開発が求められている。本研究では尿素骨格を持つ有機分子触媒が水素結合を介して反応基質を活性化するという知見から，各種イソシアネートとビス(2-アミノフェニル)ジセレニドとの反応により尿素骨格を持つジセレニド化合物の合成と触媒への活用を目的とする。現在はイソプロピル基およびシクロヘキシル基を有する新規なジセレニド化合物を合成し，過酸化水素を用いた BV 酸化に用いたところ、わずかに酸化が進行した。



1) A. Baeyer, V. Villiger, *Chem. Ber.* **1899**, 32, 3625-3633.
2) H. Ichikawa, Y. Usami, M. Arimoto, *Tetrahedron Lett.* **2005**, 46, 8665-8668.

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アズレンエステルの合成とその薬理活性

(城西大学[1]・明海大学[2]) ○古市 飛雄人[1]・三浦 航[1]・坂上 宏[2]・若林 英嗣[1]
Synthesis of Azulene Ester Derivatives and Their Pharmacological Activities ([1]*Josai University*, [2]*Meikai University*) ○ Hiyuto Furuichi,[1] Wataru Miura,[1] Hiroshi Sakagami,[2] Hidetugu Wakabayashi[1]

Our recent work is on azulene, a structural isomer of naphthalene. Azulene is very interesting because of its unique structure. We are conducting basic research on the synthesis of azulene and its applications.[1)] I have synthesized azulene ester derivatives, which are novel compounds with an ester bond at the 1-position of azulene. Furthermore, I observed the antitumor activity of azulene ester derivatives against oral cancer cells and normal oral cells. As a result, we found azulene ester derivatives that exhibit certain antitumor activity. However, a comparison of the anti-tumor activity of azulene ester derivatives with anti-cancer drugs used in actual medical practice showed that azulene ester derivatives do not show such excellent values.

Keywords : Non-benzenoid aromatic compounds; Synthesis of azulene ester derivatives; Pharmacological activity of azulenes; Antitumor activity **【4 words】**

当研究室では近年、ナフタレンの構造異性体であるアズレンの構造の特異性に着目し、基礎研究の一端としてアズレンの合成法やその応用研究[1)]を行っている。本実験ではアズレンの 1 位にエステル結合を介した全 16 種類の新規化合物であるアズレンエステル誘導体の合成を行い、口腔癌細胞と口腔正常細胞に対する抗腫瘍活性を評価した。アズレンエステル誘導体は一定の抗腫瘍活性を示したものもあったが、実際の抗がん剤と比較した結果それほど強い値は出ていないことが分かった。

	CC_{50} (μM)											
	Oral squamous carcinoma			Normal oral cells			Neuronal cells			TS	NT	TS/NT
	Ca9-22	HSC-2	mean (A)	HGF	HPC	mean (B)	PC-12	SH-SY5Y	mean (C)	(B/A)	(B/C)	(C/A)
1	>1600	427.1	>1014	1506.7	>1600	>1553	360.8	354.0	357	><1.53	>4.35	0.35
2	357.8	478.4	418	1592.1	1444.5	1518	295.9	441.2	369	3.63	4.12	0.88
3	260.5	224.9	243	1163.2	1144.9	1154	241.4	288.5	265	4.75	4.36	**1.09**
4	243.5	198.0	221	1506.0	1552.9	1529	233.0	291.1	262	**6.93**	5.84	**1.19**
5	304.3	276.1	290	>1600	>1600	>1600	196.8	337.0	267	**>5.51**	>5.99	0.92
6	667.3	614.5	641	>1600	1285.7	>1443	553.9	661.5	608	>2.25	>2.37	0.95
7	621.7	662.1	642	1245.6	1411.6	1329	592.5	589.4	591	2.07	2.25	0.92
8	389.5	513.1	451	1263.9	1332.0	1298	351.7	554.2	453	2.88	2.87	**1.00**
9	275.2	320.0	298	>1600	>1600	>1600	162.2	215.9	189	**>5.38**	>8.46	0.64
10	47.1	103.9	75	298.9	300.7	300	10.1	31.1	21	3.97	14.54	0.27
11	45.8	104.3	75	371.0	196.1	284	55.6	42.8	49	3.78	5.76	0.66
12	125.1	171.9	148	647.8	384.4	516	86.0	143.6	115	3.48	4.49	0.77
13	107.4	109.7	109	570.9	342.7	457	24.8	55.9	40	4.21	11.33	0.37
14	98.2	132.3	115	570.0	365.1	468	16.1	108.2	62	4.06	7.52	0.54
15	16.1	71.3	44	>400	201.3	>301	40.5	4.7	23	**>6.88**	>13.3	0.52
16	29.6	58.5	44	79.5	127.8	104	27.2	6.3	17	2.35	6.19	0.38
DOX	44.1	14.0	29	>1600	>1601	>1600	<12.5	<12.5	<12.5	>55.0	>128	0.43
5-FU	12.4	44.1	28	>400	>400	>400	3.1	4.4	3.79	>14.1	>105.7	0.13
CDDP	326.9	>1600	>963	>400	>400	>400	60.8	118.8	89.79	><0.4	>4.45	0.09

1) T. Wada, R. Maruyama, Y. Irie, M. Hashimoto, H. Wakabayashi *et al*. *in vivo*. **2018**, 32, 479-486.

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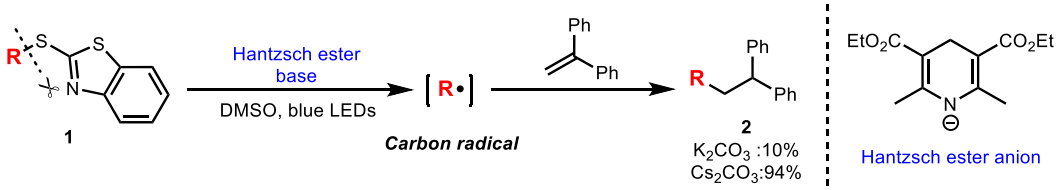
Hantzsch エステルアニオンによる青色光照射下での炭素－硫黄結合切断

(静大院総合科学技術[1]・静大工[2]) ○松根 康樹[1]・霜鳥 拓磨[1]・菊池 渚[1]・土方 陽登[2]・仙石 哲也[1]
Carbon-sulfur bond cleavage with Hantzsch ester anion under blue-light irradiation ([1]*Graduate School of Integrated Science and Technology, Shizuoka University*, [2]*Faculty of Engineering, Shizuoka University*) ○ Koki Matsune,[1] Takuma Shimotori,[1] Nagisa Kikuchi,[1] Haruto Hijikata[2], Tetsuya Sengoku[1]

Carbon-radical generation from alkyl heteroaryl sulfides is reported. The reaction of benzothiazolyl sulfides and 1,1-diphenylethylene in the presence of Hantzsch ester and inorganic base additives under blue-light irradiation afforded the corresponding adducts in moderate to good yields. The desired product was also obtained when the reaction was carried out with Hantzsch ester anions prepared in situ.
Keywords : Sulfide; Hantzsch ester; Carbon–sulfur bond; Blue LEDs

我々は、青色 LED 光照射下でアルキルベンゾチアゾリルスルホンの炭素－硫黄結合切断を伴うアルキルラジカル発生法を見出している[1)]。この手法は、炭酸カリウムと Hantzsch エステルから僅かに生じる Hantzsch エステルアニオンの光励起によるものであった。本研究では本法の拡張を目的とし、スルフィドへの適用を検討した。

スルホンの炭素－硫黄結合を実現した Hantzsch エステルと炭酸カリウムを共存させて青色 LED 光を照射する反応条件においては、ベンゾチアゾリルスルフィド (**1**) と 1,1-ジフェニルエチレンからは、わずか 10% の付加体 **2** が得られるのみであった。一方、より多くの Hantzsch エステルアニオンが発生する[2)] とされる炭酸セシウムを用いたところ、劇的に反応性が向上することが明らかとなった (収率 94%)。また、本反応は Hantzsch エステルと強塩基から調製した Hantzsch エステルアニオンを用いても進行し、30~83% で付加体を与えた。



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α-アミドマロン酸ハーフエステルを用いたイサチンへの不斉脱炭酸型アルドール反応の開発

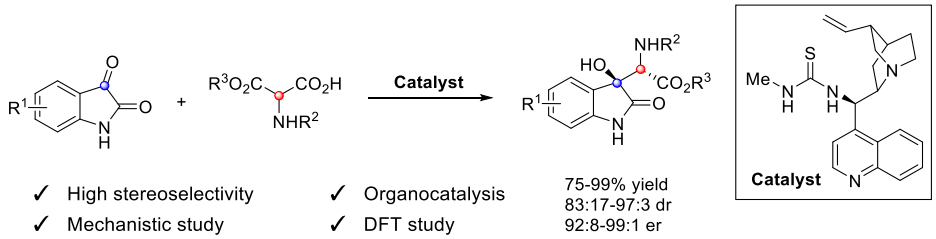
（名工大院工）○藤田 和樹・熊澤 尉吹・横井 淳平・阿部 一貴・安川 直樹・中村 修一

Development of Stereoselective Decarboxylative Aldol Reaction of α-Amido Malonic Acid Half Esters to Isatins (*Graduate School of Engineering, Nagoya Institute of Technology*)
○Kazuki Fujita, Ibuki Kumazawa, Jyunpei Yokoi, Kazuki Abe, Naoki Yasukawa, Shuichi Nakamura

α-Amino acids bearing consecutive chiral carbon centers are ubiquitous structural motifs in biologically active compounds. One of the efficient methods for the synthesis of these compounds is a stereoselective reaction of α-amido malonic acid half esters (α-amido-MAHOs). However, the reaction of α-amido-MAHOs was limited to highly reactive electrophiles such as aldehydes and aldimines. Herein, we developed the stereoselective decarboxylative aldol reaction of α-amido-MAHOs with isatins as ketones to synthesize α-amino acid derivatives bearing consecutive chiral carbon centers. A cinchona alkaloid thiourea catalyst gave products in high yields with high diastereo- and enantioselectivities. Density functional theory (DFT) calculations were conducted to clarify the origin of stereoselectivities.
Keywords: Asymmetric Synthesis; β-Hydroxy-α-Amino Acids; Consecutive Chiral Carbon Centers; α-Amido Malonic Acid Half Esters; Organocatalysis

連続不斉炭素を有するα-アミノ酸は多くの生物活性物質の部分構造に見られる重要な骨格である。この化合物を合成する手法の一つとして、分子内にアミノ酸構造を有するα-アミドマロン酸ハーフエステルを用いた不斉反応が報告されているが、アルデヒドやアルジミン等の反応性の高い基質への反応に限られていた[1)]。そこで我々は、ケトンであるイサチンを用いたα-アミドマロン酸ハーフエステルの不斉アルドール反応の開発を行った。

種々の検討の結果、シンコナアルカロイド由来のチオウレア触媒を用いることで、目的の連続不斉炭素を有する化合物が、高収率・高立体選択性で得られた。また、DFT計算による立体選択性発現機構の解明も行った[2)]。



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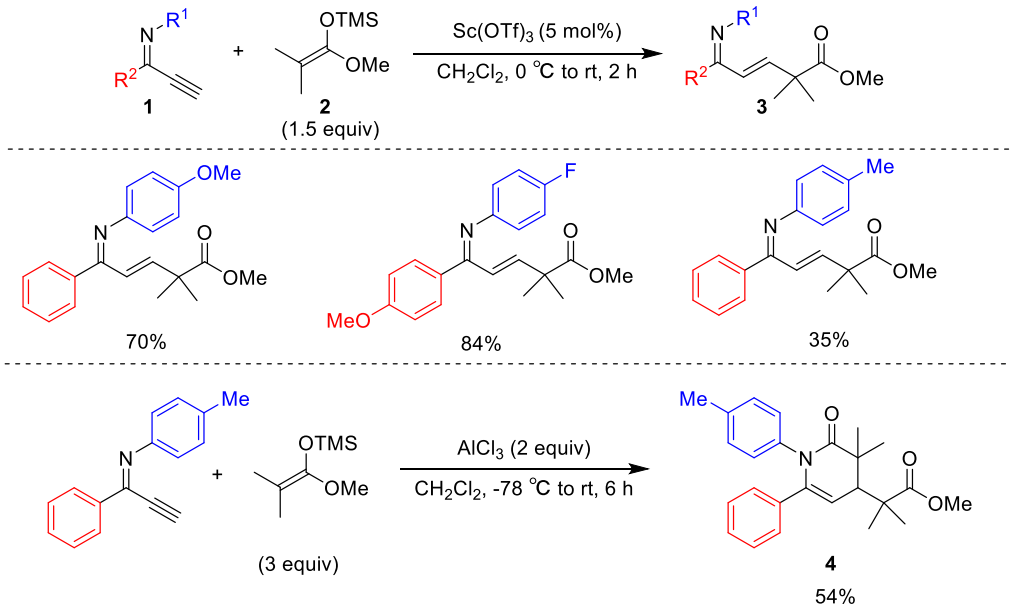
末端アルキニルイミンへのケテンシリルアセタールの共役付加反応の開発

（三重大院工）酒井 亮・○西村 仁志・八谷 巖
Development of Conjugate Addition Reactions of Ketene Silyl Acetals to Terminal Alkynyl Imines *(Graduate School of Engineering, Mie University*) Ryo Sakai, ○Hitoshi Nishimura, Iwao Hachiya

We have already reported that scandium triflate promoted domino 1,4- and 1,4-addition reactions of silyl thioacetals to dialkynyl imines to give a variety of alkynyl alkylthio- δ-lactams in moderate to good yields.[1)] We next examined Lewis acid promoted conjugate addition reactions of ketene silyl acetals **2** to terminal alkynyl imines **1**. In this presentation, we report on syntheses of δ-imino ester **3** using scandium triflate and δ-lactams **4** using alumiinum chloride.

Keywords：Conjugate Addition; δ-Imino Ester

イミンは、様々な天然物や生理活性化合物の実用的な前駆体であり、天然物合成、医薬研究において注目される含窒素化合物の 1 つである。一方で、δ−ラクタムは抗腫瘍作用、抗不安作用などを示す生物活性化合物に含まれる骨格である。今回、スカンジウムトリフラートの存在下、末端アルキニルイミン **1** に対して、求核剤としてケテンシリルアセタール **2** を作用させることにより、共役付加反応が進行し、δ−イミノエステル **3** が得られることを見出した。また、ルイス酸および求核剤の当量を変えることにより δ−ラクタム **4** が得られることを見出した。



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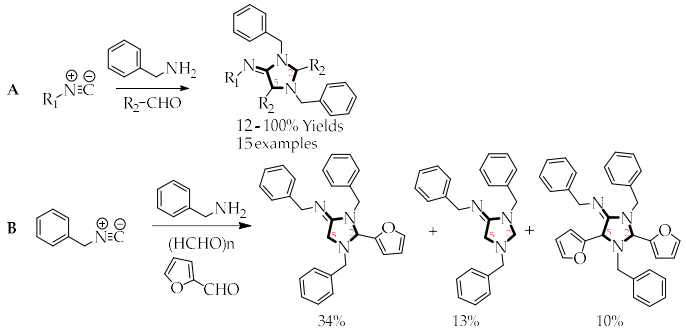
Multicomponent Synthesis of 4-Iminoimidazolidines and their Bioactivities

(*Graduate School of Nanobioscience, Yokohama City University*) ○Komoreng Oriel Hlokoane, Raku Irie, Masato Oikawa

Keywords: 4-iminoimidazolidine; multicomponent reaction; diversity-oriented synthesis; structure-activity relationship; cytotoxicity

The construction of 4-iminoimidazolidine ring was previously achieved by the reaction of alkyl isocyanide with alkyl benzimine.[1] The conventional method involved the use of commercially unavailable imines which must be predesigned prior to the reaction, thus, limiting the scope of the transformation due to the difficulty in synthesizing imine precursors. On the other hand, the 4-iminoimidazolidines had been often isolated as side products in the multicomponent Ugi-type of reactions.[2] Taking these findings into account, we envisioned a direct one-step synthesis of 4-iminoimidazolidines from commercially available three components, namely, amine, aldehyde, and isocyanide.

Under the optimized conditions of cerium (III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$) in 2,2,2-trifluoroethanol (TFE) at room temperature, the reaction was found to proceed smoothly in 24 h to afford 4-iminoimidazolidines (Scheme A). The method gave us easy access to 15 structurally diversified compounds. Furthermore, the antiproliferative activity of a series of synthesized compounds was evaluated. Compounds that were substituted at both C-2 and C-5 exhibited micromolar cytotoxicity, whereas compounds lacking substituents at the above-mentioned positions did not show cytotoxicity. Finally, to study the structure-activity relationships and the reaction mechanism, the reaction with the equimolar mixture of two different aldehydes (paraformaldehyde and furfural) was conducted to give the corresponding 4-iminoimidazolidine products with high selectivity for an analog substituted only at C-2 (Scheme B).



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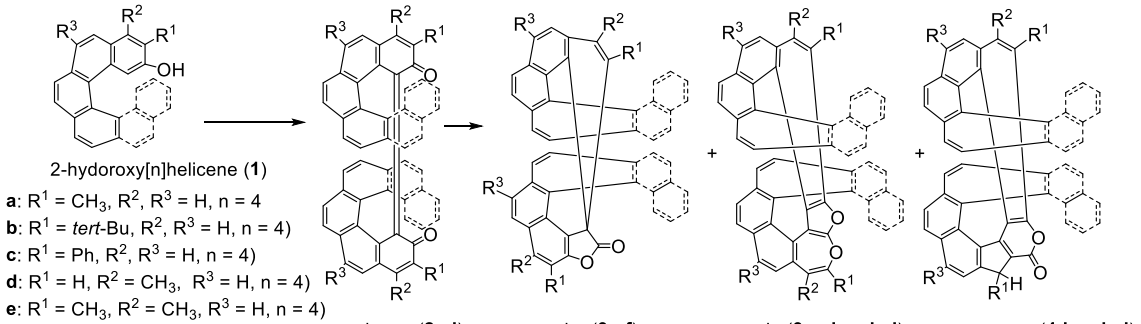
らせん型キノン誘導体から誘導される種々の含酸素ヘテロ環誘導体への転位反応

（宇都宮大院工）○上見　怜・木村なゝ実・刈込　道徳
Rearrangement Reactions of Helical Quinone Derivatives to Various Oxygen-Containing Heterocyclic Derivatives (*Graduate School of Engineering, Utsunomiya University*)
○Satoshi Joken, Nanami Kimura, Michinori Karikomi

Helical shaped quinone derivatives were synthesized via oxidative coupling reactions of benzo[*c*]phenanthrene bearing a hydroxy group at the 2-position. Upon heating these compounds, they underwent rearrangement forming oxygen-containing heterocycles. These including spiro-type compounds of cyclopentadiene and δ-lactone, fused compounds of furan and oxepine, and fused compounds of cyclopentadiene and pyranone. Introducing various substituents into the quinone derivatives revealed the effects of these substituents on the rearrangement reactions. Furthermore, similar rearrangement reactions were carried out for helical quinone derivatives synthesized from [6]helicene derivatives.
Keywords : Helicene; Rearrangement; Heterocycles; Quinone; Substituent effects

2 位にヒドロキシ基を有するベンゾ[*c*]フェナントレン誘導体の酸化的カップリング反応により、種々の置換基を導入したらせん型のキノン誘導体を合成した[1]。この化合物を加熱すると、シクロペンタジエンとδ-ラクトンのスピロ型の化合物、フラン環とオキセピンの縮環化合物、シクロペンタジエン環とピラノン環の縮環化合物などの三種類のらせん型の含酸素複素環誘導体に転位した[2]。置換基の種類や位置によってこの転位反応における置換基効果を明らかにした。さらにらせん長の長い[6]ヘリセン誘導体から合成したらせん型キノン誘導体についても同様の反応を行った。



a: R^1 = CH_3, R^2, R^3 = H, n = 4
b: R^1 = *tert*-Bu, R^2, R^3 = H, n = 4)
c: R^1 = Ph, R^2, R^3 = H, n = 4)
d: R^1 = H, R^2 = CH_3, R^3 = H, n = 4)
e: R^1 = CH_3, R^2 = CH_3, R^3 = H, n = 4)
f: R^1, R^2 = -$(CH)_4$-, R^3 = H, n = 4)
g: R^1, R^2, R^3 = H, n = 6)
h: R^1 ,R^2 = H, R^3 = Br, n = 6)
i: R^1, R^2 = -$(CH=CH)_2$-, R^3 = H, n = 6)

1) Synthesis of Helical Quinone Derivatives by Oxidative Coupling of Substituted 2-Hydroxybenzo[*c*]phenanthrenes. M. Shahabuddin, A. Akutsu, T. Kimura, M. Karikomi, *SYNTHESIS* **2017**, *49*, 1547.*J. Org. Chem.* **2010**, *75*, 7644.
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トリフルオロメトキシ基を持つジセレニドと過酸化水素を組み合わせた環境調和型 Baeyer-Villiger 酸化

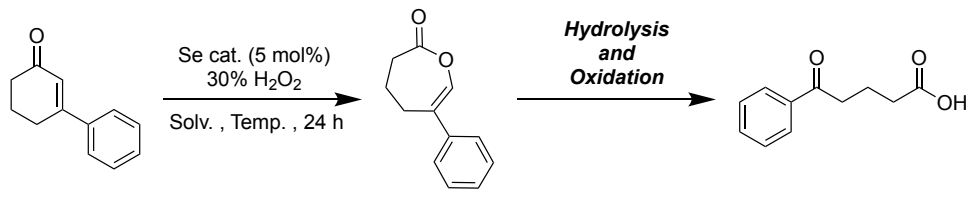
（日大生産工）○坂本 吏駒・市川 隼人

Baeyer-Villiger Oxidation with the Diselenide Bearing Trifluoromethoxy group and Hydrogen Peroxide *(College of Industrial Technology, Nihon University)* ○Riku Sakamoto・Hayato Ichikawa

Baeyer-Villiger oxidation is used to convert ketones which are readily available compounds, into more valuable esters and lactones in synthesis of natural product. Peracids used in Baeyer-Villiger oxidation is highly active, but they are explosive and requires neutralization of the corresponding carboxylic acid byproduct after the reaction. Therefore, in recent years, hydrogen peroxide, has attracted attention as a safe and an inexpensive oxidant that can replace per acids. In 2001, Sheldon *et al*. reported that diselenides with trifluoromethyl groups at 3 and 5 positions were used as catalysts for BV oxidation with hydrogen peroxide and showed high catalytic activity. In this study, BV oxidation of α, β-unsaturated cyclohexenones was performed using hydrogen peroxide in combination with a diaryldiselenide with a trifluoromethoxy group at the ortho position as a catalyst, and δ-ketocarboxylic acid was obtained in good yield on a substrate containing a phenyl group (Scheme 1).

Keywords：Baeyer-Villiger Oxidation ; Hydrogenperoxide ; Diaryldiselenide

Baeyer-Villiger（BV）酸化はカルボニル基の炭素の隣に酸素を原子挿入する反応であり，ケトンをより価値のある，エステルやラクトンに変換するために天然物合成にも使われている反応である。BV 酸化で用いる過酸は高い活性を持つ反面，爆発の危険を有しており，反応後に副生するカルボン酸の後処理が必要である。そこで近年は過酸に代わる酸化剤として酸素含有量が高く，安全で安価である過酸化水素の使用が注目されている。2001 年，Sheldon らは 3,5 位にトリフルオロメチル基が導入されたジセレニドを過酸化水素を用いた BV 酸化の触媒に用い，高い触媒活性が得られたことを報告した。本研究では過酸化水素と触媒としてオルト位にトリフオロメトキシ基を導入したジアリールジセレニドを組み合わせて，α，β-不飽和シクロヘキセノンに対する BV 酸化を行ったところ，フェニル基を有する基質においてδ-ケトカルボン酸が良好な収率で得られたので報告する(Scheme 1)。



3　　2　　1

Scheme1 Bayer-Villiger oxidation using hydrogen peroxide and diselenide catalyst

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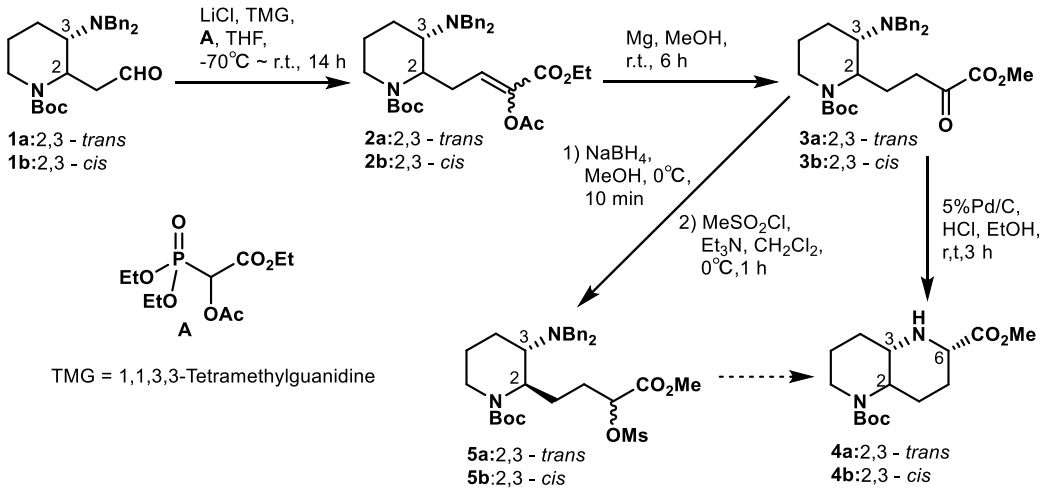
新規二環性ピペコリン酸誘導体の合成研究

(神奈川工大応用バイオ[1]・神奈川工大院工[2]) ○田村 友[1]・山本 雅彦[2]・野田 毅[1]
Synthetic Studies of New Bicyclic Pipecolic Acid Derivatives ([1]*Faculty of Applied Bioscience*, *Kanagawa Institute of Technology*, [2]*Graduate school of Engineering*, *Kanagawa Institute of Technology*) ○Yuu Tamura[1], Masahiko Yamamoto[2], Takesi Noda[1]

Peptides composed of multiple amino acids are attracting attention as a new drug discovery modality, and further development of unnatural amino acids is required. The aim of this study is to synthesize novel bicyclic pipecolinic acid derivatives. Starting from two 2-substituted 3-aminopiperidine isomers **1a** and **1b**, the α,β-unsatuitated esters **2a** and **2b** were synthesized by the Horner-Wadsworth-Emmons reaction using **A**. Deacetylation of **2a** and **2b** gave the ketones **3a** and **3b.** Deprotecton of benzyl group of **3a** and **3b** by dehydrogenaion followed by cyclization gave **4a** and **4b** as single compound respectively. The alternative syntethic route study via mesylates **5a** and **5b** in progress.

Keywords : Pipecolic acid; Piperidine; Horrner-Wadsworth-Emmons reaction

新規創薬モダリティとして複数のアミノ酸から構成されるペプチドが注目され、さらなる非天然型アミノ酸の開発が求められる。本研究は新規二環性ピペコリン酸誘導体の合成を目的としている。当研究室で開発された方法に基づき合成された 2 つの 2-置換 3-アミノピペリジンの異性体 **1a**, **1b** から出発し **A** 用いた Horner-Wadsworth-Emmons 反応を経由して **2a**, **2b** を合成した。**2a**, **2b** を脱アセチル化しケトン **3a**, **3b** へと導いた。水素添加による脱ベンジル化すると、環化も進行し、**4a**, **4b** を合成することができた。2,3-*trans* 体及び 2,3-*cis* 体はいずれもほぼ単一化合物として得られた。構造決定と異性体比を明らかにするためメシレート **5a**, **5b** を経由するルートでの **4a**, **4b** 合成を検討中である。



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超原子価ヨウ素反応剤を用いたサリチルアミド誘導体からのメタルフリージベンゾオキサゼピノン誘導体合成

（立命館大院薬）○宮本 直樹・笠井 彩理純・菊嶌 孝太郎・土肥 寿文
Metal-free dibenzoxazepinone synthesis from salicylamides mediated by hypervalent iodine reagent (*College of Pharmaceutical Sciences, Ritsumeikan University*) ○Naoki Miyamoto, Arisu Kasai, Kotaro Kikushima, Toshifumi Dohi

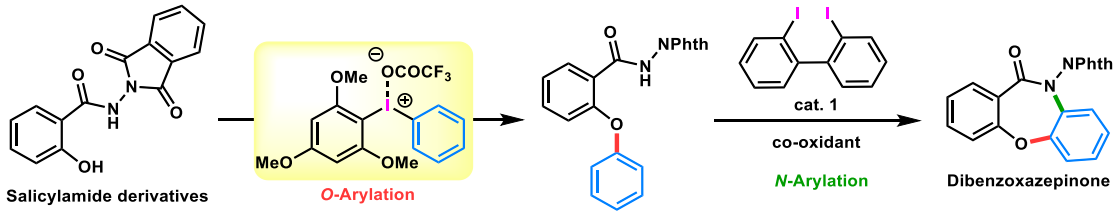
Hypervalent iodine reagents are easily accessible, non-toxic organic compounds showing unique reactivities. Recently, our group reported several catalytic C-N coupling reactions using μ-oxo hypervalent iodine(III) reagent, and *O* or *N*-arylation of phenols and *N*-alkoxyamides using aryl(2,4,6-trimethoxyphenyl)iodonium(III) salts.

Herein, we have developed a more efficient synthetic method of dibenzoxazepinone derivatives from salicylamides by hypervalent iodine-mediated successive phenol *O*-arylation and aromatic amination process. The success key of this new synthesis is the introduction of phthalimide group into salicylamide nitrogen to enable selective phenol *O*-arylation reaction.

Keywords : Dibenzoxazepinone; Hypervalent iodine(III) reagents; Phenol O-arylation; Aromatic amination

超原子価ヨウ素反応剤は合成が簡便で、毒性が低いことから、多くの酸化反応やアリール化反応に用いられている [1]。当研究室ではこれまでに、酸化反応として芳香環の酸化的 C−H アミノ化反応を報告しており [2a]、最近ではベンゾラクタム [2b] やジベンゾオキサゼピノン [2c] などの複素環化合物の合成へと展開している。また、アリール化反応として、フェノール [3a] や *N*−アルコキシアミド類 [3c] の *O*−アリール化反応や *N*−アルコキシアミド類 [3b] の *N*−アリール化反応を報告している。

今回、超原子価ヨウ素反応剤を用いたサリチルアミド誘導体のフェノール性水酸基の選択的な *O*−アリール化反応と、続く芳香環アミノ化反応によるジベンゾオキサゼピノン合成を検討した。アミドの窒素原子にフタルイミド基を導入することにより、アリール化反応をフェノール性水酸基選択的に行うことで、本合成が可能となった。



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α–イソシアノアセトニトリルによるケトン類への反応によるキラルオキサゾリン合成

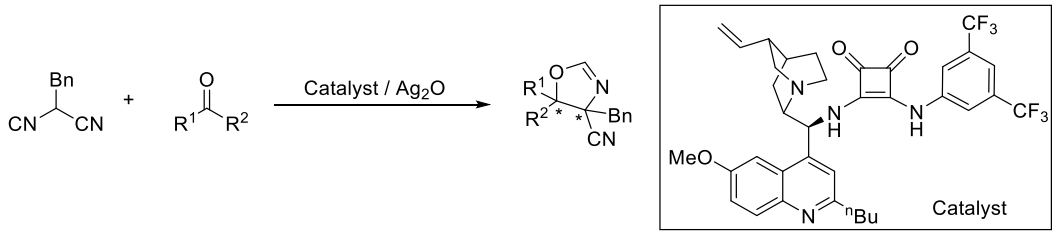
（名工大院工）○加藤 達也・安川 直樹・中村 修一
Synthesis of chiral oxazolines from the reaction of α–isocyanoacetonitriles with ketones ([1]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Tatsuya Kato, Naoki Yasukawa, Shuichi Nakamura

Chiral oxazolines have been recognized as an important backbone in various natural products. Recently various synthetic methods for chiral oxazolines using isocyanides have been developed, however, the reaction using non-activated ketones is limited. Herein we report a high yield and high enantioselective synthesis of chiral oxazolines with consecutive tetrasubstituted chiral carbons with ketones using chiral squaramide catalysts derived from cinchona alkaloids. The reaction of α–benzylisocyanoacetnitrile with acetophenone using catalyst (10 mol%) and Ag_2O (5 mol%) in *p*-xylene at 25 °C afforded corresponding oxazolines in 95% yield with 86:14 dr, 92:8 er. This catalytic system applies to the reaction using various ketones.

Keywords: Asymmetric synthesis; Chiral oxazoline; Non-activated ketones; α–Isocyanoacetonitrile

キラルオキサゾリンは様々な天然物に含まれる重要な構造である。近年、イソシアニドを用いたキラルオキサゾリンの合成手法は精力的に研究されているが、不活性なケトンを用いた反応では、利用可能な求核剤に制限があった[1)]。本研究では、シンコナアルカロイド由来のスクアラミド触媒を用いることで、ケトン類に対する連続四置換不斉炭素を有するキラルオキサゾリンを高収率・高立体選択的に合成することに成功した。

実際に、α–ベンジルイソシアノアセトニトリルとアセトフェノンの反応を、*p*-キシレン中、触媒 10 mol%、酸化銀 5 mol%存在下で行った場合、目的のオキサゾリンが95%収率、86:14 dr、92:8 er で得られた。



1) a) R. de la Campa, I. Ortín, D. J. Dixon, *Angew. Chem. Int. Ed.* **2015**, *54*, 4895; b) P. Martínez-Pardo, G. Blay, M. C. Muñoz, J. R. Pedro, A Sanz-Marco, C. Vila*, Chem. Commun.* **2018**, *54,* 2862.

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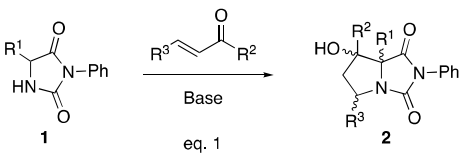
2 環性ヒダントイン構築を指向した環化反応

（神工大）○藤澤　侑輝・片倉　友弥・山口　淳一
Cyclization for construction of bicyclic hydantoin derivatives (*Department of Applied Chemistry, Kanagawa Institute of Technology*)○Yuki Fujisawa, Tomoya Katakura, Jun-ichi Yamaguchi

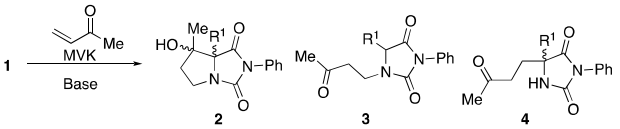
We reported that forming bicyclic hydantoin resulted in derivative amine-catalyzed conjugate addition-cyclization of hydantoin derivative with unsaturated aldehyde. Using crotonaldehyde, 4 kinds of diastereomers would be given and their ratio was clarified by ^{1}H NMR spectra. When the same conjugate addition-cyclization using unsaturated ketone instead of aldehyde was examined. While conjugate addition proceeded, cyclization is less likely to occur. It was revealed that their reactivities were different.
Keywords : Hydantoin; Cyclization; Bicyclic Heterocycle

有機アミン触媒下ヒダントイン誘導体 **1** に不飽和アルデヒド(R^2=H)を作用すると、共役付加に続いて環化が進行し 2 環性ヒダントイン誘導体 **2** を与える事を見いだしている(eq. 1)。クロトンアルデヒド(R^2=H, R^3=Me)を用いると 4 種のジアステレオマーが生成がすると考えられ、今回それらの生成比を ^{1}H NMR により明らかにすることが出来た。本反応における 4 種類のジアステレオマー比は反応温度に依存しており、室温で行った場合 2 のジアステレオマー比はほぼ同じであることが分かり、一方、50ºC で反応を行うと **2** のジアステレオマー比は、ある 1 つの異性体に偏ることが分かった。相対的立体配置については現在解析中である。

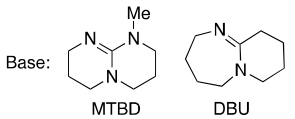


1 eq. 1 **2**

さらに、不飽和ケトンであるメチルビニルケトン(R^2=Me, R^3=H)についても同様の検討をした。その結果、共役付加は進行するものの環化は起きにくく、アルデヒドとは異なる反応性を示した(eq.2)。すなわち、クロトンアルデヒド使用時と同様な反応条件で行ったところ、2 環性ヒダントイン **2** の収率は低く、共役付加のみ進行した **3** を主生成物として与えた。副生成物として **4** も確認された。目的物 **2** は副生成物 4 とシリカゲルのクロマトグラフィーで分離しがたく、分離は $NaBH_4$ で **4** のみを変換した後に行った。単離した **2** はジアステレオマーの混合物であり、^{1}H NMR スペクトルよりいずれかの立体に偏っていることが示唆された。触媒としてグアニジン系アミン(MTBD)、アミジン系(DBU)は反応の進行は確認できた一方、アミン系(Et_3N)は進行しないことから、本反応はアミンの塩基性度に依存することが分かった。続いて、付加体 **3** の環化反応を検討したところ、環化も進行するものの **4** も生成することがわかった。**1** らは **2** への変換反応は **3** を経由して進行すると考えられるが、有機アミンを触媒とする本反応条件下では、**1** から **3** への共役付加反応は平衡反応である事が分かった。



1 **2** **3** **4** eq. 2



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アゾベンゼンユニットを有するキラル環状化合物の設計・合成および光応答性の評価

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Design, synthesis and evaluation of photoresponsive properties of chiral cyclic macro compounds containing azobenzene-unit. (*[1]Graduate School of Pharmaceutical Science, Tokyo University of Science*, *[2]Reseach Institute for Science & Technology, Tokyo University of Science, [3]Graduate School of Science, Hokkaido University*) ○ Shotaro Otaki,[1] Ryota Shibauchi,[1] Toshifumi Tojo,[1] Norio Tanada,[3] Yoshiyuki Kageyama,[3] Shin Aoki[1,2.]

In recent years, many molecular machines whose structure is changed by redox, heat, light, and other external stimuli. However, there are few examples of molecular machines whose rotation is controlled in a one-directional manner. We focused on azobenzene, which is known to undergo reversible isomerization between *cis*- and *trans*-forms upon irradiation with UV and visible light. In this study, we design and synthesize chiral cyclic compounds with azobenzene moieties to control the direction of the rotational motion of photo- and thermal isomerization by intramolecular chirality.

The chiral cyclic compounds consisting of an azobenzene unit were synthesized and their structural change upon UV and visible light irradiation was observed using NMR, UV-Vis absorption and circular dichroism (CD) spectra in organic solvents. Furthermore, the relationship between the structure and CD spectra of these compounds was studied by TD-DFT (time-dependent density functional theory). In this paper, these results will be reported.
Keywords : Molecular machine; Azobenzene; Photoisomerization; Chiral macrocycles

近年、酸化還元・熱・光などによって構造制御される分子機械が数多く報告されている。しかし、単一方向に回転を制御した分子機械の例は少ないのが現状である。我々は、紫外線および可視光線の照射により、*cis* 型と *trans* 型の間で可逆的な異性化が起こることが知られているアゾベンゼンに着目した。本研究では、アゾベンゼン骨格を有するキラル環状化合物を設計・合成し、光および熱異性化の回転運動を分子内キラリティーによって制御することを目指した。

目的のキラル環状化合物を合成し、有機溶媒中での紫外線照射と可視光照射による化合物の挙動を NMR、UV-Vis 吸収スペクトル、円二色性（CD）スペクトルを用いて観測した。さらに、TD-DFT（時間依存的密度汎関数）により、化合物の構造と CD スペクトルの関係を検討した。本発表では、これらの結果について発表する予定である。

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次亜塩素酸ナトリウム五水和物を用いた求電子的塩素化反応の研究

（東海大[1]）○嶋田玲雄[1]・岩岡道夫[1]

Study of electrophilic chlorination reactions using sodium hypochlorite pentahydrate

(1. Tokai University) ○Reo Shimada[1], Michio Iwaoka[1]

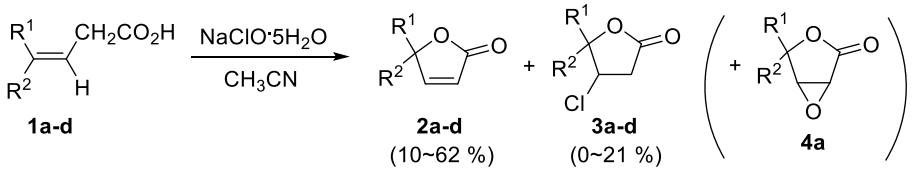
Sodium hypochlorite is widely used as a disinfectant and bleaching agent. However, its applications to organic synthetic reactions are limited in the number of cases, such as epoxidation of alkenes. In this study, we report a unique reaction, in which sodium hypochlorite pentahydrate ($NaClO·5H_2O$) acts as an electrophilic chlorinating agent.

When two equivalents of $NaClO·5H_2O$ was reacted in acetonitrile with (*E*)-5-phenylpent-3-enoic acid (**1a**) as a substrate, α,β-unsaturated lactone **2a** was obtained in 62% yield with a trace amount of chloride **3a**. When the amounts of $NaClO·5H_2O$ were increased to 3 equivalents, epoxide **4a** was obtained. Similar reaction products, i.e., unsaturated lactones **2b-d** and chlorides **3b-d**, were obtained when other substrates (**1b-d**) were employed. The reaction mechanism was proposed as follows. ClOH is liberated from $NaClO·5H_2O$ by the reaction with substrate acid **1**. The generated ClOH adds to the alkene to produce a chloronium ion intermediate, which is then cyclized to afford chloride **3**. Finally, HCl is eliminated from **3** to yield unsaturated lactone **2**.

Keywords : unsaturated carboxylic acids, electrophilic addition, cyclization, green chemistry, tandem reaction, chloronium ion intermediate

次亜塩素酸ナトリウムは、殺菌剤・漂白剤として広く用いられている。しかし、これを有機合成反応へ応用した例は、アルケンのエポキシ化など、ごく限られた反応が報告されているのみである[1]。本研究では、次亜塩素酸ナトリウム五水和物 $NaClO·5H_2O$ が求電子的塩素化剤として作用する興味深い反応を見出したので報告する。

基質として(*E*)-5-phenylpent-3-enoic acid (**1a**)を用い、アセトニトリル中で 2 当量の $NaClO·5H_2O$ を加えて撹拌したところ、α,β–不飽和ラクトン **2a** が収率 62% で得られ、ごく少量の塩化物 **3a** の生成も確認された。用いる $NaClO·5H_2O$ を 3 当量にしたところ、エポキシド **4a** が得られた。同様な反応は、別の基質(**1b-d**)を用いたときにも進行し、主として不飽和ラクトン **2b-d** と塩化物 **3b-d** が得られた。反応機構は、$NaClO·5H_2O$ から遊離した ClOH がアルケンに求電子付加し、次いで分子内環化することで塩化物 **3** となり、これから HCl が脱離することで不飽和ラクトン **2** が生じるものと考えられる。



(**a** R^1=Me, R^2=Ph; **b** R^1=H, R^2=Ph; **c** R^1=H, R^2=CH_2Ph; **d** R^1=H, R^2=Et)

[1] 桐原正之 他, *有合化*, **2020**, *78(1)*, 11-27.

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分子内にリン配位部位を有するビス（フェロセニル）ブロモスチビンの合成と、その脱臭化物イオン反応の検討

（筑波大院数理[1]・筑波大数理物質[2]・TREMS[3]）
○川元 慎也[1]・正田 浩一朗[2]・笹森貴裕[2,3]

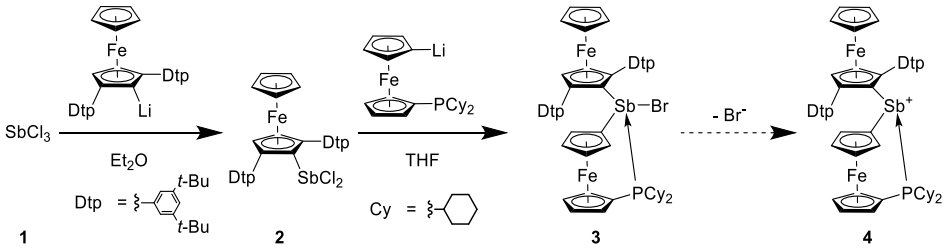
Synthesis of a Bis(ferrocenyl)bromostibine Bearing an Intramolecularly Coordinating Phosphine Moiety and Its Attempted Debromination Reaction ([1]*Graduate School of Science and Technology, Univ. of Tsukuba*, [2]*Institute of Pure and Applied Sciences, Univ. of Tsukuba,* [3]*TREMS, Univ. of Tsukuba*) ○Shin-ya Kawamoto,[1] Koichiro Masada,[2] Takahiro Sasamori[2,3]

Dicoordinated cationic species of heavier group 15 elements, such as phosphenium and stibenium ions,[1] exhibit isoelectronic structures as a silylene or a stannylene, and thus are regarded as heavier carbene analogs. They show ambiphilic reactivity due to their lone pair and vacant p-orbital as well as carbenes, which can be used for small molecule activation. However, their lability due to their extremely high electrophilicity as cationic characters should make their synthesis and isolation difficult. Recently, our group reported a phosphenium with an intramolecularly coordinating phosphine moiety.[2] Here, we will report the attempted synthesis of bis(ferrocenyl)stibenium **4** with an intramolecularly coordinating phosphine moiety. Bis(ferrocenyl)bromostibine **3** was synthesized as a precursor of the stibenium by two steps from $SbCl_3$, followed by the attempts for the debromination reaction.

Keywords : Stibenium; Ferrocene; Bis(ferrocenyl)bromostibine; Antimony; Intramolecular coordination

ホスフェニウムやスチベニウム[1]などの高周期 15 族元素の 3 価二配位カチオン種は、シリレンやスタンニレンと等電子構造を有し、カルベンの高周期元素類縁体とみなすことができる。カルベンと同様、非共有電子対と空の p 軌道を有するため求核性と求電子性を併せ持ち、小分子活性化に用いることができる。しかし、そのカチオン性に由来する高い求電子性ゆえ、その合成・単離は困難である。近年、我々は分子内にフレキシブルに配位可能なホスフィン部位を有するホスフェニウムを報告した[2]。

今回我々は、分子内に配位可能なホスフィン部位を有するビス(フェロセニル)スチベニウム **4** の合成について検討した。前駆体としてビス(フェロセニル)ブロモスチビン **3** を $SbCl_3$ から 2 段階で合成することに成功した。続くその脱臭素反応についても報告する。



[1] a) M. Olaru, D. Duvinage, E. Lork, S. Mebs, J. Beckmann, *Angew. Chem. Int. Ed.* **2018**, *57*, 10080–10084. b) M. Olaru, S. Mebs, J. Beckmann, *Angew. Chem. Int. Ed.* **2021**, *60*, 19133–19138.
[2] T. Zhang, V. Y. Lee, S. Morisako, S. Aoyagi, T. Sasamori, *Eur. J. Inrog. Chem.* **2021**, 3988–3991.

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2-シアノピリジンを用いる臭化ニッケル-DBU 触媒によるジオール類と二酸化炭素からの環状カーボネート類の合成

（大阪技術研[1]・近畿大理工[2]）○三原　正稔[1]・江崎　嘉宣[2]・兵藤　憲吾[2]・中尾　秀一[1]・中井　猛夫[1]・伊藤　貴敏[1]

Nickel Bromide-DBU-Catalyzed Synthesis of Cyclic Carbonates from Diols and CO_2 Using 2-Cyanopyridine ([1]*Osaka Research Institute of Industrial Science and Technology*, [2]*Faculty of Science and Engineering, Kindai University*) ○Masatoshi Mihara,[1] Yoshinobu Esaki,[2] Kengo Hyodo,[2] Shuichi Nakao,[1] Takeo Nakai,[1] Takatoshi Ito[1]

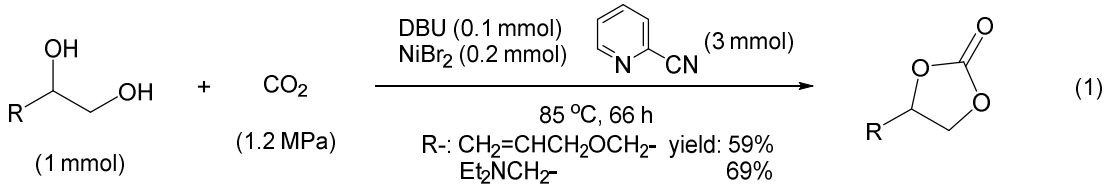
The method for synthesizing cyclic carbonates from diols and CO_2 is known to be one of the effective transformations using CO_2 as a starting material because of the by-production of only water. Although a useful method using 2-cyanopyridine and cerium oxide has already been reported,[1] we have also reported that styrene carbonate could be prepared from styrene glycol and CO_2 in a good yield by using 2-cyanopyridine, $NiBr_2$ and DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) under relatively mild conditions.[2]

Herein, we describe the application of our method to other diols bearing an olefin group or a diethylamino group to give the corresponding carbonates. In addition, we report the role of 2-cyanopyridine on the present reaction through the NMR and IR spectra of the reaction mixture.

Keywords : Carbon Dioxide; Carbonates; Diols

ジオール類と二酸化炭素から環状カーボネート類を合成する方法は、水だけを副生するため、二酸化炭素を原料として用いる有効な変換法の一つとして知られている。既に 2-シアノピリジンと酸化セリウムを用いる有用な方法が報告されているが [1]、我々も、2-シアノピリジンと臭化ニッケルと DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) を用いることにより、比較的温和な条件下で、スチレングリコールと二酸化炭素からスチレンカーボネートが、良好な収率で合成できることを報告している [2]。

ここでは、本法をオレフィン基やジエチルアミノ基を有するジオール類へ適用し、対応するカーボネート類へ誘導できることを述べる (式 1)。また、反応混合物の NMR や IR スペクトルから、本反応での 2-シアノピリジンの役割についても報告する。



(1)

1) M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2014**, *4*, 1893.
2) M. Mihara, T. Arai, K. Hyodo, S. Nakao, T. Nakai, T. Ito, *The 103th Annual Meeting of the Chemical Society of Japan*, **2023**, P3-2vn-37.

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N-(9-アントリル)チアゾリウム塩の合成と反応

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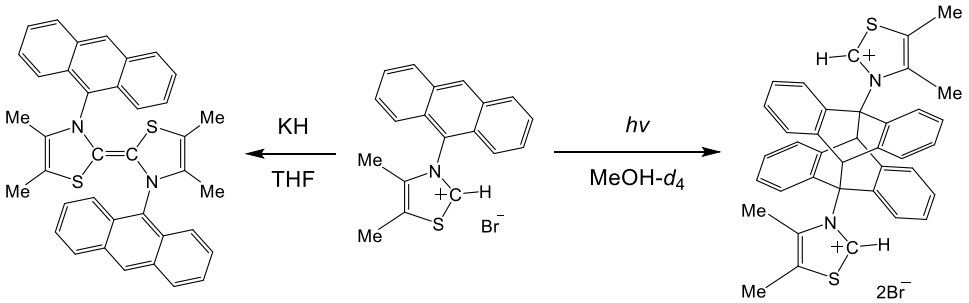
Synthesis and Reactivities of *N*-(9-Anthryl)thiazolium Salts ([1]*School of Science, Kitasato University*, [2]*The University of Alabama*, [3]*Georgia Institute of Technology*) ○ Takahide Nishikawa,[1] Yosuke Uchiyama,[1,2] Hideyo Matsuzawa,[1] Anthony J. Arduengo III[2,3]

N-(9-Anthryl)thiazolium bromide was synthesized by the reaction of 9-anthrylthioformamide with 3-bromobutan-2-one. The deprotonation of the thiazolium bromide with KH gave the corresponding thiazolium carbene dimer (**Scheme 1**). On the other hand, the corresponding thioketone and selenoketone were obtained in the deprotonation in the presence of sulfur and selenium, respectively, indicating the generation of a thiazolium carbene. To prevent dimerization of the carbene, the photodimerization of 9-anthryl moiety was investigated. The UV light irradiation to *N*-(9-anthryl)thiazolium bromide, provided a new compound, which dimerized at the anthryl moiety and it showed the aromatic proton signals at somewhat higher filed than those of anthracene in ^{1}H NMR spectrum (**Scheme 1**). In order to confirm its structure, we have investigated the synthesis of bisthiazolium bromide *via* an anthracene photodimer as a different route.

Keywords : Carbene dimer; Crystal structure; Deprotonation; Steric protection; Anthracene photodimer

N-(9-アントリル)チアゾリウムブロミドをチオホルムアミド体と3-ブロモ-2-ブタノンから合成した。THF 中 KH による脱プロトン化では、相当するカルベンの二量体が、硫黄およびセレン存在下では、それぞれ相当するチオケトン体およびセレノケトン体が得られ、チアゾリウムカルベンの発生が示唆された (**Scheme 1**)。チアゾリウムカルベンの二量化を防ぐ目的で、9-アントリル部位の光二量化を検討した。重メタノール中、*N*-(9-アントリル)チアゾリウムブロミドに紫外光を照射したところ、^{1}H NMR でアントリル部位の光二量体と思われる芳香族プロトンのシグナルが、アントラセンよりも高磁場に観測された (**Scheme 1**)。この化合物の生成を確かめるため、9-アミノアントラセンの光二量体からビスチアゾリウムブロミドの合成を検討したので、併せて報告する。



Scheme 1: Dimerization of *N*-(9-anthryl)thiazolium carbene and photodimerization of *N*-(9-anthryl)thiazolium bromide

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フェニル基を有する新規なケイ素カゴ状化合物の合成検討

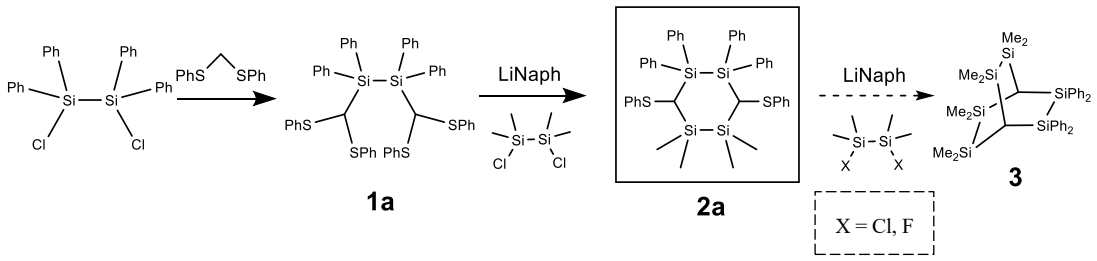
(筑波大学[1,2]) ○佐藤 弘一[1]・笹森 貴裕[2]

Attempted Synthesis of a Novel Oligosila-cage Compound bearing Phenyl Groups

([1]*Graduate School of Science and Technology, University of Tsukuba, Japan*, [2]*Department of Chemistry, Institute of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Sciences (TREMS), University of Tsukuba, Japan*)
○Koichi Sato,[1] Takahiro Sasamori,[2]

Since silicon–silicon σ/σ*-orbitals have relatively higher/lower energy level relative to those of carbon–carbon bonds, oligosilanes should exhibit unique property due to the σ-conjugations through the silicon–silicon linkages. Three-dimensional cage-like σ conjugated systems with σ bonds including silicon atoms as a skeleton are expected to be applied to organic materials and are being vigorously studied. Oligosila-cage compounds crosslinked with tetramethyldisylene chains have already been reported, and their properties have been clarified.[1] In this study, we aimed to construct a new three-dimensional silicon conjugated system of an oligosila cage compound bearing phenyl groups for fuether molecular-functionalization of this oligosilia cage compound. We report here the synthesis of 1,2,4,5-tetrasilacyclohexane derivatives as a precursor, and the attempted synthesis of the targeted oligosila cage compound using the precursors.

ケイ素間結合のσ/σ*軌道準位は、炭素-炭素結合のそれらに比べて比較的高い/低いため、オリゴシラン誘導体はケイ素-ケイ素結合のσ共役により特異な性質を示す。それゆえ、ケイ素を含むσ結合を骨格とする3次元カゴ状σ共役系は、有機材料への応用が期待され、精力的に研究されている。既に、すべてテトラメチルジシレン鎖で架橋されたケイ素カゴ状化合物が報告され、その性質が明らかとされている[1]。そこで今回我々は、このケイ素カゴ状化合物の分子修飾を可能とする目的で、ジシレン鎖の一部に複数のフェニル基を導入した新たな 3 次元ケイ素σ共役系の構築を目指した。二つのジシレン鎖から成るテトラシラシクロヘキサンを合成し、これを前駆体として目的とするカゴ状化合物の合成を検討したので報告する。



1a　2a　3

1) M. Shimizu, T. Hiyama, T. Matsubara, T. Yamabe, Organometallic. Chem. 2000, 611, 12-19.

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分子内にセレン配位部位を有する新規なかさ高いフェロセニル基の合成

（筑波大理工[1]・筑波大数理物質[2]・TREMS[3]）○浜野 竜成[1]・笹森 貴裕[2,3]

Synthesis of a new bulky ferrocenyl group bearing an intramolecularly coordinating selenium moiety. ([1]*School of Science and Engineering, Univ. of Tsukuba*, [2]*Instutute of Pure and Applied Science, Univ. of Tsukuba,* [3]*TREMS, Univ. of Tsukuba*)
○Ryusei Hamano,[1] Takahiro Sasamori[2,3]

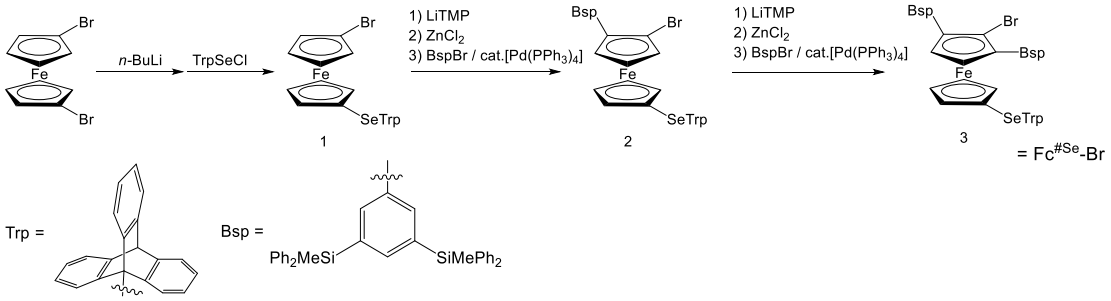
Low-coordinated species of heavier group 14 element such as silicon, e.g. a silylene, are unique chemical species that possess both extremely high electrophilicity and nucleophilicity due to their empty p orbitals and lone electron pairs, making them promising small molecule activation molecules. Conversely, since they are very reactive, their synthesis and isolation should require kinetic or thermodynamic stabilizations, by a sterically demanding substituent or a donor coordination, respectively.

We have previously developed a bulky ferrocenyl group as a redox-active steric protection group. In this study, we report the synthesis of a new bulky ferrocenyl group, compound 3, which exhibits both a kinetic and thermodynamic stabilizing effects with an intramolecular selenium-coordination moiety.

Keywords : Ferrocene; Selenium; Intramolecular coordination; Low-coordinate Organosilicon Compound

ケイ素二価化学種シリレンに代表される高周期 14 族元素低配位化合物は、空の p 軌道と孤立電子対により、極めて高い求電子性に加え、孤立電子対による求核性を併せ持つ特異な化学種であるため、小分子活性化分子として期待できる。一方、これらは非常に反応活性であるため、それらの合成・単離には、立体保護による速度論的安定化あるいはドナーの配位による熱力学的安定化が必要である。

これまで我々は、酸化還元活性な立体保護基として、かさ高いフェロセニル基を開発している[1)]。今回、立体保護による速度論的安定化効果に加え、分子内にセレン配位部位を有することで、熱力学的な安定化効果も併せ持つ、新たなかさ高いフェロセニル基として、化合物 3 を合成することに成功したので報告する。



1) . T. Sasamori, Y. Suzuki, N. Tokitoh, *Organometallics* **2014**, *33*, 6696.

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ビス(シリル)カルベノイドの発生と三塩化リンとの反応

(筑波大理工[1]・立教大理[2]・筑波大数理物質・TREMS[3])
○野元 彬弘[1]・菅又 功[2]・笹森 貴裕[3]

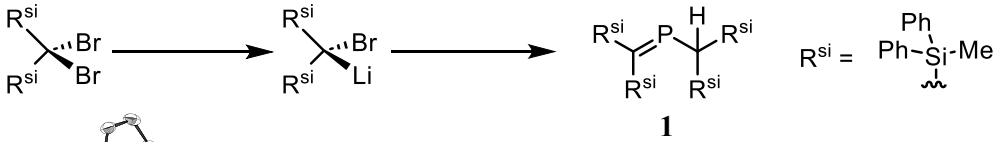
Generation of a bis(silyl)carbenoid and its reaction with phosphine trichloride

([1]*School of Science and Engineering, University of Tsukuba*, [2]*Department of Chemistry, College of Science, Rikkyo University,* [3]Institute of Pure and Applied Sciences, and TREMS, University of Tsukuba) ○Akihiro Nomoto,[1] Koh Sugamata,[2] Takahiro Sasamori[3]

Bis(silyl)carbene is a divalent carbon species bearing silyl groups, and should be of great interest due to its expected high reactivity. For example, we have reported the generation of a carbenoid bearing bulky silyl groups and its reactions with elemental sulfur to give the corresponding chalcogen-centered allene-type molecules.[1] Thus we are interested in the reaction of the carbenoid with phosphorus source in the expectation of generating several types of unsaturated species including phosphaalkenes, phosphaallenes,[2] etc. In this study, we will report the reactions of the bis(silyl)carbenoid with phosphorus trichloride to give the corresponding low-coordinated phosphorus compounds.

Keywords : carbenoid; bulky silyl group; heteroallene; phosphorus trichloride

ケイ素置換のカルベンは、ケイ素置換基の電子的影響によりユニークな反応性を示すことが期待され、興味深い化学種である。既に我々は、かさ高いシリル基を有するカルベノイドの発生と、その硫黄、セレン、テルルとの反応により、16 族元素を中心とする新規なヘテロアレン類が得られると報告している[1]。そこで、このシリル置換カルベノイドとリン化合物の反応により、ホスファアルケンやホスファアレン[2]などの種々の低配位リン化合物を与えると考えた。今回我々は、かさ高いシリル基を有するカルベノイドと、三塩化リンとの反応を行ったところ、低配位リン化合物 **1** が生成していることが判った。他の低配位リン化合物の合成検討も行ったので併せて報告する。



1

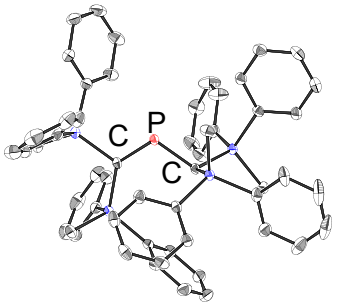


Figure. Molecular structure of **1** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

1) K. Sugamata, D. Hashizume, Y. Suzuki, T. Sasamori, S. Ishii, *Chem. Eur. J.* **2018**, *24*, 6922–6926.
2) R. Appel, J. Peters, A. Westerhaus, *Angew. Chem. Int. Ed Engl.* **1982**, *21*, 80–81.

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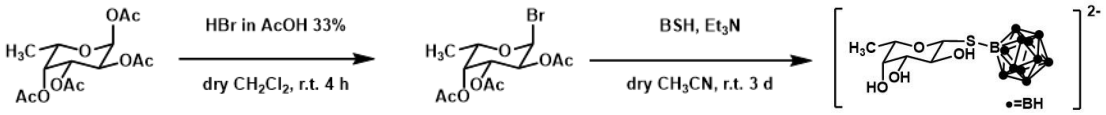
メルカプトウンデカヒドロドデカボレート/フコース複合体の合成

（岡山大環境理工 [1]・岡山大院環境生命自然科学 [2]・岡山大学術研究院環境生命自然科学 [3]） ○藤田 泰河 [1]・森原 聡 [2]・田嶋 智之 [3]

Synthesis of Mercaptoundecahydrododecaborate/Fucose Conjugate ([1]*Faculty of environmental science and technology, Okayama University,* [2,3]*Graduate school of environmental, life, natural science and technology, Okayama University,*) ○Taiga Fujita,[1] Akira Morihara,[2] Tomoyuki Tajima[3]

Mercaptoundecahydrododecaborate (BSH: $Na_2B_{12}H_{11}SH$) have been attracted much attentions from the viewpoint of boron neutron capture therapy. In order to apply the agent to tumor, intracellular uptake and tumor selectivity are required. However, BSH does not penetrate the cell membrane directly. Therefore, various derivatives of BSH have been developed by conjugation with peptides, amino acids, or sugar. In this study, we synthesized mercaptoundecahydrododecaborate/fucose conjugate.

Keywords: Boron neutron capture therapy, Boron cluster, Fucose, Thiol



メルカプトウンデカハイドロドデカボレート (BSH) は、ホウ素中性子補足療法の薬剤として注目されている。腫瘍治療へ適応するためには細胞内導入能や腫瘍細胞への選択性が重要となる。しかし、BSH は細胞膜を通過することができないため、ペプチド [1)]、アミノ酸 [2)]、糖など細胞認識部位を導入した BSH 複合体が合成されている。本研究では、BSH に細胞認識部位としてフコースを連結させた BSH/フコース複合体の合成をした。

1). I. Nakase, Y. Hattori, M. Kirihata, et al. *ACS Omega* **2020**, *5*, *36*, 22731–22738
2). Y. Hattori, et al. *J. Med. Chem.* **2012**, *55*, *15*, 6980–6984

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単層カーボンナノチューブ内包を指向したジフェロセニルジメチルスタンナンの合成

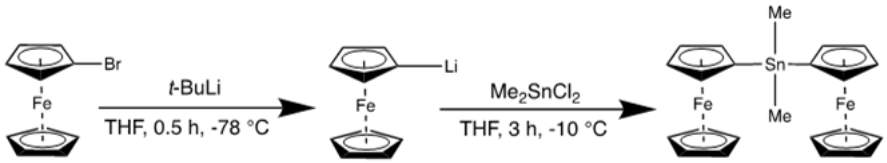
（岡山大環境理工[1]・岡山大院環境生命自然科学[2]・岡山大学術研究院環境生命自然科学[3]） ○神谷 泰地[1]・近藤佑亮[2]・田嶋 智之[3]

Synthesis of Diferrocenyldimethylstannane for Encapsulation in Single-walled Carbon Nanotubes (*Faculty of environmental science and technology, Okayama University, [2,3]Graduate school of environmental, life, natural science and technology, Okayama University)*○Taichi Kamiya[1], Yusuke Kondo[2], Tomoyuki Tajima[3]

The physical properties of inside and outside of single-walled carbon nanotubes (SWCNTs) are known to be different. NMR spectroscopy is useful to investigate the local electronic structure and environment, and the behavior of small molecules such as water and solvents inside and outside SWCNTs has been investigated by NMR. In this study, we report the synthesis of diferrocenyldimethylstannane to investigate the environment of inside-SWCNT by the measurement of ^{119}Sn NMR spectroscopy.

Keywords：Single-walled carbon nanotubes; Ferrocenyl group; Tin; NMR spectroscopy

単層カーボンナノチューブ（SWCNTs）の物理化学的性質は、内外で異なることが知られている。NMR 分光法は、局所的な電子構造や環境を調べるのに有用で、SWCNTs の内外における水や溶媒などの小分子の挙動が NMR で調べられている[1]。本研究では、 SWCNT 内の性質を ^{119}Sn NMR で調べるため、SWCNT のガイドとして有用なフェロセニル基[2]を導入したジフェロセニルジメチルスタンナンを検討した。



1) J. K. Holt and Y. Wu et. al. *Nano Lett*. **2008**, *8*, 7.
2) Y. Takaguchi et. al. *J. Am. Chem. Soc*. **2018,** *140,* 3821.

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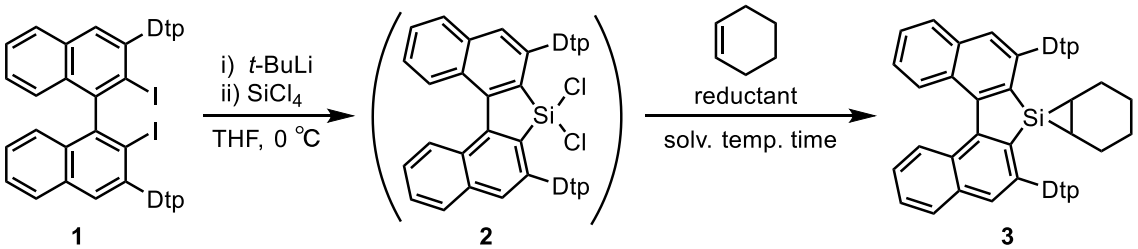
ビナフチル置換シリレンの合成検討

（筑波大院数理[1]・筑波大数理物質[2]）○金岡優[1]・森迫祥吾[2]・笹森貴裕[2]
Generation of a Binaphthalene-Ssubstituted Germylene ([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*Department of Chemistry, Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Sciences (TREMS),*
○Masaru Kanaoka,[1] Shogo Morisako,[2] Takahiro Sasamori[2]

The divalent two-coordinate silicon species, a silylene, has both nucleophilic and electrophilic properties derived from the lone-pair electrons and vacant orbital on the Si atom. Silylenes show various reactivity depending on the substituents on the Si atom. For example, carbon-substituted siylenes with small electronic perturbations to the silicon center have been revealed to be highly reactive and known that it exhibits an insertion reaction for Si-H bonds. In this study, we aimed to develop a new carbon-substituted silylene with tunable electronic structure. Herein, we report the attempted synthesis of a binaphthyl substituted silylene, bearing 2,4,6-tri-*t*-buthyl phenyl groups as bulky substituents on the binaphthyl scaffold.
Keywords : Silylene; Silicon; Binaphthalene; Metallylene

二価二配位ケイ素化学種であるシリレンは、ケイ素上の孤立電子対と空軌道に由来する求核性と求電子性を合わせ持ち、ケイ素上の置換基により多様な反応性を示す[1)]。例えば，ケイ素中心への電子的摂動が小さな炭素置換シリレンは高い反応性をもち，Si-H 結合に対する挿入反応を示すことが分かっている[2)]。しかし、一般に炭素置換シリレンはその高い反応性から自己多量化や分解反応を起こしやすく、これまでに単離・構造解析された例は限られている[1)]。そこで我々は、電子状態の制御が可能な新規炭素置換シリレンの開発を目的とした。本研究では、堅固な炭素骨格であるビナフチル骨格にかさ高い置換基である 2,4,6-tri-*t*-buthylphenyl 基が置換した、ビナフチル置換シリレンの合成検討を行った。具体的には、ジヨード体 1 のジリチオ化とそれに次ぐ $SiCl_4$ との反応によってジクロロシラン **2** の生成が示唆された。過剰量のシクロヘキセン存在下で **2** の還元反応により対応するシリレンの発生・捕捉を検討したので併せて報告する。



1 2 3

1) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479–3511. 2) M. Kira, S. Ishida, T. Iwamoto, *Chem. Rec.* **2004**, *4*, 243-253.

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ビフェニル架橋環状ホスフィンアランの合成検討

(筑波大院数理[1]・筑波大数理物質[2]・TREMS[3]) ○岩﨑貴紀[1]・笹森貴裕[2,3]

Attempted Synthesis of Cyclic Phosphine-Alane bridged by a biphenyl unit

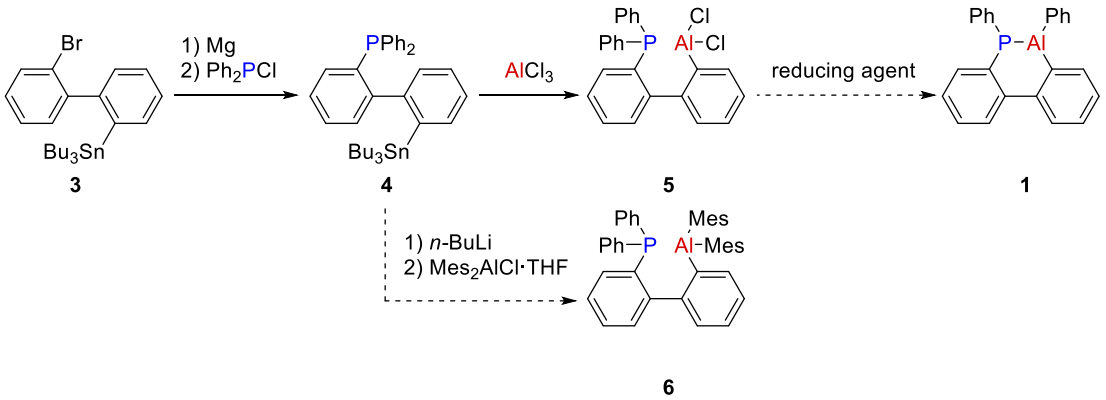
(*Graduate School of Science and Technology, Univ. of Tsukuba, Institute of Pure and Applied Sciences, Univ. of Tsukuba, TREMS, Univ. of Tsukuba*) ○Takanori Iwasaki, Takahiro Sasamori

A phosphinealane, a complex of trivalent-tricoordinate phosphine and tricoordinate aluminum compound should be interesting species as a donor-acceptor complex which is expected to be small-molecule activatable FLP.[1)] In this study, we will report the attempted synthesis of a biphenyl-bridged phosphanylalumane with the intramolecular flexible phosphorus-aluminum coordination in the molecule. Reaction of bromobiphenylstannane derivative **3** with Mg and Ph_2PCl in THF afforded the compound **4**. We also report the attempted synthesis of phosphinealane **5**, which is the precursor of phosphanylalumane **1**, and phosphinealane **6** with mesityl groups.

Keywords : Phosphinealane; FLP; Biphenyl; Phosphine; Aluminum

ホスフィンアランは、三価三配位ホスフィンが三配位アルミニウム化合物に配位下した錯体であり、小分子活性化可能な FLP として期待されるドナー・アクセプター錯体である [1)]。今回我々は、分子内にフレキシブルなリン－アルミニウム配位部位を持つ FLP として、ビフェニル架橋ホスファニルアルマン **1** を設計し、その合成について検討を行った。

ブロモビフェニルスタンナン誘導体 **3** を THF 中、Mg と反応させ Grignard 試薬とし、次いでクロロジフェニルホスフィンと反応させたところ、化合物 **4** が収率 9%で得られた。また、得られた化合物 **4** を用いて、ホスファニルアルマン **1** の前駆体となるホスフィンアラン **5** と、メシチル基をもつホスフィンアラン **6** の合成について検討を行ったので、併せて報告する。



1) a) D. W. Stephan, *J. Am. Chem. Soc.*, **2021**, *143*, 20002. (b) T. Yanagisawa, Y. Mizuhata, N. Tokitoh, *Chem. Eur. J.*, **2021**, *27*, 11273.

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トリフェニルアミン骨格をドナー部とするD-A型縮合多環化合物の合成と性質

（阪公大院理）○西山 勝貴・舘 祥光・小嵜 正敏

Syntheses and properties of donor-acceptor type fused polycyclic compounds with a triphenylamine skeleton as a donor unit (*Graduate School of Science, Osaka Metropolitan University*) ○Katsutaka Nishiyama, Yoshimitsu Tachi, Masatoshi Kozaki

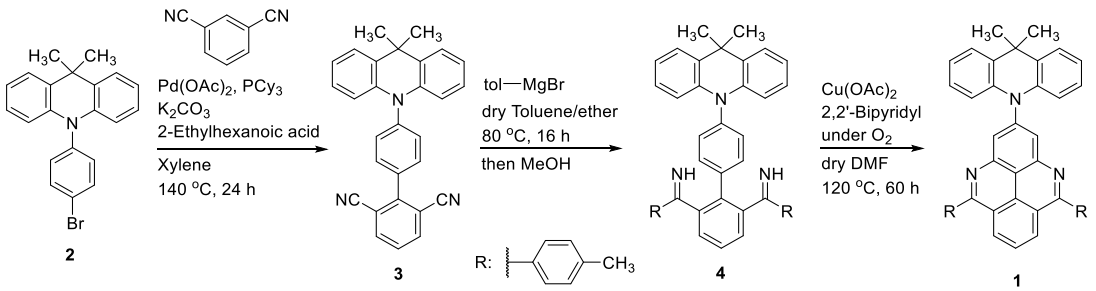
9,10-Dihydro-9,9-dimethylacridine (DDA) derivatives have attracted considerable attention due to their superior electron-donating properties and have been applied in the fabrication of organic electronic devices. In this study, we connected a 4,10-diazapyrene skeleton as an electron-accepting unit at the 10-position of the DDA unit to create a donor-acceptor type fused polycyclic compound. The 4,10-diazapyrene skeleton was synthesized in three steps with 43% yield from 10-(4-bromophenyl)-9,10-dihydro-9,9-dimethylacridine using the synthetic method established by our laboratory[1]. The UV/Vis absorption spectrum of the product was measured in CH_2Cl_2, and absorption peaks were observed at maximum wavelengths of 232, 246, 290, and 352 nm. The structure and physical properties of the compound will be discussed.

Keywords : Triphenylamine; Azapyrene; Electron donor; Electron acceptor; Heterocyclic compound

9,10-ジヒドロ-9,9-ジメチルアクリジン（DDA）誘導体は、良好な電子ドナー性をもつことから高い注目を集めており、有機発光素子を始めとする有機エレクトロニクス材料として応用されている。本研究では、電子アクセプター部として 4,10-ジアザピレン骨格を DDA 骨格の 10 位に導入することで、ドナーーアクセプター型縮合多環化合物 **1** を合成しその性質を評価した。

当研究室が開発した手法を応用して 4,10-ジアザピレン骨格を構築することで、化合物 **2** から 3 段階、収率 43%で目的化合物 **1** を合成した（Scheme 1）[1]。得られた化合物のジクロロメタン溶液を用いて紫外可視吸収スペクトルを測定したところ、極大波長 232, 246, 290, 352 nm をもつ一連の吸収が観測された。講演では、化合物の構造と物性を詳細に述べる。

Scheme 1



1) Y. Omura, Y. Tachi, K. Okada, M. Kozaki, *J. Org. Chem.* **2019**, 84, 4, 2032–2038.

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9,10-ジスチバアントラセンの合成に向けた、かさ高い置換基を有する *o*-ジブロモベンゼン誘導体の合成

(筑波大理工[1]・筑波大数理物質[2]・TREMS[3]) ○大辻 駿介[1]・正田 浩一朗[2]・笹森 貴裕[2,3]

Synthesis of an *o*-Dibromobenzene Derivative toward the Synthesis of a 9,10-Distibaanthracene, ([1]School of Science and Technology, University of Tsukuba, [2]Institute of Pure and Applied Sciences, University of Tsukuba, [3]TREMS, University of Tsukuba)
○Shunsuke Otsuji[1], Koichiro Masada[2], Takahiro Sasamori[2,3]

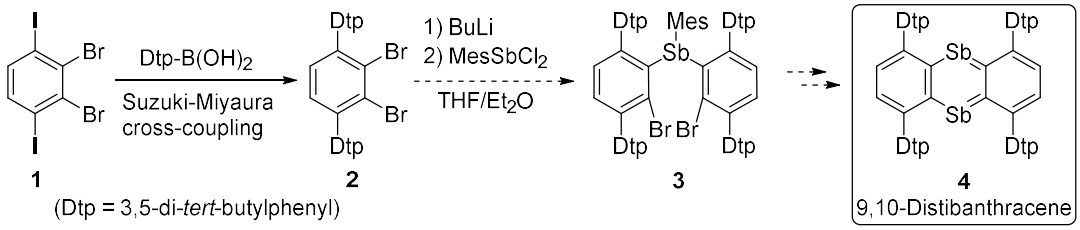
9,10-Distibanthracene is a heavier-element analog of 9,10-diazaanthracene, which contains low-coordinated antimony atoms. This compound is expected to exhibit biradical character, redox activity, and small molecule activation reactions derived from the low-coordinated heavy main-group elements. However, its synthesis has yet to be reported probably due to its high lability.[1,2] In this study, we aim to synthesize 9,10-distibanthracene **4**, where the antimony centers are protected by bulky 3,5-di-*tert*-butylphenyl (Dtp) groups.

The precursor, *o*-dibromobenzene derivative **2**, was successfully synthesized via the Suzuki-Miyaura coupling of compound **1** and the corresponding boronic acid. In addition, the conditions for introducing an antimony atom via lithiation of **2** were investigated.

Keywords: *9,10-Distibanthracene; Bulky substituent; Aromatic compound with main-group element; Antimony*

低配位アンチモン原子をアントラセン環に組み込んだ 9,10-ジスチバアントラセンは、高周期典型元素部分に由来するビラジカル性、酸化還元活性、小分子活性化反応が期待できる一方、その不安定さから現在までこれの合成は報告されていない[1,2]。本研究ではかさ高い 3,5-ジ-*tert*-ブチルフェニル(Dtp)基でアンチモン中心を保護した 9,10-ジスチバアントラセン **4** の合成に向けた検討を行った。

化合物 **1** と対応するボロン酸との鈴木-宮浦カップリングにより、かさ高い置換基を持つアンチモン上の配位子である *o*-ジブロモベンゼン誘導体 **2** を合成した。続いて **2** のリチオ化によりアンチモン原子を導入する過程について条件検討を行ったので、その結果について併せて報告する。



1) Related study on a distiba-aromatic compound: Steffenfauseweh, H.; Rottschäfer, D.; Vishnevskiy, Y. V.; Neumann, B.; Stammler, H. G.; Szczepanik, D. W.; Ghadwal, R. S. *Angew. Chem. Int. Ed.* **2023**, *62* (19), e202216003.
2) Synthesis of a 9,10-dihydrodistibanthracene derivative: Uchiyama, Y. *Heteroat. Chem.* **2011**, *22*, (3–4), 377 –387.

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かさ高いフェロセニル基を有するクロロゲルミレンのジハロアルカンへの挿入反応の検討

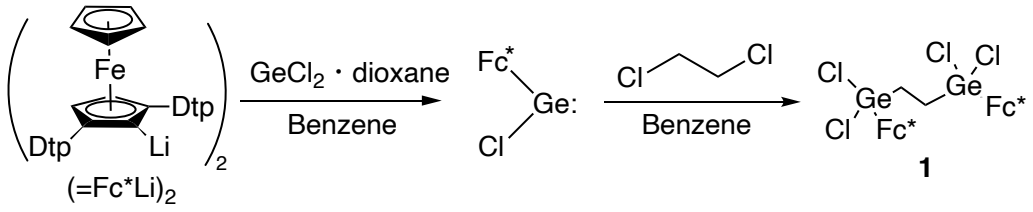
（筑波大理工[1]・筑波大数理物質[2]・TREMS[3]）○千田 裕斗[1]・笹森 貴裕[2,3]

Insertion reaction of chlorogermylene bearing a bulky ferrocenyl group into dihaloalkanes ([1]*School of Science and Engineering Univ. of Tsukuba,* [2]*Insutitute of Pure and Applied Sciences, Univ. of Tsukuba,* [3]*TREMS, Univ. of Tsukuba*)
○Hiroto Chida[1], Takahiro Sasamori[2,3]

A cyclic-digermene is expected to exhibit unique reactivity due to its expected both character of a digermene and bis-germylenes. Thus, it can be expected to work as a small molecule activation catalyst, and its chemical and physical properties are of great interest.[1] Although it is difficult to isolate such reactive low-coordinated germanium species, there are some examples of stable cyclic-digermenes bearing sterically demanding substituents. We will report here the synthesis of compound 1 as a promising precursor for the corresponding 1,2-digermacyclobutene by the insertion reaction of the chlorogermylene with a bulky ferrocenyl group[2] into a dihaloalkane.

Keywords :Organic Chemistry, Organic Elemental Chemistry, Germanium, 1,2-digermacyclobutadiene

かさ高い置換基を持つ環状ジゲルメンは、ゲルマニウム間π結合、それが解離した二つのゲルマニウム二価化学種（ゲルミレン）がもつ高い反応性に興味が持たれ、特に小分子活性化触媒としての機能発現が期待できる。しかし、その高い反応性から、単離は極めて困難であり、かさ高い置換基による速度論的安定化を施して、いくつかの単離例が報告されているのみである[1]。今回我々は、対応する1, 2-ジゲルマシクロブテンの合成前駆体として期待できる化合物**1**の合成について、かさ高いフェロセニル基を有するクロロゲルミレン[2]のジハロアルカンへの挿入反応によって検討を行ったので報告する。



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α-ヨードトルエン構造を鍵とする炭素-炭素不飽和結合の還元反応の開発とその応用範囲の検討

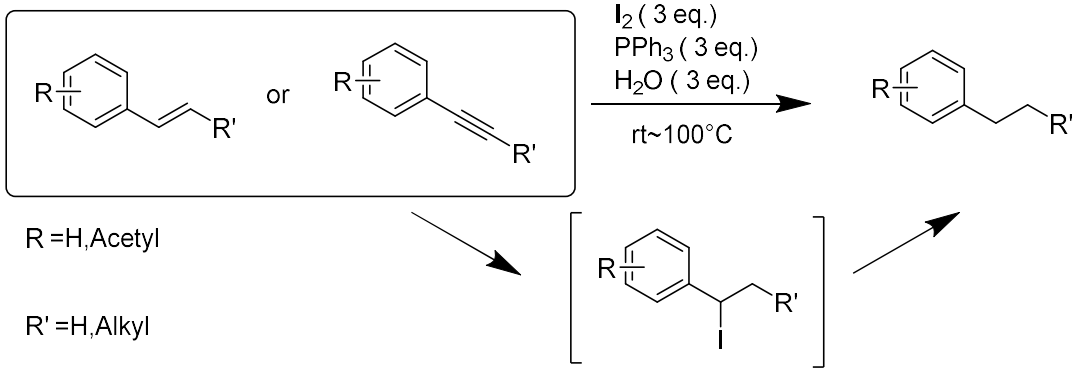
(佐賀大学[1]・大阪公立大学[2])○石角知佳[1]・天本翔大[1]・川谷瑠泉[1]・古藤田信博[1]・小川昭弥[2]・川口真一[1]

Development and application of reduction reaction of unsaturated carbon- carbon bond via α-iodotoluene structure ([1]*Saga University,* [2]*Osaka Metropolitan University*) ○Chika Ishizumi[1], Shota Amamoto[1], Rumi Kawatani[1], Nobuhiro Kotoda[1], Akiya Ogawa[2], Shin-ichi Kawaguchi[1]

Our research group has previously reported the hydroiodination of unsaturated carbon-carbon bonds using $I_2/PPh_3/H_2O$.[1,2] As a result of our investigation of the conditions, we have found a hydrogenation reaction for styrene and phenylacetylene derivatives (**Scheme 1**). In most hydrogenation reactions of carbon-carbon unsaturated bonds, the carbonyl group is also reduced, but under the present conditions, the carbonyl group is not reduced, and the hydrogenation proceeds selectively to the carbon-carbon unsaturated bond. Using this selective reaction, the synthetic method of derivatives of a natural product that are expected to have bioactivity was also investigated.

Keywords : Hydrogenation, Reduction reaction, Hydroiodination, Unsaturated bond, Styrenes

当研究グループではこれまで $I_2/PPh_3/H_2O$ を用いた、炭素－炭素不飽和結合へのヒドロヨウ素化反応を報告してきた[1,2]。条件等を検討した結果、スチレン誘導体やフェニルアセチレン誘導体を水素化する反応を見いだしたので報告する（**Scheme 1**）。炭素－炭素不飽和結合の水素化反応の多くはカルボニル基も還元してしまうが、本条件ではカルボニル基に影響を与えず、炭素－炭素不飽和結合選択的に進行することが特徴である。また、還元反応が進行する鍵となっているのは反応中間体であるα-ヨードトルエン構造であると考えている。本選択的な反応を利用して、生理活性が期待されている天然物の誘導体合成についても検討したので併せて報告する。



Scheme 1.

1) S-i. Kawaguchi, A. Ogawa, et al., *Tetrahedron Lett*. **2014**, *55*, 6779.

2) S-i. Kawaguchi, K. Nakamura, A. Ogawa, et al., *Eur. J. Org. Chem.* **2017**, 5343.

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シンコナアルカロイドアミド/亜鉛(II)触媒による α–ケチミノエステルへの不斉チオール付加反応の開発

（名工大院工 [1]）○小幡 航希 [1]・飯塚 夕夏 [1]・中村 修一 [1]

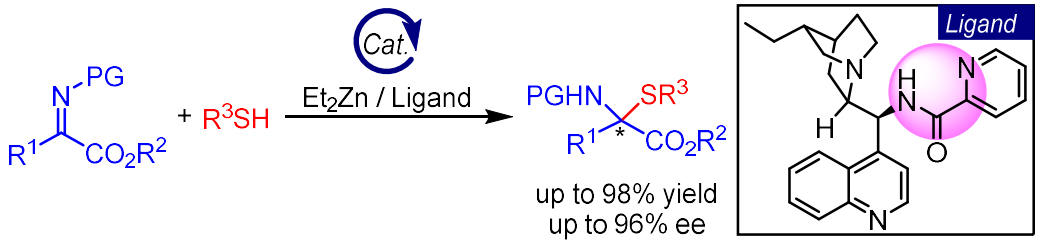
Enantioselective Addition of Thiols to α–Ketiminoesters using Cinchona Alkaloid Amide/Zinc(II) Catalysts

([1]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Kouki Obata,[1] Yuka Iizuka,[1] Shuichi Nakamura,[1]

Chiral *N*,*S*–acetals have been recognized as an important structural motif in bioactive compounds. Asymmetric nucleophilic addition to α–ketiminoesters using sulfur nucleophiles can efficiently synthesize chiral α–amino acid skeletons as well as chiral *N*,*S*–acetals. However, it has not been developed. We present here a high yield and highly enantioselective chiral *N*,*S*–acetal synthesis of various α–ketiminoesters in presence of zinc salt in combination with cinchona alkaloid amide. The reaction of benzyl mercaptan with α–phenylketiminoesters using Et_2Zn (10 mol%) and ligand (10 mol%) as a catalyst in toluene at −60 °C afforded corresponding *N*,*S*–acetals in 98% yield with 96% ee. This catalytic system applies to various ketimines/thiols bearing electron-donating or electron-withdrawing groups, and also alkyneketiminoesters.

Keywords : Chiral N,S–Acetal, Chiral Amino Acid Synthesis, Cinchona Alkaloid Catalyst, Acyclic Ketimine, Thiol Addition

キラル *N*,*S*–アセタール構造は生物活性物質に遍在しており、有用である。本構造を構築するために、近年様々なイミン類に対する硫黄求核剤の不斉求核付加反応が開発されてきたが、ほとんどが比較的反応性が高いアルジミンや立体制御が容易な環状ケチミンを用いた例である。一方、立体制御が難しい鎖状ケチミンを用いた例は 2 例のみで、基質適用範囲が限定されるため、更なる拡大が望まれる [1, 2]。この鎖状ケチミンに α–ケチミノエステルを用いればキラル α–アミノ酸骨格を同時に合成できるため合成的価値が高いが、未だ達成されていない。本研究では、シンコナアルカロイドアミドと亜鉛を組み合わせた触媒系を活用し、様々な α–ケチミノエステルから高収率・高エナンチオ選択的なキラル *N*,*S*–アセタール合成を達成した。実際に α–フェニルケチミノエステルとベンジルメルカプタンの反応を、トルエン中、ジエチル亜鉛/リガンド 10 mol%存在下で行った場合、目的の *N*,*S*–アセタールが 98%収率、96% ee で得られた。



1) *Y. Lin, H. Duan et al., Org. Biomol. Chem.* **2020**, *18*, 7431.
2) *S. Nakamura et al., Adv. Synth. Catal.* **2022**, *364*, 4271.

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スルフィドとスルホニウム部位を有するベンゼン及びナフタレン誘導体の合成と性質

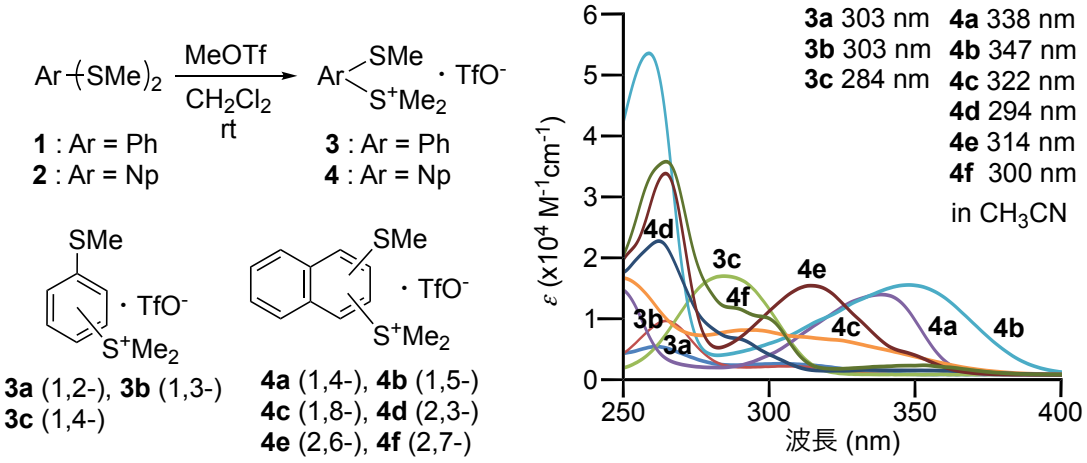
（都立大院理）○平林 一徳・高橋 蓮・北村 尚也・清水 敏夫

Synthesis and Properties of Benzene and Naphthalene Derivatives Having Sulfide and Sulfonium Groups (*Graduate School of Science, Tokyo Metropolitan University*) ○Kazunori Hirabayashi, Ren Takahashi, Naoya Kitamura, Toshio Shimizu

The reactions of benzene and naphthalene derivatives having methylthio groups **1**, **2** with methyl trifluoromethanesulfonate afforded the compounds with sulfide and sulfonium groups **3**, **4**. The UV spectra of **3** showed absorption maxima in the range of 284-303 nm. On the other hand, absorption of **4a-c** and **4d-f** were observed in the range of at 322-347 nm and 294-314 nm, respectively. Thus, the naphthalene derivatives show a significant change in absorption wavelengths depending on the position of substitution. The crystal structures of **3**, **4** were determined by X-ray analysis. In addition, the electrochemical properties of **3**, **4** were examined by cyclic voltammetry.

Keywords : Sulfonium Salts; Benzene Derivatives; Naphthalene Derivatives; Ultraviolet and Visible Absorption Spectrum; Redox Behavior

当研究室では、芳香環上に複数のスルホニウム部位を有する化合物の合成および性質について研究している。本研究では、ベンゼン環及びナフタレン環上にスルフィド部位とスルホニウム部位を有する化合物の合成を行い、その性質を調べることを目的とした。芳香環上にメチルチオ基を有する化合物 **1**, **2** とメチルトリフラートとの反応により **3**, **4** を合成した。ベンゼン環上にスルフィドとスルホニウム部位を 1 つずつ有する化合物 **3** は 284-303 nm に吸収が観測された。一方、ナフタレン誘導体 **4a-c** の場合には 322-347 nm に、**4d-f** の場合には 294-314 nm に吸収が観測され、ナフタレン誘導体の方が置換位置の違いにより吸収波長の変化が大きく、**4b** が最も長波長側に吸収を持つことがわかった。また、X 線結晶構造解析によりスルホニウム塩の結晶構造を明らかにするとともに、CV 法より酸化還元挙動の比較を行った。



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αジフルオロメチルアミノ酸の共通合成中間体の調製に関する研究

（東京工科大院工[1]・岡大院自然[2]）○白石聖弥[1]・片桐利真[1]・平松信志[2]

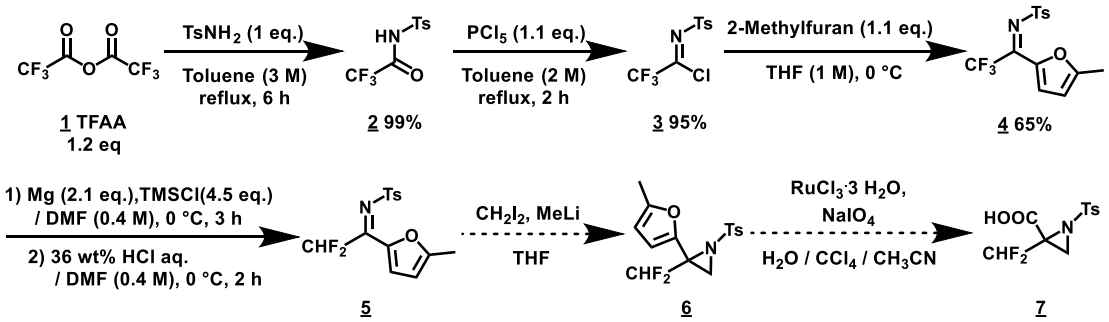
A study on preparation of a common precursor for α-difluoromethyl amino acids.

([1]*Graduate School of Engineering, Tokyo University of Technology,* [2]*Graduate School of Science and Technology, Okayama University*) ○Masaya Shiraishi,[1] Toshimasa Katagiri,[1] Shinji Hiramatsu[2]

We report on a preparation of *N*-tosyl-2-difluoromethyl-2-carboxyaziridine, a common precursor for α-difluoromethyl amino acids. Currently, preparation of aziridines from imines with using a cycloaddition reaction of carbenoid is underway.

Keywords : Organic fluorine compound; Amino acids; Synthetic Common Intermediate

α-ジフルオロメチルアミノ酸の共通合成前駆体の調製について報告する。α-ジフルオロメチルアミノ酸の共通合成前駆体となる、*N*-トシル-2-ジフルオロメチル-2-カルボキシアジリジンの合成を検討している。現在、カルベノイドの付加環化反応を用い、イミンからアジリジンの形成を検討している。



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4) J. M. Concello´n, H. Rodrı´guez-Solla, P. L. Bernad, and C. Simal, *J. Org. Chem.* **2009**, *74*, 2452.

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かさ高い置換基を有するビスホスフィド配位子の合成

(筑波大院数理[1]・筑波大数理物質[2]・TREMS[3]) ○加藤 莉子[1]・笹森 貴裕[2,3]

Synthesis of a bis(phosphide) ligand bearing sterically demanding substituents

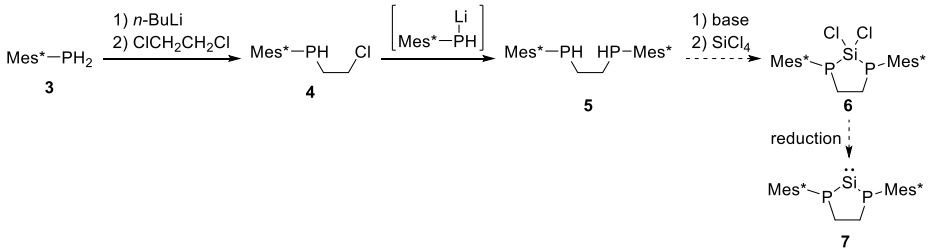
([1]*Graduate School of Science and Technology, Univ. of Tsukuba,* [2] *Institute of Pure and Applied Sciences, Univ. of Tsukuba,* [3]*TREMS, Univ. of Tsukuba*)
○Riko Kato,[1] Takahiro Samamori[2,3]

Silylenes, divalent silicon species, are highly reactive enough to activate various small molecules such as hydrogen and nitrogen molecules. However, the isolation of silylenes is difficult due to their high reactivity. Thus, they have been isolated by taking advantage of thermodynamic or kinetic stabilization. In this study, we have succeeded in synthesis of a bisphosphide ligand, which is expected to afford both thermodynamic kinetic stabilization effects to the silylene center with keeping its intrinsic high reactivity due to the moderate resonance effect from the phosphorus atom to the silicon center. In addition, we will report the attempted synthesis of the corresponding dichlorosilane bearing the bisphosphide ligand as a possible precursor for the P-substituted silylene.

Keywords : bis(phosphide) ligand; phosphorous

遷移金属触媒は汎用触媒として利用されているが、遷移金属元素の希少性や毒性の高さが問題視されており、豊富かつ低毒性な典型元素による触媒開発が期待されている。地殻中に豊富に存在するケイ素の二価化学種「シリレン」は空の p 軌道に由来する求電子性と s 性の高い孤立電子対に由来する求核性を併せ持ち、水素分子などの種々の小分子を活性化できるほどの高い反応性を示す。しかし、高い反応性ゆえに単離困難な化学種であり、これまで熱力学的安定化や速度論的安定化を駆使することで合成・単離されてきた。

今回我々は、シリレンの本来の反応性を維持しつつも、リン原子からケイ素中心への共鳴効果による熱力学的安定化とかさ高い置換基による速度論的安定化を期待できる、かさ高いビスホスフィド配位子 **5** の合成・単離に成功した[1]。また、ビスホスフィド配位子へのケイ素試薬導入によりシリレン **7** の前駆体となり得るジクロロシラン **6** の合成を検討したので報告する。



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セラニルスルファニルイミダゾ[1,5-*a*]ピリジン誘導体を配位子とした錯体の合成検討

（中部大工）○田中 陽登・饒村 修

Attempt to Synthesis of Complex with Selanyl Sulfanyl Imidazo[1,5-*a*]pyridine Ligands

(*College of Engineering, Chubu University*)
○Akito Tanaka, Osamu Niyomura

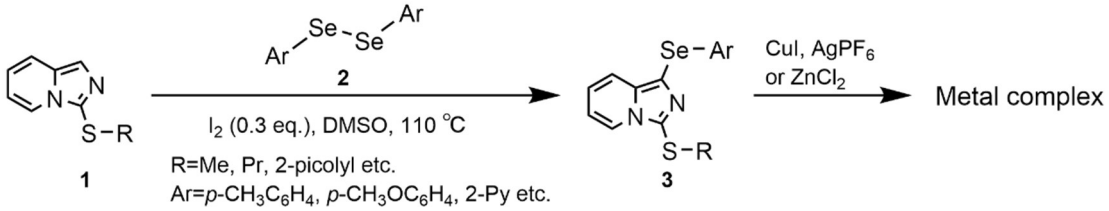
In our laboratory, we have previously synthesized compounds with sulfanyl (RS-) or selanyl (RSe-) groups on imidazopyridine skeleton and revealed their optical properties such as emission wavelength change due to complexation and halochromism. In this study, we synthesized ligand of imidazo[1,5-*a*]pyridine with 1-selanyl and 3-sulfanyl groups and attempted to synthesis group 11 and 12 metal complexes.

Various 3-sulufanyl imidazopyridines **1** were reacted with diaryldiselenides **2** to synthesized imidazopyridine derivatives **3** with selanyl group at the 1-position. For example, the reaction of sulfanyl substituent **1** (R=Pr) with diselenide **2** (Ar=2-Py) gave the corresponding product **3** in 88% yield. We attempted to synthesize metal complexes using CuI, $AgPF_6$ or $ZnCl_2$. As a result, low field shifts of the ligand were observed in these ^{1}H NMR spectra indicating the formation of the complexes. The emission spectra of the complexes were compared, revealing a short-wavelength shift of 20 to 40 nm due to complexation. The emission wavelengths were significantly changed depending on the metal.

Keywords : Imidazo[1,5-a]pyridine; Sulfanyl group; Selanyl group; Optical properties; Metal complex

これまでに当研究室では、イミダゾピリジン骨格にスルファニル基 (RS-) またはセラニル基 (RSe-) を有する化合物を合成し、その錯化による発光波長の変化やハロクロミズムなど光学特性を明らかにしてきた。本研究では、イミダゾ[1,5-*a*]ピリジン骨格の 1 位にセラニル基、3 位にスルファニル基の 2 つのカルコゲニル基を導入した配位子を合成し、11, 12 族金属錯体の合成を検討した。

種々の 3-スルファニルイミダゾピリジン **1** にジアリールジセレニド **2** を反応させ、1 位にセラニル基を導入したイミダゾピリジン誘導体 **3** を合成した。例えば、スルファニル置換体 **1** (R=Pr) とジセレニド **2** (Ar=2-Py) との反応から対応する化合物 **3** が 88%の収率で得られた。これを配位子として CuI、$AgPF_6$、$ZnCl_2$ を作用させ錯体合成を試みたところ、いずれの ^{1}H NMR においても配位子の低磁場シフトが確認され錯体の生成が示唆された。また、これらの発光スペクトルを比較したところ、錯化により 20〜40 nm ほど短波長シフトが観測され、金属の違いによっても発光波長が大きく変化することが確認された。



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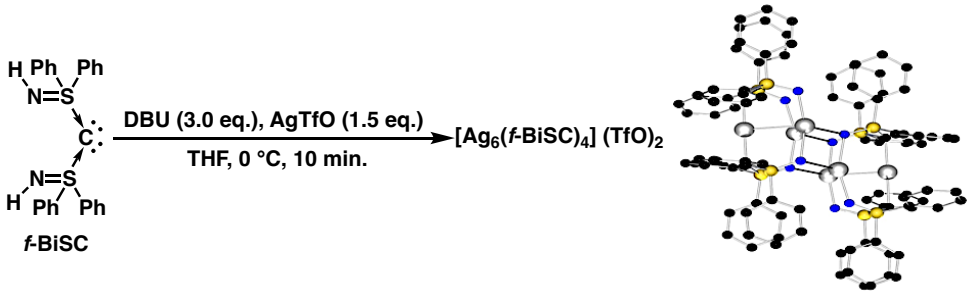
フリーなイミノ窒素を持つビスイミノスルファンカーボン(0)を配位子とした 6 核銀錯体 ([Ag$_6$(*f*-BiSC)$_4$](TfO)$_2$)の合成とその構造

（日大生産工）○野口 桂子・藤井 孝宜
Synthesis and structure of hexanuclear silver complex ([Ag$_6$(*f*-BiSC)$_4$](TfO)$_2$) with bis iminosulfanecarbone(0) ligands bearing free imino nitrogen. (*College of Industrial Technology, Nihon University*) ○Keiko Noguchi, Fujii Takayoshi

Carbones consist of two strong electron-donating ligands (L) coordinated to a central zero-valent carbon atom, which maintains four valence electrons in σ- and π-type lone pairs (LP) orbitals. (HN=SPh$_2$)$_2$C(0) has lone pairs on carbon and nitrogen atoms as metal coordination sites. We report the synthesis of a new hexanuclear silver complex [Ag$_6$(*f*-BiSC)$_4$](TfO)$_2$ with *f*-BiSC ligand. The structure of the silver complex was determined by single-crystal X-ray structure analysis. The C←Ag→C bond angle (178.03°) of the silver complex is an almost straight line. In this complex, the two-nitrogen-donor of *f*-BiSC ligand forms a bidentate pincer-type coordination mode.
Keywords : Carbones; Divalent-carbone(0) compounds; Silver complex; Polynuclear complex; Organic typical elements chemistry

0 価 2 配位炭素化学種のカルボンは中心炭素上に σ 及び π 性の非共有電子対を有するため，強い電子供与性が示される [1]。さらに中心炭素にイミノスルファンが結合した化合物は，中心炭素だけではなく窒素上の非共有電子対も金属イオンに配位できる [2,3]。本研究ではこのイミノ窒素を利用した多核金属錯体の合成を目的に，*f*-BiSC と銀 (I) イオンを反応させることで 6 核銀錯体 [Ag$_6$(*f*-BiSC)$_4$](TfO)$_2$ を合成した。実際には，アルゴン雰囲気下，*f*-BiSC (1.0 eq.) と AgTfO (1.5 eq.) を DBU 存在下，THF 中 0 °C で反応させることで配位子とは異なる ^{1}H NMR スペクトルを示す白黄色固体を得た。この白黄色固体の単結晶 X 線構造解析を行ったところ，4 つの *f*-BiSC 配位子に 6 つの銀 (I) イオンが配位子した 6 核銀錯体であることが明らかとなった。解析の結果，2 つの配位子の中心炭素と結合した銀 (I) イオン (C–Ag–C) の結合角は 178.03°とほぼ直線に近いことがわかった。配位元素が同一平面上に位置した配位形式を取るため，*f*-BiSC がピンサー型配位子として機能していることを見出した。さらにいずれの Ag–Ag 原子間距離は 3.0 Å 程度であり，金属原子間相互作用が期待できる範囲内であることがわかった。



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かさ高いフェロセニル基を有するシラン誘導体の合成とアリールリチウムとの反応性

(筑波大院数理物質[1]・筑波大数理物質[2]・TREMS[3])
○岩﨑 龍樹[1]・正田 浩一朗[2]・笹森 貴裕[2,3]

Synthesis of Silanes Bearing a Bulky Ferrocenyl Group and Their Reactivity with Aryl Lithium

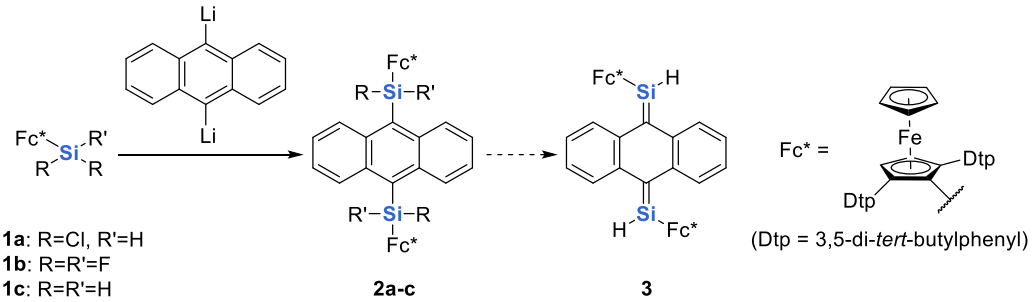
([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*Institute of Pure and Applied Sciences, University of Tsukuba,* [3]*TREMS, University of Tsukuba*)
○Ryuju Iwasaki,[1] Koichiro Masada,[2] Takahiro Sasamori[2,3]

Low-valent species of heavy main group elements, such as silicon, attract much attention for their high reactivity. *p*-Disilaquinodimethane, a quinoid-type conjugated system with silicon-carbon double bonds, has two possible electronic structures: (i) closed-shell quinoid and (ii) singlet biradical. Although this electronic property will cause characteristic reactivities and physical properties, only a few reports[1)] describe the synthesis of *p*-disilaquinodimethanes.

With this background, we aim to synthesize *p*-disilaanthraquinodimethane **3**, where unstable disilaquinodimethane moiety is protected by bulky ferrocenyl groups (Fc*) and fused with two benzene rings. In this presentation, we will report the synthesis of silanes **1a**–**c**, aiming to synthesize compound **3**. We will also report the attempted synthesis of disilaanthraquinodimethane precursors **2a**–**c** by the reaction of the resulting silane derivatives with dilithioanthracene.[2)]

Keywords : Organic Chemistry; Kinetic Stabilization; Silicon; Conjugate; Ferrocene

ケイ素など高周期典型元素の低配位化学種は、その高い反応性から注目を集めている。特に *p*-ジシラキノジメタンはケイ素-炭素二重結合を持つキノイド型共役系であり、閉殻キノイドと一重項ビラジカルの 2 つの電子構造をとりうる点で興味深い。その電子的性質から特異な反応性や物性が期待されるが、*p*-ジシラキノジメタンの報告例は極めて少ない[1)]。そこで本研究では、ジシラキノジメタンにベンゼン環を縮環し、不安定なジシラキノジメタン骨格をかさ高いフェロセニル基により保護した化合物**3**の合成を指向した。本発表では、シラン誘導体 **1a–c** の合成、ならびに得られたシラン誘導体とジリチオアントラセン[2)]との反応によるジシラアントラキノジメタン前駆体 **2a–c** の合成検討について報告する。



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1,6,2,5-ジオキサジシロシン誘導体の合成検討

（筑波大院物質[1]・筑波大数理物質・TREMS[2]）○中村 士竜[1]・笹森 貴裕[2]

Attempted Synthesis of a 1,6,2,5-Dioxadisilocine Derivative ([1]*Graduate School of Science and Technology, Univ. of Tsukuba,* [2] *Department of Chemistry, Institute of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba*) ○Shiryu Nakamura,[1] Takahiro Sasamori[2]

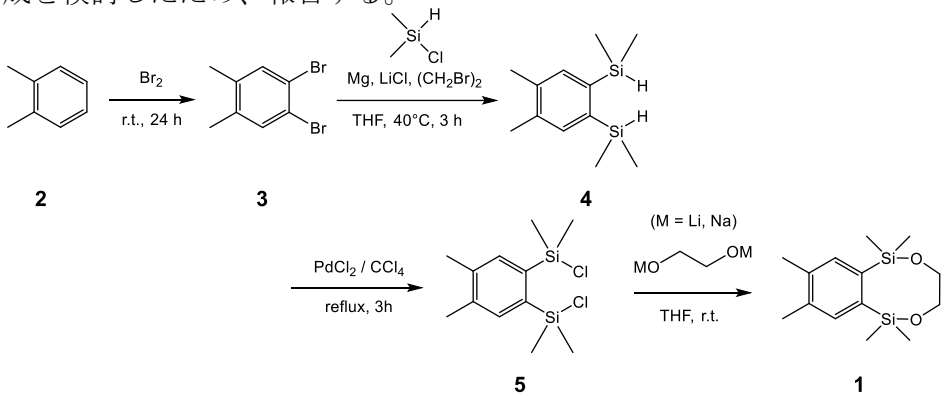
A 1,6,2,5-dioxadisilosine derivative, an eight-membered ring compound with two Si–O bonds, is known as bis-silyl protected 1,2-diol derivatives. Due to the difficulty in preparing the skeleton, there are only a few examples of synthesis of 1,6,2,5-dioxadisilosine derivative.[1] Since an alkoxysilane acts as an electrophile with the alkoxide leaving group. It is also known to be inert towars a metal-reductant such as sodium. Thus, 1,6,2,5-dioxadisilocin derivatives should be expected to work as a reduction-resistant siliyl-electrophile.

We have already reported the synthesis of a 1,6,2,5-dioxadisilosine derivative consisting of 4,5-bis(dimethylsilyl)-1,2-xylene and a catechol.[2] Here, we will report the attempted synthesis of a 1,6,2,5-dioxadisilosine derivative bearing the ethylene glycol moiety.

Keywords : 1,6,2,5-dioxadisilosine; reduction-resistant electrophile; double-silylation

分子内に Si-O 結合を 2 つ含む 8 員環構造を持つ 1,6,2,5-ジオキサジシロシン誘導体は、1,2 ジオールをシリル保護した化合物として知られているが、その環骨格形成は比較的難かしく、その合成例は限られている[1]。一般にアルコキシシランはアルコキシドを脱離基とする求電子剤として働く。また、ナトリウムなどの金属還元剤と反応しないことが知られている。これらのことから 1,6,2,5-ジオキサジシロシン誘導体は還元耐性を持つケイ素求電子剤として働くと期待できる。

既に我々は、4,5-ビス(ジメチルシリル)-1,2-キシレンとカテコールからなる 1,6,2,5-ジオキサジシロシン誘導体の合成と、その耐還元性求電子剤としての性質を報告している[2]。今回我々は、エチレングリコール部位を有する 1,6,2,5-ジオキサジシロシン誘導体の合成を検討したため、報告する。



2 3 4 5 1

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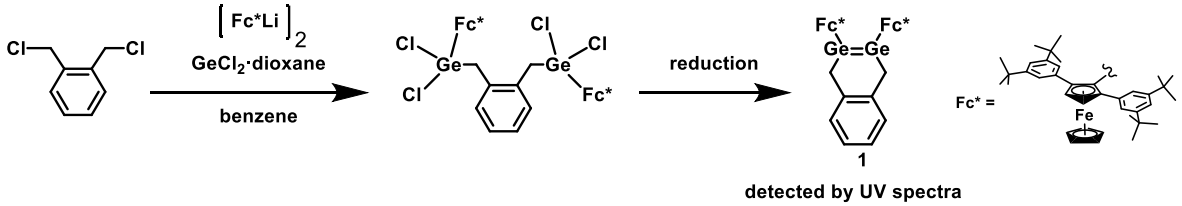
2,3-ジゲルマ-1,4-ジヒドロナフタレンの発生

（筑波大院数理[1]・筑波大数理物質・TREMS[2]）○川井 美羽子[1]・笹森 貴裕[2]
Attempted Synthesis of a Cyclic Digermene Bearing Bulky Ferrocenyl Groups ([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*Faculty of Pure and Applied Sciences, and TREMS, Univ. of Tsukuba*) ○Miwako Kawai,[1] Takahiro Sasamori[2]

A digermene, which is a double-bond compound between germanium atoms, is a unique class of compounds from viewpoints of their extremely high reactivity. A variety of digermenes with bulky substituents have been synthesized and isolated as stable compounds so far. In particular, the stable 1,2-digermabenzene, where a digermene unit was involved in the aromatic ring system, has been reported to work as a reagent for small molecule activations,[1)] though there have been still only a few examples of main-group-element catalysis. We will report here the generation of 2,3-Digerma-1,4-dihydronaphthalene **1** bearing sterically demanding ferrocenyl groups as a possible candidate of a small-molecule activator.
Keywords : Digermene; 2,3-Digerma-1,4-dihydronaphthalene; Germanium; UV/vis spectroscopy; Ferrocenyl Group

高周期 14 族元素であるゲルマニウム間の二重結合化合物であるジゲルメンは、極めて高い反応性を有する特異な化合物である。これまで、かさ高い置換基をゲルマニウム上に導入した種々のジゲルメンが安定な化合物として合成・単離され、その構造や性質が解明されてきた。特に我々は、芳香環に組み込まれた環状ジゲルメンとして 1,2-ジゲルマベンゼンの合成に成功し、これが小分子変換反応試剤として機能することを報告している[1)]。今回我々は、新たな小分子活性化剤の候補として、ジゲルメンの立体構造が *Z* に固定された 2,3-ジゲルマ-1,4-ジヒドロナフタレン **1** の合成について検討を行ったので報告する。



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ジベンゾバレレン骨格に組み込まれた含テルル 1,6-ジフェニル-1,3,5-ヘキサトリエン誘導体の合成と光物性

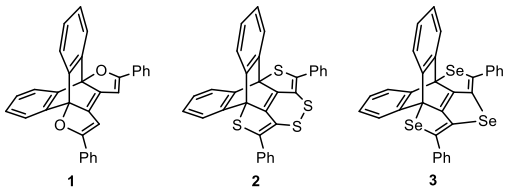
(埼玉大理[1]・埼玉大院理工[2]) ○内藤 潤[1]・中田 憲男[2]・石井 昭彦[2]

Synthesis and Optical Property of Dibenzobarrelene-fused 1,6-Diphenyl-1,3,5-hexatriene Derivatives Having Tellurium Atoms ([1]*Faculty of Science, Saitama University*, [2]*Graduate School of Science and Engineering, Saitama University*) ○Jun Naito,[1] Norio Nakata,[2] Akihiko Ishii[2]

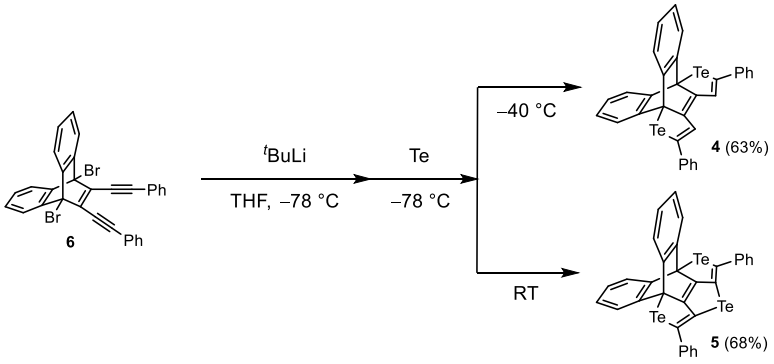
We have been studying the synthesis of 1,3,5-hexatriene derivatives fused and linked by heteroatoms with a dibenzobarrelene. In this study, we report the synthesis and optical properties of dibenzobarrelene-hexatriene derivatives having two or three tellurium atoms. The tellurium derivative **4** was synthesized by the lithiation of **6** with ^{t}BuLi followed by the treatment with tellurium powder in THF at −78 °C and then warming the reaction mixture to –40 °C. When the reaction mixture was warmed to room temperature, **5** was formed.

Keywords: Dibenzobarrelene; Hexatriene; Tellurium; Optical property

当研究室では、剛直なジベンゾバレレン骨格と融合した一連の含カルコゲン 1,3,5–ヘキサトリエン誘導体の合成とその光物性に関して研究を行っている。これまでに、酸素（**1**[1]）、硫黄（**2**[2]）およびセレン（**3**[3]）誘導体の合成に成功し、その光物性について報告している。本研究では、最も重い安定カルコゲン元素であるテルルを複数個有する誘導体の合成と光物性について報告する。



ジブロモビスエチニル体 **6** を、^{t}BuLi を用いて THF 中、–78 °C でジリチオ化し、次いでテルル粉末を加え、–40 °C に昇温して反応を行ったところ、テルル原子が 2 つ導入された誘導体 **4** が橙色結晶として収率 63%で得られた。一方、室温まで昇温した場合には、テルル原子が 3 つ導入された誘導体 **5** が赤色結晶として収率 68%で得られた。**4** および **5** は室温でほとんど蛍光を示さなかったが、77 K においては蛍光量子収率が増大する温度依存性を示した。



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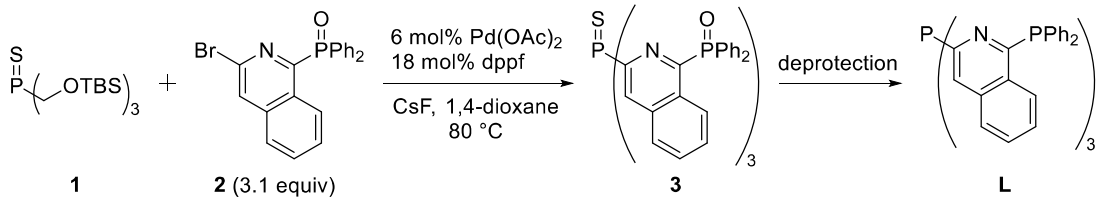
トリス[1-(ジフェニルホスフィノ)イソキノリン-3-イル]ホスフィン配位子の合成と応用

（愛媛大院理工）○狩野 竜輝・太田 英俊・林 実
Synthesis and Application of Tris[1-(diphenylphosphino)isoquinolin-3-yl]phosphine Ligand (*Grad. Sch. Sci., Eng., Ehime Univ.*) ○Ryuki Kano, Hidetoshi Ohta, Minoru Hayashi

Multinuclear metal complexes are expected to have different catalytic properties than mononuclear metal complexes. Multidentate ligands play an important role in the synthesis and creation of new functions of multinuclear metal complexes, and thus various ligands containing phosphorus and nitrogen atoms have been developed so far. Here, we report novel multidentate ligand, tris[1-(diphenylphosphino)isoquinolin-3-yl]phosphine (**L**). **L** was synthesized by the P-C cross-coupling reaction of phosphine sulfide **1** with bromoisoquinoline **2** to form compound **3** followed by the reduction of P=S and P=O groups. The complexation behaviors of **L** with transition-metal species were investigated.
Keywords : Phosphine, isoquinoline, P,N-Ligand, Multidentate Ligand, Multinuclear Metal Complex

多核金属錯体は、単核金属錯体とは異なる触媒能をもつと期待されている。その合成と新機能創出には多座配位子が重要な役割を果たしており、これまでにリン原子や窒素原子を含有する様々な配位子が開発されている。今回我々は、新規多座配位子であるトリス[1-(ジフェニルホスフィノ)イソキノリン-3-イル]ホスフィン（**L**）について報告する。**L** は、ホスフィンスルフィド **1** とブロモイソキノリン **2** の P-C クロスカップリング反応により化合物 **3** を得たのち、P=S および P=O 基を還元することで合成した。さらに、**L** と遷移金属種の錯化挙動について調査したので報告する。



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多置換イソインドロ[2,1-*a*]キノリン誘導体の設計・合成：5 位、13 位の置換基効果について

([1] 阪大院薬・[2] 生理学研究所) ○下栗　玲慈[1]・石井　宏和[2]・佐古　真[1]・村井　健一[1]・根本　知己[2]・有澤　光弘[1]

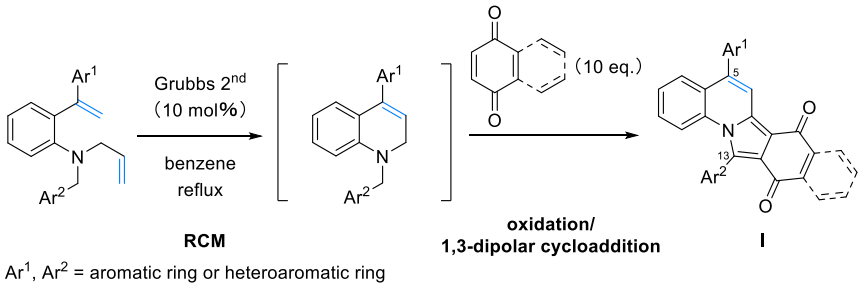
Design and Synthesis of Substituted Isoindoro[2,1-*a*]quinolines : Substituent Effects at Positions 5 and 13 ([1]Graduate School of Pharmaceutical Sciences, Osaka University, [2]National Institute for Physiological Sciences) ○Reiji Shimoguri,[1] Hirokazu Ishii,[2] Makoto Sako,[1] Kenichi Murai,[1] Nemoto Tomomi,[2] Mitsuhiro Arisawa,[1]

Fluorescent dyes are dyes that emit strong luminescence and have recently been used as organic EL materials, fluorescent reagents, and fluorescent probes. Two-photon absorption dyes can also be used for deep, clear biological imaging. However, the basic scaffolds of these dyes are limited, and there is a need to develop new basic scaffold with high absorption and fluorescence properties. Against this background, our laboratory has established a synthetic method for the fluorescent dye isoindolo[2,1-*a*]quinoline **I** via a one-pot ring-closing metathesis/oxidation/1,3-dipolar cycloaddition reaction. Using this synthetic method, we synthesized a variety of derivatives of I with heterocyclic moieties at positions 5 and 13, and gottheir respective absorption and fluorescence spectra. The two-photon excitation properties of the derivatives will also be reported.

Keywords : dye, polycyclic heterocyclic ring

蛍光色素は、強い光を発する色素であり、近年では、有機 EL 材料や蛍光試薬、蛍光プローブなどへ応用されている。また、二光子吸収色素を用いると、深部の鮮明な生体イメージングが可能である。しかし、これらの色素の基本骨格は限定的であり、高い吸光・蛍光特性を有する新規基本骨格の開発が求められている。このような背景下、当研究室ではワンポット閉環メタセシス/酸化/1,3-双極子環化付加反応を介した、蛍光色素イソインドロ[2,1-*a*]キノリン **I** の合成法を確立している。[1)]

今回、我々は本合成法を用いて、5 位、13 位に複素芳香環を導入した **I** の誘導体を種々合成し、それぞれの吸光スペクトル・蛍光スペクトルを測定した。また、各誘導体の二光子励起特性についても精査し報告する。



1) (a) *Angew. Chem. Int. Ed.*. **2013**, *52*, 1003-1007. (b) *ACS Omega* **2019**, *4*, 5064-5075. (c) *ACS Omega* **2020,** *5*, 2473-2479. (d) *Dyes and Pigments* **2023**, *212*, 111118.

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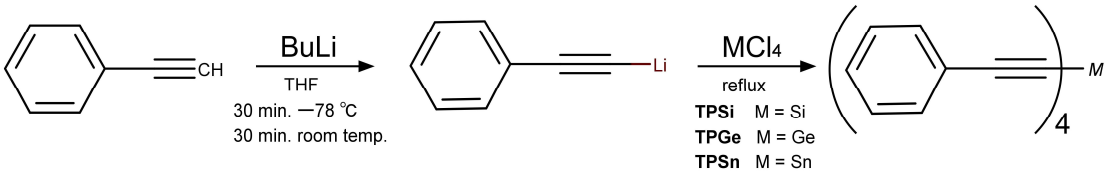
The Synthesis and Properties of Group 14 Element Compounds Bearing Four Phenylethynyl Groups

([1]*International Christian University*) ○Junji Kobayashi[1], Rika Watanabe[1]
Keywords: organometallics, conjugation, σ *- π * interaction,

In these decades, unsaturated carbon-carbon bonds which are bonded to group 14 elements have attracted huge attention by their high applicability to various reactions, such as new dendrimers and metallole compounds. This is because these compounds usually show the exclusive interaction between σ* orbital of group 14 elements and the π* orbital of carbon-carbon multiple bonds. The aim of this study is to elucidate the optical properties of tetraphenylethynyl analogs, which have the σ*-π* interaction between silicon atom and carbon-carbon triple bonds, and also the reactivities to illustrate the possibilities of further reactions.

The anions of ethynyl benzene, which were prepared by *n*-butyllithium[1], were reacted with group 14 metal chloride[2], such as $SiCl_4$, $GeCl_4$ and $SnCl_4$, to afford tetrakis(phenylethynyl)silane, tetrakis(phenylethynyl)germane and tetrakis(phenylethynyl)stannane, respectively. The red shift of UV-vis absorption maxima and emission peak in the silicon analog indicate the existence of the interactions between σ* orbital of group 14 elements and π* orbital of the carbon-carbon bond. In addition, the reduction of the silicon analog by lithium naphthalenide[3] will be also reported.



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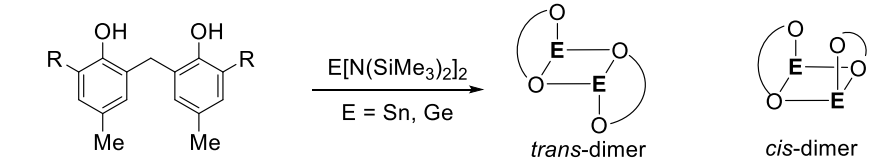
2,2′-メチレンジフェノールから誘導されるジオキシテトリレン二量体の合成、構造および CH···O 水素結合

（お茶大[1]・中央大[2]）杉原 明日香[2]・下垣内 理世[1]・石井 洋一[2]・○桑原 拓也[1]
Synthesis, structures and CH···O hydrogen bonding of dioxytetrylene dimers derived from 2,2′-methylenediphenols ([1]*Ochanomizu University*, [2]*Chuo University*) Asuka Sugihara,[2] Rise Shimogaito,[1] Youichi Ishii,[2] ○Takuya Kuwabara[1]

CH···O hydrogen bonding, which is weaker than general hydrogen bonds such as OH···O and NH···O hydrogen bonds, is mainly found in the solid-state. In this study, we demonstrate a rare example of CH···O hydrogen bonding maintained in solution even at elevated temperatures. Dioxytetrylene dimers with an E_2O_2 four-membered ring, where E = Sn, Ge, have been synthesized from the reaction of 2,2′-methylenediphenols with various steric bulkiness and Lappert's germylene and stannylene, $E[N(SiMe_3)_2]_2$. Interestingly, only **2c-Sn** adopts a cis orientation, in which the terminal ArO groups are mutually cis over the Sn_2O_2 ring. The other products were isolated as trans-dimers. All products have CH···O hydrogen bonds in the solid-state structure. Notably, significant downfield shifts were observed in the methylene proton signals of **2a-Sn** (δ 4.96), **2b-Sn** (δ 5.49) and **2c-Sn** (δ 6.25), which indicates that the hydrogen bonds are maintained even in solution.
Keywords : CH…O hydrogen bond; Stannylene; Germylene

CH···O 水素結合は OH···O や NH···O 等の一般的な水素結合と比べ弱く、その報告の多くは固体状態に集中している。今回我々は、かさ高さの異なる 2,2′-メチレンジフェノールから誘導されるテトリレンの研究を通し、溶液状態、加熱条件下でも強固な CH···O 水素結合を保持する珍しい例を見いだしたので以下報告する。

酸素のオルト位に Me, ^{t}Bu, Si^iPr_3, Si^tBuPh_2 基をもつ 2,2′-メチレンジフェノールと $Sn[N(SiMe_3)_2]_2$ の反応から、ジオキシテトリレンの二量体 **2a**–**d** を得た。Si^iPr_3 基をもつ **2c-Sn** のみ、末端のアリーロキシ基が中央の E_2O_2 四員環に対し同じ側に位置する cis 型二量体構造をとり、他の生成物は反対型に位置する trans 型二量体構造をとっていた。また、いずれの構造においてもメチレン CH と ArO 酸素原子間で CH···O 水素結合が確認された。^{1}H NMR において、メチレンシグナルは δ 4.96 (**2a-Sn**), 5.49 (**2b-Sn**), 6.25 (**2c-Sn**), 3.88 (**2d-Sn**)と、**2a**–**c** に関して顕著な低磁場シフトを示した。この結果から、低磁場シフトが観測されなかった **2d-Sn** はかさ高い Si^tBuPh_2 基の影響により溶液中で単量体へと解離する一方、他は二量体を維持しており、メチレンシグナルの低磁場シフトは固体中でみられた CH···O 水素結合が維持されていると推察される。



1a (R = Me), **1b** (R = ^{t}Bu), **1c** (R = Si^iPr_3), **1d** (R = Si^tBuPh_2)

2a-Sn, **2b-Sn**, **2d-Sn**, **2d-Ge**

2c-Sn

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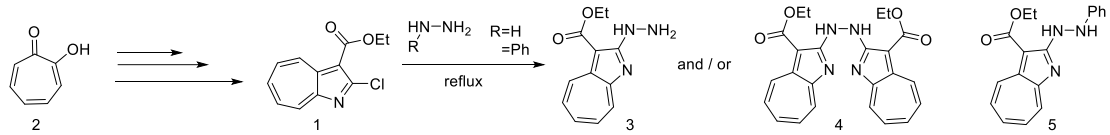
アザアズレン-2-イル基を有するヒドラジン誘導体の合成と性質

（神工大院工）山口　淳一・○大西　裕也
Preparation of derivatives bearing an azaazzulene-2-yl group and their characters (*Kanagawa Institute of Technology*) Jun-ich Yamaguchi, ○Yuya Onishi

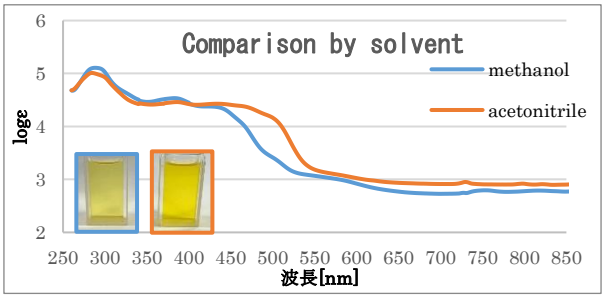
Azaazulene is kind of non-benzenoid aromatic in which a carbon atom of azulene is replaced by a nitrogen one. Although azulene derivatives are widely used in organic chemistry. few reports about azaazzulene are known. In the present work, we examined synthesis of new azaazulene derivatives in which multiple azaazulenyl groups introduced to hydrazine. Furthermore, we clarified properties of new azaazulene derivatives, especially changing coloration of new synthesized compounds.
Keywords : azaazulene ; hydrazine derivatives ; hetero ring

アズレンの炭素原子が窒素原子に置換したアザアズレン類は、その合成の困難さから、その合成研究は比較的少ない。しかし、アザアズレンの中でも比較的合成が容易な 1-アザアズレン誘導体に関する合成研究を行った。すなわち、トロポロン **2** から誘導可能な 2-クロロ-1-アザアズレン **1** を鍵化合物として、付加-脱離反応を利用した新規誘導化法についても併せて検討を行った。

トロポロン **2** より誘導したアザアズレン **1** に 2 当量のヒドラジンを作用すると、付加-脱離が進行し **3** を 95 %得た。そこで、ヒドラジンの当量を 1.2 に変えたところ、さらにアザアズレンが導入された **4** が主生成物として 35 %得られた(Scheme, Table)。このことはヒドラジンの使用量により **3** と **4** の作り分けが可能であることを示している。また、フェニルヒドラジンを用いた場合も **5** を収率 61 %で変換できた。今回合成した化合物群は黄緑色を示すものが多く、UV-可視スペクトルの比較を行った。一例として、**4** は溶媒によって呈色が異なり、400～550 nm の領域で吸収が変化することが分かった。(Figure)。



Scheme



Figure

NH_2NH_2 [eq.]	3 [%]	4 [%]
2	95	trace
1.2	31	35

$PhNHNH_2$ [eq.]	5 [%]
1.1	61

Table

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2,6-ジアズレニルピリジンの合成と色の変化

(神工大院工[1]・神工大工[2]) 山口 淳一[1]・○渡辺 比呂[1]・大西 裕也[1]・佐藤 里奈[2]
Synthesis of 2,6-Diazulenyl Pyridines and Their Changing Colorization ([1]*Graduate School of Engineering, Kanagawa Institute of Technology*、[2]*Kanagawa Institute of Technology*) Jun-ichi Yamaguchi[1],○Hiro Watanabe[1],Yuya Onisi[1], Rina Sato[2]

Pyridine bearing azulenyl groups at the 2- and 6-positions of the pyridine ring will have been unique properties. For example, we expect that its solution will change the color in the presence of acid or metal ion. Previously, we had prepared symmetrical azulenylpyridine, namely, **1**or **2**. In the present work, we prepared a symmetrical azulenylpyridine, namely, **3**. Since pyridine is a basic moiety, azulenylpyridine **1-3** will form the corresponding acid or metal ion salt.

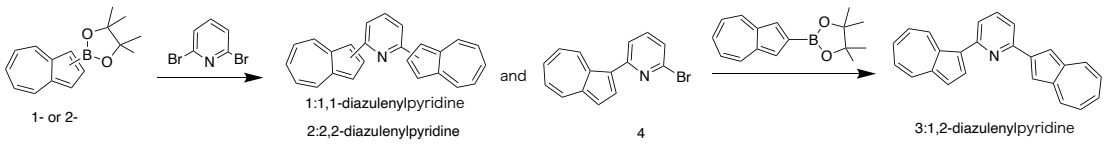
In the first task, azulenylpyridine **3** was prepared. Monoazulenylpyridine **4** was formed as a side product when **1** or **2** was prepared by a coupling reaction of azulenylboran with 2,6-dibromopyridine. We succeeded synthesis of three types diazulenylpyridines **1**, **2**, and **3**. In the second task, we examined colorization of a solution of **1**, **2**, or **3** and their salt. It was found that the colors are different in almost cases. Furthermore, we revealed that some azulenylpyridines exhibited solvatochromism.

Keywords : Azulenylpyridine; Non-benzenoid Aromatic; Colorization; Solvatochromism

アズレンは 7 員環と 5 員環が縮合した非ベンゼン系芳香族化合物であり、青色を示すことから、20 世紀初頭から興味が持たれている化合物群である。これまで当研究室では、ピリジン環の 2 位と 6 位にアズレンが置換した化合物の合成を試み、対称型 1,1-ジアズレニルピリジン **1** および 2,2-ジアズレニルピリジン **2** の合成に成功している。ピリジンは塩基性化合物であることから、塩の形成または金属イオンが配位することにより新たな性質を示すと期待できる。今回、非対称型 1,2-ジアズレニルピリジン **3** の合成に成功し、アズレニルピリジン類へ酸あるいは金属塩の添加による色の変化等について検討した。

まず、**3** の合成を行った。すなわち **1** および **2** を合成する際、1 置換体 **4** が得られ、これに異なる置換位置のアズレニルボランを作用して非対称型 1,2-ジアズレニルピリジン **3** の合成に成功した。ジアズレニルピリジン類は、アズレニル基の置換位置の違いによる 3 種類の異性体があるが、今回すべての合成に成功した。これらの化合物 **1-3** は酸塩あるいは金属塩を形成し、新たな性質が発現すると期待できる。

例えば、アズレンの置換位置の違いなどが異なる呈色を示すことが分かった。すなわち、CH_2Cl_2 中 **1** および **2** は青色を示すのに対し、**3** は青緑色を示した。これらをトリフルオロ酢酸(TFA)塩に導きそれぞれを得ることが出来た。**2** の TFA 塩はほとんど変色しないのに対し、**1** は赤色、**3** は青緑色へと変色することが分かった。さらに、ソルバトクロミズムも観測され、合わせて発表する。



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キノリンアミドオリゴマーの構造と機能評価

（慶大院薬[1]，微化研[2]）○武田 彩海[1]・シュ ウェイ[1]・熊谷 直哉[1, 2]

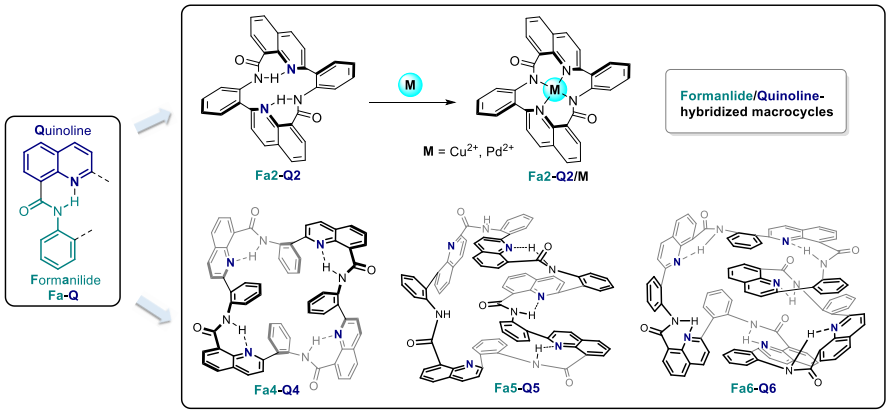
Structure and Functions of Quinoline-Based Amide Oligomers

([1]*Graduate School of Pharmaceutical Sciences, Keio University,* [2]*Institute of Microbial Chemistry*) ○Ayami Takeda,[1] Wei Xu,[1] Naoya Kumagai[1,2]

Recently, our group reported a new porphyrin-like macrocycle, TEtraQuinoline, which was synthesized via a cyclic amide comprising of two quinoline units.[1] We found that systematic modification of the amide forming reaction produced a series of cyclic quinoline-based amide oligomers, which can be regarded as formanilide (Fa)/quinoline (Q)-hybridized macrocycles (Fa-Q). Herein we present a single-step synthesis of various Fa-Q architectures, including symmetric Fa2-Q2, Fa4-Q4, and asymmetric Fa5-Q5, Fa6-Q6. We also discovered that these macrocycles have specific three-dimensional architectures due to multiple hydrogen bonds. The synthesis, X-ray crystallography, metal complexation, and physicochemical properties of these oligomers will be discussed. We are also interested in exploring novel Fa-Q compounds that may have higher ordered helical structures.

Keywords: Quinoline, Macrocycle compounds, Heterocyclic compounds

我々は近年、新規ポルフィリン様化合物であるテトラキノリン鍵中間体である大環状キノリンジアミドの合成過程において，反応条件の適切な設定により 1 工程で任意の高次環状キノリンアミドオリゴマーが優先的に得られることを見出した。単位構造である formanilide（Fa）と quinoline（Q）の単位数に基づき分類すると，対称性を持つ Fa2-Q2，Fa4-Q4，ならびに対称性を持たない Fa5-Q5，Fa6-Q6 の合成を達成した。これらの構造特性の差異は主に分子内水素結合により示現していると推察される。これらの高次構造を有した新規キノリンアミドオリゴマー類の合成，X 線結晶構造解析，物理化学的性質等の詳細を報告する。



1)W. Xu, Y. Nagata, N. Kumagai, *J. Am. Chem. Soc*, **2023**, 145, 2609-2618.

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キラルリン酸触媒を用いた 4 置換不斉炭素を有する 2,3-ジヒドロ-4-キノロンの合成

（名工大院工）○寺島 悠人・川村 稜於・松田 陽一朗・安川 直樹・中村 修一

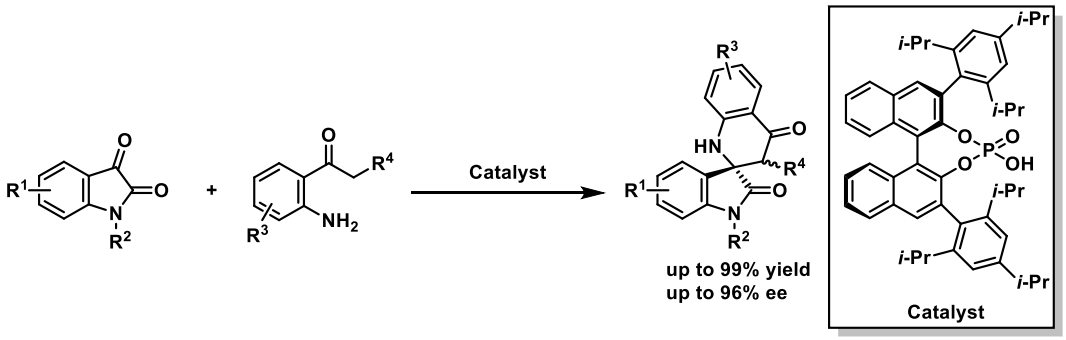
Enantioselective synthesis of tetrasubstituted 2,3-dihydro-4-quinolones using chiral phosphoric acid catalysts

(*Graduate School of Engineering, Nagoya Institute of Technology*) ○Yuto Terashima, Rio Kawamura, Yoichiro Matsuda, Naoki Yasukawa, Shuichi Nakamura

2,3-Dihydro-4-quinolones are structurally similar to 4-quinolones which are well known as a privileged structure of antibiotic agents. Therefore, 2,3-dihydro-4-quinolones are important class for updating original functionality. Enantioselective one-pot reaction of 2-aminoacetophenones with aldehydes, which proceeds via the imine formation and the subsequent intramolecular cyclization, is powerful strategy to access chiral 2-disubstituted-2,3-dihydro-4-quinolones.[1)] However, there are no reports on enantioselective synthesis of 2,2-disubstituted-2,3-dihydro-4-quinolones. Herein, we have developed the chiral phosphoric acid-catalyzed reaction of 2-aminoacetophenones with isatins to give chiral 2,2-disubstituted-2,3-dihydro-4-quinolones in high yields with high enantioselectivities. In addition, DFT calculation proposed a plausible transition state as the origin of stereoselectivity.

Keywords : Asymmetric synthesis, Organocatalyst, 2,3-Dihydro-4-quinolone , Tetrasubstituted chiral carbon

4-キノロンは抗菌薬の部分構造に広く含まれており、その類似構造である 2,3-ジヒドロ-4-キノロンは更なる機能改善が期待できる重要な化合物群である。それらの不斉合成法として、2-アミノアセトフェノンとアルデヒドとのイミン形成に続く不斉分子内環化反応が報告されている [1)]。しかし、2-アミノアセトフェノンとケトン類を用いて、2 位に 4 置換不斉炭素を有する 2,3-ジヒドロ-4-キノロンを立体選択的に合成する手法は報告例が無い。今回我々は、キラルリン酸触媒存在下、2-アミノアセトフェノンとイサチン類を出発原料とした 4 置換不斉炭素を有する 2,3-ジヒドロ-4-キノロンの合成法を開発した。また、密度汎関数法を用い、本反応の立体選択性の発現機構を解明した。



1) Y. Wang *et al., RSC Adv*. **2016**, *6*, 25375-25378.

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[P2-1vn] 23. CIP Poster

Japanese P1. Energy

[P2-1vn-01]

Observation of Water Behavior Inside Polymer Electrolyte Fuel Cells by Complementary Use of Synchrotron X-ray and Neutron Sources

○Wataru Yoshimune[1], Yuki Higuchi[1], Akihiko Kato[1], Shogo Hibi[1], Satoshi Yamaguchi[1], Yoshihiro Matsumoto[2], Hirotoshi Hayashida[2], Hiroshi Nozaki[1], Takenao Shinohara[3], Satoru Kato[1] (1. Toyota Central R&D Labs., Inc., 2. Comprehensive Research Organization for Science and Society, 3. Japan Atomic Energy Agency)

Japanese P1. Energy

[P2-1vn-02]

Orientation analysis for proton-conducting covalent organic framework (COF) membranes

○Koki Fujiu[1], Masane Kin[1], Takahiro Nishio[1], Hiroki Watanabe[1], Hiroyasu Tabe[2], Ryota Shinozaki[1], Satoshi Horike[2], Takumi Okamoto[1] (1. DENSO CORPORATION , 2. Kyoto University)

Japanese P1. Energy

[P2-1vn-03]

Development of Sulfur-Based Materials “SPAN” and Battery Creations to Realize a World's Lightest Secondary Battery and Demonstration of Long Drone Flight Time

○Kenji Kakiage[1], Shunsuke Saito[2], Masaki Kakiage[3], Toru Yano[1] (1. ADEKA CORPORATION, 2. URUTAMA.INC, 3. Gunma University)

Japanese P1. Energy

[P2-1vn-04]

Development of High-Capacity Cathode Active Materials for All-Solid-State Batteries using Organosulfur Compounds

○Takeshi Shimizu[1], Kazuki Shinoda[1], Yusei Noda[1], Kosei Nawa[1], Naoki Tanifuji[1], Hirofumi Yoshikawa[2], Mari Yamamoto[3], Atsutaka Kato[3], Masanari Takahashi[3] (1. National Institute of Technology, Yonago College, 2. Kwansei Gakuin University, 3. Osaka Research Institute of Industrial Science and Technology)

Japanese P1. Energy

[P2-1vn-05]

Improving the performance of hematite photoelectrodes for solar water splitting

○Yoshitaka Kumabe[1], Takashi Tachikawa[1,2] (1. Mol. Photosci. Res. Center, Kobe Univ., 2. Grad. Sch. of Sci., Kobe Univ.)

Japanese P1. Energy

[P2-1vn-06]

Ultra-low Excitation Intensity Visible-to-UV Photon Upconversion with High Spin Statistical Probability Factor

○Kiichi Mizukami[1], Yuya Watanabe[1], Minlang Yang[1], Nobuhiro Yanai[1,2], Takuma Yasuda[1,3], Nobuo Kimiuzka[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. IAS, Kyushu Univ.)

Japanese P1. Energy

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[P2-1vn-07]

Charge Separation Kinetics in non-fullerene acceptors by femtosecond time-resolved infrared spectroscopy

○Rintaro Adachi[1], Tomokazu Umeyama[2], Hiroshi Imahori[3], Akira Yamakata[1] (1. Okayama University, 2. University of Hyogo, 3. Kyoto University)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-08]

Highly Efficient Solar CO_2 Conversion by Coupling Silicon Solar cells with Gas Diffusion Electrolyzer using Mn(I) Complex and β-FeOOH Catalysts

○Keita Sekizawa[1], Shunsuke Sato[1], Naonari Sakamoto[1], Tomiko M Suzuki[1], Takeshi Morikawa[1] (1. Toyota Central Research and Development Laboratories)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-09]

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○Nobuyuki Nakayama[1], Isao Kotani[2], Kentaro Kotani[2], Hiroshi Haji[2], Sadayoshi Nakatsukasa[2] (1. Rigaku Kobo, LLC, 2. MAK Engineering Corporation)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-10]

Investigation of reaction mechanism of CO_2 to C_3H_7OH electrochemical conversion dinuclear Cu molecular catalysis

○Naonari Sakamoto[1], Keita Sekizawa[1], Soichi Shirai[1], Takamasa Nonaka[1], Takeo Arai[1], Shunsuke Sato[1], Takeshi Morikawa[1] (1. Toyota Central R&D Labs., Inc.)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-11]

Development of microbeads concentration method using phase separation phenomenon with temperature-responsive polymer PNIPAM

○Yui Yamashita[1], Atsushi Manaka[1,2], Mitsuhiro Ebara[2] (1. National Institute of Technology, Toyama College, 2. National Institute for Materials Science(NIMS))

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-12]

Reducion of Trace PCBs in Whale Oil by Steam Thin Film Distillation

○Arihiro Iwata[1], Tomoki Ogawa[1], Haruka Ino[1], Misato Miyamoto[1], Mitsuhiro Kishimoto[2], Kouji Yoshida[3], Takahiro Yoshida[3], Genta Yasunaga[4], Yoshihiro Fujise[4] (1. Yamaguchi Pref. Industrial Technology Institite, 2. Shimonoseki City Univ., 3. Yoshida Sogo Techno, 4. The Institute of Cetacean Research)

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[P2-1vn-13]

Complete defluorination of fluoroelastomer FKMs using subcritical water with alkaline reagents

○Jin Hamaura[1], Hisao Hori[1], Hirofumi Mukae[2], Ayane Fujishima[2] (1. Kanagawa University, 2. Daikin Industries, Ltd.)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-14]

Carboxylic Acid-Catalyzed Peptide Synthesis Using Diketopiperazine

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○Kazumasa Kon[1], Hisashi Yamamoto[1] (1. Peptide Research Centre, Chubu University)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-15]

Pd/CHA as a NOx Adsorber
-The Effect of Pd Loading methods on NOx Desorption Temperature-

○Takeshi OHTSU[1], Washiyama Shohei[1], Usami Tomoya[1], Tsunoji Nao[2], Oda Akira[1], Satsuma Atsushi[1] (1. Nagoya University, 2. Hiroshima University)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-16]

Preparation of gold nanoparticle electrocatalysts supported by single-walled CNTs and their application to aerobic oxidation of alcohols under electrochemical conditions

○Yuta Uetake[1,2,3], Honoka Nakamura[1], Rento Yabuki[1], Taiyo Shimizu[3], Ken Kokubo[3], Hidehiro Sakurai[1,2] (1. Osaka Univ., 2. ICS-OTRI, 3. AIST)

English P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-17]

Introduction to the Chemical Substances Control Act in South Korea

○YOON JIN CHO[1], YOUNGWOO CHON[1] (1. The Univ. of Inha)

Japanese P2. Resources/Environment/Green sustainable chemistry

[P2-1vn-18]

Adsorption of polycyclic aromatic hydrocarbons(PAHs) on biodegradable plastics and its effect on biodegradability

○Shodai Hino[1], Naoko Yamano[1], Norioki Kawasaki[1], Atsuyoshi Nakayama[1] (1. AIST)

Japanese P6. Featured topic: Biomass-related technologies

[P2-1vn-19]

Aliphatic Polyesters with Ester-Functionalized Side Chains Synthesized from Methacrylates

○Shin-nosuke Nishimura[1], Ryosuke Kanai[1], Tomoyuki Koga[1] (1. Doshisha Univ.)

Japanese P6. Featured topic: Biomass-related technologies

[P2-1vn-20]

Hagfish Intermediate Filament Protein LLPS-Mediated Preparation of Bioinspired Hydrogels

○Ryuki Kobayashi[1], Syunsuke Kondo[2], Jin Gong[2], Hideki Nabika[1] (1. Faculty of Science, Yamagata University, 2. Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University)

Japanese P6. Featured topic: Biomass-related technologies

[P2-1vn-21]

In silico design of the active site of chitosanase catalyzing β-1,4-glycosylation between GlcN and GlcNAc

○Mariko Kojima[1], Mehdi Davari[2], Akira Onoda[1] (1. Hokkaido University, 2. Leibniz Institute of Plant Biochemistry)

Japanese P3. New materials

[P2-1vn-22]

Development of high-speed organic crystal photoactuators toward application to soft robotics

○Yuki Hagiwara[1], Shodai Hasebe[1], Toru Asahi[1], Hideko Koshima[1] (1. Waseda University)

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Japanese P3. New materials

[P2-1vn-23]

Analysis of micro amount of CWO particles in resin

○Saihei Fujimoto[1], Katsushi Ono[1], Masaki Yano[1], Takehide Morimoto[1], Naoki Hashimoto[1] (1. Sumitomo Metal Mining Co., Ltd.)

Japanese P3. New materials

[P2-1vn-24]

Effect of electrolyte on Au anode dissolution reaction

○Shinichiro Ozawa[1], Moe Hokugo[1], Riki Yamakawa[1], Yoichi Okamoto[1] (1. National Defense Academy)

Japanese P3. New materials

[P2-1vn-25]

Modification of cationic chlorophyll derivatives to polymers containing pyridine residues and their physical properties

○Shin Ogasawara[1], Hiroaki Marumoto[1], Hitoshi Tamiaki[1] (1. Ritsumeikan University)

Japanese P3. New materials

[P2-1vn-26]

C(sp^3)–H bond functionalization promoted by a semiconductor photocatalyst and water aiming at polymer modification

○Yuji Sakai[1], Shogo Mori[2], Mineto Uchiyama[3], Masami Kamigaito[3], Susumu Saito[2,4] (1. Sch. Sci., Nagoya Univ., 2. IRCCS, Nagoya Univ., 3. Grad. Sch. Eng., Nagoya Univ., 4. Grad. Sch. Sci., Nagoya Univ.)

Japanese P3. New materials

[P2-1vn-27]

Influence of Post Annealing on Crystal Growth in Liquid Crystalline Organic Semiconductor Thin Films

○Takayuki Oka[1], Nobutaka Shioya[1], Taizo Mori[1], Takeshi Hasegawa[1] (1. Kyoto Univ. ICR)

Japanese P3. New materials

[P2-1vn-28]

Development of Triazine Derivatives Bearing Electron-Withdrawing Substituent and Their Application to TADF Emitter with Near-Infrared Two-Photon Absorption Character

○Youhei Chitose[1,2,3], Youichi Tsuchiya[3], Chihaya Adachi[1,3,4] (1. Grad. Sch. of Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. OPERA, Kyushu Univ., 4. WPI-I2CNER)

Japanese P3. New materials

[P2-1vn-29]

Novel Ethylene-based Polymers as Sustainable Elastomers

○Shigenaga Takano[1], Chikako Kuroiwa[1], Jyunichi Ishigami[1], Tomoko Kamata[1], Shojiro Kaita[1] (1. Bridgestone Corporation)

English P4. DX-related technologies

[P2-1vn-30]

Verification of required ventilation amount for evaporated gas after inflammable liquid leakage through CFD program

○YOUN HO LEE[1], Youngwoo Chon[1] (1. The Univ. of Inha)

Japanese P5. Medical care/Health care/Biotechnology

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[P2-1vn-31]

Thermo-switchable adhesive hydrogel inspired by mussel

○Hiroya Abe Abe[1], Yoshihara Daichi[1], Daigo Terutsuki[1], Matsuhiko Nishizawa[1] (1. Tohoku University)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-32]

Effects of plant polysaccharides on skin barrier function

○Ai Sugita[1], Yuki Takeuchi[1] (1. KYOWA PHARMA CHEMICAL CO.,LTD.)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-33]

Small-Molecule Aptamer for Regulating RNA Functions in Mammalian Cells and Animals

○Keisuke Fukunaga[1,3], Dhamodharan Venugopal[1], Nao Miyahira[1], Yoko Nomura[1], Mustafina Kamila[1,4], Yasuaki Oosumi[2], Kosuke Takayama[2], Akira Kanai[2], Yohei Yokobayashi[1] (1. OIST, 2. Astellas Pharma Inc., 3. Tokyo Tech, 4. MIT)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-34]

Molecular structure and biocompatibility of star polymer at water interface

○Masayasu TOTANI[1,2], Hiroharu AJIRO[2], Jun-ichi KADOKAWA[1], Tsuyoshi ANDO[2], Masao TANIHARA[2] (1. Kagoshima University, 2. Nara Institute of Science and Technology)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-35]

Membrane-deforming liposomes for highly efficient encapsulation and detoxification of huge biomacromolecules such as viruses.

○Noriyuki Uchida[1], Yunosuke Ryu[1], Teruhiko Matsubara[2], Toshinori Sato[2], Yasutaka Anraku[3], Takahiro Muraoka[1,4] (1. Tokyo Univ. Agri. Tech., 2. Keio Univ., 3. Tokyo Institute. Tech., 4. KISTEC)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-36]

Design and Synthesis of a Body Fluid-Responsive Instantly Solidifying Liquid and Dedicated Macroporous Sponges: Realizing Simple but High-Performance Hemostatic Materials

○Hiroyuki Kamata[1], Shohei Ishikawa[1], Ayano Fujisawa[1], Yuki Yoshikawa[1], Kazuyoshi Matsubara[2], Katsuyuki Hoshina[2], Takamasa Sakai[1] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. Grad. Sch. Med., The Univ. of Tokyo)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-37]

Effect of ganglioside GM1 on amyloid fibrillogenesis in the coexistence of amyloid β 40 and 42

○Kiyo Fukase[1], Hideki Nabika[2] (1. Graduate School of Sci. and Eng, Yamagata Univ., 2. Faculty of Sci, Yamagata Univ.)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-38]

Effect of cholesterol / lanosterol on DOPC membrane properties and amyloid β aggregation

○Kyohei Akiho[1], Hideki Nabika[2] (1. Graduate School of Science and Engineering, Yamagata University, 2. Faculty of Science, Yamagata University)

English P5. Medical care/Health care/Biotechnology

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[P2-1vn-39]

Contribution of Sebum and Sweat Condition to Men's Daytime Skin Appearance and Feel

○Songjie Zhang[1], Mamiko Kikuchi[1], Ai Terai[1], Jicheng Zhang[1], Shinichi Ikegaki[1], Satoru Naitou[1] (1. Kao Corporation)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-40]

Development of supramolecular gelling peptides for *in-vitro* three-dimensional tissue culture and stable collection of the tissue

○Atsuya Yaguchi Yaguchi[1], Itsuki Ajioka[2,3], Takahiro Muraoka[1,3] (1. Tokyo Univ. of Agri. and Tech., 2. Tokyo Med. and Dent. University, 3. KISTEC)

Japanese P5. Medical care/Health care/Biotechnology

[P2-1vn-41]

Development of polysaccharide modified photo cross-linked gelatin hydrogel cell scaffolds

○Hiroki Miyajima[1], Kodai Onodera[1], Yuki Hatta[1], Kaori Kojima[1], Masaru Mukai[1], Shoji Maruo[1], Kazutoshi Iijima[1] (1. Yokohama National Univ.)

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放射光 X 線と中性子の相補利用による燃料電池内部の液水挙動観察

（豊田中研[1]・総合科学研究機構[2]・原子力機構[3]）○吉宗 航[1]・樋口 雄紀[1]・加藤 晃彦[1]・日比 章五[1]・山口 聡[1]・松本 吉弘[2]・林田 洋寿[2]・野崎 洋[1]・篠原 武尚[3]・加藤 悟[1]

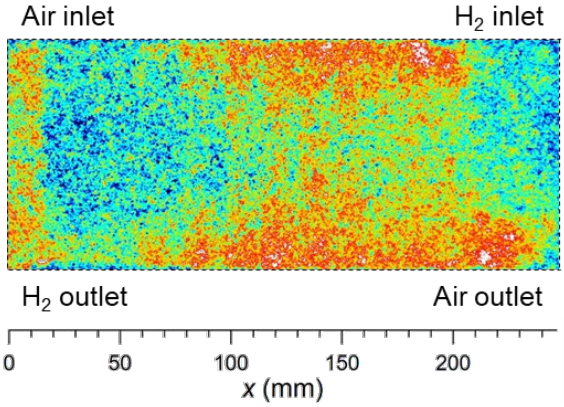
Observation of Water Behavior Inside Polymer Electrolyte Fuel Cells by Complementary Use of Synchrotron X-ray and Neutron Sources

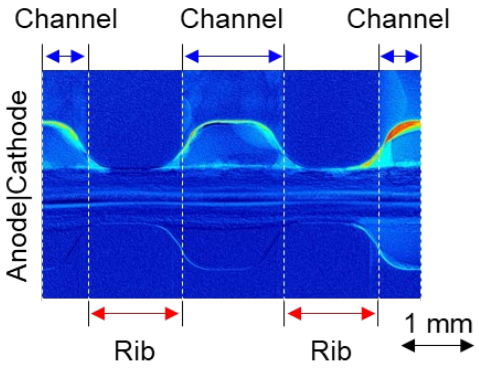
([1]*Toyota Central R&D Labs., Inc.*, [2]*Comprehensive Research Organization for Science and Society,* [1]*Japan Atomic Energy Agency*) ○Wataru Yoshimune,[1] Yuki Higuchi,[1] Akihiko Kato,[1] Satoshi Yamaguchi,[1] Yoshihiro Matsumoto,[2] Hirotoshi Hayashida,[2] Hiroshi Nozaki,[1] Takenao Shinohara,[3] Satoru Kato[1]

A multi-scale water visualization technique inside polymer electrolyte fuel cells (PEFCs) has been established using operando synchrotron X-ray and neutron radiography. It has been revealed that water back diffusion from the cathode to the anode contributes to the "drainability" inside a practical-sized PEFC for research and development of fuel cell electric vehicles. We will present details of the technique and the recent research results.

Keywords : Fuel Cell Electric Vehicle; Polymer Electrolyte Fuel Cell; Radiography; X-ray; Neutron

放射光 X 線と中性子を用いたオペランド計測技術により、固体高分子形燃料電池内部のマルチスケールな水の可視化技術を確立した。その結果、燃料電池自動車の研究開発に向けた実用的なサイズの固体高分子形燃料電池内部において、空気極から水素極への水の逆拡散が「排水性」に大きく寄与していることを明らかにしている [1]。本発表では、構築技術の詳細と最前線の研究成果について報告する。





1) Wataru Yoshimune, Yuki Higuchi, Akihiko Kato, Shogo Hibi, Satoshi Yamaguchi, Yoshihiro Matsumoto, Hirotoshi Hayashida, Hiroshi Nozaki, Takenao Shinohara, Satoru Kato, *ACS Energy Lett.* **2023**, *8*, 3485.

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プロトン伝導性共有結合有機構造体（COF）膜の配向評価

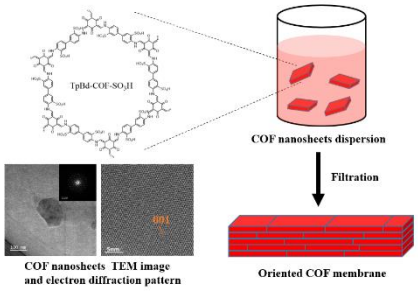
（株式会社デンソー[1]・京大 WPI-iCeMS[2]・京大院理[3]）○藤生 浩綺[1]・金 甫根[1]・西尾 隆宏[1]・渡辺弘紀[1]・田部 博康[2]・篠﨑 良太[1]・堀毛 悟史[2,3]・岡本 拓巳[1]
Orientation analysis for proton-conducting covalent organic framework (COF) membranes ([1]*DENSO CORPORATION*, [2] *WPI-iCeMS, Kyoto University,* [3] *Graduate School of Science, Kyoto University*) ○Koki Fujiu,[1] Masane Kin,[1] Takahiro Nishio,[1] Hiroki Watanabe,[1] Hiroyasu Tabe,[2] Ryota Shinozaki,[1] Satoshi Horike,[3] Takumi Okamoto,[1]

Covalent organic frameworks (COFs) are crystalline organic porous materials with periodic structures consisting of light elements. COFs with acidic groups such as sulfonic acid groups (-SO_3H) have high proton conductivity through proton transport pathways formed by acidic groups and water retained in the pores, but the conduction mechanism is not clear.

Since two-dimensional COF (2D-COF) membranes have an anisotropic structure, it is important to evaluate the overall orientation of the membrane and the COF nanosheets that form the membrane in order to clarify the mechanism of the proton conduction. In this study, we prepared highly oriented proton-conducting COF (TpBd-COF-SO_3H) membranes and analyzed their orientation by grazing incidence wide-angle X-ray scattering (GI-WAXS). We also analyzed of the crystallinity of COF nanosheets used for the deposition of 2D-COF membranes by transmission electron microscopy (TEM) and electron diffraction.
Keywords : Covalent organic framework (COF), COF nanosheets, proton conductivity, orientation, GI-WAXS

共有結合性有機構造体（COF）は軽元素で構成された周期構造を有する結晶性の有機多孔質材料である。スルホン酸基（-SO_3H）等の酸性基を付与した COF は、酸性基と COF 細孔内に保持された水から形成されるプロトン輸送パスにより、高いプロトン伝導性を有すると報告されているが、そのメカニズムは明らかになっていない [1)]。

2 次元 COF 膜は結晶学的に異方的な構造を有するため、高プロトン伝導のメカニズムを明らかにするには、膜の配向性と、膜を構成する COF ナノシートの結晶方位を評価することが重要である。本研究では、プロトン伝導性 2 次元 COF である TpBd-COF-SO_3H の高配向膜を作製し、微小角入射広角 X 線散乱（GI-WAXS）により、その配向評価を実施した。また、透過型電子顕微鏡（TEM）と電子線回折により、2 次元 COF 膜の成膜に用いた COF ナノシートの結晶性および結晶方位の評価を実施した。



1) L. Cao, Z. Jiang, *Adv. Mater.*, **2020**, *32*, 2005565
謝辞 : この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構（NEDO）の委託業務（JPNP20003）の結果得られたものです。

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硫黄系材料 SPAN の開発および電池創造による世界最軽量二次電池の実現と長時間ドローンフライトの実証

（株式会社ＡＤＥＫＡ[1]・うるたま株式会社 [2]・群馬大院理工 [3]）○撹上 健二 [1]・齊藤 俊介 [2]・撹上 将規 [3]・矢野 亨 [1]

Development of Sulfur-Based Materials “SPAN” and Battery Creations to Realize a World's Lightest Secondary Battery and Demonstration of Long Drone Flight Time ([1]*ADEKA CORPORATION*, [2]*URUTAMA.INC*, [3]*Graduate School of Science and Technology, Gunma University*) ○Kenji Kakiage,[1] Shunsuke Saito,[2] Masaki Kakiage,[3] Toru Yano[1]

ADEKA has developed sulfur-based cathode active materials “SPAN (sulfurized polyacrylonitrile: ADEKA AMERANSA SAM series)” for next generation lithium–sulfur (Li–S) secondary batteries. In this CSJ annual meeting, we (ADEKA & Gunma Univ.) report on the performance of Li–S secondary battery cells with the SPAN cathodes. An ultra-lightweight cell with the world's highest gravimetric energy density of 803 Wh/kg-cell was achieved by optimizing overall designs of the Li–SPAN pouch cell. In addition, we (ADEKA & URUTAMA) also assembled a 10 V-class Li–SPAN battery pack (246 Wh/kg-pack) and successfully flight-tested a micro-drone using the Li–SPAN battery pack. It was demonstrated that it can fly significantly longer than with usual secondary battery packs.

Keywords : SPAN; Secondary Battery; Lithium–Sulfur (Li–S); World's Lightest Weight; Drone

ＡＤＥＫＡ社は SDGs 達成のキーとなる次世代二次電池用のメタルフリー硫黄系ポリマー活物質として、硫黄変性ポリアクリロニトリル（SPAN：アデカアメランサ SAM シリーズ）を開発しており、SPAN の量産化検討と SPAN 正極･Li-metal 負極を用いたリチウム-硫黄二次電池（Li–SPAN 電池）の設計および性能実証を進めている [1,2]。

群馬大学との共同検討により、二次電池セルとして世界最軽量となる重量エネルギー密度 803 Wh/kg-cell（0.05C-rate）を有する Li–SPAN セルの実証に成功した（Fig. 1）。

また、うるたま社との共同検討により、Li–SPAN セルを 6 直列したドローン用軽量電池パック［2.27 Ah / 10.3 V / 246 Wh/kg-pack（0.1C-rate）］を試作した。マイクロドローンの飛行試験を行い、$LiCoO_2$ 正極･黒鉛負極から構成される現行 LiPo 電池パックの場合よりも 1.8 倍長時間フライトできることを実証した（Fig. 2）。

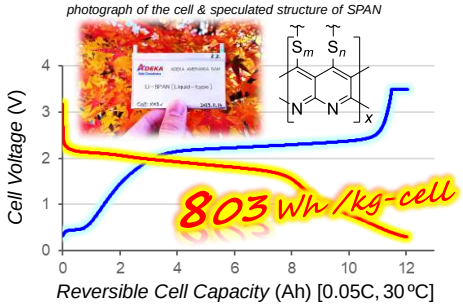

Fig. 1. Ultra-lightweight Li–SPAN pouch cell.



Fig. 2. Drone flight with the Li–SPAN battery pack.

1) 撹上健二 他, 第 64 回電池討論会, 2E17, 2E19 (2023). 2) K. Kakiage et al., Ultra-lightweight rechargeable battery: >750 Wh/kg lithium–sulfur pouch cell (Preprint : https://doi.org/10.21203/rs.3.rs-3215804/v1).

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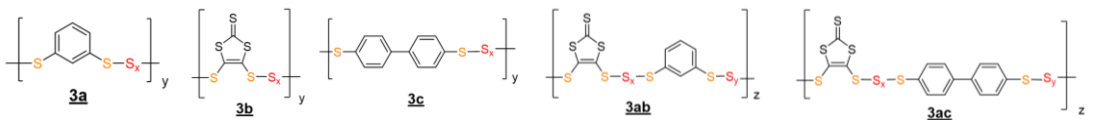
有機硫黄化合物を使用した全固体電池用の高容量正極材料開発

（米子高等専総[1]・関学大工[2]・大阪産技研[3]）○清水剛志[1]・篠田和希[1]・野田悠成[1]・那和洸星[1]・谷藤尚貴[1]・吉川浩史[2]・山本真理[3]・加藤敦隆[3]・高橋雅也[3]
High Capacity All-Solid-State Batteries including Organopolysulfides as Cathode Active Materials ([1]*Chemistry and Biochemistry Division, Department of Integrated Engineering, National Institute of Technology, Yonago College*, [2]*Graduate School of Engineering, Kwansei Gakuin University*, [3]*Osaka Research Institute of Industrial Science and Technology*) ○Takeshi Shimizu[1], Kazuki Shinoda[1], Yusei Noda[1], Kosei Nawa[1], Naoki Tanifuji[1], Hirofumi Yoshikawa[2], Mari Yamamoto[3], Atsutaka Kato[3], Masanari Takahashi[3]

Organopolysulfides, organic compounds synthesized by inverse vulcanization of monomers with radical reactive sites, have been studied as cathode active materials for next-generation rechargeable batteries based on multi-electron redox reaction of disulfide bonds. In this study, we found that 1,3-dithiol-2-thione (DMIT), one of the conductive organic molecules, enhanced the cycle performance, resulting in that the organopolysulfide including DMIT and benzene exhibited the good capacity retention and the high capacity of 1625 mAh g^{-1} as a cathode active material of an all-solid-state battery.
Keywords : Polysulfide; Inverse vulcanization; Disulfide bond; All-solid-state battery

有機ポリスルフィドは、ラジカル反応点を有するモノマーの逆加硫によって合成される有機化合物であり、ジスルフィド結合の開裂/再結合に基づく高容量次世代蓄電池の正極活物質として有用である[1]。最近では、有機ジスルフィド化合物をモノマーとした逆加硫法が開発され、多数のジスルフィド結合と様々な有機基を含む有機ポリスルフィドが液系蓄電池の高容量正極活物質として報告された[2]。しかし、これらには、ジスルフィド結合の開裂時に電解液への溶解性が高くなるため、サイクル特性が低いという問題があった。本研究では、有機基ベンゼン（BZ）、ビフェニル（BP）、1,3-ジチオール-2-チオン（DMIT）を含むジスルフィド化合物をモノマーとした逆加硫によって得た有機ポリスルフィドのサイクル特性を改善するため、固体電解質 Li_3PS_4 を用いた全固体電池を作製した。

上記の合成法により、1 種類の有機基を含む有機ポリスルフィド **3a**, **3b**, **3c**、BZ と DMIT および BP と DMIT の組からなる有機ポリスルフィド **3ab**, **3bc** を得た。これらを正極活物質とした全固体電池は、液系蓄電池よりも高いサイクル特性を示した。特に、**3b** と **3ab** がそれぞれ最も高い容量維持率と容量 1625 mAh g^{-1} を示し、前者からは DMIT の電子伝導性によって可逆な充放電が進行したこと、後者からは BZ と DMIT を含む平均分子量の小さい有機ポリスルフィド鎖由来の高容量が示唆された。



1) Z. Pan *et al*., *Adv. Energy Mater.* **2022**, *12*, 2103483.
2) T. Shimizu *et al*., *Polymers*, **2023**, *15*, 335.

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太陽光水分解システムにおけるヘマタイト光電極性能の改善

(神戸大分子フォト[1]・神戸大院理[2]) ○隈部 佳孝[1]・立川 貴士[1,2]
Improving the performance of hematite photoelectrodes for solar water splitting ([1]*Molecular Photoscience Research Center, Kobe University*, [2]*Graduate School of Science, Kobe University*) ○Yoshitaka Kumabe,[1] Takashi Tachikawa[1,2]

Hematite possessing a broad absorption band in the visible region has been gathering attention as an ideal anode material for solar water splitting systems due to its theoretically high solar-to-hydrogen conversion efficiency and excellent long-term stability. However, some shortcomings including the small mobility of minority carriers, the short hole diffusion length, and a large variation in the photoelectrochemical performance hinder its practical application. On the other hand, our research group has succeeded in improving the performance of hematite photoelectrodes by mesocrystallization with controlled crystal orientation and alignment of nanoparticles and doping of different elements. In this study, aiming for further performance improvement, we investigated the photoelectrochemical performance of hematite photoelectrodes with more than 40 different elements as dopant. In the electrode fabrication process, the improvement and homogenization of photoelectrochemical performance were achieved by optimizing the cooling process during calcination and subsequent low-temperature annealing.

Keywords : Solar water splitting; Photoelectrode; Hematite

可視光領域に幅広い吸収帯を有するヘマタイトは、理論上の高い太陽光—水素変換効率と優れた長期安定性のため、太陽光水分解システムのアノード材料として注目されている。しかし、電荷キャリアの低い移動度、短い正孔拡散長、光電気化学性能の大きなばらつきがヘマタイトの実用化を妨げている。一方、我々の研究グループではナノ粒子の結晶配向・配列を制御したメソ結晶化と、異種元素のドープによりヘマタイト光電極の性能向上に成功した[1]。本研究では更なる性能向上を目指し、40種類以上の元素をドーパントとしたヘマタイト光電極の光電気化学測定を行った (Fig. 1a)。また、電極作製プロセスの中で焼成時の冷却過程とその後の低温アニールの条件を最適化することで、電極性能の向上と均一化を達成した (Fig. 1b)。

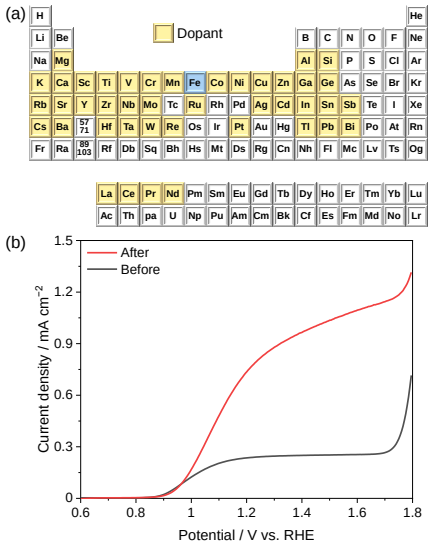

Fig. 1. (a) List of dopants. (b) The photocurrent density–potential curves before and after electrode fabrication process optimization.

1) Interfacial oxygen vacancies yielding long-lived holes in hematite mesocrystal-based photoanodes. Z. Zhang, I. Karimata, H. Nagashima, S. Muto, K. Ohara, K. Sugimoto, T. Tachikawa, *Nat. Commun.* **2019**, *10*, 4832.

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超弱励起光で駆動する高効率可視－紫外アップコンバージョン

（九大院工[1]・九大 CMS[2]・九大高等院[3]）○水上 輝市[1]・渡辺 侑哉[1]・楊 旻朗[1]・楊井 伸浩[1,2]・安田 琢麿[1,3]・君塚 信夫[1,2]

Ultra-low Excitation Intensity Visible-to-UV Photon Upconversion with High Spin Statistical Probability Factor ([1]*Grad. Sch, Eng.*, *Kyushu Univ.*, [2]*CMS*, *Kyushu Univ.*, [3]*IAS*, *Kyushu Univ.*)
○Kiichi Mizukami,[1] Yuya Watanabe,[1] Minlang Yang,[1] Nobuhiro Yanai[1,2], Takuma Yasuda,[1,3] Nobuo Kimizuka[1,2]

Triplet-triplet annihilation-based photon upconversion (TTA-UC) is an attractive methodology to convert low-energy photons to high-energy photons even under low excitation light, such as sunlight level, and it is expected to be applied to devices for photocatalysis and environmental cleanup. Herein, we have developed a heavy metal-free Vis-to-UV TTA-UC system using a TADF sensitizer and UV annihilator. The system reached a high UC efficiency of over 20%, driven under 1 sun intensity. Furthermore, the statistical probability factor exceeded the theoretical limit of 40%.
Keywords : Photon upconversion; Triplet-triplet annihilation; TADF sensitizer

三重項－三重項消滅に基づくフォトン・アップコンバージョン（TTA-UC）は、太陽光レベルの低い励起光強度（~mW cm^{-2}）で駆動する波長変換技術であり（**Fig. 1**）、太陽光を利用する太陽電池や光触媒、セラノスティクスなどへの応用が期待されている。これまでに可視－紫外 TTA-UC では、20%を超える高い UC 効率が報告されているが、三重項増感剤に重金属が含まれコストや環境負荷、生体適合性に課題がある[1]。

本研究では、TADF 増感剤と UV 発光分子を新たに設計・開発し、重金属フリーな可視－紫外 TTA-UC システムを開発した。本システムは太陽光レベル（1.4 mW cm^{-2} at 445 nm）の励起光で 20%以上の高い UC 効率を達成し、TTA 後に励起一重項が生成される確率 f 値は理論限界である 40%を超えることに成功した。

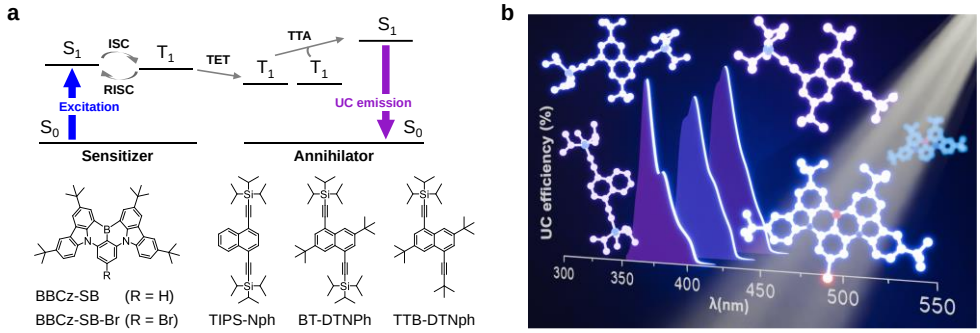

Figure 1. (**a**) TTA-UC mechanism and chemical structures of TADF photosensitizers and UV annihilators. (**b**) Schematic illustration of upconverted emission spectra for Vis-to-UV TTA-UC.

[1] N. Harada et al., *Angew. Chem. Int. Ed.*, **2021**, *60*, 142-147.

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フェムト秒時間分解赤外分光法による非フラーレン型アクセプター分子の電荷分離過程の解明

(岡山大学[1]・兵庫県立大学[2]・京都大学[3])
○安達 麟太郎[1]・梅山 有和[2]・今堀 博[3]・山方 啓[1]

Charge Separation Kinetics in non-fullerene acceptors by femtosecond time-resolved infrared spectroscopy

([1]*Okayama University*, [2]*University of Hyogo*, [3]*Kyoto University*)
○Rintaro Adachi,[1] Tomokazu Umeyama,[2] Hiroshi Imahori,[3] Akira Yamakata[1]

Non-fullerene acceptors (NFAs) have been extensively studied as organic photovoltaics materials. To further improve the performance, it is essential to understand the behavior of photoexcited charge carriers. In this study, we have examined the photodynamics on several NFAs such as DP2 and DP3 whose side chains were modified from Y6. The vibrational frequency of C≡N group attached to the NFA molecule is sensitive to the change of electron density in the molecules, and hence the femtosecond time-resolved infrared absorption measurements provide the information about the charge separation kinetics. The internal- and intra-molecular charge separation kinetics of these NFAs will be presented at the conference.
Keywords : organic photovoltaics, non-fullerene acceptors, time-resolved IR

非フラーレン型アクセプター分子（NFAs）は有機薄膜太陽電池材料として、近年盛んに研究されている。さらなる性能向上のためには、光励起キャリアの挙動を詳しく理解することが不可欠である。NFA 分子に電子受容部として付与されている C≡N 基の伸縮振動数は、電子密度の増加により低波数側にシフトする［1]。そこで本研究では、NFA 分子として最も性能が高い Y6 をベースにその側鎖を修飾した DP2, DP3 について、フェムト秒時間分解赤外分光法により C≡N 基の伸縮振動数の変化を調べた（Figure 1)。その結果、DP3 に光を照射すると、分子内電子移動によって C≡N 基の振動数は 2220 cm^{-1} から 2200 cm^{-1} に低波数シフトした。一方、PM6 や PBDB-T のようなドナー分子とブレンドすると、2200 cm^{-1} からさらに低波数シフトして 2180 cm^{-1} や 2150cm^{-1} にピークが現れた。これらのピークは分子間電荷分離によって生成したアニオン状態に帰属される。これらの結果より、時間分解赤外分光計測により分子内と分子間電荷移動過程を追跡できることを明らかにした。

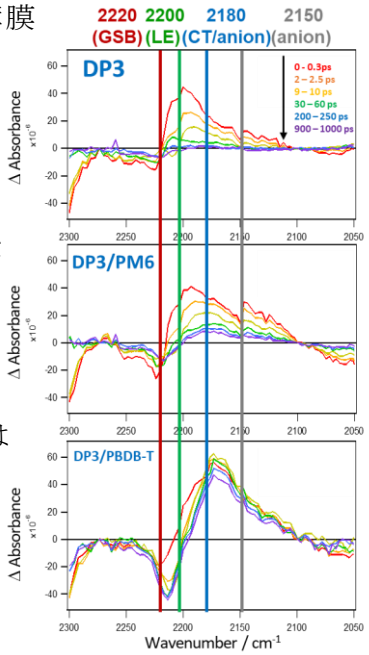

Figure 1
Transient IR absorption spectra of C≡N stretching mode of Non-fullerene acceptor films (DP3) excited by laser pulse (90 fs-duration, 800 nm pump).

[1] S. Jinnai, K. Murayama, K. Nagai, M. Mineshita, K. Kato, A. Muraoka, A.Yamakata, A. Saeki, Y. Kobori, Y. Ie J. Mater. Chem. A, 2022, 10, 20035.

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Mn 錯体およびβ-FeOOH 触媒と Si 太陽電池を用いた高効率太陽光 CO_2 電解還元

（豊田中研[1]）関澤 佳太[1]・佐藤 俊介[1]・坂本 直柔[1]・鈴木 登美子[1] ・森川 健志[1]

Highly Efficient Solar CO_2 Conversion by Coupling Silicon Solar cells with Gas Diffusion Electrolyzer using Mn(I) Complex and β-FeOOH Catalysts

([1] Toyota Central R&D Labs., Inc.) Keita Sekizawa,[1] Shunsuke Sato,[1] Naonari Sakamoto[1], Tomiko M. Suzuki,[1] and Takeshi Morikawa[1]

Solar-driven CO_2 electrolysis coupling solar cells with CO_2 electrolysis system is expected to contribute to carbon neutrality. However, the highly efficient solar-driven CO_2 electrolysis system reported previously uses precious metal catalysts for CO_2 electrolysis and requires expensive III-V semiconductors solar cells due to their high overvoltage. In this study, we aimed to drive CO_2 electrolysis at low potential by introducing molecular metal complex catalysts composed of Earth-abundant elements into a gas diffusion flow reactor. As a result, the electrochemical reactor with Mn complexes succeeded in converting CO_2 to CO with 94% selectivity at an extremely low cell voltage of 1.35 V. This CO_2 electrolysis reactor combined with silicon solar cells has realized highly efficient solar-driven CO_2 electrolysis.

Keywords : CO_2 reduction, Artificial Photosynthesis, Molecular Catalyst, Metal Complex, Gas Diffusion Electrode

CO_2 電解システムと太陽電池を直接連結した太陽光 CO_2 電解還元システムは、カーボンニュートラルに向けた有望な手段である。しかし、高い効率を実現するには、希少金属触媒と高価な宇宙用途の太陽電池が必要であり、実用には大きな課題がある。本研究では、資源量の面から実用可能な太陽光 CO_2 電解還元の実現を目指した。CO_2 還元触媒の Mn 錯体[1]と、H_2O 酸化触媒の Ni 添加 β-FeOOH[2]を、膜/電極接合体を用いたガス拡散型電解リアクターに導入した。この CO_2 電解還元システムを、市販の単結晶 Si 太陽電池に連結することで、太陽光 CO_2 電解を行った。その結果、Fig.1 に示すように、セル電圧 1.35V で CO 生成のファラデー効率 94%の高選択的な CO_2 電解を達成した。これを Si 太陽電池に接続した太陽光 CO_2 電解還元システムにより、世界最高水準の太陽光変換効率の実証に成功した[3]。発表では、詳細な反応機構解析を含めて報告する。

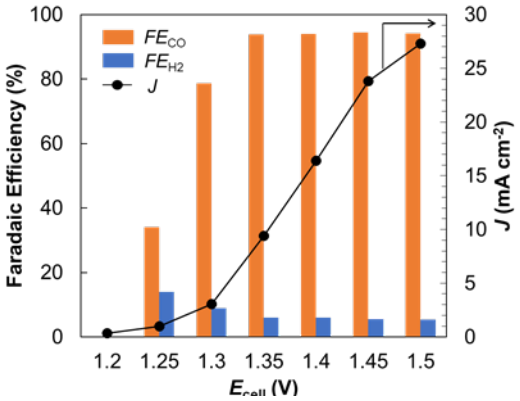

Fig.1. Faraday efficiency (FE) and current density (J) at each cell voltage (E_{cell}) in the CO_2 electrolysis

(1) S. Sato, *et al. ACS Catal.* **2018**, *8*, 4452–4458. (2) T. M. Suzuki, *et al. Bull. Chem. Soc. Jpn*. **2018**, *91*, 778-786. (3) K. Sekizawa, *et al. submitted.*

謝辞 本成果は、環境省「二酸化炭素の資源化を通じた炭素循環社会モデル構築促進事業」および NEDO「未踏チャレンジ 2050」の委託業務の結果得られた。

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マイクロスケール CSTR®による連続フロー合成／酸化および還元事例

（理楽工房[1]・マックエンジニアリング[2]）○中山伸之[1]、小谷功[2]、小谷研太朗[2]、土師浩[2]、中務定義[2]

Continuous flow synthesis / oxidation and reduction case studies using the Microscale CSTR®

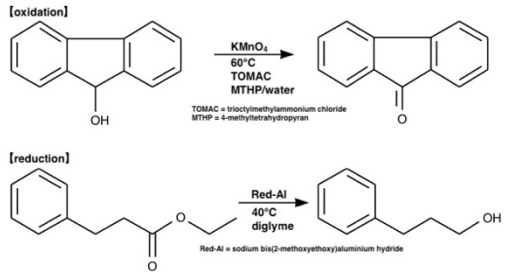
(1. Rigaku Kobo, LLC, 2. MAK Engineering Corporation)○Nobuyuki Nakayama[1], Isao Kotani[2], Kentaro Kotani[2], Hiroshi Haji[2], Sadayoshi Nakatsukasa[2]

For many years, our group has developed and marketed two types of flow reactors (PFR and CSTR) for laboratory experiments for everyday use. We report here the results of continuous flow synthesis (oxidation and reduction) using one of these flow reactors, the Microscale CSTR®, which gave good results. In addition, this type (CSTR) has been attracting attention in recent years, and several review articles have been reported[1)]. [Exp.1] 9-Fluorenone was synthesized from 9-fluorenol by continuous flow oxidation (MTHP-water two-phase system with phase transfer catalyst TOMAC, oxidant $KMnO_4$) (reaction temp. 60°C, residence time 1h, yield >95%). [Exp.2] 3-Phenylpropanol was synthesized from ethyl 3-phenylpropionate by continuous flow reduction (diglyme, reducing agent Red-Al) (reaction temp. 40°C, residence time 1h, 95% yield).

Keywords ：continuous stirred tank reactor; CSTR; continuous flow synthesis; oxidation; reduction

当グループでは、長年、普段使いのラボ実験用フローリアクターを 2 方式（PFR および CSTR）開発・市販しているが、今回、その一つであるマイクロスケール CSTR®を使って連続フロー合成（酸化および還元）を行ったところ、良好な結果が得られたので報告する。なお、近年、この方式（CSTR）が注目されており、総説も複数報告されている[1)]。

【実験 1】連続フロー酸化（MTHP-水の二相系、相間移動触媒 TOMAC、酸化剤 $KMnO_4$ を使用）により、9-フルオレノールから 9-フルオレノンを合成した（反応温度 60℃、滞留時間 1h、収率>95%）。
【実験 2】連続フロー還元（ジグリム、還元剤 Red-Al を使用）により、3-フェニルプロピオン酸エチルから 3-フェニルプロパノールを合成した（反応温度 40℃、滞留時間 1h、収率 95%）。





1) for example, N. Cherkasov, et al., *React. Chem. Eng.*, **2023**, *8*, 266.

謝辞 本研究を行うに当たりご協力頂きました滋賀県工業技術総合センターの皆様に深く感謝致します。

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CO_2-to-C_3H_7OH 変換 2 核 Cu 分子触媒の反応機構解明

(豊田中研)○坂本 直柔・関澤 佳太・白井 聡一・野中 敬正・荒井 健男・佐藤 俊介・森川 健志

Investigation of reaction mechanism of CO_2-to-C_3H_7OH electrochemical conversion dinuclear Cu molecular catalysis. (*Toyota Central R&D Labs., Inc.*,) ○Naonari Sakamoto, Keita Sekizawa, Soichi Shirai, Takamasa Nonaka, Takeo Arai, Shunsuke Sato and Takeshi Morikawa

Propanol (C_3H_7OH), requiring three CO_2 molecules, 18 electrons, and 18 protons was demonstrated to produce using a dinuclear Cu molecular catalyst capable of CO_2 adsorption and reaction intermediate retention, via a CO_2 electroreduction in aqueous solution[1]. The reaction mechanism to produce propanol from CO_2 involves over 40 processes, with unknown details. Herein, we investigated the detection of key reaction intermediates up to the formation of C_3 coupling species using *operando* surface-enhanced Raman scattering (SERS) analysis. To identify the observed reaction intermediates and to elucidate the reaction mechanism for the formation of C_3 products, DFT calculations were performed. Excellent agreement between the peaks extracted from comparing the SERS and DFT simulation spectra strongly supports the computationally inferred reaction mechanism proceeding at room temperature and applied potential. The analysis of transition state structures indicates that a crucial role in the C-C coupling progression within the Cu dinuclear molecular metal complex is forming a CO_2/CO-reduced intermediate species that forms a bridging intermediate between the two Cu active sites. The bridging intermediate can adjust the Cu-Cu distance as it progresses, drawing reducing species to one Cu side and accepting substrate on the other Cu side. New molecular design guidelines are provided as one of the basic structures of molecular catalysts for the synthesis of CO_2 reduction products that require C-C coupling.

Keywords: CO_2/CO reduction, Molecular catalyst, operando analysis, Reaction mechanism

3 分子の CO_2 と 18 電子、18 プロトンを必要とするプロパノール生成を、CO_2 の吸着・保持能力と反応中間体の保持能力を兼ね備えた新規 Cu2 核分子触媒による水溶液中 CO_2 電解還元反応で実証した。CO_2 からプロパノール生成までの反応機構は 40 以上の過程を経由する極めて複雑なものであり、その詳細は不明であった。

本発表では、局在表面プラズモン共鳴を利用した *operando* 分光分析を用い、DFT 計算と組み合わせることで C_3 カップリング種生成までの主要な反応中間体の検出・同定を検討した。さらに $^{13}CO_2$ を用いた標識実験および一酸化炭素(CO)還元反応の結果も基にして、C-C カップリング反応が進行する鍵は、2 つの銅活性サイト間に橋渡し中間体を形成する CO_2/CO 還元反応中間体の形成にあることが示唆された。反応中間体は 2 つの銅中心間の距離を柔軟に変化させながら一方の Cu 側に還元種を引き寄せ、他方の Cu 側に新たな CO_2/CO を受け入れることが DFT 計算から示唆された。CO_2/CO や反応中間体を保持でき、柔軟な活性点を有する銅 2 核分子触媒は、C-C カップリングを必要とする還元生成物の高選択的生成の実現が期待される。

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温度応答性高分子 PNIPAM の相分離現象を用いる マイクロビーズの濃縮法の開発

（富山高等専門学校[1]・国立研究開発法人物質・材料研究機構 高分子・バイオ材料研究センター スマートポリマーグループ[2]）○山下 ゆい[1]・間中 淳[1,2]・荏原 充宏[2]
Development of microbeads concentration method using phase separation phenomenon with temperature-responsive polymer PNIPAM ([1] *National Institute of Technology, Toyama College*, [2]*Smart Polymer Group, Polymer and Biomaterials Research Center, National Institute for Materials Science*) ○Yui Yamashita,[1] Atsushi Manaka,[1,2] Mitsuhiro Ebara[2]

Microbeads (MB) is very small size of microplastic, and their small particle size makes them difficult to use conventional microplastic analysis because of difficult to collect and decrease of analytical sensitivity. On the other hand, *N-isopropylacrylamide* (PNIPAM) produce small size of gel phase by temperature-dependance phase separation, and we found that MB are concentrated to the gel phase. Based on these findings, the objective this study is development of highly efficient concentration technique for microbeads with PNIPAM. As a result, it was observed that plastic particles were accumulated in the concentrated phase. Furthermore, using Raman microscope, mixed sample with polyethylene and polystyrene could be identified.
Keywords *: Micro Beads; Poly N-isopropylacrylamide (PNIPAM); Concentration*

マイクロビーズ (MB) は 0.5 mm 以下の非常に微小なマイクロプラスチックであり，微小であるゆえに生体への吸収性，有機汚染物質の吸着性が高くなるだけでなく，分析する際の捕集が難しく，FT-IR での検出感度の低下等，従来のマイクロプラスチックの分析手法が適用しにくい課題がある。一方，ポリ *N*-イソプロピルアクリルアミド (PNIPAM) は低温で水溶性，32℃を境に高温になると疎水性となるため，加温することで相分離しゲル状の沈殿物を生成する [1)]。このゲル相に種々の MB が高効率で抽出されることを見出した。そのため，本研究では PNIPAM の相分離現象を用いた MB の高効率な濃縮分離技術の開発を検討した (Fig.1) 。

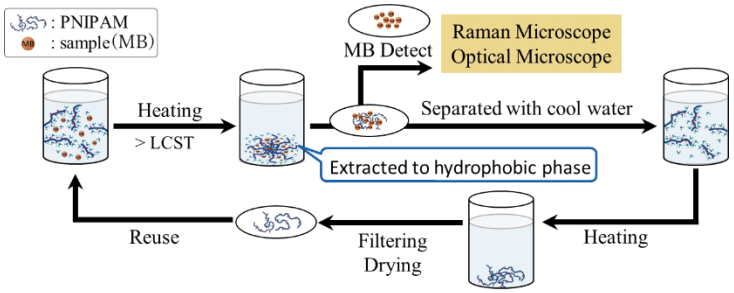

Fig.1 Overview of MB concentration method with PNIPAM

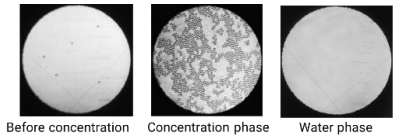

Fig.2 Micrographs observation
Sample : 10ppm of PE and PS, 20 μm, magnification : 100 times

その結果，光学顕微鏡観察において Fig.2 のように，各プラスチック微粒子が濃縮相に集積することが確認できた。また，ラマン顕微鏡を用いることで，濃縮相中のポリエチレンとポリスチレン試料のラマンスペクトルを確認することができ，混合試料中の分別同定することが可能であった。さらに，使用した PNIPAM を約 90%回収することができ繰返し使用できることが分かった。

1) Ahmed Nabil, Erika Yoshihara, Keita Hironaka, Ayman A Hassan, Gamal Shiha, Mitsuhiro Ebara, *Computational and Structural Biotechnology Journal*, **19**:3609-3617(2021).

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水蒸気薄膜蒸留による鯨油中の微量 PCB 低減法

(山口県産技セ[1]・下関市立大経[2]・吉田総合テクノ[3]・日鯨研[4]) ○岩田 在博[1]・小川 友樹[1]・猪野 陽佳[1]・宮本 美里[1]・岸本 充弘[2]・吉田 幸治[3]・吉田 貴宏[3]・安永 玄太[4]・藤瀬 良弘[4]

Reducion of Trace PCBs in Whale Oil by Steam Thin Film Distillation ([1]*Yamaguchi Prefectural Industrial Technology Institute*, [2]*Department of Economics, Shimonoseki City University,* [3]*Yoshida Sogo Techno Co., Ltd.,* [4]*The Institute of Cetacean Research*) ○Arihiro Iwata,[1] Tomoki Ogawa,[1] Haruka Ino,[1] Misato Miyamoto,[1] Mitsuhiro Kishimoto,[2] Kouji Yoshida,[3] Takahiro Yoshida,[3] Genta Yasunaga,[4] Yoshihiro Fujise[4]

Since PCBs are fat-soluble, it is difficult to remove PCBs contained in fats and oils. Because cetaceans are at the top of the food chain, they may contain trace amounts of PCBs in their whale oil, depending on the area where they were caught. In this study, we examined a steam thin film distillation method to reduce PCBs in oil of common minke whale. It was found that whale oil containing 0.76ppm of PCBs could be prepared and emulsion was formed by adding water to whale oil, and thin-film distillation under reduced pressure could efficiently reduce PCBs (Japanese Patent Application No. 2023-146282). Steam thin film distillation is considered to be effective in removing PCBs in fats and oils.

Keywords : PCBs; Oils and Fats; Steam Thin Film Distillaion

PCB（ポリ塩化ビフェニル）は、慢性毒性が認められる有機塩素化合物であり脂溶性のために生体内に取り込まれやすく、さらに残留性も高いことが知られている。鯨類は食物連鎖の頂点にあるため、捕獲海域によっては、鯨油中に微量の PCB を含んでいることがある。油脂中に含有する PCB を除去することが困難であった。本研究では、鯨油中の PCB 含有率を低減するため水蒸気薄膜蒸留法を検討した。0.76ppm の PCB を含んだミンク鯨油を調製し、鯨油に水を添加してエマルジョンを形成し、減圧下で薄膜蒸留を行うと効率よく PCB を低減できることを見出した（特願 2023-146282）。水蒸気薄膜蒸留は、油脂中の PCB 除去に有効であると考えられる。回収率の問題（Fig 1）、また蒸留操作の熱の影響により、DHA などの高度不飽和脂肪酸の含有率が低下する問題があり（Table 1）、今後改良を進めることで油脂産業で利用されることが期待される。

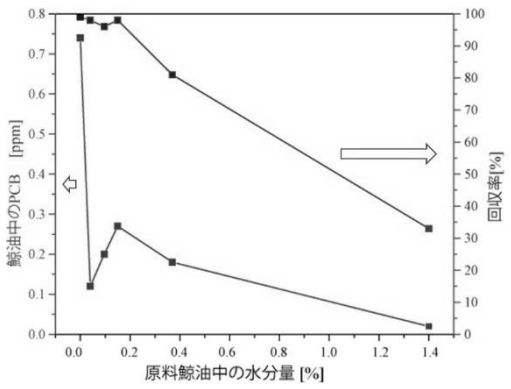

Fig 1 原料鯨油中の水分量と薄膜蒸留の結果

Table 1 蒸留前後の高度不飽和脂肪酸の組成比

	PCB[ppm]	DHA[%]	EPA[%]	DPA[%]
原料	0.76	8.4	8.4	3.5
水分量0%	0.74	7.9	8.2	3.4
水分量0.04%	0.12	7.6	8.6	3.5
水分量0.096%	0.20	6.7	7.7	3.2
水分量0.15%	0.27	7.0	8.0	3.3
水分量0.37%	0.18	7.0	7.9	3.2
水分量1.4%	0.02	7.0	7.8	3.3

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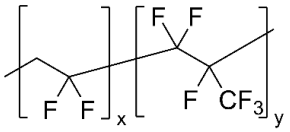
Complete defluorination of fluoroelastomer FKMs using subcritical water with alkaline reagents

([1]*Graduate School of Science, Kanagawa University,* [2]*Technology Innovation Center, Daikin Industries, Ltd*) ○Jin Hamaura,[1] Hisao Hori, [1] Hirofumi Mukae,[2] Ayane Fujishima[2]

Keywords: Subcritical water; Fluoroelastomer; Defluorination; Recycling; Artificial Fluorspar

Fluoroelastomer FKMs, which consist of vinylidene fluoride (VDF) and other monomers, are functional rubber materials widely used for fuel tube, gaskets, O-rings, electric wiring etc., owing to their high heat-, chemical resistances and high insulation. However, their recycling technologies are not fully established. These wastes can be treated by incineration. However, it requires high energy. In addition, the mine production of high-purity fluorspar (CaF_2 ore), the raw material for all fluoropolymers including FKMS, is limited in a few countries. If these materials are completely decomposed to F^- ions, F^- ions can be converted into CaF_2 by a reaction with Ca^{2+} ions. Herein we report complete defluorination of two FKMs, by use of subcritical water with alkaline reagents[1]. The first FKM is an “uncrosslinked FKM”, i.e., a poly(VDF-*co*-HFP) copolymer (x/y = 78/22) and the second FKM is a “crosslinked FKM”, which consisted of the copolymer cured with peroxide and carbon black.



Poly(VDF-*co*-HFP)

Fig. 1 shows KOH concentration dependences of the amounts of F^- and total organic carbon (TOC) formed in the reaction solutions, obtained from the reactions of (a) uncrosslinked- and (b) crosslinked FKMs at 250 ºC for 6 h. The F^- and TOC amounts increased with increasing KOH concentration. When 0.5 M of [KOH] was used, the F^- yields reached 102% and 101% for the uncrosslinked and crosslinked FKMs, respectively. The reactions caused residues. Raman spectroscopy indicated that the residue consisted of amorphous carbon. Formation of CaF_2 from the F^- ions obtained will also be reported at the presentation.

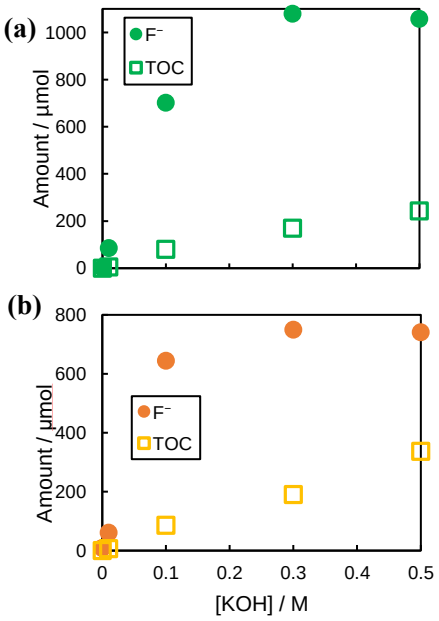


Fig. 1. Effect of KOH concentration on the amounts of F^- and TOC from (a) uncrosslinked and (b) crosslinked FKMs. Reactions were carried out at 250 ºC for 6 h.

1) J. Hamaura, H. Hori, A. Fujishima, H. Mukae, *Molecules,* **2023**, *28*, 7057.

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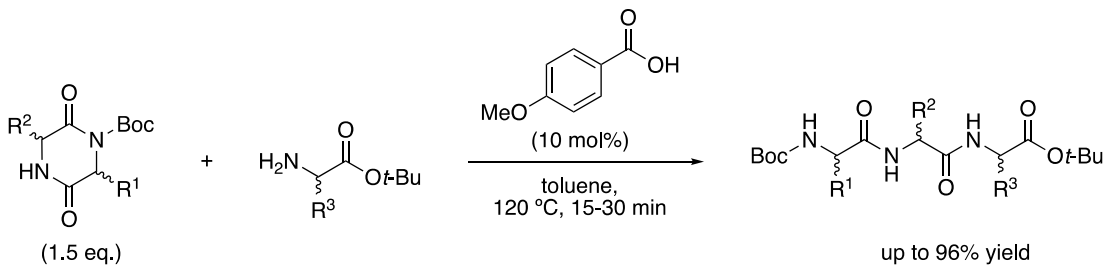
カルボン酸触媒によるジケトピペラジン類を用いたペプチド合成反応

（中部大ペプチド研究センター）○今 利真・山本 尚
Carboxylic Acid-Catalyzed Peptide Synthesis Using Diketopiperazine (*Peptide Research Center, Chubu University*) ○Kazumasa Kon, Hisashi Yamamoto

Previously, we reported the peptide elongation reaction between diketopiperazines and amino esters under neat condition to further various tripeptides.[1)] However, this reaction has room for improvement in reaction efficacy, because long reaction times (over 12 h) are necessary to synthesize tripeptides in high yields. In this investigation, we developed that carboxylic acid catalyzed peptide elongation reaction between diketopiperazines and amino esters. This carboxylic acid-catalyzed peptide elongation reaction gave the corresponding tripeptides in high yield within 15-30 min. In this presentation, I will report the investigation of the reaction conditions, and substrate scopes.
Keywords : Peptide synthesis; Diketopiperazines; Tripeptides; Carboxylic acid; Catalyst

ペプチド類は様々な生物活性化合物や医薬品などに含まれる重要な化合物である。従来の縮合剤を用いた合成法は多量の廃棄物を排出するため、廃棄物の低減を目指した縮合剤を用いない触媒的ペプチド合成法の開発が近年盛んに行われている。しかし、これまで報告されている触媒的ペプチド合成法は高い収率を得るために長時間の反応時間を必要としており反応効率に課題がある。その為、より効率的な触媒的ペプチド合成法の開発が望まれている。

一方既に当研究室では、ジケトピペラジン類とアミノエステル類とのアミド交換反応が触媒非存在下で進行し、対応するトリペプチドが良好な収率で得られることを報告している [1)]。しかし、良好な収率でトリペプチドを得るには最短でも 12 時間と長い反応時間を必要とし、反応効率に課題があった。そこで本研究ではより効率的な触媒的ペプチド合成法の開発を目指し、本反応に対して有効な触媒の検討を行なった。その結果、カルボン酸触媒が良好な触媒活性を示した。中でも *p*-メトキシ安息香酸が最も高い触媒活性を有し、本触媒による反応は最短 15 分と非常に短い反応時間で目的とするトリペプチドを高い収率で与えた。



1) W. Muramatsu, H. Yamamoto, *Chem. Sci.* **2023**, *13*, 6309-6315.

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NOx 吸着材としての Pd/CHA
- Pd 担持方法が NOx 脱離温度に与える影響 -

（名大院[1]・広大院[2]）○大津 岳士[1]、鷲山 祥平[1]、宇佐美 智也[1]、津野地 直[2]、織田 晃[1]、薩摩 篤[1]
Pd/CHA as a NOx Adsorber − The Effect of Pd Loading methods on NOx Desorption Temperature- (*1. Nagoya University, 2. Hiroshima University*) ○Takeshi Ohtsu[1], Shohei Washiyama[1], Tomoya Usami[1], Nao Tsunoji[2], Akira Oda[1], Atsushi Satsuma[1]

As diesel engine efficiency improves, NOx reduction at lower temperatures below active window of NH_3-SCR catalysts is desired. Passive NOx Adsorber (PNA) using Pd-supported zeolite (Pd/CHA) is proposed[1]. Controlling the NOx desorption temperature and the adsorption amount are important, and it is necessary to clarify the relationship between the Pd species and the PNA performances. In this study, we investigated the effects of Pd loading methods. A 1wt% of Pd was introduced using three different methods. As shown in Fig. 1A, Pd/CHA showed different NOx desorption profiles. NOx desorbed from Imp mainly below 300 ^{o}C. The contribution of aggregated Pd species was suggested by CO-FTIR. As for HTA, the desorption peaks around 190 ^{o}C, 270 ^{o}C are characteristic, which were assigned as NO_3^-(monodentate) and Pd^+-NO by NO-FTIR (Fig. 1B), respectively.
Keywords : Passive NOx Adsorber; CHA zeolite; Pd loaded material; Diesel Vehicles

ディーゼルエンジンの効率向上に伴いNH_3-SCR 触媒で浄化困難な低温での NOx 処理が課題となっている．そこで Pd 担持ゼオライト(Pd/CHA)を利用した，低温 NOx 吸着材料 (PNA) が提案されている[1]．実用化には NOx の脱離温度制御と吸着量向上が重要であり，Pd 導入量，ゼオライト，調製法に依存して形成される Pd 種との関係解明が求められている．本研究では，Pd 導入法の効果を検討した．Fig. 1A に示すように，Pd 1wt%を異なる方法で担持した Pd/CHA は異なる NOx 脱離温度特性を示した．Imp では主に 300℃以下で NOx が脱離し，CO-FTIR から Pd 凝集種の寄与が示唆された．HTA では 190℃，270℃付近の脱離 NOx が特徴的で，IR スペクトル(Fig. 1B)からそれぞれ NO_3^-(monodentate)，Pd^+-NO に帰属された．

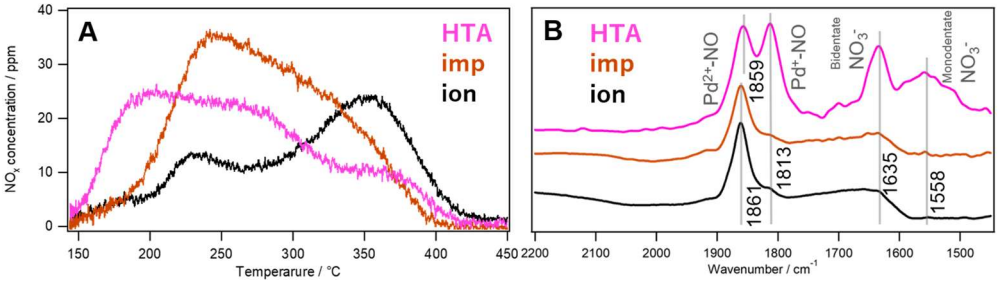

Fig. 1A NOx Temperature Programmed Desorption profiles of Pd/CHA in a flow of 8% O_2 (ion: ion exchange, imp: impregnation, HTA: Hydrothermal Aging), Fig. 1B FT-IR spectra of adsorbed NOx on Pd/CHA at 150 ºC.

1. Chen, H. Y. *et al. Catal. Letters* **146**, 1706–1711 (2016).

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単層 CNT を担体とした金ナノ粒子電極触媒の作成とアルコールの空気酸化反応への応用

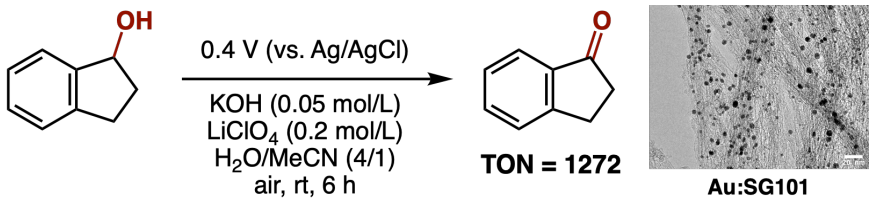
（阪大院工[1]・阪大 ICS-OTRI[2]・産総研[3]）○植竹 裕太[1,2,3]・中村 帆花[1]・矢吹 澪斗[1]・清水 太陽[3]・小久保 研[3]・櫻井 英博[1,2]

Preparation of gold nanoparticle electrocatalysts supported by single-walled CNTs and their application to aerobic oxidation of alcohols under electrochemical conditions ([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka University,* [3]*AIST*) ○Yuta Uetake[1,2,3], Honoka Nakamura[1], Yabuki Rento[1], Taiyo Shimizu[3], Ken Kokubo[3], Sakurai Hidehiro[1,2]

Electrochemical synthesis is increasingly recognized as a clean and powerful method for organic synthesis. Meanwhile, the use of electrocatalyst having nanometals have not been investigated in the fields of organic synthesis. Gold nanoparticles were immobilized on a single-walled CNT (SG101) using $HAuCl_4$ and $NaBH_4$ to give a water dispersion of Au:SG101 (3.4±0.6 nm). An electrocatalyst paper was fabricated through several simple processes such as filtration, drying and pressing, affording Au:SG101 buckypaper. This was applied for an aerobic oxidation of benzyl alcohol under electrochemical conditions, yielding corresponding ketone.

Keywords : electrochemical synthesis; electrocatalysts; carbon nanotube; gold nanoparticle; aerobic oxidation

ナノサイズの金属微粒子で修飾された電極触媒は燃料電池分野で広く研究されているが、有機電解合成におけるその活用は限定的である[1,2]。本研究では、単層 CNT 固定化金ナノ粒子触媒を用いた電極触媒の作成と、アルコールの空気酸化反応における電極触媒の役割について検討した。単層 CNT として SG101（Zeonano®SG101）[3,4]を用い、$NaBH_4$ 還元を行うことで Au:SG101（particle size: 3.4 ± 0.6 nm）の水分散液を調製し、得られた分散液を濾過・乾燥・加圧成形することで Au:SG101 バッキーペーパーを作成した。作成した Au:SG101 ペーパーをカソードに用いてアルコールの空気酸化反応を行ったところ、0.4 V (Ag/AgCl)の電圧印加条件で反応が進行し対応するケトンが得られた。



1) S. Harwood, M. Palkowitz, C. Gannett, P. Perez, Z. Yao, L. Sun, H. Abruña, S. Anderson, P. Baran, *Science* **2022**, *375*, 745.
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Comparative study on the chemical regulation law systems of Korea and Japan: Focusing on registration of chemicals less than 1 ton

([1]*Graduate School of Engineering, Inha University*, [2]*Professor of Engineering, Inha University*) ○YoonJin Cho,[1] Youngwoo Chon[2]

Keywords: Registration and Evaluation, etc. of Chemicals, REACH

Since 1991, South Korea has regulated chemicals through the "Toxic Chemical Control Act" However, incidents such as the 2011 humidifier disinfectant tragedy and the 2012 Gumi hydrofluoric acid leakage accident prompted amendments to the legislation, resulting in the enactment of the "Chemical Substance Control Act" and the "Act on the Registration and Evaluation, etc. of Chemicals" in 2015. Similarly, Japan revised its Chemical Substances Control Law in alignment with the European Union's 'REACH' regulation in 2015, demonstrating a shared goal of stringent management to prevent accidents caused by hazardous chemicals.

Recently, there has been an active movement to differentiate registration application data for chemical substances with an annual manufacturing import volume of less than 1 ton depending on the characteristics and use. In particular, discussions are underway on easing the reporting exemption requirements for new chemical substances intended to be imported in quantities of less than 0.1 tons. These efforts are mainly aimed at lowering the burden on small quantities and chemical substances for research and development purposes, and to support small and medium-sized companies to more smoothly implement the "Act on the Registration and Evaluation, etc. of Chemicals"

Therefore, this research aims to conduct a comparative analysis of legal frameworks in Japan and South Korea, specifically focusing on the registration systems for chemicals with annual production or import quantities below 1 ton.

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生分解性プラスチックへの多環式芳香族炭化水素の吸着と生分解性に及ぼす影響

（産総研[1]）○日野 彰大[1]・山野 尚子[1]・川崎 典起[1]・中山 敦好[1]
Adsorption of polycyclic aromatic hydrocarbons(PAHs) on biodegradable plastics and its effect on biodegradability ([1]AIST) ○Shodai Hino[1], Naoko Yamano[1], Norioki Kawasaki[1], Atsuyoshi Nakayama[1]

Polycyclic aromatic hydrocarbons (PAHs) are released into the environment from vehicle exhaust and cigarette smoking and have also been detected in seawater. Plastics are expected to readily adsorb PAHs due to their relatively high hydrophobicity. We have reported that antimicrobial properties on biodegradable plastic surfaces can suppress biodegradability.[1] It has also been found that increasing the hydrophobicity of the surface also reduces biodegradability.[2] Therefore, there is concern that the toxicity and hydrophobicity of PAHs may reduce their biodegradability after surface adsorption. In this study, the effect of PAHs adsorption on biodegradability was investigated.
Keywords : Biodegradable plastic; Adsorption; Polycyclic aromatic hydrocarbons(PAHs)

多環式芳香族炭化水素（PAHs）は，自動車の排気ガスやタバコの喫煙などから環境中に放出されており，海水中でも検出されている。プラスチックは比較的疎水性が高いため，PAHs を容易に吸着すると予想される。当グループでは生分解性プラスチック表面に抗菌性を付与すると，生分解性を抑制できることを報告している[1)]。また，表面の疎水性が高まることでも生分解性が低下することが分かっている[2)]。したがって，PAHs が有する毒性や疎水性によって，表面吸着後に生分解性が低下することが懸念される。そこで本研究では，PAHs の吸着による生分解性に対する影響について検討したので報告する。

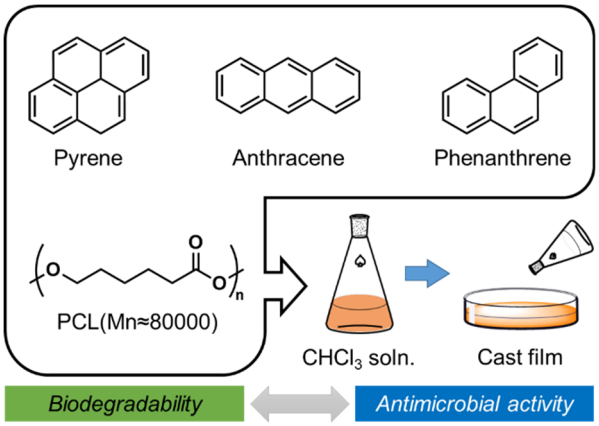

Fig. The schematic of experiment of this study.

謝辞：本研究は，JSPS 科研費(Grant No.22K18051)の支援によって得られた。

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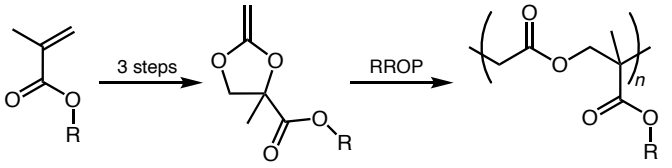
メタクリレートを出発原料に用いた側鎖にエステル基を有する脂肪族ポリエステルの合成

（同志社大理工[1]）○西村 慎之介[1]・金井 亮介[1]・古賀 智之[1]
Aliphatic Polyesters with Ester-Functionalized Side Chain Synthesized from Methacrylates ([1]*Faculty of Science and Engineering, Doshisha University*) ○Shin-nosuke Nishimura,[1] ○Ryosuke Kanai,[1] Tomoyuki Koga[1]

From the perspective of sustainable development goals (SDGs), development of biodegradable polyesters derived from biomass, replacing conventional polymers, is urgently needed. However, chemical structures of readily available biomass-derived monomers are limited; thefore, resultant polyesters have minimal variation in chemical structure, making it challenging to expand material properties and functionality. In this study, we focused on methacrylates (MAs) as a novel raw material for polyesters. MAs are known to be producible from biomass.[1)] However, poly(methacrylate) obtained through conventional vinyl polymerization of MAs is non-biodegradable. We converted MAs through a three-step reaction into five-membered cyclic ketene acetals (CKA-MAs) which are radical ring-opening polymerizable. Because of resonance stabilization of radicals generated by β-cleavage, polymerization of CKA-MAs underwent with 100% ring-opening efficiency, resulting in the aliphatic polyesters with ester-functionalized side chain with high molecular weights.
Keywords : Methacrylates; Aliphatic Polyesters; Cyclic Ketene Acetals; Radical Ring-Opening Polymerization; Biodegradable

持続可能な開発目標 (SDGs) の観点から、汎用高分子に置き換わるバイオマス由来の生分解性ポリエステルの開発が急務である。一方で、製造可能なバイオマス由来モノマーの構造が限られるため、得られるポリエステルの化学構造もバリエーションが少なく、材料特性や機能性の拡張が難しい。そこで本研究では、新たなポリエステルの原料としてメタクリレート (MAs) に着目した。MAs はバイオマスから製造できることが知られている[1)]。しかしながら、通常のビニル重合によって得られるポリメタクリレート (PMAs) は非生分解性である。本研究では、MAs を三段階の反応を経て 5 員環の環状ケテンアセタール (CKA-MAs) に変換し、ラジカル開環重合性のモノマーへと誘導した。CKA-MAs は β 開裂により生じるラジカルが共鳴安定化されるため、100%の開環率で重合が進行し、分子量が数万程度の側鎖にエステル基を有する脂肪族ポリエステルが得られることがわかった。



1) Single-Step Production of Bio-Based Methyl Methacrylate from Biomass-Derived Organic Acids Using Solid Catalyst Material for Cascade Decarboxylation–Esterification Reactions. A. Bohre, K. Avasthi, U. Novak, B. Likozar, *ACS Sustainable Chem. Eng.* **2021**, *9*, 2902.

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Hagfish 中間径フィラメントタンパク質の LLPS を介したバイオインスパイアードヒドロゲルの形成

(山形大学理学部[1]・山形大学大学院有機材料システム研究科有機材料システム専攻[2])
○小林 龍輝[1]・近藤 俊輔[2]・宮 瑾[2]・並河 英紀[1]

Formation of Bioinspired Hydrogels via LLPS of Hagfish Intermediate Filament Protein

([1]*Faculty of Science, Yamagata University*, [2]*Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University*) ○Ryuki Kobayashi,[1] Syunsuke Kondo,[2] Jin Gong,[2] Hideki Nabika[1]

Bioinspired materials inspired by the unique functions of living animals are useful. We focused on the defense function of Hagfish and investigated how intermediate filament protein (IF protein) in the exudate released in response to external stimuli are structured in vivo. We found that IF protein from Hagfish organisms has a low-complexity domain (LCD) and undergoes liquid-liquid phase separation (LLPS) in phosphate buffer solution in the presence of polymers and electrolytes that mimic the intracellular environment. Furthermore, hydrogelation was also observed, with loss of fluidity from a liquid-like state to a liquid-solid transition. We present the conditions for LLPS generation of IF protein and the properties of the hydrogels formed, with results that support the application of Hagfish IF protein to material development and a model of pathological aggregation associated with intracellular LLPS of proteins.

Keywords : Liquid-Liquid Phase Separation; Bioinspired Materials; Intermediate Filament Protein; Hydrogelation; Low Complexity Domain

生体が備える特徴的な機能から着想を得たバイオインスパイアード材料の開発は有用である。我々は Hagfish の生体防御機能に着目し、外的刺激に応答して放出される滲出液内に含まれる中間径フィラメントタンパク質 (IF protein) が細胞内においてどの様なメカニズムに従い構造化しているのかを解明し、生体由来線維タンパク質を用いた環境志向の材料開発へ向けた知見を得る事を目指した。

その結果、Hagfish 生体から抽出した IF protein は低複雑性領域 (LCD) を有している事が分かり、細胞内環境を模倣したポリマーや電解質が共存するリン酸緩衝液内において液-液相分離 (LLPS) を生じる事を発見した。更に、LCD を有する神経変性疾患原因タンパク質が関連する発病メカニズム[1)]として検討されている LLPS を介したヒドロゲル形成も確認された。我々は IF protein の LLPS 発生条件及び、形成されたゲルの性質を提示し、Hagfish IF protein を利用した材料開発への応用や、タンパク質の細胞内 LLPS が関連する病理学的凝集モデルを支持する結果を報告する。

1) Liquid-liquid Phase Separation of α-Synuclein: A New Mechanistic Insight for α-Synuclein Aggregation Associated with Parkinson's Disease Pathogenesis. Mukherjee, S.; Sakunthala, A.; Gadhe, L.; Poudyal, M.; Sawner, A. S.; Kadu, P.; Maji, S. K. *Journal of Molecular Biology.* **2023**, *435*, 167713.

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GlcN-GlcNAc 間グリコシド結合形成を触媒するキトサナーゼ活性部位の in silico 設計

（北大院地球環境科学 [1]・ライプニッツ植物科学研究所 [2]）○小島 摩利子 [1]・Mehdi Davari[2]・小野田 晃 [1]

In silico design of the active site of chitosanase catalyzing β-1,4-glycosylation between GlcN and GlcNAc ([1]*Faculty of Env. Earth Science, Hokkaido University*, [2]*Leibniz Institute of Plant Biochemistry*) ○Mariko Kojima,[1] Mehdi Davari,[2] Akira Onoda[1]

Engineering of glycohydrolytic enzymes to develop non-natural biosynthetic pathways of saccharides has attracted attention in the conversion of biomass and production of biopharmaceuticals.[1] Chitosan is a polysaccharide consisting of glucosamine (GlcN) and *N*-acetylglucosamine (GlcNAc), which is obtained from marine crustaceans, fungi, and bacteria (Fig. 1). Chitooligosaccharide, 2–20 mer of chitosan, has antibacterial activity defined by arrangements of GlcN and GlcNAc. Facile synthesis of chitooligosaccharide in which arrangements is precisely defined is challenging due to the random biodegradation by chitosanase.[2] In this study, we performed in silico design of the catalytic center of chitosanase that catalyzes non-natural β-1,4-glycosidic linkage between GlcN and GlcNAc to produce hetero-chitooligosaccharides. We computationally generated chitosanase variants with mutated residues in an active site and performed docking simulation to evaluate the specific binding with hetero-chitooligosaccharides.

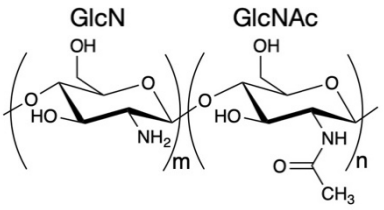

Fig. 1 Structure of chitosan.

Keywords: chitosanase, in silico design, molecular docking, glycosynthase

キトサンはグルコサミン（GlcN）と *N*-アセチルグルコサミン（GlcNAc）の β-1,4 結合により形成される多糖類であり、海洋生物の甲殻や細菌の細胞壁などから取得可能なバイオマス原料として注目されている。キトサンのオリゴマーであるキトオリゴ糖は、GlcN と GlcNAc の配列に依存した多様な抗菌作用を有するため、医薬品開発の観点からキトオリゴ糖への変換経路の開拓が求められている。キトサンの加水分解酵素であるキトサナーゼのエンジニアリングは、キトサンからキトオリゴ糖を得るために有効であるが、従来の加水分解反応では、配列が制御された均一なキトオリゴ糖を取得することは困難である。そこで本研究では、キトサナーゼの活性中心の in silico 改変により、ヘテロな GlcN–GlcNAc 結合を有するキトオリゴ糖に特異的な基質結合サイトを創出し、GlcN と GlcNAc のヘテロ糖転移反応を促進する糖転移型キトサナーゼの構築を目指す。本発表では、キトサナーゼの基質結合サイトに変異を導入した変異体モデルの構築し、ドッキングシミュレーションによりヘテロキトオリゴ糖に対する改変型キトサナーゼの結合特異性を評価したので報告する。

1) Y. Xu, *et al., Process Biochem.,* 2022. 2) I. Álvarez-Martínez, *et al., Chem. Eur. J.,* 2023.

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ソフトロボティクスへの応用に向けての高速有機結晶フォトアクチュエータの開発

(早大院先進理工[1]・早大ナノ・ライフ機構[2]) ○萩原 佑紀[1]・長谷部 翔大[1]・朝日 透[1,2]・小島 秀子[2]

Development of high-speed organic crystal photoactuators toward application to soft robotics

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*Research Organization for Nano & Life Innovation, Waseda University*) ○Yuki Hagiwara[1]・Shodai Hasebe[1]・Toru Asahi[1,2]・Hideko Koshima[2]

Mechanical organic crystals are expected to be applicable to soft robots[1]. However, their development has almost been limited to basic research in crystal chemistry, and there have been scarce engineering applications. Since 2020, we have discovered the high-speed crystal actuation by the photothermal effect[2–7] and the natural vibration,[8] and have developed a variety of high-speed mechanical organic crystals. By using the photothermal effect and the natural vibration, any crystal can actuate at high speed (milliseconds or microseconds). Moreover, actuation behavior and output properties can be designed by simulation based on thermal conduction and elastic vibration. Therefore, mechanical organic crystals are useful as a new type of actuator materials for practical applications.

Keywords : Mechanical crystals, Photothermal effect, Natural vibration, Soft robotics

光照射により動くメカニカル有機結晶はソフトロボットなどへの応用が期待されている[1]。しかしメカニカル有機結晶の開発は結晶化学的な基礎研究に留まっており、工学的に応用された例はほとんど見当たらない。我々は2020年以降、光熱効果[2–7]や固有振動[8]という、あらゆる材料で見られる現象で結晶が高速屈曲することを発見し、様々な高速メカニカル有機結晶を開発してきた。光熱効果や固有振動を用いることであらゆる結晶を高速(ミリ秒 or マイクロ秒)で動かすことができる。また動きや出力特性は熱伝導や弾性振動に基づくシミュレーションにより設計できる。このため有機結晶を新しいアクチュエータ材料として扱えるようになり、メカニカル有機結晶の研究は実際の応用段階に達した。

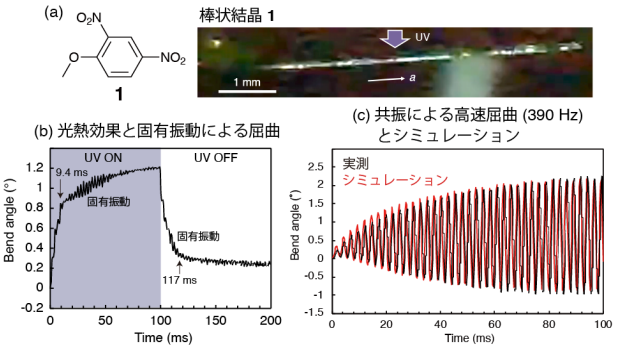

図 1. アニソール(**1**)結晶の光熱効果と固有振動による高速屈曲とシミュレーション[8]

1) *Mechanically Responsive Materials for Soft Robotics,* H. Koshima Ed., Wiley-VCH, Weinheim, **2020**. 2) Y. Hagiwara, T. Taniguchi, T. Asahi, H. Koshima, *J. Mater. Chem. C* **2020**, *8*, 4876–4884. 3) S. Hasebe, Y. Hagiwara, J. Komiya, M. Ryu, H. Fujisawa, J. Morikawa, T. Katayama, D. Yamanaka, A. Furube, H. Sato, T. Asahi, H. Koshima, *J. Am. Chem. Soc.* **2021**, *143*, 8866–8877. 4) S. Hasebe, Y. Hagiwara, K. Takechi, T. Katayama, A. Furube, T. Asahi, H. Koshima, *Chem. Mater.*, **2022**, *34*, 1315–1324. 5) S. Hasebe, Y. Hagiwara, K. Hirata, T. Asahi, H. Koshima, *Mater. Adv.*, **2022**, *3*, 7098–7106. 6) D. W. Kim, Y. Hagiwara, S. Hasebe, N. O. Dogan, M. Zhang, T. Asahi, H. Koshima, M. Sitti, *Adv. Funct. Mater.*, **2023**, *33*, 2305916. 7) S. Hasebe, Y. Hagiwara, T. Ueno, T. Asahi, H. Koshima, *Chem. Sci.*, **2024**, DOI: 10.1039/D3SC04796B. 8) Y. Hagiwara, S. Hasebe, H. Fujisawa, J. Morikawa, T. Asahi, H. Koshima, *Nat. Commun.*, **2023**, *14*, 1354.

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樹脂中における微量の CWO®粒子の解析

（住友金属鉱山株式会社 [1]）○藤本 宰平 [1]・小野 勝史 [1]・矢野 正樹 [1]・森本 健寿 [1]・橋本 直樹 [1]

Analysis of micro amount of CWO® particles in resin

([1]*Sumitomo Metal Mining Co., Ltd.*)
○Saihei Fujimoto,[1] Katsushi Ono,[1] Masaki Yano,[1] Takehide Morimoto,[1] Naoki Hashimoto[1]

Cesium tungstate (CWO®) has a hexagonal crystal structure with a composition of $Cs_{0.3}WO_3$ and has excellent near-infrared absorption (NIR), so it is used as a heat ray shielding material containing fine particles of CWO® in a resin. It is important to maintain the crystal structure of CWO® particles in the resin, which affects the NIR characteristics, but if the target particles in the resin are in trace amounts, it is difficult to analyze the crystal structure without pretreatment. Therefore, we established a method to separate and concentrate CWO® particles from the resin and analyze the crystal structure. As shown in Figure 1, particles with a $Cs_{0.3}WO_3$ composition of about several tens of nanometers in diameter were observed in the resin concentrate, and their electron diffraction pattern revealed that they were hexagonal CWO® particles.

Keywords : separation and concentration

タングステン酸セシウム（CWO®）は、$Cs_{0.3}WO_3$ 組成の六方晶構造であり、優れた近赤外線吸収（NIR）を有することから、その微粒子を樹脂に含有した熱線遮蔽材として応用されている。NIR 特性に影響する CWO®粒子の樹脂中での結晶構造の保持が重要であり、これに伴って当該粒子の結晶構造の解析を試みた。しかし、樹脂中に含有する数百 ppm レベルの微量の目的粒子を前処理なしで解析することは困難であった。そこで我々は、当該樹脂から CWO®粒子を分離濃縮して結晶構造を解析する分析技術を確立した。

分離濃縮は、当該樹脂を有機溶剤で溶解して遠心分離した後、デカンテーションした。引き続き、沈殿物中の残留溶剤を風乾したものを XRD で分析し、六方晶の化合物が沈殿物中に濃縮されていることを確認した。このため、TEM で組成と結晶構造を詳細に解析した。図 1 に結果を示す。粒径数十 nm 程度の $Cs_{0.3}WO_3$ 組成の粒子が観察され、その電子回折図形から、六方晶の CWO®粒子であることが明らかになった。

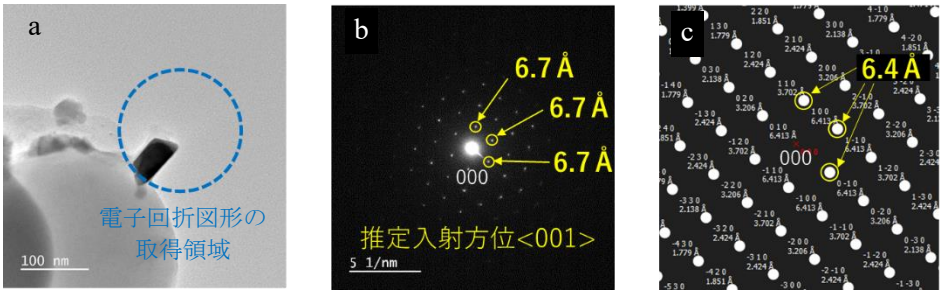

図 1　TEM 分析結果　(a)濃縮物中の CWO®粒子の TEM 像、(b)濃縮物中の CWO®粒子の電子回折図形、(c) $Cs_{0.3}(WO_3)$の入射方位[001]の電子回折シミュレーション図形 [1)]

1) Seto, Y. and Ohtsuka, M. (2022). *J. Appl. Cryst*. 55, 397-410.

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Au アノード溶解における電解質の影響

（防衛大機能材料）○小澤 真一郎・北郷 萌・山川莉輝・岡本 庸一
Effect of Electrolyte on Au Anode Dissolution Reaction (*Department of Materials Science and Engineering, National Defense Academy*) ○Shinichiro Ozawa, Moe Hokugo, Riki Yamakawa, Yoichi Okamoto

The electrolyte solution dissolving inorganic salts (Na_2SiO_3, Na_2CO_3, Na_2SO_3, etc.) was filled into a beaker with electrodes of the same material (Au, Ag, Si, etc.) as anode and cathode, and 2 A and 10 to 30 V were applied between the electrodes for a few hours.) Au nanoparticles generated by the liquid current method have the potential to be applied as useful nanomaterials in various fields if the particle size can be controlled. In this study, the effect of electrolyte on the anodic dissolution reaction of Au was investigated by electrochemical methods, UV-visible spectroscopy, and X-ray diffraction. Typical cyclic voltammograms using NaCl electrolyte solution are shown in Fig. 1. the oxidation peak current increased with increasing NaCl concentration. In the present study, we report on the effects of varying the electrolyte type (cation and anion species) and solution concentration on Au anode dissolution.
Keywords : Au anode dissolution; Electrochemical methods; Electrolyte; Nanoparticles; Electric current application

電解質として無機塩（Na_2SiO_3, Na_2CO_3, Na_2SO_4 など）を溶解した電解質溶液を、同じ材料(Au, Ag, Si など)の電極を陽極と陰極としたビーカーに充填し、電極間に 2 A、10 ～ 30 V 印加し、数時間通電したところ、電極材料に由来するナノ粒子生成を確認し報告した [1)]。この液中通電法による金属ナノ粒子の生成過程は、「H_2O の電気分解」、「電極材料のイオン化」、「生成した金属イオンの再還元による粒子成長」の 3 つの反応（いずれか 1 つの反応が律速）が同時に進行すると考えられる。液中通電法で生成する Au ナノ粒子は、粒子径を制御することができれば、様々な分野で有用なナノ材料として応用できる可能性がある。本研究では、Au のアノード溶解反応における電解質の影響について、電気化学的手法、紫外可視分光法、X 線回折法により調査した。NaCl 電解質溶液を用いたサイクリックボルタングラムを Fig. 1 に示す。NaCl 濃度の増加に伴い、酸化ピーク電流の増加（Au の溶解）を確認した。今回、電解質の種類（カチオンおよびアニオン種）、溶液濃度を変化させ、Au アノード溶解にどのような影響を及ぼすかを報告する。

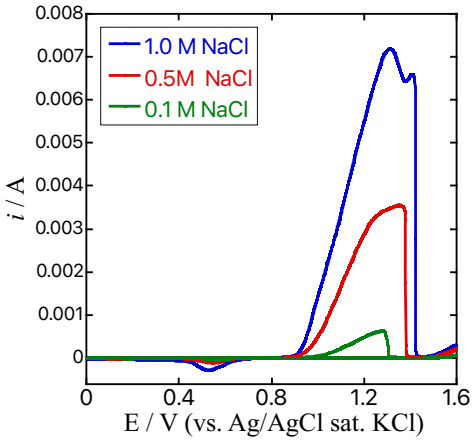

Fig.1 Typical cyclic voltammograms of NaCl electrolyte solutions.

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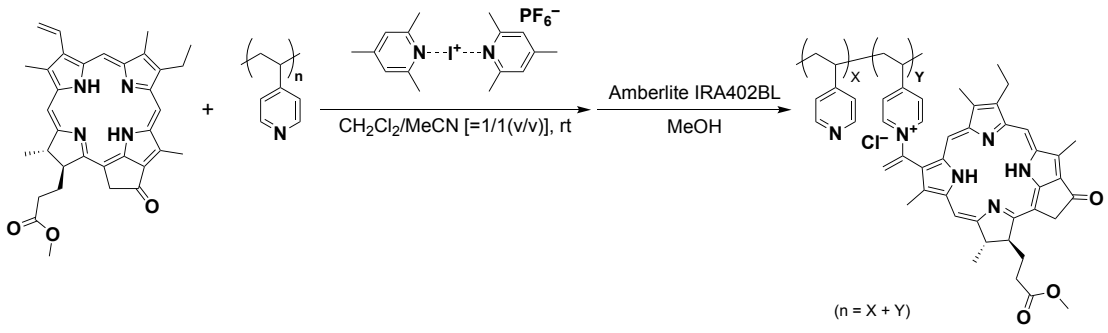
ピリジン残基を有するポリマーへのカチオン性クロロフィル誘導体の修飾とその物性

（立命館大院生命科学）○小笠原　伸・丸本　洋明・民秋　均
Modification of cationic chlorophyll derivatives to polymers containing pyridine residues and their physical properties (*Graduate School of Life Sciences, Ritsumeikan University*) ○Shin Ogasawara, Hiroaki Marumoto, Hitoshi Tamiaki

Chlorophyll(Chl)-*a* plays key roles (light harvesting antenna, energy/electron migration, and charge separation) in the primary step of the photosynthesis in living organs, and is one of the most widely distributed natural pigments. Because of its unique optical properties, so many Chl-*a* derivatives have been synthesized and investigated their optical changings. Although most of the Chl-*a* derivatives are neutral, some of them possess cationic moieties to apply photodynamic therapeutic agents for tumors or antibacterial materials. We previously reported synthesis of cationic Chl-*a* derivatives by using oxidative addition reaction to *N*-containing heteroarenes. Here a cationic chlorophyll derivative was appended via C–N^+ bonding to poly(4-vinylpyridine). On one hand, the cationic Chl-*a* derivatives were immobilized on the surface of a porous polymer containing pyridine moieties. These polymers were characterized by mainly spectroscopic techniques.
Keywords : Chlorophyll; Poly(4-vinylpyridine); Porous polymer

光線力学療法に用いるガン治療薬や抗菌材料への利用を目的として、天然のクロロフィル(Chl)-*a* のカチオン性誘導体の合成がこれまでに検討されてきた。我々は以前に酸化的付加反応によって、含窒素ヘテロ芳香環に対して Chl-*a* 誘導体を作用させることで、一段階で C–N^+結合を形成することを報告した [1), 2)]。今回同様の反応でポリ(4-ビニルピリジン)に Chl-*a* 誘導体を付加することに成功し（下のスキーム参照)、ビニルピリジンを含む不溶性の多孔質ポリマーへも同様に Chl-*a* 誘導体が付加できることを見出した。今回、それらの調製法の詳細と、種々の分析を合わせて報告する。



1) T. Takahashi, S. Ogasawara, S. Echizen, Y. Shinozaki, H. Tamiaki, *Org. Biomol. Chem.* **2019**, *17*, 5490.
2) Y. Takarada, S. Ogasawara, H. Tamiaki, *Results Chem.* **2023**, *5*, 100862.

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高分子修飾を指向した半導体光触媒と水による炭素–水素結合の官能基化反応

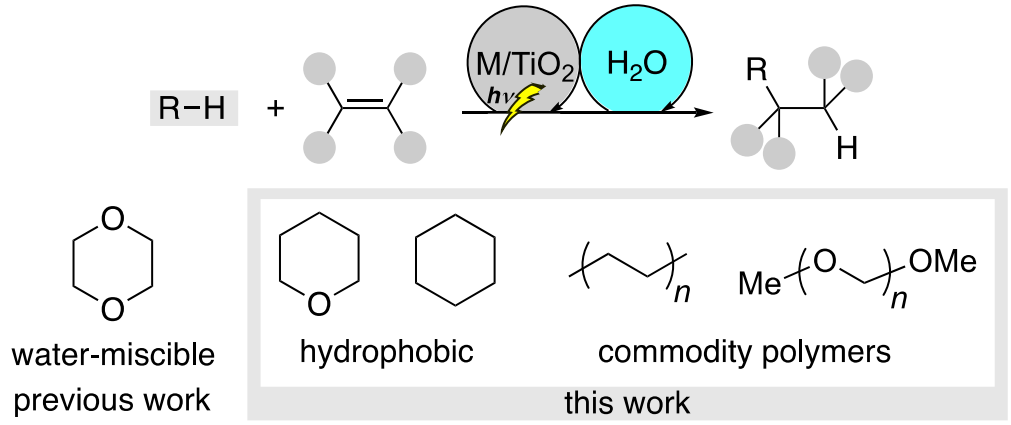
（名大理[1]・名大 IRCCS[2]・名大院工[3]・名大院理[4]）○酒井 裕司[1]・森 彰吾[2]・内山 峰人[3]・上垣外 正己[3]・斎藤 進[2,4]

C(sp^3)–H bond functionalization promoted by a semiconductor photocatalyst and water aiming at polymer modification ([1]*Sch. Sci., Nagoya Univ.*, [2]*IRCCS, Nagoya Univ.*, [3]*Grad. Sch. Eng., Nagoya Univ.*, [4]*Grad. Sch. Sci., Nagoya Univ.*) ○ Yuji Sakai,[1] Shogo Mori,[2] Mineto Uchiyama,[3] Masami Kamigaito,[3] Susumu Saito[2,4]

The development of environmentally friendly C(sp^3)–H bond functionalization will contribute to the sustainable production of organic materials. Our group reported alkylation of C(sp^3)–H bonds of water-miscible organic molecules with C=C double bonds of alkenes using a metal-loaded titanium dioxide (M/TiO_2) semiconductor photocatalyst and water without producing stoichiometric by-products.[1] In this work, we optimized the water-organic mixed solvent systems and broadened the substrate scope to rather hydrophobic organic molecules. Furthermore, we explored new functional materials derived from polyethylene glycol and polyethylene as starting materials aiming at upcycling these commodity polymers.[2]

Keywords : semiconductor photocatalyst; water; C(sp^3)–H bond functionalization; polymer modification

環境負荷低減型の炭素－水素結合の官能基化反応の開発は持続可能な物質生産に貢献する。当研究室ではこれまでに近紫外光照射下で金属担持酸化チタン (M/TiO_2) 半導体光触媒と水を併せ用いることで水に混和性の有機小分子の炭素－水素結合のアルケンによるアルキル化反応を実現した。[1] 本研究では水-有機の混合溶媒系を最適化することで基質適用範囲を比較的疎水性の有機小分子にまで拡大した。さらに汎用高分子のアップサイクリングを指向し、[2] ポリエチレングリコールやポリエチレンを出発物質に用いる新しい機能性材料の開発にも取り組んだ。



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液晶性有機半導体薄膜の結晶成長にポストアニールが及ぼす影響

（京大　化研[1]）○岡 昂徹[1]・塩谷 暢貴[1]・森 泰蔵[1]・長谷川 健[1]
Influence of Post Annealing on Crystal Growth in Liquid Crystalline Organic Semiconductor Thin Films. ([1] *Kyoto Univ. ICR.*) ○Takayuki Oka,[1] Nobutaka Shioya,[1] Taizo Mori,[1] Takeshi Hasegawa[1]

Ph-BTBT-C$_n$ has excellent performances as a p-type semiconductor for organic thin-film transistors, and its performances are enhanced by thermal annealing. We have revealed the effect of post annealing on the molecular aggregation structure in Ph-BTBT-C$_n$ thin films by a combination of X-ray diffraction and infrared spectroscopy.
Keywords : Liquid Crystalline Organic Semiconductors; Infrared Spectroscopy; X-ray Diffraction; Spin Coating

低分子有機半導体材料は, 有機物の軽量かつ柔軟な性質を利用したフレキシブルデバイスへの応用や, 溶液プロセスによる大面積加工の産業的価値の観点から注目を集めている. 特に, 2-decyl-7-phenyl[1]benzothieno[3,2-b][1]benzothiophene（Ph-BTBT-C$_{10}$; 図1）は, 有機薄膜トランジスタのp型半導体材料として大きな注目を集めている[1]. この化合物の薄膜は熱アニールによって電荷輸送特性が大幅に向上するため[1], その構造-物性相関を調べることは重要である. これまでの研究によると, 熱アニールに伴い“薄膜相”と呼ばれる薄膜に特有の結晶構造から単結晶と同じ構造である“バルク相”へと変化することが調べられている[1]. 加えて, 熱アニールの温度や室温までの冷却速度に依存して, 形成されるバルク相の分子パッキングに乱れが生じることがX線回折法（XRD）から調べられている[2]. このような分子パッキングの乱れは薄膜中の電荷輸送を阻害するため, この分子パッキングの乱れが生じる原因を解明することは重要である. 本研究では, 赤外分光法を用いて温度変化に敏感なアルキル側鎖に注目して構造解析を行い, Ph-BTBT-C$_{10}$の薄膜中で生じる分子パッキングの乱れの原因を解明し, 高品質な薄膜を得るための最適なアニール条件を明らかにする.

スピンコート法により製膜したPh-BTBT-C$_{10}$薄膜の構造を, XRDおよび赤外分光法を用いて調べた. その結果, 乱れた分子パッキングを有する薄膜においては, アルキル側鎖のコンフォメーションも一部乱れていることが明らかになった. つまり, 加熱により部分的に溶融したアルキル側鎖が分子の結晶化を阻害していることが示唆される. 発表では, アルキル鎖長やアニール温度, 冷却速度が薄膜構造に与える影響も議論し, 最適なアニール条件を検討する.

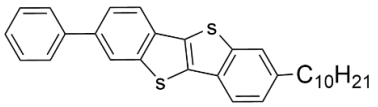

図 1　Ph-BTBT-C$_{10}$の化学構造

1) Iino, H.; et al. *Nat. Commun.* **2015**, *6*, 6828.
2) Hofer, S.; et al. *Chem. Mater.* **2021**, *33*, 1455.

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電子求引性トリアジン誘導体の開発と近赤外 2 光子応答性 TADF 発光材料への応用

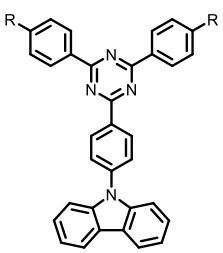
（九大院工[1]・九大 CMS[2]・九大 OPERA[3]・WPI-I2CNER[4]）○千歳 洋平[1,2,3]・土屋 陽一[3]・安達 千波矢[1,3,4]

Development of Triazine Derivatives Bearing Electron-Withdrawing Substituent and Their Application to TADF Emitter with Near-Infrared Two-Photon Absorption Character

([1]*Graduate School of Engineering, Kyushu University*, [2]*CMS, Kyushu University*, [3]*OPERA, Kyushu University*, [4]WPI-I2CNER) ○ Youhei Chitose,[1,2,3] Youichi Tsuchiya,[3] Chihaya Adachi,[1,3,4]

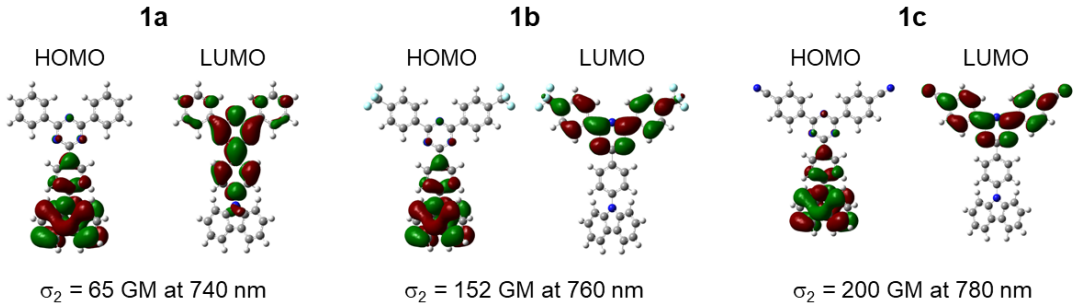
Luminescent materials that exhibit thermally-activated delayed fluorescence (TADF) are useful as imaging dyes that can improve the S/N ratio affected by the cell-derived autofluorescence. TADF materials with near-infrared two-photon absorption character will enable the bio-imaging at the deeper part of cellular tissues. In this study, we developed novel Cz-TRZ derivatives by introducing electron-withdrawing groups into the conventional 2,4-diphenyl-1,3,5-triazine (TRZ) unit, which increased the ratio of photoluminescence quantum yield of delayed fluorescence and two-photon absorption (TPA) cross-section (σ_2).

Keywords : Thermally Activated Delayed fluorescence; Two-Photon Absorption; Triazine



1a : R = H
1b : R = CF_3
1c : R = CN

熱活性化遅延蛍光(TADF)[1)]を有する発光材料は、従来の蛍光材料よりも長寿命発光を示すため、細胞由来の自家蛍光の影響を低減できるイメージング色素として有用である。近赤外領域に 2 光子吸収能を有する TADF 分子を開発することができれば、細胞深部におけるイメージングが可能となる。本研究では、従来のジフェニルトリアジン骨格に電子求引基を導入した Cz-TRZ 誘導体を開発し、遅延発光成分の量子収率の増大と 2 光子吸収能の向上に成功した。



1) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature*, **2012**, *492*, 234-238.

Acknowledgement

This work was supported by Tokuyama Science Foundation and Kyushu University Q-PIT Support Program for Young Researchers and Doctoral Students.

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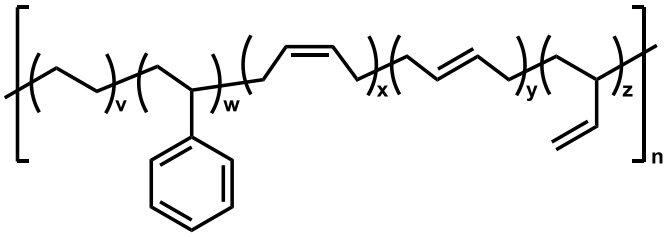
サステナブル材料としての新規エチレン系熱可塑性エラストマー

（株式会社ブリヂストン）○高野 重永・黒岩 智佳子・石上 淳一・鎌田 智子・会田 昭二郎
Novel Ethylene-based Polymers as Sustainable Elastomers (*Bridgestone Corporation*) ○ Shigenaga Takano, Chikako Kuroiwa, Jyunichi Ishigami, Tomoko Kamata, Shojiro Kaita

Bridgestone is developing a new TPE, Ethylene/Styrene/Butadiene terpolymer (ESB), as part of new materials with sustainability and circular economy. It is possible to control the main chain and higher-order structures, and as a result, various physical properties of elastomer materials can be controlled. The precisely controlled structure not only exhibits high specific strength, but also exhibits excellent properties such as self-healing and polymer degradation.
Keywords : Sustainability; Circular Economy; Thermoplastic Elastomer; Ethylene/Styrene/Butadiene; Terpolymer

化学産業におけるカーボンニュートラル化においては、資源の効率的・循環的な利用が強く求められる。その中で、化学品では需要の多いオレフィン等の基礎化学品を多目的に活用することは最も効果的な施策の一つとなりえる。ブリヂストンではサステナビリティおよびサーキュラーエコノミーを念頭においた新素材開発の一環としてエチレンを主骨格とした新規熱可塑性エラストマー（Thermoplastic Elastomer: TPE）：エチレン/スチレン/ブタジエン３元共重合体（ESB）の開発を進めている（Scheme 1）[1)2)]。TPE は非架橋でもゴムのような粘弾性を示すプラスチック材料の一つであり、省資源・省エネルギーの観点で優れたソフトマテリアルとなる。

ESB の一次構造（ポリマー組成、モノマー配列、ブタジエンユニットのミクロ構造など）は、各モノマーの仕込み比や反応条件、使用する触媒などを適切に選択することにより任意に制御することができる。これらの一次構造制御はポリマーの高次構造を精密に制御する技術につながり、その結果 ESB の材料特性（機械的強度、自己修復性、解重合性など）を大きく変化させることが可能になるなど、新素材開発における新たな分子設計指針を示すものとなった。



Scheme 1. エチレン/スチレン/ブタジエン３元共重合体（ESB）

1) 大石：特許第 6657082 号（2020）
2) 高野・柳澤・タルディフ・堀川：特許第 7155112 号 (2022)

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Verification of the required ventilation volume to prevent fire and explosion accidents in the case of a inflammable liquid leak using Computational Fluid Dynamics (CFD) program.

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Keywords: *InFlammable liquid, Fire and explosion, Required ventilation volume, CFD*

According to the 2023 hazardous materials statistics released by the the South Korean National Fire Agency, examining the trends over the past five years, the number of hazardous material accidents has shown a gradual decrease since 2018. However, in 2022, there was a notable increase of 21% compared to the previous year, with a recorded total of 80 incidents. Among the accidents in 2022, 61% were related to fire and explosions, and accidents involving inflammable liquids accounted for 74% of the total accidents.

Accidents involving inflammable liquids leading to fire or explosions often occur when leaked inflammable liquids generate gas or vapor through turbulent mixing in the atmosphere, forming an explosive atmosphere. This can be initiated by ignition sources such as static electricity. To prevent accidents, it is essential to remove the vapor generated after a leak and utilize ventilation systems to eliminate the vapor.

in this study, The analysis of fire and explosion incidents caused by inflammable liquids in South Korea in 2022 resulted in the selection of a total of seven types of materials. Accident scenarios for these seven materials were assumed, and based on 『KOSHA GUIDE P-91-2023』 leakage amounts and the time taken to reach the LEL(Lower Explosion Limit) were calculated. The material that reached the LEL in the shortest time was chosen for further analysis. In addition, according to 『KOSHA GUIDE W-1-2019』, the required ventilation amount of the ventilation system according to the leakage of the target material and the full ventilation equipment and local ventilation equipment that satisfy the relevant conditions were set and visualized in 3D. This was simulated by applying CFD (Computational Fluid Dynamics). Through this, we aim to observe changes in fluid flow over time and examine the ventilation effectiveness of full ventilation equipment and local ventilation equipment.

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ムール貝模倣温度応答性可変接着ハイドロゲル

（東北大学際研[1]・東北大院工[2]）○阿部博弥[1,2]、吉原大智[2]、照月大悟[2]、西澤松彦[2]
Thermo-switchable adhesive hydrogel inspired by mussel ([1]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University*, [2]*Graduate School of Engineering, Tohoku University*) ○Hiroya Abe[1,2], Daichi Yoshihara[2], Daigo Terutsuki[2], Matsuhiko Nishizawa[2]

On-demand underwater adhesives with remarkable adhesive and gentle detachment properties allow for a stable connection to various biomedical devices and bio-interfaces and avoid posing a significant risk of inflicting deleterious tissue damage upon detachment. Herein, we developed a hydrogel adhesive that can reversibly switch adhesion strength by temperature using thermo-responsive polymer and mussel-inspired molecules. The thermo-switchable adhesive hydrogel displayed both strong adhesion and gentle detachment with over a 1,000-fold gap in underwater adhesion strength onto a glass, Ti, Al, and Teflon substrate when exposed to temperatures above and below the lower critical solution temperature (LCST). In addition, the electrode-integrated hydrogel was maintained on the human skin and electrical signals were monitored continuously over 10 minutes above the LCST. In contrast, commercially available hydrogel electrodes quickly swelled and detached from the skin. The thermo-switchability of the bio-inspired hydrogel with robust adhesion and gentle detachment offers significant potential for biomedical applications characterized by minimally invasive procedures.
Keywords : Hydrogel, Underwater adhesion, Biomimetics

優れた接着性とマイルドな剥離性を有する水中接着剤は、様々な生体医療機器や生体界面への安定した固定を可能にし、剥離時に有害な組織損傷を与える重大なリスクを回避できる。本研究では、熱応答性ポリマーとカテコール基含有分子を用いて、温度によって接着性を可逆的に切り替えられるハイドロゲル接着剤を開発した。カテコール基はムール貝が持つ接着性分子として知られ、湿潤環境下でもさまざまな基板に接着することが可能である。本熱応答性接着ハイドロゲルは、ドーパミンが有する自己酸化重合特性を利用し、気液界面上で合成された[1)]。本ハイドロゲルは体温付近で下限臨界溶液温度（LCST）を有し、LCST を超える温度に曝されると、LCST 以下の接着性に比べガラス、チタン、アルミニウム、テフロン基板への水中接着強度に 1,000 倍以上の接着性が向上し、温度変化によって強力な接着性と穏やかな剥離性を制御できることを確認された。さらに、電極と包埋した本ハイドロゲルをヒトの皮膚上に設置することで、LCST 以上の温度で 10 分間にわたり電気信号を連続的に計測できることを確認した。対照的に、市販のハイドロゲル電極はすぐに膨潤し、皮膚から剥離した。本ハイドロゲルが有する温度切替可能な接着・剥離性を持つ水中接着剤は、低侵襲条件が必要な医工学分野への応用が期待できる。

1) “Bio-inspired Incrustation Interfacial Polymerization of Dopamine and Cross-linking with Gelatin toward Robust, Biodegradable Three-Dimensional Hydrogels” H. Abe *et al*., *Langmuir* **2021**, *37(20)*, 6201–6207.

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植物性多糖類の皮膚バリア機能への作用

（協和ファーマケミカル（株））○杉田　愛・竹内　祐希
Effects of plant polysaccharides on skin barrier function (*KYOWA PHARMA CHEMICAL CO., LTD.*) ○Ai Sugita, Yuki Takeuchi

Plant polysaccharides, which have recently been attracting attention in pharmaceutical and cosmetic fields, are known to possess various physiological effects[1]. This time, we report discovering a new effect on skin barrier function.

Polysaccharides (plant polysaccharide A and plant polysaccharide B) were prepared from residual portions of plant food products (A and B). Their efficacies were evaluated using a human 3-D cultured epidermis skin irritation model (Fig. 1). After 24 hours of applying the polysaccharide solution to the model, the amount of stratum corneum moisture content and the expression of proteins related to skin barrier function were measured. The data showed higher stratum corneum moisture content and expression of proteins related to skin barrier function compared to the control applying water. Plant polysaccharide-A showed the effect when it was applied before the addition of the barrier function-impairing substance, and plant polysaccharide-B showed the effect when it was applied after the addition of the barrier function-impairing substance. Therefore, plant polysaccharide-A is expected to prevent rough skin and plant polysaccharide-B is expected to promote healing of rough skin.
Keywords : Polysaccharide; Plant; Skin barrier function; Rough skin; Cosmetics

近年医薬・香粧品の分野で注目される植物性多糖類は、様々な生理作用を有することが知られている [1]。今回、皮膚バリア機能への新たな作用を見出したので報告する。

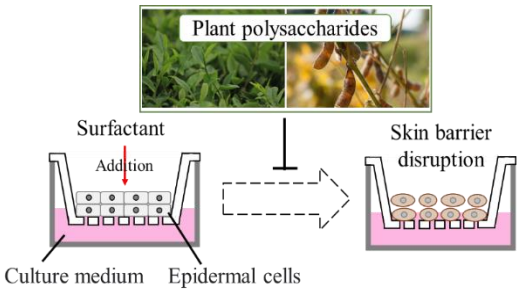

Fig. 1

2 種（A、B）の植物性食品の未利用部分より、それぞれ多糖類（植物多糖 A、植物多糖 B）を調製し、これらをヒト三次元培養表皮の肌荒れモデルを用いて効能を評価した(Fig. 1)。モデルに多糖類水溶液を塗布後、24 時間時点の角質水分量、および皮膚バリア機能関連タンパク質の発現量を測定した。結果、水のみを塗布したモデルと比較し、角質水分量、および皮膚バリア機能関連タンパク質の発現量が高くなった。植物多糖 A はバリア機能低下物質添加前、植物多糖 B はバリア機能低下物質添加後に塗布した場合に作用を示した。したがって、植物多糖 A は肌荒れ予防効果、植物多糖 B は荒れ肌治癒促進効果が期待できる。

1)　Y. Yu, M. Shen, Q. Song, J. Xie, *Carbohydr Polym,* **2018**, *183,* 91.

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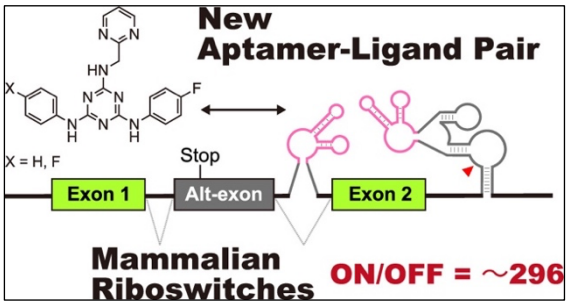
低分子化合物に結合する RNA アプタマーを用いた動物細胞機能の制御

(沖縄科学技術大学院大[1]・アステラス製薬[2]・(現所属)東工大[3]・(現所属)マサチューセッツ工科大[4]) ○福永 圭佑[1,3]・Dhamodharan Venugopal[1]・宮平 奈央[1]・野村 陽子[1]・Kamila Mustafina[1,4]・大住 康晃[2]・高山 耕輔[2]・金井 章[2]・横林 洋平[1]

Small-Molecule Aptamer for Regulating RNA Functions in Mammalian Cells and Animals
([1]*Nucleic Acid and Chemistry Engineering Unit, OIST*, [2]*Astellas Pharma Inc.*, [3]*Present affiliation: Earth-Life Science Institute, Tokyo Tech.*, [4]*Present affiliation: Department of Biological Engineering, MIT*) ○ Keisuke Fukunaga,[1,3] Dhamodharan Venugopal,[1] Nao Miyahira,[1] Yoko Nomura,[1] Mustafina Kamila,[1,4] Yasuaki Oosumi,[2] Kosuke Takayama,[2] Akira Kanai,[2] Yohei Yokobayashi[1]

We conducted *in vitro* selection of RNA aptamers against a small molecule ASP7967, a derivative of known inhibitor of KCNH3 (ASP2905). One of the selected aptamers was found to be functional in HEK293 cells, and it was used to design aptazyme-based riboswitches that can activate gene expression in the presence of the cognate ligand. An aptazyme-based riboswitch was successfully used to regulate gene expression in mice injected with AAV8 vector using orally administered ASP7967. Furthermore, by combining aptazyme-based and exon-skipping riboswitch mechanisms, an ON/OFF ratio approaching 300 was achieved with a low basal expression level in cultured cells.
Keywords : RNA Aptamer; Riboswitch; Gene Expression Control; SELEX, Small Molecule Ligand

SELEX 法を用いて低分子化合物 ASP7967 及び ASP2905 に結合する新規 RNA アプタマーを取得することに成功した[1]。また、これら化合物に応答する遺伝子発現制御デバイス（リボスイッチ）の開発を行い、哺乳動物細胞株 HEK293 及びマウスにおいて遺伝子発現制御を行うことに成功した。二つのリボスイッチ機構（アプタザイム・エクソンスキップ）を組み合わせることで ON/OFF 比 296 を実現している。また、既存のリボスイッチでは mM オーダーのリガンドが必要とされていたが[2]、AS7967／ASP2905 応答リボスイッチでは細胞に対して 5 μM の濃度で作用することが特徴である。今後、バイオ医薬品生産や遺伝子治療、細胞治療などに本遺伝子発現制御デバイスが活用されることが期待される。



1) K. Fukunaga, V. Dhamodharan, N. Miyahira, Y. Nomura, K. Mustafina, Y. Osumi, K. Takayama, A. Kanai, Y. Yokobayashi, *J. Am. Chem. Soc.* **2023**, *145*, 7820.
2) K. Mustafina, K. Fukunaga, Y. Yokobayashi, *ACS Synth. Biol.* **2020**, *9*, 19.

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水界面における星形ポリマーの分子構造と生体適合性

(鹿児島大院理工[1]・奈良先端大院物質[2]) ○戸谷 匡康[1,2]・網代 広治[2]・門川 淳一[1]・安藤 剛[2]・谷原 正夫[2]

Molecular structure and biocompatibility of star polymer at the water interface ([1]*Graduate School of Science and Engineering, Kagoshima University*, [2]*Division of Materials Science, Nara Institute of Science and Technology.* ○Masayasu Totani[1,2], Hiroharu Ajiro[2], Jun-ichi Kadokawa[1], Tsuyoshi Ando[2] and Masao Tanihara[2]

The star polymer-coated surface having a high density poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(methyl methacrylate) (PMMA) is believed to form a highly dense polymer brush-like architecture and inhibit biofouling (Fig. 1a)[1]. In this study, the surface properties of the star polymer coating were evaluated by their resistance to protein adsorption and their surface zeta (ζ)-potential to clarify the mechanism behind this inhibition of cell adhesion. The surface of the star polymer coating formed an electrically neutral diffused brush structure in water, and showed high resistance to protein adsorption. Considering all the data obtained in the study, the surface ζ-potential and anti-biofouling properties showed a correlation by controlling the molecular architecture of the coating material (Fig. 1b).

Keywords : star polymer; Molecular structure; Living polymerization; polymer/water interface

高密度のポリ(2-ヒドロキシエチルメタクリレート)(PHEMA)およびポリ(メチルメタクリレート)(PMMA)を有する星形ポリマーコート表面は、ポリマーブラシ構造を形成し、バイオファウリングが抑制されることを見出してきた(Fig. 1a)[1]。本研究では、星形ポリマーコート表面のタンパク質吸着量と表面ゼータ(ζ)電位測定を評価し、種々の細胞接着の抑制メカニズムを考察した。星形ポリマーコート表面は、水中で電気的に中性の拡散ブラシ構造を形成し、高いタンパク質吸着抑制することが示唆された。本研究で得られたデータを考慮すると、表面ζ電位と抗バイオファウリング特性は相関関係にあり、コーティング材料の分子構造を制御することにより抗バイオファウリングを示す高分子/水界面の構築が可能であることを明らかにした(Fig. 1b)。

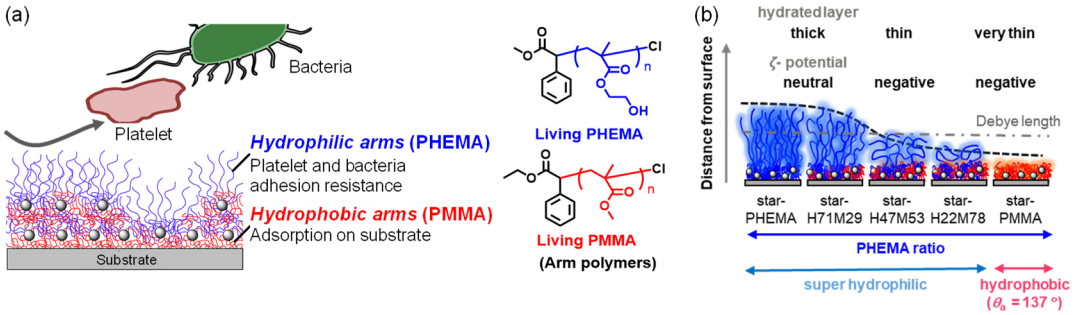

Figure 1. (a) Structure of PHEMA/PMMA heteroarm star polymer and schematic image of star polymer coatings. (b) Hypothetical illustration of correlation with the hydrated diffuse layer and ζ-potential on star polymer coatings.

1) Utilization of star-shaped polymer architecture in the creation of high-density polymer brush coatings for the prevention of platelet and bacteria adhesion. M. Totani, T. Ando, K. Terada, T. Terashima, IY. Kim, C. Ohtsuki, C Xi, K. Kuroda, M. Tanihara. *Biomater Sci.* **2014**, 2, 1172.

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ウイルスなどの巨大生体高分子の高効率封入・無毒化を可能にする膜変形リポソーム

（東農工大院工[1]、慶大理工[2]、東大院工[3]、KISTEC[4]）○内田紀之[1]・笠勇之助[1]・松原輝彦[2]・佐藤智典[2]・安楽泰孝[3]・村岡貴博[1,4]

Membrane-Deforming Liposomes for Highly Efficient Encapsulation and Detoxification of Large Biomacromolecules such as Viruses. ([1]*Tokyo University of Agriculture and Technology*, [2]*Keio University*, [3]*The University of Tokyo*, [4]*KISTEC*)

○Noriyuki Uchida[1], Yunosuke Ryu[1], Teruhiko Matsubara[2], Toshinori Sato[2], Yasutaka Anraku[3], Takahiro Muraoka[1,4]

Since viruses and bacteria are microscale huge particles, highly effective degradation reagents tend to be required to detoxify them. However, there has been a trade-off with avoiding harmful effects on human body, making material design difficult. Recently, a membrane-deforming liposome that incorporates surface-interacting microparticles such as bacteriophage virus was successfully developed. The encapsulated viruses are separated from external environments and their infectivity is drastically reduced. In this presentation, the design guideline for the membrane-deforming liposome and their functions will be reported.

Keywords: Phospholipid Bilayers; Membrane Deformation; Virus; Phage Display; Endocytosis

ウイルスや細菌はマイクロスケールの巨大な粒子であり、従来無毒化するためには分解効果の高い試薬を使用する必要があった。しかしながら、人体に対する有害な効果を抑制することとトレードオフの関係にあり、材料設計を困難なものにしてきた。最近演者は表面に相互作用するマイクロ粒子を外部溶液ごと取り込む膜変形リポソームの開発に成功した[1)–4)]。例えばマイクロスケールのファージウイルス[5),6)]を膜変形リポソームに封入すると（図１A）外部環境から遮断され、大腸菌への感染性が激減する（図１B）。本発表ではこの膜変形リポソームの設計指針、およびウイルスの封入機能に関して報告する。

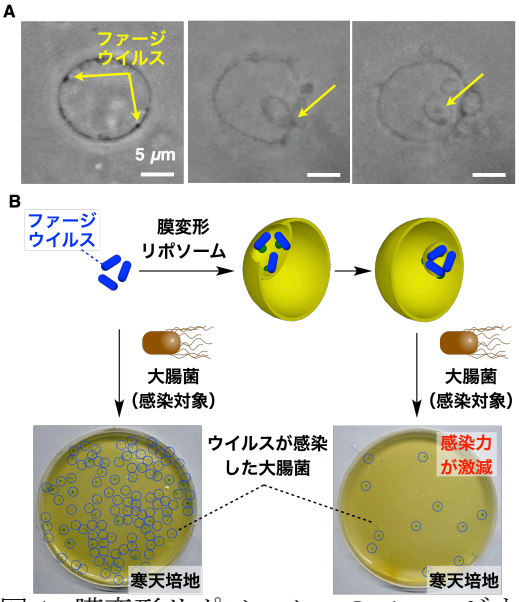

図１ 膜変形リポソームへのファージウイルスの取り込みにおける顕微鏡観察（A）と大腸菌への感染力の抑制効果（B）

1) N. Uchida, *et. al.*, *J. Am. Chem. Soc.* **2023**, *145*, 6210. 2) N. Uchida, *et. al.*, *Chem. Commun.* **2023**, *59*, 9665. 3) N. Uchida, *et. al.*, *Chem. Commun.* **2022**, *58*, 5164. 4) JP Patent 2021-077870. 5) N. Uchida, *et. al.*, *Chem. Eur. J.* **2023**, DOI: 10.1002/chem.202302261. 6) N. Uchida, *et. al.*, *Nat. Prod. Commun.* **2020**, *20*, DOI: 10.1177/1934578X20947232.

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体液応答性即時固化液および専用多孔質スポンジの設計と合成：シンプルながら高性能な止血材の実現

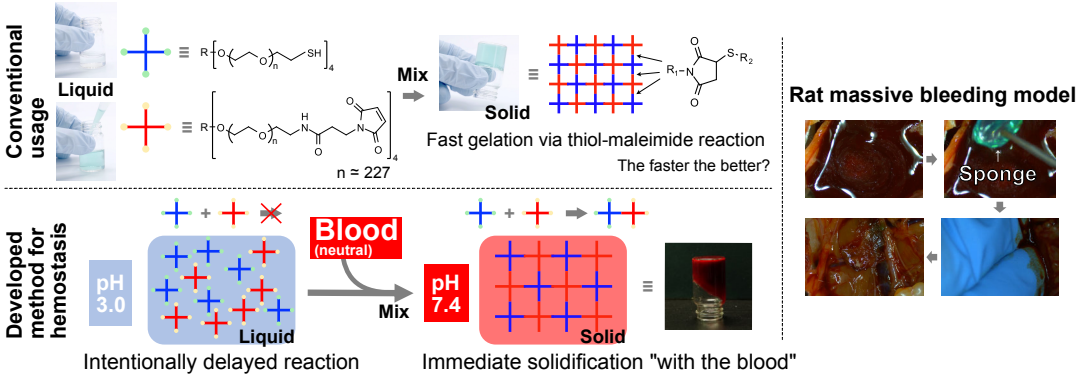
(東大院工[1]・東大院医[2]) ○鎌田 宏幸[1]・石川 昇平[1]・藤澤 彩乃[1]・吉川 祐紀[2]・松原 和英[2]・保科 克行[2]・酒井 崇匡[1]

Design and Synthesis of a Body Fluid-Responsive Instantly Solidifying Liquid and Dedicated Macroporous Sponges: Realizing Simple but High-Performance Hemostatic Materials (1 *Graduate School of Engineering, University of Tokyo*, [2]*Graduate School of Medicine, University of Tokyo*) ○Hiroyuki Kamata,[1] Shohei Ishikawa,[1] Ayano Fujisawa,[1] Yuki Yoshikawa,[1] Kazuyoshi Matsubara,[2] Katsuyuki Hoshina,[2] Takamasa Sakai[1]

We have developed a new synthetic hydrogel-based body fluid solidification liquid that does not rely on the blood coagulation reaction. This liquid consists of two tetrabranched PEG derivatives with thiol and maleimide ends, which remains liquid in weakly acidic conditions and solidify immediately under neutral conditions, such as in the presence of blood. In a rat massive hemorrhage model, when the newly designed liquid was applied together with a nonionic porous PEG sponge[1)], only the developed material successfully stopped bleeding[2)].

Keywords: Hemostatic Materials; Body Fluid Responsiveness; Instant Solidification; Nonionic Microporous Sponges; Polyethylene Glycol (PEG)

重症出血に用いられる血液凝固促進性の止血材には、感染症のリスクや抗血栓薬の影響で効果が低下する問題が残されている。我々は血液凝固反応に依存しない新しい合成ハイドロゲルベースの体液固化液を設計した。この液体はチオールとマレイミドを末端に持つ 2 種類の 4 分岐ポリエチレングリコール（PEG）誘導体からなり、弱酸性では液状を保ち、血液存在下など、中性では即時固化する。ラットの大量出血モデルで、同固化液は容易に希釈され効果が得られなかったが、新たに設計した同液を弱酸性のまま保持可能なノニオン性多孔質 PEG スポンジ [1)]と共に適用したところ、開発材のみが止血に成功した [2)]。この設計はすべての中性液体に対して有効であり、膵液漏や脳脊髄液漏など、さまざまな液体漏れに広範に応用できる可能性がある。



1) Simple Preparation of Injectable Hydrogels with Phase-Separated Structures That Can Encapsulate Live Cells. *ACS Appl. Mater. Interfaces*. **2022**, 14, 31, 35444-35453 (特願 2022-13301)
2) Hemostatic Capability of a Novel Tetra-Polyethylene Glycol Hydrogel. *Ann. Vasc. Surg*. **2022**, 84, 398-404 (特願 2020-82474)

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Amyloid-β40 と 42 の共存下でのアミロイド線維形成に対してガングリオシド GM1 が与える影響

（山形大院理工[1]・山形大理[2]）○深瀬 貴代[1]・並河 英紀[2]
Effect of ganglioside GM1 on amyloid fibrillogenesis in the coexistence of amyloid-β 40 and 42 ([1]Graduate School of Science and Engineering, Yamagata University, [2]Faculty of Science, Yamagata University) ○Kiyo Fukase,[1] Hideki Nabika[2]

Aggregates of amyloid β protein (Aβ) are formed on the surface of brain cell membranes of Alzheimer's disease (AD) patients. Since aggregation of Aβ may be involved in the onset of AD, its aggregation has been studied to clarify the pathogenic mechanism and to develop new drugs. GM1 is abundant in brain and might be a possible factor in its aggregation. Most studies have focused on either Aβ40 or Aβ42, but the two species coexist in vivo. In this study, we investigated the effect of GM1 on Aβ aggregation in the coexisting environment of the two species. As a result, aggregation was generally suppressed in the coexisting system (Fig 1, left). In addition, GM1 inhibited aggregation in the system (Fig 1, right), which was different from the results for each species alone. This difference may be attributed to the change in the morphology of the fibers. In fact, the excitation spectrum of Thioflavin-T bound to the fibers is changed.
Keywords : Amyloid-β; aggregation; Amyloid fibril; ganglioside; Alzheimer's disease

アルツハイマー病 (AD) 患者の脳細胞膜表面にはアミロイドβタンパク質 (Aβ) の凝集体の形成が確認されている。Aβの凝集は AD の発症に関与すると考えられ、発症機構解明及び創薬開発に向けて研究が進められている。中でも、ガングリオシド GM1 (GM1) は脳細胞に多く存在し、Aβの凝集に関与している可能性が示されている。多くの研究は Aβ40 又は Aβ42 の一方を対象としているが、生体内ではこの二種が共存している。本研究では、二種共存下において、GM1 が凝集に与える影響を調査した。結果、共存した系では全体的な凝集の抑制が確認された (Fig 1, left) 。加えて、GM1 の添加による凝集抑制効果が見られ (Fig 1, right) 、この結果は各々の種に添加した場合と異なるものであった。この違いは、異なる種の共存により線維の形態が変化したことに起因すると考えられ、実際、線維に結合した Thioflavin-T に由来する蛍光の励起スペクトルが変化している。

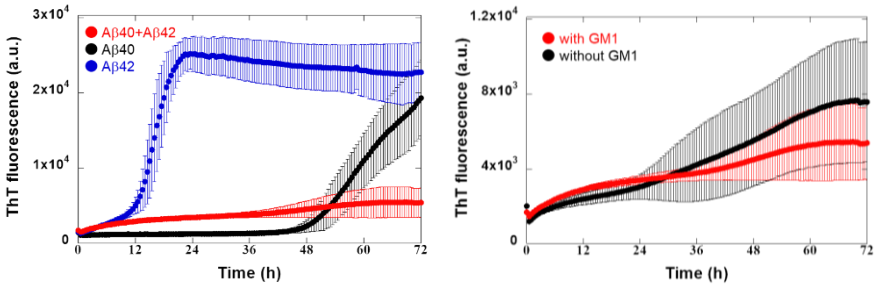

Fig 1. Aβ線維に結合した Thioflavin-T の蛍光強度の経時変化.
left) 二種共存系ならびに各 Aβ種のみにおける結果の比較. right) 二種共存系における GM1 の有無の結果の比較.

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コレステロール/ラノステロールが DOPC 膜物性およびアミロイドβ凝集挙動に与える影響

（山形大院理工[1]・山形大理[2]）○秋保恭平[1]・並河英紀[2]
Effect of cholesterol / lanosterol on DOPC membrane properties and amyloid β aggregation
([1]*Graduate School of Science and Engineering, Yamagata University*, [2]*Faculty of Science, Yamagata University*) ○Kyohei Akiho,[1] Hideki Nabika[2]

The self-assembly of amyloid β (Aβ) to form aggregates known as amyloid plaques on the neuronal surface is a feature of Alzheimer's disease (AD). Therefore, investigation of the dependence of lipid membrane composition on Aβ aggregation will lead to the identification of the causes of AD and the development of therapeutic agents for AD. In particular, cholesterol (chol) is reported to affect Aβ aggregation. On the other hand, lanosterol (lano), a precursor of chol has also been reported to exist in the brain and inhibit the aggregation of proteins. These results suggest that lano may affect on Aβ aggregation as chol. In this study, we investigated the effects of chol and lano on DOPC membrane properties and their relationship to Aβ aggregation behavior.
Keywords : Alzheimer's disease, Amyloid beta, cholesterol, lanosterol, self-assembly

アルツハイマー病（AD）は神経細胞表面にアミロイドβタンパク質（Aβ）が沈着し、アミロイド斑を形成することを特徴としている。そのため、Aβ が AD の発症に関与していると考えられ、Aβ の凝集挙動を調査することが AD の発症原因究明および創薬につながると考えられる。この凝集は神経細胞表面と相互作用しながら進行し、特にコレステロール(chol)は凝集に深く関与していると考えられる。加えて、chol はラノステロール(lano)を前駆体として生合成されており、lano 自身も神経変性タンパク質の凝集阻害効果が確認され、脳内にも存在しているため Aβ の凝集にも関与しており、AD の発症にも関わっていると考えられる。しかし、lano が Aβ の凝集に与える影響に関する研究は深く行われておらず、研究は不十分である。そこで本研究では chol もしくは lano を含んだリポソームを作成し、Aβ の凝集を調べた。その後、脂質膜物性と Aβ の凝集挙動の関連性を調査するため、表面圧-面積等温測定を用いて各条件における脂質膜物性を調査した。その結果、chol 系では濃度増加に伴って極限分子占有面積が減少したのに対して、lano 系では面積低下の効果が弱かった(図 1)。これは chol と lano の構造の違いによって生まれた差であると考えられる。最後に、得られたデータと Aβ の凝集挙動との関連性を考察した。本研究結果は lano の持つ膜物性への影響を明らかにし、AD の発症原因を突き止める一因となりうるものである。

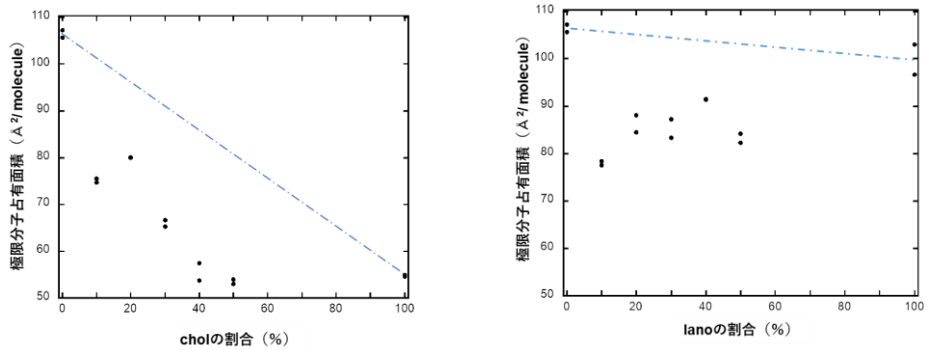

図 1. ステロール含有 DOPC 脂質膜の各濃度における極限分子占有面積. (左) chol 系. (右) lano 系

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Contribution of Sebum and Sweat Condition to Men's Daytime Skin Appearance and Feel

([1]Kao Corporation) ○Songjie Zhang[1], Mamiko Kikuchi[1], Ai Terai[1], Jicheng Zhang[1], Shinichi Ikegaki[1], Satoru Naitou[1]

Keywords: male skin condition; sebum component; sweat component; fatty acid; FT-IR imaging

Men generally perceive that their sebum and sweat levels affect the appearance and feel of their skin during the daytime. However, the contribution of each component remains unclear. Therefore, we investigated the relation between skin perception parameters, such as stickiness and pore conspicuity, and skin physio-chemical parameters, such as the composition and distribution of sweat and sebum components. For this study, we established a new skin surface chemical imaging method that uses infrared (IR) imaging.

Our findings revealed several fascinating insights:

1) The sensation of stickiness was linked to a higher content of free fatty acids in the skin surface mixture;

2) The conspicuity of pores appeared to be influenced by several factors, including sebum levels, skin pH, and the specific distribution of fatty acid salts near pores.

In conclusion, our study suggests potential relationships between perception parameters, such as stickiness and conspicuous pores, and physio-chemical parameters such as sebum level, skin pH, and the formation of fatty acid salts.

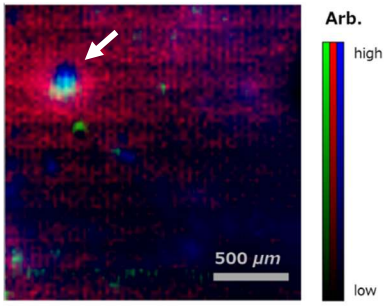

Fig. 1 Example of the distribution of sebum components on male skin in the daytime by IR imaging (Blue: esters, mainly triglycerides; Red: carboxylic acid, mainly fatty acids; Green: carboxylic acid salts, mainly fatty acid salts. Arrow: pore from a panel with conspicuous pores).

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生体組織の立体培養と回収を可能にする高強度と選択的分解性を兼ね備えた超分子ペプチドゲルの開発

(東農工大院工[1]・医科歯科大 CBIR[2]・神奈川産技総研[3])
○矢口 敦也[1]・味岡 逸樹[2,3]・村岡 貴博[1,3]

Development of supramolecular gelling peptides for *in-vitro* three-dimensional tissue culture and stable collection of the tissue ([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Center for Brain Integration Research, Tokyo Medical and Dental University*, [3]*Kanagawa Institute of Industrial Science and Technology*)

○Atsuya Yaguchi,[1] Itsuki Ajiokaka,[2,3] Takahiro Muraoka[1,3]

Three-dimensional tissue culture *in vitro*, which is currently limited, is effective in advancing the understanding of biological phenomena and in realizing new treatments for diseases. In this study, we realized a simple new three-dimensional culture method by developing novel materials. We designed a supramolecular peptide gel with sufficient mechanical strength to culture biological tissues in three dimensions and the ability to be solubilized selectively by the inhibitor, based on the assembled structure. The developed peptide gel was used as an alternative extracellular matrix for culturing mouse retina. In the cultured retinas recovered by addition of the inhibitor, three-dimensional tissue development similar to that *in vivo* was observed.

Keywords : Peptide; Self-assembly; Hydrogel; Structural Analysis; Tissue Culture

生命現象の理解進展や疾患に対する新規治療法実現には、現状限定的である生体外での三次元組織構築が有効である。本研究では、新材料開発に基づく生体組織の簡便な新規立体培養手法の実現を試みた。三次元組織培養には周囲の細胞外マトリクス(ECM)の存在が肝要だが、人工 ECM には組織培養可能な高い力学的強度と培養後の ECM 除去の両立という課題があった[1)]。

我々は、以前開発した自己集合性ペプチド JigSAP[2)]の構築するナノファイバーを構造解析し、よりファイバーへと平衡を偏らせた新しい超分子ゲル化ペプチド C-JigSAP を分子デザインした。開発した C-JigSAP は水中でゲル化し、そのゲルは生体組織の立体培養が可能な高い力学的強度と細胞接着性を示した。また、^{13}C ラベルを施し固体 NMR や IR スペクトル測定することで、C-JigSAP が分子デザイン通りに集積しナノファイバーを構築したことを明らかにした。さらには、C-JigSAP ファイバーの構造解析結果から、C-JigSAP ファイバーのみを選択的に分解するインヒビターMeA8 を新規開発した。MeA8 溶液を C-JigSAP ゲルに添加したところ、C-JigSAP ゲルは分解され分散液となった。一方、他の超分子ゲル化ペプチドとして RADA16[3)]のゲルに MeA8 溶液を添加してもゲルの分解は見られなかった。そこで C-JigSAP ゲル中に網膜組織を包埋して培養を行い、その後 MeA8 溶液の添加によって網膜組織を回収した。回収した網膜には生体内同様の異方性を持った発達が見られた。

1) F. Pampaloni, E. G. Reynaud and E. H. K. Stelzer, *Nat. Rev. Mol.* **2007**, *8*, 839-845.
2) A. Yaguchi *et al.*, *Nat. Commun.* **2021**, *12*, 6623.
3) H. Yokoi, T. Kinoshita and S. Zhang, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 8414-8419.

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多糖を複合化した光架橋ゼラチンハイドロゲル細胞足場の開発

（横国大院工[1]・横国大院理工[2]）○宮島 浩樹[1]・小野寺 晃大[2]・八田 裕貴[2]
・小島 加帆里[2]・向井 理[1]・丸尾 昭二[1]・飯島 一智[1]

Development of polysaccharide modified photo cross-linked gelatin hydrogel cell scaffolds

([1]*Faculty of Engineering, Yokohama National University*, [2]*Graduate School of Engineering Science, Yokohama National University*) ○Hiroki Miyajima[1], Kodai Onodera[2], Yuki Hatta[2], Kaori Kojima[2], Masaru Mukai[1], Shoji Maruo[1], Kazutoshi Iijima[1]

For the development of photo-printable three-dimensional cell scaffolds mimicking biological environment, we have developed cell scaffolds of photo-printable gelatin methacrylate (GelMA) hydrogels functionalized with such as hydroxyapatite. In this study, we constructed hydrogels composed of GelMA and cross-linkable polysaccharide derivatives (chitosan derivative and hyaluronic acid derivative) through Schiff base formation to promote cartilage differentiation of mesenchymal stem cells (MSCs). Gel precursor solutions were prepared by mixing GelMA, carboxymethyl chitosan (CMC), hyaluronic acid dialdehyde (HDA) and photo-initiator in basic condition. GelMA hydrogels were prepared by UV irradiation, and then gel was immersed in PBS to promote reaction between CMC and HDA. GelMA-CMC/HDA three-component gels were successfully obtained. In addition, models of GeMA-CMC/HDA three-component gels were fabricated by microstereolithography.

Keywords : Cell Scaffold; Hydrogel; Polysaccharide; Stem Cells

[緒言] 再生医療の実現に向け、生体環境を模倣した三次元細胞足場の開発が求められている。我々は光造形可能なゼラチン誘導体であるゼラチンメタクリレート（GelMA）[1)]からなるハイドロゲルの機能化手法の開発に取り組み、骨の無機成分であるヒドロキシアパタイトによる機能化を報告した[2)]。本研究では、間葉系幹細胞の軟骨誘導を促進できる材料の開発を目指し、GelMA に対し、シッフ塩基形成により架橋する多糖誘導体（キトサン誘導体およびヒアルロン酸誘導体）を複合化した、光造形可能な三成分ハイドロゲルの開発を行った。

[手順] GelMA、カルボキシメチルキトサン（CMC）、ヒアルロン酸ジアルデヒド（HDA）および光開始剤を混合し、ゲル前駆溶液とした。ハンディ UV ランプを用いてゲル前駆溶液に UV 照射した後、PBS に浸漬し、ゲル中の溶液 pH を徐々に中性に近づけ、目的のゲルを得た。また、青色レーザー光を用いた光造形にも取り組んだ。

[結果と考察] 中性条件下では CMC と HDA との反応により速やかにゲル化が起こり、光造形に用いるゲル前駆溶液は得られなかった。一方、ゲル前駆溶液を塩基性条件下で調製することで、CMC と HDA の反応によるゲル化が抑制され、ゲル前駆溶液を調製することができた。UV を照射することで溶液のゲル化が見られ、続いてゲル中の pH を低下させることでゲルが白濁する様子が観察された。まず、ゲル前駆溶液に対する UV 照射により GelMA の光架橋が誘導され、次に溶液の pH 変化により CMC/HDA の官能基間でのシッフ塩基形成による 2 種のネットワークによるゲル形成が示唆された。また、青色レーザー光による三成分ゲルからなる造形モデルを得ることにも成功した。

1) J.W. Nichol, et al., *Biomaterials* **2010**, 31, 5536-5544.
2) H. Miyajima, *et al*., *ACS Biomater. Sci. Eng*. *published online*.

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Academic Program [Poster] | 03. Physical Chemistry -Structure-：Poster

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[P1-2vn] 03. Physical Chemistry -Structure-

Japanese

[P1-2vn-01]

A study on the electric dipole moment and molecular structure of the Kr-OCS cluster by microwave double resonance spectroscopy

○Yutaro Osawa[1], Yoshihiro Sumiyoshi[1] (1. Gunma University)

English

[P1-2vn-02]

Paramagnetic ion doping in MOFs to accelerate solid-state NMR measurements

○Henric Mezzomo[1], Takuya Kurihara[1], Yasuhiro Shigeta[1], Shogo Amemori[1], Tomonori Ida[1], Motohiro Mizuno[1] (1. Kanazawa University)

Japanese

[P1-2vn-03]

Exact Analyses of ESR Spectra of Cobalt Complexes with Sizable Zero-Field Splitting Tensors

○Takeshi Yamane[1], Kenji Sugisaki[1,2,3], Kazunobu Sato[1], Kazuo Toyota[1], Daisuke Shiomi[1], Takeji Takui[1] (1. Osaka Metropolitan Univ., 2. Keio Univ., 3. JST PRESTO)

Japanese

[P1-2vn-04]

Characterization of self-assembled monolayers consisting of helical polymers: Topography modification depending on applied electric field

○Nano Kobayakawa[1], Naoya Kanbayashi[1], Taka-aki Okamura[1], Kiyotaka Onitsuka[1], Seiya Watanabe[1], Megumi Akai-Kasaya[1], Hiroyuki S. Kato[1] (1. Osaka University)

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マイクロ波2重共鳴分光法によるKr-OCSクラスターの電気双極子モーメントと分子構造に関する考察

（群馬大院理工）○大沢悠太朗・住吉吉英

A study on the electric dipole moment and molecular structure of the Kr-OCS cluster by microwave double resonance spectroscopy (*Graduate School of Science and Engineering* ,Gunma University)

○Yutaro Osawa , Yoshihiro Sumiyoshi

We performed MW-MW double resonance spectroscopy using two coherent microwaves (MW) with different frequencies on molecular clusters generated in a supersonic jet, observed the light-shift effect, and showed that the electric dipole moment of the molecular cluster can be determined from the information obtained [1]. In this study, we have applied the technique to the Kr-OCS cluster. We have newly observed total of 20 pure rotational transitions with high-J value, which has not been reported in a previous paper [2]. In combination with the transition frequencies reported in the previous paper, we have determined new molecular constants including the sextic distortion constants by least-squares analysis using an asymmetric top Hamiltonian. We also observed the light-shift effect and estimated the value of the electric dipole moment μ_b. The molecular structure was discussed based on the value of μ_b.

Keywords ; Microwave Spectroscopy; Intermolecular Interaction; Microwave Double Resonance Spectroscopy

我々は，超音速ジェット中で生成した分子クラスターに対して，異なる周波数を持つ2種類のコヒーレントなマイクロ波（MW）を用いたMW-MW二重共鳴分光を行うことでライトシフト効果を観測し，その情報から分子クラスターの電気双極子モーメントを決定できる事を示した [1]．今回，クリプトンKrと硫化カルボニル分子OCSから成るKr-OCSクラスターを対象に，過去の論文 [2]には報告されていない，回転量子数Jが大きな純回転遷移を含む遷移20本を新たに観測した．過去に報告されている遷移周波数と合わせて，非対称コマ分子のハミルトニアンを用いて最小二乗解析を行い，6次の遠心力歪定数を含めた分子定数を決定した．また，ライトシフト効果を観測し，Kr-OCSの電気双極子モーメントμ_bの値を見積もった．その情報を基に分子構造について議論した．

1）石橋泰斗，新井健太，住吉吉英，日本化学会関東支部群馬地区研究交流会 P-04 (2018)
2）F.J.Lovas and R.D.Suenram,J.Chem.Phys. **87**,2017(1987)

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Paramagnetic Ion Doping in MOFs to Accelerate Solid-State NMR Measurements

([1]*College of Science and Engineering, Kanazawa University,* [2]*Graduate School of Natural Science and Technology, Kanazawa University*) ○Henric Mezzomo,[1] Takuya Kurihara,[2] Yasuhiro Shigeta,[2] Shogo Amemori,[2] Tomonori Ida,[2] Motohiro Mizuno[2]

Keywords: Solid-state NMR, MOF, Paramagnetic Doping

Metal-organic frameworks (MOFs) are porous materials formed by metal ions and organic ligands that have been studied for gas adsorption and other applications. Solid-state NMR (SSNMR) is a powerful method in the study of local static and dynamic structures of MOFs. However, in many cases, weakness and slow relaxation rate of the NMR signal require multiple scans and a long waiting time for each scan, respectively, which lengthens the measurement time. Therefore, it is important to develop a method to shorten the measurement time to facilitate MOF research using SSNMR.

Cross-polarization (CP) can transfer the magnetization of abundant ^{1}H spins to dilute nuclear spins (^{13}C, ^{15}N, etc.) and is frequently used to enhance the intensity of the SSNMR signal. Paramagnetic metal ion doping into the sample can accelerate the NMR measurement because the interaction of the nuclear spins with the electron spins of the paramagnetic ions promotes nuclear spin relaxation.[1] In this study, we aim to accelerate CP NMR measurements of MOFs by doping paramagnetic metal ions in MOFs using a metal solid-solution approach.

ZIF-8 $[Zn(2\text{-MeIm})_2]_n$ was synthesized with various Co^{2+} doping ratios,[2] and ^{13}C CP and ^{1}H relaxation time measurements were performed. To find the optimal doping ratio, we formulated the signal acquisition efficiency per unit time (= signal-to-noise ratio/measurement time) relative to the doping ratio of paramagnetic ions and investigated the relationship between the doping ratio and the efficiency using the experimental signal intensity, linewidth, and relaxation time. Fig. 1 shows the obtained acquisition efficiency normalized to the efficiency of the undoped sample. The highest acquisition efficiency is 3.7 at a doping ratio of 0.3%. Excessive doping can reduce CP efficiency and broaden the signal due to overly fast relaxation, which in turn reduces the measurement sensitivity and the acquisition efficiency.

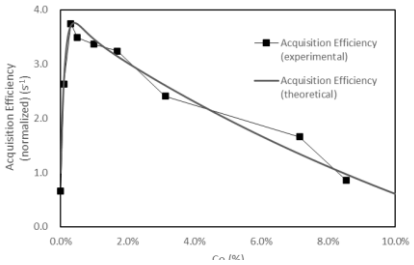

Fig. 1: Normalized acquisition efficiency relative to doping ratio

To demonstrate the effectiveness of this method, we performed ligand dynamics analysis on Co^{2+}-doped MOF-5 $[Zn_4O(1,4\text{-benzodicarboxylate})_3]_n$ using 2D ^{13}C SSNMR. The results will be discussed on the day of the presentation.

1) N. P. Wickramasinghe, et al., *Nat. Methods* **2009**, *6*, 215. 2) G. Kaur, et al., *J. Mater. Chem. A* **2016**, *4*, 14932.

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大きいゼロ磁場分裂定数を持つコバルト錯体の ESR 厳密解析法

（大阪公立大院理[1]・慶應大院理工[2]・JST さきがけ[3]）○山根 健史[1]・杉﨑 研司[1,2,3]・佐藤 和信[1]・豊田 和男[1]・塩見 大輔[1]・工位 武治[1]
Exact Analyses of ESR Spectra of Cobalt Complexes with Sizable Zero-Field Splitting Tensors ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*Graduate School of Science and Technology, Keio University,* [3]*JST PRESTO*) ○Takeshi Yamane,[1] Kenji Sugisaki,[1,2,3] Kazunobu Sato,[1] Kazuo Toyota,[1] Daisuke Shiomi,[1] Takeji Takui[1]

A fictitious spin-1/2 Hamiltonian approach is a putative method to analyze ESR spectra from high spin complexes with sizable zero-field splitting (ZFS) parameters. In this approach, the analyses result in the effective magnetic parameters such as *g*- and *A*-values (g^{eff}, A^{eff}), which are far from the theoretical true *g*- and *A*-values (g^{true}, A^{true}) obtainable from reliable quantum chemical calculations. We established the analytical procedure for analyzing the ESR spectra and determining the magnetic parameters of high spin Co(II) complexes ($S = 3/2$, $I = 7/2$) with sizable ZFS tensors. Our generalized method, which is applicable to non-collinear cases among **D**-, **g**- and **A**-tensors, is based on the analytically derived relationships between the fictitious spin-1/2 and true spin Hamiltonians.
Keywords : Electron Spin Resonance; High-Spin Metallocomplex; Quantum Chemical Calculation

ゼロ磁場分裂（ZFS）定数の大きい高スピン金属錯体は、生体内において重要な機能を持つだけでなく磁気材料への応用も期待されている。このような系の X-band（≈9.5 GHz）ESR スペクトル解析は、仮想スピン 1/2 ハミルトニアンに基づいて行われてきた。しかし、得られた磁気的パラメータ（g^{eff}, A^{eff}）は、系本来のスピン量子数に基づく量子化学計算によるパラメータ（g^{true}, A^{true}）とかけ離れており、直接の比較は困難であった。我々はこれまでにスピン量子数 $S \leq 7/2$ までの錯体に対して、スピンハミルトニアンの厳密解析解を用いて g^{eff}–g^{true} 関係式を導出し、種々の遷移金属錯体の ESR スペクトル解析に適用した[1, 2]。

本研究では、g 値および超微細相互作用定数に対する関係式を導出し、確立した ZFS 定数の大きい錯体の ESR スペクトルの一般解析法をコバルトポルフィリン錯体[1, 2]、コバルト五配位錯体[3, 4, 5]（全て $S = 3/2$, $I = 7/2$）に適用した。この手法は **D**, **g** および **A** テンソルの主軸が共軸でない場合にも適用可能である。スピンハミルトニアンの厳密エネルギー解に基づいて計算した A^{true} の E/D 依存性から理論的 A^{true} を決定し、関係式の妥当性を裏付けることができた。発表では、ESR スペクトル解析の詳細な手順、関係式を用いた磁気的パラメータの変換、他の高スピン金属錯体への応用について議論する。

1) T. Yamane, et al., *Phys. Chem. Chem. Phys.* **2017**, *19*, 24769. 2) T. Yamane, et al., *Dalton. Trans.* **2018**, *47*, 16429. 3) A. A. Fischer, et al., *Dalton. Trans.* **2017**, *46*, 13229. 4) P. Kumar, et al., *J. Am. Chem. Soc.* **2019**, *141*, 10984. 5) P. Kumar, et al., *Inorg. Chem.* **2020**, *59*, 16178.

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らせん状高分子による自己組織化単分子膜のキャラクタリゼーション：電界に応じた形状変化

(阪大理[1]・阪大院理[2]) ○小早川 なの[1]・神林 直哉[2]・岡村 高明[2]・鬼塚 清孝[2]・渡部 誠也[2]・赤井 恵[2]・加藤 浩之[2]

Characterization of self-assembled monolayers consisting of helical polymers: Topography modification depending on applied electric field ([1]*School of Science, Osaka University*, [2]*Graduate School of Science, Osaka University*) ○Nano Kobayakawa[1], Naoya Kanbayashi[2], Taka-aki Okamura[2], Kiyotaka Onitsuka[2], Seiya Watanabe[2], Megumi Akai-Kasaya[2], Hiroyuki S. Kato[2]

We attempted to fabricate self-assembled monolayers (SAMs) consisting of helical polymers in order to produce highly dense and oriented SAMs by functional polymers. In our research, the self-assembly was achieved through mercapto reaction on Au substrates by cysteinylation of the ends of previously developed helical polymers. Herein, the SAMs' structures were investigated by infrared reflection-absorbance spectroscopy (IRAS) and scanning probe microscopy (SPM). The IRAS results suggest that the molecules in SAMs are oriented standing on the Au substrate (Fig. 1a). In addition, scanning tunneling microscopy (STM) studies indicated that the film is atomically flat. In addition, they interestingly showed that their topography was altered depending on the applied sample bias (Figs. 1b-1c). In presentation, the origin of these responses in topography and physical properties are discussed.

Keywords：Chiral Polymers' SAM; Electric Field Response; Scanning Tunneling Microscope; Vibrational Spectroscopy

高機能高分子の高密度かつ高配向な分子膜作製を目標として、らせん状高分子の自己組織化単分子膜（SAM）の作製を試みた。本研究では、先に開発した らせん状高分子[1)]の末端をシステイン化することで、Au 基板上のメルカプト反応による自己組織化に成功した。この膜を赤外反射吸収分光（IRAS）や走査型プローブ顕微鏡（SPM）で解析したので報告する。IRAS の解析から、SAM 中の分子は、Au 基板に対して分子軸が立って配向していることが示唆された（Fig. 1a）。走査型トンネル顕微鏡（STM）を用いた電界応答の観測では、原子レベルで平坦な膜であることが確認された。また、走査試料電位 Vs に応じて分子の高さが伸縮する様子が確認された（Figs. 1b-1c）。発表では、この形状変化の要因と物性変化についても議論する。

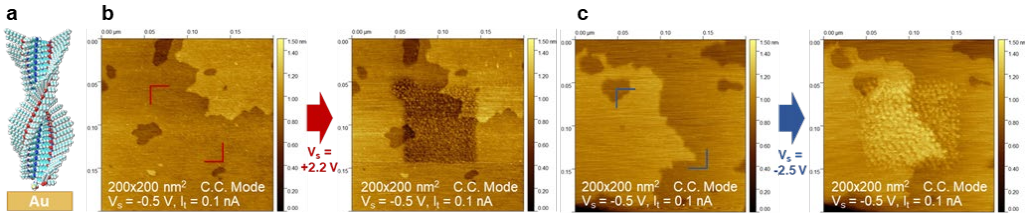

Fig. 1 Schematic structure of a helical molecule in SAMs (a), and STM images before and after electric field stimulations by scanning at Vs = +2.2 V (b) and Vs = −2.5 V (c).

1) N. Kanbayashi *et al*., *J. Am. Chem. Soc.* **2022**, *144*, 6080–6090.

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Academic Program [Poster] | 04. Physical Chemistry -Properties-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-2vn] 04. Physical Chemistry -Properties-

Japanese

[P2-2vn-01]

Solvation Gibbs energies of natural cyclodextrins

○Masao Fujisawa[1], Tomonori Ohata[2], Hiroyuki Tsutsumi[2], Hirohito Ikeda[2] (1. Dept. of Biotechnological Science, Kindai Univ., 2. Fac. of Pharmaceutical Science, Fukuoka Univ.)

Japanese

[P2-2vn-02]

Solubilization of Heated Egg White Aggregates by Direct Addition of Alkali Halides

○Takahiro Takekiyo[1], Yurina Emori[2], Kou Kato[2], Suzu Kondo[2], Taichi Matsuda[2], Rikuto Nozawa[2], Miyuu Tsumuraya[2], Atsushi Yamada[1], Yukihiro Yoshimura[1] (1. National Defense Academy, 2. Yokosuka High Scool)

Japanese

[P2-2vn-03]

High Electrically Conductive Deep Eutectic Solvents Using Organic Halides and Iodine

○Junpei Sato[1], Maharoof Koyakkat[2], Satoshi Asakura[3], Hiroyuki Kawamoto[3,4], Katsuhiko Moriyama[2], Hideaki Shirota[2] (1. Faculty of Science, Chiba University, 2. Graduate School of Science, Chiba University, 3. Ise Chemicals Corporation, 4. Chiba Iodine Resource Innovation Center)

Japanese

[P2-2vn-04]

Enhancement of hydrophobicity in oxicam group of acidic drugs by pH-induced conformational change

○Kota Moritake[1], Kanji Hasegawa[1], Tomohiro Tsuchida[1], Satoru Goto[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-05]

Distinguishing the transitions of fluorescence spectra of tryptophan-134 and 213 in BSA induced by bindings of UV filters, oxybenzone-3, and avobenzone

○Horizumi Yusuke[1], Minamide Megumi[1], Tsurushima Minori[1], Kurosawa Yuya[1], Koga Ryotaro[1], Hasegawa Kanji[1], Tsuchida Tomohiro[1], Goto Satoru[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-06]

XAS measurements for aqueous solutions of nitrogen-containing organic compounds

Haoran Xu[1], ○Takehiko Sasaki[1] (1. The University of Tokyo)

English

[P2-2vn-07]

Plasmon-influenced photoluminescence blinking behavior of lead halide perovskite quantum dots

○Tianci Wang[1], Lei Duan[1], Takuya Okamoto[1], Vasudevan pillai Biju[1] (1. Hokkaido University)

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Japanese

[P2-2vn-08]

Auger Recombination-Assisted Photoisomerization of Diarylethene Derivatives with Semiconductor Quantum Dots

○Moe Yamamoto[1], Daichi Eguchi[1], Naoto Tamai[1] (1. The Univ. of Kwansei Gakuin)

Japanese

[P2-2vn-09]

Synthesis of new magnetic acetylides containing ethynyl-substituted TTF-based derivatives

○Sodai Sasaki[1], Junichi Nishijo[1], Masaya Enomoto[2], Motoko Akita[3] (1. Meisei University, 2. Tokyo University of Science, 3. Josai University)

Japanese

[P2-2vn-10]

Crystal structures, magnetic properties, and their deuterium substitution effects of hydrogen-bonded dinuclear copper complexs, $[Cu(Eta)(Heta)(NO_3)]_2$

Tasuku Murai[1], Shinobu Aoyagi[2], ○Wataru Fujita[1] (1. Tokyo University of Marine Science and Technology, 2. Nagoya City University)

Japanese

[P2-2vn-11]

Proton Conductivity of Alginic Acid-Polyacrylic Acid-Triazole Composites

○Genta Yamamoto[1], Yasuhiro Shigeta[1], Takuya Kurihara[1], Shogo Amemori[1], Tomonori Ida[1], Motohiro Mizuno[1] (1. Kanazawa University)

Japanese

[P2-2vn-12]

Structure and properties of BEDT-TTF-based salt with indigodisulfonate, (BEDT-TTF)$_3$(indigodisulfonate) • H_2O

○Kento Yamanobe[1], Hiroki Akutsu[1], Yasuhiro Nakazawa[1] (1. Osaka University)

Japanese

[P2-2vn-13]

Electronic Properties of Azachrysene Compounds

○Nobutsugu Hamamoto[1], Makoto Inokuchi[1] (1. Sanyo-Onoda City University)

Japanese

[P2-2vn-14]

Mixed-Sequence Oligomer Salt 4P^{H}S–*X* for High Conductivity

○Takeshi Nishida[1] (1. The University of Tokyo)

Japanese

[P2-2vn-15]

Relationship between polar structure and g-tensor for (BEDT-TTF)$_2$(PO-CONHC$_2$H$_4$SO$_3$)

Sato Shiori[1], ○Ko Furukawa[1,2], Hiroki Akutsu[3], Tasuhiro Nakazawa[3] (1. Niigata Univ., 2. CCRF, Niigata Univ., 3. Osaka Univ.)

Japanese

[P2-2vn-16]

Synthesis and physical properties of fluorine-substituted TMTTF derivatives

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○Shuya Goto[1], Tatsuro Imakubo[1] (1. Nagaoka University of Technology)

Japanese

[P2-2vn-17]

Synthesis of TTF Derivatives with Hydrogen Bonding and Chiral Moieties and Characterization of One-dimensional Helical Structures Composed of TTF Derivative and F_4TCNQ Complexes.

○Fumiya Hirose[1], Sadafumi Nishihara[2,3], Tsuyoshi Minami[4], Tomoyuki Akutagawa[5], Takayoshi Nakamura[6], Yoko Tatewaki[1] (1. Tokyo Univ. of Agri. and Tech., 2. Hiroshima Univ., 3. JST PRESTO, 4. Univ. of Tokyo, 5. Tohoku Univ., 6. Hokkaido Univ.)

Japanese

[P2-2vn-18]

Preparation of Scaffolds Composed of Molecular Nanocoils and Application to Saos-2 Cell Culture

○Aoba Sasaki[1], Noritaka Maezono[1], Akira Matsumoto[2], Sadafumi Nishihara[3,4], Tomoyuki Akutagawa[5], Takayoshi Nakamura[6], Tsuyoshi Minami[2], Yoko Tatewaki[1] (1. Tokyo Univ. of Agri. and Tech, 2. Univ. of Tokyo, 3. Hiroshima Univ., 4. JST PRESTO, 5. Tohoku Univ., 6. Hokkaido Univ.)

Japanese

[P2-2vn-19]

Theoretical studies on electronic properties in iron-oxo porphyrin model complex and reaction process in P450

○Mizuki Otsuka[1], Takashi Kawakami[2,1], Marie Tsuchikawa[1], Shusuke Yamanaka[1], Mitsutaka Okumura[1], Kizashi Yamaguchi[2,1] (1. Osaka University, 2. RIKEN)

Japanese

[P2-2vn-20]

Development of a hydrogen-bonding cobalt(II)-organic framework bridged by a dicarboxylic acid linker

○Tomohiro Okano[1], Takuya Kanetomo[1], Masaya Enomoto[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-21]

Effects of desymmetrization on structures and physical properties in canted antiferromagnetic single-component molecular conductors

○shota arai[1], So Yokomori[1], Nobuyuki Matsushita[1] (1. The College of Science,Rikkyo University)

Japanese

[P2-2vn-22]

Electrical and Magnetic Properties of Axially Ligated Manganese Benzoporphyrin-based Conducting Crystals

○Kosuke Mine[1], Noriaki Hanasaki[3], Hiroshi Murakawa[3], Masaki Matsuda[2] (1. Graduate School of Science and Technology, Kumamoto University, 2. Faculty of Advanced Science and Technology, Kumamoto University, 3. Department of Physics, Osaka University)

English

[P2-2vn-23]

Magnetic monitoring electrochemical properties in strongly correlated Cu3BHT

○Yigang Jin[1] (1. Nagoya University, Graduate School of Science)

Japanese

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[P2-2vn-24]

On energy transfer to added fluorescence dopant in the solid system of near-infrared triplet-triplet annihilation photon upconversion by using quantum dot

Neeti Tripathi[1], ○Kenji Kamada[1] (1. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese

[P2-2vn-25]

Fabrication and characterization of sensitized dye solar cells with energy transfer in the presence of spiropyran derivative and cyclodextrin -SQ2/SPNO$_2$ system-

○Ryuhei Ejima[1], Michihiro Hara[1] (1. Fukui University of Technology)

Japanese

[P2-2vn-26]

Aggregate formation and multicolor fluorescence emission shown by dye blocking ESIPT sites

○Yuma Hirose[1], ken-ichi Sakai[1], Tomoyuki Akutagawa[2] (1. Chitose Inst. Sci. Tech., 2. IMRAM, Tohoku Univ.)

Japanese

[P2-2vn-27]

Creation of optical properties by controlling axial rotation in *p*-terphenyl derivatives

○Kei Kobayashi[1], Ken-ichi Sakai[1], Tomoyuki Akutagawa[2] (1. Chitose Institute of Science and Technology, 2. IMRAM)

Japanese

[P2-2vn-28]

Calculation and analysis of absorption and fluorescence spectra, and radiative and non-radiative rate constants of rubrene based on the theory of vibronic coupling

○Motoyuki Uejima[1], Hiroo Fukunaga[1], Wataru Ota[2,3], Tohru Sato[2,3] (1. MOLFEX Inc., 2. FIFC, Kyoto Univ. , 3. Graduate School of Technology, Kyoto Univ.)

Japanese

[P2-2vn-29]

Luminescent Chiral Binaphthalimide as Liquid Crystal Dopant for Enhance CPL Emission

○Yuki Yamashita[1], Chigusa Goto[1], Yugo Tsuji[1], Tsuyoshi Kawai[1], Yo Shimizu[1], Marine Louis[1] (1. Nara Institute of Science and Technology)

Japanese

[P2-2vn-30]

Synthesis of diarylethene-fused metal dithiolene complexes for the development of novel photoresponsive molecular conductors

○Kaito Wakao[1], So Yokomori[1], Ryo Nishimura[1], Masakazu Morimoto[1], Nobuyuki Matsushita[1] (1. The College of Science, Rikkyo University)

Japanese

[P2-2vn-31]

Analysis Stabilization Mechanism of Avobenzone and β-Cyclodextrin complex

○Ryotaro Koga[1], Chihiro Kuroda[1], Ryosuke Hiroshige[1], Megumi Minamide[1], Kanji Hasegawa[1], Tomohiro Tsuchida[1], Satoru Goto[1] (1. Tokyo University of Science)

Japanese

[P2-2vn-32]

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Synthesis of N-Methylcarbazole - FTCNQ

○Kota Tsuchiaki[1], Yosuke Tokuda[2], Hideo Yamakado[1,2] (1. Wakayama University, 2. Wakayama University Graduate School)

Japanese

[P2-2vn-33]

Effect of Introducing Substitutions into Anthraquinone-Based Compounds as Organic Anolytes for Aqueous Redox Flow Batteries

○Momoka Kawgauchi[1], Atsushi Okazawa[1], Kosuke Kawai[1], Masashi Okubo[1] (1. Waseda University)

Japanese

[P2-2vn-34]

Synthesis and physical properties of complexs of Methoxyphenazine and TCNQ compounds

○Kodai Ichinose[1], Yosuke Tokuda[2], Hideo Yamakado[1,2] (1. Faculty of Systems Engineering, Wakayama Univ., 2. Graduate School of Systems Engineering, Wakayama Univ.)

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天然シクロデキストリンの溶媒和ギブスエネルギー（近畿大生物理工[1]・福岡大薬[2]）〇藤澤 雅夫[1]・大波多 友規[2] 堤 広之[2] 池田 浩人[2]

Solvation Gibbs energies of natural cyclodextrins ([1]*Dept. of Biotechnological Science, Kindai University.*, [2]*Fac. of Pharmaceutical Science, Fukuoka University*) [1] 〇Masao Fujisawa[1], Tomonori Ohata[2]. Hiroyuki Tsutsumi[2], Hirohito Ikeda[2]

Cyclodextrins (CyDs) can accommodate various kinds of guest molecules in its internal cavity, recognizing the difference in structure of guest molecules in aqueous solution. We determined systematically thermodynamic functions for the molecular inclusion of simple molecules into cavities in dilute aqueous solutions using microcalorimetry, and using computational chemistry method. The water solubility is known to differ depending on the size of the inner diameter of the molecule and substituents. γ-CyD has the greatest water solubility, followed by α-CyD, β-CyD, in that order. Multiple methods have been used to determine the solvation Gibbs energy and its relationship to solubility. The Gibbs energies were calculated based on geometry optimization and frequency calculations by using Density Functional Theory (DFT)in both the gas phase and water. The Bennett acceptance ratio method was also used with molecular dynamics. Solvation Gibbs energy obtained by using energy representation (ER) method was also used with molecular dynamics. In three different ways, β-CyD had the least stable in solvation. The low water solubility of β-CyD was also supported by the number of hydrogen bonds determined by molecular dynamics.
Keywords : Solvation Gibbs Energy, DFT, Molecular Dynamics, ER, bar

シクロデキストリン(CyDs)は、水溶液中でのゲスト分子の構造の違いを認識し、その内部空洞に様々な種類のゲスト分子を収容することができる。 我々は、ミクロ熱測定と計算化学的手法を用いて、希薄水溶液中のキャビティへの単純分子の分子包接に関する熱力学関数を系統的に決定した。CyD の水に対する溶解度は分子の内径の大きさと置換基によって異なることが知られている。γ-CyD の水溶性が最も高く、次いでα-CyD、β-CyD の順である。溶媒和ギブスエネルギーと溶解度との関係を決定するために、複数の方法が用いて明らかにすることを企てた。溶媒和ギブスエネルギーは、気相と水相の両方で密度汎関数理論（DFT）を用いて、構造最適化と振動数計算に基づいて計算された。また、分子動力学法を用いてベネット受容比法を用いた。さらにエネルギー表現(ER)法を用いて得られた溶媒和ギブスエネルギーも分子動力学法を用いて決定した。3 つの異なる方法で、β-CyD は最も溶媒和安定性が低かった。β-CyD の低い水溶性は、分子動力学法によって決定された水素結合の数によっても支持された。

1) Enthalpy and entropy changes on molecular inclusion of pentane derivatives into α-cyclodextrin cavities in aqueous solutions. T. Kimura, S. Fujie, T. Yukiyama, M. Fujisawa, T. Kamiyama, H. Aki *J. Incl. Phenom. Macrocycl. Chem.* **2011**, *70*, 269.

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アルカリ金属塩の直接添加による卵白の熱凝集体の可溶化

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Solubilization of Heated Egg White Aggregates by Direct Addition of Alkali Halides
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Solubilization and recovery techniques of water-insoluble protein aggregates such as heated-egg white and amyloid aggregates are related to the reconstruction technique of protein aggregation.[1)] Recently, we have investigated the solubilization of amyloid aggregates of bovine insulin and human α-synuclein by direct addition of alkali halides. Lithium iodide (LiI) showed a strongest solubilization ability among alkali halides.[2)] As a next step, we have investigated the direct additional effect of ten alkali halides on the solubilization of heated egg white aggregates (HEWA) using FTIR spectroscopy. The present finding is that LiI and cesium iodide (CsI) showed a high solubilization ability for HEWA among the studied salts. The solubilization ability of salts for HEWA depends on the competition between the ionic radius and the heat of hydration of salts.
Keywords : Heated Egg White; Solubilization; Alkali Halides; FTIR Spectroscopy

規則性凝集体であるアミロイド凝集体や不規則性凝集体である熱蛋白質凝集体を天然状態に戻す技術は、医薬品や蛋白質工学の分野で重要な課題である[1)]。最近、我々は、アルカリ金属の直接添加によるウシ由来 insulin 及びヒト由来 α-synuclein のアミロイド凝集体の可溶化効果を調べた[2)]。その結果、10 種類のアルカリ金属塩の中で、ヨウ化リチウム(LiI)が最も高い可溶化効果を示すことを明らかにした。そこで、次のステップとして、アルカリ金属塩による熱蛋白質凝集体の可溶化に着目した。本研究では、10 種類のアルカリ金属塩の直接添加による卵白の熱凝集体の可溶化を FTIR 分光法により用いて調べた。その結果、卵白の熱凝集体に対して LiI とヨウ化セシウム(CsI)が高い可溶化能を示した。塩による卵白の熱凝集体の可溶化は、イオン半径と塩の水和熱の競合性に依存することが示唆された。

1) Bacterial inclusion bodies: Discovering their better half. U. Rinas, E. Garcia-Fruitós, J. L. Corchero, E. Vázquez, J. Seras-Franzoso, A. *Trend Biochem. Sci*., **2017**, *42*, 726.
2) Dissolution of amyloid aggregates by direct addition of alkali halides. T. Takekiyo, N. Yamada, T. Amo, C. T. Nakazawa, A. Asano, T. Ichimura, M. Kato, Y. Yoshimura, *J. Mol. Liq.*, **2023**, *369*, 120849.

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有機ハロゲン化物塩とヨウ素から成る高導電性深共晶溶媒

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Highly Conductive Deep Eutectic Solvents Using Organic Halides and Iodine

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Deep eutectic solvents (DESs) are a new class of solvents that become liquid at room temperature due to the eutectic effect when two or more substances (typically solids) are mixed at a certain composition. Most DESs are electrically conductive because they contain an organic or a metal salt as a constituent, while their high viscosity makes them less electrically conductive. In this presentation, we will report a study of DESs composed of organic halide salts (chloride, bromide, and iodide salts of choline and 1-ethyl-3-methylimidazolium) and iodine, which possess high electrical conductivities. The electrical conductivity of the DESs studied increased as increasing the molar ratio of the iodine to the organic halide salt. Comparing the chloride, bromide, and iodide mixtures with the same molar ratio, the iodide salts showed the highest electrical conductivity. A 1:2.5 mixture of choline iodide and iodine showed an electrical conductivity of as high as 41.7 mS cm^{-1}. In addition, the slope of the electrical conductivity to the molar ratio is clearly steep in the iodide salt DESs. The phase diagrams of the mixtures will be also discussed.
Keywords: deep eutectic solvent, organic halide, iodine, high electrical conductivity

深共晶溶媒（DES）とは，2種類以上の物質（典型的には固体）をある特定の組成で混ぜた時に共晶効果により室温で液体状態になる物質をいう。多くのDESは，有機塩や金属塩を構成物質として含むため導電性を有しているものの，高い粘性のため導電性はあまり高くない。今回の発表では，有機ハロゲン化物塩（コリン及び1-エチル-3-メチルイミダゾリウムの塩化物塩，臭化物塩，及びヨウ化物塩）とヨウ素から成る高い導電性を有する深共晶溶媒の研究結果を報告する。本研究で検討した深共晶溶媒においてハロゲン種に注目すると，ヨウ化物塩によるDESが最も高い導電性を示した。また，いずれの系も有機ハロゲン化物塩に対するヨウ素のモル比が大きくなるほど電気伝導率が高くなった。このモル比に対する電気伝導率の傾きは，ヨウ化物塩のDESにおいて明らかに大きいことが分かった。コリンのハロゲン化物塩とヨウ素から成るDESの中では最も高い導電性を示すものはヨウ化コリンとヨウ素の1:2.5混合物であり，その電気伝導率は25 ℃で41.7 mS cm^{-1}であった。当日の発表ではこれらの相図についても議論を行う。

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pH 依存的なオキシカム系酸性薬物のコンフォメーション変化による疎水性の増強

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Enhancement of hydrophobicity in oxicam group of acidic drugs by pH-induced conformational change (*Faculty of Pharmacy, Tokyo University of Science*) ○Kota Moritake, Kanji Hasegawa, Tomohiro Tsuchida, Satoru Goto

Acidic non-steroidal anti-inflammatory drugs cause drug-induced kidney damage by transporting across the renal membranes. This transportation is related to hydrophobicity, which is variable depending on pH. Conventionally, it is known that compounds with carboxylic acids have a high possibility of dimerization, and methanol (MeOH) increases their pK_a. The UV-Vis measurement and singular value decomposition determined the pK_a of propionates, naproxen (NPX) and ketoprofen (KTP), and oxicams meloxicam (MLX) and piroxicam (PRX). For NPX and KTP, their pK_a values increased depending on MeOH concentration. It means the acidity has decreased, considering that dehydration by MeOH reduces the amount of hydration water around the carboxyl group, promoting dimerization of NPX or KTP, making acid dissociation less likely to occur. On the other hand, the pK_a of MLX and PRX decreased depending on MeOH concentration. It means the acidity has increased, suggesting oxicams have intramolecular hydrogen bonds and are stabilized by hydrophobic hydration. MeOH facilitates acid dissociation due to its inability to maintain a hydrophobic hydration state for MLX and PRX. We will show the results of fluorescence measurement, and discuss the state of dimerization in NPX and conformational changes of MLX or PRX.
Keywords : partition confficient; acid dissociation constant; high-performance liquid chromatography; non-steroidal anti-inflammatory drugs; hydrophobicity

酸性薬物である非ステロイド性抗炎症薬は腎膜を介した輸送により薬剤性腎障害を引き起こす．輸送には薬物の疎水性が関与し，解離性薬物の場合 pH に応じて変化する．カルボン酸を有する化合物は二量体化する可能性が高く，メタノール (MeOH) によって pK_a が上昇することが知られている．プロピオン酸系のナプロキセン (NPX) とケトプロフェン (KTP)，オキシカム系のメロキシカム (MLX) とピロキシカム (PRX) の種々の pH における UV-Vis スペクトルを測定し，特異値分解を行うことで pK_a を決定した． MeOH 存在/非存在下での pK_a を比較すると，NPX と KTP は MeOH 濃度依存的に pK_a が増加した．これは酸性度が低下したことを意味している．MeOH の脱水により，カルボキシル基周辺の水和水が減少し，NPX と KTP の二量体化が促進されることで酸解離が起きにくくなったと考えられた．MLX と PRX は MeOH 濃度依存的に pK_a が低下した．これは酸性度が増加したことを意味している．MLX と PRX は分子内水素結合を有しているため，水中では疎水性水和によって安定化されていたが，MeOH により疎水性水和が維持できず，酸解離が起きやすくなったと考えられた．当日は励起・蛍光スペクトル測定の結果を示し，NPX が多量体を形成する様子と，MLX と PRX のコンフォメーション変化について検討した結果を述べる．

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UV 吸収剤であるオキシベンゾン-3 及びアボベンゾンの結合により誘導される BSA 中のトリプトファン-134 および 213 の蛍光スペクトル遷移の識別

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Distinguishing the transitions of fluorescence spectra of tryptophan-134 and 213 in BSA induced by bindings of UV filters, oxybenzone-3, and avobenzone ([1]*Faculty of Pharmacy, Tokyo University of Science*, [2]*Graduate School of Pharmaceutical Sciences, Tokyo University of Science*) Megumi Minamide,[1] Yusuke Horizumi,[2] Minori Tsurushima,[1] Ryotaro Koga,[2] Kanji Hasegawa,[2] Yuya Kurosawa,[2] Tomohiro Tsuchida,[1] Satoru Goto[1]

Ketoprofen (KTP) known as an analgesic anti-inflammatory drug involves a photo-allergic reaction by haptenization, and active ingredients in sunscreens have also been reported to involve similar issues. Oxybenzone-3 (OBZ) and avobenzone (ABZ) are currently used as commercial ultraviolet-light filters for sunscreens, they have similar structures of benzophenone skeleton with photoexcitability as KTP. In this study, to determine the chemical modification of these compounds on bovine serum albumin (BSA) which is abundant in the blood, we investigated an interaction between BSA and these compounds using a Stern–Volmer plot analysis and trajectory analysis with singular value decomposition (SVD) of the tryptophan (W) fluorescence spectrum of BSA. As a result, The W fluorescence in the presence of ABZ showed a blue shift in its peak and had two binding sites with different affinities by Langmuir analysis. On the other hand, that in the presence of OBZ showed a red shift, indicated adsorption on the W residue present in the hydrophobic region and coating hydrophilic W residue present in the hydrophilic region.

Keywords : BSA intrinsic fluorescence; benzophenone derivatives; singular value decomposition (SVD); Langmuir adsorption isotherm; Hill's plot

鎮痛消炎剤であるケトプロフェン（KTP）はハプテン化による光アレルギー反応を伴うが，日焼け止め有効成分でも同様の問題が報告されている．市販の日焼け止め用紫外線フィルターとして現在用いられているオキシベンゾン-3 (OBZ) およびアボベンゾン (ABZ) は，KTP と同様に光励起性のあるベンゾフェノン骨格の類似構造を持つ．本研究では，血中に多く存在するウシ血清アルブミン（BSA）に対する OBZ 及び ABZ の化学修飾を決定するため，BSA のトリプトファン（W）蛍光から Stern-Volmer プロット解析および特異値分解 (SVD) 計算によるトラジェクトリー解析を用いて，薬物と BSA の相互作用様式を調べた．その結果，ABZ による W 蛍光は青方偏移を示し，ラングミュア解析から親和性の異なる 2 つの結合部位が観察された．一方で OBZ では赤方偏移を示し，疎水性領域に存在する W 残基への吸着，又親水性領域に存在する W 残基への被覆が示唆された．

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含窒素有機化合物水溶液の XAS 測定

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XAS Measurements for Aqueous Solutions of Nitrogen Containing Organic Compounds ([1]*Graduate School of Frontier Sciences, The University of Tokyo*) Haoran Xu,[1] ○Takehiko Sasaki[1]

Nitrogen-containing organic compounds are important as ionic liquids and amino acids. In this study N K-edge and C K-edge XAS measurements were conducted for aqueous solutions of imidazole, 1-ethylimidazolium chloride and various amino acids. For the analysis of obtained spectra, quantum chemical calculations were achieved for determining structures of solutes in aqueous solutions, followed by XAS simulations. Dependence on the charge state, PH and hydrogen bonding are discussed.
Keywords : XAS; Aqueous Solution; N K-edge; EmimCl

含窒素有機化合物は、イオン液体やアミノ酸として重要である。本研究では、イミダゾール、１－エチルイミダゾリウムクロリド、種々のアミノ酸の水溶液について、N K 端 及び C K 端 軟 X 線吸収分光法の測定を行った。液体サンプルの XAS 測定は、長坂らが開発した装置を使用して PF BL7A で実施した[1]。 SiC 膜を備えた液体サンプルセルを採用し、液体層の厚さはセル周囲の He ガス圧力によって制御した。 1-エチル-3-メチルイミダゾリウムクロリド (EmimCl) 0.20 M および 0.10 M 水溶液試料 の N-K XAS スペクトルを図 1 に示す。すべての場合において、401.0 eV に鋭いピークが見つかり、この位置が濃度や置換基に依存せずにイミダゾリウム N 原子に固有であることがわかった。また、他の関連する窒素含有分子の N-K XAS スペクトルも測定した。ピーク位置は窒素原子の電荷量に依存することがわかった。

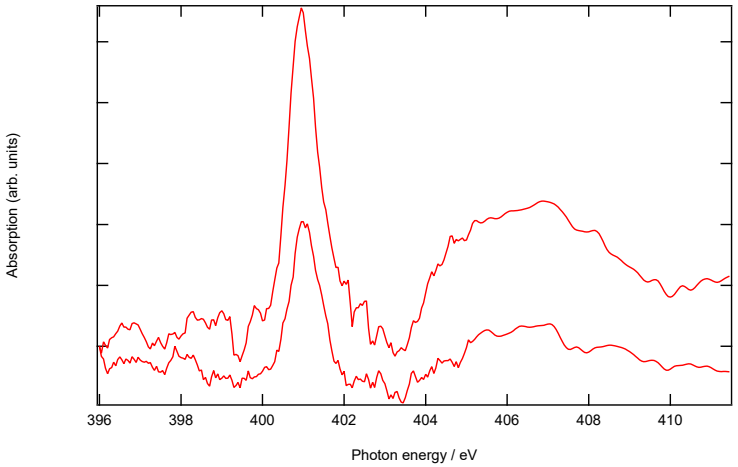

図 1 N-K XAS spectra measured for EmimCl aqueous solutions (Upper 0.20 M, Lower 0.10 M)

測定結果の解析のために、量子化学計算を行い、水溶液中の溶質分子の構造を求め、XAS シミュレーション計算を行った。中性、またはイオン状態による違い、PH の効果、水素結合の効果に関して議論を行う。

1) M. Nagasaka *et al.*, *J. Electrosc. Relat. Phenom.* **200** (2015) 293.

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Plasmon-influenced photoluminescence blinking behavior of lead halide perovskite quantum dots

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Keywords: Plasmon; lead halide perovskite; quantum dot; photoluminescence; blinking

Lead halide perovskite quantum dots (PQDs) show excellent optical and electronic properties due to the halogen- and size-dependent bandgap engineering. Single PQDs show photoluminescence (PL) blinking due to charging-discharging process induced by Auger ionization, which is further complexed by intermittent carrier trapping and de-trapping[1]. The PL of the PQDs can be enhanced or quenched by coupling the QD exciton with the localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs)[2]. However, plasmonic effects of Au NPs on the PL blinking behavior of PQDs are yet to be understood entirely. Here, we investigate the plasmon-influenced PL blinking behavior of PQDs on the Au NP films.

We synthesized ligand-free or ligand-capped methylammonium lead iodide ($MAPbI_3$) PQDs, respectively, by a spray or the ligand-assisted reprecipitation (LARP)[3] method. The LSPR substrate was prepared by tethering a monolayer of Au nanorods (NRs) on silanized glass substrate (Figure 1). Next, PQDs were deposited on the Au NR film (Figure 1). The PQD-Au film was excited by a 532 nm cw laser, where the Au LSPR couples with proximal PQDs, thus affected the PL. Using an electron-multiplying CCD camera, we recorded the emitted photons from the LSPR-coupled or -uncoupled PQDs. PQDs on glass substrate without Au NRs, were also studied as control samples.

$MAPbI_3$ PQDs illustrated clear on-off two states blinking. The blinking trajectories changed after coupling with Au NRs, showing PL intensity enhancement in most cases. We discussed the blinking change and intensity enhancement in terms of the effect of ligands.

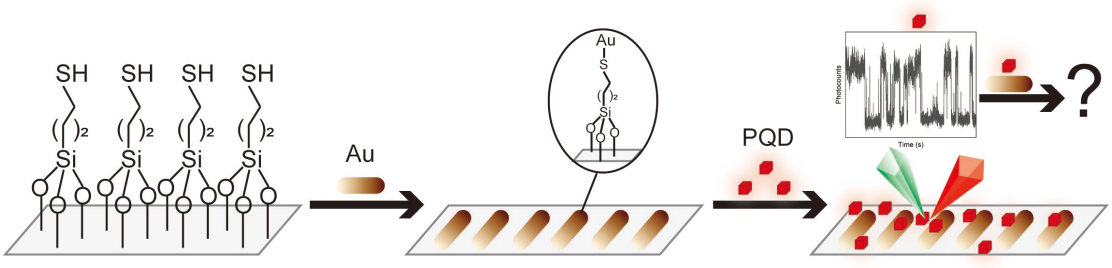

Figure 1. A scheme of Au NR tethered on a glass substrate and PQDs on the Au NR film.

1) C. Galland, Y. Ghosh, A. Steinbrück, M. Sykora, J.A. Hollingsworth, V.I. Klimov, H. Htoon, *Nature* **2011**, *479*, 203. 2) X. Yang, D. Su, X. Yu, P. Zeng, H.G. Liang, G.Z. Zhang, B.X. Song, S.L. Jiang, *Small* **2023**, *19*, 2205659. 3) F. Zhang, H.Z. Zhong, C. Chen, X.G. Wu, X.M. Hu, H.L. Huang, J.B. Han, B.S. Zou, Y.P. Dong, *ACS Nano* **2015**, *9*, 4533.

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半導体量子ドットを用いたジアリールエテン誘導体の Auger 再結合支援による光異性化反応

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Auger Recombination-Assisted Photoisomerization of Diarylethene Derivatives with Semiconductor Quantum Dots (*Graduate School of Science and Technology, Kwansei Gakuin University*) ○Moe Yamamoto Daichi Eguchi, Naoto Tamai

Colloidal semiconductor quantum dots (QDs) show efficient Auger recombination compared with the bulk due to the exciton confinement. Despite the generation of excited carriers in higher energy states through Auger recombination in QDs, the extraction of higher energy carriers is challenging due to the rapid relaxation from higher energy states. In the present study, we constructed hybrid systems of QDs and diarylethene derivatives and examined the effects of Auger recombination on the isomerization reaction. We found that the Auger recombination-assisted photoisomerization was induced by the multiple exciton generation in QDs at non-resonant excitation wavelength for a diarylethene derivative.

Keywords : Auger Recombination; Semiconductor Quantum Dots; Diarylethene Derivatives; Photoisomerization

半導体量子ドット(QDs)は、励起子間の相互作用である Auger 再結合がバルク半導体と比べて高効率で起こる [1]。この Auger 再結合では高エネルギー状態のキャリアが生成する。この高エネルギー状態を利用した物質変換は可能であると考えられるが、Auger 再結合により生成した高エネルギーキャリアの緩和時間は数百 fs 程度であるため利用が難しい。本研究では、QDs とジアリールエテンの複合系を構築し、Auger 再結合支援光異性化を見出したので報告する。

既報に従い、ジアリールエテン誘導体カドミウム錯体 ($Cd(DAE)_2$) と粒径の異なる CdSe QDs を合成した [2]。Z-type の配位子交換により、$Cd(DAE)_2$ と CdSe QDs を複合化した (DAE/CdSe HSs)[3]。複合化前後で CdSe QDs の発光量子収率は概ね維持しており、新たに表面欠陥を導入せずに複合体を構築することができた。この構築した複合体 (DAE は開環体) に対してパルスレーザー (520 nm) を照射すると、DAE の開環体のみでは光異性化が起きないにも関わらず、DAE/CdSe HSs では光異性化反応が進行した (図 1)。この開環体から閉環体への光異性化反応の速度は、励起光強度が大きくなるにつれ非線形的に増加するという依存性が観測され、多励起子生成が関与した Auger 再結合支援の光異性化が起きていることを示唆している。発表当日は、この過程の粒径依存性も報告する。

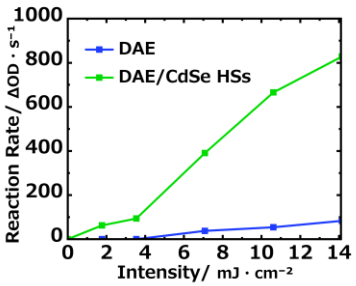

図 1. DAE/CdSe HSs (緑) と $Cd(DAE)_2$ (青) の初速度法により算出した光異性化速度の励起光強度依存性 (520 nm, 60 fs)

[1] Gyot-Sionnest *et. al*., *Chem.Rev.*, **2021**, *121*, 2325−2372. [2] Y. Charles Cao *et. al.*, *Angew.Chem.Int.Ed.*, **2008**, *47*, 8639 [3] Du-Jeon Jang *et. al., J.Phys.Chem.C*, **2021**, *125*, 22929.

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TTF 系分子を用いた新規磁性アセチリド錯体の作成

（明星大院[1]・東京理科大[2]・城西大[3]）○佐々木 創大[1]・西條 純一[1]・榎本 真哉[2]・秋田 素子[3]
Synthesis of new magnetic acetylides containing ethynyl-substituted TTF-based derivatives ([1]*Meisei University,* [2]*Tokyo University of Science*, [3]*Josai University*) ○Sodai Sasaki,[1] Junichi Nishijo,[1] Masaya Enomoto,[2] Motoko Akita[3]

Molecular magnetic materials have a low magnetic transition temperature due to weak spin-spin interactions. To overcome this weakness, we are developing Cr complexes with Tetrathiafulvalene (TTF) ligands, which are expected to exhibit strong intermolecular exchange interactions mediated by the stacking of TTF-based radical ligands. In this presentation, a $[CrCyclam(C_2MeTTF(SC_5H_{11})_2)_2]^+$ complex (Fig. 1) was synthesised by introducing two thiopentyl groups into the TTF backbone and coordinating them to CrCyclam to enhance solubility. This was combined with the magnetic anion $[Ni(mnt)_2]^-$ to give crystals of $[CrCyclam(C_2MeTTF(SC_5H_{11})_2)_2][Ni(mnt)_2]_3$ (Fig. 2). The TTF units of the adjacent $[CrCyclam(C_2MeTTF(SC_5H_{11})_2)_2]^+$ complexes sandwich a $[Ni(mnt)_2]^-$. This three-layered unit has a spin of S=1/2 at low temperature, and forms a ferrimagnetic chain with Cr^{3+}, where strong intra-chain interaction of $2J / k_B$ =－35 K was observed. The other two $[Ni(mnt)_2]^-$ complexes from non-magnetic dimer.
Keywords : Molecule-based magnetic material, Chromium, Acetylide, Tetrathiafulvalene

分子性磁性体はスピン間の相互作用が弱く磁気転移温度が低いという課題がある。この弱点を克服するべく、我々はテトラチアフルバレン(TTF)を配位子とした Cr 錯体の開発を行っている。TTF は酸化によりラジカルカチオンとなり、それが積層することによって強い分子間磁気相互作用の実現が期待される。本研究では、溶解度の向上を狙って TTF 骨格にチオペンチル基を 2 つ導入し CrCyclam に配位させた $[CrCyclam(C_2MeTTF(SC_5H_{11})_2)_2]^+$錯体(図 1)を合成、これと磁性アニオンである $[Ni(mnt)_2]^-$を組み合わせ、$[CrCyclam(C_2MeTTF(SC_5H_{11})_2)_2][Ni(mnt)_2]_3$ の結晶(図 2)を得た。この結晶は、積層した TTF-$[Ni(mnt)_2]^-$-TTF と Cr^{3+}がフェリ鎖を形成しており、強い鎖内相互作用 $2J / k_B$＝－35 K と弱い鎖間反強磁性相互が存在した。また、その鎖間には 2 分子の$[Ni(mnt)_2]^-$がダイマーとなり非磁性化している。

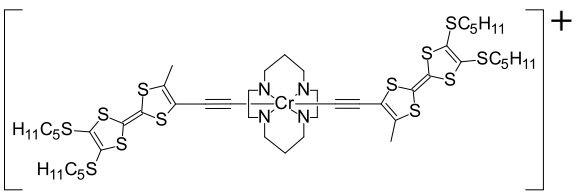

図 1 $[CrCyclam(C_2MeTTF(SC_5H_{11})_2)_2]^+$ 錯体

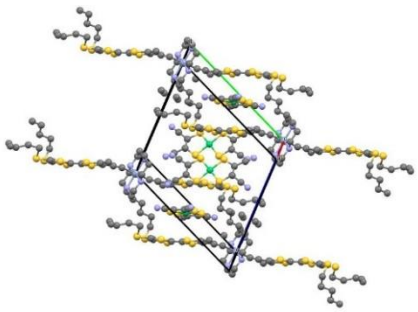

図 2 得られた結晶の構造

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水素結合を有する銅二核錯体[Cu(Eta)(Heta)(NO_3)]$_2$の結晶構造と磁性における重水素置換効果

（東京海洋大海洋工[1]・名市大院理[2]）村井 奨[1]・青柳 忍[2]・○藤田 渉[1]
Crystal Structures, Magnetic Properties, and their Deuterium Substitution Effects of Hydrogen-bonded Dinuclear Copper Complexes, [Cu(Eta)(Heta)(NO_3)]$_2$ ([1]*Faculty of Marine Engineering, Tokyo University of Marine Science and Technology*, [2]*Graduate School of Science, Nagoya City University*) Tasuku Murai,[1] Shinobu Aoyagi[2], ○Wataru Fujita[1]

The title compound, [Cu(II)(Eta)(Heta)(NO_3)]$_2$ (Eta = $H_2NCH_2CH_2O^-$, Heta = $H_2NCH_2CH_2OH$) (the hydrogen derivative **H**), reported by Bertrand et al.,[1)] has the copper dimer structure via O•••H–O strong hydrogen bonds, as shown in Fig. 1. In the dimer, an antiferromagnetic interaction works via the hydrogen bonds. In this presentation, crystal structures, magnetic properties, and their deuterium substitution effects of the complex were studied.

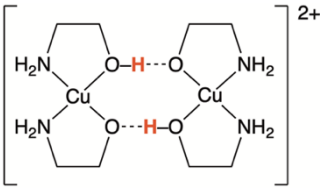

Fig. 1. Molecular structure of **H**.

The derivative **D** with the deuterated hydroxy and amino groups was prepared by mixing of $Cu(NO_3)_2$•$3D_2O$ and $D_2NCH_2CH_2OD$ in MeOD, and was identified by IR spectroscopy. Xray structure analyses revealed that the **D** derivative was isostructural with **H**. We found that these derivatives showed structural phase transitions to the low temperature phases at 118 K for **H**, and 126 K for **D**. Magnetic measurements revealed that the *g*-factors and the magnetic coupling constants $2J/K_B$, estimated from the Bleany-Bowers model, were 2.024 and –51.9 K for **H**, and, 2.039 and –51.3 K for **D**, respectively. It is concluded that there was little difference in magnetism between **H** and **D**. We will show the detailed data at the presentation venue.

A part of this work was conducted in Institute for Molecular Science, supported by ARIM of MEXT. Proposal Numbers JPMXP12232MS1030.
Keywords : Hydrogen Bond; Crystal Structure; Magnetic Properties; Structural Phase Transition; Deuterium Substitution

表題の物質 [Cu(Eta)(Heta)(NO_3)]$_2$ (Eta = $H_2NCH_2CH_2O^-$, Heta = $H_2NCH_2CH_2OH$)（**H**）は、Fig. 1 に示すように、２つの単核錯体が水素結合を介して二量体構造を形成し、この二量体間には水素結合を介して磁気的相互作用が働くことが知られている[1)]。本研究ではこの物質について、結晶構造の温度依存性、磁気測定、さらには水素結合部位の重水素置換を行った際の構造物性への影響について検討を行った。重水素置換体（**D**）は $Cu(NO_3)_2$•$3D_2O$ と $D_2NCH_2CH_2OD$ とを重メタノール中で混合することによって、調製した。**H** と **D** の結晶構造を検討したところ、**H** は 118 K 以下で、**D** は 126 K 以下でそれぞれ低温相へ相転移を示すことを発見した。一方、これらの磁気的性質を検討したところ、有意な差は認められなかった。詳細は当日報告する。

1) J. A. Bertrand et al. *Inorg. Chem*. **1980**, *19*, 2022.

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アルギン酸/ポリアクリル酸/1,2,3-トリアゾール複合体のプロトン伝導性

（金沢大理工[1], 金沢大院自然[2]）○山本源太[1]・重田泰宏[2]・栗原拓也[2]・雨森翔悟[2]・井田朋智[2]・水野元博[2]

Proton Conductivity of Alginic Acid-Polyacrylic Acid-Triazole Composites ([1]*School of Chemistry, College of Science and Engineering, Kanazawa University, Graduate School of Natural Science and Technology, Kanazawa University*) ○ Genta Yamamoto,[1] Yasuhiro Shigeta[2], Takuya Kurihara[2], Shogo Amemori[2], Tomonori Ida[2], Motohiro Mizuno[2]

Solid electrolytes that can act as proton conductors even under high temperature conditions of 100℃ or higher include composites of 1,2,3-triazole (Tz) and polymers. One of them is the composite of Tz, polyacrylic acid (PAA), and alginic acid (AA), (1-x) AA-xPAA-yTz (x and y indicate the ratio of PAA and Tz, respectively). High proton conductivity of these composites is considered to originate from the continuous proton transfer (Grotthuss Mechanism) with Tz as the carrier. However, the detailed kinetics of 1,2,3-triazole has not been clarified. Then, we prepared a composite of 1,2,3-Tz and a polymer and investigated the kinetic properties of 1,2,3-Tz by solid-state ^{2}H NMR measurements.

Keywords : Proton Conductivity; Solid Electrolyte; Solid State NMR

高温でも高いプロトン伝導性を示す電解質材料の開発が進められており、高分子にプロトンキャリアとしてトリアゾール(Tz)を加えた複合体もその一つである[1)]。本研究では、ポリアクリル酸(PAA)、アルギン酸(AA)と 1,2,3-Tz を用いた複合体 (1-x) AA-xPAA-yTz を調製し、プロトン伝導性を調べた。また、固体 ^{2}H NMR 測定により 1,2,3-Tz の運動性を調べ、プロトン伝導性との関係を考察した。

(1-x) AA-xPAA-yTz の膜は、1,2,3-Tz 及び PAA、AA の比率を変えて蒸留水中で混合し、数日間乾燥させることで得た。得られた膜を 50℃で 24 時間真空乾燥し、それぞれの膜について電気伝導率を測定した。固体 ^{2}H NMR測定ではTzの炭素と結合した水素を重水素化した 1,2,3-Tz-d_2 を用いて作製した複合体膜を用いた。

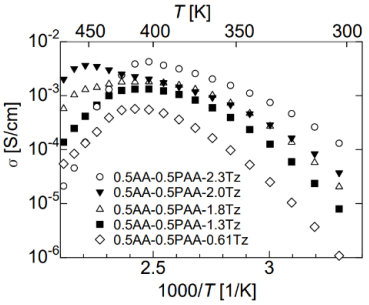

図 1 0.5AA-0.5PAA-yTz におけるプロトン伝導率の温度変化

図 1 に 0.5AA-0.5PAA-yTz（y=2.3, 2.0, 1.8, 1.3, 0.6）のプロトン伝導率の温度変化を示す。1,2,3-Tz の導入量が増えるにつれてプロトン伝導率は増大し、y=2.3 では 403 K で最大値 4.0×10^{-3} S/cm となった。^{2}H NMR のスペクトルでは高温でシャープなピークが現れ、1,2,3-Tz が等方回転運動することが分かった。また、Tz の導入量を増やすと Tz の運動性が向上し、プロトン伝導率の増大に繋がることが分かった。

1) R. Watanabe, T. Kurihara, Y. Shigeta, S. Amemori, N. Yamaguchi, F. Ishii, T. Ida, and M. Mizuno, *Solid State Ionics*, **399**, 116299 (2023).

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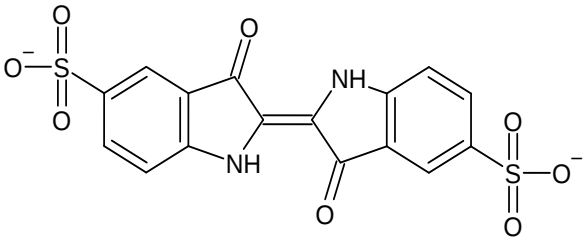
インディゴジスルホン酸を対アニオンとする BEDT-TTF 塩、(BEDT-TTF)$_3$(インディゴジスルホン酸)・(H_2O)の構造と物性

（阪大院理）○山延 謙斗・坏 広樹・中澤 康浩

Structure and properties of BEDT-TTF-based salt with indigodisulfonate, (BEDT-TTF)$_3$(Indigodisulfonate)・(H_2O) (*Graduate School of Science, Osaka University*) ○Kento Yamanobe, Hiroki Akutsu, Yasuhiro Nakazawa

We have prepared the title BEDT-TTF salt by electrocrystallisation using indigo carmine as an electrolyte, which is expected to become a dipole oscillator. BEDT-TTF trimer possessing a twisted stack and indigodisulfonate stack alternatively along the *b* axis. The outer molecules of the trimer have much larger charge(+0.82) than that of the inner molecule(+0.36).

Keywords：Organic Conductors; BEDT-TTF; dipole oscillator



Indigodisulfonate

インディゴなどの色素分子は分子全体に渡って広い共役系を持ち、導体内に導入すると振動分極を起こすことが期待できる。振動双極子を有する分子を有機導体に導入することで、振動分極と伝導電子との相互作用によってより高温の有機超伝導体の実現が期待されている。本研究では、インディゴジスルホン酸に注目し、今回は、BEDT-TTF 分子との電解を行うことにより表題の結晶を得ることが出来たので報告する。

インディゴカーミンと BEDT-TTF 分子を THF 18 mL、EtOH 2 mL、H_2O 1 mL の混合溶媒中で電解を行ったところ、黒色針状結晶が得られた。構造解析の結果、組成は(BEDT-TTF)$_3$(Indigodisulfonate)・H_2O （**1**）であった。Fig.1 に結晶構造を示す。晶系は triclinic、空間群は $P\bar{1}$であった。*b* 軸方向に沿って BEDT-TTF 3 量体とインディゴジスルホン酸が交互にスタックしていたが、この 3 量体内で BEDT-TTF はねじれてスタックしており、3 量体の内側(+0.36)より外側(+0.82/規格化後)の分子の方がずっと大きな価数を有していた。また、BEDT-TTF 分子は *a* 軸方向に沿って横方向には接触していた。予備的な伝導度測定の結果、半導体的挙動を示し、ρ_{RT}= 2.42 Ω･cm、*E*a = 0.053 eV であった。詳しくは当日報告する。

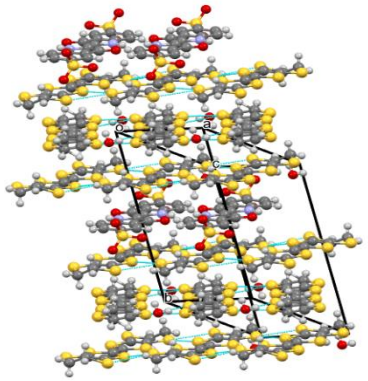


Fig.1. 結晶 **1** の結晶構造(点線は S…S 接触(< 3.70 Å))
(a = 6.6011(3), b = 15.2343(6), c = 16.2938(8) Å, α = 79.440(4), β = 80.204(4), γ = 77.779(4)°, Z = 2, V = 1559.52(13) Å^3, R = 8.80 %, T = 290 K)

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アザクリセン化合物群の電子特性

（市立山口東理大 [1]）○濱本 信次 [1]・井口 眞 [1]
Electronic Properties of Azachrysene Compounds ([1]*Department of Applied Chemistry, Faculty of Engineering, Sanyo-Onoda City University*)○Nobutsugu Hamamoto,[1] Makoto Inokuchi

Chrysene has a minimum framework of phenacene-type polycyclic aromatic hydrocarbons (PAHs) belonging to C_{2h} point group according to the molecular symmetry. Azachrysene compounds, where a carbon atom of chrysene is replaced by a nitrogen one, show different electronic properties depending on the position of nitrogen atom. In this study, we systematically examined an effect of a nitrogen atom on electronic properties, notably a molecular orbital energy diagram and a UV-Vis spectrum for a series of azachrysene compounds by theoretical calculations and experimental observations.
Keywords : Aromatic compound; Quantum chemical calculation; UV-Vis spectrum

フェナセン型の多環式芳香族炭化水素 (PAHs) は、分子構造の対称性によって 2 種類 (C_{2v} と C_{2h}) に分類される。先行研究において、C_{2v} 対称性に属する PAHs の最小骨格化合物である phenanthrene に着目し、その類縁体である窒素原子が 1 つ導入された azaphenanthrene において、窒素原子の導入位置による電子物性、特に分子軌道と紫外可視吸収スペクトルの違いを明らかとした [1)]。本研究では、C_{2h} 対称性に属する PAHs の最小骨格化合物である chrysene に窒素原子が導入された azachrysene の電子物性に関する窒素原子位置依存性を実験・理論の両面から系統的に明確にすることを目的とした。

1-azachrysene の紫外可視吸収スペクトルの実験・計算結果、及び chrysene の計算結果を Figure 1 に示す。chrysene を含むフェナセン型 PAHs の第一励起 (S_1) 及び第二励起 (S_2) 状態は Platt の記法で L_b 及び L_a と表記され、これら励起状態への電子遷移に伴う振動子強度は前者の方が小さい [2)]。これに対して、1-azachrysene では、S_1 状態の電子遷移に伴う振動子強度が S_2 状態のそれより大きい計算結果を得た。azaphenanthrene では、窒素原子導入に伴い、S_1 及び S_2 状態に主に関与する分子軌道の形状に大きな変化が生じていた [1)] が、1-azachrysene では比較的小さな変化しか生じていなかった。電子物性の詳細、及びその他の azachrysene の結果については当日報告する。

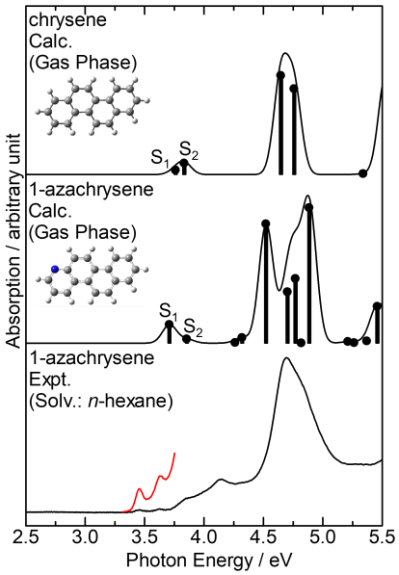

Figure 1. Excited states of chrysene and 1-azachrysene as obtained from the TD-B3PW91 calculations. The experimental absorption spectrum of 1-azachrysene is shown in the bottom panel.

1) N. Hamamoto *et al.*, *Phys. Chem.* **2022**, 552, 111370.
2) M. Baba *et al.*, *J. Phys. Chem. A* **2013**, 117, 13524.

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高伝導化を指向した新規オリゴマー型電荷移動塩 4P^{H}S-*X*

（東大物性研）○西田武志，藤野智子，小野塚洸太，森初果
Mixed-Sequence Oligomer Salt **4P^{H}S**–*X* for High Conductivity (*ISSP, The Univ. of Tokyo*)
Takeshi Nishida, Tomoko Fujino, Kota Onozuka, Hatsumi Mori

Oligomer-based conductors have rich structure-determining factors that can systematically tune their electronic structures. We have been developing oligomeric conductor series modeled on doped PEDOT[1–3]. Recently, we reported that a tetrameric (**P-S-S-P**) salt single crystal consisting of two types of monomoer units: ethylenedithiothiophene (**S**) and dimethypropylenedioxythiophene (**P**) which exhibits excellent room temperature conductivity and metallic state above room temperature. However, the relatively bulky **P** units at the termini reduced the effective intermolecular interactions. In this study, we developed a tetrameric salt in which a less-bulky propylenedioxythiophene was introduced in place of **P**, aiming to achieve even higher conductivity. This time, we will report on the synthesis and physical properties of this new tetramer (**P^{H}-S-S-P^{H}**).
Keywords : Oligomer, Charge transfer complex; Molecular crystal; Electrical conductivity; Band filling

低分子と高分子の間に位置するオリゴマー型伝導体は，豊富な構造制御因子をもち，構造の設計によって伝導性を自在に制御しうる理想的な材料である．我々はドープ型 PEDOT をモデルとしたオリゴマー伝導体材料を開発してきた [1–3]．最近ではエチレンジチオチオフェン（**S**）およびジメチルプロピレンジオキシチオフェン（**P**）の２種のユニットからなる４量体 **4PS**（**P-S-S-P**）の電荷移動塩単結晶が優れた室温伝導度を示すうえ、室温以上で金属化することを見出した [4]．しかし，末端に導入した，比較的嵩高い **P** ユニットが有効な分子間相互作用を低減させていた。そこで本研究では，さらなる高伝導化を目指し，**P** の代わりに嵩の低いプロピレンジオキシチオフェンを導入した 4 量体塩を開発した．本発表では，この新規 4 量体 **4P^{H}S** (**P^{H}-S-S-P^{H}**) の電荷移動塩の合成と物性に関して報告する．

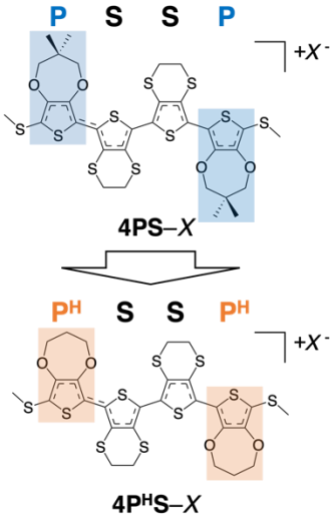

図 1. 新規混合配列型 4 量体の電荷移動塩の構造

1) Kameyama, R.; Fujino, T.*; Dekura, S.; Kawamura, M.; Ozaki, T.; Mori, H.* *Chem. Eur. J.* **2021**, *27*, 6696–6700. Front Cover. 2) Kameyama, R.; Fujino, T.*; Dekura, S.; Mori, H.* *Phys. Chem. Chem. Phys.*, **2022**, *24*, 9130–9134. 3) Kameyama, R.; Fujino, T.*; Dekura, S.; Imajo, S.; Miyamoto, T.; Okamoto, H.; Mori, H.* *J. Mater. Chem. C*, **2022**, *10*, 7543–7551. 4) Onozuka, K.; Fujino, T.*; Kameyama, R.; Dekura, S.; Mori, H.* *J. Am. Chem. Soc.* **2023**, *145*, 15152–15161.

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(BEDT-TTF)$_2$(PO-CONHC$_2$H$_4$SO$_3$)における結晶内分極と g テンソルの相関

(新潟大理[1]・新潟大 CCRF[2]・阪大院理[3])佐藤 栞[1]・○古川 貢[1,2]・坏 広樹[3]・中澤 康浩[3]
Shiori Sato[1], ○Ko Furukawa[1,2], Hiroki Akutsu[3], Yasuhiro Nakazawa[3]([1]*Faculty of Science, Niigata Univ.*, [2]*CCRF, Niigata Univ.*, [3]*Grad. School of Sci., Osaka Univ.*)

It has been reported the anomalous temperature dependence of the resistivity around 70 K in κ-β''- (BEDT-TTF) (PO-CONHC$_2$H$_4$SO$_3$). In order to clarify the relationship between the mechanism and the crystal structure, the temperature dependence of the g-tensor for κ-β''-(BEDT-TTF) (PO-CONHC$_2$H$_4$SO$_3$) was examined by using single-crystal ESR spectroscopy. At room temperature, the g-tensor estimated from an observed ESR signal originates from BEDT-TTF. On the other hand, the ESR spectrum at 5 K is composed of two ESR signals. We will discuss the relationship between the temperature dependence of the g-tensor and the polarized crystal structure.
Keywords : Organic Conductor, polarized structure, Single-crystal ESR, g-tensor

電荷移動錯体 κ-β''-(BEDT-TTF)$_2$(PO-CONHC$_2$H$_4$SO$_3$)は結晶状態で分極が生じ、70 K 付近で抵抗率に異常が見られることが報告されている[1)]。しかし、機能性メカニズムと構造との相関は解明されていない。本研究では、単結晶 ESR により g テンソルの温度依存性を解明し、電子状態変化と構造との相関解明が目的である。

図 1、2 に室温と 5 K における単結晶 ESR スペクトル(B_0 // z)を示した。室温では 1 つの ESR 信号から得られた g テンソルは BEDT-TTF に帰属できた。一方、5 K では、2 つの ESR 信号の和として解釈できた。つまり 5 K では、室温とは異なる 2 つの g テンソルの存在を示唆しており、低温における結晶内分極構造を反映することを示唆する結果を得た。当日は、g テンソルの温度依存性と構造との相関を議論する。

1) Hiroki Akutsu *et al.*, *Chem. Mater.*, 23, 762-764 (2011).

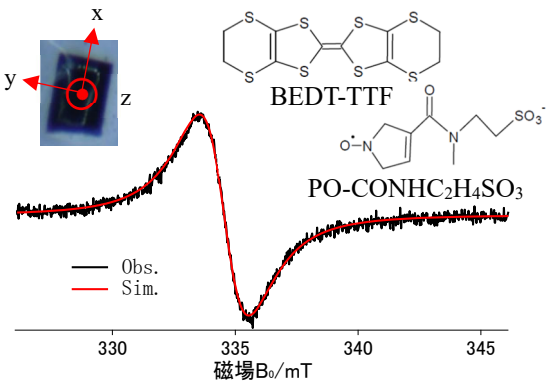

図 1：室温における実測(黒)とシミュレーション(赤)ESR スペクトル(B_0//z)。挿入図は、結晶外形に対する座標軸の定義と分子構造を示す。

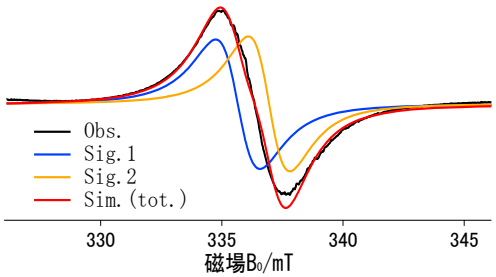

図 2：5 K における実測(黒)とシミュレーション(赤) ESR スペクトル(B_0//z)。シミュレーションは、sig.1(青)と sig.2(黄)の和で表記した。

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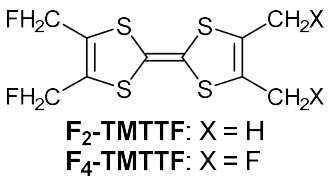
フッ素置換 TMTTF 誘導体の合成と物性

(長岡技科大)○後藤 脩哉・今久保 達郎
Synthesis and physical properties of fluorine-substituted TMTTF derivatives (*Nagaoka University of Technology*) ○Shuya Goto, Tatsuro Imakubo

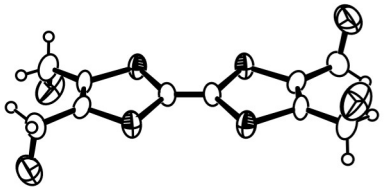
Fluorine has the largest electronegativity among all elements and is also the closest to hydrogen in atomic radius among all main group elements. For the sake of preservation of crystal structure and modification of electronic structure of known organic conductors, we have been working on selective fluorination of the hydrogen atom on the methyl group of tetramethyltetrathiafulvalene (TMTTF), which is one of the basic donor molecules in TTF-based organic conductors. In this presentation, we will report on the development of a synthetic route to the fluorine-substituted TMTTF derivatives, F_2-TMTSF and F_4-TMTSF, together with their crystal structure and electronic properties.

Synthesis of F_2-TMTSF and F_4-TMTSF has been accomplished by a $P(OEt)_3$ mediated cross-coupling reaction between 4,5-bis(fluoromethyl)-1,3-dithiole-2-thione and 4,5-dimethyl-1,3-dithiole-2-thione. Figure 1 shows molecular structure and crystal parameters of F_4-TMTSF. The neutral F_2-TMTTF has low crystallinity and crystallization conditions for the preparation of single crystals are currently under investigation. Electrochemical properties of these new donors will also be reported on the day of the conference.
Keywords : Tetrathiafulvalene; fluorine substitution; organic conductor



フッ素は、全元素中で電気陰性度が最大であると同時に典型元素の中で van der Waals 半径が水素に最も近い元素である。我々は、既知の有機伝導体の結晶構造を維持したまま電子構造を変化させる目的で、TTF 系有機伝導体における基本的なドナー分子の一つである tetramethyltetrathiafulvalene (TMTTF) のメチル基の水素を選択的にフッ素置換した誘導体の研究を進めている。本発表では、TMTTF のフッ素置換誘導体である F_2-TMTTF および F_4-TMTTF の合成法の開発と、中性分子の結晶構造および電子物性について報告する。

F_2-TMTTF および F_4-TMTTF の合成は、4,5-bis(fluoromethyl)-1,3-dithiole-2-thione と 4,5-dimethyl-1,3-dithiole-2-thione を $P(OEt)_3$ を用いてクロスカップリングさせることにより行った。Figure 1 に、F_4-TMTTF の分子構造と結晶構造パラメータを示す。中性の F_2-TMTTF については結晶性が低いことから、単結晶育成の条件を検討中である。当日は、これらの新規ドナー分子の電気化学測定の結果についても併せて報告する。



Crystal data for F_4-TMTTF: *Monclinic*, $P2_1/n$,
$a = 4.119(2)$, $b = 22.370(11)$, $c = 6.849(3)$ Å,
$\beta = 95.063(8)$ deg., $V = 628.7(5)$ Å^3, $Z = 2$,
$R = 0.0786$, $wR = 0.1809$, $GOF = 1.010$ for $I > 2\sigma(I)$,
$R = 0.1341$, $wR = 0.2132$, $GOF = 1.017$ for all data.

Figure 1. Molecular structure and crystal parameters for F_4-TMTTF.

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水素結合とキラル部位を有する TTF 誘導体の合成と F_4TCNQ 錯体を用いた 1 次元螺旋組織体の評価

(農工大[1]・広島大[2]・JST さきがけ[3]・東大[4]・東北大[5]・北大[6]) ○廣瀬 史哉[1]・西原 禎文[2,3]・南 豪[4]・芥川 智行[5]・中村 貴義[6]・帯刀 陽子[1]

Synthesis of TTF Derivatives with Hydrogen Bonding and Chiral Moieties and Characterization of One-dimensional Helical Structures Composed of TTF Derivative and F_4TCNQ Complexes

(Tokyo Univ. of Agri. and Tech.[1], Hiroshima Univ.[2], JST PRESTO[3], Univ. of Tokyo[4], Tohoku Univ.[5], Hokkaido Univ.[6]) ○ Fumiya Hirose[1], Sadafumi Nishihara[2,3], Tsuyoshi Minami[4], Tomoyuki Akutagawa[5], Takayoshi Nakamura[6], Yoko Tatewaki[1]

In recent years, the field of molecular electronics has been the focus of much research interest because of increasing expectation for more downsized and high-performance electronic devices. In particular, research on nanoscale devices consisting of functionalized molecules has been widely studied.

In this study, we synthesized a TTF derivative *S*-UM-TTF-Ts (Fig. 1), a disk-like molecule with multiple π-conjugation and hydrogen bonding moieties at the molecular center and a chiral moiety at the molecular end, to prepare a one-dimensional helical structure. *S*-UM-TTF-Ts forms a CT complex when mixed with an acceptor molecule, F_4TCNQ. The one-dimensional helical structure was obtained by dropping a solution of the *S*-UM-TTF-Ts complex dissolved in DMSO onto a mica substrate. AFM images of this one-dimensional helical structure indicated that the size was 30 nm in height, 6 nm in width, and 20 nm in pitch. The electrical conductivity of the one-dimensional helical structure in the bulk state was 2.3×10^{-3} S/cm, indicating semiconducting behavior. The electromotive force of one-dimensional helical structures will be reported.

Keywords : Charge Transfer Complexes, One-dimensional Helical Structures, Induced Electromotive Force

近年、電子デバイスのさらなる小型化や高性能化への期待から、分子エレクトロニクス分野が大きな注目を集めている。特に、機能性を有する分子を集積して構築したナノスケール素子に関する研究が盛んに行われている。

本研究では、1 次元螺旋組織体の作成を目的に、分子中心部分に複数のπ共役、水素結合部位を、分子末端にキラル部位を導入したディスク上分子である TTF 誘導体 *S*-UM-TTF-Ts (図 1)を合成した。*S*-UM-TTF-Ts はアクセプター分子である F_4TCNQ と混合することで CT 錯体を形成する。この錯体の DMSO 溶液をマイカ基板上に滴下することで、1 次元螺旋組織体が得られることが明らかとなった。この 1 次元螺旋組織体の AFM 像から、サイズは高さ 30 nm、幅 6 nm、ピッチ 20 nm であることが分かった。この 1 次元螺旋組織体のバルク状態での電気伝導度は、2.3×10^{-3} S/cm であり、半導体的な挙動を示した。1 次元螺旋組織体の起電力については、当日報告する。

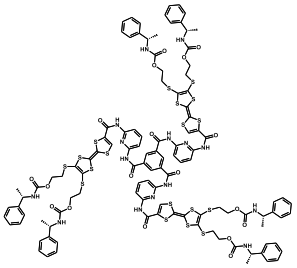

図 1　***S*-UM-TTF-Ts の分子構造**

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分子性ナノコイルを用いたスキャホールドの作成と細胞培養への応用

(1. 農工大院工、2. 東大生研、3. 広島大院先進理工、4. JST さきがけ、5. 東北大多元研 、6. 北大電子研) ○佐々木 青葉[1]、前園 宜孝[1]、松本 彬[2]、西原 禎文[3,4]、芥川 智行[5]、中村 貴義[6]、南 豪[2]、帯刀 陽子[1]
Preparation of Scaffolds Composed of Molecular Nanocoils and Application to Saos-2 Cell Culture (1. Tokyo Univ. of Agri. and Tech, 2. Univ. of Tokyo, 3. Hiroshima Univ., 4. JST PRESTO, 5. Tohoku Univ., 6. Hokkaido Univ.) ○Aoba Sasaki[1], Noritaka Maezono[1], Akira Matsumoto[2], Sadafumi Nishihara[3,4], Tomoyuki Akutagawa[5], Takayoshi Nakamura[6], Tsuyoshi Minami[2], Yoko Tatewaki[1]

Research on regenerative medicine and engineering has been reported in a large field of science and engineering, from the field of medicine to that of science and engineering. In particular, there is a need to develop new scaffold materials that effectively function the cells required for regeneration. It has been shown that external stimulation of cells with electric or magnetic fields promotes differentiation and proliferation.

In this study, a new scaffold was prepared based on a molecular coil composed of ***R*-TTF-4UM** which is TTF with hydrogen bonding and chiral moieties and F_4TCNQ. The induced electromotive force generated by this molecular nanocoil is used as a stimulus to increase the number of Saos-2 cells. Specifically, a molecular scaffold was prepared by casting a 5 mM(***R*-TTF-4UM**)(F_4TCNQ) complex solution on a glass dish. One hundred thousand Saos-2 cells were grown on the scaffold and cultured under magnetic field conditions, and MTT assay showed that the cell growth was approximately doubled under magnetic field application, indicating that the electrical charge induced efficient cell proliferation proceeded.
Keywords : Nanocoils; Organic Conductor; TTF Derivatives; Scaffolds

再生医工学に関する研究は医学分野から理工学分野まで広い範囲に渡り報告がなされており、特に再生に必要な細胞を効果的に機能させる新規スキャホールド材料の開発が求められている。また、これまでに、細胞に電場や磁場等の外部刺激を加えることによって分化や増殖が促進されることが明らかとなっている。

本研究では TTF に水素結合、キラル部位を付与した ***R*-TTF-4UM** と F_4TCNQ からなる分子性コイルを用いて新規スキャホールドを作成した。この分子性ナノコイルの誘導起電力を刺激として利用することで、Saos-2 細胞の増殖を促進させる。

具体的には、ガラスディッシュに 5 mM(***R*-TTF-4UM**)(F_4TCNQ)錯体溶液をキャストし、分子性スキャホールドを作成した。その上に、Saos-2 細胞 100,000 個を播種し、磁場印加条件下で培養した。MTT アッセイにより磁場印加下においては細胞増殖率が約 2 倍となり、外部電気刺激による効率的な細胞増殖の進行が示唆された。

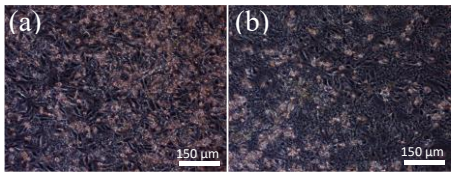

Figure 1 Optical microscopy images of Saos-2 cells (a) with magnetic field (b) without magnetic field

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鉄ポルフィリン-酸素モデル錯体の高精度計算と P450 の反応機構の理論的解明への適用

（阪大院理[1]・理研[2]）○大塚 瑞生[1]・川上 貴資[2,1]・土川 真理恵[1]・山中 秀介[1]・奥村 光隆[1]・山口 兆[2,1]
Theoretical studies on electronic properties in iron-oxo porphyrin model complex and reaction process in P450 ([1]*Graduate School of Science, Osaka University*, [2]*Center for Computational Science, RIKEN*) ○Mizuki Otsuka,[1] Takashi Kawakami,[2,1] Marie Tsuchikawa,[1] Shusuke Yamanaka,[1] Mitsutaka Okumura,[1] Kizashi Yamaguchi[2,1]

Iron-oxo porphyrin model complex is the main target to study the nature of hemoglobin, cytochrome and P450 etc. Thus, theoretical studies on electronic properties in the series of this complex have to be carried out by using accurate theoretical methods. High-valent iron ions are strong and important oxidants and contribute to oxygen-transfer in catalytic process. The active intermediate is widely known as radical cation species (Cpd I), where Fe(IV) ion is stabilized by oxygen and porphyrin ligand. Since higher oxidation state Fe(V) is also feasible with stronger ligands, electron-transfer from Fe ion to porphyrin is interesting to study the catalytic ability of Cpd I. In this study, we start to investigate relative stabilities among all possible electronic configuration by UB3LYP methods under broken-symmetry (BS) approach. Post-HF methods are also employed in order to reveal more accurate electronic properties.
Keywords : iron-oxo porphyrin complex; P450; hybrid-DFT method; broken-symmetry approach

シトクロム P450 は、自然界で最も汎用性の高い酵素の 1 つであり、特定の酸化還元酵素ファミリーに属する酵素の総称である。この酵素は、様々な有機化合物を酸化する反応により、ホルモンの生合成や解毒、薬物代謝を行うことが知られている。P450 の化学反応性は非常に多様であるが、最も一般的にはアルカン分子の水酸化を行う。この触媒に関係する活性中心は鉄ポルフィリン-酸素モデル錯体と呼ばれる活性中間体であり、鉄イオンが IV 価から III 価に変化する。この活性中間体は、ラジカルカチオン種 Cpd I : [(Fe(IV)=O)($Por^{+\cdot}$)]である[1]。本研究では軸配位子に Cl^-が配位した錯体において、Broken-Symmetry(BS)アプローチにて UB3LYP 計算、及び post-HF 計算により解析を行った。

鉄イオンの *d* 電子やポルフィリンのラジカル電子は磁気スピンを持つため、それらの局所スピンによるスピン多重度も考慮すると、例えば $^2[^3(Fe(IV)=O)\ ^2(Por^{+\cdot})]^+Cl^-$ (左肩の数値はスピン多重度)と表現できる。これらを、ポルフィリンの占有軌道の対称性(a_{1u}, a_{2u})に関連付けて、$^2A_1$, $^2A_2$ と表現する。加えて、より高い多重度となる $^4A_1$, $^4A_2$ も相対安定性の議論を実行するために採用した。同様に、鉄イオンからポルフィリンに分子内電子移動して鉄イオンがより高原子価となった ^2E : $^2[^2(Fe(V)=O)\ ^1(Por)]^+Cl^-$ も考慮した。これら全ての電子状態 $^2A_1$, $^2A_2$, $^4A_1$, $^4A_2$, ^2E, ...の解を作成し解析した。

1) DFT and ab initio study of iron-oxo porphyrins: May the have a low-lying iron(V)-oxo electromer ? M. Radon, E. Broclawik, K. Pierloot, *J. Chem. Theory Comput.* **2011**, *7*, 898.

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ジカルボン酸系有機リンカーが架橋する水素結合性コバルト(II)ー有機構造体の開拓

（東理大院理）○岡野朋博・金友 拓哉・榎本 真哉
Development of a hydrogen-bonding cobalt(II)-organic framework bridged by a dicarboxylic acid linker (*Tokyo University of Science*) ○Tomohiro Okano, Takuya Kanetomo, Masaya Enomoto

Hydrogen-bonded metal-organic frameworks (H-MOFs) exhibit a flexible porous structure and a highly crystalline nature. Recently, we reported a novel cobalt(II) complex $[Co(HL)_2]\cdot(DMF)_{1.2}(H_2O)_{2.4}$ (**1**·solv), where H_2L is 2,2':5',2''-terpyridine-5,5''-diyl bis(carboxylic acid).[1] Compound **1** had an H-bonded diamond framework. To control of the physical properties in the H-MOFs, we have focused on co-crystalline H-MOFs including the H-bond-active metal complex and organic linker units. In this study, a novel co-crystalline H-MOF $[Co(H_2L)(L)][Co(HL)_2](IPA)_3\cdot(MeOH)(H_2O)_{5.5}$ (**2**·solv) was synthesized, where IPA is isophthalic acid. There were direct H-bonds between the ligands with IPA and indirect H-bonds *via* H_2O. Thermal analysis and variable-temperature powder X-ray diffraction (VT-PXRD) measurement revealed that the desorption of solvent with increasing of temperature does not change the crystal structure. Magnetic measurement of both **2**·solv and the desolvated sample exhibited the spin transition (ST) behavior (Fig. 1). We will report on the crystalline-solvent-dependence of the ST behavior for **2**.
Keywords : cobalt(II) complexes; spin transition; hydrogen bonding

H-MOF は柔軟な多孔質構造および結晶性の高さなどが特徴である。これまでカルボキシ基を有するテルピリジン配位子 (H_2L) と Co^{2+}イオンから成る錯体 **1**·solv が H-MOF になることを報告した [1]。錯体 **1** は水素結合を介したダイヤモンド型骨格を持っている。加熱による溶媒脱離後、中心金属 Co^{2+}イオンは ST 挙動を示した。本研究では、物性制御を目的に、水素結合活性な有機化合物を架橋分子として内包する新奇 H-MOF の開発を行った。具体的には、イソフタル酸 (IPA) を含む共結晶 **2**·solv を合成した。構造解析より、配位子および IPA のカルボキシ基同士の直接的な水素結合および水分子を介した間接的な水素結合がそれぞれ見られた。熱分析と VT-PXRD 測定より、溶媒脱離は結晶性の低下を伴うものの構造は変化しないことがわかった。磁気測定より、**2**·solv は ST 挙動を示した。一方、**2** も ST 挙動を示唆する結果を与えたが、その変化は緩やかであった(Fig. 1)。本発表では結晶溶媒の吸脱着に伴う磁気挙動について報告する。

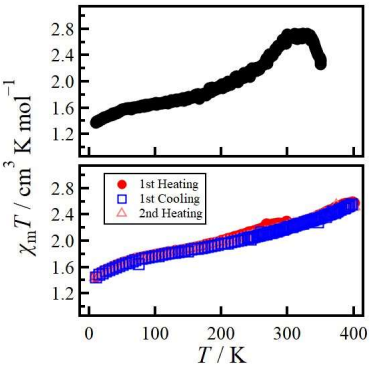

Fig. 1. $\chi_m T$ vs. T plots for (top) **2**·solv and (bottom) the desolvated **2**.

1) Kanetomo, T. et al., *Dalton Trans.*, **2022**, *51*, 5034.

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傾角反強磁性単一成分分子性導体における分子非対称化による構造・物性への影響

（立教大理）○荒井翔太・横森創・松下信之
Effects of desymmetrization on structures and physical properties in canted antiferromagnetic single-component molecular conductors (*College of Science, Rikkyo University*)
○Shota Arai, So Yokomori, Nobuyuki Matsushita

Canted antiferromagnetism (CAF) showing spontaneous magnetization is rare in especially molecular conductors, and thus its structure-property relationships have not been revealed. In our previous works, a family of alkoxybenzene-fused Au dithiolene complex crystals exhibiting CAF have been found. In this presentation, crystal structures and magnetic properties of obtained two kinds of crystals based on a newly synthesized asymmetric complex (Fig.1a, **Au2OPr2OBu**) will be reported and discussed as its CAF properties.
Keywords : Metal dithiolene complex; single-component molecular crystal; canted antiferromagnetism; single crystal

傾角反強磁性体とは反強磁性的磁気秩序を持つにも関わらず、全てのスピンが特定の方向に傾くことで強磁性的磁気挙動を示す磁性体である。特にπ電子非局在系の分子性導体においては傾角反強磁性を示す例はわずかであり[1,2]、その構造物性相関に関する系統的研究は行われていない。こうしたなか、最近我々はジエトキシベンゼン縮環 Au ジチオレン錯体 (Fig.1, **Au4OEt**)からなる単一成分中性ラジカル結晶が約 10 K 以下で傾角反強磁性を示すことを見出した。先行研究ではこの **Au4OEt** に加え、非対称化したエトキシプロポキシ体 (**Au2OEt2OPr**)とプロポキシ体 (**Au4OPr**)が同形で傾角反強磁性を示す一方、ブトキシ体 (**Au4OBu**)は分子配列が著しく変化し傾角反強磁性が消失することが明らかとなっている。

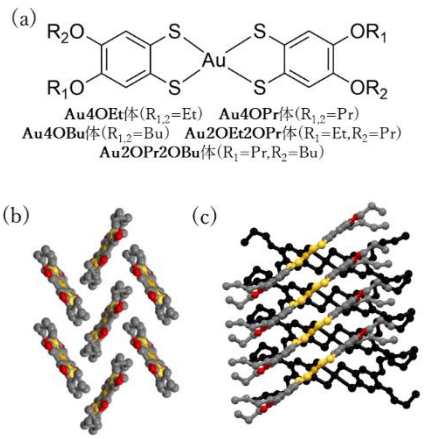

Figure 1. (a)ジエトキシベンゼン縮環型 Au ジチオレン錯体の構造
(b)**Au2OPr2OBu** の板状結晶の結晶構造
(c)**Au2OPr2OBu** の針状結晶の結晶構造

本研究では、その間の非対称錯体であるプロポキシブトキシ体 (**Au2OPr2OBu**)の合成、結晶化ならびにその磁気測定を行った。興味深いことに、板状と針状の異なる 2 種類の結晶が得られ、それぞれ **Au4OEt** と **Au4OBu** と同形で 1 次元 π-π スタッキング構造と 2 次元ヘリンボーン構造を構築していた。発表では、傾角反強磁性の発現が期待できる板状結晶の磁気特性の結果も交えて、報告・議論する予定である。

(1) X. Yu *et al.*, *J. Am. Chem. Soc*., **2012**, 134, 2264
(2) R. Ishikawa *et al.*, *J. Phys. Soc. Jpn*., **2018**, 87, 064701.

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軸配位子を有するマンガンベンゾポルフィリン導電性結晶の電気・磁気特性

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Electrical and Magnetic Properties of Axially Ligated Manganese Benzoporphyrin-based Conducting Crystals ([1]*Graduate School of Science and Technology, Kumamoto University*, [2]*Faculty of Advanced Science and Technology, Kumamoto University*, [3]*Department of Physics, Osaka University*) ○ Kosuke Mine,[1] Noriaki Hanasaki,[3] Hiroshi Murakawa[3], Masaki Matsuda[2]

Axially ligated iron phthalocyanine conductors exhibit the giant negative magnetoresistance effect caused by the strong π-d interaction between conducting π electrons and localized d spins. This effect can be modulated by changing a central metal ion, axial ligands, and/or a macrocyclic ligand. In this study, $Ph_4P[Mn^{III}(tbp)^{1.5-}L_2]_2$ (tbp = tetrabenzoporphyrin, L = CN, Br, or Cl) were fabricated, and their temperature dependence of the electrical resistivity, temperature dependence of the magnetic susceptibility, and magnetic field dependence of the resistance were measured to verify the influence of molecular modification on the negative magnetoresistance effect.

Keywords : Molecular Conductors; π-d Systems; Benzoporphyrin; Magnetoresistance Effect

軸配位型鉄フタロシアニン$[Fe^{III}(Pc)L_2]$（L = axial ligand）(Fig. 1)からなる導電体$Ph_4P[Fe^{III}(Pc)^{1.5-}(CN)_2]_2$は、π 伝導電子と局在 d スピンの間の強力な磁気的相互作用によって巨大な負の磁気抵抗効果を示す[1]。$Ph_4P[Fe(Pc)(CN)_2]_2$が示す負の磁気抵抗効果は大環状配位子や軸配位子の置換などの分子修飾によって変調を受ける[2,3]。本研究では、分子修飾が負の磁気抵抗効果に及ぼす影響の系統的検証の一つとして、軸配位型マンガンベンゾポルフィリン$[Mn^{III}(tbp)L_2]$からなる導電体$Ph_4P[Mn^{III}(tbp)^{1.5-}L_2]_2$の作製とそれらが示す磁気抵抗効果を評価した。

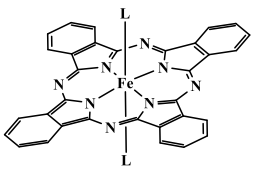

Fig. 1. Molecular Structure of $Fe(Pc)L_2$.

導電性結晶の作製条件を検討した結果、$Ph_4P[Mn(tbp)L_2]_2$（L = CN, Br, or Cl）の作製に成功した。このうち、$Ph_4P[Mn(tbp)(CN)_2]_2$及び$Ph_4P[Mn(tbp)Br_2]_2$の磁化測定を行ったところ、前者のMn^{III}は低スピン状態（$S=1$）、後者のMn^{III}は高スピン状態（$S=2$）であった。また、電気抵抗の磁場依存性測定を行ったところ、$Ph_4P[Mn(tbp)Br_2]_2$では、同形の結晶で最大の負の磁気抵抗効果を示す$Ph_4P[Fe(Pc)(CN)_2]_2$に匹敵するほど巨大な負の磁気抵抗効果が発現した。

当日は$Ph_4P[Mn(tbp)L_2]_2$の電気特性及び磁気特性から得られる知見をもとに、分子修飾が負の磁気抵抗効果に及ぼす影響について議論する。

1) N. Hanasaki, *et al.*, *Phys. Rev. B*, **2000**, *62*, 5839–5842.
2) D. E. C. Yu, *et al.*, *J. Mater. Chem.*, **2009**, *19*, 718–723.
3) M. Nishi, *et al.*, *Dalton Trans.*, **2016**, *45*, 16604–16609.

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Magnetic monitoring electrochemical properties in strongly correlated Cu-BHT

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Keywords: magnetic properties; electrochemical properties; antiferromagnetic

Two-dimensional (2D) π−d conjugated coordination polymers (CPs) have found widespread application as active materials in secondary batteries[1]. Despite their success, the underlying reason for their high charge storage capacity remains unclear. Some studies have suggested a mechanism involving the formation of multiple radicals on a single organic ligand. However, to date, no conclusive evidence supports this mechanism, and it stands in contrast to the established resonance theory[2]. In this study, we employed various magnetometric techniques to track the formation and concentration of paramagnetic species during the electrochemical process of 2D strongly correlated Cu-BHT (BHT = benzenehexathiolate)[3]. Surprisingly, the spin concentration of the fully reduced (discharged at 1.5 V) electrode was found to be very minimal, significantly lower than that expected for a "diradical" form. More intriguingly, we simultaneously observed a significant temperature-independent paramagnetic term. This observation suggests an enhancement of delocalized π electrons in the discharged state, pointing towards a mechanism where π-electron bands accept/donate electrons during the charge/discharge process in this strongly correlated system.

(1) Wada, K.; Sakaushi, K.; Sasaki, S.; Nishihara, H. *Angew. Chem.Int. Ed.* **2018**, *57* (29), 8886−8890.

(2) Zeng, Z.; Shi, X.; Chi, C.; Lopez Navarrete, J. T.; Casado, J.; Wu, J. *Chem. Soc. Rev.* **2015**, *44* (18), 6578−6596.

(3) T. Takenaka, K. Ishihara1, M. Roppongi. *Sci. Adv.* **2021**, 7, eabf3996.

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量子ドットを用いた近赤外変換三重項-三重項消滅光フォトンアップコンバージョン固体系における添加蛍光ドーパントへのエネルギー移動について

（産総研ナノ材）トリパティ ニーティ・○鎌田 賢司
On Energy Transfer to Added Fluorescence Dopant in The Solid System of Near-Infrared Triplet-Triplet Annihilation Photon Upconversion by Using Quantum Dot (*NMRI, AIST*) Neeti Tripathi, ○Kenji Kamada

For the solid system of near-infrared triplet-triplet photon upconversion (TTA-UC) by using PbS quantum dot as sensitizer (guest) and an anthradithiophene derivative (TES-ADT) as emitter (host), we added tetraphenyldibenzoperiflanthene (DBP) as fluorescent dopant and observed the emission from DBP. On this energy transfer to the fluorescence dopant, we report dependence of emission quantum yield for direct excitation on DBP-concentration and discuss the relation with the upconversion properties.
Keywords : Energy Transfer; Fluorescent Dopant; Photon Upconversion; Solid System; Quantum Dot

我々は太陽電池応用に向け 980 nm 以長の近赤光を吸収する増感剤としてPbS量子ドット(QD)を用い, 配位子交換でQDコアに吸着可能なanthradithiophene誘導体 (TES-ADT) をトランスミッター兼発光体とした固体系三重項-三重項消滅(TTA)光アップコンバージョン(UC)を報告して来た [1]。その際，マトリクスである TES-ADT が固体状態で顕著な蛍光消光を示すことが問題であった。

これに対し，蛍光ドーパントとして tetraphenyldibenzoperiflanthene (DBP) を添加し，溶液キャスト法にて作製した混合固体で DBP からと考えられる UC 発光を得た [2]。TES-ADT マトリクスへの DBP のドープ量を増加させると蛍光ピークの長波長化 (660 nm→700 nm) と蛍光量子収率の向上 (2.5%→23%) が認められた (Fig.1a)。1 mol%を超えるドープ量では構造の無い幅広いスペクトル形状を示した。固体にドープされた DBP の蛍光スペクトルは，一般に振動微細構造の明確なものが報告されているが, 今回の構造の無い発光スペクトルはアモルファス固体によるものと考えられる。また時間分解蛍光測定では，両成分間のエネルギー移動を示す長波長での立ち上がりが観測された(Fig.1b)。発表においては，エネルギー移動に関わる蛍光特性と UC 特性との関係を含めて議論する。

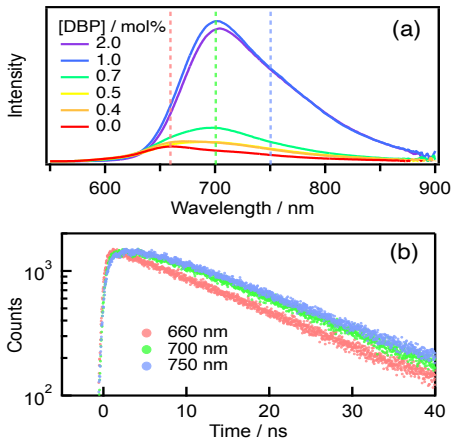

Fig. 1. (a) Change in fluorescence spectrum of TES-ADT film by doping of DBP. Dashed lines show the wavelengths of decay measurements. (b) Its decay profiles at 2.0 mol%-DBP.

1) N. Tripathi, M. Ando, T. Akai, K. Kamada, *J. Mater. Chem. C* **2022**, 10, 4563.
2) N. Tripathi, K. Kamada, *ACS Appl. Nano Mater.* ***Accepted***.

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スピロピラン誘導体とシクロデキストリンを含むエネルギー移動を伴う色素増感太陽電池の作製と評価-SQ2/SPNO$_2$ 系-

（福井工大院工）○江島隆平，原　道寛*

Fabrication and characterization of sensitized dye solar cells with energy transfer in the presence of spiropyran derivative and cyclodextrin -**SQ2/SPNO$_2$** system-

(*Department of Applied Science and Engineering, Fukui University of Technology*)
Ryuhei Ejima, Michihiro Hara*

We fabricated sensitized dye solar cells (DSSCs) based on **SQ2-dye** /1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran **(SPNO$_2$)** with incorporated photochromic molecules and investigated their control photoelectric conversion properties and the fabrication of color-changing DSSCs through external light stimulation. We found that the photoelectric conversion efficiency and absorption properties of these DSSCs increased after UV irradiation and decreased after visible light irradiation. The **SPNO$_2$** on the DSSCs photoisomerized from spiropyran form to photomerocyanine form (**PMC**) by the UV irradiation. This suggests that the mechanism of the improved photoelectric conversion properties in the DSSCs is energy transfer from **PMC** to **SQ2-dye** by FRET.

Keywords : Cyclodextrin; photochromic molecules; sensitized dye solar cells; energy transfer; spiropyran derivative

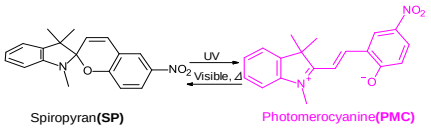

Fig. 1 Schematic of isomerization of **SPNO$_2$**(1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran).

色素増感太陽電池(DSSC)の高効率化の手段として共増感やエネルギー移動が注目されている。エネルギー移動の一つに，γ-シクロデキストリン(**CD**)共存下で **SPNO$_2$** の光異性体であるフォトメロシアニン型(**PMC**)から **SQ2** 色素へのエネルギー移動(FRET)が報告されている [1)]。また，フォトクロミック分子と **CD** 層を含む DSSC において，Vis 照射により **PMC** を光異性化させることで,光電変換特性が減少することを報告している [2)]。本研究ではスクアレイン系色素である **SQ2** 色素，**CDs(α-, β-, γ-CD)**，スピロピラン誘導体の一つである **SPNO$_2$** (1,3,3-Trimethyl indolino - 6'- nitrobenzopyrylospiran :**SPNO$_2$**）(Fig.1)に TiO_2 電極を浸漬させる事で **SQ2/CDs/SPNO$_2$** の DSSC の作製と評価を行った。フォトクロック分子を含むデバイスの可能性として，外部光刺激による光電変換特性の制御，色が変化する DSSC の作製を検討した。

SQ2/CDs/SPNO$_2$ 電極の透過率の外部光応答性は，540 nm において、UV5 分間照射で減少し，Vis5 分間照射で増加し，**SQ2/CDs** 電極に吸着した **SPNO$_2$** が外部光照射で **PMC** に光異性化し，それに伴い色が変化することが示唆された。また，**SQ2/CDs/SPNO$_2$** 素子の $IPCE_{580}$ は UV 光 5 分間照射後増大し、Vis 光 5 分間照射後減少した。このことから，光異性化した **PMC** が関与していることが示唆され，光電変換のメカニズムとして，**PMC** から **SQ2** へのエネルギー移動(FRET)後，TiO_2 への電子注入への過程が示唆された。また、Vis 光照射によって、その過程が抑制されることを示唆した。よって，**SQ2/CDs/SPNO$_2$** 素子において外部応答刺激による色の変化と光電変換特性の制御の可能性を示した。また、**SQ2/CDs/PMC** 電極及び **CDs/PMC** 電極の蛍光寿命, FRET 効率, **CD** による影響についても報告する。

1）Viktoras Dryza and Evan J. Bieske，*J. Phys. Chem. C,* **2015**, *119*, 14076–14084.
2） T. Takeshita, T. Umeda, and Michihiro Hara, *J. Photochem. Photobiol. A*, **2017**, *333*, 87-91.

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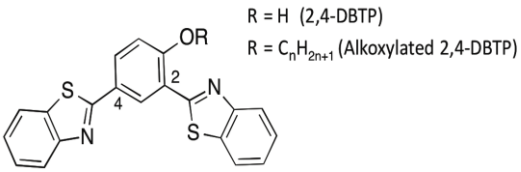
ESIPT 部位を塞いだ色素が示す会合体形成と多色蛍光発光

（千歳科技大[1]・東北大多元研[2]）○廣瀬 夕真[1]・坂井 賢一[1]・芥川智行[2]
Aggregate formation and multicolor fluorescence emission shown by dye blocking ESIPT sites (*[1]Chitose Inst. Sci. Tech.*, *[2]IMRAM, Tohoku Univ.*) ○Yuma Hirose,[1] Ken-ichi Sakai,[1] Tomoyuki Akutagawa[2]

2,4-Bis(1,3-benzothiazol-2-yl)phenol (2,4-DBTP) is an excited-state intramolecular proton transfer (ESIPT) type of fluorophore that exhibits solvent-dependent white fluorescence despite being a single molecular species. Although alkoxylated 2,4-DBTP with its hydroxy group blocked is unable to assume the occurrence of ESIPT, we found that it shows unique fluorescence properties: largely Stokes-shifted strong fluorescence in solid, and multicolor fluorescence in solution depending on the solvent type and fluorophore concentration.

Keywords : Fluorescence; ESIPT; Aggregate

励起状態分子内プロトン移動（ESIPT）型色素である2,4-bis(1,3-benzothiazol-2-yl)-phenol (2,4-DBTP)は，溶媒の影響により単一の分子種でありながら白色蛍光を示す。本研究では，分子内水素結合を構成するヒドロキシ基をアルコキシ化してしまうとESIPTを想定することは出来なくなるにも関わらず，結晶状態においてはESIPTで誘起される構造変化に相当した大きなストークスシフトをもつ蛍光が，一方で溶液状態においては溶媒の種類や色素濃度によって多彩な蛍光色を示すことを見出した。



粉末試料は 570 nm 付近に極大をもつ橙色蛍光を示し，Stokes シフトの大きさは ESIPT を起こす 2,4-DBTP のそれに匹敵する（図 1 左）。この蛍光は粉末をアセトンに溶解すると観測されず，代わりに 400 nm 付近に極大をもつ青紫蛍光が現れた（**図 1** 右）。濃度上昇に伴ってこの蛍光の強度は著しく低下する一方，今度は 500 nm 付近に極大をもつ青緑色蛍光が現れた。その際，無色の溶液も黄色に着色し，会合体に由来すると思われる Stokes シフトの小さい鏡像関係の吸収・蛍光スペクトルが確認された。現在，このような現象のメカニズムの解明を進めている。

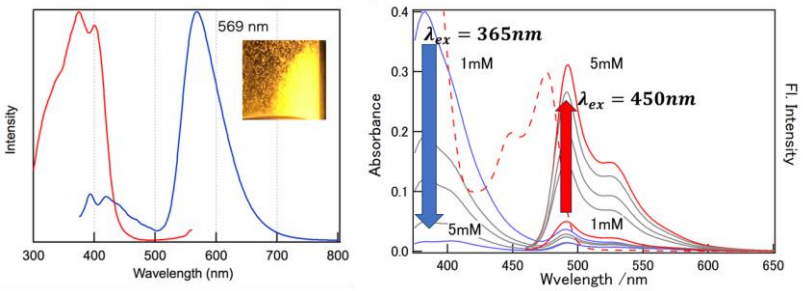


図 1　アルコキシ化 2,4-DBTP の（左）粉末の蛍光・励起スペクトルと（右）アセトン溶液中での蛍光スペクトルの色素濃度依存性。赤の点線は 5mM での吸収スペクトル。

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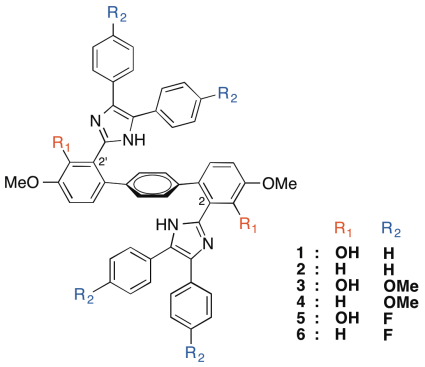
p-ターフェニル誘導体の軸回転制御による光機能性の創出

（千歳科技大院[1]・東北大多元研[2]）○小林 圭[1]・坂井 賢一[1]・芥川 智行[2]
Creation of optical properties by controlling axial rotation in *p*-terphenyl derivatives ([1]*Chitose Institute of Science and Technology*, [2]*IMRAM, Tohoku University*) ○Kei Kobayashi,[1] Kenichi Sakai,[1] Tomoyuki Akutagawa[2]

p-Terphenyl (*p*-TP) is a fluorescent molecule consisting of three benzene rings linearly linked by a single bond, and its photocycle involves rotation around the single bond. Here, we investigated the correlation between the rotation barrier and fluorescence properties of molecules with bulky diphenylimidazole (DPI) groups at the 2 and 2' positions of the benzene rings at both ends. The X-ray structural analysis revealed that the dihedral angle between the phenyl groups of the TP skeleton is 74.1°, which is greatly twisted by the DPI group, and that a strong NH-π interaction exists. We will report the correlation between the strength of NH-π interactions and fluorescence properties, including the results of ^{1}H-NMR and IR.

Keywords : Fluorescence; Terphenyl; Intramolecular Hydrogen Bond; NH- π interaction

p-ターフェニル(*p*-TP)は３つのベンゼン環を単結合で直線上に連結した蛍光性の分子であり，その光サイクルには単結合まわりの回転が関与している。本研究では, 両端のベンゼン環の 2 及び 2'位に嵩高いジフェニルイミダゾール(DPI)基を導入した分子を対象にして(右)，回転障壁と蛍光特性の相関を調べることを目的とした。そこで，DPI 基に隣接する 3,3'位への水酸基の導入(R_1 = OH)による分子内水素結合の効果や，フェニル基末端の置換基効果(R_2 = OMe, F)も鑑みて，合計 6 種類の誘導体を合成し蛍光特性を系統的に評価した。



1 には励起状態分子内プロトン移動(ESIPT)反応を起こし得る分子内水素結合が存在し，粉末状態でも強い青色蛍光 (Φ_{fl} = 0.30)と，9,000 cm^{-1} を超える大きな Stokes シフトが確認された。R_1 が OH 基の **3** や **5** でも同様の結果が得られた一方，ESIPT が想定出来ない **2, 4, 6** でも Stokes シフトの大きな蛍光が観測された。**1** の X 線構造解析の結果から，TP 骨格のフェニル基間の二面角は 74.1° と DPI 基によって大きく捻れていることと，強固な NH-π 相互作用の存在が確認された(**Fig. 1**)。現在，**1~6** における NH-π 相互作用の強さと蛍光特性の相関について，^{1}H-NMR や IR の結果も含めて考察している。

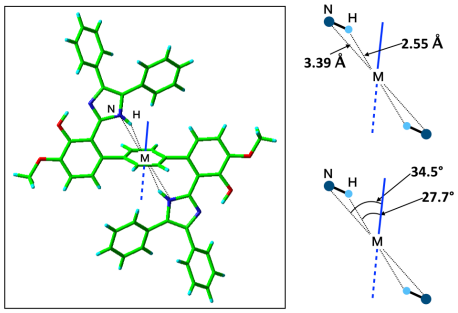


Fig. 1 Structural parameters of the NH-π interaction recognized in the crystal of 1

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振電相互作用理論に基づくルブレンの吸収・蛍光スペクトルおよび輻射・無輻射速度定数の計算と解析

（MOLFEX[1]・京大福井セ[2]・京大院工[3]）○上島 基之[1]・福永 宏雄[1]・大田 航[2,3]・佐藤 徹[2,3]

Calculation and analysis of absorption and fluorescence spectra, and radiative and non-radiative rate constants of rubrene based on the theory of vibronic coupling

([1]*MOLFEX, Inc.*, [2]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [3]*Graduate School of Engineering, Kyoto University,*) ○Motoyuki Uejima[1], Hiroo Fukuanaga[1], Wataru Ota,[2,3] Tohru Sato[2,3]

The vibronic coupling (VC) between the electronic and vibrational states, provides complex electronic spectral shapes due to the vibronic progressions, and induces non-radiative transitions. In particular, in the spin-mixed crude adiabatic (SMCA) representation, the non-radiative transition can be regarded as a one-phonon emission/absorption process driven by the VC, and the internal conversion and intersystem crossing can be treated in a unified manner. The normal modes can be classified into the promoting mode, which is involved in phonon emission/absorption, and the accepting mode, which receives the electron excitation energy. The origin of the VC can be analyzed by the vibronic coupling density, which facilitates the design of finely tuned molecules with respect to the spectral shape and non-radiative transitions.

In this study, we have calculated the absorption and fluorescence spectra of rubrene, and the radiative and non-radiative rate constants in the framework of SMCA picture, and compared them with the experiments. The vibrational modes that greatly contribute to the vibronic progressions and non-radiative transitions were assigned. The origin of the VCs was analyzed using the vibronic coupling density.

Keywords： Internal Conversion; Intersystem Crossing; Vibronic Coupling

電子状態と振動状態との間の相互作用である振電相互作用は振電プログレッションを与え、電子遷移スペクトルに複雑なスペクトル形状をもたらす[1)]。また振電相互作用は無輻射遷移の駆動力でもある。特に混合スピン粗断熱表現において無輻射遷移は振電相互作用を介した一フォノン放出、吸収過程とみなせ、内部転換と系間交差を統一的に扱うことができる[2)]。これらの振動モードにおける振電相互作用の起源は振電相互作用密度[3)]により解析でき、さらにはスペクトル形状や無輻射遷移を制御した分子設計への応用を可能にする。

本研究では混合スピン粗断熱描像に基づいてルブレンの吸収・蛍光スペクトルおよび輻射・無輻射遷移の速度定数を計算し、実測との比較を行った。振電プログレッションや無輻射遷移に寄与する主要な振動モードの帰属を行い、その振電相互作用の起源を振電相互作用密度理論により解析した。

1) Y. Shigemitsu, M. Uejima, T. Sato, K. Tanaka, Y. Tominaga, *J. Phys. Chem. A*, **2012**, *116*, 9100.
2) W. Ota, M. Uejima, N. Haruta, T. Sato, *Bull. Chem. Soc. Jpn.* in press.
3) T. Kato, N. Haruta, and T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation* (Springer, 2021).

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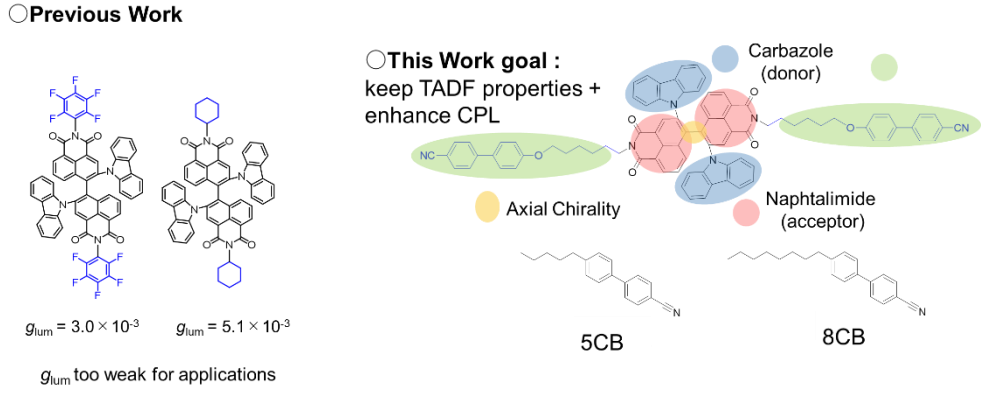
CPL 発光増強のための液晶ドーパントとしての発光性キラルビナフタルイミド

（奈良先端科学技術大学院大学[1]）○山下友希[1]・後藤千草[1]・辻雄伍[1]・河合壮[1]・清水洋[1]・Marine Louis[1]

Recently, strong CPL materials with g-value have attracted much attention due to their potential applications in chemical sensors, biological probes, 3D displays, and LCD backlighting. Also, Luminescent nematic liquid crystal materials, such as 5CB, doped with chiral fluorescent dyes have attracted great interest because of their ability to amplify the inherent molecular chirality and circularly polarized luminescence (CPL) properties. Research our laboratory has binaphthalimide derivatives CPL and Thermally Activated Delayed Fluorescence (TADF) properties. However, the g-value of the CPL is only about 3.0 x 10^{-3}. Therefore, in this study, we modified binaphthalimide derivative and investigated its luminescence properties in solution and dispersed in liquid crystal materials.

Keywords　: Liquid Crystal; Circularly Polarized Luminescence; Delayed Emission

近年、化学センサー、生物学的プローブ、3D ディスプレイ、液晶ディスプレイのバックライトなどへの応用が期待されることから、g 値を有する強い CPL 材料が注目されている。また、ネマチック液晶にキラル蛍光色素をドープした発光性ネマチック液晶材料が、ドーパント固有の分子キラリティを増幅できるとして大きな関心を集めている。当研究室で、ビナフタルイミド誘導体が CPL および TADF 特性を持つことが明らかにされたが、CPL の g 値は約 3.0×10^{-3} にとどまっている。本研究では、ビナフタルイミド誘導体を修飾し、溶液中および液晶材料中に分散させた状態での発光特性を調べた。



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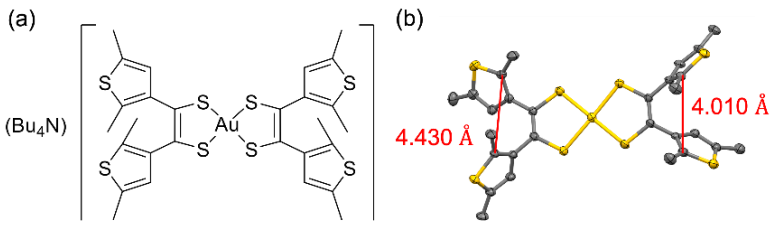
新規な光応答性分子性導体の開発を目指した ジアリールエテン縮環金属ジチオレン錯体の合成

（立教大理）○若尾 海斗・横森 創・西村 涼・森本 正和・松下 信之
Synthesis of diarylethene-fused metal dithiolene complexes for the development of novel photoresponsive molecular conductors (*College of Science, Rikkyo University*)
○Kaito Wakao, So Yokomori, Ryo Nishimura, Masakazu Morimoto, Nobuyuki Matsushita

Metal dithiolene complexes have been developed to exhibit various physical properties such as magnetism and electrical conductivity, and its external-stimuli responsivities (e.g., temperature and pressure) in the solid states. However, there are few reports of photoresponsive molecular conductors/magnets based on metal dithiolene complexes. Thus, we focused on diarylethenes, which are known as a photochromic molecule in the crystalline phases, and synthesized diarylethene-fused metal dithiolene complexes to develop novel photoresponsive physical properties. In this presentation, crystal structures and properties of newly synthesized Au(2Me-BTDT)$_2$ complexes will be reported.
Keywords : Metal dithiolene complex, Photochromism, Single crystal, Diarylethene

金属ジチオレン錯体は固体状態で磁性や電気伝導性など様々な物性を示すことで知られる酸化還元活性な金属錯体である [1]。この錯体からなる結晶群では各種電子物性を熱、圧力や電場によって変調・調節可能な例が多く報告されているものの、光応答性の電子機能性を示す結晶の報告例は少ない。そこで我々が注目したのが、フォトクロミック分子の一つとして盛んに研究されているジアリールエテンである [2]。ジアリールエテンは結晶相でもフォトクロミック特性を示し、さらにその前後において共役長変化があり有意な物性変調が期待できると考えられる。本研究では、新規光応答物性の開拓を目的として、下図 a に示した新規ジアリールエテン縮環金属ジチオレン錯体の合成を着手した。

2Me-BTDT の配位子前駆体を合成し、それに固体状態で 365 nm の紫外光を照射することで淡黄色から赤色に変化するフォトクロミズムが観測された。さらに中心金属に Au を用いたジアリールエテン縮環 Au 錯体の合成および単結晶化・結晶構造解析に成功した（図 b）。発表では、この Au 錯体塩結晶の結晶構造およびその基礎物性について報告する予定である。



(a) (Bu_4N)[Au(2Me-BTDT)]の構造式
(b) (Bu_4N)[Au(2Me-BTDT)]の結晶構造

1) (a) A. Kobayashi *et al.*, *Chem. Rev.*, **2004**, 104, 5243. (b) R. Kato, *Chem. Rev.*, **2004**, 104, 5319.
2) M. Irie *et al.*, *Chem. Rev.*, **2014**, 114, 12174.

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β-シクロデキストリンの包接作用におけるアボベンゾンの安定化機構の解析

(東京理大薬[1]) 古賀 遼太郎[1]・黒田 千尋[1]・弘重 涼介[1]・南出 恵[1]・長谷川 寛治[1]・槌田 智裕[1]・後藤 了[1]
Analysis Stabilization Mechanism of Avobenzone and β-Cyclodextrin complex ([1] *Graduate School of Pharmaceutical Sciences, Tokyo University of Science*) Ryotaro Koga,[1] Chihiro Kuroda,[1] Ryosuke Hiroshige,[1] Megumi Minamide,[1] Kanji Hasegawa,[1] Tomohiro Tsuchida,[1] Satoru Goto[1]

The effectiveness of sunscreen is evaluated based on its UV absorption capacity and the durability of its effect. Reactivity and photostability of sunscreen are important for this. It has been reported that these properties depending on the hydrophobic drug encapsulated in β-cyclodextrin (CD). In this study, we aimed to assess the effectiveness of CD on UV absorbers. Avobenzone (ABZ), curcumin (CUR), and oxybenzone (OBZ) were prepared in 50% (v/v) acetonitrile/water solution containing 0-4 mM CD. UV-A (320-400 nm) was irradiated to promote the compounds' photolysis reaction. We conducted the UV-Vis spectrum of compounds from 0 to 72h after UV-A irradiation and the kinetic analysis using the primary reaction formula. UV-Vis spectra of ABZ and CRU show their photolysis under the UV-A irradiated, and the kinetics analysis revealed that the rate constant *k* values of ABZ and CRU are decreased at the CD concentration dependent manner. Conversely, it wasn't observed the photolysis reaction of OBZ. These results show that CD improves the photostability of ABZ and CRU. Therefore, it is possible to become an effective stabilizer for UV absorbate.
Keywords : Cyclodextrins, sunscreen, Avobenzone, the stability, inclusion complex

紫外線 (UV) 吸収剤による日焼け止め効果には，UV 吸収能や効果持続性が指標である． UV 吸収能には分子の反応性が，効果持続性には分子の光安定性が重要である．これらの性質は，β-シクロデキストリン (CD) が包接する疎水性薬物の種類によって挙動が異なることが報告されている．本研究では液相中で CD と UV 吸収剤の包接複合体を調製し，UV 吸収剤に対する CD の有効性を検討した．

0-4 mM CD を含むアボベンゾン(ABZ)，オキシベンゾン (OBZ)，クルクミン (CUR) 溶液を，50% (v/v) アセトニトリル/水共溶媒で調製した．包接複合体の形成は，各薬物の CD 濃度依存的な溶解度向上によって確認した．それぞれの溶液に UV-A (320-400 nm) を 0-72 時間照射し，経時的に UV-Vis スペクトルを測定して光分解反応を追跡した．この反応に対する UV-Vis スペクトルの速度論的解析より，ABZ と CUR では光分解反応が観察され，反応速度定数 *k* が CD 濃度依存的に減少することが明らかになった．一方，OBZ の光分解反応は CD 有無に関わらず観察されなかった．これらの結果から CD は ABZ，CUR において UV に対する光安定性を向上させることが分かった．また，CD が UV 吸収剤に対する有効な光安定剤として機能する可能性が示唆された．

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N-メチルカルバゾール-FTCNQ の合成

(和歌山大システム工[1]・和歌山大院システム工[2])
○土明 倖大[1]・徳田 遥祐[2]・山門 英雄[1,2]
Synthesis of N-methylcarbazole-FTCNQ ([1]*Faculty of System Engineering, Wakayama University*, [2]*Graduate School of System Engineering, Wakayama University*) ○ Kota Tsuchiaki,[1] Yosuke Tokuda,[2] Hideo Yamakado[1, 2]

Commonly, a charge Transfer (CT) complex of carbazole (Cz) as an electric donor and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as an electric acceptor is known[1)] and Cz-TCNQ has 2 crystal structures[2)] and electric resistivity of Cz-TCNQ is $7.0 \times 10^{10}\ \Omega \cdot cm$ at room temperature[1)]. This time, a CT complex of N-methylcarbazole (MeCz) as an electric donor and 2-fluoro-7,7,8,8-tetracyanoquinodimethane (FTCNQ) as an electric acceptor were synthesized. Spectra of infrared absorbance were measured, and a peak shift of nitrile was observed.
Keywords : N-methylcarbazole; FTCNQ; CT complex; Infrared; spectra

従来、ドナーにカルバゾールを、アクセプターに 7,7,8,8-テトラシアノキノジメタン(TCNQ)を用いた電荷移動錯体が知られており[1)]、その結晶構造は 2 種類あり[2)]、電気伝導性は室温で$7.0 \times 10^{10}\ \Omega \cdot cm$である[1)]。本研究では、ドナーに N-メチルカルバゾール(MeCz)を、アクセプターに 2-フルオロ-7,7,8,8-テトラシアノキノジメタン(FTCNQ)を用いた(Fig.1 参照)新規電荷移動錯体を作成した。得られた黒色の錯体の赤外吸収スペクトルを測定したところ、原料の FTCNQ の CN 基に由来する 2220 cm^{-1} 付近の鋭いピークが、MeCz-FTCNQ では 2205 cm^{-1} 付近になだらかに現れた。(Fig.2 参照)　FTCNQ の CN 基のピークは MeCz-FTCNQ となる際に、15 cm^{-1} 程度低い端数側にシフトしており、DA 間での電荷移動を反映しているものと考えられる。

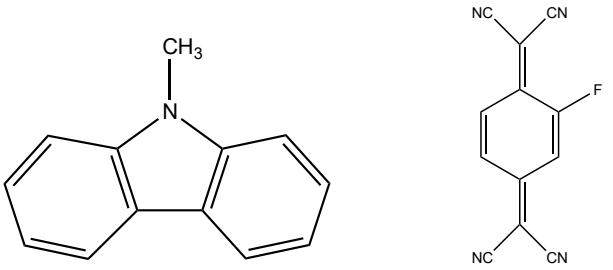

Fig.1 MeCz(left) and FTCNQ(right)

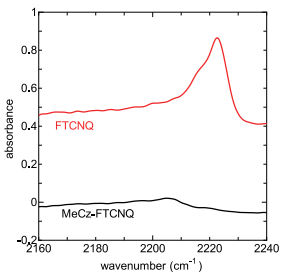

Fig.2 Spectra of Infrared absorbance

1) Akimasa Taniguchi, Seiichi Kanda, Takeshi Nogaito, Shigekazu Kusabayashi, Hiroshi Mikawa and Kazuo Ito, Bull. Chem. Soc Jpn., Vol. 37, No. 9, 1386-1388, **1964**.
2) Hayao Kobayashi, Bull. Chem. Soc Jpn., Vol. 46., 2675-2683, **1973** .

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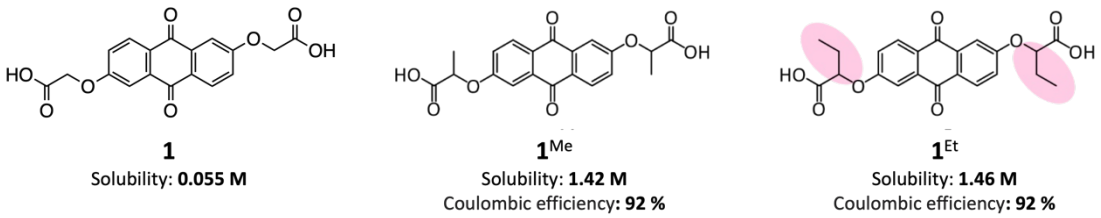
水系レドックスフロー電池用有機負極液としてのアントラキノン系化合物の置換基導入の効果

（早大先進理工）○川口桃佳・岡澤　厚・川合航右・大久保將史
Effect of Introducing Substitutions into Anthraquinone-Based Compounds as Organic Anolytes for Aqueous Redox Flow Batteries (*School of Advanced Science and Engineering, Waseda University*) ○Momoka Kawaguchi, Atsushi Okazawa, Kosuke Kawai, Masashi Okubo

Redox flow batteries (RFBs) have recently attracted research attention as the promising candidate of grid-scale load-leveling technology for renewable energy. Commercial RFBs use vanadium ions as active materials, but their low energy density and high cost hinder wide deployment in electrical grids. To address these issues, we focused on anthraquinone derivatives solely consisting of abundant elements. For example, anthraflavic acids with substituents at 2,6-positions are promising high-capacity anolytes due to their two-electron redox ability, long cycle life, and high solubility.[1] In this work, we further improve the cycle stability by introducing a sterically bulkier substituent into the side chain of the anthraflavic acid derivative $\mathbf{1}^{Me}$. Indeed, we successfully achieved the high solubility and high coulombic efficiency of $\mathbf{1}^{Et}$. We will also discuss other derivatives with different-size substituents.
Keywords : Redox Flow Battery; Redox Active Materials; Cycle Stability; Anthraquinone; Steric Effect

レドックスフロー電池（RFB）は再生可能エネルギーの電力変動を平準化する大規模蓄電池の候補として注目されている。現行の商用 RFB は活物質にバナジウムイオンを使用しているが、エネルギー密度が低くコストが高いという課題がある。この課題を解決するため、我々は希少元素を使用しない安価なアントラノン系化合物に着目した。2,6-位に置換基を持つアントラフラビン酸は 2 電子酸化還元能と高い溶解度から高容量な負極液活物質として期待される [1)]。そこで我々は、既報のアントラフラビン酸誘導体 $\mathbf{1}^{Me}$ の側鎖に嵩高い置換基を導入することによって立体保護を強め、サイクル安定性の向上を目指した。実際、合成した $\mathbf{1}^{Et}$ は $\mathbf{1}^{Me}$ に匹敵する溶解性とクーロン効率を得た。当日は、サイズの異なる置換基を導入した際の溶解度と、電気化学特性の違いについても議論する。



1) R. G. Godon, M. J. Aziz, et al., *ACS Energy Lett.* **2023**, *8*, 600.

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メトキシフェナジンと TCNQ 誘導体を用いた錯体の合成と物性

(和歌山大システム工 [1]・和歌山大院システム工 [2])・○一瀬 航大 [1]・徳田 遥祐 [2]・山門 英雄 [1,2]

Synthesis and physical properties of complexs of Methoxyphenazine and TCNQ compounds

(1. Faculty of Systems Engineering, Wakayama Univ., 2. Graduate School of Systems Engineering, Wakayama Univ.) ○Kodai Ichinose[1], Yosuke Tokuda[2], Hideo Yamakado[1,2]

It has been reported that a complex using phenazine as a donor and 2-fluoro-7,7,8,8-tetracyanoquinodimethane (hereinafter referred to as FTCNQ) as an acceptor has an alternating laminated structure. 1) In this study, a new complex using methoxyphenazine with a methoxy group introduced into the phenazine ring as a donor and FTCNQ as an acceptor was created by the concentration method. X-ray crystal structure analysis was performed to clarify the crystal structure. It was found to be an alternating laminated complex in the triclinic system. The space group is $P\bar{1}$.The lattice constants were 8.3793 Å, 8.4244 Å, and 15.5762 Å for a, b, and c, respectively, and 77.950°, 74.774°, and 72.482° for α, β, and γ, respectively.

Keyword :Physical properties, Charge-transfer complex, TCNQ compounds, Methoxyphenazine

ドナーにフェナジン、アクセプターに 2-フルオロ-7,7,8,8-テトラシアノキノジメタン(以下､FTCNQ とする)を用いた錯体が交互積層構造をとることが報告されている。[1)]今回、ドナーにはフェナジン環にメトキシ基を導入したメトキシフェナジン、アクセプターに FTCNQ を用いた新規の錯体を濃縮法にて作成した。X線結晶構造解析を行い、結晶構造を明らかにした。三斜晶系で交互積層型錯体であることがわかった。空間群は $P\bar{1}$。格子定数は a,b,c はそれぞれ 8.3793Å, 8.4244Å, 15.5762 Å、α、β、γ はそれぞれ 77.950°,74.774°,72.482°であった。

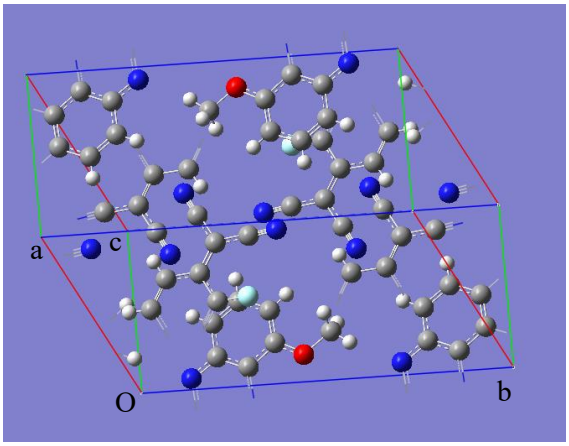

Fig. 1　メトキシフェナジン-FTCNQ 錯体の結晶構造

1)　酒井賢作、山門英雄、分子科学討論会 2015、1P042、2015.

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Academic Program [Poster] | 05. Physical Chemistry -Chemical Kinetics and Dynamics-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 3(理工スポーツホール [1階] アリーナ)

[P3-2vn] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Japanese

[P3-2vn-01]

Effect of intramolecular hydrogen bond on photoisomerization of hemiindigo

○Reona Yoshida[1], Takayuki Murai[1], Sora Ishikawa[1], Yu Matsunaka[1], Yuki Shimizu[1], Yugo Isawa[1], Risa Kojima[1], Yutaka Nagasawa[1] (1. Ritsumeikan Univ.)

Japanese

[P3-2vn-02]

Size-Dependent Single-photon Emission of Cesium Lead Iodide Perovskite Nanocrystals

○Nicholas Huang[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

Japanese

[P3-2vn-03]

Photoisomerization dynamics of *N*,*N*'-substituted indigo derivatives with aromatic substituents

○Yuki Shimizu[1], Takayuki Murai[1], Sora Ishikawa[1], Yu Matsunaka[1], Yugo Isawa[1], Reona Katayama[1], Risa Kojima[1], Yutaka Nagasawa[1] (1. The Univ. of Ritsumeikan)

Japanese

[P3-2vn-04]

Construction of Photoresponsive Quantum Dot Assemblies Using Azobenzene Derivatives

○Manato Kiriyama[1], Naoki Kubo[1], Sadahiro Masuo[1] (1. Kwansei gakuin university)

Japanese

[P3-2vn-05]

Photocleavage reaction of asymmetric spiropyran SBP-β-AP with a large aromatic substituent on one side

○Yugo Isawa[1], Yu Matsunaka[1], Takayuki Murai[1], Sora Ishikawa[1], Yutaka Nagasawa[1] (1. Ritsumeikan University)

Japanese

[P3-2vn-06]

Energy transfer in $CsPbBr_3$ perovskite nanocrystals – pentacene system

○Seiju Koyama[1], Miyu Yoshioka[1], Sadahiro Masuo[1] (1. kwansei gakuin university)

Japanese

[P3-2vn-07]

Development of transient grating method for studies on biomolecular reactions in microenvironments

○Akito Nishino[1], Yusuke Nakasone[1], Kosuke Nishitani[1], Moeto Nagai[2], Masahide Terazima[1] (1. Kyoto University, 2. Toyohashi University of Technology)

Japanese

[P3-2vn-08]

Energy transfer in a CdZnS/ZnS quantum dot – perylene bisimide system

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○Ami Goto[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

Japanese

[P3-2vn-09]

Development of nanoscopic photoexcitation method by using triplet-triplet annihilation up-conversion emission

○Makoto Yamada[1], Hirotaka Kageyama[1], Haruki Nagae[1], Hayato Tsurugi[1], Syoji Ito[1,2], Hiroshi Miyasaka[1] (1. The Univ. of Osaka, 2. RILACS, Osaka Metropolitan Univ.)

Japanese

[P3-2vn-10]

Constructing One-Dimensional Arrangements of Heterogenous Quantum Dots using Molecular Assemblies

○Megumi Tomonaga[1], Naoki Kubo[1], Sadahiro Masuo[1] (1. Kwansei Gakuin University)

English

[P3-2vn-11]

Understanding the DNA hybridisation kinetics under optical condensation with simultaneous single particle detection

○Bhagya Lakshmi Sankaramangalam Balachandran[1], Shuichi Toyouchi[2,4], Syoji Ito[1,4], Shiho Tokonami[3,4], Takuya Iida[2,4] (1. Graduate School of Engineering Science, Osaka University, 2. Graduate School of Science, Osaka Metropolitan University, 3. Graduate School of Engineering, Osaka Metropolitan University, 4. Research Institute for Light-induced Acceleration System (RILACS), Osaka Metropolitan University)

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分子内水素結合がヘミインジゴの光異性化反応に及ぼす影響

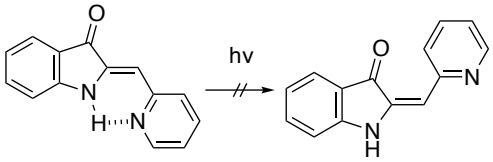
（立命館大学[1]）○片山 礼央奈[1]・郁井 孝行[1]・石川 宙[1]・松中 由有[1]・清水 優輝[1]・伊澤 有悟[1]・小島 理沙[1]・長澤 裕[1]

Effect of Intramolecular Hydrogen Bonding on Photoisomerization of Hemiindigo

([1]*Ritsumeikan University*) ○ Reona Katayama,[1] Takayuki Murai,[1] Sora Ishikawa,[1] Yu Matsunaka,[1] Yuki Shimizu,[1] Yugo Isawa,[1] Risa Kojima,[1] Yutaka Nagasawa,[1]

Indigo and hemi-indigo derivatives exhibit photochromism due to reversible E-Z isomerization under visible light, and application as photoswitches is expected. For this purpose, separated absorption bands of the E- and Z-forms are required. In the case of pyrrole hemiindigo derivatives, an intramolecular hydrogen bond (IHB) formed only in the E-form, shifts the absorption band to longer wavelengths. However, photoexcited intramolecular proton transfer (ESIPT) induced by IHB is known to inhibit the photoisomerization. In fact, for 2-(2-Pyridylmethylidene) indolin-3-one (2PDMI, shown below), which forms IHB only in the Z form, is nonfluorescent and does not exhibit photoisomerization. [1] Hence, in order to examine the possibility of ESIPT occurring in 2PDMI, we investigated its excited state dynamics by femtosecond time-resolved transient absorption (fsTRTA) spectroscopy. The results showed that the excited state lifetime of 2PDMI in methanol solution was as short as 2.0 ps, and the deactivation to the ground state occurred efficiently without any signs of an intermediate state.
Keywords： Photochromism; Hemiindigo; Transient Absorption spectroscopy

インジゴやヘミインジゴ誘導体は可視光による可逆的な E-Z 異性化によるフォトクロミズムを示し、フォトスイッチとしての応用も期待されている。そのためには E 体と Z 体の吸収帯が離れている必要があり、E 体でのみ分子内水素結合(IHB)を形成するため、吸収スペクトルが長波長シフトするピロールヘミインジゴ誘導体等が開発されている。しかし、インジゴのように IHB によって光励起分子内プロトン移動(ESIPT)が誘導される場合、異性化は阻害されることが知られている。実際、Z 体でのみ IHB を形成する 2-(2-Pyridylmethylidene)indolin-3-one (2PDMI、下図)は、無蛍光性で光異性化を起こさない。[1] そこで、2PDMI について ESIPT が起こる可能性を検討するため、フェムト秒時間分解過渡吸収（fsTRTA）スペクトル測定法により、その励起状態ダイナミクスを観測した。その結果、メタノール溶液では 2PDMI の励起状態寿命は約 2.0 ps と非常に短く、無輻射失活による消光が効率的に起こっていることが判明したが、中間状態的なものは観測できなかった。クロロホルム溶液においては、2.3 ps に加え、微弱な 38 ps 程度の寿命成分(10 %)も観測されたので、今後その正体を検討していく予定である。



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$CsPbI_3$ ペロブスカイトナノ結晶における単一光子発光のサイズ依存性

（関西学院大理工）○ニコラス フアン・増尾 貞弘

Size-Dependent Single-Photon Emission of Cesium Lead Iodide Perovskite Nanocrystals

(*Kwansei Gakuin University*) ○Nicholas Huang, Sadahiro Masuo

Several nm sized-perovskite nanocrystals (PNCs) have been known to exhibit single-photon emission by Auger recombination.[1] We recently elucidated the relationship between single-photon emission and its size up to 25 nm for $CsPbBr_3$ PNC.[2] In this work, we investigated the relationship between the single-photon emission, and the size of $CsPbI_3$ PNC, which have a larger Bohr diameter than that of $CsPbBr_3$.

Fig. 1 shows the simultaneous measurement of the cross-sections of single PNCs measured by atomic force microscopy (AFM) (a, c) and their photon-correlation histograms (b, d). In the case of several nm sized single PNCs, low central peak at 0 ns in the photon-correlation histograms is observed (Fig. 1d), indicating single-photon emission. On the other hand, PNCs with sizes about 20 nm showed a high central peak at 0 ns, indicating multiphoton emission (Fig. 1b). From these results, we found that $CsPbI_3$ shows size dependent single-photon emission. We report a more detailed relationship between size and single-photon emission compared to that of $CsPbBr_3$.

Keywords : Perovskite Nanocrystal; Quantum Dot; Single-Photon

数 nm サイズのペロブスカイトナノ結晶 (PNC) は、オージェ再結合により単一光子発光を示す [1]。我々は最近、$CsPbBr_3$ PNC について、サイズと単一光子発生の相関を詳細に解明することに成功した [2]。本研究では、ボーア直径が $CsPbBr_3$ PNC より大きい $CsPbI_3$ PNC について、サイズと単一光子発光の相関を検討した。

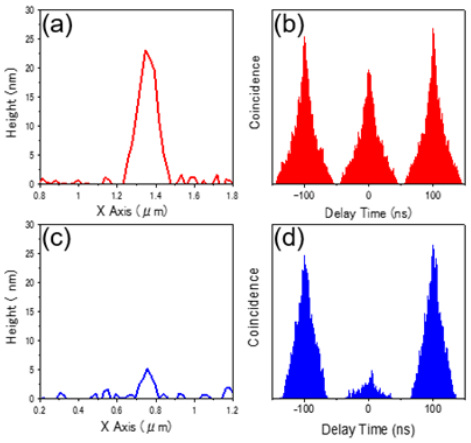

Fig. 1 AFM cross-sections (a, c) and photon-correlation histograms (b, d) obtained to single $CsPbI_3$ PNCs

Fig. 1 には、サイズの異なる２つの PNC について、AFM 測定から得られた断面図 (a, c) と単一粒子分光から得られた光子相関ヒストグラム (b, d) を示す。数 nm の単一 PNC (c)では、光子相関ヒストグラムの中央のピークが低いため、単一光子発光を示すことがわかった。一方、20 nm 程度の PNC (a)では、中央のピークが高いため、多光子発生を示すことがわかった。

これらの結果より、$CsPbI_3$ は $CsPbBr_3$ と同様にサイズに相関を示すという知見が得られた。$CsPbBr_3$ と比較して、より詳細なサイズと単一光子発光の関係について報告する。

1) Y. Park, S. Guo, N. Makarov, V. Klimov, *ACS Nano*, **2015**, *9*, 10386-10393.
2) H. Igarashi, M. Yamauchi, S. Masuo, *J. Phys. Chem. Lett.,* **2023**, *14*, 2441-2447.

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芳香族置換基を付加した *N,N'*-インジゴ誘導体の光異性化ダイナミクス

（立命館大学 [1]）○清水 優輝 [1]・邨井 孝行 [1]・石川 宙 [1]・松中 由有 [1]・伊澤 有悟 [1]・片山 礼央奈 [1]・小島 理沙 [1]・長澤 裕 [1]

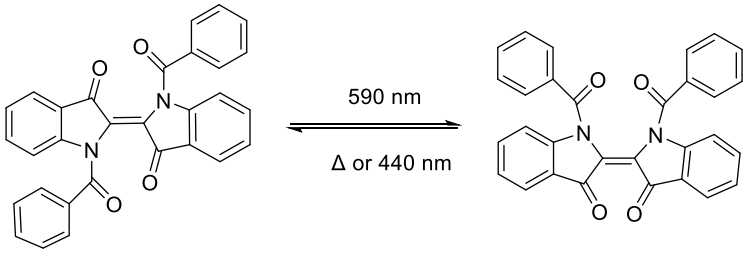
Photoisomerization dynamics of *N,N'*-substituted indigo derivatives with aromatic substituents

([1]*Ritsumeikan University*)○Yuki Shimizu,[1] Takayuki Murai,[1] Sora Ishikawa,[1] Yu Matsunaka,[1] Yugo Isawa,[1] Reona Katayama,[1] Risa Kojima,[1] Yutaka nagasawa,[1]

N,N'-Diacetylindigo (DAI) exhibits *trans-cis* photoisomerization, in which the *cis*-form is thermally unstable and returns to the *trans*-form even in the dark, *i.e.*, T-type photochromism. Furthermore, *cis*-form of DAI exists in two rotamers (head-head and tail-tail), depending on the orientation of the methyl moiety (head) and the carbonyl moiety (tail) of the two acetyl groups. When the methyl moiety of the acetyl group of DAI is replaced with phenyl or naphthalene, steric hindrance increases and π-π interaction is also expected to get involved. Therefore, we conducted a comparative study to examine how these effects affect the photoisomerization reaction utilizing low-temperature measurements and femtosecond time-resolved transient absorption (TRTA) spectroscopic measurements. In this study, we have synthesized N,N'-dibenzoylindigo (DBI) and N,N'-dinaphthoylindigo (DNI), and compared them with DAI. The femtosecond TRTA spectroscopic measurements revealed that the excited state lifetime of DBI and DNI are extremely shorter than that of DAI, i.e., 2.1 ns.[1)]

Keywords : Photoisomerization ; Indigo ; Transient Absorption

N,N'-ジアセチルインジゴ（DAI）は光照射によりトランス-シス異性化反応すが、シス型は熱的に不安定であり、暗所においてもトランス型に熱的に戻る T 型フォトクロミズムを起こす。さらに DAI のシス体には、２つのアセチル基のメチル部位（head）とカルボニル部位（tail）の向きにより、２つの回転異性体（head-head と tail-tail）が存在する。DAI のアセチル基のメチル部位をフェニルやナフタレンで置換すると、立体障害が大きくなり、π-π 相互作用の関与も予想される。そこで、これらの効果が光異性化反応にどのような影響をおよぼすか、低温測定やフェムト秒時間分解過渡吸収スペクトル測定等により比較検討した。本研究では、*N,N'*-ジベンゾイルインジゴ（DBI）と *N,N'*-ジナフトイルインジゴ（DNI）を合成し、DAI との比較を行った。フェムト秒時間分解過渡吸収スペクトル測定を行った結果、DAI の励起寿命 2.1 ns [1)]に比べ、DBI と DNI の寿命はそれぞれ 60 ps と 100 ps と非常に短いことが明らかとなった。



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アゾベンゼン誘導体を用いた光応答性量子ドット集合構造の構築

(関西学院大理工)○桐山 真翔・久保 直輝・増尾 貞弘

Construction of Photoresponsive Quantum Dot Assemblies Using Azobenzene Derivatives

(*Kwansei Gakuin University*) ○Manato Kiriyama, Naoki Kubo, Sadahiro Masuo

The assemblies of semiconductor quantum dots (QDs) are expected to create new physical properties that are not realized by single QDs. Our research group has reported the construction of one-dimensional assemblies of QDs using self-assembling properties of organic molecules and the energy transfer between QDs within the structures[1,2]. However, the stimulus-responsive properties have not been realized. In this study, we attempted to construct photoresponsive assembly of CdSe/ZnS QDs (**QD**) by using azobenzene derivative (**1**, Fig. 1a) having self-assembling ability and photoresponsivity. Transmission electron microscopy (TEM) images showed that the **1** formed assemblies in apolar solvent (Fig. 1b). In addition, the assemblies were disassembled by UV light irradiation, indicating the photoresponsivity of the assemblies (Fig. 1c). Furthermore, we evaluated the formation of **QD** arrangement structure and the energy transfer between **QD**s by mixing the **QD** with the **1** assemblies.

Keywords : Quantum Dot; Self-Assembly; Azobenzene; Photoresponsivity: Supramolecular Structure

半導体量子ドット(QD)は、集合することで単体とは異なる物性の発現が期待できる。当研究グループは、有機分子集合体を利用したQDの一次元配列構造の構築と、QD間エネルギー移動を報告してきた[1,2]。しかしながら、有機分子特有の刺激応答性の付与は実現されていない。そこで本研究は、CdSe/ZnS QD（**QD**）と**QD**への吸着部位と水素結合部位を有するアゾベンゼン誘導体（**1**, Fig. 1a）を用い、光応答性を示す一次元配列構造の構築を試みた。透過型電子顕微鏡（TEM）観察より、低極性溶媒中における**1**の集合体形成を確認した（Fig. 1b）。また、UV光照射により構造の分解が確認され、**1**の集合体が光応答を示すことを明らかにした（Fig. 1c）。さらに、この集合体に対して**QD**を混合し、**QD**配列構造の構築と**QD**間エネルギー移動についても検討した。

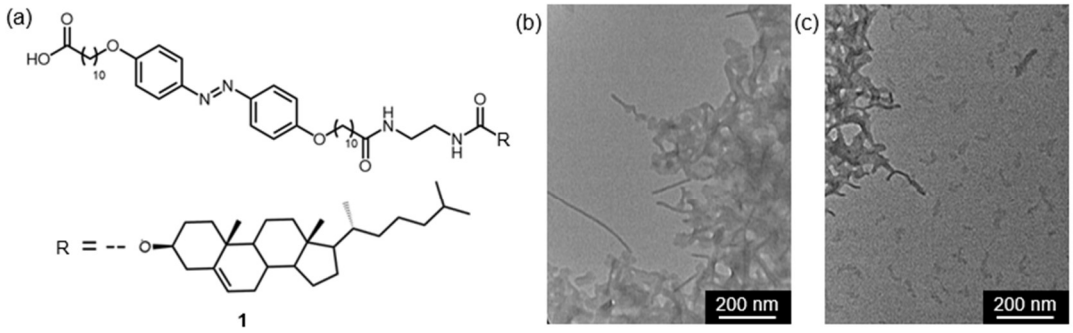

Fig. 1 (a) Molecular structure of **1**. (b) TEM image of **1** assemblies. (c) TEM image of the assemblies after UV irradiation.

1) M. Yamauchi, S. Masuo, *Chem. Eur. J.* **2019**, *25*, 167-172.
2) M. Yamauchi, K. Nakatsukasa, N. Kubo, H. Yamada, S. Masuo, *Angew. Chem. Int. Ed.* **2023**, e202314329.

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片側に大きな芳香族置換基を有する非対称スピロピラン SBP-β-AP の光開環反応

(立命館・生命)　○伊澤 有悟・松中 由有・邨井 孝行・石川 宙・長澤 裕
Photocleavage reaction of asymmetric spiropyran, SBP-*β*-AP, with a large aromatic substituent on one side (Ritsumeikan Univ. Life Sciences)　○Yugo Isawa, Yu Matsunaka, Takayuki Murai, Sora Ishikawa, Yutaka Nagasawa

2,2'-spirobi[2H-1-benzopyran] (SBP) is a photochromic spiropyran with a C_2-symmetric molecular structure with two equivalent C-O spiro bonds, one of which could be cleaved by UV irradiation. In the case of an asymmetric SBP derivative, SBP-*β*-AP (Fig. 1), with one of the phenyl groups of SBP replaced with an anthracene, the cleavage probabilities of the C-O spiro bonds are no longer equivalent. In this study, we observed the photochromic reaction of SBP-*β*-AP at low temperatures and confirmed whether the cleaving C-O bond depends on excitation wavelength. [1] When SBP-*β*-AP was irradiated with UV light at low temperatures, the absorption spectra of the photoproduct changed depending on the excitation wavelength (248 nm, 365 nm, 405 nm). In addition, the lifetimes of the colored species were different, suggesting existence of photoproducts that depend on excitation wavelengths.

Keywords : Photochromism, photo-cleavage reaction, time-resolved spectroscopy

2,2'-spirobi[2H-1-benzopyran] (SBP)は C_2 対称な分子構造のスピロピラン類であり、紫外光照射によって 2 つの等価な C-O スピロ結合のうち、どちらか一方が開裂して着色するフォトクロミズムを示す。SBP 誘導体である SBP-β-AP は、SBP の片側のベンゼン環をアントラセンに置換した非対称な構造をした分子である。そのため、C-O スピロ結合の開裂確率が等価ではなくなり、図 1 のように二つの異なる光開環生成物が生じることが期待される。[1] 本研究では、低温下で SBP-β-AP に紫外光照射した際のフォトクロミズムの測定を行い、励起波長(248 nm, 365 nm, 405 nm)に依存性して開裂する C-O 結合が変化するか確認した。その結果、励起波長に依存して光反応生成物の吸収スペクトルが変化し、加えて時間変化を観測すると、異なる 2 つの寿命が得られ、二種類の開環体が存在することが判明した。これらのことより、長波長励起の場合、おもにアントラセン側の C-O 結合が開裂するのに対し、短波長励起の際にはベンゼン環側も開裂するようになることが示唆される。

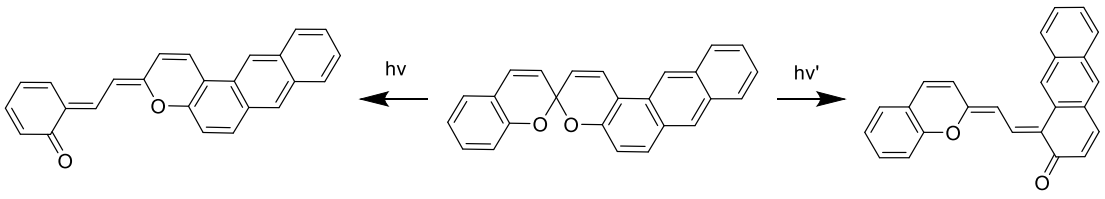

Figure 1. Photochromism of SBP-β-AP

References

[1] M. Vladimir I. Chem. Rev. 2004, 104, 2751-2776.

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$CsPbBr_3$ ペロブスカイトナノ結晶ーペンタセン間のエネルギー移動

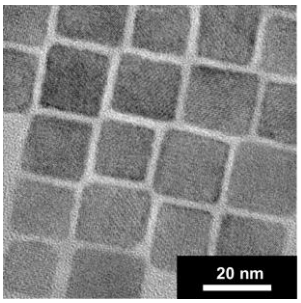
（関西学院大理工）○小山征重・吉岡 美結・増尾 貞弘
Energy Transfer in $CsPbBr_3$ Perovskite Nanocrystals-Pentacene System
(*Kwansei Gakuin University*) ○Seiju Koyama, Miyu Yoshioka, Sadahiro Masuo

To realize the efficient use of generated excitons in quantum dots (QDs), we have been investigated the energy transfer (ET) from multiple excitons in the QDs to dye molecules adsorbed on the QDs. Recently, we have reported that the Auger recombination (AR) occurs faster than ET in a system in which perylene bisimide molecules were adsorbed on a CdSe/ZnS QDs[1]. In this work, we have investigated the ET between multiple pentacene (Pc) molecules adsorbed on PNCs with size of 8 nm and 20 nm in solution and at the single PNC level. The ET from PNCs to Pc was observed by spectroscopic measurement. Furthermore, we investigated the ET from multiple excitons in a PNC to Pc at the single PNC level.
Keywords : Perovskite Nanocrystals; Nanocrystal; Pentacene; Energy Transfer

我々は励起子の有効活用を目的とし、半導体量子ドット(QD) に生成する複数の励起子から、QD 表面に吸着させた複数の有機色素へのエネルギー移動 (ET) を検討してきている。これまでの研究から、CdSe/ZnS QD にペリレンビスイミド誘導体を吸着させた系では、ET よりもオージェ再結合 (AR) が速く起こることがわかった[1]。そこで本研究では、8 nm 程度の $CsPbBr_3$ ペロブスカイトナノ結晶 (PNC) と、弱い量子閉じ込め効果により AR 速度が遅い 20 nm 程度の PNC (Fig.1a) を用いる。アクセプター分子としてペンタセン (Pc, Fig.1b) を PNC に吸着させ、溶液中、および単一 PNC レベルで ET を検討した。

溶液中において、8 nm 程度の PNC-Pc の発光スペクトル、および発光寿命測定により、PNC から Pc への ET の観測に成功した。20 nm 程度の PNC についても、ET、および複数励起子の取り出しについて検討したので詳細を報告する。

(a)



(b)

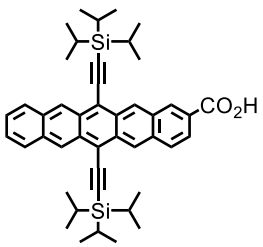


Fig.1 (a) TEM image of PNCs with a size of 20 nm. (b) Chemical structure of Pc.

1) M. Yoshioka, M. Yamauchi, N. Tamai, and S. Masuo, *Nano Lett.* **2023**, *23,* 2311548-11554.

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微小空間内での生体分子反応研究に向けた過渡回折格子法の開発

（京都大学[1]・豊橋技術科学大学[2]）〇西野晶翔[1]・中曽根祐介[1]・西谷公佑[1]・永井萌土[2]・寺嶋正秀[1]

Development of Transient Grating Method for Studies on Biomolecular Reactions in Microenvironments (*[1]Kyoto University, [2]Toyohashi University of Technology*) 〇Akito Nishino,[1] Yusuke Nakasone,[1] Kosuke Nishitani,[1] Moeto Nagai,[2] Masahide Terazima[1]

Most biomolecular reactions occur within microscopic spaces (pL ~ fL), such as cells. In these microenvironments, confinement effects could be observed, such as promotion of phase separation of proteins, and a reduction in diffusion coefficient[1)]. Although there are several methods for analyzing localization and steady-state diffusion in such microenvironments, there is no established method for observing molecular reaction dynamics in these confined spaces. The transient grating (TG) method offers ability to measure conformational changes and intermolecular reactions of biomolecules with high temporal resolution. In this study, we have enhanced its spatial resolution by using a highly light-collecting lens to apply the TG method to the analysis of reactions in small spaces. Currently, we have achieved a spatial resolution of approximately 10 μm, and we have conducted TG measurements of photosensor proteins using this setup. Additionally, we are currently developing a microchamber designed for confining proteins in microscopic spaces.

Keywords: Transient Grating Method; Microscopic Space; Biomolecular Reactions; Confinement Effect; Microscope

生体分子反応の多くは細胞のような微小空間内（pL～fL）で起こる。このような微小空間内では、タンパク質の相分離の促進や拡散係数の減少といったいわゆる「閉じ込め効果」が観測されることがある[1)]。微小空間内での分子の局在化や定常的な拡散を計測する手法はいくつか存在するが、生体分子の反応ダイナミクスを高感度かつ高時間分解能で観察できる手法は確立されていない。そこで本研究では過渡回折格子法（TG 法）の空間分解能を高めることで、細胞のような微小空間内での反応解析を実現することを目的とした。TG 法はタンパク質の高次構造変化や分子間反応を高い時間分解能で測定することができる分光学的手法であるが、従来法はバルク溶液中での測定に最適化されており、空間分解能は 1 mm 程度であった。そこで我々は集光性の高いレンズを用いた TG 法を開発し、現在までに約 10 μm の空間分解能を達成した。このセットアップで光センサータンパク質の TG 信号を得ることに成功しており、現在はタンパク質を微小空間に閉じ込めるために微細加工セルの開発を進めている。

1）Chiho Watanabe, Yuta Kobori, Johtaro Yamamoto, Masataka Kinjo, and Miho Yanagisawa, *J. Phys. Chem. B* **2020**, *124*, 1090-1098.

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CdZnS/ZnS 量子ドットからペリレンビスイミドへのエネルギー移動評価

（関西学院大理工）○後藤 亜美・増尾 貞弘

Energy Transfer in a CdZnS/ZnS Quantum Dot - Perylene Bisimide System

(*Kwansei Gakuin University*) ○Ami Goto, Sadahiro Masuo

To realize the efficient use of generated excitons in quantum dots (QDs), we have been investigated the energy transfer (ET) from multiple excitons in QDs to dye molecules adsorbed on the QDs. Recently, we have shown that Auger recombination (AR) occurs faster than ET in a system in which perylene bisimide (PBI) molecules are adsorbed onto CdSe/ZnS QDs [1]. It is known that the AR rate is inversely proportional to the volume of QDs. Therefore, in this work, we evaluated ET using CdZnS/ZnS QDs (Fig. 1a) with a size of approximately 10 nm and three types of PBIs (Fig. 1b) as acceptor molecules. The PBIs were adsorbed onto CdZnS/ZnS QDs, and ET was observed by spectroscopic measurements. Furthermore, we investigated the ET from multiple excitons in a CdZnS/ZnS QDs to PBIs at the single QD level.
Keywords : Perylene Bisimide; Nanocrystal; Quantum Dot; Energy Transfer; Single Molecule

我々は励起子の有効活用を目的とし、量子ドット（QD）に生成する複数の励起子から複数の有機色素へのエネルギー移動（ET）を検討してきている。これまでの研究から、CdSe/ZnS QD にペリレンビスイミド誘導（PBI）を吸着させた系では、ET よりもオージェ再結合（AR）が速く起こることがわかった [1]。AR の速度は、QD の体積に反比例することが知られている。そこで、本研究では、粒径が 10 nm 程度の CdZnS/ZnS QD（Fig. 1a）を作製し、3 種類の PBI（Fig. 1b）をアクセプター分子として ET を評価した。CdZnS/ZnS QD に PBI を吸着させ、発光スペクトル、および発光寿命測定から ET を観測した。単一 QD レベルで評価を行い、CdZnS/ZnS QD から PBI への多励起子取り出しを評価したので詳細を報告する。

(a) (b)

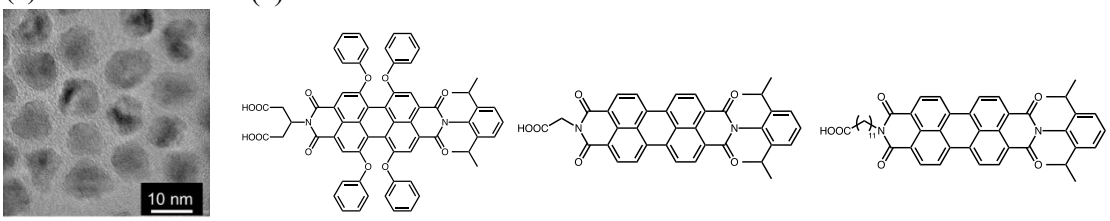

Fig.1 (a) TEM images of CdZnS/ZnS QDs. (b) Chemical structures of PBI derivatives.

1) M. Yoshioka, M. Yamauchi, N. Tamai, and S. Masuo, *Nano Lett.* **2023**, *23*, 11548-11554.

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三重項-三重項消滅アップコンバージョン発光を用いたナノ局在励起法の開発

（阪大院基礎工[1]・阪公大 LAC-SYS 研[2]）山田真琴[1]・蔭山浩崇[1]・長江春樹[1]・劒隼人[1]・伊都将司[1,2]・宮坂博[1]

Development of nanoscopic photoexcitation method by using triplet-triplet annihilation up-conversion emission

([1]*Graduate School of Engineering, Osaka University*; [2]*RILACS*)
Makoto Yamada[1], Hirotaka Kageyama[1], Haruki Nagae[1], Syoji Ito[1,2], Hiroshi Miyasaka[1]

Nanometric photoexcitation technique leads to super-resolved fluorescence imaging and photochemical nanofabrication. Local photoexcitation in an area < 200 nm is in general difficult owing to the diffraction limit of light. To overcome this limitation, we have utilized in the present study nanoparticles (NPs) exhibiting up-conversion (UC) emission as nanometric light sources. We prepared NPs consisting of an Os complex and rubrene (OsRu-NPs) exhibiting triplet-triplet annihilation UC emission at VIS wavelength region under photoexcitation with a CW near-infrared (NIR) laser. We measured the UC emission of the NPs in conjugated solids and investigated the excitation energy transfer from the NPs to the surrounding medium for evaluating the performance of the prepared nanoparticles as a nanometric excitation source.
Keywords : Up-conversion emission; Local photoexcitation; Triplet-triplet annihilation

励起状態のナノ局在化は，超解像イメージングや光化学的ナノ加工への展開が期待できる。しかし，光の回折限界のため，200 nm より微小な空間スケールに可視光程度のエネルギーをもつ励起状態を局在生成することは一般的には困難である。本研究では三重項-三重項消滅アップコンバージョン（TTA-UC）ナノ粒子を局所励起源として，超解像ナノ励起実現を目指す。文献[1)]に基づき TTA-UC 発光を示すオスミウム-ルブレン混合系のナノ粒子(OsRu-NPs)を作製した。PVA 固体膜中の単一 OsRu ナノ粒子の発光挙動及び共役固体中での発光・励起移動挙動を観測し，調製したナノ粒子の励起源としての性能を評価した。

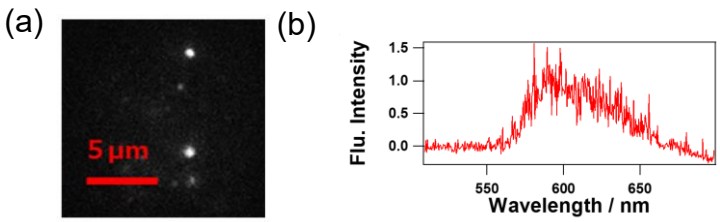

Fig. 1. (a) Fluorescence image of single OsRu-NPs in a PVA solid film (λ_{ex}=940 nm). (b) Fluorescence spectrum of single OsRu-NP.

1) S. Amemori, Y. Sasaki, N. Yanai, and N. Kimizuka, *J. Am. Chem. Soc.* **2016**, *138*, 8702-8705.

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分子集合を利用した異種量子ドットの一次元配列構造の構築

（関西学院大理工）○友永 愛・久保 直輝・増尾 貞弘
Constructing One-Dimensional Arrangements of Heterogeneous Quantum Dots Using Molecular Assemblies (*Kwansei Gakuin University*) ○Megumi Tomonaga, Naoki Kubo, Sadahiro Masuo

Quantum dot (QD) assemblies can show novel photophysical properties derived from the arrangement structures. Recently, our research group reported constructing one-dimensional arrangements of CdSe/ZnS QDs using one-dimensional assemblies of a cholesterol derivative (**Chol**, Fig. 1a). However, energy migration between the QDs with emission quenching was observed in the homogeneous QD arrangements. In this work, we attempted constructing one-dimensional arrangements of heterogeneous QDs consisting of perovskite nanocrystals (**PNC**, Fig. 1b) and the CdSe/ZnS QDs (**csQD**, Fig. 1c) using the **Chol** assemblies to discuss the energy transfer in the QD arrangements. Transmission electron microscopic observation revealed that the **PNC**s and **csQD**s can be adsorbed along the one-dimensional assemblies of **Chol**. Furthermore, the energy transfer between the **PNC** and **csQD**s was evaluated by the spectroscopic measurements.
Keywords : Quantum Dot; Perovskite Nanocrystal; Self-Assembly; Energy Transfer

集合した量子ドット (QD) は、集合構造に由来した新たな光機能の発現が期待される。当研究室では、QD への吸着部位を有するコレステロール誘導体 (**Chol**, Fig.1a) の一次元集合体を用い、CdSe/ZnS QD の一次元配列構造の構築に成功した [1]。しかしながら、この構造内では同種の QD 間でエネルギー移動が起こり、QD が消光してしまう [1]。そこで本研究は、ペロブスカイトナノ結晶 (**PNC**, Fig. 1b) と CdSe/ZnS QD (**csQD**, Fig. 1c) からなる異種 QD 一次元配列構造の構築を試みた。低極性溶媒中において **Chol** 集合体と **PNC** および **csQD** を混合すると、**Chol** の一次元集合体に沿って **PNC** と **csQD** が吸着可能であることが、透過電子顕微鏡観察により明らかになった。さらに、各種分光測定により、**PNC** と **csQD** 間のエネルギー移動について評価した。

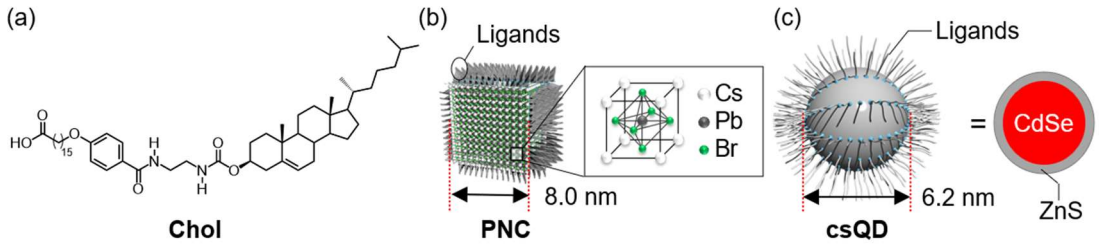

Fig. 1 Chemical structures of **Chol** (a), **PNC** (b), and **csQD** (c).

1) M. Yamauchi, K. Nakatsukasa, N. Kubo, H. Yamada, S. Masuo, *Angew. Chem. Int. Ed.* **2023**, e202314329.

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Understanding the DNA hybridization kinetics under optical condensation with simultaneous single particle detection

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Science, Osaka Metropolitan University,* [3]*Graduate School of Engineering, Osaka Metropolitan University,* [4]*Research Institute for Light-induced Acceleration System (RILACS), Osaka Metropolitan University*) ○ Bhagya Lakshmi Sankaramangalam Balachandran,[1] Shuichi Toyouchi,[4] Syoji Ito,[1,4] Shiho Tokonami,[3,4] Takuya Iida[2,4]

Keywords: Optical Condensation; Single Particle Microscopy; DNA hybridization; Kinetics

DNA hybridization is a process that occurs when two single-stranded DNA having a complementary sequence identify themselves. This molecular recognition process has been used in biomedical research for the detection of various infectious and genetic diseases. In general, earlier diagnosis requires the detection of a small number of DNAs and, for this purpose targeted DNA is replicated by polymerase chain reaction (PCR) technique until the number of the DNA reaches to enough concentration. Though this method is effective, the DNA replication takes long time and, it is difficult to apply the method to detect DNA in situ. While we have recently developed a method, named optical condensation (OC), to locally condense molecules by using fluidic process induced through photothermal conversion,[1] the OC can accelerate several biochemical reactions by gathering and trapping molecules to a small volume. Although we have already demonstrated the advantages of the optical condensation, the detailed molecular processes have not been well understood. The present study hence aims to the elucidation of the molecular dynamics under OC at the single molecule level.

The sample consists of two cover glasses sandwiched with a spacer. The top cover glass has nanofilm Au islands on which the thiolated probe DNA is immobilized via Au-S linkage. A matching target DNA tagged with a fluorescent dye will be injected between the cover glasses which then interacts with the probe DNA. The hybridization events between the probe and the target DNAs are marked by blinking of fluorescent spots which is observed using an EMCCD camera connected to the fluorescence microscope. Study on a control Au island within the same sample with no probe DNA or using a mismatch target DNA will help to distinguish the hybridization process. OC can also be performed under the same setup with a different excitation laser.

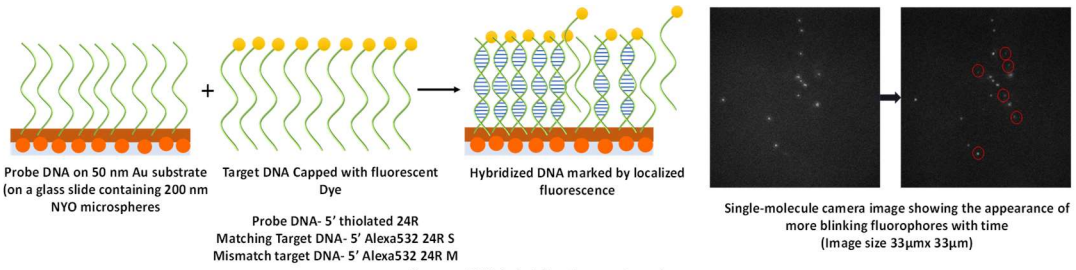

Figure : DNA hybridisation on Au substrate

1) T.Iida et al., *Sci. Rep*. **2016**, *6*, 37768.

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Academic Program [Poster] | 07. Inorganic Chemistry：Poster

Tue. Mar 19, 2024 1:00 PM - 2:30 PM JST | Tue. Mar 19, 2024 4:00 AM - 5:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-2pm] 07. Inorganic Chemistry

Japanese

[P1-2pm-01]

Synthesis of metal oxide nanoparticles employing amino acid hydrochloride as a structure-directing agent and their dispersion control

○Yuto Hibi[1], Nagisa Hattori[1], Takashi Sugiura[1], Kazuhiro Manseki[1] (1. Gifu University)

Japanese

[P1-2pm-02]

Synthesis of magnesium ionic conductive solid electrolite and composition dependence of crystal structure and electric propert

○Shota Tange[1], Naoya Kinokiri[1], Rie Shimanouchi[1] (1. Kochi University)

Japanese

[P1-2pm-03]

Immobilization of molybdate ion in inorganic amorphous materials by vacuum freeze drying method

○HUIXIN LIU[1], Akihiko Kajinami[1] (1. Kobe University)

Japanese

[P1-2pm-04]

Synthesis of Lambda-phase Trititanium Pentoxide by Block Copolymer Method

○Kazuya Yamaguchi[1] (1. University of Tsukuba)

Japanese

[P1-2pm-05]

Immobilization of Cesium Ion in Inorganic Amorphous Materials by Vacuum Freeze-Drying Method

○Naoki Hamada[1], Akihiko Kajinami[1], HUIXIN LIU[1] (1. Kobe University)

Japanese

[P1-2pm-06]

Study of the synthesis conditions for tetragonal zirconium dioxide

○Yuki Konno[1], Natsuki Asano[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. University of Tokyo)

Japanese

[P1-2pm-07]

Synthesis method of zirconium dioxide

○Natsuki Asano[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. University of Tokyo)

Japanese

[P1-2pm-08]

Synthesis method for gallium-substituted tetratitanium heptoxide ($Ti_{4-x}Ga_xO_7$) and evaluation of its magnetic properties

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○Tomoko Kubota[1], Riku Seiki[1], Akito Fujisawa[1], Akhmad Fadel Fadilla[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. The Univ. of Tsukuba, 2. The Univ. of Tokyo)

Japanese

[P1-2pm-09]

Flow-type LP-ALD process for the preparation of α-Fe_2O_3 thin films

○Mitsuki Takayanagi[1], Yohei Yamane[1], Naoki Osaka[1], Kentarou Mori[1] (1. College of Industrial Technology, Nihon University)

Japanese

[P1-2pm-10]

Examination of crystal structure control by elements substutution in cyclosilicate compounds

○Rie Futagami Shimanouchi[1], Hayato Osawa[1], Takuro Ikeda[1] (1. Kochi University)

Japanese

[P1-2pm-11]

Luminescence property of lead halide perovskite single crystals controlled by lanthnide ions

○Mizuki Noto[1], Tomohide Yamada[2], Ayumi Ishii[2] (1. Teikyo University of Science, 2. Waseda University)

Japanese

[P1-2pm-12]

Development of lanthanide based up-conversion materials with multicolor luminescence

○Ryusuke Mizoguchi[1], Truptimayee Behera[2], Ryota Komatsuzaki[2], Ayumi Ishii[2] (1. Teikyo Univ. of Sci., 2. Waseda Univ.)

Japanese

[P1-2pm-13]

Synthesis and luminescent copper(I) carbene complexes

○Kanta Nakamura[1], Taro Tsubomura[1] (1. Seikei University)

Japanese

[P1-2pm-14]

Electrochemical Ag nanoparticles synthesis inside MOF

○Junya Kato[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-15]

Pb nanoparticle synthesis within COF by electrochemical reduction method

○Weihua Wang[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-16]

Synthesis and evaluation of Cu(BDC-NH_2) MOF oriented film by casting method

○Takumi Nishigaki[1], Qiyuan ZHANG[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-17]

Fabrication of oriented crystalline thin film of cationic MOF by casting method

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○Taisei Sato[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-18]

Construction of oriented COF film by casting method

○Koichi Takano[1], Tomoyuki Haraguchi[1] (1. Tokyo University Of Science)

Japanese

[P1-2pm-19]

Construction and evaluation of MOF oriented films with three-dimensional framework by casting method

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Japanese

[P1-2pm-20]

Fabrication and Evaluation of Oriented Crystalline Zn_3(TCPP)(DABCO) MOF Thin Film by Casting Method

○Jiahao Zhang[1], Qiyuan Zhang[1], tomoyuki haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-2pm-21]

Construction of Aluminosilicate Frameworks from Double-Four-Ring-Type Molecular Precursor

○Yurika Ohnishi[1], Akira Imaizumi[2], Akinori Honda[1], Ho-Chol Chang[1] (1. Faculty of Science and Engineering, Chuo Univ., 2. Graduate School of Science and Engineering , Chuo Univ.)

Japanese

[P1-2pm-22]

Creation of molecular-sized electride compounds by using tin oxide cluster as a base material

○Takamasa Tsukamoto[1,2], Mayumi Otake[1], Nozomi Yoshida[3], Tatsuya Moriai[3,4], Kimihisa Yamamoto[3,4] (1. IIS, The Univ. of Tokyo, 2. JST-PRESTO, 3. Lab. for Chemistry and Life Science, Tokyo Tech, 4. JST-ERATO)

Japanese

[P1-2pm-23]

Efficient reducibility of layered polysilane (LpSi)
for selective recovery of platinum ions from
aqueous media

○Masataka Ohashi[1], Goto Yasutomo[1], Nakano Hideyuki[1] (1. TOYOTA CENTRAL R&D LABS., INC.)

Japanese

[P1-2pm-24]

Does the origin of montmorillonite affect cesium ion exchange behavior?

○Noriko Suzuki[1], Masato Sawada[1], Reishi Moriya[1] (1. Showa Pharmaceutical University)

Japanese

[P1-2pm-25]

Organically modified layered silicates dispersing in a polyurethane foam

○Haruna Sasaki[1], Tomonori Watanabe[1], Tomohiko Okada[1] (1. Shinshu University)

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Japanese

[P1-2pm-26]

Development of microporosity by the selective leaching of fluorine muscovite mica ceramics

○Daichi Aoyagi[1], Tomohiro Yamaguchi[1], Seiichi Taruta[1] (1. Shinshu University)

Japanese

[P1-2pm-27]

Formation of Zn-Al LDHs as coating on a Zn plate by the homogeneous precipitation method using a polyhydroxoaluminum complex solution

○Issei Kokubo[1], Tomohiro Yamaguchi[1], Seiichi Taruta[1] (1. Shinshu University)

Japanese

[P1-2pm-28]

Synthesis and Evaluation of Sodium-doped Hydrogen Boride Sheets with controlling dopant amount

○Shohei Shimozato[1], Miwa Hikichi[1], Shinichi Ito[1], Natsumi Noguchi[1], Kosuke Takeshita[1], Takahiro Kondo[1] (1. The Univ. of Tsukuba)

Japanese

[P1-2pm-29]

^{1}H solid state NMR spectra of lanthanoid nitrate hydrate

○Mineyuki Hattori[1], Emiko Oonuma[1] (1. NMIJ, AIST)

Japanese

[P1-2pm-30]

Catalytic activity of water-soluble fluorinated chlorin iron(III) complexes

○Shino Nakashima[1], Reina Ishikawa[1], Haruo Akashi[1] (1. Okayama University of Science)

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アミノ酸塩酸塩を構造制御試薬とする金属酸化物ナノ粒子の合成と分散性制御

(岐阜大工[1]) ○日比 祐斗[1]・服部 凪紗[1]・杉浦 隆[1]・萬関 一広[1]

Synthesis of metal oxide nanoparticles employing amino acid hydrochloride as a structure-directing agent and their dispersion control ([1]*Faculty of Engineering, Gifu University*)
○Yuto Hibi,[1] Nagisa Hattori,[1] Takashi Sugiura,[1] Kazuhiro Manseki[1]

Nanostructured tin oxide (SnO_2) particles and their thin-films have been regarded as useful energy materials in the production of perovskite solar cells. In this paper, we present a novel synthesis and dispersion control of SnO_2 nanoparticles employing amino acid hydrochloride as a structure-directing agent (SDA) in the solution synthesis. This provides a new strategy for the size-tuning of sub-10 nm SnO_2 nanocrystals. Moreover, the SnO_2 dispersion/aggregation can be solely controlled by changing the reaction temperature. Our method of using an amino acid hydrochloride in the SnO_2 synthesis will have an advantage for the performance optimization of solar cells as well as further the development of functional nanomaterials based on versatile metal oxide nanoparticles.

Keywords : Tin oxide nanoparticles; Structure directing agents

ナノ構造を制御した酸化スズ微粒子および薄膜は、ペロブスカイト太陽電池向けに応用可能なエネルギー材料として興味深い。本研究では、低温の溶液合成法を利用し、構造制御試薬（SDA）としてアミノ酸塩酸塩を添加する酸化スズナノ粒子の新たな合成法と分散性制御技術について報告する。水/エタノール混合溶媒中、L-フェニルアラニンメチルエステル塩酸塩の共存下、塩化スズ(IV)の重縮合反応で形成する酸化スズナノ粒子の形態・凝集状態について調べた。70℃および 80℃の 2 種の温度条件で得られる微粒子を XRD 測定、高分解能 TEM 観察により分析したところ、共に微粒子サイズが 2～3 nm 程度の酸化スズが単相で形成し、サイズ分布が非常に小さいことが分かった。Figure 1 に 70℃試料の TEM 像の例を示す。また、70℃に比べ、80℃の試料では、酸化スズ粒子の凝集が顕著となり、分散性に大きな差が見られた。これらの温度条件の試料ではラマンスペクトルも大きく異なることが判明した。結晶成長との相関について合わせて報告する。本研究で見出したアミノ酸塩酸塩を SDA とする酸化スズナノ粒子の合成法は、太陽電池材料としての応用だけでなく、多種にわたる高機能性金属酸化物ナノ粒子の創製に有効活用できる。

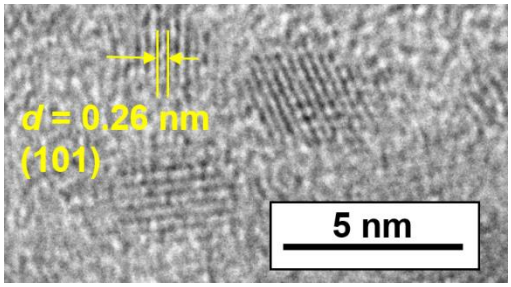

Figure 1 SDA を用いて合成した酸化スズナノ粒子の TEM 像(70℃合成の例)

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マグネシウムイオン伝導性を示す固体電解質の合成と結晶構造および電気的物性の組成依存性

（高知大理工 [1]）○丹下 翔太 [1]・木ノ桐 尚哉 [1]・島内 理恵 [1]

Synthesis of magnesium ionic conductive solid electrolyte and composition dependence of crystal structure and electric properties.

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Although lithium-ion batteries, which are widely used at present, are excellent batteries, they also have disadvantages such as lack of resources for lithium metal to be used and being dangerous. Magnesium ion batteries are attracting attention as safe batteries with excellent resourceability, but they have a disadvantage of having large anion interactions.

In this study, Mg^{2+} ion conductive material promising as this electrolyte material is newly synthesized to reduce anion interaction by replacing ions responsible for skeletal structure and aim for high ion conductivity. We synthesized $Mg_{0.5}Ti_2(PO_4)_3$ with NASICON type known as highly ionic conductive crystal structure and its solid solution $Mg_{0.5+x}(Ti_{1-x}Al_x)_2(PO_4)_3$ using hydrothermal synthesis method.

Keywords : Solid electrolyte; Ionic conductor; Solid solution; Mg^{2+} conductor

現在広く用いられているリチウムイオン電池は優れた電池であるが、使用するリチウム金属の資源が乏しく危険である欠点も持っている。マグネシウムイオン電池は資源性に優れ安全な電池として注目を集めているが、アニオン相互作用が大きいという欠点がある。本研究ではこの電解質材料として有望な Mg^{2+}イオン伝導性物質を新規合成し骨格構造を担うイオンを置換することでアニオン相互作用を減少させ高イオン伝導性を目指した。

まず高イオン伝導性が期待できる結晶構造として NASICON 型に着目し、水熱合成法により NASICON 型 $Mg_{0.5}Ti_2(PO_4)_3$ およびその固溶体２種(1) $Mg_{0.5+x}(Ti_{1-x}Al_x)_2(PO_4)_3$ と(2) $Mg_{0.5+1.5x}Ti_2(P_{1-x}Si_xO_4)_3$ を合成した。(1)についてはテフロン内張り型オートクレーブに、$Al(CH_3CO_2)_3$、$(CH_3COO)_2Mg・4H_2O$、$[(CH_3)_2CHO]_4Ti$、H_3PO_4 水溶液を所定の割合で混合密閉し 200℃、5 時間で水熱合成を行った。吸引ろ過し、乾燥させた後、さらに 800℃、1 時間電気炉内で焼成した。今回合成できた固溶体(1)について Rietveld 解析で精密化した結晶構造データから VESTA を用いて結合距離と多面体体積を計算した結果、チタン酸素八面体、マグネシウム酸素八面体、リン酸素四面体のそれぞれの多面体体積と原子間距離が x の値に対応して変化したことが確認できた。このうちマグネシウム酸素多面体の体積変化を図１に示す。またゾルゲル法により同じく NASICON 型の $Mg_{0.5}Ti_2(PO_4)_3$、およびリン酸塩型の $Mg_{0.5}Zr_2(PO_4)_3$ も合成できる条件を見出した。

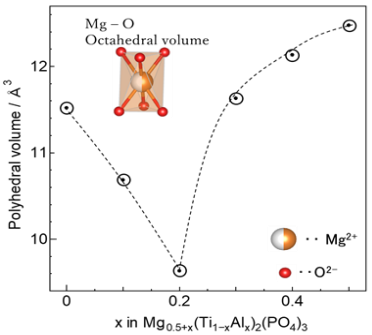

図１　マグネシウム酸素八面体体積の組成 x 依存性

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真空凍結乾燥法によるモリブデン酸イオンの無機アモルファス材料への固定化に関する研究

（神戸大院工）○LIU HUIXIN、梶並 昭彦
Immobilization of molybdate ion in inorganic amorphous materials by vacuum freeze drying method (*Graduate School of Engineering, kobe University*) ○ HUIXIN LIU, Akihiko Kajinami

The treatment of Mo ions in the high-level wastes generated from reprocessing of spent nuclear fuel has been an international issue. The main treatment method is to immobilize Mo ions in glass by melt-quenching method. However, Mo component is easily volatilized at high temperatures. Therefore, a technology that can synthesize the glass at low temperature is desired. Our laboratory has been investigating a method for synthesizing glass at low temperatures by vacuum freeze drying (FD) method. In this study, we attempted to create an inorganic amorphous material that can immobilize Mo ions in large quantities by the FD method. That is, $Fe(NO_3)_3$, Na_2SiO_3 , and Na_2MoO_4 solutions were mixed at specified molar ratios, the pH was adjusted to neutral, to get a hydrolyzed gel. The gel was quickly cooled by liquefied nitrogen and the water was removed by vacuum freeze drying method. The effect of Mo content with the glass composition was investigated. In addition, the chemical stability was evaluated by an elution test.

Keywords：vacuum freeze drying method, Immobilization, iron silicate glass, molybdate ion

使用済み核燃料の再処理から生じる高レベル放射性廃棄物の一つである Mo イオンの処理は国際的な課題となっている。Mo イオンの主な処理方法は、溶融急冷法によりガラス成分と混合して固定化させるが、高温で揮発しやすいため、低温で非晶質固体に強く固定化する技術が望まれている。当研究室では、エネルギー消費量を削減できる真空凍結乾燥法（FD 法）という低温でガラスを合成する方法を検討してきた。本研究では、FD 法により Mo イオンを大量かつ強く固定化できる無機アモルファス材料の作成を試みた。すなわち、$Fe(NO_3)_3$ 溶液と Na_2SiO_3 溶液と Na_2MoO_4 溶液を所定モル比で混合し、pH を中性に調整し、加水分解ゲルを作成した。それを真空凍結乾燥により水分を除去し、水洗して余分の塩を除去し、Mo 含有鉄ケイ酸塩ガラス試料を合成した。試料中の Mo イオン含有濃度を調べ、ガラス組成による影響について調べた。また、試料の化学的な安定性を調べるため、浸出実験を PCT 法[1)] により行った。

その結果、得られたガラスには最大 23wt%まで Mo イオンを含有できることが明らかとなった。また溶出試験により、溶融急冷法で合成したガラスよりも安定に Mo イオンを固定化できることが明らかとなった。

1）ASTM Int'l , C1285-02 (2008).

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Synthesis of Lambda-phase Trititanium Pentoxide by Block Copolymer Method

([1] *Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba*, [2] *Department of Chemistry, School of Science, The University of Tokyo*)
○K. Yamaguchi,[1] Y. Araki,[1] T. Kubota,[1] R. Seiki,[1] S. Ohkoshi,[2] H. Tokoro[1]
Keywords: Titanium oxide: Phase transition: Synthesis method

Lambda-phase trititanium pentoxide (λ-Ti_3O_5) exhibits a reversible phase transition with beta-phase trititanium pentoxide (β-Ti_3O_5) upon various external stimuli such as light and heat, and is expected to be applied as a heat storage material that can release heat under applied pressure.[1,2] In this study, we developed a synthesis method of λ-Ti_3O_5 nanocrystals by preparing a precursor using a block copolymer and studied the properties of pressure-induced phase transition of the samples.[3]

A mixed solution of Ti powder, H_2O_2, and NH_3 was prepared in a glass vessel, and stirred in an ice bath below 2 ℃ for 2 h. The obtained yellow solution was added to block copolymer and stirred in an ice bath below 2 ℃ for 4 h. Heated to 70 ℃ with stirring and then, we gained a yellow powder by centrifugation, and drying. The obtained yellow powder was sintered under hydrogen at a flow speed of 0.3 dm^3 min^{-1} and 1100 ℃ for 5 h to give Ti_3O_5 as a black powder.

The powder X-ray diffraction (PXRD) pattern and Rietveld analysis indicated that the obtained sample is λ-Ti_3O_5 (monoclinic, space group *C*2/m; a = 9.8369 Å, b = 3.7841 Å, c = 9.9690 Å, β = 91.2270 °) (Fig. 1). A pressure-induced phase transition was confirmed with the threshold of pressure at 300 MPa, and the pressure-produced β-Ti_3O_5 returned to λ-Ti_3O_5 by heating up to 475 K with the accumulated heat energy of ca. 105 kJ L^{-1}.

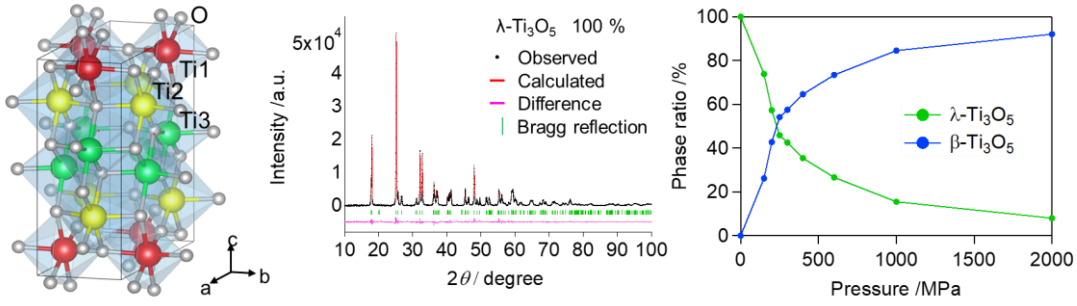

Fig. 1: Crystal structure (left), PXRD patterns with Rietveld analysis (middle) and pressure dependence of phase fractions of λ and β (right).

1) S. Ohkoshi, Y.Tsunobuchi, T. Matsuda, K. Hashimoto, A. Namai, F. Hakoe, H. Tokoro, ***Nature Chem.***, 2, 539 (2010). 2) H. Tokoro, M. Yoshikiyo, K. Imoto, A. Namai, T. Nasu, K. Nakagawa, N. Ozaki, F. Hakoe, K. Tanaka, K. Chiba, R. Makimura, K. Prassides, S. Ohkoshi, ***Nature Commum.***, 6, 7037 (2015). 3) Y. Araki, S. Ohkoshi, H. Tokoro, ***Mater. Today Energy***, 18, 100525 (2020).

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真空凍結乾燥法によるセシウムイオンの無機アモルファス材料への固定化

（神戸大学大学院工学研究科 [1]）○濱田 直輝 [1]・梶並 昭彦 [1]・LIU HUIXIN [1]

Immobilization of Cesium Ion in Inorganic Amorphous Materials by Vacuum Freeze-dry Method ([1]*Graduate School of Engineering, Kobe University*) ○Naoki Hamada,[1] Akihiko Kajinami,[1] HUIXIN LIU[1]

The objective of this study was to synthesize iron phosphate glasses by vacuum freeze-drying method and to immobilize cesium ions on them. Generally, iron phosphate glasses are synthesized by melting and quenching. Vacuum freeze-drying method has not been used to synthesize iron phosphate glass. In this study, we have synthesized iron phosphate glasses containing cesium ions by vacuum freeze-drying method. XRD and XPS analyses were performed on this glass. As shown in Figure 1, the XRD results showed that the fabricated samples were amorphous. In addition, the XPS results in Figure 2 show that the iron phosphate glass fabricated by the FD method can contain more than 7 wt% of cesium ions.

Keywords : Vacuum Freeze-Drying Method; Iron Phosphate Glass; Immobilization; Cesium Ion; Leaching Rate

本研究では、真空凍結乾燥法により鉄リン酸塩ガラスの合成を行い、そこにセシウムイオンを固定化することを目的とした。一般的に、鉄リン酸塩ガラスは溶融急冷法によって合成されるが、真空凍結乾燥法により合成された鉄リン酸塩ガラスがどれだけセシウムイオンを固定化できるのかあまり研究がされていない。そこで我々は真空凍結乾燥法を用いてセシウムイオンが入った鉄リン酸塩ガラスを合成した。
このガラスについてXRD、XPSの分析を行った。図1に示すようにXRDの結果からは作製した試料が非晶質であることが分かった。また、図2のXPSの結果からは、FD法で作製された鉄リン酸塩ガラスはセシウムイオンを7wt%以上含有できることが明らかとなった。

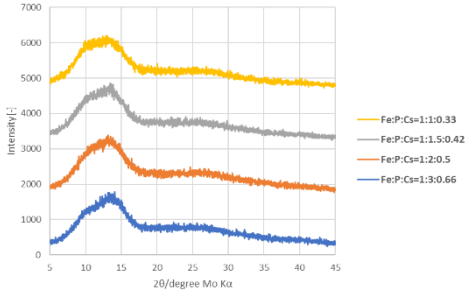

Fig.1 XRD pattern of cesium containing iron phosphate glass synthesized by vacuum freeze drying method.
The 'Fe:P:Cs' shows preparation ratio of iron, phosphor and cesium.

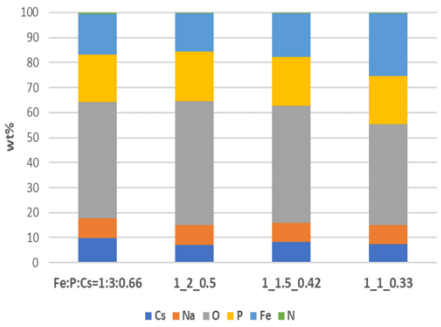

Fig.2 Composition of cesium containing iron phosphate glass synthesized by vacuum freeze drying method.

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Study of the synthesis conditions for tetragonal zirconium dioxide

([1]*Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba*, [2]*Department of Chemistry, School of Science, The University of Tokyo*) ○Yuki Konno,[1] Natsuki Asano,[1] Shin-ichi Ohkoshi,[2] Hiroko Tokoro[1]

Keywords: Zirconium dioxide; Structural phase transition; Zirconia

Introduction Zirconium dioxide (ZrO_2) is an attractive material that used in solid oxide fuel cells due to its high ionic conductivity. It is known that ZrO_2 is monoclinic at room temperature but undergoes structural phase transition to tetragonal (1170 ℃-2370 ℃), and to cubic (2370 ℃). Our research group reported that tetragonal ZrO_2 can be obtained at room temperature by sintering a precursor obtained by dropping an NH_3 aqueous solution into an aqueous $ZrCl_4$ solution and performing rapid cooling. In this study, we investigated the effect of changes concentration of ammonia aqueous solution during precursor synthesis on the appearing fraction of tetragonal ZrO_2.

Synthesis A solution of H_2O, $ZrCl_4$, and NH_3 (sample **1**: 9.6 mL, sample **2**: 19.2 mL, sample **3**: 38.4 mL) was prepared in a flask and stirred at 50 ℃ for 20 hours and formed precipitate. The precipitate was obtained by centrifugation, washed with ethanol, and heated at 60 ℃ for 24 h on a hot plate. After treatment at 200 ℃ for 10 minutes, precursors were heat with a sweep rate of 4 ℃/min up to 900 ℃ and sintered for 1 hour. After that, the samples were rapidly cooled with water. The powder X-ray diffraction (PXRD) measurements were performed to study the crystal structure of the samples.

Result and Discussion Rietveld analyses were performed for samples **1, 2** and **3**. Sample **1** had 24.51% tetragonal ($a = b = 3.5963$ Å, $c = 5.1863$ Å,) and 75.83% monoclinic (a =5.1451 Å, b = 5.2071 Å, c = 5.3141 Å, β = 99.197 °) (Fig. 1a), sample **2** had 30.29% tetragonal ($a = b$ = 3.5963 Å, c = 5.1867 Å,) and 69.71% monoclinic (a =5.1451 Å, b = 5.2073 Å, c = 5.3152 Å, β = 99.211°) (Fig. 1b). Sample **3** had 31.93% tetragonal ($a = b$ = 3.5962 Å, c = 5.1869 Å,) and 68.07% monoclinic (a = 5.1448 Å, b = 5.2075 Å, c = 5.3159 Å, β =99.173 °) (Fig. 1c). These results indicated that the higher concentration of NH_3 solution for precursor synthesis, the higher formation of tetragonal ZrO_2. In addition, crystalline size of the tetragonal and monoclinic phases were estimated by Rietveld analysis, i.e., ca. 15.3 nm and 16.5 nm for sample **1**, 14.7 nm and 16.45 nm for sample **2**, and 13.3 nm and 12.9 nm for sample **3**, tetragonal and monoclinic phases, respectively. Both crystallite sizes were decreased as the concentration of NH_3 solution increased. These results suggest that as the concentration of the NH_3 aqueous solution in the precursor synthesis increases, the crystallite sizes decrease, then formation of tetragonal phase increases.

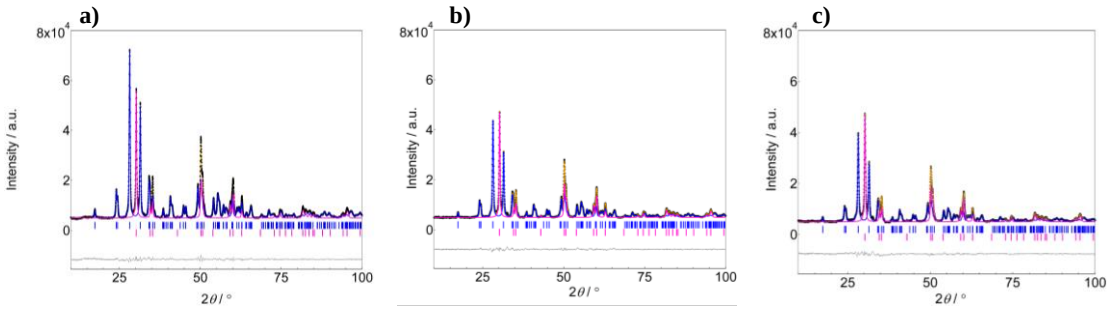

Fig. 1: XRD patterns and Rietveld analyses of (a) Sample **1**, (b) Sample **2**, and (c) Sample **3.** Dots, blue, pink, orange, and gray lines are the observed plots, calculated monoclinic, tetragonal, total XRD pattern, and XRD difference between observed and calculated, respectively. Blue and pink bars represent the calculated positions of the Bragg reflections of monoclinic and tetragonal phases.

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Stabilization of tetragonal phase of zirconium dioxide at room temperature

([1] *Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba,* [2] *Department of Chemistry, School of Science, The University of Tokyo*)
○N. Asano[1], Y. Konno[1], S. Ohkoshi[2], H. Tokoro[1]
Keywords: Zirconia; Zirconium dioxide; Structural phase transition

Introduction Zirconium dioxide ZrO_2 is colorless and transparent material. It has a monoclinic structure at room temperature, a tetragonal structure between 1170 ℃ and 2370 ℃, and a cubic structure above 2370 ℃. In the previous work, we synthesized a precursor using zirconium tetrachloride ($ZrCl_4$) as starting material and obtain a tetragonal structure at room temperature by sintering and rapid cooling. In this work, we study the sintering-temperature dependence of rate of the produced tetragonal structure.
Synthesis Solution of H_2O, $ZrCl_4$, and NH_3 was prepared in a flask and stirred at 50 ºC for 20 h to form precipitate. The precipitate was obtained by centrifugation, washed with ethanol, and heated at 60 ˚C for 24 h on a hot plate. After treatment at 200 ℃ for 10 minutes, 0.4 g of precursor was heated with a sweep rate of 4 ℃/min up to 870 ℃ (Sample **1**) and 900 ℃ (sample **2**), ans 930 ℃ (sample **3**)for 5min. Then, the samples were rapidly cooled.
Result and Discussion XRD patterns and Rietveld analyses of **1**, **2** and **3** are shown in Fig. **1a**, **1b** and **1c**, respectively. **1** had a tetragonal phase of 35.18 % (lattice constants $a = b =$ 3.5975 Å、c = 5.1904 Å) and a monoclinic phase of 64.82 %（a = 5.1414 Å、b = 5.2103 Å、c = 5.3261 Å、β = 99.214 °）. **2** had a tetragonal phase of 31.00 % (lattice constants $a = b =$ 3.5978 Å、c = 5.1910 Å) and a monoclinic phase of 69.00 %.（a = 5.1415 Å、b = 5.2103 Å、c = 5.3263 Å、β = 99.212 °）. **3** had a tetragonal phase of a tetragonal phase of 30.17% (lattice constants $a = b$ = 3.5980 Å, c = 5.1911 Å) and a monoclinic phase of 65.83 %(a = 5.1420 Å、b = 5.2103 Å、c = 5.3166 Å、β = 99.209 °). These results indicated that the lower the sintering temperature, the more tetragonal phase was produced.

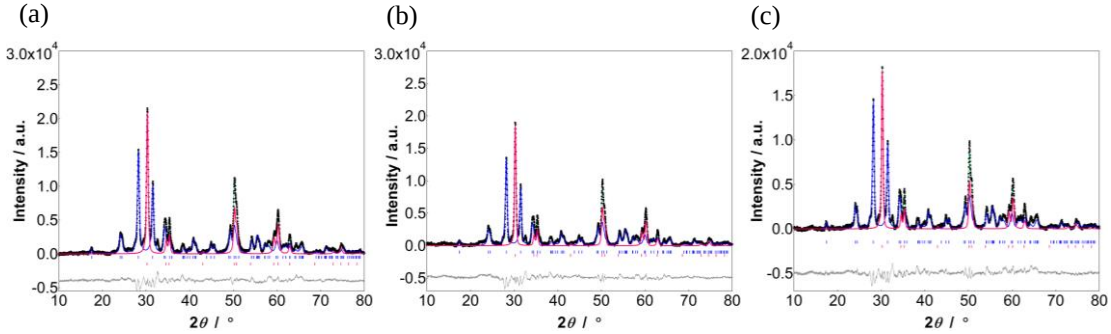

Fig. 1 The XRD patterns and Rietveld analysis for sample **1** (a), sample **2** (b) and sample **3** (c). Black dots, green lines, and gray lines are the observed, calculated, and the residual patterns, respectively. Blue bars, pink bars represent the calculated positions of the Bragg reflections of monoclinic and tetragonal phases, respectively.

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Synthesis method for gallium-substituted tetratitanium heptoxide ($Ti_{4-x}Ga_xO_7$) and evaluation of its magnetic properties

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Keywords: Titanium Oxide, Synthetic Method, Metal-Semiconductor Phase Transition

[Introduction] Tetratitanium heptoxide, Ti_4O_7, exhibits metal-semiconductor phase transition. The metal-substituted tetratitanium heptoxide is expected to control the electrical conductivity and the phase transition behavior. In this study, we developed a synthesis method to obtain gallium-substituted titanium heptoxide, $Ti_{4-x}Ga_xO_7$, and study the effect of gallium-substitution on the crystal structure.

[Method] A mixture solution of H_2O, $TiCl_4$ and NH_3 was prepared in a flask, and stirred at 50°C for 20 h. These precipitates were separated via centrifugation, washed with ethanol, and dried at 60°C for 24 h. The precipitates were calcinated under the hydrogen flow, forming a black powder sample. Five samples were synthesized with different Ga composition: **Ga0** (sintering temperature = 1000℃, [Ga]/[Ga+Ti] = 0%), **Ga1** (900℃, 19%), **Ga2** (900℃, 21%), **Ga3** (900℃, 23%), **Ga4** (900℃, 26%).

[Result] Elemental analyses by X-ray fluorescence (XRF) spectroscopy suggested the samples formulas were $Ti_{4.00}O_7$ (**Ga0**), $Ti_{3.93}Ga_{0.07}O_7$ (**Ga1**), $Ti_{3.91}Ga_{0.09}O_7$ (**Ga2**), $Ti_{3.87}Ga_{0.13}O_7$ (**Ga3**), $Ti_{3.75}Ga_{0.25}O_7$ (**Ga4**). X-ray diffraction (XRD) patterns and Rietveld analyses indicated that the crystal structure of **Ga0** was triclinic (space group *P*1; $a = 5.5982$ Å, $b = 7.1238$ Å, $c = 12.4604$ Å, $\alpha = 95.056°$, $\beta = 95.145°$, $\gamma = 108.783°$), and those of **Ga1**-**Ga4** was also triclinic. However, the lattice constants changed with increasing Ga substitution. For example, for **Ga4**, the *a*-axis decreased to 5.5940 Å, the *b*-axis increased to 7.1265 Å, and the *c*-axis decreased to 12.4530 Å. The α and γ angles increased to 95.101 ° and 108.816 °, respectively, while the β angle decreased to 95.123°. These changes were suggested to be a change in the crystal structure caused by the Ga substitution.

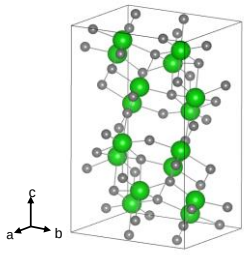

Fig. 1 Crystal structure of Ti_4O_7.

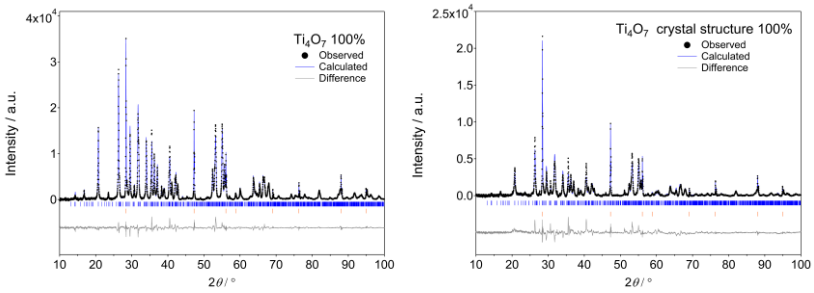

Fig. 2 XRD pattern and Rietveld analysis of **Ga0** (left) and **Ga4** (right).

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フロー型液相原子層堆積法によるα-Fe_2O_3薄膜の作製

（日大生産工）○高柳 充希・大坂 直樹・森 健太郎・山根 庸平

Flow-type LP-ALD process for the preparation of α-Fe_2O_3 thin films (College of Industrial Technology, Nihon University) ○Mitsuki Takayanagi, Naoki Osaka, Kentarou Mori, Yohei Yamane

LP-ALD (Liquid-Phase Atomic Layer Deposition) is a solution process that inherits the advantages of gas-phase ALD, but does not require high temperatures or high vacuum, and thus enables low-cost film deposition. The purpose of this study is to automate LP-ALD for α-Fe_2O_3 film deposition using the similar process as gas-phase ALD. The prepared films are yellowish brown, highly transparent, and strongly adhere to the substrate, while the XRD pattern suggests that the films are amorphous. Currently, we are exploring deposition conditions for the direct formation of crystalline α-Fe_2O_3.

Keywords : Thin film, Metal oxide, Deposition system

原子層堆積法(Atomic Layer Deposition: ALD)は複数の前駆体ガスを基板表面に交互に流すことにより，原子層ごとに膜形成する手法であり，近年，デバイスの微細化が進む中で需要が高まっている．しかし，その多くが真空条件を必要とすることから，プロセスのスケールアップが妨げられている. 昨今注目が集まっている液相原子層堆積法(Liquid-phase ALD: LP-ALD)は，気相 ALD の主な利点を受け継ぎながらも，溶液プロセスであるため，高温，高真空環境が不要であり，簡便な装置での低コストの製膜が可能となる [1].

本研究ではα-Fe_2O_3を対象物質とし，LP-ALD の手順を自動化させてフロー型製膜装置に適用することで, 気相 ALD と同等のプロセスで製膜を行うことを目的とした. 作製した膜の外観, および XRD パターンを Fig.1 に示す．膜は黄褐色で透明度が高く，基板との高い密着性を示した．一方，XRD パターンはブロードなピークのみが現れ，α-Fe_2O_3 に対応するピークは確認できなかったことから，作製された膜が非晶質であることが示唆された．現在，結晶質α-Fe_2O_3の直接形成を目指し，さらなる製膜条件の探索を進めている．

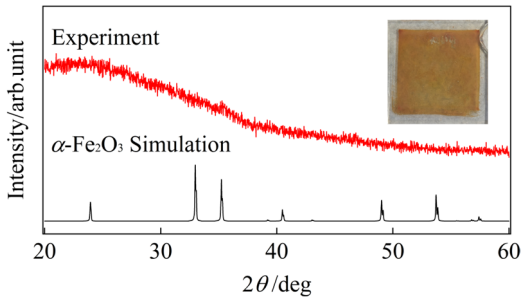

Fig.1 薄膜の外観および XRD パターン

1) Graniel, O., Puigmartí-Luis, J., & Muñoz-Rojas, D. *Dalton Trans.*, **2021**, 50 (19), 6373-6381.

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シクロケイ酸塩化合物における元素置換による構造制御の試み

（高知大理工[1]）○島内 理恵[1]・大澤 勇斗[1]・池田 拓朗[1]
Examination of crystal structure control by elements substitution in cyclosilicate compounds.
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A zirconium cyclosilicate-based compound has a zirconium-oxygen-silicon 7-membered ring channel characteristic in its structure. In sodium salts, K^+ is known to be incorporated therein and is used as a treatment for hyperkalemia. This study focused on potassium salts and attempted to shorten the synthesis time by hydrothermal synthesis.

First, precursors were synthesized from aqueous solutions of three starting substances: colloidal silica, $ZrCl_2O$ $8H_2O$ and KOH. The precursor was placed in an autoclave and hydrothermal synthesis was carried out at 250 °C for 6 hours, and potassium zirconium cyclosilicate was obtained by suction filtration, drying and firing at 800 °C. In addition, $ZrCl_2O$ $8H_2O$ among the starting substances were replaced with titanium tetraisopropoxide in a fixed ratio, and synthesis was carried out according to the same procedure to obtain potassium zirconium titanium cyclosilicate. From the result of XRD measurement, a possibility that the size of the crystal lattice can be controlled by substituted solid solution of Zr and Ti is found.
Keywords : Hydro thermal synthesis; Zirconium cyclosilicates; Solid solution; Ionic exchange

シクロケイ酸ジルコニウム系化合物は構造中に特有のジルコニウム-酸素-ケイ素 7 員環のチャンネルを持つ。ナトリウム塩においてはここに K^+を取り込むことが知られており、高カリウム血症の治療薬として用いられている。本研究ではカリウム塩に着目し、水熱合成による合成時間の短縮を試みた。また Zr^{4+}を Ti^{4+}で置換した固溶体の合成を試み、結晶構造の詳細について調べ、他イオンの交換可能性を考察した。

まずコロイダルシリカ、$ZrCl_2O$・$8H_2O$、KOH の三種の出発物質の水溶液から前駆体を合成し、オートクレーブに入れ 250℃で 6 時間水熱合成を行い、吸引ろ過および乾燥、800℃焼成によりシクロケイ酸ジルコニウムカリウムを得た。また出発物質のうち $ZrCl_2O$・$8H_2O$ を所定の割合でチタン（Ⅳ）テトライソプロポキシドに置き換えた。Zr：Ti＝10：0～0：10 の混合比において同様の手順で合成を行った。得られた試料について XRD 測定、SEM 観察等で評価を行った。

シクロケイ酸ジルコニウムチタンカリウム固溶体の結晶相が Zr と Ti の混合割合により変化する様子を調べた。Zr：Ti＝10：0～4：6 までは同一のパターンであった。図 1 に Zr：Ti＝4：6～0：10 の試料の XRD 測定結果を示す。これより Zr と Ti の置換固溶により結晶格子の大きさを制御できる可能性を見出した。

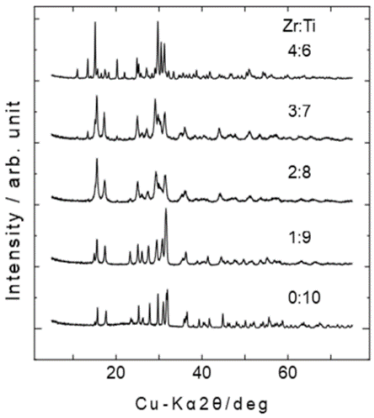

図 1 シクロケイ酸ジルコニウムチタンカリウム固溶体の XRD パターン

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希土類イオンによるハロゲン化鉛ペロブスカイト単結晶の発光制御

(帝京科学大院理工[1]・早稲田大先進理工[2]) ○能登 瑞樹[1]・山田 知英[2]・石井 あゆみ[2]

Luminescence property of lead halide perovskite single crystals controlled by lanthanide ions

([1]*Graduate School of Science and Engineering, Teikyo University of Science*, [2]*School of Advanced Science and Engineering, Waseda University*)
○Mizuki Noto,[1] Tomohide Yamada,[2] Ayumi Ishii[2]

Lead halide perovskites are known to exhibit strong luminescence in the visible region. In this study, we prepared perovskite crystalline thin films doped with Yb ions and succeeded in observation of high-brightness near-infrared luminescence through the quantum-cutting energy transfer. To control the energy-transfer based luminescence in perovskites, we have tried to fabricate the single crystal. In this presentation, we discuss the structure and luminescence properties of perovskite single crystals doped with lanthanide ions.

Keywords : Lead halide perovskite; Single crystal; Lanthanide ion; Luminescence; Energy transfer

近赤外領域に発光を示す材料は、セキュリティや情報通信分野、生体イメージングなどでの応用が期待されている。本研究では、高効率な近赤外発光を促すため、量子切断（quantum-cutting）による一光子吸収二光子発光過程を利用した新しい近赤外発光材料の開発を進めている。これまでに、ペロブスカイト（$CsPbCl_3$）構造の一部を近赤外領域に発光準位を持つ希土類イオン（Yb^{3+}、Er^{3+}）で置換した薄膜を作製し、ペロブスカイトから希土類イオンへの量子切断型のエネルギー移動を促すことで、100％を超える量子効率の近赤外発光の発現に成功した [1,2]。一方で、薄膜やナノ粒子内で生じるペロブスカイトー希土類間でのエネルギー移動は、欠陥構造や置換位置が不明瞭であることから、そのメカニズムについては未解明な点が多い。そこで本研究では、量子切断型エネルギー移動を構造的視点から明らかにすることを目的とし、単結晶化による精密な構造決定を試みた。ここでは、希土類イオンを添加したペロブスカイト単結晶構造と発光特性との相関について議論する。

Yb^{3+}を含むペロブスカイト（$CsPbCl_3$）単結晶は溶媒蒸発法により作製した（$CsPbCl_3$:Yb^{3+}）。蛍光 X 線分析の結果から、結晶内に Yb^{3+}が導入されたことが確認された。$CsPbCl_3$:Yb^{3+}単結晶の XRD 測定の結果を Fig. 1 に示す。立方晶のペロブスカイト構造に由来する回折ピークが観測されたことから、Yb^{3+}が結晶格子の Pb^{2+}位置に置換されたと考えられる。$CsPbCl_3$:Yb^{3+}単結晶は、$CsPbCl_3$ のバンド間遷移に対応する 400 nm での光励起により、Yb^{3+}の $^2F_{5/2}$→$^2F_{7/2}$遷移に帰属される近赤外発光を 984 nm に示す。984 nm でモニターした励起スペクトルは $CsPbCl_3$ の吸収スペクトルと一致したことから、Yb^{3+}の近赤外発光は、結晶格子内において形成した $CsPbCl_3$ の励起子準位からPb^{2+}位置に存在するYb^{3+}へのエネルギー移動により生じたものと考えられる。

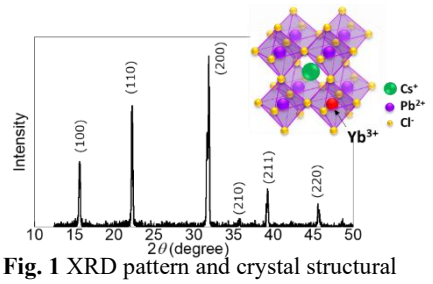

Fig. 1 XRD pattern and crystal structural model of $CsPbCl_3$:Yb^{3+} single crystal.

1) A. Ishii, T. Miyasaka, *Adv. Science* **2020**, *7*, 1903142.
2) A. Ishii, T. Miyasaka, *J. Chem. Phys.* **2020**, *153*, 194704.

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ハイブリッド型希土類アップコンバージョン粒子の合成と発光波長制御

(帝京科学大院理工[1]・早稲田大先進理工[2])
○溝口 隆介[1]・Truptimayee Behera[2]・小松﨑 涼太[2]・石井 あゆみ[2]
Development of Lanthanide Based Up-conversion Materials with Multicolor Luminescence
([1]*Graduate School of Science and Engineering, Teikyo University of Science*, [2]*School of Advanced Science and Engineering, Waseda University*)
○Ryusuke Mizoguchi,[1] Truptimayee Behera,[2] Ryota Komatsuzaki,[2] Ayumi Ishii[2]

In this study, we have developed lanthanide-based hybrid materials with up-conversion (UC) luminescence properties, and succeeded in improving the green UC emission efficiency of Er(III)-based materials to >5% by controlling the crystal and interface structure of the particles. In this report, control of the UC emission color by construction of hybrid structure with Mn(II) or Tm(III) has been reported.
Keywords : Up-conversion; Lanthanide ion; Hybrid; Energy Transfer

希土類イオンによるアップコンバージョン（UC）発光は、発光効率が著しく低く（1%程度）、励起光源に強いレーザー光が必要であるなど、応用には多くの課題がある。これに対し、石井らは、有機色素の高い吸収能を利用した色素増感型コアシェルナノ粒子を開発し、微弱な近赤外照射による UC 発光（緑や青）の発現に成功している[1,2]。本研究では、更なる発光機能の向上を目指し、結晶構造・サイズの最適化による UC 発光の高効率化およびエネルギー緩和過程の最適化による発光波長の制御を進めている。ここでは、Er 系 UC 粒子の発光強度および発光波長に対する結晶構造や金属イオンドーピングの効果について議論する。

希土類酸化物および酢酸マンガン(II)を用い、三種の Er 系粒子（$NaYF_4$:Yb,Er、$NaYb_{1-x}Er_xF_4$:Mn^{2+}および $NaErF_4$:Yb, Tm@$NaYF_4$）を合成した。$NaYF_4$:Yb, Er は、980nm 励起により $^2H_{9/2}\rightarrow{}^4I_{15/2}$, $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ および $^4F_{9/2}\rightarrow{}^4I_{15/2}$ 遷移に帰属される UC 発光を 410, 530, 540 および 654 nm に示す（Fig. 1）。$NaYF_4$:Yb, Er の緑色発光に対し、$NaYb_{1-x}Er_xF_4$:Mn^{2+}および $NaErF_4$:Yb, Tm@$NaYF_4$ では、$^4F_{9/2}\rightarrow{}^4I_{15/2}$ 遷移に由来する赤色発光が強く観測された。Mn^{2+}の $^4T_1$ 準位は Er^{3+} の $^2H_{11/2}$ および $^4S_{3/2}$ 準位と隣接していることから、$NaYb_{1-x}Er_xF_4$:Mn^{2+}において緑色発光が消光したと示唆される。$NaErF_4$:Yb, Tm@$NaYF_4$ における赤色 UC 発光の発現は、Er^{3+}-Tm^{3+}間での交差緩和により $^4F_{9/2}$ 準位が優先的に形成された結果である。

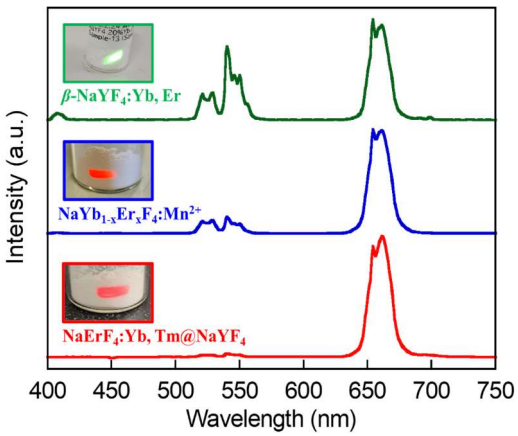

Fig.1 UC luminescence spectra of Er-based UC particles (λ_{ex} = 980 nm). Insets show UC emissions under NIR light irradiation (980 nm, 100 mW).

1) A. Ishii, et. al, *Adv. Photon. Res.* **2023**, 4, 2200222.
2) A. Ishii, *Electrochemistry* **2021**, 89, 544–551.

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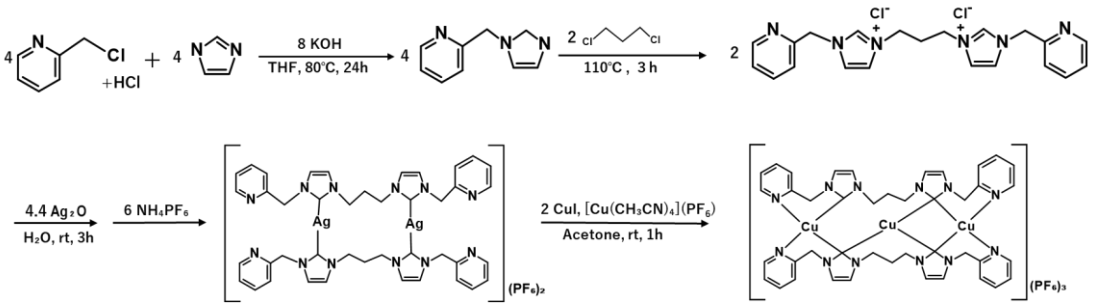
銅(I)カルベン多核錯体の合成と発光

（成蹊大院 [1]）○中村 寛太 [1]・坪村 太郎 [1]
Luminescent copper(I) carbene complexes ([1] *Seikei University*)
○Kanta Nakamura,[1] Taro Tsubomura,[1]

Imidazole, which has an N-heterocyclic structure, is often used as a carbene ligand precursor because it is easy to handle and synthesize, and because it forms complexes that exhibit luminescence, and these complexes exhibit various luminescent properties and chromic behavior. We have studied Cu(I) complexes using a ligand in which two N-heterocyclic carbene units are connected by a propylene chain, and found that they emit light in solids and solutions. Furthermore, we have been studying how dinuclear complexes synthesized by changing substituents change their luminescent color upon mechanical stimulation[1]). When the terminal substituent was a pyridylmethyl group, a trinuclear complex in which three Cu atoms exist in a linear manner, which is rarely reported, was synthesized. In this study, we aimed to synthesize this copper complex and investigate in detail its luminescence, which is still unknown. We also investigated the copper complexes with a similar trinuclear complex structure.
Keywords : carbene complex; copper complex; luminescence

N-複素環構造を持つイミダゾールは、取り扱いやすさ、合成の簡便さ、そして発光を示す錯体を形成することからカルベン配位子の原料としてよく用いられ、その配位子を用いた錯体には様々な発光特性やクロミック挙動がみられ注目されている。

これまで 2 つの N-複素環カルベンユニットがプロピレン鎖で連結された配位子を用いた Cu(I)錯体の研究を行い、固体及び溶液中で発光を示す事を見出した。さらに置換基を変えることで合成される二核錯体が機械的刺激などで発光色が変化するなどを研究してきた [1]。その際、末端の置換基をピリジルメチル基にした場合、Cu が 3 つ直線状に存在する報告例の少ない三核錯体が合成された。本研究ではこの銅錯体の合成を行い、まだ未解明である発光について詳細に調査することを目的とした。また、三核錯体の構造をもつ他の銅錯体の存在を探究した。



1) S. Ogawa, H. Katsuragi, T. Ikeda, K. Oshima, S. Satokawa, Y. Yamazaki, T. Tsubomura, *Dalton Trans*., **2021**, *50*, 8845.

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電気化学的な還元法による MOF 内部での Ag ナノ粒子合成

（東理大院理 [1]）○加藤 準也 [1]・原口 知之 [1]
Ag nanoparticle synthesis inside MOF by electrochemical reduction method ([1]*Graduate School of Science, Tokyo University of Science*) ○Junya Kato[1], Tomoyuki Haraguchi[1]

Metal Organic Frameworks (MOF) are crystalline materials with high porosity formed by self-assembly of metal ions and organic ligands. Recently, many studies have been carried out to construct composites of metal nanoparticles and MOFs for catalysts. In this study, Ag nanoparticles were formed in the pores of HKUST-1 by electrochemical reduction. The retention of the structure was confirmed by single crystal X-ray structure analysis for HKUST-1 after the reduction. Elemental mapping of the HKUST-1 single-crystal cross section by SEM-EDS confirmed that silver was introduced into the pores, showing that silver was distributed throughout the cross section.
Keywords : Metal Organic Frameworks; metal nanoparticles

多孔性配位高分子(MOF)は、金属イオンと有機配位子が自己集合して形成された高い空孔率を持つ結晶性材料である。選択的なガス分離・貯蔵を可能とする MOF と高い触媒活性を持つ金属ナノ粒子を組み合わせた複合材料を作製する研究は近年数多く行われている。[1)] しかしながら、従来の化学的な還元法では MOF 細孔内で密にナノ粒子を形成することは困難であった。そこで本研究では HKUST-1（$Cu_3(BTC)_2$）の細孔内で電気化学的な還元法によって Ag ナノ粒子を形成させた。

Figure に示すように、作製した Ag@HKUST-1 の SEM-EDS による結晶断面の元素マッピングによって、結晶断面全体に銀が分布していることから、細孔内に銀が導入されていることが確認された。また、XPS 測定によって細孔内に導入された銀イオンが還元されていることが確認された。さらに単結晶 X 線構造解析から、電気還元前後で HKUST-1 の骨格構造が保持されていたことが確認された。

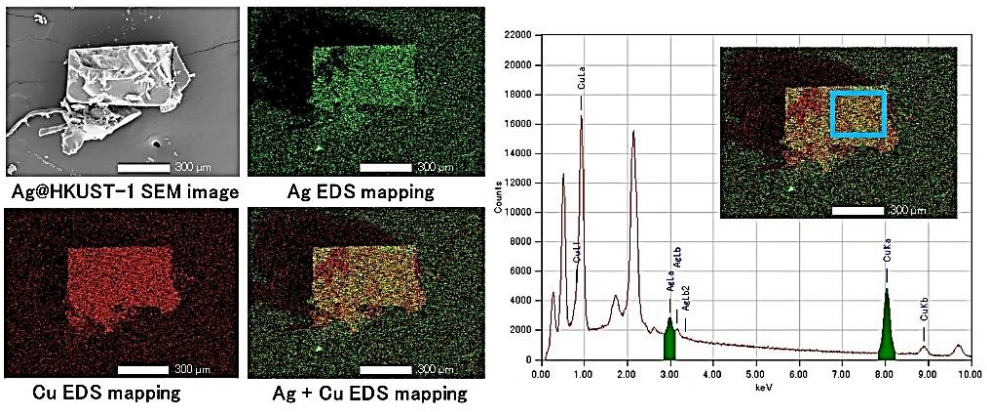

Figure. Ag@HKUST-1 の元素マッピング

1)Y. Liu, et al., *Adv. Mater*. **2010**, *22*, 4112

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電気化学的な還元法による COF 内部での鉛ナノ粒子の合成

(東理大院理 [1]) ○王 威樺[1]・原口 知之[1]

Pb nanoparticle synthesis within COF by electrochemical reduction method ([1]*Graduate School of Science, Tokyo University of Science*) ○Weihua Wang,[1] Tomoyuki Haraguchi[1]

Covalent Organic Frameworks (COFs) are crystalline porous structures formed through covalent bond between organic molecules, having functionalities like gas separation and catalysis. Metal nanoparticles within a COF form a composite material, garnering attention for catalytic applications. However, conventional chemical reduction methods used in previous studies pose a challenge in achieving a densely packed nanoparticle distribution within the COF pores. In this study, we introduced Pb^{2+} ions into COF-300 and synthesized Pb@COF-300 through an electrochemical reduction method.

Keywords : Covalent Organic Frameworks; Metal nanoparticles

共有結合性有機構造体（COF）は、有機分子同士の共有結合によって形成される結晶性多孔体で、ガス分離や触媒作用などの機能を示す。COF 内部に金属ナノ粒子を包接した金属ナノ粒子/ COF 複合材料が触媒などの観点から近年注目されている [1)]。しかしながら、従来の化学還元法では COF 細孔内にナノ粒子を密に形成することは困難である [2)]。そこで、本研究では COF-300 の細孔に Pb^{2+}を導入し、電気化学的な還元法で鉛ナノ粒子を形成し、Pb@COF-300 の合成を行った。

COF-300 単結晶が $Pb(NO_3)_2$ の DMF 溶液に対して安定であることを確認し、COF-300 の細孔内に $Pb(NO_3)_2$ を導入し、電気化学的な還元法で鉛ナノ粒子を形成することで Pb＠COF-300 を作製した。

また、Figure に示すように SEM-EDS の元素マッピングを行ったところ、電気還元後の結晶断面に鉛が分布していることが明らかとなり、細孔内に鉛が導入されていることが確認された。さらに、還元後の Pb@COF-300 の XPS 測定によって、鉛イオンが還元されていることが確認された。

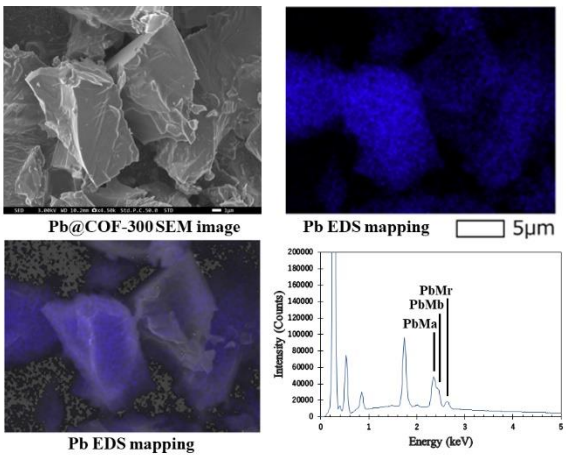

Figure. Pb@COF-300 の元素マッピング

1) Bing-Jian Yao, et al., *ACS Appl. Mater. Interfaces*. **2018**, 10, 20448−20457.
2) Kae Jye Si, et al., *Adv. Sci.* **2018**, 5, 1700179.

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Cu(BDC-NH_2) MOF 配向膜のキャスト法による構築と評価

（東理大院理[1]）○西垣　拓海[1]・張　啓原[1]・原口　知之[1]
A Synthesis and evaluation of Cu(BDC-NH_2) MOF oriented film by casting method ([1]*Graduate School of Science, Tokyo University of Science*) ○Takumi Nishigaki[1], Qiyuan ZHANG[1], Tomoyuki Haraguchi[1]

In this study, MOF alignment films were easily prepared using the casting method. we synthesized Cu(BDC-NH_2) MOF nanosheets by combining 2-aminoterephthalic acid (BDC-NH_2), an amino-substituted derivative of BDC, with Cu^{2+} ions. The result of powder X-ray diffraction measurement and IR measurement proved that the target nanosheet was synthesized. Furthermore, oriented MOF thin films with a two-dimensional structure were easily constructed by using a casting method in which the resulting colloidal solution of nanosheets was spontaneously dropped and dried on a substrate. The high orientation and crystallinity of the obtained thin films were demonstrated by the results of the thin film X-ray diffraction measurement.
Keywords : Metal Organic Frameworks; thin film

多孔性配位高分子(MOF)は金属イオンと有機配位子の自己集合によって形成される設計性の高い多孔性材料である。近年、MOF 配向膜を構築することでデバイスに応用する研究がなされているが、従来の MOF 配向膜の作製は、Layer-by-Layer 法[1)]などの複雑な手法にほぼ限られてきた。一方、当研究室では MOF ナノシート、Cu(BDC)のコロイド溶液を基板上に滴下・乾燥させるだけの簡便なキャスト法によって二次元 MOF 配向膜を構築できることを既に報告している[2)]。本研究では、プロトン伝導性などの物性面での展開が期待できるテレフタル酸のアミノ基置換体、 2-aminoterephthalic acid (BDC-NH_2)を用いて Cu(BDC-NH_2)の MOF ナノシートを作製した。さらに、このナノシートを用いて二次元 MOF 配向膜をキャスト法で構築し、得られた膜について構造評価を行った。

合成したバルクについて赤外分光分析(IR)、元素分析から同定を行った。さらに図に示すように粉末 X 線回析(XRD)測定から、得られた回析パターンがシミュレーションとよく一致していることから、目的の Cu(BDC-NH_2)が合成されたことを確認した。また薄膜 XRD 測定から、out-of-plane 方向(基板垂直方向)および in-plane 方向(基板水平方向)においてそれぞれ独立な回折パターンが観測され、得られた薄膜は高い配向性と結晶性をもつことが示唆された。

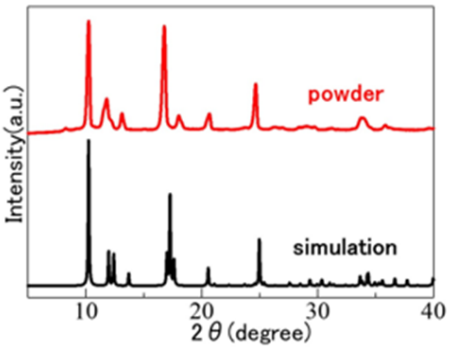

図 Cu(BDC-NH_2)のXRDパターン

1)T. Haraguchi, et al., *J. Am. Chem. Soc*. **2021**, 143, 16128 16135
2)Y.Fujii,et al., The 103rd CSJ Annual Meeting,**2023**

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カチオニックなフレームワークからなる MOF 配向膜のキャスト法による構築

(東理大院理) ○佐藤 泰聖[1]・張 啓原[1]・原口 知之[1]

Fabrication of oriented crystalline thin film of cationic MOF by casting method

([1]*Graduate School of Science, Tokyo University of Science*) ○Taisei Sato[1], Qiyuan Zhang[1], Tomoyuki haraguchi[1]

Metal-Organic Frameworks (MOFs), which are formed by self-assembly of metal ions and organic ligands, have various applications such as gas storage and separation, and so on. Recently, highly oriented crystalline MOF thin films have been intensively desired, which are expected to be applied as functional devices such as gas sensors, membranes, and so on. We have already succeeded in fabricating oriented crystalline MOF thin films by-casting method using a colloidal solution of charge-neutral MOF nanosheets. In this study, we fabricated 2D ELM-12 - $[Cu(bpy)_2(OTf)_2]$ thin film on a substrate using the casting method.

First, we synthesized ELM-12 MOF nanosheets through the solution diffusion method. Next, we fabricated 2D ELM-12 thin film on a substrate using the casting method. The pillar ligand SiF_6^{2-} was then introduced to form 3D MOF thin film of $[Cu(bpy)_2SiF_6]$. High crystallinity and orientation of the films were confirmed by X-ray diffraction measurements in both parallel (in-plane) and vertical (out-of-plane) directions to the substrate.

Keywords：Metal-Organic Frameworks, Thin film.

金属イオンと有機配位子の自己集合によって形成される多孔性配位高分子(MOF)はガスの貯蔵・分離、触媒などの様々な機能を示す。近年、高い配向性と結晶性を有する MOF 薄膜はセンサーや分離膜としての応用が期待されている。我々は電荷中性の MOF ナノシートのコロイド溶液を用いて乾燥･塗布するだけの簡便なキャスト法による MOF 配向膜の構築に既に成功している。[1] 本研究ではアニオン性無機配位子を含むカチオニックフレームワークを有する MOF である ELM-12、$[Cu(bpy)_2(OTf)_2]$ (OTf = Trifluoromethanesulfonate) を用いて、キャスト法による MOF 配向膜の構築と評価を行った。

既報[2]に従い MOF ナノシート、ELM-12 を合成した。次に ELM-12 のコロイド溶液を用いてキャスト法により、薄膜を作製した。さらに、この薄膜に対してアニオン性無機ピラー配位子として SiF_6^{2-}を導入することにより三次元骨格を有する MOF、$[Cu(bpy)_2SiF_6]$の配向膜も作製した。図 1 に示すように ELM-12 配向膜について X 線回折(XRD)測定を行ったところ、Out-of Plane 方向(基板垂直方向、図左)ではレイヤー間の周期構造由来の(*h*00)の回折ピークのみが、In-plane(基板水平方向、図右)ではレイヤー内の周期構造由来の(0*kl*)の回折ピークのみが観測され、膜が高い結晶性と配向性を有することが明らかとなった。吸着特性を含む詳細については当日報告する。

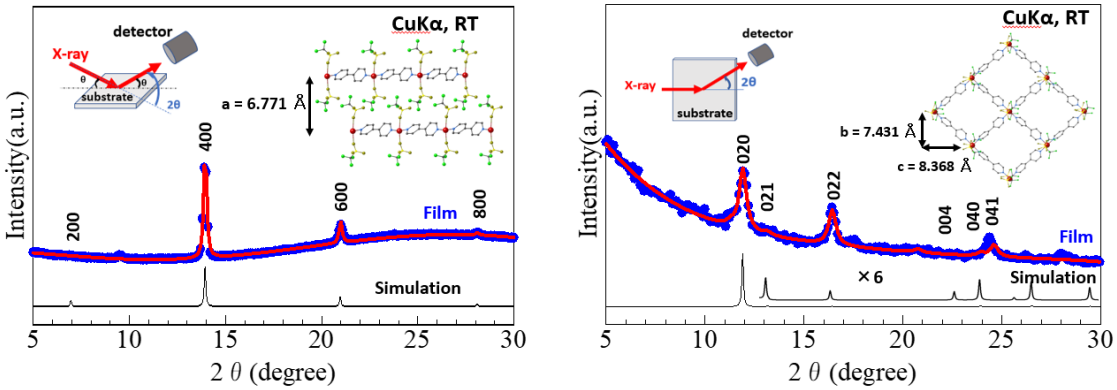

図 1　ELM-12 配向膜の XRD パターン(CuK α, RT) : Out-of-Plane(左)、In-Plane(右)

1) T. Haraguchi *et al., 70th JSCC*, **2020**.
2) A. Kondo *et al., J. Am. Chem. Soc.*, **2011**, 133, 10512-10522.

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キャスト法による COF 配向膜の構築

(東京理科大学 [1]) ○高野 浩一 [1]、張 啓原 [1],原口 知之 [1]
Construction of COF-oriented film by casting method (Graduate School of Science, Tokyo University of Science[1]) ○Koichi Takano[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1]

Covalent organic frameworks (COFs) are crystalline porous materials with potential applications in catalytic reactions and gas storage. In recent years, there have been numerous reports on the construction of COF-oriented films as part of efforts to develop functional surface devices. In this study, COF-1 was synthesized, dispersed in acetonitrile and toluene solution, and drop-cast onto a substrate. The resulting thin film, upon drying, exhibited high crystallinity and orientation, as indicated by X-ray study.
Keywords : Covalent Organic Framework; thin film

共有結合性有機構造体（COF）は結晶性多孔体であり高い比表面積や熱安定性から触媒、ガス貯蔵などへの応用が期待される。近年、機能性表面デバイスの開発を目指す上で、COF 配向膜の構築に関する研究が多く報告されている。本研究では、COF-1 のコロイド溶液を基板に滴下・乾燥させる簡便なキャスト法で COF-1 薄膜を構築し、配向性などを評価した。既報 [1]に従い 1.4-phenylene diboronic Acid を 1.4 ジオキサン：メシチレン溶媒として、ソルボサーマル法により COF-1 を合成した。アセトニトリル:トルエン溶液に分散させコロイド溶液にし、基板上に塗布し乾燥させ薄膜を作製した。膜の構造と配向性を評価するため X 線回折測定を行ったところ、in-plane 方向（基板水平方向、左図）ではレイヤー内周期構造由来の(*hk*0)に帰属される回折ピークのみが観測され、out-of-plane 方向（基板垂直方向、右図）ではレイヤー間周期構造由来の(00*l*)に帰属される回折ピークのみがそれぞれで独立に観測され、膜は高い結晶性と配向性を有していることが明らかとなった。

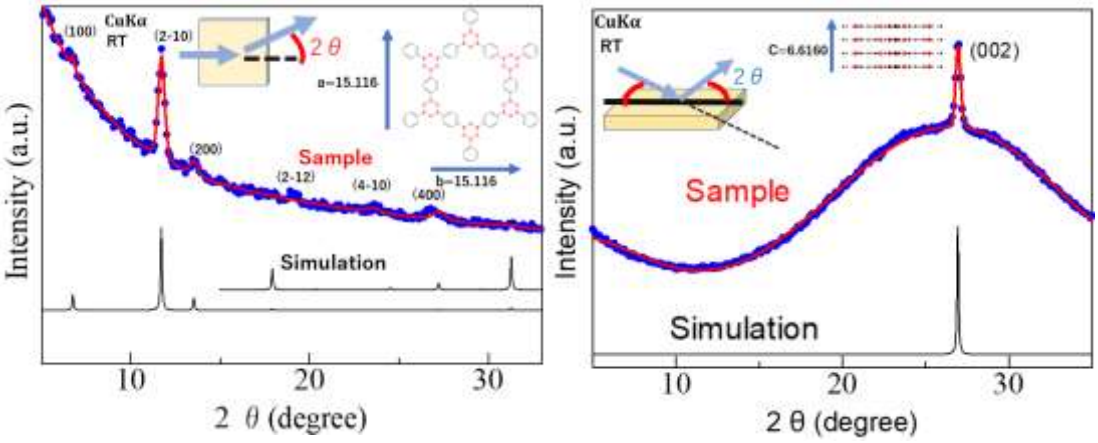

Fig. 1 COF-1 の XRD パターン(CuKα, RT): in-plane (左)、out-of-plane (右)

1) John W. Colson, et al., Science. **2011**, 332, 228−231.

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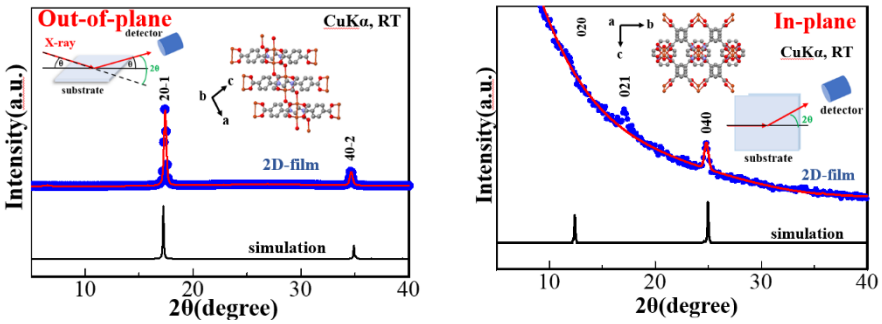
三次元骨格を有する MOF 配向膜のキャスト法による構築と評価

（東理大院理 [1]）○藤井　祐輔 [1]・チョウ　ケイゲン [1]・原口　知之 [1]
Construction and evaluation of MOF oriented films with three-dimensional framework by casting method.([1]*Graduate School of Science, Tokyo University of Science*) ○ Yusuke Fujii[1],Qiyuan Zhang[1], Tomoyuki Haraguchi[1]

Metal-Organic Frameworks (MOFs) are formed through the self-assembly of metal ions and organic ligands. Recently, MOF thin films have been expected to be applied as functional devices, though the methods of fabricating such films have been limited to complicated techniques. In this study, we successfully fabricated Cu(BDC) thin film and $Cu_2(BDC)_2(DABCO)$ thin film using casting method. First, we synthesized MOF nanosheets, Cu(BDC), by the solution diffusion method. Next, we fabricated a 2D-MOF thin film of Cu(BDC) on a substrate using the casting method. After introducing DABCO as a pillar ligand, the 3D-MOF thin film of $Cu_2(BDC)_2(DABC)$ was constructed. X-ray diffraction measurements of the films show their high crystallinity and orientation.
Keywords : Metal Organic Frameworks; thin film

金属イオンと有機配位子の自己集合によって形成される多孔性配位高分子は、ガスの貯蔵などへの応用が期待されている。近年、MOF を配向膜としてデバイス応用することが期待されているが、膜作製は複雑な方法に限られている。我々は MOF ナノシート、CuTCPP のコロイド溶液をガラス基板に滴下・乾燥させる簡便なキャスト法で MOF 配向膜の作製に成功している [1]。本研究では MOF ナノシート、Cu(BDC)を用いたキャスト法による MOF 配向膜を作製した後に、ピラー配位子として DABCO を導入することにより三次元骨格を持つ MOF 配向膜を作製した。得られた膜の構造と配向性について検討するため薄膜 X 線回折測定を行った。Cu(BDC)薄膜(図 1)、$Cu_2(BDC)_2(DABCO)$薄膜ともに、out-of-plane 方向(基板垂直方向)ではレイヤー間の周期構造由来の回折ピークのみが観測された。また in-plane 方向(基板水平方向)ではレイヤー内の周期構造由来の回折ピークが観測された。それぞれの XRD パターンは独立に観測され、シミュレーションと一致したことからそれぞれの膜が高い配向性を有することが明らかとなった。



図．Cu(BDC) MOF 配向膜の XRD パターン out-of-plane（左）、in-plane（右）

1) T. Haraguchi, et al., 70th JSCC, 2020.

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キャスト法による Zn_3(TCPP)(DABCO) MOF 配向膜の構築

(東京理科大学 [1]) ○張 嘉浩 [1]、張 啓原 [1]、原口 知之 [1]
Fabrication and Evaluation of Oriented Crystalline Zn_3(TCPP)(DABCO) MOF Thin Film by Casting Method (Graduate School of Science, Tokyo University of Science[1]) ○Jiahao Zhang[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1]

Recently, there has been significant research focused on the fabrication of crystalline-oriented Metal-organic framework (MOF) thin films, with potential applications as functional surface materials. In this study, we fabricated a 2D-oriented crystalline MOF: Zn_3(TCPP) thin film by casting method. Then 3D-oriented crystalline MOF thin film was formed by introducing DABCO. The high crystallinity and controllable orientation of the obtained films were confirmed by thin film X-ray diffraction measurement.
Keywords : Metal-Organic Framework, ,Thin Film, Surface

多孔性配位高分子（MOF）は、金属イオンと有機配位子の自己集合から形成され、ガス貯蔵材料や触媒などの機能を示す。MOF を配向膜にすることにより、ガス分離膜、触媒、プロトン伝導膜としての応用が期待されているが、これまでの MOF 配向膜の作製は、Layer-by-Layer 法などの煩雑な手法にほぼ限られていた。本研究では、MOF ナノシート、Zn_3(TCPP) (TCPP＝Tetrakis(4-carboxyphenyl)porphyrin)のコロイド溶液を使用しキャスト法で二次元層状 MOF 配向膜を構築した [1]。更に、1,4-Diazabicyclo[2.2.2]octane (DABCO) を得られた薄膜に導入し、三次元 MOF、Zn_3(TCPP)(DABCO)の配向膜を構築した。

得られた薄膜の構造と配向性について検討するために薄膜 X 線回折(XRD)測定を行った。Fig.1 に示すように膜の in-plane 方向ではレイヤー内の周期構造由来の(hk0)に帰属される回折ピークのみが、out-of-plane 方向ではレイヤー間の周期構造由来の(00l) に帰属される回折ピークのみが観測され、膜が高い結晶性と配向性を有することが明らかとなった。

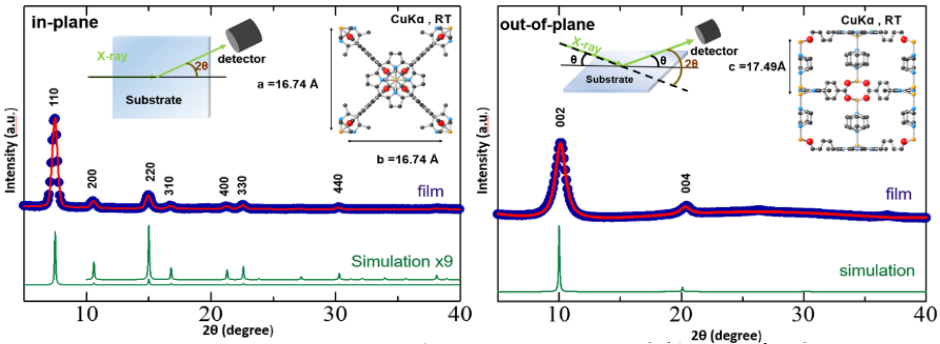

Fig. 1 Zn_3(TCPP)(DABCO)の XRD パターン(CuKα, RT): in-plane (左)、out-of-plane (右)

1) T. Haraguchi, et al., *The 72nd Conference of JSCC*. **2020**, 3A-06 .

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Double-Four-Ring 型分子プリカーサーを用いたアルミノシリケート構築

（中大理工[1]・中大院理工[2]）○大西 祐里香[1]・今泉 暁[2]・本田 暁紀[1]・張 浩徹[1]
Construction of Aluminosilicate Frameworks from Double-Four-Ring-Type Molecular Precursor ([1]*Faculty of Science and Engineering, Chuo University*, [2]*Graduate School of Science and Engineering, Chuo University*) ○Yurika Ohnishi[1], Akira Imaizumi,[2] Akinori Honda,[1] Ho-Chol Chang[1]

Zeolites, which possess great industrial importance, have been synthesized using discrete Al and Si sources under hydrothermal conditions. Although a variety of zeolites have been achieved by the conventional methods, further development of the method for rational zeolite construction based on the composition and structure of starting materials is an urgent issue. Therefore, we applied a single-source molecule precursor $[NMe_4]_4[Al_4Si_4O_{12}(OH)_8]\cdot 13H_2O$ (**[MP]**) with double-four-ring (D4R)-type core structure, which is a common unit in certain zeolite frameworks, as a precursor. Interestingly, LTA-type zeolite, which can be construct by linking only the D4R units, was formed under a wider range of Na^+ ion content and temperature than when using discrete Al and Si sources. These results indicate an important effect of the structure of starting materials during the aluminosilicate framework construction.
Keywords : Aluminosilicate; Molecular precursor; Hydrothermal synthesis; LTA-type zeolite

従来の水熱反応を利用したゼオライト合成は、別々の Al および Si 源を用いる点から、組成や構造の制御が困難であった。一方で、出発物質として予めゼオライトの部分構造および組成を有する分子プリカーサーを用いることで、その構造を保持したゼオライトの選択的形成が期待される。本研究では、double-four-ring (D4R)型骨格を有する$[NMe_4]_4[Al_4Si_4O_{12}(OH)_8]\cdot 13H_2O$[1] (**[MP]**, Fig. 1a) をプリカーサーとして用い、D4R 骨格のみから構築可能なゼオライトの合成を検証した。

[MP]へ *x* 当量 (*x* = 1, 4, 及び 8) の NaOH あるいは NaCl を添加して得たゲルを *y* ℃ (*y* = 100, 150, 及び 200)で水熱反応させると(**P-*x*NaOH-*y***, **P-*x*NaCl-*y***)、1 あるいは 4 当量において**[MP]**と近い Si/Al 比 (0.9–1.2) を有する D4R 型骨格のみから構築される LTA 型ゼオライトが生成した(Fig. 1a-c)。別々の Al および Si 源を用いた従来の方法に比べ(**P_{conv}-*x*NaOH-*y***, **P_{conv}-*x*NaCl-*y***)、**[MP]**を用いた方が広範囲の Na^+濃度および温度で LTA 型ゼオライトが得られた(Fig. 1b-e)。これらの結果は出発物質の構造が LTA 型ゼオライト形成に影響することを示す興味深い結果である。

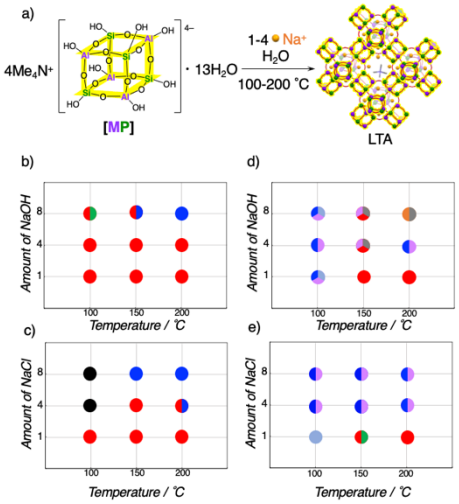

Fig. 1 a) **[MP]**からの LTA 型ゼオライト合成スキーム, b) **P-*x*NaOH-*y***, c) **P-*x*NaCl-*y***, d) **P_{conv}-*x*NaOH-*y***, 及び e) **P_{conv}-*x*NaCl-*y*** の生成物プロット図 (*x* = 1, 4, 8, 及び *y* = 100, 150, 200 ℃). ● = Amorphous, ● = LTA, ● = FAU, ● = SOD, ● = GIS, ● = CAN, ● = JBW, ● = 不明相.

Reference: [1] Smolin, Y. I.; Shepelev, Y. F.; Ershov, A. S.; Hoebbel, D. *Sov. Phys. Dokl.* **1987**, *32*, 943–945.

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酸化スズクラスターを基盤材料とする分子サイズエレクトライドの創成

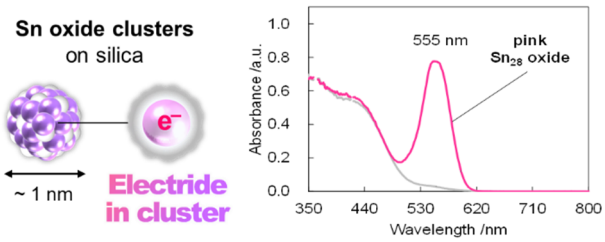
（東大生研[1]・JST-さきがけ[2]・東工大化生研[3]・JST-ERATO[4]）○塚本 孝政[1,2]・大竹 真由美[1]・吉田 希生[3]・森合 達也[3]・山元 公寿[3,4]

Creation of Molecular-sized Electride Compounds by Using Tin Oxide Cluster as a Base Material ([1]*IIS, The Univ. of Tokyo*, [2]*JST-PRESTO*, [3]*Lab. Chem. Life Sci., Tokyo Tech*, [4]*JST-ERATO*) ○ Takamasa Tsukamoto[1,2], Mayumi Otake[1], Nozomi Yoshida[3], Tatsuya Moriai[3], Kimihisa Yamamoto[3,4]

In this study, we investigated the creation of molecular-sized electrides with unpaired electrons by using 1 nm clusters as a base material. In particular, by focusing on tin oxide clusters, it was discovered that they exhibited significant coloration originating with unpaired electrons when through a specific synthesis scheme. ESR measurements and observations of temperature-dependent UV-vis absorption changes revealed that the clusters have a cage-like substructure containing unpaired electrons.

Keywords : Atomic clusters; Tin oxides; Electrides

対アニオンとして電子そのものを持つエレクトライド（電子化物）は、結晶中の格子欠陥やナノ包摂空間等のバルク固体中での単離が報告される一方で、相対的に反応性の高い分子サイズのエレクトライドはこれまで合成が困難とされてきた。本研究では、新たに分子サイズ(1 nm)のクラスター[1]を基盤材料とし、内部に不対電子を有する分子サイズエレクトライドの合成を試みた。高分子カプセルを用いる独自のクラスター合成法[2-4]を応用し、様々な条件でのクラスター合成を検討した結果、特定の合成スキームを経ることで、ピンク色の特徴的な発色を示す酸化スズクラスターを得ることに成功した（図）。この可視光吸収帯は、周辺温度に依存した可逆的な強度・波長変化を起こす、バルク結晶等の欠陥構造に存在する不対電子と同様の性質を示したことから、当該クラスターが内部に電子の閉じ込めを可能とするケージ様構造を有していることが示唆され、実際に、ESR による磁性測定により不対電子を持つことを明らかにした。加えて、当該クラスターは、周辺の雰囲気（Air、N_2、CH_2Cl_2 蒸気、CH_3OH 蒸気等）によって大きな色調変化（赤～紫～水色）を伴う、顕著なクロミズムを示すことを見出した。この現象は、孤立電子と周辺環境との距離が非常に近い、分子性エレクトライド特有の性質であると考えられた。



1) T. Tsukamoto, et al., *Nature Rev. Chem.* **2021**, *5*, 338.
2) T. Tsukamoto, et al., *Nature Commun.* **2018**, *9*, 3873.
3) T. Tsukamoto, et al., *Acc. Chem. Res.* **2021**, *54*, 4486.
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層状ポリシランの還元性を利用した白金イオンの選択的還元回収

（豊田中研）○大橋 雅卓・後藤 康友・中野 秀之
Efficient reducibility of layered polysilane for selective recovery of platinum ions from aqueous media（Toyota Central R&D Labs., Inc.）○Ohashi Masataka, Goto Yasutomo, Nakano Hideyuki

Platinum (Pt) ions dissolved in artificial seawater were recovered using layered polysilane (LpSi), which is a stacking of hydrogen-terminated monatomic silicon layers. Hydrosilyl groups (≡Si-H) in LpSi selectively reduced Pt ions to form Pt nanoparticles (Pt-NPs) on LpSi. The formed Pt-NPs can be isolated from LpSi by simple treatment with an alkaline solution. Moreover, the resulting Pt-NP loaded LpSi catalysed the H_2 evolution reaction in water splitting as an electrocatalyst, and H_2 evolution proceeded quantitatively for the supplied charges.
Keywords : Layered polysilane; Platinum nanoparticle; Hydrosilyl group; Selective reduction; Resources recovery

【緒言】 水素終端されたシリコン単原子層の積層体である層状ポリシラン（LpSi）は、還元性官能基（ヒドロシリル基：Si－H）が高密度に存在する層間空間を有している。本研究では LpSi の還元作用を利用し、様々なイオン種を含む水系媒体中に溶存させた白金イオン（Pt^{4+}）の還元回収を検討した。

【実験】 水系媒体には種々のイオン種が混在する人工海水を用いた。塩化白金酸を溶解させた人工海水に LpSi を添加し室温撹拌することで Pt^{4+}の還元回収を評価した。

【結果・考察】 Pt^{4+}を含む人工海水に LpSi を添加すると LpSi の色調が黄色から暗緑色へと変化した。生成した暗緑色 LpSi の XRD 及び TEM 観察からは LpSi 上に 30–100 nm の Pt ナノ粒子（Pt-NPs）が形成している事を確認した（Fig. 1）。一方、人工海水由来のイオン種は LpSi に殆ど吸着/担持していなかった。また FTIR スペクトルからは Pt-NPs の形成に伴い Si－H 振動の大幅な減衰が確認された。以上の結果は、人工海水中の希薄な Pt^{4+}が LpSi の Si－H 基によって選択的に還元され Pt-NPs として LpSi 上に回収された事を示している。Pt-NPs が担持した LpSi（Pt/LpSi）をアルカリ処理すると、LpSi の Si 骨格が分解して Pt-NPs が簡便に単離回収された。また導電性担体に塗布した Pt/LpSi を電極触媒とする水電解反応では、LpSi 上の Pt-NPs が触媒活性点として機能し、投入電荷に対して定量的に水素生成反応が進行した。

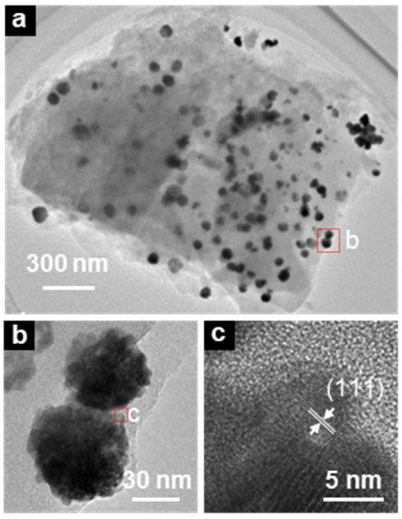

Fig. 1 HRTEM images of Pt/LpSi (a) and formed Pt-NPs on LpSi (b, c)

M. Ohashi, Y. Goto, H. Nakano, *New J. Chem.* **2023**, *47*, 10638–10644.

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産地によってモンモリロナイトのセシウムイオン交換挙動は異なるのか？

（昭和薬大・薬）○鈴木　憲子・澤田　雅斗・守谷　礼司

Does the origin of montmorillonite affect cesium ion exchange behavior? (*Department of Analytical Chemistry of Medicines, Showa Pharmaceutical University*) ○Noriko Suzuki, Masato Sawada, Reishi Moriya.

Bentonite deposits are formed through hydrothermal denaturation of volcanic ash deposited by volcanic eruptions and other processes. Bentonite deposits are found in the United States, Europe, China, and other parts of the world. It is also produced in Japan, such as Niigata, Yamagata and so on. Montmorillonite is the main component of bentonite and is a silicate mineral with a 2:1 layered structure. It is well known that it has exchangeable cations between the layers, so that the ion-exchange properties will be observed. In this study, we examined the cesium ion exchange of two types of montmorillonite (Tsukinuno and Mikawa), which are distributed by the Clay Science Society of Japan. The CEC of smectite clay minerals is 100-150 meq/100 g, so there was no difference in sorption in the low concentration range, but there was a significant difference in the high concentration range.

Keywords : clay minerals, montmorillonite, cesium ion, ion exchange.

ベントナイトは火山噴火などによって堆積した火山灰などが熱水変性などを経て鉱床を生成する。ベントナイト鉱床は米国、欧州、中国など世界各地に存在し、我が国でも新潟県、山形県などで産出している。モンモリロナイトはベントナイトの主成分で、2 : 1 型の層状構造をもつ珪酸塩鉱物である。層間に交換性陽イオンをもち、イオン交換性を示すことが知られている。本研究では、日本粘土学会より領布されている２種類のモンモリロナイト（月布、三川）のセシウムイオン交換について検討した。

三川モンモリロナイトは月布モンモリロナイトと比べクリストバライト、雲母、角閃石、少量の石英、長石などの不純物を含む。したがって、Si や K を多く含み、Al や Na が少ない。この不純物によりセシウムに対するイオン交換挙動が月布と異なることが予想された。所定の初期濃度による各モンモリロナイトのセシウムイオン収着率を Fig. 1 に示した。スメクタイト系粘土鉱物の陽イオン交換容量は 100～150 meq/100 g なので低濃度領域では収着量の差は見られないが、高濃度域では大きな違いがあった。

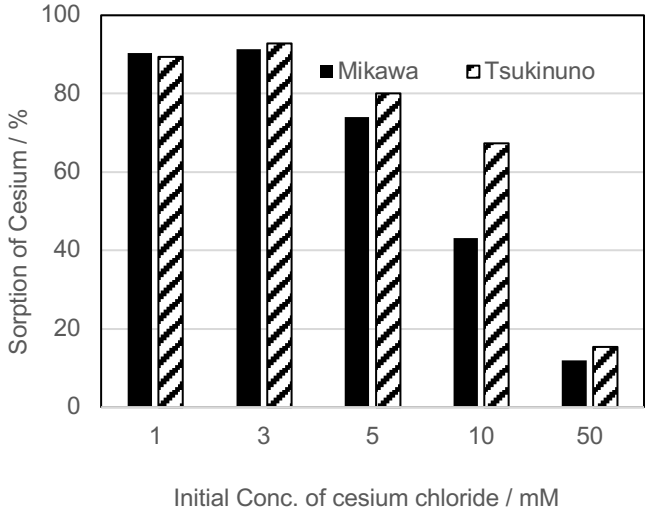

Fig. 1 Sorption of cesium ion by the initial concentration.

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ポリウレタンフォームへの有機修飾した層状ケイ酸塩の分散

（信州大工）○佐々木　春奈・渡邉　朋憲・岡田　友彦
Dispersion of organically modified layered silicates in polyurethane foam (*Faculty of Engineering, Shinshu university*) ○Haruna Sasaki, Tomonori Watanabe, Tomohiko Okada

A polyurethane foam (PUF) has been used as a thermal insulation material; however, the performance has degraded because of replacing the insulation gases in babbles with air. The aim of this study is to disperse a nanosheet (layered silicate) in PUF as a gas barrier for improving thermal insulation performance. Here, we examined that organically modified montmorillonites prepared though cation-exchange reactions with quaternary ammoniums (hexadecyldimethylbenzylammonium, dioleyldimethylammonium or bis(2-hydroxyethyl) dimethylammonium), were mixed with polyols, followed by reacting with an isocyanate. Whereas the polyols were scarcely intercalated into the bis(2-hydroxyethyl) dimethylammonium-form, high dispersion of the nanosheets was found in PUF owing to the increase in polarity from polyol to polyurethane by the polymerization reactions.

Keywords : Layered silicates; Polyurethane foam; Organic modification; Dispersion; Polymer-clay hybrids

ポリウレタンフォーム（PUF）は、ポリオ―ルとイソシアネートの重合反応により生成し、気泡層の多孔質構造を持つ。断熱材として用いられるが、気泡層の断熱ガスが空気と入れ替わることで断熱性能が経年劣化することが課題となっている。本研究では、断熱ガスと空気の置換を遅延させ、断熱性能を向上させることを目的に、層状ケイ酸塩（モンモリロナイト）のナノシートを PUF 中に分散させる方法を検討した。

4 級アンモニウム（ヘキサデシルジメチルベンジルアンモニウム（$C_{16}B$）、ジオレイルジメチルアンモニウム（$2C_{18=}$）、ビス(2-ヒドロキシエチル)ジメチルアンモニウム（$2C_2OH$））との陽イオン交換反応により調製した有機修飾モンモリロナイトをポリオ―ルと混合し、続いてイソシアネートと反応させ PUF を調製した。$C_{16}B$ または $2C_{18=}$ で修飾したモンモリロナイトの(001)回折線は、ポリオ―ル混合後により低角側に現れたことから、ポリオールの層間取り込みにより層間距離が拡大した。一方、$2C_2OH$ で修飾した場合では、ポリオ―ル混合前後で(001)回折線の位置が変化せず、ポリオールは層間に取り込まれなかった。イソシアネートと反応させて得られた PUF の SAXS 測定の結果、q = 0.01~0.1 nm^{-1} における散乱強度は、$C_{16}B$、$2C_{18=}$、$2C_2OH$ の順に減少した。特に、$2C_2OH$ 型モンモリロナイトを添加した PUF での散乱強度は無添加の PUF とほぼ一致したことから、 μm 級の凝集粒子はほとんど存在しないと解釈できる。ポリオールから PUF へと重合すると極性が高くなり、ヒドロキシ基を持つ $2C_2OH$ と PUF との親和性が高まったため、モンモリロナイトが PUF へ良好に分散したと考えられる。以上のように、モンモリロナイトの有機修飾に用いる 4 級アンモニウムの官能基は PUF への分散性に影響を与えることがわかった。

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フッ素白雲母系マイカセラミックスの選択溶解によるミクロ多孔化

（信州大院総合理工[1]・信州大工[2]）○青柳 大知[1]・山口 朋浩[2]・樽田 誠一[2]

Development of microporosity by the selective leaching of fluorine muscovite mica ceramics

(*[1]Graduate School of Science and Technology, Shinshu University・[2]Faculty of Engineering, Shinshu University*)
○Daichi Aoyagi,[1] TomohiroYamaguchi,[2] Seiichi Taruta[2]

Fluorine muscovite mica ceramics were prepared using kaolinite and potassium hexafluorosilicate as raw materials by firing at 600℃. Selective leaching of powder sample of the mica ceramics was attempted to develop microporosity using H_2SO_4 at 50℃. Micropores formed depending on the acid-treatment conditions. Specific surface area of the acid-treated product obtained by a 12 h acid-treatment using 0.125 M H_2SO_4 reached 119 m^2/g. Upon acid-treating under more severe conditions, specific surface area of the acid-treated product decreased.

Keywords：Fluorine Muscovite; Mica Ceramics; Selective Leaching; Micropore

【緒言】層状ケイ酸塩鉱物を酸処理すると、鉱物種および酸処理条件に依存してシリカリッチな多孔体が生成する。マイカセラミックスは機械加工性を有し、そのマイカ相に多孔性を付与できれば、吸着能やイオン交換能などの化学的機能の発現が期待できる。本研究では、カオリナイトを用いて作製したフッ素白雲母[$KAl_2(AlSi_3O_{10})F_2$]系マイカセラミックス粉末の酸処理によるミクロ多孔化を試みた。

【実験方法】カオリナイト(＜45 μm)とケイフッ化カリウムを、モル比 1.5:0.6 で全量が 0.5 g となるように秤取・混合した。これを 75 MPa で真空一軸加圧成形し、600℃で 6 時間焼成してマイカセラミックス試料とした。75 μm 以下に粉砕したマイカセラミックス試料 0.15 g を 0.025~1 M の硫酸 15 mL 中で、室温または 50℃で 6~48 時間攪拌して酸処理した。生成物を蒸留水で洗浄し、60℃で 24 時間乾燥させて酸処理試料とした。各試料について、XRD および窒素吸脱着等で分析・評価した。

【結果と考察】マイカセラミックス試料粉末を 0.25 M の硫酸を用いて室温または 50℃で 24 時間酸処理したところ、いずれの酸処理試料もマイカの周期構造を維持していることが分かった。また、酸濃度をより大きくした場合でも、周期性はやや低下するものの酸処理試料はマイカ構造を維持した。処理温度を 50℃として 24 時間酸処理したところ、酸濃度を大きくするにつれて生成物の比表面積は増大し、0.125 M の硫酸で処理をしたときに生成物の比表面積が最も増大した。一方で、さらに酸濃度を大きくすると、酸処理生成物の比表面積は低下した。また、酸処理生成物のミクロ孔容積は低濃度の酸を用いたときに大きく、酸濃度を大きくすると低下した。0.125 M の硫酸を用いて 50℃で 6-48 時間酸処理したところ、生成物の比表面積およびミクロ孔容積はともに 12 時間で最大となり、BET 比表面積は 119 m^2/g に達した。

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ポリヒドロキソ Al 錯体水溶液を用いる均一沈殿法による Zn 板表面への Zn-Al 系 LDH 膜の析出

（信州大院総合理工[1]・信州大工[2]）○小久保　一誠[1]・山口　朋浩[2]・樽田　誠一[2]

Formation of Zn-Al LDHs as coating on a Zn plate by the homogeneous precipitation method using a polyhydroxoaluminum complex solution

([1]*Graduate School of Science and Technology, Shinshu University*, [2]*Faculty of Engineering, Shinshu University*) ○Issei Kokubo[1], Tomohiro Yamaguchi[2], Seiichi Taruta[2]

Zn-Al layered double hydroxides (LDHs) were prepared as coating on a Zn plate by the homogeneous precipitation method using a polyhydoroxoaluminum complex solution. LDH particles were deposited on a Zn plate after a reaction time of 6 h, and the Zn plate was completely covered by LDH particles for reaction times longer than 24 h. LDH particles were selectively deposited on the surface of the Zn plate in the initial stage of reaction. Subsequently, LDH particles were also deposited besides the surface of the Zn plate after a reaction time of 12 h.

Keywords：Layerd double hydroxide; Zinc; Homogeneous precipitation method; LDH coating

層状複水酸化物（LDH）は、$[M^{2+}_{1-x}M^{3+}x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x+}$の一般式で示される層状化合物である。本研究では Zn 板を Zn 源としても利用する均一沈殿法により、Zn 板表面に Zn-Al 系 LDH を膜状に析出させ、その析出挙動を明らかにすることを目的とした。また析出する LDH 粒子の形態制御の可能性も検討した。

ポリヒドロキソ Al 錯体(PHA)水溶液を蒸留水で希釈し($[Al^{3+}]$ = 0.05 または 0.15 M)、そこに Zn 板(45×15×0.3 mm)と $ZnCl_2$(Zn/Al = 0.12)および尿素(尿素/Al = 2.0)を加えた。その後約 100℃で 3 ~ 48 時間還流した。還流後の生成物を蒸留水で洗浄し、60℃で 48 時間乾燥させ、Zn 板試料とフラスコ内沈殿物試料を得た。これらを XRD および SEM で分析し、LDH 膜の析出挙動を調査した。

Zn 板試料の XRD を測定したところ、いずれの濃度の PHA 水溶液を用いた場合も、還流時間を 6 時間以上とした場合に Zn 板上に LDH が生成することがわかった。また 0.05 M の PHA 水溶液を用いた方が、Zn 板上での LDH の成長が速いことが示唆された。フラスコ内沈殿物中には、0.05 M の PHA 水溶液を用いた場合では 12 時間以上、0.15 M の PHA 水溶液を用いた場合では 18 時間以上の反応で LDH が生成した。すなわち、反応時間の初期には LDH が Zn 板上に選択的に析出し、その後、基板表面以外でも LDH が析出するようになると判断される。Zn 板試料を SEM 観察したところ、0.05 M の PHA 水溶液を用いた場合には 24 時間以上の反応で Zn 板が完全に被覆されたが、0.15 M の PHA 水溶液を用いた場合には完全な被覆に 48 時間を要した。また 0.05 M の PHA 水溶液を用いた場合には、0.15 M の PHA 水溶液を用いた場合よりもアスペクト比の高い LDH 粒子が観察され、反応条件の制御によって LDH 粒子の析出形態を制御できる可能性が示唆された。

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ナトリウム添加量を変化させたホウ化水素シートの合成と評価

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Synthesis and Evaluation of Sodium-doped Hydrogen Boride Sheets with Controlling Dopant Amount

([1]*University of Tsukuba*) ○Shohei Shimozato[1], Miwa Hikichi[1], Shinichi Ito[1], Natsumi Noguchi[1], Kosuke Takeshita[1], Takahiro Kondo[1]

Hydrogen Boride (HB) sheet is composed of hydrogen and boron. Previous theoretical studies predict that decoration of HB sheets by alkali metal atoms such as Li have the property of controlling the physical adsorption and desorption of molecular hydrogen by simply controlling the hydrogen pressure at room temperature. In this study, we challenge to synthesis and evaluate Na-doped HB sheets by titrating with NaOH.

FTIR for Na-doped HB shows the peak associated with Boron-Hydrogen groups of HB sheets shifted to lower wavelength compared with HB sheets by Na introduction. XPS shows the Na1s peak and the negatively charged B peak which only HB sheets have. In addition, when HB sheets titrated with NaOH to pH11 was heated to 1200℃, needle-like structure were observed in SEM and XPS shows the B peak shifted to lower binding energy than the negatively charged B peak. These results suggest that a new material based on HB, whose properties were changed by the decoration by Na, was synthesized.

Keywords : Hydrogen Boride (HB) sheet; sodium; titration; needle-like structure

ホウ素と水素で構成される 2 次元状のシート物質であるホウ化水素（HB）シートは、既往の理論研究によると Li などのアルカリ金属原子で修飾することにより、室温での水素圧力の制御だけで水素分子の物理吸着と脱離を制御できる特性があることが知られている。本研究では、HB シートは水中では酸性になることを生かし、NaOH で滴定をすることで Na を修飾した HB シートを調製し評価することを目的とした。

NaOH を滴下した HB シートについて、FTIR では HB シート BH 基由来のピークの低波長側へのピークシフトが観測され、XPS では Na1s と HB シート特有の負に帯電した B の両方が観測された。これは HB シートの BH 基の H が Na に置換されたこと、及び Na 導入により BH 基の BH 結合が弱くなったことを示唆している。また pH11 まで滴定を行った試料はより酸性側の試料と比べて FTIR、EEM-ABS、水素放出特性などが大きく異なっていた。さらにこの pH11 の試料を 1200℃まで加熱すると針状試料が観測され、XPS では負に帯電した B よりもさらに低エネルギーへシフトしたピークが観測された。以上の結果により Na を導入することで性質が変化した HB シートを基軸とした新物質が合成されたことが示唆された。

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ランタノイド硝酸塩水和物の ^{1}H 固体 NMR スペクトル

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^{1}H solid state NMR spectra of lanthanoid nitrate hydrate
([1]NMIJ, AIST) Mineyuki Hattori[1], Emiko Oonuma[1]

Solid-state NMR spectra of lanthanide nitrate hydrates of Sc, Y, and La~Lu were acquired. For Sc, Y, La, and Lu without magnetism, widening due to symmetrical 1H dipole interaction with no shift during MAS rotation at 600 MHz and 0~12 kHz was observed to be sharpened by increasing the width and speeding of rotation. In the nitrates of intermediate magnetic lanthanides, shifted asymmetric broad spectra and sharpening patterns were observed. The pattern varied depending on the anisotropy and magnitude of the magnetism on the lanthanide ions.
Keywords : nuclear magnetic resonance, lanthanoid, hydrate

概要（Summary）：Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu の硝酸塩・水和物の固体 NMR スペクトルを取得した。
実験（Experimental）：NMR 測定は、Bruker Avance III HD 600WB を用いて行った。^{1}H 測定周波数は 600.395 MHz である。外径 4 mm のジルコニアローターを用い、マジック角回転（MAS）速度を 0~12 kHz とした。パルス系列はシングルパルス（SP）法および DEPTH 法を用いた。
結果と考察（Results and Discussion）：磁性のない Sc, Y, La, Lu については、600MHz、0～12kHz の MAS 回転中の対称な ^{1}H の双極子相互作用による広幅と回転の高速化により先鋭化した。磁性のある Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb の硝酸塩・水和物では、シフトのある非対称な広幅と先鋭化パターンが観測された。図 1.に ^{1}H MAS NMR スペクトルを示す。ランタノイドイオン上の磁性の異方性や大きさに依存して変化した。

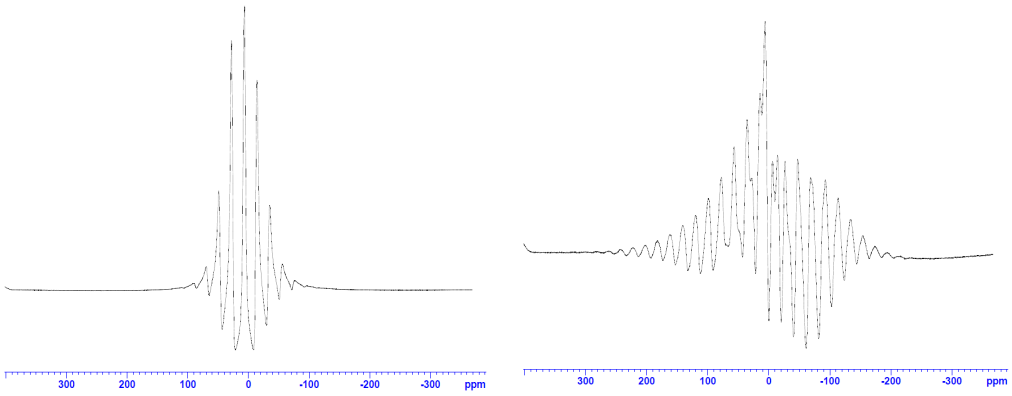

図 1. 左)$ScNO_3$・nH_2O の ^{1}H NMR (12kHz)、右)$CeNO_3$・nH_2O の ^{1}H NMR (12kHz)

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水溶性フッ素化クロリン鉄（III）錯体の触媒活性

（岡山理科大）○中島 しの・赤司 治夫
Catalytic activity of water-soluble fluorinated chlorin iron (III) complexes (*Institute of Frontier Science and Technology, Okayama University of Science*)
○ Shino Nakashima, Haru Akashi

We have reported that Zn(**TFPC**) (H_2**TFPC** = 5,10,15,20-tetrakis(pentafluorophenyl)-2,3-(methano(N-methyl)iminoethano) chlorin) shows an excellent catalytic activity for highly selective oxidation of benzylamines. [1)]

In this study, we prepared iron complexes with sugar-conjugated fluorochlorins (Figure 1, **FeCl(TFPC)-SGlc**, **FeCl(TFPC)-SMan**, **FeCl(TFPC)-SMal**). Using these complexes as catalysts, we conducted oxygenation reactions of olefins under an oxygen atmosphere and in the presence of sodium borohydride. Particularly, in the oxygenation reaction of cycloolefins, the catalytic reaction proceeds with high efficiency compared to **FeCl(TFPC)** without sugar conjugation (Scheme 1, Table 1).

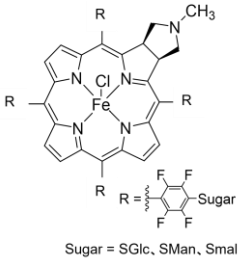

Figure 1 **FeCl(TFPC) -Sugar.**

Scheme 1

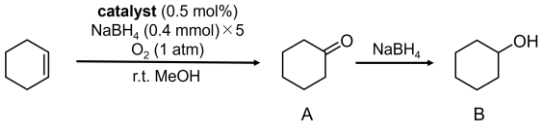

Table 1 Oxygenation reaction of cyclohexene

catalyst	substrate (%)	A (%)	B (%)	total	TON
FeCl(TFPC)	28	3	69	100	144
FeCl(TFPC)-SMal	0	3	97	100	200

Keywords : Iron complex; Metal complex catalyst; Oxygenation

我々は、Zn(**TFPC**) (H_2**TFPC** = 5,10,15,20-tetrakis(pentafluorophenyl)-2,3-(methano(N-methyl)iminoethano) chlorin)が、ベンジルアミンの酸化反応の優れた触媒になることを報告している。[1)]

本研究では、H_2**TFPC** にグルコース、マンノース、およびマルトースを連結した配位子を合成し、糖連結フッ素化クロリンを配位子とする鉄錯体（Figure 1, **FeCl(TFPC)-SGlc**、**FeCl(TFPC)-SMan**、**FeCl(TFPC)-SMal**）を合成した。これらの錯体を触媒として、酸素雰囲気下、水素化ホウ素ナトリウム共存下で、オレフィンの酸素化反応を行ったところ、特に、シクロオレフィン類の酸素化反応において、糖を連結していない**FeCl(TFPC)**と比較して、高効率で触媒反応が進行することを明らかにしたので報告する(Scheme 1, Table 1)。

(1) K. Marui, K. Moriwaki, H. Akashi, A. Nomoto, M. Ueshima, S. Yano and A. Ogawa, *Synthesis*, **2016**, 48(1), 31 - 42.

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Academic Program [Poster] | 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 4(理工スポーツホール [1階] アリーナ)

[P4-2vn] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Japanese

[P4-2vn-01]

Development of the electrochemical methylation reaction of organic molecules.

○Shoya Banzawa[1], Yuma Morii[1], Yutaka Saga[1], Tetuya Kambe[1], Mio Kondo[1,2,3], Shigeyuki Masaoka[1] (1. Osaka University, 2. Tokyo Tech., 3. JST PRESTO)

Japanese

[P4-2vn-02]

Study on energy conversion via quantum tunneling of proton-coupled electron transfer

○Tatsushi Nakayama[1], Bunji Uno[2] (1. Gifu Pharmaceutical University, 2. Gifu University of Medical Science)

Japanese

[P4-2vn-03]

π-Facial Selectivity and Reaction Mechanism of the Hydroboration of Allylic Substituted Alkenes

○Shotaro Ogawa[1], Kaname Takaoka[1], Daisuke Kaneno[1] (1. Kochi Univ.)

Japanese

[P4-2vn-04]

Regioselectivity and Reaction Mechanism on Tricyanovinylation Reaction of *N*-Substituted Pyrroles

○Ayako Hidaka[1], Yoshiaki Sasaki[1], Sora Takahashi[1], Saori Arisawa[1], Ryota Tani[1], Daisuke Kaneno[1] (1. Kochi Univ.)

Japanese

[P4-2vn-05]

Development of dicyanomethylation of styrene derivatives over Platium-loaded TiO_2

○Ryo Takeda[1] (1. National Institute of Technology, Miyakonojo College)

Japanese

[P4-2vn-06]

Development of molecules exhibiting circularly polarized luminescence based on cyclodextrins as a chiral source

○Kentaro Takaji[1], Hajime Shigemitsu[1], Toshiyuki Kida[1] (1. Osaka University)

Japanese

[P4-2vn-07]

Suppression of Quinine, an Antimalarial Drug, Photosensitized Singlet Oxygen Generation by Catechol Related Molecules

○Yuto Yoshimoto[1], Mikio Yagi[2], Azusa kikuchi[2] (1. Yokohama national university engineering, 2. Yokohama national university)

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Japanese

[P4-2vn-08]

New Phosphate Protecting Group Deprotected by PET Using Visible LED

○Aoi Murakami[1], Mugen Yamawaki[1] (1. National Institute of Technology, Fukui College)

Japanese

[P4-2vn-09]

Synthesis of diarylethene-subporphyrazine hybrids and their photochemical properties

○Nanari Tamiya[1], Taichi Muto[2], Mihoko Yamada[2], Tsuyoshi Kawai[2], Akuto Takagi[1], Tadashi Mizutani[1] (1. Doshisha University, 2. Nara Institute of Science and Technology)

Japanese

[P4-2vn-10]

Investigation of fluorescence properties and the emission mechanism of mesoionic 1,3-diaryltetrazolium compounds

○Yuta MATSUKAWA[1], Hitoshi TAMIAKI[1] (1. Ritsumeikan University)

Japanese

[P4-2vn-11]

Synthesis and Circularly Polarized Emission Properties of Bis-1,8-Naphthalimide Derivatives and Their Analogues

○Mami Naoe[1], Shiori Eguchi[1], Hiroshi Takashima[1], Yoshitane Imai[2], Norimitsu Tohnai[3], Shoko Yamazaki[4], Eiji Nakata[5] (1. Nara Women's University, 2. Kindai University, 3. Osaka University, 4. Nara University of Education, 5. Kyoto University)

Japanese

[P4-2vn-12]

Development of Visible-light-induced π-Extension of Perylene Diimide Derivatives and its Regioselectivity

○Shingo Miyano[1], Kenshin Norizuki[1], Keisuke Fujimoto[1], Tetsuya Sengoku[1], Masaki Takahashi[1] (1. Shizuoka University)

Japanese

[P4-2vn-13]

1,10-Phenanthroline-Based Octahedra Induced by Protonation of a Nitrogen Atom: Structures and Emission Properties

○Hiroshi Takashima[1], Naokazu Yoshikawa[1], Shoko Yamazaki[2], Norimitsu Tohnai[3], Eiji Nakata[4] (1. Nara Women's University, 2. Nara University of Education, 3. Osaka University, 4. Kyoto University)

Japanese

[P4-2vn-14]

Chiroptical properties of difluoroboron complexes with optically-active-7-iminomethylindole ligands

○Ryosuke Horio[1], Masahiro Ikesita[2], Yoshitane Imai[3], Takashi Tsuno[2], Seika Suzuki[3] (1. Graduate School of Industrial Technology, Nihon University, 2. College of Industrial Technology, Nihon University, 3. Graduate School of Science and Engineering, Kindai University)

Japanese

[P4-2vn-15]

Synthesis and Characterization of BODIPY with Phosphorus-based Substituents

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○Daiki Ito[1], Shota Yamagishi[1], Keisuke Fujimoto[1], Masaki Takahashi[1] (1. Shizuoka University)

Japanese

[P4-2vn-16]

A Singlet Oxygen Sensor bearing Triphenylimidazole

○Yuna Fukuoka[1], Takato Kurashina[1], Mikio Yagi[1], Azusa Kikuchi[1] (1. Yokohama National University)

Japanese

[P4-2vn-17]

Development of new photoswitches by modifying thermally stable stiff-stilbene skeleton

○Soseki Kurokawa[1], Keiichi Imato[1], Naoki Kaneda[1], Ichiro Imae[1], Yousuke Ooyama[1] (1. The Univ. of Hiroshima)

Japanese

[P4-2vn-18]

Persistent Room-Temperature Phosphorescence exhibited by organic compounds with triazine skeleton.

○Masaya Sugimoto[1], Daisuke Aoki[1], Tatsuo Taniguchi[1], Takashi Karatsu[1] (1. Chiba University)

Japanese

[P4-2vn-19]

Effect of crystals forming conglomerates on Persistent Room-Temperature Phosphorescence

○Kyoshiro Tanno[1], Daisuke Aoki[1], Tatsuo Taniguchi[1], Masami Sakamoto[1], Takashi Karatsu[1] (1. Chiba University)

Japanese

[P4-2vn-20]

Synthesis of Heterocyclic Compounds by Photocyclization of *N*-Substituted-*o*-alkynylaniline Derivatives

○Kan Wakamatsu[1], Risa Shirahama[1], Teruaki Nakamura[1], Yotaro Omae[1] (1. Okayama University of Science)

Japanese

[P4-2vn-21]

Internal Conversion as a Phonon-Emission/Absorption Process: Role of Vibronic Couplings and Energy Gap

○Tohru Sato[1,2], Wataru Ota[1,2], Motoyuki Uejima[3] (1. Fukui Institute for Fundamental Chemistry, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. MOLFEX, Inc.)

Japanese

[P4-2vn-22]

Oxidation reactions of phenanthrene derivatives using organic acridinium-type photo-redox catalyst

○Shou Yasui[1], Takeshi Kawase[1], Jun-ichi Nishida[1] (1. Grad. School. of Engi., Univ. of Hyogo)

Japanese

[P4-2vn-23]

Transient and Persistent One-electron σ-Bonded Radical Cations Generated by Photoinduced Electron Transfer

○Kanata Wada[1], Ryohei Takayasu[1], Takuya Ogaki[1], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ.)

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Japanese

[P4-2vn-24]

Sodium salt of terphenyl caboxylate as an anode for Na-ion batteries were synthesized and investigated

○YUUKI KAMOCHI[1], Kanata Takahashi[1], Naoaki Yabuuchi[2], Makoto Miyasaka[1] (1. Tokyo Denki University, 2. Yokohama National University)

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有機分子の電気化学的メチル化反応の開発

(阪大院工[1]・東工大院理[2]・JST さきがけ[3])○ばん澤　翔也[1]・森井　佑真[1]・嵯峨　裕[1]・神戸　徹也[1]・近藤　美欧[1,2,3]・正岡　重行[1]
Development of the electrochemical methylation reaction of organic molecules. ([1]*Graduate School of Engineering, Osaka University,* [2]*Tokyo Tech.,* [3]*JST PRESTO*)○Shoya Banzawa,[1] Yuma Morii,[1] Yutaka Saga,[1] Tetuya Kambe,[1] Mio Kondo,[1,2,3] Shigeyuki Masaoka.[1]

The 'magic methyl effect' is a significant technology that can dramatically improve the activity of pharmaceuticals through the introduction of methyl groups into the structure. Among them, methylation of unactivated C(sp^3)-H bonds serves as an attractive strategy because unactivated C(sp^3)-H bonds exist in versatile pharrmaceuticals. However, there have been few examples to achieve methylation of unactivated C(sp^3)-H bonds. In this study, we aimed to develop the electrochemical methodology for the methylation reaction of unactivated C(sp^3)-H bonds under mild conditions by using a versatile and safe methylation reagent. In this presentation, the details of the reaction development will be given.
Keywords : Electrochemical Synthesis ; Methylation; Magic Methyl Effect

「マジックメチル効果」は、医薬分子へのメチル基導入によって、分子の構造柔軟性及び標的タンパク質との相互作用を制御することで、医薬活性を劇的に向上しうる最先端の創薬技術[1)]である。その中でも医薬分子に汎用的に存在し、かつ反応性の低い不活性 C-H 結合を自在にメチル化することは、様々な医薬分子に対する「マジックメチル効果」による活性の向上が見込めることから、魅力的な化学変換である。しかしながら、不活性 C-H 結合へのメチル化反応は困難な化学変換であり、これまでの報告例は数例[2)]に留まっている。加えてそれら先駆的報告例においても、危険な金属試薬や爆発性のある過酸の使用など過酷条件を必要としていた。

本研究では、汎用的かつ安全なメチル化試薬と電気化学的手法を組み合わせた、穏和条件における有機分子中不活性 C-H 結合のメチル化反応の開発を目的とした。反応開発の詳細について当日報告する。



1) J. Huang, Z Chen, J. Wu, *ACS Catal*, **2021**, *11*, 10713−10732.
2) a) K. Feng, R. E. Quevedo, J. T. Kohrt, M. S. Oderinde, M. C. White, *Nature* **2020**, *580*, 621. b) A. Vasilopoulos, S. W. Krska, S. S. Stahl, *Science* **2021**, *372*, 398. c) L. F. T. Novaes, J. S. K. Ho, K. Mao, K. Liu, M. Tanwar, M. Neurock, E. Villemure, J. A. Terrett, S. Lin, *J. Am. Chem. Soc.* **2022**, *144*, 1187. d) E. Mao, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2023**, *145*, 2787.

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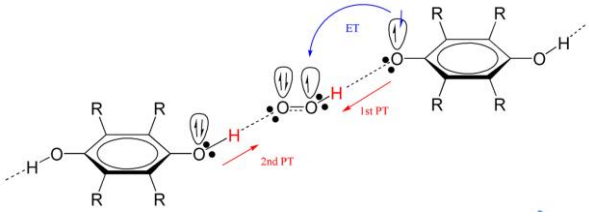
プロトン電子共役移動反応の量子トンネルを使ったエネルギー変換に関する研究

（岐阜薬大[1]、岐阜医療科学大薬[2]）○中山 辰史[1]・宇野 文二[2]
Study on energy conversion via quantum tunneling of proton-coupled electron transfer
([1]*Department of Pharmacy, Gifu Pharmaceutical University*, [2]*Department of Pharmacy, Gifu University of Medical Science*) ○Tatsushi Nakayama,[1] Bunji Uno[2]

Living organisms achieve highly efficient energy conversion through quantum tunneling of proton-coupled electron transfer (PCET) reactions. Among them, the 2PCET (concerted two-proton coupled electron transfer) reaction between superoxide ($O_2^{\bullet-}$) and hydroquinone (H_2Q) derivatives exhibits particularly efficient electron transfer[1,2)] and is expected to be used industrially as a new energy conversion technology. In this study, we aimed to elucidate the factors that further improve the efficiency of the 2PCET reaction between H_2Q derivatives and $O_2^{\bullet-}$ using electrochemical and computational methods. We analyzed the 2PCET reaction between electrogenerated $O_2^{\bullet-}$ and methyl and chloro substituted H_2Q derivatives in DMF solvent, and observed that the 2PCET reaction was promoted by both of the substituents. The electronic inductive effect (*I* effect) of electron-donating/withdrawing substituents suppresses/promotes proton transfer and promotes/suppresses electron transfer (+*I*/−*I*), resulting in a net leveling of *I* effect and enhanced resonance effect for the 2PCET.
Keywords : proton-coupled electron transfer, superoxide radical anion, electrochemistry, computational chemistry, hydroquinone derivatives

生物は、プロトン電子共役移動（PCET）反応の量子トンネルを介した高効率なエネルギー転換を実現している。その中で、スーパーオキシド（$O_2^{\bullet-}$）とハイドロキノン（H_2Q）の間の 2PCET（2 プロトンと 1 電子の協奏移動）反応[1)]は、特に効率的な電子移動を具現化し、新規のエネルギー転換技術として産業活用が期待される。当研究は、電気化学・計算化学手法を用い、H_2Q－$O_2^{\bullet-}$間の 2PCET 反応を更に効率化する要素を解明する。DMF 溶媒中で酸素の一電子還元により電解生成させた $O_2^{\bullet-}$とメチル基・クロル基を置換した H_2Q 類の 2PCET 反応を解析し、置換基効果により効率化する様子を観測した。電子供与性/吸引性の置換基の電子誘起効果（*I* 効果）は、プロトン移動を抑制/促進し電子移動を促進/抑制するが、PCET 反応では *I* 効果が水平化により相殺され、共鳴効果（*R* 効果）が作用していることが明らかとなった。



1) Reactivities of 1,2-, 1,3-, and 1,4- Dihydroxynaphthalenes toward Electrogenerated Superoxide in *N*,*N*-Dimethylformamide through Proton-coupled Electron Transfer. T. Nakayama, B. Uno, *Electrochim.Acta.* **2022**, *436*, 141467.

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アリル位置換アルケンのヒドロホウ素化反応におけるπ面選択性と反応機構

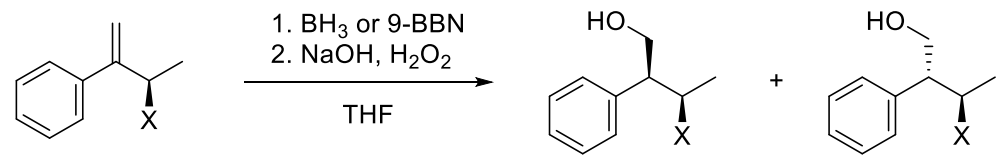
（高知大院総合）○小川 渉太郎・高岡 要・金野 大助
π-Facial Selectivity and Reaction Mechanism of the Hydroboration of Allylic Substituted Alkenes (*Graduate School of Integrated Arts and Sciences, Kochi University*) ○Shotaro Ogawa, Kaname Takaoka, Daisuke Kaneno

Hydroboration of terminal olefin which afford the primary alcohol with anti-Markovnikov adduct selectively is useful and important process in organic synthesis. π-Facial selectivities and reactivities of hydroboration of 3-substituted 2-phenyl-1-butenes were examined with BH_3 and 9-BBN in THF. It was revealed that selective trends were reversed in hydroboration by BH_3 or 9-BBN. MO calculation analysis of the mechanism of this reaction suggested that the reverses of π-facial selectivities result from intra- and intermolecular steric repulsion of the reacting species. Further structural analysis by MO calculation suggested that for substrates with oxygen substituents, the formation of intramolecular hydrogen bonds in the transition state structure would strongly affect the selectivity.
Keywords : Hydroboration; π-Facial Selectivity; MO Calculation

立体選択性の制御及び予測は有機合成上非常に有用であり、様々な反応における選択性発現機構の理論的解明が活発に行われている。本研究では、アリル位に置換基を有するアルケンのヒドロホウ素化反応における、π面選択性発現機構の解明を目的として、アリル位に置換基を有する鎖状アルケンをモデル分子として実験及び分子軌道計算を用いて解析を行った。

まず、モデル基質となる2-フェニル-1-ブテン類を種々合成し、BH_3及び9-BBNによるヒドロホウ素化反応を行い、置換基及びヒドロホウ素試薬の違いによるπ面選択性の変化を調査した。その結果、BH_3を用いた場合と9-BBNを用いた場合で選択性の逆転が見られた。更に、アリル位に酸素置換基を持つ基質と持たない基質においても選択性の逆転が見られた。

また、この反応について分子軌道計算を行い、詳細な反応機構の解析を試みたところ、π面選択性の変化は、ヒドロホウ素試薬の立体構造の違いや、アリル位置換基が酸素置換基を有する場合に形成される分子内水素結合に起因することが分かった。



X = OMe, OPh, OTBS, OH,
Et, ^{t}Bu, Cl, SMe

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N-置換ピロールのトリシアノビニル化反応における配向性と反応機構

（高知大院総合[1]・高知大理[2]）○飛鷹 絢子[1]・佐々木 義章[1]・高橋 大空[2]・有澤 佐織[2]・谷 涼太[2]・金野 大助[1]

Regioselectivity and Reaction Mechanism on Tricyanovinylation Reaction of *N*-Substituted Pyrroles ([1]*Graduate School of Integrated Arts and Sciences, Kochi University*, [2]*Faculty of Science, Kochi University*) ○ Ayako Hidaka,[1] Yoshiaki Sasaki,[1] Sora Takahashi,[2] Saori Arisawa,[2] Ryota Tani,[2] Daisuke Kaneno[1]

The reactivity and regioselectivity of the substitution reaction between pyrroles and tetracyanoethylene are affected by the substitution of nitrogen atoms in the pyrrole ring. Reaction mechanism analysis based on molecular orbital calculations suggested that the reaction actually proceeds via a stable intermediate, which was observed experimentally.
Keywords : Pyrrole Derivatives; Regioselectivity; Reaction Mechanism; Solvent Effect; Molecular Orbital Calculation

芳香族ヘテロ環化合物であるピロールは，テトラシアノエチレン(TCNE)によって容易に求電子置換反応を起こしトリシアノビニル体を生成することが知られているが[1], 生成物であるトリシアノビニル体は 2 位置換体と 3 位置換体の混合物であり，その生成比は窒素上の置換基や反応に用いた溶媒種によって大きく変化する。本研究では，様々な *N*-置換ピロールのトリシアノビニル化における反応速度の変化や配向性を実験により検証し，量子化学計算を用いて反応機構を明らかにすることを目的とした。

溶媒にアセトンを用いて実験を行った結果，*N* 上の置換基によって反応速度は大きく異なり，無置換やアルキル基の場合では室温で反応が進行した一方で，ベンゼン環を有する置換基が導入された場合では，室温条件下では反応は進行せず，加温が必要であった。配向性については，無置換の場合は 2 位置換体が優先的に得られたのに対し，置換基が導入された場合では 3 位置換体が優位に生成された。

N-置換ピロールのトリシアノビニル化反応（アセトン溶液中）

R	time (h)	temp.	Product ratio(%)[a]	
			2 位置換体	3 位置換体
H	1	r.t.	63	37
CH_3	1	r.t.	21	79
i-Pr	1	r.t.	-	100
Phenyl	24	reflux	-	100
Benzyl	24	reflux	-	100

[a]Determind by ^{1}H NMR spectroscopy.

[1] V. N. Drichkov, L. N. Sobenina, T. I. Vakul'skaya, I. A. Ushakov, A. I. Mikhaleva, B. A. Trofimov, *Synthesis*, **2008**, *16* , 2631.

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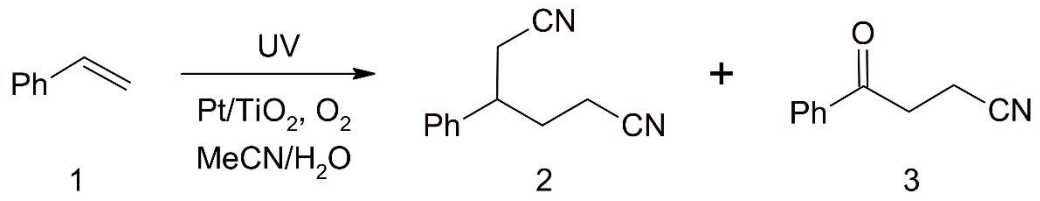
Pt/TiO_2 によるスチレン誘導体のジシアノメチル化反応の開発

（都城高専）○武田凌・畠山楓花・岡部勇二・山下敏明
Development of dicyanomethylation of styrene derivatives over platium-loaded TiO_2 (*National Institute of Technology(KOSEN), Miyakonojo College*) ○Ryo Takeda, Huka Hatakeyama, Yuji Okabe, Toshiaki Yamashita

Cyano-containing compounds are used as precursors in pharmaceuticals and polymer synthesis, since cyano groups can be easily converted to various functional groups. Yoshida et al. found that photocyanomethylation of benzene and cyclohexane using Pd/TiO_2.[1] On the other hand, we found that photocyanomethylation of styrene (**1**) with MeCN in the presence of Pt/TiO_2 results in the formation of dinitrile (**2**) and γ-ketonitrile (**3**), resulting in the 1,2-functionalization reaction of two cyanomethyl or carbonyl groups into **1** (Scheme. 1). The ratios of **2** and **3** formation depended on the catalyst used and the dissolved oxygen. In addition, the reaction was adapted to various styrene derivatives. Density functional theory (DFT) calculations were also performed to clarify the reaction mechanism.
Keywords : Dicyanomethylation; Styrene; Acetonitrile; Pt/TiO_2

シアノ基は様々な官能基に容易に変換できるため、シアノ基含有化合物は医薬品や高分子合成における前駆体として利用されている。吉田らは、Pd/TiO_2 を用いて、ベンゼンやシクロヘキサンの光シアノメチル化反応を見出している[1]。一方、当研究室ではスチレン(**1**)の光シアノメチル化反応を行うと、ジニトリル(**2**)および γ-ケトニトリル(**3**)を合成することができ、ワンポットでシアノメチル基やカルボニル基の 2 つを **1** に導入する 1,2-官能基化反応を見出した（Scheme. 1）。**2** と **3** の生成比は、用いる触媒および溶存酸素に依存することがわかった。また、本反応が種々のスチレン誘導体にも適応できることを確認し、反応機構を明らかにするために密度汎関数理論（DFT）計算を実行した。



Scheme. 1　Dicyanomethylation of styrene (**1**)

1) E. Wada, T. Takeuchi, Y. Fujimura, A. Tyagi, T. Kato, H. Yoshida, *Catal. Sci. Technol.,* **2017**, 7, 2457.

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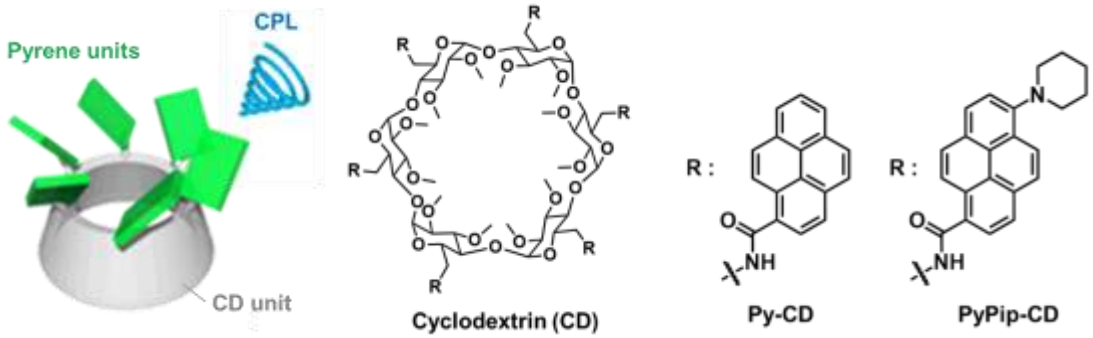
シクロデキストリンをキラル源とした円偏光発光分子の創出

(阪大院工)　○髙司 健太郎・重光 孟・木田 敏之
Development of molecules exhibiting circularly polarized luminescence based on cyclodextrins as a chiral source (*Graduate School of Engineering, Osaka University*)
○Kentaro Takaji, Hajime Shigemitsu, Toshiyuki Kida

Circularly polarized luminescence (CPL) holds potential for diverse applications in 3D displays and biosensing. Consequently, CPL-active organic molecules with superior brightness and anisotropy have been intensely required. Our group has successfully developed a cyclodextrin (**CD**) derivative featuring multiple pyrenyl groups, exhibiting a robust CPL property (g_{lum}: 1.2×10^{-2}, $\Phi = 0.39$). However, further enhancement in CPL properties is crucial for the practical applications. In this study, we synthesized a novel **CD** incorporating a push-pull type pyrene with high quantum yield. The CPL properties of **CD**s bearing pyrenyl units will be discussed.
Keywords: Circularly polarized luminescence; Chirality; Chiroptical properties; Cyclodextrin; Polycyclic aromatic compound

円偏光発光 (CPL)は 3D ディスプレイやバイオセンシングなどの様々な分野への応用が期待されており、高輝度かつ高異方性の CPL を示す材料が求められている。これまでに、ビナフチルやペリレン骨格などを有する様々なキラル分子の CPL 特性についての研究が行われてきた。しかしながら、CPL 分子を実際に応用するためにはさらなる CPL 特性の向上が必要である。我々はシクロデキストリン(**CD**)に複数のピレンを修飾した分子を合成し、優れた CPL 特性を示すこと (g_{lum}: 1.2×10^{-2}, $\Phi = 0.39$) を明らかにしてきた [1)]。本研究では、更なる CPL 特性の向上を目指し、高い量子収率が期待される電子求引性のアミド基と電子供与性のピペリジル基を有する push-pull 型ピレン [2)]を修飾した **PyPip-CD** を合成し、CPL 特性を評価した。本発表では、無置換ピレンを修飾した **Py-CD** と円偏光発光特性を比較し、置換基が与える影響を議論する。



1) H. Shigemitsu, K. Kawakami, Y. Nagata, R. Kajiwara, S. Yamada, T. Mori, T. Kida, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202114700.
2) Y. Niko, Y Cho, S. Kawauchi, G. Konishi, *RSC Adv.*, **2014**, *4*, 36480.

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抗マラリア薬キニーネ光増感一重項酸素のカテコール関連化合物による生成抑制

（[1]横浜国大院理工）○吉本 雄翔[1]・八木 幹雄[1]・菊地 あづさ[1]

Suppression of Quinine, an Antimalarial Drug, Photosensitized Singlet Oxygen Generation by Catechol Related Molecules ([1]*Graduate School of Engineering Science, Yokohama National University*) ○Yuto Yoshimoto,[1] Mikio Yagi,[1] Azusa Kikuchi[1]

The cinchona alkaloid quinine (QN) is well known for its pharmaceutical applications as an antimalarial. QN has affinity for melanin and accumulates in melanin-rich areas of the body, eye, hair and skin. These tissues are frequently exposed to solar radiation and artificial light. Energy transfer from the lowest photoexcited triplet state of QN to ground-state oxygen generates singlet oxygen. Singlet oxygen shows a characteristic phosphorescence band at 1274 nm. In this study, we have studied the suppression of QN-sensitized singlet oxygen generation by catechol related molecules through the measurements of time-resolved near IR phosphorescence.

Keywords: Quinine; Catechol; Singlet oxygen

抗マラリア薬のキニーネ(QN)はメラニンとの親和性が高く，皮膚などにおいて光に曝露されやすい[1)]。QN は励起三重項エネルギーを基底状態の酸素分子に移動させ一重項酸素を生成する光増感分子である[2,3)]。一重項酸素は 1274 nm に特異的な微弱りん光を発する。本研究では，パルスレーザー励起による時間分解近赤外発光測定を行い，カテコール関連化合物を用いて QN 光増感一重項酸素生成を抑制する方法について検討した。一重項酸素の生成抑制機構を明らかにするために，過渡吸収測定を行った。QN は pK_a 値に従って中性(QN)，一プロトン付加体(QNH^+)および二プロトン付加体(QNH_2^{2+})となるため，溶液の pH を変化させて測定を行った。

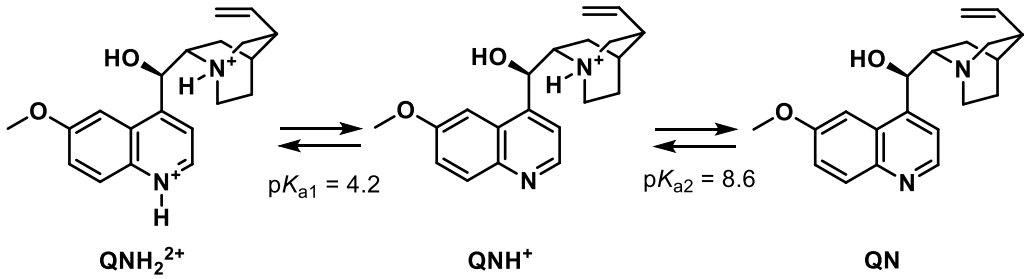

Figure 1. Molecular structures of QN, QNH^+, and QNH_2^{2+}.

1) S. Kristensen et al., *J. Photochem. Photobiol. B* **1994**, *26*, 87.
2) A. G. Morten et al., *Photochem. Photobiol*. **1999**, *69*, 282.
3) Y. Suzuki, M. Yagi, A. Kikuchi, *Photochem. Photobiol. Sci*. **2023**, *22*, 2851.

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可視光 LED 使用による PET によって脱保護される新たなリン酸保護基の開発

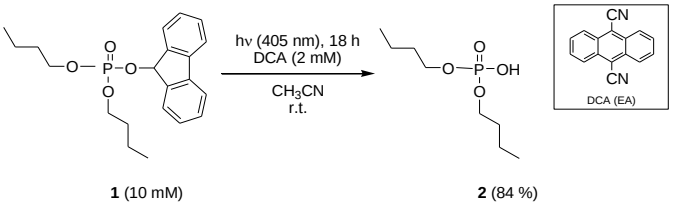
（福井工業高等専門学校 [1]）○村上 葵 [1]・山脇 夢彦 [1]
New Phosphate Protecting Group Deprotected by PET Using Visible LED ([1]*National Institute of Technology, Fukui College*) ○Aoi Murakami,[1] Mugen Yamawaki,[1]

Nucleic acid molecules are extremely difficult to synthesize because they decompose easily in the presence of heat or water. New protective groups that can be deprotected under mild conditions are needed. We have reported a desorption reaction based on photoinduced electron transfer (PET) through a two-molecule photoredox system using electron donor (ED) and electron acceptor (EA) molecules using visible light. In this study, we developed new PET-deprotected protecting groups for organophosphorus compounds.

An acetonitrile solution (CH_3CN) containing protecting phosphate **1** (10 mM) and 9.10-dicyanoanthracene (DCA, 2 mM) under an argon atmosphere for 18 h at room temperature was irradiated (18 W Blue LED) to yield deprotected phosphate **2** in a high yield (84%). The byproduct of acetonitrile added via the Ritter reaction to the fluorene eliminated by PET was confirmed by GC-MS measurements. The use of 1,2,4,5-tetracyanobenzene as an electron acceptor resulted in the formation of CT complexes with fluorene to improve photodeprotection.
Keywords : nucleic acid; organophosphorus compounds; two-molecule visible organic photoredox catalyst; photoinduced electron transfer

核酸分子は熱や水で容易に分解し合成は極めて難しいため、穏和な条件下で脱保護可能な新しい保護基が求められている。当研究室では、可視光を用いて電子供与体と電子受容体の光誘起電子移動反応 (PET) を利用した脱離反応を報告している [1)]。本研究では、PET を用いた有機リン化合物に対する新たな保護基の開発を行った。

リン酸ジブチルにフルオレンを導入したリン酸保護化合物 **1** と 9,10-ジシアノアントラセン (DCA) をアセトニトリル中で室温 Ar 雰囲気下、18 W Blue LED (405 nm) の光を 18 時間照射したところ、フルオレンが脱離し脱保護体 **2** が 84 %の収率で得られた。GC-MS 分析結果から、副生成物としてフルオレンが脱離した後にカチオン経由によって、溶媒であるアセトニトリルが脱離したフルオレンに Ritter 反応で付加した化合物が生成していることがわかった。電子受容体として 1,2,4,5-テトラシアノベンゼンを用いた場合、CT 錯体形成により高効率で反応が進行することを確認した。



1) M. Yamawaki, Y. Okita, T. Yamamoto, T. Morita, Y. Yoshimi, *Tetrahedron* **2017**, *73*, 7239-7244.

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ジアリールエテン-サブポルフィラジンハイブリットの合成と分光特性

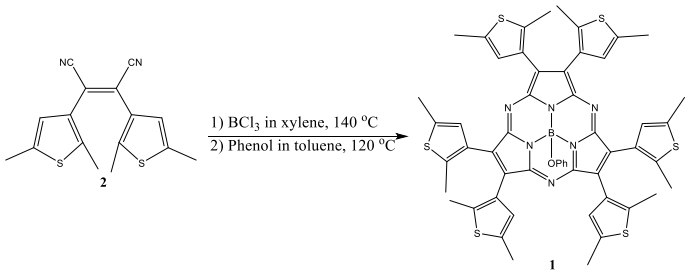
民谷 虹晴[1]、水谷 義[1]、河合 壯[2]、山田 美穂子[2]、高木 阿久斗[1]、武藤 太一[2]

(1. 同志社大学、2. 奈良先端科学技術大学院大学)

Nanari Tamiya[1], Tadashi Mizutani[1], Tsuyoshi Kawai[2], Mihoko Yamada[2], Akuto Takagi[1], Taichi Muto[2]
(1. Doshisha University, 2. Nara Institute of Science and Technology)

Diarylethene derivatives are well-known photochromic compounds, which have attracted much attention because of their potential technological applications in optical recording. The switching properties of these derivatives can be modulated by hybridization with other dyes. Tian et al. reported that the hybrid of diarylethene and porphyrazine showed photochromism. We prepared the hybrid of subporphyrazine and diarylethene. We found that a new band appeared at around 700 nm in the UV-vis spectrum after irradiation with 365 nm light.

ジアリールエテン誘導体はフォトクロミック化合物であり、光記録への技術的応用が期待されている。これを他の色素と複合化することでフォトクロミズムを制御できる可能性があり、ポルフィラジンとジアリールエテンのハイブリットがフォトクロミズムを示すことが報告された。今回サブポルフィラジンとジアリールエテンのハイブリットを合成したところ、365nm の光を照射すると 700nm 付近に新しい吸収バンドが出現した。



1 H. Tian, *et al.*, *Adv. Mater.*, **2002**, *14*, 918.
2 Z. Li, *et al.*, *Coord. Chem. Rev.*, **2023**, *493*, 215325.
3 M. S. Rodríguez-Morgade, *et al.*, *Chem. Eur. J.*, **2005**, *11*, 354.

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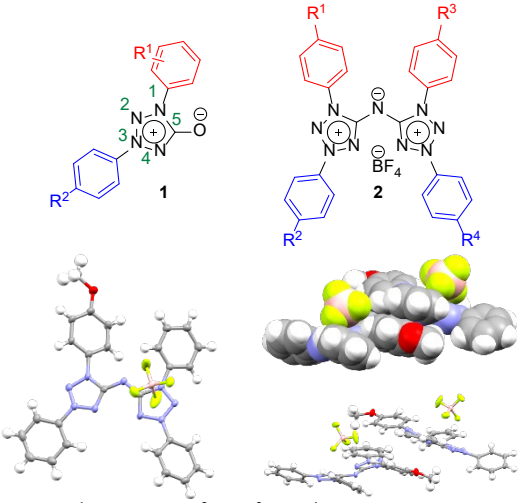
1, 3–ジアリールテトラゾリウム系蛍光性メソイオン化合物の発光特性と機構研究

（立命館大生命科学）〇松川 裕太・民秋 均
Investigation of fluorescence properties and the emission mechanism of mesoionic 1,3-diaryltetrazolium compounds
(*College of Life Sciences, Ritsumeikan University*) 〇Yuta Matsukawa, Hitoshi Tamiaki

Mesoionic compounds are dipolar five- or six-membered heterocyclic betains where both the negative and positive charge are delocalized and cannot be represented satisfactorily by any one polar structure. We previously synthesized tetrazolium mesoionic olates **1** and bistetrazolioamides **2** bearing methoxy group(s) at the 1- and/or 3-phenyl groups and disclosed their high fluorescence quantum yields up to 81%. Here, their fluorescence spectra were measured and the quantum yields were determined under various acid concentrations. Their molecular structures were analyzed by single crystal X-ray diffraction to reveal the intermolecular interactions based on arrangement of the molecules. Their theoretical calculations were examined to disclose the photophysical processes of these emissive tetrazolium mesoionic compounds.

Keywords : Electronic absorption; Fluorescence; Optical property; Organic fluorescent dye; Betaines

我々はこれまでに、単一の極性構造で表現し得ない複素 5–6 員環ベタイン (= メソイオン)[1] のうち、テトラゾリウム系メソイオンの一種であるオレート **1** およびビステトラゾリオアミド **2** (右図) が、CH_2Cl_2 中において 81%の高い量子収率で強い蛍光性を示すことを明らかにした。[2,3] 今回は、プロトン濃度や溶媒といった外的要因へのスペクトル依存性を調べるために、種々の溶媒中で酸(無)添加条件下での紫外可視吸収と蛍光発光/励起スペクトル測定を行った。また、単結晶 X 線構造解析によって結晶中における分子配列に基づく分子間相互作用を明らかにしたほか、量子化学計算により溶液中のスペクトルにおける吸収極大の帰属を行い、これらテトラゾリウム系蛍光性メソイオン化合物の光物理過程を解明したので報告する。



2a: R^1 = OMe, R^2 = R^3 = R^4 = H
R = 5.46%, *wR* = 14.26%, GOF = 1.07
単斜, $P2_1/n$, *Z* = 4, α = γ = 90º, β = 91.605º,
a = 18.572 (2), b = 7.4503 (7), c = 19.025 (2)

1) IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by McNaught, A. D. and Wilkinson, A. Blackwell Scientific Publications, Oxford, **1997**.
2) Y. Matsukawa, H. Tamiaki, 103rd CSJ Annual Meeting (2023), **2023**, K604-2am, Chiba.
3) Y. Matsukawa, H. Tamiaki, IKCOC-15, **2023**, PB(C)-20, Kyoto.

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ビス-1,8-ナフタルイミド誘導体およびその類縁体の合成と円偏光発光特性

（奈良女大理[1]・近畿大理工[2]・阪大院工[3]・奈良教育大[4]・京大エネ研[5]）○直江麻美[1]・江口詩織[1]・高島弘[1]・今井喜胤[2]・藤内謙光[3]・山崎祥子[4]・中田栄司[5]
Synthesis and Circularly Polarized Emission Properties of Bis-1,8-Naphthalimide Derivatives and Their Analogues ([1]*Nara Women's University,* [2]*Kindai University,* [3]*Osaka University*, [4]*Nara University of Education,*[5]*Kyoto University*) ○ Mami Naoe,[1] Shiori Eguchi,[1] Hiroshi Takashima,[1] Yoshitane Imai,[2] Norimitsu Tohnai,[3] Shoko Yamazaki,[4] Eiji Nakata[5]

When excimer luminescent molecules containing planar polycyclic aromatic hydrocarbon chromophores are in a chiral environment, one can usually expect to observe a strong CPL. We have studied the luminescence properties of optically active bis-1,8-NI derivatives (*D,L*-LybNI, *D,L*-LyMebNI) and their reference compounds (*D,L*-NorNI) in several solvents as shown in Fig. 1 and 2 for comparison. The CPL spectra of *D,L*-LybNI and *D,L*-LyMebNI all showed relatively large $|g_{lum}|$ values in the highly polar solvents of MeCN and MeOH, and the $|g_{lum}|$ values in MeCN for *D,L*-LyMebNI were 1.9 x 10^{-3}(*D*) and 1.6 x 10^{-3}(*L*), respectively. We successfully observed an effective CPL derived from intramolecular excimer formation. With the aim of observing intramolecular excimer formation in various solvents and CPLs exhibiting higher $|g_{lum}|$ values, we have synthesized analogues of optically active bis-1,8-NI derivatives with further extended π-electron planes.
Keyword : Optical Properties; Fluorescence; Naphthalimide; Circularly Polarized Luminescence; Excimer

円偏光発光（CPL）を発する有機発光色素は、その光物理的挙動により大きな注目を集めており活発に研究されている。平面性の多環芳香族炭化水素発色団を含むエキシマー発光分子がキラルな環境にある場合、通常強い CPL の観察が期待できる。これまでに、Fig 1,2 に示したような光学活性ビス-1,8-NI 誘導体(*D,L*-LybNI, *D,L*-LyMebNI)およびその参照化合物(*D,L*-NorNI)の発光特性について、いくつかの溶媒中での比較検討を行った。CPL スペクトルは、*D,L*-LybNI, *D,L*-LyMebNI でいずれも MeCN と MeOH の高極性溶媒中で比較的大きい$|g_{lum}|$値を示し、*D,L*-LyMebNI における MeCN 中での$|g_{lum}|$値はそれぞれ 1.9 x 10^{-3}(*D*), 1.6 x 10^{-3}(*L*)であった。分子内エキシマー形成由来の効果的な CPL の観測に成功した。また、様々な溶媒での分子内エキシマー形成と、より高い$|g_{lum}|$値を示す CPL を観測することを目的として、光学活性ビス-1,8-NI 誘導体のπ電子平面をさらに拡張させた類縁体の合成を行った。

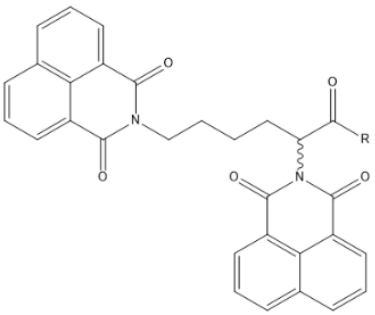

Fig.1. Structures of *D,L*-LybNI (R=OH) and *D,L*-LyMebNI (R=OCH_3).

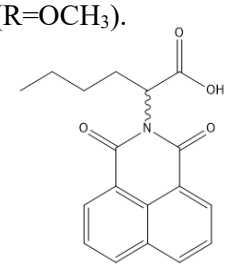

Fig.2. Structure of *D,L*-NorNI.

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ペリレンジイミド誘導体の可視光駆動型π拡張反応の開発とその位置選択性

（静岡大工[1]）○宮野 伸吾[1]・法月 健真[1]・藤本 圭佑[1]・仙石 哲也[1]・高橋 雅樹[1]
Development of Visible-light-induced π-Extension of Perylene Diimide Derivatives and its Regioselectivity ([1] *Faculty of Engineering, Shizuoka University*) ○Shingo Miyano,[1] Kenshin Norizuki,[1] Keisuke Fujimoto,[1] Tetsuya Sengoku,[1] Masaki Takahashi[1]

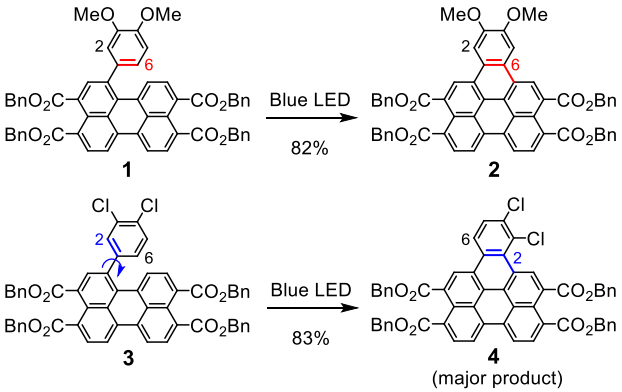
Perylene diimides are attractive functional molecules as luminescent materials and organic semiconductors. Visible-light-induced π-extension is one of the useful chemical modifications, which proceeds via photochemical electrocyclic reaction followed by oxidative dehydrogenation.

In this work, we revealed that the π-extension reaction of perylene tetraester (PTE) **1**, which contains a 3,4-dimethoxyphenyl group, proceeds regioselectively at the 6-position of the aryl group to afford symmetric isomer **2** by only irradiating a blue LED (8.6 W, 465 nm). On the other hand, the cyclization reaction of 3,4-dichlorophenyl-substituted PTE **3** proceeded selectively at the 2-position, resulting in the preferential formation of the asymmetric isomer **4**. Experimental and theoretical investigations for various PTEs with different aryl groups revealed that the π-extension reactions proceed regioselectively at positions with higher double bond character.

Keywords : Perylene Diimide, Photocyclization, Regioselectivity, Luminescent Material, Organic Semiconductor

ペリレンジイミド誘導体は発光材料・半導体材料として有用であり、化学修飾による様々な機能化が可能である。有用な修飾反応の一つに可視光照射によるπ拡張反応が挙げられ、電子環状反応-脱水素化を経由したπ拡張反応が円滑に進行することが知られている。

本研究では、3,4-ジメトキシフェニル基を有するペリレンテトラエステル (PTE) **1** のπ拡張反応が青色 LED (8.6 W, 465 nm) の照射のみで円滑に進行し、アリール基の 6 位で環化した対称異性体 **2** が選択的に得られることを見出した。一方、3,4-ジクロロフェニル基を有する **3** の環化反応は 2 位選択的に進行し、非対称異性体 **4** が優先的に得られた。様々なアリール基を持つ PTE の光環化反応について実験的および理論的考察を行ったところ、置換基によってアリール基上の結合交替に差が生じ、より二重結合性の高い位置で選択的な環化反応が進行することを明らかにすることができた。



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1, 10–フェナントロリン誘導体のプロトン化により誘起された八面体構造と発光特性

（奈良女大理[1]・奈良教育大[2]・阪大院工[3]・京大エネ研[4]）○高島　弘[1]・吉川　直和[1]・山崎　祥子[2]・藤内　謙光[3]・中田　栄司[4]

1,10-Phenanthroline-Based Octahedra Induced by Protonation of a Nitrogen Atom: Structures and Emission Properties

(*[1]Faculty of Science, Nara Women's University*, *[2]Nara University of Education*, *[3]Graduate School of Engineering, Osaka University*, *[4]Institute of Advanced Energy, Kyoto University*) ○ Hiroshi Takashima,[1] Naokazu Yoshikawa,[1] Shoko Yamazaki,[2] Norimitsu Tohnai,[3] Eiji Nakata[4]

Although a few metal-free octahedral compounds based on nitrogen-containing ligands are known, the realization of mixed ligand compounds remains difficult. To obtain an improved understanding of this class of compounds, two new octahedral compounds, [(tmphenH)(phen)]PF_6, and [(tmphenH)(tmphen)]PF_6 (where tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline and phen = 1,10-phenanthroline), were synthesized. The relationship between the emission properties, as evaluated using experimental measurements and theoretical calculations, and structures of the protonated compounds was studied. In addition, differences between the atomic charge distributions and geometries in the ground and singlet excited states were investigated using density functional theory calculations. Both complexes formed hydrogen-bonded octahedrons in acetonitrile solution, even in the excited state. Furthermore, in [(tmphenH)(tmphen)]PF_6, the addition of a methyl substituent suppressed thermal vibrations, resulting in a higher emission intensity.

Keywords : Octahedral Compound; Phenanthroline; Planarity; Hydrogen Bond; Emission

含窒素配位子に基づくメタルフリーな八面体化合物はいくつか知られているが、混合配位子化合物の実現は依然として困難である。このクラスの化合物の理解を深めるために、2 つの新しい八面体化合物、[(tmphenH)(phen)]PF_6 と[(tmphenH)(tmphen)]PF_6（tmphen = 3,4,7,8-テトラメチル-1,10-フェナントロリン、phen = 1,10-フェナントロリン）を合成した[1)]。本研究では、実験的測定と理論計算により、発光特性とプロトン化化合物の構造との関係を調べた。さらに、基底状態と一重項励起状態における原子電荷分布と形状の違いを密度汎関数理論(DFT)計算により調べた。

[(tmphenH)(phen)]PF_6 と[(tmphenH)(tmphen)]PF_6 はともにアセトニトリル溶液中では励起状態でも水素結合した八面体を形成していた。さらに、[(tmphenH)(tmphen)]PF_6 においては、メチル置換基を追加することによって、熱振動が抑制され発光強度が高くなることが明らかになった。

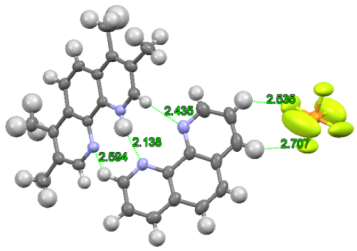

Figure. Crystal structure of [(tmphenH)(phen)]PF_6.

1) N. Yoshikawa, S. Yamazaki, A. Nakaoku, Y. Manabe, N. Tohnai, E. Nakata, H. Takashima, *ChemistrySelect*, **2023**, *8*, e202303561.

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光学活性 7-イミノメチル置換インドールを配位した ジフルオロボロン錯体の光学特性

（日大院生産工[1]・日大生産工[2]・近大院総理工[3]）○堀尾　亮佑[1]・池下 雅広[2]・今井義胤[3]・鈴木聖香[3]・津野 孝[2]

Chiroptical properties of difluoroboron complexes with optically-active-7-iminomethylindole ligands

([1]*Graduate School of Industrial Technology, Nihon University*, [2]*College of Industrial Technology, Nihon University, Graduate school of Science and Engineering, kindai University*)
○Ryosuke Horio,[1] Masahiro Ikeshita,[2] Yoshitane Imai,[3] Seika Suzuki,[3] Takashi Tsuno[2]

The *N^N* ligands (**1-3**) are composed of an indole and an imino group bearing chiral-alkyl chain, similar to the 2,2-dipyrromethne (*N^N*) ligand in BODIPY, which is well-known as a good fluorescent dye. The boron complexes (**4-6**) prepared using ligands **1-3** is expected to have high quantum yields and CPL properties.

先に本研究室ではイミノ基にキラリティーを導入した Schiff 塩基(*O^N*)ホウ素錯体の円偏光発光(CPL: Circularly Polarized Luminescence)について検討し、イミノ基上のキラリティーが異方性因子に十分に影響を与える知見を得ている [1)]。本主題中の *N^N* 配位子(**1-3**)は、良好な蛍光色素として知られている BODIPY の 2,2-dipyrromethne (*N^N*)配位子と似たインドール環とイミノ基から構成されており、さらにイミノ基のアルキル部位にキラリティーを導入したものである。配位子 **1-3** を用い調製されるホウ素錯体(**4-6**)は、高い発光収率と CPL 特性が期待される。今回、**4-6** の発光特性について報告する。

合成したホウ素錯体 **4-6** の円二色性 (CD)スペクトルを測定したところ、350 nm から 430 nm の範囲で *R* 体は正、*S* 体は負のコットン効果を示した。また、**4-6** は DCM 中で緑色から青色の発光（Figure 1）を示し、固体状態では DCM 中と比較してブルーシフトした。**4**,**5** の DCM 中における CPL は、*R* 体は正、*S* 体は円偏光発光を示し、異方性因子(g_{lum} 値)は **4** が 1.2×10^{-3} であり、**5** は 2.1×10^{-3} と求められた。

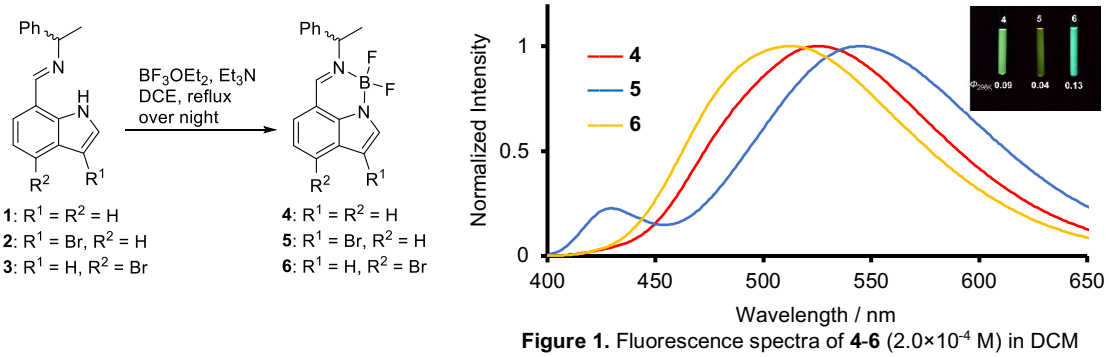

Figure 1. Fluorescence spectra of **4-6** (2.0×10^{-4} M) in DCM

1) M. Ikeshita, T. Suzuki, K. Matsuda, M. Kitahara, Y. Imai, T. Tsuno, *Phys. Chem. Chem. Phys.* **2022**, *24*, 15502. M. Ikeshita, H. He, M. Kitahara, Y. Imai, T. Tsuno, *RSC Adv.* **2022**, *12*, 34790. M. Ikeshita, T. Oka, M. Kitahara, S. Suzuki, Y. Imai, T. Tsuno, *Chem. Lett.* **2023**, *52*, 556. M. Ikeshita, T. Oka, M. Kitahara, Y. Imai, T. Tsuno, *ChemPhotoChem*, **2023**, *7*, e202200318.

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リン官能基が置換した BODIPY の合成と物性評価

（静岡大工 [1]）○伊藤 大貴 [1]・山岸 翔太 [1]・藤本 圭佑 [1]・高橋 雅樹 [1]
Synthesis and Characterization of BODIPY with Phosphorus-based Substituents ([1]*Faculty of Engineering, Shizuoka University*) ○ Daiki Ito,[1] Shota Yamagishi,[1] Keisuke Fujimoto,[1] Masaki Takahashi[1]

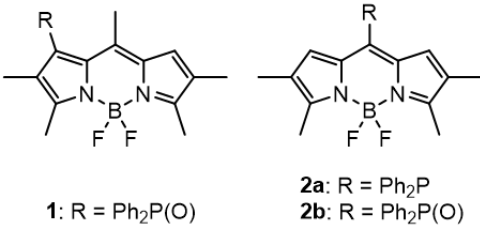
Boron dipyrromethene (BODIPY) is an attractive fluorescent material in the field of imaging applications due to its high stability and fluorescent quantum yield, and its chemical modification allows for various functionalizations. In this study, we developed novel BODIPY derivatives by introducing phosphorus-based substituents which are capable of coordinating to metal atoms and imparting strong electron-accepting properties.

The synthesis of **1**, with a phosphorus-substituent at the 1-position, was achieved through a palladium-catalyzed phosphinylation of the corresponding bromide. Additionally, the synthesis of compounds **2a** and **2b**, with phosphorus-substituent at the 8-position, was achieved through aromatic nucleophilic substitution reactions. Investigation of the optical and redox properties revealed that the phosphino group in **2a** quenched the luminescence, while compounds **1** and **2b** retained highly luminescent property. Furthermore, the substitution effect was more pronounced at the 8-position than at the 1-position, highlighting that **2b** displayed higher electron-accepting properties.

Keywords：Boron-dipyrromethene; phosphino group; phosphinyl group; fluorescent property; electron-accepting property

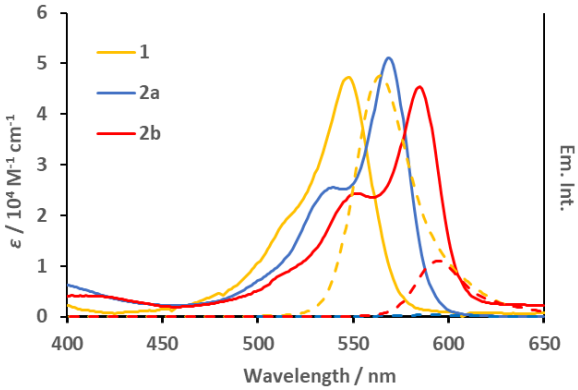
ボロンジピロメテン（BODIPY）は高い安定性と発光量子収率を有することからイメージング応用において有用な発光色素であり、その化学修飾により様々な機能化が可能である。本研究では、金属原子への配位能や強い電子受容性の付与が可能なリン官能基を導入することにより、新規 BODIPY 誘導体の開発を試みた。

リン官能基を１位に導入した BODIPY **1** の合成は対応する臭素体に対するパラジウム触媒を用いたホスフィニル化反応により達成した。また、８位に導入した化合物 **2a**, **2b** の合成は芳香族求核置換反応により達成した。合成した化合物の光学特性および酸化還元電位を調査した結果、ホスフィノ基を有する **2a** はその発光性が消失する一方で、ホスフィニル基を有する **1, 2b** は高い発光性を保持することが分かった。また、置換基効果は 1 位よりも 8 位において大きく、**2b** がより高い電子受容性を示すことが明らかとなった。



1: R = $Ph_2P(O)$

2a: R = Ph_2P
2b: R = $Ph_2P(O)$



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トリフェニルイミダゾール誘導体による一重項酸素センサーの開拓

(1 横浜国大理工，2 横浜国大院理工）○福岡 悠奈 1・倉品 鷹人 2・八木 幹雄 2・菊地 あづさ 2

A Singlet Oxygen Sensor Bearing Triphenylimidazole ([1]*College of Engineering Science, Yokohama National University,* [2]*Graduate School of Engineering Science, Yokohama National University*)○Yuna Fukuoka,[1] Takato Kurashina,[2] Mikio Yagi,[2] Azusa Kikuchi[2]

The accumulation of singlet oxygen ($^1O_2$) and the consequent oxidative stress produced may lead to skin damage and accelerated aging. $^1O_2$ shows a characteristic phosphorescence band at 1274 nm. The imidazole structures exist in many purines such as guanosine, xanthine, theophylline, and the reactions with $^1O_2$ take place by attack on the imidazole portion. The study of the detection of $^1O_2$ to investigate the loss mechanism of biological activity by photosensitized oxidation of imidazole ring is of great interest. In this study, we have synthesized novel $^1O_2$ sensors, triphenylimidazole (TPI) derivatives, and studied the reaction with $^1O_2$ through the measurements of fluorescence and time-resolved near IR phosphorescence.

Keywords: 2,4,5-Triphenylimodazole; Singlet oxygen sensor

グアノシン，キサンチン，テオフィリンのような多くのプリン誘導体の部分構造であるイミダゾールは一重項酸素（$^1O_2$）と反応し，エンドペルオキシド体を経て，ヒドロペルオキシド体を生成することが報告されている[1-3]。イミダゾール部位の光増感酸化による生理活性機能失活機構解明には，$^1O_2$ との反応を感度良く簡便に定量検出する方法が求められる。$^1O_2$ の検出方法の一つに，$^1O_2$ とアントラセンの[4+2]環化付加反応によるエンドペルオキシド体生成を利用した蛍光応答型 $^1O_2$ センサーが報告されてる[4-7]。

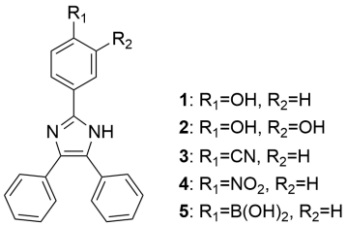

Figure 1. Molecular structures of TPI derivatives.

本研究では，TPI 誘導体（Figure 1）のイミダゾール部位の $^1O_2$ 光酸化反応特性に着目し，蛍光応答型 $^1O_2$ 検出方法について検討した。$^1O_2$ は 1274 nm に特異的な微弱りん光を発するため，TPI 誘導体によるローズベンガル光増感 $^1O_2$ 消光についてパルスレーザー励起による時間分解近赤外発光測定から確認した。

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熱安定なスティッフスチルベン骨格の改変による新しい光応答性分子スイッチの開発

（広島大工[1]・広島大院先進理工[2]）○黒川漱石[1]・今任景一[2]・兼田直輝[2]・今榮一郎[2]・大山陽介[2]

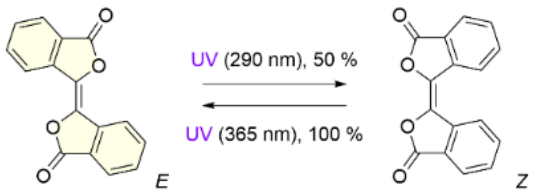
Development of New Photoswitches by Modifying Thermally Stable Stiff-Stilbene Skeleton

([1]*School of Engineering, Hiroshima University*, [2]*Graduate School of Advanced Science and Engineering*, *Hiroshima University*) ○Soseki Kurokawa,[1] Keiichi Imato,[2] Naoki Kaneda,[2] Ichiro Imae,[2] Yousuke Ooyama[2]

Molecular photoswitches have been widely used as molecular machines due to the small structures, simple motions, and the advantages of photostimulation. Particularly, stiff stilbene (SS) attracts considerable attention as a photoswitch offering large structural changes and high thermal stability, and its use started recently.[1)] We found that sterically hindered stiff stilbene (HSS), in which the surround of the central C=C bond in the SS skeleton is modified with four methoxy groups, shows higher photoisomerization yields and larger motions than SS and still has high thermal stability (half-life = ca. 1000 years at room temperature).[2)] However, the photoisomerization yields, thermal stability, and durability are not enough for practical use. In this study, we aim to develop new photoswitches that improve the above properties by modifying the SS skeleton. We found that an SS-based photoswitch, in which the ethylene groups in the two five-membered rings were changed to the ester bonds, was thermally stable and reversibly isomerized by photoirradiation.

Keywords: Molecular Switch; Molecular Machine; Photoisomerization; Thermal Stability

光可逆的に異性化する分子スイッチは、小さな構造やシンプルな動き、光刺激の利点などから分子マシンとして広範な分野で利用されている。その中でもスティッフスチルベン（SS）は、大きな構造変化と高い熱安定性を有する分子スイッチとして注目され、最近になって利用が始まった[1)]。我々はSSの中心C=C結合周辺に4つのメチル基を修飾したヒンダードスティッフスチルベン（HSS）がSSに比べて、より高い光異性化率や大きな構造変化を示し、同時に高い熱安定性（室温半減期 = 約1000年）を持つこと見出した[2)]。しかし、HSSでも光異性化率や熱安定性、耐久性などは実用に十分ではなかった。そこで本研究では、SS 骨格の改変により上記課題を解決した新しい分子スイッチを開発することを目的とした。今回、SS骨格の5員環エチレンをエステル結合に変換した分子が熱安定な分子スイッチとして可逆的に光異性化することを見出した。



1) D. Villarón, S. J. Wezenberg, ***Angew. Chem. Int. Ed.*** **2020**, *59*, 13192.
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トリアジン骨格を有する有機化合物が示す室温長寿命りん光

（千葉大院工）○杉本 真也・青木大輔・谷口 竜王・唐津 孝
Persistent Room-Temperature Phosphorescence of Compounds with triazine skeleton
(*Graduate School of Engineering, Chiba University*) ○Masaya Sugimoto, Daisuke Aoki, Tatsuo Taniguchi, Takashi, Karatsu

Persistent room-temperature phosphorescence (pRTP) is important for imaging applications. Although efficiency and brightness of pRTP is crucial, however, the design of pRTP is difficult because the detailed mechanism of pRTP is still unclear. In this study, we found that a series of compounds with triazine skeleton without metals and heavy atoms showed pRTP and have different luminescence properties such as emission wavelength, quantum yield and lifetime depending on the substituents. The purpose of this study is to elucidate the mechanism of pRTP by prepared crystals using a group of compounds with triazine skeleton. Emission characteristics was investigated and discussed by measurement of emission spectrum, single-crystal XRD, and TD-DFT calculation.
Keywords：triazine; persistent Room-Temperature Phosphorescence (pRTP), single crystal X-ray structure analysis

有機化合物の光照射により生成した一重項励起状態からの発光を蛍光，項間交差を経て，三重項励起状態からの発光をりん光と呼ぶ。りん光の中でも特に，固相，室温大気下で発光寿命が 100 ms を超えるりん光は「室温長寿命りん光 (persistent room-temperature phosphorescence; pRTP) 」と呼ばれ，近年注目されている。金属や重原子を用いない有機りん光材料は，低コストで低毒性などの利点があり，バイオイメージングやデータの暗号化などへの応用が期待されている。しかし，pRTP を示す分子の報告例は多くなく，発現メカニズムも未解明な点が多く残るため，分子設計が困難である。

本研究では，トリアジン骨格を有する化合物群 (Fig.1) において pRTP の発現を確認し，置換基の変化によりそれぞれ異なる発光特性を有することを確認した。これら化合物群において，単結晶 X 線構造解析，TD-DFT 計算を用いて発光特性の差異の要因となる要素を調査することで，pRTP の詳細な発現メカニズムの解明を目指した。

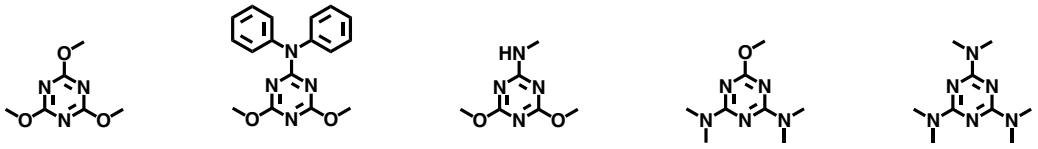

Fig.1 Some of the investigated compounds with triazine skeletons

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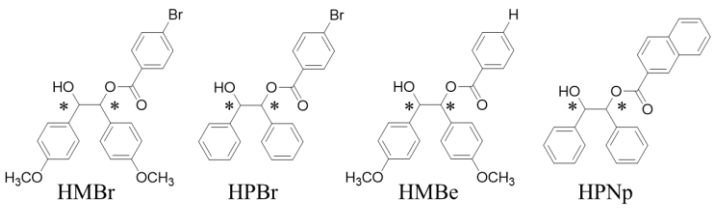
コングロメレートを形成する結晶が室温長寿命りん光に与える影響

（千葉大院工）○丹野 亨志郎・青木 大輔・谷口 竜王・坂本 昌巳・唐津 孝
Effect of crystals forming conglomerates on Persistent Room-Temperature Phosphorescence (*Graduate School of Engineering, Chiba University*) ○Kyoshiro Tanno, Daisuke Aoki, Tatsuo Taniguchi, Masami Sakamoto, Takashi Karatsu

The luminescence characteristics of persistent Room-Temperature Phosphorescence (pRTP) from monoacylated hydrobenzoin derivatives having various substituents were investigated. It has been reported that monoacylated hydrobenzoins have different crystal states depending on the substituent. In this study, it was also confirmed that acylated derivatives of hydrobenzoin have different crystal structures. By investigating the phosphorescence characteristics of these materials, we elucidated the crystal structure that contributes to pRTP characteristics.

Phosphorescence lifetimes (τ_p) of HMBr, HPBr, HMBe, and HPNp (structures showed below the text), all of which are derivatives of monoacylated hydrobenzoin, were measured in the crystalline state, and it was observed that HMBe had significantly smaller phosphorescence lifetimes than others. HPNp crystal is observed to be conglomerate, but the other three crystals were observed to be racemic by single crystal X-ray structure analyses. It was observed that the molecular structure of HMBe, which has a short phosphorescence lifetime, is significantly different from other molecular structures, suggesting that the decrease in the emission lifetime is due to this molecular structure and its effect on intermolecular interaction in the crystal.
Keywords : conglomerate, persistent Room-Temperature Phosphorescence, single crystal X-ray crystallography, monoacylated benzoin

有機発光材料は低コスト，低環境負荷という利点を持ち，多岐にわたり研究されている。その中でも固体状態で 100 ms 以上の寿命を持つりん光を室温長寿命りん光（pRTP）と呼び，応用が期待されている。しかし，一方でりん光を発する有機化合物の分子設計には未解明な部分が多く残されているという課題点がある。本研究では置換基によって異なる結晶状態を有することが報告されている，モノアシル化ヒドロベンゾインについて発光特性調査を行った。いずれもモノアシル化ヒドロベンゾインの誘導体である HMBr，HPBr，HMBe, HPNp（下図参照，*印は不斉炭素原子）のりん光寿命(τ_p)を結晶状態で測定したところ，HMBe のりん光寿命は著しく小さいことが観測された。また，単結晶 X 線構造解析にて HPNp はコングロメレート結晶であり，他の 3 つはラセミ結晶であることが観測された。また，りん光寿命の短い HMBe の分子構造が他の分子構造と大きく異なることが観測され、発光寿命の低下はこの分子構造と，それに基づく分子間相互作用への影響に起因することが示唆された。



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N-置換-*o*-アルキニルアニリン誘導体の光環化を経由する複素環合成

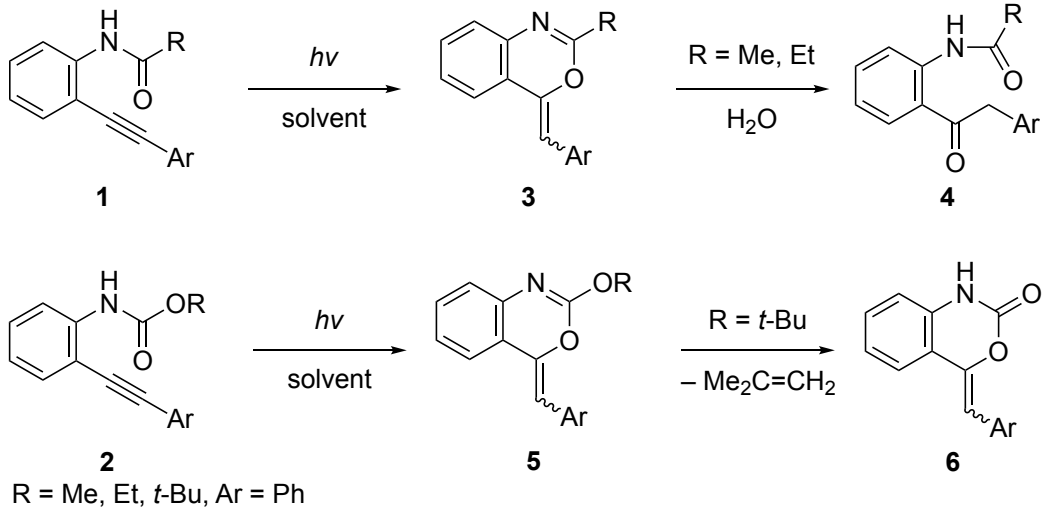
（岡山理大理）○若松 寛・白濱 理沙・中村 輝晃・大前 陽太郎

Synthesis of Heterocyclic Compounds by Photocyclization of *N*-Substituted-*o*-alkynylaniline Derivatives (*Faculty of Science*, *Okayama University of Science*) ○Kan Wakamatsu, Risa Shirahama, Teruaki Nakamura, Yotaro Omae

We reported photoreaction of *o*-alkynylaniline or its *N*-sulfonyl derivatives produced indole derivatives (5-*endo*-*dig*), while for the *N*-acyl derivatives **1** ($\lambda > 280$ nm, 2 h, in toluene) NMR analysis revealed the formation of benzoxazine derivatives **3** (6-*exo*-*dig*), and **3** was successfully isolated (94%) at R = *t*-Bu.[1] In this work, the carbamate ester **2** was irradiated under the same conditions, and the corresponding benzoxazine **5** was obtained with an isolation yield of 61–62% at R = Me, Et. Instead, at R = *t*-Bu, the dealkylated product **6** (benzoxazinone) was obtained with an isolation yield of 63%. The reaction mechanism will be discussed with both experimental product analysis and DFT calculation.

Keywords: Organic Photoreaction, Intramolecular Cyclization, Benzoxazine, Computational Chemistry

o-アルキニルアニリンまたはその *N*-スルホニル誘導体の光反応ではインドール誘導体（5-*endo*-*dig*）を生成するが，*N*-アシル誘導体 **1** ではトルエン中光照射（$\lambda > 280$ nm）2 時間後の NMR 解析でベンゾオキサジン誘導体 **3**（6-*exo*-*dig*）の生成が認められ，R = *t*-Bu では **3** の単離に成功している（収率 94%）.[1] 今回，カルバミン酸エステル **2** を同条件で光反応させたところ，R = Me, Et ではベンゾオキサジン **5** が単離収率 61〜62%，R = *t*-Bu では脱アルキル化したベンゾオキサジノン **6** が単離収率 63%で得られた．本発表では反応機構を生成物解析および DFT 計算結果をもとに考察する．



1) 若松，川原，大前，白濱，中村，山田，第 33 回基礎有機化学討論会（2023），岡山，1P104.

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フォノンの放出・吸収過程としての内部転換:
振電相互作用定数とエネルギーギャップの依存性

（京大福井セ[1]・京大院工[2]・MOLFEX[3]）○佐藤 徹[1,2]・大田 航[1,2]・上島 基之[3]

Internal Conversion as a Phonon-Emission/Absorption Process: Role of Vibronic Couplings and Energy Gap ([1]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*MOLFEX, Inc.*) ○Tohru Sato,[1,2] Wataru Ota,[1,2] Motoyuki Uejima[3]

An analytical expression for the rate constant of internal conversion (IC) was derived based on the crude adiabatic representation. All vibrational modes were considered to be on an equal footing in the rate constant expression. Based on this expression, we investigated the role of vibronic couplings and electronic energy gap in IC processes, using 9-fluorenone as an illustrative example. Vibrational modes with strong off-diagonal vibronic coupling constants (VCCs) give rise to non-radiative transitions. In contrast, vibrational modes with strong diagonal VCCs constitute the final vibronic states that accept the excess electronic energy between the initial and final electronic states. Therefore, vibrational modes are classified into promoting and accepting modes based on their roles. We identified important promoting modes responsible for one-phonon emission and accepting modes that contribute greatly to the final state. A Franck-Condon envelope, which describes the density of final vibronic states, explains the dependence of the rate constant on the electronic energy gap. VCC can be visualized as a spatial distribution of its density form, i.e., vibronic coupling density (VCD). The VCD concept is expected to facilitate the design of functional molecules with IC processes understood in terms of electronic states and vibrational modes.

Keywords : Nonradiative Transition; Internal Conversion; Vibronic Coupling

粗断熱表現を用いたフェルミの黄金律に基づき、分子の全振動モードを考慮した内部転換速度定数の解析的表式を導出した[1,2]。内部転換は振電相互作用を駆動力としたフォノン放出過程とみなせる。得られた解析的表式により、振電相互作用の選択則に基づきながら、振動モードをフォノン放出に関与するモード（促進モード）と電子励起エネルギーを受け取るモード（受容モード）に分類することができる。また、終振電状態の状態密度を表すフランク・コンドン包絡線により、速度定数のエネルギーギャップ依存性を説明することができる。粗断熱表現を用いることで、振電相互作用の起源を振電相互作用密度[3]により明らかにし、内部転換を制御した分子設計に応用することが可能である。計算によって得られた９―フルオレノンの内部転換速度定数は実験値を良く再現した。

1) W. Ota, M. Uejima, T. Sato, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 582.
2) W. Ota, M. Uejima, N. Haruta, T. Sato, *Bull. Chem. Soc. Jpn.* in press.
3) T. Kato, N. Haruta, and T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation* (Springer, 2021).

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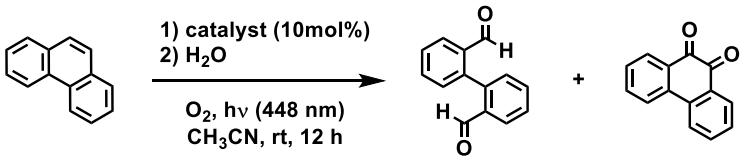
アクリジニウム系有機光レドックス触媒を利用したフェナントレン誘導体の酸化反応

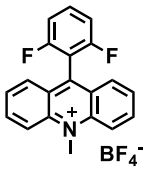
（兵庫県立大院工）○安井 菖・川瀬 毅・西田 純一
Oxidation reactions of phenanthrene derivatives using organic acridinium-type photo-redox catalyst (*Grad. School of Engineering, University of Hyogo*) ○Shou Yasui, Takeshi Kawase, Jun-ichi Nishida

Organic synthesis under mild condition using visible light is attracting great attention. It is known that acridinium dyes exhibit high oxidizing ability when irradiate with visible light and can be used as photocatalyst for one-electron oxidation of substrates.[1)] Since they are a non-metallic molecule and the reaction proceeds at room temperature, they are an extremely important catalyst from the perspective of green chemistry. We have discovered a new oxidation reaction using an acridinium catalyst with an orthodifluorobenzene skeleton. Oxidation products made from phenanthrene are important intermediates for functional compounds, but they are synthesized under harsh conditions using chromium-oxide based reagents and ozone. This time, we have demonstrated that photoredox catalyst can be used in reaction to obtain these intermediates. Furthermore, we investigated the synthesis of new acridinium compounds.

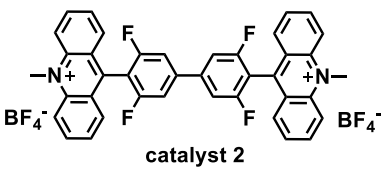
Keywords : Acridinium; photoredox catalyst; oxidation reaction; phenanthrene; visible light photocatalyst

可視光線を利用した温和な条件での有機合成が注目されている。アクリジニウム色素は、可視光照射に際して高い酸化力を発現し、基質の一電子酸化光触媒として利用できることが知られている。[1)] 非金属分子であり、常温で反応が進行するため、グリーンケミストリーの観点からも非常に重要な触媒である。私たちはオルトジフルオロベンゼン骨格を持つアクリジニウム触媒を利用した新しい酸化反応を見いだした。フェナントレンを原料とした酸化生成物は機能性化合物の重要な中間体であるが、酸化クロム系試薬やオゾンを利用した強い条件で合成されている。今回光レドックス触媒がこれらの中間体を得る反応に利用できることを明らかにした。さらに新しいアクリジニウム系化合物の合成も検討した。





catalyst 1



catalyst 2

1)S. Fukuzumi *et al., J. Am. Chem. Soc.*, **2004**, *126*, 15999–16006

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光誘起電子移動で生ずる過渡的および持続的一電子σ結合型ラジカルカチオン

（阪公大院工）○和田 佳成太・高安 凌平・大垣 拓也・松井 康哲・池田 浩

Transient and Persistent One-electron σ-Bonded Radical Cations Generated by Photoinduced Electron Transfer (*Grad. Sch. of Eng., Osaka Metro. Univ.*) ○Kanata Wada, Ryohei Takayasu, Takuya Ogaki, Yasunori Matsui, Hiroshi Ikeda

A radical cation **1**$^{\bullet+}$ generated by an electron-transfer reaction of a diary-substituted cage compound **1** (Fig.) has a property of one-electron σ-bond.[1] Generally, radical cations are thermodynamically more stable when they have a large number of strong electron-donating groups. In fact, the radical cation **1a**$^{\bullet+}$ having an *N,N*-diphenylamino (Ph_2N) group is stable enough to be isolated.[2] However, the radical cation **1b**$^{\bullet+}$ having two Ph_2N groups are not isolated because of its facile rearrangement reaction.[3] In this study, to investigate more systematically into substituent effects on radical cations **1**$^{\bullet+}$, we conducted photoinduced and non-photoinduced electron-transfer reactions of **1b–g** with various electron-donating groups. As a result, the lifetime and absorption wavelength of **1c**$^{\bullet+}$–**f**$^{\bullet+}$ become longer in the order of increasing the electron-donating ability of aryl groups. In the presentation, we will give the details of the properties of **1**$^{\bullet+}$, including the result of the density functional theory calculations.
Keywords: Laser Flash Photolysis; Back Electron Transfer; Lifetime; Rearrangement Reaction; Hammett Plot

ジアリール置換かご型化合物 **1** の電子移動反応で生ずるラジカルカチオン **1**$^{\bullet+}$(Fig.)は，一電子 σ 結合性を有する [1]．一般にラジカルカチオンは強い電子供与基を数多く有するほど熱力学的に安定である．実際，*N,N*-ジフェニルアミノ（Ph_2N）基を一つ有するラジカルカチオン **1a**$^{\bullet+}$は単離される [2]．しかし，Ph_2N 基を二つ有するラジカルカチオン **1b**$^{\bullet+}$は転位反応を速やかに起こすため単離されない [3]．そこで本研究では，**1**$^{\bullet+}$の安定性に対する置換基効果を系統的に調査すべく，種々の電子供与基をもつアリール誘導体 **1b–g** の光誘起および非光誘起による電子移動反応を行った．その結果，アリール基の電子供与性が増大する順に，**1c**$^{\bullet+}$–**f**$^{\bullet+}$は長寿命化し，その吸収は長波長化した．発表では密度汎関数理論計算の結果も含め，**1**$^{\bullet+}$の特性について詳細に議論する．

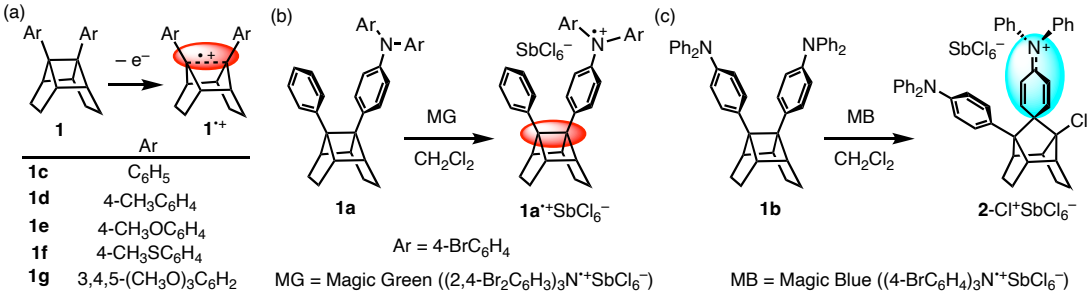

Fig. Generation of (a) **1**$^{\bullet+}$ from **1**, (b) **1a**$^{\bullet+}SbCl_6^-$ from **1a** with MG and (c) **2**-$Cl^+SbCl_6^-$ from **1b** with MB.

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SIB 用負極材料としてのターフェニルトリカルボン酸塩の合成と評価

（東電大工[1]・東電大院[2]・横国大[3]）○鴨打 悠希[1]・高橋 海七太[2]・藪内 直明[3]・宮坂 誠[2]

Sodium salt of terphenyl carboxylate as an anode for Na-ion batteries were synthesized and investigated

([1]*Department of Applied Chemistry, School of Engineering, Tokyo Denki University*, [2] *Materials Science and Engineering, Graduate School of Engineering, Tokyo Denki University* [3]*Department of Chemistry and Life Science, Yokohama National University*)
○Yuuki Kamochi[1], Kanata Takahashi[2], Yabuuchi Naoaki[3], Makoto Miyasaka[2]

Today, Sodium-ion batteries (SIBs) are being developed as an alternative to Lithium-ion batteries (LIBs). However, it has been reported that the graphite anode material used in LIBs does not work in SIBs, and it is necessary to develop a new anode material for SIBs.

Our laboratory studying anode materials for SIBs, especially focusing on them extended with disodium terephthalate (Na_2TP)[1),2)]. More recently, we advance research based on the report that carboxylate-introduced compounds in Na_2TP (**TBC**) improved cycling properties[3)].

In this study, we synthesized **Tri-TP1**, and evaluated its electrochemical properties (**Fig.1**). In addition, **Tri-TP** isomers were compared their electrochemical properties for SIBs.

今日、リチウムイオン電池(LIB)の代替材料としてナトリウムイオン電池(SIB)の開発が進められている。しかし、LIB で用いられていた黒鉛負極材料は SIB では機能しないことが報告されており、新たな負極材料を開発する必要がある。

当研究室では SIB 用負極材料の研究を行っており、特に Hu らにより報告されたテレフタル酸二ナトリウム(Na_2TP)を拡張した負極材料に着目している[1),2)]。

最近では、Luo らの Na_2TP にカルボキシレートを導入した化合物(TBC)はサイクル特性が向上するという報告をもとに研究を進めている[3)]。

本研究では **Tri-TP1** の合成及び電気化学特性評価を行った(**Fig.1**)。加えて、**Tri-TP** 異性体を比較し、電気化学特性の変化を SIB 用負極材料の面から評価する。

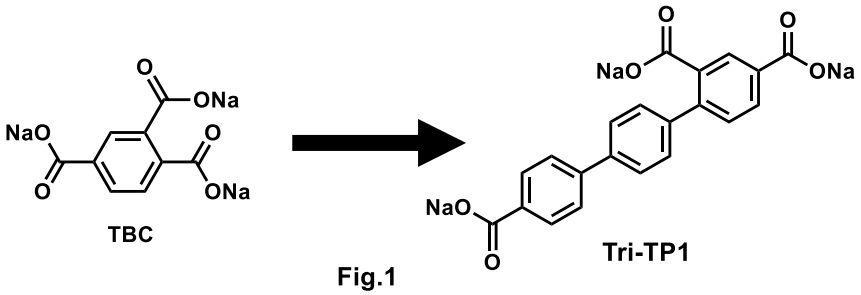

Fig.1

1) Hu, Y. *et al., Adv. Energy Mater.,* **2012***, 2, 962-965.*
2) Miyasaka, M. *et al., Polymer J.,***2022***,54,111-1118.*
3) Luo, C. *et al., J. Power Sources.,* **2020***, 453, 227904.*

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Academic Program [Poster] | 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-：Poster

Tue. Mar 19, 2024 3:45 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:45 AM - 8:15 AM UTC Poster Site 5(理工スポーツホール [1階] アリーナ)

[P5-2vn] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Japanese

[P5-2vn-01]

Development of novel synthetic method for chiral phosphine-containing β-amino acid precursors through asymmetric conjugate addition reaction

○Kosei Miyake[1], Kazuki Fujita[1], Akane Iwamura[1], Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

Japanese

[P5-2vn-02]

Asymmetric Aza-Friedel-Crafts Reaction of 2-Naphthols and Imines Using Chiral Phosphoric Acid Ctalysts

○Tomoki Marui[1], Akira Yanagisawa[1] (1. Chiba University)

Japanese

[P5-2vn-03]

Highly Chemoselective Triflation of Phenols Using *N*-Trifluoromethanesulfonylimidazole

○Momoko Ishikawa[1], Ranmaru Terasawa[1], Honoka Jinda[1], Emi Ikebe[1], Yukiko Fujiyama[1], Tsubasa Hirata[1], Manabu Hatano[1], Junki Nitta[2], Takako Yamazaki[2], Ren Tomita[2], Katsuhiro Akiyama[2] (1. Kobe Pharmaceutical University, 2. Central Glass Co., Ltd.)

Japanese

[P5-2vn-04]

Development of stereoselective reactions using tertiary alkyl halides

○Naoki Tsuchiya[1], Takashi Nishikata[1] (1. The Univ. of Yamaguchi)

Japanese

[P5-2vn-05]

Study on Efficient Introduction of Silyl Protecting Groups into Borneol and Isoborneol as Secondary Alcohols

○Yoshikazu Hiraga[1,2], Koya Tayama[2], Mio Sugiura[2], Yuki Takahashi[2], Baohe Lyu[1], Ryukichi Takagi[3] (1. Graduate School of Science and Technology, Hiroshima Institute of Technology, 2. Hiroshima Institute of Technology, 3. Graduate School of Science, Hiroshima University)

English

[P5-2vn-06]

Selective Monooxidation of Symmetric Dialdehydes in Aqueous Media

Pullaiah Kattanguru[1], Ren Ogawa[1], Yutaro Suzuki[1], ○Satomi Niwayama[1] (1. Muroran Institute of Technology)

Japanese

[P5-2vn-07]

Gold-Catalyzed Tandem Allylation/Enyne Cycloisomerization of Propargyl Acetate with Allylsilanes

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○Yoshikazu Horino[1], Shota Nakagawa[1], Nene Murata[1], Sota Akima[1] (1. Chitose Inst. Sci. Tech.)

Japanese

[P5-2vn-08]

Transformation focused on the carbonyl groups of fluorinated benzocyclobutenones

○Jo Kashiwabuchi[1] (1. Gunma university)

Japanese

[P5-2vn-09]

Stereoselective Synthesis of (*Z*)-*anti*-Homoallylic Alcohols Using Palladium-Catalyzed Three-Component Reaction

○Ayumu Natsubori[1], Mizuki Akagawa[1], Yoshikazu Horino[1] (1. Chitose Inst. Sci. Tech.)

Japanese

[P5-2vn-10]

O-Alkylation of α-Ketoamides Suppressing the Hydride Reduction

○Maika Yasue[1], Ayaki Yamamoto[1], Isao Mizota[1] (1. Mie University)

Japanese

[P5-2vn-11]

Thiazolidine Amide Synthesis Utilizing Umpolung of α-Imino Amide

○Kotomi Kanda[1], Takehiro Shimizu[1], Isao Mizota[1] (1. Mie University)

English

[P5-2vn-12]

Synthesis of 5-spiroproline derivatives by organocatalytic enantioselective [3+2] cycloaddition between enals and isatinimines

○Qian Liu[1], Kazuaki Kudo[1] (1. The University of Tokyo)

Japanese

[P5-2vn-13]

Development of 1,4-oxazin-2-one Synthesis Utilizing Umpolung Reaction to α-Hydrazonoketone

○Nozomi Hoshiai[1], Keiji Oshima[1], Isao Mizota[1] (1. Mie University)

English

[P5-2vn-14]

Dynamic kinetic resolution of axially chiral heterobiaryl N-oxides via peptide catalyzed aldol reaction

○JIAQI TIAN[1], Kazuaki Kudo[1] (1. The University of Tokyo)

Japanese

[P5-2vn-15]

Quaternary Amino Ester Synthesis Utilizing Tandem Umpolung/Radical AdditionReaction of α-Iminoester

○Yuki Ito[1], Isao Mizota[1] (1. Mie University)

English

[P5-2vn-16]

Synthesis of α-chloro-β-ketoesters and chlorine-containing polyketides via decarboxylative condensation of chloromalonic acid half-esters

○Yihao Shi[1], Kazuaki Kudo[1] (1. The University of Tokyo)

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Japanese

[P5-2vn-17]

[Withdraw] Synthesis of Functionalized C_2 Symmetric Compounds with Dibenzosuberane Skeleton and Their Use in Organic Synthesis

○Yusei Minagawa[1], Takanori Shibata[1] (1. Waseda University)

Japanese

[P5-2vn-18]

Study on Alkoxylation of Alkyl Halide under External Electric Field

○Asato Gake[1], Gen Onodera[1], Hironobu Tahara[1], Taichi Otsuji[1], Tsutomu Fukuda[1], Masanari Kimura[1] (1. Nagasaki University)

Japanese

[P5-2vn-19]

Direct Synthesis of Thioamide from Ketones

○Ishin Tomiya[1], Kengo Hyodo[1] (1. Kindai University)

Japanese

[P5-2vn-20]

Synthesis of substituted cyclobutanones and application to *y*-aminobutyric acid esters.

○Yuhao Wu[1], Issin Tomiya[1], Kengo Hyodo[1] (1. Kindai University)

Japanese

[P5-2vn-21]

Development of rapid electrochemical thiol-ene click reaction in a microfluidic reactor

○Kakeru Yamamoto[1], Kenta Arai[1] (1. Tokai Univ.)

Japanese

[P5-2vn-22]

Green Manufacturing: Reaction Condition Optimization for the Pseudo-Steady Flow Synthesis of the Functional Group Evaluation Kit

○Tomoki Sugimura[1], Kohei Sato[1], Tetsuo Narumi[1], Nobuyuki Mase[1] (1. Shizuoka University)

Japanese

[P5-2vn-23]

Fine Bubble Organic Chemistry: Development of Atmospheric Pressure Gas-Liquid Phase Reactions of Highly Viscous Liquids Using a Microporous Method

○Houto MORITA[1], Hiroto SAKURAI[2], Kohei SATO[1], Tetsuo NARUMI[1], Nobuyuki MASE[1] (1. Shizuoka University, 2. Shizuoka University Graduate School of Integrated Science and Technology)

English

[P5-2vn-24]

Microwave Flow Chemistry: Estimation Dielectric Loss Tangent Using Machine Learning

○Azmi Aisi[1], Kohei Sato[1], Tetsuo Narumi[1], Nobuyuki Mase[1] (1. Shizuoka Univ.)

Japanese

[P5-2vn-25]

Hydrogen/deuterium exchange of acyl hydrogens in cyclodextrin D_2O solutions

○Takatoshi Kawaji[1], Yuua Nishikawa[1] (1. NIT, Wakayama College)

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Japanese

[P5-2vn-26]

Single-process desalting of pyridine hydrochloride derivatives and water forbidden reactions using integrated flow reactors

○Hiroki Soutome[1,2], Yusuke Kimuro[3], Yosuke Ashikari[2], Aiichiro Nagaki[2] (1. AGC Inc., 2. Hokkaido University, 3. Juzen Chemical Corp.)

Japanese

[P5-2vn-27]

PCBM Synthesis by using Flow Photoreactor

○Shuhei Sumino[1], Yuya Tanaka[2], Michihisa Murata[2], Fukashi Matsumoto[1], Toshiyuki Iwai[1], Takatoshi Ito[1] (1. ORIST, 2. Osaka Institute of Technology)

Japanese

[P5-2vn-28]

Exploring the application of Highly volatile organic compounds in flow reactions

○Kensuke Muta[1,2], Kazuhiro Okamoto[2], Aiichiro Nagaki[2] (1. Central Glass Co., Ltd., 2. The Univ. of Hokkaido)

Japanese

[P5-2vn-29]

Alkylation of β-dicarbonyl compounds by microwave irradiation in the presence of $NaHSO_4/SiO_2$

○Keisuke Kumada[1], Mamiko Hayakawa[1], Shinpei Suzuki[1], Tadashi Aoyama[1] (1. College of Science and Technonology, Nihon University)

Japanese

[P5-2vn-30]

Synthesis of Esters and Amids under Microwave Irradiation and Investigation of Their Reaction-Promoting Effects

○Riko Arai[1], Hirokazu Iida[1] (1. Kanto Gakuin University)

Japanese

[P5-2vn-31]

A simple synthesis of 4-phenylbutanoic acid and related compounds using microwave irradiation

○Akane Takahashi[1], Mika Sakai[1], Ai Tsudo[1], Hirokazu Iida[1] (1. Kanto Gakuin Univ.)

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不斉共役付加反応による新規キラルリン含有 β-アミノ酸前駆体合成法の開発

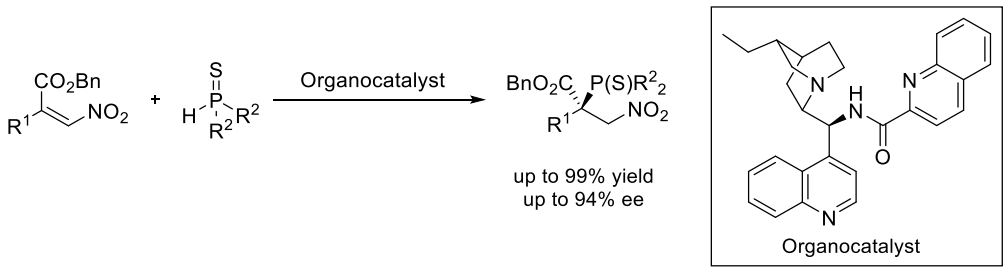
（名工大工[1]）○三宅 航成[1]・藤田 和樹[1]・岩村 朱音[1]・安川 直樹[1]・中村 修一[1]
Development of novel synthetic method for chiral phosphine-containing β-amino acid precursors through asymmetric conjugate addition reaction ([1]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Kosei Miyake[1], Kazuki Fujita[1], Akane Iwamura[1], Naoki Yasukawa[1], Shuichi Nakamura[1]

Chiral β-amino acids are important structural motifs found in various biologically active compounds and pharmaceuticals. One of the efficient methods for the synthesis of chiral β-amino acids is the enantioselective conjugate addition reactions of some nucleophiles with β-nitroacrylates. However, there are no reports for the synthesis of phosphine-containing chiral β-amino acids bearing the tetrasubstituted carbon center through the enantioselective conjugate addition reactions to β-nitroacrylates. Herein, we report the synthesis of phosphine-containing chiral β-amino acid precursors by the enantioselective conjugate addition reaction to β-nitroacrylates using phosphine sulfides as nucleophiles. The organocatalyst with the unique skeleton which was developed in our laboratory enables the reaction to proceed in high yield and high enantioselectivity. Especially, the conversion of the heteroarene amide part of the organocatalyst from 2-picolinamide to 2-quinolinamide improves the enantioselective control.

Keywords: Asymmetric synthesis; Conjugated addition reaction; β-Amino acid precursors; Organocatalyst; Chiral tetrasubstituted carbon center

キラルβ-アミノ酸は様々な生物活性物質や医薬品の部分骨格に見られる重要な構造モチーフである。この構造モチーフを合成する手法の一つとして、β-ニトロアクリル酸エステルへの不斉共役付加反応が数多く報告されているが、四置換不斉炭素を構築し、かつキラルリン含有β-アミノ酸を合成した例はなかった。そこで我々は、ホスフィンスルフィドを用いた不斉共役付加反応によるキラルリン含有β-アミノ酸前駆体の合成を行った。

本研究では、当研究室で開発した基本骨格を含む有機触媒を用いることで高収率、高立体選択的な反応開発を実現した。特に触媒構造におけるヘテロアレーンアミド部分をピコリンアミドから 2-キノリンアミドに変えることで更なる立体制御が可能になった。



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キラルリン酸触媒を用いた 2-ナフトール類とイミン類との不斉アザ-フリーデル-クラフツ反応

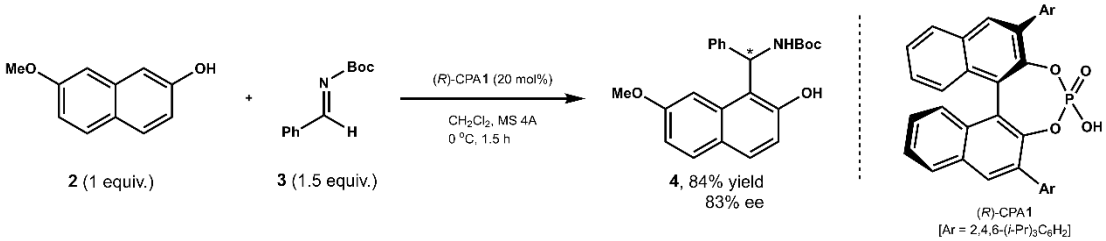
（千葉大院融合理工[1]・千葉大院理[2]）○丸井 友貴[1]・柳澤 章[2]
Asymmetric Aza-Friedel-Crafts Reaction of 2-Naphthols and Imines Using Chiral Phosphoric Acid Catalysts (*Chiba University*)○Tomoki Marui[1], Akira Yanagisawa[2]

The benzylamine motif is a useful substructure found not only in natural products but also in pharmaceuticals. Since aromatic C-H bonds can be converted to chiral benzylamines, the enantioselective aza-Fridel-Crafts reaction has attracted notice. An efficient skeleton-forming reaction of 2-naphthols with *N*-Boc imines is, however, still undeveloped today[1)]. We have previously developed enantioselective chiral amine synthesis reactions using chiral silver catalysts or chiral tin catalysts[2,3)]. Here, we attempted an asymmetric aza-Friedel-Crafts reaction between 2-naphthols and imines using chiral phosphoric acid catalysts, and report the results. As a result of various studies, a chiral binaphthol phosphoric acid having bulky substituents at the 3,3'-positions showed excellent catalytic activity and yielded the target chiral amines with good enantioselectivity.

Keywords : Asymmetric Aza-Friedel-Crafts Reaction; Chiral Phosphoric Acid; 2-Naphthol; Imine; Betti Base

ベンジルアミンは、天然物のみならず医薬品にもしばしばみられる有用な化合物群である。不斉アザ-フリーデル-クラフツ反応は、芳香族の C-H 結合をキラルなベンジルアミンへと変換する反応として注目されてきた。しかしながら、2-ナフトール類と *N*-Boc イミン類の効率的な骨格形成反応は未だ達成されていない[1)]。当研究室ではこれまでに、不斉銀触媒や不斉スズ触媒を用いたエナンチオ選択的キラルアミン合成反応を開発している[2,3)]。そこで今回、キラルリン酸触媒を用いた 2-ナフトール類とイミン類との不斉アザ-フリーデル-クラフツ反応を試みたので、その結果を報告する。

種々検討の結果、3,3'-位にかさ高い置換基を有するキラルビナフチルリン酸 **1** がすぐれた触媒活性を示し、目的とするキラルアミン **4** を良好なエナンチオ選択性で与えた。



2 (1 equiv.)　**3** (1.5 equiv.)　**4**, 84% yield, 83% ee　(*R*)-CPA**1** [Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$]

1) Niu, L.-F.; Xin, Y.-C.; Wang, R.-L.; Jiang, F.; Xu, P.-F.; Hui, X.-P. *Synlett* **2010**, *5*, 765.
2) Yanagisawa, A; Kasahara, S.; Takeishi, A.; Marui, T. *Synlett* **2022**, *33*, 2019.
3) Yanagisawa, A; Takagi, K.; Horiguchi, M.; Dezaki, K.; Marui, T.; Saito, E.; Ebihara, T.; Russell, G. M.; Watanabe, T.; Midorikawa, K. *Asian J. Org. Chem.* **2023**, *12*, e202300213.

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N-トリフルオロメタンスルホニルイミダゾールを用いるフェノール類の高化学選択的トリフリル化反応

(神戸薬大薬[1]・セントラル硝子株式会社[2]) ○石川 桃子[1]・寺澤 蘭丸[1]・神田 萌乃夏[1]・池部 絵美[1]・藤山 幸子[1]・平田 翼[1]・波多野 学[1]・新田 純基[2]・山﨑 貴子[2]・富田 廉[2]・秋山 勝宏[2]

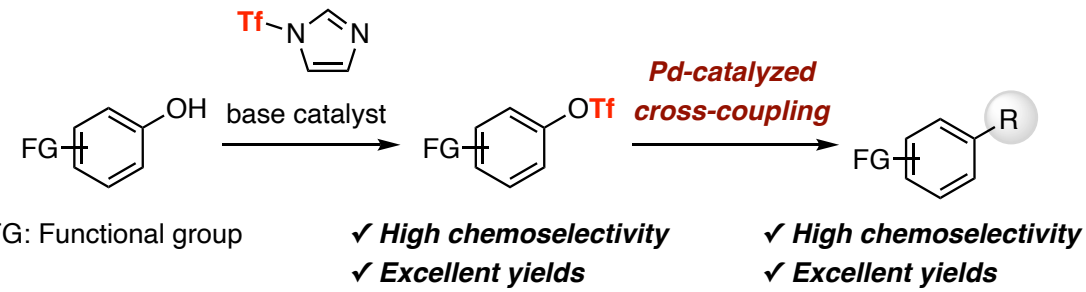
Highly Chemoselective Triflation of Phenols Using *N*-Trifluoromethanesulfonylimidazole

([1]*Faculty of Pharmaceutical Sciences, Kobe Pharmaceutical University*, [2]*New-STEP Research Center, Central Glass Co. Ltd.*) ○Momoko Ishikawa,[1] Ranmaru Terasawa,[1] Honoka Jinda,[1] Emi Ikebe,[1] Yukiko Fujiyama,[1] Tsubasa Hirata,[1] Manabu Hatano,[1] Junki Nitta,[2] Takako Yamazaki,[2] Ren Tomita,[2] Katsuhiro Akiyama[2]

Aryl triflates (ArOTf), which can be synthesized by trifluoromethanesulfonylation (triflation) of the hydroxy groups of phenols, are used as substrates for transition metal-catalyzed coupling reactions such as the Suzuki-Miyaura reaction, and are therefore important in organic synthesis. However, the reaction using conventional trifluoromethanesulfonic anhydride (Tf_2O) is often non-selective when the substrates have other reactive functional groups, and undesired byproducts are given. In this study, we developed a highly chemoselective triflation of phenols using *N*-trifluoromethanesulfonylimidazole, and the desired *O*-triflated products were obtained in high yields. We will propose the reaction mechanism of the chemoselective triflation of the hydroxy groups of phenols, and show some Pd-catalyzed transformations of the obtained *O*-triflated products.

Keywords: *Triflation; Chemoselectivity; Phenol; Sulfonylation; Coupling reaction*

フェノール類のヒドロキシ基をトリフルオロメタンスルニル化（トリフリル化・Tf化）することで合成できるアリールトリフラート（ArOTf）は、鈴木-宮浦反応に代表される触媒的カップリング反応の基質として用いられるため、有機合成上重要である。ところが、反応性の高いトリフルオロメタンスルホン酸無水物（Tf_2O）を用いるフェノール類のトリフリル化反応では、競合する他の官能基も非選択的に反応しうるため、しばしば混合物を与える。我々は *N*-トリフルオロメタンスルホニルイミダゾールを用いることで、フェノール性のヒドロキシ基を高化学選択的かつ高収率でトリフリル化できることを見出した。反応機構の考察とパラジウム触媒を用いるカップリング反応による誘導も発表する。



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第三級アルキルハロゲン化物に対する立体選択的反応の検討

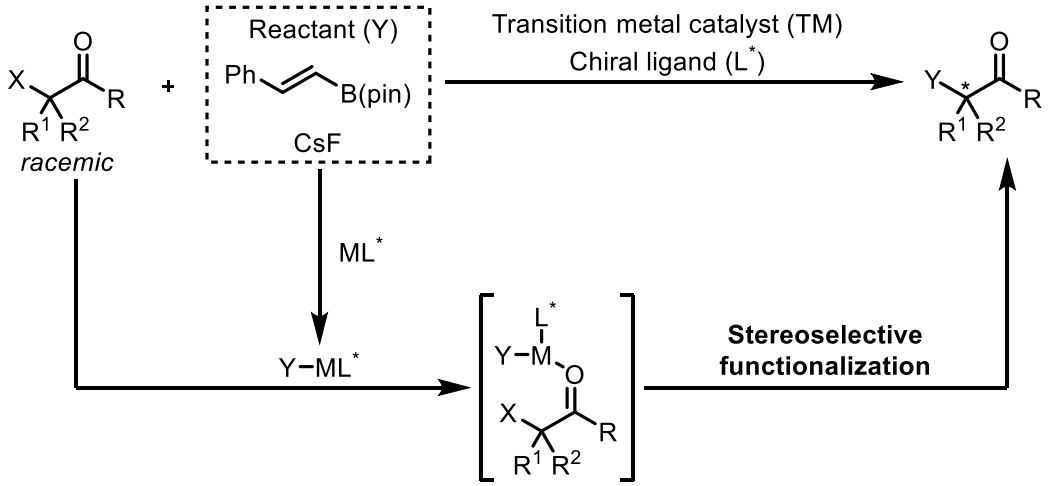
（山大院創成[1]） ○土屋　直輝[1]・西形　孝司[1]

Development of stereoselective reactions using tertiary alkyl halides ([1]Graduate School of Sciences and Technology, Yamaguchi University)
○Naoki Tsuchiya,[1] Takashi Nishikata[1]

Quaternary carbon compounds are very important skeleton including natural products or physiologically active compounds. As synthesis method of their compounds, various substitution reaction to tertiary alkyl electrophile has been developed using transition metal catalyst. However, since substitution reaction to tertiary alkyl electrophile often require harsh reaction conditions, there are still many limitations on the development of stereoselective substitution to tertiary alkyl electrophile. In this research, we examined various stereoselective substitution reaction of α-halocarbonyl compounds in the presence of chiral transition metal catalyst.
Keywords：Tertiary alkyl halides, Stereoselective reaction, Chiral transition metal catalyst

四置換炭素骨格は生理活性分子などの様々な有用物質に含まれる重要な骨格である。この四置換炭素骨格を形成するために、遷移金属触媒を利用した第三級アルキル化合物に対する官能基導入反応の開発が盛んに研究されている。しかし、第三級アルキル化合物に対する官能基導入反応ではしばしば過酷な反応条件が必要となるため、不斉空間を制御しながら官能基導入を行う立体選択的官能基化反応の開発には未だ制限が多いのが現状である。今回我々は、第三級アルキルハロゲン化物に対して、キラル遷移金属触媒存在下、様々な反応剤を作用させることで、立体選択的官能基化反応が進行するか調査した。

例えば、以下に示したα-ハロカルボニル化合物に対して、アルケニル誘導体やフッ化セシウムなどの反応剤を作用させた立体選択的官能基導入反応においてキラル配位子の検討を実施した。その結果、立体選択的フッ素化反応の検討で、キニーネ配位子を使用すると若干の立体選択性を発現した。



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第二級アルコールとしてのボルネオールおよびイソボルネオールに対する効率的シリル保護基導入に関する研究

（広島工業大院生命[1]・広島工業大生命[2]・広島大院先進理工[3]）○平賀良知[1,2]・田山馨彩[2]・杉浦美桜[2]・高橋侑希[2]・呂　保鶴[1]・高木隆吉[3]

Study on efficient introduction of silyl protecting groups into borneol and isoborneol as secondary alcohols ([1]*Graduate School of Science and Technology*, *Hiroshima Institute of Technology*, [1]*Hiroshima Institute of Technology*, [3]*Graduate School of Advanced Science and Engineering*, *Hiroshima University*) ○Yoshikazu Hiraga[1,2], Koya Tayama[2], Mio Sugiura[2], Yuki Takahashi[2], Baohe Lyu[1], Ryukichi Takagi[3]

Various reaction conditions have been reported for the introduction of silyl protecting groups into secondary alcohols. Previously, we discovered that silyl protecting groups (TBDPS, TBDMS, TIPS, TPS) can be efficiently introduced to secondary alcohols in the presence of iodine and iodide ions. Here, we investigated the effects of iodine and iodide ions, as well as the effect of the polarity of reaction solvents used, in order to examine the optimal conditions for introducing various silyl protecting groups into the hydroxyl groups of borneol and isoborneol as secondary alcohols.

Keywords : Silyl protective group, Secondary alcohol, Iodine, Iodide ion, Borneols

これまでに，第二級アルコールへの *tert*-ブチルジフェニルシリル（TBDPS）基など様々なシリル保護基導入を検討した。その際，ヨウ素（I_2）およびヨウ化物イオンの存在下で，効率的にシリル保護基が導入できることを見出した。[1)] 本研究では，嵩高い第二級アルコールとして，ボルネオールとイソボルネオールを用い，それぞれのヒドロキシ基への TBDPS 基の導入における溶媒および添加剤の検討を行った。

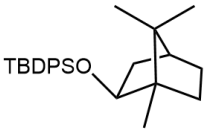
塩基はイミダゾールを用い，反応溶媒として，テトラヒドロフラン（THF）とアセトニトリル（MeCN），添加剤として，I_2 とヨウ化カリウム（KI）の効果を調査した。

ボルネオールに TBDPS を導入する際，溶媒に THF を用いると，添加剤は I_2 より KI の方が効果的であった。

一方，MeCN を用いた場合，いずれの添加剤であっても TBDPS 基が導入できた。特に，添加剤を KI にすると，反応は定量的であった。

イソボルネオールは，構造的な嵩高さから，いずれも低収率であった。溶媒を MeCN，添加剤を KI の条件が最も収率が高かった。現在，他のシリル保護基導入における溶媒効果および添加剤の効果を調査している。

Table 1. Effect of solvent and additive in the formation of TBDPS protected borneol and isoborneol

Product				
Solvent	THF	MeCN	THF	MeCN
Addtive	I_2 KI	I_2 KI	I_2 KI	I_2 KI
Yield (%)	36 60	66 100	0 1	2 31

Reaction conditions: Borneol or isoborneol (1.0 mmol), imidazole (3.0 mmol), additive (3.0 mmol), TBDPS-Cl (1.1 mmol), solvent (5.0 mL), 25℃. Yields were determined by ^{1}H NMR spectra of the reaction mixture after 24 h.

1) 平賀，永井，高木，杉浦，他，日本化学会第 103 春季年会，P4-2am-09（2023）.

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Selective Monooxidation of Symmetric Dialdehydes in Aqueous Media

(*Graduate School of Engineering, Muroran Iinstitute of Technology*) ○Pullaiah Kattanguru, Ren Ogawa, Yutaro Suzuki, ○Satomi Niwayama*

Keywords: Desymmetrization; Water-mediated Reaction; Monooxidation; Symmetric Dialdehyde; Formyl-Carboxylic Acid

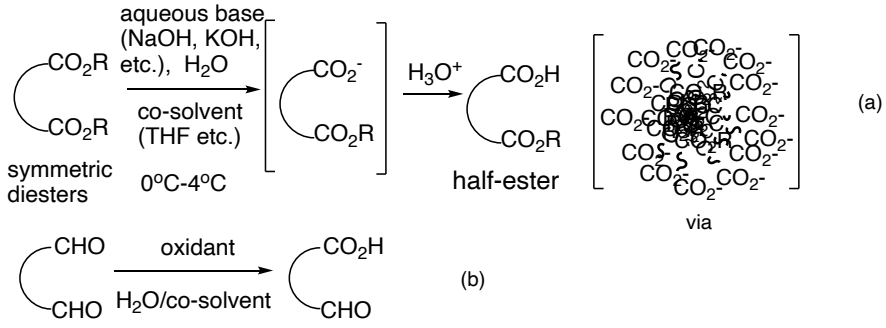
Organic reactions mediated by water are typical green chemistry. Many symmetric compounds are inexpensive or can be prepared on a large scale at low cost. Therefore, desymmetrization reactions of symmetric compounds in aqueous media significantly advance the development of environmentally-benign and practical organic synthesis, although distinguishing the two identical functional groups in symmetric compounds is a non-trivial task.

Earlier, we reported highly efficient and practical selective monohydrolysis reactions of symmetric diesters without enzymes (Scheme 1a).[1] The mechanism has been proposed to proceed through intermediary micellar aggregates, in which the hydrophilic carboxylate anions formed by the hydrolysis are directed outward and the remaining hydrophobic groups including the ester groups are directed inward.[2]

According to this mechanism, it should be possible to desymmetrize symmetric compounds when the desymmetrization leads to change of hydophilicity/hydrophobicity. Therefore, we reasoned that selective monooxidation of symmetric dialdehydes can produce formyl-carboxylic acids in aqueous media, since the formyl groups in the starting symmetric dialdehydes are hydrophobic, and their oxidation yields carboxyl groups, which are hydrophilic (Scheme 1b).

We investigated various conditions such as oxidizing reagent, co-oxidant, co-solvent, reaction time, and temperature on improvement of the reactivity and selectivity. The best conditions apply 1.1 equivalents of H_5IO_5 with 0.02 equivalents of a co-oxidant PCC in H_2O containing CH_3CN as a co-solvent (H_2O/CH_3CN=10/1). The reaction conditions are simple, mild, and practical, yielding the corresponding formyl carboxylic acids in modest to high yields.

Scheme 1



1) For example, a) S. Niwayama, *J. Org. Chem*. **2000**, *65,* 5834. b) T. Barsukova, T. Sato, H. Takumi, S. Niwayama, *RSC Adv.* **2022**, *12*, 25669. 2) S. Niwayama, Y. Hiraga, *ACS Omega*. **2023**, *8*, 33819.

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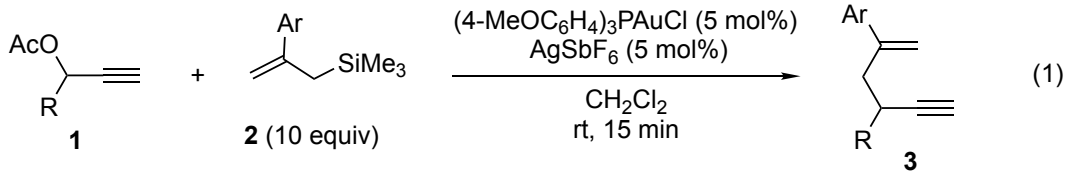
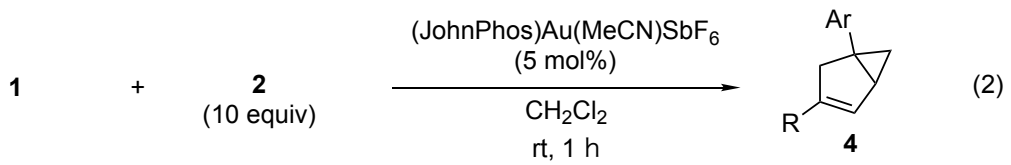
金触媒によるプロパルギル位アリル化と環化異性化のタンデム反応

（公立千歳科技大[1]）○堀野 良和[1]・中川 翔太[1]・村田 寧々[1]・秋間 想太[1]
Gold-Catalyzed Tandem Allylation/Enyne Cycloisomerization of Propargyl Acetate with Allylsilanes ([1]*Department of Applied Chemistry and Bioscience, Chitose Institute of Science and Technology*) ○Yoshikazu Horino,[1] Shota Nakagawa,[1] Nene Murata,[1] Sota Akima[1]

It is known that the reaction of propargylic acetates with allylsilanes in the presence of Lewis acids leads to propargylic allylation to give 1,5-enynes. A similar allylation of propargylic alcohols occurs with gold (III) catalyst, but the yield is significantly lower when the reaction is carried out in the presence of gold (I) catalyst. In this study, we found that when the reaction was carried out using propargylic acetate **1** and allylsilane **2** having an aryl group at the β-position in the presence of a gold (I) catalyst, the propargylic allylation of **1** proceeded successfully to afford 1,5-enynes **3** (eqn 1). Furthermore, a tandem allylation/1,5-enyne cycloisomerization proceeded to afford bicyclo[3.1.0]hexene derivatives **4** when (JohnPhos)Au(MeCN)SbF_6 was applied (eqn 2).
Keywords : Gold; Allylation; Cycloisomerization; Allylsilanes; Tandem Reaction

ルイス酸存在下、プロパルギルアセテートとアリルシランとの反応を行うと、プロパルギル位アリル化反応が進行し 1,5−エンイン化合物が得られることが知られている[1]。三価の金触媒を用いても同様のプロパルギル位アリル化反応が進行するが、一価の金触媒で行うと収率が著しく低下する[2]。今回、一価の金触媒存在下、プロパルギルアセテート **1** と β 位にアリール基を有するアリルシラン **2** を用いて反応を行うと、プロパルギル位アリル化反応が首尾良く進行し 1,5−エンイン化合物 **3** が得られることを見出した（式 1）。さらに、(JohnPhos)Au(MeCN)SbF_6 触媒存在下で反応を行うと、プロパルギル位アリル化反応と環化異性化反応が連続的に進行しビシクロ[3.1.0]ヘキセン誘導体 **4** を与えることも見出した（式 2）[3]。





1) T. Schweir, M. Rubin, V. Gevorgyan, *Org. Lett.* **2004**, *6*, 1999.
2) M. Georgy, V. Boucard, O. Debleds, C. D. Zotto, J.-M. Campagne, *Tetrahedron*, **2009**, *65*, 1758.
3) J. P. Reeds, A. C. Whitwood, M. P. Healy, I. J. S. Fairlamb, *Chem. Chem*. **2010**, *46*, 2046.

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フッ素化ベンゾシクロブテノンのカルボニル部位の変換反応

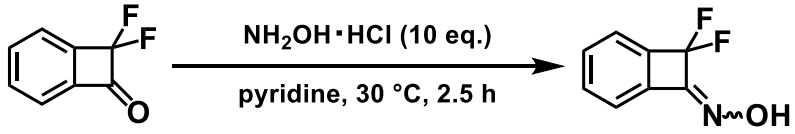
（群馬大院理工[1]）○柏渕　城[1]・杉石露佳[1]・網井秀樹[1]
○Jo Kashiwabuchi,[1] , Tsuyuka Sugiishi,[1] Hideki Amii[1]
(1*Graduate School of Science and Technology, Gunma University*)

Transformation focused on the carbonyl groups of fluorinated benzocyclobutenones

Indoline is useful for many pharmaceutical intermediates and is synthesized by ring expansion reaction using DIBAL. However, the introduction of a difluoromethylene group into indoline has not yet been reported. In this study, we have achieved the synthesis of fluorinated benzocyclobutenone oximes from fluorinated benzocyclobutenones for synthesis of indolines with difluoromethylene group.
In fact, by using 10 equivalents of hydroxylamine hydrochloride and pyridine as a solvent for fluorinated benzocyclobutenones, the fluorinated benzocyclobutenone oximes were obtained in 59% isolated yield, including the geometric isomers, *E* and *Z* forms. Furthermore, we will present synthetic application of difluoro benzocyclobutenone oximes
Keywords : Fluorine, Difluoromethylene group, Benzocyclobutenone, Oxime

インドリンは多くの医薬品中間体などに利用されており、現在はベックマン転位やDIBAL を用いた環拡大反応を用いて合成する手法がある[1]。しかし、インドリンへのジフルオロメチレン基の導入は未だに報告例がない。本研究では、ジフルオロメチレン基を有するインドリン合成を目指し、フッ素化ベンゾシクロブテノンからフッ素化ベンゾシクロブテノンオキシムの合成を試みた。

実際に、フッ素化ベンゾシクロブテノンに対し、ヒドロキシルアミン塩酸塩 10 当量と溶媒としてピリジンを用いることで、目的のフッ素化ベンゾシクロブテノンオキシムを、幾何異性体である*E*体と*Z*体の混合物として、単離収率 59%で得ることができた。



59%

本発表では、フッ素化ベンゾシクロブテノンオキシムの変換反応についても述べる。

1)　Cho, H.; Iwama, Y.; Sugimoto, K.; Mori, S.; Tokuyama, T. *J. Org. Chem.* **2010**, *75*, 627-636.

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パラジウム触媒を用いた三成分連結反応によるホモアリルアルコール誘導体の合成

（公立千歳科技大[1]）○夏堀 歩[1]・赤川 美月[1]・堀野 良和[1]

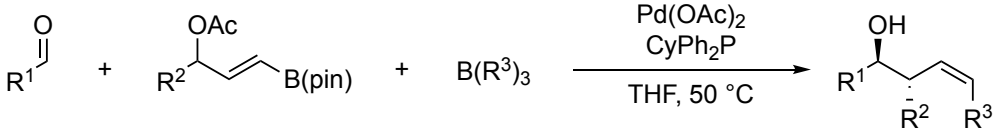
Stereoselective Synthesis of (*Z*)-*anti*-Homoallylic Alcohols Using Palladium-Catalyzed Three-Component Reaction

([1]*Department of Applied Chemistry and Bioscience, Chitose Institute of Science and Technology*) ○Ayumu Natsubori,[1] Mizuki Akagawa,[1] Yoshikazu Horino[1]

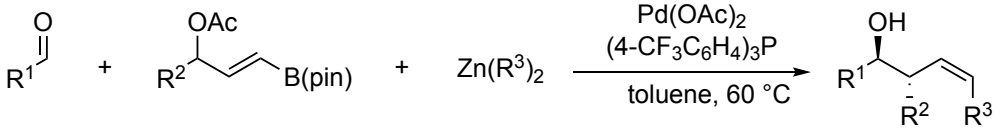
Multi-component reactions are useful synthetic methods as they not only shorten the reaction process but also enable efficient stereoselective synthesis of target molecules. We have reported the palladium-catalyzed three-component reaction of 3-(pinacolatoboryl)allyl acetates, aldehydes, and triorganoboranes that provides wide variety of functionalized (*Z*)-*anti*-homoallylic alcohols (eqn. 1).[1)] However, the method offers narrow functional group tolerance as the trialkylboranes used in this reaction was prepared by hydroboration of the corresponding alkenes. On the other hand, organozinc reagents are easily prepared by either the direct insertion of zinc metal or transmetallation with zinc salts. In this study, we investigated a three-component coupling reaction using organozinc reagents instead of the trialkylboranes, and found that a highly diastereoselective three-component coupling reaction proceeded to give (*Z*)-*anti*-homoallyl alcohols (eqn. 2).

Keywords : Palladium; Allylation; Three-Component Reaction; Homoallylic Alcohols

多成分連結反応は、反応工程を短縮できるだけでなく、目的分子を効率よく立体選択的に合成することもできるため有用な合成手法である。当研究室では、パラジウム触媒を用いた三成分連結反応により、*Z* 体の *anti*-ホモアリルアルコール誘導体が立体選択的に得られることを報告している（式 1）[1)]。しかしながら、有機ホウ素反応剤はヒドロホウ素化反応によって調製していたため、多くの場合、導入できる置換基 R^3 はアルキル基に限定され、アリール基やメチル基の導入は困難であった。また、官能基許容性が低い問題点もあった。そこで本研究では、有機亜鉛化合物を用いることで、導入できる置換基 R^3 の一般性の拡張と官能基許容性により優れた反応開発を目指した。トリアルキルホウ素反応剤の代わりに有機亜鉛反応剤を用いた三成分連結反応を検討したところ、高ジアステレオ選択的な三成分連結反応が進行し、*Z* 体の *anti*-ホモアリルアルコールが与えることを見出したので報告する（式 2）。



(1)



(2)

1) Y. Horino, A. Aimono, H. Abe, *Org. Lett.* **2015**, *17*, 2824.

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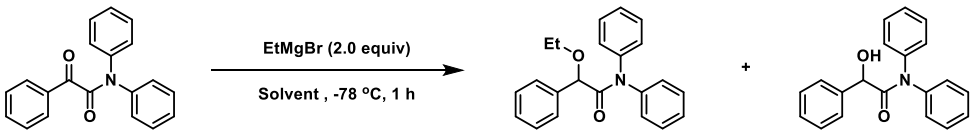
還元反応を抑制する *α*-ケトアミドの *O*-アルキル化反応の開発

（三重大院工）○安江 舞花・山本 彩輝・溝田 功
O-Alkylation of *α*-Ketoamides Suppressing the Hydride Reduction (*Graduate School of Engineering, Mie University*) ○Maika Yasue, Ayaki Yamamoto, Isao Mizota

Ether (R-O-R') is one of the most fundamental class of organic compounds widely existing around us. Among them, α-alkoxy carbonyl compounds are very important skeletons in that they are found in natural products and biologically active compounds, and are also synthetic intermediates of such compounds. In particular, α-alkoxy amides are known as compounds having fungicidal and PDE10A inhibitory (antipsychotic) effects, and many synthetic methods have been reported so far. We have already developed umpolung reactions of α-imino esters (*N*-alkylation) and integrated reactions utilizing *N*-alkylation. In this study, we examined the umpolung reaction (*O*-alkylation) of α-ketoamides suppressing the hydride reduction from Grignard reagents.
Keywords : α-Ketoamide; Umpolung Reaction; O-Alkylation; α-Alkoxy Carbonyl Compound; Hydride Reduction

当研究室では *α*-イミノエステルに対する *N*-アルキル化反応が円滑に進行することを見出し、多くの反応集積化に成功している。[1,2]今回 *α*-ケトアミドに対する極性転換反応（*O*-アルキル化）において副生成物である還元体を抑制し選択的に *O*-アルキル化が進行する条件を検討したので報告する。

α-ケトアミド **1** に対しエチル Grignard 反応剤を 2.0 当量、また様々な種類の溶媒や添加剤を用いて、-78 ℃で 1 時間反応させ、副生成物 **3** である還元体とともに目的の *O*-エチル化体 **2** を得た。



1 2 3

Entry	Solvent	Yield (%) 2	3	Entry	Solvent	Yield (%) 2	3
1	DCM	40	51	4	Xylene	44	42
2	Benzene	31	16	5	Mesitylene	50	23
3	Toluene	33	21	6	Pyridine	23	17

1) I. Mizota, M. Shimizu, *Chem. Rec.* **2016**, *16*, 688.
2) I. Mizota, Y. Nakamura, S. Mizutani, N. Mizukoshi, S. Terasawa, M. Shimizu, *Org. Lett.* **2021**, *23*, 4168.

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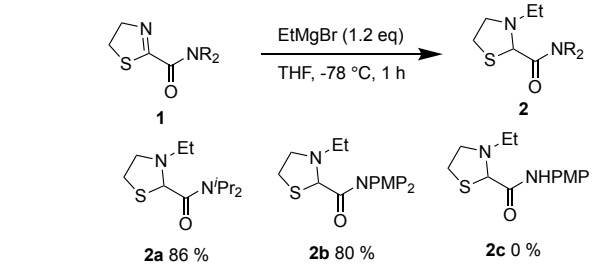
α-イミノアミドの極性転換を活用するチアゾリジンアミド合成

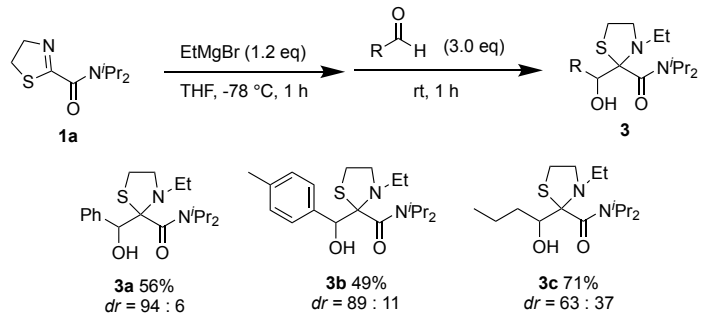
（三重大院工）○神田 琴巳・清水 健弘・溝田 功
Thiazolidine Amide Synthesis Utilizing Umpolung of α-Imino Amide (*Graduate School of Engineering, Mie University*) ○Kotomi Kanda, Takehiro Shimizu, Isao Mizota

We have already reported that the umpolung reaction of α-imino esters with organometallic reagents proceeded smoothly to give corresponding *N*-alkylated products in high yields. In this study, we examined umpolung reactions of α-imino amides with a thiazoline skeleton to afford the desired thiazolidine products.We also found tandem *N*-alkylated / aldol reaction proceeded to give the product in good to high yields.
Keywords : α-Imino Amide; Umpolung Reaction; N-Alkylation; Thiazoline Skeleton; Thiazolidine Amide

当研究室では α-イミノエステルに対し、有機金属反応剤を用いることで、極性転換反応である *N*-アルキル化が円滑に進行することを見出し報告している。[1-3)]今回出発物質としてチアゾリン骨格含有 α-イミノアミドに対する極性転換反応を検討し、生物活性物質にみられるチアゾリジンアミドを合成することに成功したので報告する。

チアゾリン骨格を有する α-イミノアミド **1** に対し、THF 溶媒中 EtMgBr を作用させたところ、対応するチアゾリジアミド **2** を得た。また、*N*-アルキル化後、求電子剤としてアルデヒドを作用させ、反応が円滑に進行し、対応するアミノアルコール **3** を得た。





1) Y. Niwa, M. Shimizu, *J. Am. Chem. Soc.* **2003***, 125*, 3720.
2) I. Mizota, Y. Shimizu, *Chem. Rec.* **2016***, 16*, 688.
3) I. Mizota, C. Ueda, T. Yun, Y. Tsujimoto, M. Shimizu, *Org. Lett*. **2018**, *20,* 2291.

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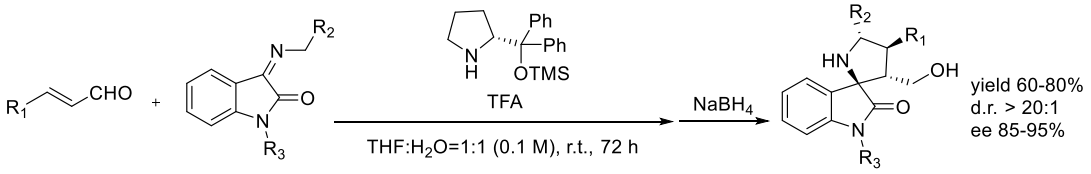
Synthesis of 5-spiroproline derivatives by organocatalytic enantioselective [3+2] cycloaddition between enals and isatinimines

(*Institute of Industrial Science, The University of Tokyo*) ○Qian Liu, Kazuaki Kudo

Keywords: Asymmetric Synthesis, Organocatalysis, [3+2] Cycloaddition, 5-Spiroproline Derivatives, Aqueous Conditions

5-spiroproline derivatives, especially spiro[proline-5,3'-oxindole]s are known to show specific bioactivity such as antibacterial, antimalarial or antitubercular activities.[1] Therefore, stereocontrolled synthesis of such class of compounds is highly important. So far, they have been prepared by [3+2] cycloaddition of isatin-derived azomethine ylides. The reaction includes the formation of imines from a glycinate ester and the isatin, followed by the ylide formation and the cycloaddition. In many cases the cycloaddition occurs in a highly diastereoselective manner.[2] However, an enantioselective version of this cycloaddition has not been developed to date. Due to this situation, bioassays have been carried out only with racemates. On the other hand, there are several reports on the asymmetric synthesis of spiro[pyrrolidine-2,3'-oxindoles] by chiral amine catalysts.[3] In those papers, there is no example for the synthesis of a spiro[proline-5,3'-oxindole].

This time, our group has established the catalytic enantioselective synthesis of spiro[proline-5,3'-oxindole]s. In the presence of 20 mol% of Hayashi-catalyst, the [3+2] cycloaddition of N-alkoxycarbonylmethyl isatinimines and enals proceeded in a highly stereoselective manner. The key factor was the use of water as a co-solvent. In the absence of water, the reaction proceeded sluggishly with lower stereoselectivity.



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α-ヒドラゾノケトンに対する極性転換反応を活用した 1,4-オキサジン-2-オン合成

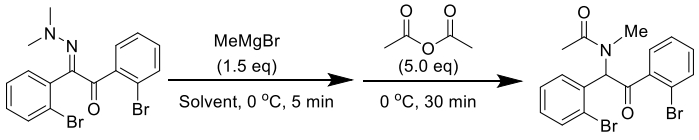
（三重大院工）○星合 希美・大島 慶二・溝田 功
Development of 1,4-Oxazin-2-one Synthesis Utilizing Umpolung Reaction to α-Hydrazonoketone (*Graduate School of Engineering, Mie University*) ○Nozomi Hoshiai, Keiji Oshima, Isao Mizota

We have already reported the umpolung *N*-alkylation of α-iminoester with various organometallic reagents proceeded to give the corresponding *N*-alkylated products in high yields. We succeeded in the synthesis of 1,4-oxazin-2-one utilizing tandem *N*-alkylation/reduction of α-hydrazonoketone as a novel starting material in good to high yields.

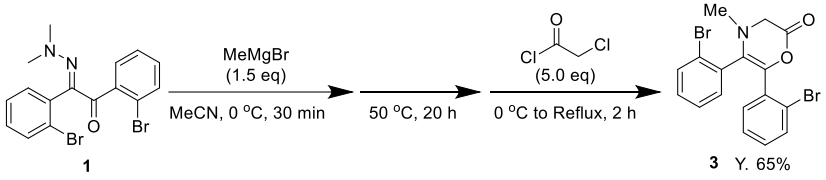
Keywords: α-Hydrazonoketone, Umpolung Reaction, N-Alkylation, Hydride Reduction, 1,4-Oxazin-2-one

当研究室では α-イミノエステルに対し、有機金属反応剤を用いることで、極性転換反応である *N*-アルキル化が良好に進行することを既に見出している。[1-3]今回新たな出発物質として α-ヒドラゾノケトンを用い、有機金属反応剤と反応させることで窒素上置換基の脱離およびヒドリド還元を伴った α-アミノケトン合成に成功した。さらに、クロロアセチルクロリドを連続的に反応させることで、*N*,*O*-ジアルキル化した 1,4-オキサジン-2-オンを得ることにも成功した。

α-ヒドラゾノケトン **1** に対し MeMgBr を 1.5 当量、アセトニトリル溶媒中 0 ℃で 30 分間反応させた後、5.0 当量の無水酢酸を加えることで、α-アミノケトン **2** を得た。また、*N*-メチル化後、50 ℃で 20 時間攪拌し、クロロアセチルクロリド 5.0 当量を加えることで、1,4-オキサジン-2-オン **3** を得た。



Entry	Solvent	Yield (%)	Entry	Solvent	Yield (%)
1	THF	82	5	Hexane	8
2	Et_2O	43	6	DMF	trace
3	DCM	79	7	MeCN	96
4	Toluene	58	8	EtCN	62



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Dynamic kinetic resolution of axially chiral heterobiaryl N-oxides via peptide catalyzed aldol reaction

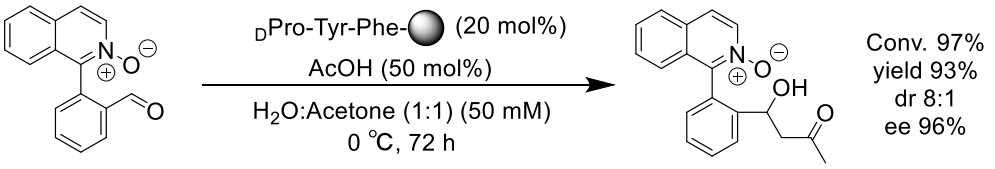
(*Institute of Industrial Science, The University of Tokyo*) ○Jiaqi Tian, Kazuaki Kudo

Keywords: Peptide Catalyst; Heterobiaryl N-Oxides; Aqueous Media; Dynamic Kinetic Resolution; Aldol Reaction

Axially chiral heterobiaryl N-oxides have attracted increasing attention due to their widespread presence in natural products, bioactive molecules, and functional materials. The asymmetric synthesis of chiral heterobiaryl N-oxides typically involves multiple steps, leading to reduced yields. Kinetic resolution of racemic mixtures is a common method to obtain axially chiral compounds. However, like other resolution techniques, it is constrained by a maximum theoretical yield of only 50%. Addressing this limitation, dynamic kinetic resolution emerges as an effective approach in response to the challenge. Notably, since Clayden and Turner's group reported biological dynamic kinetic resolution using enzymes in 2016,[1] only two dynamic kinetic resolutions employing organic catalysts have been published.[2][3] There remains a scope for the development of reactions in this context.

Our group has been consistently dedicated to advancing enantioselective reactions catalyzed by resin-bound peptides.[4] These immobilized peptides offer advantages due to their straightforward synthesis and potential for reusability. In 2005, we successfully developed a resin-supported tripeptide/zinc chloride catalyst system for the direct asymmetric aldol reaction of acetone with aldehydes in aqueous media, achieving as high as 84% ee.[5]

This time, we have successfully extended the application of this aldol reaction to the dynamic kinetic resolution of axially chiral substrates. Through a systematic screening of reaction conditions, we have achieved a significantly high diastereoselectivity (8:1) and improved enantioselectivity (96% ee) for the main isomer. Ongoing efforts are focused on exploring further substrate expansion and potential applications of the obtained products.



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α-イミノエステルの極性転換/ラジカル付加を活用する四級アミノエステル合成

（三重大院工）○伊藤 裕基・溝田 功

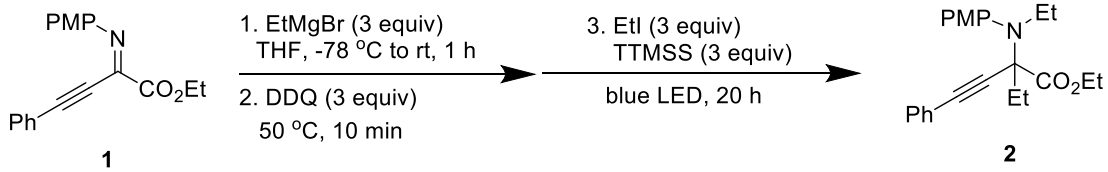
Quaternary Amino Ester Synthesis Utilizing Tandem Umpolung/Radical Addition Reaction of α-Iminoester (*Graduate School of Engineering, Mie University*) ○Yuki Ito, Isao Mizota

We have already reported that the umpolung reaction of α-iminoesters with organometallic reagents proceeded smoothly to give corresponding *N*-alkylated products in good to high yields. In 2023, we also developed the tandem *N*-alkylation/Claisen rearrangement of α-imino allylesters to afford γ,δ-unsaturated quaternary α-amino esters in good to high yield. In this study, we investigated the new type of tandem *N*-alkylation/radical addition reaction to α-iminoester to give the quaternary amino esters.

Keywords : α-Iminoester, Umpolung Reaction, N-Alkylation, Tandem Reaction, Radical Addition

当研究室では、α-イミノエステルに対し有機金属反応剤を用いることで、極性転換反応である *N*-アルキル化が円滑に進行し、対応する *N*-アルキル化体が良好な収率で得られることを見出している。[1-4]今回 α-イミノエステルへの *N*-アルキル化/酸化により調製したイミニウム塩に対し、光照射下で調製したラジカルを付加させることで、四級アミノエステルを合成することに成功したので報告する。

β,γ-アルキニル α-イミノエステル **1** に対し、EtMgBr を 3 当量、THF 溶媒、-78 ℃から室温で反応させ *N*-エチル化を進行させたのち、酸化剤に DDQ を 3 当量用い、50 ℃で反応させイミニウム塩を系内調製した。その後、ヨウ化エチルを TTMSS とともに blue LED 照射下反応させたところ、望みの四級アミノエステル **2** を得ることができた。



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2) I. Mizota, M. Maeda, K. Imoto, M. Shimizu, *Org. Lett.* **2020**, *22*, 3079.
3) I. Mizota, Y. Nakayama, S. Mizutani, S. Terasawa, M. Shimizu, *Org. Lett.* **2021**, *23,* 4168.
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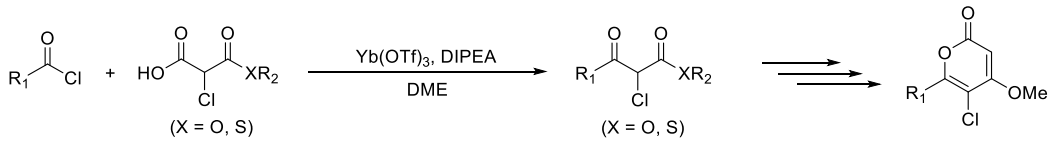
Synthesis of α-chloro-β-ketoesters and chlorine-containing polyketides via decarboxylative condensation of chloromalonic acid half-esters

([1]*The University of Tokyo*) ○Yihao Shi,[1] Kazuaki Kudo[1]

Keywords: Decarboxylative Condensation; α-Chloro-β-ketoesters; Chlorine-containing Polyketides; Ytterbium Triflate

Chlorine is one of the most common heteroatoms found in small-molecule drugs and natural products. In some bioactive compounds, the substitution of hydrogen atom with chlorine profoundly improves their activity and potency. Conventional late-stage chlorination methods with a variety of chlorination reagents such as elemental chlorine, metal chlorides, NBS, and TCCA are well-known reactions. However, these methods are greatly limited by low chemical selectivity, site selectivity, and functional group compatibility. Existing solutions require extra steps for protecting group manipulation, directing group manipulation, harsh reaction conditions, and delivering moderate yields.[1] On the other hand, we have previously demonstrated an effective method for the decarboxylative condensation of malonic acid half-thioester into β-ketothioesters mediated by Grignard reagents, and further iteratively synthesis of polyketides.[2] Taking this finding into account, we envisioned that introducing chlorine atoms at designated sites, and synthesis of inert sites selective chlorinated polyketides, would be feasible by utilizing decarboxylative condensation of chloromalonic acid half-oxyester (Cl-MAHO).

Mediated by $Yb(OTf)_3$, the Cl-MAHO underwent decarboxylative condensation toward 3-phenylpropionyl chloride to afford α-chloro-β-ketoester in 89% yield. Different from precedent magnesium-mediated decarboxylation condensation,[3] this method prevents the metal-halogen exchange on halogen-containing acyl chloride substrates and Cl-MAHO, allowing us to easily obtain α-chloro-β-ketoesters with a variety of functional groups. This method is also suitable for obtaining α-bromo-β-keto ester from bromomalonic acid half-ester. In addition, this $Yb(OTf)_3$ mediated C-C bond formation could be applied to the synthesis of 4-methoxy-5-chloro-2-pyrone in 29% overall yield. This product was successfully derivatized to a variety of potentially biologically active compounds by palladium-catalyzed cross-coupling reactions.



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ジベンゾスベラン骨格を有する官能基化された C_2 対称化合物の合成と有機合成における利用

（早大先進理工）○皆川 有成・柴田 高範

Synthesis of Functionalized C_2 Symmetric Compounds with Dibenzosuberane Skeleton and Their Use in Organic Synthesis

(*School of Advanced Science and Engineering, Waseda University)* ○ Yusei Minagawa, Takanori Shibata

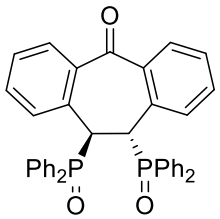
As represented by the axially chiral binaphthyl skeleton, asymmetric skeletons serve as chiral sources for chiral ligands and chiral organocatalysts, and the development of new asymmetric skeletons is crucial for the advancement of asymmetric synthetic chemistry. Therefore, we here investigated the asymmetric synthesis of functionalized C_2 symmetric compounds with a dibenzosuberane skeleton. There have been few examples of asymmetric catalysts and ligands possessing a seven-membered ring as the core skeleton and their use in organic synthesis.

In this research, C_2 symmetric diphosphine oxide **1** and diol **2**, as well as diamine **3**, possessing a dibenzosuberane skeleton, were synthesized. Optical resolution of the racemic compounds was achieved via chiral HPLC column or crystallization of their diastereomeric salts. Furthermore, we evaluated the synthesized optically active compounds as chiral catalysts or chiral ligand.

Keywords : Dibenzosuberane Skeleton, 7-Membered Ring Compound, Chiral Catalyst, Chiral Ligand

軸不斉ビナフチル骨格に代表されるように、キラル骨格は不斉配位子、不斉有機触媒における不斉源であり、新規なキラル骨格の開発は不斉合成化学の発展において重要である。そこで今回我々は、ジベンゾスベラン骨格を有する官能基化された C_2 対称化合物の不斉合成を目指した。これまで、七員環を基本骨格とする不斉触媒および配位子の合成や有機合成への応用は報告例が少ない。

本研究ではジベンゾスベラン骨格を有する C_2 対称のジホスフィンオキシド **1** およびジオール **2**、ジアミン **3** を合成し、キラルカラムを用いた HPLC による光学分割、あるいはジアステレオマー塩の結晶化による光学分割を達成した。さらに、合成した化合物を不斉触媒または不斉配位子として有機合成に応用し、その不斉骨格の評価を行った。



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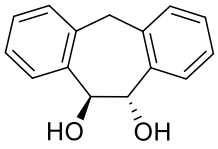

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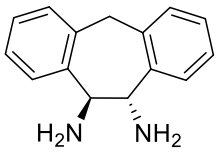

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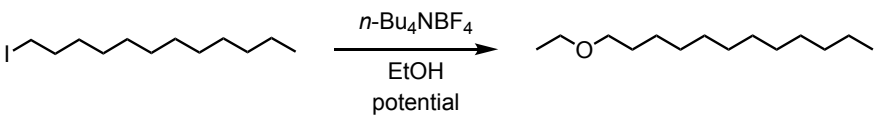
外部電場中におけるハロゲン化アルキルのアルコキシ化反応に関する検討

（長崎大院工）○我毛 麻人・小野寺 玄・田原 弘宣・尾辻 太一・福田 勉・木村 正成
Study on Alkoxylation of Alkyl Halide under External Electric Field (*Graduate School of Engineering, Nagasaki University*) ○Asato Gake, Gen Onodera, Hironobu Tahara, Taichi Otsuji, Tsutomu Fukuda, Masanari Kimura

In organic synthesis, Lewis acids are often used as catalysts to reduce the activation energy by inducing an electric polarization of organic molecules. However, Lewis acids are unstable under air and require special handling techniques. In addition, they must be removed after the reaction. On the other hand, if an external electric field could be used to induce an electric polarization instead of a Lewis acid catalyst, it would be a simple and useful “catalyst” for organic synthesis. In this case, there is no concern about stability under air, and the “catalyst” can be removed by turning off the switch. Actually, an organic synthesis using an external electric field was reported in 2016.[1)] However, it is difficult to use this methodology generally in organic synthesis, because it requires a special reaction field. In this system, starting materials should be supported on electrodes. We have investigated the alkoxylation of alkyl halide under an external electric field in order to construct a more versatile reaction system. We found that the reaction of 1-iodododecane with ethanol by using *n*-Bu_4NBF_4 as an electrolyte under voltage application proceeded to give 1-ethoxydodecane in 8% yield. A longer voltage-application time increased the yield of the product to 19%. This substitution reaction did not proceed in the cases of the polarity reversal and without electrodes. These results suggest that the voltage application is essential in this reaction system.

有機合成反応では，有機分子の電気分極を誘導することで活性化エネルギーが低下することが知られており，そのための触媒としてルイス酸がしばしば用いられる。しかし，ルイス酸は空気中で不安定なことが多く，取り扱いには専門的な技術が必要とされる。また，反応終了後には除去する必要がある。一方，外部電場による電気分極の誘導をルイス酸のように”触媒”として利用することができれば，空気中での安定性を気にする必要もなく，スイッチを切れば除去できる簡便な”触媒”となると考えた。実際に，外部電場を活用した有機合成反応が 2016 年に報告されている [1)]。しかし，この反応では電極上に出発物質を担持する限定的な反応場が用いられており，有機合成に汎用的に用いることは難しい。そこで，我々は外部電場を用いてより汎用性の高い反応系を構築するべく，外部電場中におけるハロゲン化アルキルのアルコキシ化反応について種々検討した。

電解質として *n*-Bu_4NBF_4 を溶解させたエタノール中に 1-ヨードドデカンを加え，電圧を印加することで置換反応が進行し，1-エトキシドデカンが収率 8%で得られた。さらに，電圧印加時間を伸ばすことで目的物の生成量は 19%まで向上した。この置換反応は，電極の極性を反転させた場合や電極を使用しない場合には進行しないことから，電圧の印加が必須である。



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・ケトンからの直接的チオアミド合成法の開発

Direct Synthesis of Thioamide from Ketones. (近大院)　○富家　唯深・兵藤　憲吾
(*Faculty of Science and Engineering, Kindai University*) ○ Ishin Tomiya, Kengo Hyodo

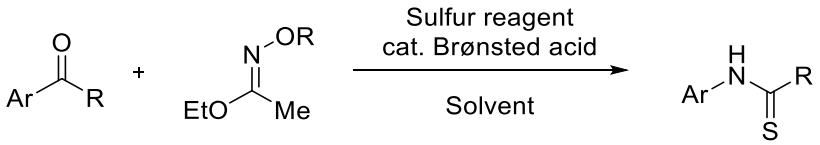
Syntheses of organic compounds having a sulfur heteroatom have been in the interest of many groups. This has been performed mainly through the reactions of thionating agents, the important ones of which is phosphorus decasulfide and Lawesson's reagent etc. [1]

On the other hand, in our laboratory, we have synthesized secondary amides directly and catalytically from ketones using relatively stable oxime reagents as equivalents of unstable and explosive hydroxylamine derivatives. [2] In this study, we will apply this reaction to thioamide synthesis by using various sulfur sources instead of water. We expected the reaction would be proceeded *via* the addition of sulfur to nitrilium ion and sulfur. Under this strategy, we will attempt direct and catalytic thioamide synthesis and investigate the reaction conditions. In this presentation, we will introduce the details.

Keywords : Thioamide, Beckmann rearrangement, Transoximation.

硫黄原子を有する有機化合物の合成は，現在多くの関心を集めている．五硫化二リンやローソン試薬は，主に S 化剤としてチオアミド合成などの反応に用いられており，現在もなお重要な試薬である．[1]

一方で, 当研究室ではこれまでに不安定で爆発性があるヒドロキシルアミン誘導体の等価体として，比較的安定なオキシム試薬を用いて，ケトンから直接的かつ触媒的に二級アミドを合成した．[2] この反応ではオキシム試薬からケトンへのオキシム転移及びベックマン転位より生じたニトリリウムイオンに対して, 水が付加反応を起こすことによりアミドが生成する．本研究では，S 源となる試薬を求核剤として求核付加反応を起こすことで, 直接的かつ触媒的にチオアミド合成を行えるのではないかと考えた．ケトンから直接的にチオアミドを合成する方法はほとんどなく，私たちはこの合成戦略のもと，反応条件を種々検討した．



Scheme 1. 脱アセチル型アミノ化反応を応用したチオアミド合成

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2) K. Hyodo, G. Hasegawa, N. Oishi, K. Kuroda, K. Uchida, *J. Org. Chem.* **2018**, *83,* 13080–13087.

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置換型シクロブタノン類の合成と γ-アミノ酪酸エステル類への応用

(近大院)　○武　宇浩・富家　唯深・兵藤　憲吾

Synthesis of Substituted Cyclobutanones and Application to γ-aminobutyric acid esters

(*Graduate school of Science and Engineering, Kindai University*) ○Yuhao Wu, Ishin Tomiya, Kengo Hyodo

γ-Aminobutyric acid (commonly known as GABA, figure 1) plays a role as an inhibitory neurotransmitter that relieves stress, calms excitement, and induces relaxation. γ-Aminobutyric acid appears to be a ring-opened product of cyclobutanone introduced with nitrogen. Previous research in our laboratory reported that an amide was created by introducing nitrogen into a ketone using an original oxime reactant [1),2)] In this research, we established an efficient synthesis method for cyclobutanones, synthesized various cyclobutanones, and developed ring-opening reactions using them (Figure 2).

In the presence of an acid catalyst, an oxime transfer reaction occurs between a ketone and an oxime reagent, followed by a Beckmann rearrangement, and finally, methanol added causes alcoholysis of the nitrilium ions generated after the Beckmann rearrangement. γ-aminobutyric acid esters were obtained.

Keywords: Cyclobutanone, [2+2] cyclization, Ring-opening reaction, γ-Aminobutyric acid.

γ-アミノ酪酸 (通称 GABA, figure 1)は抑制系の神経伝達物質として，ストレスを和らげ，興奮を鎮め，リラックスをもたらすなどの役割を果たす. γ-アミノ酪酸はシクロブタノンの窒素導入し，開環した生成物と見られる．当研究室の先行研究は，オリジナルのオキシム反応剤 [1)]を使い，ケトンに窒素を導入し，アミドができたことを報告した．[2)]今回の研究ではシクロブタノン類を効率的な合成手法の確立と様々なシクロブタノン類の合成を行い，それらを用いた開環反応の開発を実施した (Figure 2).

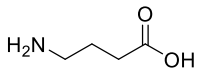

Figure 1. γ-アミノ酪酸の構造

酸触媒存在下，ケトンとオキシム試薬との間でオキシム転移反応を起こし，その後続けてベックマン転位，最後に添加したメタノールにより，ベックマン転位後に生じたニトリリウムイオンが加アルコール分解を起こすことで，γ-アミノ酪酸エステル類を得られた.

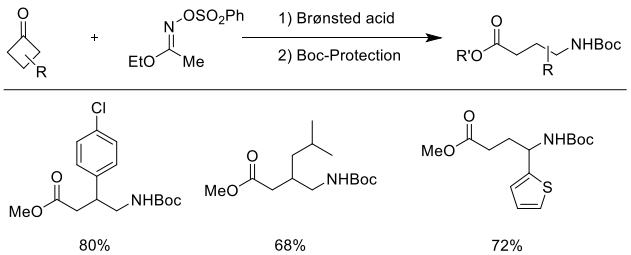

Figure 2. シクロブタノン類からの γ-アミノ酪酸エステル類の合成例

1) K. Hyodo, K. Togashi, N. Oishi, G. Hasegawa, K. Uchida, *Org. Lett.* **2017**, *19*, 3005-3008.
2) K. Hyodo, G. Hasegawa, N. Oishi, K. Kuroda, K. Uchida, *J. Org. Chem.* **2018**, 83, 13080-13087.

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マイクロフローリアクター内における迅速な電気化学的チオール-エンクリック反応の開発

（東海大理化 [1]，東海大先進生命研 [2]）○山本 駆流 [1]・荒井 堅太 [1,2]
Development of rapid electrochemical thiol-ene click reaction in a microfluidic reactor ([1]*Department of Chemistry, School of Science, Tokai University,* [2]*Institute of Advanced Biosciences, Tokai University*) ○Kakeru Yamamoto,[1] Kenta Arai[1,2]

Thiol-ene click reaction is an oxidative radical addition that occurs between thiols and olefins. Although this reaction, which is initiated by one-electron oxidation of a thiol, allows selective bimolecular coupling, the use of radical initiators and photocatalysts is unfavorable in terms of synthetic cost and green chemistry. Electrolytic microreactor (ECMR) has a flow channel sandwiched between electrodes and enables rapid and efficient electrolysis of organic compounds owing to the high specific surface area and short diffusion distance in the flow channel.[1] Applying the electrolysis by ECMR to thioradical generation, a low-cost and clean radical addition could be developed (Fig. 1).

When the electrochemical flow reaction of mixture of thiol **1** and olefin **2** was firstly conducted as a model reaction, sulfide **3** was obtained in up to 67% isolated yield within 5 min under optimal conditions. In the presentation, we will discuss the substrate scope of this reaction system and its applicability to chemical modification of biomolecules.
Keywords : Catalyst; Telluride; Peptide; Thiol; Oxidation

チオール-エンクリック反応はチオールおよびオレフィン間の酸化的ラジカル付加反応である。チオールの一電子酸化反応によって開始される本反応は、選択的な二分子間カップリングを可能にするが、ラジカル開始剤や光触媒の使用は、合成コストと環境科学の観点から改善が求められている。電解マイクロリアクター(ECMR)はフローチャネルが金属電極に挟まれた構造をもち、流路内の高い比表面積と短い拡散距離により迅速で効率的な有機電解反応を可能にする。ECMR による電解反応をチオラジカル生成に応用することで、低コストでクリーンなラジカル付加反応を開発できるものと考えた（Fig. 1）。

はじめにモデル反応として、チオール **1** とオレフィン **2** の混合溶液の電解フロー反応を行ったところ、最適条件下において反応時間 5 分以内でスルフィド **3** を最大単離収率 67%で得ることができた。発表では、本反応の基質一般性および生体分子の化学修飾への応用可能性についても議論する。

[1] *ChemistryOpen* **2014**, 3, 23–28.

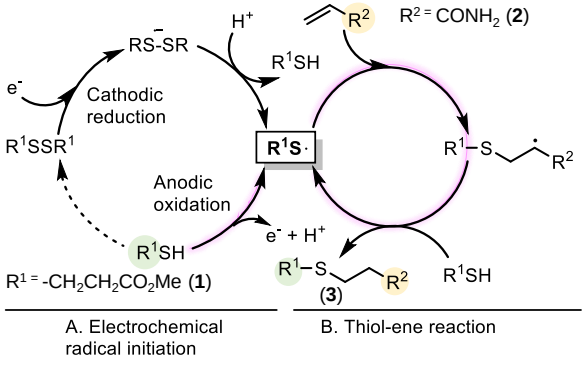

Fig. 1: Proposed mechanism of electrochemical radical initiation for thiol-ene reaction of thiol **1** and olefin **2**.

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グリーンものづくり：官能基評価キット合成における非定常フロー反応条件最適化法の開発

（静岡大工）○杉村 茂紀・佐藤 浩平・鳴海 哲夫・間瀬 暢之

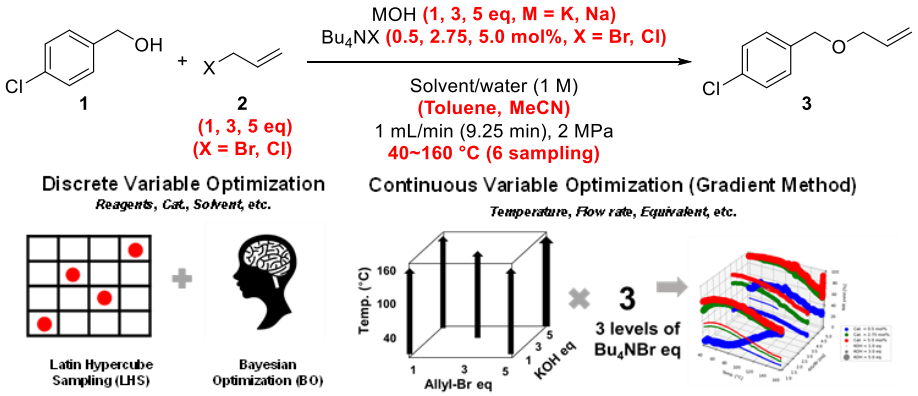
Green Manufacturing: Reaction Condition Optimization for the Pseudo-Steady Flow Synthesis of the Functional Group Evaluation Kit (*Faculty of Engineering, Shizuoka University*)

○Tomoki Sugimura, Kohei Sato, Tetsuo Narumi, Nobuyuki Mase

The Functional Group Evaluation (FGE) kit is a valuable set of compounds for comprehensive reaction analysis. Some compounds, however, face supply issues, requiring efficient synthetic routes. We herein describe the flow synthesis and reaction optimization for allyl 4-chlorobenzyl ether. A combination of Latin hypercube sampling and Bayesian optimization was applied to discrete variable optimization, identifying optimal conditions with 83% probability from 8 of 16 experiments. For continuous variables (equivalents of Allyl-Br, KOH, Bu_4NBr), we set three levels and applied our developed gradient method for temperature, comprehensively collected data from 15 experiments. We created a regression model based on the obtained data to predict the conditions for a yield greater than 99%, minimizing the usage of reagents.

Keywords : Green manufacturing; Flow chemistry; Discrete variable optimization; Functional group evaluation kit; Bayesian optimization

官能基評価（FGE）キットは、反応に対して官能基が与える包括的な情報を収集するために、大嶋らのグループによって開発された有用な化合物群である [1]。しかし、一部の化合物は供給面に課題があり、効率的合成法の開発が求められている。そこで、これら化合物の 1 つであるアリル 4-クロロベンジルエーテルのフロー合成と迅速反応条件最適化に取り組んだ。離散型変数である試薬類と溶媒の最適化は、ラテン超方格法による初期検討条件の設定と、続くベイズ最適化を組み合わせて実施した。この結果、全 16 通りの組み合わせの中から 8 実験を実施すれば 83%の確率で最適条件を特定できることが明らかになった。連続型変数である当量（Allyl-Br、KOH、Bu_4NBr）について 3 水準を設定し、温度に対して我々の開発したグラジエント法を適用した [2]。全 15 実験を実施し、データを網羅的に収集した。得られたデータを基に回帰モデルを作成し、使用試薬が最小となる収率＞99%となる条件を予測した。



1) Ohshima, T. *et al., Bull. Chem. Soc. Jpn.* **2023**, *96,* 465. 2) Mase, N. *et al.* 2022 Asia-Pacific Microwave Conference (APMC), **2022**, 169.

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ファインバブル有機化学：微細孔方式による高粘性液体の常圧気相—液相反応の開発

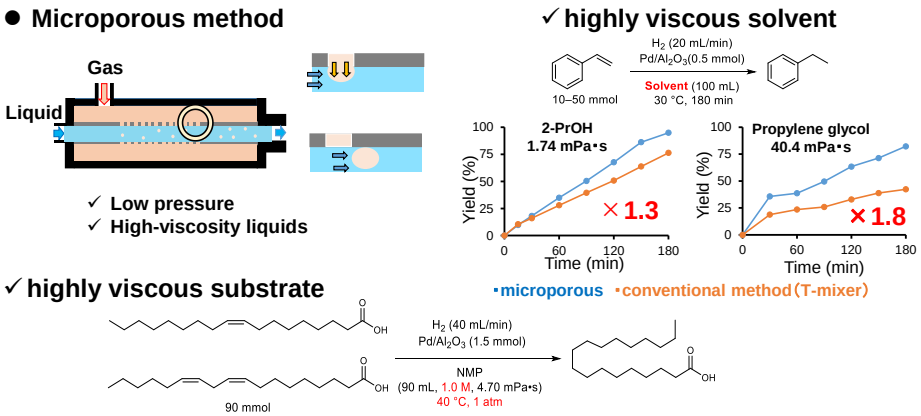
(静岡大工[1]・静岡大院総[2]) ○盛田 鵬人[1]・櫻井 大斗[2]・佐藤 浩平[1,2]・鳴海 哲夫[1,2]・間瀬 暢之[1,2]

Fine Bubble Organic Chemistry: Development of Microporous-Mediated Gas-Liquid Phase Reactions of Highly Viscous Liquids Under Atmospheric Pressure ([1]*Shizuoka University,* [2]*Graduate School of Integrated Science and Technology, Shizuoka University*) ○Houto Morita,[1] Hiroto Sakurai,[2] Kohei Sato,[1,2] Tetsuo Narumi,[1,2] Nobuyuki Mase[1,2]

Fine bubbles (FB), with a diameter of less than 100 μm, offer better gas solubility than regular bubbles, and their applicability to gas-liquid reactions has been demonstrated. Herein, we describe FB generation by the microporous method, which does not require high-pressure components and is suitable for high-viscosity liquids. This method was successfully applied to catalytic hydrogenations even in high-viscosity solvents. The developed technique also enabled efficient hydrogenation of highly viscous substrates, namely oleic acid and linoleic acid, affording the desired products at 40 °C and ambient pressure.

Keywords : Fine bubble; Microbubble; Ultra-fine bubble; Microporous; Catalytic hydrogenation

ファインバブル（FB）は直径 100 μm 以下の気泡の総称であり、通常の気泡と比較して優れた気体溶解性を示す。我々は気—液反応において、気体を FB として供給することで反応性が向上することを示してきた[1-2]。しかし、FB 発生の原理上、加圧が必要であり高粘性液体への適用は制限されてきた。本研究では、高圧部を必要としない FB 発生方式として微細孔方式を採用し、気—液反応に適用した。微細孔方式では微細孔膜外側から気体を滲出させ、膜内側を流れる液体の剪断力による押出しで FB を常圧で発生できる。本手法を接触水素化反応に適用したところ反応は円滑に進行し、溶媒の粘度上昇に伴う反応性の低下は認められなかった。本手法を高粘性基質であるオレイン酸およびリノール酸の水素化反応に適用し、40 ℃・常圧で生成物を得た。



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2) Iio, T.; Nagai, K.; Kozuka, T.; Sammi, A. M; Sato, K.; Narumi, T.; Mase, N.; *Synlett* **2020**, *31*, 1919.

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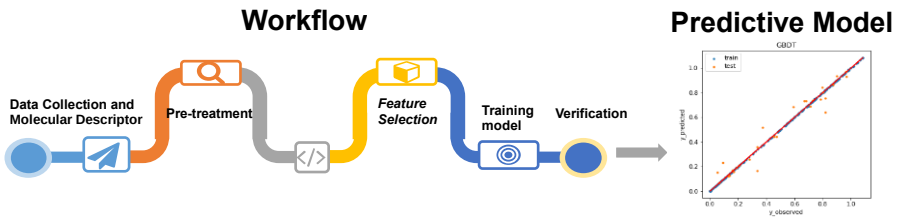
Microwave Flow Chemistry: Estimation Dielectric Loss Tangent Using Machines Learning

(*Graduate School of Integrated Science and Technology, Shizuoka University*)
○Aisi Azmi, Kohei Sato, Tetsuo Narumi, Nobuyuki Mase
Keywords: Flow Chemistry, Microwave, Machine Learning, Dielectric Loss Tangent, Molecular Descriptors

Microwave heating is an effective and unique method, offering advantages such as accelerated reactions and selective heating of materials. However, setting the operating parameters can be challenging due to the variation in heating efficiency, which depends on the physical properties of the target material. One crucial parameter is the dielectric loss tangent, which characterizes a material's ability to convert microwave energy into heat. Despite its importance, experimentally measuring the dielectric loss tangent is technical, as it varies with compounds, temperature, and frequency. Machine learning (ML) techniques have great potential in various scientific and engineering applications.[1,2] They can effectively capture complicated patterns and relationships in large datasets, thus enabling the development of predictive models.[3] Considering this potential, we describe a machine-learning method to estimate the dielectric loss tangent.

This study used molecular descriptors to represent chemicals and collected data on the dielectric loss tangent from literature. The dataset was divided into training and testing data. The proposed model was trained using different algorithms, and the best results were obtained with nonlinear Gradient-boosted decision trees (GBDT) algorithms, which produced excellent performance with significant metrics and the ability to capture complex non-linear relationships in data. This allows GBDT to capture intricate patterns and complexities within the data that linear models might miss.[4] The model performance shows that the predicted tan d values are in good agreement with the experimental ones, with the root mean square error (RMS) being 0.002 (R^2=0.99) and 0.06 (R^2=0.95) for the test set. Thus, the present model is more useful in predicting compounds' dielectric loss tangent values.



1) Horikoshi, S., Serpone, N. *Chem. Rec*. **2019**, *19*, 118; 2) Michael, G., *et al. Chem. Sci.* **2021**, *12*, 11473; 3) Schmidt, J., *et al. npj Comput. Mater.* **2019**, *5*, 83; 4) Gonzalez, S. C., *et al. Energy Fuels* **2021**, *35*, 9332.

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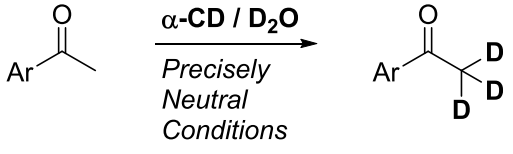
シクロデキストリン重水溶液を用いたアシル基水素の重水素交換反応

（和歌山高専 [1]）○河地 貴利 [1]・西川 侑亜 [1]
Hydrogen/deuterium exchange of acyl α-hydrogens using cyclodextrin D_2O solutions ([1]*Department of Applied Chemistry and Biochemistry, National Institute of Technology, Wakayama College*) ○Takatoshi Kawaji,[1] Yuua Nishikawa[1]

The development of a method to exchange specific hydrogen atoms in biomolecules into its isotopes (^{2}H = D, ^{3}H = T) under mild conditions will contribute to medicinal chemistry and life science research. Usually, hydrogen/deuterium (H/D) exchange of the α-position hydrogens of the acyl group proceeds efficiently via enol or enolate in D_2O with an acid or base catalyst. On the other hand, the H/D exchange on biomolecules that have vulnerable sites for an acids and bases have to be conducted under precisely neutral conditions. In this study, we used a D_2O solution of α-cyclodextrin (α-CD) to discover the H/D exchange reaction of acetyl methyl hydrogens under neutral and normal pressure conditions without the addition of acid, base or heavy metal catalysts. When an acetophenone (33 mM) D_2O solution was kept at 50°C and the deuteration rate of acetyl methyl hydrogen was followed by integral of methyl signals in ^{1}H NMR spectra, the reaction rate was significantly accelerated by the coexistence of α-CD (10–100 mol%).
Keywords：Hydrogen/Deuterium Exchange, Cyclodextrin, Deuterium Oxide, Acyl Group

生体分子中の特定水素原子を穏和な条件下に水素同位体 (^{2}H = D, ^{3}H = T) へ交換する手法の開発は薬化学および生命科学研究に寄与する。通常、アシル基α-位水素の水素/重水素 (H/D) 交換は、D_2O 中、酸または塩基触媒の作用によりエノールまたはエノラートを経由して効率的に進行する。一方、酸や塩基に脆弱な部位を持つ生体分子に対しては真に中性の条件下に H/D 交換反応を進行させる必要があるが、中性かつ穏和な温度・圧力下でのアシル基水素 H/D 交換反応はこれまでに殆ど知られていない [1)]。本研究では、α-シクロデキストリン (α-CD) の D_2O 溶液を用い、酸塩基および重金属触媒を添加しない中性・常圧下でのアセチルメチル水素の H/D 交換反応を見出した。

アセトフェノン (33 mM) D_2O 溶液を 50°C に保持し、アセチルメチル水素の重水素化率を ^{1}H NMR スペクトルのメチルシグナル積分値を用いて追跡したところ、α-CD を共存 (10－100 mol%) させることによって反応速度の有意な加速が認められた。



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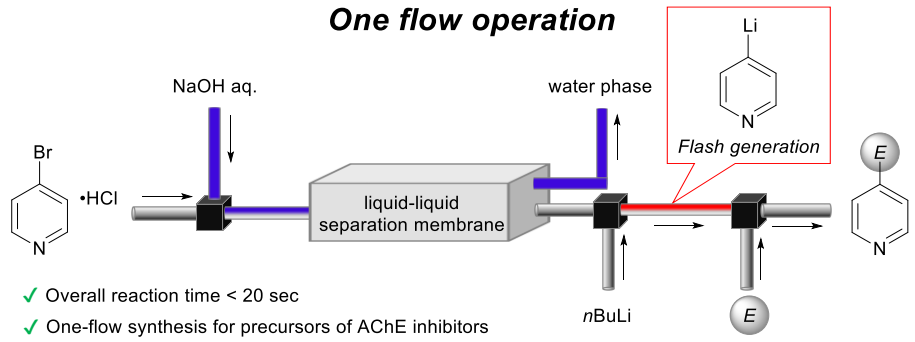
集積型リアクターを用いたピリジン塩酸塩の脱塩と禁水反応の単工程化

（北大院理[1]・AGC 株式会社[2]・十全化学株式会社[3]）○早乙女広樹[1,2]・木室佑亮[1,3]・芦刈洋祐[1]・永木愛一郎[1]
Single-process desalting of pyridine hydrochloride and water-forbidden reactions using integrated reactors (*Graduate School of Science, Hokkaido University*[1], *AGC Inc.*[2], *Juzen Chemical Co*[3]) ○Hiroki Soutome, Yusuke Kimuro, Yosuke Ashikari, and Aiichiro Nagaki

Commercially available low-stability compounds often require stabilizers or exist as salts. Pyridine derivatives, for instance, are sold as hydrochloride salts due to oligomerization. In the case of water-prohibited reactions, a pretreatment process of desalting followed by separation, dehydration, and evaporation is necessary, but decomposition of the unstable desalted compounds is feared in this process. In this study, we successfully integrated flow microreactors and a liquid-liquid separator to perform desalting, halogen-lithium exchange reaction, and subsequent reaction with electrophiles in a single-flow, using 4-bromopyridine hydrochloride as a model. This one-flow system allowed skipping the drying step, enabling the reaction completed in less than 20 seconds. The Suzuki coupling reaction was allowed to be integrated, yielding the pharmaceutical precursor.
Keywords : Flow microreactor; One-flow operation; Flash chemistry; Bromopyridine hydrochloride; Liquid-liquid separate membrane

不安定化合物の中には、安定化剤の添加や塩の状態で保存・市販されるものが珍しくない。例えば、ピリジン系化合物には多量化などの副反応を抑制するため塩酸塩として市販されるものがあり、反応前には塩基性水溶液による脱塩処理が必要である。特に禁水反応を行う場合は、前処理として脱塩後に分液・脱水・乾固といった水分除去の工程が必須だが、この工程の間に不安定な脱塩体の分解が懸念される。

今回我々は、フローマイクロリアクターと液－液分離装置を集積化し、4-ブロモピリジン塩酸塩をモデルとして、脱塩と、禁水反応であるハロゲン－リチウム交換反応および続く求電子剤との反応の単工程化に成功した[1]。この集積化システムでは有機溶媒の脱水が不要であり、全工程を 20 秒以内に完結可能である。さらにこの集積反応によりボロン酸エステルを合成し、連続的に鈴木カップリング反応を行うことにより医薬品前駆体の高速合成を実証した。



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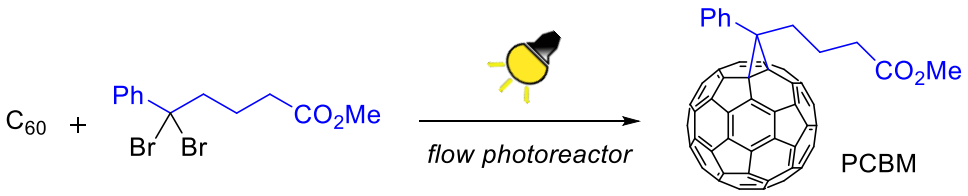
光フロー法における PCBM 合成の検討

(大阪技術研[1]・大阪工大[2]) ○隅野 修平[1]・田中 雄也[2]・村田 理尚[2]・松元 深[1]・岩井 利之[1]・伊藤 貴敏[1]
PCBM Synthesis by using Flow Photoreactor ([1]*ORIST*, [2]*Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology*) ○Shuhei Sumino,[1] Yuya Tanaka,[2] Michihisa Murata,[2] Fukashi Matsumoto,[1] Toshiyuki Iwai,[1] Takatoshi Ito[1]

PCBM, a fullerene derivative, is used as an acceptor molecule for organic thin-film solar cells. However, reports on the synthesis methods of PCBM are limited, and conventional methods often result in low yields. Recently, we reported that PCBM can be obtained in high yield by discovering a photosynthetic method. In this paper, we report on the results of our investigations aimed to high yields by using flow photo system.
Keywords : Fullerene; PCBM; Photo Reaction; Flow Reaction

炭素 60 個からなるフラーレンは電気伝導性、熱伝導性、などの点において優れた特性を有する次世代の炭素素材として注目されており、さらにフラーレンを修飾したフラーレン誘導体は有機薄膜太陽電池のアクセプター材料として注目されている。代表格である $PC_{61}BM$ ([6,6]-Phenyl-C_{61}-Butyric Acid Methyl Ester) の合成法は、Wudl らの超高温条件による手法[1]や Jin らの過剰のマンガンなどの金属と反応させる手法[2]がある。また、我々が見出した硫黄イリドを用いる合成法[3]もあるが、いずれも収率面に課題が残っている。

最近我々は、フラーレンの光応答性に注目し、ジブロマイドを反応基質とした PCBM を含むメタノフラーレンの光合成を達成した[4]。本光合成法を PCBM の効率的合成法と昇華すべく光フロー化への適応検討を行った。発表では、その結果について詳細を述べる。



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2) W. Si, X. Zhang, S. Lu, T. Yasuda, N. Asao, L. Han, Y. Yamamoto, T. Jin, *Sci. Rep.* **2015**, *5*, 13920.
3) T. Ito, T. Iwai, F. Matsumoto, K. Hida, K. Moriwaki, Y. Takao, T. Mizuno, T. Ohno, *Synlett* **2013**, *24*, 1988−1992.
4) S. Sumino, F. Matsumoto, T. Iwai, T. Ito, *J. Org. Chem.* **2021**, *86*, 8500-8507.

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高揮発性有機化合物のフロー反応への適用探索

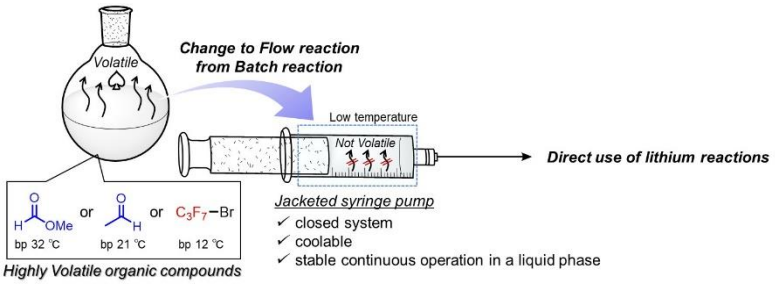
（セントラル硝子株式会社[1]・北大院理[2]）○牟田 健祐[1]・岡本 和紘[2]・永木 愛一郎[2]
Exploring the Application of Highly Volatile Organic Compounds in Flow Reactions ([1]*Central Glass Co., Ltd.*, [2]*Graduate school of science, Hokkaido University*) ○Kensuke Muta,[1] Kazuhiro Okamoto,[2] Aiichiro Nagaki[2]

Low molecular weight substances such as volatile organic compounds (VOCs) play crucial roles for highly atom-economy in organic synthesis. Furthermore, they are easily purified through distillation or other methods due to their volatile nature, making them highly favorable from an industrial standpoint. However, incorporating VOCs into the reactions contingent upon meticulous residence time control is a formidable challenge due to their too high volatility even at room temperature. We found that VOCs with boiling points (bp) near or below room temperature were successfully applied to the fast flow reactions with organolithium compounds using a jacketed syringe pump.

We initially adopted methyl formate (bp 32°C) as a model substrate, which enabled the formylation of organolithium species using a jacketed syringe pump in flow. This flow system was successfully delivered to the continuous operation for over 30 minutes. Moreover, this methodology was successfully expanded to the application of acetaldehyde (bp 21 °C) and heptafluoropropyl bromide (bp 12 °C).

Keywords： Flow microreactor; Volatile organic compounds; Organolithium reagents

揮発性有機化合物 (VOCs) のような低分子量化合物は、その原子効率の高さから有機合成において極めて重要な役割を果たし、さらに蒸留等の方法で容易に精製可能であるため、工業プロセス的観点からも有用性は高い。しかしながら、室温付近に沸点を持つ VOCs は、その揮発性の高さからフロー条件下で精密な反応を行うことは困難であった。我々は冷却ジャケット付きシリンジポンプを使用することで、室温付近またはそれ以下の沸点をもつ VOCs を有機リチウムとの高速反応に適用可能であることを見出した。



我々はまずモデル VOCs としてギ酸メチル (沸点32℃) を採用し、ジャケット付きシリンジポンプを用い、フロー条件下、有機リチウム種のホルミル化反応に適用し、30分間の連続運転も可能であった。また本手法は、より低沸点でVOCsあるアセトアルデヒド (沸点21℃)、ヘプタフルオロプロピルブロミド (沸点12℃) に適用拡大できた。

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$NaHSO_4/SiO_2$ 存在下マイクロ波照射による β−ジカルボニル類のアルキル化反応

（日大理工）○熊田　佳祐・早川　麻美子・鈴木　眞平・青山　忠

Alkylation of β-dicarbonyl compounds by microwave irradiation in the presence of $NaHSO_4/SiO_2$ (*College of Science and Technology, Nihon University*)○Keisuke Kumada, Mamiko Hayakawa, Shinpei Suzuki, Tadashi Aoyama

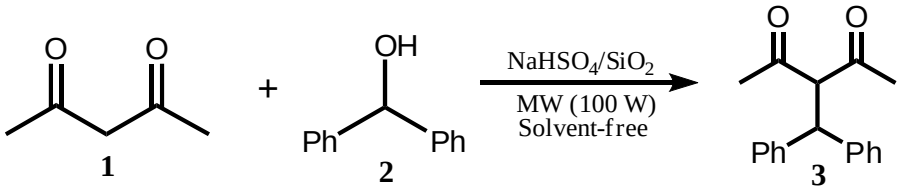
Recently microwave assisted organic synthesis have been taken much attention. Notable differences between conventional and microwave assisted organic synthesis are: conventional organic synthesis is carried out by conductive heating with external heat sources such as oil baths whereas microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules. Thus, microwave assisted organic synthesis can reduce a reaction time dramatically and allow solvent-free synthesis. Recently we have reported alkylation by using acetyl acetone and benzylic alcohols in the presence of Silica-gel supported sodium hydrogen sulfate in dichloroethane. In this presentation we introduce an alkylation of β-dicarbonyls using MW in the absence of solvents (Scheme).

For example, 3-(benzhydryl)pentane-2,4-dione **3** was obtained at 99 % by adding $NaHSO_4/SiO_2$ (1.0 g) to a mixture of acetylacetone **1** (6 mmol) and diphenylmethanol **2** (2 mmol) and microwaving at 100 W output until 60 °C.

Keywords : Alkylation, Alcohol, Microwave, Solid acid, Solvent free

マイクロ波(MW)を用いた有機合成反応は、外壁からの熱伝導により徐々に内部が加熱される外部加熱とは異なり、容器内の物質を直接加熱するため反応時間の短縮が可能となり、近年では多くの反応が MW を用いて行われている。先に我々は、シリカゲル担持硫酸水素ナトリウム($NaHSO_4/SiO_2$)存在下、アルコールを用いた β-ジカルボニル類の α-位アルキル化が効率的に進行することを報告した[1]。そこで、本研究では $NaHSO_4/SiO_2$ 存在下、無溶媒中マイクロ波を照射することでより簡便な β-ジカルボニル類の α-位アルキル化を検討した(Scheme)。

例えば、アセチルアセトン **1**（6 mmol）とジフェニルメタノール **2**（2 mmol）の混合液に $NaHSO_4/SiO_2$（1.0 g）を加え、出力 100 W で 60 ℃になるまでマイクロ波を照射したところ 3-(ベンズヒドリル)ペンタン-2,4-ジオン **3** が 99 %で得られた。同様の手法で、ジフェニルメタノール類を用いた反応では 90～99 %の収率で対応するアルキル化化合物が得られた。また、1-フェニルエタノール類を用いた反応では 69～97 %の収率で対応するアルキル化化合物が得られた。



1　**2**　**3**

1)　T. Aoyama, S.Miyota, T. Takido, K. kodomri, *Synlett* **2011**, *20*, 2971-2976

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マイクロ波を利用したエステル・アミドの簡便合成とその反応促進効果に関する考察

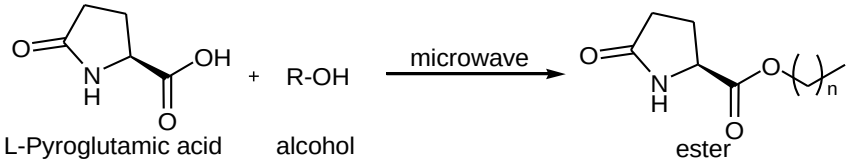
（関東学院大院工[1]） ○荒井 りこ[1]・飯田 博一[1]
Synthesis of Esters and Amids under Microwave Irradiation and Investigation of Their Reaction-Promoting Effects ([1]*Graduate School of Engineering, Kanto Gakuin University*) ○ Riko Arai,[1] Hirokazu Iida[1]

Microwaves possess several characteristics, including higher heating efficiency than conventional heating such us oil baths and the ability to heat the target substance selectively even if the solution consists of mixed components. It is also thought microwaves have a reaction-promoting effect that is not found in conventional heating. Even though it had been studied for many years, the details haven't been clarified yet. In this study, we investigated short-time synthesis of esterification and amidation reactions while microwave irradiation without catalyst and/or solvent. In addition, we investigated the effects that accelerate reactions by comparison the reaction conditions using a low-temperature microwave device.

In the esterification, we performed the reactions between L-pyroglutamic acid and alcohols under microwave irradiation. The reaction progress was found according to shortening the chain length of the alcohol to yield corresponding ester up to 93%.

Keywords : Reaction-promoting effects; Esterification; Amidation; No catalysts and solvents reaction

マイクロ波にはいくつかの特徴があり、オイルバス等を用いた従来加熱より加熱効率が高いこと、溶液が混合成分で構成されている場合でも目的物質への選択的加熱が可能であることなどが挙げられる。また通常加熱にはない非熱的な反応促進効果があるとされ、長年研究が行われているが、詳細は未だ解明されていない。本研究ではエステル化やアミド化反応において無触媒・無溶媒でマイクロ波照射を行い、短時間での合成を検討した。また低温マイクロ波装置を用いて反応条件を比較し、それに基づき反応促進効果の本質について考察を行った。L-ピログルタミン酸のアルコール溶液にマイクロ波を 200 W、150℃で 60 分照射してエステル化を試みた。アルコールの鎖長を短くしながら反応進行を比較したところ、使用したアルコールがヘキサノールの時にエステルは最高収率 93%で得られた。



L-Pyroglutamic acid　alcohol　ester

Entry	alcohol	ester	yield
1	R=$C_{12}H_{25}$ (Dodecanol)	n=11	84%
2	R=C_8H_{17} (Octanol)	n=7	92%
3	R=C_6H_{13} (Hexanol)	n=5	93%

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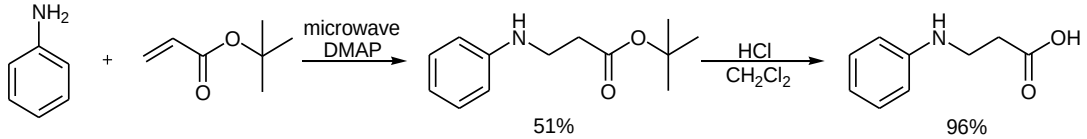
マイクロ波照射法を用いた４-フェニル酪酸等の簡便な合成法の検討

（関東学院大院工[1]・理工[2]）○高橋 朱音[1]・酒井 美佳[2]・都藤 藍[2]・飯田 博一[1]
A Simple Synthesis of 4-Phenylbutanoic Acid and Related Compounds using Microwave Irradiation ([1]*Graduate School of Engineering, Kanto Gakuin University*, [2]*College of Science and Engineering, Kanto Gakuin University*) ○Akane Takahashi,[1] Mika Sakai,[2] Ai Tsudo,[2] Hirokazu Iida[1]

Microwaves are used in the synthesis of pharmaceuticals and cosmetics. Microwave irradiation method does not require heat conduction and directly heats reactants or reaction solvents, so it possesses advantages to perform rapid internal heating and easy temperature control. 4-Phenylbutanoic acid is a type of chemical chaperone and is known to prevent protein aggregation, which is one of the causes of neurodegenerative diseases. 4-PBA and its analogues have been suggested to promote plant growth. In this study, we investigated a simple method for the synthesis of 4-PBA, its derivatives, and analogues by using microwave irradiation reactions such as Friedel-Crafts reaction and Michael addition. In addition, we investigated the reaction using low-temperature microwave device to know whether reactions proceeded a heating effect or a microwave effect.
Keywords : microwave irradiation; 4-phenylbutanoic acid analogue; a short time method

マイクロ波照射法は熱伝導を必要とせず、直接反応物または反応溶媒を加熱するため、迅速に内部を加熱できることや温度調節がしやすいことが利点として挙げられる[1,2]。そのため、現在では医薬品や化粧品などの化学合成にも利用されている。4-フェニル酪酸（4-PBA）はケミカルシャペロンの一種であり、神経変性疾患の原因の一つであるたんぱく質の凝集を改善することが知られている。また、植物の成長にも関与できうると示唆されている。本研究では、Friedel-Crafts 反応や Michael 付加反応などマイクロ波照射が有効な反応を用いて、短工程で簡便な 4-PBA やその誘導体、類似体の合成法を検討した。



さらに、低温マイクロ波でも反応の進行を確認、合成を行い、加熱効果なのかマイクロ波効果なのかを明らかにする検討も行ったので併せて報告する。

1) H. Iida, K. Takahashi, Y. Akatsu and K. Mizukami, *Current Microwave Chem.,* **4(2)**, 108-114 (2017).
2) H. Iida, M. Okawa, S. Leeanansaksiri, and K. Takahashi, *Lett. Org. Chem.*, **19(8)**, 608-615 (2022).

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Academic Program [Poster] | 17. Biofunctional Chemistry, Biotechnology：Poster

Tue. Mar 19, 2024 1:00 PM - 2:30 PM JST | Tue. Mar 19, 2024 4:00 AM - 5:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-2pm] 17. Biofunctional Chemistry, Biotechnology

Japanese

[P2-2pm-01]

Study on optimization of synthesis of a cyclodextrin dimer for the practical application of dual antidote against carbon monoxide and cyanide poisoning.

○Takashi Onishi[1], Atsuki Nakagami[1], Kitagishi Hiroaki[1] (1. Doshisha university)

Japanese

[P2-2pm-02]

Coordination behavior of sulfide ions to porphyrin iron complexes in aqueous solution and cellular environment

○Riria Honda[1], Atsuki Nakagami[1], Hiroaki Kitagishi[1] (1. Doshisha University)

Japanese

[P2-2pm-03]

Synthesis and secondary Structure of collagen model peptides incorporating N-terminal His-tag

○Raraho Kanda[1] (1. Ryukoku University)

Japanese

[P2-2pm-04]

Development of a calcium ion concetration-resposive imaging probe for intracellular redox behavior

○Yuhei Sato[1], Rumi Mikami[1], Kenta Arai[1] (1. Tokai Univ.)

Japanese

[P2-2pm-05]

Modification of golg nanorods with peptides containing cell recognition sequence and evaluation of their anti-cancer drug loading performance

○Conoha Yamaoka[1], Takahito imai[1], Masahiro asano[1], Kin-ya Tomizaki[1] (1. Ryukoku University Faculty of Advanced and Technology)

Japanese

[P2-2pm-06]

Indole-3-butyric Acid Derivative (JAX-44) Promoting Lateral Root Elongation

○Ami Watanabe[1], Kazuki Arai, Haruka Yamamoto, Takeshi Yamada[2], Kota Ibe[1], Sentaro Okamoto[1] (1. Kanagawa University , 2. Kobe Pharmaceutical University)

Japanese

[P2-2pm-07]

Development of novel fluorescent DNA probes containing bis-pyrene unit

○Yuta Kanezawa[1], Saika Kobayashi, Katsuhiko Matsumoto, Yoshio Saito[1] (1. Nihon University)

Japanese

[P2-2pm-08]

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Design and studies of o-keto benzaldehyde derivatives as a probe for efficient fluorescent lysine modification

○Guosheng Gao[1], Mariko Aso[1] (1. Kyushu University)

Japanese

[P2-2pm-09]

Fluorescence properties and excited-state calculations of amino group-modified GFP dyes

○Takashi Kanamori[1], Yuki Sadai[1], Kenji Hida[1], Hiroya Asami[2], Hideya Yuasa[1] (1. Tokyo Institute of Technology, 2. Gakushuin University)

English

[P2-2pm-10]

Toward the measurement of micellar dipole potentials by voltage sensitive dyes

○Minami Nakada[1], Makoto Roppongi[2], Toru Oba[3] (1. Department of Material and Environmental Chemistry, Utsunomiya University, 2. Center for Instrumental Analysis, Utsunomiya University, 3. Department of Materials and Environmental Chemistry, Graduate School of Utsunomiya University)

Japanese

[P2-2pm-11]

Discovery and utilization of pseudo-luciferase activities in non-luminescent proteins

○Ryo Nishihara[1,2], Ryoji Kurita[1,3] (1. National Institute of Advanced Industrial Science and Technology, 2. JST PREST, 3. University of Tsukuba)

English

[P2-2pm-12]

Synthesis and photophysical properties of novel solvatochromic fluorescent dyes with quinolone-based molecular wires

○Satoshi Saito[1], Makoto Roppongi[1], Toru Oba[1] (1. The Univ. of Utsunomiya)

Japanese

[P2-2pm-13]

Control of molecular assembly of platinum(II) complex bearing thymine subsitutents by selective hydrogen bonding with adenine oligomer

○Shun Fujii[1], Manabu Nakaya[1] (1. Graduate school of Science Josai University)

Japanese

[P2-2pm-14]

Synthesis and characterization of a mitochondria transfer signal peptide derivative.

○Soshin Saita[1], Kin-ya Tomizaki[1] (1. Ryukoku University Faculty of Advanced Science and Technology)

Japanese

[P2-2pm-15]

Synthesis and Properties of Schiff Base-Modified Chlorophyll Derivatives

○Hodaka Imose[1], Tomohiro Miyatake[1] (1. Ryukoku University)

Japanese

[P2-2pm-16]

Synthesis and evaluation of membrane-localizable gefitinib ligands targeting the epidermal growth factor receptor

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○Keishi Mitamura[1], Keita Tsutsui[2], Masaru Yoshikawa[2], Shinya Tsukiji[2] (1. Fac. of Eng., Nagoya Inst. of Tech., 2. Grad. Sch. of Eng. Nagoya Inst. of Tech.)

Japanese

[P2-2pm-17]

Development of a novel environmentally responsive pterin-type fluorescent probes

○Saki Nakai[1], Yasushi Kawai[1], Tetsuya Takemoto[1], Muyon Asami[1] (1. Nagahama Institute of Bio-Science and Technology)

Japanese

[P2-2pm-18]

Photodynamic effect of coumaryl alcohol derivative-modified 5-aminolevulinic acid

○Hideki Azuma[1], Kosuke Morita[1], Rin Fukushima[1], Takeshi Nagasaki[1] (1. Osaka Metropolitan Univ.)

Japanese

[P2-2pm-19]

Preparation of plasmonic chip sensor chip by visible light of photo-responsible molecule

○Kyohei Asano[1], Syohei Horio[1], Yasunori Nawa[1], Mutsuo Tanaka[2], Keiko Twa[1] (1. Kwansei Gakuin University, 2. Saitama Institute of Technology)

Japanese

[P2-2pm-20]

Effect of linker length on conjugation-extended pterin-type fluorescence probes

○Haruka Nishitani[1], Yasushi Kawai[1] (1. Nagahama Institute of Bio-Science and Technology)

English

[P2-2pm-21]

Development of photo-triggered DNA double-strand invasion method targeting long chain oligonucleotides oriented to genome manipulation

○ZUMILA HAILILI[1], JUNLING MO[1], Fujimoto Kenzo[1] (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-22]

Development of crosslinking to purine bases in DNA accelerated by reversible DNA photo-crosslinking

○Junling Mo[1], Rei Hirahara[1], kenzo Fujimoto[1] (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-23]

Synthesis and properties of oligonucleotides conjugated with sugar ligands for selective cell delivery

○Daiki Shimamura[1], Remi Arie[1], Shuri Kaneyama[2], Aya Miyauchi[2], Koji Seio[1], Yoshiaki Masaki[1] (1. Sch. Life Sci. Tech., Tokyo Tech., 2. Showa Univ.)

Japanese

[P2-2pm-24]

Photo-control of intracellular RNA behavior using artificial nucleic acids with photo-crosslinking

○QINGYUAN HUANG[1] (1. Japan Advanced Institute of Science and Technology)

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Japanese

[P2-2pm-25]

Development of novel DNA photo-crosslinking that enables switching of crosslink sites by peripheral sequences.

○touya odai[1], junling MO, kenzo fujimoto (1. Japan Advanced Institute of Science and Technology)

Japanese

[P2-2pm-26]

Effect of polyvinyl alcohol on G-quadruplex formation

○Takahiro Nakamura[1], Ryoko Uda[1] (1. National Institute of Technology (KOSEN), Nara College)

Japanese

[P2-2pm-27]

Synthesis of guanosine tetra phosphate analogue has photoreactive biotinylation linker.

○Yudai Suzuki[1], Yukine Suda[1], Ayano Iwake[1], Yoshiaki Masaki[1], Kohji Seio[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese

[P2-2pm-28]

Structures of DNAs having diphenylanthracene- or pyrene-modified deoxycytidine

○Ryosuke Izumi[1], Aoi Okamoto[1], Mitsunobu Nakamura[1], Tadao Takada[1] (1. University of Hyogo)

Japanese

[P2-2pm-29]

Structures of DNAs having pyrene-modified deoxyguanosine and deoxyadenosine

○yuto nakajima[1], yojiro takiguti[1], mitunobu nakamura[1], tadao takada[1] (1. University of Hyogo)

Japanese

[P2-2pm-30]

Fluorescence properties of C5-heteroaryl-pyrimidine nucleosides and post-synthetic modification of DNA

Miu Hara[1], Keita Kudo[1], Kie Sakurai[2], Wakaba Yoshizawa[2], ○Hiroaki Ozaki[1] (1. Graduate School of Science and Technology, Gunma University, 2. School of Science and Technology, Gunma University)

Japanese

[P2-2pm-31]

Development of RNA-binding small molecules that recognize specific nucleobase based on hydrogen bonding

○Kosuke Tsuzuki[1,2], Kazumitsu Onizuka[1,2], Ryosuke Nagasawa[1,2], Emi Miyashita[3], Kaoru Richard Komatsu[3], Hirohide Saito[3], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku University, 2. Department of Chemistry, Tohoku University, 3. CiRA, Kyoto University)

Japanese

[P2-2pm-32]

Increased sensitivity of HCR-based nucleic acid detection using the concentration effect of microbeads

Yu Yasuhara[1], ○Takashi Sakamoto[1] (1. Wakayama Univ.)

Japanese

[P2-2pm-33]

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Synthesis of novel nucleopeptides with oxime bonds

○Yukino Fukushima[1], Toda Hiroki[1], Moriguchi tomohisa[1] (1. Gunm University)

Japanese

[P2-2pm-34]

Development of a photothermal-induced drug release system using DNA-modified gold nanoparticles

○Kento Noguchi[1], Takuya Yui[1], Mitsunobu Nakamura[1], Tadao Takada[1] (1. University of Hyogo)

Japanese

[P2-2pm-35]

Synthesis and properties of oligonucleotides having 7-pyridyl-7-deazadeoxyguanosine

Kento Miyaji[1], ○Narumi Habu[1], Kohji Seio[1], Yoshiaki Masaki[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese

[P2-2pm-36]

Synthesis of novel diphenylsilylpyrene derivatives directed to fluorescent labeling of DNA

○Mayuko Hoshiba[1], Tomohisa Moriguchi[1] (1. The Univ. of Gunma)

Japanese

[P2-2pm-37]

Effect of introduction of guanidino group on complex formation of G-quadruplex and thioflavin T derivative

○Yuuka Shiratori[1], Tomoaki Nakamura[2], Tomoko Wariishi[2], Yuka Kataoka[2], Masayasu Kuwahara[2] (1. Nihon University, 2. Grad. Sch. Integrated Basic Sci, Nihon Univ.)

Japanese

[P2-2pm-38]

Effect of tetraphenylethylene derivative-modified DNA on the stability of G-quadruplexes

○MAAYA KIYOSE[1] (1. TOKYO UNIVERSITY OF TECHNOLOGY GRADUATE SCHOOL)

Japanese

[P2-2pm-39]

Molecular Dynamics Study on the Difference in Molecular Fluctuations between Wild Type and G93A Mutant of Superoxide Dismutase 1

○Kazuaki Fukushima[1], Noriko Fujiwara[1] (1. Hyogo Medical University)

Japanese

[P2-2pm-40]

Development of Oxidative Protein Folding Catalysts Involving Chaperone-like Activity

○Yuki Iwata[1], Yuya Nishizawa[1], Kenta Arai[1] (1. Tokai Univ.)

Japanese

[P2-2pm-41]

Chemical synthesis of new long-acting insulin via an easily modifiable insulin as a key precursor.

○Rikana Takahashi[1], Kenta Arai[1] (1. Tokai Univ.)

English

[P2-2pm-42]

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The effect of sorbitol addition on the asymmetric reduction of ketones using cyanobacterium *Synechocystis* sp. PCC 6803

○Satsuki Fukui[1], Hideo Kojima[1], Satomi Takeda[1], Rio Yamanaka[2] (1. Osaka Metropolitan University, 2. Himeji Dokkyo University)

English

[P2-2pm-43]

Lipase-catalyzed alkoxycarbonylation in the presence of a solid acid catalyst

○Yuto Yamamoto[1], Hideo Kojima[1] (1. Osaka Metropolitan University)

English

[P2-2pm-44]

Lipase-catalyzed alkoxycarbonylation in the deep eutectic solvent/water system

○Taito Nagamoto[1], Yuto Yamamoto[1], Hideo Kojima[1] (1. Osaka Metropolitan Univercity)

English

[P2-2pm-45]

Asymmetric reduction of keto esters using *Pisum sativum* as a whole-cell biocatalyst

○Ryota Shimamoto[1], Yuya Machi[1], Hideo Kojima[1], Satomi Takeda[1] (1. Osaka Metropolitan University)

English

[P2-2pm-46]

Biotransformation of cyclohexane to ε-caprolactone using *Arabidopsis thaliana* as a whole-cell biocatalyst

○Yuya Machi[1], Jina Yoshida[1], Hideo Kojima[1], Satomi Takeda[1] (1. Osaka Metropolitan University)

Japanese

[P2-2pm-47]

In vitro selection of streptavidin-binding cyclic peptide aptamers by cDNA display

○Daiki Katakura[1] (1. Saitama University)

Japanese

[P2-2pm-48]

Enzymatic metabolic reactions compartmentalized in a liposome with a skeletal DNA nanostructure

○Futa Komatsubara[1,2], Eiji Nakata[1], Lin Peng[1], Hiroaki Konishi[1,2], Takashi Morii[1] (1. Institute of Advanced Energy, Kyoto University, 2. Graduate School of Energy Science, Kyoto University)

Japanese

[P2-2pm-49]

Prediction and Validation of Proline-containing Tripeptides with Angiotensin I-converting Enzyme Inhibitory Activity

○Mizuho Tanaka[1], Yuki Fujimoto[1], Toshiya Hatakenaka[1,2], Tamaki Kato[1] (1. Kyushu Institute of Technology, 2. Vital Resources Applied Laboratory)

Japanese

[P2-2pm-50]

Functional Regulation of Oxidative Enzymes Through On/Off Switching of Electron Transfer Chain

○Satoshi Hasegawa[1], Ryota Kato[1], Daisuke Umeno[1] (1. Waseda University)

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Japanese

[P2-2pm-51]

Protein Folding Promotion Using Redox-Active Liquid-Liquid Phase Separation Materials

○Yukino Yamashita[1], Takahiro Muraoka[1,2] (1. Grad. Sch. of Eng. Tokyo Univ. of Agri. and Tech., 2. KISTEC)

English

[P2-2pm-52]

Improved Degradation of Polyethylene Terephthalate Film by Cutinase Using 1-Dodecyl-1*H*-1,2,3-Triazole-4-Carbaldehyde Surfactant.

○JOEL MUYOMBA[1], MD SADIKUR RAHMAN SHUVO[1], AKIRA ONODA[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

Japanese

[P2-2pm-53]

Preparation and properties of chymotrypsin chemically modified with benzoxaborole

○Ryoga Tsuchiya[1], Yamato Yoshida[1], Shin Ono[1] (1. Kanazawa Institute of Technology)

Japanese

[P2-2pm-54]

Detection of TEV protease by pore blockage in Outer Membrane Protein-G Nanopore mutation

○Haruka Suzuki[1], Tosiyuki Tosaka[1], Kouki Kamiya[1] (1. Grad. Sch. Sci. Tec., Gunma Univ.)

Japanese

[P2-2pm-55]

Enzyme integration by YK peptide tag fusion in E. coli and its effect on 3-hydroxybutyrate synthesis.

○Bungo Kozasa[1], Nakayama Sae[1], Masahiro Hashimoto[1], Takayuki Miki[1,2], Hisakazu Mihara[1] (1. School of Life Science and Technology, Tokyo Institute of Technology , 2. School of Engineering,The University of Tokyo)

Japanese

[P2-2pm-56]

Examination of proximity and reaction efficiency of enzymes by external stimulation

○Momoka Takazawa[1], Koki Kamiya[2] (1. School of Science and Technology, Gunma Univ., 2. Graduate School of Science and Technology, Gunma Univ.)

Japanese

[P2-2pm-57]

Investigation of crystallization of crystallized protein expressed using cell-free protein synthesis

○Yume Kosuge[1], Koki Kamiya[2] (1. School of Science and Technology, Gunma Univ., 2. Graduate School of Science and Rechnology, Gunma Univ.)

English

[P2-2pm-58]

Synthesis of self-assembling peptides conjugated with integrin-targeting peptides as biomaterials for cancer cell culture.

○MAN LI[1], Hisakazu Mihara[1], Hiroshi Tsutsumi[1] (1. Tokyo Institute of Technology, School of Life Science and Technology)

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English

[P2-2pm-59]

Enhancing antitumor efficacy by glutathione-depleted nanophotosensitizers with photo-triggered strong hyperthermia and ROS generation

○Wen-Hsuan Chiang[1], Yu-Hsin Chen[1], I-Ju Liu[1] (1. National Chung Hsing University)

Japanese

[P2-2pm-60]

Synthesis of Gold Nanorods Modified with Hepatocellular Carcinoma Targeting Sequence Peptides and Verification of Their Photothermal Effects

○Shoya Fujimoto[1], Takahito Imai[1], Masahiro Asano[1], Masayuki Yamazaki[1], Kin-ya Tomizaki[1] (1. Ryukoku University)

English

[P2-2pm-61]

Wireless charging-mediated angiogenesis and nerve repair by adaptable microporous hydrogels

○Shang-Hsiu Hu[1] (1. National Tsing Hua University)

Japanese

[P2-2pm-62]

Intracellular behavior of peptide heterodimers labeled with FRET probes

○Karen Tanaka[1], Masayuki Yamasaki[1], Kin-ya Tomizaki[1] (1. Ryukoku University)

Japanese

[P2-2pm-63]

RNA encapsulation and photo-responsive release by caged coacervates based on liquid-liquid phase separation

○Akinari Bando[1], Kazunori Watanabe[1], Takashi Ohtsuki[1], Mizuki Kitamatsu[2], Yuuki Kanazaki[2] (1. Okayama University, 2. Kindai University)

Japanese

[P2-2pm-64]

Synthesis of Amphiphilic Imidazolyl Porphyrinatozinc Having a Fatty Amide Group, and Their Introduction to Lipid Bilayer Membrane.

○Miki Oono[1], Kazuma Yasuhara[2], Akiharu Satake[1] (1. Tokyo University of Science, 2. NARA INSITUTE of SCIENCE and TECHNOLOGY)

Japanese

[P2-2pm-65]

Synthesis of Imidazolyl Porphyrinatozinc Having a Maleimide Group Linked with Different Methylene Groups, and Their Self-organization in Lipid Bilayer Membrane.

○Yohei Yanase[1], Kazuma Yasuhara[2], Akiharu Satake[1] (1. Tokyo University of Science, 2. NNARA INSTITUTE of SCIENCE and TECKNOLOGY)

Japanese

[P2-2pm-66]

Monitoring ERK activity in cancer cells following photothermal stimulation

○Kenji Omori[1] (1. Graduate School / Faculty of Information Science and Technology, Hokkaido University)

Japanese

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[P2-2pm-67]

Photoinduced cytotoxicity of diarylethene based on photoswitching isomerization

○Norikazu Maruyama[1], Kimio Sumaru[2], Kana Morishita[2], Kingo Uchida[1] (1. Ryukoku University, 2. National Institute of Advanced Industrial Science and Technology)

Japanese

[P2-2pm-68]

A microbail BOD biosensor by a FRET based intercellular ATP measurment

○Yuto Kanno[1], Yuta Tateno[1], Takuo Akimoto[1] (1. Tokyo University of Technology)

Japanese

[P2-2pm-69]

Detection of landmines using FRET based Microbial biosensor

○Taiga Yoshizawa[1], Kai Nishimura[1], Suzuna Nakajima[1], Takuo Akimoto[1] (1. Tokyo University of Technology)

Japanese

[P2-2pm-70]

Bacterial cellulose-based hydrogels carrying sulfated galactosides as naked-eye monitoring systems of carbohydrate-carbohydrate interactions

○Jiayu Dong[1], Teruaki Hasegawa[1] (1. Toyo Univ.)

Japanese

[P2-2pm-71]

Synthetic studies of lipid-peptide antigen conjugation for targeting multiple factors on antigen-presenting cells

○Shunya Kikuchi[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Keio University)

Japanese

[P2-2pm-72]

Fusogenic liposomes containing pH-responsive malachite green

○Kaede Nikaido[1], Ryoko Uda[1] (1. National Institute of Technology (KOSEN), Nara College)

Japanese

[P2-2pm-73]

Protein pairs which change FRET based fluorescent color for an intercellular pH indicator.

○Shuzo Homma[1], Sohki Miyazaki[1], Takuo Akimoto[1] (1. Tokyo University of Technology)

Japanese

[P2-2pm-74]

Synthesis and molecular properties of gossypols having multiple carbohydrates

○Kotomi Ishikawa[1], Teruaki Hasegawa[1] (1. Toyo Univ.)

Japanese

[P2-2pm-75]

Luminescence of a Firefly luciferin on the plasmonic chip

○Hitomi Yamanaka[1], Yasunori Nawa[1], Keiko Tawa[1] (1. Kwansei Gakuin University)

Japanese

[P2-2pm-76]

Development of polymeric micelles containing photosensitizer for deep tissue photodynamic therapy

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○Hayato Yao[1], Yohiyuki Uruma[1], Batbayar Altannavch[1], Kunishige Onuma[2], Masahiro Inoue[2], Chung Yu Lin[3], Ping Shan Lai[3] (1. NIT(KOSEN), Yonago College, 2. The Univ. of Kyoto, 3. NCHU)

Japanese

[P2-2pm-77]

Microbial degradation process of biodegradable polymer directly monitored by QCM andElectrochemistry

○Maika Yoshimura[1], Takuma Otsuki[1], Yasumasa Takenaka[2], Tomohiro Hiraishi[2], Hideki Abe[2], Noriyuki Asakura[1,2] (1. Tokyo Institute of Technology, 2. RIKEN)

Japanese

[P2-2pm-78]

Fundamental investigation and understanding of characteristics from engineering aspects relating to the production of valuable material through plants

Akito Matsushima[1], ○Tsubasa Hirabayashi[1], Mizuki Saegusa[1], Hiroki Muramatsu[1], Sho Yoshida[1], Naoko Nishida[1] (1. Chiyoda Corporation)

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一酸化炭素とシアン化合物の同時解毒剤実用化に向けたシクロデキストリンダイマーの合成条件最適化に関する検討

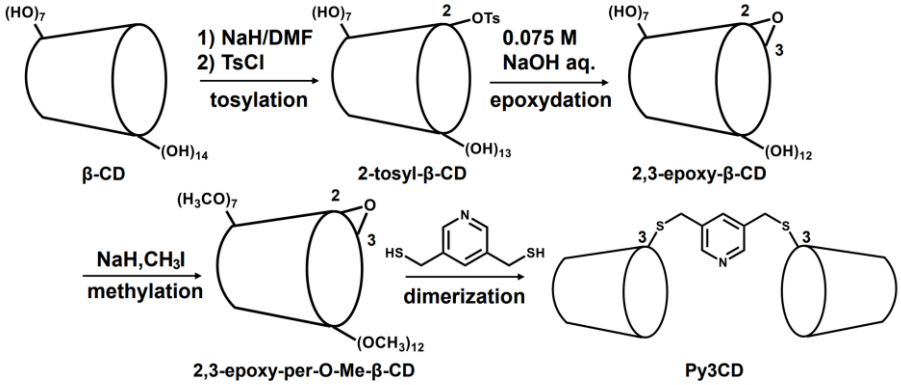
(同志社大理工) ○大西隆史・中上敦貴・北岸宏亮

Study on optimization of synthesis condition of a cyclodextrin dimer for the practical application of dual antidote against carbon monoxide and cyanide poisoning. (*Faculty of Science and Engineering, Department of Molecular Chemistry and Biochemistry, Doshisha University*) ○Takashi Onishi, Atsuki Nakagami, Hiroaki Kitagishi

We have previously reported an effective dual antidote, “hemoCD-Twins”, against carbon monoxide and cyanide poisoning. Cyclodextrin dimer, “Py3CD”, is one of the components in hemoCD-Twins. However, it is difficult to synthesize Py3CD in large quantities using current synthetic methods. And it is not possible to conduct necessary experiments for the practical application. In this study, we optimized the synthetic condition of Py3CD for mass production. Especially, we reconsidered the purification processes in tosylation step to separate β-cyclodextrin by recrystallization in substitute of column chromatography. As a result, whereas previous way was conducted in 30％ yield in 2-3 days, this simple and scalable way was conducted in 16% yield in 1 day.

Keywords: cyclodextrin, antidote, synthetic condition, purification processes, optimization

我々は火災ガスの中で毒性の高い一酸化炭素とシアン化水素に対する同時解毒剤「hemoCD-Twins」を以前報告した[1)]。しかし、この解毒剤の構成要素であるシクロデキストリンダイマー(Py3CD)は現在の合成方法では大量合成が困難であり、実用化に向けた実験を十分に行うことができない。そのため、本研究では Py3CD の大量合成に向けて合成条件の最適化を行い、特に Py3CD 合成のトシル化段階における精製操作を見直し、現在主に精製に用いられているカラムクロマトグラフィーの代わりに再結晶を用いて出発物質である β−シクロデキストリンの分離を行った。その結果、以前まで 2〜3 日の工程において収率 30%で行っていた分離を 1 日の作業に短縮し、収率 16%で、簡便かつスケーラブルな方法で合成することに成功した。



Scheme.1 Synthetic route of Py3CD.

1） Q. Mao et al., *PNAS*, **2023**, Vol. 120, No. 9, e2209924120.

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水中および細胞環境におけるポルフィリン鉄錯体への硫化物イオンの配位挙動

(同志社大理工) ○本田 里々愛・中上 敦貴・北岸 宏亮

Coordination behavior of sulfide ions to porphyrin iron complexes in aqueous solution and cellular environment

(Fuculty of Science and Engineering, Department of Molecular Chemistry and Biochemistry, Doshisha University) ○Riria Honda, Atsuki Nakagami, Hiroaki Kitagishi

Hydrogen sulfide (H_2S) is one of the gas-transmitting substances produced in vivo and it is believed to have physiological functions. However, since there are multiple pathways for the synthesis of H_2S in vivo (Fig. 1)[1], it is difficult to create a deficient state for the search of physiological functions. Therefore, many physiological functions of H_2S remain to be elucidated. We have reported a supramolecular complex "hemoCD" composed of a cross-linked methylated cyclodextrin dimer and a water-soluble iron porphyrin as an artificial heme protein model that functions in water. In the present study, we investigated the sulfide scavenging ability and coordination behavior of hemoCD-I (Fig. 2)[2] in water, and found that hemoCD-I strongly scavenges sulfide in water. We also examined the ability of hemoCD-I to capture sulfide in the intracellular environment.

Keywords : cyclodextrin, porphyrin, hydrogen sulfide, sulfide ions, heme protein

硫化水素（H_2S）は生体内で産出されるガス伝達物質の中の１つであり、生理機能を有するとされている。しかし、生体内における H_2S の合成経路は複数存在する(Fig. 1)[1]ため、生理機能探索のための欠乏状態を作るのは困難である。そのため、H_2S の生理機能に対して、未解明な点が多く残されている。我々は架橋されたメチル化シクロデキストリン二量体と水溶性鉄ポルフィリンから構成される超分子錯体“hemoCD”を水中で機能する人工ヘムタンパク質モデルとして報告している。本研究ではhemoCD-I (Fig. 2)[2]による水中における硫化物の捕捉能および配位挙動について検討を行い、水中においてhemoCD-Iが硫化物を強く捕捉することを見出した。また、細胞内環境における硫化物の捕捉能について検討を行った。

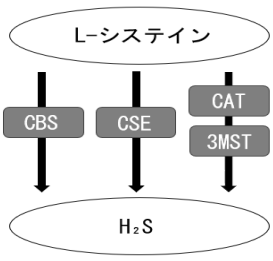

Fig 1. Synthetic pathways of endogenous H_2S.

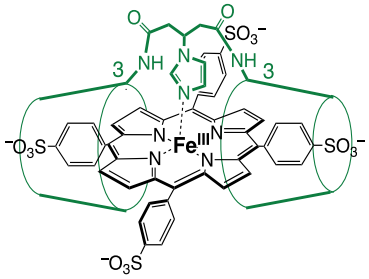

Fig 2. Structure of a sulfide receptor, hemoCD-I.

1) Mikami, Y.; Kimura, H., *Commun Integr Biol.* **2012**, *5*, 169–171.
2) Kitagishi, H.; Kano, K., Chem. *Commun*. **2021**, *57*, 148.

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N 末端に His タグを組み込んだコラーゲンモデルペプチドの合成および二次構造評価

（龍谷大先端理工）〇神田ららほ・富﨑欣也

Synthesis and secondary Structure of collagen model peptides incorporating N-terminal His-tag

(Department of Materals Chemistry, Ryukoku Univ) ○Raraho Kanda, Kin-ya Tomizaki

Titanium has attracted attention as a material for implants because of its high corrosion resistance and biocompatibility, and is already in practical use. However, the risk of bacterial infection due to low initial cell adhesion efficiency to titanium surface is an issue. Efforts have been made to improve initial cell adhesion by chemical etching of the surface or surface modification with polymers and bone-forming proteins, etc. However, but the problem has not yet been satisfactorily solved. For example, when natural collagen is used, there are issues such as the risk of zoonosis from terrestrial organisms and denaturation temperatures of aquatic organisms different from mammals. To improve these conditions, the use of chemically synthesized collagen model peptides (CMP), which have a low risk of infection, excellent denaturation temperature, and easy function control, is considered to be effective. In this study, we synthesized a new collagen model peptide incorporating two types of sequences: a cell adhesion site (GFOGER) that specifically binds to integrins on cell surface and a His-tag that is designed to associate CMPs with copper ions for antibacterial effects.

Keywords：collagen model peptide ; a cell recognition site ; a His tag ; titanium ; antibacterial

チタンは耐腐食性および生体適合性が高いことから、インプラントの材料として注目され、すでに実用化されている。しかし、チタン表面への初期細胞接着量が少ないことによる細菌感染のリスクが課題として挙げられる。対応策として、表面の化学エッチングや高分子・骨形成タンパク質などによる表面修飾により、初期細胞接着量を増大させるなど取り組まれているが、完全な問題解決には至っていない。例えば、天然コラーゲンを用いる場合、陸生生物由来の人獣共通感染症のリスクや水生生物由来の変性温度が哺乳類と異なるといった課題がある。そこで、それらを改善するために感染症のリスクが少なく変性温度の制御が容易な化学合成されたコラーゲンモデルペプチド（CMP）の利用が効果的と考える。本研究では、細胞表面のインテグリンと特異的に結合する細胞接着部位（GFOGER）および銅イオンと CMP の錯形成による抗菌効果の付与を目指し His タグの二種の配列を取り込んだ新規コラーゲンモデルペプチドを合成し、銅イオン存在下における二次構造評価により His タグの性質を調査した。

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カルシウムイオン濃度に応答する細胞内酸化還元挙動のイメージングプローブの開発

（東海大理化[1]，東海大先進生命研[2]）○佐藤悠平[1]・三神瑠美[1,2]・荒井堅太[1,2]

Development of a calcium ion concetration-resposive imaging probe for intracellular redox behavior

([1]*Department of Chemistry, School of Science, Tokai University,* [2]*Institute of Advanced Biosciences, Tokai University*) ○Yuhei Sato,[1] Rumi Mikami,[1,2] Kenta Arai[1,2]

The endoplasmic reticulum (ER), a storage of calcium ion (Ca^{2+}), regulates concentration of Ca^{2+} in other organelles by releasing and incorporating Ca^{2+}. Excessive Ca^{2+} in the cytosol leads to increase in reactive oxygen species, which in turn induces imbalance of the redox environment in the cells and eventually cell death. We previously developed cyclic diselenide (SeSe) compounds that catalytically reduce hydrogen peroxide, a reactive oxygen species.[1] More recently, we also developed a SeSe compound that is reductively activated to a diselenol species ([SeH,SeH]), which has reducing ability against oxidative factors, in a concentration-dependent manner of intracellular Ca^{2+}.[2] The amount of [SeH,SeH] produced in the cell also depends on the concentration of reducing factors such as glutathione. Consequently, a technique to quantify the intracellular production of [SeH,SeH] could allow real-time observation of redox behavior in living cells. Therefore, in this study, we attempted to develop a fluorescent probe to monitor both Ca^{2+} concentration and redox balance. Using a redox model compound fused with a Ca^{2+} chelator as a starting material, a compound conjugated with a fluorescent dye was obtained in three steps. In the presentation, we will report on the design, synthesis, and fluorescent properties of the compound.

Keywords : Fluorescence; Redox; Oxidative Stress; Calcium Ion

カルシウムイオン(Ca^{2+})の貯蔵庫である小胞体(ER)は、Ca^{2+}の放出と取り込みによって、他の細胞小器官中のCa^{2+}濃度を調節している。サイトゾル中のCa^{2+}濃度の過剰な増加は、活性酸素種の増加を招き、細胞内の酸化還元バランスの崩壊、ひいては細胞死を誘発する。以前我々は、活性酸素種である過酸化水素を触媒的に還元する環状ジセレニド(SeSe)化合物を開発した[1]。さらに最近我々は、細胞内の Ca^{2+}の濃度依存的に酸化的因子に対して活性なジセレノール種([SeH,SeH])へと還元的に活性化される SeSe 化合物を開発した[2]。細胞内での[SeH,SeH]の生成量は、グルタチオン(GSH)などの還元因子の濃度にも依存する。故に、[SeH,SeH]の細胞内の生成量が定量化できれば、生細胞のレドックス挙動をリアルタイムで観測できるものと考えられる。そこで、本研究ではCa^{2+}濃度と酸化還元バランスの両方を観測する蛍光プローブの開発を目指した。Ca^{2+}キレーターを融合した酸化還元モデル化合物を出発物質として蛍光色素を接合した化合物を 3 段階で合成した。本発表では、合成化合物のデザイン、合成、および化合物の蛍光特性について報告する。

[1] *Bioorg. Med. Chem*. **2021**, 29, 115866. [2]日本化学会 第 103 春季年会 2023 予稿集 D1411-2pm-02.

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細胞認識部位含有ペプチドによる金ナノロッドの修飾と抗ガン剤の担持性能評価

(龍谷大先端理工)○山岡湖ノ波[1]・今井崇人[1]・浅野昌弘[2]・富﨑欣也[1]

Modification of gold nanorods with peptides containing a cell recognition sequence and evaluation of their anti-cancer drug loading performance(*[1]Materials Chemistry Course, [2]Ecology and Enviromental Engineering Course, Faculty of Advanced Science and Technology, Ryukoku University*)○Conoha Yamaoka[1], Takahito Imai[1], Masahiro Asano[2], Kin-ya Tomizaki[1]

Tumor-targeted combination therapies have received increasing attention in recent years. The combination of chemotherapy and photothermal therapy (PTT) is considered to be effective for cancer treatments. The RGDS peptide, which recognizes integrins α5β1 overexpressed in cancer cells and induces cellular adhesion, is used to direct the gold nanorods to cancer cells. 11-Mercapto undecanol (11MUD) is also used to provide hydrophobic space to load anti-cancer drug doxorubicin (Dox) on the surface of gold nanorods. In this study, we verify the loading and releasing performances of Dox by near-infrared light irradiation.

First, gold nanorods were synthesized by the CTAB (hexadecyltrimethylammonium) method and surface-modified with mPEG-SH (polyethleneglycol methyl ether thiol) in aqueous solution for 30 minutes. Then, 11MUD was used to modify the surface of the nanorods in aqueous solution for 30 minutes. Finaly, RGDS peptide was attached to the surface of the nanorods in aqueous solution for 24 hours to synthesize the target product. Physicochemical properties of the target product were evaluated by UV-vis, zeta potential, TEM, and IR measurements.

Keywords: Peptide; Gold nanorod; Doxorubicin

近年、腫瘍を標的とする併用療法が注目されている。その中でも、化学療法と光熱療法(PTT)の併用は効果的であると考えられる。本研究では、ガン細胞に過剰発現しているインテグリンの$\alpha 5 \beta 1$ を認識し細胞接着を誘発する RGDS ペプチド及び 11-メルカプトウンデカノール(11MUD）により金ナノロッドを修飾し、ペプチドと 11MUD の疎水環境に抗ガン剤ドキソルビシン(Dox)を担持させる。今回は Dox の担持性能と近赤外照射による放出能を検証した。

まず、CTAB(ヘキサデシルトリメチルアンモニウム)法を用いて金ナノロッドの合成を行った。得られた金ナノロッドにポリエチレングリコールメチルエーテルチオールを加え 30 分間水溶液中で反応させ表面修飾した。次いで、11MUD を加え 30 分間水溶液中で反応させ表面修飾した。最後に、RGDS ペプチドと 24 時間水溶液中で反応させることにより AuNR-PEG-11MUD-peptide(AuNR-P-M-p)の合成を行い、UV-vis、ゼータ電位、TEM, IR 測定によって物性評価を行った。

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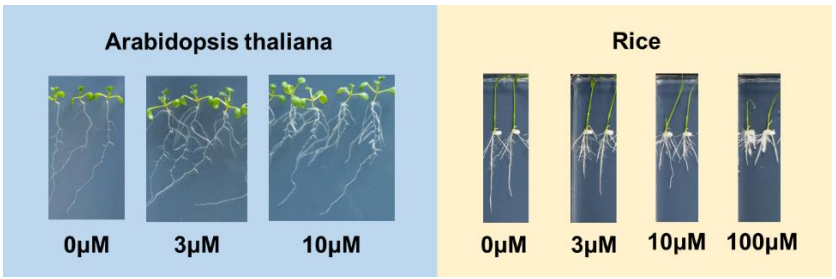
代謝されて側根伸張の促進作用を示す IBA 誘導体

(神奈川大学) ○渡邊 愛美，荒井 一輝，山本 春佳，山田 健，伊部公太，中川理絵，岡本 専太郎

Indole-3-butyric Acid Derivative (JAX-44) Promoting Lateral Root Elongation (*Kanagawa University*) ○Ami Watanabe, Kazuki Arai, Haruka Yamamoto, Takeshi Yamada, Kota Ibe, Rie Nakagawa, Sentaro Okamoto

Indole-3-acetic acid (IAA) and indole-3-butyric acid (IBA) are known as plant hormone auxins. On the course of our investigation on synthesis and propetiy of auxin derivatives, we discovered one of IBA derivatives, JAX-44, that promotes lateral root elongation under agar culture conditions in *Arabidopsis*. Mass spectrometry analysis of extracts of the root of *Arabidopsis* cultured with deuterated JAX-44 revealed that JAX-44 was metabolically converted to IBA within the plant. It can be asummed that the generated IBA exhibited a lateral root elongation effect. In addition, an increase in root hairs was observed in rice.
Keywords: Auxin; IBA Derivative; Lateral Root Elongation

インドール-3-酢酸(IAA)およびインドール-3-酪酸(IBA)は植物ホルモンオーキシンとして知られている。我々は，これらの誘導体の合成と作用を検討する中で，シロイヌナズナの寒天培地育成条件下で側根伸長の促進作用を示す IBA 誘導体(JAX-44)を見いだした。重水素化 JAX-44 を用い，質量分析を行ったところ，植物体内で JAX-44 は IBA へ代謝変換されていることが分かった。生成された IBA が側根伸長作用を示したと考えられる。また，イネでは根毛の増加が見られた。



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ビスピレンユニットを有する蛍光核酸を用いた新規 DNA プローブの開発

(日大院工[1]・理化学研究所[2]) ○金澤 優多[1]・小林 彩夏[1]・松本 桂彦[2]・齋藤 義雄[1]

Design and synthesis of novel fluorescent DNA probes containing bis-pyrene unit for DNA detection

([1]School of Eng. Nihon Univ., [2]RIKEN) ○Yuta Kanezawa[1], Saika Kobayashi[1], Katsuhiko Matsumoto[2], Yoshio Saito[1]

Environmentally sensitive fluorescent (ESF) molecules that demonstrate a change in emission wavelength in response to a microenvironmental change are potentially powerful probes for the investigation of the interactions and functions of biomolecules. ESF nucleosides have reported and are widely used for the detection of nucleic acid sequences and structural studies of nucleic acids. However, there remains the challenge of discovering ESF nucleosides that are capable of discriminating target DNA sequences through significant changes in fluorescence wavelength. We wish to report herein a unique fluorescent probe containing bis-pyrene-labeled 8-aza-3,7-dideaza-2'-deoxyadenosine that can discriminate target DNA sequences.

Keywords:Nucleoside; DNA; Fluorescence

蛍光核酸塩基周辺の環境変化に応じて蛍光スペクトルを大きく変化させる蛍光ヌクレオシドを開発することができれば、核酸の二重鎖形成などに伴う環境変化を発光強度や波長の違いで簡単に識別でき、遺伝子診断や核酸の構造解析のためのツールとして非常に有用である。まず本研究では、ピレンエキシマー発光を利用した新しい蛍光核酸プローブの開発を目指して、プリン塩基の C3 位と C7 位を同時に修飾することができる 8-アザ-3,7-ジデアザアデノシン誘導体をデザイン・合成した。さらに、これに 2 つのピレンユニットを導入することで、エキシマー形成が可能な蛍光核酸を開発した。この新規蛍光核酸を導入した蛍光核酸プローブに標的となる DNA 鎖を加えたところ、プローブと標的 DNA の間で二重鎖が形成され、プローブ単独時に見られたエキシマー発光が消失した。このことから、本研究で開発した核酸プローブを用いることで、標的核酸の有無をエキシマー発光の有無により識別できることがわかった。

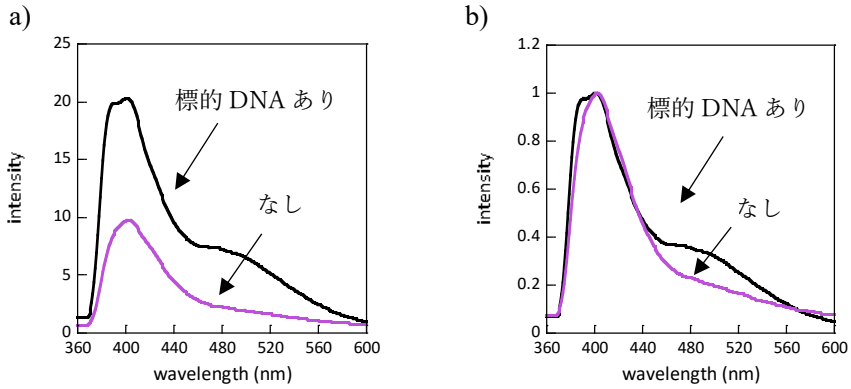

Figure 1. (a) Fluorescence spectra of ODN(^{2py37z}A), (b) Normalized fluorescence spectra of ODN(^{2py37z}A).

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Design and studies of o-keto benzaldehyde derivatives as a probe for efficient fluorescent lysine modification

([1]*Graduate School of Pharmaceutical Science, Kyushu University*,) ○Gao Guosheng,[1] Aso Mariko,[1]

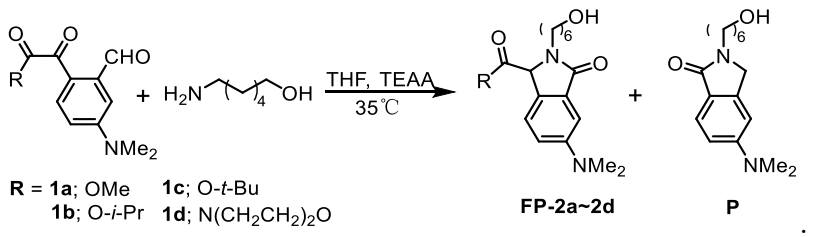
Keywords: Fluorescent Modification, Lysine Modification, Solvatochromic Fluorescence

Fluorescent labeling is a powerful method to study biomolecules. We have developed a series of o-keto benzaldehyde derivatives, which convert lysine residues of proteins to fluorophore achieving turn-on fluorescent protein modification. In this study, we designed benzaldehyde derivatives containing o-ketoester or o-ketoamide groups, to facilitate rapid fluorescent lysine modification by electron withdrawing properties of ester and amide. Ligands for selective targeting can be also connected through ester or amide linkages.

A series of benzaldehydes containing o-ketoester or o-ketoamide groups were synthesized and their reactions with amine in a 1:1 mixture of THF and TEAA buffer (100 mM, pH 7) were studied as a model for lysine modification. Reaction of methyl ester **1a** (10 mM) with 1 equiv. of amine afforded "non-fluorescence product" (**P**) and "fluorescence product" (**FP-2a**) in 33 and 30 %, respectively. Reaction of isopropyl ester **1b** gave similar results. However, *t*-butyl ester **1c** afforded **FP-2c** exclusively in 90 % yield and reaction rate was faster than other esters under the same conditions. Compared to o-ketoesters, o-ketoamides reacted slowly. Overnight-reaction of morpholine amide **1d** yielded **FP-2d** in 76%**.** Studies in detail indicated that **FP-2c** formation from *t*-butyl ester **1c** was rapid and efficient even at 50 μM with 3 equiv. of amine.

In addition, we found that FPs were solvatochromic fluorophores exhibiting linear correlation between solvent polarity and fluorescence properties such as intensity and λ_{emmax}.

Obtained data indicated that benzaldehyde derivatives with o-ketoester designed in this study were identified as promising molecules for lysine modification. Preparation of fluorescent antibody-drug conjugate is an attractive application and incorporation of ligand for targeting and drug release system will be studied.



R = **1a**; OMe **1c**; O-*t*-Bu
1b; O-*i*-Pr **1d**; $N(CH_2CH_2)_2O$

FP-2a~2d **P**

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アミノ基修飾 GFP 色素の蛍光特性と励起状態計算

（東工大生命[1]・学習院大理[2]）○金森 功吏[1]・定井 佑樹[1]・飛田 健司[1]・浅見 祐也[2]・湯浅英哉[1]

Fluorescence properties and excited-state calculations of amino group-modified GFP dyes

([1]*School of Life Science and Technology, Tokyo Institute of Technology*, [2]*Department of Chemistry, Faculty of Science, Gakushuin University*) ○Takashi Kanamori,[1] Yuki Sadai,[1] Kenji Hida,[1] Hiroya Asami[2], Hideya Yuasa[1]

In cellular fluorescence imaging, turn-on type fluorescent probes that specifically turn on fluorescence in the presence of a target molecule are attracting attention. These molecules emit almost no fluorescence in the absence of the target molecule, enabling rapid *in vivo* imaging with reduced background fluorescence. Fluorescent molecular rotors (FMRs), which exhibit fluorescence when intramolecular rotation is inhibited in the excited state, are of interest as fluorescent molecules that exhibit these properties.

In this study, we aimed to develop a turn-on type fluorescent probe for cellular fluorescence imaging that turns on fluorescence in the presence of target molecules or in response to the intracellular viscous environment. GFP dyes are composed of a benzylideneimidazolinone skeleton. We aimed to develop the derivatives with excellent fluorescence response. We introduced various alkylamines into the benzene ring of GFP dyes as electron-donating groups. In addition, we synthesized a series of derivatives in which a phenyl group was introduced into the benzene ring of GFP dyes. We evaluated their fluorescent properties and excited-state dynamics to understand the effect of these substituents on the fluorescence properties. In this presentation, these details will be reported.

Keywords : Fluorescent probe; GFP fluorophore; Fluorescent molecular rotor; Excited state dynamics

細胞の蛍光イメージングにおいて、標的分子存在下で特異的に蛍光を on にする turn-on 型蛍光プローブが注目されている。この分子は、標的分子非存在下ではほとんど蛍光を発しないため、in vivo でのイメージングにおいて、迅速かつバックグランド蛍光の低減したイメージングが可能になる。このような性質を示す蛍光性分子として、励起状態での分子内回転が抑制された際に蛍光を示す、蛍光性分子ローター（FMR）が注目されている。FMR は、非拘束状態では分子内でのねじれ等を伴う無輻射失活によって励起状態から緩和する。

本研究では、細胞の蛍光イメージングにおいて、標的分子存在下や細胞内の粘度環境に応答して蛍光を on にする turn-on 型蛍光プローブ開発を目指した。鍵となる蛍光分子として、FMR の一種である GFP 色素誘導体を用いることとした。本研究では、ベンジリデンイミダゾリノン骨格からなる GFP 色素を基本骨格として用い、蛍光応答に優れた誘導体の開発を志向し、GFP 色素のベンゼン環に種々の電子供与基(アルキルアミン)や、イミダゾリン環にフェニル基を導入した一連の誘導体の合成およびその蛍光特性を評価した。さらに、これらの置換基が蛍光特性に与える影響を理解するため、励起状態ダイナミクスの計算を行った。本発表ではこれらの詳細について報告する。

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界面活性剤分子膜の電気的環境を蛍光プローブで計測する

(宇都宮大工[1]・宇都宮大機器分析センター[2]) ○中田みなみ[1]・六本木誠[2]・大庭 亨[1]

Toward the measurement of micellar dipole potentials by voltage sensitive dyes

([1]*Faculty of Engineering, Utsunomiya University*, [2]*Center for Instrumental Analysis, Utsunomiya University*) ○Minami Nakada,[1] Makoto Roppongi,[2] Toru Oba[1]

Voltage-sensitive dyes (VSDs) are useful tools to visualize electric activity of live cells such as neural tissues, cardiac muscles, and mitochondria. VSDs have been evaluated by patch-clamp experiments on neurons. However, patch-clamp experiments are inadequate for facile screenings for efficient development of the dyes. We have studied facile dye screenings using micellar dipole potentials. Stark shift (*ex*. Di-4-ANEPPS, *ca*. 16.5 nm) was observed by fluorescence changes of the micellar aqueous solution (10 mM SDS) by increasing bulk ionic strength (NaCl, 0 to 200 mM). Compound b, on the other hand, showed 2.0-nm red-shift of the fluorescence maximum by the same environmental change. We will report evaluation of possible VSDs.

Keywords：dipole potential, micelle, membrane potential

膜電位感受性色素は、生体膜の電気的環境を介して細胞機能の出力を与える分子プローブである。膜電位感受性色素の評価ではパッチクランプ法で神経細胞に対する試験が行われることが多い。しかし、パッチクランプ法は特殊な技術を要する分析法であり、多数の候補分子を何度もスクリーニングして蛍光プローブの合成開発サイクルを効率良く進めていく方法としては適していない。我々はより簡便な評価法として、界面活性剤ミセルの dipole potential を利用する方法を検討してきた。本発表では、我々が開発した分子を含め、種々の蛍光プローブの検討結果を報告する。

色素 **a**〜**c** を内包させた SDS ミセル分散液に NaCl 水溶液を滴下し、色素の蛍光変化を検討した（**Figure 1, Table 1**）。NaCl 濃度 0 mM から 200 mM への変化にしたがって、**a** (Di-4-ANEPPS) の最大蛍光波長は 16.5 nm ほど浅色シフトした。これは神経細胞の膜電位が変化するときに観測される蛍光変化と同様である。また、b と c との比較から、電位応答には分子ワイヤー部が必要であると考えられた。

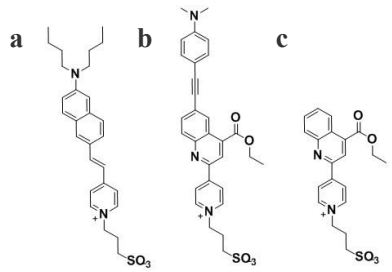

Figure 1. 色素 **a**〜**c** の分子構造.

Table 1. 色素 **a**〜**c** の蛍光変化.

	最大蛍光波長 [nm]	Peak shift [nm]	蛍光強度の変化
a	632.0	−16.5	2.59
b	560.5	+2.0	2.57
c	556.5	—	0.78

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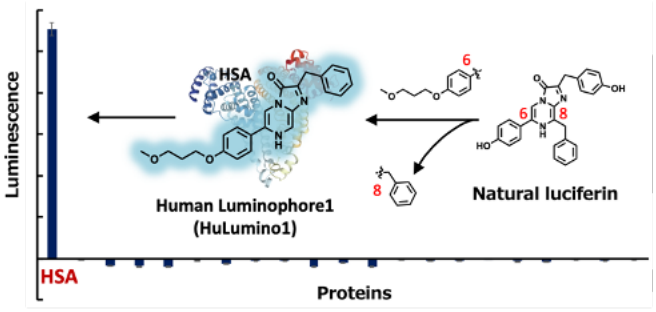
非発光タンパク質における擬似ルシフェラーゼ活性の発見と利用

（産業技術総合研究所[1]・JST さきがけ[2]・筑波大学[3]）○西原 諒[1,2]・栗田 僚ニ[1,3]
Discovery and utilization of pseudo-luciferase activities in non-luminescent proteins ([1]*National Institute of Advanced Industrial Science and Technology*, [2]*JST PREST*, [3]*University of Tsukuba*)○Ryo Nishihara,[1,2] Ryoji Kurita,[1,3]

Luminous organisms, such as *fireflies* and *sea pansy Renilla reniformis*, generate bioluminescence (BL), which is the light emission in the absence of external energy sources. In the core of BL, an enzymatic reaction occurs involving a bioluminescent substrate (luciferin) and enzyme (luciferase). In this presentation, we suggest that the introduction of appropriate exogenous luminescent substrates reveals pseudo-luciferase activity of non-bioluminescent proteins, which can significantly differ from the conventional function of the protein and has potential for use in quantitative luminescent analysis of proteins without any labeling procedures, including transgene introduction of luciferase from luminous organisms[1-3].

Keywords : Bioluminescence; Luminescence; Luciferase; Luciferin

ホタルなどの発光生物は、発光基質ルシフェリンとそれに対応する発光酵素ルシフェラーゼの酵素反応で発光する。本発表では、「発光生物由来の酵素でしか、生物発光反応を触媒できない」という常識から脱却し、ヒト由来タンパク質や他のタンパク質にもこれまで見出されてこなかった擬似的なルシフェラーゼ活性があることを発見、これら擬似ルシフェラーゼ活性は、標的タンパク質のラベル化や発光生物由来のルシフェラーゼを必要としない、新たなタンパク質発光分析技術として利用可能であることを提案する[1-3]。



擬似ルシフェラーゼ活性発見の例：天然基質の化学構造を変えると、ヒト血清アルブミン(HSA)がルシフェラーゼのように機能した。

1) Coelenterazine analogue with human serum albumin-specific bioluminescence. R. Nishihara, T. Tomita, K. Niwa, R. Kurita, *Bioconjugate Chem.* **2020**, *31*, 2679-2684.
2) Mix-and-read bioluminescent copper detection platform using a caged coelenterazine analogue. R. Nishihara, R. Kurita, *Analyst.* **2021**, *146*, 6139-6144.
3) Pseudo-Luciferase Activity of the SARS-CoV-2 Spike Protein for *Cypridina* Luciferin. R. Nishihara, H. M. Dokainish, Y. Kihara, H. Ashiba, Y. Sugita, R. Kurita, *ACS Cent. Sci.* **2023**, in press.

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新規なキノリン系ソルバトクロミック蛍光色素の合成と性質

（宇都宮大工[1]・宇都宮大機器分析センター[2]）○齊藤聡志[1]・六本木 誠[2]・大庭 亨[1]

Synthesis and photophysical properties of novel solvatochromic fluorescent dyes with quinolone-based molecular wires

([1]*Faculty of Engineering, Utsunomiya University*, [2]*Center for Instrumental Analysis, Utsunomiya University*) ○Satoshi Saito,[1] Makoto Roppongi,[2] Toru Oba[1]

We have studied development of voltage-sensitive dyes having a quinolone-based molecular wire. We synthesized new derivatives including amphiphilic ones and examined their fluorescence solvatochlomism. The one with a sulfo group at the end of the molecular wire showed the visible absorption maxima at 426 nm and 328 nm and the fluorescence maximum at 547 nm. Stokes shifts observed in 1-hexanol was 136 nm, while that in methanol was 123 nm. These data will be compared with those of the other analogs possessing carboxy, malonic acid, pyridinium, and thiomorphorine moieties as hydrophilic groups.

Keywords：solvatochromism, molecular wire, quinoline, voltage sensitive dye, membrane potential

我々は高感度な膜電位感受性色素の開発を最終目標として、キノリン骨格を含む分子ワイヤーを持つ色素を合成してきた。本研究では、これらの分子に種々の親水性官能基を導入した色素を合成し、その蛍光特性を検討した。分子ワイヤー末端にホルミル基を導入した後、亜硫酸水素イオンを付加させて化合物 **4** を合成した（**Fig. 1**）。スルホン酸を導入した **4** はメタノール中で 426 nm と 328 nm に吸収ピークを、547 nm に蛍光ピークを与えた。1-ヘキサノール中での Storks シフトは 136 nm であったのに対し、メタノール中では 123 nm であった。**4** を SDS ミセルに内包すると、ミセルの表面電位の変化に伴って（NaCl, 0→200 mM）蛍光強度が 7.3 倍に増加した。親水基としてカルボキシ基（**3**）、ピリジニウム（**5**）、マロン酸（**6**）、チオモルホリン（**7**）を導入した誘導体の性質についても報告する。

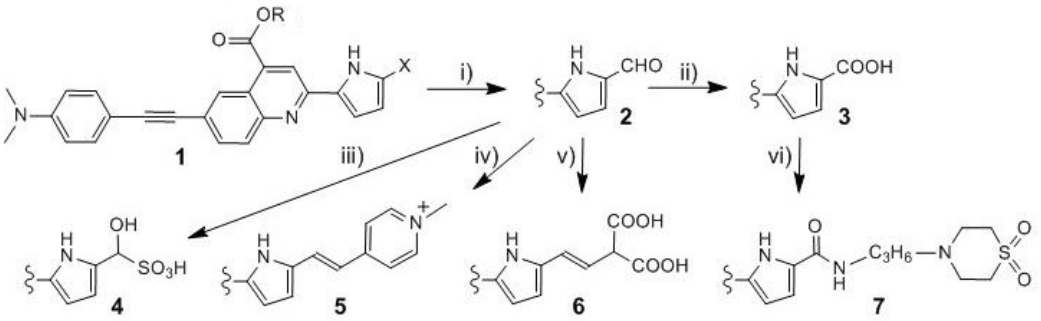

Fig. 1. キノリン系色素の誘導体化. i) $POCl_3$, DMF; ii) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene; iii) $NaHSO_3$; iv) 2,4-dimethylpyridinium, piperidine; v) malonic acid, piperidine; iv) 4-(3-aminopropyl)thiomorpholine 1,1-Dioxide, EDC, DMAP, Et_3N.

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アデニンオリゴマーを鋳型とした選択的水素結合による白金(II)錯体の集積制御

（城西大院理）○藤井 駿・仲谷 学
Control of molecular assembly of platinum(II) Complex bearing thymine substituents by selective hydrogen bonding with adenine oligomer (*Graduate School of Science, Josai University*) ○Shun Fujii, Manabu Nakaya

Molecular metal complexes change own functions variously depending on the molecular assemblies, and the control of the formation of molecular assemblies is an important key for achieving to give flexible functionalities. However, it is still difficult to control the assembly nature of complex molecules, and this is a major problem should be solved. In recent research, DNA have been found to be useful as a template for the arrangement of small molecules.

In this study, salophene-type platinum(II) complex bearing thymine (T) substituent (**T-Pt**) was synthesized, and was hybridized with various number of adenine (A) oligomers. The melting experiments using A_{10}-mer revealed that the melting temperature (T_m) decreased with increasing the amount of **T-Pt**. This suggests the molecular arrangement of **T-Pt** was quantitatively occurred between A_{10}-mer, however duplex formation was not occurred. A detailed discussion will be going on the presentation.

Keywords : Platinum(II) complex, DNA template, Molecular assembly.

金属錯体は、分子集積状態の変化に起因して様々に物性を変化させることから集積状態の制御が高機能化の重要な鍵とされ勢力的に研究が行われている。しかし、錯体分子の自在な集積状態の制御は、溶媒分子や錯体分子の様々な分子間相互作用に依存するため未だ困難であり現在も解決すべき大きな課題である。そこで、DNA を鋳型とした錯体分子の集積状態制御が報告されてきた [1]。DNA を鋳型に用いることで DNA の選択的塩基対形成を利用した錯体分子の自在な配列制御が可能になる。

本研究では、核酸塩基のチミン(T)を導入したサロフェン型白金(II)錯体（**T-Pt**）を合成しアデニン(A)オリゴマー（A_{10}-mer）との複合化を行った。任意の塩基数をもつアデニンオリゴマーに対して、**T-Pt** の比率を変えながら融解測定を行った。融解測定の結果より、**T-Pt** の等量が増えるにつれて融解温度（T_m 値）は減少した。このことから、**T-Pt** とアデニンオリゴマーとの定量的な相互作用形成は確認されたが、DNA 二重鎖形成などによる構造安定化は見られないことがわかった。分光測定の詳細な議論は当日に行う予定である。

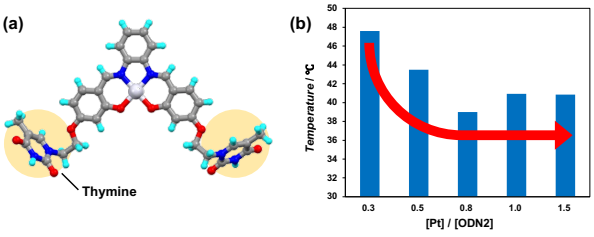

図 (a) **T-Pt** の単結晶構造解析。(b) **T-Pt** とアデニンオリゴマー（A_{10}-mer）複合体の T_m 値の変化。

1) T. Govindaraju, *et. al., Chem. Commun*., **2015**, *51*, 5493

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ミトコンドリア移行シグナルペプチド誘導体の合成と特性評価

（龍谷大先端理工[1],龍谷大農[2]）○齋田颯心[1]、山﨑正幸[2]、富﨑欣也[1]

Synthesis and characterization of a mitochondria transfer signal peptide derivative.

(Ryukoku University Department of Materials Chemistry[1], Ryukoku University Department of Food Sciences and Human Nutrition[2]) ○Soshin Saita[1], Masayuki Yamazaki[2] , Kin-ya Tomizaki[1]

Mitochondria are cell organelles playing important rules of ATP production and apoptosis. We are focusing on the design, synthesis, structural characterization, and cytotoxicity of the molecules of mitochondria transfer signal (MTS) derived from aldehyde dehydrogenase tethering a self-assembling peptide. In this research, we designed and synthesized peptides in which some amino acids of the MTS sequence were lacked and characterized their structures by spectroscopic measurements.

MTSΔC-p, which lacks the C-terminal sequence of MTS and MTSΔN-p, which lacks the N-terminal sequence of MTS were synthesized by Fmoc solid phase synthesis. CD spectra showed that both peptides were in random conformation in PBS, but formed α-helices in TFE and SDS-containing PBS. Cytotoxicity evaluation on HeLa cells showed resulted in cell viability about 50% for both peptides at a peptide concentration of 10 μM.

Keyword: Peptide, Mitochondria

ミトコンドリアは ATP の合成やアポトーシスに関与する細胞小器官である。当研究室ではアルデヒドデヒドロゲナーゼ由来のミトコンドリア移行シグナルペプチド(MTS)誘導体の設計、合成、構造特性評価、細胞毒性について研究をすすめている。これまでに、自己集合化ペプチドの N 末端に、MTS 配列の一部のアミノ酸を置換して結合させたペプチド（MTS-p）を設計および合成し、分光学的測定によってそれらの構造・特性を調べてきた。本研究では、MTS の C 末端側配列を欠損させた MTSΔC-p および N 末端側配列を欠損させた MTSΔN-p をそれぞれ Fmoc 固相合成法で合成し、構造と細胞毒性を調べた。CD 測定の結果、いずれのペプチドも PBS 中でランダム構造であるが、TFE 中および SDS 含有 PBS 中ではα-ヘリックス構造を形成した。また HeLa 細胞を対象とする細胞毒性評価では、いずれのペプチドも 10 μM において細胞生存率約 50%であった。

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シッフ塩基を有するクロロフィル誘導体の合成と物性

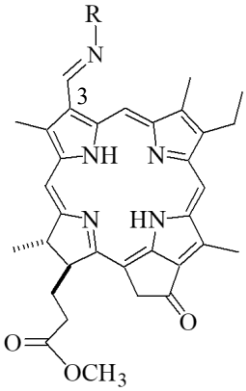
（龍谷大先端理工）○妹背 帆高・宮武 智弘
Synthesis and Properties of Schiff Base-Modified Chlorophyll Derivatives (*Faculty of Advanced Science and Technology, Ryukoku Univ.*) ○Hodaka Imose, Tomohiro Miyatake

Chlorophyll derivatives are known to change their spectroscopic properties depending on the substituents at the peripheral positions. In this study, we synthesized novel chlorophyll derivatives with a Schiff base moiety and examined their physical properties. The cast film of the chlorophyll derivatives exhibited red-shifted absorption bands due to pigment-pigment interactions. Heating treatment of the solid-state chlorophyll assemblies showed thermochromism with further red-shifted absorption bands.

Keywords: Chlorophyll, Self-Aggregation, Schiff Base

光合成色素であるクロロフィル類は可視～近赤外領域に特徴的な光吸収をもつ。クロロフィル骨格の 3 位（図 1）に導入された置換基は、その光吸収に大きな影響を与えることが知られており、天然系ではビニル基、ホルミル基、アセチル基などをもつ色素が存在している。

本研究では 3 位にシッフ塩基をもつクロロフィル誘導体（図 1）を合成し、その物性を検討した。まず天然より抽出したクロロフィル *a* を原料とし、3 位にビニル基をもつ誘導体を得た。このビニル基をホルミル基へと酸化した後、アミンを縮合させることで 3 位にシッフ塩基をもつ誘導体 **1**（R=$CH_2CH_2CH_2CH_3$）、および **2**（R=C_6H_5）をそれぞれ合成した。これらの誘導体はクロロホルムに溶解し、**1** は 676 nm に Qy 吸収波長を示した。一方、フェニル基を持つ **2** はより長波長側の 685 nm に吸収帯を示し、共役系の拡張による効果がみられた。つぎに誘導体 **1**, **2** のクロロホルム溶液をガラス板に滴下した後、溶媒を留去することでクロロフィルのキャストフィルムを作製した。このフィルムは溶液中の吸収帯よりも長波長にシフトした Qy 吸収帯を与え（**1**: 690 nm, **2**: 706 nm）、固体フィルムにおいてクロロフィルは色素間相互作用を持つことがわかった。また、このフィルムを加温すると Qy 吸収帯がそれぞれ長波長にシフトした（**1**: 714 nm, **2**: 737 nm）。このスペクトル変化は化合物の分解を伴っていないことから、この誘導体が形成する分子集積体の構造変化がサーモクロミズムを引き起こしたと考えられる。さらにシッフ塩基をもつ誘導体 **1**, **2** のアセトン溶液に金属塩を加えると、その分光学的特性が変化することを見出したのであわせて報告する。



1: R=$CH_2CH_2CH_2CH_3$
2: R=C_6H_5

図 1. シッフ塩基を有するクロロフィル誘導体

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上皮成長因子受容体を標的とした局在性ゲフィチニブの合成と評価

（名工大工[1]・名工大院工[2]）○三田村 啓史[1]・筒井 啓太[2]・吉川 優[2]・築地 真也[1,2]

Synthesis and evaluation of membrane-localizable gefitinib ligands targeting the epidermal growth factor receptor ([1]*Faculty of Engineering,* [2]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Keishi Mitamura[1], Keita Tsutsui[2], Masaru Yoshikawa[2], Shinya Tsukiji[1,2]

In general, small-molecule inhibitors are used in a way that they diffuse uniformly within the cell. However, considering that many target proteins, including cancer-/disease-causing proteins, are localized at specific membranes or organelles, positioning inhibitors to the site of target proteins is expected to (dramatically) improve their inhibitory effect. To demonstrate the validity of such an enhanced inhibitory effect by inhibitor localization, we set out to develop self-localizable gefitinib derivatives targeting the epidermal growth factor receptor (EGFR) at the plasma membrane (PM). In this presentation, we report the design and synthesis of gefitinib derivatives that localize to intracellular membranes, including the inner leaflet of the PM, and evaluate their localization and activity properties in cells.

Keywords: Inhibitor, Gefitinib, Epidermal growth factor receptor, Plasma membrane, Fluorescent probe

タンパク質の活性を阻害する低分子阻害剤は、ケミカルバイオロジーや創薬の柱となるモダリティの一つである。従来、これらの阻害剤は、細胞内を均一に拡散させて使用されてきた。一方、増殖因子受容体や Ras、p53 の変異体をはじめ、がん・疾患関連タンパク質の多くは、細胞膜、核内など、特定の膜やオルガネラに局在している[1-3]。そのため、細胞内の特定部位に局在しているタンパク質を標的とする場合、従来のように“阻害剤を細胞全体に拡散させる”のではなく、“阻害剤を標的タンパク質と同じ場所へ共局在させる”ことで、その阻害効果を劇的に向上させられるかも知れない。また、阻害剤を標的と共局在化させることで、親和性が十分でない阻害剤でも高い標的阻害活性を発揮させられる可能性や、オフターゲットの低減、あるいはごく少量の投与で効く薬剤の創製などに繋がるかも知れない。このようなアイデアのもと、我々のグループでは現在、標的タンパク質と共局在する「局在性阻害剤」の開発に着手している。

本研究では、局在性阻害剤の概念実証を目指し、上皮成長因子受容体（epidermal growth factor receptor, EGFR）に対する低分子阻害剤ゲフィチニブの局在性誘導体の開発を行った。本発表では、細胞膜インナーリーフレットに局在するゲフィチニブ誘導体群の設計と合成、および蛍光プローブを用いた各種阻害剤の局在・活性評価などの詳細を報告する。

1) A. E. Wakeling et al., *Cancer Res*. **2002**, 62, 5749−5754. 2) D. Kim et al., *Nature* **2023**, 619, 160−166. 3) J. R. S. Clarke et al., *ACS Pharmacol. Transl. Sci*. **2022**, 5, 1169−1180.

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環境変化に応答する新規プテリン型蛍光プローブの開発

（長浜バイオ大バイオサイエンス）○中井 咲輝・河合 靖・竹本 哲也・朝見 武永

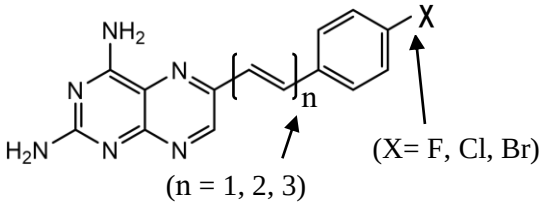
Development of novel environmentally responsive pterin-type fluorescent probes (*Faculty of Bioscience Nagahama Institute of Bio-Science and Technology*) ○Saki Nakai, Yasushi Kawai, Tetsuya Takemoto, Muyon Asami

Pterin is the generic term for natural pteridine compounds and also known as a fluorescent molecule. In this study, diaminopteridine derivatives with a substituted phenyl group linked by a conjugated linker have been synthesized as novel fluorescent probes. The number of double bonds in the linker was 1 to 3, and F, Cl, or Br were introduced as a substituent. Fluorescence measurements of the synthesized compounds in various solvents with different polarities showed that these compounds emit fluorescence in organic solvents, and their fluorescence properties changed with the polarity of the solvents. Some compounds are fluorescent solvatochromic molecules whose fluorescence wavelength changed with polarity. Furthermore, the fluorescence properties varied greatly depending on the length of the conjugated linker and the substituents. Since many of these compounds are quenched in water and respond sensitively to environmental changes, they are expected to be applied as fluorescent probes to detect specific proteins.

Keywords : Fluorescence Probe; Pterin; Environmental Response

プテリンは天然プテリジン化合物の総称であり、蛍光分子としても知られている。本研究では新規蛍光プローブの開発を目的に、プテリンの誘導体であるジアミノプテリジンを基本骨格として、様々な置換基を有するベンゼン環を共役系リンカーで繋いだ化合物を新たに合成した。リンカーの二重結合の数は 1〜3 個、置換基は F, Cl, Br を導入した。

合成した化合物を極性の異なる各種溶媒を用いて蛍光測定を行った結果、有機溶媒中で蛍光を発し、溶媒の極性に応じて蛍光特性が変化した。いくつかの化合物では、極性に応じて蛍光波長が変化する蛍光ソルバトクロミック分子であることを見出した。また、共役系の長さや置換基によって蛍光特性が大きく異なった。これらの化合物の多くは水中で消光しており、環境変化に敏感に応答することから、特定のタンパク質を検出する蛍光プローブとしての応用が期待できる。



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クマリルアルコール誘導体修飾 5-アミノレブリン酸の光線力学的効果

（阪公大院工 [1], 阪公大工 [2]）○東　秀紀 [1]・森田昂祐 [1]・福島　凛 [2]・長崎　健 [1]
Photodynamic effect of coumaryl alcohol derivative-modified 5-aminolevulinic acid
([1]*Graduate School of Engineering*, [2]*Faculty of Engineering*, *Osaka Metropolitan University*)
○Hideki Azuma, [1] Kosuke Morita,[1] Rin Fukushima,[2] Takeshi Nagasaki[1]

Recently, we found that 4-((*E*)-3-Hydroxyprop-1-enyl) phenyl acetate (HPA), a coumaryl alcohol derivative, reduces the intracellular reduced glutathione (GSH) level. In this study, we examined the modifying effect of HPA on ALA-PDT using HPA-functionalized ALA. Unfortunately, PDT activity of HPA-ALA was lower than that of a membrane permeable analogue Hex-ALA against mouse carcinoma Colon26 cells. However, HPA-ALA showed high cell death activity against mouse melanoma B16BL6 cells under the photoirradiation, although high cytotoxic effect of HPA-ALA was also observed under no irradiation condition. HPA-ALA may also act as an inhibitor against some kind of receptor (or transporter) on the cell surface of the melanoma cells.

*Keywords : Photodynamic Therapy; Coumaryl alcohol; Glutathione; Reactive oxygen species; 5-Amino*levulinic *acid; Quinone methide*

我々は以前、クマリルアルコール誘導体 4-((*E*)-3-Hydroxyprop-1-enyl) phenyl acetate (HPA) に細胞内グルタチオン量を低下させる効果があることを見出した。そこで今回、5-アミノレブリン酸（ALA）に HPA を修飾した HPA-ALA を合成し、ALA-PDT における HPA の修飾効果を評価した。マウス大腸がん由来 Colon26 細胞に対しては、HPA-ALA の PDT 活性は膜透過性の Hex-ALA よりも低くなった。一方、マウスメラノーマ由来 B16BL6 細胞に対しては、Hex-ALA では PDT 活性が見られなかったのに対し、HPA-ALA は高い細胞傷害性を示したが非照射下でも毒性が見られた。この細胞毒性は HPA&ALA では見られないことから、HPA-ALA はそれ自体でメラノーマに対して何らかの作用を示すことが示唆された。また、GSH を不活性化させて PDT 活性を向上させるため、HPA をベースによりチオール基と反応しやすいキノンメチド前駆体についての検討も行ったので報告する。

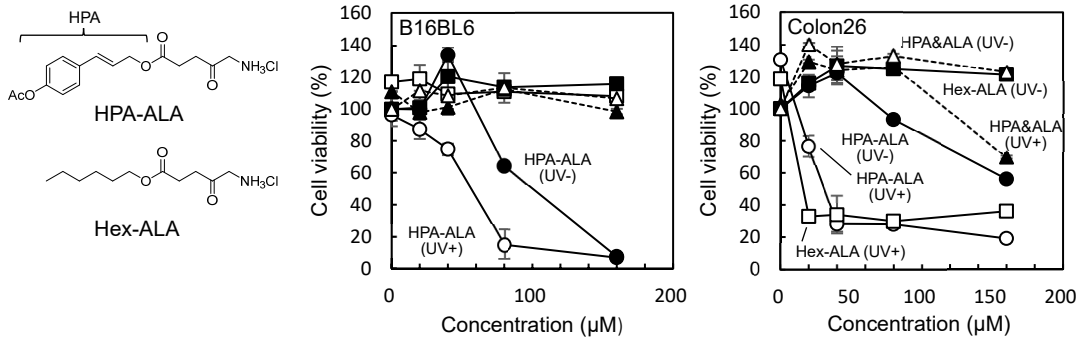

Fig. 1　Photodynamic effect of HPA-ALA against mouse melanoma B16BL6 and mouse carcinoma Colon26 cells.

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光応答性分子の可視光照射によるプラズモニックチップセンサーチップの調製

（関西学院大理工[1]・埼玉工業大工[2]）○浅野恭平[1]・堀尾祥平[1]・名和靖矩[1]・田中睦生[2]・田和 圭子[1]

Preparation of plasmonic chip sensor chip by visible light of photo-responsible molecule

(*[1]School of science and technology, Kwansei Gakuin University, [2]Saitama Institute of Technology*)○Kyohei Asano,[1] Shohei Horio,[1] Yasunori Nawa,[1] Mutsuo Tanaka,[2] Keiko Tawa[1]

Highly sensitive multiple detection of biological interactions has been performed by the enhanced electric field on a plasmonic chip. The enhanced electric field was utilized for not only enhanced fluorescence but also promotion of photochemical reactions. In this study, in order to improve the detection sensitivity, B-O-MBA was synthesized as a new O-MBA molecule and immobilized on the chip surface. In addition, Cy5-maleimide was reacted with the intermediates of B-O-MBA formed by exposure to visible light at a wavelength of 410nm. Fluorescence images were taken with upright-inverted microscope and fluorescence enhancement and binding density of Cy5-M were evaluated from the ratio of fluorescence intensities inside exposure spot to that outside.

Keywords : Plasmon, Fluorescence Microscopy, Enhanced Fluorescence, Biosensor, Photochemical Reaction.

当研究室では、波長サイズの周期構造を持つ金属薄膜で覆われたプラズモニックチップを使用し、この上に結合した蛍光分子の表面プラズモン共鳴による増強蛍光で、高感度な蛍光バイオセンサーの開発に取り組んできた。このプラズモニックチップによる増強電場は蛍光増強だけでなく、光化学反応を促進する場として用いることもでき、これまでに 3-(2-formyl-3-methylphenyl)thio)propionic acid (P-O-MBA)を用いて UV 光照射スポットのみ捕捉分子を結合させてアレイ化し、生体相互作用の高感度マルチアレイ検出を行ってきた。本研究ではより高感度な相互作用検出を行うために、プラズモンとの結合効率の大きい可視光で光反応する 4-((2-formyl-3-methylphenyl)thio)benzoic acid (B-O-MBA)（Fig.1）を合成した。B-O-MBA をチップ表面に修飾し、正立倒立蛍光顕微鏡下で波長 410nm の光をチップ裏面より照射して反応中間体を形成し、Cy5-マレイミド(Cy5-M)を Diels-Alder 反応で結合した。撮影した蛍光像（Fig.2）の解析から可視光照射スポット内外の蛍光強度を評価することで、蛍光増強度や Cy5-M の結合密度を明らかにした。

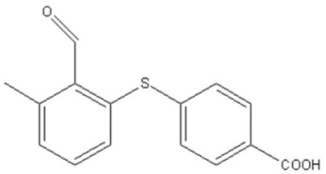

Fig.1 Molecular structure of B-O-MBA

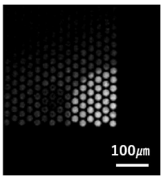

Fig.2 Fluorescence image of Cy5-M reacted with B-O-MBA by exposure to visible light

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接近/乖離による共役拡張プテリン型蛍光プローブのリンカーの鎖長の効果

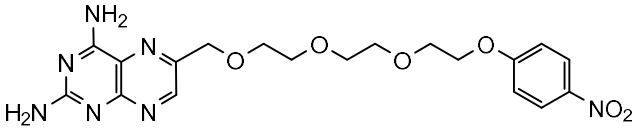
（長浜バイオ大院バイオサイエンス）○西谷悠、河合靖

Effect of linker length on conjugation-extended pterin-type fluorescence probes (*Graduate School of Bioscience, Nagahama Institute of Bio-Science and Technology*) ○Haruka Nishitani, Yasushi Kawai

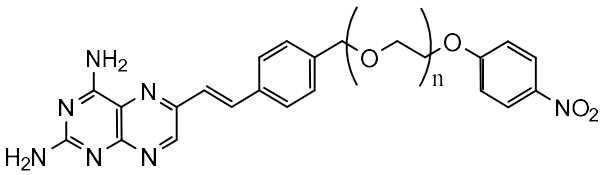
Contact/separation type fluorescence probe **2** based on conjugation-extended diaminopteridine have been reported. Further improvement is desired due to poor off/on efficiency of this probe. We have synthesized a probe **3** with a shorter chain length of the linker moiety. These probes **2** and **3** are expected to quench under hydrophilic conditions as the fluorescence pterin moiety and nitrophenyl quencher group contact with each other. In contrast, under hydrophobic conditions, they are considered to show fluorescence emission as the pterin moiety and nitrophenyl group separated from each other. Therefore, they can be expected to be applied as environment-responsive fluorescent probes. The evaluation of the effect of linker chain length on the fluorescence properties of these new probes will be reported.

Keywords：fluorescence probe, pterin, fluorescence imaging

これまでに共役拡張ジアミノプテリジンを用いた接近/乖離型蛍光プローブ **2** を報告した。これはプテリンの特性で蛍光の off/on 効率が悪いというプローブ **1** の問題を改善することができたが、off/on 効率のさらなる改善が望まれている。そこでリンカー部位の鎖長を短くしたプローブ **3** を新たに合成した。これらのプローブ **2** と **3** は親水性環境で消光基のニトロフェニル基が蛍光基のプテリンに接近して消光し、疎水性環境では乖離して蛍光を発するという、環境応答型の蛍光プローブとしての利用が期待できる。本講演では、これらの新規プローブの蛍光特性におけるリンカー鎖長の効果を評価したので報告する。



1



n=3：**2**

2：**3**

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ゲノム操作を志向した光を用いた長鎖オリゴ核酸への DNA２本鎖侵入法開発

（北陸先端大バイオ機能 [1]）○ZUMILA HAILILI[1]・MO JUNLING[1]・藤本　健造 [1]
Development of photo-triggered DNA double-strand invasion method targeting long chain oligonucleotides oriented to genome manipulation ([1]Biofunctional Medical Engineering Research Area, *Japan Advanced Institute of Science and Technology*) ○ZUMILA HAILILI,[1] MO JUNLING,[1] Fujimoto Kenzo[1]

Natural DNA restriction enzymes bind duplex DNA with high affinity at multiple sites. For artificial restriction moieties, however, it is difficult to open long-range double-strand DNA for efficient cleavage. In our previous research we have reported photo-induced double-duplex invasion (pDDI) methods using 3-cyanovinylcarbazole nucleoside (^{CNV}K)[1,2]. ^{CNV}K is an ultra-fast photo-cross-linker developed by our lab. ^{CNV}K can form covalent bond to pyrimidine bases in -1 position in its complementary strand within 1 s under 366 nm UV irradiation. And it has succeeded in achieving double-duplex invasion. However, the inter-probe cross-linking of the ^{CNV}K-containing probes has been a major drawback in gaining maximum invasion rate. We have confirmed that replacing the pyrimidine at the cross-linking site in the probes with 5-cyanouracil (^{CN}U) can suppress inter-probe cross-linking while maintaining the pDDI efficiency[3]. In this study, we investigated the condition for improving the overall pDDI efficiency using a long-range dsDNA as a template. And for pDDI probes, photo-cross-linkable ODNs containing ^{CNV}K and ^{CN}U as inter-probe cross-linking suppresser were tested.
Keywords : Genome Manipulation; DNA Photo-cross-linker; Double Duplex Invasion

遺伝子工学等で日常的に用いられている制限酵素は、二重鎖 DNA に対して高い親和性を有し配列選択的に DNA を切断する。一方、人工制限酵素では、優れた切断能力を有しているとしても、そもそも長鎖二本鎖 DNA 引き剥がすこと自体が困難である。我々の以前の研究では、3-シアノビニルカルバゾールヌクレオシド（^{CNV}K）を用いた光誘導二重鎖侵入（pDDI）法を報告している [1,2]。^{CNV}K は当研究室が開発した超高速光架橋剤である。^{CNV}K は、366nm の紫外線照射下で 1 秒以内に相補鎖の-1 位のピリミジン塩基と共有結合を形成することができる。しかし、^{CNV}K を含むプローブのプローブ間架橋は、最大侵襲率を得る上で大きな欠点であった。我々は、プローブの架橋部位のピリミジンを ^{CN}U で置換することにより、pDDI 効率を維持した上プローブ間架橋を抑制できることを確認している [3)]。本研究では、長距離 dsDNA を鋳型として、pDDI 全体の効率を向上させるための条件を検討した。そして、pDDI プローブとして、プローブ間架橋抑制剤として ^{CNV}K と ^{CN}U を含む光架橋性 ODN を試験した。

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可逆的光架橋により高速化したプリン塩基への架橋反応開発

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Development of crosslinking to purine bases in DNA accelerated by reversible DNA photocrosslinking

(Biofunctional Medical Engineering Research Area, Japan Advanced Institute of Science and Technology)
○Mo Junling, Rei Hirahara, Kenzo Fujimoto

Crosslinking between DNA strands is known to lead to applications such as SNP typing, regulation of transcription and translation, and treatment of genetic diseases. It is also known that cross-linking between DNA strands requires a long time to cross-link to purine bases. We have previously reported on photo-manipulation of nucleic acids using photoresponsive artificial nucleic acids, mainly 3-cyanovinylcarbazole nucleoside (^{CNV}K), which is a photo-crosslinking element[1]. Photoresponsive artificial nucleic acids incorporating these photocrosslinking elements into DNA strands exhibit regioselective photocrosslinking reactions by [2+2] photoreduction with pyrimidine bases such as thymine and cytosine present in DNA and RNA strands upon photoirradiation. In addition, we have recently developed 4-methylpyranocarbazole nucleoside (^{MEP}K), which shows selective photocrosslinking only to thymine, and reported the results of the crosslinking method[2]. While there are many examples of crosslinking to pyrimidine bases, crosslinking to purine bases has not been reported very often. Moreover, it is known that purine base crosslinking requires a long time when crosslinking between DNA strands. Therefore, we have conducted experiments to investigate the possibility of improving the speed of crosslinking to purine bases via reversible DNA photo crosslinking using the already developed ultrafast photo-crosslinker (^{CNV}K).

Keywords：crosslinking to purine bases; photocrosslinking;

DNA 鎖間の架橋は SNP タイピング・転写及び翻訳の制御・遺伝性疾患の治療といった応用に繋がることが知られている。また、DNA 鎖間を架橋する際にプリン塩基への架橋には長時間必要であることも知られている。我々はこれまで光架橋素子 3-cyanovinylcarbazole nucleoside (^{CNV}K)を中心とした光応答性人工核酸を用いた核酸類光操作法について報告している [1]。この光架橋素子を DNA 鎖に組み込んだ光応答性人工核酸は光照射により，DNA 鎖や RNA 鎖内に存在するチミンやシトシンといったピリミジン塩基と[2+2]光還化することで，位置選択的な光架橋反応を示す。また、最近クロスリンク法に関して､チミンにのみ選択的な光架橋を示す 4-methylpyranocarbazole nucleoside (^{MEP}K)の開発に成功し、その結果について当研究室より報告している [2]。この様にピリミジン塩基への架橋例は多いのに対しプリン塩基への架橋についてはあまり報告されていない。しかも、DNA 鎖間を架橋する際にプリン塩基への架橋には長時間必要であることも知られている。そこで、我々は既に開発済みの超高速光クロスリンカー（^{CNV}K）による可逆的な DNA 光クロスリンクを経由させることでプリン塩基への速度を向上させられないかと考え実験をおこなったので報告する。

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細胞選択的送達を目指した糖リガンド修飾アンチセンス核酸の合成と性質

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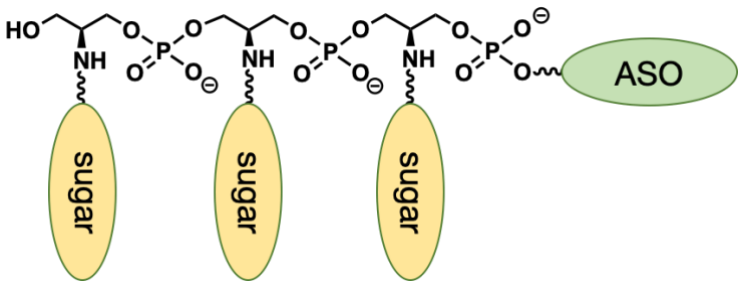
Synthesis and properties of oligonucleotides conjugated with sugar ligands for selective cell delivery ([1]*Sch. Life Sci. Tech., Tokyo Tech,* [2]*Showa Univ*) ○Daiki Shimamura[1], Remi Arie[1], Shuri Kaneyama[2], Aya Miyauchi[2], Koji Seio[1], Yoshiaki Masaki[1]

Antisense oligonucleotides (ASOs) are used as therapeutic agents targeting RNA. ASOs exhibit therapeutic effects when they are taken up by the target cells. However, ASOs can also be taken up by non-targeted cells, leading to side effects. Therefore, there have been widely studied to develop methods for selectively delivering ASOs to target cells using ligand molecules that bind to receptors highly expressed in those cells. There have been studies on ligand molecules such as cholesterol, tocopherol, sugars, peptides, aptamers, and antibodies.

In this study, we focused on sugars as ligand molecules. It is known that the interaction between a single sugar molecule and sugar-binding receptors is relatively weak, but the multivalent effect, achieved by multiple sugars binding, greatly enhances the interaction. Therefore, we synthesized ASOs having multiple sugar molecules. The details will be reported.

Keywords : Antisense oligonucleotide; small-molecule ligand; sugar conjugation

アンチセンス核酸（ASO）は RNA を標的とした治療薬として用いられる。ASO を体内に投与し、標的の細胞に取り込まれることで薬効を発揮するが、標的外の細胞にも送達され、副作用の原因となる。そこで標的細胞で発現している受容体等に結合するリガンド分子を利用し、選択的に薬物を標的細胞へ送達する方法が広く研究されてきている。ここでリガンド分子として、コレステロールやトコフェロール、糖などの低分子、ペプチド、アプタマー、抗体などが利用されている。本研究では、リガンド分子として、糖に着目した。単一の糖分子と糖認識受容体の相互作用は弱いが、複数の糖が結合するマルチバレント効果により、相互作用が大幅に増強することが知られている。そこでセリノールをリンカーとして用い、糖分子を複数個導入した ASO の合成を行った。合成した ASO の性質を評価したのでその詳細を報告する。



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光クロスリンク能を有する人工核酸を用いた細胞内 RNA 挙動の光制御

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Photocontrol of intracellular RNA behavior using artificial nucleic acids with RNA photo-crosslinking.(Biofunctional Medical Engineering Research Area, Japan Advanced Institute of Science and Technology) ○Huang Qingyuan, Mo Junling, Kenzo Fujimoto

Antisense nucleic acids bind to intracellular RNA in a sequence-specific manner and can suppress the expression of target genes. Some antisense nucleic acids are already on the market and are considered one of the approaches that are being studied for practical use. These antisense nucleic acids contain various modifications, such as Peptide Nucleic Acid (PNA) and Locked Nucleic Acid (LNA), which can greatly improve the binding strength to the target. On the other hand, we have reported a method of photo-manipulation of nucleic acids using chemically modified photoresponsive artificial nucleic acids. We have also succeeded in suppressing the expression of target genes by introducing these photoresponsive artificial nucleic acids into cells as antisense nucleic acids and irradiating them with light. For example, DNA containing 3-cyanovinylcarbazole (^{CNV}K)[1], a photoresponsive artificial nucleic acid, can be photocrosslinked to pyrimidine bases in the complementary strand after a few seconds of photoirradiation. We have already succeeded in controlling the thermal stability of DNA nanostructures and in detecting RNA independent of the higher-order structure of RNA. Recently, we have also succeeded in developing 4-methylpyranocarbazole nucleoside (^{MEP}K)[2], a photoresponsive element that can be photocrosslinked by visible light. In this report, we describe the photocontrol of intracellular RNA behavior using artificial nucleic acids containing these original photoresponsive elements.
Keywords : 4-methylpyranocarbazole; photocrosslinking;

アンチセンス核酸は細胞内 RNA に配列特異的に結合し、標的の遺伝子発現を抑制できる。既に上市されているアンチセンス核酸もあり、実用化に向けて研究が進んでいるアプローチの一つとされている。これらアンチセンス核酸は様々な修飾を含んでおり、Peptide Nucleic Acid(PNA)や Locked Nucleic Acid(LNA)などの骨格を変更したものは標的に対し、結合力を大きく向上することができる。

一方、我々はこれまで化学的に修飾を施した光応答性人工核酸を用いた核酸類光操作法を報告している。またこの人工核酸をアンチセンス核酸として細胞内に導入し、光照射を行うことで標的遺伝子の発現を抑制することにも成功している。例えば、光応答性人工核酸である 3-cyanovinylcarbazole(^{CNV}K)[1] を含む DNA は数秒の光照射で相補鎖中のピリミジンと光架橋することができる。既に、DNA ナノ構造体の熱的安定性の制御や RNA の高次構造に依存しない RNA 検出にも成功している。また最近では可視光により光クロスリンク可能な光応答素子 4-methylpyranocarbazole nucleoside (^{MEP}K)[2] の開発に成功している。今回、これら研究室独自の光応答素子を含む人工核酸を用いた細胞内 RNA 挙動の光制御をおこなったので報告する。

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周辺配列によって架橋位置をスイッチング可能な新規 DNA 光反応の開発

（北陸先端科学技術大学院大学　バイオ機能医工学研究領域）○小田井柊也・莫竣凌・藤本健造

Development of novel DNA photo-crosslinking that enables switching of crosslink sites by peripheral sequences.

(Biofunctional Medical Engineering Research Area, Japan Advanced Institute of Science and Technology)
○Touya Odai, Mo Junling, Kenzo Fujimoto

We have previously reported on photochemical manipulation of nucleic acids using photo-responsive artificial nucleic acids. These methods can be divided into two major categories: photoligation, in which nucleic acids are linked together using light depending on the template DNA sequence, and photocrosslinking[1], in which nucleic acids are directly cross-linked to the template DNA or RNA. In the photocrosslinking method, we have succeeded in developing 4-methylpyranocarbazole nucleoside (^{MEP}K), which selectively crosslinks thymine only, and have reported the results from our laboratory[2]. In that paper, we showed that ^{MEP}K photocrosslinks at 400 nm, which is a weakly phototoxic visible light source. On the other hand, there have been few reports on DNA ligation using weakly phototoxic visible light. In this study, we report the development of a novel DNA photoreaction in which ligation and crosslinking can be controlled with visible light by switching the cross-linking position according to the surrounding sequence of ^{MEP}K. In the future, nucleic acid probes containing ^{MEP}K that can largely switch reactions according to the sequence information will be used to correctly read nucleic acid information in living cells by light, which is expected to lead to the development of intracellular nucleic acid analysis.
Keywords : 4-methylpyranocarbazole; photocrosslinking; photligation

我々はこれまで光応答性人工核酸を用いた核酸類光操作法について報告している。この操作法は鋳型となる配列に依存して光を用いて核酸同士を繋げる光ライゲーション法と鋳型に対して直接架橋する光クロスリンク法[1]の２つに大別される。光クロスリンク法に関して、チミンにのみ選択的な光架橋を示す 4-methylpyranocarbazole nucleoside (^{MEP}K)の開発に成功し、その結果について当研究室より報告している。その論文の中で ^{MEP}K が光毒性の弱い可視光の 400 nm で光架橋していることを明らかにしている[2]。一方、光毒性の弱い可視光で DNA 同士を繋げるライゲーションについては報告例はほとんどなかった。今回、^{MEP}K の周辺配列によって架橋位置をスイッチングすることで、ライゲーションとクロスリンクを可視光で制御可能な新規 DNA 光反応を開発したので報告する。今後、この配列情報に従って大きく反応をスイッチング可能な ^{MEP}K を含む核酸プローブを用いることにより、生細胞内の核酸情報を正しく光で読み取ることが可能となるため細胞内核酸解析への発展が期待される。

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グアニン四重鎖形成に及ぼすポリビニルアルコールの影響

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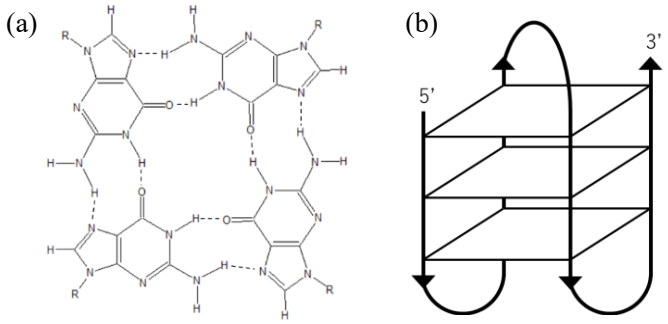
Effect of polyvinyl alcohol on G-quadruplex formation (Department of Chemical Engineering, National Inst. of Tech., Nara College) ○Takahiro Nakamura, Ryoko Uda

G-quadruplex (G4) has a structure with stacked G-quartet planes (Scheme) and is known for the effect on the inhibition of telomerase. Therefore, this structure has attracted attention in cancer therapy. Mechanism of G4 formation has been studied under the conditions with the ionic concentration of cellular environments and molecular crowding. For example, there have been many investigations of the effect of alcohol or polyethylene glycol on G4 structures. We have focused on polyvinyl alcohol (PVA) to afford molecular crowding environment, which has been seldom reported. The purpose of this work is to investigate the effect of PVA on the formation of G4. We used oligonucleotides having the sequence observed in human telomer region. The results of circular dichroism spectra indicated that PVA induced formation of antiparallel G4. From the measurements using fluorescence probe, polarity change of aqueous solution caused by the addition of polymer hardly affects the formation of G4.
Keywords : G-quadruplex; molecular crowding; polyvinyl alcohol

グアニン四重鎖は G カルテット平面が積層した構造を持ち、テロメラーゼに対して阻害効果を有することが知られている。そのため、がん治療の点から注目されている構造である。これまでに細胞内環境のイオン濃度や分子クラウディングを再現し、グアニン四重鎖形成のメカニズムなどが研究されてきた。例えば、アルコールやポリエチレングリコールを添加し、グアニン四重鎖構造への影響を調べた研究には多数の報告がある。そこで本研究では、報告例の少ないポリビニルアルコールを用いて分子クラウディング環境を作り、グアニン四重鎖構造の形成にどのような影響をもたらすのかを調べることを目的とした。試料には、ヒトテロメア領域にみられる塩基配列を有するオリゴヌクレオチドを用いた。円二色性スペクトル測定より、ポリビニルアルコールはアンチパラレル型グアニン四重鎖構造を誘起することが分かった。また、蛍光プローブを用いた評価から、ポリマー添加による水溶液の極性変化は、グアニン四重鎖の形成にほとんど影響しないことが分かった。



Scheme (a) Chemical structure of G-quartet. (b) Antiparallel G-quadruplex structure. Squares correspond to G-quartets.

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光架橋ビオチンリンカーを有するグアノシンテトラリン酸誘導体の合成

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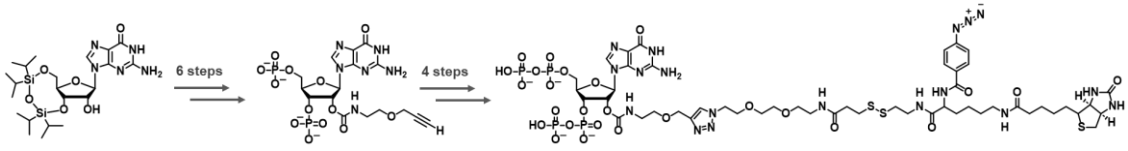
Synthesis of guanosine tetraphosphate analogue having photoreactive biotinylation linker

(1. Sch. Life Sci. Tech., Tokyo Tech.) ○Yudai Suzuki[1], Yukine Suda[1], Ayano Iwake[1], Yoshiaki Masaki[1], Kohji Seio[1]

Guanosine tetraphosphate (ppGpp) is present in bacteria and is known to act as a second messenger in the stringent response[1]. Recently, ppGpp was found to be present not only in bacteria but also in eukaryotes. However, the detailed mechanism remains unclear. To elucidate the mechanism, it is necessary to comprehensively identify the proteins that bind ppGpp. In the past, there have been reports of studies using compounds in which a linker was introduced into the pyrophosphate moiety[2] and a linker was introduced into the base moiety[3]. However, this method cannot identify the protein that binds to the pyrophosphate or base. Therefore, in this study, we designed and synthesized a compound in which a linker with a photoreactive group and biotin was attached to the 2′ position of ppGpp

Keywords : pGp, ppGpp, second messenger, stringent response, phosphoramidite,

グアノシンテトラリン酸（ppGpp）は細菌に存在し、緊縮応答のセカンドメッセンジャーとして働くことで知られる[1]。近年、ppGpp が細菌のみでなく真核生物にも存在することが明らかとなった。しかし、その詳細なメカニズムは依然不明である。このメカニズムを解明するためには ppGpp と結合するタンパク質の網羅的な同定を行うことが必要である。過去にはピロリン酸部にリンカーを導入した化合物[2]や塩基部にリンカーを導入した化合物[3]による研究の報告がある。しかし、この手法ではピロリン酸部や塩基部に結合するタンパク質を同定することが出来ない。そこで本研究では、ppGpp の 2′位に光架橋基とビオチンを持つリンカーを付与した化合物の設計・合成を行った。



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ジフェニルアントラセンまたはピレン修飾シチジンを有するDNAの合成とその構造

（兵庫県立大院工）○泉 了介・岡本 蒼生・中村 光伸・高田 忠雄

Synthesis and structure of DNA with diphenylanthracene or pyrene-modified cytidine

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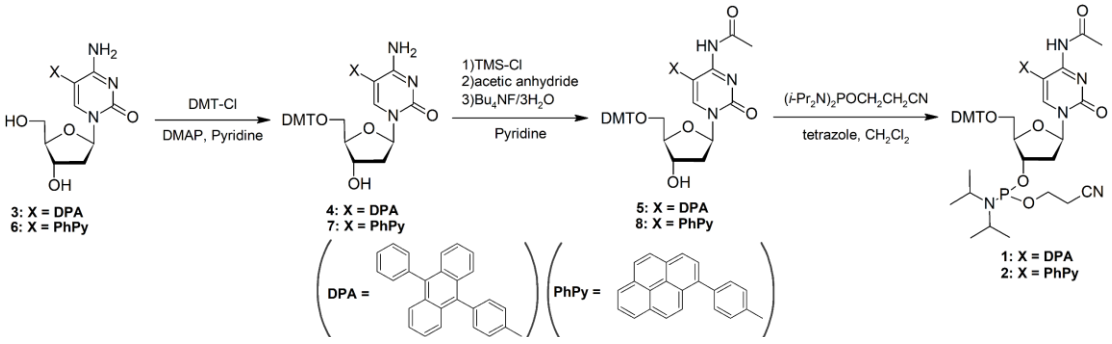
DNA normally assumes a right-handed double-helix (B-form), but under certain pH, salt concentration conditions, and temperature, it assumes a left-handed double-helix (Z-form). The B-Z transition of DNA can be regarded as a molecular switching system and is expected to be utilized for biosensors. Although there have been many studies on molecular switching systems based on B-Z conformational transitions using pyrene, only a few reports use 9,10-diphenylanthracene (DPA) as a fluorescent probe. In this study, to clarify the sequence behavior between dye molecules on duplex DNA by DNA conformational transition, we investigated the synthesis of DNA with G-C repeating sequence using DPA or 1-phenylpyrene-modified cytidine and investigated its properties.

Keywords: Association, DNA, Structural transition, 9,10-diphenylanthracene, Pyrene

DNA は通常右巻き二重らせんの B 型構造を形成するが、特定の外部刺激により左巻き二重らせんの Z 型構造を形成する。このような DNA の B-Z 構造転移は分子スイッチとしてみなすことができ、バイオセンサーなどへの応用が期待できる。これまでピレンを用いた B-Z 構造転移による分子スイッチに関する多くの研究が行われてきたが、9,10-ジフェニルアントラセン(DPA)を蛍光プローブとして用いた研究例は多くはない。本研究では DNA 構造転移による二重鎖 DNA 上の色素分子間の配列挙動を明らかにするために、DPA または 1-フェニルピレン(PhPy)を修飾したシチジンを用いて G-C 繰返し配列を持つ DNA の合成を検討し、その特性を調査した。



Scheme 1 Synthesis of **1** and **2**.

DNA1 5' - CGC G**C(DPA)**G CGC GCG - 3'
DNA2 5' - CGC GCG **C(DPA)**GC GCG - 3'
DNA3 5' - CGC G**C(DPA)**G **C(DPA)**GC GCG - 3'
DNA4 5' - CGC G**C(PhPy)**G CGC GCG - 3'
DNA5 5' - CGC GCG **C(PhPy)**GC GCG - 3'
DNA6 5' - CGC G**C(PhPy)**G **C(PhPy)**GC GCG - 3'

Figure 1 Sequences of DPA or PhPy modified DNAs.

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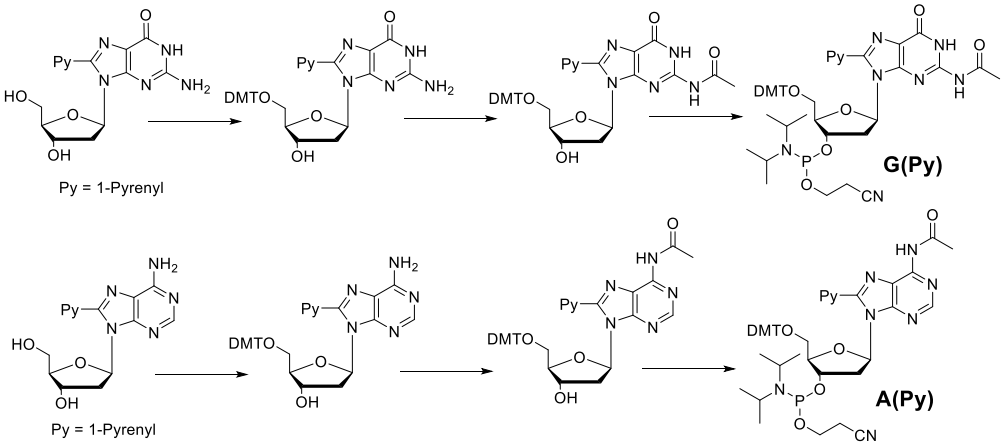
ピレンを連結したグアノシンおよびアデノシンを有するDNAの合成とその構造

（兵庫県立大院工）○中島 悠斗・○瀧口 遥二郎・中村 光伸・高田 忠雄
Structures of DNAs having pyrene-modified deoxyguanosine and deoxyadenosine (*Graduate School of Engineering, University of Hyogo*) ○ Yuto Nakajima, ○ Yojiro Takiguchi, Mitsunobu Nakamura, Tadao Takada

B- to Z-DNA transitions play a crucial role in biological systems and have attracted interest for their applications in DNA nanotechnology. DNA and DNA analogs have also been used as templates to construct helical chromophore associations with π-interactions. In this work pyrene labeled guanosine or adenosine DNAs having alternating purine-pyrimidine repeats were synthesized to investigate the pyrene association on DNA duplexes. Molecular dynamics (MD) simulations of the B-form and Z-form **DNAs** were performed to elucidate the structures. The pyrenes of **DNAs** were placed in the major groove of the duplex without intercalating.
Keywords : *Pyrene*; *Molecular Association*; *DNA*; *B-Z Transition*

DNAは特定の環境下において、右巻きのB-型から左巻きのZ-型の二重らせんに構造を変化させることが知られている。このようなDNAの構造転移を利用し、分子スイッチとして用いることができれば、バイオセンサーなどへの活用が期待できる。本研究ではピレンを有するプリンーピリミジン繰返し配列のDNAを合成し、さらに分子動力学計算によっても構造転移による DNA 上のピレン間の配列挙動を検討した。

ホスホリルアミダイト法による固相合成に対応したピレン修飾アミダイトをScheme 1に従い合成した。このアミダイトを用いて、Figure 1に示すDNAの合成を行った。分子動力学計算により、**DNA1**、**DNA2** のB-型およびZ-型二重らせん上のピレンはインターカレートすることなく二重らせんの主構に位置し、B-Z構造転移によりピレン間のコンフォメーションが変化した。



Scheme 1. Syntheses of **G(Py)** and **A(Py)**.

DNA1: 5'-CGC GC**G(Py)** CGC GCG-3'
3'-GCG CGC **G(Py)**CG CGC-5'

DNA2: 5'-CGC GC**A(Py)** TGC GCG-3'
3'-GCG CGT **A(Py)**CG CGC-5'

Figure 1. Sequences of DNAs.

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C5-ヘテロアリール-ピリミジンヌクレオシドの蛍光特性と DNA 合成後修飾

(群馬大院理工[1]・群馬大理工[2]) 原未羽[1]・工藤圭太[1]・櫻井希衣[2]・吉澤若葉[2]・○尾崎広明[1]

Fluorescence properties of C5-heteroaryl-pyrimidine nucleosides and post-synthetic modification of DNA ([1]*Graduate School of Science and Technology, Gunma University*, [2]*School of Science and Technology, Gunma University*) Miu Hara,[1] Keita Kudo,[1] Kie Sakurai,[2] Wakaba Yoshizawa,[2] ○Hiroaki Ozaki[1]

C5-Heteroaryl-pyrimidine nucleosides have unique spectroscopic properties. Emission wavelength of 5-benzofuranyl-2′-deoxyuridine and 5-benzofuranyluridine increased with increasing the solvent polarity[1,2], similar to 5-naphthyl-2′-deoxyuridine[3]. 5-Indolyluridine has also similar photophysical properties and additionally, the fluorescence was quenched by high-polarity solvents such as water[1]. In this study, fluorescent C5-heteroaryl-2′-deoxyuridines were synthesized and their spectroscopic properties were investigated. The heteroaryl groups were incorporated into DNA by post-synthetic Suzuki-Miyaura cross-coupling reactions, and the probe properties were evaluated.

Keywords : DNA probe, fluorescence property, environmental responses

ヘテロ環化合物を C5 位に直接結合した 2´-デオキシウリジンはユニークな蛍光特性を持つ．これまでに多くの研究例があるベンゾフラン修飾ヌクレオシドは高い環境応答性を持ち，蛍光極大値は極性溶媒中でより長波長になる[1,2]．これはナフタレン修飾ヌクレオシドと類似した分光学的特性である[3]．また，ベンゾフランのヘテロ原子を窒素としたインドール修飾ヌクレオシドも同様の環境応答性を持ち，さらに水のような高極性溶媒中では著しく消光する[1]．我々はこのインドールの特性に着目し，DNA への組み込みを検討した．修飾 DNA 合成において，インドールの環内アミノ基の保護が必要となる．本研究では，保護基を用いずに DNA 合成後に鈴木・宮浦クロスカップリング反応でインドールを結合した．その合成と得られた修飾 DNA の蛍光特性を報告する．また，同様にアクリドン誘導体についての検討結果も併せて報告する．

1) A microenvironment-sensitive fluorescent pyrimidine ribonucleoside analogue: Synthesis, enzymatic incorporation, and fluorescence detection of a DNA abasic site, A. A. Tanpure, S. G. Srivatsan, *Chem. Eur. J.* **2011**, 17, 12802.
2) Controlling the fluorescence of Benzofuran-modified uracil residues in oligonucleotides by triple-helix formation, T. Kanamori, H. Ohzeki, Y. Masaki, A. Ohkubo, M. Takahashi, K. Tsuda, T. Ito, M. Shirouzu, K. Kuwasako, Y. Muto, M. Sekine, K. Seio. *ChemBioChem* **2015**, 16, 167.
3) Wavelength shifting oligonucleotide probe for the detection of adenosine of a target DNA with enhanced fluorescence signal, S. S. Bag, M. K. Pradhan, S. K. Das, S. Jana, R. Bag, *Bioorg. Med. Chem. Lett.* **2014**, 24, 4678.

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水素結合に基づき特定の塩基を認識する RNA 結合分子の開発

（東北大多元研[1]・東北大院理[2]・京大 CiRA[3]）○都築航祐[1,2]・鬼塚和光[1,2]・長澤瞭佑[1,2]・宮下映見[3]・小松リチャード馨[3]・齊藤博英[3]・永次史[1,2]

Development of RNA-binding small molecules that recognize specific nucleobase based on hydrogen bonding

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,* [2]*Graduate School of Science, Tohoku University*, [3]*CiRA, Kyoto University*)
○Kosuke Tsuzuki,[1,2] Kazumitsu Onizuka,[1,2] Ryosuke Nagasawa,[1,2] Emi Miyashita,[3] Kaoru Richard Komatsu,[3] Hirohide Saito,[3] Fumi Nagatsugi[1,2]

RNA takes various higher order structures, and small-molecules capable of recognizing specific RNA 3D-structure are promising drug candidates. Despite its growing interest, it is still not easy to develop the RNA-targeted small molecules that bind strongly and selectively to particular structured RNAs. Therefore, development of related technologies and molecules is desired. Using “Barcode microarray[1)]”, a high-throughput screening method allows to evaluate RNA-small molecules interactions, we recently discovered that the G-clamp-monomer exhibits site- and base-selective binding to guanine. In this study, here we present the development of RNA-targeted small molecules designed to bind to specific nucleobases based on complementary hydrogen bonding. The interactions between the synthesized small molecules and RNA structure library were analyzed using the barcode microarray. In this poster presentation, we plan to provide detailed reports on the design, synthesis, and the scanning results of the small molecules developed.

Keywords : RNA; RNA-binding Molecules; Large-scale Analysis; Hydrogen Bonding; DNA Microarray

近年、RNA 標的創薬はオリゴ核酸に加え、経口投与可能な小・中分子でも効果を期待できる標的が増え、飛躍的に進展している。RNA は様々な高次構造をとることが知られているが、特定の高次構造を持つ RNA に選択的かつ強固に結合する分子の開発は未だ容易ではないため、関連する技術や分子の開発が望まれている。以前我々は RNA-低分子間相互作用を大規模に解析することが可能であるバーコードマイクロアレイ法[1)]を用い、G-clamp の低分子が特定の位置にある G 塩基を認識し結合することを見出した。そこで本研究では G-clamp 以外で特定の核酸塩基を、相補的な水素結合を介して認識する RNA 結合分子の開発を行った。さらに合成した分子の RNA-小分子間相互作用を、バーコードマイクロアレイ法を用い大規模に解析した。本発表では分子の設計・合成・解析結果について詳しく報告する予定である。

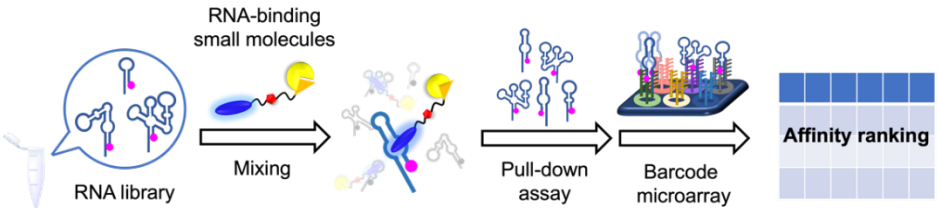

Fig 1. Schematic illustration of the large-scale analysis of RNA-small molecules interactions

1) H. Saito, *et. al.*, *Nat. Commun.* **2020**, 11, 6275.

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マイクロビーズへの濃縮効果を利用した HCR による核酸検出の高感度化

（和歌山大シス工[1]・和歌山大院シス工[2]）安原 優[1]・○坂本 隆[1,2]
Increased sensitivity of HCR-based nucleic acid detection using the concentration effect of microbeads ([1]*Faculty of Systems Engineering, Wakayama University*, [2]*Graduate School of Systems Engineering, Wakayama University*) Yu Yasuhara,[1] ○Takashi Sakamoto,[1,2]

In hybridization chain reaction (HCR)[1], the signal can be amplified non-enzymatically under isothermal conditions to detect the target nucleic acid, so that simple and sensitive detection of nucleic acids is possible. In addition, by applying the label-free HCR (LF-HCR, Figure 1)[2] that developed recently and that does not require fluorescent labeling of oligo DNA, we can perform inexpensive on-site clinical testing (POCT; point of care testing). However, the detection sensitivity of LF-HCR is far from that of the PCR-based method, and a further improvement in detection sensitivity has been required. Therefore, in this study, we tried to improve the detection sensitivity by adsorbing HCR products on microbeads and increasing the local concentration. As the results, we report that we succeeded in significantly improving the detection sensitivity (about a 10^6-fold increase in detection limit) by adding microbeads having an amino group to the reaction solution of LF-HCR and quantifying the fluorescence of the microbeads under a fluorescence microscope.
Keywords: Nucleic acids detection; Hybridization chain reaction; Microbeads

ハイブリダイゼーション連鎖反応（HCR）[1] では等温条件下、非酵素的に信号を増幅し標的核酸を検出できることから、核酸の簡便な高感度検出が可能である。また、我々が独自に開発したオリゴ DNA の蛍光ラベルを必要としないラベルフリーHCR（LF-HCR, Figure 1）[2] を適用することで、核酸配列に基づく安価な臨床現場即時検査（POCT; point of care testing）を実現できると期待できる。しかし、LF-HCR の検出感度は PCR 法には到底及ばず、さらなる検出感度の改善が求められていた。そこで本研究では HCR 産物をマイクロビーズに吸着し、局所濃度を増大させることによる検出感度の改善を試みた。結果、LF-HCR の反応溶液に、アミノ基を持ったマイクロビーズを添加し、顕微鏡下でマイクロビーズの蛍光を定量することで、顕著な検出感度の改善（10^6 倍程度の検出限界の向上）に成功したので報告する。

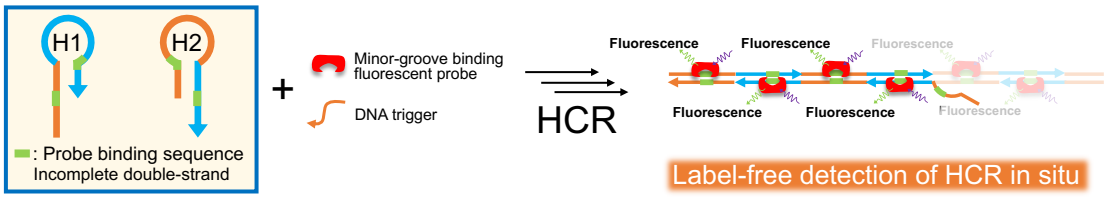

Figure 1. Schematic drawing of label-free HCR[2]

1) R. M. Dirks, N. A. Pierce, *Proc. Natl. Acad. Sci. U. S. A.*, **2004**, 101, 15275–15278.
2) T. Sakamoto, R. Yamada, *ChemBioChem*, **2019**, 20, 1242–1245.

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オキシム結合をもった新規ヌクレオペプチドの合成

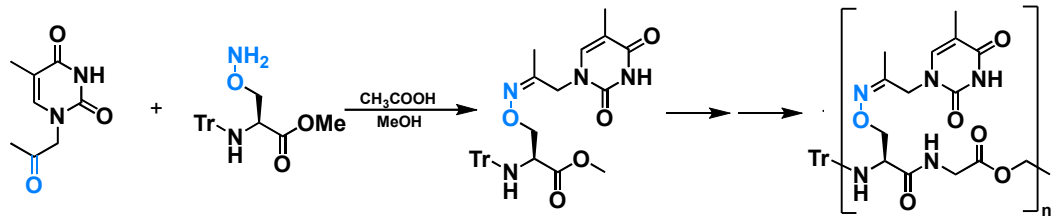
（群馬大院理工）○福島 由乃・戸田 皓紀・森口 朋尚
Synthesis of novel nucleopeptides with oxime bonds (*Graduate School of Science and Technology, Gunma University*) ○Yukino Fukushima, Koki Toda, Tomohisa Moriguchi

In recent years, chemically modified artificial nucleic acids have garnered attention as prospective next-generation drugs. Among these modified nucleic acid analogs, there are nucleotides with a peptide backbone resembling the structure of natural nucleic acids. This α-amino acid backbone closely mimics the natural form, allowing for potential enhancements in functionality through the introduction of functional groups. However, it's been observed that the incorporation of amide bonds in the side chains reduces solubility as chain length increases, posing challenges in synthesizing long-chain nucleopeptides.

In this study, our focus was on designing a novel nucleotide analog with a modified nucleotide backbone, where the amide bond in the side chain is replaced by an oxime bond. The target nucleopeptide monomer was synthesized via a condensation reaction between a thymine derivative with a carbonyl group and a serine derivative with an aminooxy group. Notably, this reaction proceeds almost quantitatively without requiring condensing agents. Subsequently, oligomers were synthesized, and their properties, including stability with the complementary strand, were thoroughly investigated.

Keywords : nucleopeptides; oxime bonds

近年、次世代医薬品として化学修飾された人工核酸が注目されている。骨格修飾された核酸類縁体の中に、ペプチド骨格を含む核酸類縁体としてヌクレオチドがある。これはより天然型に近いαアミノ酸を骨格に持つ構造である。官能基を導入することで機能を向上させることが可能である。しかし、側鎖にもアミド結合を導入すると、鎖長が長くなるにつれて溶解度が低下し、長鎖のヌクレオペプチドの合成が困難になる。そこで本研究では、このヌクレオチド骨格のうち、側鎖のアミド結合をオキシム結合に変換した新規核酸類縁体をデザインした。オキシム結合は縮合剤を必要とせず、カルボニル基をもつチミン誘導体とアミノオキシ基をもつセリン誘導体を脱水縮合することにより、目的のヌクレオペプチドモノマーを合成した。その後オリゴマーを合成し、相補鎖との安定性などの性質について調べる。



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DNA 修飾金ナノ粒子を活用した光熱誘導型薬物放出システムの開発

（兵庫県立大工）○野口拳斗・由里拓也・中村光伸・高田忠雄
Development of a photothermal-induced drug release system using DNA-modified gold (*Graduate School of Engineering, University of Hyogo*) ○Kento Noguchi, Takuya Yuri, Mitsunobu Nakamura, Tadao Takada

The development of Drug Delivery Systems (DDS) that precisely control the pharmacokinetics of drugs to minimize side effects while maximizing therapeutic effects is garnering attention. Particularly, DDS that use light as an external stimulus enable spatiotemporal control of drug release, and research in this area is actively being conducted. In this study, we aimed to develop a system that effectively releases drugs by utilizing the localized heat generated from the interaction between gold nanoparticles (AuNP) and light. We synthesized DNA-modified gold nanoparticles (AuNP-DNA) and created complexes by binding AuNP-DNA with DNA intercalators, such as ethidium bromide and daunomycin. Next, we investigated how these drug molecules are released using the localized heat generated on the surface of the AuNP due to light absorption. The release of drug molecules was examined by observing the fluorescence changes of the bound molecules upon dissociation from DNA.
Keywords : DNA; Gold Nanoparticles; Photothermal Effect; Fluorescence; Drug Delivery

薬物の体内動態を精密にコントロールすることにより、副作用を最小限に抑えつつ治療効果を最大化するドラッグデリバリーシステム（DDS）の開発が注目されている。特に、光を外部からの刺激として用いる DDS は、薬物放出の時空間制御が可能であり、その研究が活発に行われている。本研究では、金ナノ粒子（AuNP）と光の相互作用によって生じる局所熱を利用して、薬剤を効果的に放出するシステムの開発を目指した。

DNA で表面修飾された AuNP は球状核酸と呼ばれ、ヌクレアーゼに対する耐性が高く生体内で安定に存在するため、効果的なドラッグキャリアーとして機能する。そこで、DNA で表面修飾された金ナノ粒子を作製し、それらに DNA インターカレーターであるエチジウムブロマイドとドウノマイシンを結合させた複合体を作製した。次に、AuNP の光吸収によって生じる表面の局在熱を使用して、これらの薬剤分子がどのように放出されるかを検討した(Fig.1)。薬剤分子の放出は DNA からの解離に伴う結合分子の蛍光変化の観測によって調べた。

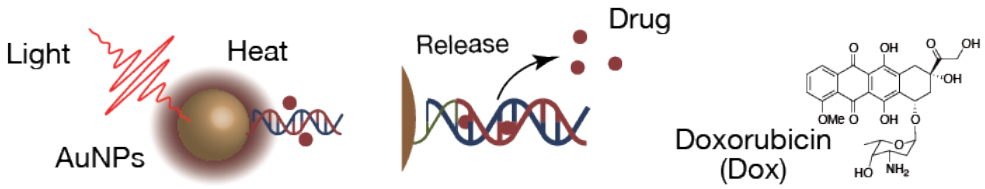

Fig.1 Drug release from DNA-modified gold nanoparticles through photothermal effect.

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7 位にピリジル基を導入した 7-デアザデオキシグアノシンを含むオリゴヌクレオチドの合成と性質

（東工大生命理工[1]）宮地 健人[1]・○羽生 愛深[1]・清尾 康志[1]・正木 慶昭[1]

Synthesis and properties of oligonucleotides having 7-pyridyl-7-deazadeoxyguanosine

([1]*Sch. Life Sci. Tech., Tokyo Tech.*) Kento Miyaji,[1] ○Narumi Habu,[1] Kohji Seio,[1] Yoshiaki Masaki[1]

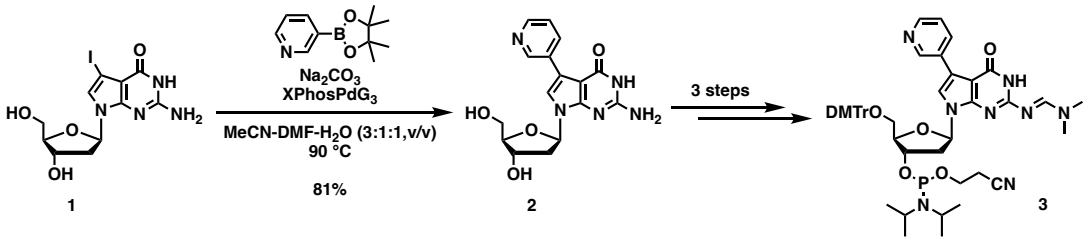
Nucleic acid-protein interactions play a crucial role in the gene expression and functional regulation of nucleic acids. Therefore, we aimed to alter these interactions by introducing chemical substituents into the major groove, one of the important interaction sites. In this study, we synthesized and evaluated oligonucleotides containing 7-deazadeoxyguanosine with a pyridyl group at the 7th position.

By following the reported procedure, we synthesized 7-iodo-7-deazadeoxyguanosine.[1)] Then, we investigated the incorporation of a pyridyl group into 7-iodo-7-deazadeoxyguanosine (**1**). Utilizing XPhos PdG3 as a catalyst, known for its high reactivity and stability, we successfully suppressed the formation of the deiodinated derivative and obtained an 81% yield of the 7-pyridyl-7-deazadeoxyguanosine (**2**). In this presentation, we will report in detail on the investigation of Suzuki-Miyaura coupling conditions and the characterization of the synthesized oligonucleotides.

Keywords : Chemically modified oligonucleotide; DNA; modified nucleobase

核酸-タンパク質の相互作用は、遺伝子発現や核酸の機能制御に大きく関わっている。そこで、その相互作用に重要な部位であるメジャーグルーブに置換基を導入した修飾核酸により核酸-タンパク質相互作用を変化させることを目指した。本研究では修飾核酸として、7 位にピリジル基を導入した 7-デアザデオキシグアノシンを含むオリゴヌクレオチドの合成および評価を行うこととした。

既知の合成法[1)]を参考に、7-ヨード-7-デアザグアノシン (**1**) に対して、ピリジル基の導入検討を実施した。その結果、高い反応性と安定性を持つ XPhos PdG3 を触媒として用いた際に、脱ヨード体の生成を抑制し、7-ピリジル-7-デアザグアノシン (**2**) を 81%の収率で得ることに成功した。本発表では、鈴木・宮浦カップリングの条件検討および合成したオリゴヌクレオチドの性質評価について詳細に報告する。



1) *Chem. Commun.*, **2016**, *52*, 3809-3812.

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新規ジフェニルシリルピレン誘導体の合成と蛍光特性

（群大院理工工[1]）森口朋尚[1]・○干場 真由子[1]・森口朋尚[1]

Synthesis of novel diphenylsilylpyrene derivatives directed to fluorescent labeling of DNA

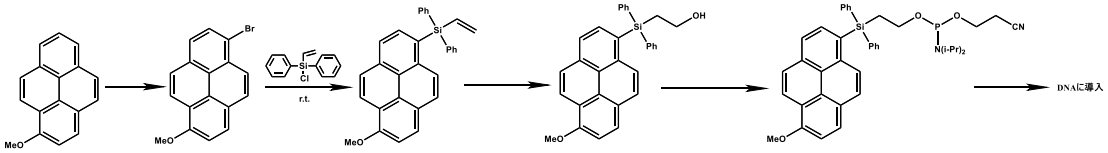
([1]*Graduate School of Science and Technology, Gunma University*)○Mayuko Hoshiba[1]・Tomohisa Moriguchi,[1]

In recent years, genetic analysis using fluorescent-labeled nucleic acids has involved extensive research into fluorescent substances for incorporation into probes. There is an increasing demand for near-infrared fluorescent labeling agents with excellent chemical and photochemical stability, enabling real-time detection within living organisms. Achieving longer emission wavelengths and heightened fluorescence intensity has become a primary focus.

Within our laboratory, our focus has centered on studying silylated pyrene derivatives, where pyrene is modified with silicon atoms. This study specifically delves into enhancing the fluorescent properties of silylated pyrene by concentrating on the substituents on the silicon. We synthesized new silylated pyrene derivatives by introducing a diphenyl group, aiming to augment their fluorescence. This synthesis involved incorporating a diphenyl group into vinylsilane as a silylating agent and subsequently reacting it with pyrene. The fluorescence properties resulting from these introduced substituents were thoroughly elucidated and evaluated as potential fluorescent probes.

Keywords : Fluorescent Labeling Agents; Silylated pyrene

近年、蛍光標識核酸を用いた遺伝子解析ではプローブに導入する蛍光物質について長らく研究が行われている。蛍光物質には生体内でリアルタイム検出を可能にするような化学的安定性と光化学的安定性に優れた近赤外蛍光標識剤の必要性が高まっており、発光波長の長波長化、さらに蛍光強度の増強が目標となってきた。当研究室では、蛍光性をもつピレンをケイ素原子で修飾したシリル化ピレン誘導体の研究を行ってきた。本実験ではシリル化ピレンのケイ素上の置換基に注目し、ジフェニル基を導入した新規シリル化ピレン誘導体の合成を行い、蛍光特性の改良を試みた。ビニルシランにジフェニル基を導入したシリル化剤とし、ピレンと反応させることで合成を行った。置換基の導入による蛍光特性を明らかにし、蛍光プローブとしての評価を行う。



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グアニン四重鎖／チオフラビンT誘導体の複合体形成におけるグアニジノ基の導入効果

（日大文理学部[1]・日大院総合基[2]）○白鳥 悠香[1]・中村 友昭[2]・割石 智子[2]・片岡 由佳[2]・桒原 正靖[2]

Effect of introduction of guanidino group on complex formation of G-quadruplex and thioflavin T derivative ([1]*College of Humanities and Sciences, Nihon University,* [2]*Graduate School of Integrated Basic Science, Nihon University*) ○Yuuka Shiratori,[1] Tomoaki Nakamura,[2] Tomoko Wariishi,[2] Yuka Kataoka,[2] Masayasu Kuwahara[1,2]

Thioflavin T (ThT) derivatives are fluorescent compounds that bind to amyloid and are used to detect amyloid fibrils that cause neurodegenerative diseases[1]. ThT is also useful as a probe for guanine quadruplex (G4)[2,3]. Previous research has shown that several thioflavin T derivatives with substituents at the N^3 position exhibit different fluorescent properties depending on the topology of G4s[4]. Meanwhile, L-arginine is one of the proteinogenic amino acids, and the guanidino group on Its side chain is known to contribute to complex stabilization and molecular recognition through hydrogen bonding with exocyclic amino groups of nucleobases and electrostatic interactions with phosphate groups in DNA and RNA[5]. In this study, we newly synthesized ThT derivatives with L-arginine or L-ornithine introduced at the N^3 position, and evaluated their binding affinity and fluorescence properties for several G4s with different topologies. By comparing and verifying these results, the effects of the guanidino group were investigated.

Keywords : Thioflavin T, L-Arginine, G-quadruplex, Fluorescent compounds

チオフラビンT(ThT) 誘導体はアミロイドに結合し蛍光を発する化合物であり、神経変性疾患を引き起こすアミロイド線維の検出に用いられている[1]。また、ThTはグアニン四重鎖 (G4) に対するプローブとしても有用である[2,3]。これまでの研究で、N^3位に置換基を導入したいくつかのチオフラビンT誘導体がG4のトポロジーの違いによって異なる蛍光特性を示すことを明らかにした[4]。一方、L-アルギニンはタンパク質構成アミノ酸のひとつであり、その側鎖にみられるグアニジノ基は、DNAやRNA中の核酸塩基の環外アミノ基と水素結合を形成したりリン酸基と静電相互作用したりすることで、複合体の安定化や分子認識に寄与している[5]。そこで本研究では、L-アルギニンもしくはL-オルニチンをN^3位に導入したThT誘導体を新たに合成し、トポロジーの異なるいくつかのG4に対して結合親和性や蛍光特性の評価等を行い、それらの結果を比較検証することで、グアニジノ基の効果を検討した。

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グアニン四重鎖の安定性に対するテトラフェニルエチレン誘導体修飾 DNA の効果

（東京工科大学大学院工学研究科 [1]・東京工科大学 工学部 [2]）○清瀬 茉紋 [1]・須磨岡 淳 [2]

Effect of tetraphenylethylene derivative-modified DNA on the stability of G-quadruplexes ([1]*Tokyo University of Technology Graduate School of Engineering,* [2]*Tokyo University of Technology School of Engineering*) ○Maaya Kiyose,[1] Jun Sumaoka[2]

Sequences that can form guanine quadruplexes (G-quadruplexes) are abundant in disease-causing regions, including cancer; ligands that stabilize G-quadruplexes are known to suppress telomerase activity and gene overexpression. In this study, tetraphenylethylene (TPE) was used as the basic skeleton of the ligand. By modifying DNA with it, we expected it to selectively bind to and stabilize any G-quadruplexes (Fig. 1).

Incubation of DNA modified with a TPE derivative at the 5' end (Fig. 2) with DNA forming the G-quadruplexes was performed, and thermal stability was evaluated by circular dichroism spectroscopy (CD) measurement. The thermal melting temperature (Tm) of the G-quadruplexes differed by 3.7°C between the addition of DNA modified with the TPE derivative and unmodified DNA. The stability of the G-quadruplexes was not affected by the addition of TPE derivative-modified DNA when a mismatch was introduced into the DNA sequence forming the double-stranded DNA. In the presentation, the effects of TPE derivatives with modified linkers and TPE derivatives with functional groups will also be reported.

Keywords : Nucleic Acid; G-quadruplexes; tetraphenylethylene

グアニン四重鎖（G4 構造）を形成し得る配列はがんを含む疾患の要因となる領域に多く存在している。G4 構造を安定化させるリガンドはテロメラーゼ活性の抑制や遺伝子の過剰発現を抑制することが知られている。本研究では、リガンドの基本骨格としてテトラフェニルエチレン(TPE)を用いた。これを DNA に修飾することで、任意の G4 構造と選択的に結合し安定化することを期待した(図 1)。

5’ 末端に TPE 誘導体を修飾した DNA(図 2)と G4 構造を形成する DNA をインキュベートし、円偏光二色性分光法（CD）測定により熱安定性の評価を行った。測定結果をもとに熱融解温度（Tm）を算出したところ、TPE 誘導体で修飾した DNA と未修飾の DNA との間に約 3.7℃の温度差を確認した。また、二本鎖を組む DNA 配列にミスマッチを導入すると TPE 誘導体修飾 DNA を加えても G4 構造の安定性に影響はなかった。発表ではリンカーを変更した TPE 誘導体や官能基を導入した TPE 誘導体の効果についても報告する。

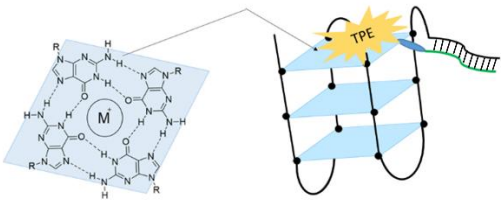

図 1　G4 構造と研究戦略

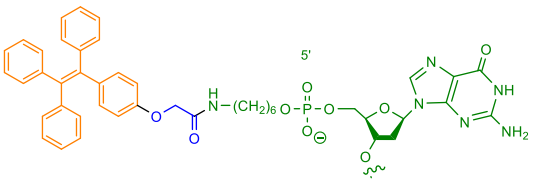

図 2　TPE 誘導体修飾 DNA の構造

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スーパーオキシドディスムターゼ 1 の野生型と G93A 変異体の分子の揺らぎの違いに関する分子動力学的研究

（兵庫医大医）○福島和明・藤原範子
Molecular Dynamics Study on the Difference in Molecular Fluctuations between Wild Type and G93A Mutant of Superoxide Dismutase 1 (*School of Medicine, Hyogo Medical University*)
○Kazuaki Fukushima, Noriko Fujiwara

Superoxide dismutase 1 (SOD1) is an enzyme that converts superoxide radical anions into hydrogen peroxide and oxygen molecules, which are harmful to organisms. Mutants of SOD1 are known to cause amyotrophic lateral sclerosis (ALS), which is more unstable and prone to aggregation, but the pathogenesis mechanism is still unknown.

In this study, we performed five 300-ns molecular dynamics simulations of wild-type SOD1 and the ALS-causing G93A mutant using Gromacs. In the results of the simulations, the root mean square fluctuation (RMSF) of each residue showed that there were large fluctuations in the metal-binding loop (Loop IV) and the electrostatic loop (Loop VII). A comparison of the root mean square deviation (RMSD) of these two loops revealed that the metal-binding loop in WT and the electrostatic loop in G93A had larger values, indicating that the loops that fluctuated significantly varied with mutations.

Keywords : Superoxide Dismutase 1; Amyotrophic Lateral Sclerosis; G93A Mutant; Molecular Dynamics

スーパーオキシドディスムターゼ 1（SOD1）は、生体にとって有害なスーパーオキシド（O_2^-）を酸素（O_2）と過酸化水素（H_2O_2）に不均化して消去する酵素である。一方で、SOD1 の変異体には、筋萎縮性側索硬化症（ALS）の原因となるものが 200 種類以上知られている。ALS 変異体は不安定で凝集しやすい性質を持つが、ALS 発症機構は未解明である。

本研究では、野生型（WT）SOD1 と ALS 変異体である G93A について、両者の動的な性質の違いを明らかにするために、Gromacs を用いて分子動力学（MD）シミュレーションを行った。計算に用いた WT の初期構造は X 線解析によって明らかにされた座標（PDBID:3t5w）を用い、ここから取り出した単量体の構造を水和して、エネルギー最小化、*NVT* 平衡化、*NPT* 平衡化を行った。このように平衡化した構造を用いて 1.0 bar、310 K で 300 ns のシミュレーションを 5 回行った。また、G93A 変異体については、WT の初期構造を基に初期構造を作成し、平衡化したのちに同様の条件でシミュレーションを 5 回行った。

シミュレーションの結果、各残基の平均二乗揺らぎ（RMSF）では、金属結合ループ（Loop IV）と静電ループ（Loop VII）に大きな揺らぎがあることが示された。また、この二つのループの平均二乗偏差（RMSD）を比較したところ、WT では金属結合ループ、G93A では静電ループの値が大きく、変異によって大きく揺らぐループが変化することが明らかになった。

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シャペロン様活性を包含した酸化的タンパク質フォールディング触媒の開発

（東海大理化[1]，東海大先進生命研[2]）○岩田 悠希[1]・西沢 優也[1]・荒井 堅太[1,2]

Development of Oxidative Protein Folding Catalysts Involving Chaperone-like Activity

([1]*Department of Chemistry, School of Science, Tokai University,* [2]*Institute of Advanced Biosciences, Tokai University*) ○Yuki Iwata,[1] Yuya Nishizawa,[1] Kenta Arai[1,2]

Biosynthesized proteins exert their physiological functions by gaining a unique three-dimensional structure with forming disulfide (SS) bonds in the endoplasmic reticulum (ER). This SS formation-coupled folding, i.e., oxidative folding, is effectively promoted by protein disulfide isomerase (PDI), an ER-resident enzyme, which can recognize and capture structurally immature proteins. We previously reported that water-soluble diselenide (SeSe) compounds catalyze oxidative folding by a reaction mechanism similar to that of PDI.[1] Meanwhile, cyclodextrins (CDs), which is cyclic oligosaccharides composed of multiple D-glucoses, can include hydrophobic molecules and is therefore expected to recognize hydrophobic regions exposed on the molecular surface of structurally immature proteins. In this study, we attempted to develop a new SeSe-based oxidative folding catalyst conjugated with a heptameric CD (β-CD) as a substrate recognition sensor. β-CD dimers **A** and **B** were synthesized via a key precursor, in which only one of the 3- or 6-position hydroxy groups of β-CD was tosylated. We are currently evaluating the catalytic function of the obtained compounds for oxidative folding and their affinity for denatured proteins.

Keywords : Catalyst; Folding; Protein; Selenium; Disulfide

生合成された蛋白質は、小胞体内においてジスルフィド(SS)結合の形成と共に固有の三次元構造を獲得することで生理機能を発揮する。この酸化的 folding は、小胞体内在酵素である protein disulfide isomerase (PDI)が構造未熟な蛋白質を認識・捕捉し、SS 形成を触媒することで効果的に促進される。以前我々は、水溶性ジセレニド(SeSe)化合物が、PDI と同様の反応機構によって酸化的 folding を触媒することを報告した[1]。一方で、D-グルコースからなる環状オリゴ糖である cyclodextrin(CD)は、疎水性分子を包接できることから、構造未成熟な蛋白質の分子表面に露出した疎水性領域を認識する機能を有するものと期待される。本研究では、基質認識センサーとして 7 量体 CD (β-CD)を接合した SeSe 系酸化的 folding 触媒の開発を目指した。β-CD が有する 3 位あるいは 6 位のヒドロキシ基のうち 1 つだけをトシル化した鍵前駆体を経由し、β-CD ダイマー**A** および **B** を合成した。現在、得られた化合物の酸化的 folding 触媒機能を評価するとともに、変性蛋白質との親和性についても評価を進めている。

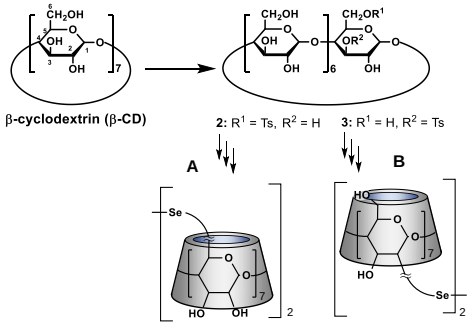

Fig. 1: β-CD ダイマー**A**・**B** の合成。

[1] *Chem Asian J.* **2020**, *15*, 2646–2652.

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易化学修飾インスリンを鍵前駆体とした新規持効型インスリン製剤の化学合成

(東海大院理化[1]・東海大先進生命研[2]) ○髙橋 莉奏[1]・荒井 堅太[1,2]
Chemical synthesis of new long-acting insulin via an easily modifiable insulin as a key precursor. ([1]*Graduate School of Science, Tokai University*, [2]Institute of Advanced Biosciences, Tokai University) ○Rikana Takahashi,[1] Kenta Arai[1,2]

Insulin, which is a hypoglycemic drug for diabetics, is a globular protein consisting of two different polypeptide chains (A- and B-chains) stabilized by three disulfide bonds. Insulin must be dispersed as the monomeric state in the blood to exert its biological effect. Utilizing this property, this study attempts to design and synthesize new long-acting insulins that readily associate with insulins or other biomolecules in the subcutaneous and blood after injection, from which the monomeric insulin slowly dissociate. The component peptides, A-chain and B-chain analogue having an azide group were prepared by a general solid-phase peptide synthesis method, and folding of the prepared peptides were subsequently conducted to yield peptide **1a** as a key precursor. Then, various insulin formulation candidates were synthesized via click reaction using peptide **1a**. In the presentation, we will show the synthetic protocol of the formulation candidates and discuss their potential pharmacological applications based on the assessments on their structural and physicochemical properties.
Keywords : Click Chemistry; Azide; Triazole; Folding; Drug Discovery

糖尿病患者が利用する血糖降下製剤として知られる insulin は、異なる二本のポリペプチド鎖 (A 鎖・B 鎖)から成る球状蛋白質であり、3 つのジスルフィド結合で立体構造が安定化されている。insulin は、モノマーとして血液中に分散することで血糖降下作用を発現する。この特性を利用し、本研究では insulin モノマーが自身あるいは他の生体分子と会合し、注射投与後の皮下や血中で徐々にモノマーが解離するような新規持効型 insulin の設計と合成を試みた（**Fig. 1**)。ペプチド固相合成法によって A 鎖およびアジド基を有する B 鎖類縁体を調製し、続けて 2 本のペプチド鎖を folding させることで insulin 製剤候補の鍵前駆体となる **1a** を合成した。**1a** を用いたクリック反応によって、様々な持効型 insulin 製剤候補を調製した。本発表では、製剤候補の具体的な合成方法を示すとともに、構造と物理化学的特性に関する評価に基づき、合成 insulin の薬理応用の可能性について議論する。

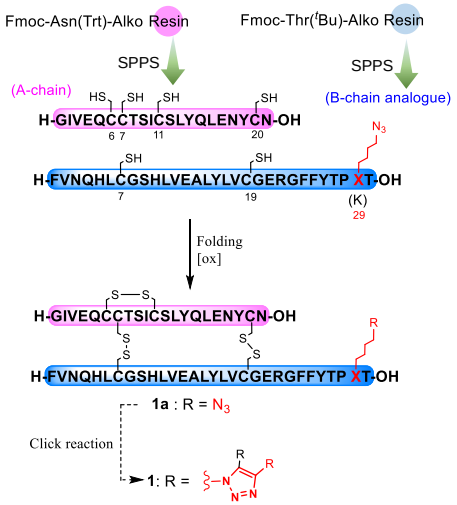

Fig. 1: B 鎖にアジド基を有するインスリン類縁体 **1a** の化学合成とクリック反応を利用した持効型インスリン製剤候補 **1** への変換。

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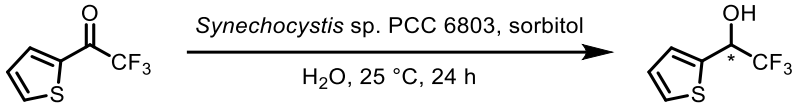
The effect of sorbitol addition on the asymmetric reduction of ketones using cyanobacterium *Synechocystis* sp. PCC 6803

([1]*Department of Chemistry, Graduate School of Science, Osaka Metropolitan University,* [2]*Department of Biological Chemistry, Graduate School of Science, Osaka Metropolitan University,* [3]*Faculty of Pharmaceutical Sciences, Himeji Dokkyo University*)
○Satsuki Fukui[1], Hideo Kojima[1], Satomi Takeda[2], Rio Yamanaka[3]
Keywords: Cyanobacterium; Asymmetric Reduction; Ketones; Sorbitol Addition

Optically active alcohols are crucial as versatile chiral intermediates in the pharmaceutical and agrochemical industries. Utilizing whole-cell biotransformation through the asymmetric reduction of prochiral ketones represents a potent approach for generating such optically active alcohols. This method is particularly advantageous due to the availability and recycling of reducing cofactors (e.g., NAD(P)H) within the cells. Despite these advantages, the challenge of achieving high yields persists in whole-cell biotransformation processes. In a previous study, we reported on the effect of incorporating organic solvent additives in the asymmetric reduction of β-keto esters, employing the cyanobacterium *Synechocystis* sp. PCC 6803.[1] Building on this, our current investigation explores the potential of sorbitol addition to enhance the yield of asymmetric ketone reduction using *Synechocystis* sp. PCC 6803.

The wild-type strain of *Synechocystis* sp. PCC 6803 was cultivated in BG-11 medium and exposed to fluorescent light (20 μmol m^{-2} s^{-1}) at 25 °C for 10 days. The asymmetric reduction of ketone **1** (0.05 mg/mL) to chiral alcohol **2** was performed using the cyanobacterial strain ($Abs_{680\text{-}750}$ 0.33). This reaction took place in the presence of sorbitol (0.5 M) under either red LED light illumination (660 nm, 10 μmol m^{-2} s^{-1}) or in darkness at 25 °C for 24 hours (Scheme 1). Yields and enantiomeric excess (ee) were quantified using gas chromatography. Notably, the addition of sorbitol resulted in an increased yield of **2** under dark conditions, as detailed in Table 1.



1 **Scheme 1** **2**

Table 1.

Light cond.	Sorbitol (M)	**2**/%	**2**/%ee (config.)
light	none	34	33 (*S*)
dark	none	10	25 (*S*)
light	0.5	30	33 (*S*)
dark	0.5	35	24 (*S*)

1) S. Tanaka, H. Kojima, S. Takeda, R. Yamanaka, T. Takemura, *Tetrahedron Lett.*, **2021**, *77*, 153249

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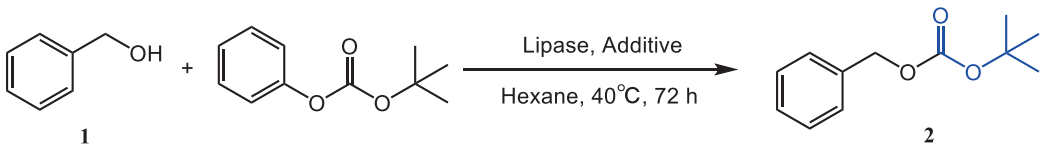
Lipase-catalyzed alkoxycarbonylation in the presence of a solid acid catalyst

(*Department of Chemistry, Graduate School of Science, Osaka Metropolitan University*)
○Yuto Yamamoto, Hideo Kojima
Keywords: Lipase, Alkoxycarbonylation, Solid Acid Catalyst, Alkyl Phenyl Carbonates

Lipases have been widely utilized in organic synthesis due to their high activity, high selectivity, and ease of handling under mild reaction conditions. Many studies have been reported on the lipase-catalyzed synthesis of carboxylate esters. However, few studies have been reported on the lipase-catalyzed synthesis of carbonate esters. We have previously developed the lipase-catalyzed *tert*-butoxycarbonylation of primary alcohols using di-*tert*-butyl dicarbonate.[1] In this research, we have investigated the lipase-catalyzed alkoxycarbonylation of alcohols using alkyl phenyl carbonate in the presence of a solid acid catalyst.

For example, the reaction of benzyl alcohol with *tert*-butyl phenyl carbonate (5 equiv.) was carried out in the presence of *Candida rugosa* lipase (lipase/**1** = 20 (w/w)) in hexane at 40°C for 72 h to afford carbonate **2** (Scheme 1). We found that the addition of SiO_2 increased the yield of carbonate **2** (Table 1). Thus, a solid acid catalyst like SiO_2 was shown to work in the lipase-catalyzed *tert*-butoxycarbonylation.



1 **2**

Scheme 1

Table 1

Lipase	Additive (mg)	Yield (%)[a)]
Candida rugosa lipase	-	39
	SiO_2 (130)	84

a) Determined by Gas Chromatography.

1) N. Kishi, H. Kojima, *ChemistrySelect*, **2019**, *4*, 9570-9572.

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Lipase-catalyzed alkoxycarbonylation in the deep eutectic solvent/water system

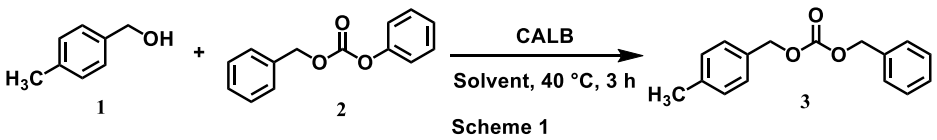
(Graduate School of Science, Osaka Metropolitan University) ○Taito Nagamoto, Yuto Yamamoto, Hideo Kojima

Keywords: Lipase, Aqueous Deep Eutectic Solvent, Alkoxycarbonylation, Alkyl Phenyl Carbonate

As alternatives to organic solvents, deep eutectic solvents (DESs), which are prepared by mixing a hydrogen bond acceptor and a hydrogen bond donor with heating until a liquid is formed, have been acknowledged as green solvents. Among them, aqueous DESs (DESs/water systems) have recently been evaluated as solvents in lipase-catalyzed reactions. Lipases have been widely utilized in organic synthesis due to their high activity and selectivity, and their ease of handling under mild reaction conditions.

The alkoxycarbonyl group has been employed as a protecting group for alcohols and amines. Recently, enzymatic protecting techniques have gained increasing importance in the promotion of green and sustainable chemistry. In this research, we have investigated the lipase-catalyzed alkoxycarbonylation using alkyl phenyl carbonate in the DESs/water systems.

For example, the reaction of 4-methylbenzyl alcohol (**1**) with benzyl phenyl carbonate (**2**) (3 equiv.) was carried out in the presence of *Candida antarctica* lipase B (CALB) (lipase/**1** = 5 (w/w)) in a solution (4 mL) with different ratios of DES (choline chloride/urea/water or choline chloride/glycerol/water (1:2:1))/hexane (1:4) at 40 °C for 3 h (Scheme 1). The results showed that the aqueous DES (choline chloride/urea/water)–hexane mixed solvents were superior to hexane in the benzyloxycarbonylation of 4-methylbenzyl alcohol (Fig. 1).



Scheme 1

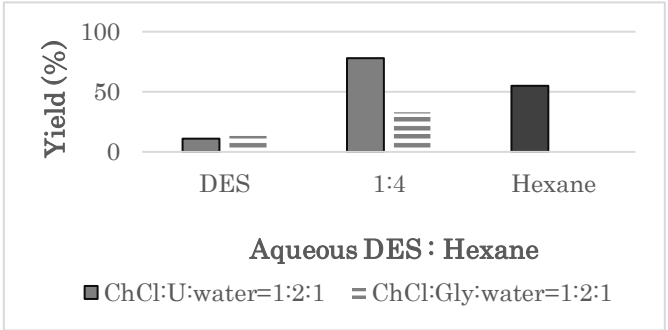


Fig. 1

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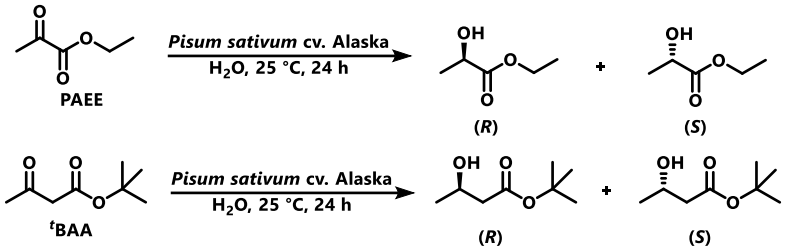
Asymmetric reduction of keto esters using *Pisum sativum* as a whole-cell biocatalyst

(*Graduate School of Science, Osaka Metropolitan University*) ○Ryota Shimamoto, Yuya Machi, Hideo Kojima, Satomi Takeda

Keywords: *Pisum sativum*, Asymmetric Reduction, Keto Esters, Whole-cell Biocatalyst

Pea (*Pisum sativum*) is widely cultivated throughout the world because it is easy to grow and inexpensive. Polyphenols obtained from peas by extraction have a wide range of pharmacological activities and have been applied to nutraceuticals, but there are few examples of their use as biocatalysts for material transformations. In this study, we investigated the use of *Pisum sativum* as a whole-cell biocatalyst for the preparation of optically active α- or β-hydroxy esters, which are used as chiral building blocks for the synthesis of pharmaceuticals and agrochemicals.

Pisum sativum cv. Alaska was grown under fluorescent light (40 μmol m^{-2} s^{-1}) at 25 °C for 14 days. The seedlings, sterilized in 0.5% sodium hypochlorite solution, were used for the reaction. The seedlings (200 mg) were added to the aqueous solution of α- or β-keto ester (5 mL) and allowed to react under the illumination of light (L) (40 μmol m^{-2} s^{-1}) or in the dark (D) for 24 h at 25 °C (Scheme 1). The product was extracted with ether. Yield and enantiomeric excess (*ee*) were determined by gas chromatography. In all cases, the corresponding alcohols were obtained with good to high ee values. The results are shown in Table 1.



Scheme 1

Table 1. Asymmetric reduction of keto esters using *Pisum sativum* cv. Alaska.

Substrate	Light cond.	Yield (%)[a]	*ee* (%)[a]
PAEE	L	14	88 (*R*)
PAEE	D	20	86 (*R*)
^{t}BAA	L	89	>99 (*S*)
^{t}BAA	D	60	>99 (*S*)

[a]Determined using GC. All values represent the mean of three experimental results.

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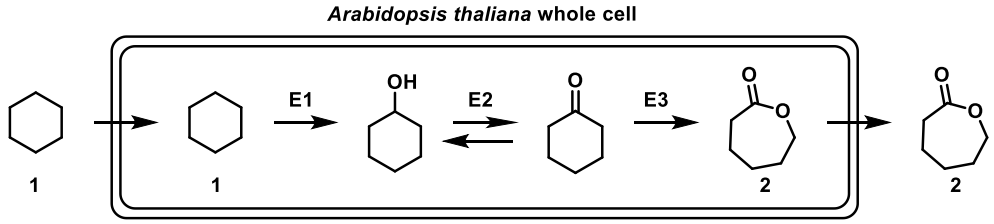
Biotransformation of cyclohexane to ε-caprolactone using *Arabidopsis thaliana* as a whole-cell biocatalyst

(*Graduate School of Science, Osaka Metropolitan University*) ○Yuya Machi, Jina Yoshida, Hideo Kojima, Satomi Takeda

Keywords: Enzymatic Cascade Reaction; *Arabidopsis thaliana*; ε-Caprolactone; Whole-cell Biocatalyst

The synthesis of high-value-added substances often involves multi-step reactions, requiring isolation and purification of products at each step. Recently, cascade reactions consisting of multiple enzymes have attracted much attention. By using such enzymatic cascade reactions, multiple chemical transformations can be performed continuously without the need to isolate intermediate products. Furthermore, in the enzymatic cascade reactions using whole cells, the coenzyme regeneration system is provided as an intrinsic cellular metabolic pathway, and a one-pot reaction system can be constructed, enabling multi-step molecular transformations under simpler and less expensive conditions. Previously, we have reported on the use of *Arabidopsis thaliana* (*A. thaliana*) as a whole-cell biocatalyst to synthesize optically active alcohols by asymmetric reduction of ketones.[1] Since *A. thaliana* is known as a model plant, which is easy to cultivate and its entire genome has already been analyzed, it is easy to obtain mutant strains in which specific enzymes are disrupted or strongly expressed. In this study, we investigated the whole-cell enzymatic cascade reaction from cyclohexane (**1**) to ε-caprolactone (**2**) (Scheme 1).

A. thaliana seeds were sown on agar medium and incubated under light (40 μmol m^{-2} s^{-1}) at 22°C for 2 weeks. 100 mg of the plants was added to 5 mL of phosphate buffer solution (pH 7.0) containing substrate (0.5 mM) and the reaction mixture was incubated under light (40 μmol m^{-2} s^{-1}) or in the dark at 25°C for 24 h (Scheme 1). After the reaction, the plant was removed and the mixture was extracted with ether. The yields were determined by gas chromatography. We found that **2** was produced in 15% yield under light conditions and 11% yield under dark conditions from **1**.



Scheme 1

1) S. Takeda *et al*., *Plant Biotechnol*., **28**, 77–82 (2011).

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cDNA display によるストレプトアビジン結合環状ペプチドアプタマーの試験管内進化

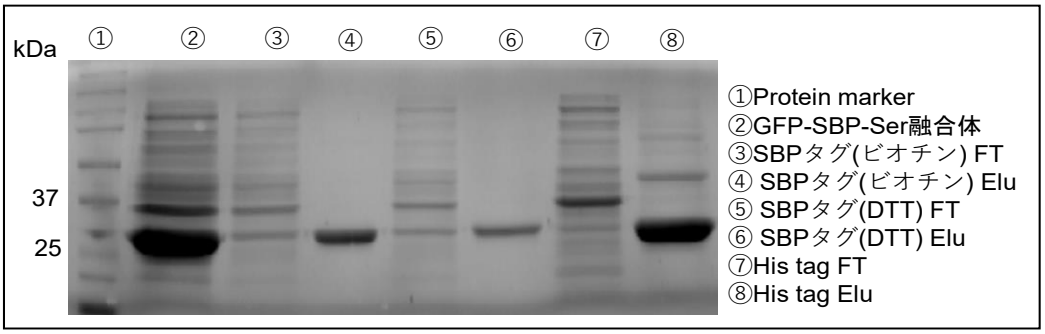
(埼玉大学大学院理工学研究科[1]・株式会社 Epsilon Molecular Engineering[2]) 今友樹[1]、○片倉大起[1]、望月祐樹[2]、根本直人[1,2]
In vitro selection of streptavidin-binding cyclic peptide aptamers by cDNA display ([1]Graduate School of Science＆Engineering, Saitama University, Japan, [2]Epsilon Molecular Engineering, Japan) Tomoki Kon[1], ○Daiki Katakura[1], Yuki Mochizuki[2], Naoto Nemoto[1,2]

Biotin has been known to have high affinity with streptavidin. On the other hand, its high affinity for streptavidin makes it difficult to purify biotinylated protein with a streptavidin-immobilized column because of denaturation of the target molecule. Although a linear SBP (streptavidin binding protein) tags have already been developed in previous studies, we aimed to develop more shorter cyclic peptide aptamer tags. In this study, we screened by cDNA display with a 20-residue cyclic peptide library and obtained some cyclic peptide tag candidates that bind to streptavidin.

The protein (GFP) fused with this peptide tag was expressed in *E.coli* and compared between the new SBP-tagged purification and His-tagged purification. As a result, the purification efficiency of SBP-tag purification is lower than that of His-tag purification, but the number of nonspecific bands is fewer. We will try to improve the purification efficiency by considering the elution conditions.
Keywords : cDNA display, cyclic peptide aptamer, affinity tag

ビオチンはストレプトアビジンとの高い親和性を有することが知られている。一方、ストレプトアビジン固定化カラムで精製する際はその強力な結合力のために厳しい条件下での分離となり、標的分子の変性が課題となる。先行研究ですでにリニアな SBP (streptavidin binding protein) タグが開発されているが、我々はより短い環状化ペプチドアプタマータグの開発を目指した。本研究では 20 残基の環状化ペプチドライブラリを提示する cDNA display を用いてスクリーニングを行い、ストレプトアビジンに結合する配列を取得した。

実際にこのタグを融合したタンパク質 (GFP) を大腸菌で発現させ新規 SBP タグ精製と His tag 精製とで比較した。その結果、新規 SBP タグ精製では His tag 精製に比べ精製効率は低いものの、非特異バンドは少なかった。溶出条件の検討で精製効率の改善を試みる。



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リポソームで区画化した酵素代謝反応システム

（京大エネ研 [1]）（京大エネ科 [2]）○小松原 風汰 [1,2]・Peng Lin[1]・中田 栄司 [1]・小西 宏明 [1,2]・森井 孝 [1]

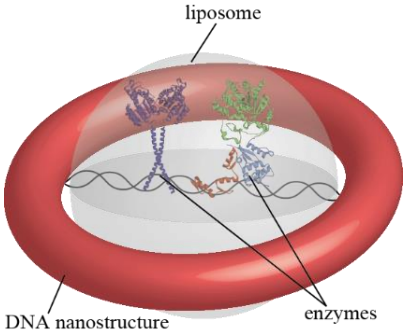
Enzymatic metabolic reactions compartmentalized in liposome with a skeletal DNA nanostructure ([1]*Institute of Advanced Energy, Kyoto University*) ([2]*Graduate School of Energy Science, Kyoto University*)○Futa Komatsubara[1,2], Peng Lin[1], Eiji Nakata[1], Hiroaki Konishi[1,2], Takashi Morii[1]

Metabolic reactions take place with high efficiency and precision in the cell, where an enormous number of molecules are densely mixed. It is believed that increasing the concentration of intermediates enhances the enzymatic reaction rate by compartmentalizing substrates and enzymes in intracellular organelles. Quantitative evaluation of such compartment is necessary for understanding its actual benefit and for the development of artificial organelles.

In this research, we have designed an enzymatic metabolic reaction system on a ring-shaped DNA nanostructure that could be compartmentalized with liposome to construct an artificial organelle. Controlling the number and location of enzymes within a defined size of liposome would allow quantitative evaluation of the metabolic reaction in the compartment.

Keywords : Enzyme metabolic reaction; DNA nanostructure; Compartment; Liposome

細胞内は様々な生体分子が高密度で共存した夾雑な環境にあるにもかかわらず、代謝反応が高精度かつ高効率で進行する。そのひとつの機構として、基質と酵素が特定の区画に分けられることによる局所的な反応中間体の濃度の上昇があげられる。本研究では、リング状 DNA ナノ構造体 [1]に分子数を制御して配置した酵素 [2)3)]を、リポソームに内包して人工細胞小器官の作製することにより、区画化された代謝反応を定量的に評価する。



1) Self-assembly of size-controlled liposomes on DNA nanotemplates. Y. Yang, J. Wang, H. Shigemitsu, W. Xu, W. M. Shih, J. E. Rothman, C. Lin, *Nat. Chem.* **2016**, *8*, 476-483.

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3) Spatially Organized Enzymes Drive Cofactor-Coupled Cascade Reactions. T. A. Ngo, E. Nakata, M. Saimura, T. Morii, *J. Am. Chem. Soc.* **2016**, *138*, 3012-3021.

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アンジオテンシンⅠ変換酵素阻害活性を有するプロリン含有トリペプチドの機械学習による予測と検証

(九州工業大学[1]・バイタルリソース応用研究所[2]) ○田中瑞穂[1]・藤本雄樹[1]・畠中登志也[1,2]・加藤珠樹[1]

Prediction and Validation of Proline-containing Tripeptides with Angiotensin I-converting Enzyme Inhibitory Activity ([1]*Kyushu Institute of Technology*, [2]*Vital Resources Applied Laboratory*) ○Mizuho Tanaka,[1] Yuki Fujimoto,[1] Toshiya Hatakenaka,[1,2] Tamaki Kato[1]

Angiotensin I-converting enzyme (ACE I) is an enzyme associated with increased blood pressure and various inhibition studies have been conducted to alleviate hypertension. Some short-chain peptides are known to have ACE I inhibitory potential and many of them contain proline. In this study, we focused on tripeptides that contain proline and have ACE I inhibitory activity and attempted to use machine learning to predict those with high inhibitory activity. First, the IC_{50} of known inhibitory peptides were collected from an online database. Next, docking simulations of these inhibitory peptides and ACE I were performed using MOE to collect data on the interaction. The relationship between the collected data and IC_{50} was learnt by PyCaret, and the learning results were used to predict candidate inhibitory peptides for tripeptides containing proline in the sequence. Several tripeptides predicted to have high ACE I inhibitory activity were selected and synthesized by conventional peptide solid-phase synthesis using the Fmoc strategy, and the ACE I enzyme inhibitory activity was measured in vitro.

Inhibitory activity measurements showed that some of the predicted tripeptides had inhibitory activity at μM to tens of μM levels. This demonstrates the applicability of machine learning prediction methods to the screening of peptides with inhibitory activity.

Keywords : Hypertension, Angiotensin I-Converting Enzyme, Machine learning, PyCaret

アンジオテンシンⅠ変換酵素（ACEⅠ）は血圧上昇に関連する酵素であり、高血圧の緩和に向けてさまざまな阻害研究が行われている。短鎖ペプチドにも ACEⅠ阻害能を持つものがあり、またその多くはプロリンを含んでいることが知られている。本研究では、プロリンを含み ACEⅠ阻害能を持つトリペプチドに着目し、機械学習を用いて阻害活性が高いものを予測する手法を試みた。まず、既知の阻害ペプチドの IC_{50} をオンラインデータベースから収集した。次に、これら阻害ペプチドと ACEⅠのドッキングシミュレーションを MOE を用いて行い、相互作用に関するデータを収集した。収集したデータと IC_{50} との関連を PyCaret により学習させ、この学習結果を配列内にプロリンを含むトリペプチドに用いて阻害ペプチド候補を予測した。ここで ACEⅠ阻害活性が高いと予測されたトリペプチドを複数選択し、Fmoc 戦略を用いた通常のペプチド固相合成法により合成し ACEⅠ酵素阻害活性の in vitro 測定を行った。

阻害活性測定の結果、予測されたトリペプチド中には μM レベルの阻害活性を有するものがあった。機械学習による予測手法が阻害能を持つペプチドのスクリーニングに適用可能であることを示している。

1) Prediction and Validation of Proline-containing Tripeptides with Angiotensin I-converting Enzyme Inhibitory Activity Using Machine Learning Models. T. Hatakenaka, Y. Fujimoto, T. Kato, *Letters in Drug Design & Discovery*, **2023**, in press.

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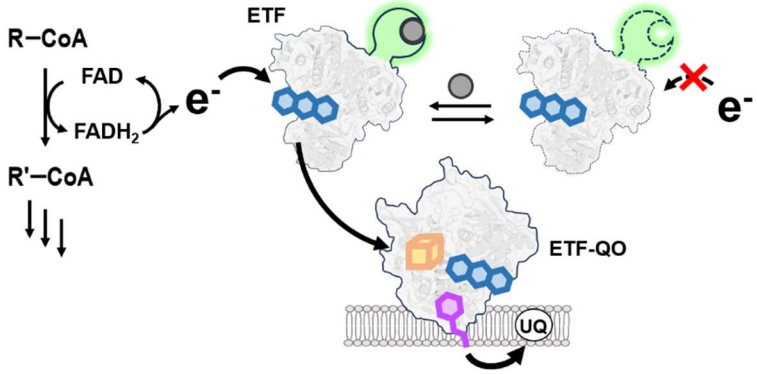
電子伝達鎖のスイッチングによる酸化酵素活性の外的制御

（早稲田大学[1]）○長谷川 悟史[1]・加藤涼大[1]・梅野 太輔[1]
Functional Regulation of Oxidative Enzymes Through On/Off Switching of Electron Transfer Chain ([1]*Waseda University*) ○Satoshi Hasegawa,[1] Ryota Kato,[1]Daisuke Umeno[1]

Dynamic control of engineered metabolic pathways is often achieved by turning on and off the expression of biosynthetic genes. Here, we sought to implement the regulator domain directly to the key biosynthetic genes, specifically by controlling the electron transfer chain required for the catalytic turnover of oxidation enzymes. Electron transfer flavoprotein (ETF) is a protein that regenerates FAD necessary for oxidative reactions by discarding electrons drawn from the cofactor $FADH_2$ into quinone sink through a chain of electron transfers. In this study, we attempted to develop an on/off control system for the synthesis of fatty acids and organic acids by externally controlling the electron-transfer function of the ETF protein. We searched for peptide tag insertion sites in ETF_{α}, ETF_{β}, and ETF_{QO}, which are responsible for electron transfer, without impairing their functions. We found 2, 1, and 3 insertion sites for ETF_{α}, ETF_{β}, and ETF_{QO}, respectively. *E. coli* strain expressing the tag-inserted ETF_{α} exhibited conditional induction of oxidative process by the addition of targeted molecules.
Keywords: Synthetic Biology, Biosensor, Metabolic Engineering, Intracellular Electron Transfer

人工的な代謝経路のダイナミック制御は，おもに生合成遺伝子発現誘導の ON/Off によって実現することが多い．我々は，生体内の酸化反応で消費される補因子の再生サイクルに着目した。電子伝達フラボタンパク質（ETF）は，補因子 $FADH_2$ から引き抜かれた電子を電子伝達の連鎖によってキノンに捨て，酸化反応に必要な FAD を再生させるタンパク質である。本研究では，ETF タンパク質の電子伝達機能を ON/Off することによって，脂肪酸・有機酸の合成を ON/Off 制御する系の開発を試みた。

電子伝達を担う ETF α，ETF β，ETF-QO に対し，機能を損なわずペプチドタグを挿入できる部位を探索した．それぞれ，2, 1, 3 箇所の挿入可能部位を見出すことができた. なかでも ETF α にペプチドタグを挿入して作出した融合タンパク質を発現した大腸菌株は, ペプチドと相互作用する分子の培地添加によって有意にその生産が増加することを見出した。



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酸化還元活性を付与した液液相分離材料によるタンパク質フォールディング促進

（農工大院工[1]・神奈川産技総研[2]）○山下 有希乃[1]・村岡 貴博[1,2]

Protein Folding Promotion Using Redox-Active Liquid-Liquid Phase Separation Materials

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*KISTEC*)
○Yukino Yamashita,[1] Takahiro Muraoka,[1,2]

Proteins are functional macromolecules notable for mediating various vital biological reactions as well as pharmaceuticals. Folding into the native conformation is essential for proteins to express the biological functions. Non-native and misfolded proteins cannot work properly and also aggregate via intermolecular contacts between exposed hydrophobic amino acid residues. The protein aggregation causes some serious problems such as decrease in the yields of functional proteins and pathology. Artificial materials that promote protein folding have been developed. Although a number of synthetic materials, such as nanogels and thiol compounds, that promote folding have been developed, the previous systems require time-consuming chromatographic purification at the final step.

In this study, we focus on liquid-liquid phase separation systems to facilitate the separation of native proteins after the folding reactions. Liquid-liquid phase separation triggered by hydrophobic interactions could isolate the non-native proteins that expose hydrophobic surfaces. We have developed the thermo-responsive phase separation materials based on elastin-like polypeptide.

Keywords : Liquid-Liquid Phase Separation; Protein Folding; Elastin-like Polypeptide

タンパク質はあらゆる生命現象に重要な役割を果たすとともに、製薬材料としても注目される機能性高分子である。タンパク質の生物学的機能の発現には、天然構造へのフォールディングが不可欠である[1)]。非天然構造体は、生物学的機能を発現できないことに加え、露出した疎水部が分子間会合することで凝集を形成する。凝集体は天然構造形成の収率を低下させる原因であるとともに、神経変性疾患などの原因となる。凝集体の抑制と天然構造収率の増加の重要性から、天然構造形成を促す効果を持った人工材料が開発されてきた。例としてナノゲル[2)]やチオールを有した合成分子[3)]が報告されている。これら材料によるフォールディングは均一な系であり、最終的にはクロマトグラフィーによる分離が必要とされる。

本研究では、より簡便に天然構造体を分離可能な系の構築に向け、疎水性相互作用により形成する液液相分離を利用し、表面が比較的親水的な天然構造を分離することを着想した。温度応答的に相分離を形成するエラスチン類似ペプチドを基盤とする材料を開発した。

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3) S. Okada *et al., Chem. Sci.* **2023**, 14, 7630-7636.

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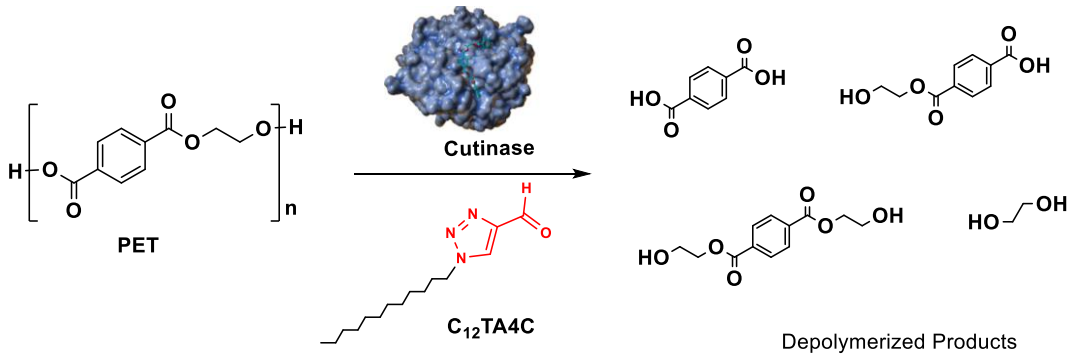
Improved Degradation of Polyethylene Terephthalate Film by Cutinase Using 1-Dodecyl-1*H*-1,2,3-Triazole-4-Carbaldehyde Surfactant

([1]*Graduate School of Environmental Science, Hokkaido University,* [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Joel Muyomba,[1] MD Sadikur Rahman Shuvo,[1] Akira Onoda.[1,2]

Keywords: PET; Biodegradation; Surfactants; Enzyme activity

The use of enzymes for the biodegradation of PET is still under investigation for improvement; Cutinase is one of the PET hydrolyzing enzymes that has been shown to have the highest degradation activity toward PET film compared to other enzymes.[1] Research to improve its activity has mainly focused on modifying cutinase through enzyme engineering. Our group previously reported that modified cutinase with 1-hexyl-1*H*-1,2,3-triazole-4-carbaldehyde (C_6TA4C) showed improved activity compared to the unconjugated enzyme.[2] However, due to the increased hydrophobic nature of the longer alkyl chain of triazole carbaldehydes, the conjugation of enzymes using longer alkyl triazoles became improbable. We therefore used 1-dodecyl-1*H*-1,2,3-triazole-4-carbaldehyde (C_{12}TA4C) as a surfactant to modify the PET film surface making PET chains more accessible for the enzyme. C_{12}TA4C was observed to improve the catalytic activity of cutinase without conjugation. The triazole surfactant was then compared to the effect of the anionic surfactant on cutinase since anionic surfactant had been demonstrated to improve PETase enzyme activity on PET.[3]



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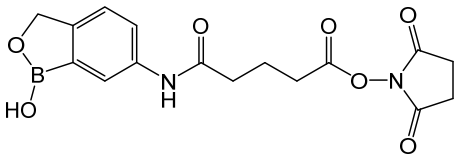
ベンゾオキサボロールで化学修飾されたキモトリプシンの調製とその性質

（金工大応化）○土谷 涼翔・吉田 大和・小野 慎
Preparation and properties of chymotrypsin chemically modified with benzoxaborole (*Department of Applied Chemistry, Kanazawa Institute of Technology*) ○Ryoga Tsuchiya, Yamato Yoshida, Shin Ono

Benzoxaborole is a derivative of phenylboronic acid and has a binding affinity for cis-diol compounds. Recently, benzoxaborole has attracted much attention for its application because of its sugar-binding ability even at neutral pH. We have introduced benzoxaboroles into the Lys side chains of enzymes and investigated the changes in the characteristics of the enzymes. In this study, we introduce several benzoxaboroles into the Lys side chains of chymotrypsin and report the changes in enzymatic activity and properties of the enzyme by adding sugar-binding properties.
Keywords : Benzoxaborole; Chemical modification; Chymotrypsin; Enzymatic activity; Sugar-binding ability

ベンゾキサボロール (benzoxaborole, Bob) は，ガラクトースやマンノースなどのシスージオール構造を持つ化合物に対して，選択的に認識して結合する特性を持っているため，医薬品や糖センサーへの応用が注目されている[1]．そこで，タンパク質の Lys 残基にランダムに Bob を導入することで糖鎖を認識する機能を付与し，既知タンパク質の機能を変換する研究を行っている．

今回，Bob のアミノ誘導体（5-Amino-2-(hydroxymethyl)phenylboronic Acid Cyclic Monoester）をグルタリル化後，*N*-ヒドロキシサクシンイミド活性エステルに導いた Bob 修飾分子 (Bob-NH-Glt-NHS) を用い，既知タンパク質としてキモトリプシン（Csin）を採用して，Bob 誘導体が結合したランダム Bob (Bob^{r}MCsin) を調製した．得られた Bob^{r}MCsin のペプチド基質に対する加水分解速度は，天然の Csin のものに相当することがわかり，導入された Bob 部分はペプチド基質の加水分解活性には影響しないことが示された．さらに，Bob^{r}MCsin のアガロースゲルやアルギン酸ゲルへの親和性を評価しているので合わせて報告する．



Bob-NH-Glt-NHS の構造

1) Recent Developments in the Chemistry and Biological Applications of Benzoxaboroles. A. Adamczyk-Woźniak, K. M. Borys, A. Sporzyński, *Chem. Rev.* **2015**, *115*, 5224−5247.

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OmpG ナノポア変異体のポア閉塞による TEV プロテアーゼの検出

（群大院理工 [1]）○鈴木 遥香 [1]・登坂 俊行 [1]・神谷 厚輝 [1]

Detection of TEV protease by pore blockage in Outer Membrane Protein-G Nanopore mutation

([1]*Graduate School of Science and Engineering, Gunma University*) ○ Haruka Suzuki,[1] Tosiyuki Tosaka,[1] Kouki Kamiya[1]

Outer membrane protein (Omp) forms a nano-sized pore and transports ions and nutrients. The pore of outer membrane protein G (OmpG) that is one of the Omp family has a β-barrel structure. Recently, it has been reported that DNA and antibodies are detected using OmpG. The detection of protease which is the purpose of this study enables the sensing of diseases for the identification of kinds of cancer. In this study, we developed a detection method of protease using OmpG nanopore mutation that was conjugated with linker containing some kinds of protease recognition sites. First, we prepared the OmpG nanopore mutation with the linker containing the TEV protease recognition site and examined the length of the linker that induces pore blockage. We investigated differences in single-channel currents of OmpG before and after cutting the linker using a patch-clamp amplifier (Figure 1).

Keywords : Nanopore; TEV protease; Patch-clamp amplifier

外膜タンパク質 Omp (Outer membrane protein) は、ナノサイズの孔(ポア)を形成し、細胞内外のイオンや栄養物の輸送を行っている。Omp ファミリーのひとつである OmpG はβ-バレル構造をもつ膜貫通外膜タンパク質であり、1 本のポリペプチド鎖からナノポアを形成する。近年，OmpG を用いて DNA や抗体の検出ができることが報告されている。本研究の目標であるプロテアーゼの検出が可能になれば，がんの種類の同定など疾病のセンシングが可能になる。本研究では，複数種類のプロテアーゼ認識配列を含むリンカーをナノポアに付加することで，プロテアーゼの種類を検出する。まず，TEV プロテアーゼ認識配列をひとつ含む単純なリンカーを OmpG ナノポアに連結して，ポアの閉塞が起こるリンカーの長さを検討した。リンカー切断前後のイオン透過性の変化を人工膜のパッチクランプ法で測定した(Figure 1)。

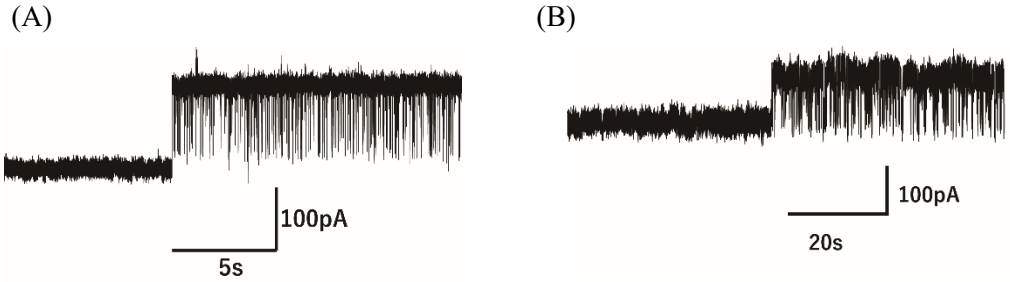

Figure 1 (A)The signal of OmpG mutation. (B)The signal of OmpG mutation with the linker.

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大腸菌内での YK ペプチドタグ融合による酵素集積化と 3-ヒドロキシ酪酸合成への影響

(東京工大院生命理工[1]・東大院工[2]) ○小笹 文吾[1]・中山 彩恵[1]・橋本 匡浩[1]・三木 卓幸[1,2]・三原 久和[1]

Enzyme integration by YK peptide tag fusion in E. coli and its effect on 3-hydroxybutyrate synthesis([1]*School of Life Science and Technology, Tokyo Institute of Technology,* [2]*School of Engineering, The University of Tokyo*). ○ Bungo Kozasa[1], Sae Nakayama[1], Masahiro Hashimoto[1], Takayuki Miki[1,2], Hisakazu Mihara[1]

Cells are leveraged as factories for mass production by modifying the metabolic pathways to produce desired compounds. The integration of enzymes is essential in this process. Local concentration of enzymes accelerates the cascade reactions by transferring the intermediates from one enzyme to another.

We aimed to establish a more straightforward strategy for enzyme accumulation by using self-assembling peptide tags. Previously, we have developed YK peptides, composed of repeats of tyrosine and lysine, self-assembled intracellularly. In this study, we fused the YK11 peptide to β-ketothiolase (PhaA), (*S*)-3-hydroxybutyryl-CoA reductase (Hbd), and propionate CoA transferase (Hbd) for efficient production of (*S*)-3-hydroxybutyrate. We expressed these enzymes in *E. coli*, and the yield of 3-hydroxybutyrate was evaluated. Unexpectedly, the fusion of the peptide tag resulted in a 60% decrease in yield.

To confirm the cause of the yield decrease, we examined each enzyme's activity in the soluble and insoluble fractions of the lysate. The results showed that PhaA lost its activity dramatically, while the expression of Hbd was significantly reduced. Of note, despite the significant decrease in the activity of the respective enzymes in the cell lysate, the intracellular evaluation showed only a 60% yield decrease. This study indicates the necessity to construct and evaluate in living cells.

Keywords: Enzyme engineering, Peptide engineering, Self-assembling peptides, Metabolon

細胞は物質生産の場として活用されている。細胞内の代謝経路を改変し、望みの化合物を生産する。その上で、酵素集積化が重要視される。酵素が濃縮することで、酵素間での中間体の受け渡しが迅速化され、カスケード反応が促進される。

我々は、より簡便に酵素を集積化する戦略として、自己集合化ペプチドタグを用いることを考案した。これまで、我々はチロシンとリシンを繰り返した YK ペプチドは、細胞内で自己集合することを見出している。そこで本研究では YK11 ペプチドをβ-ケトチオラーゼ(PhaA)、(*S*)-3-ヒドロキシブチリル-CoA 還元酵素(Hbd)、プロピオン酸 CoA トランスフェラーゼ(Hbd)に融合し、(S)-3-ヒドロキシ酪酸の効率的な生成を目指した。その結果、予想外なことに、大腸菌内で 3-ヒドロキシ酪酸の生成量評価を行なったところ、ペプチドタグの融合によって 60%の収率の低下が見られた。

収率低下の原因を確認すべく、破砕液の可溶性画分、不溶性画分それぞれを用いて各酵素の活性の変化を調べた。その結果、PhaA はペプチド融合によって劇的に活性が失われ、また Hbd はペプチド融合によって発現量が大幅に低下したことが要因であることがわかった。同時に、興味深い点として、細胞破砕液中でのそれぞれの酵素活性は大幅に低下しているにも関わらず、細胞内での評価は 60%の収率低下にとどまった。本研究から、細胞内での直接的な酵素集積化の構築と評価の必要性が明白となった。

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外部刺激応答による酵素の近接と反応効率の検討

(群馬大理工[1]・群馬大院理工[2]) ○髙沢桃花[1]・神谷厚輝[2]
Examination of proximity and reaction efficiency of enzymes by external stimulation ([1] *School of Science and Technology, Gunma University*, [2]*Graduate School Science and Technology, Gunma University*)○Momoka Takazawa, Koki Kamiya[2]

It has been reported that cascade reactions of the multiple enzymes connected with a protein linker were more efficient than the reactions of isolated enzymes. The change of an active and inactive of enzyme cascade reactions by this approach is difficult because multiple enzymes are bonded to the linker. In this study, we introduce an amino acid sequence of zinc finger to the linker between multiple enzymes in order to change the active and inactive of the reactions. An accumulation of zinc finger domains that were promoted by an external stimulation such as metal ions caused a proximity of enzymes.
Keywords : Enzyme; Linker; Metal Ion

酵素カスケード反応が様々な細胞小器官で行われているため、近年では細胞小器官を模倣した人工細胞モデルの区画化の研究が進められている[1]。人工細胞の区画化では、中間体の局所的な高濃度化などの利点があり、酵素反応を効率よくかつ連続的に進めることができる。人工系において、酵素の逐次反応を効率良く行うためには酵素の近接が重要である。我々の研究室では、DNA と RNA を利用した三又構造の酵素複合体を作製した[2]。この複合体はフリーな酵素と比較して反応効率が 7 倍程度上昇したことを明らかにしている。DNA は酵素の近接に多く利用されているが、DNA は負電荷を帯びているため、タンパク質機能の影響を及ぼす可能性があると考えた。

そこで本研究では、外部刺激に金属イオンを用いて、酵素の近接と反応効率の上昇を目指した。リンカーにジンクフィンガー配列を導入した ECFP と EYFP 複合体を大腸菌で発現させ、大腸菌を破砕した後、可溶化部を His tag 精製、ゲルろ過クロマトグラフィーを行った。SDS-PAGE をした結果、複合体の精製に成功した(Fig.1)。亜鉛イオンの有無による FRET 測定を行った結果、亜鉛イオンを含まない方は EYFP/ECFP 比が 1.6 倍だったのに対し、亜鉛イオンを加えて蛍光タンパク質を近接した方では 2.9 倍と FRET 効率が上昇した(Fig.2)。当日は、蛍光タンパク質を酵素に変え、酵素反応の効率上昇について発表する予定である。

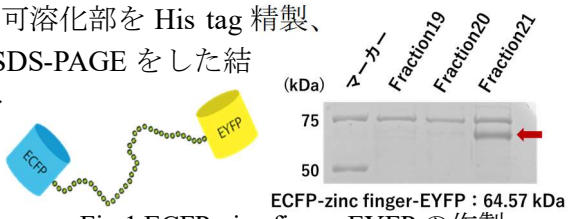

Fig.1 ECFP-zinc finger-EYFP の作製

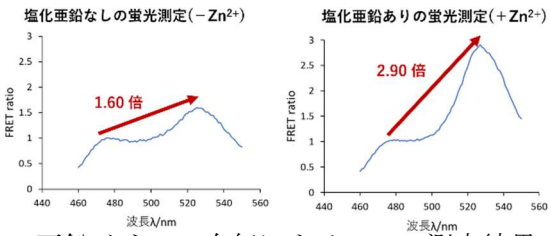

Fig.2 亜鉛イオンの有無による FRET 測定結果

1) Anna H., et al,, *Trends Cell Bi*ol. **2012**, 22, 12
2) Aoi Mameuda., et al,, *Anal. Chem.* **2023**, 95, 9548-9554

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無細胞タンパク質発現系で発現させた結晶化タンパク質の結晶化の検討

（群大理工[1]・群大院理工[2]）○小菅 友萌[1]・神谷 厚輝[2]
Investigation of crystallization of crystallized protein expressed using cell-free protein synthesis ([1]*School of Science and Technology, Gunma University*, [2]*Graduate School of Science and Technology, Gunma University*) ○Yume Kosuge,[1] Koki Kamiya[2]

In living cells, biopolymers exist at high density is called a molecular crowding state. The proximity of the enzymes causes an efficient cascade reaction. Our goal constructs an efficiency bioreactor system that mimics intracellular conditions using an artificial cell model. In this study, we use Cry3Aa of a crystallized protein for generating the enzyme proximity. Cry3Aa proteins spontaneously form crystals in the bacterium *Bacillus thuringiensis* (*Bt*). Water-soluble proteins are entrapped within the nanoporous channels of Cry3Aa crystals. It takes about three days to form Cry3Aa crystals in *Bt* cells. In this study, we examine conditions of the crystal formation of Cry3Aa synthesized using a cell-free protein synthesis. Crystal formation of Cry3Aa was investigated using a dynamic light scattering (DLS) measurement, microscope observation, and protein electrophoresis.
Keywords : Cell-free protein synthesis; Protein; Crystallization

細胞内では、生体高分子が高密度に存在する状態を分子クラウディング状態という。この状態において、近接化した酵素によって効率的なカスケード反応が生じる。我々は、人工細胞モデルを用いて、細胞内の酵素近接状態を再現することで、効率的なバイオリアクターシステムの構築を目指している。酵素同士の近接の手段として結晶化タンパク質である Cry3Aa を用いる。Cry3Aa は、バチルス・チューリンゲンシス(*Bt*)細菌の中で自然に結晶を形成するタンパク質であり、Cry3Aa 結晶のナノ多孔質チャネル内に酵素等を封入できることが報告されている [1)]。Cry3Aa の発現と結晶形成を *Bt* 細胞で行うと、約 3 日の時間を要する [2)]。本研究では、無細胞タンパク質発現系を用い、Cry3Aa を発現させ、細胞外における結晶形成の条件を検討する。Cry3Aa の結晶形成は、動的光散乱(DLS)、顕微鏡観察、タンパク質電気泳動によって検討した(Fig.1)。

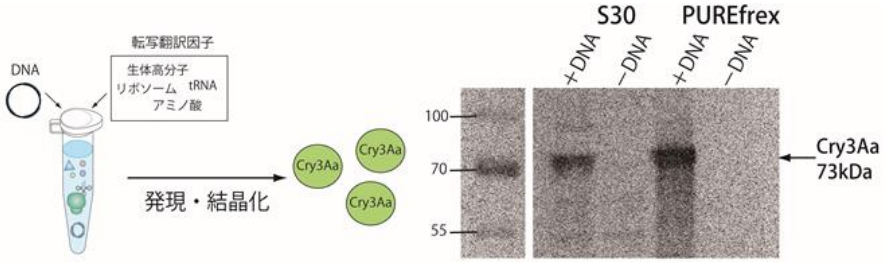

Fig.1 結晶化タンパク質 Cry3Aa の無細胞タンパク質発現

1) Bradley S. Heater. et al, Journal of the American Chemical Society, Vol.142 (2020), pp.9879-9883
2) Qian Sun. et al, Bioconjugate Chemistry, Vol.33 (2022), pp.386-396

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Synthesis of self-assembling peptides conjugated with integrin-targeting peptides as biomaterials for cancer cell culture

(*School of Life Science and Technology, Tokyo institute of Technology*)
○Li Man, Hisakazu Mihara, Hiroshi Tsutsumi
Keywords: Self-assembling peptide, Integrin-targeting peptide

Malignancy of tumors is not only dependent on cellular properties, but also dependent on the milieu around tumor tissues, which is called tumor microenvironment. In the tumor microenvironment, one of the key components is extracellular matrices (ECMs). ECM proteins can bind to integrins on cancer cell membranes. The integrin can regulate various activities of cancer cells—adhesion, proliferation, apoptosis, metastasis and etc[1,2]. Many biologically active motif sequences which can bind to integrins have been identified from ECM proteins.
Previously, we developed a short self-assembling peptide $(FFiK)_2$ which could self-assemble into beta-sheet structure and form stable and transparent hydrogel for cell culture scaffolds[3]. However, $(FFiK)_2$ does not have biological activities to regulate cancer cell functions. The conjugation of integrin-targeting bioactive sequences with $(FFiK)_2$ can regulate cancer cell bioactivities via ECM-integrin interaction.
In this research, $(FFiK)_2$ derivatives conjugated with integrin-targeting peptides were designed and synthesized. Then, cell adhesion and proliferation activities of functionalized $(FFiK)_2$ derivatives were investigated.

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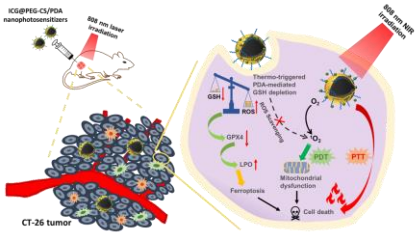
Enhancing antitumor efficacy by glutathione-depleted nanophotosensitizers with photo-triggered strong hyperthermia and ROS generation

(*Department of Chemical Engineering, National Chung Hsing University, Taiwan*)
Wen-Hsuan Chiang, Yu-Hsin Chen, I-Ju Liu
Keywords: Nanophotosensitizers; Polydoapmine, Thermo-enhanced GSH depletion; NIR-triggered ROS generation; Dual-modal cancer phototherapy

Dual-modal phototherapy based on the combination of photodynamic therapy (PDT) and photothermal therapy (PTT) has emerged as a promising strategy for cancer treatment. However, the poor photostability and photothermal conversion efficiency (PCE) of organic small-molecule photosensitizers, and the intracellular glutathione (GSH)-mediated reactive oxygen species scavenging result in unsatisfactory antitumor efficacy of dual-modal phototherapy. To address these issues, in this study, a versatile nanophotosensitizer system was successfully fabricated by ingenious incorporation of indocyanine green (ICG) into PEGylated chitosan (PEG-CS)-decorated polydopamine (PDA) via multiple π-π stacking, hydrophobic and electrostatic interactions. The attained ICG@PEG-CS/PDA nanophotosensitizers exhibited the outstanding photothermal stability, high PCE (ca 62.8 %), prominent singlet oxygen-generating and PDA-mediated GSH-consuming capability. After being internalized by CT26 cells, these nanophotosensitizers under 808 nm near-infrared (NIR) laser irradiation effectively produced singlet oxygen with the aid of thermo-enhanced intracellular GSH depletion to promote mitochondrial damage and lipid peroxide formation, thus eliciting ferroptosis and apoptosis. The in vivo antitumor efficacy studies further demonstrated that the ICG@PEG-CS/PDA nanophotosensitizers markedly inhibited CT26 tumor growth by NIR-activated intense hyperthermia and redox homeostasis disruption without systemic toxicity. Our study presents a new strategy to augment antitumor effect of dual-modal phototherapy by ICG@PEG-CS/PDA nanophotosensitizers.



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肝細胞ガン標的ペプチドで修飾した金ナノロッドの合成とフォトサーマル効果の検証

(龍谷大先端理工)○藤本翔也[1]・今井崇人[1]・浅野昌弘[2]・山﨑正幸[3]・富﨑欣也[1]

Synthesis of Gold Nanorods Modified with Hepatocellular Carcinoma Targeting Sequence Peptides and Verification of Their Photothermal Effects ([1]*Department of Materials Chemistry, Ryukoku University, Ecology and Environmental Engineering Course, Faculty of Advanced Science and Technology,* [3]*Department of Food Sciences and Human Nutrition, Ryukoku University*) ○Shoya Fujimoto[1], Takahito Imai[1], Asano Masahiro[2], Masayuki Yamasaki[3]and Kin-ya Tomizaki[1]

Recently, photothermal therapy using gold nanorods with photothermal conversion properties has attracted attention as a minimally invasive therapeutic strategy for the selective treatment of cancers. In this study, we are focusing on DDS using SP94 peptide, which specifically binds to GRP78, a glucose-regulated protein on the cell membrane of hepatocellular carcinoma. In this study, we modified sufaces of gold nanorods with the hepatocellular carcinoma target peptide, charaacterized their complexation, and verified the difference in photothermal effects using two types of cancer cells.

First, gold nanorods were synthesized using the CTAB (hexadecyltrimethylammonium) method and surface-modified with mPEG-SH (polyethyleneglycol methyl ether thiol) in aqueous solution for 30 minutes. Then, SP94-tethering RU188 peptide was used to modify the surface of the nanorods in aqueous solution for 24 hours to synthesize the target product. The cytotoxicity of the target product was evaluated in human hepatocellular carcinoma (HepG2) and human cervical carcinoma (HeLa) after irradiation with 808 nm NIR at 2 W/cm2 for 5 min.

Keywords : Peptide ; Gold nanorod ; Hepatocellular Carcinoma

近年、光熱変換特性をもつ金ナノロッドを用いたフォトサーマル療法が低侵襲治療戦略としてガン細胞の選択的治療に注目されている。本研究では、肝細胞ガンの細胞膜上に多く存在するグルコース制御タンパク質である GRP78 と特異的に結合する SP94 ペプチドを用いた DDS を指向している。今回、金ナノロッドに肝細胞ガン標的ペプチドを用いて表面修飾を行い、その複合化評価と二種類のガン細胞を用いた PTT の検証を行った。

まず、CTAB (ヘキサデシルトリメチルアンモニウム) 法を用いて金ナノロッドを合成し mPEG-SH (ポリエチレングリコールメチルエーテルチオール) を 30 分間水溶液中で表面修飾した。次いで SP94 配列を含む RU188 ペプチドにより 24 時間水溶液中で表面修飾 し目的物の合成を行った。この目的物をヒト肝細胞がん(HepG2)とヒト子宮頸がん(HeLa)に添加し 808 nm NIR を 2W/ cm^2 の強度で 5 分間照射した際の細胞毒性を評価した。

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Wireless charging-mediated angiogenesis and nerve repair by adaptable microporous hydrogels

(*Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, Hsinchu 300044, Taiwan.*) ○Shang-Hisu Hu

Keywords: Drug delivery; functional polymer; wireless charging; hydrogel; traumatic brain injury

Traumatic brain injury causes inflammation and glial scarring that impede brain tissue repair, so stimulating angiogenesis and recovery of brain function remain challenging. Here we present an adaptable conductive microporous hydrogel consisting of gold nanoyarn balls-coated injectable building blocks possessing interconnected pores to improve angiogenesis and recovery of brain function in traumatic brain injury. We show that following minimally invasive implantation, the adaptable hydrogel is able to fill defects with complex shapes and regulate the traumatic brain injury environment in a mouse model. We find that placement of this injectable hydrogel at peri-trauma regions enhances mature brain-derived neurotrophic factor by 180% and improves angiogenesis by 250% in vivo within 2 weeks after electromagnetized stimulation, and that these effects facilitate neuron survival and motor function recovery by 50%. We use blood oxygenation level-dependent functional neuroimaging to reveal the successful restoration of functional brain connectivity in the corticostriatal and corticolimbic circuits.[1]

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FRETプローブで標識したペプチドヘテロダイマーの細胞内挙動

（龍谷大先端理工[1]・龍谷大農[2]）○田中かれん[1]・山﨑正幸[2]・富﨑欣也[1]

Intracellular behavior of peptide heterodimers labeled with FRET probes

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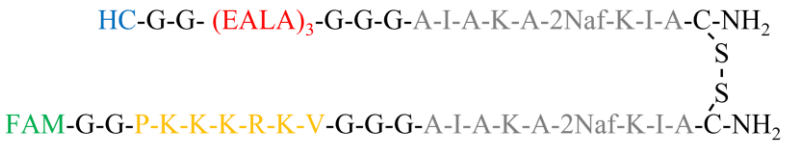
In recent years, research on drug delivery systems targeting cellular organelles has attracted much attention. However, when drugs are taken into cells by endocytosis, endosomal escape of drugs is a bottleneck to cytoplasmic distribution. Therefore, disrupting the endosomal membrane facilitates endosomal escape of drugs and efficient drug delivery. In our previous study, to improve drug escape from endosomes, two different types of peptides were dimerized, in which the N-terminus of a drug carrier peptide (Cap-p) [1)] was modified with a pH-responsive fusogenic peptide (GALA peptide) [2)] and a nuclear localization signal peptide (NLS) to form a disulfide bond-mediated peptide heterodimer (GALA-NLS), respectively. In this study, we synthesized a peptide labeled with two different fluorescent dyes (HC-GALA-NLS-FAM) and observed the localization of heterodimers in cells using FRET.

Keywords : endocytosis; endosome; pH-responsive fusogenic peptide ; FRET

近年、細胞小器官を標的としたドラックデリバリーシステムの研究が注目されている。しかし、薬剤がエンドサイトーシスにより細胞内へ取り込まれる際、エンドソームによる内包が細胞質送達への障壁となる。したがって、エンドソーム膜を乱すことで薬物のエンドソーム脱出が促進され、効率的な薬物送達が可能となる。先行研究では、エンドソームからの薬物の脱出を誘導するために、薬物キャリアペプチド (Cap-p) [1)] の N 末端に pH 応答性膜融合ペプチド (GALA peptide) [2)] および核移行シグナルペプチド (NLS) を修飾した 2 つのペプチドをヘテロ二量化し、ジスルフィド結合を介したペプチドヘテロダイマー (GALA-NLS) を合成した。本研究では、GALA-NLS を 2 種類の蛍光色素で標識したペプチド (HC-GALA-NLS-FAM) を合成し、細胞内還元環境におけるヘテロダイマーの挙動を FRET を利用して観察した。

HC-GALA-NLS-FAM :



1) Tomizaki, K.-Y. et al. *Molecules* **2017**, 22, 1916.
2) Nanda K.Subbarao, et al. *Biochemistry* **1987**, 26, 2964-2972.

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・液–液相分離に基づくケージドコアセルベートによる RNA の内包および光応答的放出

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RNA encapsulation and photo-responsive release by caged coacervates based on liquid-liquid phase separation

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Recent studies have reported a His-rich peptide that forms microdroplets (coacervates) by liquid-liquid phase separation, which could deliver RNA into cells. Intracellular delivery of RNA is important for elucidating RNA functions and RNA-induced intracellular phenomena. Since the above peptide coacervates do not have the ability to transport RNA into target cells, this study aims to develop a mechanism to make these coacervates photoresponsive so that RNA is released from the coacervates and functions only in cells irradiated with light. Specifically, we prepared caged coacervating peptides with a lysine residue to which a photodegradable protecting group was added, and attempted to disperse and release RNA by light after their intracellular introduction. The mechanism of action proposed here is based on chemical changes in the peptide due to dissociation of the photodegradable protecting group. To date, we have prepared caged coacervating peptides and demonstrated that photodegradation of the peptides, formation of coacervates, and internalization of siRNA are possible.

最近、ある種の His-rich ペプチドが液-液相分離による微小液滴（コアセルベート）を形成し、RNA を内包して細胞内に運びうることが、報告されている。RNA の細胞内送達は、RNA 機能や RNA の引き起こす細胞内現象を解明するうえで重要である。上記のペプチドコアセルベートは狙った細胞内に RNA を運ぶ能力がないため、本研究では、このコアセルベートに光応答性を付与し、光照射した細胞内のみで RNA を放出し機能させるような仕組みを開発する。具体的には、光分解性保護基を付加したリシン残基を導入したケージドコアセルベートペプチドを作成し、その細胞内導入後に光照射による分散と RNA 放出を試みた。ここで想定している作用機序は、光分解性保護基の解離によるペプチドの化学的変化に基づいている。現在のところ、ケージドコアセルベートペプチドを作製し、その光分解、および、コアセルベートを形成、siRNA の内包などが可能であることを証明できた。

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尾部に脂肪酸アミドを有する両親媒性イミダゾリル亜鉛ポルフィリンの合成と二分子膜への導入

（東理大理二[1]・奈良先端大物質[2]）○大野幹[1]・安原主馬[2]・佐竹彰治[1]
Synthesis of Amphiphilic Imidazolyl Porphyrinatozinc Having a Fatty Amide Group, and Their Introduction to Lipid Bilayer Membrane. ([1] *Faculty of Science Division II, Tokyo University of Science*, [2] *Division of Materials Science, Nara Institute of Science and Technology*) ○ Miki Oono,[1] Kazuma Yasuhara,[2] Akiharu Satake[1]

The purpose of this study is to functionalize liposomes based on self-organization of functional imidazolyl porphyrinatozinc (**ImZnP**). In our previous studies, we have observed that **ImZnP** having a fran-protected maleimide group self-organized in lipid bilayer membrane as a head-tail coordination manner. Here, we plan to prepare **ImZnP 1** having a fatty amide group, which is expected to self-organize in lipid bilayer membrane by the imidazolyl-zinc coordination with assist of hydrogen bonding interactions among the amide groups.
Keywords : Liposome; Porphyrin; Supramolecular polymer; Coordination; Hydrogen bond

リン脂質からなるリポソーム膜は生体膜モデルとして知られている。我々は機能性イミダゾリル亜鉛ポルフィリン(**ImZnP**)の脂質二分子膜内自己組織化を基軸としたリポソームの機能化を目指している。イミダゾリル部を頭部、その対角のメソ位置換基を尾部とすると、膜内で **ImZnP** を頭－尾型の配位ポリマーとして伸長させるためには、イミダゾールー亜鉛の配位に加え、尾部間の非共有結合性相互作用が有効と考えられる。そこで本研究では尾部に脂肪酸アミドを導入した **ImZnP 1** を新規に合成し、リン脂質リポソーム膜内での自己組織化挙動を調査することを目的とした。（結果）様々な脂肪酸アミドを系統的に合成するために尾部に NHBoc 基を有する **ImH_2P 2** を合成した。続いてトリフルオロ酢酸を用いて Boc 基の脱保護を行ったところ、目的のアミノ体の他に複数の副生成物が観測された。これらの副生成物は脂肪酸アミド導入後も分離が困難であった。そこで脂肪酸アミドを有するアルデヒドとイミダゾールカルバルデヒド、エーテル鎖を有するジピロメタンの縮合反応によって **ImZnP 1** を合成することに成功した。合成した **ImZnP 1** を用いてリポソーム膜内自己組織化について発表予定である。

Fig. 1

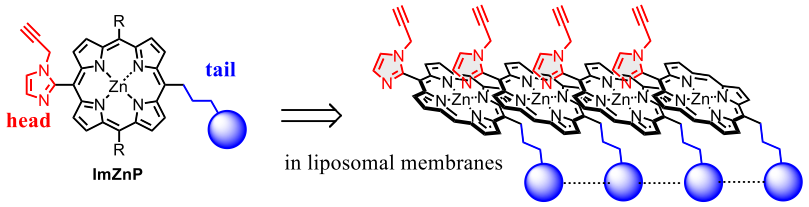
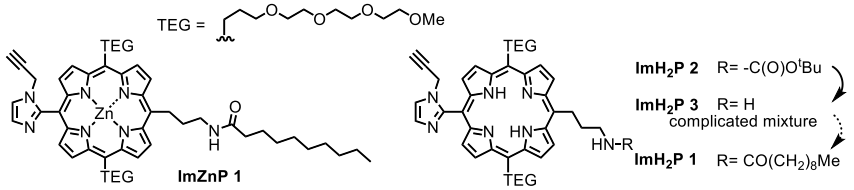


Fig. 2



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異なるメチレン鎖長で架橋したマレイミド基を有する両親媒性イミダゾリル亜鉛ポルフィリンの合成と二分子膜中での自己組織化

(東理大理二[1]・奈良先端大院物質[2]) ○梁瀬遥平[1]・安原主馬[2]・佐竹彰治[1]

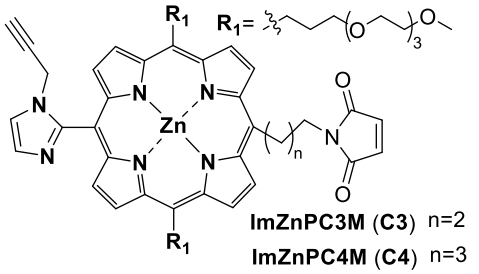
Synthesis of Imidazolyl Porphyrinatozinc Having a Maleimide Group Linked with Different Methylene Groups, and Their Self-organization in Lipid Bilayer Membrane.

([1] *Faculty of Science Division II, Tokyo University of Science*, [2] *Division of Materials Science, Nara Institute of Science and Technology*) ○ Yohei Yanase,[1] Kazuma Yasuhara,[2] Akiharu Satake[1]

A liposomal bilayer membrane composed of phospholipids is a two-dimensional space with a few nm thick front and back surface. Our goal is to functionalize a vesicle by self-assembling functional imidazolyl zinc porphyrin (**ImZnP**) derivatives within the lipid bilayer. **ImZnP** having a maleimide group linked with propylene, **ImZnPC3M** (**C3**), gave coordination polymer in the membrane of POPC liposomes, whereas the corresponding head-head dimer is formed in acetonitrile and Triton X-100 aqueous solution. Here, another **ImZnP** having a butylene linker, **ImZnPC4M** (**C4**), was synthesized. The self-assemble property of **C4** in POPC liposome was compared with that of **C3** to assess the effect of methylene length between the porphyrin and the maleimide group.

Keywords : supramolecular polymer, liposome, zinc porphyrin, coordination

リン脂質で構成されるリポソームの二分子膜は厚さ数 nm の表裏のある 2 次元空間である。我々はこの二分子膜内で機能性イミダゾリル亜鉛ポルフィリン誘導体を自己組織化させ、二分子膜内の機能化を目指している。先行研究では亜鉛ポルフィリンの 1 つのメソ位 (頭部) に*N*−プロパルギルイミダゾリル基、そして対面するメソ位 (尾部)にメチレン基3つを介してフラン保護されたマレイミド基を連結した**ImPZnMFu** を合成した。**ImPZnMFu** はアセトニトリルやトリトン X-100 のミセル中では頭−頭型の二量体を選択的に形成するのに対し、リン脂質(POPC)リポソーム中では頭−尾型ポリマーを形成した。本研究では頭−尾型ポリマーを形成する要素として、マレイミドとポルフィリンをつなぐメチレン鎖の長さの影響を調べるために、プロピレン基とブチレン基をそれぞれ有するポルフィリン **ImZnPC3M (C3)**と **ImZnPC4M (C4)** を合成し、POPC リポソーム膜内での自己組織化挙動を比較した。(結果) メンブランフィルターを用いた押し出し法によって作成した直径 100 nm の POPC リポソームに **C3** の DMSO 溶液を添加し、吸収スペクトル変化を追跡すると 380~550 nm 領域にブロードな吸収帯が現れ、約 30 分で変化が緩やかになった。この観測は **C3** が膜内で頭−尾型ポリマーを形成していることを示している。一方、**C4** の 30 分後の 380~500 nm 領域の吸収帯は **C3** に比べて狭く、変化もまだ続いていたことから、頭−尾型ポリマーの形成速度が **C3** に比べて低いことがわかった。



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光熱刺激に伴うがん細胞の ERK 活性モニタリング

（北海道大学情報科学院 [1]・名古屋工業大学 [2]）○大森　健司 [1]・山口　和志 [1]・Farsai Taemaitree[1]・根本　知己 [2]雲林院　宏 [1]

Aziridination of Styrene Derivatives Using Iminoiodinane Catalyzed by Iodine and Ammonium Iodide ([1]*Faculty of Information Science and Technology, Hokkaido University*, [2]*Nagoya Institute of technology*) ○Kenji Omori,[1]Kazushi Yamaguchi,[1] Farsai Taemaitree,[1] Tomomi Nemoto[2], Hiroshi Uji,[1]

Prior research has focused on photothermal therapy, in which cancer is treated using gold nanoparticles that generate a photothermal effect when exposed to excitation light. The detailed bioactive response of cancer cells when they are exposed to heat in the course of this therapy is unknown.

In addition, ERK, a signaling molecule involved in the regulation of cell fate such as division and death, is known to be abnormally upregulated in cancer cells.

The purpose of this study was to observe the ERK activity response of cancer cells in real time using the corresponding fluorescence changes and to elucidate the dynamics of ERK activity upon local photothermal stimulation.

In the experiment, gold nanoparticles, which generate photothermal effects, were uniformly distributed on cancer spheroids, which are 3-dimensional multicellular systems, and the ERK activity was compared between the cells heated by irradiation with excitation light and those heated without excitation light.

Keywords : photothermal therapy; ERK activity

先行研究では、励起光を当てることで光熱効果を発生する金ナノ粒子を用いてがんを治療する光熱治療がある。この治療の過程において細胞が熱を受けた際のがん細胞の詳細な生理活性応答は不明となっている。

また、分裂や死といった細胞運命の制御に係わるシグナル分子である ERK はがん細胞で異常に昂進することが知られている。

本研究の目的はがん細胞の ERK 活性応答をそれに対応する蛍光変化を用いてリアルタイムで観察し光熱局所刺激を与えた時の ERK 活性動態を解明することである。

実験では３次元多細胞系であるがんスフェロイド上に光熱効果を発生させる金ナノ粒子をおおよそ均一に分布させ、励起光を照射することで細胞を加熱した際にさせなかったものとの ERK 活性の比較を行った。

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異性化の光スイッチングに基づくジアリールエテンの光誘起細胞毒性

（龍谷大[1]・産総研[2]）○丸山 徳一[1]・須丸 公雄[2]・森下 加奈[2]・内田 欣吾[1]

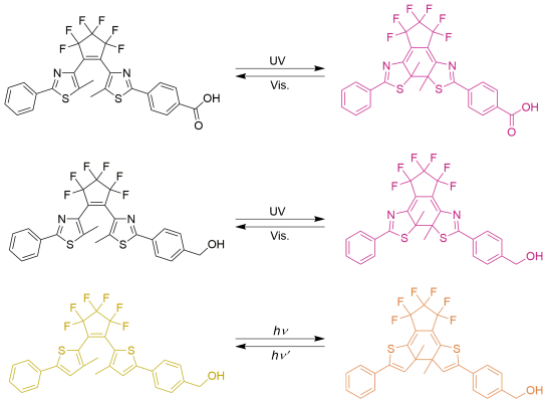
Photoinduced cytotoxity of diarylethene based on photoswitching isomerization

([1]*Ryukoku University*, [2] National Institute of Advanced Industrial Science and Technology)
○Norikazu Maruyama,[1] Kimio Sumaru,[2] Kana Morishita,[2] Kingo Uchida.[2]

Diarylethene (DAE) is a photochromic compound that is reversibly isomerized by light. We have reported that the double-strand breaks of DNA are induced by repetitive cyclization and cycloreversion reactions when planar and hydrophobic DAE closed-ring isomers are intercalated between base pairs of DNA upon irradiation with blue light where both isomers have the absorbance. In this study, we report a new DAE derivative that exhibits photoinduced cytotoxicity (Scheme 1). Previous DAE derivatives were likely to stabilize between base pairs after DNA intercalation and remained in the DNA, causing side reactions. Therefore, we designed and synthesized DAE derivatives with additional hydrophilic substituents and investigated whether they could be expelled from DNA due to increased hydrophilicity. We also report the observation of cell killing by short-term irradiation with UV light at 365 nm using these derivatives, which is different from previously reported photocytotoxicity.

Keywords : Photochromism; Diarylethene; dark toxicity; Photoinduced cytotoxicity

ジアリールエテン(DAE)は光により可逆的に異性化するフォトクロミック化合物である。我々は分子平面性の高く疎水性の高いDAEの閉環体がDNAの塩基対間に挿入された状態で開環/閉環両異性化を起こす波長の光を照射することでDNAのdouble-strand breaksを誘起し、光照射部の細胞のみを殺傷することを報告している[1)]。本研究では、新たに光誘起細胞毒性を示したDAE誘導体について報告する (Scheme 1)。過去のDAE誘導体はDNA挿入後、塩基対間で安定化しDNAに残留することで副反応の原因となる可能性が高い。その為、親水性置換基を追加したDAE誘導体を設計・合成し、親水性の増加によるDNAからの排出が可能であるかを検討した。また、これらの誘導体を用いて以前に報告した光殺傷とは異なるUV光365 nmの短時間照射による細胞殺傷も観察された為、同時に報告する。



Scheme 1. 本研究で使用した DAE 誘導体の分子構造とフォトクロミック反応

1) Y. Nakagawa, T. Hishida, E. Hatano, K. Sumaru, K. Morishita, K. Kirito, S. Yokojima, Y. Sakamoto, S. Nakamura, K. Uchida, *J. Med. Chem,* **2023**, 66, 5937-5949.

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FRETによる細胞内ATP測定を指標としたBODセンサー

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A microbial BOD biosensor by FRET based intercellular ATP measurement.
(Sch. of Biosci. and Biotechnol., Tokyo Univ. of Technol.) ○Yuto Kanno, Yuta Tateno, Takuo Akimoto

Biochemical oxygen demand(BOD)is an important indicator of organic pollution, and is evaluated as oxygen consumptions by microorganisms to decompose organic materials. In this study, we focused on the relationship between the intercellular ATP of microorganisms and BOD to achieve a simple BOD measurement. For this, ε subunit, ATP-binding protein whose conformation can be changed by ATP, fused with fluorescent proteins of CFP and YFP was used. By using the microorganism expressing the fusion protein, it is expected that BOD can be measured by FRET based fluorescence change of microorganisms. Concretely, the microorganism exhibits blue fluorescence for high BOD, while yellow green fluorescence can be observed for low BOD. In this study, Saccharomyces cerevisiae BY4741 gph (Glycogen Phosphorylase) Δ strain expressing the fusion protein was used to measure FRET ratio at BOD concentrations of 0, 10, 20, 50, 100 and 500 mg/L. The FRET ratio was found to be increased with increasing BOD concentration. A calibration curve was obtained from 0 to 100mg/L, suggesting that it is possible to determine BOD from the FRET ratio.

Keywords : Biosensor, FRET, BOD

BOD(生物化学的酸素要求量)とは微生物が試料水中の有機物を分解するために必要な酸素量を表しており、有機汚染の重要な指標である。本研究では、BOD を簡単に測定するために微生物内の ATP 量が BOD と相関することに着目した。ATP に特異的に結合する ATP 結合タンパク質のεサブユニットと蛍光タンパク質の CFP と YFP を用いることで BOD を微生物の蛍光変化によって測定できると期待される。本方法では BOD が高い試料水では微生物が青色に蛍光し、BOD が低い試料では黄緑色に微生物が蛍光すると考えられる。

実験では、εサブユニット遺伝子を導入した *Saccharomyces cerevisiae* BY4741 gph(Glycogen Phosphorylase)Δ株を使用した。*S.cerevisiae* を SC 培地で 2 日間培養し、BOD 濃度が 0、10、20、50、100、500 mg/L の試料水に懸濁した時の蛍光スペクトルから FRET ratio を求めた。その結果、濃度増加に伴い FRET ratio が高くなることが分かった。また、0~100mg/L で検量線が得られ、FRET ratio から未知濃度の BOD を求めることが可能であると示唆された。

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FRET を利用した地雷を検出する微生物バイオセンサーの開発

（東京工科大･応用生物）○吉澤 太我・西村 快・仲島 紗那・秋元 卓央
Detection of landmines using FRET based Microbial biosensor
(Sch. of Biosci. and Biotechnol., Tokyo Univ. of Technol.)○Taiga Yoshizawa,Kai Nishimura, Suzuna Nakazima, Takuo Akimoto

2,4-dinitrotoluene (DNT) is a component of explosive material, and has been reported to be leaked into the soil around landmines. In this study, DNT resposive microbial biosensor was developed for detection of buried landmines. In this method, Tobacco Vein Mottling Virus (TVMV) protease was expressed in microbe using yqjF promoter which is DNT responsive gene promoter. The landmines were detected by fluorescence change of microbe based on Förster Resonance Energy Transfer (FRET). For FRET, a fusion protein consisting of GFP and RFP connected with a linker peptide containing TVMV protease recognition sequence was used. In absence of DNT, FRET based red fluoresce can be observed, while in the presence of DNT, green fluorescence can be observed.
In this experiment, TVMV protease was firstly added to GLR to examine the change of FRET ratio and, consequently, 0.124 to 0.082 decrease was evaluated. Next, TVMV was induced with a final concentration of 1 mM DNT, and the FRET ratio was measured

Keywords：2,4-dinitrotoluene, Tobacco Vein Mottling Virus protease, Fluorescence Resonance Energy Transfer

地雷の周辺の土壌には、火薬成分の 2,4-dinitrotoluene(DNT)が漏出していることが報告されている。そこで本研究では、埋設地雷の発見を目的とする DNT をターゲットとした微生物バイオセンサーの開発を行った。本方法では、DNT に応答する *yqjF* promotor を利用し Tobacco Vein Mottling Virus (TVMV) protease を発現させ、Förster Resonance Energy Transfer (FRET)の蛍光変化による地雷の検出を目標とした。FRET には､GFP と RFP を TVMV が認識する Linker で繋げた融合タンパク質(GLR)を用いた。この場合 DNT 非存在下では、FRET により GLR の RFP が蛍光する。DNT 存在下では、TVMV Linker を切断されることで FRET が起きず GFP が蛍光する。

実験では、まず GLR と TVMV を混合した場合の FRET ratio の変化を調べた。その結果、FRET ratio が 0.124 から 0.082 まで減少した。次に終濃度 1mM DNT により TVMV を誘導し FRET ratio を測定した。

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バクテリアヒドロゲルを用いた硫酸化ガラクトース間相互作用の裸眼評価

（東洋大院生命[1]・東洋大生命[2]・東洋大バイオナノ[3]）○Jiayu Dong[1]・長谷川 輝明[2,3]

Bacterial cellulose-based hydrogels carrying sulfated galactosides as naked-eye monitoring systems of carbohydrate-carbohydrate interactions ([1]*Graduate School of Life Sciences, Toyo University, Department of Life Sciences, Toyo University,* [2]*BNEL, Toyo University*) ○Jiayu Dong[1], Teruaki Hasegawa[2,3]

Some bioprocesses are triggered by carbohydrate-carbohydrate interactions (CCIs) between glycosphingolipids (GSLs) on the surface of neighboring cells. For example, the myelin sheath is a multilayered membrane in the nervous system that encircles axons and promotes the saltatory conduction of neural signals. Galactosylceramide (GalCer) and 3-sulfogalactosylceramide (sulfatide, 3SGalCer) are believed to act as essential GSLs for triggering proper myelination, and knockout mice lacking one or both exhibit abnormal myelination and the resultant molecular and physiological defects.

To assess CCIs between GalCer and 3SGalCer, we prepared bacterial cellulose (BC) based hydrogels carrying galactosides (BC-Gal) and those carrying 3-sulfogalactosides (BC-3SGal). Cation-mediated self-assembly of the BC-based hydrogels was monitored in aqueous media. The most stable assembly between BC-Gal and BC-3SGal was achieved in the presence of Ca^{2+}, indicating strong interactions between Gal and 3SGal mediated by Ca^{2+}.

Keywords : Carbohydrate-Carbohydrate Interactions, Bacterial Cellulose, Hydrogel

スフィンゴ糖脂質は細胞表面に豊富に存在し、細胞間シグナル伝達、細胞接着、宿主免疫などの生物学的認識プロセスにおいて重要な役割を担っている。例えば神経系の跳躍伝導を誘導するミエリンの形成は、スルファチド（3SGalCer）とガラクトシルセラミド（GalCer）間の強い相互作用により引き起こされており、片方または両方の欠損によって異常な髄鞘形成や様々な分子的・生理的欠陥を示すことが知られている。

我々は 3SGalCer と GalCer との間の CCIs のメカニズムを解明するため、3 位もしくは 4 位に *O*-硫酸基を導入したガラクトシルアジドを化学合成したのち、末端アルキンを導入したバクテリアセルロース（BC）から構成されるヒドロゲルとカップリングさせることで、各種硫酸化 Gal を導入したヒドロゲル（BC-3SGal および BC-4SGal）を合成した。水溶液中におけるこれらのヒドロゲルの会合挙動を裸眼観察することで、硫酸化ガラクトース間に働く糖鎖間相互作用を評価した。その結果、Ca^{2+}共存下においてガラクトースと3位硫酸化ガラクトースの間に強いCCIsが働くことが分かった。

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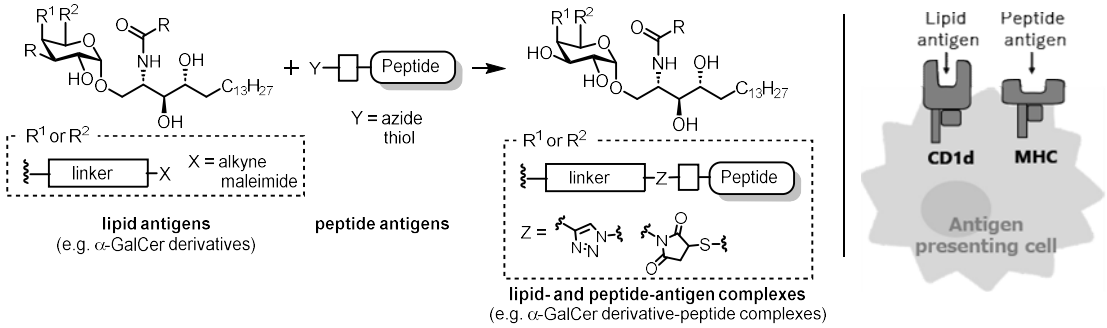
抗原提示細胞の複数因子を標的とする脂質抗原-ペプチド抗原複合体の合成研究

（慶大理工）○菊地 隼矢・松丸 尊紀・藤本 ゆかり
Synthetic studies of lipid-peptide conjugation for targeting multiple factors on antigen-presenting cells (*Graduate School of Science and Technology, Keio University*) ○Shunya Kikuchi, Takanori Matsumaru, Yukari Fujimoto

On antigen-presenting cells, MHC and related molecules recognize peptide- and lipid-antigens, and play a crucial role in the immunomodulatory system. In the case of lipid antigen presentation, CD1d presents lipid antigens to NKT cells via the TCR to induce various cytokines. In this study, we designed conjugated molecules that combine peptide antigens with lipid antigens such as α-GalCer and its derivatives[1] to target multiple MHC-related factors expressed on antigen-presenting cells. For the conjugation of the antigens, linkers containing alkynes or maleimides was applied to the glycolipids, and azide lysines or cysteines was introduced to the peptide antigens. Using these linkers for the conjugation reaction with Huisgen cyclization or Mc-thiol reaction, we achieved the synthesis of the peptide- and lipid-antigen conjugated molecules and analyzed their functions.
Keywords : Organic Synthesis; Glycolipids; Antigen Presentation; Innate Immune Receptors; Complex Molecules

抗原提示細胞上には、ペプチドや脂質等の抗原を認識する MHC や関連分子が存在し免疫調節に関わっており、MHC 分子によるペプチド抗原提示とともに、CD1 特に CD1d により脂質抗原が NKT 細胞に提示され様々なサイトカインを誘導する。本研究では、抗原提示細胞上での抗原提示機能の詳細な解明のため、代表的な脂質抗原であるα-GalCer やその誘導体 [1]とペプチド抗原を複合化した分子を設計した。糖脂質の 4 位もしくは 6 位にアルキンやマレイミドを含むリンカーを結合し、ペプチド抗原には末端にアジド化リジンもしくはシステインを導入することで、Huisgen 環化や Mc-thiol 反応により目的の抗原複合化分子の合成を達成し、その機能を解析した。



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膜融合性を有する pH 応答型マラカイトグリーンリポソーム

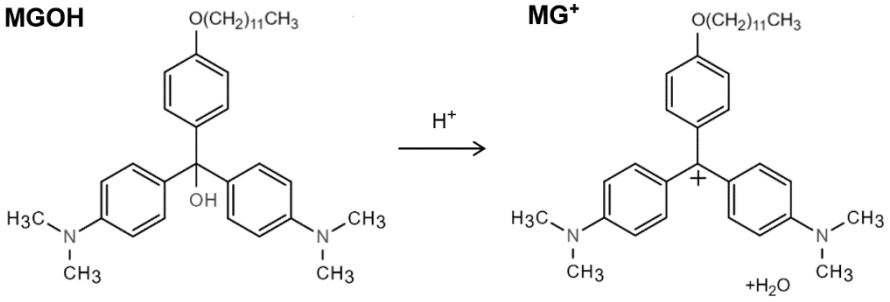
（奈良高専物質工）○二階堂 楓・宇田 亮子
Fusogenic liposomes containing pH-responsive malachite green (*Department of Chemical Engineering, National Inst. of Tech., Nara College*) ○Kaede Nikaido, Ryoko Uda

Malachite green carrying a long alkyl chain (MGOH) is ionized to become an amphiphilic molecule (MG^+) under acidic conditions (Scheme). In this work, we prepared liposomes containing neutral and lipophilic MGOH and investigated the fusogenicity of the liposomes under acidic conditions. After MGOH-containing liposomes are endocytosed, MGOH is expected to be ionized owing to endosomal acidic environment. The ionization of MGOH perturbs the membrane packing and promotes fusion with the endosomal membrane. MGOH-containing liposomes can be used as drug carriers which delivers drugs to cytoplasm by escaping from endosomes.

Membrane mixing assay revealed that MGOH-containing liposomes were fused under acidic conditions. The assay for mixing aqueous contents was carried out and the aqueous contents was mixed under the acidic conditions consistent with that for membrane mixing. The two assays also revealed that the ionization of MGOH promotes membrane fusion at the concentrations up to 2.0 mol%, above which it favors membrane solubilization over fusion.
Keywords : Fusogenic; Liposome; pH; Malachite green

長鎖アルキル基を有するマラカイトグリーン（MGOH）は酸性環境下でイオン化し両親媒性分子 MG^+となる（Scheme）。そこで本研究では、中性体で脂溶性の MGOH をリポソーム膜に含有させたものを調整し、融合性を調べることを目的とした。MGOH 含有リポソームは、エンドサイトーシス後、エンドソームの低 pH 環境下で MG^+となり、リポソーム膜を乱してエンドソーム膜との融合を誘起することが期待できる。MGOH 含有リポソームをドラッグキャリアとして用いれば、脱エンドサイトーシス経路での細胞質への効率の良い薬物送達が可能になる。

リポソームと MGOH 含有リポソームの膜融合実験の結果から、MGOH 含有リポソームは低 pH 環境下で膜融合することが明らかになった。内水相混合実験の結果から、膜融合実験と同条件下で内水相が混合することが明らかになった。また、これらの実験結果から、MGOH 濃度がリポソームの脂質の 2.0 mol%以上では、リポソームの崩壊が促進することが明らかになった。



Scheme Ionization of malachite green carrying a long alkyl chain (MGOH) induced by acidic conditions.

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pH によって蛍光色変化するタンパク質ペアの探索

（東京工科大学・応用生物）○本間柊蔵・宮崎爽輝・秋元卓央
Protein pairs whose fluorescent color changes depending on pH
(Sch. of Biosci. and Biotechol., Tokyo Univ. of Techol.) ○Shuzo Homma, Sohki Miyazaki, Takuo Akimoto

Abstract: Protein pairs whose fluorescent color can be changed by Förster Resonance Energy Transfer (FRET) have been developed to monitor intercellular pH, channels on cell membranes and to measure organophosphorus pesticides. By selecting pH-insensitive protein as a donor and pH-sensitive protein as an acceptor, FRET based fluorescence color can be changed depending on pH. A typical protein pair is CYP-YFP; however, the change of fluorescent color is not sufficient. In this study, we selected pHuji and pHoran4, red fluorescent proteins, as pH-sensitive fluorescent proteins and TagGFP and mAmetrine, green fluorescent proteins, as donor proteins to develop protein pairs that show sufficient change of fluorescence color depending on pH. The protein pairs of pHuji-TagGFP and pHuji-mAmetrine were constructed and suspended in different pH buffers. As a result, the protein pairs showed green color at lower pH due to low FRET ratio and red color at higher pH due to high FRET ratio with excitation light (430nm, 480 nm).

keyword: Förster Resonance Energy Transfer, pH, Fluorescent Protein

生体内 pH や細胞膜上チャネルのモニタリング、有機リン系農薬の測定をするために Förster Resonance Energy Transfer (FRET)により蛍光色変化するタンパク質ペアが開発されている。ドナータンパク質を pH 感受性が低く、アクセプタータンパク質を pH 感受性が高くすることで、pH によって FRET 効率の変化とともに蛍光色が変化するタンパク質ペアを作製できる。代表的なタンパク質ペアとして CYP-YFP ペアが存在するが、蛍光色が大きく変化しないという問題点がある。本研究では、アクセプタータンパク質として pH 感受性蛍光タンパク質である赤色蛍光の pHuji と pHoran4、ドナータンパク質として緑色蛍光タンパク質の TagGFP と mAmetrine に着目し、pH による蛍光変化が明瞭になるタンパク質ペアを探索することを試みた。

pHuji-TagGFP、pHuji-mAmetrine のタンパク質ペアを異なる pH バッファー(pH5～9)に懸濁し、励起光(430nm, 480nm)を照射した。その結果、タンパク質ペアは pH5 では FRET ratio は低く、蛍光色は緑色を示した。一方で、pH9 では FRET ratio は高く、蛍光色は赤色を示した。

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ゴシポールをコアとする新規糖クラスターの合成とその分子特性

（東洋大生命[1]・東洋大バイオナノ[2]）○石川 琴微[1]・長谷川 輝明[1,2]
Synthesis and molecular properties of gossypols having multiple carbohydrates ([1]*Department of Life Sciences, Toyo University,* [2]*BNEL, Toyo University*) ○Kotomi Ishikawa,[1] Teruaki Hasegawa[1,2]

Gossypol (Gos) is a yellow pigment from cottonseed and is known to have antibacterial, anticancer, and antiviral activity. However, the unstable nature in various solvents, the highly light-sensitive nature, and the poor water-solubility of Gos make its application quite difficult. To overcome these problems and apply Gos to medicinal chemistry, we have been synthesizing Gos derivatives with improved stability, water solubility, and cell-targeting properties. Through our research, we have already reported on preparing Gos derivatives carrying two carbohydrate units through the chemical modification of the formyl groups of Gos.[1)] On the other hand, in this study, the hydroxyl groups of Gos were chemically modified using chloro 3,5-di(azidomethyl)benzoate. Since the resulting Gos derivative has 12 azide groups ($GosAz_{12}$), it is possible to introduce a variety of functional groups on the Gos scaffold through click chemistry. For example, in this work, we converted $GosAz_{12}$ into a gossypol derivative with 12 lactoside appendages ($GosLac_{12}$) using propargyl lactoside. Detailed synthetic procedures and the molecular properties of $GosLac_{12}$ will be presented in the poster session.
Keywords : gossypol; dendrimer; glycocluster

ゴシポール（Gos）は綿実由来の黄色色素であり、抗菌活性や抗酸化活性のほか、抗ウイルス活性やがん細胞増殖抑制効果など、多様な生理活性を有することも知られている。しかし溶媒や光に対する不安定さやナフタレン環に起因する難水溶性のため、これらの生理活性を有効利用した実例はあまり存在しない。本研究室では化学修飾によって安定性や水溶性を向上させ、同時に細胞標的性も付与した Gos 誘導体の合成に取り組んでおり、これまでに Gos のアルデヒド基に対する化学修飾により 2 残基の糖鎖を導入した Gos 誘導体の作成とその生理活性について報告している[1)]。

一方で本研究では、Gos のヒドロキシ基に対して 3, 5-ジ(アジドメチル)安息香酸クロライドを用いた化学修飾を行った。この結果得られた Gos 誘導体は 12 個のアジド基を有するため、クリック反応にて様々な機能性基を更に多数導入可能である。例えば今回の実験ではプロパルギルラクトシドを結合させることで、12 残基のラクトース（Lac）を導入した Gos 誘導体へと変換することに成功した。得られた Lac 修飾 Gos（$GosLac_{12}$）の特性評価を行ったところ、溶媒に対する安定性および水溶性が Gos と比べて大幅に向上した。今後、レクチンに対する親和性評価や大腸菌に対する抗菌活性についても評価を行い、その結果も併せて報告する予定である。

1) Y. Amano, M. Nakamura, S. Shiraishi, N. Chigira, N. Shiozawa, M. Hagio, T. Yano, and T. Hasegawa, *Carbohydr. Res.* 458–459 (2018) 67-76. DOI: 10.1016/j.carres.2018.02.001.

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プラズモニックチップ上のホタルルシフェリン発光

（関西学院大[1]）○山中 瞳[1]・名和 靖矩[1]・田和 圭子[1]
([1]*Graduate school of science and technology, Kwansei Gakuin Univ.*) Luminescence of a Firefly luciferin on the plasmonic chip ○Hitomi Yamanaka,[1] Yasunori Nawa,[1] Keiko Tawa[1]

The bioluminescence of luciferin is excited by a chemical reaction with adenosine triphosphate (ATP) catalyzed by luciferase, and the bioluminescence from the excited state to the ground state is observed. In our laboratory, target molecules have sensitively detected using enhanced fluorescence with a plasmonic chip, which is a substrate with a wavelength-size periodic structure on its surface and coated with thin metal films. In this study, we aim to enhance bioluminescence using a plasmonic chip.

400 nm pitch-plasmonic chip with an array of concentric patterns called Bull's eyes was fabricated and coated with silver and SiO_2 films in which a film thickness was prepared as 100nm and 30nm, respectively. Just after luciferin, luciferase, and ATP were mixed, the mixed solution was dropped onto a glass substrate and a plasmonic chip, and then the luminescence image and microscopic luminescence spectra ware measured using an upright microscope. As a result, plasmon-enhanced luminescence was observed in the emission spectra on the plasmonic pattern (Fig.1).

Keywords : Luciferin ; Plasmon ; Luminescence

ルシフェリンの生物発光はアデノシン三リン酸（ATP）との化学反応がルシフェラーゼに触媒され、生成物が励起状態となり基底状態に戻る際に蛍光が発される現象である。ルシフェリン、ルシフェラーゼが過剰にあれば発光量は ATP 量に依存するため発光強度から ATP 量を定量することが可能であり、この定量法は食品の安全管理や細胞内の ATP 量の測定に利用されている。これまで当研究室ではプラズモニックチップとよばれる表面に波長サイズの周期構造を持ち、金属薄膜でコーティングされた基板を用いた増強蛍光イメージングによる高感度分子検出が研究されてきた。本研究では、プラズモニックチップを利用した生物発光増強を目指す。

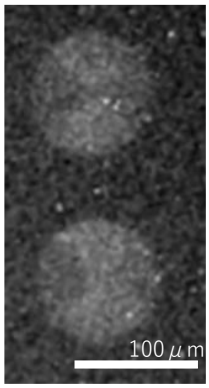

Fig.1 Plasmon-enhanced luciferin luminescence on the plasmonic pattern

ピッチ 400 nm の Bull's eye とよばれる同心円パターンがアレイ化された構造で、銀と SiO_2 がそれぞれ膜厚 100 nm、30nm に調製されたプラズモニックチップを作製した。ルシフェリン（0.41 mM）、ルシフェラーゼ（2.8 μM）、ATP（0.14 mM）で、混合後すぐにガラス基板とプラズモニックチップ上に滴下し、発光像と顕微発光スペクトルを顕微鏡で計測した。その結果、発光像においてプラズモニックチップパターン上でのプラズモン増強発光が観察された(Fig.1)。

[謝辞] 光硬化性樹脂をご提供いただいた東洋合成株式会社に感謝いたします。

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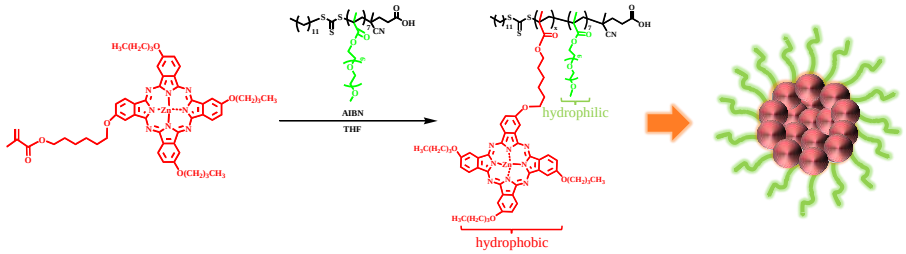
組織深部への光線力学療法を志向した光増感剤含有高分子ミセルの開発

（米子高専物質[1]・京大医[2]・国立台湾中興大理化）○八尾 颯斗[1]・Batbayar Altannavch[1]・粳間 由幸[1]・小沼 邦重[2]・井上 正宏[2]・Chung-Yu Lin[3]・Ping-Shan Lai[3]

Development of polymeric micelles containing photosensitizer for deep tissue photodynamic therapy ([1]*National Institute of Technology, (KOSEN)Yonago College*, [2]*Kyoto University*, [3]*National Chung Hsing University*)
○Hayato Yao[1], Batbayar Altannavch[1], Yoshiyuki Uruma[1], Kunishige Onuma[2], Masahiro Inoue[2], Chung-Yu Lin[3], Ping-Shan Lai[3]

Recently, one of the promising treatments for cancer, photodynamic therapy (PDT), has been attracting attention because it is noninvasive, nontoxic, and nontoxic, with little risk of damaging normal cells. PDT is a treatment method that utilizes a photochemical reaction using light and a photosensitizer. However, there is a problem with photosensitizers remaining in the body after PDT treatment, which can cause photosensitivity to sunlight. The concept of drug delivery systems (DDS) is gaining attention as a methodology to solve this problem. We investigated the utilization of polymeric micelles as nanocarriers for DDS, which have advantages such as specific accumulation in tumors and low toxicity. In this study, we synthesized a block copolymer containing a photosensitizer and evaluated its micellization by NMR and its photocytotoxicity in HeLa cells.
Keywords : Photodynamic Therapy; Photosensitizer; Drug Delivery System; Polymeric Micelle

近年，癌の有望な治療法の一つである光線力学療法(PDT)は正常な細胞を傷つけるリスクが少なく，非侵襲的で患者の負担が少ないことから期待されている．PDT は，光と光増感剤を使用し，光化学反応を利用する治療法である．しかし，PDT 治療後、体内に残った光増感剤が太陽光により光線過敏症を引き起こす問題がある．この問題を解決する方法として，ドラッグデリバリーシステム(DDS)の考え方が注目されている．DDS は体内での薬物分布を制御することで，薬物の効果を最大限に高め，副作用を最小限に抑えることを目的とした技術である．そこで私たちは，腫瘍への特異的集積，低毒性などの利点を持つ高分子ミセルを DDS のナノキャリアとして用いることを検討した．本研究では，光増感剤含有ブロック共重合体の合成を行い，NMR を用いてミセル化の評価及び HeLa 細胞を用いた光細胞毒性の評価を行った．



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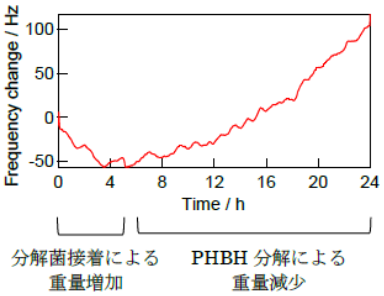
生分解性ポリマーの微生物による分解のリアルタイム QCM 計測と電気化学的解析

（東京工業大学[1]・理化学研究所[2]）○吉村 舞夏[1]、大槻 拓馬[1]、竹中 康将[2]、平石 知裕[2]、阿部 英喜[2]、朝倉 則行[1]
Microbial degradation process of biodegradable polymer directly monitored by QCM and electrochemistry ([1]*Tokyo Institute of Technology*, [2]*RIKEN*) ○ Maika Yoshimura[1], Takuma Otsuki[1], Yasumasa Takenaka[2], Tomohiro Hiraishi[2], Hideki Abe[2], Noriyuki Asakura[1]

Biodegradable polymers are decomposed by the action of microorganisms. Each biodegradable polymer is different in the properties of degradation because microbial community in the environment such as soil, ocean, river, etc. is not uniform. To clarify the properties provides important insight into development of biodegradable polymers that are suitable for utilizing in various environment. The biodegradation in the environment proceed through a few steps; that is adhesion of bacteria to the polymer, polymer degradation by extracellular enzymes of the bacteria, and then additional adhesion and degradation in the same time. In this study, real-time measurement of mass change in the biodegradation process was investigated. The biodegradable polymer PHBH (copolymer of hydroxybutanoic acid and hydroxyhexanoic acid) film was formed on the gold surface of quartz crystal and put the quartz crystal in mineral medium. PHBH degrading bacteria was injected into the medium, and mass change was monitored by QCM (Quartz Crystal Microbalance) method. Mass increase due to bacteria adhesion and mass decrease by PHBH degradation were observed. In order to analyze degree of degradation and to investigate PHBH film condition, cyclic voltammetry and electrochemical impedance spectroscopy were carried out.
Keywords : Biodegradable Polymer, Quartz Crystal Microbalance, Electrochemistry

生分解性ポリマーは自然環境中の微生物によって分解される。土壌や海など環境ごとに存在する微生物群は異なるので、ポリマーごとに分解される環境は異なる。そこで、微生物による分解過程を明らかにし、それをもとに様々な環境で分解されるポリマーを設計することが期待されている。環境中では分解菌がポリマー表面に接着し、その後分解菌が分泌した酵素によりポリマーの分解が開始する。本研究ではポリマーの重量変化を計測することによりこれらの過程をリアルタイムで観察した。生分解性ポリマーPHBH（ヒドロキシブタン酸とヒドロキシヘキサン酸の共重合体）の膜を水晶振動子金表面に作製し、培地中に静置した。その後分解菌を添加して QCM（水晶振動子マイクロバランス）法で重量変化を測定した。その結果、分解菌の接着による重量増加と PHBH の分解による重量減少が見られた。また、QCM と同時測定が可能なサイクリックボルタンメトリーを用いて分解の進行を調べた。さらに、電気化学インピーダンス法を用いて膜の分解の詳細な解析を行った。



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植物による有用物質生産技術に関するエンジニアリング観点の基礎検討及び特性理解

（千代田化工建設株式会社[1]）松嶋　全人[1]・○平林　翼[1]・三枝　瑞季[1]・村松　弘樹[1]吉田 翔[1]・西田 尚子[1]
Fundamental investigation and understanding of characteristics from engineering aspects relating to the production of valuable material through plants ([1]*Bio & Pharm Technology Development Section, Technology Development Department, Frontier Business Division, Chiyoda Corporation*) Akito Matsushima[1], ○Tsubasa Hirabayashi[1], Mizuki Saegusa[1], Hiroki Muramatsu[1], Sho Yoshida[1], Naoko Nishida[1]

With the ongoing advancements in research and development for the production of valuable compounds from plants, there is still a lack of practical demonstration of such production. The implementation of engineering technologies aimed at commercialization is needed, yet there are few reports that systematically organize the production techniques for valuable compounds from plants, taking into consideration an engineering perspective. Especially in plant cultivation, which is a crucial step in production, it remains a personalized process and poses a hurdle for industrialization.

The process of compound production through plants can be divided into two processes: the upstream process, which involves cultivation and recombination, mainly relying on biotechnological approaches such as plants and microorganisms, and the downstream process, which involves extraction and purification and relies on chemical and industrial processes. The scientific fields to be considered for evaluation are diverse.

Through extensive study in our lab, we have identified and attempted to understand the challenges in plant production techniques. In this presentation, we aim to discuss the challenges and characteristics of compound production through plants, with the hope of contributing to the future development of plant-based compound production.
Keywords : hydroponic culture, recombinant, plant made pharmaceuticals, secondary metabolism, purification

植物の有用物質生産に関する研究開発が進む中、その生産実証は未だ少ない。商用化を目指したエンジニアリング技術の社会実装が求められる中、植物の有用物質の生産技術を整理した報告は少なく、エンジニアリング観点を持った一連の生産技術を俯瞰し議論した場は存在しなかった。特に、植物栽培は生産に重要な工程であるが、属人的な工程であり、工業化へのハードルとなる。

植物による物質生産工程は、栽培や遺伝子組換えから成る上流工程と、抽出・精製を成す下流工程に二分できるが、上流は植物や微生物等のバイオが主となる技術構成で、下流は化学・工業を主とした技術構成となり、検討する科学分野が多岐に渡る。

我々はラボでの検討を重ね、植物の生産技術の課題を抽出し、理解を試みた。本発表では、植物による物質生産の課題及びその特性を議論する事により、植物の物質生産の発展と今後に寄与することを期待する。

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Academic Program [Poster] | 20. Materials Chemistry -Basic and Application-：Poster

Tue. Mar 19, 2024 10:00 AM - 11:30 AM JST | Tue. Mar 19, 2024 1:00 AM - 2:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-2am] 20. Materials Chemistry -Basic and Application-

Japanese

[P1-2am-01]

Heterogeneous photoreaction in photomechanical crystals: evaluation of a cooperative effect by simultaneous tracking of reaction progress and crystal shape

○Shin Ozamoto[1], Hikaru Sotome[1], Daichi Kitagawa[2], Seiya Kobatake[2], Hiroshi Miyasaka[1] (1. Graduate School of Engineering Science, Osaka University, 2. Grad. Sch. of Eng., Osaka Metropolitan Univ.)

English

[P1-2am-02]

Luminescent Properties of Room-Temperature Liquid-Crystalline Trinuclear Gold(I) Complex

○Abhilash Sahu[1], Tamon Nakao[1], Kohsuke Matsumoto[1], Ganesan Prabusankar[2], Osamu Tsutsumi[1] (1. Ritsumeikan University , 2. Indian Institute of Technology Hyderabad)

Japanese

[P1-2am-03]

Synthesis of a methacryl monomer having a 2-aminopyridyl group and its application to photo-adhesive materials

○Hinata Okada[1], Masahiro Furutani[1] (1. Natioal Institute of Technology, Fukui College)

Japanese

[P1-2am-04]

Chemical analysis of solid components separated from mucilage of roots of Tororo-aoi

Makoto Kono[1], ○Masahiro Furutani[1], Chika Shimada[1] (1. Natioal Institute of Technology, Fukui College)

Japanese

[P1-2am-05]

Synthesis of a methacryl monomer having a hydroxypyridyl group and its application to photo-adhesive materials

○Miku Matsui[1], Masahiro Furutani[1] (1. Natioal Institute of Technology, Fukui College)

Japanese

[P1-2am-06]

Development of dissimilar bonding technology using sheet material.

○Yuya Nakazawa[1], Kenji Harada[1], Masaki Ozaki[1], Atsushi Fumikura[1] (1. Sumitomo Osaka Cement Co.,Ltd.)

Japanese

[P1-2am-07]

Preparation and Characterization of Transparent Alicyclic Polyimide Aerogel

○Masaki Negoro[1], Kazuyoshi Kanamori[1] (1. Kyoto University)

Japanese

[P1-2am-08]

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Degradation factors due to environmental conditions of giant surface potential of vacuum-deposited diarylethene films

○Tsuyoshi Tsujioka[1], Junwei Shen[2], Shinichiro Nakamura[2] (1. Osaka Kyoiku University, 2. Kumamoto University)

Japanese

[P1-2am-09]

Development of Molecular Crystals of Platinum Complexes Equipped with Substituted Heteroaromatic Groups

○Rintaro Ishikawa[1], Tomohiro Seki[1] (1. Department of Chemistry, Faculty of Science, Shizuoka University)

Japanese

[P1-2am-10]

Synthesis and Aggregation-Induced Emission Properties of Dibenzoylmethanato Boron Difluoride Complexes with an Alkyl Group at the α-position

○Kazunori Ichihara[1], Haruto Koide[1], Naoto Miyasaka[1], Keita Makabe[1], Kotaro Moriya[1], Kazumitsu Minemura[1], yushi Fujimoto[3], Fuyuki Ito[2,3] (1. Suwaseiryo High school, 2. Inst. of Edu., Shinshu Univ, 3. Grad. Sch. of Sci. and Tech., Shinshu Univ)

Japanese

[P1-2am-11]

Development of Stimuli-Responsive Molecular Crystals of Benzoselenophene Platinum Complex

○Akihito Yano[1], Tomohiro Seki[1] (1. Department of Chemistry, Faculty of Science, Shizuoka University)

Japanese

[P1-2am-12]

Fabrication of Thermoelectric Films Containing π-Conjugated Nickel Complexes with Vinylthiophene Units

○Iku Miyatake[1], Tomoya Yaoita[1], Devon Aditya Jobs[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese

[P1-2am-13]

Synthesis and Properties of Novel D–π–A Type Molecules Bearing Bridged Bithiophene π-Spacers

○Miyu Ueda[1], Ryo Nagayama[2], Naoya Suzuki[1,2], Shintaro Kodama[1,2], Takeshi Maeda[1,2], Shigeyuki Yagi[1,2] (1. Graduate School of Engineering, Osaka Metropolitan University, 2. College of Engineering, Osaka Prefecture University)

Japanese

[P1-2am-14]

Evaluation of film materials using TEMPO oxidized CNF

○Yusaku Koitabashi[1], Yuji Kimura[1] (1. Nihon University)

Japanese

[P1-2am-15]

Synthesis and Photo-degradation behavior of polyphthalaldehydes with oxime ether terminals

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○Hirokazu Hayashi[1], Hideki Tachi[1], Kanji Suyama[2] (1. Osaka Research Institute of industrial Science and technology, 2. Osaka Metropolitan University)

Japanese

[P1-2am-16]

Gas separation property of MOF801-PDMS composite membranes fabricated by in situ synthesis of MOF in gel under various condition.

○Takara Nishikawa[1], Takuya Kurihara[1], Yasuhiro Shigeta[1], Shogo Amemori[1], Tomonori Ida[1], Motohiro Mizuno[1] (1. Kanazawa Universuty)

Japanese

[P1-2am-17]

Imaging X-ray photoelectron analysis of polyelectrolyte multilayers deposited on polyethylene terephthalate filaments

○Ginga Watanabe[1], Aoi Yoshimitsu[1], Shota Yasuda[1], Toyoaki Hirata[1], Kenji Hisada[1] (1. University of Fukui)

Japanese

[P1-2am-18]

Synthesis and characterization of PAMAM dendrimer/water-soluble polymer membranes for CO_2 separation

○Keisuke Serizawa[1], Yuji Kimura[1] (1. Nihon University)

Japanese

[P1-2am-19]

Accelerated aging test of polypropylene material used in ankle-foot orthosis

○Yoshihiro Mihara[1], Shin Murahara[1], Toshiaki Horiuchi[1] (1. Hokkaido Univ. of Science)

Japanese

[P1-2am-20]

Preparation and properties evaluation of solid acid catalyst on cedar

○Yui Igaki[1], Takumi Akinaga[1], Ryuki Ikeda[1], Yuko Shikami[2], Toshiyuki Miyauchi[2] (1. Gradute of Chubu University, 2. Chubu University)

Japanese

[P1-2am-21]

Evaluation of Optical Properties in Water Soluble Lanthanide Complex Nanoparticles

○Shunsuke Kobashi[1], Yoshinori Okayasu[1], Yuki Nagai[1], Yoichi Kobayshi[1] (1. Ritsumeikan University)

Japanese

[P1-2am-22]

Investigation of chromism and molecular orientation of aromatic amine intercalated between layers of tetrasilicicfluormica

○Reira Kinoshita[1], Shin'ichi Ishimaru[1] (1. Tokyo Denki University)

Japanese

[P1-2am-23]

Fabrication of Yellow Luminescent Dy Hydroxide Nanoparticle-Based Composite Films

○Hidetoshi Miyazaki[1], Wataru Kato[1] (1. Shimane University)

Japanese

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[P1-2am-24]

Development of slow-release material of corrosion inhibitor for plating film by the intercalation into layered double hydroxide

○Junna Taki[1], Daiyu Kodama[2], Yoshiumi Kohno[3] (1. Graduate School of Engineering, Shizuoka University , 2. Kamiya Riken Co., 3. School of Engineering, Shizuoka University)

Japanese

[P1-2am-25]

Chlorophyll/organo-modified clay composites as a stable green colorant

○Asuka Ueda[1], Yoshiumi Kohno[2], Masashi Shibata[3], Ryo Watanabe[2], Choji Fukuhara[2] (1. Graduate School of Engineering, Shizuoka University , 2. School of Engineering, Shizuoka University, 3. School of Biotechnology, Tokyo University of Technology)

Japanese

[P1-2am-26]

Introduction of carboxyl group to single-molecule magnets and construction of thin film using air-liquid interface

○Miki Yamada[1], Akane Mizoguchi, Yoji Horii, Takashi Kajiwara (1. Nara Women's University)

Japanese

[P1-2am-27]

Preparation of Au nanocubes supported on magnetic Fe_3O_4 and its catalytic performance of alcohol oxidation reaction

○Mutsumi Nagafune[1], Riko Kawahara[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P1-2am-28]

Preparation of hemispherical gold nanoflowers supported on cerium oxide for alcohol oxidation reaction

○Yuta Jino[1], Asuka Kasuga[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P1-2am-29]

Improved Electrochromic Properties and Addition of Layered Inorganic-imidazoline Covalently Bonded Hybrid for Ru(II)-based Metallo-supramolecular Polymer

○Kazuko Fujii[1], Dines Chandra Santra[1], Manas Kumar Bera[1], Kazuhiko Sakata[1], Takatsugu Wakahara[1], Ritsuko Nagahata[2], Masayoshi Higuchi[1] (1. National Institute for Materials Science, 2. National Institute for Advanced Industrial Science and Technology)

Japanese

[P1-2am-30]

Intercalation of gemini quaternary ammonium into zirconium phosphate

○Hiroaki Katsuzaki[1], Takeru Kasuga[1], Takayuki Tsukegi[1], Osamu Yoshimura[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-2am-31]

Preparation of concave gold nanorods supported alumina for alcohol oxidation reaction

○Kousuke Kinoshita[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P1-2am-32]

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Formation of Metal Oxide Multilayer for Optic Materials by Electrochemical Depositions

○Mitsuru Watanabe[1], Yuro Saegusa[2], Naoaki Ito[2], Hiroyuki Enomoto[2,3], Seiji Watase[1] (1. Osaka Research Institute of Industrial Science and Technology, 2. Osaka Electro-Commun. Univ., 3. Grad. Sch. of Eng., Osaka Electro-Commun. Univ.)

Japanese

[P1-2am-33]

Study of evaluation method for the mechano-bactericidal effect in water

○Satoshi Toba[1,2], Ryo Yamano[1,2], Yukari Miyazaki[2], Nobuaki Negishi[2], Naoko Kurosaki[1] (1. Chiba Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-2am-34]

Dynamic deformation of three-dimensionally microfabricated temperature-responsive hydrogels

○Shunsuke Nagahama[1,2] (1. Kyoto University of Advanced Science, 2. Waseda University)

Japanese

[P1-2am-35]

Separation and analysis of volatile sulfur compounds using disulfide compounds

○Shuta Miura[1], Yasuko Yamada Maruo[1] (1. Grad. Sch. Eng, Tohoku. Inst. Tech.)

Japanese

[P1-2am-36]

Effect of substrates on an acetone detection using porous material-substrate sensors

○Kaito Murayama[1], Yasuko Yamada Maruo[1], Sei Sakano[2] (1. Grad.Sch.Eng Tohoku Inst Tech, 2. Tohoku Inst Tech)

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光メカニカル結晶の不均一光反応：反応率と結晶形状の同時追跡による協同効果の評価

（阪大院基礎工[1]・阪公大院工[2]）○尾座本 晋[1]・五月女 光[1]・北川大地[2]・小畠誠也[2]・宮坂 博[1]

Heterogeneous Photoreaction in Photomechanical Crystals : Evaluation of a Cooperative Effect by Simultaneous Tracking of Reaction Progress and Crystal Shape ([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Engineering, Osaka Metropolitan University*) ○Shin Ozamoto,[1] Hikaru Sotome,[1] Daichi Kitagawa,[2] Seiya Kobatake,[2] Hiroshi Miyasaka[1]

We have investigated a heterogeneous photoreaction in a photomechanical crystal using low-frequency Raman microscopy, aiming to elucidate correlation between the photoreaction at the molecular level and macroscopic change of crystalline shape. Raman mapping measurements under photoirradiation revealed that the photoreaction took place heterogeneously from the edge to the center of the crystal. Furthermore, simultaneous measurements of Raman spectra and transmission images showed that the crystal shape changes nonlinearly in proportion with the reaction progress at the molecular level. These results will be discussed in detail from the viewpoints of hierarchy of responses.

Keywords : Photomechanical Crystals, Low-Frequency Raman Microscopy, Reaction Kinetics, Cooperative Effect, Organic Crystals

光照射により変形する光応答性結晶は、電気回路などを必要とせず光照射のみで力学的な仕事を可能とするアクチュエータやソフトロボットとして有望な先端材料である。これらの結晶中の光反応は溶液中とは異なり、隣接する分子との相互作用により不均一に進行することが多く、協同効果に代表されるように特異的な反応挙動を示す場合も多い[1]。本研究では、光メカニカル挙動を示すジスチリルピラジン結晶を対象に、分子レベルの光反応と結晶形状との相関解明を目的として、顕微低波数ラマン分光を用いてその不均一光反応を調べた。光照射下でラマンマッピングを行うことにより、光反応が結晶の端から中央に向かって伝播する様子を確認した。さらに、併せて透過像を同時追跡することで、結晶形状が分子レベルの反応の進行に対して非線形に変化し協同的な光反応が進行していることが分かった。

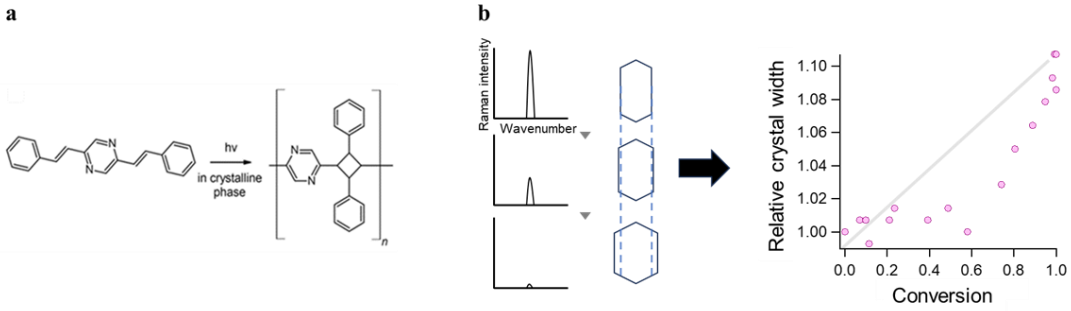

Figure 1. (a) Photopolymerization reaction of 2,5-distyrylpyrazine in the crystalline phase. (b) Correlation between relative crystal width and conversion

[1] K. Morimoto et al., *Angew. Chem. Int. Ed.* **2022**, *61*, e202212290.

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Luminescent properties of Room-Temperature Liquid-Crystalline Trinuclear Gold(I) Complexes

([1]*Department of Applied Chemistry, Ritsumeikan University*, [2]*Departmrnt of Chemistry, Indian Institute of Technology Hyderabad*) ○Abhilash Sahu,[1] Tamon Nakao,[1] Kohsuke Matsumoto,[1] Ganesan Prabusankar,[2] Osamu Tsutsumi[1]

Keywords: liquid-crystal, aggregation-induced emission, gold complexes

Aggregation-Induced Emission (AIE), characterized by photoluminescence only within aggregates, holds significant promise for applications in display devices and bioimaging. Given that luminescent properties are intricately tied to the aggregated structure, effective control of these aggregates is crucial to unleash their full potential in various applications. Utilizing liquid-crystalline trinuclear gold(I) complexes developed in our group, we have successfully altered their aggregated structure and photoluminescence behavior through a phase transition.[1)] In the present study, we meticulously explored the liquid-crystalline behavior and photophysical properties of trinuclear gold(I) complexes bearing branched alkyl chains via an ester linkage (Fig. 1).

Remarkably, the incorporation of branched chains led to a substantial reduction in the melting point, with the complex exhibiting an impressively low melting temperature of –15 °C. Consequently, this complex demonstrated a discotic nematic phase ranging from –15 °C to its thermal decomposition temperature of 285 °C, surpassing the temperature range reported in previous studies and extending into room temperature. In the discotic nematic phase at room temperature, the complex showed vibrant red phosphorescence at 730 nm, boasting an impressive quantum yield of 37%. The disappearance of phosphorescence in dilute solutions indicated the complex is AIE active, attributed to aurophilic interactions, similar to previously reported complexes.

Furthermore, the manipulation of molecular alignment in the discotic nematic phase through shearing stress enabled the complex to exhibit polarized luminescence. These findings contribute valuable insights into the design of room-temperature liquid-crystalline materials with enhanced luminescent features, showcasing their potential for diverse applications.

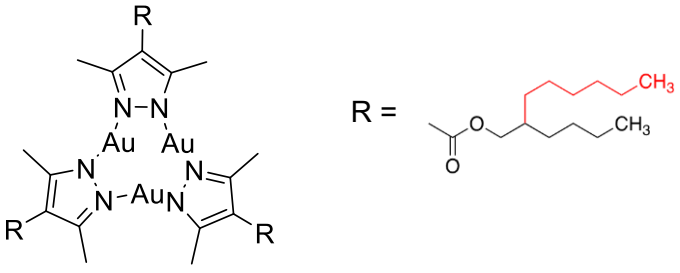

Figure 1. The molecular structure of Au complexes used in this study.

1) Kuroda, Y. *et al*., *Commun Chem.* **2020**, *3*, 139.

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日本化学会 第104春季年会 (2024)

2-アミノピリジル基を有するメタクリルモノマーの合成および光接着材料への応用

（福井高専）○岡田 ひなた・古谷 昌大

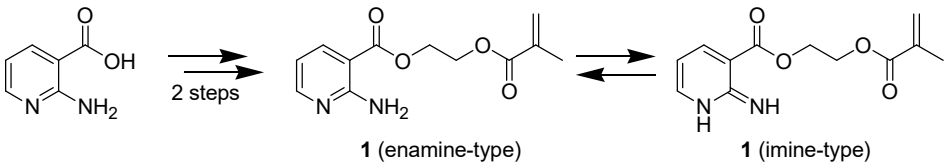
Synthesis of a Methacryl Monomer Having a 2-Aminopyridyl Group and Its Application to Photo-adhesive Materials

(*National Institute of Technology, Fukui College*)
○Hinata Okada, Masahiro Furutani

Adhesion of dissimilar materials has been required for manufacturing processes of industrial products. In addition, photo-adhesion is one of useful manufacturing technologies because it realizes local adhesion in a short time without heating. On the other hand, it is known that keto-enol tautomerization reaction of 2-substituted pyridine changes polarity of the molecule. In this work, we designed and synthesized a photo-adhesive monomer **1** having a 2-aminopyridyl group that undergoes inime-enamine tautomerization reactions. Monomer **1** was used for a methacryl photo-adhesive material of dissimilar substrates. Monomer **1** was synthesized as a white solid in a 2.4% yield. UV-Vis spectral measurement revealed that monomer **1** was mainly tautomerized into imine-type structure. Monomer **1** was then mixed with 2-hydroxyethyl methacrylate (HEMA), and a photo-radical initiator, which was used as a photo-adhesive material. In a glass-glass photo-adhesive sample, 11.4 MPa of shear stress was recorded. Photo-adhesion between glass and polypropylene was also observed.

Keywords : 2-Aminopyridyl Group; Methacryl Monomer; Photo-adhesive Material; Tautomerization; Radical UV Curing

今日の工業製品の製造過程において、異種材料どうしの接着は大きなニーズの一つである。また、加熱を伴わない光接着は、短時間で局所的な接着が可能であることから、その有用性が認められている。一方、2 位置換ピリジンのケト・エノール互変異性化反応では、分子の極性を変化させることが知られている。そこで本研究では、イミン･エナミン互変異性化反応を起こす 2-アミノピリジル基を光接着モノマーに導入することを試みた。そして、同モノマー**1** を異種材料用メタクリラート光接着材料に組込んだ。モノマー**1** の収率は 2.4%であり、白色固体として得られた。UV-Vis スペクトル測定より、**1** は主にイミン型で存在することがわかった。次に、**1** と 2-ヒドロキシエチルメタクリラート（HEMA）および光ラジカル開始剤を混合して溶液を調製し、光接着材料とした。ガラスーガラス光接着試料において接着強度は 11.4 MPa となった。また、ガラスーポリプロピレンの光接着を確認した。



Monomer for photo-adhesion of dissimilar materials

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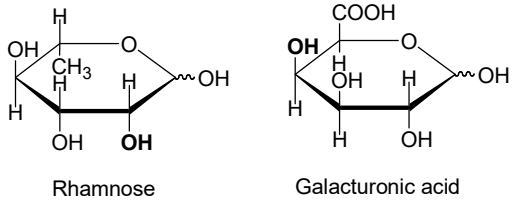
トロロアオイ根粘液から分離した固形分の化学分析

（福井高専）河野 真琴・○古谷 昌大・嶋田 千香
Chemical Analysis of Solid Components Separated from Mucilage of Roots of Tororo-aoi
(*National Institute of Technology, Fukui College*)
Makoto Kono, ○Masahiro Furutani, Chika Shimada

Mucilage extracted from roots of Tororo-aoi (*Abelmoschus manihot*), called as “Neri”, is used for producing Japanese traditional handmade papers. Main components of polysccharides of the mucilage are rhamnose and galacturonic acid.[1)] It is known that the viscosity becomes low dramatically under preservation even in refrigerator in a few days. In this report, chemical substances of cooling mucilage samples were subjected to chemical analyses such as gel permeation chromatography (GPC) measurements and continuous ^{1}H-NMR spectral measurements. Solid components were obtained in yields of 3-5 mg per 1 g of mucilage, from each sample by freeze-drying. The analytical results were compared between individuals being subjected to different cultivation methods which watering was enough (**MW**) or not (**LW**).
Keywords : Tororo-aoi (Abelmoschus manihot); Chemical Analysis; Japanese Traditional Handmade Paper; Mucilage; Cultivation Method

トロロアオイ根粘液は「ねり」と呼ばれ、和紙の原料の一つとして使用される。その主成分は糖鎖であり、成分糖としては下図に示すラムノースやガラクチュロン酸が知られる[1)]。通常、根粘液は冷蔵保存されるが、数日間でその粘性が著しく低下する。本研究では、粘性低下の化学的な原因の有無を調査するため、GPC や ^{1}H-NMR といった測定機器を用いて、冷蔵保存されている粘液試料中の化学物質について分析を試みた。試料としては、栽培時に水を多めに与えたトロロアオイ（**MW** 群）と、潅水を極力与えなかったトロロアオイ（**LW** 群）より、それぞれ根粘液を用意した（n = 3）。

各粘液試料を凍結乾燥することによって、粘液 1 g あたり 3〜5 mg の分析用固形分を得た。これを DMF に溶解し GPC 測定を行ったところ、分子量約 50 万の高分子量成分が検出された。**LW** 群では、分子量約 20 万の成分も併せて検出された。一方、重水を用いた ^{1}H-NMR 測定ではポリラムノガラクチュロン酸由来ピークが見られたが、**LW** 群では低分子量成分由来と考えられるピークも高磁場側に検出された。各ピーク強度は、基準ピーク強度に対して時間経過とともに減少した。



1) Y. H. Han, M. Yanagisawa, T. Enomae, A. Isogai, T. Ishii, *JAPAN TAPPI JOURNAL* **2005**, *59*, 1067.

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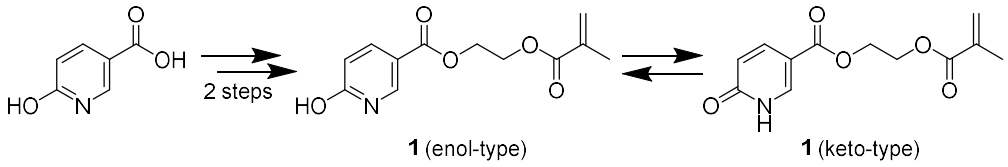
ヒドロキシピリジル基を有するメタクリルモノマーの合成および光接着材料への応用

（福井高専）○松井 実玖・古谷 昌大
Synthesis of a Methacryl Monomer Having a Hydroxypyridyl Group and Its Application to Photo-adhesive Materials (National Institute of Technology, Fukui College)
○Miku Matsui, Masahiro Furutani

Various kinds of adhesives have been developed for adhesion between dissimilar materials, which the adhesives often mimic adhesive proteins secreted by mussels for adhesion to moist surfaces. It is well-known that such proteins contain catechol groups. In this work, hydroxypyridyl groups that were chemically similar to catechol group were introduced into adhesive methacryl monomers. We adopted 6-hydroxypyridyl group to exclude the possibility of intramolecular hydrogen bonding. By utilizing the keto-enol tautomerization reactions involving polarity change, photo-adhesive materials were designed. A novel adhesive monomer **1** was synthesized using 6-hydroxynicotinic acid and 2-hydroxyethyl methacrylate (HEMA) as starting compounds in a 10% yield. A photo-adhesive material was consisted of **1**, HEMA, a photo-radical initiator, and at least amount of THF. Polypropylene, copper (untreated or treated with *conc.* HNO_3), stainless steel, aluminum, zirconia, and glass substrates were used to photo-adhesion toward glass substrates, resulting in *ca.* 3-7 MPa of adhesive strength.
Keywords : Hydroxypyridyl Group; Methacryl Monomer; Photo-adhesive Material; Dissimilar Material; Keto-enol Tautomerization Reaction

ムラサキイガイが湿った表面に固着する際に分泌する接着タンパク質を模倣して、様々な万能型の接着材料が合成されている。本研究では、接着タンパク質に多く含まれるカテコール構造に類似したヒドロキシピリジル基を有するメタクリルモノマーを設計、合成した。分子内水素結合の可能性を排除するため、6-ヒドロキシピリジル基を用いた。一方、極性変化を伴うケト - エノール互変異性化反応を利用するかたちで、万能型光接着材料を作製した。主原料として 6-ヒドロキシニコチン酸と 2-ヒドロキシエチルメタクリラート（HEMA）を用いて、新規接着モノマー**1** を収率 10%で合成した。接着モノマー**1** と HEMA、光ラジカル開始剤、必要最少量の THF を用いて光接着材料を調製した。被着体としてポリプロピレン、銅（未処理および濃硝酸処理）、ステンレス、アルミニウム、ジルコニア、およびガラスの各基板を用意し、それぞれガラスとの異種材光接着を試みたところ、約 3〜7 MPa の接着強度を得た。



Monomer for photo-adhesion of dissimilar materials

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シート材を用いた異種接合技術の開発

（住友大阪セメント株式会社）○中澤 悠哉・文倉 篤志・原田 健司・尾崎 雅樹
Development of dissimilar bonding technology using sheet material (Sumitomo Osaka Cement Co., Ltd.) ○Yuya Nakazawa, Atsushi Fumikura, Kenji Harada, Masaki Ozaki

Abstract: Sheet adhesives not only provides uniform layer thickness, but also reduces thermal stress between materials. However, the sheet adhesive has a problem in that if there is a recess on the adhesive surface, the adhesive layer is curved and a gap is generated between the adhesive layer and the material. In this work, we developed a method to form an adhesive layer with no gaps and a uniform thickness in the recesses on the surface of a substrate by using a combination of sheet adhesive and liquid adhesive.
Keywords: Dissimilar bonding; Sheet adhesive; Heat curing

［緒言］

異種材料の接合において、面内の接合強度や熱的特性のばらつき低減の観点から接合層厚みの均一化は重要である。接合技術として高分子材料からなるシート接着剤による接着は、層厚みが均一となることに加え、異種材料間の熱応力を緩和できるため有望である。しかし、シート接着剤では、接着面に局所的な凹部がある場合には、接着層が湾曲し、基材との間に隙間が発生する問題があった。本研究では、接着面に局所的な凹部がある基材に対して、シート接着剤と液状接着剤を併用することにより、凹部の部分に隙間がなく、層厚みが均一な接着層ができる手法を開発した。

［実験・結果］

評価サンプルは以下の手順で作製した；ⅰ)接着面がアルミ基材から凹んだセラミックス部を有する複合基材を準備、ⅱ)アルミ基材の平滑部上に凹部部分を取り除いたエポキシシート接着剤を仮貼り、ⅲ)凹んだセラミックス部上にシリコーン液状接着剤を適量塗布、ⅳ)別のセラミックス基材を両接着剤の上に載せ、130℃、0.5MPa にて加熱・加圧し接合。評価方法として、接着層の断面観察および層厚みを測定することにより、凹部においても平滑部と同様に接着層厚みが均一であることが確認された。

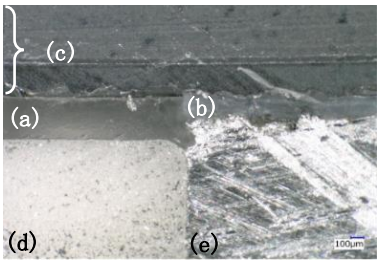

Fig.1 Cross-sectional SEM image of bonded body of dissimilar materials.
Adhesive layer of (a) Liquid, (b) Sheet, (c) Integrated ceramic plate,
(d) Ceramic material“recessed area”, (e) Aluminum plate“smooth area”

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透明な脂環式ポリイミドエアロゲルの作製と評価

（京大院理 [1]）○根来 大基 [1]・金森 主祥 [1]

Preparation and Characterization of Transparent Alicyclic Polyimide Aerogels ([1]*Graduate School of Science, Kyoto University*,) ○Masaki Negoro,[1] Kazuyoshi Kanamori[1]

Aerogels are highly porous solids synthesized in liquid-phase systems and subsequent supercritical drying. Although aerogels are a good candidate for thermal insulation window due to their visible-light transparency and low thermal conductivity, their low mechanical strength limits the application. Various chemical compositions have been explored to improve their mechanical resistance; especially, polyimide aerogels have been widely studied because of their high mechanical strength. However, suppressing their yellowish color and opacity is still challenging. In this study, polyimide aerogels with suppressed color and opacity were prepared by using an alicyclic monomer.

Keywords : Aerogels; Porous Materials; Polyimides; Thermal Insulator

湿潤ゲルを超臨界乾燥することにより得られるエアロゲルは、低密度の多孔体であり、優れた断熱性および透明性を示すことから透明断熱材としての応用が期待されている。しかし、機械的強度が低く壊れやすいため、実用化は困難である。

ポリイミド系のエアロゲルは良好な機械的強度を示すため、透明断熱材への応用が期待できる。しかし、一般的な芳香族ポリイミドはその難溶性ゆえに、ゲル化する際に巨視的な相分離を起こし、粗大化した細孔構造を形成するため、エアロゲルの透光性は非常に低い。一方で、脂環式構造を有するポリイミドは溶媒に対し高い溶解性を示すため、巨視的な相分離の抑制とエアロゲルの透光性向上に有効であると考えられる [1)]。本研究では、脂環式ポリイミドからなるエアロゲルの作製方法を探索し、細孔構造の粗大化を抑制することにより、高い透光性を示すエアロゲルの作製法を明らかにした。

作製したポリイミドエアロゲルは、9 mm 厚で文字を視認できる程度の透光性を示し、SEM 像より微細な細孔構造を有していることが確認できた（**Figure 1**）。以上より、脂環式構造の導入がポリイミドエアロゲルの細孔構造の微細化および透光性の向上に有効であることがわかった。

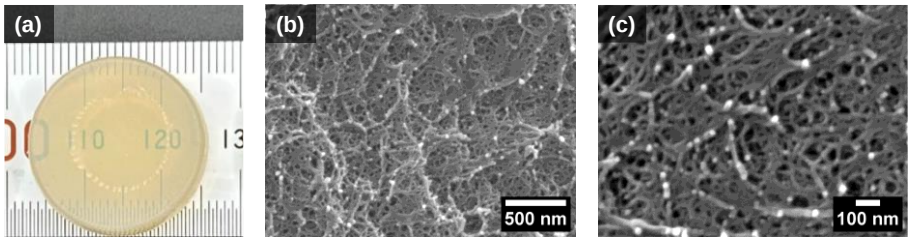

Figure 1. (a) Appearance and (b,c) SEM images of the prepared polyimide aerogel.

1) Properties of Alicyclic Polyimides with Bis-spironorbornane Structure Prepared in Various Solvents. T. Matsumoto, H. Ozawa, E. Ishiguro, S. Komatsu, *J. Photopolym. Sci. Technol.* **2016**, *29*, 237.

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Degradation factors due to environmental conditions of giant surface potential of vacuum-deposited diarylethene films

([1]*Osaka Kyoiku University*, [2]*Kumanoto University*) ○Tsuyoshi Tsujioka,[1] Junwei-W Shen,[2] Shinichiro Nakamura[2]

Keywords: Diarylethene; Giant surface potential; Vacuum deposition

In vacuum-deposited organic films, it is known that molecules spontaneously orient themselves, resulting in the generation of Giant Surface Potential (GSP).[1,2)] In certain diarylethene vacuum-deposited films, the largest levels of negative GSP have been observed, but their magnitude decreases due to various environmental factors.[3)] The primary factors include high temperature, light, and humidity.

Above the glass transition temperature, molecular orientation becomes disrupted, leading to the disappearance of GSP. As shown in Fig. 1, the negative GSP (-155 V) of a 1μm-thick DE-2A film obtained by evaporation disappeared after only a few seconds of UV irradiation (λ=365 nm, 330 μW/cm^2). Since the negative GSP did not recover even with visible light irradiation, photoisomerization reactions are ruled out as the cause. Due to the thick film (~ 1 μm), UV penetration is limited to the surface, where light is completely absorbed. Therefore, the disappearance of GSP is attributed to the diffusion of carriers generated by surface light absorption. Photo-generated positive carriers are trapped on the negative GSP, while negative carriers flow out externally. Using a similar line of reasoning, the surface conductivity increases in a high-humidity environment and results in a decrease in GSP due to carrier influx from the external environment to the surface.

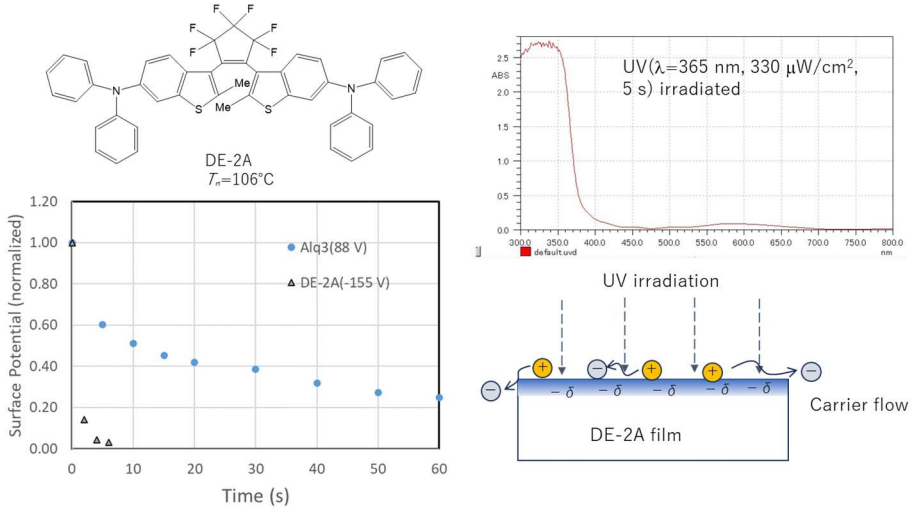

Fig. 1 GSP degradation of DE-2A upon UV irradiation

1) Y. Tanaka, et al., Sci. Rep., 10. 6648 (2020).
2) M. Tanaka, et al., Nat. Mater., 21. 819 (2022).
3) T. Tsujioka, et al., 10th International Symposium on Photochromism ISOP 2023 (Nara), CL25.

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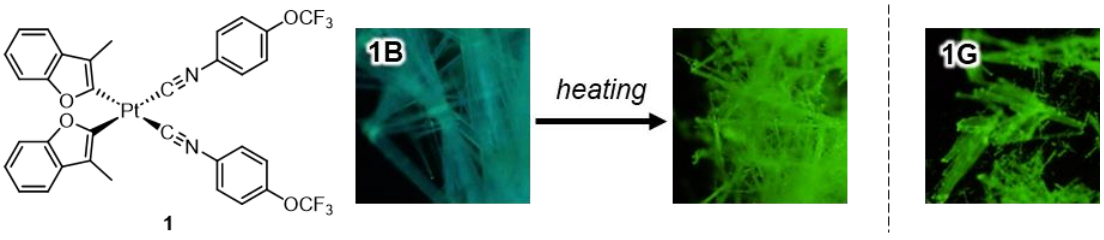
置換ヘテロ芳香環を有する白金錯体からなる分子結晶の開発

（静大理）○石川 倫太郎・関 朋宏
Development of Molecular Crystals of Platinum Complexes Equipped with Substituted Heteroaromatic Groups (*Faculty of Science, Shizuoka University*) ○ Rintaro Ishikawa, Tomohiro Seki

We have found that arylation of dichloroplatinum complexes is a promising molecular design strategy for imparting stimuli-responsiveness.[1)] In particular, introduction of unsubstituted benzofuran groups has been confirmed to produce a variety of stimuli-responsive properties. Herein, we prepared methylated analogue **1** to construct molecular arrangements different from the corresponding unsubstituted benzofuryl platinum complexes owing to steric repulsion. **1** showed stimulus-responsive properties such as luminescent mechano- and thermochromism. Blue-emitting crystal (**1B**) and green-emitting crystal (**1G**) of **1** can be selectively prepared by vapor diffusion methods using $CHCl_3$/*n*-pentane and CH_2Cl_2/*n*-pentane, respectively. The luminescent color of **1G** did not change by mechanical or thermal stimulation. Contrary, the solid sample of **1B** showed luminescent mechano- and thermochromism, to lead to emission color change from blue to green. In this presentation, we will discuss the details of the phase transition behavior of **1B** and the crystal structure obtained after external stimuli.
Keywords: molecular crystals; platinum complex; phase transition; photoluminescence

当研究室では最近、塩化白金錯体に対するアリール化が刺激応答性の付与を可能にする分子設計戦略であることを見出した[1)]。特にアリール基としてベンゾフランのようなヘテロ芳香環を導入すると、多様な刺激応答性を発現することを明らかにしている[1)]。本研究ではベンゾフランにメチル基を導入し、立体反発により無置換体とは全く異なる結晶構造の形成を目指し、メチル化体 **1** を合成した。**1** は発光性メカノクロミズムや温度変化に伴う相転移などの刺激応答性を示した。

1 は、$CHCl_3$/*n*-pentane の蒸気拡散法により青色発光結晶（**1B**）と、CH_2Cl_2/*n*-pentane の蒸気拡散法により緑色発光結晶（**1G**）を形成した。**1G** に対し、機械的刺激の印可や温度変化を与えても発光色は変化しなかった。一方で、**1B** に対して機械的刺激を与えると、緑色発光へと変化する発光性メカノクロミズムを示した。同様に、**1B** を加熱することによっても発光色が緑色に変化した。本発表では、**1B** の相転移挙動の詳細や外部刺激を印可した後の結晶構造に関しても議論する。



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1) T. Seki, D. Korenaga, *Chem. Eur. J.*, **2023**, *29*, e202302333.

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α位をアルキル基で置換したジベンゾイルメタンフッ化ホウ素錯体の合成と凝集誘起発光特性

（長野県諏訪清陵高等学校[1]・信州大[2]）○市原 一模[1]・小井出 遥斗[1]・宮坂 直人[1]・真壁 啓太[1]・守谷 虎太朗[1]・峯村 和光[1]・藤本 悠史[2]・伊藤 冬樹[2]
Syntesis and Aggregation-Induced Emission Properties of Dibenzoylmethanato Boron Difluoride Complex with Alkyl Group at α-position ([1]*Suwa Seiryo High School, Nagano Prefecture*, [2]*Shinshu University*) ○Kazunori Ichihara[1], Haruto Koide[1], Naoto Miyasaka[1], Keita Makabe[1], Kotaro Moriya[1], Kazumitsu Mineumra[1], Yushi Fujimoto[2], Fuyuki Ito[2]

Recently, organic molecules with aggregation-induced emission (AIE) properties have attracted much attention. While AIE molecules have weak emission in the solution states, strong emission shows in the crystalline states. Morris et al. have reported that BF2DBM molecules substituted with a methyl group at the α-position exhibit AIE properties. In this study, we tried to synthesize BF2DBM substituted by alkyl chains at the α-position in order to investigate the dependence of carbon numbers for the AIE properties.
Keywords : dibenzoylmethanato boron difluoride complex; aggregation-induced emission; alkyl group

近年，溶液中ではほとんど発光せず，固体状態で強く発光する凝集誘起発光（AIE）特性を有する有機分子が着目されている．Morris らは，溶液中で高蛍光量子収率を示すジベンゾイルメタンフッ化ホウ素錯体（BF_2DBM）誘導体について，そのα位プロトンをメチル基で置換した $MeBF_2$ は，AIE 特性を有することを報告している[1]．そこで，本研究では，$MeBF_2$ のメチル基を炭素数の異なる直鎖アルキル基（エチル，*n*-プロピルおよび *n*-ブチル基）で置換した BF_2DBM 誘導体（Fig. 1；それぞれ $EtBF_2$，*n*-$PrBF_2$ および *n*-$BuBF_2$）を新たに合成し，その AIE 特性を評価した．

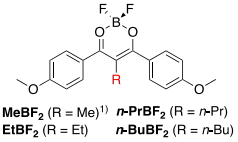

Fig. 1. アルキル置換 BF_2DBM 誘導体.

異なる水の体積割合（f_w）での，$EtBF_2$ および *n*-$PrBF_2$ の水/アセトン混合溶液の蛍光特性を調査した．Fig. 2 に各 f_w の蛍光スペクトルを示す．f_w=0-50%では，$EtBF_2$ および *n*-$PrBF_2$ のいずれも蛍光はほとんど観測されなかった．f_w の増加にともない蛍光強度は増強し，f_w=90%では，いずれの分子も 480 nm 付近にピークを有する蛍光スペクトルを示した．これは，溶解度の減少にともない凝集体を形成することで，AIE を発現したことを示唆している．さらに，$EtBF_2$ および *n*-$PrBF_2$ の単結晶の蛍光スペクトルは，それぞれ 505 および 514 nm 付近にピークを示した．当日は，*n*-$BuBF_2$ の光物理特性，および単結晶の蛍光特性を踏まえてそれぞれの分子での結晶多形の存在についても議論する．

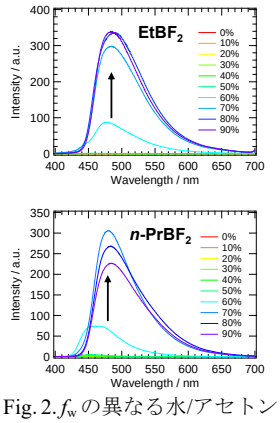

Fig. 2. f_w の異なる水/アセトン混合溶液中でのアルキル置換 BF_2DBM 誘導体の蛍光スペクトル.

1) W. A. Morris, M. Kolpaczynska, C. L. Fraser, *J. Phys. Chem. B*, **2016**, *120*, 22539.

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ベンゾセレノフェン白金錯体からなる刺激応答性分子結晶の開発

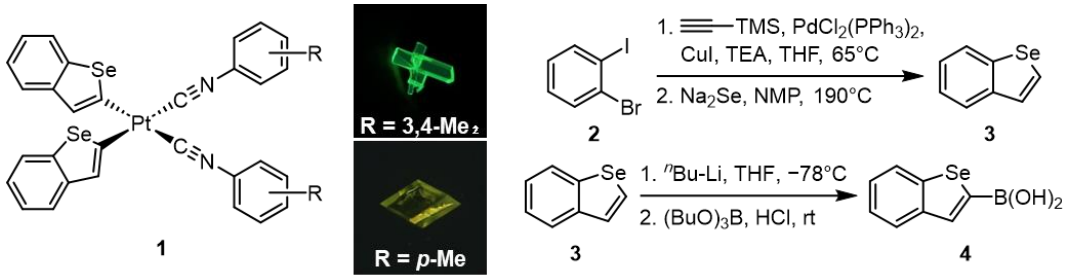
（静大理）○矢野 彰人・関 朋宏

Development of Stimuli-Responsive Molecular Crystals of Benzoselenophene Platinum Complex (*Faculty of Science, Shizuoka University*) ○Akihito Yano, Tomohiro Seki

Introduction of heteroaromatic rings such as benzofuran/thiophene to a dichloroplatinum complexes allowed to provide various stimuli-responsive properties[1]. Since benzofuryl and benzothiophenyl platinum complexes more often showed unique responses than those bearing other aryl groups, we focus on benzoselenophenyl platinum complexes **1** containing selenium, a homologue of oxygen and sulfur. The crystal of **1** showed the photoluminescence and stimuli-responses different from those of the benzofuryl platinum complexes. From compound **2**, precursor **4** was prepared by a three-step reaction[2]. Novel benzoselenophenyl platinum complexes were prepared by the reaction with a dichloroplatinum complex. It was found that the solid sample of **1** often showed green or yellow luminescence irrespective of a substituent R. This is in contrast to the corresponding benzofuryl platinum complexes, which showed a wide range of emission colors from blue to orange. The origin of the luminescent color and stimuli-responsive properties of **1** will be also discussed in this presentation.
Keyword: molecular crystals; mechanochromism; platinum complex

我々は塩化白金錯体に対してベンゾフランやベンゾチオフェンなどのヘテロ芳香環を導入することで発光性メカノクロミズムやサーモ・ベイポクロミズムなど様々な刺激応答性を発現することを報告している[1]。ベンゾフランやベンゾチオフェン白金錯体がその他のアリール基よりも豊富な応答を示したため、本研究では酸素と硫黄の同族元素に着目しヘテロ芳香環にセレンを含むベンゾセレノフェン白金錯体 **1** を合成した。その結果、**1** は対応するベンゾフラン白金錯体と比較して異なる発光色や刺激応答性を示したので報告する。

2 を出発物質として、2 段階の反応によって **3** を合成し、そのホウ素化により **4** を得た[2]。**4** と塩化白金錯体とのカップリングによりベンゾセレノフェン白金錯体を新規に合成した。配位子上に様々な置換基 R を有する **1** の結晶は、そのほとんどが緑色や黄色の発光を示す傾向にあることがわかった。これは、対応するベンゾフラン白金錯体の結晶が青色から橙色まで幅広い発光色を示すことと対照的である。本発表では、**1** の発光色の起源やその外部刺激応答性についても議論する。



1) T. Seki, D. Korenaga, *Chem. Eur. J.*, **2023**, *29*, e202302333
2) Y. He, J. Quinn, Y. Deng, Y. Li, *Org. Electron.,* **2016***, 35,* 41–46

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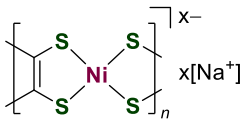
ビニルチオフェン構造を含むπ共役ニッケル錯体の製膜法と熱電変換特性

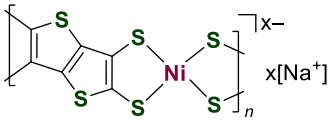
（阪工大工）○宮武 郁・矢尾板 朋也・ジョブス デフォンアディティア・村田 理尚
Fabrication of Thermoelectric Films Containing π-Conjugated Nickel Complexes with Vinylthiophene Units (*Faculty of Engineering, Osaka Institute of Technology*) ○Iku Miyatake, Tomoya Yaoita, Devon Aditya Jobs, Michihisa Murata

π-Conjugated nickel-ethenetetrathiolate (NiETT) has attracted substantial interest on account of the unusual properties, which include high conductivity in the solid state. However, given the insolubility in common solvents, new ligands and a facile coating method need to be developed. In this study, we designed and synthesized a π-conjugated ligand with a vinylthiophene structure. We will discuss the thermoelectric properties of the newly obtained film of the π-conjugated nickel complex.
Keywords : Thermoelectric Conversion; Nickel Complexes; Organic Semiconductors; π-Conjugated Systems; n-Type Semiconductors

ニッケルエテンテトラチオラート (NiETT) は、大気安定な n 型半導体として、フレキシブル熱電変換デバイスへの応用が期待されている [1,2]。当研究室では以前に、チエノチオフェン骨格を含むニッケル錯体 **1** を合成し、その塗布膜が高い導電性を示すことを報告した [3]。本研究では、ビニルチオフェン骨格を含有するπ共役配位子を含むニッケル錯体を合成し，その塗布膜の熱電変換特性を調べた。



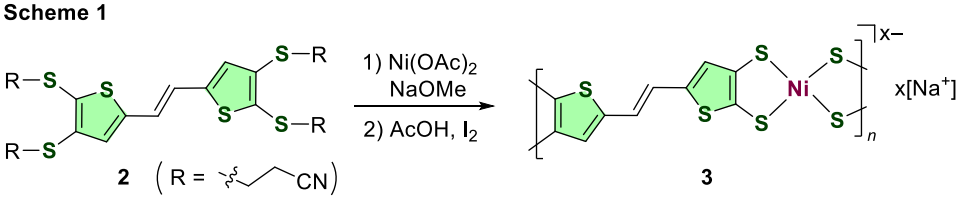
NiETT



1

まず、ビニルチオフェン骨格を含有する配位子前駆体 **2** を独自に合成し、その構造を単結晶 X 線構造解析により確認した。次に，**2** の塩基による脱保護と錯形成を進行させた後、酸化することによりワンポットでニッケル錯体 **3** に変換した (Scheme 1)。得られた錯体 **3** は不溶性であったが、溶液プロセスによる製膜を行うことができた。熱電変換特性についても報告する。

Scheme 1



2 (R =) **3**

1) A. K. Menon, R. M. W. Wolfe, S. R. Marder, J. R. Reynolds, S. K. Yee, *Adv. Funct. Mater.* **2018**, *28*, 1801620. 2) K. Ueda, Y. Yamada, T. Terao, K. Manabe, T. Hirai, Y. Asaumi, S. Fujii, S. Kawano, M. Muraoka, M. Murata, *J. Mater. Chem. A* **2020**, *8*, 12319. 3) K. Ueda, R. Fukuzaki, T. Ito, N. Toyama, M. Muraoka, T. Terao, K. Manabe, T. Hirai, C.-J. Wu, S.-C. Chuang, S. Kawano, M. Murata, *J. Am. Chem. Soc.* **2022**, *144*, 18744.

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架橋ビチオフェンをπスペーサーとする新規D–π–A型分子の合成と物性

（阪公大院工[1]・阪府大工[2]）○上田 未侑[1]・永山 諒[2]・鈴木 直弥[1,2]・小玉 晋太朗[1,2]・前田 壮志[1,2]・八木 繁幸[1,2]

Synthesis and Properties of Novel D–π–A Type Molecules Bearing Bridged Bithiophene π-Spacers ([1]*Graduate School of Engineering, Osaka Metropolitan University*, [2]*College of Engineering, Osaka Prefecture University*) ○Miyu Ueda,[1] Ryo Nagayama,[2] Naoya Suzuki,[1] Shintaro Kodama,[1] Takeshi Maeda, [1] Shigeyuki Yagi[1]

D–π–A type molecules consisting of electron donating and accepting groups linked by a π-conjugated spacer exhibit strong absorption in the visible region and emission with a large Stokes shift due to their intense intramolecular charge transfer (ICT) characters. However, the extension of the π-conjugation system in such molecules leads to a decrease in photostability due to the high reactivity of their π-electron-enriched structures. In this study, we have synthesized novel D–π–A type molecules bearing a carbonyl-bridged bithiophene as a π-conjugated spacer (Fig. 1) and evaluated the absorption and emission properties as well as the photostability. The absorption spectra of **1**–**3** in dichloromethane at room temperature showed absorption maxima (λ_{abs}) at 569 nm, 628 nm, and 667 nm, respectively, and the λ_{abs}s of **2** and **3** were red-shifted in comparison with that of **1**, indicating that stronger acceptors in **2** and **3** enhanced the ICT character. In addition, **2** and **3** had a second absorption band in the visible region, showing panchromatic absorption properties.

Keywords : D–π–A Type Molecule; Photostability; Panchromatic Absorption; Stokes Shift; Intramolecular Charge Transfer

電子ドナー・アクセプターの両原子団をπ共役スペーサーで連結したD–π–A型分子は、可視領域での強い光吸収やStokesシフトの大きな発光など、特徴的な光学・発光特性を示し、これまで色素増感太陽電池やバイオイメージングなどに応用されてきた。本研究では、新規D–π–A型分子の創出を目的として、ドナー部位にジフェニルアミノフェニル基を、π共役リンカー部位にカルボニル架橋ビチオフェン骨格をそれぞれ有する一連の新規D–π–A型分子**1**–**3**を合成し（Fig. 1）、それらの光学・発光特性および耐光性について評価した。ジクロロメタン中、室温下において**1**–**3**の吸収スペクトルを測定したところ、それぞれ、569 nm、628 nm、667 nmに吸収極大λ_{abs}を示し、**2**と**3**のλ_{abs}は**1**に比べて長波長化していることから、強いアクセプター基の導入による分子内電荷移動の促進が長波長化の原因であると考えられる。また、**2**と**3**は第二吸収帯を可視領域に有することから、全色吸収型のスペクトル特性を示した。

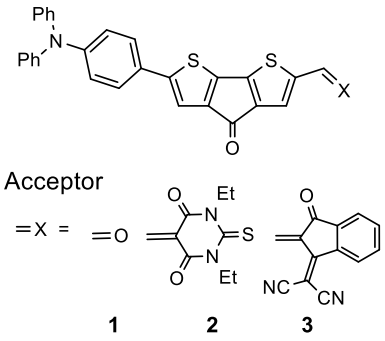

Fig. 1. Structures of **1**–**3**.

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TEMPO 酸化セルロースナノファイバーを用いたフィルム材料の物性評価

（日本大学[1]）○小板橋 優作[1]・木村 悠二[1]
Evaluation of film materials using TEMPO oxidized CNF ([1]*Nihon University*) ○Yusaku Koitabashi,[1] Yuji Kimura[1]

Plastic products derived from petroleum are causing ocean pollution and fossil fuel depletion problems. Half of the plastic waste is packaging films and containers, and the development of alternative materials for these products is considered a solution to these problems. Biobased polymers are expected to be used to solve the problem.

In this study, we tried to develop a bioplastic. Currently, the cost and mechanical strength of bioplastics are inferior to those of petroleum-derived plastics. Therefore, we combined biobased polymers such as starch and TEMPO oxidized CNF to solve the problem. Results showed that stress and hardness increased with increasing amounts of TEMPO-oxidized CNF. Film materials can replace petroleum-derived plastic products.
Keywords：film, starch, cellulose, natural resources, biomass

石油由来のプラスチックは，海洋汚染や化石燃料の枯渇問題を引き起こす原因となっている．プラスチックゴミとして排出される大半は包装フィルムや容器であるため，これらの代替材料を開発することで環境問題の解決につなげることができる．

本研究では，石油由来の包装フィルムの代替品となるバイオプラスチックの開発を目指した．現状のバイオプラスチックは，コストと機械的強度において石油由来の包装フィルムに劣っているため，安価なデンプンと TEMPO 酸化 CNF などの天然由来高分子を組み合わせることで，これらの問題を解決できると考えた．

実験手順は，10 wt%のデンプン溶液，所定濃度の粘土鉱物分散液，セルロース(デンプンに対して 30 wt%)のポリマー溶液およびクリセリン(デンプンに対して 30 wt%)を混合してフィルム材料を作製した．その結果，セルロースを添加していない材料は形状の維持が困難な硬くて脆い材料であったが，セルロースを添加することで形状の維持が可能な硬い材料となった。セルロース添加有無の DSC を Fig.1 に示す．Fig.1 より，a と b のピークはフィルム材料が保持している H_2O であると考えられる．ピーク面積は a＞b であるため，セルロースを添加したフィルム材料の方が H_2O を多く保持していると考えられる．また，セルロースの添加によって H_2O 量が増加したため，低温で蒸発しやすくなりピークが b から a にシフトしたと考える．ピーク面積とピークのシフトからセルロース添加の有無によって H_2O 量に差があり，材料物性に影響していると考える．このことから，形状の維持が不可能であった材料に，セルロースを添加することで形状の維持が可能となった．この結果から，セルロース添加により材料物性が向上し，包装フィルムなどの幅広い用途での使用が可能であると考える．

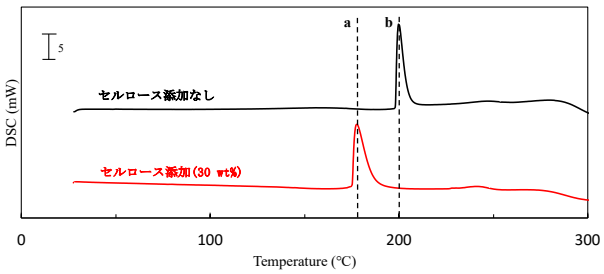

Fig.1 DSC of film materials.

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解重合が可能なオキシムエーテル末端ポリフタルアルデヒドの合成とその光分解挙動

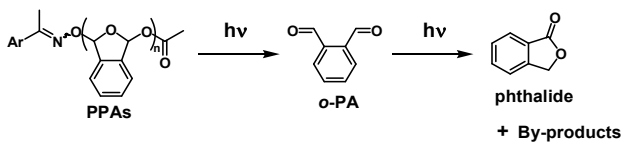
（大阪技術研[1]・阪公大　基幹教育[2]）○林 寛一[1]・舘 秀樹[1]・陶山 寛志[2]

Synthesis and Photo-degradation behavior of polyphthalaldehydes with oxime ether terminals

([1] *Izumi Center, Osaka Research Institute of Industrial Science and Technology*, [2] *Faculty of Liberal Arts, Sciences and Global Education Osaka Metropolitan University*)
○Hirokazu Hayashi,[1] Hideki Tachi,[1] Kanji Suyama[2]

The degradation and recycling of polymeric materials are growing public interests recently, and the molecular design of degradable polymers is highly important. Herein the syntheses and photochemical behavior of photolabile polyphthalaldehydes (PPAs) with oxime terminals are reported. *o*-Phthalaldehyde (*o*-PA) was polymerized with acetonaphthone oxime as initiators in the presence of DBU at －80 °C and terminated with acetic anhydride. The incorporation of naphthyl oxime ether units and acetyl terminals was confirmed by NMR, UV, and IR spectral measurements. The repeating units in obtained PPAs were about 100. When PPAs were irradiated with UV light (>310 nm) in $CHCl_3$, peaks due to *o*-PA appeared. These spectral changes clearly indicated the proceeding of photo-depolymerization of PPAs.
Keywords : Photo-depolymerization; Polyphthalaldehyde; Oxime ether

一般に、架橋樹脂の分解は難しく、リサイクルには適していない。本研究では、後で架橋樹脂に誘導可能なユニットを組み込んだ解重合性ポリマーを開発することを目的に、オキシムを重合開始剤として末端に導入したポリフタルアルデヒド(PPA)の重合を行い、その光分解性について調査した。PPA の重合例を次に示す。Ar 雰囲気下、*o*-フタルアルデヒド(*o*-PA)(7.16 mmol)の CH_2Cl_2 溶液に、1-アセトナフトンオキシム(0.092 mmol)と DBU(0.090 mmol)を加え、－80 °C でアニオン重合を行った。重合停止剤には無水酢酸（0.18 mmol）を用いた。得られた PPA(1NaPPA)は、メタノールを用いて再沈殿を行い、白色固体を得た（ポリマー収率 42%）。この 1NaPPA の $CDCl_3$ 溶液の光照射後の NMR スペクトルから、PPA の主鎖由来のピークの減少と、*o*-PA 由来のピークの出現を確認した。また、UV スペクトルから、290-320nm 付近の吸収スペクトルの減少が観測された。さらに NMR スペクトルでのベンジル位のメチレン基由来ピークの出現に加え、IR スペクトルからは、C=O (1780cm^{-1})由来の吸収の増加が観測された。これらのことから、本光反応では分解生成した *o*-PA から、フタリドへの光異性化の進行を推察した。予想される PPA の光分解反応を Scheme 1 に示す。また、多置換 PPA の結果についても報告する。



Scheme 1. Plausible photoreaction of PPAs with oxime ether terminals.

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様々な反応条件でのゲル中における MOF の合成を利用した MOF801-PDMS 複合膜の作製とガス分離特性

(金沢大理工[1], 金沢大院自然[2], 金沢大ナノマリ[3]) ○西川卓良[1]・栗原拓也[2]・重田泰宏[2,3]・雨森翔悟[2,3]・井田朋智[2]・水野元博[2,3]

Gas separation property of MOF801-PDMS composite membranes fabricated by in situ synthesis of MOF in gel under various condition.

([1]*College of Science and Engineering, Kanazawa Univ.,*[2]*Graduate School of Natural Science and Technology, Kanazawa Univ.,*[3]*NanoMaterials Research Institute, Kanazawa Univ*) ○Takara Nishikawa[1], Takuya Kurihara[2], Yasuhiro Shigeta[2,3], Shogo Amemori[2,3], Tomonori Ida[2], Motohiro Mizuno[2,3]

Mixed-Matrix Membranes (MMM) compositing polymers and metal organic frameworks (MOF) are expected to have both self-standing nature and high gas separation properties. However, it remains a challenge to improve a dispersity of the MOF in the MMM. We have previously reported the MMM obtained by in situ synthesis of MOF801 in polydimethylsiloxane (PDMS) gel, demonstrating good dispersion of MOF801 in the MMM. However, optimal reaction conditions for the MMM have not been studied. In this work, we investigated effects of film thickness for the in situ synthesis method. MMMs were fabricated using PDMS with thicknesses of 300-400 μm and 600-700 μm. And IR spectra and PXRD measurements indicated successful hybridization of MOF801 and PDMS in both MMMs. We will also report the gas permeation properties of these fabricated MMMs.

Keywords: Metal-Organic Frameworks, PDMS, Mixed Matrixed Membrane, Gas Separation

金属−有機構造体（Metal-Organic Frameworks, MOF）を高分子中に分散させた MOF-混合マトリックス膜（Mixed-Matrix Membrane, MMM）は自立性と高いガス分離特性を持つガス分離膜として期待されている。一方、高分子中における MOF の凝集等が課題となっている。これまでに本研究室では MMM 内での MOF 分散向上を目的とし、ゲル内で MOF 合成を行う in situ 合成による MMM 作製を行ってきた(Fig.1)。具体的にはフマル酸と Zr オキソクラスターで構成される MOF801 とポリジメチルシロキサン(PDMS)の MMM を作製し、MOF のマクロな凝集の抑制を報告している[1)]。一方、この MMM 作製においてガス分離に最適な作製条件の検討はされてはいない。そこで、本研究では異なる膜厚の PDMS を用い、膜厚が MMM 作製、ガス分離特性に及ぼす影響を検討した。実際に、膜厚が 300-400 μm と 600-700 μm の PDMS を用い、in situ 合成を行うことで MMM を作製した。IR スペクトル、PXRD 測定により、どちらも MOF801 と PDMS の複合化が確認された。当日は得られた MMM のガス透過試験の評価も合わせて報告する。

1) S. Amemori, T. Nishikawa, A. Tomura, S. Nagame, T. Kurihara, M. Mizuno al., MRM2023/ IUMRS-ICA2023, 2023, C1-O501-05

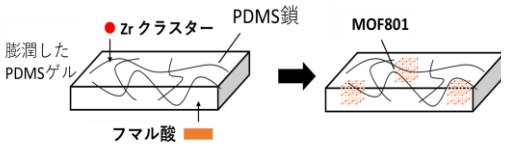

Fig.1. in situ 合成の概略図

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ポリエチレンテレフタレートフィラメント上に積層した高分子電解質多層膜のイメージングＸ線光電子分析

（福井大院工）○渡辺 銀雅・吉光 蒼生・安田 将大・平田 豊章・久田研次
Imaging X-ray Photoelectron Analysis of Polyelectrolyte Multilayers Deposited on Polyethylene Terephthalate Filaments (*Graduate School of Engineering, University of Fukui*)
○Ginga Watanabe, Aoi Yoshimitsu, Syota Yasuda, Toyoaki Hirata, Kenji Hisada

In the finishing process of synthetic fibers, it is desirable to establish a technology to coat each filament with a nanofilm. Polyelectrolyte multilayers (PEMUs) with alternating layers of polycations and polyanions have a nanometer-order periodic structure and can be a sustainable fiber finishing processing method because it is an organic solvent-free technique. Since the only ionizable functional group on the polyethylene terephthalate (PET) surface is the terminal carboxyl group, PEMUs were deposited after pretreatment with a photobase generator. Polydiallyldimethylammonium chloride (PDDA) and sodium polystyrene sulfonate (PSS) were deposited on PET fabrics. The modified fabrics were etched by sputtering Ar gas cluster ion beams and analyzed for elemental composition distribution by imaging XPS measurements. The deposited PEMUs were slightly rich in PDDA, but both components were uniformly distributed in the in-plane and depth directions.

Keywords : Polyelectrolyte multilayers; Imaging X-ray photoelectron analysis; Polyethylene terephthalate; Photobase generator

合成繊維の機能加工において, 各フィラメントをナノ薄膜で被覆する技術が望まれている。ポリカチオンとポリアニオンを交互積層した高分子電解質多層膜（PEMU）はナノメートルオーダーの周期構造を有しており [1]，有機溶剤フリーの加工法であることから，繊維の持続可能な機能加工法として期待が持てる [2]。ポリエチレンテレフタレート（PET）表面にある電離可能な官能基は末端カルボキシル基のみであるため，光塩基発生剤により前処理した後にPEMUを積層した。ポリジアリルジメチルアンモニウムクロリド（PDDA）とポリスチレンスルホン酸ナトリウム（PSS）のPEMUを積層したPETフィラメント表面にArガスクラスターイオンビームをスパッタしてエッチングし，イメージングXPS測定で元素組成分布を分析した（図１）。積層されたPEMUは若干PDDAリッチであったが，面内および深さ方向に対して両成分が一様に分布していること明らかにした。

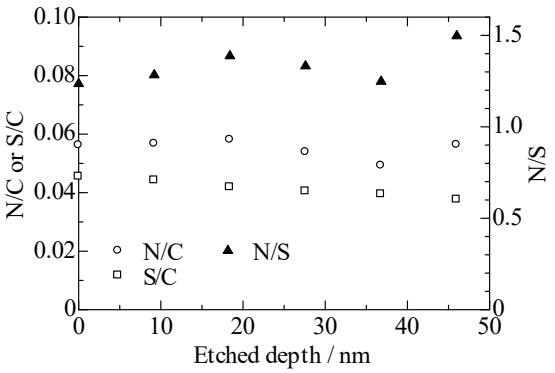

Fig. 1. PEMUを5.0サイクル積層したPET布表面近傍の元素組成分布.
○: N/C, □: S/Cおよび▲: N/S.

1) Decher *et al*., *Science*, **227**, 1232-1237 (1996).
2) Dubus *et al*., *J. Appl. Polym. Sci.*, **101**, 3286-3290 (2006).

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CO_2 分離を目的とした PAMAM デンドリマー/水溶性ポリマー膜の合成および物性評価

（日本大学）○芹澤　佳翼・木村　悠二
Synthesis and characterization of PAMAM dendrimer/water-soluble polymer membranes for CO_2 separation (*Nihon University*)　○Keisuke Serizawa, Kimura Yuji

Technologies to separate and capture CO_2 emitted from thermal power plants and factories are attracting attention as a countermeasure against global warming. Among these technologies, CO_2 separation using membranes is being considered because of its potential to reduce costs and energy consumption. In this study, membranes were synthesized by adding a water-soluble polymer to polyamidoamine (PAMAM) dendrimers[1] that exhibit excellent affinity for CO_2. The physical properties of the membranes, such as stress and strain, were evaluated.

Figure 1 shows the results of stress and strain for the addition rates of PEG and PVA. 100% PEG resulted in membranes with high strain. The film with 100% PVA showed better stress and strain than the film with a mixture of PEG and PVA, although the strain was not as high as that of 100% PEG. I think that when PEG and PVA were mixed, the structure of the film became non-uniform, which adversely affected the physical strength of the film.

Keywords : PAMAM dendrimer; Water-soluble polymer; CO_2 separation

地球温暖化対策技術として，火力発電所や工場で排出される CO_2 を分離回収する技術が注目されている。中でも，コストや消費エネルギーの削減が期待できる膜を利用した CO_2 の分離が検討されている。本研究では，CO_2 と優れた親和性を示すポリアミドアミン（PAMAM）デンドリマー[1]に水溶性高分子を添加し，膜を合成した。この膜の応力や歪みなどの物性を評価した。

PEG および PVA の添加率に対する応力と歪みの結果を図 1 に示す。PEG100％の場合歪みが大きい膜を得た。また，PVA100% の場合，PEG100%の歪みには劣るものの，PEG と PVA を混合したものに比べて応力と歪みに優れた膜を得た。PEG と PVA を混合した場合，膜の構造が不均一となり物理的な強度に悪影響をおよぼしたと考える。

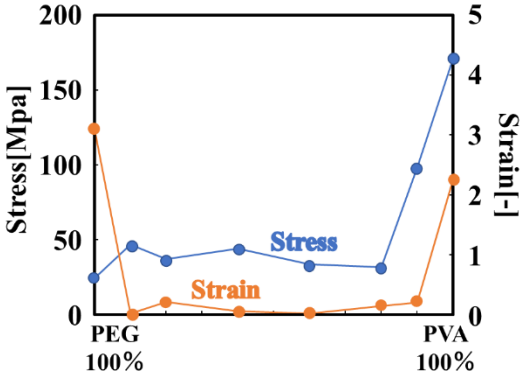

図1. PAMAM デンドリマー/PEG/PVA 膜の応力および歪み

1) J. H. Lee, J. Y. Lim, M. S. Park, J H Kim, *Macromolecules*, 2018, **51**, 8800-8807

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短下肢装具に用いられるポリプロピレン材の加速劣化試験

（北海道科学大学[1]）○三原 義広[1]・村原 伸[1]・堀内 寿晃[1]
Accelerated aging test of polypropylene material used in ankle-foot orthosis ([1]*Hokkaido University of Science*) ○Yoshihiro Mihara,[1] Shin Murahara,[1] Toshiaki Horiuchi,[1]

Ankle-foot orthosis (AFO) is primarily manufactured by stretching polypropylene sheet material. Oxidative degradation of polypropylene may occur due to temperature changes and exposure to light, resulting in crack initiation. In this study, we conducted surface observations and mechanical tests on used AFOs utilizing various spectroscopic methods. We investigated the efficacy of employing these techniques to diagnose orthotic degradation. The mechanical and structural properties of the AFOs were evaluated through X-ray Photoelectron Spectroscopy, tensile tests, Raman Microscopy, and Fourier-transform infrared spectroscopy with attenuated total reflectance before and after ultraviolet testing. Additionally, we examined the surface undulation of polypropylene after 8 years of use.
Keywords：Plastic, Aging, UV irradiation

プラスチック製短下肢装具は、おもにポリプロピレン(PP)のシート材を軟化し、吸引成形によって製作される。積雪寒冷地での装具の使用は、紫外線や温度変化の影響で PP 材が酸化促進され、PP の内部構造の変化により装具の劣化が加速される可能性がある。本研究では、使用された短下肢装具に対して、さまざまな分光学的手法による表面構造の観察および試料の力学的特性の測定を行い、これらの手法が装具の劣化判断に有効であるかを検討した。さらに、8 年間使用された短下肢装具を切断し、母趾球部、ふくらはぎ、くるぶし、かかとの各部位から試料を取得し、劣化状況を確認した。分光学的手法には、赤外分光光度計（FTIR）、顕微ラマン分光装置、X 線光電子分光装置、原子間力顕微鏡を用い、酸化により生成されるカルボニル基(C=O)の測定や表面構造の観察を行った。力学的特性の測定には引っ張り試験を用いた。

PP 材の表面構造に関しては、紫外線照射時間が増加するにつれてカルボニル基が増加し、照射表面の変色や亀裂の発生も確認された。FTIR による測定では、紫外線照射 24 時間後の PP 試料で 1750cm^{-1} 付近の C=O 伸縮振動について、ピーク強度の増加が顕著であった。カルボニル基の増加に伴い、PP 材の引張強さが低下する傾向が認められた。さらに、装具歩行による変形外力の集中が考えられる箇所で、カルボニル基のピーク強度が他の部分よりも大きかった。

装具に用いられるポリプロピレンは、使用環境や経年に伴い、高分子の主鎖の切断によって脆化し、表面に亀裂が生じることがある。装具の各部位において、カルボニル基のピーク強度に違いがあったことから、装具の劣化はポリプロピレン自体の経年劣化だけでなく、装具の使用に伴う変形外力などの影響も考えられる。

装具の劣化は、装具の形状、使用頻度および生活環境などによって異なる。分光学的な手法を活用することで客観的かつ迅速に PP の内部構造を把握できれば、交換時期の提案につながり、装具使用者の安全に寄与できる。

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スギを基体とする固体酸触媒の合成とその物性評価

（中部大院工[1]・中部大工[2]）○井垣 侑生[1]・秋永 拓未[1]・池田 琉稀[1]・爾見 優子[2]・宮内 俊幸[2]
Preparation and properties evaluation of solid acid catalyst on cedar ([1]*Graduate of Chubu University*, [2]*Chubu University*) ○Yui Igaki,[1] Takumi Akinaga,[1] Ryuki Ikeda,[1] Yuko Shikami,[2] Toshiyuki Miyauchi,[2]

Sulfuric acid is an important catalyst in the chemical industry, but it generates a lot of energy for disposal and separation from products. Solid acid is expected to reduce the environmental burden compared to sulfuric acid. Therefore, this research prepared the solid acid by pretreating cedar, a plant-derived biomass, and then introducing sulfonic acid group. The solid acid was characterized by measuring acidity, surface observation, and surface analysis, and its properties were evaluated. In addition, the solid acid will be used as a catalyst in the esterification. Ethyl acetate was observed by adding the solid acid to acetic acid and ethanol. Therefore, we report that the prepared solid acid could be used as a catalyst.
Keywords : Biomass; Solid acid; Catalyst

【背景】硫酸は化学工業において重要な触媒であるが、生成物との分離や廃棄処理に多くのエネルギーを生じる。それに代わり固体で酸性を示す固体酸触媒は分離が容易であり、繰り返し使用できるため環境負荷を軽減できると期待されている。さらに、固体酸触媒はエステル化や加水分解反応において利用が可能である。そこで、本研究では生体高分子である植物由来バイオマスを前処理した後、硫酸・発煙硫酸によってスルホン化することで固体酸を合成した。この固体酸の物性評価を行い、触媒としての応用を試みた。
【実験】植物由来バイオマスであるスギおが屑を塩酸で前処理し、樹皮等の不純物を除去した。その後、硫酸・発煙硫酸を直接作用させ、スルホン基を導入する直接法によって固体酸を合成した。合成した固体酸を SEM と XPS を用いて、表面観察、結合状態などの物性評価を行った。また、固体酸の評価において酸性度を滴定によって算出した。さらに、エステル化反応の触媒として利用を検討した。
【結果および考察】化学処理をしたスギの表面観察を SEM で行った(Fig.1)。化学処理を行う前のスギ(a)の表面はなめらかであるが、塩酸で前処理(b)をするとその表面は荒れ、硫酸処理(c)をするとさらに荒いものとなった。また、XPS を用いて表面の結合状態を測定したところ硫酸処理後では、168 eV 付近に-C-SO_3H 由来ピークが検出され、スルホン基の導入が明らかであった。さらに、酢酸とエタノールに触媒として固体酸を加えたところ、酢酸エチルが確認された。従って、合成した固体酸はエステル化の触媒として利用が可能であった。

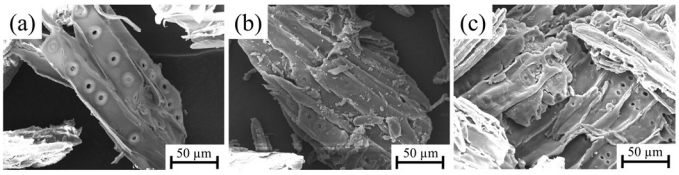

Fig. 1 SEM picture of chemical modified cedar sawdust
(a)Cedar sawdust; (b)Cedar sawdust-H; (c)Cedar sawdust-SO_3H.

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水溶性希土類錯体ナノ粒子における光学特性評価

（立命館大生命科学[1]・JST さきがけ[2]）小橋 俊介[1]・岡安 祥徳[1]・永井 邑樹[1]・小林 洋一[1,2]

Evaluation of Optical Properties in Water-Soluble Lanthanide Complex Nanoparticles

([1]*College of Life Sciences, Ritsumeikan Univ.*, [2]*PRESTO JST*) ○Shunsuke Kobashi[1], Yoshinori Okayasu[1],Yuki Nagai[1] , Yoichi Kobayashi[1,2]

Europium (III) complexes have unique luminescent properties and are expected to be applied to fluorescence lifetime imaging. However, water dispersibility and high photodurability are indispensable for bioimaging applications. In this study, we prepared water-soluble Eu(III) complexes nanoparticles (NPs, Fig.1a) by the reprecipitation method, and evaluated their optical properties and photodurability.

The absorption and emission spectra of the $Eu(PhDK)_3$ in acetonitrile and $Eu(PhDK)_3$ NPs in water were similar. On the other hand, the luminescence quantum yield of NPs was significantly lower than that in acetonitrile. Repeated UV light irradiation experiments revealed that $Eu(PhDK)_3$ NPs exhibit higher photodurability than that in acetonitrile.

Keywords：Lanthanide complexes; photodurability; reprecipitation; water-soluble nanoparticles;

ユーロピウム（Eu(III)）錯体は、色純度の高い発光やミリ秒程度の発光寿命などの特徴的な発光特性を有することから、センサーや発光材料として応用されている。一方、これらの性質を生命科学分野に応用するには、水分散性や連続観察に耐えうる高い光耐久性が求められる。本研究では、それらの機能を有する希土類錯体機能材料を見出すことを目的として、β-ジケトナート配位子を有する単核および複核の Eu(III)錯体 ($Eu(PhDK)_3$、$Eu_2(BTP)_3$)の水溶性ナノ粒子(NPs)を再沈法によって合成し、それらの光物性や安定性を評価したので報告する。

$Eu(PhDK)_3$ のテトラヒドロフラン（THF）溶液をミリ Q 水に急速に加え、その後ドデシル硫酸ナトリウムを加えた。反応溶液を 65°C で 10 分間加熱撹拌することにより、それぞれの NPs 水溶液を調製した。$Eu(PhDK)_3$ NPs 水溶液と $Eu(PhDK)_3$ のアセトニトリル溶液の吸収、発光スペクトル形状はきわめて類似していた。一方、発光量子収率はアセトニトリル溶液では 32%であったのに対し、NPs 水溶液では 0.14%と大幅に減少した。また、それぞれの溶液に紫外光（365 nm, 600 mW cm^{-2}）を 60 分照射すると、アセトニトリル溶液では、配位子由来の吸収が 95%減少した。一方、$Eu(PhDK)_3$ NPs 水溶液では、48%に留まることがわかった(Fig. 1b)。複核の $Eu_2(BTP)_3$ でも同様に、NPs 水溶液ではより高い光耐久性を示した。さらに $Eu_2(BTP)_3$ NPs では、水溶性ナノ粒子化による発光量子収率の減少が $Eu(PhDK)_3$ NPs よりも小さいことが明らかになった。

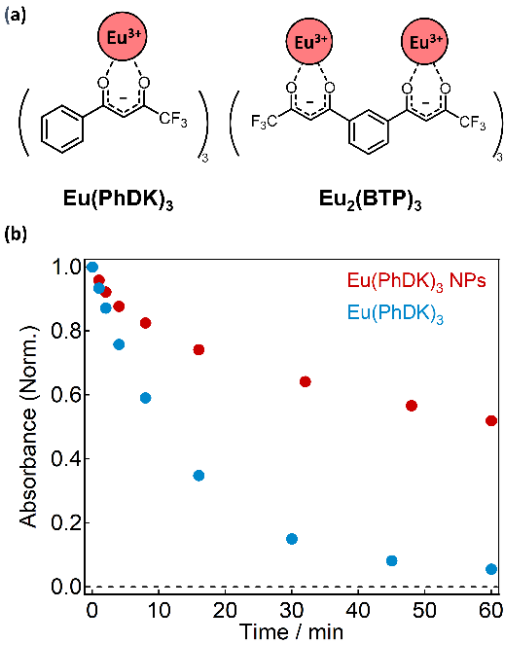

Fig.1 (a) Molecular structures of the Eu(III) complexes. (b) Relative absorbance at 321 nm under light irradiation (365 nm, 600 mW cm^{-2}) to $Eu(PhDK)_3$ in acetonitrile and $Eu(PhDK)_3$ NPs in water.

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フッ化四ケイ素雲母の層間にインターカレートされた芳香族アミンのクロミズムと分子配向の検討

（電機大院工）○木下麗羅・石丸臣一
Investigation of chromism and molecular orientation of aromatic amine intercalated between layers of tetrasilicicfluormica (*Graduate School of Engineering, Tokyo Denki University*)
○Reira Kinoshita, Shin'ichi Ishimaru

Chromism is a phenomenon in which the color of a substance changes reversibly in response to external stimuli. Vapochromism, in which a color change occurs due to vapor, is an example of a chemical substance that is used as external stimuli. Because it can detect volatile organic compounds with a color change, it is expected to be used as the chemical sensors to detect harmful organic compounds in the environment. Several vaporochromic materials have been reported so far, but most are complexes of minor metals such as platinum. Therefore lower-cost and more readily available materials are desirable. We have previously demonstrated that a composite material "TMB-mica" obtained from 3,3',5,5'-tetramethylbenzidine (TMB), a simple organic compound, and a clay mineral (mica), which is an environmentally friendly substance, changes the color when exposed to acetonitrile and water. We found that the TMB molecules in the intercalation compounds took two orientations, parallel and perpendicular, to the clay layers. The higher the TMB content, the more the perpendicular component. The sample color was yellow with less TMB content and green with more TMB content. In this research, we investigated time variation of XRD patterns after exposure to solvent vapor to clarify the mechanism of chromism in this material. The orientation of TMB gradually changed from parallel to perpendicular as the amount of adsorbed solvent molecules increased. In the presentation, we also report on studies using different types of clay minerals.
Keywords : Chromism; Clay minerals; Acetonitrile; Chemical sensors; 3,3',5,5'-tetramethylbenzidine

クロミズムとは、外部刺激によって物質の色が可逆的に変化する現象である。化学物質を外部刺激とするものとして、蒸気によって色変化が生じるベイポクロミズムが挙げられる。揮発性有機化合物を色の変化によって検知できるため、環境中の有害有機化合物を検知する化学センサーとしての利用が期待される。ベイポクロミック材料はこれまでにもいくつか報告されているが、多くは白金などレアメタルの錯体であり、より安価で入手しやすい材料が望ましい。我々は以前に、単純な有機化合物である3,3',5,5'-テトラメチルベンジジン(TMB)と環境調和性の高い粘土鉱物(mica)から得られる複合材料 TMB-mica のアセトニトリルや水に対するベイポクロミズムを報告した。以前の調査の結果、TMB は粘土層間で層に対して平行に配向している成分と垂直に配向している成分が混在していることがわかっている。TMB 含有量が多いほど垂直成分が多くなる。試料の色は TMB 含有量の少ないものは黄色で、多いものは緑色であった。そこで本報告では、TMB-mica のクロミズムのメカニズムを検討するため、色調に対して TMB の分子配向に違いがあることに着目し、溶媒蒸気曝露後の XRD パターンの時間変化を調査した。溶媒分子の吸着量の増加によって TMB の配向が徐々に平行から垂直に変化した。発表ではホストである粘土鉱物の違いによる変化についても報告する予定である。

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黄色発光 Dy 水酸化物ナノ粒子ベース複合膜の合成

（島大院自然科学）○宮崎　英敏・加藤　航
Fabrication of Yellow Luminescent Dy Hydroxide Nanoparticle-Based Composite Films
([1]*Graduate School of Natural Science, Shimane University*) Hidetoshi Miyazaki, Wataru, Kato

Dysprosium (Dy)-based phosphors are used as complementary color materials for blue light-emitting diodes. Furthermore, Dy-based fiber lasers are expected to be the next-generation high-power mid-infrared laser light source. In this study, yellow-emitting Dy-based composite films were prepared using anhydrous dysprosium nitrate $Dy(NO)_3$ and urethane resin, and their microstructures and fluorescence properties were evaluated. By increasing the amount of water added during membrane synthesis, permeation was observed in the resulting membranes, but the Dy^{3+} derived 570 nm emission peak increased. Infrared absorption spectra showed that the Dy-OH absorption peak increased as the amount of water added in the sample increased, confirming that the 570 nm peak emission was derived from Dy-OH based particles. Transmission electron microscopy showed that the particles were a few nm in diameter, and it was inferred that Dy-OH nanoparticles were responsible for the yellow 570 nm emission.
Keywords : Composites; Dysprosium; photoluminescence

ジスプロシウム(Dy)を用いた蛍光体は青色発光ダイオードの補色材料に用いられており、さらには Dy 系ファイバー レーザーは次世代の高出力中赤外レーザー光源として期待されている。本研究では、無水硝酸ジスプロシウム $Dy(NO)_3$ とウレタン樹脂を用いて、黄色発光 Dy ベース複合膜を作製し、微構造および蛍光特性を評価した。膜を合成する際に、水の添加量を増加させることで、得られた膜は失透が観察されたが、Dy^{3+}由来の 570nm 発光ピークは増大した。赤外吸収スペクトルで確認した所、試料中の水添加量が増加するに従って Dy-OH 吸収ピークが増大したことから、570nm ピークの発光は Dy-OH ベース粒子由来であることが確認された。透過型電子顕微鏡観察では粒子が数 nm であることが観察され、Dy-OH ナノ粒子が黄色 570nm 発光に起因することが推察された。

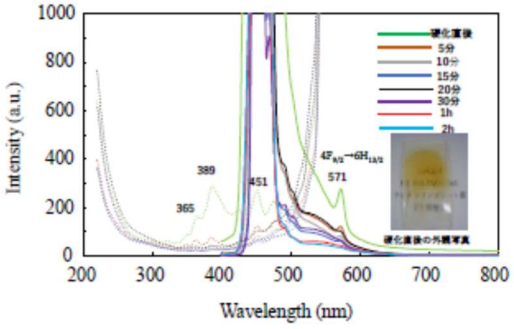

図 1. Dy-コンポジット膜の蛍光および励起スペクトル

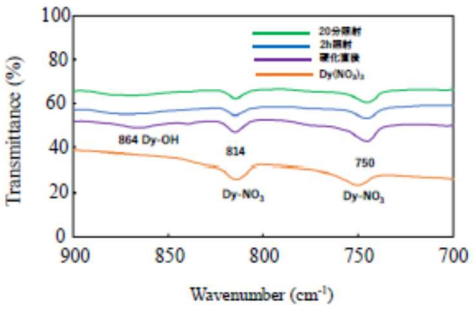

図 2. Dy-コンポジット膜の FT-IR スペクトル

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層状複水酸化物への複合化によるめっき膜腐食抑制剤徐放材料の開発

（静岡大院工[1]・神谷理研[2]・静岡大工[3]）○滝 純名[1]・小玉 大雄[2]・河野 芳海[3]
Development of slow-release material of corrosion inhibitor for plating film by the intercalation into layered double hydroxide ([1]*Graduate School of Engineering, Shizuoka University*, [2] *Kamiya Riken Co.*, [3] *School of Engineering, Shizuoka University*) ○Junna Taki,[1] Daiyu Kodama,[2] Yoshiumi Kohno[3]

Phosphinic acid (PA) can be expected to protect the plating film as an internal corrosion inhibitor. However, PA cannot work as the corrosion inhibitor for a long time because of its instability. In this study, PA was intercalated into the interlayer of anion-exchangeable layered double hydroxides (LDH) to give a slow-release ability.

The composites (PA/LDH) were prepared by coprecipitation method. Raw materials of LDH, divalent and trivalent metal nitrates, were mixed in an aqueous solution, and the sodium salt of PA was dropped into the solution with NaOH to incorporate PA into the interlayer during the formation of the LDH layered structure. PA/LDH was stirred in water to test the slow-release ability of PA from the interlayer of composites. The released PA was determined by oxidation-reduction titration with $KMnO_4$ to calculate the release rate of PA.

The result of the slow-release test is shown in Fig. 1. Continuous release of PA was still observed after 96 h of stirring, showing that PA remained in the interlayer of LDH. Therefore, we concluded that PA was composited not on the surface of LDH but in the interlayer and immobilized by an electrostatic interaction with the hydroxide sheet of LDH.

We will further report the effects of metal species and layer charge density of LDH on the amount of intercalated corrosion inhibitor and slow-release ability.

Keywords： Phosphinic Acid; Corrosion Inhibitor; Plating; Layered Double Hydroxide; Slow-release

次亜リン酸（PA）をめっき膜中に添加すると腐食抑制剤として働くため，めっき膜の保護が期待される。しかし，PA は不安定な物質なので，腐食抑制効果の長期継続が課題である。本研究では，アニオン交換性を有する層状複水酸化物(LDH)の層間へ PA を複合化することで徐放性能を付与した。

複合体(PA/LDH)は，LDH の原料である二価と三価の金属硝酸塩の混合溶液に，PA のナトリウム塩を NaOH 水溶液と共に滴下し，得られた懸濁液を加熱して LDH 層構造の生成時に PA を層間に取り込む共沈法により調製した。得られた PA/LDH を水中で攪拌し，複合体の層間から溶出する PA の徐放性能を確認した。溶出した PA を過マンガン酸カリウムによる酸化還元滴定で定量し，PA の放出率を算出した。

Mg-Al LDH での徐放試験結果を Fig. 1 に示す。96 h 攪拌後も，PA の徐放が確認され，LDH の層間に PA が残存していた。このことから，PA は LDH の表面ではなく，層間に複合化され，LDH の水酸化物シートとの静電相互作用によって層間に PA が固定化されたと考えた。

さらに，LDH の金属種や層電荷密度が，腐食抑制剤の複合化量と徐放性能に与える影響を報告する。

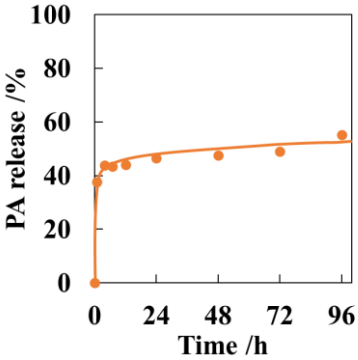

Fig. 1 Time course of released PA from PA/LDH prepared by coprecipitation.

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安定な緑色着色材としてのクロロフィル/有機修飾粘土複合体

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○上田　あすか[1]・河野　芳海[2]・柴田　雅史[3]・渡部　綾[2]・福原　長寿[2]

Chlorophyll/organo-modified clay composites as a stable green colorant

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○Asuka Ueda[1], Yoshiumi Kohno[2], Masashi Shibata[3], Ryo Watanabe[2], Choji Fukuhara[2]

The use of chlorophyll (Chl) as a colorant requires improved stability. In this study, we tried to improve the photostability of Chl by the adsorption between hydrotalcite (HT) interlayers organo-modified with anionic surfactants.

Lauric acid (C12), myristic acid (C14), and stearic acid (C18) were used as surfactants. The organo-modified HT (o-HT) was prepared by a conventional reconstruction method. The composites Chl/o-HT were prepared by the adsorption of Chl dissolved in MeOH on o-HT. As a reference sample, a composite Chl/S was prepared by mixing silica (S) and Chl. Each composite was irradiated with visible light from 100 W halogen lamp, and the photostability was evaluated from the degradation rate approximated by a first-order reaction.

Fig. 1 shows the degradation rate analysis of each Chl composite under visible irradiation. Chl/o-HT was more photostable than Chl/S, showing that the adsorption between the layers inhibited the contact of Chl with oxygen. Since the stability of composites with C12 and C14 were especially high, we concluded that the stability depended on the packing density of the surfactant between the layers.

Keywords : light stability; colorant; hydrotalcite; chlorophyll; surfactant

クロロフィル(Chl)を着色材として使用するには安定性の向上が必要である。本研究では，ハイドロタルサイト(HT)層間をアニオン性界面活性剤で有機修飾し，層間を疎水性にすることで Chl を HT 層間へ吸着し，光安定性の向上を試みた。

界面活性剤として，ラウリン酸(C12)，ミリスチン酸(C14)，ステアリン酸(C18)を用いた。有機修飾した HT (o-HT)は再構築法で調製した。これに Chl のメタノール溶液を加え，Chl を疎水的相互作用により o-HT に自発吸着させた複合体を調製した(Chl/o-HT)。参照試料として多孔質シリカ(S)と Chl を物理混合した複合体を調製した(Chl/S)。各複合体に 100 W ハロゲンランプからの可視光を照射し，一次反応近似した劣化速度から光安定性を評価した。

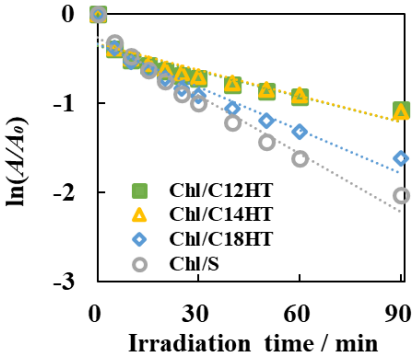

Fig.1 First-order degradation rate analysis of each Chl composites during 90 min of visible irradiation.

Fig. 1 に各 Chl 複合体の可視光照射下での劣化速度解析を示す。Chl/o-HT は Chl/S よりも光安定性が高かった。Chl/o-HT では Chl が HT 層間で保護され，劣化要因である酸素と Chl との接触が抑制されたため光安定性が向上したと考えた。特に C12 と C14 での光安定性が高いことから，光安定性は HT 層間での界面活性剤の充填密度に依存すると考えている。

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カルボキシ基導入単分子磁石の合成と気液界面を利用した薄膜の構築

(奈良女大理[1])○山田 実季[1]・溝口 茜子[1]・堀井 洋司[1]・梶原 孝志[1]

Metal-organic nanosheet composed of single-molecule magnet ([1]*Nara Women's University*) ○Miki Yamada,[1] Akane Mizoguchi,[1] Yoji Horii,[1] Takashi Kajiwara[1]

Single-molecule magnets (SMMs) can be applied to ultrahigh-density magnetic memory because of their magnetic bistability at the molecular level. However, the formation of two-dimensional arrays with homogeneous and large areas to access an individual has been a challenge. Recently, our group has succeeded in constructing thin films with perpendicular magnetic anisotropy, by the reaction single-molecule magnets involving pyridyl groups and Pd^{2+} ions as linkers at air-liquid interface[1].

In this study, we synthesized a new SMM with carboxyl groups as coordination sites and reacted it with Cu^{2+} ions at air-liquid interface to construct a thin film (**1**) with a paddle-wheel structure. **1** deposited on a quartz substrate exhibited successive increase in absorbance upon layer-by- layer process, indicating successful stacking.

Keywords : single-molecule magnets, thin film, metal-organic frameworks

分子でありながら磁石としての性質を有する単分子磁石は、超高密度記録媒体への応用が期待されているが、均一かつ大面積な二次元配列の形成が課題となっている。当研究室では、配位サイトとしてピリジル基を有する単分子磁石とリンカーであるPd^{2+}イオンを気液界面で反応させることで磁気記録媒体に有利な垂直磁気異方性を有する薄膜を構築することに成功している[1]。

今回、より強固な薄膜の構築を目指して、配位サイトとしてカルボキシ基を導入した単分子磁石を新規に合成し、気液界面でリンカーである Cu^{2+}イオンと反応させることでパドルホイール骨格を有する薄膜 (**1**) を構築した(図 1)。**1** を石英基板に転写し薄膜の吸収スペクトルを測定したところ、積層プロセスの繰り返しにともなう吸光度の上昇が見られ、layer-by-layer 法による積層化が可能であることが明らかになった(図 2)。

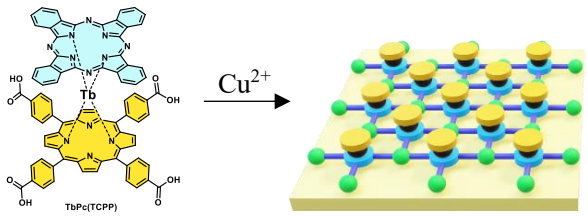

図 1. 単分子磁石と Cu^{2+}との気液界面における反応

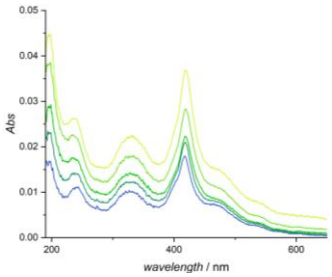

図 2. 積層化にともなう吸光度の上昇

[1] I. Aratani *et al., J. Mater. Chem. C,* **2023**, *11*, 2082–2088

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磁気応答性を持つ酸化鉄担持金ナノキューブの調製とアルコール酸化反応の触媒特性評価

（東京理科大学）○長船 六海・河原 莉子・伊村 芳郎

Preparation of Au nanocubes supported on magnetic Fe_3O_4 and its catalytic performance of alcohol oxidation reaction (*Tokyo University of Science*)○Mutsumi Nagafune, Riko Kawahara, Yoshiro Imura

The catalytic property of Au nanocrystals is changed by their shape and support.[1)] Au nanocrystals with magnetic response are expected as novel nanomaterials for easy recovery and reuse.[1)] Previously, we reported that the catalytic activity of alumina-supported Au nanocubes was higher than that of supported spherical Au nanoparticles of similar size. In this study, we prepared Fe_3O_4-supported Au nanocubes with magnetic response and examined the catalytic performance. The Au nanocubes were prepared by reducing gold ions in an aqueous solution containing cetyltrimethylammonium chloride (CTAC) and ascorbic acid. TEM image showed Au nanocubes were obtained (Figure 1). Au nanocubes were supported on Fe_3O_4 and washed with water for the removal of CTAC. Fe_3O_4-supported Au nanocubes had a magnetic response and high catalytic performance for the oxidation reaction of 1-phenylethyl alcohol.
Keywords : Nanocube; Gold; Nanocrystal; Magnetic response

ナノキューブやナノフラワーなどの異方形態金ナノ結晶は、特異的な触媒特性を示すことが知られている[1)]。また、磁気応答性を持つナノ結晶は、使用後の回収が容易なため、新規な機能性ナノ材料として期待されている[1)]。これまでにアルミナ担持金ナノキューブが、1-フェニルエチルアルコールの酸化反応に対して、担持球状金ナノ粒子よりも高い触媒活性能を示すことを報告した。そこで本研究では、磁気応答性を持つ四酸化三鉄に担持した金ナノキューブを調製し、その触媒特性について検討した。

金ナノキューブの調製は、保護剤であるセチルトリメチルアンモニウムクロリド(CTAC)水溶液に塩化金酸を加えた後、アスコルビン酸を用いて還元することで行った。透過型電子顕微鏡(TEM)観察を行ったところ、Figure 1のような金ナノキューブを形成していることがわかった。四酸化三鉄担持金ナノキューブは、金ナノキューブ分散溶液を水により数回洗浄し、四酸化三鉄を加えた後に 24 時間攪拌して調製した。担持後に水で洗浄し、CTAC の除去を行った。担持洗浄後もナノキューブの形状に変化はなかった。さらに、調製した四酸化三鉄担持金ナノ結晶は、磁気応答性を持つこともわかった。触媒特性は、1-フェニルエチルアルコールからアセトフェノンを生成する酸化反応を用いて調べた。その結果、四酸化三鉄担持金ナノキューブは磁気応答性を持つだけでなく、アルミナ担持金ナノキューブと同様に高い触媒活性能を示すことも分かった。

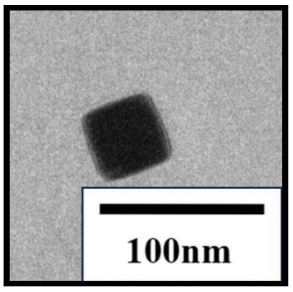

Figure 1. TEM image of Au nanocube.

1) Y. Imura, R. Kan, R. Akiyama, H. Saito, C. Morita-Imura, T. Kawai, *ACS Omega*, **2020**, *5*, 15755-15760.

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酸化セリウム担持半球状金ナノフラワーの調製とアルコール酸化反応に対する触媒性能

（東京理科大学）○神尾 悠太・春日 あすか・伊村 芳郎
Preparation of hemispherical gold nanoflowers supported on cerium oxide for alcohol oxidation reaction (*Tokyo University of Science*)○Yuta Jino, Asuka Kasuga, Yoshiro Imura

The catalytic properties of Au nanocrystals depend on shape and support. Previously, we reported Au nanoflowers supported on alumina showed high catalytic performance for alcohol oxidation.[1)] Cerium oxide support is expected to be more effective than alumina in improving catalytic activity. Moreover, it is known that increasing the Au/support interface leads to improvement of the catalytic activity. In this study, we prepared Au nanoflowers and hemispherical Au nanoflowers supported on cerium oxide and examined catalytic performance for the alcohol oxidation reaction. The catalytic performance of cerium oxide-supported Au nanoflowers was higher than alumina-supported Au nanoflowers. In addition, cerium oxide-supported hemispherical Au nanoflowers with large Au/support interface showed high catalytic performance compared to cerium oxide-supported Au nanoflowers.
Keywords : Nanoflower; Gold; Cerium Oxide; Alcohol oxidation

金ナノ結晶の触媒特性は、形態や担持する担体による影響を強く受けることが知られている。これまでに、アルミナ担持金ナノフラワーがアルコール酸化反応に対して高い触媒活性能を持つことを報告した[1)]。酸化セリウムはアルミナよりも触媒活性能の向上効果が高いため、担体として酸化セリウムを用いることで更なる触媒活性能の向上が期待できる。また、担体を用いた触媒活性能の向上効果は、担体と金ナノ結晶との接合界面部が大きくなるにつれ増加する。そこで本研究では、酸化セリウム担持金ナノフラワーと担持半球状金ナノフラワーを調製し触媒特性を評価した。

保護剤であるメラミンと塩化金酸からなる水溶液にアスコルビン酸を添加し、30分経過すると金ナノフラワーが形成し、その後、担体（アルミナあるいは酸化セリウム）を加えると担持金ナノフラワーが得られた。ここで、アスコルビン酸を添加後すぐに酸化セリウムを添加することで、担体との接合界面が大きい担持半球状金ナノフラワーが形成した。これらの担持金ナノ結晶を水で繰り返し洗浄し、保護剤除去後も形態に変化は見られなかった（Figure 1）。

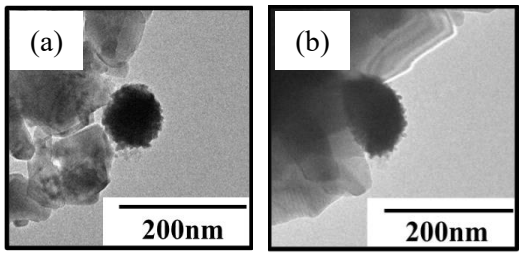

Figure 1 TEM images of (a) Au nanoflowers and (b) hemispherical Au nanoflowers supported on cerium oxide.

触媒特性は、1-フェニルエチルアルコールからアセトフェノンを生成する酸化反応を用いて評価した。その結果、酸化セリウムを担体として用いることで、金ナノフラワーの触媒活性能が向上することが示された。さらに、形状を半球状金ナノフラワーにすることでアセトフェノン生成速度が向上した。

1) Y. Imura, S. Furukawa, K. Ozawa, C. Morita-Imura, T. Kawai, T. Komatsu, *RSC advances*, **2016**, 6, 17222-17227.

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層状無機-イミダゾリン共有結合体添加による Ru(II)メタロ超分子ポリマーのエレクトロクロミック特性向上

（物材機構[1]・産総研[2]）○藤井　和子[1]、Dines Chandra Santra[1]、Manas Kumar Bera[1]、坂田　和彦[1]、若原　孝次[1]、長畑　律子[2]、樋口　昌芳[1]

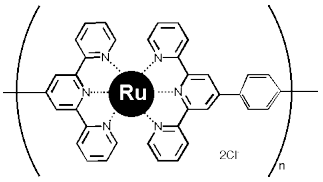
Improved Electrochromic Properties and Addition of Layered Inorganic-imidazoline Covalently Bonded Hybrid for Ru(II)-based Metallo-supramolecular Polymer

([1]*National Institute for Materials Science,* [2]*National Institute for Advanced Industrial Science and Technology*) ○Kazuko Fujii,[1] Dines Chandra Santra,[1] Manas Kumar Bera,[1] Kazuhiko Sakata,[1] Takatsugu Wakahara,[1] Ritsuko Nagahata,[2] Masayoshi Higuchi[1]

Metallo-supramolecular polymers (MSP) exhibit the metal-to-ligand charge transfer (MLCT) absorptions in visible reason. The appearance/disappearance of MLCT absorption is switched by the electrochemical redox of the metal ion in MSPs, namely MSPs are electrochromic (EC) materials.[1)] We have previously reported improvements in the EC properties, e.g., optical memory of Ru(II)-based MSP (**polyRu**, **Scheme**) by adding layered inorganic-imidazoline covalently bonding hybrids (LIIm).[2)] LIIm is an inorganic-organic hybrid consisting of inorganic layers and imidazolyl group locating between and covalently bonding with the inorganic layers.[3)] In this work, we study properties of composites consisting of **polyRu** and LIIm and discuss the improved EC properties.

PolyRu and LIIm were synthesized as per previous reports.[1, 3)] LIIm was added to **polyRu** to prepare **polyRu**-LIIm composites. Spin-coated films and EC devices of **polyRu**-LIIm composites were prepared. These samples were characterized by thermogravimetric and differential thermal analysis (TG-DTA), cyclic voltammetry, *in-situ* spectro-electrochemical measurements, and so on.

Keywords : Metallo-supramolecular polymer, Electrochromism, Layered material, Layered inorganic-organic hybrid, Ruthenium



Scheme. Ru(II)-based MSP (polyRu)

メタロ超分子ポリマー(MSP)では、金属から有機リガンドへの電荷移動吸収（MLCT）を制御することでエレクトロクロミック（EC）特性が発現する[1)]。MSP の記憶特性等 EC 特性の向上を層状無機-イミダゾリン共有結合体（LIIm）との複合化により既に達成した[2)]。LIIm は層状の無機部分とイミダゾリン基が共有結合で一体化した層状の化合物である[3)]。本研究では、金属イオンがルテニウムの MSP（**polyRu**, **Scheme**)と LIIm の複合体の特性を評価し、EC 特性向上について議論する。

PolyRu 及び LIIm は、既報[1, 3)]に従い合成した。**PolyRu** に LIIm を添加し、**polyRu**-LIIm 複合体を調製した。また、**polyRu**-LIIm 複合体のスピンコート膜やデバイスも作製した。これらの試料は、熱重量-示差熱分析（TG-DTA)、サイクリックボルタンメトリー、*in-situ* 電気化学-分光測定等で評価した。これらの評価結果に基づき、**polyRu**-LIIm 複合体の EC 特性の向上について議論する。

1) Han, F. et al, *J. Am. Chem. Soc.*, (2008)　2) Fujii, K. et al., *ACS Appl. Polym. Mater.* (2023)
3) Fujii, K. et al., *J. Inorg. Organometallic Polym. Mater.* (2021)

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リン酸ジルコニウムへのジェミニ型第四級アンモニウムのインターカレーション

（金沢工業大学[1]）○勝崎 大耀[1]・春日 丈[1]・附木 貴行[1]・吉村 治
Intercalation of gemini quaternary ammonium into zirconium phosphate ([1] *Kanazawa Institute of Technology*) ○ Hiroaki Katsuzaki[1], Takeru Kasuga[1], Takayuki Tsukegi[1] and Osamu Yoshimura[1]

Gemini quaternary ammonium salts (QAS) have two hydrophilic groups and two hydrophobic chains in one molecule or exhibit high antibacterial activity against Gram-positive and Gram-negative bacteria, as well as a broad antibacterial spectrum. The purpose of this research is to intercalate α-type zirconium phosphate (α-ZrP) and γ-type zirconium phosphate (γ-ZrP) into Gemini QAS salt, and evaluate and compare the antibacterial performance, heat resistance, and water resistance. As a result, it was found that the interlayer distance of the γ-composites was wider than that of the α-composites. Regarding heat resistance, weight loss was observed between 200°C and 330°C for both α- and γ-composites, and weight loss was suppressed compared to Gemini QAS alone, confirming improved heat resistance. Based on the content of Gemini QAS in the composites, Gemini QAS with short spacers such as **12-2-12** and **12-3-12** in α-ZrP is thought to bind to one adsorption site per molecule. Both α- and γ-composites showed high antibacterial activity. It was also found that the antibacterial performance depends on the antibacterial performance of the inserted Gemini QAS. The samples of **12-5-12**/α-ZrP and **12-5-12**/γ-ZrP exposed at 300°C for 10 minutes maintained high antibacterial performance without any significant decrease in antibacterial performance. **【197 words】**

Keywords : Gemini QAS; Antimicrobial; Inorganic layered compounds, Intercalation **【4 words】**

ジェミニ型第四級アンモニウム（QAS）は、1 分子中に親水基、疎水鎖を 2 つ有し、グラム陽性菌やグラム陰性菌に対して高い抗菌活性、また、広い抗菌スペクトルを持つ。本研究の目的は、α 型リン酸ジルコニウム（α-ZrP）と γ 型リン酸ジルコニウム（γ-ZrP）にジェミニ型 QAS をインターカレートし、特性の評価を行い、抗菌性能、耐熱性、耐水性が優れた複合体の比較検討を行う。その結果、γ-複合体の層間距離が α-複合体よりも広いことがわかった。耐熱性については、α-複合体、γ-複合体ともに 200℃-330℃の間で重量減少が見られたが、ジェミニ型 QAS 単体と比較して重量減少が抑制され、耐熱性が向上していることが確認された。 複合体のジェミニ型 QAS の含有量から、α-ZrP に **12-2-12** や **12-3-12** などの短いスペーサーのものは、1 分子あたり ZrP 層間の一つの吸着サイトに結合したと示唆された。α-複合体および γ-複合体は、いずれも高い抗菌活性を示した。また、複合体の抗菌性能はインターカレートされたジェミニ型 QAS の抗菌性能に依存することが判明した。**12-5-12**/α-ZrP 、**12-5-12**/γ-ZrP を 300℃、10 分間曝露した試料は、抗菌性能の大幅な低下もなく、高い抗菌性能を維持した。**【464 文字】**

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アルミナ担持表面凹型金ナノロッドの調製とアルコール酸化反応に対する触媒特性

（東京理科大学）○木下 公介・伊村 芳郎
Preparation of concave gold nanorods supported alumina for alcohol oxidation reaction
(*Tokyo University of Science*) ○Kousuke Kinoshita, Yoshiro Imura

Anisotropic nanocrystals are attractive as catalysts with novel catalytic performance. Previously, we reported that alumina-supported Au nanorods had a high catalytic performance for alcohol oxidation compared with alumina-supported spherical Au nanoparticles.[1)] In this study, we prepared concave Au nanorods (AuCNRs) supported on alumina and examined their catalytic performance for oxidation reaction from 1-phenylethyl alcohol to acetophenone. The AuCNRs were prepared with the seed growth method using cetyltrimethylammonium bromide as a capping agent. Alumina-supported AuCNRs were obtained by adding alumina powder to the dispersion. In addition, we prepared alumina-supported spherical Au nanoparticles by heating alumina-supported AuCNRs at 200°C to compare their catalytic activity. The acetophenone formation rate of alumina-supported AuCNRs was higher than that of alumina-supported spherical Au nanoparticles.
Keywords : Nanorod; Gold; Nanocrystal; Alcohol oxidation reaction

異方形態金ナノ結晶は、球状金ナノ粒子とは異なる触媒特性を持つことが知られている[1)]。これまでに、アルコール酸化反応に対して、アルミナ上に担持した金ナノロッドが球状金ナノ粒子よりも高い触媒活性能を示すことを報告した[1)]。金ナノロッドの側面が凹型となった表面凹型ナノロッドにおいても、高い触媒活性能が期待できる。そこで、本研究ではアルミナ担持表面凹型金ナノロッドを調製し、その触媒特性を評価した。

表面凹型金ナノロッドは、保護剤にセチルトリメチルアンモニウムブロミド（CTAB）を用いたシード成長法により合成した (Fig.1)。さらに、表面凹型金ナノロッド分散液から CTAB を洗浄操作により取り除いた後に、アルミナを加えることでアルミナ担持表面凹型金ナノロッドを得た。担持表面凹型金ナノロッドに UV オゾン処理を行った後に、触媒特性評価を行った。また、形状による影響について調べるため、担持表面凹型金ナノロッドを 200℃で 3 時間焼成し、担持球状金ナノ粒子を調製した。触媒特性は、1-フェニルエチルアルコールからアセトフェノンを生成する酸化反応により評価した。その結果、担持表面凹型金ナノロッドは、担持球状金ナノ粒子よりも高いアセトフェノン生成速度を示すことがわかった。

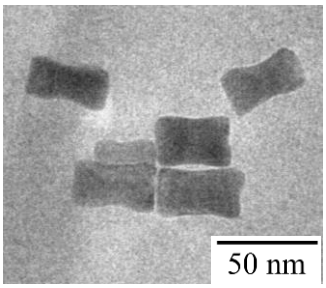

Fig. 1 TEM image of concave Au nanorods.

1) Y. Imura, K. Fukuda, H. Saito, M. Maniwa, Y. Kurihara, C. Morita-Imura, T. Kawai, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 1685-1689.

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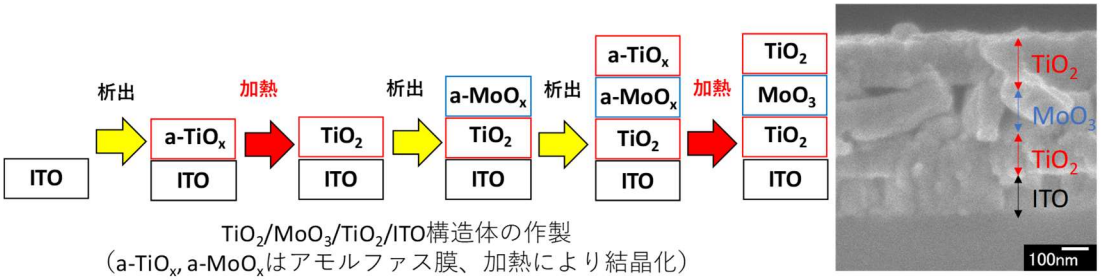
光学材料を目指した金属酸化物積層体の電解析出

（阪技術研[1]・阪電通大工[2]・阪電通大院工[3]）○渡辺　充[1]・三枝　佑路[2]・伊藤　尚晃[2]・榎本　博行[2,3]・渡瀬　星児[1]
Formation of Metal Oxide Multilayer for Optic Materials by Electrochemical Depositions
([1]*Osaka Research Institute of Industrial Science and Technology*, [2]*Osaka Electro-Commun. Univ.*, [3]*Grad. Sch. Of Eng., Osaka Electro-Commun. Univ*) ○Mitsuru Watanabe,[1] Yuro Saegusa,[2] Naoaki Ito,[2] Hiroyuki Enomoto[2,3] Seiji Watase[1]

We have been investigating the deposition of metal oxides by electrochemical method. Electrodeposition is a simple method, which is able to carry out under ambient condition of aqueous solution with relatively inexpensive apparatus. We have achieved the formation of transparent titanium oxide thin film on a transparent electrode by electrodeposition. In this report, we have tried the formation of transparent multilayer of titanium oxide and molybdenum oxide and achieved to obtain transparent $TiO_2/MoO_3/TiO_2$/ITO tri-layer structure. Such structure is potentially optic material because the difference of refractive index between titanium oxide and molybdenum oxide is sufficiently large. Since both TiO_2 and MoO_3 as-deposited films are amorphous, heat treatment of the films is required for the crystallization. Although MoO_3 layer will be broken by usual crystallization, transparent tri-layer structure could be obtained because MoO_3 layer was supported by TiO_2 layer in the both sides. Their formation conditions and optical properties will be reported.
Keywords : Electrodeposition; Transparent oxide films; Titanium oxide; Molybdenum oxide; Optic materials

電解析出法は比較的簡素な装置を用いて室温の水溶液から電極上に析出させる手法であり、我々はそれを用いて金属酸化物の析出について検討してきた。我々はこれまで、電解析出法によって透明電極上に透明な酸化チタン膜を形成することに成功している。今回、酸化チタンと酸化モリブデンの透明な積層体について検討した結果、$TiO_2/MoO_3/TiO_2$/ITO という３層の構造体を作製することができた。酸化チタンと酸化モリブデンは比較的大きな屈折率差があるため、このような構造体は光学材料として利用できる可能性がある。As Depo の膜では酸化チタン、酸化モリブデンはいずれもアモルファスであり、結晶化のために熱処理が必要である。特に、酸化モリブデンは結晶化の際に膜が崩壊してしまうため、酸化チタン膜に挟んだ状態で熱処理を行うことで透明な構造体が得られた。構造体の作製条件やその光学特性について報告する。



$TiO_2/MoO_3/TiO_2$/ITO構造体の作製
（a-TiO_x, a-MoO_xはアモルファス膜、加熱により結晶化）

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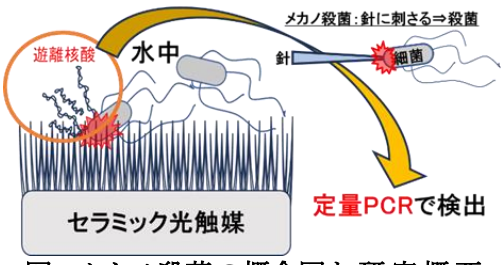
水中におけるメカノ殺菌効果評価法の検討

（千葉工大院[1]・産総研[2]）○鳥羽 悟史[1,2]・山野 凌[1,2]・宮崎 ゆかり[2]・根岸 信彰[2]・黒﨑 直子[1]
Study of evaluation method for the mechano-bactericidal effect in water ([1] *Graduate School, Chiba Institute of Technology,* [2] *National Institute of Advanced Industrial Science and Technology*) ○Satoshi Toba,[1,2] Ryo Yamano,[1,2] Yukari Miyazaki,[2] Nobuaki Negishi,[2] Naoko Kurosaki,[1]

Particularly in developing countries, drinking water contaminated with microorganisms is a significant issue, leading to the spreading of infectious diseases. This is due to economic factors such as the lack of water purification facilities. Meanwhile, developing countries have high solar radiation levels, so it's thought that water purification by inexpensive titanium dioxide photocatalysts using sunlight is feasible. However, there is a problem that the performance of photocatalytic disinfection is affected by weather conditions such as low UV radiation. Therefore, we focused on mechano-bactericidal phenomenon[1]. This effect is a phenomenon that which bacteria are sterilized when they pierce the needle structure. By supporting them on photocatalysts, we expect that mechano-bactericidal effect and photocatalytic sterilization will become a water purification technology unaffected by weather conditions.

This study evaluated the mechano-bactericidal effect using aragonite of needle structure supported on photocatalysts. Currently, little is known about the mechano-bactericidal effect in water and there is no established evaluation method. Therefore, an evaluation method for the mechano-bactericidal effect in water was investigated. As a result, the quantitative PCR method can be used to detect eluted DNA outside the bacteria due to the effect, and it is useful as an evaluation method for that effect in water.

Keywords：waterborne disease, photocatalyst, mechano-bactericidal effect, water purification, aragonite



図．メカノ殺菌の概念図と研究概要

途上国を中心に微生物汚染された飲料水による水系感染症が問題となっている。この原因として、経済的要因による水浄化設備の未整備が挙げられる。一方で、途上国は日射量が多いことから、太陽光を利用した安価な酸化チタン光触媒による水浄化が可能と考えられている。しかし、光触媒殺菌の性能が紫外線低照射時など天候に左右される問題がある。そのため、光触媒に針状構造を担持し、針状構造に細菌が刺さることで殺菌される現象であるメカノ殺菌効果[1]を付与することで、天候に左右されない水浄化技術になると期待できる。

本研究では、光触媒に担持した針状アラゴナイトの水中におけるメカノ殺菌効果の評価を行った。今まで水中におけるメカノ殺菌効果は殆ど知られておらず、確立された評価法がないことから、その評価法を検討した。その一つとして、定量 PCR によるメカノ殺菌効果由来の菌体外に溶出した DNA の検出を検討した。その結果、水中メカノ殺菌の評価法として定量 PCR は有用であることが確認された。

1) Ivanova, E. P.et al. *Small,* 8(16),2489-2494 (2012).

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立体的に微細加工した温度応答性ハイドロゲルの動的な変形

（KUAS[1]・早大[2]）○長濱 峻介[1,2]

Dynamic deformation of three-dimensionally microfabricated temperature-responsive hydrogels. ([1]*Nagamori Institute of Actuators, Kyoto University of Advanced Science*, [2]*Future Robotics Organization, Waseda University*)○Shunsuke Nagahama[1,2]

We fabricated a mass-producible mold by transferring a pattern fabricated by grayscale lithography onto a flexible material, and developed a method for fabricating a micro-structured hydrogel using the mold. Since polymerization using only stimuli-responsive polymers caused polymerization failure when using a mold made of PDMS[1)], the molded gel was obtained by polymerizing NIPAM gel in the mold using Agar gel, a physical cross-linked gel, as a scaffold.

Using this technique, a structure was fabricated in which the hydrogel had a pattern with different surface area on the top and bottom surfaces of the transfer, resulting in a difference in deformation during contraction and swelling by the temperature-responsive polymer and bending (Fig. 1; a pattern designed with a diameter of about 100 um was used). Upon heating and cooling, the deformation behavior during heating and cooling in water was confirmed, as shown in Fig 2.

Keywords : Stimuli-responsive material; Hydro-gel; Micro-structure; Mold production;

グレースケールリソグラフィにより加工したパターンを柔軟材料に転写することで量産可能な型を製作し、その型を用いて微細構造を有するハイドロゲルを製作する手法を構築した。なお、PDMS で製作した型を用いた場合に刺激応答性ポリマーのみで重合すると重合不良を引き起こしたため [1)]，物理架橋ゲルである Agar ゲルを足場として NIPAM ゲルを型内で重合することで成型されたゲルを得た。

本技術を用いて、転写上面と下面で表面積の異なるパターンをハイドロゲルに持たせることで、温度応答性高分子による収縮・膨潤時の変形量の差が生じ屈曲する構造を製作した（図１。直径 100um 程度で設計したパターンを使用した）。加熱及び冷却により、図２のように水中での加熱・冷却時に変形する挙動が確認できた。

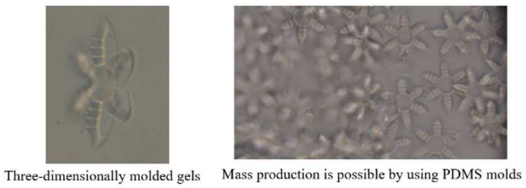

Fig.1 Molded gels with fine patterns

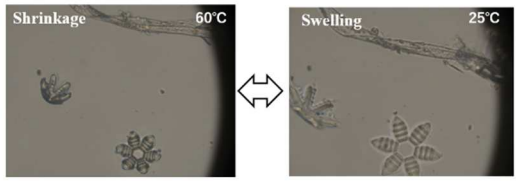

Fig.2 Shrinkage and swelling behavior due to heating and cooling

1) Polymerization failure when using PDMS molds has been reported. Shunsuke Nagahama, 71st SPSJ Annual Meeting, 2P3B021, 2022

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ジスルフィド化合物を用いた揮発性硫黄化合物の分離分析法の検討

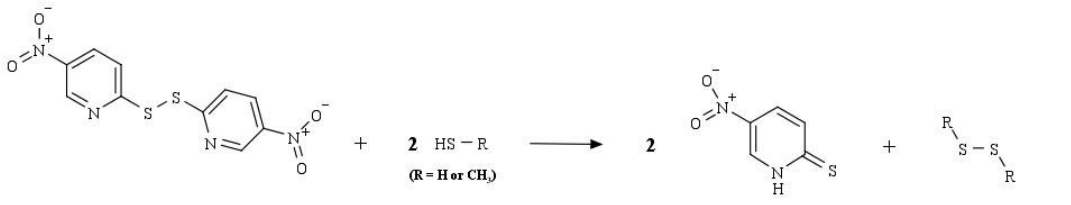
（東北工大院工 [1]）・○三浦 秀太 [1]・丸尾 容子 [1]

Separation and analysis of volatile sulfur compounds using disulfide compounds ([1]*Graduate School of Engineering, Tohoku Institute of Technology*) ○Shuta Miura,[1] Yasuko Yamada Maruo[1]

Hydrogen sulfide and methyl mercaptan, volatile sulfur compounds (VSCs) in exhaled breath, are known as biomarkers of periodontal disease. They have similar chemical structures, making them difficult for selective detection on various gas sensors, such as semiconductor gas sensors. We had developed a sensor element for VSC using a reaction between 2,2'-Dithiobis (5-nitropyridine) (DTNP) and VSC on fiber substrates. In this study, we focused on the reactivity and adsorption properties of hydrogen sulfide and methyl mercaptan on the sensor. When the sensor element was exposed to hydrogen sulfide and methyl mercaptan, respectively, both reacted with DTNP to generate 5-nitro-2-thiopyridine (NTP). The differences were observed in adsorption rate and NTP production rate between hydrogen sulfide and methyl mercaptan. Based on the results, we investigated a separation and analysis method for both chemicals and aimed to develop gas sensors capable of selective detection.

Keywords: Materials chemistry; Colorimetric analysis; Adsorption; Volatile sulfur compounds; Separation.

呼気中に含まれる揮発性硫黄化合物である硫化水素及びメチルメルカプタンは歯周病のバイオマーカーとして知られている。それらは化学構造が類似しており、半導体ガスセンサをはじめとした様々なガスセンサにおいてそれらを選択的に検出することが困難となっている [1)]。本研究では、ジスルフィド化合物である 2,2'-Dithiobis (5-nitropyridine)(DTNP)と繊維基板を組み合わせてガスセンサを作製し、ガス状硫化水素及びメチルメルカプタンのガスセンサに対する反応性、吸着特性の違いに着目した。作製したガスセンサを硫化水素及びメチルメルカプタンにそれぞれ曝露したところ、両者ともに DTNP と反応を示し、5-nitro-2-thiopyridine (NTP)が生成された。また、作製したガスに対する吸着速度、NTP 生成速度に有意差が見られた。これらを用いて両物質の分離分析法を検討し、選択的に検出可能なガスセンサを開発することを目的とした。



1) K. Lim et al. *Sensors and Actuators: B. Chemical* 2021, 348, 130665.

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多孔材料センサを用いたアセトン検出方法における基板種の検討

（東北工大院工[1]・東北工大[2]）○村山　海斗[1]・丸尾　容子[1]・坂野　聖[2]
Effect of substrates on an acetone detection using porous material-substrate sensors ([1]*Graduate School of Engineering, Tohoku Institute of Technology*, [2] *Tohoku Institute of Technology*) ○ Kaito Murayama,[1] Yasuko Yamada Maruo,[1] Sei Sakano[2]

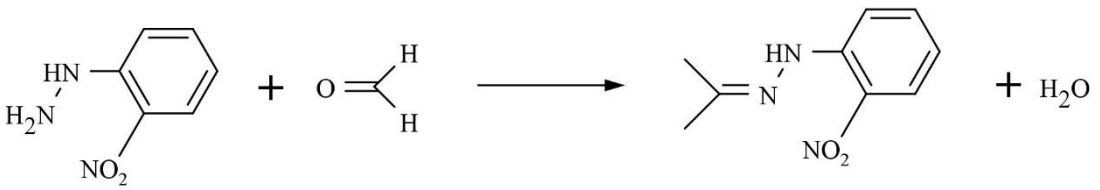
Human exhaled breath contains a variety of volatile organic compounds, some of which are associated with specific diseases. Since acetone in exhaled breath is associated with diabetes and lipid metabolism, we are developing a simple sensor element that could be a tool for health monitoring using the colorimetric reaction between acetone and nitrophenylhydrazine (NPH). In this study, we have evaluated the effect of substrate material on the sensor's performance. Three types of material were tested.

In the case of cellulose, the NPH reacted with the cellulose, and a spectral change was observed without exposing to acetone atmosphere. For a porous glass substrate, spectral changes dependent of the acetone concentrations were observed, and acetone could be detected in a short time with high sensitivity. When a quartz substrate containing organic binder was used, spectral changes similar to that of porous glass were observed, however the sensitivity was low (<one-tenth), and that thought to be different surface area.

Keywords : Acetone; Colorimetric Analysis; Porous Material

人間の呼気には様々な揮発性有機化合物が含まれており特定の疾患と関連のある物質が存在している。呼気に含まれるアセトンには糖尿病や脂質代謝に関連があることから、これを利用し健康管理のツールとして用いることのできる簡易センサを開発している。本研究では簡易センサにおいて検出に用いるアセトンとニトロフェニルヒドラジンの比色反応に及ぼす基板材料の影響について、3 種類の材料を用いて評価したのでその結果を報告する。

セルロースの基板では検出試薬がセルロースと反応しアセトンを曝露せずともスペクトル変化が見られ、アセトンセンサに用いることは不可能という結果となった。次に多孔質ガラスを用いた結果、短時間かつ高感度にアセトンを検出可能であるという結果が得られた。さらに有機バインダー入り石英基板を用いた結果、多孔質ガラスと似たスペクトル変化が見られたが表面積が狭いことも起因し、感度は多孔質ガラスの数分の一となった。



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Academic Program [Poster] | 22. Resources Utilization Chemistry, Environmental and Green Chemistry : Poster

Tue. Mar 19, 2024 10:00 AM - 11:30 AM JST | Tue. Mar 19, 2024 1:00 AM - 2:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-2am] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Japanese

[P2-2am-01]

Synthesis of sulfated cellulose pulp with a swollen fiber structure and application to completely dispersed cellulose nanofibers

○Ayato Nishimura[1], Sonoka Otsuka[1] (1. Marusumi Paper Co., Ltd.)

Japanese

[P2-2am-02]

Development and evaluation of water-based paint for wood using cellulose nano fiber and ultraviolet absorber

○Shunpei Kuma[1], Yuki Taguri[1], Keiji Hoaki[1], Masayuki Yano[1] (1. Industrial Technology Center of Saga)

Japanese

[P2-2am-03]

Effect of calcium salt additives on the crystal phase of calcined calcium phytate

○Kazuki Maeda[1], Yoshiki Aoto[1], Satoru Dohshi[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese

[P2-2am-04]

Preparation of transparent sulfated pulp desperation

○Sakura Morimitsu[1], Ayato Nishimura[1] (1. Marusumi Paper Co., Ltd.)

Japanese

[P2-2am-05]

Research on the development of an efficient degradation method for lignin and its application

○Tsubasa Kojima[1], Yoshiyuki Uruma[1], Tomohiro Yamada[2], Hirofumi Maekawa[2], Matsumi Doe[3], Kan Wakamatsu[4] (1. National Institute of Technology, Yonago College., 2. Nagaoka University of Technology, 3. Osaka Metropolitan University., 4. Okayama University of Science)

Japanese

[P2-2am-06]

Antibacterial activity of Polyethylene Glycol (PEG)-Modified Lignin

○Akane Sakaguchi-Mikami[1], Miku Takagi[1], Nagisa Hara[1], Takashi Yamashita[1] (1. Tokyo Univ. of Technology)

Japanese

[P2-2am-07]

Mechanical properties of network polymers based on epoxidized marine oils and preparation of bio-based composite

○Yohtaro Inoue[1] (1. Osaka Research Institute of Industrial Science and Technology)

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Japanese

[P2-2am-08]

Synthesis of MOFs using various metal ions with Azobenzene-4,4'-dicarboxylic acid ligands.

○Teppei Kagaya[1], Shigeki Furukawa[1] (1. College of Industrial Technology, Nihon University)

Japanese

[P2-2am-09]

Development of the detection method of pathogenic viruses in the environment water and its application

○Yuzu Ueki[1], Takeji Takamura[1] (1. Kanagawa Institute of Technology)

Japanese

[P2-2am-10]

Preparation of supported Ni catalysts using carbon nanotubes as supports and the investigation of their permanence in reduction reactions

○Yuika Aoki[1], Naoki Toyama[1], Hiroe Kimura[2], Norifumi Terui[2], Shigeki Furukawa[1] (1. Nihon University, 2. National Institute of Technology, Ichinoseki College)

Japanese

[P2-2am-11]

Synthesis of silica hollow spheres supported on transition metal catalysts and their reduction of *p*-nitrophenol

○Maki Ueshima[1], Kenzo Deguchi[2], Shinobu Ohki[2], Yuuki Mogami[2], Naoki Toyama[1], Shigeki Furukawa[1] (1. Nihon University, 2. National Institute for Materials Science)

Japanese

[P2-2am-12]

Capture of low concentration CO2 by using silica with amino groups

○Liao Hansheng[1], YAMAZOE SEIJI[1], KIKKAWA SOUICHI[1] (1. Tokyo Metropolitan University)

Japanese

[P2-2am-13]

Highly efficient capture and release system of low-concentration carbon dioxide using solid-liquid phase separation.

○Li Xuanbing[1], CAO FURONG[1], Souichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P2-2am-14]

Analyses of extracted compounds from bottle caps with organic solvents

○Keisuke Nakagawa[1], Yukimi Iwamoto[1], Masahiro Furutani[1], Tomoya Kataoka[2] (1. Natioal Institute of Technology, Fukui College, 2. Ehime University)

Japanese

[P2-2am-15]

Research in the cause of abnormal daily variation of ozone concentration in Ho Chi Minh City, Vietnam

○Norimichi Takenaka[1], Yusuke Fujii[1], Hien Thi To[2] (1. Osaka Metropolitan University, 2. Vietnam National University Ho Chi Minh)

Japanese

[P2-2am-16]

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Nitrite production from carbon dioxide on snow and ice surfaces in nature

○Arisa Hinoshita[1], Ayane Yamamura[1], Yusuke Fuji[1], Izumi Noguchi[2], Hiroki Motomichi[3], Keiichi Sato[4], Norimichi Takenaka[1] (1. Osaka Metropolitan University, 2. Hokkaido Research Organization Industrial Technology and Environment Research Headquarters Institute of Energy, Environment and Geology, 3. National Institute for Disaster Prevention Science and Technology Snow and Ice Disaster Prevention Research Center, 4. Asian Air Pollution Research Center Atmospheric Research Department)

Japanese

[P2-2am-17]

Synthesis of mesoporous silica-titania hollow spheres and their methylene blue decomposition and hydrogen generation reactions

○Naoki Toyama[1], Kouki Mizumura[1], Asa Hayashi[1], Shigeki Furukawa[1] (1. Nihon University)

Japanese

[P2-2am-18]

Studies on oil and fat accumulation and Triglyceride lipase gene expression in *Microchloropsis gaditana*

○Ayumu Watanabe[1], Tomoe Komoriya[1], Shigeki Furukawa[1] (1. Nihon University)

Japanese

[P2-2am-19]

Copper free Sonogashira coupling reaction catalyzed by a complex of palladium-bistheophyllines

○Katsuya Kaikake[1], Asuma Shingo[1], Ren-Hua Jin[1] (1. Kanagawa University)

Japanese

[P2-2am-20]

Effect of plasticisers, additives and stabilisers on the dechlorination reaction of polyvinyl chloride under hydrothermal conditions

○Satomi Hosokawa[1], Douglas Hungwe[1], Kenji Sugiyama[1], Yuki Yamasaki[1] (1. Hosei University)

Japanese

[P2-2am-21]

Preparation of a cation exchanger based on some biomass and adsorption characteristics of metal ions

○Takumi Akinaga[1], Yui Igaki[1], Ryuki Ikwda[1], Toshiyuki Miyauchi[2], Yuko Shikami[2] (1. Gradute of Chubu University, 2. Chubu University)

Japanese

[P2-2am-22]

Investigation of flow synthesis conditions utilizing Bayesian optimization of antimicrobial spike particles

○Takahiro Nakae[1], So Ito[1] (1. KRI, Inc.)

Japanese

[P2-2am-23]

Fabrication and Evaluation of Dye-sensitized Solar Cells Using Extracts from Aquatic Organisms

○Masaharu Komatsu[1] (1. Tokai University)

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膨潤した繊維構造を有する硫酸エステル化セルロースパルプの合成と完全孤立型セルロースナノファイバーへの応用

（丸住製紙）○西村 朱十・大塚 園果

Synthesis of sulfated cellulose pulp with a swollen fiber structure and application to completely dispersed cellulose nanofibers (*Marusumi Paper Co., Ltd.*) ○Ayato Nishimura, Sonoka Otsuka

Cellulose nanomaterials, such as cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs), have been prepared by the combination of chemical modification of cellulose pulp (CP) and its difibrillation. Chemically modified CPs can disintegrate a completely dispersed CNFs with a fiber width of 3–4 nm, which is the smallest unit of a cellulose fiber. CNFs have attracted attention as promising natural nanofibers with various useful properties, including extremely high aspect ratio, high stiffness, and low thermal expansion. In this study, sulfated CPs (SCPs) were synthesized by a CP/sulfamic acid/urea reaction system, and their fiber morphology was investigated. SCPs were synthesized by absorbing an aqueous solution of sulfamic acid (H_2NSO_3H, 0.62 mmol) and urea (H_2NCONH_2, 0.25–2.5 mmol) onto CPs (100 g), removing water by drying, and reacting at 393 K for 30 min. In addition, the fiber morphology of SCPs is discussed in terms of the relationship between fiber shape and water retention value, which affects the defibration behavior of CNFs.

Keywords : Cellulose; Sulfation; Cellulose Nanofiber; Swollen Fiber Structure

近年、製紙原料のセルロースパルプ (CP) を用いたナノマテリアル調製に関する研究が数多くなされている [1)]。本研究では、CP を硫酸エステル化した硫酸エステル化 CP (SCP) を合成し、繊維特性を評価した。さらに SCP スラリーを高圧ホモジナイザーで微細化処理 (解繊) しセルロースナノファイバー (CNF) への応用も行った。

SCP は水を介してスルファミン酸 (H_2NSO_3H、0.62 mmol) と尿素 (H_2NCONH_2、0.25–2.5 mmol) を CP (100 g) に担持させ、393 K で 30 分反応させることにより高収率で得た。SCP の硫酸エステル基導入は 0.79–1.33 mmol/g であった。加えて、スルファミン酸≧尿素 (モル比) で得られた SCP は繊維幅方向への膨潤が観察された (**Figure 1**)。この膨潤繊維構造はパルプ保水度の向上に寄与していた。0.6 wt% SCP スラリーを 60 MPa で解繊したところ、5 回の処理以内に繊維幅 3–4 nm の CNF が得られた。この CNF 分散液はヘイズ 2%以下の高透明性を示した。

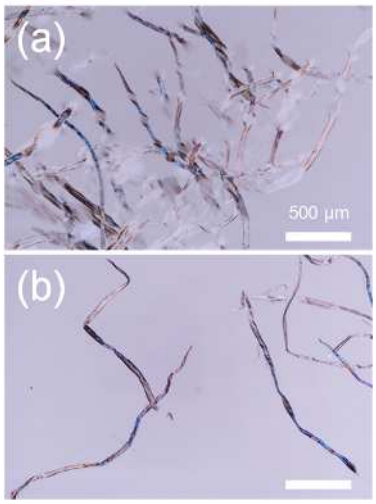

Figure 1 Optical micrographs of (a) SCPs and (b) original CPs.

1) Isogai, A.; Bergström, L. Preparation of cellulose nanofibers using green and sustainable chemistry. *Current Opinion in Green and Sustainable Chemistry* **2018,** *12*, 15-21.

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セルロースナノファイバーと紫外線吸収剤を利用した木材用水性塗料の開発と評価

（佐賀県工技セ[1]）○久間俊平[1]・田栗有樹[1]・帆秋圭司[1]・矢野昌之[1]
Development and evaluation of water-based paint for wood using cellulose nano fiber and ultraviolet absorber ([1]*Industrial Technology Center of Saga*) ○Shunpei Kuma[1], Yuki Taguri[1], Keiji Hoaki[1], Masayuki Yano[1]

There are increasing needs for wood paints that have a low environmental impact as well as woody feel and high weather resistance. However, transparent water-based paints that do not impair the woody feel and have a low environmental impact have a problem with weather resistance. In this study, water-based paints ware developed with silicone, which has good weather resistance, as the main component and biomass-derived additives with low environmental impact were added. As additives, cellulose nano fiber (CNF), which is derived from bamboo and has high strength, high elasticity, and ferulic acid (figure1), which is manufactured from rice bran and has UV absorption ability and antioxidant properties, were added. In practice, a paint mixture of silicone emulsion and CNF was applied to quartz glass. As a result, transmittance was reduced due to light scattering. The addition of ferulic acid further reduced the transmittance due to absorption of ultraviolet rays (figure2). Next, after the aqueous paints were applied to the wood, the wood was irradiated with ultraviolet light. The results of the evaluation of the color change over time, painted wood's changes were suppressed.
Keywords : cellulose nano fiber; ultraviolet absorber; water-based paint

木材用塗料について、木質感や高耐候性等の性能と共に低環境負荷であることが求められている。しかし、木質感を損なわず低環境負荷である透明系水性塗料は、耐候性に課題がある。本研究では、耐候性に優れるシリコーンを主成分とし、低環境負荷のバイオマス由来添加剤を加えた水性クリア塗料を開発した。添加剤として、竹由来で、高強度・高弾性の性能を有するセルロースナノファイバー（CNF）及び米ぬかより製造可能で、紫外線吸収能や酸化防止機能を有するフェルラ酸（図１）等を添加した。

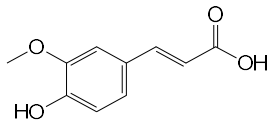

図１　フェルラ酸の構造式

実際に、シリコーンエマルションと CNF を混合した塗料を石英ガラスに塗布した。その結果、光散乱により透過率は低下した。また、さらにフェルラ酸を添加することで紫外線が吸収され、より透過率は低下した（図２）。次に、それらの水性塗料を木材に塗布した後、紫外線を照射した。色の経時変化を評価した結果、塗装木材の変色を抑制することができた。

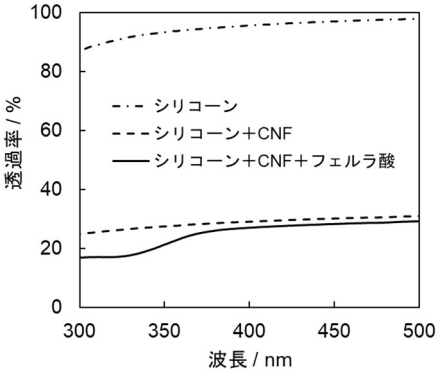

図２　塗膜の透過率

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フィチン酸カルシウム焼成物の結晶相に対する添加カルシウム塩の影響

（大阪技術研）○前田 和紀・青戸 義希・道志 智
Effect of calcium salt additives on the crystal phase of calcined calcium phytate (Osaka Research Institute of Industrial Science and Technology)○Kazuki Maeda, Yoshiki Aoto, Satoru Dohshi.

Calcium phosphates have been used in a variety of applications such as biomaterials, catalyst supports, and fluorescent materials. Hence, sustainable synthesis methods of calcium phosphates have been developed with natural calcium sources such as eggshells. However, natural phosphorus sources were rarely used for the synthesis of calcium phosphates. In this study, phytic acid found in plants was used as a biomass-phosphorus source, and the synthesis conditions of calcium phosphate using phytic acid were investigated. Calcium phytate was synthesized by the reaction of phytic acid with calcium chloride. Moreover, calcium phytate was mixed with various calcium salts (calcium chloride, calcium carbonate, and calcium oxide) to adjust the Ca/P ratio, and the mixture was calcined for 3 h in air at 1100 °C. When the Ca/P ratio was adjusted to 1.67, the X-ray diffraction patterns of the products were consistent with β-tricalcium phosphate (β-TCP), hydroxyapatite (HAP), and calcium oxide, respectively（Figure 1）. However, the ratio of β-TCP to HAP for three products was changed dependent on the kind of the calcium salt additives, indicating that calcium salt additives can affect the reaction selectivity in the calcination process.
Keywords： Phytic acid; Calcium phosphates; Biomass

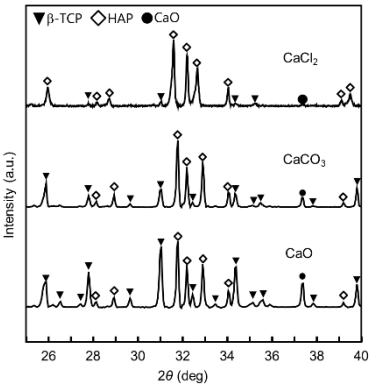

Fig. 1: XRD patterns of synthesized calcium phosphates from precursors containing different calcium salt.

リン酸カルシウムは生体材料など様々な場面で用いられているが、持続可能なリン原料を用いたリン酸カルシウムの合成法は限られている。本研究では、植物バイオマスのフィチン酸をリン資源として活用したリン酸カルシウムの合成ルートについて検討した。まず、フィチン酸と塩化カルシウムを水溶液中で反応させてフィチン酸カルシウムを合成し、リン酸カルシウムの合成原料とした。続いて Ca/P 比を調整するためにフィチン酸カルシウムと各種カルシウム塩（塩化カルシウム、炭酸カルシウム、酸化カルシウム）を物理混合した後、空気中で 1100 ℃、3 時間焼成し、得られた生成物を X 線回折によって定性した。Ca/P 比を 1.67 に調整した場合、生成物は、ハイドロキシアパタイト、リン酸三カルシウム、および少量の酸化カルシウムであった。しかし、その生成比率は混合したカルシウム塩によって異なっており（図 1）、添加塩が生成物の選択性に影響を与えることがわかった。

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透明な硫酸エステル化セルロースパルプ水分散液の調製

（丸住製紙）○森光 さくら・西村 朱十
Preparation of transparent sulfated cellulose pulp dispersion (*Marusumi Paper Co., Ltd.*) ○ Sakura Morimitsu, Ayato Nishimura

Cellulosic fiber surface modification has attributed attention to an important technology for the preparation of cellulose-derived materials. Cellulose pulps (CPs), one of the most important abundant materials that can be easily produced in large quantities by pulping method using wood chips, figure fiber shape that the fiber length 1-3 mm and width 20-40 μm. In this study, we performed a sulfation of CP to synthesize sulfated cellulose pulp (SCP) with functional properties. The sulfation was performed as follows. CP was soaked in an aqueous solution mixed with sulfamic acid and urea. The mixture was heated in an oven for 3 h to remove water. After the drying process, the dried CP material containing sulfamic acid and urea was reacted in an oven at 140°C for 30 min, and washed with pure water and sodium bicarbonate. The SCP was adjusted at 0.6 wt% using pure water. The SCP showed high dispersibility in water and transparency.
Keywords : Cellulose; Cellulose Pulp; Sulfation; Swollen Fiber Structure; Transparency;

近年、セルロースパルプ（CP）の水酸基を化学修飾させることによって、新たな特性を見出すという研究結果が報告されている [1)]。本研究では、CP にスルファミン酸と尿素を使った硫酸エステル化法を応用することで、硫酸エステル化セルロースパルプ（SCP）の合成を試みた。さらに SCP の繊維形態や分散液物性の評価を行った。

SCP の合成は、スルファミン酸と尿素を混合した水溶液に CP を含浸させ、水分を完全に飛ばした後、140℃で 30 分間加熱反応して行った。純水を用いて 0.6 wt%に調製した SCP 分散液を、石英セルに入れて 1 分間静置後の様子を観察した（**Figure 1**）。その結果、SCP は水中で未反応の CP に比べ高い分散性を維持していた。また、分散液の透明性について注目すると、SCP 分散液は高い透明性を有していることが示された。

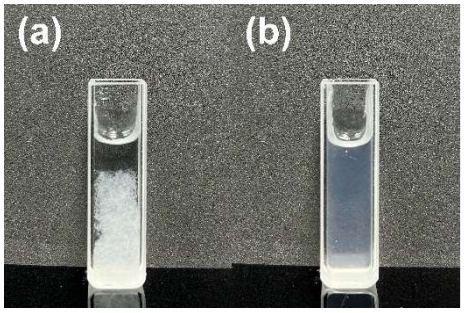

Figure 1 Dispersibility evaluation of (a) original CP and (b) SCP.

1) Yang, X.; Biswas, S. K.; Han, J.; Tanpichai, S.; Li, M. C.; Chen, C.; Sailing, Z.; Atanu K. D.; Yano, H. Surface and interface engineering for nanocellulosic advanced materials. *Advanced Materials* **2021**, *33*(28), 2002264.

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リグニンの効率的分解法の開発とその応用に関する研究

(・米子高専物質 [1]・長岡技科大 [2]・大阪公大 [3]・岡山理大 [4]) ○小島 翼 [1]・粳間 由幸 [1]・山田 知宏 [2]・前川 博史 [2]・土江 松美 [3]・若松 寛 [4]

Research on the development of an efficient degradation method for lignin and its application

([1]*National Institute of Technology, (KOSEN) Yonago College,* [2]*Nagaoka University of Technology,* [3]*Osaka Metropolitan University.,* [4]*Okayama University of Science*) ○Tsubasa Kojima[1], Yoshiyuki Uruma[1], Tomohiro Yamada[2], Hirofumi Maekawa[2], Matsumi Doe[3], Kan Wakamatsu[4]

Woody biomass is attracting attention as a new biomass resource that may replace fossil resources. Lignin is one of the woody biomasses and an aromatic polymer in the cell walls of wood. Lignin has a complex structure makes it difficult to decompose and is currently not completely utilized. In general, lignin degradation is costly, requiring a lot of energy and chemicals. Therefore, it is necessary to develop an efficient and inexpensive lignin degradation method for utilizing lignin. Lignin is an aromatic polymer with phenylpropanoid as the basic unit, and about 50% of the bonds between unit to unit are β-O-4.[1)] In this study, four different lignin models with β-O-4, 2-(2-methoxyphenoxy)-1-phenylethanol (**1a**), 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**1b**), Guaiacylglycerol-β-guaiacylether (**1c**), 1-(3, 4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1, 3-diol (**1d**), were degraded by organic electrolysis, and the structure of the degradation products and the degradation mechanism of β-O-4 were clarified. [2)] Furthermore, electrolysis was performed on three isolated lignin samples, successfully achieving the cost-effective and efficient decomposition of lignin compared to conventional decomposition methods.

Keywords : Lignin, Organic Electrolytic Reaction, Carbon Electrode, Lignin models, β-O-4

木質バイオマスは化石資源に代わる新たなバイオマス資源として注目されている。リグニンは木質バイオマスの一つで、木材の細胞壁中に存在する芳香族高分子であり複雑な構造をしているため分解されにくく、現在では完全に利用されていない。一般的にリグニンの分解は多くのエネルギーと薬品を必要とするため利用にはコストがかかる。そのため木質資源の有効利用にはリグニンの安価で効率的な分解法の開発が必要である。リグニンはフェニルプロパノイドを構造単位とする芳香族高分子でありその単位間結合は約 50%が β-O-4 結合である。[1)]本研究では β-O-4 結合を有する 4 種類のリグニンモデル 2-(2-methoxyphenoxy)-1-phenylethanol (**1a**), 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (**1b**), Guaiacylglycerol -β- guaiacylether (**1c**), 1-(3, 4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1, 3-diol (**1d**)を有機電解法によって分解し、分解物の構造と β-O-4 結合の分解メカニズムを明らかにした。[2)]さらに、3 種類の単離リグニンの電解を行い従来の分解法より低コストで効率的にリグニンの分解に成功した。

1) Chakar, F. S; Ragauskas, A. J. *Ind. Crops. Prod*, **2004**, 20, 131-141.
2) Y. Uruma, T. Yamada, T. Kojima, T. Zhang, C. Qu, M. Ishihara, T. Watanabe, K. Wakamatsu, and H. Maekawa, *RSC Adv.*, **2023**, 13, 17991-18000.

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ポリエチレングリコール修飾リグニンの抗菌作用の検討

(東京工科大[1])○三上 あかね[1]、髙木 美空[1]、原 汀[1]、山下 俊[2]
Antibacterial activity of Polyethylene Glycol (PEG)-Modified Lignin ([1]*Department of Medical Technology, School of Healthsciences,* [2]*Graduate School of Bionics, Computer and Media sciences, Tokyo University of Technology*)○Akane Sakaguchi-Mikami[1], Miku Takagi[1], Nagisa Hara[1], Takashi Yamashita[2]

Lignin, a major component of wood, is a polyphenolic polymer and its molecular structure varies depending on the plant species and the extraction process. Glycol lignin (GL) is extracted from Japanese cedar with polyethylene glycol. Since GL has less structural heterogeneity as well as high thermal stability, it has been thus expected as a sustainable alternative to petroleum polymer materials. Our previous study showed that a GL-containing plastic had a significant antibacterial activity against *Staphylococcus aureus*, and its potential as a novel antibacterial plastic material. The mechanism for GL antibacterial activity is, however, still unclear.

Here, we report the antibacterial evaluation of free GL to investigate the potential of GL as a novel antibacterial substance and a functional plastic material. The number of viable Gram-positive (G+) and -negative(G-) bacteria significantly decreased by incubation in GL-containing solution, indicating that free GL had antibacterial activity against both G+ and G- bacteria. On the other hand, the antibacterial effect of GL-containing plastics varied depended on the polymer types, suggesting that GL affinity of polymer components and the surface structure of a plastic may affect its antibacterial function. Further studies on GL antibacterial mechanisms may enable its application as antibacterial substances and plastic materials.
Keywords : Lignin, Antibacterial activity, Functional plastic materials

植物細胞壁構成成分であるリグニンはフェノール性高分子化合物であり，由来植物種及び抽出法によって異なる分子構造を持つ．ポリエチレングリコール(PEG)を用いて抽出されたスギ由来 PEG 修飾グリコールリグニン(glycol lignin; GL)は，高い均一性と耐熱性を有し，プラスチック代替素材等として応用が期待されている．演者らはこれまでに，数種類の GL 含有プラスチックがグラム陽性細菌に対して抗菌活性を有することを示したが，その抗菌作用機序は明らかになっていない．そこで本研究では GL 単体の細菌に対する抗菌作用の評価を行い，GL の新規抗菌性物質及び機能性樹脂素材としての検討を行った．まずグラム陽性及び陰性細菌を GL 添加溶液中にてインキュベートしたところ非添加溶液に比べて生菌数の減少が見られ，GL がグラム陽性及び陰性細菌に対して抗菌性を有することが示された．また，GL 含有プラスチックに細菌培養液を添加しインキュベート後，プラスチック表面から回収された生菌数は，複数のポリマーにおいて，GL 含有量増加に伴って著しく減少し，その挙動はポリマー及び細菌の種類によって異なった．これらの結果から，ポリマー素材と GL の親和性，また評価材表面構造の違いが GL 含有プラスチックの抗菌作用に影響することが示唆された．今後，GL の抗菌活性機序の詳細解析を行うことで高抗菌性 GL の開発及び GL の抗菌性樹脂素材としての応用が期待される．

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エポキシ化水産油から作製したネットワークポリマーの機械特性の評価とバイオベース複合材料の作製

（大阪技術研）○井上　陽太郎
Mechanical properties of network polymers based on epoxidized marine oil and preparation of bio-based on composite materials (Osaka Research Institute of Industrial Science and Technology) ○Yohtaro Inoue

Epoxidized fish oil (EFO) and epoxidized whale oil (EWO) were prepared by introducing epoxy groups to fish oil and whale oil rich in polyunsaturated fatty acids. Then EFO or EWO were mixed 4-methylcyclohexane-1,2- dicarboxylic acid anhydride (MHPA) and were cured to obtain network polymers. The breaking stress of the network polymer synthesized by EFO and 0.65 eq MHPA showed about 9.0 MPa. Paper (cellulose) was impregnated with EFO and MHPA solution, and were cured to obtain bio-based composite materials.

［緒言］魚油は、フィッシュミールの製造過程で生産され、主に養殖魚飼料添加用油脂として利用されている。また、水産加工残滓（魚あら）を原料として魚油は製造されている。同じく水産動物油である鯨油は、かつては、灯火用、潤滑剤、農業資材など多岐にわたり使用され身近な存在であった。現在は鯨肉生産が主であり、鯨肉加工時に排出される鯨油は産業廃棄物として廃棄され、ほとんど活用されていない。水産廃棄物リサイクルの効率化はゴミ減量化の進展と食品廃棄物の再生利用の増大に直結するため、魚油および鯨油の高度利用に伴う付加価値の向上が望まれている。

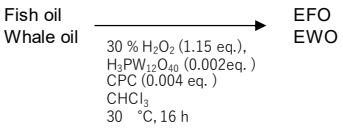

Fig. 1 Synthesis of EFO and EWO.

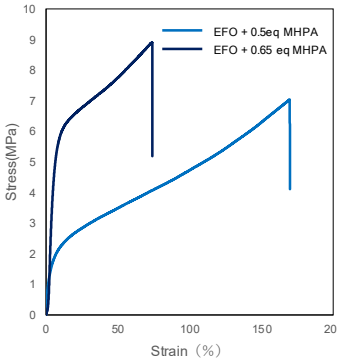

Fig. 2 Stress – strain curves of network polymers.

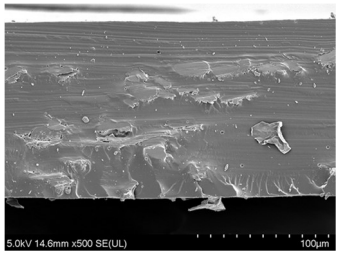

Fig. 3 SEM image of EFO-cellulose composite.

［結果および考察］ 図 1 に示すようにエポキシ化魚油（EFO）およびエポキシ化鯨油（EWO）を合成した。次に、EFO のエポキシ基に対し、0.5 当量の 4-メチルシクロヘキサン-1,2-ジカルボン酸無水物（MHPA）および 1 wt%の 2-エチル-4-メチルイミダゾール（EMI）を混合し、80 ℃で 3 時間、続いて 140 ℃で 24 時間加熱したところ、透明性を有し柔軟な熱硬化性樹脂を得た。得られた熱硬化性樹脂について引張試験を行ったところ、EFO-0.5eqMHPA では、破断強度が約 7.0 MPa を示し、EWO-MHPA では破断強度は約 5.3 MPa を示した。さらに、EFO-0.65eq のとき、破断強度は 9.0 MPa まで向上した（Fig. 2）。さらに、EFO および 1wt%の熱潜在性硬化剤を含浸させ、熱プレス（150 ℃, 2hr, 2 MPa）することにより、バイオベース複合材料を作製した（Fig. 3）。

［謝辞］JSPS 科研費 21K12318 の助成を受けて実施しました。

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アゾベンゼン-4,4'-ジカルボン酸を配位子とする各種金属イオンを用いた MOFs の合成

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Synthesis of MOFs using various metal ions with azobenzene-4,4'-dicarboxylic acid ligands.

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We have focused on metal organic frameworks (MOFs), which have attracted attention as adsorbents that selectively adsorb atmospheric CO_2 and enable separation at low energy cost. In this study, we attempted to synthesized new MOFs with azobenzene-4,4`-dicarboxylic acid (ADA) as a ligand, which are expected to undergo chromatic and structural changes[1)] during CO_2 adsorption. MOFs were synthesized using group 2 metal ions (M = Mg, Ca, Sr, Ba) and period 3 metal ions (Fe, Co, Cu, Zn) and Al, and their crystal structures, specific surface areas and CO_2 adsorption capacities were measured and compared. The results of CO_2 adsorption and desorption on MOF (M-ADA) by group 2 metal ions and ADA are shown in Figure 1. Among the group 2 metal ions, the Mg-MOF showed the highest value of CO_2 adsorption. Based on these results, it is suggested that this may be due to differences in the crystal structure of the metal ions. In addition, hysteresis adsorption/desorption behavior was observed depending on the interaction with the sorbent, confirming that the interaction between CO_2 and MOFs is not a simple physical adsorption.

Keywords : Inorganic and Complex Chemistry, Organometallics Chemistry, Coordination Polymers, CO_2 Absorbent, MOFs

我々は大気中の CO_2 を選択的に吸着し，エネルギーコストが低い分離を可能とする吸着材として注目されている金属有機構造体である MOFs (Metal Organic Frameworks)に着目した.

本研究ではアゾベンゼン-4,4`-ジカルボン酸(ADA)を配位子とし，CO_2 の吸着時に色相変化に色相変化や構造変化 [1)]が期待できる新たな MOFs の合成を試みた.

MOFs の合成は，2 族の金属イオン(M = Mg, Ca, Sr, Ba)および第 3 周期の金属イオン(Fe, Co, Cu, Zn), Al を用いて行い，両者の結晶構造や比表面積および CO_2 吸着量の測定比較を行った. 2 族の金属イオンと ADA による MOF(M-ADA)の CO_2 吸脱着結果を図 1 に示した. 2 族の金属イオンの中でも CO_2 の吸着量が高い値を示したのは，Mg-MOF であった．この結果を踏まえ金属イオンの結晶構造の違いに由来する可能性が示唆された．また，吸着質との相互作用によってヒステリシスな吸脱着の挙動が観測されたことから, CO_2 と MOFs 間の相互作用が単純な物理吸着ではない事を確認した.

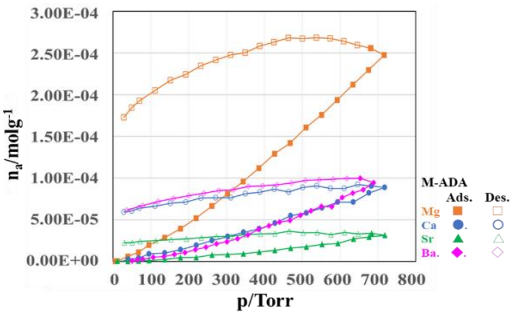

図 1 M-ADA の CO_2 吸脱着等温線

1) Kun-Yu. Wang, Zhentao Yang, nature Protocols (2023) pp.604-625.

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環境水中の病原性ウィルスの簡易検出方法の開発とその応用

（神奈川工科大学[1]）高村 岳樹[1]・○植木 柚[1]
Development of the detection method of pathogenic viruses in the environment water and its application ([1]Kanagawa Institute of Technology) Takeji Takamura[1], ○Yuzu Ueki[1]

Noroviruses (NoV) can contaminate water sources through sewage and survive for extended periods in the environment. This means they can accumulate in bivalves and other organisms in rivers, leading to human infection. To prevent the spread of disease and protect public health, it is crucial to analyze NoV in environmental water. Currently, the most common method for detecting NoV involves RNA extraction using the commercially available RNA kit, followed by rRT-PCR. However, this method can be complicated and time-consuming. We aimed to create a quick and easy method for detecting Norovirus. We discovered that RNA extraction using Chelex100, a simple nucleic acid extraction method, was effective for our purposes. In addition, using a microfluidic chip for real-time reverse transcription polymerase chain reaction (rRT-PCR) can reduce the operation time to 30 minutes. Currently, the sensitivity of this method is being verified, and researchers are testing its effectiveness in real-world samples.

Keywords： Environmental measurement, Pathogen

下水などを通じて環境水中に放出されたノロウィルス（NoV）は、同環境下で長期間生存することが知られている。そのため NoV は河川下流域の二枚貝等に濃縮され、最終的にヒトに対して感染を引き起こす可能性がある。このため、環境水中の NoV の分析は公衆衛生の観点や感染拡大状況を把握することに役立つことが期待される。現在の NoV の検出方法は、市販キットによる RNA 抽出、rRT-PCR 法が主流であるが、処理の煩雑さや判定結果を得るまでの時間が長いなどの欠点を有する。そこで、簡易かつ迅速な NoV の検出方法の開発について検討した。その結果、簡易な核酸抽出法として知られる Chelex100 を用い、かつマイクロ流路チップを用いる rRT-PCR 法を利用することで RNA 抽出から約 30 分で結果を得ることができた。同法の感度の確認、及び実環境試料からの回収について現在検討を行っている。

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カーボンナノチューブを担体とした担持 Ni 触媒の調製と還元反応への耐久性評価

（日本大学[1]・一関工業高等専門学校[2]）○青木 唯夏[1]・外山 直樹[1]・木村 寛恵[2]・照井 教文[2]・古川 茂樹[1]

Preparation of supported Ni catalysts using carbon nanotubes as supports and the investigation of their permanence in reduction reactions ([1]*Nihon University*, [2]*National Institute of Technology, Ichinoseki College*) ○Yuika Aoki,[1] Naoki Toyama,[1] Hiroe Kimura,[2] Norifumi Terui,[2] Shigeki Furukawa[1]

Carbon nanotubes (CNTs) are used in various fields due to their unique structure and shape. When the CNTs are used as supports, the Ni catalyst are probably supported on the defective of the surface on the CNTs. In this study, we prepared supported Ni catalysts using multi-walled CNTs with many defective structures and evaluated their effect on the reduction reaction of *p*-nitrophenol. As a result of examining the concentration of Ni precursor supported on multi-walled CNTs, the catalyst prepared at 15 mass% shows high activity. Furthermore, this catalyst showed rate of decrease relative to the initial concentration of over 90% up to the 10th test, and was more permanent than the single-walled CNTs supported Ni catalysts as shown in Figure 1.
Keywords : Carbon Nanotubes; Supported Catalysts; Reduction Reaction; Nickel

カーボンナノチューブ(CNTs)は，その構造および形状の特異性から，さまざまな分野に利用されている．CNTs を担体とした場合，Ni 触媒は CNTs の表面の欠陥に担持されることが考えられる．そこで本研究では，担体として欠陥構造の多い多層 CNTs を用いて担持 Ni 触媒を調製し，*p*-ニトロフェノールの還元反応に与える影響と耐久性について評価した. 多層 CNTs に担持させる Ni 前駆体濃度について検討した結果，15 mass%で調製した触媒が高い活性を示すことがわかった．さらに図 1 に示すようにこの触媒は，10 回目まで 90%以上の減少率を示し，比較対象である単層 CNTs 担持 Ni 触媒より耐久性があることがわかった．

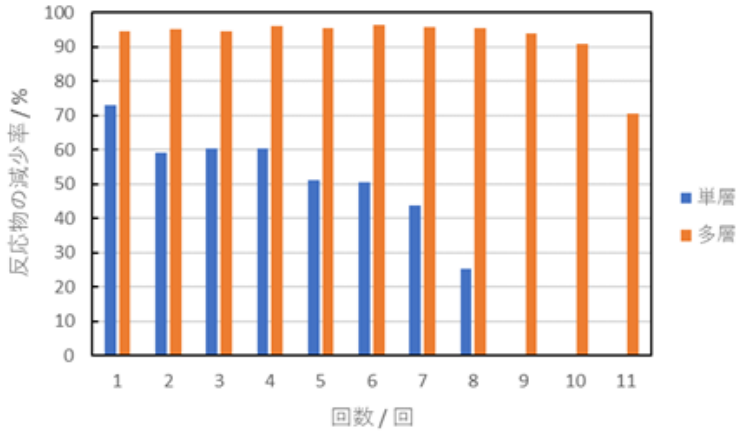

図 1 多層および単層 CNTs 担持 Ni 触媒を繰り返し使用したときの反応物の減少率

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球状中空シリカ担持遷移金属触媒の合成とその *p*-ニトロフェノールの還元反応

（日本大学[1]・物質・材料研究機構[2]）上嶋真季[1]・出口健三[2]・大木忍[2]・最上祐貴[2]・外山直樹[1]・古川茂樹[1]

Synthesis of silica hollow spheres supported on transition metal catalysts and their reduction of *p*-nitrophenol

([1]*Nihon University*, [2]*National Institute for Materials Science*) Maki Ueshima[1], Kenzo Deguchi[2], Shinobu Ohki[2], Yuuki Mogami[2], Naoki Toyama[1], Shigeki Furukawa[1]

Hollow spheres expected to increase the specific surface area due to the presence of hollow spaces. In this study, we synthesized transition metals such as Ni, Co, and Fe catalysts were supported on silica hollow spheres, and investigated the effects of their catalysts on the reduction reaction of *p*-nitrophenol. Silica hollow spheres were synthesized using polystyrene particles as templates. Ni, Co, and Fe precursors were supported on the surface of the synthesized silica hollow spheres using an impregnation method to obtain the desired supported catalysts. Co, Ni, and Fe catalysts supported on silica hollow spheres were evaluated in the reduction reaction of *p*-nitrophenol, and the first-order reaction rate constants were calculated as shown in Figure 1. From this result, the first-order reaction rate constant of Co, Ni, and Fe catalysts supported on silica hollow spheres were 0.0576, 0.0232, and 0.0002 min^{-1}, respectively. Meanwhile, the activation energy was calculated from the results of activities at various temperatures, it was confirmed that the value of the activation energy in the presence of Co supported catalyst was the lowest in the all catalysts.

Keywords : Silica Hollow Spheres; Transition Metal Catalysts; P-nitrophenol

球状中空体は，中空空間の存在により比表面積を増加させることが期待できる．本研究では，球状中空シリカに Co，Ni および Fe といった遷移金属を担持させた触媒の合成を行い，それぞれの触媒が *p*-ニトロフェノールの還元反応に与える影響について検討した．球状中空シリカは，ポリスチレン粒子をテンプレートした方法で合成した．合成した球状中空シリカに Co，Ni および Fe 前駆体を含浸法で表面に担持させ，目的の担持触媒を得た．これらの触媒を *p*-ニトロフェノールの還元反応で評価し，一次反応速度定数を算出した結果を図 1 に示す．この結果から，球状中空シリカ担持 Co，Ni および Fe 触媒の一次反応速度定数は，それぞれ 0.0576，0.0232 および 0.0002 min^{-1} であった．また，各温度で活性試験を行った結果から活性化エネルギーを算出したところ Co を担持させた触媒の値が最も低くなることが確認できた．

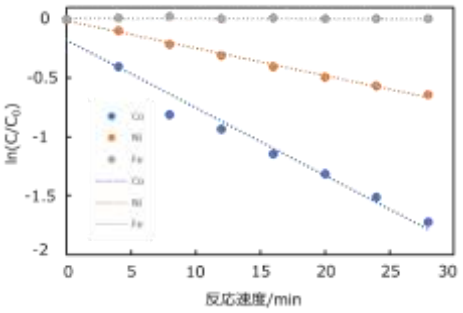

図 1　球状中空シリカ担持 Co，Ni および Fe 触媒を用いたときの一次反応速度式図

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アミノ基を有するシリカを用いた低濃度 CO_2 の回収

(都立大院理) 廖瀚声，吉川聡一，山添誠司

Capture of low concentration CO_2 by using silica with amino groups

(*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University*)
Hansheng Liao, Soichi Kikkawa, Seiji Yamazoe

Direct air capture (DAC) that captures emitted low-concentration CO_2 directly from the atmosphere has achieved great attention in recent years. Solid CO_2 adsorbents, such as silica modified the surface with amines, are expected to be suitable for DAC due to their ease of recovery and regeneration, selectivity for CO_2 adsorption, and moisture resistance[1]. We have previously reported the solid CO_2 adsorbents with a high density of amines that was obtained by the sol-gel synthesis of silica having organic functional group, and following modification of the surface organic functional group with diamines[2]. The resulting material can efficiently adsorb 400 ppm CO_2, desorb the captured CO_2 at 80°C with the absorption/desorption repeatedly out of degradation. As this method can be widely applied to compounds containing amino groups, this study examines the optimization of synthesis conditions, scale-up, and survey of types of amines modified, with the aim of developing silica materials with even greater low-concentration CO_2 adsorption performance.
Keywords: Carbon dioxide, Low concentration, Silica gel, Amine functionalization, CO_2 Absorption/Desorption

これまでに排出された大気中の低濃度 CO_2 を直接回収する Direct Air Capture（DAC）が近年注目されている．シリカなどの表面にアミンを修飾した固体 CO_2 吸着剤は，回収・再生が容易であり，CO_2 吸着への選択性や耐湿性があるため DAC に向けた CO_2 吸収剤として期待される[1]．我々はこれまでに，ゾルーゲル法により有機修飾シリカを合成し，表面有機鎖をジアミンで修飾することで，高密度なアミンを有する固体 CO_2 吸着剤を報告してきた[2]．得られた材料は 400 ppm の CO_2 を高効率で吸着し，回収した CO_2 を 80℃で脱離可能であり，繰り替えしの吸着・脱離に対しても劣化せず使用できる．本手法はアミノ基を有する化合物に広く適用できるため，本研究では，本手法の合成条件最適化，スケールアップ，及び用いるアミン種を検討し，更なる低濃度 CO_2 の吸着性能を有するシリカ材料の開発を検討した．

1) E. S. Sanz-Perez *et al*., *Chem. Rev.* **2016**, *116*, 11840.
2) 吉川，片岡，山添，第 103 回日本化学会春季年会，K207-3pm-05.

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固液相変化を用いた低濃度二酸化炭素の高効率回収放出システム

(都立大院理) ○李 烜冰，Furong Cao，吉川 聡一，山添 誠司

Highly efficient capture and release system of low-concentration carbon dioxide using solid-liquid phase change of diamine (*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University*) Xuanbing Li, Furong Cao, Soichi Kikkawa, Seiji Yamazoe

It is essential to establish a direct air capture (DAC) system that capture already emitted atmospheric CO_2 in order to reduce atmospheric CO_2 concentration. The solid-liquid phase separation type of amine absorbent, which captures CO_2 as a solid deposit, has attracted attention because of highly efficient reaction rate of amine absorbent with low-concentration CO_2[1]. We reported that a DMSO solution of diamine can absorb low-concentration CO_2 with high efficiency and can also release the captured CO_2 at a low temperature of 60°C[2]. In this study, we developed a CO_2 absorption system based on gas-liquid contact between diamine and low-concentration CO_2 gas to achieve highly dense CO_2 capture. When 400 ppm CO_2 gas was distributed at 50 sccm to diamine (1.0 mmol), >99% CO_2 absorption efficiency was maintained for >13 h. The presentation will show the absorption of low concentration of CO_2 and desorption property of the captured CO_2 by this system.

Keywords: Absorption and desorption of carbon dioxide, low concentration of carbon dioxide, contact of gas and liquid phase

既に排出された CO_2 を回収し大気中の CO_2 濃度を低減するには、大気中の CO_2 を直接回収する（DAC）システムの確立が必須である。CO_2 を固体析出物として回収する固液相分離型のアミン吸収液は、アミン吸収液と低濃度 CO_2 の高効率な反応を実現できるため注目されている[1]。我々は、ジアミンの DMSO 溶液が低濃度 CO_2 を高効率で吸収し、また、60℃の低温で CO_2 を放出できることを報告した[2]。本研究では、より高密度での CO_2 捕集を実現するため、ジアミンと低濃度 CO_2 ガスとの気液接触による CO_2 吸収システムを検討した。400 ppm の CO_2 ガスを 50 sccm でジアミン（1.0 mmol）に流通したところ、13 時間以上にわたって>99%の CO_2 を吸収できることを確認した。発表では、本システムによる低濃度 CO_2 の回収、及び、回収した CO_2 の脱離特性について報告する。

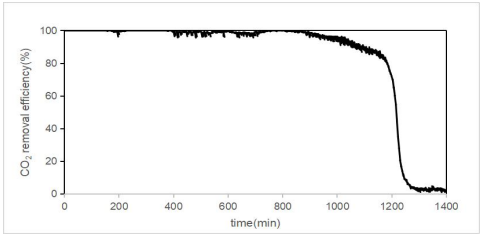

Figure 1.CO_2 removal efficiency

1) a) P. Luis *et. al.*, *Desalination* **2016**, *380*, 93−99. b) X. Jin *et. al.*, *Sep. Purif. Technol.* **2022**, *298*, 120630. c) F. Inagaki *et. al.*, *J. Am. Chem. Soc.* **2017**, *139*, 4639−4642., 2) S. Kikkawa *et. al.*, *ACS Environ. Au* **2022**, *2*, 354−362.

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ボトルキャップからの有機溶媒抽出物の分析

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Analyses of Extracted Compounds from Bottle Caps with Organic Solvents

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○Keisuke Nakagawa,[1] Yukimi Iwamoto,[1] Masahiro Furutani,[1] Tomoya Kataoka[2]

It is known that plastic wastes are fragmented by external stimuli such as ultraviolet light and heat, although the mechanism is still unknown. In addition, efflux behavior of low-molecular-weight additives is also unknown which are used in manufacturing of plastic products. In this preliminary work, we focused on bottle caps made from polyethylene, and tried to extract low-molecular-weight compounds from them by using several organic solvents. Acetone and tetrahydrofuran (THF) were used, for example, and the extracted amounts were measured. Identification of the extracted compounds was also tried by GC-MS and ^{1}H-NMR measurements. Instead of conventional Soxhlet method, we adopted an extraction method without any heating.

It was found that THF extracted chemical compounds better than other organic solvents from a bottle cap per unit mass where it took total 3 h and *ca.* 200 mL of solvent amount. After preparative thin layer chromatography (PTLC, using chloroform as eluent) purification, a low-molecular-weight compound that had both aromatic and alkyl moieties was suggested by ^{1}H-NMR spectral measurement.

Keywords: Bottle Cap; Extracted Compound; Plastic Waste; Polyethylene; Soxhlet Method

プラスチックごみは、紫外線や熱などの外部刺激に曝されることによって微細化される。しかし、その機構の詳細はわかっていない。また、プラスチック製品の製造において種々の低分子量化合物が添加されるが、微細化過程におけるそれらの流出挙動についても明らかになっていない。本研究では、プラスチックごみからの添加物の流出状況を把握するための前段階として、効率的な抽出操作に向けた予備的知見の取得を目的とした。ポリエチレン製ボトルキャップを対象試料とし、種々の有機溶媒を用いた低分子量化合物の抽出を試みた。抽出量を計測するとともに、GC-MS 測定や ^{1}H-NMR スペクトル測定などによる化学構造の推定を試みた。また、従来のソックスレー抽出の代替方法として、非加熱での抽出方法を検討した。

試料 1 g から得られる抽出物の量を有機溶媒間で比較したところ、テトラヒドロフラン（THF）の場合が最も多くなった。抽出は非加熱で行われ、抽出時間は計 3 時間、必要な溶媒量は計 200 mL 程度であった。得られた抽出物を分取薄層クロマトグラフィー（PTLC，展開溶媒：クロロホルム）によって精製し、精製物の一つについて ^{1}H-NMR スペクトルを測定したところ、芳香環やアルキル部分を有する化合物の存在が示唆された。

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ベトナムホーチミンの異常なオゾン濃度変動の原因解明

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Research in the cause of abnormal daily variation of ozone concentration in Ho Chi Minh City, Vietnam ([1]*Graduate School of Sustainable System Sciences, Osaka Metropolitan University*, [2]*Faculty of Environmental Sciences, Vietnam National University-Ho Chi Minh City*) ○ Norimichi Takenaka,[1] Yusuke Fujii,[1] Hien To Thi[2]

As a result of measuring the concentration of pollutants in the air with automatic measuring instruments from 2012 to 2014 in Ho Chi Minh City, Vietnam, abnormal fluctuations only in the ozone concentration during the rainy season were observed. The reason for this is expected to be due to HONO because HONO is one of the main sources of OH radical. HONO is formed mainly by the reaction of NO_2 with water on the particle surface. The concentration of $PM_{2.5}$ is extremely high, and this is a major air pollution problem in Ho Chi Minh City. In fact, when we measured the HONO concentration using the filter pack method in Ho Chi Minh City, it is found that the HONO concentration itself was higher than that in Osaka, and the ratio of $HONO/NO_2$ was the highest among those measured in the world. Therefore, it was assumed that HONO is efficiently generated from NO_2 due to the high humidity and high $PM_{2.5}$ concentration during the rainy season in Ho Chi Minh. It is speculated that the abnormal fluctuations in ozone concentration during the rainy season were due to a combination of several factors, including high humidity during the rainy season, and HONO being easily dissolved in water.

Keywords : Ozone concentration variation, Gaseous nitrous acid , $PM_{2.5}$, Nitrogen dioxide, Ammonia

ベトナムホーチミンで 2012 年から 2014 年にかけて大気中の種々の汚染物質濃度を自動測定器で測定した結果、雨期のオゾン濃度変動だけ異常な変動を観測した。その原因として、HONO の関与が推測された。HONO は、OH ラジカルの主発生源の 1 つであるためであり、粒子表面上で NO_2 と水との反応により生成される経路がその大きな発生源であると報告されている。また、$PM_{2.5}$ の濃度は極めて高く、これがホーチミン市の大気汚染の大きな問題となっている。実際に、ホーチミン市でフィルターパック法で HONO 濃度を測定したところ、HONO 濃度自体も大阪よりも高く、さらに NO_2 との比は $HONO/NO_2$ は世界で報告されている中でも最も高い値を示した。従って、ホーチミンの雨期の高湿度と高い $PM_{2.5}$ 濃度により、効率よく NO_2 から HONO が生成していると推定された。雨期は湿度も高く、HONO は水に溶解しやすいなど、いくつかの要因が重なったために、雨期のオゾン濃度は異常な変動を示したものと推察した。

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雪表面における二酸化窒素からの硝酸や亜硝酸生成

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Production of Nitric Acid and Nitrous Acid from Nitrogen Dioxide on Snow and Ice Surfaces

([1]*Osaka Metropolitan University, [2]Industrial Technology and Environment Research Department, Hokkaido Research Organization, [3]Snow and Ice Research Division, National Research Institute for Earth Science and Disaster Resilience, [4]Asia Center for Air Pollution Research, Japan Environmental Sanitation Center*) ○Arisa Hinoshita,[1] Ayane Yamamura,[1] Yusuke Fuji,[1] Izumi Noguchi[2], Hiroki Motoyoshi[3], Keiichi Sato[4], and Norimichi Takenaka.[1]

During dendritic snowfall, there was an increase in nitric acid in the snow. However, no research has been conducted on the cause so far. It is expected that nitrogen dioxide will react on the snow surface, producing nitric acid and nitrous acid, and that nitrous acid will change to nitric acid through volatilization or oxidation with ozone or hydrogen peroxide. Therefore, we expected that nitrate ions would increase in dendritic snow with a large surface area. In this research, we filled a glass tube with the artificial snow and poured nitrogen dioxide into it. Then, we conducted experiments to see if there was a change in the concentration of the gas generated before and after the reaction between the snow and ice surface and nitrogen dioxide. We used NOx meter and a continuous nitrous acid concentration measuring device to measure the gas concentration and analyzed the snow after the experiment using by ion chromatograph.

In fact, as a result of reacting snow made using ultrapure water with nitrogen dioxide, when nitrogen dioxide and nitrogen monoxide are removed from the total product, most of it is nitric acid, and more than ten percent is nitrous acid. In the future, we will conduct similar experiments using natural snow and aim to elucidate this process.

Keywords : nitrogen dioxide; nitrous acid; nitric acid; snow; surface reaction

樹枝状の降雪時に、雪に硝酸が増加するという結果があった[1)]。しかし、その原因についての研究はこれまで行われていない。二酸化窒素が雪の表面で反応し、硝酸と亜硝酸を生じ、亜硝酸は揮散もしくはオゾンや過酸化水素による酸化で硝酸に変化するプロセスが予想される。そのため、表面積の大きな樹枝状の雪の時に硝酸イオンの増加が起こるのではないかと予想した。そこで本研究では、ガラス管に、人工雪を詰め、その中に二酸化窒素を流し、雪氷面と二酸化窒素の反応の前後で発生する気体の濃度に変化が生じるかどうか実験を行った。気体の濃度測定には、NOx 計、亜硝酸濃度の連続測定装置を用い、実験後の雪はイオンクロマトグラフを用い、分析をした。

実際に、超純水を用いて作製した雪と二酸化窒素を反応させた結果、全生成物から二酸化窒素と一酸化窒素を除いた場合、ほとんどが硝酸となり、十数%が亜硝酸である結果を得た。今後は自然雪を用いた同様な実験を行い、このプロセスの解明を目指す。

1)Influence of the growth mechanism of snow particles on their chemical composition. Tsuneya Takahashi, Tatsuo Endoh, Kenichiro Muramoto, Chie Nakagawa, And Izumi Noguchi, Atmos. Environ. 1996, **30**, 1683-1692.

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メソポーラス球状中空シリカ-チタニアの合成とそのメチレンブルー分解および水素生成反応

（日本大学）○外山 直樹・水村 光希・林 亜咲・古川 茂樹
Synthesis of mesoporous silica-titania hollow spheres and their methylene blue decomposition and hydrogen generation reactions (*Nihon University*) ○Naoki Toyama, Kouki Mizumura, Asa Hayashi, Shigeki Furukawa

In this study, mesoporous silica-titania hollow spheres with various Si/Ti molar ratios were synthesized, and we investigated their activities influence on the hydrolysis of ammonia borane and the methylene blue decomposition reaction. Mesoporous silica-titania hollow spheres were synthesized by a sol-gel method using polystyrene particles as templates. First, transmission electron microscopy (TEM) results for samples synthesized at Si/Ti molar ratios of 10, 30, and 100 were shown in Figure 1. The presence of hollow space was observed the difference contrast. Furthermore, the shell thickness and void spaces were similar morphologies. The photocatalytic activity of these samples was evaluated by the methylene blue decomposition. These results suggested that the activity increased with decreasing Si/Ti molar ratios. In addition, we found that the hydrolysis of ammonia borane was produced high hydrogen generations in the presence of sample with Si/Ti molar ratio of 30.
Keywords : Mesoporous, Hollow Spheres, Silica-Titania, Methylene Blue, Ammonia Borane

本研究では, 各 Si/Ti モル比のメソポーラス球状中空シリカ-チタニアの合成を行い, アンモニアボラン加水分解およびメチレンブルーの分解反応に与える影響について検討した．メソポーラス球状中空シリカ-チタニアは，ポリスチレン粒子をテンプレートとしたゾル-ゲル法で合成した．まず，Si/Ti モル比 10，30 および 100 で合成した試料を透過型電子顕微鏡（TEM）で観察した結果を図 1 に示す．コントラストの差から，中空空間の存在が確認できた．さらに，中空壁厚や粒径は同程度のであることが示唆された．これらの試料を用いてメチレンブルーの分解で光触媒を評価した．この結果から，Si/Ti モル比が減少するに伴い活性が増大した．さらにアンモニアボラン加水分解反応は，Si/Ti モル比 30 の試料の水素発生量が多いことがわかった．

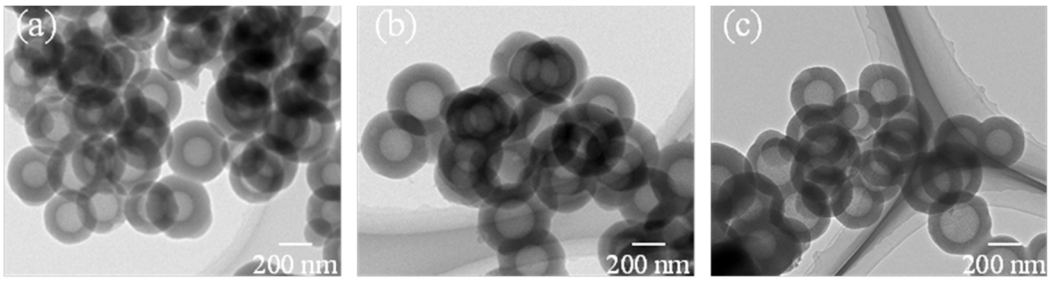

図 1 メソポーラス球状中空シリカ−チタニアの TEM 写真
Si/Ti モル比 / - (a)10，(b)30，(c)100

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Microchloropsis gaditana の油脂蓄積量と Triglyceride lipase 遺伝子発現量に関する研究

（日本大学）○渡邊　歩，小森谷友絵，古川茂樹

Studies on Oil and Fat Accumulation and Triglyceride Lipase Gene Expression in *Microchloropsis gaditana*

(Nihon University) ○Ayumu Watanabe, Tomoe Komoriya, Shigeki Furukawa

Microalgae produce large amounts of Triacylglycerol, a feedstock for biodiesel fuel. TAG is accumulated in large amounts when microalgae are cultured under stress conditions. However, when the stress is removed, TAG is degraded to Diacylglycerol and Free fatty acid by the hydrolytic enzyme Triglyceride lipase. Therefore, it is difficult to maintain growth and TAG accumulation in microalgae.

In this study, we investigated the relationship between TAG accumulation and Triglyceride lipase gene expression under stress and non-stress conditions by nitrogen source ($NaNO_3$) concentration, aiming to regulate the expression level of Triglyceride lipase gene for increasing TAG accumulation. Microalgae *Microchloropsis gaditana* were first cultured for 15 days at $NaNO_3$ concentrations (0,75 and 150 mg/L) and light intensity of 20 μmol photons・m^{-2}・s^{-1}. During incubation, microalgae were sampled over time, and TAG accumulation was measured using lipid fluorescence analysis and Triglyceride lipase gene expression was measured using quantitative real-time PCR. The results showed that TAG accumulated in larger amounts in the $NaNO_3$ concentration of 0 mg/L (under stress) than in other conditions, but there was no relationship between TAG accumulation and Triglyceride lipase gene expression. On the other hand, at $NaNO_3$ concentration of 150 mg/L (non-stressed), there was a relationship between TAG accumulation and Triglyceride lipase gene expression.

Keywords : Triglyceride lipase; Triaclyglycerol accumulation; Microchloropsis gaditana

微細藻類はバイオディーゼル燃料の原料である Triacylglycerol(以後 TAG)を多量に生産できるため着目されている．TAG は微細藻類をストレス環境下で培養することにより多量に蓄積されるが, ストレスの解消により, TAG は加水分解酵素 Triglyceride lipase により Diacylglycerol と Free fatty acid に分解される．そのため藻類の増殖と TAG の微細藻類内の蓄積を維持することは難しい．

そこで本研究では TAG 蓄積量の増加のための Triglyceride lipase 遺伝子の発現量の制御を目的とし, 窒素源($NaNO_3$)濃度によるストレスと非ストレス下における TAG 蓄積量と Triglyceride lipase 遺伝子発現量の関係性を調査した．実験は，微細藻類 *Microchloropsis gaditana* を $NaNO_3$ 濃度 0，75，150 mg/L，光強度 20 μmol photons・m^{-2}・s^{-1} で 15 日間培養させた．培養中は経時的にサンプリングし，TAG 蓄積量は脂質蛍光分析を用いて，Triglyceride lipase 遺伝子発現量は定量的リアルタイム PCR を用いて測定した．その結果，$NaNO_3$ 濃度 0 mg/L(ストレス下)では，他の条件と比較して全体的に多く TAG を蓄積したが，TAG 蓄積量と Triglyceride lipase 遺伝子発現量との関係性は見られなかった．一方で，$NaNO_3$ 濃度 150 mg/L(非ストレス下)では，TAG 蓄積量と Triglyceride lipase 遺伝子発現量の関係性があることがわかった．

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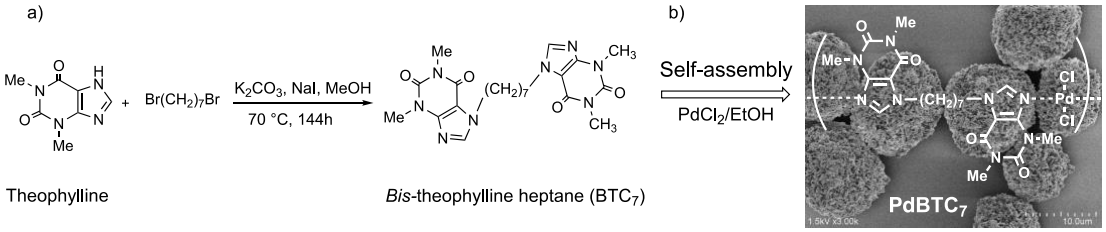
テオフィリンパラジウム触媒を用いた銅フリー薗頭カップリング反応

（神奈川大化学生命）○貝掛 勝也・新郷 明日真・金 仁華
Copper free Sonogashira coupling reaction catalyzed by a complex of palladium-bistheophyllines (*Department of Applied Chemistry, Faculty of Chemistry and Biochemistry, Kanagawa University*) ○Katsuya Kaikake, Asuma Shingo, Ren-Hua Jin

The catalytic performance of a bisteophylline palladium catalyst ($PdBTC_7$), which has high catalytic activity and excellent recycling performance in the Suzuki-Miyaura coupling reaction, were investigated for the Sonogashira coupling reaction. $PdBTC_7$ effectively played as catalyst for the Sonogashira coupling reaction at low temperature (40 ºC) under the air. Moreover, it was revealed that the reaction proceeds well without copper additive in the presence of triethylamine. *Keywords : Theophylline; Palladium; Sonogashira coupling reaction; copper free; green catalyst*

２分子のテオフィリンをヘプチル鎖により連結した配位子(BTC_7)を合成し、パラジウムと錯形成させたパラジウムビステオフィリン触媒($PdBTC_7$)を合成した(Scheme 1)。



Scheme 1. a) Synthesis of *bis*-theophylline heptane (BTC_7) as a ligand, b) the preparation of $PdBTC_7$ catalyst.

$PdBTC_7$を鈴木−宮浦カップリング反応における触媒として用いたところ、ブロモベンゼンとフェニルボロン酸を用いたモデル反応において、$PdBTC_7$が連続 10 回の使用に耐えうること、さらに、反応系中に塩素イオンを添加すると、触媒は 20 回のリサイクルにも適応できることが判明した[1)]。その堅牢性から触媒をカラム充填した循環式反応装置では、驚異的な 50 回リサイクルも可能であった[2)]。そこで本研究は$PdBTC_7$触媒が薗頭カップリング反応用触媒として機能するかを検討するためハロゲン化アリルとエチニルベンゼンを基質に条件検討を行った。水/40℃/トリエチルアミンの条件下、高転化率で反応が進行した。本条件下でエチニルピリジンも容易に反応した。本触媒を用いることで、通常必要とされる銅助触媒が存在しなくても反応が効率的に進行した。すなわち、$PdBTC_7$は完全に銅フリーパラジウム触媒として機能することが明らかとなった。

【参考文献】Suzuki-Miyaura coupling reaction using *bis*-theophylline-palladium catalyst has been reported. 1) K. Kaikake, N. Jou, G. Shitara, R.-H. Jin, *RSC Advances.*, **2021**, 11, 35311–35320. 2) K. Kaikake, K. Matsuo R.-H. Jin, *Catal. Commun.*, 181 **2023**, 106727.

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水熱条件下でのポリ塩化ビニルの脱クロロ化反応における，可塑剤，添加剤，安定化剤の影響

（法政大経多摩研究開発センター[1]・法政大生命 [2]・法政大経済 [3]）○細川 さとみ [1]・Douglas Hungwe[1]・杉山 賢次 [2]・山﨑 友紀 [3]
Dechlorination of Polyvinyl Chloride with Amines under Hydrothermal Conditions ([1]*Reserch & Development Center, Hosei University*, [2]*Faculty of Bioscience and Applied Chemistry, Hosei University*, [3] *Faculty of Economics, Hosei University*) ○Satomi Hosokawa,[1] Hungwe Douglas,[1] Kenji Sugiyama,[2] Yuki Yamasaki[3]

Polyvinyl chloride (PVC) has been widely used as a general-purpose resin. However, most incinerated PVC wastes including the chlorine are supposed to cause the environmental hazardous pollution. We have been successfully established the dechlorination of PVC in the presence of sodium hydroxide under hydrothermal conditions[1)]. In this study, the effects of plasticisers, additives and stabilizers on the hydrothermal treatment of PVC have been investigated in a viewpoint of practical application. The significant effect of the plasticizer was found to cause the decrease of dechlorination, while the additives and stabilizers showed little effect under the same condition.
Keywords : PVC; Dechlorination; Plasticiser; Additive; Stabilizer

ポリ塩化ビニル (PVC) は、その強度、耐候性、難燃性の高さから、電線被覆、サッシや水道管などに広く利用されている。一方で、PVC のケミカルリサイクルは困難であり、これ等に関する知見は、いまだ不足している。当研究室では、水熱システムを用いた実用的な PVC 脱クロロ化反応の確立を目的とし、これまでに NaOH 水溶液やアミン類存在下、回転軸付き電気炉を用いた水熱反応により、効率的に PVC の脱クロロ化反応が進行することを明らかにしている [1)]。

本研究では、水熱条件下での PVC の脱クロロ化反応における添加剤（炭酸カルシウム）、安定化剤（ステアリン酸亜鉛およびカルシウム）、可塑剤（フタル酸ジイソノニル）の影響を検討した。可塑剤存在下で脱クロロ化率が大きく低下した一方で、添加剤や安定化剤の影響はわずかだった。本発表では、さらに、実際のプロダクトを用いた脱クロロ化反応に関しても言及する。

塩基存在下でのPVC脱クロロ化率 (%)

反応条件	PVC	PVC + 添加剤	PVC + 安定化剤	PVC + 可塑剤
NaOH (1 M), 230 ºC, 1 h	30	44	47	8
Urea (10 mmol), 180 ºC, 3 h	61	63	63	10
Et_3N (10 mmol), 180 ºC, 1 h	58	53	55	52

PVC: TK-1000 (信越工業株式会社, 100 mg), 添加剤 ($CaCO_3$, 20 mg), 安定化剤 (ステアリン酸亜鉛 , 0.3 mg + ステアリン酸カルシウム, 0.5 mg), 可塑剤 (フタル酸ジイソノニル, 100 mg)

1) 山﨑友紀，細川さとみ，ダグラス・ホンゴウィ：廃棄物資源循環学会論文誌, 34 巻, pp. 30-43 (2023)

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種々のバイオマスを基体とする陽イオン交換樹脂の合成と金属イオンの吸着特性

（中部大院工[1]・中部大工[2]）○秋永 拓未[1]・井垣 侑生[1]・池田 琉稀[1]・宮内 俊幸[2]・爾見 優子[2]
Preparation of a cation exchanger based on some biomass and adsorption characteristics of metal ions ([1]*Graduate of Chubu University*, [2]*Chubu University*) ○Takumi Akinaga,[1]Yui Igaki,[1] Ryuki Ikeda,[1] Toshiyuki Miyauchi,[2]Yuko Shikami,[2]

Using of biomass contributes to the SDGs. The biomass were pretreated with autoclave or hydrochloric acid. Untreated cedar, autoclaved cedar and cedar treated by HCl each were oxidized with solid potassium permanganate to give a weakly acidic cation exchange resins with a carboxyl group. Since density of the cation exchange resins were more than 1.0 g mL^{-1}, ion cation exchange resin did not float in the water, and was able to be applied to the column operation. Then copper ion was adsorbed on cation exchange resin using a batch method. From this result the best maximum adsorption capacities was untreated cedar 70.4 mg g^{-1}.
Keywords : Cation exchange resin; Woody biomass; Herbaceous biomass; Exchange Capacity; Copper ion

【背景】本研究では、SDGs の達成を目指し、バイオマスを基体とする化学材料の開発を行っている。これまでのバイオマスに関する研究では、主成分であるセルロース、リグニンおよびヘミセルロースを分離し利用してきたが、本研究では、植物由来バイオマスに官能基を導入することで、陽イオン交換樹脂を合成したのでここに報告する。
【実験】陽イオン交換樹脂を合成するために、種々のバイオマスへ前処理として塩酸およびオートクレーブを用いた。次に前処理をしたバイオマスへカルボキシ基を交換基として導入するために、過マンガン酸カリウムで酸化処理し、弱酸性型陽イオン交換樹脂を得た。
【結果および考察】前処理をしたスギの表面観察を SEM で行った(Fig.1)。前処理を行う前のスギ(a)と比較して、オートクレーブ処理(b)をすると可溶性有機成分が取り除かれたため表面はなめらかになった。一方、塩酸で前処理(c)を行うと表面は荒いものとなった。バイオマスを化学材料として扱うときの欠点としては、水に浮くことだが、酸化処理を加えることで、ほとんどのバイオマスにおいて密度が 1.0 g mL^{-1} 以上になり、その欠点を克服することが出来た。さらに、バッチ法で Cu^{2+}の飽和吸着量を算出したところ、前処理を加えなかったスギが最も高い値であった(70.4 mg g^{-1})。この結果から 2.22 meq g^{-1} の交換容量を得ることができた。市販の陽イオン交換樹脂と比較しても本研究で合成した陽イオン交換樹脂の方が良好の値が得られた。

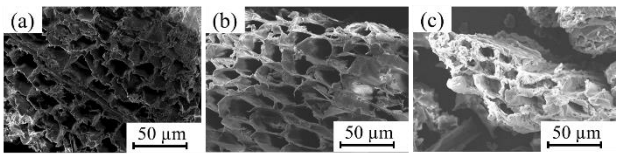

Fig.1 SEM picture of chemical modified cedar sawdust
(a)Cedar sawdust; (b)Autoclaved cedar sawdust;
(c)Cedar sawdust treated by HCl

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抗菌スパイク粒子のベイズ最適化を活用したフロー合成条件検討

（株式会社ＫＲＩ）○中江 隆博・伊藤 聡
Investigation of flow synthesis conditions utilizing Bayesian optimization of antimicrobial spike particles (KRI, Inc.) ○Takahiro Nakae, So Ito

Dragonfly and cicada wings have antimicrobial properties derived from their nano-sized spike structures, and nanostructures that mimic them have been reported to exhibit structural bactericidal properties.[1)] KRI has been studying antimicrobial spike particles that mimic these structures.[2)] A method to prepare antimicrobial spike particles with desired properties in a highly reproducible, high-yield, and scalable synthetic method will be essential for industrial applications. Flow synthesis is one of the low environmental impact chemical processes due to its reproducibility and scalability by numbering up. In addition, flow synthesis has less uncertainty derived from experimental manipulations, making it suitable for the use of machine learning.[3)] In this presentation, we will report the results of our study by utilizing Bayesian optimization to examine the conditions of flow synthesis.
Keywords : flow synthesis, Bayesian optimization, Antimicrobial spike particles, biomimetics

トンボやセミの羽根はナノサイズのスパイク構造に由来する抗菌性を有しており、これを模したナノ構造は構造殺菌を示すことが報告されている [1)]。構造殺菌は物理ダメージに由来し長期的効果が期待できることと、細菌類だけでなくカビに対して有効であり、ウィルスへの効果も期待されている。KRI ではこれを模した抗菌スパイク粒子に関する研究に取り組んでいる [2)]。所望の特性を発揮する抗菌スパイク粒子を高い再現性、高い収率、かつスケーラブルな合成手段で調製する手法は工業利用の応用に必須となる。フロー合成は再現性とナンバリングアップによるスケールアップ性から、低環境負荷な化学プロセスの 1 つです。また、フロー合成では実験操作に由来する不確実性が少なく、機械学習の活用に適している [3)]。フロー合成の条件検討にベイズ最適化を活用し検討を行った結果について報告する。

1) Bactericidal activity of black silicon. E. P. Ivanova, J. Hasan, H. K. Webb, G. Gervinskas, S. Juodkazis, V. K. Truong, A. H. Wu, R. N. Lamb, V. A. Baulin, G. S. Watson, J. A. Watson, D. E. Mainwaring, R. J. Crawford *Nat Commun.* **2013**, *4*, 2838.
2) 昆虫の羽の機能を再現した抗菌、防カビ、抗ウイルス機能表面の開発, KRI プレスリリース 2021 年 3 月 3 日。 https://www.kri-inc.jp/press/1275615_11456.html
3) Exploration of flow reaction conditions using machinelearning for enantioselective organocatalyzed Rauhut–Currier and [3+2] annulation sequence. M. Kondo, H. D. P. Wathsala, M. Sako, Y. Hanatani, K. Ishikawa, S. Hara, T. Takaai, T. Washio, S. Takizawa, H. Sasai, *Chem. Commun.* **2020**, *56*, 1259-1262.

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水棲生物からの抽出液を使用した色素増感太陽電池の作製および評価

（東海大海洋）○小松 真治
Fabrication and Evaluation of Dye-sensitized Solar Cells Using Extracts from Aquatic Organisms (*School of Marine Science and Technology, Tokai University*) ○ Masaharu Komatsu

Dye-sensitized solar cells (DSSCs) use natural dyes to replace expensive chemical synthesis processes with easily extractable dyes that are non-toxic and environmentally friendly. Pigments obtained from organisms such as bacteria, cyanobacteria, microalgae, and yeast are poorly developed and could represent a promising potential alternative source. The photovoltage and *I-V* characteristics of the fabricated DSSC were measured under irradiation with LED light. The open-circuit photovoltage measured under visible light irradiation of DSSC was about 370 mV for both DSSC purified from wakame extract and Aplysia extract. This photovoltage remained stable for 1 hour. The maximum output was 1.57 μW/cm^2 for DSSC purified from extract from wakame and 2.57 μW/cm^2 from extract from Aplysia. Currently, batteries are being created and evaluated using other aquatic organisms. In addition, we have created a DSSC in which individual photosynthetic pigments separated from the extract by chromatography are adsorbed onto titanium oxide electrodes, and are exploring requirements for battery optimization.
Keywords : Aquatic Organisms; Extract; Photosynthetic Pigment; Dye-sensitized Solar Cells

色素増感太陽電池（DSSC）は、希少金属としてルテニウムや有害金属の鉛を使う太陽電池で、高くて 13～16%の光エネルギー変換効率が達成されている。天然色素の使用で、高価な化学合成プロセスを、毒性がなく環境に優しい容易に抽出可能な色素に置き換えられる。細菌、シアノバクテリア、微細藻類、酵母などの生物から得られる色素は、十分に開発されておらず、有望で潜在的な代替源になり得る。本研究では、DSSC に利用する水圏生物に由来する新規増感色素の開発を行うことで、カラフルで高効率な DSSC を開発する。本講演では、様々な水棲生物からの抽出液を用いた色素吸着操作によって作製した DSSC の光起電力および *I-V* 特性について報告する。

酸化チタン電極を各種水棲生物からの抽出液中への浸漬処理することで、DSSC を作製した。作製した DSSC への可視光照射下で、光起電力および *I-V* 特性を測定した。

DSSC への可視光照射下にて測定した開回路下での光起電力は、ワカメからの抽出液から作製した DSSC では 366 mV、アメフラシからの抽出液からのものでは 370 mV であった。この光起電力は、1 時間安定に保持された。最大出力は、ワカメからの抽出液から作製した DSSC で 1.57 μW/cm^2、アメフラシからの抽出液からのもので 2.57 μW/cm^2 であった。現在、他の水棲生物でも電池を作製し、評価しているところである。また、抽出液からクロマトグラフィーにて分離された個々の光合成色素を酸化チタン電極へ吸着させた DSSC を作製し、電池の最適化についての要件について模索している。

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Academic Program [Poster] | 01. Education and History of Chemistry：Poster

Wed. Mar 20, 2024 10:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:00 AM - 2:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-3am] 01. Education and History of Chemistry

Japanese

[P1-3am-01]

Alkaline Hydrolysis Reaction of Prussian Blue Suspension in the Presence of Alkaline Earth Metal Ions

○Tadatsugu Yamaguchi[1] (1. Hyogo University of Teacher Education)

Japanese

[P1-3am-02]

Development of teaching materials using a decomposition reaction on aspartame

○Akino Uchiyama[1], Shizuka Takami[2], Tadatsugu Yamaguchi[1] (1. Hyogo University of Teacher Education, 2. National Institute of Technology, Niihama College)

Japanese

[P1-3am-03]

Estimation of the Stokes Radius for Transition Metal Ions and Complexes by Electrophoresis on Filter

○Syusuke Koizumi[1], Hidekazu Arii[1] (1. University of Miyazaki)

Japanese

[P1-3am-04]

Aerobic oxidation of oils accelerated by iron compounds of animal origin in foods

○Kiko Takenouchi[1], Masayuki Inoue[1] (1. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-05]

Suppression effect of amino acids on air oxidation of lipids plant oils catalyzed by iron (III) salts

○Yukino Tanigawa[1], Masayuki Inoue[2] (1. Graduate School of Science, Tokyo University of Science, 2. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-06]

Hydration of alkynes with sulfuric acid silica gel

○Kohei Yamada[1], Masayuki Inoue[2] (1. Graduate School of Science, Tokyo University of Science, 2. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-07]

Mechanism of oxidation of sugars by copper (II) compounds in alkaline aqueous solutions

○Akari Matsubara[1], Masayuki Inoue[2] (1. Graduate School of Science, Tokyo University of Science, 2. Faculty of Science, Tokyo University of Science)

Japanese

[P1-3am-08]

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Development of microscale experimental teaching materials to distinguish aromatic carboxylic acid through neutralization reactions.

○Ueda Tatsuya[1], Masatada Matsuoka[1] (1. Fukuoka Univ.)

Japanese

[P1-3am-09]

Development of Quantitative Experiments Using Iodine Clock Reaction -Experiments to estimate the concentration of an unknown sample from the reaction time-

○Sanefuji Shota[1], Masatada Matsuoka[1] (1. Fukuoka Univ.)

Japanese

[P1-3am-10]

Formation of a Pd catalyst layer using an Anionic Surfactant and Subsequent Fabrication of a Glucose Fuel Cell

○Takahiro Suzuki[1] (1. Otsuma Ranzan Junior and Senior High School)

Japanese

[P1-3am-11]

New Development of Microscale Experiments: Science exhibitions after Covid-19

○Marina Kawata[1], Yuna Moriwaki[1], Reina Ono[1], Chika Takahashi[1], Yumiko Takagi[1], Kazuko Ogino[2] (1. Kagawa University, 2. Tohoku University)

Japanese

[P1-3am-12]

Consideration of Methods for Shape Control and Comparison of Physical Properties in Vinylon Synthesis Using Acetaldehyde

○Kotone Ai[1], Mio Watanabe[2], Izumi Imai[1] (1. Toho University, 2. Fuzikawaguchiko High School)

Japanese

[P1-3am-13]

Development of an evaluation method to visualize the environmental load and safety of chemical experiments in secondary education

○Moeka Kudo[1], Masashi Yamada[2], Izumi Imai[1] (1. Toho university, 2. Graduate school of science, Toho University)

Japanese

[P1-3am-14]

PuzMol: Molecule-building Puzzle

○Norifumi Yamamoto[1] (1. Chiba Tech)

Japanese

[P1-3am-15]

BasePairPuzzle: An experiential molecular model that reproduces hydrogen bonds with magnetic force

○Jiro Kondo[1], Shota Nakamura[2] (1. Sophia University, 2. StudioMIDAS Inc.)

Japanese

[P1-3am-16]

Developing Human Resources for Women in Science with Sechi Kato as a Role Model

○YASUNAO KURIYAMA[1], Mizue Kissho[1,2] (1. Yamagata University, 2. Science Studio Marie)

Japanese

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[P1-3am-17]

Development of a simple and highly precise visual type polarimeter equipped with a constant temperature bath

○Tetsumaru Uzawa[1], Izumi Imai[1] (1. The Univ. of Toho)

Japanese

[P1-3am-18]

Development of a Simple Colorimeter using a White-color LED and a Color sensor IC

○Yasutada Suzuki[1], Natsumi Sakai[1], Syunichi Oshima[1], Mune-aki Sakamoto[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-3am-19]

Introduction to chemical experiments in class using hydrophilic polymer

○Masayuki Toyoshima[1], Tatsuya Takahashi[1] (1. Tokyo Metropolitan College of Industrial Technology)

Japanese

[P1-3am-20]

Color reaction of pH change using anthocyanin of rough extract via Butterfly pea

Ken Nozawa[1], Masahide Niboshi[1], Nagi Itou[1], Hiroki Oka[1], Shiho Goto[1], ○Tatsuya Takahashi[1], Masayuki Toyoshima[1] (1. Tokyo Metropolitan College of Industrial Technology)

Japanese

[P1-3am-21]

Chem Tube: A group of students for producing video teaching materials for chemistry experiments (4)

○Saki Takanashi[1], Sona Okamoto[1], Jiro Ito[1], Junya Ataka[1], Ryota Inomata[1], Yutaro Ogawa[1], Akinari Futamura[1], Ikuhiro Tanida[1], Shin Ono[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-3am-22]

Chem Tube: A group of students for producing video teaching materials for chemistry experiments (5)

○Shin Ono[1], Ikuhiro Tanida[1] (1. Kanazawa Institute of Technology)

Japanese

[P1-3am-23]

New Development of Microscale Experiments: Experimental Classes after Covid-19

○Reina Ono[1], Yuna Moriwaki[1], Marina Kawata[1], Chika Takahashi[1], Yumiko Takagi[1], Kazuko Ogino[2] (1. Kagawa University, 2. Tohoku University)

Japanese

[P1-3am-24]

Development of Multi Sided Liberal Arts Educaion Based on Historical Peppermint Industry of Kitami, Hokkaido
- An attempt to create an educational material which incorporate feelings of people

○Mitsunori Izumi[1] (1. Tokai Univ.)

Japanese

[P1-3am-25]

Application of Generative AI to Inquiry Based Experiments at College of Technology

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○Hirotoshi Sato[1], Kozo Fukumoto[2], Aiko Oshio[1] (1. Kobe City College of Technology, 2. University of the Ryukyus)

Japanese

[P1-3am-26]

Development of teaching materials for chemical experimentation using quantum chemical simulations: An estimate of XPS spectra of organic compounds

○Tsugiko Takase[1], Fuga Miyazawa[1], Katsuhiko Yamaguchi[1] (1. Fukushima University)

Japanese

[P1-3am-27]

Attempts to develop chemistry-based liberal arts for students who are not good at chemistry

○Tamotsu Sugimori[1] (1. University of Toyama)

Japanese

[P1-3am-28]

Current State and Challenges in General Chemistry Education within the Model Core Curriculum of the National Institute of Technology

○Junko Ninomiya[1] (1. National Institute of Technology, Oita College)

Japanese

[P1-3am-29]

Educational Effectiveness of Face-to-Face and On-Demand Practice in Chemistry Experiments

○Toshiyuki Katsumata[1] (1. Tokyo Medical and Dental University)

Japanese

[P1-3am-30]

Designing of Organic Chemistry Experiment Classes for University Students Using Aromatic Compounds

○AKIKO KIDO[1], Naoya Iwasaki[1], Takayuki Suzuki[1] (1. Tokyo Denki University)

Japanese

[P1-3am-31]

Chemistry-based Approach to High School Biology in Closer Connection with University Education

○Yuriko Kai[1], Hiroyuki Oshikane[2] (1. Kanagawa Institute of Technology, 2. Osaka University)

Japanese

[P1-3am-32]

From "resonance" to "delocalization": The Terms and Usages on Electron Delocalization in Conjugate Systems for Organic Chemistry in University Fundamental Education

○Masato M. Ito[1] (1. Soka Univ.)

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日本化学会 第104春季年会 (2024)

アルカリ土類金属イオン存在下におけるプルシアンブルー液のアルカリ加水分解反応

（兵教大）○山口 忠承 [1]

Alkaline Hydrolysis Reaction of Prussian Blue Suspension in the Presence of Alkaline Earth Metal Ions (*Hyogo University of Teacher Education*) ○Tadatsugu Yamaguchi[1]

A Prussian blue suspension undergoes a hydrolysis reaction with an alkaline solution such as an aqueous sodium hydroxide solution or an aqueous potassium hydroxide solution. The reaction rate of hydrolysis of a Prussian blue suspension varies greatly depending on the coexisting potassium ions and sodium ions. In this study, I analyzed the reaction rate of Prussian blue suspension in the presence of alkaline earth metal ions, with the aim of using it as teaching materials for experiments on reaction rates.

Keywords : Alkaline earth metal ions; Prussian blue; Alkaline hydrolysis reaction; Teaching Material

プルシアンブルー液は、水酸化ナトリウム水溶液、または、水酸化カリウム水溶液のアルカリ溶液の添加により加水分解反応が起こることが報告されている。[1)]プルシアンブルー液の加水分解の反応速度は、共存するカリウムイオンやナトリウムイオンによって反応速度が大きく異なる。本研究では、アルカリ土類金属イオンとプルシアンブルーを用いた反応速度に関する実験教材の開発を目的として、アルカリ土類金属イオン存在下におけるプルシアンブルー液の反応速度の解析を行った。

アルカリ金属を用いた場合の実験方法 [2)] を参考にして、プルシアンブルー液の分解反応は分光光度計で測定することにより解析を行った。市販試薬から調製したプルシアンブルー液 3.0 mL に、0.01 M (mol/L) の水酸化マグネシウム溶液、0.01 M の水酸化ストロンチウム溶液、0.01 M の水酸化バリウム溶液をそれぞれ 0.3 mL 加えると、水酸化マグネシウム溶液、水酸化ストロンチウム溶液の添加した場合は、白色沈殿生成と共に藍色のプルシアンブルーが凝集する現象が見られた。唯一、水酸化バリウム溶液の添加の際は凝集せず、プルシアンブルーのアルカリ加水分解反応が起こった。また、水酸化バリウム溶液を添加した場合は、同一周期の水酸化セシウム溶液と比べて大きな反応速度の差があることが確認できた。

この実験結果を元にして、プルシアンブルーの含まれる市販のあいいろの水彩絵の具液を用いて、同一物質量の水酸化物イオン添加時に、目視により反応速度の差が確認できるかについて検討を行った。図 1 の写真に示すように添加する陽イオンの種類によって反応速度に関する差が確認できた。

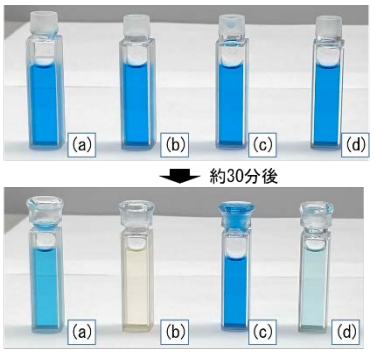

図1 プルシアンブルーの分解反応
(a) NaOH, (b) KOH, (c) CsOH, (d) $Ba(OH)_2$

1) 山口忠承，八木春佳，尾關徹，科学教育研究，**2022**，46，154-173.

2) 山口忠承，化学と教育，**2023**，71，150-151.

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アスパルテームの分解反応を用いた化学実験教材の開発

（兵教大[1]・新居浜高専環境材料工[2]）○内山亜希乃[1]・高見 静香[2]・山口 忠承[1]

Development of Chemical Experiment Teaching Materials Using a Decomposition reaction on Aspartame ([1]*Hyogo University of Teacher Education*, [2]*Department of Environmental Materials Engineering*, *National Institute of Technology, Niihama College*) ○ Akino Uchiyama,[1] Shizuka Takami,[2] Tadatsugu Yamaguchi[1]

Aspartame, which is known as an artificial sweetener, is decomposed by acid into two types of amino acids: aspartic acid and phenylalanine. We developed teaching materials for chemical experiments using aspartame as a starting material, with the aim of developing teaching materials for teaching how to purify the two types of amino acids produced and how to analyze amino acids. We tried to practice teaching materials in lectures at the University.

Keywords : Aspartame; Amino Acid; Paper Chromatography; Nuclear Magnetic Resonance

人工甘味料として知られているアスパルテームは、酸による分解反応によりアスパラギン酸とフェニルアラニンの２種類のアミノ酸が得られる。生成する２種のアミノ酸の精製の方法や、アミノ酸の分析の方法が学べる化学教材の開発を目的として、アスパルテームを原料にした化学実験教材の開発を行った。

アスパルテームの分解反応を、アミノ酸自動分析の試料調製法を参考にして行った。アスパルテーム 0.5 g を、６M 塩酸存在下 110℃の条件下で 24 時間加熱還流を行った。原料が、２種類のアミノ酸に分解したことは、No.50 のろ紙を用いたペーパークロマトグラフィー（展開溶媒：１-ブタノール:水：酢酸=４：１：２）の混合溶媒を用いて試料を展開した。ニンヒドリン溶液を噴霧後、加熱することによりに確認できた。この際、市販の２種類のアミノ酸と原料のアスパルテームをペーパークロマトグラフィーの分析のために比較として用いると、反応が起こっていることを確認できた。また、原料と生成物の化学構造の違いを調べるため、アスパルテーム分解後のアミノ酸の試料を、陽イオン交換樹脂に酸性条件下で吸着させ、流出時の液のｐH を大きくすることによる手法を用いてアミノ酸の分離を試みた。pH1～pH5 程度の条件下の流出液（A）試料では、アスパラギン酸が得られ、pH11 程度の条件下の流出液（B）試料はフェニルアラニンが主に得られることを、ペーパークロマトグラフィーによって確認した（図１）。（A）試料と（B）試料から水を蒸発させた２つの試料を、それぞれ、卓上型核磁気共鳴装置で調べると、（A）試料からはアスパラギン酸が得られていることと、(B) 試料からはフェニルアラニンが多く含まれていることを確認した。令和５年 10 月に大学院の講義で、上記の方法を用いて教材実践を行った。アミノ酸の確認の手法と精製の必要性が学べる化学教材であることを確認した。

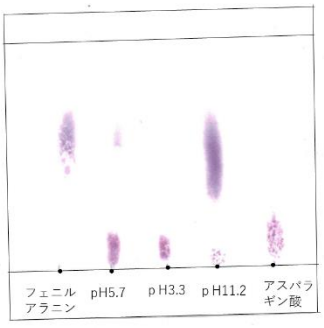

図１. 流出液の分析の結果

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ろ紙電気泳動を利用した遷移金属イオンおよび錯イオンの流体力学的半径の評価

（宮崎大教育）○小泉 秀介・有井 秀和
Estimation of the Stokes radius for transition metal ions and complexes by electrophoresis on filter (*Faculty of Education, University of Miyazaki*) ○Shusuke Koizumi, Hidekazu Arii

An electrophoresis on a filter is well known one of experiments to understand an ion in the lecture of junior high school. We focus on the evaluation of scale and charge of ions by the electrophoresis. We present about the estimation of hydrodynamic radius (Stokes radius) of transition metal ions and complexes bearing monodentate or bidentate ligands. The Stokes radii of Cu^{2+} and Co^{2+} for electrophoresis on a filter were 2.8 and 3.2 Å, respectively, estimated from the migration distance and time. The radii are consistent with those calculated from the corresponding limiting molar conductivities. For the complexes, the Stokes radii of $[Co(NH_3)_6]^{3+}$ and $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$ were obtained at 4.7 and 7.0 Å (Figure 1), respectively, which depends on the bulkiness of ligand although they are more than the expected radii.
Keywords : Stokes Radius; Transition Metal Ion; Complex; Electrophoresis on Filter

ろ紙上での金属イオンの電気泳動は、中学校でイオンが電荷を帯びていることの理解に利用される実験手法の一つである。電圧を印加した水中をイオンが移動するとき、イオンの大きさや電荷により移動速度が変化することが知られている。これを踏まえて我々は、ろ紙電気泳動を用いて金属イオンの大きさや電荷を簡便に比較できる実験手法の確立を目指している。本研究では、遷移金属イオンや、単座あるいは二座配位子を持つ錯イオンを用いて、それぞれの流体力学的半径を評価した。

0.1 M KNO_3水溶液を染み込ませたろ紙に塩化銅を置き、電圧を一定時間印加するとCu^{2+}イオンの移動が観測された。移動距離と電圧の印加時間から移動速度を求め、それを用いて流体力学的半径を算出すると2.8 Åであった。同様にCo^{2+}イオンで実験を行うと3.2 Åであり、これらの値は対応するイオンの極限モル伝導率から求めた流体力学的半径と一致していた。錯イオンである$[Co(NH_3)_6]^{3+}$や$[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$ (Figure 1) ではそれぞれ4.7 Åと7.0 Åであった。流体力学的半径は配位子の嵩高さにより増加していると考えられるが、その値は予測されたものよりも大きかった。発表では、その他の遷移金属イオンや錯イオンとも比較・検討し、その詳細を述べる。

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食品中の動物性鉄化合物によって加速される油脂の酸化

（東理大理 [1]）○竹之内紀子 [1]・井上正之 [1]
Aerobic oxidation of oils accelerated by iron compounds of animal origin in foods（*1Faculty of Science, Tokyo University of Science*）○Kiko Takenouchi[1], Masayuki Inoue[1]

Oils are used in various subjects such as "Chemistry", "Science and Our Daily Life", "Home Economics" and "Art and Design" at the high school level. Oils in food are thermally oxidized under aerobic conditions during the cooking process. In our laboratory, we have studied the effects of food ingredients on the aerobic oxidation of oils and the possibility of using them as teaching materials for experiments. In this study, iron (II) phthalocyanine and hemin were investigated as model compounds to explore the catalytic activity of iron compounds of animal origin such as hemoglobin.
Keywords : Oils; Aerobic oxidation; Catalyst; Iron compounds of animal origin

油脂は高等学校理科（「化学」，「科学と人間生活」）や「家庭科」，「美術」など複数の教科で扱われ，日常生活に密着した素材である。我々の研究室では食品の成分が油脂の酸素酸化に与える影響を検討し，実験教材化するための検討を行っている。食品中に含まれる油脂は，金属イオンの触媒作用によって加熱時に空気酸化される。本研究では，ヘモグロビンなどの動物性の鉄化合物の触媒作用を探索するために，モデル化合物であるフタロシアニン鉄（Ⅱ）FePc と鉄（Ⅲ）イオンを含むヘミン（図 1）およびヘモグロビン Hb を用いる検討を行った。

触媒における Fe^{2+} と Fe^{3+} の物質量をヘモグロビン 1.00 g における Fe^{2+} の量に相当する 62.4 μmol に揃えてアマニ油 11.0 g に添加し，空気を送りながら 30 分間加熱したところ，触媒としてフタロシアニン鉄（Ⅱ）が最も効率よく作用したがヘモグロビンでは酸化が進行しなかった。なお反応の進行は ^{1}H-NMR（溶媒：$CDCl_3$）を測定し，酸化の影響を受けやすい油脂分子中のビスアリル位における水素原子数の減少によって評価した（図 2）。

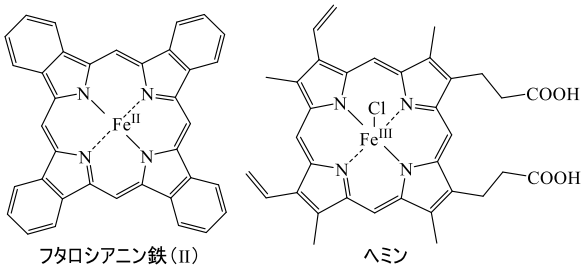

図 1　検討した触媒

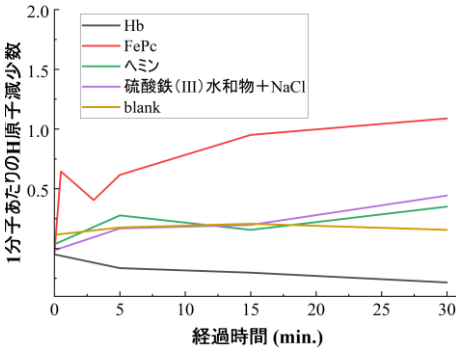

図 2　ビスアリル位における水素原子数の変化

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鉄（III）塩を触媒とする油脂の空気酸化におけるアミノ酸の抑制効果

（東理大院理[1]・東理大理[2]）○谷川 千乃[1]・井上 正之[2]
Suppression effect of amino acids on air oxidation of lipids plant oils catalyzed by iron (III) salts ([1]*Graduate School of Science, Tokyo University of Science*, [2]*Faculty of Science, Tokyo University of Science*) ○Yukino Tanigawa,[1] Masayuki Inoue[2]

In our laboratory, the effect of food components on the aerobic oxidation of oils has been studied in order to use as a teaching material for experiments. We have already studied an experimental method for rapid oxidation of linseed oil by adding a mixture of hydrated iron (III) sulfate and sodium chloride as a catalyst and blowing air into the mixture while heating. In this study, we investigated the effect of moisture in the air on the oxidation of linseed oil. We also investigated the effect of some α-amino acids as catalytic inhibitors.
Keywords : Aerobic oxidation of oils; Ferric salts; Amino acids

我々の研究室では食品中の成分が油脂の空気酸化に与える影響に着目し，これを実験教材とするための検討を行っている。当研究室では既に硫酸鉄（III）水和物と塩化ナトリウムの混合物（mol 比 $Fe^{3+}:Cl^{-}=1:4$）を，触媒として油脂に対して 0.50wt%添加し，97℃に加熱しながら空気を吹き込むことでアマニ油を迅速に酸化させる実験法が検討されている。本研究では，この反応における空気中の水分の影響を調査すると共に，食品中に含まれ酸化防止効果が報告されているアミノ酸のうち，4 種類の α-アミノ酸をアマニ油 11 g に対して 0.5 mmol 添加し，酸化に与える影響を過酸化物価（POV）[1]および ^{1}H-NMR（溶媒：$CDCl_3$）によって評価した。その結果，本検討で用いた α-アミノ酸のうち，アスパラギン酸以外には顕著な抑制効果が見られた（図 1）ことから，アミノ酸の側鎖の種類によって触媒を抑制する効果が異なることが分かった。また FT-IR による分析によって，そのメカニズムを考察した。

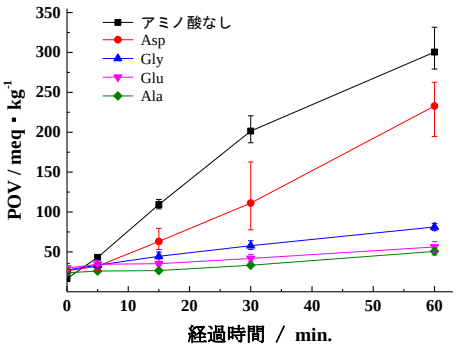

図 1　POV の時間変化

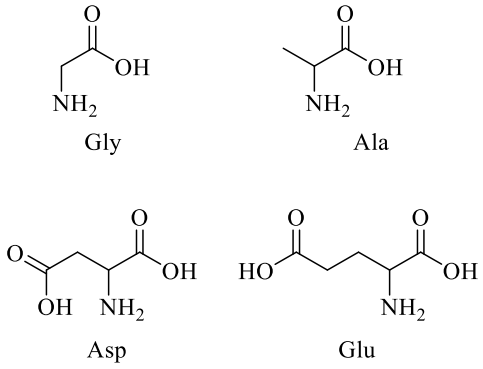

図 2　検討した α-アミノ酸

1)　日本油化学会，日本油化学会制定基準油脂分析試験法，日本油化学会，**2013**，p.2.5.2.2-2013.

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日本化学会 第104春季年会 (2024)

硫酸シリカゲルを用いたアルキンの水和

（東理大院理[1]・東理大理[2]）○山田 康平[1]・井上 正之[2]
Hydration of alkynes with sulfuric acid silica gel([1]Graduate School of Science, Tokyo University of Science, [2] Faculty of Science, Tokyo University of Science)○Kohei Yamada[1], Masayuki Inoue[2]

The hydrationof unsymmetrical alkynes can serve as an advanced experimental material for learning keto-enol equilibrium and the Markovnikov rule. We have previously reported experiments about the hydration of phenylacetylene using concentrated sulfuric acid solution and surfactants, which posed challenges due to the long reaction time and the handling of high-concentration sulfuric acid solution at high temperatures.

In this study, we explored experimental materials about the hydration of alkynes with a short reaction time using sulfuric acid-supported silica gel (sulfuric acid silica gel). When phenylacetylene was reacted with sulfuric acid silica gel, a mixture of concentrated sulfuric acid and silica gel at a mass ratio of 1:1, acetophenone was formed with a low yield (17% yield) due to the progressing carbonization. However, phenylacetylene was reacted with sulfuric acid silica gel, prepared with 12 mol/L sulfuric acid solution and silica gel at a mass ratio of 1:1, the yield of acetophenone increased to 48% in 1 minute.

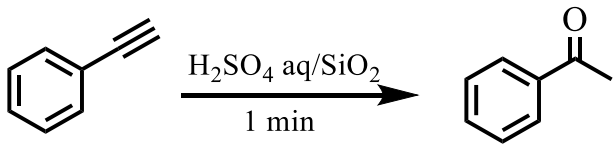
We also investigated detection of acetophenone utilizing iodoform reaction, 2,4-dinitrophenylhydrazine solution, and commercially available ketone paper for urine testing.

Keywords : *Hydration of Phenylacetylene* ; *Sulfuric Acid Supported on Silica Gel* ; Acetophenone

非対称アルキンの水和反応は、ケト-エノール平衡およびマルコフニコフ則を学習する発展的な実験教材になる。すでに当研究室では、濃度の高い硫酸水溶液と界面活性剤の組み合わせによるフェニルアセチレンの水和の実験を報告している[1)]。この方法では反応時間が長いこと、高濃度の硫酸水溶液を高温で扱うことに問題があった。

本研究では、当研究室で継続的に用いられている硫酸担持シリカゲル（硫酸シリカゲル）を使用して、短時間で進むアルキンの水和反応の実験教材を検討した。フェニルアセチレンを濃硫酸とシリカゲルを質量比 1：1 で混合した硫酸シリカゲルと反応させると、炭化が進行して生成物であるアセトフェノンは低収率（17%）でしか生成しなかった。しかしフェニルアセチレンを、12 mol/L 硫酸水溶液とシリカゲルを質量比 1：1 で混合した硫酸シリカゲルと、加熱することなく 1 分間反応させることで、アセトフェノンの収率が 48%に向上した。

あわせてヨードホルム反応や 2,4-ジニトロフェニルヒドラジン溶液、市販の尿検査用ケトン紙を用いるアセトフェノンの検出法を検討した。



1）上原智，井上正之，化学と教育 **2015**，*64*，244.

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塩基性水溶液中における銅（Ⅱ）化合物による糖類の酸化のメカニズム

（東理大院理 [1]，東理大理 [2]）○松原朱里 [1]・井上正之 [2]

Mechanism of oxidation of sugars by copper (II) compounds in alkaline aqueous solutions

([1]*Graduate School of Science Tokyo University of Science,* [2]*Faculty of Science Tokyo University of Science*) ○Akari Matsubara,[1] Masayuki Inoue[2]

Monosaccharides such as glucose, mannose and fructose are known to have reducibility. We have previously reported that the reducibility of sugars is attributed to the α-hydroxycarbonyl structure by comparing reaction rates[1)]. In this study, the mechanism of oxidation of such reducing sugars under basic conditions was discussed by HPLC analysis of the reaction products of glucose, mannose and fructose with Benedict's reagent.

Keywords : Products of Benedict's Reaction; *Glucose*; *Mannose*; *Fructose*

グルコース，マンノース，フルクトースなどの単糖は塩基性水溶液中で還元作用を示す。すでに我々は，反応速度を比較することで還元性の原因が α-ヒドロキシカルボニル構造であることを報告している [1)]。本研究では，実際にグルコース，マンノース，フルクトースとベネジクト試薬との反応生成物を分析することによって，生成物の観点から塩基性条件における糖の酸化のメカニズムについて考察した。

試料糖とベネジクト試薬を反応させ HPLC を用いて得られた試料を分析したところ，生成物の出現ピークパターンに共通部分が見られた（図 1)。この結果から各糖とベネジクト試薬との反応は共通の中間体（エンジオラート）を経由して進行していると考えられる（図 2)。詳細について，講演で報告する。

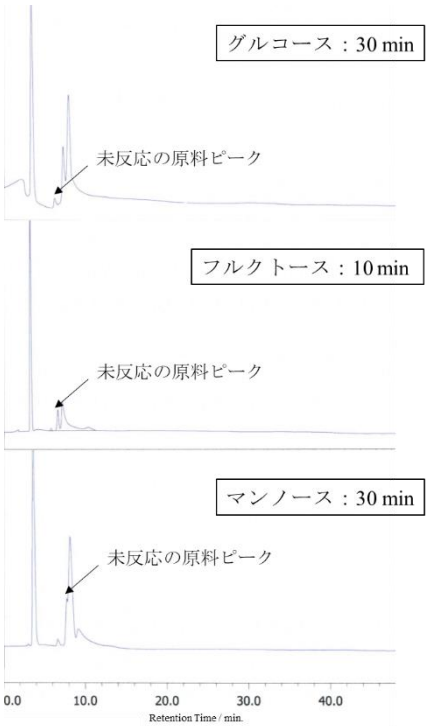

図 1　HPLC による糖とベネジクト試薬との反応生成物の分析結果

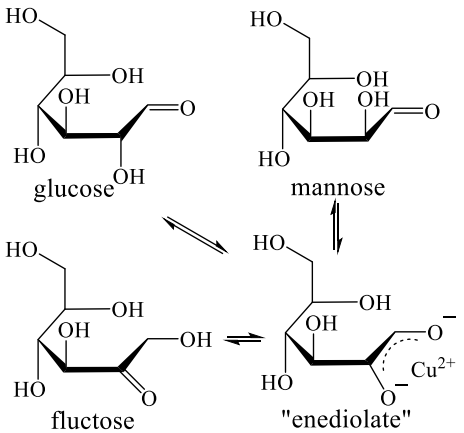

図 2　各糖の酸化における中間体

1)　増田泰大，今野貴幸，井上正之，化学と教育，**2020**，*68*，434.

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芳香族カルボン酸を中和反応で区別するマイクロスケール実験教材

（福岡大理）○上田　竜也・松岡　雅忠

Development of microscale experimental teaching materials to distinguish aromatic carboxylic acid through neutralization reactions.

(*Faculty of Science, Fukuoka University*)
○Ueda Tatsuya and Matsuoka Masatada

Based on the awareness of the issue in chemical education of promoting the understanding of quantification of chemical reactions through experiments, a student experiment to determine the molecular weight of aromatic carboxylic acid by neutralization reaction was investigated. Since aromatic carboxylic acid is poorly soluble in water, a solution prepared by dissolving aromatic carboxylic acid in ethanol was used for titration with aqueous sodium hydroxide. As a result of the experiment, the molecular weights of benzoic acid, salicylic acid, and acetylsalicylic acid were determined almost accurately. Then, a microscale experiment using a plastic dropper was developed and practiced in a high school class. This experimental method's advantage is avoiding the use of glassware and electronic balance.

Keywords : Acid-base Titration, Microscale Experiment, Molecular Weight, Aromatic Carboxylic Acid

実験を通じて化学反応の定量性への理解を促進するという視点から，中和反応により芳香族カルボン酸の分子量を求める生徒実験[1,2]の反応条件を検討した。

芳香族カルボン酸は水に難溶なため，エタノール溶液を調製し，これを水酸化ナトリウム水溶液で滴定した。実験の結果，代表的な芳香族カルボン酸（安息香酸，サリチル酸，アセチルサリチル酸）でほぼ正確に分子量を求めることができた。

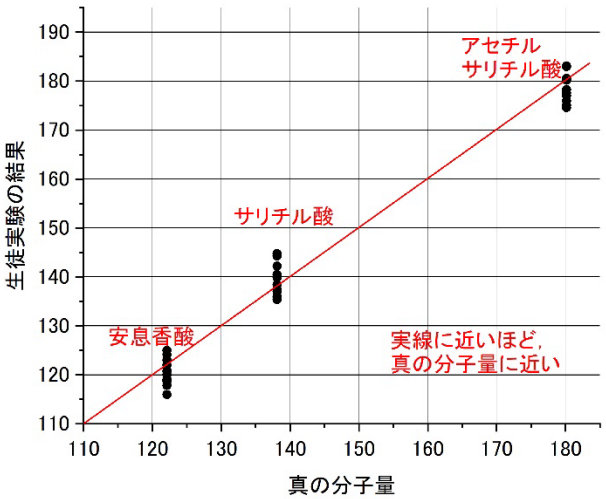

図　中和滴定を利用した分子量の推定

そして，プラスチックスポイトを用いるマイクロスケール実験を開発した。この実験方法は，生徒実験では電子天秤を使用しないことや，逆滴定を回避できることがメリットといえる。

模擬授業の結果からは，分子量の離れた 3 種類の芳香族カルボン酸を区別することが可能であることがわかり，質量，物質量，分子量を関連付ける生徒実験として適していると考えられる。

1) 松岡雅忠，化学と教育 **2023**, *71*, 152.　2) 志賀裕樹，化学と教育 **2007**, *55*, 168.

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時計反応を利用した定量実験の開発 －反応時間から濃度を推定する実験－

（福岡大理）○實藤　匠汰・松岡　雅忠

Development of Quantitative Experiments Using Iodine Clock Reaction -Experiments to estimate the concentration of an unknown sample from the reaction time-

(*Faculty of Science, Fukuoka University*)
○Sanefuji Shota and Matsuoka Masatada

A clock reaction is a chemical reaction in which the entire solution changes color instantaneously after a certain time. It is popular as a chemical demonstration, and is often used in experiments to calculate the reaction rate. This study attempted to develop the clock reaction (Landolt reaction) into an experiment to quantify an object. First, the relationship between the molar concentration of two aqueous reagent solutions and the time required for the color change was investigated to find appropriate reaction conditions. Then, based on the graph of concentration and time, an experimental teaching material was developed to estimate the concentration of an aqueous potassium iodate solution of unknown concentration. Such quantitative experiments deepen the learning about reaction rates and are also suitable for learning activities involving group discussions.

Keywords : Clock Reaction; Landolt Reaction; Reaction rate

時計反応とは，一定時間後に溶液全体が瞬間的に色変化する化学反応を指す。化学デモンストレーションとして人気があるほか，反応速度を算出する実験もよく実践される[1,2]。

本研究では時計反応（ランドルト反応）を，対象物を定量する実験へと発展させることを試みた。まず，2 種類の試薬水溶液のモル濃度と色変化までの時間との関係を調査し，適切な反応条件を模索した。

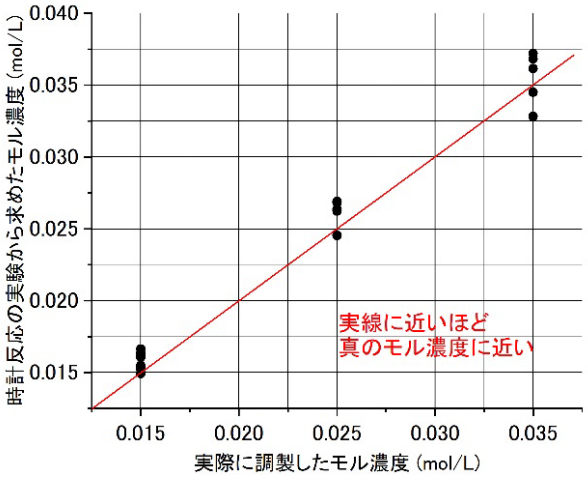

図　時計反応を利用した未知溶液の定量

そして，モル濃度と時間のグラフをもとに，濃度未知のヨウ素酸カリウム水溶液の濃度を推定する実験教材の開発を行った。高校生を対象とする模擬授業では，ヨウ素酸カリウム水溶液のモル濃度を大まかに見積もることが可能であることが判明した。呈色までの時間変化に着目する定量実験は，反応速度に関する学習事項の深化につながるだけでなく，グループでの話し合いを取り入れた学習活動を行う上でも適していると考えられる。

1) Xavier Creary and Karen M. Morris, *J. Chem. Educ.* **1999**, *76*, 530-531.　2) 池本勲訳，B. Z. Shakhashiri 著，教師のための化学実験　ケミカルデモンストレーション 6，丸善，**1998**.

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陰イオン界面活性剤を用いたパラジウム触媒層の形成とグルコース形燃料電池の作製

（大妻嵐山高[1]）○鈴木　崇広[1]

Formation of a Palladium Catalyst Layer Using an Anionic Surfactant and Subsequent Fabrication of a Glucose Fuel Cell ([1]*Otsuma Ranzan Junior and Senior High School*)

○Takahiro Suzuki[1]

In this experiment, students fabricated a glucose fuel cell, checked the operation of a solar motor, and investigated the cell performance. First, a fuel cell catalyst was prepared by plating palladium on two nickel wire meshes using an aqueous palladium chloride solution containing sodium dodecyl sulfate, an anionic surfactant that helped in achieving uniform palladium plating. Next, a cell was fabricated by sequentially placing a potassium hydroxide solution containing glucose, nickel wire mesh with the palladium catalyst, cellophane membrane, and another nickel wire mesh with the palladium catalyst in a plastic container. Using this method, a glucose fuel cell was easily fabricated in ~30 min, which is extremely short compared to the time required in conventional fabrication processes.

Keywords：Oxidation/Reduction, Electrochemistry, Plating, Metals

グルコース燃料電池（式 1、2）の触媒として、電極（ニッケル金網）にパラジウムめっきを施す際に、塩化パラジウム水溶液に陰イオン界面活性剤であるドデシル硫酸ナトリウムを添加することによって、均一で剥がれにくい触媒層を形成することができた（図 1）。次に、プラスチック製容器にグルコースを含む水酸化カリウム溶液、パラジウム触媒付きニッケル金網、セロハン膜、パラジウム触媒付きニッケル金網を順に重ねて電池を作製した（図 2）。この方法により、グルコース燃料電池を約 30 分で簡単に製造できた。この実験は、グルコース燃料電池の作製を実際に体験できるだけでなく、めっきの原理やグルコースの還元性についても学ぶことができる。

陰極　$C_6H_{12}O_6 + 2OH^- \rightarrow C_6H_{12}O_7 + H_2O + 2e^-$　$E° = -0.853$ V　（式 1）

陽極　$1/2O_2 + H_2O + 2e^- \rightarrow 4OH^-$　$E° = 0.403$ V　（式 2）

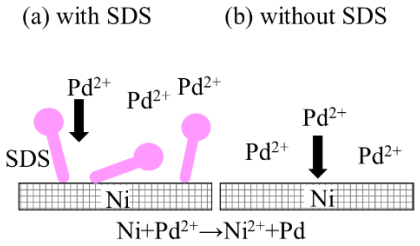

図 1　パラジウムめっきの概要

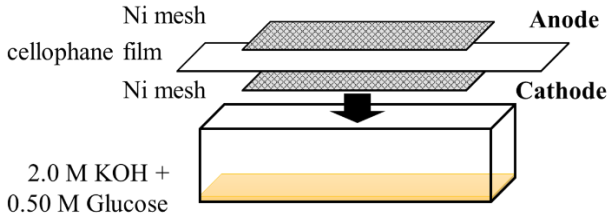

図 2　グルコース燃料電池の構成

1) Takahiro Suzuki, Misaki Fujino, Yoji Yamada, *J. Chem. Educ.* **2023**, *100* (12), 4780–4785.

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マイクロスケール実験の新しい展開：コロナ後のサイエンス展

(香川大教育[1]・東北大理[2]) ○川田 茉里奈[1]・森脇 ゆな[1]・小野 玲奈[1]・高橋 智香[1]・高木 由美子[1]・荻野 和子[2]

New Development of Microscale Experiments: Science exhibitions after Covid-19 ([1]*Faculty of Education, Kagawa University*, [2]*Faculty of Science, Tohoku University*) Marina Kawata,[1] Yuna Moriwaki,[1] Reina Ono,[1] Chika Takahashi,[1] Yumiko Takagi,[1] Kazuko Ogino[2]

Microscale chemistry can be used to conduct environmentally friendly experiments by setting up appropriate reaction systems. Various reports have been made on this method as a way to recapture the concept of experimentation. It has been reported that microscale experiments can be used to experimental classes that take into account the prevention of COVID-19 infection. It is reported that the detail of a new science exhibition under micro-scaling and infection control consideration of the SDGs.

Keywords : Microscale Chemistry; Science Exhibition

マイクロスケールケミストリーには様々な利点があり、３蜜を回避するのに有効であることから，コロナ感染予防に配慮した実験授業ができることが報告されている[1-3]。オンラインサイエンス展においてもマイクロスケール化は有効であった。コロナ下で実施したオンラインサイエンス展の工夫や，質疑応答に対する好意的な評価は多く，オンライン実施の良さを体感できた。2023年度は、感染対策を講じた上で、従来の対面での児童生徒を対象にしたサイエンス展に加えて、海外協定大学と合同の食育プログラム、本年採択されたJST女子中高生の理系進路選択支援プログラムを共同で開催した。本年度実施の概要及び、実施の工夫について紹介する（図１）。

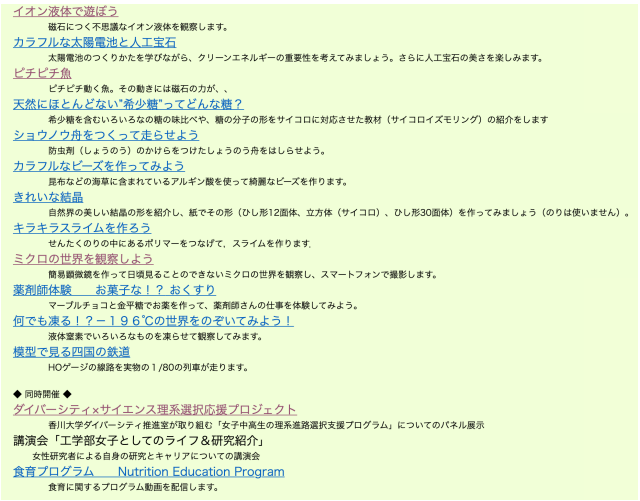

Fig. 1 実施プログラム一覧
http://www.kms.ac.jp/~yakubutu/wakuwaku2023.html

1) S. Thompson, Chemtrek-Small Scale Experiments for General Chemistry, 1st ed., Prentice Hall, New Jersey, 1989, Chap.7, pp.114-136.
2) マイクロスケール化学実験-マイクロスケール実験の広場から-荻野 和子編, 日本化学会関東支部, 2005年
3) COVID-19蔓延下におけるマイクロスケール実験の有用性，荻野和子，片岡久美子，猪俣慎二，生田博将，高瀬つぎ子，高木由美子，高橋智香，化学と教育, 70(1), 44-47, 2022.

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アセトアルデヒドを用いたビニロン合成における形状制御と物性比較の方法の検討

（東邦大[1]・山梨県立富士河口湖高[2]）○藍 ことね[1]・渡辺 美緒[2]・今井 泉[1]
Consideration of Methods for Shape Control and Comparison of Physical Properties in Vinylon Synthesis Using Acetaldehyde ([1]*Toho University*, [2]*Fuzikawaguchiko High School*) ○Kotone Ai,[1] Mio Watanabe,[2] Izumi Imai[1]

This research aims to develop experimental teaching materials synthesizing vinylon using Acetaldehyde. Specifically, the first step was to control the product shape, and the second was to compare the product's physical properties (tensile strength) before and after acetalization. In the first step, we added 10 mL of 9 % polyvinyl alcohol (PVA) solution and 5 mL of Na_2SO_4 solution to a petri dish and then heated for 10 minutes to dry. As a result, we synthesized thin and uniform vinylon with thicknesses ranging from 0.13 to 0.37 mm. In the second step, we added 5 mL of Na_2SO_4 solution to 10 mL of PVA solution, heated and dried, and acetalized by reacting with 10 mL of Acetaldehyde. Also, we synthesized vinylon acetalized with formaldehyde, which is conventionally used, for comparison[1)]. We measured tensile strength with a digital force gauge (IMADA Corporation, DST-500N) using each 1 cm x 3 cm sample. As a result, the vinylon with Acetaldehyde had greater tensile strength (Fig. 1). Therefore, the developed experimental teaching materials are more helpful and exploratory regarding safety and quantitatively measurable.
Keywords : Vinylon; Acetaldehyde; Tensile Strength

本研究では，アセトアルデヒドを用いたビニロン合成の実験教材の開発を目的とする。具体的には，第一段階として生成物の形状制御，第二段階としてアセタール化前後の物性比較（引張強度）を実施した。第一段階として，9 %ポリビニルアルコール（PVA）水溶液 10 mL，Na_2SO_4 水溶液 5 mL をシャーレに加えた後，10 分間加熱して乾燥させた。その結果，厚さが 0.13～0.37 mm の均一なビニロンが合成された。第二段階として，PVA 水溶液 10 mL に Na_2SO_4 水溶液 5 mL を加え，加熱・乾燥させた後，アセトアルデヒド 10 mL を反応させてアセタール化した。また，比較のために従来用いられるホルムアルデヒドでアセタール化したビニロンも合成した[1)]。引張強度の測定は，1 cm×3 cm の各試料を用いてデジタルフォースゲージ（株式会社イマダ，DST-500N）で実施した。その結果，アセトアルデヒドを用いたビニロンの方が，引張強度が大きくなった（図 1）。よって，開発した実験教材は，安全性及び定量的に測定可能な観点から，より活用しやすく探究的な教材であることが示唆された。

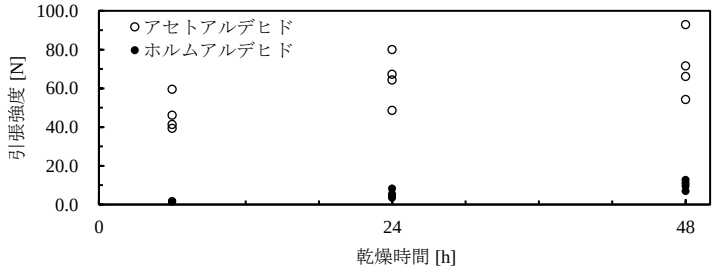

図 1. アセトアルデヒドとホルムアルデヒドを用いたビニロンの引張強度

1）守本昭彦，化学と教育，**1990**，38，194-195

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中等教育の化学実験における環境負荷及び安全性を可視化する評価方法の開発

（東邦大[1]・東邦大院理[2]）○工藤 萌香[1]・山田 将司[2]・今井 泉[1]

Development of an evaluation method to visualize the environmental impact and safety of chemical experiments in secondary education ([1]*Toho University*, [2]*Graduate School of Science, Toho University*) ○Moeka Kudo,[1] Masashi Yamada,[2] Izumi Imai[1]

This research aims to develop an evaluation method that visualizes experiments' environmental load and safety in junior high school sciences (chemistry field) and high school chemistry. Specifically, we evaluate using the three indicators of environmental load, "energy," "reagents," and "waste," and the three indicators of safety, "several labels under the Globally Harmonized System of Classification and Labelling of Chemicals," "concentration used," and "experiment time."

We configured the standards as 1 for the first quartile from the minimum value, 2 for the median value from the first quartile, 3 for the third quartile from the median value, and 4 for the maximum value from the third quartile. Then, we visualized the environmental load and safety level on a 12-point scale by adding the evaluation results of the three indicators (Figure 1). In Figure 1, Experiments in the first quadrant are more concerned with environmental impact and safety. However, the results suggested that it is necessary to pursue further improvements in environmental load and safety in many experiments.

Keywords： experimental teaching materials evaluation; green and sustainable chemistry

本研究では、中学校『理科』（化学分野）（n＝21）、高等学校『化学基礎』・『化学』（n＝31）の実験における環境負荷及び安全性を可視化する評価方法の開発を目的とする。具体的には、環境負荷の指標として「エネルギー」、「試薬」、「廃棄物」の 3 指標、安全性の指標として「化学品の分類および表示に関する世界調和システムのラベル数」、「使用濃度」、「実験時間」の 3 指標を用いて評価する。

最小値から第一四分位値を 1、第一四分位値から中央値を 2、中央値から第三四分位値を 3、第三四分位値から最大値を 4 と基準を設定し、3 指標の評価結果を足し合わせた 12 段階で環境負荷と安全性の程度をそれぞれ可視化した（図 1）。図 1 では右上に位置する実験ほど環境負荷と安全性に配慮した実験であるが、多くの実験において環境負荷及び安全性の向上をさらに追求する必要があることが示唆された。

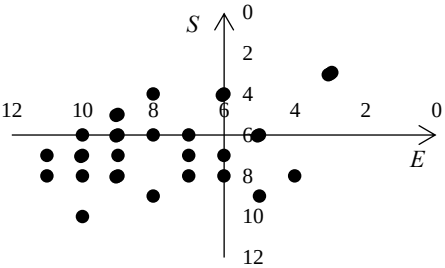

図 1　環境負荷（E）・安全性（S）評価の結果

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分子パズル PuzMol（パズモル）の開発と教育実践

（千葉工業大学）山本 典史

PuzMol: Molecule-Building Puzzle

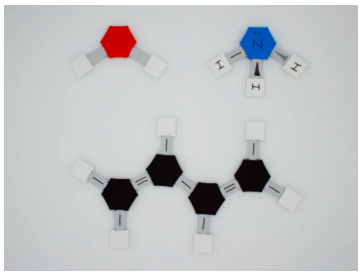
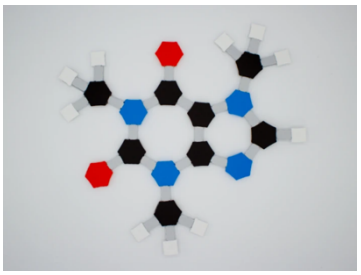
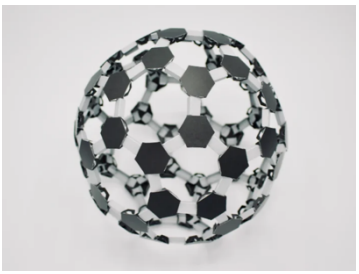
(*Chiba Tech*) Norifumi Yamamoto

PuzMol[1] is a molecular puzzle that serves as both a paper craft and a web application, with the aim of improving accessibility in chemistry education. The papercraft version can be easily assembled without the use of scissors or glue, making it suitable even for young children. The web application allows instant access from any location with an Internet connection, using devices such as PCs, smartphones, or tablets. PuzMol is commonly employed in educational settings as an affordable molecular model, making it an ideal tool for teaching students about molecular structures while engaging their interests through the enjoyment of puzzle-solving. In this presentation, I will demonstrate how PuzMol can be utilized as both a learning resource to promote learning in the classroom and a means of communication to convey the excitement of scientific discoveries.

Keywords : Molecular Model; Educational Toy; Communicative Tool; Teaching Aid

PuzMol[1]は「**化学の学びをもっと身近に**」することをめざして、身近で安価な材料の紙製の**ペーパークラフト**として、さらに、いつでもどこでもだれでもすぐに使える**ウェッブアプリ**として開発した、**分子のパズル**です。紙でつくったペーパークラフト版の PuzMol は、ハサミや接着剤を用いずに、**幼児や小学生でも、安全に・簡単に**組み立てることができます。ウェッブアプリ版は、パソコン・スマートフォン・タブレットなどのインターネットのアクセス環境があれば、**いつでも・どこでも・だれでも・すぐに**使うことができます。

PuzMol は学校の授業などで、**手軽に組み立て・自由に組み替えができる分子模型、分子のカタチの成り立ちをパズルのように解きながら楽しく学べる教材**として、幅広く活用されてきました。本発表では、ペーパークラフト版 PuzMol を実際に手に取っていただきながら、開発の経緯、そして、子どもたちの探究心を育む**知的玩具**、授業での主体的な学びを促す**学習教材**、科学の楽しさを伝える**コミュニケーションツール**として PuzMol を活用したいくつかの教育実践について、ご紹介します。

1) https://puzmol.com

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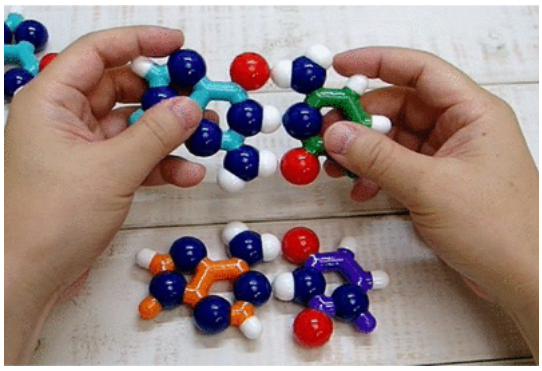
水素結合を磁力で再現した体感型分子模型「BasePairPuzzle」

（上智大理工[1]・㈱スタジオミダス[2]）○近藤 次郎[1]・中村 昇太[2]
BasePairPuzzle: An experiential molecular model that reproduces hydrogen bonds with magnetic force ([1]*Faculty of Science and Technology, Sophia University*, [2]*StudioMIDAS Inc.*)
○Jiro Kondo,[1] Shota Nakamura[2]

Various molecular models and computer graphics applications have been developed to understand chemical structures and life phenomena based on them. However, these existing tools do not allow us to experience the attraction and repulsion between molecules. Therefore, we have developed a new experiential molecular model, "BasePairPuzzle," that focuses mainly on molecular interactions in which hydrogen bonds are reproduced by the magnetic force of neodymium magnets.[1)]

The S and N poles of a neodymium magnet are placed at the positions of a hydrogen atom (hydrogen bond donor) and a lone pair (hydrogen bond acceptor) of the models, respectively, so that the user can experience hydrogen bonding as a magnetic force between their fingers and hands. As the students play with several models, they will stick to each other on their own with the assistance of the neodymium magnets, and the students will notice for themselves that there are some attractive and repulsive forces between the models. The BasePairPuzzle is truly a puzzle that helps users understand the principles and diversity of molecular interactions for themselves.



Keywords: Molecular Model, Nucleic Acids, Base Pair, Hydrogen Bond, Active Learning

化学構造やそれに基づく生命現象を理解するために、様々な分子模型やコンピューターグラフィックスのアプリケーションが開発されてきた。しかし、これらの既存のツールでは、分子同士が「引き合う・反発する」という性質を体感することはできない。そこで我々は、分子の相互作用に主眼を置き、水素結合をネオジム磁石の磁力で再現した新しい体感型分子模型「BasePairPuzzle」を開発した。[1)]

ネオジム磁石の S 極と N 極を分子模型の水素原子（ドナー）と非共有電子対（アクセプター）の位置にそれぞれ配置しており、水素結合を磁力として手のひらで体感することができる。いくつかの模型で遊んでいるうちに、ネオジム磁石の助けを借りて分子模型同士が勝手に引き合うため、学習者は分子間に引力や斥力があることに自然と気が付くはずである。BasePairPuzzle はまさに分子間相互作用の原理や多様性を学習者自身で理解するためのパズルとして教育現場で使うことができる。

1) J. Kondo, S. Nakamura, "BasePairPuzzle: Molecular Models for Manipulating the Concept of Hydrogen Bonds and Base Pairs in Nucleic Acids" *J. Chem. Edu.* **2023**, *100*, 946.

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加藤セチをロールモデルに理系女子人材育成を

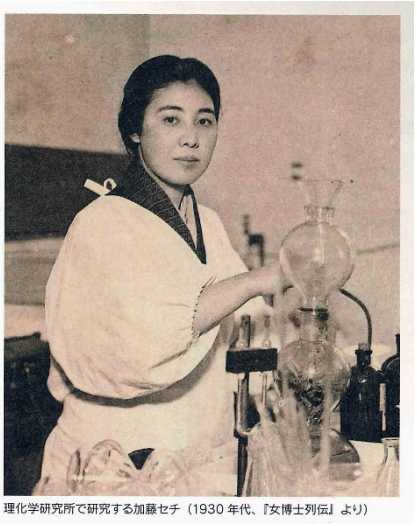
（山形大理[1]・サイエンススタジオマリー[2]）○栗山　恭直[1]・吉祥　瑞枝[2]
Developing Human Resources for Women in Science with Sechi Kato as a Role Model
([1]*School of Science, Yamagata University*, [2]*Science Studio Marie*) ○Yasunao Kuriyama,[1] Mizue Kissho[2]

Sechi Kato was the third woman from Yamagata to receive a PhD in Japan. She worked as a researcher at RIKEN. We will present her activities and the program for human resource development for women in science using her as a role model.
Keywords : Sechi Kato; Woman in Science

山形大学では、平成 3 年度から JST の理系女子進路選択支援プログラムに採択され「ヤマガタ夢☆未来 Girls プロジェクト」を実施している。その中で現役の女性研究者や技術者をロールモデルとして紹介してきた。[1)]

女性理学博士の先人として黒田チカは有名であり、東北大の博物館等でも資料として公開されている。黒田チカに続いて日本で 3 番目に理学博士になったのが山形県出身の加藤セチである。山形県出身の加藤セチをロールモデルとして多くの人に知ってもらい、理系女子を増やすことをプロジェクトに取り入れることにした。

加藤セチは、1893 年の山形県三川町で生まれ、鶴岡高等女学校を退学後、山形県女子師範学校（現　山形大学地域教育文化学部）を卒業後、小学校教師になるが東京女子高等師範学校に進学、卒業後北海道の北星高等女学校で教えながら北海道帝国大学に全科目履修専科生として入学、修了後に結婚した。その後理化学研究所に勤務し、1931 年に京都帝国大学より「アセチレンの重合」を主論文として理学博士を授与された。理化学研究所で研究を続けた。1960 年から 15 年間理科ゼミとよばれる勉強会を毎月開催した。一般向けだが、高校の教員が参加者の中心だった。1989 年に死去した。[2)]


理化学研究所で研究する加藤セチ（1930 年代、『女博士列伝』より）

加藤セチの誕生日の前日の 10 月 2 日に山形大学で生誕 120 年のイベントを開催した。午前中が加藤セチが研究に使用した分光に関する親子対象の実験講座、午後には、加藤セチとマリキュリーに関する講演と大学と県試験場の研究者の座談会を行った。

1)　ヤマガタ夢☆未来 Girls プロジェクト https://yumemirai-girlsproject.aiyweb.com/.
2)　前田侯子：『加藤セチ博士の研究と生涯』ジェンダー研究, 第 7 号（2004）, p.87

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恒温槽を備えた，簡便で高精度な目視型の旋光計の開発

（東邦大学[1]）○鵜沢 哲丸[1]・今井 泉[1]
Development of a simple and highly accurate visual polarimeter equipped with a constant temperature bath ([1]*Toho University*) ○Tetsumaru Uzawa,[1] Izumi Imai

We developed a simple and sophisticated polarimeter by converting the light from a light source into two types of polarization using two polarizing plates with different planes of polarization and measuring the light by comparing the transmittance. This polarimeter can control the temperature since it has a constant temperature bath that supplies water at a constant temperature, which is adjusted by a thermostat and a water pump (Figure 1). Furthermore, this polarimeter operates even while stirring a solution with a stirrer bar, as is commonly done in typical chemical reactions, so it can be measured using the same equipment used for conventional reactions. Therefore, the reaction rate of sucrose hydrolysis was measured from 10 °C to 30 °C in 5 °C increments. By graphing the results, we could accurately confirm the temperature dependence (Figure 2).
Keywords： Polarimeter, Reaction Rate, Arrhenius plot, Sucrose, Constant Temperature Bath

光源からの光を，異なる偏光面をもつ 2 枚の偏光板で 2 種類の偏光にして，透過率を比較することで測定する，簡便で精巧な旋光計を開発した。また旋光計に，サーモスタットと水流ポンプで調整した恒温水を流す恒温槽を備えることで温度制御を可能とした（Figure 1）。さらに，本旋光計は，一般的な化学反応で行うように，撹拌子を入れて溶液を撹拌した状態でも使用できる。そのため，反応容器のまま旋光度の測定ができ，反応追跡が容易である。そこで，ショ糖の加水分解の反応速度[1)]を 10 ℃から 5 ℃刻みで，30 ℃まで測定した。その結果をグラフ化すると精度よく温度依存性を確認することができた（Figure 2）。

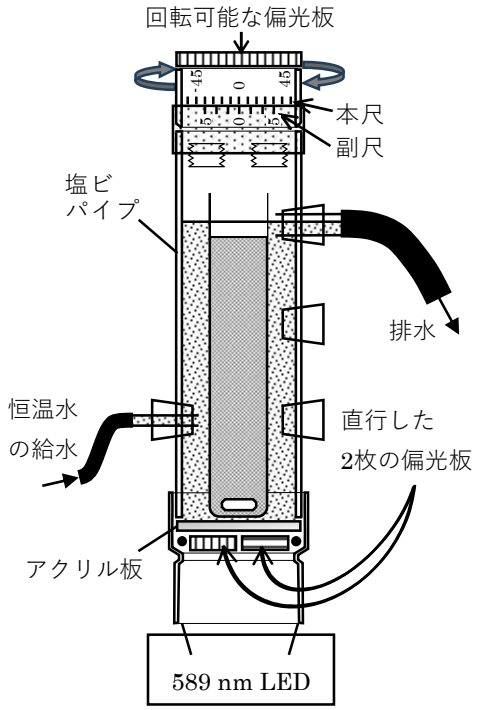

Figure 1. 恒温槽を備えた旋光計

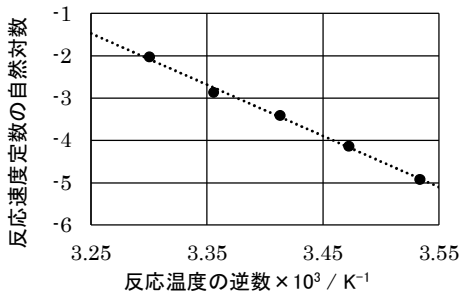

Figure 2. ショ糖の加水分解のアレニウスプロット

1) 千原秀昭, 物理化学実験法, 第 5 版, 東京化学同人, **2011**, 134.

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白色 LED と半導体色センサーを用いる小型・簡易な光電比色計の開発と分析化学・環境化学の教材としての利用

（金工大バイオ化学[1]）○鈴木 保任[1]・坂井 夏美[1]・大嶋 俊一[1]・坂本 宗明[1]

Keywords : White-color LED; Color sensor; Photometric colorimeter; Educational materials
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【緒言】 高校の科学部などの活動において、実験結果を評価するには何らかの分析操作が必要であり、一般にパックテスト、検知管といった簡易分析法が用いられている。分光光度計は安価な装置であるが、高校への導入は困難である。一方、LED を光源に用いる比色計は、波長が限定されるものの実用的な性能を有する。以前、サイエンスパートナシッププログラムの援助で比色計キットを開発し、高校生らの実習に提供できた。近年はマイクロコントローラー (マイコン) や光センサーの機能が向上していることから、より簡便な比色計を開発し、高校科学部の実験体験の教材に用いた。

【装置】 光源には可視域に平坦な発光スペクトルを有する太陽光 LED を用いた。検出器には赤、緑、青の 3 色の強度を測定できる色センサーを用いた。色センサーは個別の波長の LED を組み合わせるよりも測定波長の半値幅が大きく、感度が低下するという欠点があるが、光源が一つで済み、アナログデジタル変換機能を内蔵することから、部品点数を大幅に減らせた。マイコンに測光値を取り込み、吸光度を計算してディスプレイに表示した。電源は USB から供給し、PC と接続すれば吸光度データを送信することもできる。筐体は光造形型 3D プリンターで製作した。セルホルダーは光路長 10 mm のセルに対応する。大きさは 64×57×55 mm と小型である。



図 1 比色計の外観

【結果と考察】 石川県内高校理科部の生徒が実験体験に訪れた際に、ナフチルエチレンジアミンとスルファニルアミドを用いる亜硝酸体窒素の定量実験を行った。4 台の比色計を製作し、1 グループ 5 人程度で標準溶液および河川水のピペッティング、メスフラスコによる希釈などの操作を行い、試作した比色計で緑色の吸光度を測定した。1 グループが調製に失敗したが、他のグループの検量線の決定係数は 0.99 以上であり、失敗したグループも含めて得られた検量線の式の平均は、$Abs = (1.03 \pm 0.04)\, C + (0.009 \pm 0.003)$ と機差も小さかった。

今回は小型化のために表面実装部品を用いて製作したが、より大きい部品を用いて設計しなおし、高校生や学部生が自分達で組み立てられるようキット化も試みる。

1. 鈴木保任，高橋徹，高柳俊夫，本水昌二，川久保進，分析化学，**59**，125 (2010).

本研究の一部は、日本学術振興会科学研究費補助金「基盤研究（C）」（21K1227900）の支援によりなされたことを付記し、ここに謝意を表します。

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日本化学会 第104春季年会 (2024)

親水性高分子を用いた化学実験の授業導入

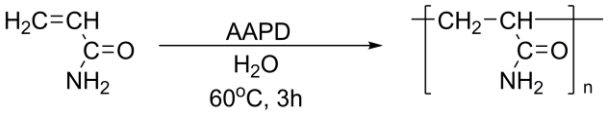
（都立産業技術高等専門学校[1]）〇豊島 雅幸[1]・髙橋　龍也[1]

Introduction to chemical experiments in class using hydrophilic polymer

(*[1]Tokyo Metropolitan College of Industrial Technology*) 〇Masayuki Toyoshima,[1] Tatsuya Takahashi[1]

We incorporated a series of experiments into the class, selecting hydrophilic acrylic amide as the monomer and utilizing radical polymerization with water as the solvent. After polymerization (Scheme), the obtained polymer underwent dialysis purification, and a comparative analysis between the monomer and polymer was conducted using NMR and FT-IR. As a result, we successfully synthesized the polymer using a straightforward method. While pre-experiment lectured faced challenges in student comprehension, post-experiment focused on comparative changes allowed students to appreciate the correspondence of ^{1}H NMR peaks to specific hydrogen atoms (Fig.), facilitating enhanced understanding. Additionally, the difficulty in observing changes through FT-IR emphasized the need to approach measurements from multiple perspectives, enabling the exploration of advanced concepts.

Keywords : Radical polymerization, Hydrophilic polymer, Analysis of structure, Chemical experiment



Scheme Polymerization of acrylamide

親水性物質であるアクリルアミドをモノマーに選択し、水を溶媒としてラジカル重合により、重合し(Scheme)、得られた高分子を透析精製した上で、NMR, FT-IR によるモノマーとポリマーの比較を一連の実験手法を授業に組み込んだ。その結果、簡便な手法で重合進行を確認できた。さらに実験前に解析についての講義では学生の理解が進まなかったが、実験後は変化の比較に注目させることで、^{1}HNMR (Fig.) のピークがどの水素に対応しているかを実感し、理解促進が図られた。また FT-IR では変化が検出しにくいことから、測定に関して複数の視点から検討する必要性を学ぶ発展的内容まで実施できた。

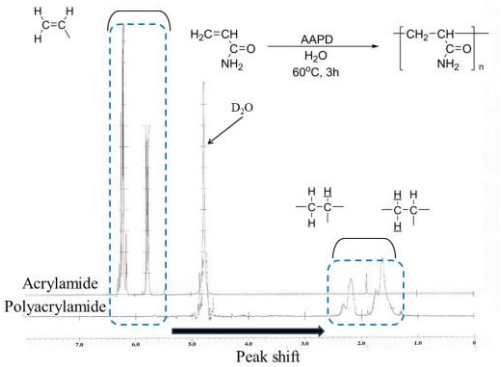


Fig. ^{1}HNMR of monomer and polymer.

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蝶豆から粗抽出したアントシアニンの pH 変化による呈色反応

（都立産業技術高等専門学校[1]）野澤　賢[1]・二星　聖英[1]・伊藤　凪[1]・岡　宏樹[1]・後藤　詩歩[1]・○髙橋　龍也[1]・豊島　雅幸[1]

Color reaction of pH change using anthocyanin of rough extract via Butterfly pea ([1]*Tokyo Metropolitan College of Industrial Technology*) Ken Nozawa[1], Masahide Niboshi[1], Nagi Itou[1], Hiroki Oka[1], Shiho Goto[1], Tatsuya Takahashi[1] and Masayuki Toyoshima[1]

Butterfly pea contained lots of anthocyanin and became the subject of beautiful tea due to vibrant color change.

We attempted rough extract of anthocyanin by boiling commercially available butterfly pea. After extraction, we observed distinct color change at pH levels using the freeze-dried anthocyanin extract such as pink at pH 1, purple at pH 4, blue at pH 7, green at pH 10 and yellow at pH 14. Additionally, when used as an indicator for neutralization titration, as the same results to phenolphthalein were obtained, confirming its functionality as a simple indicator.

Keywords : Neutralizing titration, Anthocyanin, Color reaction, Indicator

バタフライピー(蝶豆) はアントシアニン類の一種であるテルナチンを豊富に含み、その鮮やかな色調変化から”映え茶”として近年話題となっている。

本研究では市販のバタフライピーを煮出すことで、アントシアニンを粗抽出を試みた。抽出後、凍結乾燥させただけのアントシアニン含有物を用いて、既知 pH による色調変化を確認したところ、pH 1 において桃色、pH 4 において紫色、pH 7 において青色、pH 10 において緑色、そして pH 14 において黄色を呈色し (Fig. 1)、明確な変化が確認された。また、中和滴定の指示薬として用いたところ、フェノールフタレインのような簡易的な指示薬としての機能が確認 (Fig. 2) できた。

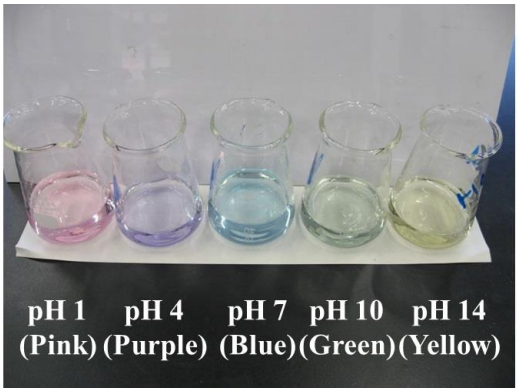

Fig. 1 Color change of pH level

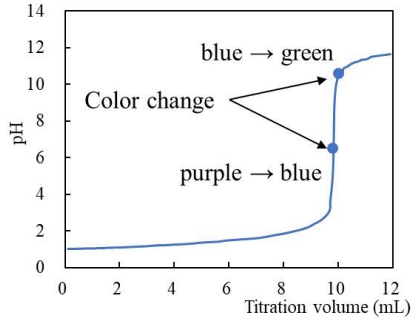

Fig. 2 The curve of neutralization titration (0.1 M HCl – 0.1 M NaOH)

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化学実験の動画教材を制作する学生グループ Chem Tube (4)

（金工大応化）○高梨 咲・岡本 蒼奈・伊藤 慈朗・安宅 純哉・猪股 諒太・小川 悠太朗・二村 映成・谷田 育宏・小野 慎
Chem Tube: A group of students for producing video teaching materials for chemistry experiments (4) (*Department of Applied Chemistry, Kanazawa Institute of Technology*) ○Saki Takanashi, Sona Okamoto, Jiro Ito, Junya Ataka, Ryota Inomata, Yutaro Ogawa, Akinari, Futamura, Ikuhiro Tanida, Shin Ono

Chem Tube is an extracurricular activity group composed of students belonging to Department of Applied Chemistry, Kanazawa Institute of Technology, and its purpose is to support chemistry education by producing videos that explain the principles and experimental operations of chemistry experiments. We will introduce the latest activities and the educational effects.
Keywords : Chem Tube; Chemistry experiments; Extracurricular activity; Video teaching materials

Chem Tube は金沢工業大学応用化学科に所属する学生で構成された課外活動グループで，化学実験の原理や実験操作を説明する動画制作とそれを利用した化学教育の支援を目的としている．Chem Tube の前身である化学実験・研究紹介動画制作プロジェクト（2017～2019）において，「マイクロピペット使用法」と「光学顕微鏡の使い方」の動画を制作し，基礎実験の予習用動画教材として継続して利用している．2020 年よりプロジェクト名を Chem Tube に改め，下表に示す動画を制作してきた [1–3].

2023 年ではまず初めに，新人メンバーが早く動画制作に慣れるように，全メンバーを縦割りにして各学年を含む 3 グループに分け，同一のテーマ（ホールピペットの使い方）に関する動画を制作し，互いにその動画に対する意見を出し合って評価する機会を作った．また，各学年グループでの実験動画制作や実験以外の化学教育用動画の制作も行っているので，2023 年の Chem Tube の活動を紹介する．

表 1. ChemTube で制作してきた動画の例

活動年	制作した動画タイトル
2020	メスフラスコの洗浄法，ポリアニリンの合成，PCR のやりかた
2021	緩衝液の調製，アガロースゲル電気泳動，抗酸化作用の測定
2022	テスター・ノギスの使用法，分光光度計の使用法
2023	ホールピペットの使い方，pH メーターの校正方法，色が変わる粘土

1) 化学実験の動画教材を制作する学生グループ Chem Tube，高鳥萌・大橋滉樹・古谷幸一・坂上晴香・谷田育宏・小野慎，第 101 春季年会，P1-2am-05，2021 年 3 月.
2) 化学実験の動画教材を制作する学生グループ Chem Tube (2)，和田佳純・山口紗生・山村凛・水野皓太・松井景亮・阿部雅美・嶺村一稀・小間大和・谷田育宏・小野慎、第 102 春季年会，P1-3am-03，2022 年 3 月.
3) 化学実験の動画教材を制作する学生グループ Chem Tube (3)，阿部雅美・嶺村一稀・小間大和・猪又冬花・谷田育宏・小野慎、第 103 春季年会，P1-3pm-07，2023 年 3 月.

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化学実験の動画教材を制作する学生グループ Chem Tube (5)

（金工大応化）○小野 慎・谷田 育宏
Chem Tube: A group of students for producing video teaching materials for chemistry experiments (5) (*Department of Applied Chemistry, Kanazawa Institute of Technology*) ○Shin Ono, Ikuhiro Tanida

Chem Tube is an extracurricular activity group composed of students belonging to Department of Applied Chemistry, Kanazawa Institute of Technology, and its purpose is to support chemistry education by producing videos that explain the principles and experimental operations of chemistry experiments. We will present our extra-curricular activities from 2017 to date and discuss their educational effects.
Keywords : Chem Tube; Chemistry experiments; Extracurricular activity; Video teaching materials

Chem Tube は金沢工業大学応用化学科に所属する学生で構成された課外活動グループで，化学実験の原理や実験操作を説明する動画制作とそれを利用した化学教育の支援を一つの目的としている．Chem Tube の前身である化学実験・研究紹介動画制作プロジェクト（2017～2019）は，授業などの正課以外で応用化学科の学生が集まる機会を作る試みとして，プロジェクト参加を希望した 2 年次生 1 名と 4 年次生 1 名が共同して「マイクロピペット使用法」の動画を制作することから始まった．このプロジェクト活動は，応用化学科のオナーズプログラムとして 2017 年度から採用されたものである．当該 4 年次生は自らの卒業研究（学生実験用動画教材の作成とその効果）のために，制作した動画を 2 年次生の基礎実験の予習用動画教材として提供し，学生へのアンケート調査を実施して，その教育効果を検証した．一方我々も，この活動の経緯と教育効果をまとめて報告した [1,2]．その後，本プロジェクトに参加する学生たちが増え，2020 年よりプロジェクト名を Chem Tube に改めて，課外活動を継続している．

現在，実験に限らず動画教材は大いに活用され，大学だけでなく，予備校や高校の教員らによって，YouTube にアクセスフリーの動画が投稿されており，有用なものが数多く見受けられる．このような動画教材の活用に教育効果があることは広く認識されている．一方，本プロジェクトのように，動画教材を制作するという経験を通して学生自身がどのように変化したのかという観点からの報告はあまりない．

今回，2017 年から現在までの本プロジェクト活動を紹介し，この活動に参加した学生たちの変化や成長について議論したい．

1) 学生実験用動画の制作と化学教育における活用，小野慎・谷田育宏，教育改革 ICT 戦略大会，2018 年 9 月．
2) 学生実験用動画教材の開発と e-シラバスを利用した視聴システムによる教育的効果，谷田育宏・小野慎，工学教育研究（KIT Progress），No.27，pp.153-162，2019.

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マイクロスケール実験の新しい展開:遠隔教育における改良

(香川大教育[1]・東北大学[2]) ○小野 玲奈[1]・森脇 ゆな[1]・川田 茉里奈[1]・高橋 智香[1]・高木 由美子[1]・荻野 和子[2]
New Developments in Microscale Experiments: Improvements in Distance Learning Education (*Faculty of Education, Kagawa University*) Reina Ono, Yuna Moriwaki, Marina Kawata, Chika Takahashi, Yumiko Takagi, Kazuko Ogino

Microscale experiments have various advantages such as saving reaction and handling time, cutting costs and using reagents, reducing the amount of waste chemicals by setting an appropriate reaction system. Because of it does not use a laboratory and/or expensive equipment, it is a method that can utilize the ingenuity of the teachers and review the concept of the experimental education. It is used that the findings to micro-scale our current student experiments without changing the concept of those experiments.

Keywords : Micro Scale Chemistry; Small Scale Chemistry; Distance Learning Education

マイクロスケールケミストリー[1,2]は、スケールを小さくした適切な反応系を設定することで、１）反応時間が短縮できる、２）生徒一人一人が実験に参加できる、３）試薬と経費の節約と廃棄物の少量化を図ることができる、４）実験結果が一目瞭然であるなどの利点がある。さらに、場所を選ばす実験できるため、従来の実験室や実験器具は必ずしも必要でなく、実験のコンセプトそのものを捉え直すことができる方法として、様々な報告がなされてきた[2]。マイクロスケール実験は３蜜を回避するのに有効であることから，コロナ感染予防に配慮し，マイクロスケール実験を大幅に導入してきた。[3]また、香川大学は全学をあげて SDGs 教育を実施している。

2023 年前期は、人数制限を撤廃し実験授業でマイクロスケール化を行ったものを工夫して実施することにした。１）分族実験，２）Ｉ族～Ⅳ族の金属の陽イオンの各個反応及び系統分析について、マイクロスケール実験を行った。必要に応じて、各自のスマートホンのカメラ機能を使って画像写真を撮影し、その結果は、レポートとともに Moodle に提出させた。系統分析の場合は，沈殿および溶液を採取するために遠心分離を行い、各個実験と同様ラボトップの指示に従って実験を行った。実施の詳細について報告する。

1) S. Thompson, Chemtrek-Small Scale Experiments for General Chemistry, 1st ed., Prentice Hall, New Jersey, 1989, Chap.7, pp.114-136.
2) マイクロスケール化学実験-マイクロスケール実験の広場から-荻野 和子編，日本化学会関東支部, 2005年
3) COVID-19蔓延下におけるマイクロスケール実験の有用性，荻野和子，片岡久美子，猪俣慎二，生田博将，高瀬つぎ子，高木由美子，高橋智香，化学と教育, 70(1), 44-47, 2022.

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北海道北見地方のハッカを題材とした多面的リベラルアーツ教育の深耕　ー歴史を伝える人々の想いを化学実験教材に織り込む試みー

（東海大生物）和泉 光則

Development of Multi Sided Liberal Arts Educaion Based on Historical Peppermint Industry of Kitami, Hokkaido
- An attempt to create an educational material which incorporate feelings of people (*School of Biological Sciences, Tokai University*) ○Mitsunori Izumi

Kitami used to be known as the city of the world's No.1 Hakka (japanese peppermint) production in early 20th century. Its history started from the reclamation by Tondenhei in 1901 and ended in 1983 with the closure of the Hokuren Kitami Hakka Factory. It may construct effective liberal-arts educational materials, from the multiple viewpoints of chemistry, biochemistry, industry and industrial history. I'm practicing it at the university chemical experiment class. I carried out interviews to nine persons who promotes the historical Kitami Hakka. Although the mint industry in Kitami faded away regrettably in 1983, most of the respondents mentioned, "I don't remember much." Such valuable information without evidence is difficult to remain in the literature. So I am going to create an educational booklet on the peppermint in Kitami region, which notes the feelings and passions of them.
Keywords : japanese peppermint; kitami city; liberal arts; educational booklet

[目的] かつて生産量世界一を誇った北海道北見地方の薄荷は、水蒸気蒸留→遠心分離→再結晶という天然物の単離工程、明治～平成の産業史、さらには天然物化学、タンパク質の構造と機能といった多彩かつ文理融合的な教育の素材と言え、大学基礎化学実験の有効な文理融合的リベラル・アーツ教育素材となり得る[1]。今回、授業の副教材として利用するブックレットを作製するために、北見在住の 9 名の人物から聞き取りを行った。

[方法] 対象者は北見市内の主要観光施設等、販売会社、保存団体のメンバーおよび元メンバー、教師から計 9 名を選んだ。原則として一人ずつ、北見市において 40 分～2 時間程度の聞き取りを行った。聞き取りの内容は①幼少期の想い出、②業務等に関わっている中で思うこと、③未来に向けて思うこと、等。

[結果と考察] 惜しまれながら消えていった北見の薄荷産業であるが、1983 年のホクレン北見薄荷工場閉鎖というセンセーショナルな出来事について、聞き取った対象者の殆どが「あまり覚えていない」と語るなど、エビデンスを伴う歴史文献にはない、人間味ある情報が、聞き取り結果には織り込まれていた。現在、2024 年度の授業に活用することを目指し、ブックレットを作製中である。

※本研究は東海大学総合研究機構「クラウドファンディング型社会発信研究補助計画」の援助を受けて行ったものである。

1) 北海道北見地方のハッカ（薄荷）（講座 ご当地の化学［北海道／北海道支部］），和泉光則，化学と教育 2016，64 巻（4），188-191.

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高専における探究型実験への生成 AI の活用

(神戸市立高専一般科[1]・琉球大学教育学部[2]) ○佐藤　洋俊[1]・福本　晃造[2]・大塩　愛子[1]
Application of Generative AI to Inquiry Based Experiments at College of Technology
([1]*Department of General Education, Kobe City College of Technology*, [2]*Faculty of Education, University of the Ryukyus*) ○Hirotoshi Sato,[1] Kozo Fukumoto,[2] Aiko Oshio[1]

Generative AI was applied actively for inquiry-based experiments in chemistry class at a college of technology. After a brief lecture on the use of generative AI, students used generative AI to obtain hints and conducted experiments. If the hints didn't work, students reused the generation AI or did trial and error by using their investigation to achieve their goal. After the experiment, students submitted the initial pair of their questions and answers generated by the AI, and the final pair. The pairs of questions and answers showed difference of students' skills and answers from generative AI accordingly. Results of questionnaire showed the usefulness, limitations, and precautions of generative AI in chemical experiments. Through the questionnaire, students compared and evaluated the answers from generative AI with their own trial and error.

Keywords：Generative AI, Inquiry Based Experiment, College of Technology

高専の教養化学において、探究型実験に生成 AI を活用した。生成 AI 利用について簡単なレクチャーを行った後、学生は iPad とブラウザのチャット機能を通して生成 AI に質問を入力し、実験遂行のためのヒントを得た上で実験を行った。その通りに実験がうまくいかない場合は生成 AI を再活用したり自分たちで調べた内容を試したりして、目標を達成した。実験後に学生が初期に作成した質問と生成 AI の回答、最終の質問と回答を提出してもらい、学生の活用スキルの変化とそれに合わせた AI の回答の変化を観察した。アンケートを実施し、生成 AI からの回答と自分たちの試行錯誤を比較して評価してもらい、化学実験における生成 AI の有用性とその限界、注意点などを探った。

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量子化学シミュレーションを用いた学生実験教材の開発
－有機化合物の XPS スペクトルの推定－

（福島大学 [1]）○高瀬 つぎ子 [1]、宮沢 風我 [1]、山口 克彦 [1]

Development of teaching materials for chemical experimentation using quantum chemical simulations: An estimate of XPS spectra of organic compounds

([1]Fukushima University) Tsugiko Takase[1], Fuga Miyazawa[1], Katsuhiko Yamaguchi[1]

X-ray Photo-electron Spectroscopy (XPS) is an effective analytical tool for analyzing the chemical state of a surface. Conventionally, it has been used to compare measured XPS spectra with a database that covers chemical shifts in XPS spectra due to functional groups. By doing this, the chemical state of the surface has been analyzed. This time, we used quantum chemical simulation to estimate the influence of functional groups on the electron energy level (C1s, N1s, O1s F1s, Cl2p, S2p,Si2p) in the ground state, and compared it with the actually measured XPS spectrum.. *Keywords：Quantum chemical simulation, XPS, Polymer*

X 線光電子分光分析（XPS）は，表面の化学状態を分析するための有効な分析手段であり, 従来,「官能基による XPS スペクトルの化学シフトを網羅したデータベース」と実測の XPS スペクトルを比較することで, 表面の化学状態の解析が行われてきた. 量子化学シミュレーション（DFT 計算）を用いて XPS スペクトルの推定を行う場合、通常の UV-VIS 領域での電子遷移と異なり、束縛状態から連続状態（真空中）への電子遷移であるため、汎用の DFT 計算ソフトを用いて推定することは困難であったが, 近年、「DFT 計算(基底状態の分子軌道のエネルギー(C1s）推計)を用いて，官能基を含むグラフェン結晶の XPS スペクトルの帰属を行う」という試みも行われている [1)]. 今回，この手法を利用して，DFT 計算を用いて，特性の異なる官能基（CHO 系官能基，N, F, Cl 等を含む官能基）がポリマーの分子軌道のエネルギー（C1s 等）に対して与える影響を推定し，実測の XPS スペクトル [2)]との相関を検討した（Fig.1 参照；官能基含むポリマー約 50 種類）. その結果，①広いエネルギー領域で，DFT 計算によって推計されたポリマーの分子軌道のエネルギー(C1s, O1s, F1s 等)と実測 XPS スペクトルのピークエネルギーが非常に良い相関を示すこと②推計された C1s のエネルギーを用いて，官能基の違いによる XPS スペクトル（C1s）の化学シフトが定性的説明できることが明らかになった. このように，基底状態の分子軌道のエネルギーと XPS スペクトルとの相関を明らかにすることは，XPS の原理を理解するための一助になると考えられる.

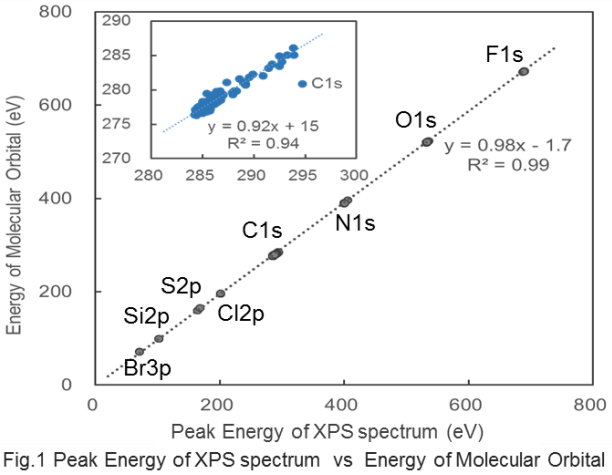

Fig.1 Peak Energy of XPS spectrum vs Energy of Molecular Orbital

1) Y. Yamada. H. asuda *et.al.*, *J Mater Sci* **2013** *48:8171–8198*
2) The XPS of Polymer Database **2000**

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化学に対する苦手意識の払拭を目指した化学系教養科目の試み

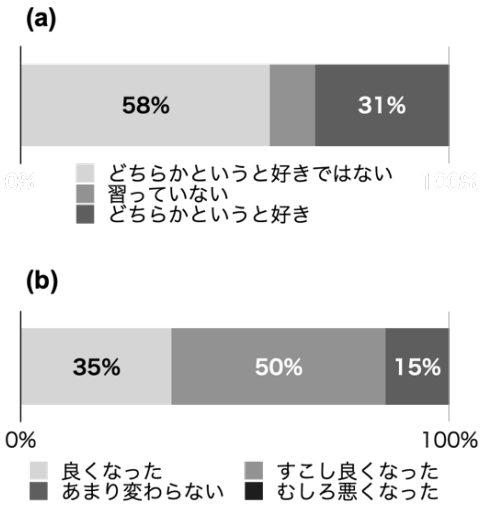
（富山大教養[1]）○杉森 保[1]
Attempts to develop chemistry-based liberal arts for students who are not good at chemistry
([1]*Institute of Liberal Arts and Sciences, University of Toyama*) ○Tamotsu SUGIMORI[1]

We designed and implemented a course to give students who had avoided chemistry an opportunity to approach chemistry from a medium- to long-term perspective, and to provide them with the opportunity to learn chemistry on their own throughout their lives. The course was designed to provide a chemical perspective based on a policy of focusing on the properties of water, a familiar chemical substance, and then delving into what is responsible for its characteristics, so that the course would not be limited to rote memorization. The majority of the students were not very good at chemistry in the first class, but their awareness improved by the end of the class.

Keywords : general education, scientific literacy, class design, lifelong learning, teaching plactice

大学入学時までに科学（化学）を避けてきた学生に，中長期的な視点で化学に近づく機会を与え，生涯にわたって自ら学ぶきっかけとなる授業を設計し実施することを試みた．シラバスに「化学が苦手な学生向け」と明示した上で，特に事項の暗記ばかりにならないように工夫しながら構成した．

この授業では「身の回りにあふれる化学物質の代表としての水」に目を向けることから，「そもそもなぜ水はいろいろなものを溶かすのか」「水に溶けないものにはどういう特徴があるのか」といった直感的で素朴な疑問を掘り下げることで，まず「その物質が持つ性質が何に起因するのか」「物質は何によって特徴付けられるのか」といった観点を提供することから始める形で授業を構築した．履修者には初回の授業で入学前の理科（物理・化学・生物）に対する印象などを回答してもらった．毎回の授業，および最終回にも Moodle のフィードバック機能を利用してアンケートを適宜実施し，回答を得た．初回の授業時に履修者の過半数は化学に苦手意識をもっていたが，終了時にはその意識に改善傾向がみられた（図）．自由記述の内容から，満足度は高く，内容に加えて毎回の授業で双方向的な要素を含めたことも一定の効果があったと考えている．発表では 2023 年度の授業実践も含めた取り組みと結果についても報告する．



図．2022 年度の当該授業における（a)初回授業時の化学に対する印象（回答数 123），(b)終了時に尋ねた化学への印象の変化（回答数 108）

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高専のモデルコアカリキュラムにおける一般化学の現状と課題

（大分工業高等専門学校）○二宮 純子[1]
Current State and Challenges in General Chemistry Education within the Model Core Curriculum of the National Institute of Technology
([1] *National Institute of Technology, Oita College*) ○Junko Ninomiya,[1]

Commencing from the academic year of 2018, all National Institutes of Technology in Japan, henceforth denoted as KOSEN, have instituted educational curricula in conformity with the Model Core Curriculum (MCC). Approximately 60-70% of the comprehensive syllabus at each KOSEN aligns with the MCC, while the remaining segment capitalizes on the distinctive characteristics and uniqueness of each KOSEN. The General Chemistry component within the MCC mirrors the content covered in "Basic Chemistry" and "Chemistry" within a conventional high school setting. However, it is imperative to note that the General Chemistry program at MCC omits the topics of reaction rates/chemical equilibrium, inorganic chemistry, and organic chemistry.

Conversely, owing to the revision of the Courses of Study slated for the year 2022, certain aspects of high school chemistry will undergo modification. Specifically, alterations will be introduced to enthalpy notation, mandatory inclusion of entropy, electron orbitals, and composite orbitals. These adjustments have been deliberated from the vantage point of fostering a seamless transition between high school and university levels of education. Given that numerous KOSEN students proceed to higher education institutions, it becomes imperative for them to attain proficiency in the realm of chemistry, encompassing the aforementioned modifications in KOSEN General Chemistry. Our investigation will scrutinize the prevailing status of general chemistry education at Oita National College of Technology, an establishment lacking a dedicated department for chemistry, and delve into the associated challenges.
Keywords : the Model Core Curriculum; general chemistry education

2018 年度から全国の工業高等専門学校（以下 KOSEN）ではモデルコアカリキュラム（MCC）に準拠した教育プログラムが実施され、各 KOSEN では全カリキュラムの 60～70%を MCC に対応し、残りを各 KOSEN の特徴や独自性を活かしたカリキュラムが設定されている。MCC の一般化学は、普通科の高等学校の「化学基礎」「化学」の学習内容に相当する。しかし、MCC の一般化学には、反応速度・化学平衡、無機化学と有機化学は含まれていない。一方、2022 年度から学習指導要領の改訂により、高校化学の内容が一部変更され、特にエンタルピー表記、エントロピー必修化、電子軌道、混成軌道については、高大接続の観点から議論されてきた。KOSEN では、大学へ進学する学生が多いことから、KOSEN の一般化学においても、これらの変更点を含めた化学の内容を習得する必要が生じている。化学系の専門学科をもたない大分高専の一般化学教育の現状を分析し、その課題について検討する。

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化学実験における対面実習とオンデマンド実習の教育効果

勝又 敏行 (東京医科歯科大学教養部)

Educational Effectiveness of Face-to-Face and On-Demand Practice in Chemistry Experiments
(*College of Liberal Arts and Sciences, Tokyo Medical and Dental University*) Toshiyuki Katsumata

We introduced on-demand experiments with video assignments in chemistry experiments. We tested whether there was a change in the educational effect of both face-to-face and on-demand experiments on the analysis of metal ions. The experiments were conducted twice for the analysis of metal ions using hydrogen sulfide, and the detection rate of metal ions in the experiments and the progress of the experiments were compared. The experiments compared whether there was a change in the detection rate of metal ions between the group that performed the face-to-face experiment and the group that performed the on-demand experiment first and the group that performed the on-demand experiment and then performed the face-to-face experiment, but no significant difference was found. The progress of the experiments was also similar. We also examined differences in educational effects due to changes in the teaching format of the face-to-face experiments.

化学実験において、ビデオ課題を用いたオンデマンド実習の導入を行った。金属イオンの分析実験を対象として、対面の実験とオンデマンド実験の両方の実験を行うことにより、教育効果に変化があったのかを検証した。実験は硫化水素を用いた金属イオンの第１属から５属までの分析を２回にわたり行い、実験における金属イオンの検出率や実験の進捗状況を比較した。実験は対面実験を行ってからオンデマンド実験を行うグループと、オンデマンド実験を行ってから対面実験を行うグループで金属イオンの検出率に変化があるかを比較したが、有意な差は見られなかった。実験の進捗状況も同程度であった。対面実験の授業形態の変更による教育効果の差についても検討を行った。

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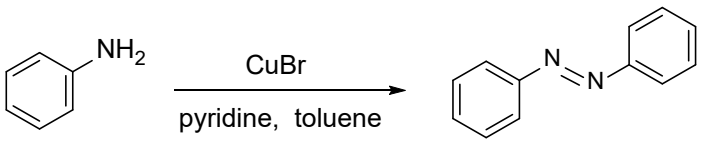
日本化学会 第104春季年会 (2024)

芳香族化合物を用いる大学生のための有機化学実験の授業構築

（電機大工）○木戸 晶子・岩﨑 直也・鈴木 隆之
Designing of Organic Chemistry Experiment Classes for University Students Using Aromatic Compounds（*Sch. Eng., Tokyo Denki Univ.*）○Akiko KIDO, Naoya IWASAKI, Takayuki SUZUKI

In organic chemistry experiments for university students, we study teaching methods with the aim of helping students master basic skills in organic synthesis and deepen their understanding of reaction mechanisms and analytical methods. In the present study, an attempt was made to introduce the new one-step synthesis of aniline to azobenzene[1] to student experiments, instead of the previously conducted synthesis of nitrobenzene to azobenzene. With this synthesis method, it is expected to understand the sequential synthesis scheme following the synthesis of nitrobenzene to aniline in the previous year. To identify the product, the simple TLC method was employed. In addition, the isomerization behavior of the resulting azobenzene was also observed in the class. Specifically, the operations of irradiating the solution samples with UV light of a certain wavelength using a handy LED light followed by UV-visible spectroscopic measurement were repeated and the obtained absorption spectra were analyzed. This is expected to provide students with an understanding of various analytical methods in organic chemistry.
Keywords : organic chemistry experiment, aniline, azobenzene, isomerization, UV-visible spectroscopy

大学生のための有機化学実験授業において、有機合成の基礎的な操作の習得と、反応機構および分析方法の理解を深めることを目的とした指導について検討している。今回は、従来行っていたニトロベンゼンからアゾベンゼンへの合成に替え、新たにアニリンからアゾベンゼンへの一段階による合成[1]の学生実験への導入を試みた。この合成方法により、前年次のニトロベンゼンからアニリンへの合成に続く連続的な合成スキームの理解が期待される。生成物の確認方法としては簡便なTLC法を用いた。さらに得られたアゾベンゼンの異性化挙動の観察も授業内で行った。具体的には、ハンディタイプのLEDライトを用い溶液サンプルに一定波長の紫外線を照射した後、紫外可視分光法による測定を行うことを繰り返し、得られた吸収スペクトルを解析した。これにより様々な分析方法の理解が期待される。



1) Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed*. **2010**, *49*, 6174.

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高大接続に焦点を当てた生物教育への化学的アプローチ

（神工大教育開発センター[1]・阪大院薬[2]）○甲斐　由理子[1]・押鐘　浩之[2]
Chemistry-based Approach to High School Biology in Closer Connection with University Education ([1] *Educational Development Center, Kanagawa Institute of Technology,* [2] *Graduate School of Pharmaceutical Sciences*, *Osaka University*) ○Yuriko Kai,[1] Hiroyuki Oshikane[2]

In recent years, the connections between school stages have been greatly focused in view of scientific education, thus regarded to be of high importance. In addition, the Course of Study in Japan high school was drastically revised in 2008, where updated molecular biology contents were newly described. However, it makes much harder for high school students to grasp molecular biological subjects such as PCR and electrophoresis since basic knowledge in chemistry is strictly required [1)]. Although the best way to understand the principles of the experiments is to perform the experiments, however, it has been quite demanding to carry out molecular biological experiments due to the limited equipment in high schools. We have thus developed the experimental protocols for high school students without any special need for expensive laboratory equipment [2)].

We herein introduce the educational effects of molecular biology experiments in high schools combined with the rigid chemical backgrounds through the development of DNA barcoding experiments, where each student can freely choose the samples of interest for species identification.

Keywords :　High School-University Connection; Biological Chemistry; Molecular Biological Experiments

近年、上級学校への進学にともなう学修者の学業面でのつまずきが問題となっており、理科教育においても各学校間における学びの円滑な接続が重要視されている。一方、平成 20 年の学習指導要領改訂以降、高等学校の生物分野では分子生物学の内容が新しく加わったが、PCR 法や電気泳動法といった分子生物学実験の原理を理解するためには、生物学だけではなく化学的な基礎知識も必要となるため、高校・大学間における学びのハードルの一因となってきた [1)]。実験原理を理解するための最良の方法は、実習を通した涵養に他ならないが、一般的な高等学校では設備面、予算面等の問題により、分子生物学的な実習を取り入れることは難しかった。そこで、発表者らはこれまで一般的な高等学校でも実施可能な、出来るだけ高額な設備・機器に頼らない分子生物学実験プロトコールを考案してきた [2)]。

本発表では、高校化学の知識をベースとした DNA バーコーディング技術を応用し、生徒が自由に持ち寄った身近なサンプルにより生物種同定を実施できるプロトコールの導入およびその教育効果の検証について紹介する。

1) 甲斐 由理子, 押鐘 浩之「理系学生の初年次教育における異学年合同学習の実践と効果」神奈川工科大学研究報告（紀要）A47 号, pp 45-48, 2023 年
2) 針谷 桃華, 橋場 美穂, 甲斐 由理子, 押鐘 浩之 「高等学校の授業実態に即した 分子生物学実験の実践と考察」神奈川工科大学研究報告（紀要）A47 号, pp. 29-37, 2023 年

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「共鳴」から「非局在化」へ:有機化学の専門基礎教育のための共役系での電子の非局在化に関する用語について

（創価大理工）○伊藤 眞人

From “Resonance” to “Delocalization”: the Terms and Usages on Electron Delocalization in Conjugated Systems for Organic Chemistry in University Fundamental Education

(*Faculty of Science and Engineering, Soka University*) ○Masato M. Ito

Delocalization of π-electrons in a conjugated system has been Referred to as "resonance", without any description of its theoretical basis. So are the "resonance formula", which combines classical structural formulas to understand the delocalized electron distribution, and "resonance effect" which refers to the electronic effect of the substituent on the conjugated system. The concepts underlying these terms are very useful in understanding the delocalization of π-electrons in conjugated systems, based on traditional structural formula. Indeed, it is much more widely used than its synonym “mesomery” [1], especially in the basic education of organic chemistry in universities, including in Fundamental education. However, the electronic theory (hypothesis) concerning the "resonance" in its name is now known to have no proper theoretical background. Therefore, in the previous annual meeting, it was proposed to use an alternative term "delocalization", which expresses the essence of the behavior of electrons that make up a conjugated system, instead of "resonance", to express the contents corresponding to the above concept.[2] This time, by using this term, an attempt is exemplified to construct teaching materials for organic chemistry in basic university education. An overview of the teaching materials is available on the website.[3]

Keywords : Organic Chemistry, University Fundamental Education, Conjugated System, Mesomery, Delocalization Effect

共役系でのπ電子等の非局在化には「共鳴」という用語が用いられている。その理論的基盤が示されることはない。非局在化の様子を理解するために古典的な構造式を複数組み合わせて用いる「共鳴式」や、置換基の共役系に対する電子効果をさす「共鳴効果」も同様である。これらの根底にある概念は，共役系でのπ電子の非局在化の様子を，伝統的な構造式に基づいて理解するには非常に有用である。実際，「共鳴」という用語は，特に大学有機化学の基礎教育以上では，同義語「メソメリー」[1]よりもはるかに広範囲に用いられている。しかしながらその名前にある「共鳴」に関する電子理論（仮説）は，今日では正当な理論的基盤を持たないことがわかっている。そこで一昨年の年会では，「共鳴」ではなく，共役系を構成する電子の挙動の本質を表す「非局在化」という用語を用いて上記に対応する内容を表現することを提案した[1]。今回は，この用語を用いて，大学の基礎教育での有機化学の教材を構築する試みを例示する。教材の全体像はホームページに公開されている[3]。

1) P. Sykes (久保田尚志訳), 「有機反応機構 第 5 版」東京化学同人 (1984) p. 26 など.
2) 日化第 102 春季年会講演予稿集, D202-2pm-03 (2022).
3) 伊藤眞人「有機化学のページ」, url = https://home.soka.ac.jp/chem/yuki/shiryo.html.

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Academic Program [Poster] | 08. Catalysts and Catalysis：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-3vn] 08. Catalysts and Catalysis

Japanese

[P1-3vn-01]

Degradation mechanism of ruthenium oxide electrocatalysts during oxygen evolution reaction

○Kazuki Obigane[1], Kosuke Beppu[1], Fumiaki Amano[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-02]

Utilization of low-energy electron beam for the immobilization of Pd nanoparticle catalyst on polymer substrate by radiation irradiation method

○Ryohei Iwano[1], Satoshi Seino[1], Naoto Uegaki[1], Fumiyasu Ishiguro[1], Yuji Ohkubo[1], Takashi Nakagawa[1] (1. Osaka Univ.)

Japanese

[P1-3vn-03]

Greenhouse gas conversion reaction catalyzed by precise nickel clusters

○Tatsuya Moriai[1,2], Takamasa Tsukamoto[2,3,4], Makoto Tanabe[2,5], Tetsuya Kambe[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. for Chemistry and Life Science, Tokyo Tech, 2. JST-ERATO, 3. Inst. of Industrial Science, The Univ. of Tokyo, 4. JST-PRESTO, 5. Ctr. for Integrated Sciences and Humanities, Fukushima Medical Univ.)

English

[P1-3vn-04]

Size effect of V group metal oxide clusters on base catalytic property

○Supisara Hongpuek[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

English

[P1-3vn-05]

Precise separation of mixed metal oxide clusters by HPLC

○Nattamon Panichakul[1], Tomoki Matsuyama[1], Soichi Kikkawa[1], Koichi Kikuchi[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-06]

Study on the correlation between photoelectrochemical properties and photocatalytic activities of various GaN:ZnO powders

○Shuji Sekimori[1], Hiroka Sandaiji[1], Shintaro Abe[1], Natsudogi Iwasa[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Graduate School of Science and Technology, Shinshu University, 2. Graduate School of MedicineScience and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4. PRESTO, Japan Science and Technology Agency)

Japanese

[P1-3vn-07]

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Optimization of the synthesis conditions for GaN:ZnO solid solution depending on water content of starting materials

○Hiroka Sandaiji[1], Natsutogi Iwasa[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Graduate School of Science and Technology, Shinshu University, 2. Graduate School of Medicine, Science and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4. PRESTO, Japan Science and Technology Agency)

Japanese

[P1-3vn-08]

Effects of temperature near the photocatalyst under light illumination in aqueous suspension on hydrogen evolution rate

○Mika Hirata[1], Hiroto Inuduka[1], Yosuke Kageshima[1,2], Katsuya Teshima[1,2], Hiromasa Nishikiori[1,2] (1. Shinshu University, 2. RISM)

Japanese

[P1-3vn-09]

Modification of polymer layer containing phosphate functional groups to surface of hydrogen-evolving photocatalytic particles

○Kiyoharu Yamamura[1], Masataka Yamamoto[1], Yousuke Kageshima[1,3], Katsuya Teshima[1,3], Kazunari Domen[2], Hiromasa Nishikiori[1,3] (1. Shinshu University, 2. The Univ. of Tokyo, 3. RISM)

Japanese

[P1-3vn-10]

Water Splitting under Visible Light Irradiation over a Tiny Amount of Ru-Doped $SrTiO_3$ Photocatalyst Prepared by Various Synthesis Methods

○Chisato Hanafusa[1], Yoshiya Ueki[1], Motonori Ando[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese

[P1-3vn-11]

Hydrogen production by photoreforming of organic waste using CdS/ZnS composite photocatalyst via MOF precursor.

○Yusei Kumai[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese

[P1-3vn-12]

Hydrogen production by water splitting using carbon-based metal-free photocatalyst

○Eitaro Nishimura[1], Morio Nagata[1] (1. Tokyo University of Science)

English

[P1-3vn-13]

Pelletized photoelectrodes for photoelectrochemical water splitting

○Surya Pratap Singh[1], Kosuke Beppu[1], Fumiaki Amano[1] (1. Tokyo Metropolitan University, Faculty & Graduate School of Urban Environmental Sciences)

Japanese

[P1-3vn-14]

Development of Visible-Light Photocatalyst for the Conversion of Glucose to Fungicide

○Mana Akita[1], Sho Usuki[1], Kazuya Nakata[1] (1. Tokyo University of Agriculture and Technology)

Japanese

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[P1-3vn-15]

Synthesis of aragonite immobilized photocatalysts exhibiting mechano-bactericidal effects and its evaluation of bactericidal performance

○Ayako Gomi[1,2], Kaoru Igarashi[1], Yukari Miyazaki[2], Nobuaki Negishi[2], Ryo Yamano[1,2], Satoshi Toba[1,2] (1. Chiba Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology)

Japanese

[P1-3vn-16]

Photocatalytic nitrate generation from water and air on tungsten oxide loaded with noble metal

○Kazuki Miyata[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Osaka University)

Japanese

[P1-3vn-17]

Photocatalytic hydrogen peroxide generation on ion-exchange resin-incorporated resorcinol-formaldehyde semiconducting resins

○Yoshihiro Nishiyama[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Graduate School of Osaka University)

Japanese

[P1-3vn-18]

Infrared-responsive covalent organic framework (COF) photocatalysts with metal ions atomically immobilized with hydrogen peroxide generation ability

○Kei Oyama[1] (1. Kyushu Institute Technology)

Japanese

[P1-3vn-19]

Development of g-C_3N_4 with high degradation activity for phenol

○Naoko Taki[1], Sho Usuki[1], Kazuya Nakata[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P1-3vn-20]

Visible light responsive photocatalytic methane production using graphite-type carbon nitride (PCN)

○Tatsuki Kanazawa[1], Teruhisa Ohno[1] (1. Kyushu Institute of Technology)

Japanese

[P1-3vn-21]

Photocatalytic hydrogen production and selective CO_2 reduction using nitrogen-rich carbon nitride (C_3N_5)

○Kosei Ito[1], Kei Noda[1] (1. Keio Univercity)

Japanese

[P1-3vn-22]

Photocatalytic Roles of Vacancy Sites on Iron nanoparticle supported Zirconium oxide for CO_2 photoconversion

○Ayana Omata[1], Keisuke Hara[1], Tomoki Oyumi[1], Kaori Niki[1], Yasuo Izumi[1] (1. Chiba University)

Japanese

[P1-3vn-23]

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Production of Rare Sugars by Electrochemical Oxidation of Monosaccharide

○Kio Kawakatsu[1], Sho Usuki[1], Yasuaki Einaga[2], Kazuya Nakata[1] (1. Tokyo University of Agriculture and Technology, 2. Keio University)

Japanese

[P1-3vn-24]

Development of Pt/C-based electrocatalysts intended for direct oxidation of cellulose dissolved in a strong alkaline aqueous solution

○Kenta Maeda[1], Yosuke Kageshima[1], Katsuya Teshima[1], Hiromasa Nishikiori[1] (1. Shinshu University)

Japanese

[P1-3vn-25]

Development of Helical Organocatalyst Based on (*cis*, *cis*)-Diphenylurea

○Fumi Takeda[1], Mayumi Kudo[2], Mamika Ogura[1], Yayoi Orihara[3], Minami Odagi[3], Kazuo Nagasawa[3], Aya Tanatani[1] (1. Ochanomizu University, 2. National Institute of Technology, Gunma College, 3. Tokyo University of Agriculture and Technology)

Japanese

[P1-3vn-26]

Mechanism of organic dye decomposition using persulfate activated by carbon catalysts with varied surface oxidation states

○Urushidate Ryusuke[1], Shimoda Syuhei[2], Suzuki Keita[3], Fukuoka Atsushi[2], Takada Tomoya[1] (1. Chitose Institute of Science and Technology, 2. Institute for Catalysis, Hokkaido University, 3. Faculty of engineering, Hokkaido University)

Japanese

[P1-3vn-27]

Development of catalytic reaction system utilizing vibration energy

○Ryuichi Fujikake[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-28]

Dehydrogenation of ammonia on the $CoAl_n$(n=10-13) cation clusters

○Kazuki Kodaira[1], Shoji Kudo[1], Hidenori Matsuzawa[1] (1. Chiba Institute of Technology)

Japanese

[P1-3vn-29]

Catalytic reaction and the mechanism over vibro-catalyst using low-frequency vibration

○Yuto Oba[1], Taiki Uno[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

Japanese

[P1-3vn-30]

Effect of reaction temperature on gas phase decomposition of dibromomethane using iron-supported alumina

○Daisuke Fujimoto[1], Liu Dan[1] (1. National Institute of Technology, Ariake College)

Japanese

[P1-3vn-31]

Effect of sodium chloride on the asymmetric ring-opening reaction of epoxides by Plant-based Organic Molecular Catalyst

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○Koichi Wada[1], Yasuo Kato[2], Makoto Hibi[2], Yuki Takeuchi[1], Tatsuhiro Asano[1] (1. Kyowa Pharma Chemical Co., Ltd, 2. Toyama Prefectural University)

Japanese

[P1-3vn-32]

Fabrication of metal nanoparticles by electrolytic reduction of composite metal oxides

○Toshiaki Oka[1], Soichi Kikkawa[1], Seiji Yamazoe[1] (1. Tokyo Metropolitan University)

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酸素発生反応における酸化ルテニウム触媒の劣化機構

（東京都立大院都市環境科学[1]）○帯金 一貴[1]・別府 孝介[1]・天野 史章[1]

Degradation Mechanism of Ruthenium Oxide Electrocatalysts during Oxygen Evolution Reaction ([1]*Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*)
○Kazuki Obigane,[1] Kosuke Beppu,[1] Fumiaki Amano[1]

The electrocatalysts for oxygen evolution reaction (OER) at high current density are exposed to harsh conditions including high anodic potential and acidity. Ruthenium oxide (RuO_2) catalysts exhibit high OER activity, but the stability under acidic conditions is lower than that of expensive iridium oxides. The degradation mechanism and strategy to enhance stability remain unclear for RuO_2 electrocatalysts. This study investigates the dissolution of Ru species from the RuO_2 particles with different crystallinity, aiming to understand the degradation mechanism of RuO_2 during acidic OER. Among the tested catalysts, RuO_2 calcined at 350 °C showed the highest stability in the durability test. Figure 1 summarizes the amount of Ru species that remained on the electrode surface and dissolved in the electrolyte solutions after the deactivation. The residues were determined by SEM-EDS analysis, while the dissolved amounts were quantified using ICP-OES. The samples prepared at calcination at 280 and 300 °C had significant missing in the Ru species detection, attributed to the detachment of RuO_2 aggregates during the stability test.
Keywords: Oxygen Evolution Anode; Ruthenium Dioxide; Deactivation; Water Splitting

大電流での水素製造を指向した場合、酸素発生反応（OER）触媒の表面は酸性かつ高電位条件となる。酸化ルテニウム（RuO_2）はこのような条件下でも高い OER 活性を示すが、耐久性の低さに問題がある。しかし、RuO_2 触媒の劣化機構や耐久性向上のための触媒設計指針はいまだ明らかとなっていない。本研究では、焼成温度を変えることで作製した結晶化度の異なる RuO_2 触媒を用いて、耐久性試験前後の触媒状態や Ru 種の溶出量を評価し、劣化機構の差異を調べた。

調製した触媒の中で、350ºC で焼成した RuO_2 が最も高い耐久性を示した。耐久性試験後の Ru 種の定量結果を図 1 に示す。電極表面上に残留した RuO_2 は SEM-EDS 分析により求めた。電解液中に溶出した Ru 種は ICP-OES により定量した。280°C および 300°C で焼成して調製した試料では、Ru 種の検出量が大幅に少ないことがわかった。これは、耐久性試験中に RuO_2 粒子凝集体が電極から脱落したためである。

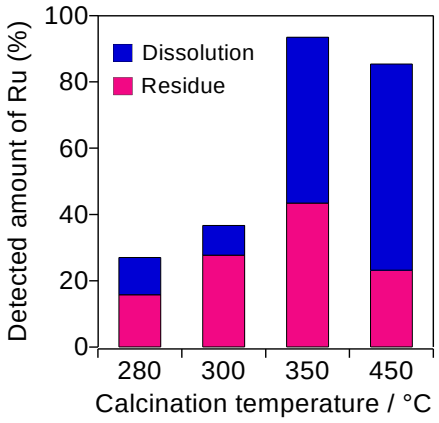

Figure 1. Amount of Ru species remained on the electrode surface and dissolved in the electrolyte solutions after the stability test.

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放射線照射法による樹脂基材表面への Pd ナノ粒子触媒固定化技術における低エネルギー電子線の適用

（阪大院工）○岩野 凌平・清野 智史・上垣 直人・石黒 文康・大久保 雄司・中川 貴
Utilization of low-energy electron beam for the immobilization of Pd nanoparticle catalyst on polymer substrate by radiation irradiation method (*Graduate School of Engineering, Osaka University*) ○Ryohei Iwano, Satoshi Seino, Naoto Uegaki, Fumiyasu Ishiguro, Yuji Ohkubo, Takashi Nakagawa

Palladium (Pd) nanoparticle catalysts can be immobilized on polymer substrates by irradiating that substrate immersed in Pd ion aqueous solution. Previous investigations have predominantly focused on employing high-energy electron beams or gamma-rays as radiation sources. The utilization of low-energy electron beams stands as a preferable option, particularly in industrial applications and for materials exhibiting low radiation resistance. In this study, we investigated the applicability of low-energy electron beams in a radiation-based method of immobilizing Pd nanoparticles on polymer substrates. Synthesis conditions and the chemical state of the Pd nanoparticles and the polymer substrates are discussed.

Keywords : Low-energy electron beam, Polymer substrate, Nanoparticles, Palladium, Catalyst

Pd イオン水溶液に浸漬した樹脂基材に放射線を照射することで、Pd ナノ粒子触媒を基材表面に固定化できることが報告されている[1]。既往研究では、高エネルギー電子線（4.8 MeV）やガンマ線を利用した検討が行われている。低エネルギー電子線を線源として利用することで、工業的応用の可能性が広がり、また低放射線耐性物質への適用も期待できる。本研究では、当該手法における低エネルギー電子線の適用可能性の検討を行った。Pd イオン水溶液に浸漬した ABS 樹脂基板に 175 keV の電子線を照射することで、Pd ナノ粒子を固定化した。得られた Pd/ABS の Pd3d-XPS スペクトルを Figure 1 に示す。高エネルギー電子線を用いた場合と同様、Pd の電子状態として、金属状態および樹脂表面に導入された官能基に配位した状態とが共存していることが分かった。適用する放射線種が、Pd の固定化状態や、無電解めっき触媒としての性能に及ぼす影響について議論する。

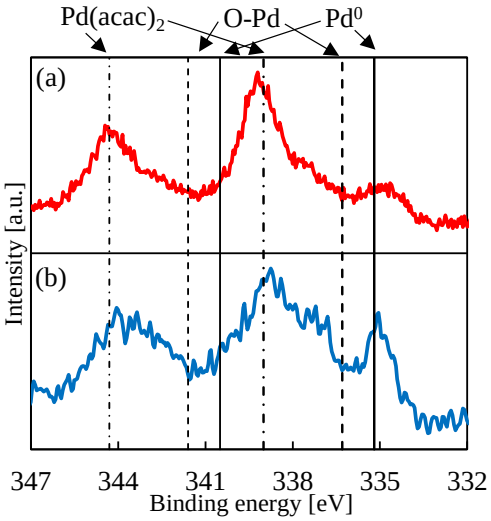

Figure 1. Pd3d-XPS spectra of Pd/ABS prepared by irradiated with (a) 4.8 MeV electron beams (previous research), and (b) 175 keV electron beams.

1) N. Uegaki et al., *Nanomaterials*, 12(9), 1463.

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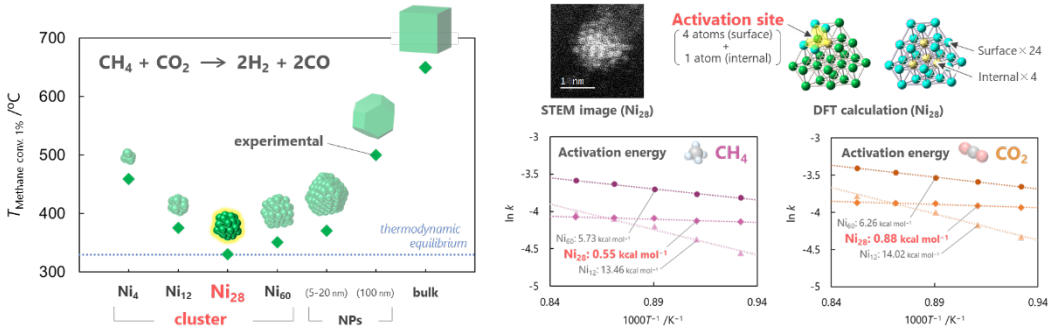
精密ニッケルクラスターを触媒とした温室効果ガス変換反応

（東工大化生研 [1]・JST-ERATO[2]・東大生研 [3]・JST-さきがけ [4]・福島県医大総合科学教育研究セ [5]）○森合 達也 [1,2]・塚本 孝政 [2,3,4]・田邊 真 [2,5]・神戸 徹也 [1,2]・今岡 享稔 [1,2]・山元 公寿 [1,2]
Greenhouse gas conversion reaction catalyzed by precise nickel clusters ([1]*Lab. for Chemistry and Life Science, Tokyo Tech*, [2]*JST-ERATO*, [3]*Inst. of Industrial Science, The Univ. of Tokyo*, [4]*JST-PRESTO*, [5]*Ctr. for Integrated Sciences and Humanities, Fukushima Medical Univ.*) ○ Tatsuya Moriai,[1,2] Takamasa Tsukamoto,[2,3,4] Makoto Tanabe,[2,5] Tetsuya Kambe,[1,2] Takane Imaoka,[1,2] Kimihisa Yamamoto[1,2]

Metal clusters have attracted much attention due to their unique structure and reactivity not found even in nanoparticles (NPs). We have successfully synthesized various clusters by using the original phenyl azomethine dendrimer as a template molecule[1)]. In this work, we prepared Ni clusters with a fine-controlled atomicity and evaluated their catalytic performance through dry reforming of methane (DRM). These clusters were identified by STEM/EDS observation and XAFS analysis while their properties were evaluated through XPS measurements and temperature-programmed reduction. Furthermore, they were applied to DRM as catalysts, revealing a size and atomicity-dependent catalytic performance. Among them, the 28-atom cluster exhibited outstanding performance and low activation energy due to its unique structure.
Keywords : Cluster; Dendrimer; Nickel; Greenhouse gas; Catalyst

金属クラスターは、粒径約 1 nm の極微小物質であり、従来のナノ粒子にも見られない構造や反応性を有することから近年注目を集めている。我々は、これまでに独自に開発した樹状高分子であるデンドリマーを用いた鋳型合成法により、様々な金属クラスターの合成に成功してきた [1)]。本研究では、核数を制御した Ni クラスターを合成し、これらをメタンのドライリフォーミング（DRM）反応に対する触媒能を評価した。合成したクラスターについて、STEM/EDS 観察や XAFS 解析から同定を行い、XPS 分析や昇温還元測定により化学状態を評価した。また、これらを DRM 触媒として応用したところ、触媒活性が触媒のサイズ・核数に依存して変化することが明らかとなった。その中でもとくに 28 核クラスターが特異な幾何構造に起因する優れた活性を持つことが示され、反応の活性化エネルギーを大きく低下させることに成功した。



1) T. Moriai *et al.*, *Angew. Chem. Int. Ed.* **2020**, *59*, 23051–23055.

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Size effect of V group metal oxide clusters on base catalytic property

(*[1]Tokyo Metropolitan University*) ○Supisara Hongpuek,[1] Hiroki Nagakari,[1] Soichi Kikkawa,[1] Seiji Yamazoe[1]

Keywords: Polyoxometalate; group V metal oxide cluster; base catalysis

Acid and base catalysts are essential for industrial processes in petroleum chemistry and biomass conversion. Group V transition metal oxide clusters, such as $[Ta_6O_{19}]^{8-}$,[1)] $[Nb_6O_{19}]^{8-}$,[1)] and $[Nb_{10}O_{28}]^{6-}$,[2)] have been reported as base catalyst to show the Brønsted and Lewis base catalysis for Knoevenagel condensation reaction and CO_2 fixation reaction, respectively. The base property came from highly negative natural bonding charge of the surface O atoms, as calculated by DFT calculations. However, the origin of the strong basicity of V group metal oxide clusters is not fully understood yet. In this study, we synthesized group V transition metal oxide clusters composed of different number of metal oxo units by microwave-assisted hydrothermal method and the following bottom-up condensation synthesis, and investigated their base catalytic property to understand size-dependent reactivity trends and the origin of their basicities (Figure 1).

Tetra-*n*-butylammonium (TBA) salt of $[Ta_6O_{19}]^{8-}$ (**TBA-Ta6**) was synthesized by a microwave-assisted hydrothermal method as reported.[3)] **TBA-Ta6** was synthesized by acidification of $K_8[Ta_6O_{19}]\cdot nH_2O$ to obtain $Ta_2O_5\cdot nH_2O$, which then reacted with 10% tetrabutylammonium hydroxide (TBAOH) aqueous solution using microwave-assisted hydrothermal method. TBA salt of $[Ta_{10}O_{28}]^{6-}$ (**TBA-Ta10**) was obtained by heating **TBA-Ta6** in toluene for 30 hours and keeping it to stand at −20°C for a couple days, as reported.[4)] The obtained samples were characterized by Fourier-transform infrared spectroscopy, electrospray ionization-mass spectroscopy, and other techniques and plied to Knoevenagel condensation reaction to evaluate their base catalytic property.

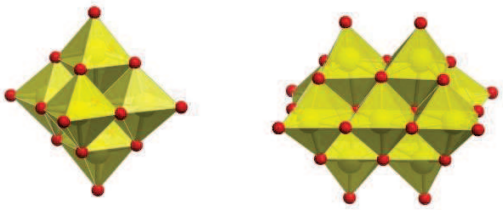

Figure 1. The structure of $[Ta_6O_{19}]^{8-}$ and $[Ta_{10}O_{28}]^{6-}$.

1) S. Hayashi *et al*., *J. Phys. Chem. C*, **2018** ,*122*, 29398. 2) S. Hayashi *et al*., *Chem. Asian J* **2017**, *12*, 1635. 3) M. A. Rambaran *et al*., *Eur. J. Inorg. Chem.*, **2019**, 3913 (2019). 4) M. Matsumoto *et al*., *Inorg. Chem.* **2013**, *52*, 7825.

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Synthesis, separation, and purification of V group metal oxide clusters

(Graduate School of Science, Tokyo Metropolitan University) ○Nattamon Panichakul, Tomoki Matsuyama, Soichi Kikkawa, Koichi Kikuchi, Seiji Yamazoe
Keywords: Anionic cluster; Polyoxometalate, Base catalysis; HPLC techniques; Microwave-assisted synthesis

Metal oxide clusters (polyoxometalates, POMs) have been known as acid catalysts, photocatalysts, and redox catalysts. Recently, the findings and application of metal oxide clusters as base catalysts have been reported, such as Lindqvist-type V-group metal oxide clusters $[M_6O_{19}]^{8-}$ (M = Nb, Ta) for Knoevenagel condensation and CO_2 fixation reactions due to the highly negative natural bonding charge of the surface O atoms.[1] We have reported that the Lindqvist-type Ta-Nb mixed hexametalates with tetrabutyl ammonium cation, $TBA_6H_2[Ta_xNb_{6-x}O_{19}]$ (will be called as TBA-$Ta_xNb_{6-x}O_{19}$), exhibited activity for CO_2 fixation reaction to styrene oxide (SO) and the product selectivity toward the CO_2 fixation reaction to form styrene carbonate (SC) could be tuned by the composition of the clusters.[2] Precisely, a single TaO_6 unit doped TBA-$Ta_1Nb_5O_{19}$ exhibited selective formation of SC with suppression of an undesired byproduct formation came from SO polymerization (Figure 1). We considered that the terminal oxygen site coordinated to a single Ta atom act as a CO_2 activation site and the activated CO_2 attacked SO to form SC. By obtaining the TBA-$Ta_2Nb_4O_{19}$ with two TaO_6 units surrounded by NbO_6 units, the catalytic activity shall be improved. Thus, composition and geometric isomer control of $[Ta_xNb_{6-x}O_{19}]^{8-}$ ions should have great influences upon the catalytic trends. In this study, we synthesized TBA-$Ta_xNb_{6-x}O_{19}$ and applied HPLC techniques to gain further insights on purification of $[Ta_xNb_{6-x}O_{19}]^{8-}$ ions.

Accordingly, TBA-$Ta_xNb_{6-x}O_{19}$ were prepared by modified microwave-assisted hydrothermal method. The mixture of $K_8Ta_6O_{19}{\cdot}nH_2O$ and $K_8Nb_6O_{19}{\cdot}nH_2O$ in a certain molar ratio was treated by HCl aq. Then, the mixture was dispersed in TBAOH aq. and irradiated by the microwave in a glass tube to obtain the TBA-$Ta_xNb_{6-x}O_{19}$. Characterization of obtained samples were done via ESI-MS and FT-IR prior to the CO_2 fixation reaction to SO to confirm the product selectivity reproduced as reported. In addition, the results on cluster separation and purification of $[Ta_xNb_{6-x}O_{19}]^{8-}$ ions by HPLC techniques will be reported in the presentation.

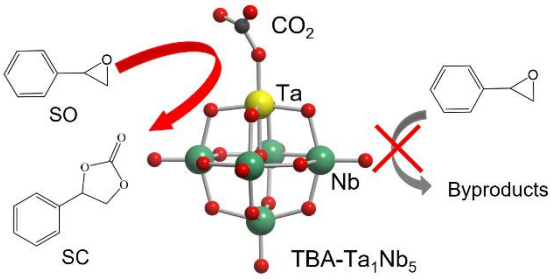

Figure 1. CO_2 fixation mechanism into SO to form SC over TBA-$Ta_1Nb_5O_{19}$.[2]

1) S. Hayashi, N. Sasaki, S. Yamazoe, T. Tsukuda, *J. Phys. Chem. C*, **2018**, *122*, 29398. 2) V. Chudatemiya, M. Tsukada, H. Nagakari, S. Kikkawa, J. Hirayama, N. Nakatani, T. Yamamoto, S. Yamazoe, *Catalysts*, **2023**, *13*, 442.

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種々の GaN:ZnO 粉末の光電気化学特性と光触媒活性の相関の検討

(信大院総合理工[1]・信大院総合医理工[2]・信大先鋭材料研[3]・JST さきがけ[4])○関森 柊二[1]・三大寺 広花[1]・阿部 慎太郎[1]・岩佐 捺伽[2]・久富 隆史[3,4]・堂免 一成[3]

Study on the correlation between photoelectrochemical properties and photocatalytic activities of various GaN:ZnO powders ([1]*Graduate School of Science and Technology*, *Shinshu University*, [2]*Graduate School of Medicine, Science and Technology, Shinshu University,* [3]*Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University,* [4]*PRESTO, JST*) ○Shuji Sekimori,[1] Hiroka Sandaiji,[1] Shintaro Abe,[1] Natsutogi Iwasa,[2] Takashi Hisatomi,[3,4] Kazunari Domen[3]

GaN:ZnO photocatalyst powders with different compositions were synthesized in sealed evacuated tubes by varying the synthesis and post-treatment conditions. The powders were then processed into photoelectrodes by the particle transfer method and their photoelectrochemical properties were investigated. The samples with improved water splitting activity tended to exhibit photocurrent onset potential at more negative potentials, suggesting a correlation between photoelectrochemical properties and photocatalytic water splitting activity.
Keywords: Oxynitride, particle transfer, visible light, composition, band gap

真空封管法を用いることで波長 550 nm までの光を吸収して水分解反応に活性な GaN:ZnO 粉末を合成できる[1]。しかし、水素生成活性や水の完全分解活性は酸素生成活性に比べて低く、高効率な可視光水分解の実現に向けて原因の究明が望まれる。本研究では真空封管加熱及び後処理の条件を変えることで組成の異なる種々の GaN:ZnO 粉末を合成し、それを粒子転写法により光電極に加工して、光電気化学的特性と光触媒活性の相関を検討した。

Zn_3N_2、Ga_2O_3、$ZnCl_2$ を真空封管中で反応させて GaN:ZnO を得た。調製した GaN:ZnO は種々の助触媒を担持してもほとんど水分解活性を示さなかったが、溶融塩処理すると吸収端が短波長化して明瞭な可視光水分解活性を示すようになった。GaN:ZnO の電流電位特性を比較すると、溶融塩処理により水分解反応に活性化された試料では、光電流開始電位及び光照射時の開回路電位がともに卑な電位にシフトしていた（図 1）。これらは電荷分離効率の向上を反映していると考えられる。

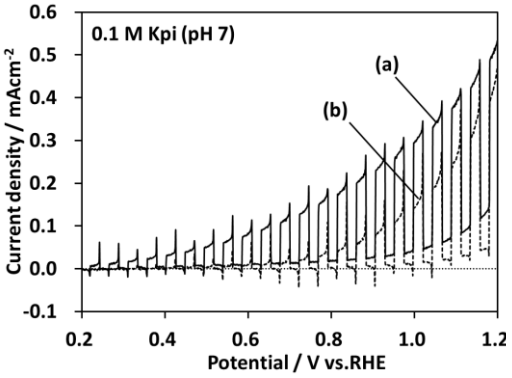

図 1　IrO_2 を担持した GaN:ZnO の疑似太陽光照射下における電流電位特性。(a) 溶融塩処理なし、(b) 溶融塩処理あり。

1) Liu *et al. ACS Catal.* **2022**, *12*, 14637.

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出発原料の含水量に応じた GaN:ZnO 固溶体の合成条件最適化

（信大院工[1]・信大先鋭材料研[2]・ JST さきがけ[3]）○三大寺 広花[1]・岩佐 捺伽[1]・久富 隆史[2,3]・堂免 一成[2]

Optimization of the synthesis conditions for GaN:ZnO solid solution depending on water content of starting materials ([1]*Graduate School of Science and Technology, Shinshu University,* [2]*Research Initiative for Supra-Materials, Shinshu University,* [3]*PRESTO, JST*) ○ Hiroka Sandaiji,[1] Natsutogi Iwasa,[1] Takashi Hisatomi,[2,3] Kazunari Domen[2]

ZnO-rich GaN:ZnO solid solutions with high oxygen evolution activity can be synthesized by heating a mixture of Zn_3N_2, poorly crystalline Ga_2O_3, Zn, and zinc halide in sealed evacuated tubes. In this study, in order to improve the reproducibility of the GaN:ZnO synthesis and the controllability of its composition, the relationship between the water content in Ga_2O_3 and the amount of Zn added was investigated. The addition of Zn was found to suppress the formation of oxide impurities resulting from the water content in the poorly crystalline Ga_2O_3.

Keywords : Water content, Oxygen source、*Sealed evacuated tube*、*Visible light*、*Water splitting*

Zn_3N_2、低結晶性 Ga_2O_3、Zn、ハロゲン化亜鉛の混合物を真空封管中で加熱することで、ZnO 含有量が高く、硝酸銀水溶液からの酸素生成反応に優れた活性を発揮する GaN と ZnO の固溶体（GaN:ZnO）を合成できる[1)]。本研究では、低結晶性 Ga_2O_3 の含水量と原料中に添加する Zn の量の関係を検討し、GaN:ZnO 合成の組成の制御性及び再現性の向上を図った。

低結晶性 Ga_2O_3 は $Ga(NO_3)_3{\cdot}xH_2O$ を 200℃で 18 時間熱分解して調製した。熱重量分析により求めた含水量は 16 wt%であった。低結晶性 Ga_2O_3、Zn_3N_2、ZnI_2、Zn を 1:1:2:y（y = 0-1）のモル比で混合し、真空封管中で加熱して GaN:ZnO を合成した。

Zn 添加量 y が低い領域では不純物として $ZnGa_2O_4$ が生成したが、y が 0.35 以上の場合に GaN:ZnO が単相で生成した。添加した Zn は低結晶性 Ga_2O_3 の水分に由来する酸化物の副生を抑制する役割をしていると考えられる。GaN:ZnO の酸素生成活性は Zn 添加量 y によらず同程度であった（図 1）。講演では、調製条件に応じて低結晶性 Ga_2O_3 の含水量が異なる場合に Zn 添加量 y を検討した結果について議論する。

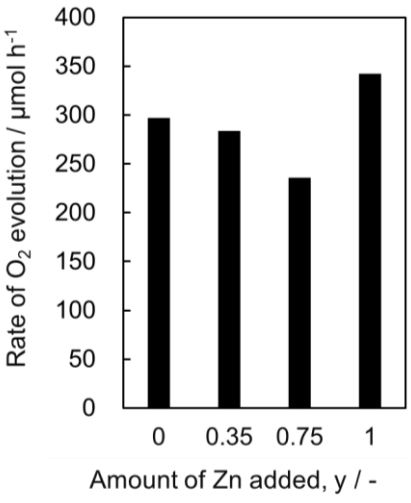

図 1　Zn 添加量 y を変化させて合成した GaN:ZnO の酸素生成活性。原料中 Ga_2O_3 の含水量は 16 wt%。

1) 三大寺ら、第 132 回触媒討論会 1C13 A1(2023)

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光照射下の水系懸濁液中における光触媒近傍の温度が水素生成速度に与える影響

(信州大工 [1]・信州大先鋭材料研 [2]) ○平田 美佳 [1]・犬塚 寛人 [1]・影島 洋介 [1,2]・手嶋 勝弥 [1,2]・錦織 広昌 [1,2]

Effects of Temperature near the Photocatalyst under Light Illumination in Aqueous Suspension on Hydrogen Evolution Rate ([1]*Faculty of Engineering*, *Shinshu University*, [2]*Research Initiative for Supra-Materials*, *Shinshu University*) ○ Mika Hirata,[1] Hiroto Inuzuka,[1] Yosuke Kageshima,[1,2] Katsuya Teshima,[1,2] Hiromasa Nishikiori[1,2]

We have previously reported that the local heat induced by visible and infrared light absorption by electronic defects and cocatalysts on TiO_2 particles accelerates the photocatalytic hydrogen production rete. In this study, we tried to increase the number of defects introduced into TiO_2 particles and to further promote the hydrogen production reaction by using $NaBH_4$, which has stronger reducing power, as a reducing agent during preparation of the reduced TiO_2. The effect of temperature near the photocatalytic particles in an aqueous suspension under light irradiation on the photocatalytic reaction rate was also evaluated.

Fig. 1 shows the dependence of hydrogen evolution activity of the $NaBH_4$-reduced TiO_2 on $NaBH_4$ mass ratio. During the photocatalysis, Pt nanoparticles were loaded on the reduced TiO_2 as a cocatalyst. Although the photocatalytic activities showed the volcano-type trend according to the amount of $NaBH_4$, all the reduced TiO_2 specimens unfortunately suffered from the deteriorated activity compared with the pristine TiO_2. Thus, improvement of reduction method might be necessary. In the presentation, the effect of temperature of the reaction solution under light irradiation on the hydrogen production rate will also be discussed.

Keywords : Photocatalysts; Black Titania; Oxide; Photothermal Effects; Reaction Temperature

これまでに、TiO_2 粉末上の電子欠陥や助触媒微粒子の可視～赤外域での光吸収に起因する光発熱が、光触媒的な水素生成反応を促進することを報告している [1)]。本研究では、還元 TiO_2 調製時に、還元力がより強い $NaBH_4$ を還元剤として使用することで、TiO_2 微粒子への欠陥導入量の増大及びそれによる水素生成反応の更なる促進を試みた。また、光照射下の水系懸濁液中における光触媒微粒子近傍の温度が、光触媒反応速度へ及ぼす影響についても評価した。

$NaBH_4$ 還元 TiO_2 の水素生成活性の、$NaBH_4$ 質量比依存性を Fig.1 に示す。活性評価時には助触媒として Pt 微粒子を還元 TiO_2 に担持した。$NaBH_4$ 添加量に対して水素生成活性は火山型を示す傾向にあるが、未処理の TiO_2 の場合と比べ活性は低下しており、還元方法の改善が必要と考えられる。発表では、光照射下の反応溶液の温度が水素生成速度に与える影響についても議論する。

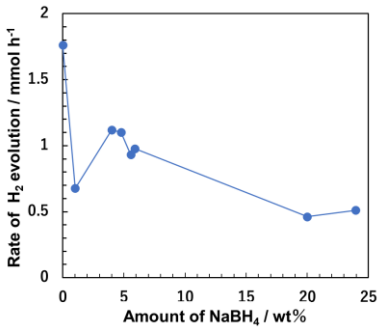

Fig. 1 The dependence of H_2 evolution rate on the amount of $NaBH_4$ used during the reduced TiO_2 preparation.

1) Y. Kageshima, *et al.*, *J. Phys. Chem. C* **2023**, *127*, 37, 18327–18339.

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水素生成用光触媒粉末表面へのリン酸系官能基含有ポリマーの修飾

(信州大工[1]・信州大先鋭材料研[2]・東大[3]) ○山村 清遥[1]・山本 雅隆[1]・影島 洋介[1,2]・手嶋 勝弥[1,2]・堂免 一成[2,3]・錦織 広昌[1,2]
Modification of Polymer Layer Containing Phosphate Functional Groups to Surface of Hydrogen-Evolving Photocatalytic Particles ([1]*Faculty of Engineering, Shinshu University*, [2]*Research Initiative for Supra-Materials, Shinshu University*, [3]*The University of Tokyo*) ○ Kiyoharu Yamamura,[1] Masataka Yamamoto,[1] Yosuke Kageshima,[1,2] Katsuya Teshima,[1,2] Kazunari Domen,[2,3] Hiromasa Nishikiori[1,2]

We have reported that modification of visible-light responsive photocatalyst surface using silane-coupling reagents containing phosphonate groups enhances the photocatalytic hydrogen evolution activity. In this study, the surface of Rh-doped $SrTiO_3$ (Rh:STO) was modified with polymer layer containing phosphate functional groups, intended for increasing of concentration of buffering groups at the vicinity of photocatalyst surface and the resultant further improvement of the hydrogen evolution activity. Figure 1 shows the XPS spectra of Rh:STO without the surface modification, specimen modified with the conventional silane coupling reagent containing one phosphonate group per molecule, and specimen modified with phosphate-polymer layer. The Si and P signals observed from the polymer-modified specimen were significantly larger than the case of the conventional phosphonate-modified one, implying the increased concentration of buffering groups at the surface. In the presentation, more detailed characterizations and hydrogen evolution activity obtained by the polymer-modified Rh:STO will also be discussed.
Keywords : Photocatalysts, Hydrogen Evolution, Phosphate Groups, Silane-Coupling Treatment, Polymerization

これまでに、可視光応答型光触媒表面にホスホン基を有するシランカップリング剤を修飾することで、水素生成活性を向上可能であることを報告している[1)]。本研究では、光触媒近傍の緩衝性官能基の濃度の増大とそれによる更なる水素生成活性の向上を目指し、Rh ドープ $SrTiO_3$ (Rh:STO)表面へのリン酸系官能基を有するポリマーの修飾を試みた。未修飾の Rh:STO、1 分子あたり 1 つのホスホン基を有する既往のシランカップリング剤で修飾した試料、及びリン酸系ポリマーで修飾した試料の XPS スペクトルを Fig. 1 に示す。ポリマー修飾体から得られた Si 及び P のシグナルは、既往のホスホン基修飾体に比べ大幅に増大しており、表面近傍の緩衝性官能基濃度の増大が示唆された。発表では、ポリマー修飾した Rh:STO のより詳細なキャラクタリゼーションや水素生成活性についても議論する。

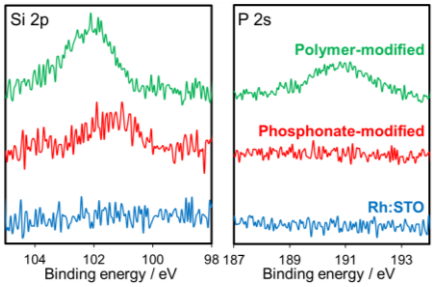

Fig. 1 XPS spectra of Rh:STO with and without surface modification.

1) Y. Kageshima, *et al.*, *Angew. Chem. int. Ed.* **2021**, *60*, 7, 3654-3660.

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種々の合成法により調製した Ru 微量ドーピング $SrTiO_3$ 光触媒を用いた可視光水分解

（東理大理[1]・東理大総研カーボンバリュー[2]）○花房 ちさと[1]・植木 義也[1]・安藤 宗徳[1]・山口 友一[1,2]・工藤 昭彦[1,2]

Water Splitting under Visible Light Irradiation over a Tiny Amount of Ru-Doped $SrTiO_3$ Photocatalyst Prepared by Various Synthesis Methods ([1]*Faculty of Science, Tokyo University of Science*, [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Chisato Hanafusa[1], Yoshiya Ueki[1], Motonori Ando[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2]

We have reported that the photocatalytic water splitting activity under visible light over $SrTiO_3$:Ru,Sb,Al extensively enhanced by doping a small amount of Ru, the $SrCl_2$-flux treatment, and loading CrO_x/Rh and CoOOH cocatalysts[1,2] by the photodeposition method.[3] However, the activity is low at the present stage. In the present study, we investigated the photocatalytic water splitting under visible light over fine $SrTiO_3$:Ru,Al particles prepared by various synthesis methods.

SEM images showed that fine $SrTiO_3$:Ru,Al particles were obtained by the polymerized complex method following the $SrCl_2$-flux treatment compared with the samples prepared by a solid-state reaction following the $SrCl_2$-flux treatment. Additionally, the sample showed the efficient water splitting activity under visible light irradiation.

This presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Keywords : water splitting; metal oxide; doping Ru; visible light; green hydrogen production

当研究室では微量ドーピング，フラックス処理，および光電着法による CrO_x/Rh および CoOOH 助触媒の共担持[1,2]によって，$SrTiO_3$:Ru,Sb,Al 光触媒を用いた可視光水分解の高活性化に成功している[3]．しかし，未だ活性は低いという課題がある．水分解活性を向上させるためには光触媒粒子の微小化が重要である．そこで本研究では，錯体重合法などの種々の合成法を用いて $SrTiO_3$:Ru,Al 微粒子を調製することで可視光水分解の高活性化を目指した．

錯体重合法を用いて調製した後，フラックス処理を施した試料の SEM 像を観察したところ，従来の固相合成後にフラックス処理を施した試料よりも小粒径の粒子が得られたことがわかった．そして，本光触媒は可視光照射下における水分解において従来のものよりも高い活性を示した．

この成果は，国立研究開発法人新エネルギー・産業技術総合開発機構（ＮＥＤＯ）の委託業務の結果得られたものである．

1) T. Takata, K. Domen *et al.*, *Nature*. **2020**, *581*, 411.
2) K. Maeda, K. Domen *et al.*, *Nature*. **2006**, *440*, 295.
3) 植木，山口，工藤，第 132 回触媒討論会，2C10 (2023).

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MOF 前駆体を経由した CdS/ZnS 複合光触媒を用いた有機廃棄物の光改質による水素生成

（東京理科大工 [1]）○隈井 祐成 [1]・永田 衞男 [1]
Hydrogen production by photoreforming of organic waste using CdS/ZnS composite photocatalyst via MOF precursor([1]*Faculty of Engineering, Tokyo University of Science*)
○Yusei Kumai,[1] Morio Nagata,[1]

The use of photocatalysts to decompose household waste and hydrogen production can solve both waste and energy problems. We are aiming to improve the activity of hydrogen production by photoreforming of organic waste using sulfide photocatalysts. The sulfide photocatalyst via MOF precursor reported so far is a stand-alone photocatalyst. Therefore, we aimed to further improve the hydrogen production activity by combining cadmium sulfide (CdS) and zinc sulfide (ZnS).

In this study, the composite of CdS and ZnS was prepared via cadmium (Cd) and zinc (Zn) MOF precursors. Hydrogen production was significantly enhanced in the CdS and ZnS composite photocatalyst compared to the single photocatalyst.

Keywords : photocatalyst, photoreforming, Hydrogen production, Metal Organic Frameworks

光触媒を用いて、家庭ごみを分解し、水素を生成することでごみ問題とエネルギー問題を同時に解決できる。我々は硫化物系光触媒を用いて有機廃棄物の光改質による水素生成活性の向上を目指している。これまでに報告した有機金属骨格(MOF)前駆体経由の硫化物系光触媒は単体である [1]。そこで、硫化カドミウム(CdS)と硫化亜鉛(ZnS)の複合で更なる水素生成活性向上を目指した。

本研究では、CdS と ZnS との複合をカドミウム(Cd)と亜鉛(Zn)の MOF 前駆体を経由して作製した。CdS と ZnS の複合光触媒において単体と比較して水素生成量が著しく向上した(下図)。

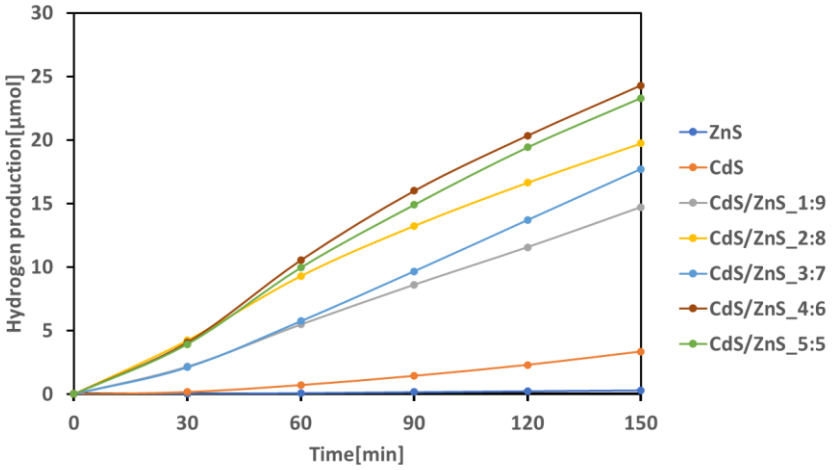

Figure 1：ZIF-8 前駆体を経由した光触媒の光改質による水素生成

1) H. Nagakawa, M. Nagata, *Adv. Mater. Interface*, **2022**, 9, 2101581.

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炭素系メタルフリー光触媒を用いた水分解による水素生成

（東京理科大工 [1]）○西村 英太郎 [1]・永田 衞男 [1]

Hydrogen production by water splitting using carbon-based metal-free photocatalyst ([1]*Faculty of Engineering, Tokyo University of Science*) ○Eitaro Nishimura,[1] Morio Nagata[1]

Photocatalytic hydrogen production is attracting attention because it does not emit carbon dioxide. The use of metal co-catalysts such as Pt on photocatalysts has been considered as highly efficient method, but high cost is one of the problems. Reduced Graphene Oxide (rGO) has been gathering attention as an alternative material to metal co-catalysts. Although photocatalytic studies using rGO have been widely researched, many of them require complicated processes and extreme conditions[1)]. In this study, we aimed to prepare graphitic carbon nitride($g\text{-}C_3N_4$)/rGO metal-free composite photocatalysts by a simple method and to improve the hydrogen production.

Using one-pot hydrothermal synthesis, we successfully reduced GO to rGO and loaded rGO on $g\text{-}C_3N_4$ simultaneously, resulting in improved hydrogen production. When we loaded 12.5 wt% rGO on $g\text{-}C_3N_4$, hydrogen production rate was four times higher than that of pure $g\text{-}C_3N_4$.
Keywords : Photocatalyst; Hydrogen Production; Metal-free; Carbon Materials; Reduced Graphene Oxide

光触媒による水素生成は二酸化炭素を排出しない製法として注目されている。高効率な水素生成法として Pt などの金属助触媒を光触媒に担持する研究が知られているが、コストが高いという問題がある。金属助触媒の代替物として、還元型酸化グラフェン(rGO)が注目を集めており、rGO を用いた光触媒の研究は広く行われているが、複雑なプロセスや過激な条件を要するものが多い[1)]。本研究では、簡易的な方法によりカーボンナイトライド($g\text{-}C_3N_4$)/rGO メタルフリー複合光触媒を作製し、水素生成量を向上させることを目的とした。

水熱合成法を用いて、GO の還元・$g\text{-}C_3N_4$ への rGO の担持をワンポットで同時に達成し、水素生成量を向上させることができた。$g\text{-}C_3N_4$ に 12.5wt%の rGO を担持した時、水素生成速度は $g\text{-}C_3N_4$ 単体の 4 倍となり、水素生成量の向上を達成した(下図)。

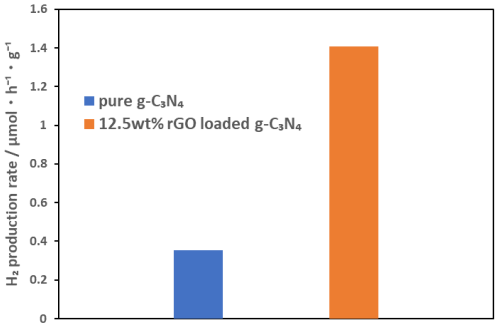

Figure 1. $g\text{-}C_3N_4$ 単体と rGO を担持した $g\text{-}C_3N_4$ の水素生成速度の比較

1) Quanjun Xiang, Jiaguo Yu, and Mietek Jaroniec, J. Phys. Chem. C **2011**, 115, 15, 7355–7363

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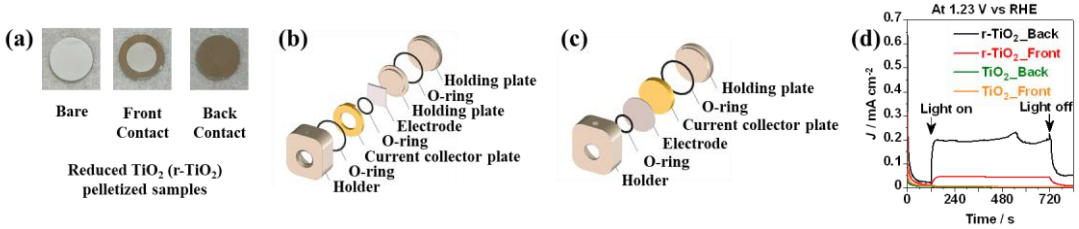
Pelletized Photoelectrodes for Photoelectrochemical Water Splitting

([1]*Faculty and Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*) ○Surya Pratap Singh,[1] Kosuke Beppu,[1] Fumiaki Amano[1]

Keywords: Bismuth Vanadate; Titanium Dioxide; Pelletized Photoelectrode; PEC; Water Splitting

Photoelectrochemical (PEC) water splitting to produce molecular oxygen and hydrogen is a promising method to address the energy problems in modern times.[1] Usually, metal oxide semiconductors supported on two-dimensional (2D) substrates such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO), and three-dimensional (3D) substrates such as titanium felt (Ti-felt) are used as the electrodes in the PEC water splitting cells.[2] In the present study, we developed the pelletized electrodes of metal oxide semiconductors such as titanium dioxide (TiO_2) and bismuth vanadate ($BiVO_4$) and used them as photoanodes for the PEC water splitting in a neutral aqueous media.

$BiVO_4$ was prepared by ball milling followed by calcination at 923 K. XRD patterns showed the formation of monoclinic fergusonite $BiVO_4$. Commercial TiO_2 (99.99 % rutile) was used. The pelletized sample was prepared by mixing the powder with a 5% polyvinyl alcohol (PVA) binder and then pressing it into a pellet of 0.5 mm thickness. The pellet was calcined at 773 K and then sintered at 1073 K. The TiO_2 pellet was further reduced in a hydrogen flow at 973 K to increase the conductivity. Ohmic contacts were made by sputtering gold (Au) layer (sputtering time 1 min, thickness ~70 nm) on the front and rear side of the pelletized samples (Fig. a). The Au front- and back-contacted pelletized samples were fit into the front- (Fig. b) and back-contact (Fig. c) current collecting holders (EC Frontier). The PEC cell consisted of the pelletized photoelectrodes as working electrodes (irradiation area 0.5 cm^2), Ag/AgCl as a reference electrode, Pt wire as a counter electrode, and 0.2 M Na_2SO_4 (pH 6.8) as the electrolyte in a conventional three-electrode system. Upon UV-light irradiation (365 nm LED, intensity 40 mW cm^{-2}), a photocurrent developed with reduced TiO_2 (r-TiO_2) pelletized photoanodes and Au-back contacted photoanode showed enhanced photocurrent (0.2 mA cm^{-2} at 1.23 V vs RHE) (Fig. d) possibly due to low diffusion length. $BiVO_4$ pelletized photoanode also showed a small photocurrent upon visible light irradiation.



1) T. Hisatomi, J. Kubota, K. Domen *Chem. Soc. Rev.* **2014**, *43*, 7520. 2) C.X.M. Ta, Y. Furusho, F. Amano *Appl. Surf. Sci.* **2021**, *548*, 149251.

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グルコースを殺菌剤に変換する可視光応答型光触媒の開発

（農工大 BASE）○秋田真那・臼杵翔・中田一弥
Development of Visible-Light Photocatalyst for Conversion of Glucose to Fungicide (*Tokyo University of Agriculture and Technology*) ○Mana Akita, Sho Usuki, Kazuya Nakata

Bacteria that cause food poisoning and infectious diseases and deteriorate the sanitary environment are a constant problem. Especially for bacteria that are difficult to sterilize, disinfectants with a broad antimicrobial spectrum are needed. Peracetic acid is one of the organic peroxides and has been used as a disinfectant with a broad antimicrobial spectrum. However, it is manufactured by adding hydrogen peroxide and sulfuric acid to acetic anhydride and distilling it, which is problematic because of its high environmental impact. Previously, our laboratory has successfully converted EtOH to peracetic acid and inactivated highly durable spores by using a visible light-responsive WO_3 photocatalyst. Based on this result, in this study, we used glucose, a biomass-derived compound, as a raw material and PdO_x-loaded WO_3 (PdO_x/WO_3) photocatalyst. The formation of organic peroxides with strong bactericidal activity was examined under mild conditions of visible light and ambient temperature and pressure. As a result, the formation of organic peroxides was confirmed by dispersing PdO_x/WO_3 in a glucose solution and irradiating it with visible light (Fig. 1). When antimicrobial tests were conducted using this organic peroxide solution, the survival rate of *E. coli* was reduced by 5.3 log in 15 min.
Keywords : Photocatalyst; Organic peroxides; Fungicide; Glucose; Biomass

食中毒や感染症を引き起こし、衛生環境を悪化させる細菌が恒常的に問題となっている。特に殺菌が困難な細菌に対しては抗菌スペクトルの広い殺菌剤が必要となる。過酢酸は有機過酸化物の一つであり、抗菌スペクトルが広い殺菌剤として使用されているが、無水酢酸に過酸化水素および硫酸を加えて蒸留することで製造されているため環境負荷が高いことが問題であった。これまで当研究室では、可視光応答型である WO_3 系光触媒を用いることで EtOH を過酢酸へと変換し、高耐久性の芽胞を不活化することに成功した[1]。この知見を踏まえ、本研究ではバイオマス由来の化合物であるグルコースを原料として、PdO_x を担持した WO_3 光触媒を用いて、可視光下かつ常温常圧の温和な条件下で、強力な殺菌作用をもつ有機過酸化物の生成を検討した。

実際に、グルコース水溶液に PdO_x を担持した WO_3 (PdO_x/WO_3)を分散し、可視光を照射することで、有機過酸化物の生成が確認された(Fig. 1)。また、この有機過酸化物溶液を用いて抗菌試験を行ったところ、大腸菌の生存率は 15 分で 5.3 log 減少した。

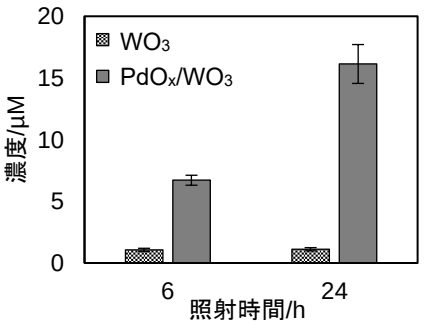

Fig. 1 WO_3 または PdO_x/WO_3 を用いたグルコース転換による有機過酸化物の生成

1) Y. Yamaguchi, K. Nakata *et al., Sci. Rep.,* **2016**, *6*, 33715.

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メカノ殺菌効果を発現するアラゴナイト担持光触媒の合成と評価

(千葉工大院工[1]・産総研[2])○五味 彩子[1,2]・五十嵐 香[1]・宮崎 ゆかり[2]・根岸 信彰[2]・山野 凌[1,2]・鳥羽 悟史[1,2]

Synthesis of aragonite immobilized photocatalysts exhibiting mechano-bactericidal effects and its evaluation of bactericidal performance ([1]Graduate School of Engineering, Chiba Institute of Technology, [2]National Institute of Advanced Industrial Science and Technology) ○Ayako Gomi,[1,2] Kaoru Igarashi,[1] Yukari Miyazaki,[2] Nobuaki Negishi,[2] Ryo Yamano,[1,2] Satoshi Toba[1,2]

The lack of access to safe and controlled drinking water services is particularly prevalent in developing countries, thus necessitating the development of low-cost and simple bacterial purification systems in drinking water for such areas. As a solution, attention was paid to inexpensive photocatalysis and the mechano-bactericidal effect, in which bacteria pierce the needle-like shape and cause a physical bactericidal effect.

In a previous study, aragonite with a needle-like crystal, was successfully deposited on a photocatalyst by using Contrex, and aragonite was observed to sting bacteria[1)].

Therefore, we prepared an artificial mineral water that simulate the composition of Contrex, and the research aimed at synthesizing nanoneedles from it, evaluating their bactericidal effect, and creating a path toward industrial production. It was found that nanoneedles could be stably deposited on photocatalysts by using a photocatalytic reaction. We also found conditions for the selective synthesis of aragonite nanoneedles.

keywords: photocatalyst; Mechano-bacterial effect; Drinking water purification; Aragonite

安全に管理された飲料水サービスを受けられていないのは特に途上国に多いのが現状であるため、このような地域に向けた低コストかつ簡易的な飲料水中細菌汚染浄化システムの開発が必要である。この解決策の一つとして、安価な光触媒と針状形状(ナノニードル)に細菌が刺さることで物理的な殺菌効果をもたらすメカノ殺菌効果に注目した。

先行研究では、市販のミネラル水である Contrex を用いることで針状結晶であるアラゴナイトの光触媒上への析出に成功し、アラゴナイトが細菌に刺さる様子も観察した[1)]。

そこで、本研究では Contrex の組成を模倣した人工的なミネラル水を調製し、それを原料としたナノニードル合成、その殺菌効果評価、さらに工業的な生産に向けた筋道を作ることを目的とした研究を行った。光触媒反応を用いることでナノニードルを安定して光触媒上に析出させられることが分かった。さらに選択的にアラゴナイトナノニードルを合成する条件も見出した。

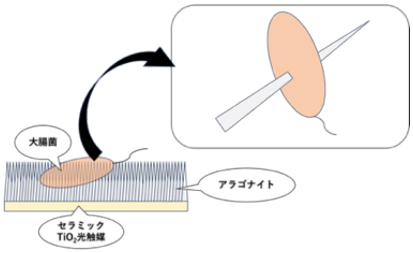

図. アラゴナイト担持光触媒による メカノ殺菌効果模式図

1) N. Negishi. et. al , Aqueous mechano-bactericidal action of acicular aragonite crystal, Scientific reports, **11**, 19218 (2021).

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助触媒担持酸化タングステン光触媒による水と空気からの硝酸生成

（阪大院基礎工）○宮田 和樹・白石 康浩・平井 隆之
Photocatalytic nitrate generation from water and air on tungsten oxide loaded with noble metal (*Graduate School of Engineering Science, Osaka University*) ○Kazuki Miyata, Yasuhiro Shiraishi, Takayuki Hirai

NO_3^- is a versatile chemical for the synthesis of fertilizers, polymers, and dyes. Currently, nitrate is manufactured by the Ostwald process under high temperature conditions. In addition, the process needs NH_3 produced by the Haber-Bosch process with H_2 and N_2 under high temperature and high pressure conditions. Therefore, photocatalytic NO_3^- production from water and air under ambient condition is desirable. Here, we report that tungsten oxide (WO_3) photocatalyst loaded with noble metal cocatalysts such as Pt and Pd successfully generates NO_3^-. Noble metals were loaded by means of microwave heating of ethylene glycol solutions containing metal precursors and WO_3 particles. The noble metal cocatalysts trap the photoexcited electrons and enhance the charge separation, resulting in an enhancement of N_2 oxidation.
Keywords : Photocatalyst; tungsten oxide; noble metal; nitrate

NO_3^- は、肥料、火薬、染料の原料となる、化学工業の根幹をなす重要な化合物である。現在、NO_3^- は、NH_3 を高温条件下で酸化するオストワルト法により合成されている。また、NH_3 は高温・高圧条件下、多量の水素を用いるハーバー・ボッシュ法により製造されている。したがって、光触媒により空気中の N_2 を直接酸素酸化する反応（$1/2N_2 + 5/4O_2 + 1/2H_2O \rightarrow HNO_3$, $\Delta G^o = +25.3$ kJ mol^{-1}）が可能となれば、常温常圧下で NO_3^- を合成する省エネルギープロセスとなる。本研究では、可視光応答型光触媒である WO_3 に Pt および Pd を助触媒として担持した Pt(x)/WO_3、Pd(x)/WO_3 光触媒 [x = Pt, Pd 仕込み量 (wt%)] が本反応を進行させることを見出した。

助触媒の担持は、Pt および Pd 源を溶解したエチレングリコールに WO_3 粒子を懸濁させ、マイクロ波を照射する方法により行った。Figure 1 には、各触媒を水に懸濁させ、空気流通下で紫外光（$\lambda > 300$ nm）を 96 時間照射した場合の HNO_3 生成量をまとめている。無担持の WO_3 はほとんど活性を示さないが、助触媒を担持することにより活性が飛躍的に増大することが分かる。WO_3 上で生成した励起電子を助触媒粒子が捕捉することにより正孔との再結合を抑制され、N_2 分子の酸化が促進されたと考えられる。

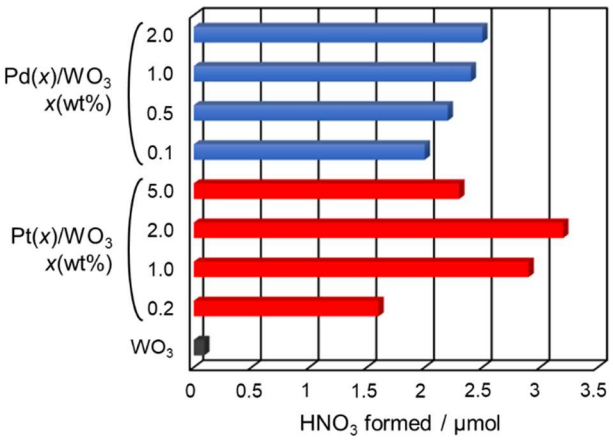

Figure 1. Amount of HNO_3 formed by photoreaction in pure water containing the respective catalysts under UV light (96 h).

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イオン交換樹脂複合レゾルシノール半導体樹脂による光触媒型過酸化水素生成

（阪大院基礎工）○西山　佳宏・白石 康浩・平井　隆之
Photocatalytic hydrogen peroxide generation on ion-exchange resin-incorporated resorcinol-formaldehyde semiconducting resins (*Graduate School of Engineering Science, Osaka University*) ○Yoshihiro Nishiyama, Yasuhiro Shiraishi, Takayuki Hirai

We prepared ion-exchange resin (Amberlite)-incorporated resorcinol-formaldehyde (RF) semiconducting resin. The pristine RF resin is spherical particles with ~3 μm diameter owing to its slow polymerization. In contrast, the Amberlite-incorporated resin is smaller particles with ~200 nm diameters owing to rapid polymerization with ion-exchange resin as a crystallization nuclei. The incorporated resins have enlarged specific surface area and exhibited ~1.3 times higher photocatalytic activity than pristine RF resin for H_2O_2 generation owing to the enhanced water oxidation and oxygen reduction reactions. However, the incorporation of excess amount of Amberlite decreased the photocatalytic activity because the large amount of insulator incorporated decreased the electronic conductivity of the resin.
Keywords : Photocatalysis, Hydrogen peroxide, RF resin, Ion exchange resin, Particle size

レゾルシノールーホルムアルデヒド（RF）半導体樹脂は、太陽光照射下、水と酸素からの H_2O_2 を進行させる光触媒として機能する [1]。本研究では、さらなる高活性化を目的とした。自動乳鉢により粉砕した強酸性陽イオン交換樹脂（Amberlite）の存在下で RF 樹脂を合成し、イオン交換樹脂複合 RF（RF(*x*)）を調製した（*x* はレゾルシノール 800 mg に対して複合した Amberlite 量(mg)を示す）。RF 樹脂生成における重縮合は遅く、粒径 3 μm 程度の球状粒子が生成する。一方、複合樹脂では、Amberlite のポリスチレン骨格を結晶核とした重縮合が進行すること、ならびに末端スルホン酸基の静電反発による会合の抑制により、粒径 200 nm 程度の小粒子が生成する。これらの樹脂を光触媒反応に用いたところ（Figure 1）、複合樹脂はその大きな比表面積により反応が促進された。特に、RF(60)触媒では、RF 樹脂の 1.3 倍程度の H_2O_2 生成活性を示した。一方、過剰に Amberlite を複合した RF(200)は、さらに比表面積が増加するものの活性は低下した。これは絶縁体である Amberlite を多量に複合することにより、導電性が低下したためと考えられる。したがって、適切な量の Amberlite を結晶核として用いることにより、比表面積の大きな高活性 RF 半導体樹脂を調製できることが分かった。

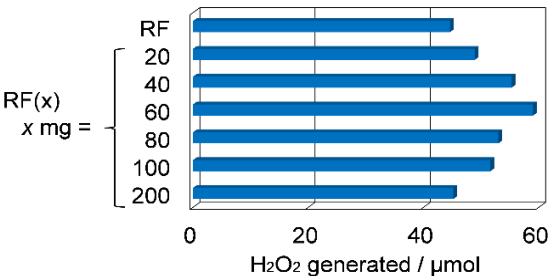

Figure 1. Amount of H_2O_2 generated on the respective RF and RF(*x*) resins during visible light irradiation [conditions: water (30 mL), catalyst (50 mg), O_2 (1 atm), Xe lamp (λ >420 nm), 298 K, 6 h.]

1)Y. Shiraishi, T. Takii, T. Hagi, S. Mori, Y. Kofuji, Y. Kitagawa, S. Tanka, S. Ichikawa, T. Hirai, *Nat. Mater*. **18**, 985 (2019)

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過酸化水素生成能を有する金属イオンを原子上に固定した赤外光応答性共有結合性有機骨格(COF)光触媒の開発

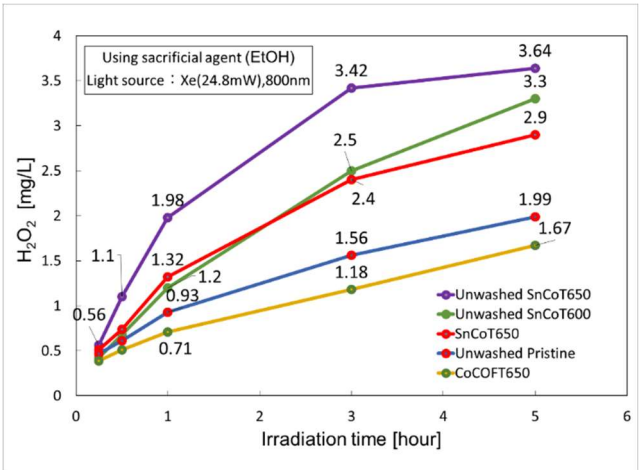
（九州工業大学[1]）○大山 慧[1]・横野 照尚[1]
Infrared-responsive covalent organic framework (COF) photocatalysts with metal ions atomically immobilized with hydrogen peroxide generation ability ([1]*Kyushu Institute Technology*)○Kei Oyama,[1]Teruhisa Ohno[1]

Infrared light, which accounts for about 51% of sunlight, has low energy, making it difficult for conventional photocatalysts to synthesize H2O2 in infrared light. The covalent organic framework (COF) has an ultra-high porosity and a huge internal surface area exceeding 6.000m2g-1. The band gap (Eg) can be controlled in the range of 1.29~2.34 eV by selecting the precursor, and the synthesis of H2O2 can be extended from visible light to infrared light. In this study, we attempted to control the band gap and improve the hydrogen peroxide production ability by loading a metallic element on a covalent organic framework (COF). In fact, when 5 wt% of tin was mixed with unsupported COF, the desired amount of hydrogen peroxide production was about 2.3 times higher than that of unsupported COF. Furthermore, when 5 wt% of sodium cobalt phosphate was added there, the hydrogen peroxide production was significantly improved.
Keywords : Photocatalyst; Water splitting; Covalent organic frameworks; Hydrogen peroxide

太陽光の約 51%を占める赤外線はエネルギーが低く、従来の光触媒では赤外光での H_2O_2 合成が困難である。共有結合性有機骨格(COF)は、超高空隙率と 6.000m^2g^{-1} を超える巨大な内部表面積を有する。また前駆体の選択によりバンドギャップ(Eg)の制御が 1.29~2.34 eV の範囲で可能であり、H_2O_2 の合成を可視光から赤外光まで拡張することが可能となる。

本研究では、共有結合性有機骨格(COF)に金属元素を担持させることでバンドギャップを制御し、過酸化水素生成能を向上させることを試みた。

実際に、スズを 5wt%分、無担持 COF に混合させた場合、目的の過酸化水素生成量が無担持のものと比べて約 2.3 倍向上した。さらに、そこにリン酸コバルトナトリウムを 5wt%添加したところ、過酸化水素生成量は著しく向上した。



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フェノール分解活性の高い g-C_3N_4 の開発

（農工大 BASE）○瀧 奈緒子・臼杵 翔・中田 一弥
Development of g-C_3N_4 with high degradation activity for phenol (*Tokyo University of Agriculture and Technology*) ○Naoko Taki, Sho Usuki, Kazuya Nakata

Endocrine disrupting chemicals (EDCs) affects living organisms even in trace amounts, and their effects on living organisms have been reported mostly in aquatic environments. As a means to safely remove EDCs from water, photocatalyst which can decompose organic chemicals under light irradiation is expected. Photocatalysts have the advantage that reactions can be controlled by turning light irradiation on and off, and have a low environmental impact because they do not produce the byproducts that are produced when oxidants or reducing agents are used. Especially, g-C_3N_4 is a metal-free photocatalyst consisting only of carbon and nitrogen atoms, and is expected to have a low impact on the human body. However, g-C_3N_4 has a low specific surface area due to its layered structure, and its degradation activity for phenol, a typical model chemical for organic pollutants, is low. In this study, we examined the characterization and evaluation of phenol-degrading activity using g-C_3N_4 by preparing thin layered structure. As a result, it was found that the phenol degradation activity of g-C_3N_4 was improved by preparing thin layered structure.
Keywords : Water purification; Photocatalyst; Graphitic carbon nitride; Phenol

内分泌系かく乱化学物質(EDCs)は、微量でも生物に影響を与える化学物質として知られており、その生物への影響は多くが水域にて報告されている。安全に水中の EDCs を除去する手段として、光照射下で有機物を分解可能な光触媒が注目されている。光触媒は光照射の ON/OFF によって反応を制御でき、かつ酸化剤や還元剤を利用した際に生成するような副生成物がなく環境負荷が小さい利点をもつ。特に g-C_3N_4 は炭素および窒素のみから構成されるメタルフリー光触媒であることから人体への影響も小さいことが期待される。しかし、既往の g-C_3N_4 は層状構造をもつため比表面積が小さく、有機系汚染物質の代表的なモデル物質であるフェノールの分解活性が低い [1]。本研究では、フェノール分解活性の高い g-C_3N_4 の開発を目指し、g-C_3N_4 の層状構造を薄層化し、物性およびフェノールの分解活性を調査した。その結果、薄層化により g-C_3N_4 のフェノール分解活性は向上したことが明らかとなった（図 1）。

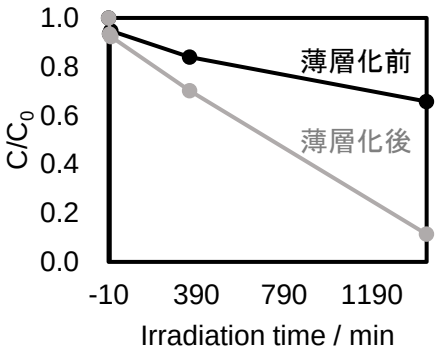

図 1. 薄層化した g-C_3N_4 によるフェノール分解の経時変化

1) An optimized and general synthetic strategy for fabrication of polymeric carbon nitride nanoarchitectures. J. Zhang, F. Guo, X. wang. *Adv. Funct. Mater*. **2013**, 23, 3008-3014.

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グラファイト型窒化炭素(PCN)を用いた可視光応答性光触媒反応によるメタン生成

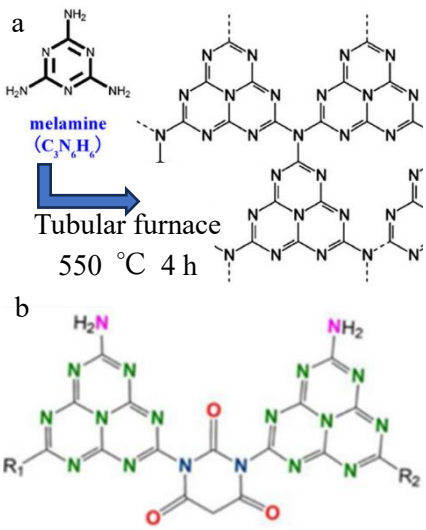
(九州工業大学大学院工学部工学専攻[1]) 金澤 辰紀[1], 横野 照尚[1]
(Kyushu Institute Of Technology graduate school[1]) Kanazawa tatuki[1], Ohno Teruhisa[1]

The photocolbe reaction, in which methane is produced from acetic acid by exposing a photocatalyst to ultraviolet light in an aqueous acetic acid solution, has been reported. In order to develop a methane production system with less environmental impact by using sunlight, a renewable energy source, we focused on PCN, a visible light responsive photocatalyst. However, PCN has the disadvantage of low charge separation efficiency. To solve this problem, we aimed to improve the methanogenic performance of PCN by supporting Pt as an auxiliary catalyst and doping heteroatoms in the CN heterocyclic ring structure.

Pt-loaded PCN showed maximum activity at 0.5 wt% to 1.0 wt% Pt. PCNBA, in which the band structure was controlled by modifying the PCN structure, showed higher activity at lower BA concentrations.

酢酸水溶液中で光触媒に紫外線を当てると酢酸からメタンが生成する光コルベ反応が報告されている。この反応を再生可能エネルギーである太陽光を利用することで環境負荷の少ないメタン生成システムの開発を目指すために可視光応答性の光触媒であるPCNに注目した。しかし電荷分離効率が低いという欠点があり、これを解決するためにPt助触媒の担持や、CN複素環構造内へのヘテロ原子ドープなどの方法を取り、PCNのメタン生成性能の向上を目指した。

白金担持PCNは0.5wt%から1.0wt% Ptで最大活性を示した。またPCN構造を修飾してバンド構造を制御したPCNBAは、BA濃度が低いほど高い活性を示した。



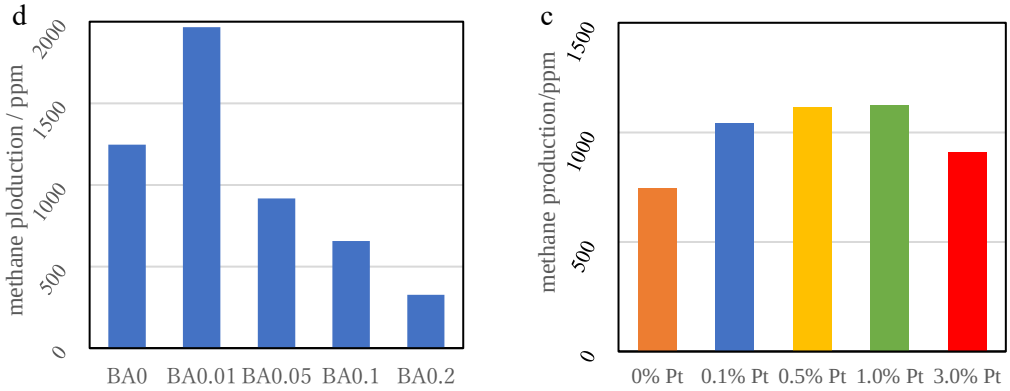


Figure 1. a) Synthesis and structure of PCN, b) Structure of PCNBA, c) Methane production of Pt-loaded PCN, d) Methane production of PCNBA (0.5 wt% Pt-loaded)

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窒素リッチな窒化炭素（C_3N_5）による光触媒水素生成と選択的 CO_2 還元

（慶大院理工 [1]）○伊藤 皇聖 [1]・野田 啓 [1]

Photocatalytic hydrogen production and selective CO_2 reduction using nitrogen-rich carbon nitride (C_3N_5)

([1]*Graduate School of Science Engineering, Keio University*,) ○Kosei Ito,[1] Kei Noda,[1]

Carbon nitride (g-C_3N_4) is attracting attention as an inexpensive, semi-permanently synthesizable, visible light responsive, metal-free photocatalyst. On the other hand, the low reaction efficiency and the tendency of catalyst degradation have been major impediments to its practical application.

The nitrogen-rich carbon nitride (C_3N_5) synthesized in this study showed improved reduction efficiency of nitro blue tetrazolium chloride solution, H_2 production from Triethanolamine solution (10%), and oversaturated CO_2 solution compared to g-C_3N_4. In addition, multiple cycle experiments showed that C_3N_5 did not exhibit catalytic degradation. Investigation of the surface structure, internal structure, and energy bands of C_3N_5 indicates that the increase in π-electrons due to the nitrogen enrichment induced a negative shift of valence band and a narrowing of band gap, and that this effect probably contributed most to the enhancement and stability of the photocatalytic properties.

Keywords : photocatalyst; nitrogen-rich carbon nitride*; H_2 production; CO_2 reduction; π electron*

窒化炭素（g-C_3N_4）は安価かつ半永久的に合成可能な可視光応答を有する金属フリー光触媒として注目を集めている。一方、反応効率が低く、触媒劣化が起こりやすいことが実用化への大きな足かせとなっていた。

本研究で作成した窒素リッチな窒化炭素（C_3N_5）は、g-C_3N_4 に対してニトロブルーテトラゾリウムクロリド溶液の還元効率、トリエタノールアミン溶液(10%)からの H_2 生成効率、過飽和 CO_2 溶液の還元効率が向上していた。さらに複数回のサイクル実験の結果、触媒劣化を示さなかった。C_3N_5 の表面構造、内部構造、エネルギーバンドを調査した結果、窒素リッチになったことでのπ電子の増加が価電子帯の負方向へのシフトとバンドギャップの縮小を誘発しており、この影響が光触媒特性の向上と安定に最も寄与したと考えている [1)]。



g-C_3N_4



C_3N_5

1) Highly efficient hydrogen production and selective CO_2 reduction by C_3N_5 photocatalyst using only visible light. K. Ito, K. Noda, *Phys. Chem. Chem. Phys.* **2024**,*26,153-160*.

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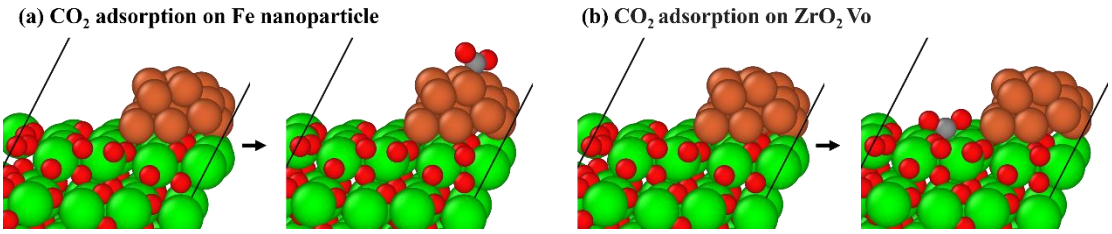
Fe–ZrO_2 による CO_2 の光還元反応の理論的考察

（千葉大院理 [1]）○尾亦 彩奈 [1]・大弓 知輝 [1]・原 慶輔 [1]・二木 かおり [1]・泉 康雄 [1]
Theoretical Study of CO_2 Photoreduction Reaction Using Fe–ZrO_2 ([1]*Graduate School of Science and Engineering, Chiba University*) ○Ayana Omata,[1] Tomoki Oyumi,[1] Keisuke Hara,[1] Kaori Niki,[1] Yasuo Izumi[1]

The catalytic reduction of carbon dioxide (CO_2) by zirconium oxide (ZrO_2), which has oxygen vacancy with the emission of carbon dioxide (CO_2) to convert it into fuel, has attracted attention. In previous studies, detailed calculations of activation energy revealed the photocatalytic cycle when using Co–ZrO_2 photocatalyst. [1-3] In this study, a process for the conversion of CO_2 to CH_4 using inexpensive iron is proposed. The site-dependent adsorption energy of CO_2 was calculated to be −0.71 eV on Fe nanoparticles and −2.48 eV on the ZrO_2, suggesting the contribution of V_O¨ sites. In this presentation, the optimization of catalyst design and the pathway from CO_2 to CH_4 using Fe–ZrO_2 are discussed.
Keywords : Zirconium Oxides; Iron supported Zirconium Oxide; Photoreduction; Methanation; Carbon dioxide reduction

排出された二酸化炭素(CO_2)を回収して燃料に変換する、酸素欠陥(V_O¨)を持つ酸化ジルコニウム(ZrO_2)による CO_2 の光触媒的還元が注目されている。以前の研究では活性化エネルギーを詳細に計算することで、Co–ZrO_2 光触媒使用時に V_O¨が関与した光触媒反応サイクルを提唱した。[1-3] 本研究では安価な鉄を使用した CO_2 の CH_4 への変換過程を提案する。CO_2 吸着エネルギーは、鉄ナノ粒子上には−0.71 eV、 ZrO_2 上には −2.48 eV で吸着することが計算され、やはり V_O¨の関与が示された。発表では触媒設計の最適化と、Fe–ZrO_2 が CO_2 を CH_4 に変換するプロセスを提案する。



1) H. Zhang, Y. Izumi, et al., *J. Am. Chem. Soc.*, **2019**, *141*, 6292.
2) H. Zhang, Y. Izumi et al., *Angew. Chem. Int. Ed.*, **2021**, *60*, 9045.
3) K. Hara, Y. Izumi et al., *J. Phys. Chem. C*, **2023**, *127*, 1776.

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単糖の電気化学的酸化による希少糖の生成

（農工大 BASE[1]・慶應大理 [2]）○川勝 葵央 [1]・臼杵 翔 [1]・栄長 泰明 [2]・中田 一弥 [1]
Production of Rare Sugars by Electrochemical Oxidation of Monosaccharide ([1]*Tokyo University of Agriculture and Technology,* [2]*Keio University*) ○Kio Kawakatsu,[1] Sho Usuki,[1] Yasuaki Einaga,[2] Kazuya Nakata[1]

“Rare sugars” is defined by the International Society of Rare Sugars as "monosaccharides and their derivatives being rare in nature." Currently, rare sugars are expected to be utilized in various fields such as pharmaceuticals, pesticides, and food additives, and there is a demand for the development of new methods to produce rare sugars. The typical synthetic methods for rare sugars are broadly classified into biological methods using enzymes and chemical methods using oxidizing agents. In the former, challenges include the high cost of enzymes and constraints related to reaction conditions derived from factors such as the optimal temperature and pH for enzymes. In the latter, challenges include the need for hazardous reagents in the reaction, complex reaction pathways, and difficulties in isolating the target chemicals. In our research laboratory, we confirmed the generation of the rare sugar erythrose from the natural monosaccharide glucose using a photocatalyst. Electrocatalysis, similar to photocatalysis, allows reactions to proceed under mild conditions at room temperature and atmospheric pressure, with the additional advantage of being able to control the reaction through factors such as the applied potential etc. However, there are few reports of rare sugar production from monosaccharides using electrocatalysis. In this study, we examined the oxidation of the monosaccharide glucose to generate the rare sugars erythrose and glycolaldehyde using electrochemical decomposition with a boron doped diamond electrode.
Keywords : Rare sugar; Boron doped diamond electrode; Electrochemical oxidation

希少糖は「自然界での存在量が少ない単糖とその誘導体」と国際希少糖学会により定義されている。現在、希少糖は医薬品や農薬、食品添加物など多様な分野での利用が期待されており、希少糖を生産する新たな方法の開発が求められている。希少糖の代表的な合成方法は、酵素を用いた生物学的な方法と、酸化剤などを用いた化学的な方法に大別される。前者では、酵素自体が高価であることや、酵素の至適温度や至適 pH などに由来する反応条件の制約等の課題がある。後者では、反応に危険な試薬が必要、反応経路が煩雑で目的物質の単離が難しい等の課題がある。当研究室では、光触媒を用いて、天然型単糖であるグルコースから希少糖であるエリトロースが生成されることを確認した。電極触媒は光触媒と同様に常温常圧の穏やかな条件下で反応を進めることができ、さらには電位などによって反応を制御できる利点を有する。しかし、電極触媒を用いた単糖からの希少糖の生成の報告例はほとんど無い。本研究では、ボロンドープダイヤモンド電極を用いた電気分解により、単糖であるグルコースを酸化して希少糖であるエリトロースおよびグリセルアルデヒドを生成することを明らかにした。

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強塩基水溶液中に溶解したセルロースの直接酸化を志向した Pt/C 電極触媒の開発

(信州大工[1]・信州大先鋭材料研[2]) ○前田 賢汰[1]・影島 洋介[1,2]・手嶋 勝弥[1,2]・錦織 広昌[1,2]

Development of Pt/C-Based Electrocatalysts Intended for Direct Oxidation of Cellulose Dissolved in a Strong Alkaline Aqueous Solution ([1]*Faculty of Engineering, Shinshu University,* [2]*Research Initiative for Supra-Materials, Shinshu University*) ○ Kenta Maeda,[1] Yosuke Kageshima,[1,2] Katsuya Teshima,[1,2] Hiromasa Nishikiori[1,2]

We have reported that cellulose dissolved in a strong alkaline aqueous solution could be directly oxidized in an electrochemical manner by using various metal electrodes. However, previous study mainly focused on a fundamental investigation employing disk electrodes. Intended for future application to fuel cell devices, improvement in current through designing of electrocatalyst materials should be necessary. In this study, we developed Pt-based electrocatalysts loaded on carbon black supports to improve the electrocatalytic activity for direct oxidation of cellulose in liquid.

The current-potential curves of Pt rotating disk electrode (RDE) and Pt catalyst loaded on carbon black (Pt/C) in aqueous cellulose solution are compiled in Fig. 1. The Pt/C exhibited higher cellulose oxidation current than the planar electrode possibly due to the increased electrochemically active surface area (ECSA). In the presentation, more detailed characterizations for Pt/C catalysts, such as ECSA, double layer capacitance, and oxygen evolution/reduction reaction activities, will also be discussed.

Keywords : Cellulose, Oxidation, Fuel Cell, Biomass, Electrocatalysts

これまでに、種々の金属電極を用いて、強塩基水溶液中に溶解させたセルロースを電気化学的に直接酸化可能であることを報告してきた[1)]。しかしこれまでの検討はディスク電極を用いた基礎検討であり、将来的に燃料電池デバイス等への展開を志向した際には、電極触媒材料の設計による電流向上が不可欠となる。本研究では、液相中セルロースの直接酸化活性の向上を志向して、カーボンブラック担体に担持した Pt 系電極触媒を開発した。

Pt 回転ディスク電極 (RDE) 及びカーボンブラック担持 Pt 触媒 (Pt/C) の、セルロース水溶液中における電流-電位曲線を Fig.1 に示す。電気化学的活性表面積 (ECSA) の増大により、Pt/C は平板電極に比べ高いセルロース酸化電流を示した。発表では、ECSA、二重層容量、酸素生成／還元活性等、Pt/C 触媒のより詳細なキャラクタリゼーションについても議論する。

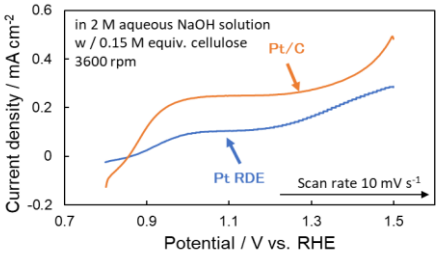

Fig. 1 Current-potential curves for Pt disk and Pt/C in 2 M aqueous NaOH solution containing cellulose equivalent to 0.15 M glucose.

1) Y. Kageshima, *et al.*, *J. Phys. Chem.* C **2021**, *125*, 27, 14576–14582.

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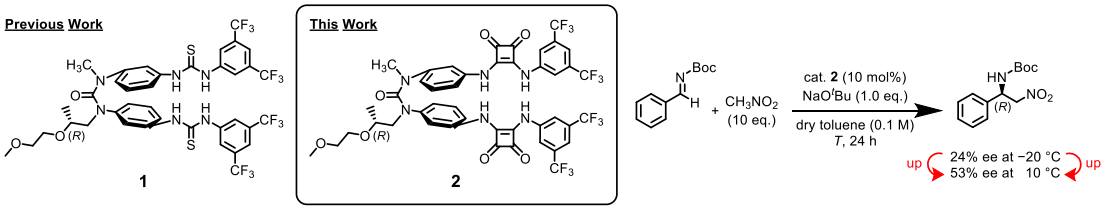
cis 型芳香族ウレアを骨格としたらせん分子触媒の開発

（お茶大院理[1]・群馬高専[2]・東京農工大院工[3]）○武田史[1]・工藤まゆみ[2]・小倉麻珠華[1]・折原弥生[3]・小田木陽[3]・長澤和夫[3]・棚谷綾[1]
Development of Helical Organocatalyst Based on (*cis*, *cis*)-Diphenylurea ([1]*Graduated School of Science, Ochanomizu University,* [2]*National Institute of Technology, Gunma College,* [3]*Graduated School of Engineering, Tokyo University of Agriculture and Technology*) ○Fumi Takeda, Mayumi Kudo, Mamika Ogura, Yayoi Orihara, Minami Odagi, Kazuo Nagasawa, Aya Tanatani

Asymmetric organocatalysts generally have rigid chiral backbones, while those with flexible backbones are expected to respond to external stimuli, such as solvents, pressure, and temperature in an entropy-driven manner. We have studied the development of asymmetric organocatalysts by using the dynamic helical structure of (*cis*, *cis*)-diphenylurea as a backbone, and one of the derivatives with preferential one-handed helical conformation was shown to act as an organocatalyst in the asymmetric aza-Henry reaction. In this work, we designed and synthesized (*cis*, *cis*)-diphenylurea derivative **2** bearing squaramides. The organocatalyst **2** was also effective for the asymmetric aza-Henry reaction, and it showed the entropy-driven behavior in the enantioselection process.
Keywords : Asymmetric Organocatalyst; (cis, cis)-Diphenylurea; Dynamic Helical Structure

不斉有機触媒は一般に堅固な骨格を有しているが、一方で、柔軟な不斉骨格を有する触媒は溶媒や温度などの外部環境応答性を有するユニークな機能を発揮する可能性がある。演者らは、動的らせん構造を形成する cis 型芳香族ウレア [1]を骨格とした不斉有機触媒の開発を試みた。先行研究において、光学活性側鎖を導入することで一方のらせんの巻き方向を優先させた cis 型芳香族ウレアに、基質認識部位としてチオウレア基を導入した化合物 **1** が、aza-Henry 反応において不斉触媒として働くことを見いだした [2]。

本研究では、化合物 **1** の基質認識部位をスクアルアミド基に代替した化合物 **2** を合成し、立体構造の解析および触媒機能の検討を行った。その結果、化合物 **2** も aza-Henry 反応の不斉触媒として機能した。興味深いことに **2** は、温度の上昇とともに反応性およびエナンチオ選択性が向上することがわかり、熱力学的な解析からエントロピー駆動型触媒であることが明らかとなった。



1) Kudo, M. *et al*. *J. Org. Chem.* **2009**, *74*, 8154–8163.
2) Kudo, M. et al. Proceedings of the Symposium on Molecular Chirality 2018, P.136.

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酸化状態を変化させた炭素触媒表面での過硫酸塩活性化による有機色素分解のメカニズム

(公立千歳科技大[1]・北大触媒研[2]・北大院工[3])○漆舘 琉介[1]、下田 周平[2]、鈴木 啓太[3]、福岡 淳[2]、髙田 知哉[1]

Mechanism of organic dye decomposition using persulfate activated by carbon catalysts with varied surface oxidation states ([1]*Chitose Institute of Science and Technology,* [2]*Institute for Catalysis, Hokkaido University,* [3]*Faculty of engineering, Hokkaido University*) ○Ryusuke Urushidate[1], Shuhei Shimoda[2], Keita Suzuki[3], Atsushi Fukuoka[2], Tomoya Takada[1]

We studied the influence of surface oxidation state of carbon catalyst surface on oxidative Rhodamine B (RhB) decomposition through persulfate activation. The mechanism of the RhB decomposition was also discussed. The RhB decomposition was enhanced by using the highly reduced carbon catalysts. Rhodamine 110 (Rh110) was also formed as a product of the RhB decomposition; the carbon catalysts with oxidized surface preferentially provided Rh110. The main active species produced were OH• and $^1O_2$. The catalysts with oxidized surface contributed to the generation of $^1O_2$. Consequently, $^1O_2$ converted RhB into Rhodamine 110 (Rh110), while OH• directly decomposed RhB into final decomposition products. Generation of both $^1O_2$ and OH• was suppressed under existence of positive charge scavenger. Formation of positive charge is thus essential for the generation of the active species.

Keywords : carbon catalyst, persulfate, oxidation state, oxidative decomposition

Advanced Oxidation Processにおいて炭素触媒表面で過硫酸塩 (PS) を活性化させて有機物を分解する方法は、メタルフリーかつPSが安価という利点から注目を集めている。この方法での分解速度や活性種は炭素触媒表面の化学構造の違いに影響されると考えられている。本研究では、化学構造のうち酸化状態に着目し、PS活性化によるRhBの触媒的酸化分解のメカニズムと炭素触媒表面の酸化状態の関係について検討した。

RhBの分解過程でRh110の生成が確認され（Fig.1）、その生成量は炭素触媒表面の酸化が進むほど増加した。一方、RhBの分解速度はより還元された炭素触媒ほど速くなった。生成する活性種は主にOH•と$^1O_2$であり、触媒表面の酸化が進行すると、分解反応に対する$^1O_2$の寄与が大きくなった。OH•を捕捉するとRh110の生成量が増加し、$^1O_2$を捕捉するとRh110の生成量が減少したことから、$^1O_2$はRhBをRh110へと変化させ、OH•はRhBを最終分解生成物まで分解することが示唆された。正電荷を消去する条件ではRhBが分解されなかったため、両方の活性種の生成に正電荷の存在が関与すると考えられる。

本研究は、文部科学省マテリアル先端リサーチインフラ（ARIM）事業および触媒科学計測共同研究拠点のオンデマンド型共同利用・共同研究の一環として実施された。

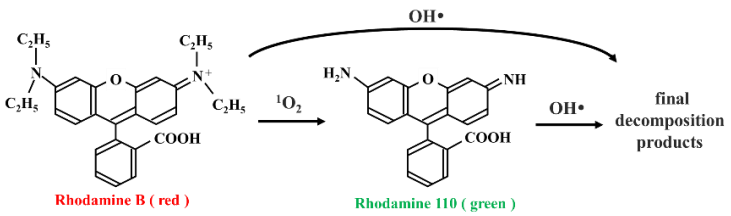

Fig. 1 Proposed RhB decomposition pathway.

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振動エネルギーを利用した新規触媒反応系の開拓

（都立大理[1]）○藤掛　隆一[1]・吉川　聡一[1]・山添　誠司[1]
Development of vibro-catalytic reaction system utilizing vibration energy ([1]*Tokyo Metropolitan University*) ○Ryuichi Fujikake,[1] Soichi Kikkawa,[1] Seiji Yamazoe[1]

Piezo-catalysts, which drive redox reactions by utilizing mechanical energy input to piezoelectric elements, are attracting attention from the viewpoint of energy harvesting in recent years. For example, it is reported that $BiTiO_3$ can promote mechanochemical organic synthesis by mixing in ball milling[1)] and that $BiFeO_3$ nanosheet is active for water splitting and dye degradation by irradiation of ultrasonic[2)]. We focused on a low frequency vibration that generated in our daily lives and reported that reaction system that a piezoelectric element made of $Pb(Zr,Ti)O_3$ coated with Ag acted as the vibro-catalyst that promoted H_2 oxidation by applying vibration at 200 Hz (Figure 1)[3)]. We proposed that the electronic state of Ag could be tuned accompanied by the potential change of the surface of piezo-electric material under vibration to promote the reaction. In this research, we attempted to develop a new vibro-catalytic reaction using other substrates.
Keywords : vibro-catalyst, piezoelectric material, hydrogen production

圧電素子に加わった機械的エネルギーを用いて酸化還元反応を起こす，圧電触媒がエネルギーハーヴェスティングの観点から近年注目を集めている．例えば，圧電材料である $BaTiO_3$ をボールミルで攪拌するメカノケミカル有機合成や[1)]，$BiFeO_3$ のナノシートに超音波振動を印加する水分解や色素分解[2)]が報告されている．我々は，生活環境中で発生する低周波振動に着目し，Ag を蒸着した $Pb(Zr,Ti)O_3$（PZT）圧電素子が 200 Hz 程度の振動印加により H_2 酸化反応を駆動する振動触媒として機能することを報告した（図１）[3)]．振動に伴う圧電材料表面の電位変化に伴い Ag 種の電子状態が変調し反応が進行したと考えている．本研究では振動触媒反応を異なる基質へと展開し，その結果について報告する．

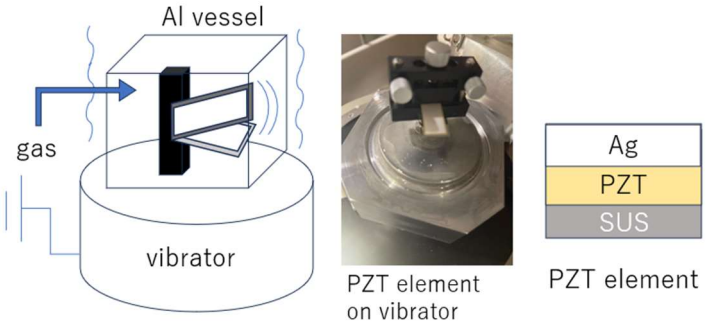

図１．PZT圧電素子を用いた振動触媒反応系

1) K. Kubota *et al.*, *Science*. **2019**, *366*, 6472. 2) H. You *et al.*, *Angew. Chem. Int. Ed*. **2019**, *131*, 11905.
3) 宇野，山添ら，第 128 回触媒討論会 A1，1F10 (2021)

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$CoAl_n$(n=10-13)カチオンクラスターによるアンモニアの脱水素反応の検討

（千葉工大院工）○小平 和輝・工藤 翔慈・松澤 秀則

Dehydrogenation of Ammonia on the $CoAl_n$(n=10-13) Cation Clusters (*Graduate School of Engineering, Chiba Institute of Technology* ○ Kazuki Kodaira, Shoji Kudo, Hidenori Matsuzawa

The dehydrogenation of ammonia (NH_3) on the $CoAl_n^+$ (n=10-13) clusters were examined theoretically. Three intermediates (INT) and three transition states (TS) are appeared in the reaction. The reaction pathway of dehydrogenation is classified according to the adsorption site of NH_3. One is the adsorption of NH_3 on the Al atom (Path1), and another is that on the Co atom (Path2). The activation energies of the reaction of Path1 are lower than those of Path2 except n=13. From the energetic analyses of the difference in the total energy of TS1 between Path1 and Path2, it is found that the difference in the adsorption energy of the NH_2 on the cluster surface affects the stability of TS1. Furthermore, electron transfer from the cluster to NH_2 is related to the adsorption energy.

Keywords : Dehydrogenation; Metal Cluster

近年水素社会の実現のため、金属クラスターを触媒とした NH_3 の脱水素反応により水素を得る研究が行われている [1]。そこで我々は新規触媒の開発を目指し、Al クラスターに Co を 1 原子ドープした $CoAl_n^+$ (n=10-13)クラスターを触媒とする NH_3 の脱水素反応の反応経路を理論的に検討した。検討したすべてのクラスター上で NH_3 の脱水素反応が進行し、n=13 を除いて Fig. 1 の $CoAl_{11}^+$のように NH_3 が Al 原子に吸着した経路（Path1）の方が、Co 原子に吸着した経路（Path2）よりも活性化エネルギーがより低かった。Path1 と Path2 の TS1 のエネルギー差はΔE=-26.8kcal/mol (Paht1 が安定なときはマイナス)で、クラスターのエネルギー差（+13.2 kcal/mol）＋NH_2 の吸着エネルギー差(-27.8kcal/mol)＋H 原子の相互作用の差(-11.0 kcal/mol)は-25.6kcal/mol でΔE に近い。したがって、NH_2 の吸着エネルギーの差が TS1 のエネルギー差に大きく影響しており、この吸着エネルギーの大きさは、NH_2−クラスター間の電子移動量が、Path1 で 0.49eC、Path2 で 0.23eC という結果と矛盾しない。

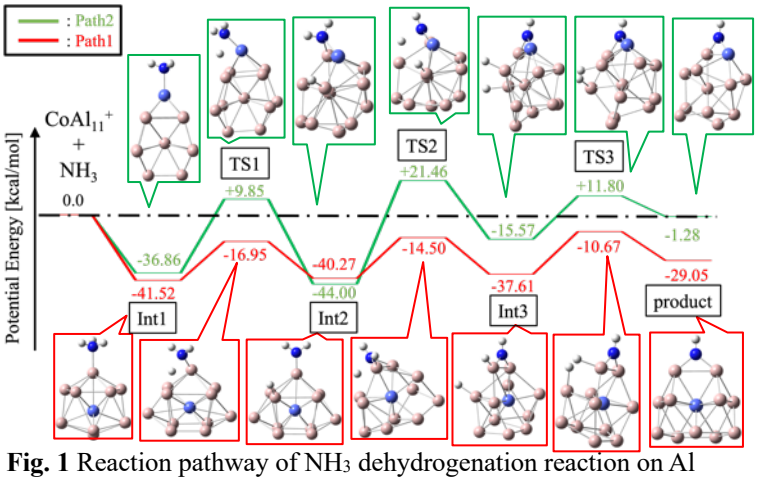

Fig. 1 Reaction pathway of NH_3 dehydrogenation reaction on Al adsorption and Co adsorption of NH_3 in $CoAl_{11}^+$

1) L. Geng, C. Cui, Y. Jia, H. Wu, H. Zhang, B. Yin, Z. Sun, Z. Luo, *J. Phys. Chem. A*, **2020**, 124, 5879.

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低周波振動による触媒反応とそのメカニズムの考察

（都立大院理）○大庭 佑斗・宇野 太喜・吉川 聡一・山添 誠司

Catalytic reaction and the mechanism over vibro-catalyst using low-frequency vibration (*Tokyo Metropolitan University*) ○Yuto Oba, Taiki Uno, Soichi Kikkawa, Seiji Yamazoe

Low-frequency vibration of 1~200 Hz that is emitted by ambient vibrations such as automobile engines and factory operations is one of unutilized energy. Catalytic systems utilizing mechanical energies represented by vibration as electronic energy that was converted by piezoelectric materials have been studied. However, while catalytic reactions by irradiation of ultrasound to piezoelectric materials are numerously reported, there are only a few reports on catalytic reactions using <1000 Hz unutilized vibrations, such as ambient vibrations. We have reported the vibro-catalytic system that promotes H_2 oxidation reactions by applying 150 Hz resonance vibration to a piezoelectric thick film device consisting of $Pb(Zr,Ti)O_3$ (PZT) thick film having a perovskite structure fixed on a stainless steel plate with Ag electrode deposited on PZT surface. In this study, we studied on the mechanism of the vibro-catalytic reactions and fabrication of the PZT thick film device to design the catalytic active sites on the catalyst surface.

Keywords : Vibrocatalyst; Piezoelectric material; Ambient vibration;

自動車のエンジンや工場の操業などの環境振動に伴い排出される 1~200 Hz 程度の低周波振動は未利用エネルギーの一種である. 振動に代表される機械エネルギーを圧電材料を用いて電気エネルギーへと変換し利用する触媒システムが検討されている. しかし, これまでに圧電材料に超音波を照射する触媒反応は多く報告されている一方で, 環境振動のような 1000 Hz 以下の未利用振動を利用した触媒反応例はごくわずかである [1]. 我々は, ペロブスカイト型の構造を持つ $Pb(Zr,Ti)O_3$（PZT）の厚膜をステンレス板に成型し Ag 電極を塗布した圧電厚膜素子に 150 Hz の共振振動を印加することで H_2 酸化反応が進行する振動触媒システムを報告してきた [2]. 本研究では, このような振動触媒反応のメカニズムについて考察を行なうとともに, 触媒表面の活性点制御の観点から圧電厚膜素子の作製を検討した.

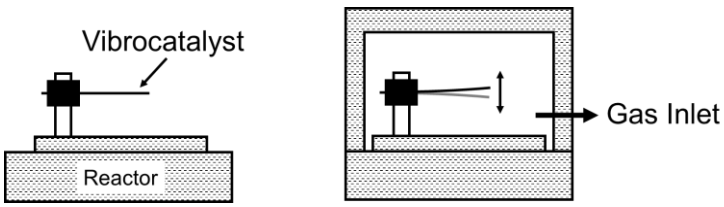

Fig. Reaction vessel

1) M. B. Starr, J. Shi, X. Wang, *Angew. Chem. Int. Ed.*, **2012**, 51, 5962.
2) 宇野，山添ら，第 130 回触媒討論会 P12 (2022).

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鉄担持アルミナを用いたジブロモメタンの気相分解における反応温度の影響

（有明高専[1]）○藤本 大輔[1]、劉 丹[1]
Effect of reaction temperature on gas phase decomposition of dibromomethane using iron-supported alumina ([1]*National Institute of Technology, Ariake College*) ○FUJIMOTO, Daisuke,[1] LIU, Dan[1]

The iron-supported catalyst was prepared by passing iron-rich spring water through activated alumina. Decomposition experiment using this catalist was carried out. dibromomethane at a concentration of approximately 1000 ppm was passed through the reaction tube at 300 °C that this catalist set. The removal rate was always showed around 50% for 6 hours from the start of the decomposition experiment. At that time, it was found that the removal rate changed significantly by changing the amount of water vapor contained in the gas and the temperature of the reaction tube.

Keywords : Iron supported catalysts; dibromomethane

鉄担持アルミナを設置した300 ℃の反応管に、約 1000ppm のジブロモメタン(DBM)を流速 2.5 L/min で、水蒸気添加量を変化させて 2 時間通気した際の DBM 分解率の経時変化を図 1 に示した。シリカゲルを通気させた乾燥空気(6.2×10^3ppm)では分解実験開始直後から 2 時間まで、常に分解率約 50%程度を示したが、水蒸気量を 1.7×10^4ppm とした際、DBM 分解率は約 70%まで上昇した。しかし、それ以上の水蒸気量では分解率 70%を示し、分解率に変化はなかった。

次に水蒸気量を 1.7×10^4ppm とし、反応管温度を 250℃、350℃として分解実験を行った結果を図 2 に示す。反応管温度を 250℃とした場合は約 60%の分解率を示した。また同じ触媒を用いて 250℃で同様の実験を繰り返したところ、分解実験を繰り返すたびに分解率は徐々に低下し、10%程度となった。それに対して反応管温度 350℃では、約 80%の分解率を示し、同じ触媒を用いて同様の実験を繰り返し行っても分解率は変化しなかった。

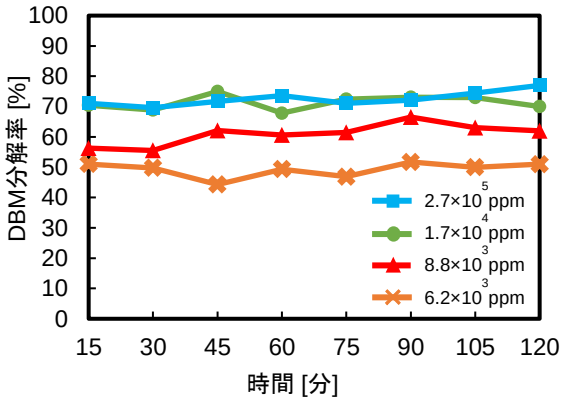

図 1 各水蒸気濃度における DBM の気相分解実験の結果

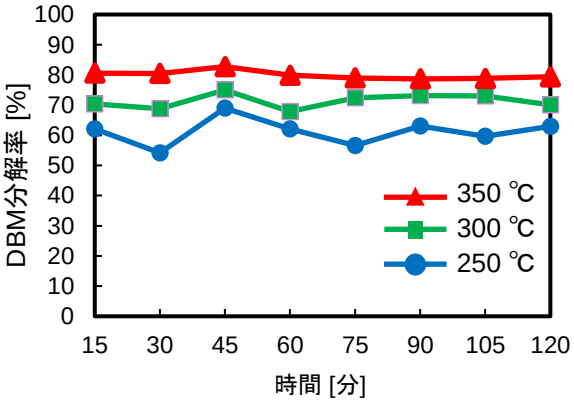

図 2 各反応管温度における DBM の気相分解実験の結果

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植物由来有機分子触媒によるエポキシド不斉開環反応に及ぼす塩化ナトリウムの影響

（富山県大・生医工研セ [1]・協和ファーマケミカル(株) [2]）○和田浩一 [2]・加藤康夫 [1]・日比 慎 [1]・竹内祐希 [2]・浅野健裕 [2]

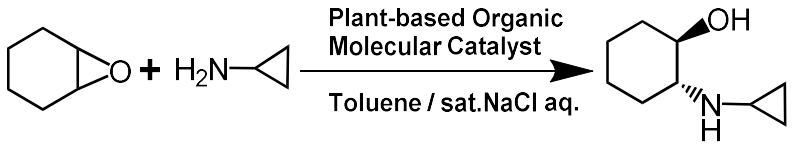
Effect of sodium chloride on the asymmetric ring-opening reaction of epoxides by Plant-based Organic Molecular Catalyst

([1] *Biotechnol. Res. Cent., Toyama Pref. Univ.,* [2] *Kyowa Pharma Chemical Co., Ltd.*) ○Koichi Wada,[2] Yasuo Kato,[1] Makoto Hibi,[1] Yuki Takeuchi,[2] Tatsuhiro Asano [2]

Keywords : organocatalyst, epoxide, asymmetric ring opening, sodium chloride, aminoalcohol

我々はこれまで、植物の乾燥粉末が有機溶媒中でアミン付加を伴うエポキシドの不斉開環反応を触媒することを報告している [1-3]。その触媒活性には酵素タンパク質ではなく多糖類が関与していると推定されることから、植物由来有機分子触媒 (Plant-based Organic Molecular Catalyst：POMC) と名付けた。

本触媒反応の立体選択性発現のためには塩化ナトリウムと少量の水を添加した有機溶媒中での反応が必須であったが、検討の結果、80%以上の飽和食塩水中でも立体選択性を示すことが分かった。加えて、トルエン/飽和食塩水の二相系反応を用いることで、触媒の入れ替えなしに 21 回の繰返し反応(総反応時間約 1000 時間)を行うことができた。なお、有機溶媒中での反応において、塩化カリウムは塩化ナトリウムと同様の添加効果を示したが、二相系反応では飽和塩化カリウム溶液を用いた場合立体選択性は発揮されなかった。



1) Catalytic asymmetric amination of meso-epoxide using soy polysaccharide. (Soyafibe S-DN) Y. Takeuchi, T. Asano, K. Tsuzaki, K. Wada, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 678.
2) Asymmetric amination of meso-epoxide with vegetable powder as a low-toxicity catalyst. Y. Takeuchi, T. Asano, K. Tsuzaki, K. Wada, H. Kurata, *Molecules* **2020**, *25*, 3197
3) 国際特許公開 WO/2023/191088

We have reported a catalytic asymmetric amination of epoxides catalyzed by plant powder and the activity was attributed to polysaccharides but not proteins[1-3], which resulted to name the catalyst as “Plant-based Organic Molecular Catalyst” (POMC). For the expression of the stereoselectivity, the reaction was carried out in an organic solvent system supplemented with sodium chloride (NaCl) and small amount of water. In this study, we found that POMC showed enough stereoselectivity in an aqueous solution over 80% saturation of NaCl. We also succeeded a repeated (21 times, nearly 1000 h) batchwise reaction by using two-phase (toluene/sat. NaCl aq.) reaction system. The selectivity was drastically decreased in two-phase system when saturated potassium chloride was used as an additive although it was comparable when the reaction was carried out in organic solvent.

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複合金属酸化物の電解還元によるナノ粒子合成

（都立大理）○岡 俊明[1]・吉川 聡一[1]・山添 誠司[1]
Fabrication of metal nanoparticles by electrolytic reduction of composite metal oxides
(*Department of Chemistry*, *Tokyo metropolitan University*) ○Toshiaki Oka, Soichi Kikkawa, Seiji Yamazoe

Alloy nanoparticles (NPs) consist of more than two elements have attracted attention because their geometric and electronic interaction lead to their superior catalytic property compared to single-element metal NPs catalysts. To increase the effective surface area for catalytic reaction, alloy NPs are often dispersed on a support material. The supported alloy NPs is synthesized by thermal decomposition of metal salt precursor, however, the active surface area is limited due to aggregation by high temperature treatment. We focused on alloy NPs synthesis method by electrochemical reduction in liquid phase, which can avoid the heat treatment. We have found that intermetallic compound NPs can be obtained by electrochemical reduction of Cu-In mixed metal oxide over carbon powder. In this study, we synthesized Ag-In mixed metal oxide, $AgInO_2$, and evaluated the structure of metal NPs formed by electrochemical reduction of $AgInO_2$. In addition, we evaluated the electrocatalytic property of obtained metal NPs for electrochemical reduction of CO_2, confirming the production of H_2, CO and HCOOH.

Keywords： *Electrochemical reduction, Metal nanoparticles, Electrocatalyst*

複数の元素からなる合金ナノ粒子は，その幾何・電子的作用により単一元素の金属ナノ粒子に比べて優れた触媒機能を示すことから注目されている[1)]．触媒反応に有効な表面積を増やすため，このような合金ナノ粒子は支持体に分散担持して用いられる．担持合金ナノ粒子の合成は，担体上での金属塩前駆体の熱分解により行われるが，高温での熱処理を経るため生成するナノ粒子は凝集しており，触媒として有効な表面積が低いことが課題である．我々は，熱処理を経ない合金ナノ粒子の合成法として，液相中での電気化学的還元による合金ナノ粒子合成に着目した．これまでに，Cu と In の複合金属酸化物粒子をカーボン粉末と混合し，電極上で電気化学的に還元することで，金属間化合物のナノ粒子が得られることを見出している[2)]．本研究では，本手法の一般化のため，Ag と In からなる複合金属酸化物 $AgInO_2$ を合成し，電解により形成する金属ナノ粒子の構造を評価した．また，得られたナノ粒子について CO_2 の電気化学還元に対する電極触媒特性を評価し，H_2，CO，および HCOOH の生成を確認した．

1) Y. Nakaya, S. Furukawa, *Chem. Rev.* **2023**, *123*, 5859.
2) 幸林，吉川，山添，第 90 回 電気化学大会，3M04.

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Academic Program [Poster] | 09. Coordination Chemistry, Organometallic Chemistry：Poster

Wed. Mar 20, 2024 1:00 PM - 2:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:30 AM UTC Poster Site 1 (理工スポーツホール [1階] アリーナ)

[P1-3pm] 09. Coordination Chemistry, Organometallic Chemistry

Japanese

[P1-3pm-01]

Synthesis and Reactions of Mononuclear Vanadium(II) Phenoxide Complexes

○Toyama Yudai[1], Ishida Yutaka[1], Kawaguchi Hiroyuki[1] (1. Tokyo Institute of Technology)

Japanese

[P1-3pm-02]

Synthesis of Titanium and Zirconium Complexes Having Sterically Hindered Tripodal Tetradentate [O_3C] Ligands

○Masato Komura[1], Yutaka Ishida[1], Hiroyuki Kawaguchi[1] (1. Tokyo institute of technology)

Japanese

[P1-3pm-03]

Catalytic primary alcohol oxidation by copper(II)-phenoxyl radical complexes under aerobic condition

○Marina Yoshii[1], Yuichi Shimazaki[1] (1. College of Science, Ibaraki University)

Japanese

[P1-3pm-04]

Syntheses and crystal structures of novel Cu(I)-C_2H_4 coordination polymers bridged by 2,2':4',4''-terpyridine

○Sho Yoshimura[1], Masahiko Maekawa[1], Kunihisa Sugimoto[1], Takayoshi Kuroda[1] (1. Kindai university)

Japanese

[P1-3pm-05]

Construction of Six-membered Silacycle Frameworks by Barbier Reaction

○Kaori Noguchi[1], Mai Tsugaya[1], Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

Japanese

[P1-3pm-06]

Introduction of Alkynyl Groups to the Ends of Oligosilanes

○Mizuki Wamme[1], Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

Japanese

[P1-3pm-07]

Introduction of thiolate into silylene bridged palladium hexanuclear clusterand functional development

○Suda Tetsuro[1], Sunada Yusuke[2,3,4] (1. Faculty of Science and Engineering, Chuo University, 2. Graduate School of Engineering, The University of Tokyo, 3. Institute of Industrial Science, The University of Tokyo, 4. JST PRESTO)

English

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[P1-3pm-08]

Substitution reactions of cobalt cubane complexes by bridging bis-pyridine molecules

○Wataru Ishikawa[1], Toshi Nagata[1] (1. Meijo University)

Japanese

[P1-3pm-09]

Synthetic Study of Silyllithium Bearing Benzodiazaborolanyl Group

○Gai Kadoishi[1], Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

English

[P1-3pm-10]

Synthesis of Copper Complexes of Dipicolylamines with Various Degrees of Steric Hindrance and Their Electrochemical Behaviors

○Yumiko Kitamura[1], Toshi Nagata[1] (1. Meijo University)

Japanese

[P1-3pm-11]

Synthesis and Intramolecular C-H Bond Activation of Low-valent Cobalt Complexes Supported by Electron-Donating Diamide Ligands

○Suiho Kobayashi[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

Japanese

[P1-3pm-12]

Silylation of an oxo-molybdenum dimeric complex $(^{t}BuC_5H_4)_2Mo_2Se_2O_2$

○Takeru Hayakawa[1], Shinji Inomata[1] (1. Fukushima University)

English

[P1-3pm-13]

Redox Properties of a Composite Material of Boron-oxide Layers and a Pentanuclear Cluster

○Nicole Sallier de la Tour[1,2], Maho Imai[1], Tetsuya Kambe[1], Yutaka Saga[1], Mio Kondo[1,3,4], Shigeyuki Masaoka[1] (1. Osaka University, 2. Heidelberg University, 3. Tokyo Institute of Technology, 4. JST PRESTO)

Japanese

[P1-3pm-14]

Synthesis and properties of heterometallic multinuclear complexes with an intense electronic interaction among metal centers

○Akira Hasegawa[1], Masaya Sakamoto[1], Misa Tomoda[1,2,3], Yutaka Saga[1], Tetsuya Kambe[1], Mio Kondo[4,1,5], Shigeyuki Masaoka[1] (1. Osaka University, 2. Institute for Molecular Science, 3. The Graduate University for Advanced Studies, 4. Tokyo Institute of Technology, 5. JST PRESTO)

Japanese

[P1-3pm-15]

Synthesis of a novel metal–organic framework consisting of tetravalent metal cation and tetracarboxylate ligand

○Haruka Kusumi[1], Masaaki Sadakiyo[1] (1. Tokyo Univ. of Sci.)

Japanese

[P1-3pm-16]

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Synthesis, structure, and multinuclear reactivities of unsymmetrical dinuclear platinum complex containing diethyl sulfides as co-ligands

○Junnosuke Miyamura[1], Shota Knamori[2], Kzuhiro Uemura[1] (1. Faculty of Engineering, Gifu Univ., 2. Graduate School of Natural Science and Technology, Gifu Univ.)

Japanese

[P1-3pm-17]

Synthesis of Cu9 Hydride Clusters Supported by Linear Tetraphosphine Ligand

○Madoka Shimada[1], Yurika Komura[1], Seina Sakabe[1], Takayuki Nakajima[1], Tomoaki Tanase[1] (1. Nara Women's University)

Japanese

[P1-3pm-18]

Synthesis and Evaluation as Metal Fluorescent Sensor of Novel Schiff Base [2+2] Macrocycles

○Michiru Matsuoka[1], Yuki Yamaguchi[1], Makoto Miyasaka[1] (1. Tokyo Denki University)

Japanese

[P1-3pm-19]

Synthesis and Structure iron(II) complex of $[Fe(tppz)_2]^{2+}$ constructed by terpyridine moiety

○Mao Kihara[1], Zi Lang Goo[1], Masahiko Maekawa[1], Takayoshi Kuroda-Sowa[1], Kunihisa Sugimoto[1] (1. Kindai University)

English

[P1-3pm-20]

Syntheses and Structures of Aminoalcohol-ligated Mononuclear and Dinuclear Samarium Complexes

○Kulsum Bano[1], Tetsuro Kusamoto[1], Hayato Tsurugi[1] (1. Osaka University)

Japanese

[P1-3pm-21]

Synthesis of Tetranuclear Iron-oxo Complexes Having Bipyridonate Ligands

○Aina Sakamoto[1], Yasuyuki Ura[1] (1. Nara Women's University)

Japanese

[P1-3pm-22]

Synthesis on dinuclear cobalt complexes with the triply bridge structures by the oxygen- or nitrogen- donor ligands.

○Ryosei Ito[1], Tomoyo Misawa[1], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

Japanese

[P1-3pm-23]

Syntheses and characterization of Tridentate Abnormal NHC Pd(II) Complexes

○Ai Watanabe[1], Takeyoshi Yagyu[1] (1. Nagoya Institute of Technology)

Japanese

[P1-3pm-24]

Syntheses of ruthenium complexes bearing a macrocyclic ligand consisting of two bis(imino)pyrrole units

○Karin Yasue[1], Tomoyo Misawa[1], Yasuhiro Funahashi[2], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ., 2. Osaka Univ.)

Japanese

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[P1-3pm-25]

Effect of multinuclear structures on the selective formation of heterometallic cyclic complexes using flexible tripeptides

○Haruka Hasegawa[1], Ryosuke Miyake[1] (1. Ochanomizu University)

Japanese

[P1-3pm-26]

Synthesis of metal-organic rhombic dodecahedra with trimesic acid derivatives

○Ryohei Yoshida[1], Ayana Miyata[1], Shun Tokuda[1], Shuhei Furukawa[1] (1. Kyoto University)

Japanese

[P1-3pm-27]

Effects of axial ligand on Ru(II) complexes with both hydrogenated metal and organic ligands

○Asato Morihara[1], Dai Oyama[1], Tsugiko Takase[1], Ito Keiya (1. Fukushima University)

Japanese

[P1-3pm-28]

Development of ternary metallic MOFs incorporating multiple luminescent centers

○ZHOU YAO[1] (1. Kyushu University)

Japanese

[P1-3pm-29]

Structures and Solid-State Photoluminescence of Novel Polymorphic Platinum(II) Complexes Containing a Pyridylthiazole Ligand

○Ren Hashimoto[1], Ryota Nakamura[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo)

Japanese

[P1-3pm-30]

Structures and Reativity of Heterogeneous Dinuclear Dinitrogen Complexes using Vanadium and Chromium Ions

○Yuji Kajita[1], Yoshiaki Kokubo[2] (1. Aichi Institute of Technology, 2. Tokyo Institute of Technology)

Japanese

[P1-3pm-31]

Effect of Highly-Coordinated Iron Complex on Redox Flow Battery Performance

○Soshi Kodama[1], Atsushi Okazawa[1], Kosuke Kawai[1], Masashi Okubo[1] (1. Waseda University)

Japanese

[P1-3pm-32]

Fabrication of two-dimensional oriented thin film $[NPr_4][MnCr(C_2O_4)_3]$ by casting method

○Yuki Funahashi[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1] (1. Graduate School of Science, Tokyo University of Science)

Japanese

[P1-3pm-33]

Synthesis and magnetic properties of cyano-bridged Fe^{II}-W^{IV} complex incorporated three-types of organic ligands

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○Daiki Kobayashi[1], nagashima syuntarou[1], Wang Junhao[1], Ohkoshi Shinichi[2], Tokoro hiroko[1] (1. The Univ. of Tsukuba, 2. The Univ. of Tokyo)

Japanese

[P1-3pm-34]

Control of Emission States of Mixed Crystals of Platinum(II)/Palladium(II) Complexes by Mixing Ratio

○Kaito Segawa[1], Masaki Yoshida[2], Masako Kato[2] (1. Kwansei Gakuin Univ. Graduate school of Science and Technology., 2. Kwansei Gakuin Univ. School of Biological and Environmental Sciences.)

Japanese

[P1-3pm-35]

Synthesis and Properties of Platinum Complexes with 2,3'-Bipyridine

○Masashi HASHIMOTO[1], Kazushi Takemoto[1], Hideo Konno[2] (1. Josai Univ., 2. AIST)

Japanese

[P1-3pm-36]

Creation of a Novel Calcium Ion Conductor Using a Metal–Organic Framework

○Takahiro Erikawa[1], Masaaki Sadakiyo[1] (1. Tokyo Univ. of Sci.)

Japanese

[P1-3pm-37]

Dependence of Guest-Induced Ionic Conductivity on Cationic Species in Divalent Ion-Containing Metal–Organic Frameworks

○Kaori Taniguchi[1], Sadakiyo Masaaki[1] (1. Tokyo Univ. of Sci.)

English

[P1-3pm-38]

Self-assembly behavior of porphyrins having terpyridine sites by metal ions

○Tomoya Abe[1], Joe Otsuki[1], Kosuke Sugawa[1] (1. Nihon Univ.)

Japanese

[P1-3pm-39]

Synthesis and gas adsorption properties of the fluorinated three-dimensional porous coordination polymer

○Yuki Saito[1], Xin Zheng[1], Shin-ichiro Noro[1,2] (1. Fac. of Env.Earth Sci., Hokkaido Univ., 2. Grad. Sch. of Env. Sci., Hokkaido Univ.)

Japanese

[P1-3pm-40]

Fabrication of Oriented Crystalline Pillared-Layer-Type MOF Thin Film Using the Casting Method and Analysis of the Spin-Crossover Phenomena

○QIYUAN ZHANG[1], TOMOYUKI HARAGUCHI[1] (1. Tokyo University of Science)

English

[P1-3pm-41]

The complex formation behavior of porphyrins with phenylbisbipyridine introduced at positions 5 and 15

○Aguri Akitomi[1], Joe Otsuki[1], Sugawa Kosuke[1] (1. Nihon Univ.)

Japanese

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[P1-3pm-42]

Electrochemical Properties of *C*3-Symmetric Schiff Base Nickel Complexes with Thienyl Groups

Yuri Oshima[1], Teturo Furukawa[1], ○Naoto Kuwamura[2], Noriko Chikaraishi[1], Masakazu Hirotsu[1] (1. Graduate School of Science, Kanagawa University, 2. Kogakuin University)

Japanese

[P1-3pm-43]

The π-electronic system-dependence on the energy relaxation process of triboluminescence of the chiral lanthanide complexes

○Daisuke Hayauchi[1], Reo Ohno[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

English

[P1-3pm-44]

Ligand- and aggregation-dependent photoluminescence in nitrogen-centered pentagold(I) clusters protected by *N*-heterocyclic carbenes

○Leonado Hayato Takeshige[1], Xiao-Li Pei[1], Pei Zhao[2], Koichi Nagata[1], Hitoshi Ube[1], Zhen Lei[1], Masahiro Ehara[2], Mitsuhiko Shionoya[1] (1. The University of Tokyo, 2. Institute for Molecular Science)

Japanese

[P1-3pm-45]

Investigation of protonation-deprotonation behavior of azophenines as ligands for metal complexes in solution

○Noriya Nakamaru[1], Yuka Inagaki[1], Keiji Ohno[2], Takashi Fujihara[3] (1. Grad. Sch. Sci., Eng., Saitama Univ, 2. Jpn. Women's Univ, 3. CACS, Saitama Univ)

Japanese

[P1-3pm-46]

Synthesis and Properties of Tris(salen)-Type Macrocyclic Ligands with *N*-Heterocyclic Building Blocks Introduced onto the Outer Periphery

○Takumi Kitajima[1], Shohei Tashiro[1], Mitsuhiko Shionoya[1] (1. Grad. Sch. of Sci.; The Univ. of Tokyo)

Japanese

[P1-3pm-47]

Magnetic properties of a one-dimensional copper(II) compound bridged by a terpyridine-based biradical ligand

○Kazuki Ochiai[1], Takuya Kanetomo[1], Masaya Enomoto[1] (1. Tokyo University of Science)

Japanese

[P1-3pm-48]

The phase transition behavior of fatty acids in metal–organic frameworks

○Rei Yoshii[1], Genki Hatakeyama[1], Kunyi Leng[1], Teppei Yamada[1] (1. The University of Tokyo)

Japanese

[P1-3pm-49]

Structural and Physical Properties of Dto-bridged Iron Mixed Valence Complexes with Intercalation of Polarizable Cations

○Takashi Oba[1], Masaya Enomoto[1], Takuya Kanetomo[1] (1. Tokyo University of Science)

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English

[P1-3pm-50]

Synthesis and Photochemical Properties of Phthalocyanine Complexes Bearing Fluorine and Alkyl Groups

○HongFeng Liu[1], Kei Murata[1], Kazuyuki Ishii [1] (1. IIS, The Univ. of Tokyo)

Japanese

[P1-3pm-51]

Luminescence spectra of glassy europium complexes with linolic acid and phenanthroline derivative

○Kota Chikaraishi[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

Japanese

[P1-3pm-52]

Identification of luminescent species contributing to induced CPL of a Eu(III) complex with Δ(Λ)-Co(III) complexes by time-resolved CPL spectroscopy

○Juri Yamashita[1], Munetaka Iwamura[1], Koichi Nozaki[1], Taro Tsubomura[2] (1. Grad. Sch. Sci. Eng., Univ. Toyama, 2. Seikei Univ.)

English

[P1-3pm-53]

Spin state changes of luminescent cobalt(II) complexes bearing bulky substituent in the solid state and solution

○Manabu Nakaya[1], Naoki Izumiyama[1] (1. Josai University)

Japanese

[P1-3pm-54]

Luminescence spectra of valinamide-bipyridine lanthanide complexes with a series of alkyl groups

○Reo Ohno[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

Japanese

[P1-3pm-55]

Design, Synthesis, and Complexation Behavior of Sulfur-Embedded TriQuinoline (t-TQ)

○Ryo Otani[1], Toi Kobayashi[1], Naoya Kumagai[1,2] (1. Graduate School of Pharmaceutical Sciences, Keio University, 2. Institute of Microbial Chemistry)

English

[P1-3pm-56]

Synthesis and Characterization of Iron (II) Complex with an Unsymmetrical Heterocyclic Multidentate Azine Ligands, (2-Pyridyl)(4-imidazolyl)azine

○Kennedy Mawunya Hayibor[1], Yukinari Sunatsuki [2], Takayoshi Suzuki[1,3] (1. Graduate School of Natural Science and Technology, Okayama University, 2. Advanced Science Research Center, Okayama University, Okayama , 3. Research Institute for Interdisciplinary Science, Okayama University, Okayama)

Japanese

[P1-3pm-57]

Development of LB films of lanthanide complexes with photochromic and polarized luminescence properties

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○Junya Kondo[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

English

[P1-3pm-58]

Mechanism of water molecule adsorption/desorption and phase transition in cobalt terpyridine complex crystals

○Yusaku Kobayashi[1], Otsuki Joe[1], K Sugawa[1] (1. The Univ. of NIhon)

Japanese

[P1-3pm-59]

Development and chromism control of visible-transparent and UV/NIR-absorbing dyes based on mixed-valence clusters

○Tomoki Kamada[1], Takashi Morino[1], Naoki Shimomoto[1], Yasuko Osakada[2], Mamoru Fujitsuka[2], Yoshiki Ozawa[1], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo, 2. SANKEN, Osaka University)

Japanese

[P1-3pm-60]

Synthesis of Rare-Earth Phthalocyanine Double-Decker Complexes and Their Chiral Induction

○Tomohito Mori[1], Kei Murata[1], Kazuyuki Ishii[1] (1. IIS, The Univ. of Tokyo)

Japanese

[P1-3pm-61]

Synthesis and phase transition behavior of Fe(III) ion-based plastic crystal aimed at endowing vapor response

○Yasuhiro Shigeta[1], Motohiro Mizuno[1] (1. Nanomaterials Research Institute, Kanazawa University)

Japanese

[P1-3pm-62]

Synthesis of a novel donor-acceptor molecular assembly composed by Rh binuclear unit with a bulky dicarboxylic acid ligand and an electron acceptor molecule

○Fuminori Kimura[1], Kazuya Otsubo[1] (1. Tokyo University of Science)

Japanese

[P1-3pm-63]

Chiral induced spin selectivity of magnetic coordination molecular chain

○Kubo Karin[1], Zhongyue ZHANG[1], Sekine Yoshihiro[1], Hayami Shinya[1] (1. Kumamoto University)

Japanese

[P1-3pm-64]

Synthesis of Pd_6L_8 and Pd_6L_4 cages from triptycene-based tripodal shaped ligands

○Hiromu Yamamoto[1], Masahiro Yamashina[1], Shinji Toyota[1] (1. Tokyo Tech.)

Japanese

[P1-3pm-65]

Effects of cationic surfactants on the emission properties of $[Au(CN)_2]^-$ oligomers

○Ryo Okada[1], Daichi Inoue[1], Koichi Nozaki[1], Munetaka Iwamura[1] (1. Sch. of Sci., Univ. of Toyama)

English

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[P1-3pm-66]

Optical and Magnetic Properties of Octacyanidemetalate Ionic Crystals with Alkali Cations and Glycine

○Tatsuya Konishi[1], Kunal Kumar[1], Kazuki Nakamura[1], Yuuki Mineo[1], Taiki Sakaguchi[1], Koji Nakabayashi[1], Shin-ichi Ohkoshi[1] (1. The University of Tokyo)

Japanese

[P1-3pm-67]

Formation of porphyrin dimer by coordination bonding and supramolecular host function

○Shigeki Miyazaki[1], Ken Sato[1], Kosuke Sugawa[2], Joe Otsuki[2] (1. Graduate School of Science and Technology, Nihon University, 2. College of Science and Technology, Nihon University)

Japanese

[P1-3pm-68]

Rapid CO_2 Fixation Using a Trinuclear Zn(II) Cryptate Complex and Analysis of its Structure State

○Masakazu Murase[1], Yoshifumi Maegawa[1], Masataka Ohashi[1], Yasutomo Goto[1], Naonari Sakamoto[1], Takamasa Nonaka[1], Takeshi Uyama[1], Takeo Arai[1] (1. Toyota Central R&D Labs., Inc.)

English

[P1-3pm-69]

Heterogenized Cationic Ru(II) Polypyridine Complexes for Visible-Light Photoredox Catalysis

○Seong Huh[1], Jongseo Kim[1] (1. Hankuk University of Foreign Studies)

Japanese

[P1-3pm-70]

Synthesis and Reaction of the anionic vanadium thionitrosyl complex with an [ONO] ligand

○Daichi Sugawara[1], Yutaka Ishida[1], Hiroyuki Kawaguchi[1] (1. Tokyo Institute of Technology)

Japanese

[P1-3pm-71]

Electrochemical CO_2 reduction using a Re(I) complex catalyst and carbamate as a CO_2 source

○Kenshu Nemoto[1], Osamu Ishitani[1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

English

[P1-3pm-72]

Mechanisms of hydrosilylation of carbonyl compounds catalyzed by rhodium-phosphine complexes: The rate enhancement by proximate two Si-H groups

○Hideo Nagashima[1], Yoshihito Shiota, Kazunari Yoshizawa (1. Kyushu University)

Japanese

[P1-3pm-73]

Development of the dehydrogenation coupling reactions of group 14 hydrides mediated by iron catalyst

○TAEWOO KIM[1], Yusuke Sunada[1,2,3] (1. Graduate School of Engineering, The University of Tokyo, 2. Institute of Industrial Science, The University of Tokyo, 3. JST PRESTO)

Japanese

[P1-3pm-74]

Development of the Asymmetric Friedel-Crafts Alkylation Using the Chiral Rare Earth Organophosphate

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○Shoko Suzuki[1], Yudai Tsukada[1], Natsumi Oyama[1], Misaki Sogen[1], Yasuo Yokoyama[2] (1. The Kyoto University of Education, 2. National Institute of Technology, Akita College)

Japanese

[P1-3pm-75]

CO_2 Hydrosilylation Catalyzed by Tetranuclear Copper Hydride Complex Supported by Tridentate Phosphine Ligand

○Konoka Baba[1], Takayuki Nakajima[1], Tomoaki Tanase[1] (1. Nara Women's University)

Japanese

[P1-3pm-76]

Photo and electrochemical properties of Ru complexes immobilized on Al-containing mesoporous silica thin films on ITO electrodes.

○Narumi Nakano[1], Shunpei Harada[1], Ayano Yamada[1], Masaya Okamura[1], Shiro Hikichi[1] (1. Kanagawa University)

Japanese

[P1-3pm-77]

Synthesis of Hydrogels with Thermoresponsive Crosslinked Domains Containing Iridium Complex for Ammonia Sensing and Selective Catalytic Reaction

○Shohichi Furukawa[1], Ida Shohei[2], Fujita Ken-ichi[1] (1. Kyoto university, 2. The University of Shiga prefecture)

English

[P1-3pm-78]

Photoinduced Carbon-Heteroatom Cross-Coupling Catalyzed by Nickel Naphthyridine Complexes

○PAVAN KUMAR VARDHANAPU[1], Janet Bahri[1], Julia Khusnutdinova[1] (1. Okinawa Institute of Science and Technology Graduate University)

Japanese

[P1-3pm-79]

Pd/Fe-catalyzed Synthesis of Terminal Acetals from Terminal Alkenes

○Nanako Fukui[1] (1. nara women's university)

Japanese

[P1-3pm-80]

Catalytic hydrogenation of CO_2 at mild conditions using a photo-activated (PNNP)Ir complex

○Koki Taga[1], Bendik Grømer[1], Jieun Jung[1], Susumu Saito[1,2] (1. Graduate School of Science, 2. Integrated Research Consortium on Chemical Sciences)

Japanese

[P1-3pm-81]

Photocatalytic Reduction of Carbon Dioxide using β-Ketoimine Boron Complexes

○Riku Urita[1], Yuma Hisata[2], Tatsuki Morimoto[1] (1. Tokyo University of Technology Graduate School, 2. Tokyo University of Technology)

Japanese

[P1-3pm-82]

Expression of the Reaction Selectivity and the Substituent Effect in Coupling Reactions by Reducing the Catalyst Loading

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Tomohiro Shibata[1], ○Hiroto Saga[1], Hana Kimura[1], Misa Kawase[1], Yoshimasa Matsumura[1], Osamu Shimomura[1], Atsushi Ohtaka[1] (1. Osaka Institute of Technology)

English

[P1-3pm-83]

Synthesis and Characterization of Uio-67 MOFs Incorporated with Photocatalytic Components for Solar Energy Conversion

○Qingen Zheng[1], Kosei Yamauchi[1], Ken Sakai[1] (1. Kyushu Univ.)

Japanese

[P1-3pm-84]

Theoretical study of reduction of nitrite into NO by copper(II) complexes

○Yoshihito Shiota[1], yohei Kametani[1], Kazunari Yoshizawa[1] (1. Kyushu University)

Japanese

[P1-3pm-85]

Reactivity of Nickel Complexes bearing Two α-Cyanocarboanion Ligands

○Natsuki Nogaki[1], Hajime Kameo[1], Hiroyuki Matsuzaka[1] (1. Osaka Metropolitan University)

Japanese

[P1-3pm-86]

Catalytic Reactions with Monodentate Phosphine-Based Cu-MOF

○Shouki Yui[1], Marina Koga[1], Hiroyuki Arafune[2], Takahiro Sawano[3], Ryo Takeuchi[1] (1. Aoyama Gakuin University, 2. National Institute of Technology, Tsuruoka College, 3. Shimane University)

English

[P1-3pm-87]

Photo-accelerated decomposition of ammonia borane with phosphine-ligated gold clusters

○Shaojing Yan[1], Tomotaka Nakajima[1], Yukatsu Shichibu[1,2], Haru Hirai[3], Tatsuya Tsukuda[3], Katsuaki Konishi[1,2] (1. Grad. Sch. of Env. Sci., Hokkaido Univ., 2. Fac. of Env. Earth Sci., Hokkaido Univ., 3. Sch. of Sci., Tokyo Univ.)

Japanese

[P1-3pm-88]

DFT study on a reaction mechanism of nitric oxide reduction by copper complex with in-built proton-donating functional group

○Yohei Kametani[1], Ryoga Toyoshima[1], Yoshihito Shiota[1], Kazunari Yoshizawa[1] (1. IMCE, Kyushu Univ.)

Japanese

[P1-3pm-89]

Antimicrobial properties of metal complexes bearing salicylideneaniline ligand

○Arisa Niinobe[1], Satoshi D. Ohmura[1] (1. National Institute of Technology, Niihama College)

Japanese

[P1-3pm-90]

Development of Pd(II) complex catalyst with tridentate *N*-heterocyclic carbene ligand immobilized on reduced graphene oxide

○Hina Yamada[1], Yagyu Takeyoshi[1] (1. Nagoya Institute of Technology)

Japanese

[P1-3pm-91]

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Polarized light induced optical anisotropy PMMA films of containing [Ni(dmit)$_2$] complexes and azobenzene compound

○Taiga Imae[1], Akinori Honda[2], Daisuke Nakane[1], Takashiro Akitsu[1], Kazuo Miyamura[1] (1. Tokyo University of Science, 2. Chou University)

Japanese

[P1-3pm-92]

Synthesis and Cation Recognition Capacity of Novel Redox-Active Platinum Complexes with Oligoethylene Glycoxy Chains

○Sota Inoue[1], Akinori Honda[2], Akinobu Nakada[2,3], Ho-Chol Chang[2] (1. Graduate School of Science and Engineering, Chuo Univ., 2. Faculty of Science and Engineering, Chuo Univ., 3. Graduate School of Engineering, Kyoto Univ.)

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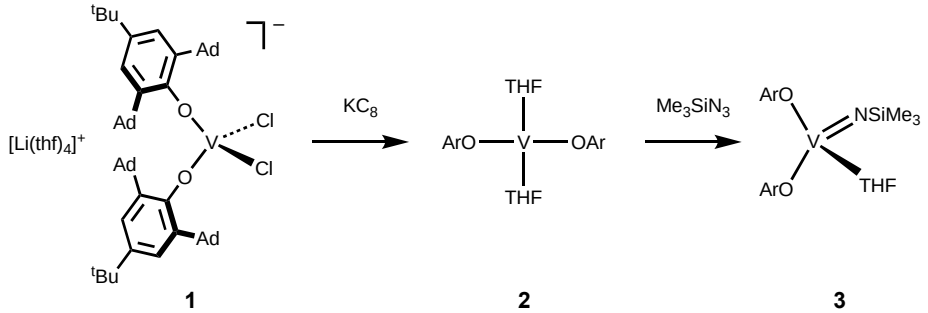
単核バナジウム(II)フェノキシド錯体の合成と反応

（東工大理）○外山 雄大・石田 豊・川口 博之
Synthesis and Reactions of Mononuclear Vanadium(II) Phenoxide Complexes (*School of Science*, *Tokyo Institute of Technology*) ○Yudai Toyama, Yutaka Ishida, Hiroyuki Kawaguchi

Coordinatively unsaturated low-valent vanadium complexes are expected to be reactive and offer an opportunity to study novel transformations of inactive molecules. Here we report the synthesis and the reactions of mononuclear vanadium(II) complexes having ortho-adamantyl-substituted phenoxides (OAr). When $VCl_3(thf)_3$ was treated with 2 equiv of LiOAr, the bis(phenoxide) vanadium(III) compound **1** was obtained as an ate complex. Reduction of **1** with KC_8 afforded the neutral V(II) complex **2**. The geometry of **2** was found to be square planar with the phenoxide ligands arranged in a trans fashion. Next we investigated the reducing capability of **2**. For example, treatment of **2** with trimethylsilyl azide produced the imido complex **3** along with oxidation of the metal center from V(II) to V(IV). The complex **3** adopts a tetrahedral geometry with an imido, one THF molecule, and two phenoxide ligands.

Keywords : vanadium; phenoxide ligand; low-valent complex

配位不飽和な低原子価バナジウム錯体は高い反応性を示すことが知られている。本発表では、アダマンチル基(Ad)をオルト位に導入した嵩高いフェノキシド配位子(OAr)を用いた単核バナジウム錯体の合成と反応について報告する。フェノキシド配位子のリチウム塩 LiOAr と $VCl_3(thf)_3$ を 2:1 で反応させることで、錯体 **1** が得られた。続いて、錯体 **1** に KC_8 を作用させると、バナジウムは V(III)から V(II)に還元され、単核錯体 **2** が生成した。X 線構造解析の結果、錯体 **2** は平面四配位構造をとり、フェノキシド配位子は trans 位に位置していることが明らかになった。次に、錯体 **2** の反応を検討した。例えば、錯体 **2** と Me_3SiN_3 を反応させると、錯体 **3** が得られた。反応過程で錯体 **2** は 2 電子還元剤として作用している。錯体 **3** はイミド基、THF、および 2 つのフェノキシド配位子が結合した四面体構造をとる。



1 **2** **3**

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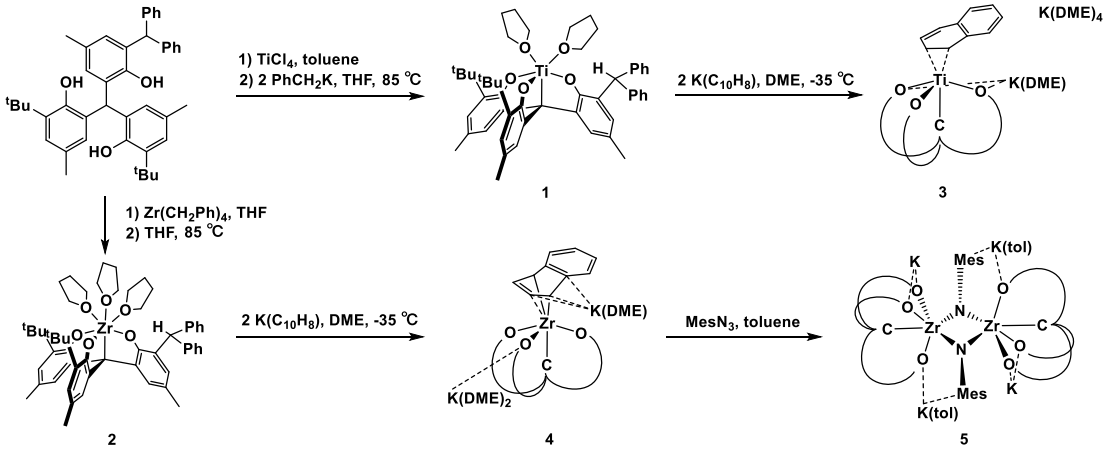
嵩高い三脚型四座[O_3C]配位子を用いたチタンおよびジルコニウム錯体の合成

（東工大理）○小村 公人・石田 豊・川口 博之
Synthesis of Titanium and Zirconium Complexes Having Sterically Hindered Tripodal Tetradentate [O_3C] Ligands (*School of Science, Tokyo Institute of Technology*) ○Masato Komura, Yutaka Ishida, Hiroyuki Kawaguchi

We have studied the coordination chemistry of multidentate phenoxide ligands and their use in the synthesis of metal complexes capable of activating small molecules. Here we report on titanium and zirconium complexes with tripodal the tetradentate [O_3C] ligand having an ortho-diphenylmethyl-substituted phenoxide unit. Treatment of $TiCl_4$ with 1 equiv of the ligand precursor $H_3[O_3CH]$ followed by addition of 2 equiv of $PhCH_2K$ afforded the titanium complex **1**. The analogous zirconium complex **2** was prepared by the reaction of $Zr(CH_2Ph)_4$ with $H_3[O_3CH]$. The reaction of **1** and **2** with 2 equiv of $K(C_{10}H_8)$ produced the corresponding naphthalene complexes **3** and **4**, respectively. The X-ray crystal structures revealed that the naphthalene unit is bound to Ti and Zr in an η^2 and η^4 mode, respectively. The complexes **3** and **4** can behave as a two-electron reductant along with release of naphthalene. For example, the reaction of **4** with mesityl azide resulted in extrusion of N_2 and naphthalene, giving the imido-bridged dinuclear complex **5**.

Keywords : zirconium; titanium; multidentate ligand

我々は多座フェノキシド配位子を用いた錯体の合成と反応について研究を進めている。[1] 本発表では、フェノキシド部位のオルト位にジフェニルメチル基を導入した三脚型四座配位子[O_3C]を用いたチタンおよびジルコニウム錯体の合成と反応について報告する。チタン金属への[O_3C]配位子の導入は段階的に行った。配位子前駆体 $H_3[O_3CH]$と $TiCl_4$ を 1:1 で反応させたのち、2 当量の $PhCH_2K$ を加えることで、チタン錯体 **1** が得られた。一方、ジルコニム錯体 **2** は $Zr(CH_2Ph)_4$ と $H_3[O_3CH]$の反応から得られた。錯体 **1** および **2** に $K(C_{10}H_8)$を作用させると、ナフタレン錯体 **3** および **4** が得られた。X 線構造解析より、ナフタレンは Ti および Zr 金属にそれぞれ η^2 および η^4 配位していることが明らかになった。これらナフタレン錯体は 2 電子還元剤として働く。例えば、錯体 **4** と有機アジド $MesN_3$ の反応では、ナフタレンと N_2 が脱離するとともに、イミド架橋二核錯体 **5** が得られた。



1) Y. Nakanishi, Y. Ishida, H. Kawaguchi. *Dalton Trans*. **2016**, *45*, 15879.

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大気下における銅(II)-フェノキシルラジカル錯体を用いた第一級アルコールの触媒的酸化

（茨城大学理学部）○吉井 万里奈・島崎 優一
Catalytic primary alcohol oxidation by copper(II)-phenoxyl radical complexes under aerobic condition (*College of Science, Ibaraki University*) ○Marina Yoshii, Yuichi Shimazaki

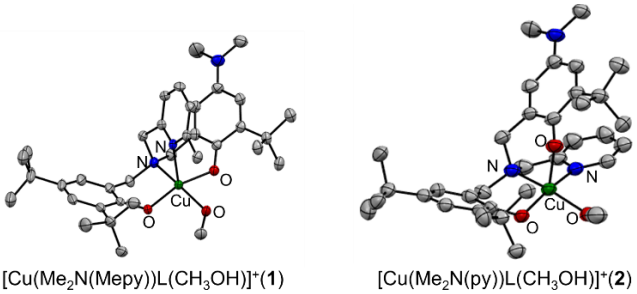
Galactose oxidase is the phenoxyl radical containing enzyme, which catalyzes a primary alcohol of the 6-position of galactose to the corresponding aldehyde by oxygen molecule. In order to know catalytic reactivity of the Cu(II)-phenoxyl radical, two Cu complexes were synthesized using tetradentate tripodal ligand having two phenol moieties, one of which has a *p*-*N*,*N*-dimethylamino group.

Reaction of Cu(II) ion with the phenolate ligands gave phenoxyl radical complexes in the presence of oxygen molecule. These Cu(II)-phenoxyl radical complexes showed the catalytic oxidation reactivity of benzyl alcohol to form benzaldehyde.

Keywords : Copper complexes, phenoxyl radical, oxidation, oxygen molecule, catalyst

ガラクトースオキシダーゼは銅含有酵素であり、酸素分子を用いて一級アルコールをアルデヒドへ酸化する酵素である。この活性種は銅(II)-フェノキシルラジカルであることが知られている。そこで本研究では、銅(II)-フェノキシルラジカルを用いた酸素分子による一級アルコールの酸化触媒の構築について検討した。

2 つの異なるフェノール部位を有し、一方のパラ位にジメチルアミノ基を導入した四座配位子を用いて、2 種の銅(II)-フェノキシルラジカル錯体の合成に成功した。 フェノキシルラジカルがエカトリアル位に配位した[Cu(Me_2N(Mepy))L(CH_3OH)]ClO_4 (**1**)[1] を室温、大気下で過剰のベンジルアルコールと反応させたところ、触媒として機能し、GC-MS により触媒回転数はおおよそ 5 と見積もられた。一方、フェノキシルラジカルがアキシャル位に配位した類似の錯体[Cu(Me_2N(py))L(CH_3OH)]ClO_4（**2**）を用いたところ、ベンズアルデヒドの生成が確認されたが、錯体 **1** と比べて触媒としての機能は低下していることが判明した。これらの実験結果から、錯体 **1** は酸素分子と反応し触媒として回転していることが示唆され、フェノキシルラジカルがアキシャル位に配位している方が有利であることが判明した。



[Cu(Me_2N(Mepy))L(CH_3OH)]$^+$(**1**)　　[Cu(Me_2N(py))L(CH_3OH)]$^+$(**2**)

図 1. 銅(II)-フェノキシルラジカル錯体(**1**)、(**2**)の結晶構造

1) T. Suzuki *et. al*., *Chem Eur. J.,***2019**, *25*, 15805-15814

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2,2':4',4''-terpyridineに橋かけされた新規なCu(I)-エチレン配位高分子の合成と構造

(近畿大理工[1]，理工総研[2]) ◯吉村 祥[1]，前川 雅彦[2]，杉本 邦久[1]，黒田 孝義[1]
Syntheses and crystal structures of novel Cu(I)-C_2H_4 coordination polymers bridged by 2,2':4',4''-terpyridine; (Kindai University) ◯Sho Yoshimura, Masahiko Maekawa, Kunihisa Sugimoto, Takayoshi Kuroda-Sowa

The reactions of $[Cu(MeCN)_4]X$ (X=BF_4, PF_6) with 2,2':4',4''-terpyridine (2,2':4',4''-terpy) in MeOH under C_2H_4 preferentially afforded trinuclear Cu(I) complex $[Cu_3(4,4\text{-terpy})_2(C_2H_4)_2](BF_4)_3$ (**1**) and 1D zigzag chain Cu(I) coordination polymer $[Cu(4,4\text{-terpy})(C_2H_4)]PF_6\}_n$ (**2**) depending on counter anions.
Keywords : Cu complexes, C_2H_4 adducts, Coordination polymers, X-ray Crystal structures, multidentate nitrogen ligands

【目的】これまでキレート部位とターミナル部位を有する多座窒素配位子である2,2':5',4''-terpyridineや2,2':6',4''-terpyridineとCu(I)イオンを反応させると，合成溶媒や対アニオン選択的に多様なメタラマクロサイクリックや配位高分子錯体が自己組織化すること報告してきた(M. Maekawa et al, *Inorg. Chim. Acta*, **497**, 2019, 119088; **528**, 2021, 120628)。本研究では類縁配位子として2,2':4',4''-terpyridine (4,4-terpy)を新たに合成し，対アニオンの異なるCu(I)イオンと反応させ，新規なCu(I)-4,4-terpy/C_2H_4錯体の単離・単結晶化を試み，そのX線構造および性質を特徴付けた。

【実験・結果】(1) 2,2':4',4''-terpyridine (4,4-terpy)の合成. 4,4-terpyは無水トルエン中，$[Pd(PPh_3)_2]Cl_2$を触媒とし，4-bromo-2,2'-bipyridineと4-trimethylstannylpyridineを反応させ合成した (収率: 0.74 g, 61.0 %)。

(2) Cu(I)-4,4-terpy/C_2H_4錯体の合成および構造. C_2H_4雰囲気下，MeOH中，$[Cu(MeCN)_4]X$ (X=BF_4, PF_6)と4,4-terpyをモル比2:1で反応させ，反応溶液をエーテルで拡散させると，対アニオン選択的に$[Cu_3(4,4\text{-terpy})_2(C_2H_4)_2](BF_4)_3$ (**1**)の赤色結晶と$[Cu(4,4\text{-terpy})(C_2H_4)]PF_6\}_n$ (**2**)の黄色結晶が得られた。X線構造解析の結果，錯体**1**は2つの4,4-terpyがtail-to-tail形式を取り，ターミナル部位のCu(I)イオンは二配位構造を，またキレート部位のCu(I)イオンはC_2H_4が配位し三配位構造を取り，三核Cu(I)-4,4-terpy/C_2H_4錯体であることが明らかとなった(Fig. 1)。一方，錯体**2**は異なる2つの一次元ジグザグ鎖構造から構成されたCu(I)-4,4-terpy/C_2H_4高分子錯体であり，同形のいずれの鎖状構造も4,4-terpyはhead-to-tail形式を取り，4,4-terpyのキレート部位と橋かけ部位とC_2H_4が配位した四配位構造のCu(I)イオンが*c*軸に沿って，順次繋がった構造を有することが明らかとなった(Fig. 2)。

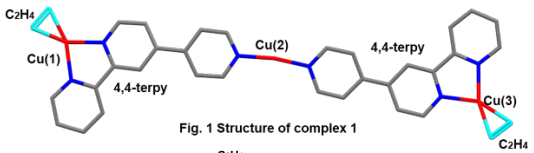

Fig. 1 Structure of complex 1

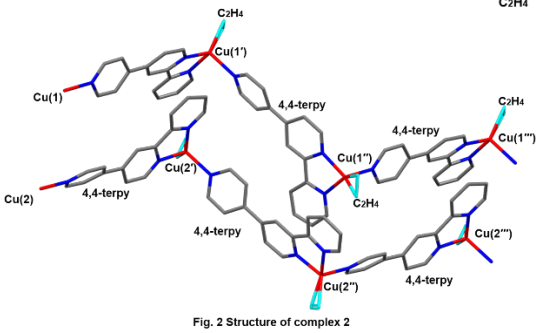

Fig. 2 Structure of complex 2

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バルビエ反応による六員環シラサイクル骨格の構築

(法政大院理工[1]・法政大生命[2])○野口香織[1]・津ヶ谷真唯[1]・河内敦[2]

Construction of Six-membered Silacycle Frameworks by Barbier Reaction ([1]*Graduate School of Science and Engineering, Hosei University*, [2]*Faculty of Bioscience and Applied Chemistry, Hosei University*) ○Kaori Noguchi,[1] Mai Tsugaya,[1] Atsushi Kawachi[2]

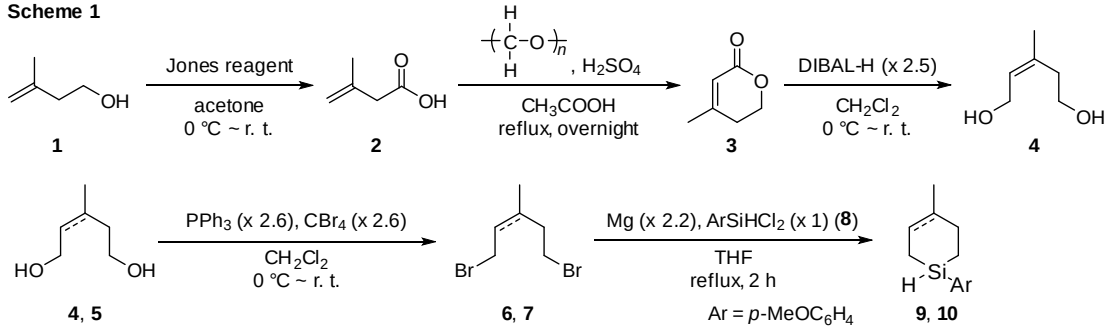
Six-membered cyclic compounds containing silicon atoms and their analogues are attracting attention from the viewpoint of pharmaceuticals and functional material synthesis. Here, we synthesized silacyclohexene and silacyclohexane frameworks **9** and **10** by Barbier reaction of a mixture of dibromopentene **6** or dibromopentane **7**, magnesium metal, and dichlorosilane **8**. The structures of **9** and **10** were determined by NMR spectroscopies and mass spectrometry. Dearylation-chlorination on the silicon atoms in **9** and **10** and introduction of organic groups will be also reported.

Keywords : Barbier Reaction; Silane; Silacyclohexane; Silacyclohexene; Cyclization Reaction

生物活性化合物の炭素原子をケイ素原子に置換する“silicon switch”が医薬品や機能性分子合成の分野で注目を集めている。環状モノテルペンは，リモネンなど多くの天然物の基本骨格を成している。今回我々は，このケイ素置換体である 1-シラ-3-シクロヘキセンおよび 1-シラ-3-シクロヘキサン骨格の構築をおこなった[1)]。

ホモアリルアルコール **1** を出発物質とし，Jones 酸化によりカルボン酸 **2** を得た。酢酸中でカルボン酸 **2**，パラホルムアルデヒド，硫酸を加熱還流することでラクトン **3** を得た。ラクトン **3** を DIBAL により還元しジオール **4** を得た。ジオール **4** および **5** をそれぞれジクロロメタン中，四臭化炭素，トリフェニルホスフィンと反応させ，ジブロモペンテン **6** およびジブロモペンタン **7** を得た。これらと金属マグネシウムおよびアリールジクロロシラン **8** を THF 中で混合し加熱することで(Barbier 反応)，1-シラ-3-シクロヘキセン **9** および 1-シラ-3-シクロヘキサン **10** を合成することに成功した。生成物の構造は各種 NMR スペクトルおよび質量分析により決定した。ケイ素原子上の脱アリール塩素化と有機基の導入についても検討したので併せて報告する。

Scheme 1



1) 津ヶ谷真唯，野口香織，河内敦，第 50 回有機典型元素化学討論会，PO-85（2023）.

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オリゴシラン末端へのアルキニル基の導入

（法政大院理工[1]・法政大生命[2]）○分目 瑞希[1]・河内 敦[2]

Introduction of Alkynyl Groups to the Ends of Oligosilanes

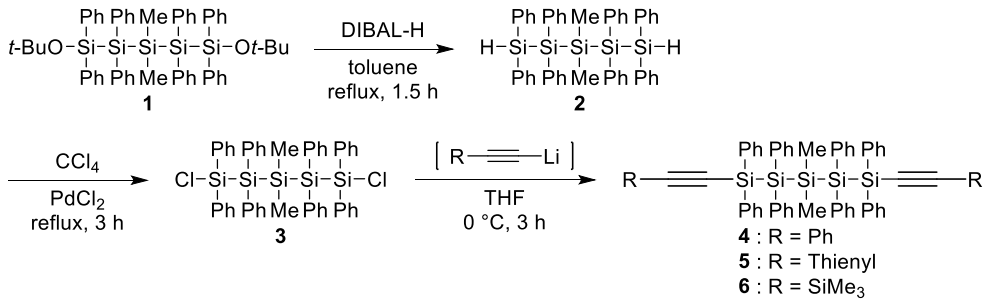
（[1]*Graduate School of Science and Engineering, Hosei University*, [2]*Faculty of Bioscience and Applied Chemistry, Hosei University*） ○Mizuki Wamme,[1] Atsushi Kawachi[2]

Oligosilanes have unique properties due to the σ-conjugation of Si-Si bonds. Our group has reported the synthesis of oligosilanes by the reaction of [2-(alkoxy)disilanyl]lithium with various chlorosilanes. In this study, we introduced alkynyl groups to the ends of oligosilanes for the purpose of expanding the conjugated system. Dihydropentasilane **2** was prepared by reduction of di(*tert*-butoxy)pentasilane **1** with DIBAL-H. Dichloropentasilane **3** was obtained from chlorination of **2**. α,ω-Bis(phenylethynyl, thienylethynyl, or silylethynyl) pentasilanes **4-6** were prepared by reaction of the corresponding lithium acetylides and dichloropentasilane **3**. UV-vis absorption spectroscopy and TD-DFT calculations of the bis(alkynyl)pentasilanes were performed.

Keywords : Oligosilane; σ-Conjugation; UV-vis Spectra; TD-DFT Calculation

当研究室ではこれまでに[2-(アルコキシ)ジシラニル]リチウムと種々のクロロシランとの反応によるオリゴシランの合成を報告している[1)]。本研究では共役系の拡張を目的として，ペンタシラン末端へのフェニルエチニル，チエニルエチニルおよびシリルエチニル基の導入をおこなった。DIBAL-H でジ(*tert*-ブトキシ)ペンタシラン **1** を還元することで，ジヒドロペンタシラン **2** を得た(Scheme 1)。これをパラジウム触媒存在下で四塩化炭素と加熱還流することで，ジクロロペンタシラン **3** を得た。各種リチウムアセチリドとジクロロペンタシラン **3** との反応により，α,ω-ビス(アルキニル)ペンタシラン **4-6** の合成をおこなった。得られたビス(アルキニル)ペンタシラン **4-6** の UV-vis スペクトル測定と TD-DFT 計算をおこなった。

Scheme 1



1） Matsuo, T.; Yamaguchi, T.; Hirohata, T.; Nakamoto, M.; Yamamoto, Y.; Maeda, Y.; Kawachi, A. *Eur. J. Inorg. Chem*. **2021**, 4096-4102.

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シリレン架橋パラジウム 6 核クラスターへのチオラート導入と機能開拓

(中央大理工[1]・東大生研[2]・JST さきがけ[3]) ○須田鉄郎[1]・砂田祐輔[2,3]
Development of thiolate-introduced palladium hexanuclear cluster supported by silylene ligands ([1]Faculty of Science and engineering, Chuo University, [2]Institute of Industrial Science, The University of Tokyo, [3]JST PRESTO) ○Tetsuro Suda,[1] Yusuke Sunada[2,3]

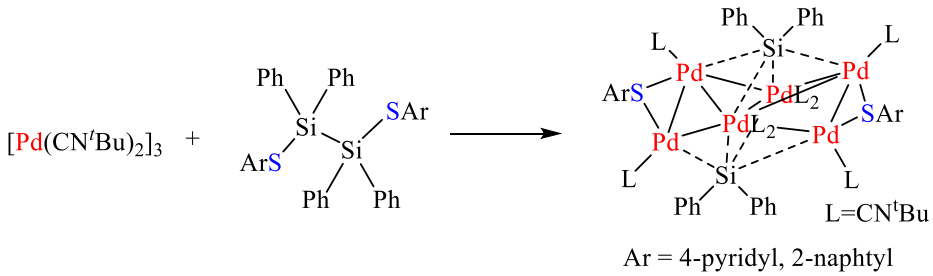
We have focused on the synthesis of metal clusters bearing organosilicon ligands, and their catalytic functions in organic synthesis. In our previous study, it has been discovered that hexanuclear palladium cluster supported by both Cl and silylene ligands was found to be facilely synthesized by the reaction of $[Pd(CN^tBu)_2]_3$ and $Si_2Ph_4Cl_2$.[1]

In this presentation, we wish to describe the synthesis of a silylene-bridged hexanuclear palladium cluster in which thiolate ligands were introduced in an aforementioned hexanuclear palladium cluster. In addition, structural details of the obtained cluster as well as its functions will also be reported.

Keywords : Palladium; Cluster; Silylene; Insertion; Thiolate ligand

当研究室では、有機ケイ素配位子を有する金属クラスターの合成およびその触媒機能開発に関する研究を行ってきた。特に、低原子価遷移金属種の Si-Si 結合への挿入活性に立脚した金属クラスター合成を行っている。例えば、cyclotetrasilane への低原子価 Pd 種の挿入により得られる平面状 Pd4 核クラスターが、アルケンの水素化に対し高活性を示すことを見出している。さらに最近、パラジウム前駆体として $[Pd(CN^tBu)_2]_3$、ケイ素化合物として $Si_2Ph_4Cl_2$ を反応させることでシリレンおよび塩素架橋配位子を有するパラジウム 6 核クラスターの合成を報告した。本研究では、disilane 内に事前にチオラート部位を導入した $Si_2Ph_4(SR)_2$ (R=4-pyridyl, 2-naphtyl)と $[Pd(CN^tBu)_2]_3$ との反応から、チオラート部位を有するパラジウム 6 核クラスターの合成を行った(Scheme 1)。本反応では、定量的に 6 核クラスターのみが得られることを NMR スペクトルによる反応追跡から明らかにしている。得られたクラスターの構造や反応性についても併せて報告する。

(1) Shimamoto, K.; Sunada, Y., *Chem. Eur. J.* **2019**, *25*, 3761–3765.



Scheme 1. Synthesis of Pd6 clusters supported by both thiolate and silylene ligands.

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Substitution reactions of cobalt cubane complexes by bridging bis-pyridine molecules

(*Graduate School of Science and Technology, Meijo University*) ○Wataru Ishikawa, Toshi Nagata

Keywords: Cobalt Cubane, Pyridine, Ligand Exchange

Background. Cobalt cubane complexes (such as $Co_4O_4(OAc)_4(py)_4$) have attracted much attention as candidate for water oxidation catalyst in artificial photosynthesis system.[1] The feature of these complexes is that they are capable of cooperative actions of multiple cobalt centers, and they can be treated as well-defined molecules from a synthetic point of view. We aim to synthesize highly functional molecules based on the cobalt cubane structure. In order to establish synthetic strategies, we carried out substitution reactions on cobalt cubane complexes by bridging bis-pyridine molecules.

Synthesis. The cobalt cubane complexes are prepared from $Co(NO_3)_2{\cdot}6H_2O$, CH_3COONa, pyridine derivative and 30% hydrogen peroxide by stirring under reflux for 4 h in methanol.[2] Substitution reactions were conducted by stirring cobalt cubane complexes and pyridine derivatives under reflux for 16 h in CH_3CN.

Results and discussion. We tried to synthesize $Co_4O_4(OAc)_4(DMAP)_4$ (Y=N$(CH_3)_2$) by substitution reactions (Figure 1). When $Co_4O_4(OAc)_4(py)_4$ (X=H) was used as the starting material, the product contained much impurities as revealed by ^{1}H NMR. On the other hand, when $Co_4O_4(OAc)_4(4\text{-CNpy})_4$ (X=CN) was used as the starting material, the reasonably pure product was obtained in 42% isolation yield. These results suggested that substitution reaction proceeded smoothly when the pyridine derivative in the starting material had an electron-withdrawing group. We also synthesized $Co_4O_4(OAc)_4(4\text{-MeOpy})_4$ (Y=OMe) and $Co_4O_4(OAc)_4(4\text{-Mepy})_4$ (Y=Me) by substitution reactions of $Co_4O_4(OAc)_4(4\text{-CNpy})_4$ (X=CN) (Figure 1). The isolated yields of the products were 64% and 31%, respectively. These results suggested that the pyridine derivatives that had electron-donating groups substituted smoothly. Finally, we synthesized cobalt cubane complexes with bridging structure by substitution reactions of $Co_4O_4(OAc)_4(4\text{-CNpy})_4$ and bpop (1,3-bis(4-pyridyloxy)propane). After column chromatography, the product was obtained in 15% isolated yield (Figure 2).

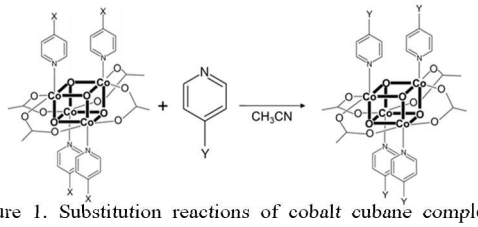

Figure 1. Substitution reactions of cobalt cubane complexes

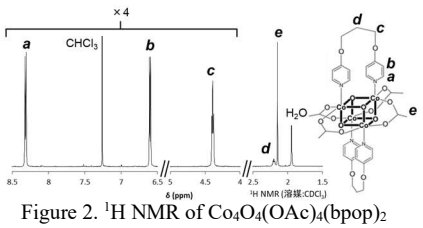

Figure 2. ^{1}H NMR of $Co_4O_4(OAc)_4(bpop)_2$

1) N. S. McCool *et al*., *J. Am. Chem. Soc.,* **2011**, *133*, 11446-11449.

2) R. Chakrabarty *et al*., *Inorg. Chem.,* **2007**, *46*, 9450-9462.

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ベンゾジアザボロラニル基を有するシリルリチウムの合成研究

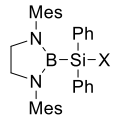
（法政大院理工[1]・法政大生命科学[2]）○角石 凱[1]・河内 敦[2]

Synthetic Study of Silyllithium Bearing Benzodiazaborolanyl Group（[1]*Graduate School of Science and Engineering, Hosei University*, [2]*Faculty of Bioscience and Applied Chemistry, Hosei University*）○Gai Kadoishi,[1] Atsushi Kawachi[2]

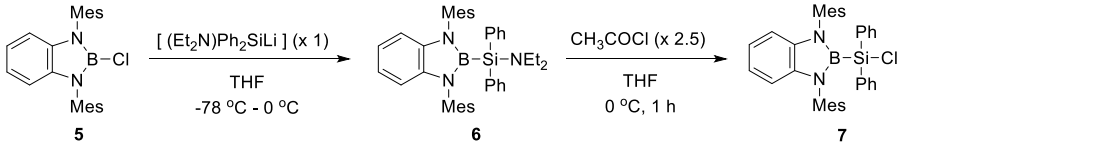
We previously reported the preparation and reactions of boron-substituted silyllithium **2** bearing cyclic diaminoboryl group. Here, we report the preparation of silyllithium **4** bearing benzodiazaborolanyl group. (Borylsilyl)stannane **3** as the precursor of **4** was prepared in a manner similar to that of **1**. Reaction of **3** with *n*-BuLi afforded boron-substituted silyllithium **4**, which was reacted with chlorotrimethylsilane to afford disilane **8**.

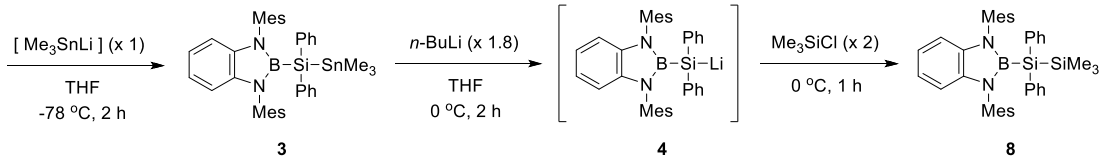
Keywords ; Silyllithium, Silylstannane, Borylsilane, Silane, Borane

われわれは昨年の日本化学会春季年会で，シリルスタンナン **1** のスズ-リチウム交換反応によるホウ素置換シリルリチウム **2** の合成と反応について報告している[1)]。今回，同様の手法により，ベンゾジアザボロラニル基を有するシリルスタンナン **3** からシリルリチウム **4** を合成することに成功したので報告する。クロロボラン **5** を(アミノシリル)リチウムと反応させることでアミノボリルシラン **6** を合成し，**6** を官能基変換することでクロロボリルシラン **7**，シリルスタンナン **3** を合成した。シリルスタナン **3** を *n*-ブチルリチウムと THF 中，0℃で 2 時間反応させたところホウ素置換シリルリチウム **4** が生成した。これをクロロシランで捕捉することで，ホウ素置換ジシラン **8** を得た。



1: X = $SnMe_3$
2: X = Li





1) 小和田雄太，河内敦，日本化学会第 103 春季年会，K503-2am-06 (2023).

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Synthesis of Copper Complexes of Dipicolylamines with Various Degrees of Steric Hindrance and Their Electrochemical Behaviors

(Graduate School of Science and Technology, Meijo University) ○Yumiko Kitamura, Toshi Nagata

Keywords: Copper complex, Dipicolylamine, Steric Hindrance

Introduction. Cu(I) complexes with dipicolylamine derivative ligands have been reported to possess interesting reactivity, such as reduction of carbon dioxide [1]. In this study, 15 copper complexes were synthesized with dipicolylamine derivatives having primary to tertiary alkyl groups on amine nitrogen ($[L_RCu(I)(CH_3CN)]$, $[L_RCu(I)Cl]$, $[L_RCu(II)Cl_2]$, $[L_RCu(II)Cl](ClO_4)$, $[L_RCu(II)(ClO_4)_2]$; L = ligand, R = *n*-Pr, *i*-Pr or *t*-Bu), and their redox properties were evaluated.

Synthesis. L_{tBu} (*t*-butyldipicolylamine) was obtained by overnight reaction of 2-chloromethylpyridine hydrochloride, *t*-butylamine, K_2CO_3, and KI in CH_3CN. L_{iPr} and L_{nPr} ligands were obtained by reaction of 2-pyridine carboxyaldehyde, *i*-propyl- or *n*-propylamine, and sodium triacetoxyborohydride in CH_2Cl_2 for 18 h. Cu(I) complexes were obtained by stirring the corresponding ligands with $[Cu(CH_3CN)_4]BF_4$ or CuCl in CH_3CN for 1 h. Cu(II) complexes were obtained by heating the ligands with $CuCl_2$ or $Cu(ClO_4)_2$-$6H_2O$ in MeOH at reflux overnight. The structures of Cu(II) complexes were determined by X-ray structure analysis (Fig. 1a), whereas the structures of Cu(I) complexes were estimated by quantum chemical calculations (Fig. 1b).

Electrochemistry. The voltammograms of $[L_RCu(II)Cl](ClO_4)$ for the three ligands are shown in Fig. 2. The Cu(I) state becomes more stable with the alkyl group having larger steric hindrance of the ligand. The similar tendency was found for the other complexes synthesized in this study.

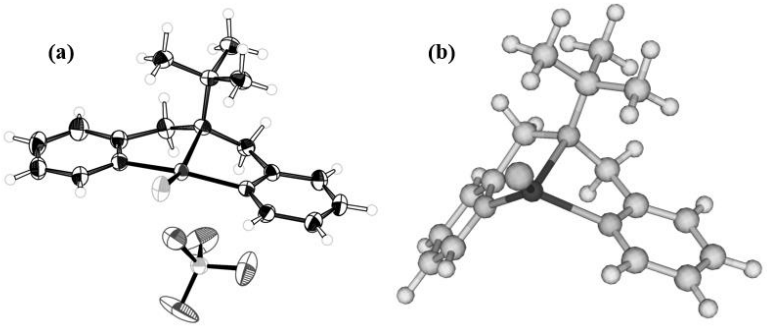

Figure 1 (a) X-ray structure of $[L_{tBu}Cu(II)Cl](ClO_4)$ (b) Calculated structure of $[L_{tBu}Cu(I)Cl]$

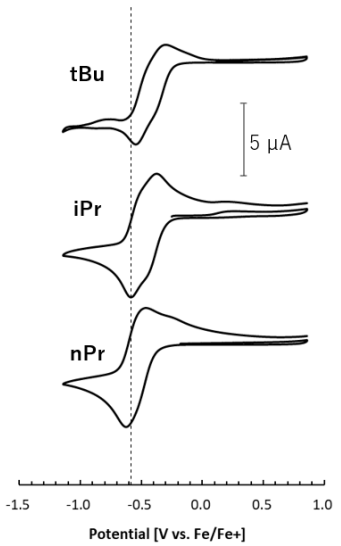

Figure 2 Voltammograms of $[L_RCu(II)Cl](ClO_4)$

[1] Angamuthu. R.; Byers. P.; Lutz. M.; Spek. A. L.; Bouwman. E., *Science*, **2010**, *327*, 313-315.

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電子供与性ジアミド配位子を導入した低原子価コバルト錯体の合成および分子内 C-H 結合活性化

（阪大院理）○小林 翠穂・畑中 翼・舩橋 靖博

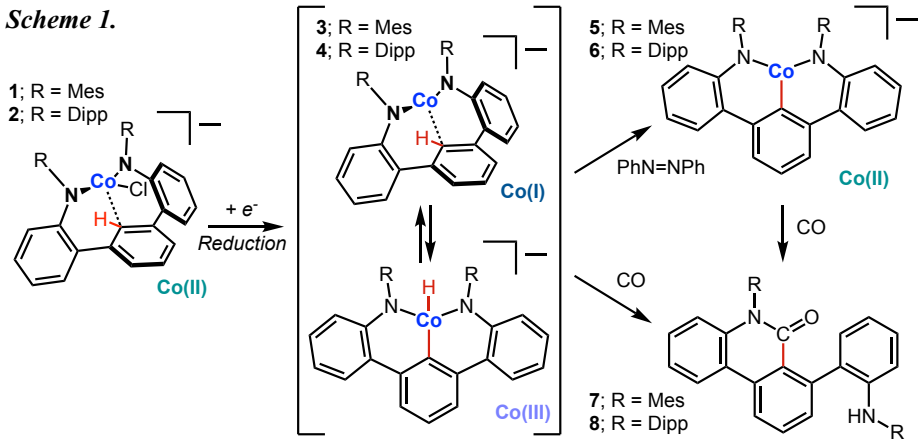
Synthesis and Intramolecular C–H Bond Activation of Low-valent Cobalt Complexes Supported by Electron-Donating Diamide Ligands (*Osaka Univ.*) ○Suiho Kobayashi, Tsubasa Hatanaka, Yasuhiro Funahashi

To achieve stoichiometric C–H bond activation by low-valent cobalt, we performed synthesis and reactions of cobalt complexes having terphenyl diamide ligands. The cobalt(II) complexes **1** and **2** were synthesized by reaction of cobalt chloride with potassium salts of the ligands. Reduction of complexes **1** and **2** was found to provide anionic cobalt(I) complexes **3** and **4**, respectively. Reactions of the reduced complexes **3** and **4** with azobenzene resulted in C–H bond cleavage to form cobalt(II) complexes **5** and **6**. Furthermore, reactions of the complexes **3**-**6** with CO were found to afford C–C/C–N bond formation between the ligands and CO to produce organic compounds **7** or **8**.
Keywords : C-H Bond Activation; Coordinatively Unsaturated Complexes; Electron-donating Ligands; Low-valent Cobalt; Oxidative Addition

低原子価コバルト錯体は、C–H 結合活性化における有用な触媒として注目を集める一方、同じく重要となる量論反応については報告例が限られている。本研究では、低原子価コバルト錯体による量論的 C–H 結合活性化を観察するために、ターフェニルジアミド配位子を有するコバルト錯体の合成と反応を行った。

窒素原子上の置換基が異なる 2 種類の配位子のカリウム塩に対して塩化コバルトを反応させることで Co(II)錯体 **1**、**2** をそれぞれ得た。さらに、得られた錯体の還元反応を行うことで、アニオン性 Co(I)錯体 **3** および **4** を得ることができた(**Scheme 1**)。錯体 **3** や **4** にアゾベンゼンを作用させた場合には分子内 C–H 結合切断反応が進行し錯体 **5**、**6** が得られること、また CO を作用させた場合には C–H 結合修飾反応が進行し有機化合物 **7**、**8** が得られることがわかった。以上の反応から、錯体 **3** や **4** は溶液状態において可逆的な C–H 結合切断反応を起こしていることが示唆された。

Scheme 1.



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オキソーモリブデン二核錯体($(^tBuC_5H_4)_2Mo_2Se_2O_2$)のシリル化反応

(福島大共生システム理工[1]) ○早川 武流[1]・猪俣 慎二[1]
Silylation of an oxo-molybdenum dimeric complex ($(^tBuC_5H_4)_2Mo_2Se_2O_2$) (*[1]Faculty of Symbiotic System Science, Fukushima University)* ○Takeru Hayakawa,[1] Shinji Inomata [1]

Oxo-molybdenum complexes can serve as models for metal-containing proteins such as a molybdenum oxidase.[1)] Previously, we succeeded the synthesis of organometallic type oxo-molybdenum complexes $(RC_5H_4)_2Mo_2Se_2O_2$, from thermal reaction of $(RC_5H_4)_2Mo_2(CO)_6$ (R = H, Me, ^{t}Bu, $SiMe_3$) with grey selenium.[2)] We report here the reactivity of an oxo complex $(^tBuC_5H_4)_2Mo_2Se_2O_2$ towards trimethylchlorosilane.

The reaction of $(^tBuC_5H_4)_2Mo_2Se_2O_2$ with two equiv. of Me_3SiCl in xylene at room temperature afforded a complex $[(^tBuC_5H_4)_2Mo_2Se_2(OSiMe_3)_2]^{2+}(Cl^-)_2$ in 46% yield, in which both oxo ligands were silylated. In the IR absorption spectrum, the Mo=O stretching band at 892 cm^{-1} observed in the starting material disappeared and a Si-O stretching band newly appeared at 1153 cm^{-1}. Interestingly, the product was easily hydrolyzed to give the starting oxo-molybdenum complex in 53% yield.
Keywords : Molybdenum complex; Oxo complex; Silylation

オキソーモリブデン錯体は，モリブデンオキシダーゼ等のモデル錯体となりうる，生物無機化学的に重要な化合物である。[1)]我々は，モリブデンカルボニル二核錯体$(RC_5H_4)_2Mo_2(CO)_6$ (R = H, Me, ^{t}Bu, $SiMe_3$)と灰色セレンとの熱反応により，2 つのオキソモリブデン部位($(RC_5H_4)Mo=O$)が 2 つのセレニド配位子で架橋された有機金属型の二核錯体$(RC_5H_4)_2Mo_2Se_2O_2$ の合成を報告している。[2)]今回，$(^tBuC_5H_4)_2Mo_2Se_2O_2$ とトリメチルクロロシランの反応について報告する。

キシレン中室温で反応を行ったところ，2 つのオキソ配位子がどちらもシリル化された二核錯体$[(^tBuC_5H_4)_2Mo_2Se_2(OSiMe_3)_2]^{2+}(Cl^-)_2$ が収率 46%で得られた。赤外吸収スペクトルは，出発物質でみられた 892 cm^{-1} の Mo=O 伸縮振動が消失し，1153 cm^{-1} に Si-O 伸縮振動があらわれた。また，生成物は容易に加水分解され，出発物質であるオキソーモリブデン二核錯体が収率 53%で得られることがわかった。

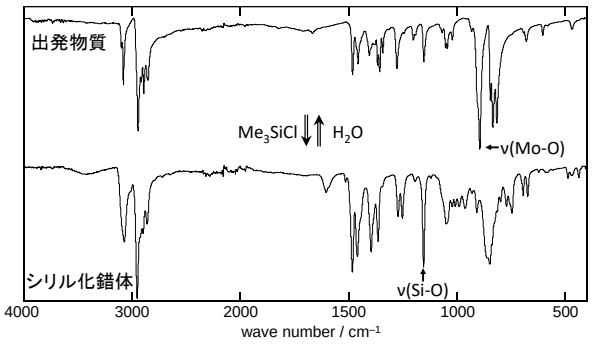

図　赤外吸収スペクトルの変化

1) Donahue, J. P.; Goldsmith, C. R.; Nadiminti, U.; Holm, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 12869
2) Takeru Hayakawa, Tsugiko Takase, Shinji Inomata, The 103rd CSJ Annual meeting (2023)

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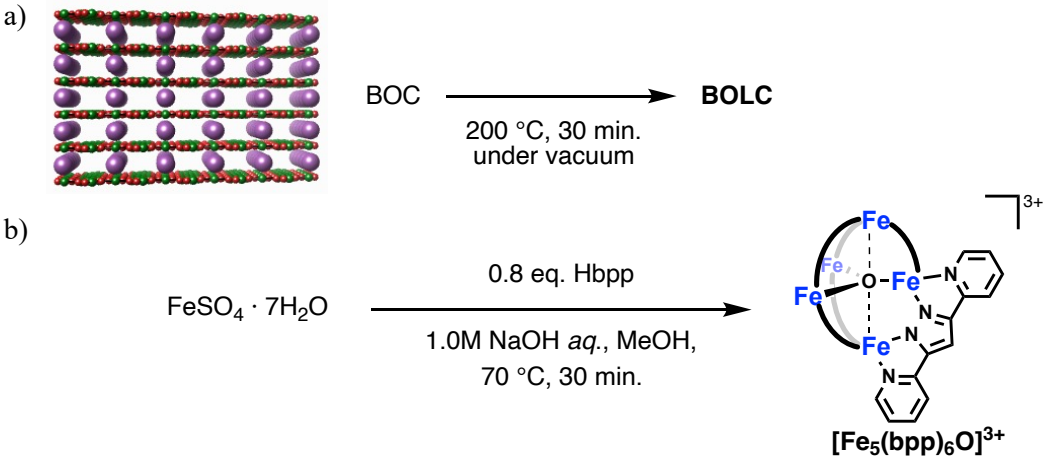
Redox Properties of a Composite Material of Boron-oxide Layers and a Pentanuclear Cluster

([1]*Osaka University,* [2]*Heidelberg University,* [3]*Tokyo Institute of Technology,* [4]*JST PRESTO*)
○ Nicole Sallier de la Tour[1,2], Maho Imai[1], Tetsuya Kambe[1], Yutaka Saga[1], Mio Kondo[1,3,4], Shigeyuki Masaoka[1]

Keywords: Multinuclear metal complex, Boron-oxide layers, Redox activity

The boron oxide layer is a new type of inorganic material with liquid crystallinity, anisotropic electron transfer and high thermal stability.[1] The reduction and oxidation properties are essential for tuning the electronic properties of the two-dimensional structure.[2] In this work, we have investigated oxidation or reduction properties of a boron oxide layer by combining it with a pentanuclear iron cluster. The pentanuclear iron cluster with highly promising catalytic activity has been reported by our group, demonstrating multi-step redox behavior.[3]

The boron oxide liquid crystal (BOLC) is achieved by heating the boron oxide crystal (BOC) (Scheme 1a). The preparation of the pentanuclear iron cluster was conducted as follows with bpp^- ligands (Hbpp: 3,5-bis(2-pyridyl)pyrazole) (Scheme 1b). This study investigates the chemical and electronic interactions between the boron oxide layer and the pentanuclear iron cluster using cyclic voltammetry, revealing notable changes in the redox properties of both materials.



Scheme 1. Preparations of a) boron oxide liquid crystal and b) $[Fe_5(bpp)_6O]^{3+}$.

[1] T. Kambe, S. Imaoka, M. Shimizu, R. Hosono, D. Yan, H. Taya, M. Katakura, H. Nakamura, S. Kubo, A. Shishido, K. Yamamoto, *Nat. Commun.* **2022**, *13*, 1037.[2] T. Kambe, H. Nishihara, K. Yamamoto, *Dalton Trans.* **2023**, *52*, 15297–15302. [3] M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata, S. Masaoka, *Nature* **2016**, *530*, 465–468.

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強い電子的相互作用を有する異種金属多核錯体の合成および物性評価

(阪大院工[1]・東工大院理[2]・JST さきがけ[3]) ○長谷川 暉[1]・坂本 雅也[1]・友田 美紗[1]・嵯峨 裕[1]・神戸 徹也[1]・近藤 美欧[1,2,3]・正岡 重行[1]
Synthesis and properties of heterometallic multinuclear complexes with an intense electronic interaction among metal centers ([1]*Graduate School of Engineering, Osaka Univ.;* [2]*School of Science, Tokyo Institute of Technology;* [3]*JST PRESTO*) ○ Akira Hasegawa[1] ・ Masaya Sakamoto[1] ・ Misa Tomoda[1] ・ Yutaka Saga[1] ・ Tetsuya Kambe[1] ・ Mio Kondo[1,2,3] ・ Shigeyuki Masaoka[1]

Heterometallic multinuclear complexes can exhibit specific functions including reactivities, magnetic properties, and luminescence properties. Such properties can be tuned by the kind of metal ions with the arranged positions. In this work, we have investigated heterometallic multinuclear complexes with ruthenium ions, including Ru_2Cu_3, Ru_2Cu_2, Ru_2Cu_2Zn, Ru_2CuZn and Ru_2Ni_3 with bpp^- ligands (Hbpp = 3,5-Bis(2-pyridyl)pyrazole). In our presentation, we report on the synthesis by using the metal-substitution method with tetrabutylammonium hydroxide as a base and properties of prepared complexes.
Keywords: Heterometallic Multinuclear Complex; Substitution of Metal Ions

異種金属多核錯体は多電子の移動に起因した特異な反応性・磁気特性および光物性等が発現できる物質であり、構成する金属イオンの種類・配置を制御することで新規機能の発現や電子物性の精密な制御が期待できる。今回、Tetrabutylammonium Hydroxide (TBAOH)を用いた金属イオンの置換手法を駆使することで、Ru イオンを含む異種金属多核錯体：**Ru_2Cu_3**, **Ru_2Cu_2**, **Ru_2Cu_2Zn**, **Ru_2CuZn**, **Ru_2Ni_3** を架橋配位子である 3,5-Bis(2-pyridyl)pyrazole (Hbpp)を用いて構築した。

まず、$RuCl_3 \cdot nH_2O$ と Hbpp を反応させ、単核錯体$[Ru(Hbpp)_3](ClO_4)_2$ を得た[1]。得られた錯体を Cu^{2+}と反応させ、$[Ru_2Cu_3OH(bpp)_6](ClO_4)_3$ (**Ru_2Cu_3**)を合成した (Fig. 1)。

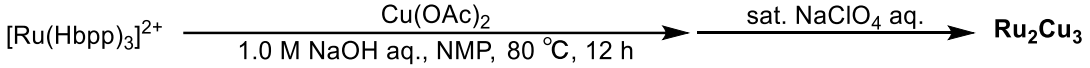

Fig. 1 **Ru_2Cu_3** の合成スキーム

次に、TBAOH の処理により生成した欠損四核錯体 **Ru_2Cu_2** を Zn^{2+}と反応させ、**Ru_2Cu_2Zn** を合成した。そして、塩基処理により、欠損４核錯体 **Ru_2CuZn** が得られていることが ESI-TOF-MS により示唆された。これを駆使した５種金属混合型５核錯体 **$RuCuZnM^1M^2$** (Fig. 2)の合成について検討した。中央部分の金属を Ni に変更した **Ru_2Ni_3** についても合成し、その金属脱離特性についても検討した。当日は、これら多核金属錯体の合成および反応性を含む物性の評価について発表する。

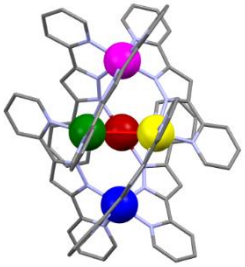

Fig. 2 異種金属五核錯体

1) H. Izu et al., ChemRxiv Preprint, DOI: 10.33774/chemrxiv-2021-n3jtl.

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四価金属カチオンとテトラカルボン酸を用いた新規配位高分子の合成

（東理大[1]）○久住 遥香[1]・貞清 正彰[1]
Synthesis of a Novel Metal–Organic Framework Consisting of Tetravalent Metal Cation and Tetracarboxylate Ligand ([1]*Tokyo University of Science*) ○ Haruka Kusumi,[1] Masaaki Sadakiyo[1]

Metal–organic frameworks (MOFs) are the porous solids constructed by metal ions or metal oxide clusters and organic ligands. MOFs have various porous structures and have been applied for gas storage, separation, and catalysis in recent years. Therefore, thermal and chemical stabilities are important for diverse applications. MOFs constructed with tetravalent metal ions have been widely studied because of their excellent thermal and chemical stabilities. However, there are not many reports on various structures of MOFs with tetravalent metal ions. In this study, we synthesized a novel Zr-based MOF with a tetracarboxylate ligand, TCPP (Tetrakis(4-carboxyphenyl)porphyrin). The obtained samples were identified by X-ray powder diffraction (XRPD) and nitrogen adsorption isotherms measurements. Results of XRPD showed that a novel framework was formed. Nitrogen adsorption isotherm measurements at 77 K also indicated the apparent porosity of the novel compound.
Keywords : Metal–organic framework; Porous solid

金属イオンまたは金属酸化物クラスターと架橋配位子が自己組織化することにより形成される構造体は配位高分子(PCP または MOF)として知られている。MOF は、その多様な細孔構造を用いて、ガス貯蔵、分離、触媒などへの応用が期待され、近年盛んに研究されている。熱的・化学的安定性は様々な分野で MOF を利用する際に重要な要素となるが、これまでの研究から、高価数の金属カチオンを用いた MOF は優れた熱的・化学的安定性を示す傾向があることが知られている[1)]。一方で、MOF は二価および三価の金属カチオンを用いたものが多く、これらと比較して四価金属カチオンにより骨格構造が構築された多孔性 MOF の報告例は未だ限られている。本研究では、Zr^{4+}とテトラカルボン酸である TCPP (Tetrakis(4-carboxyphenyl)porphyrin)を用いた新規な多孔性 MOF の合成を試みた。合成した試料は粉末 X 線回折(XRPD)測定、窒素吸着等温線測定等を用いて同定した。様々な合成条件で合成を行ったところ、原料および既存の MOF とは異なる XRPD パターンを示す試料が確認され、新規 MOF(化合物 1)の合成が示唆された。77 K における窒素吸着等温線測定を行った結果(図 1)、低圧部分から多量の吸着を示したことから、合成した試料が多孔性を有していることが確認された。

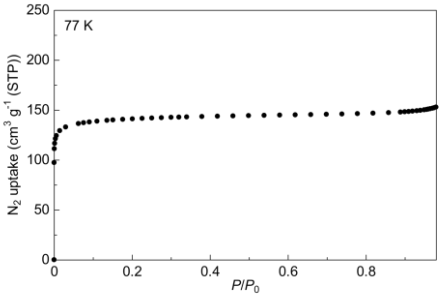

図 1. 化合物 1 の窒素吸着等温線

1) J. H. Cavka, S. Jakobsen, U Olsbye, et al., *J. Am. Chem. Soc*. **2008**, *130*, 13850-13851.

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ジエチルスルフィドが配位した非対称白金複核錯体の構造と多核反応性

(岐阜大工[1]・岐阜大院自然科技[2]) ○宮村 洵之介[1]・金森 章太[2]・植村 一広[1]

Synthesis, structure, and multinuclear reactivities of unsymmetrical dinuclear platinum complex containing diethyl sulfides as co-ligands

([1]*Faculty of Engineering, Gifu University*, [2]*Graduate School of Natural Science and Technology, Gifu University*) ○Junnosuke Miyamura,[1] Shota Kanamori,[2] Kazuhiro Uemura[1]

Toward the multinuclear one-dimensional compounds with metal-metal bonds, we have tried to synthesize mononuclear platinum complex containing diethyl sulfide (Et_2S) as co-ligands, because it is possible to be removed- in the synthetic process. According to the previous report, *cis*-$[Pt(Et_2S)_2Cl_2]$ was synthesized, which was stirred with $AgNO_3$ in H_2O. After removing white powder, the addition of *cis*-$[Pt(piam)_2(NH_3)_2]$ (piam = pivalamidate) and excess $NaClO_4$ afforded dinuclear *cis*-$[Pt_2(piam)_2(NH_3)_2(Et_2S)_2](ClO_4)_2$. Each Pt is bridged by two piam ligands with Pt---Pt distance of 3.1317(5) Å, where one Pt are coordinated with two NH_3, and the other is with two Et_2S as co-ligands.

Keywords : Dinuclear Complex; Unsymmetrical; Ligand Exchange; Multinucleation;

我々は、白金にアンモニアとピバルアミダートが 2 つずつ配位した、*cis*-$[Pt(piam)_2(NH_3)_2]$ (piam = pivalamidate)を用いて、一次元多核化を検討している。この白金単核錯体は配位フリーの酸素原子が他の金属を補足するため、容易に複核および三核化することが可能である。本研究では、アンモニアの替わりに、脱離可能なジエチルスルフィド（Et_2S）を補助配位子に、同様の白金単核錯体および多核化を検討した。既報を参考に、*cis*-$[Pt(Et_2S)_2Cl_2]$を合成した。H_2O 中で 2 等量の硝酸銀を加え、析出した白色粉末を除去後、*cis*-$[Pt(piam)_2(NH_3)_2]$を加え、過剰量の $NaClO_4$ を加えると緑色粉末が析出した。この緑色粉末を再結晶し、単結晶 X 線構造解析したところ、複核錯体の $[Pt_2(piam)_2(NH_3)_2(Et_2S)_2](ClO_4)_2$（図 1）であった。白金は 2 つの piam で架橋され、白金間距離は 3.1317(5) Å であった。また、片方の白金には 2 つの NH_3 が、他方には 2 つの Et_2S が配位した非対称構造であり、白金の酸化数は＋2 と考えられる。さらに、銅との三核化、さらなる多核化の検討結果も発表する予定である。

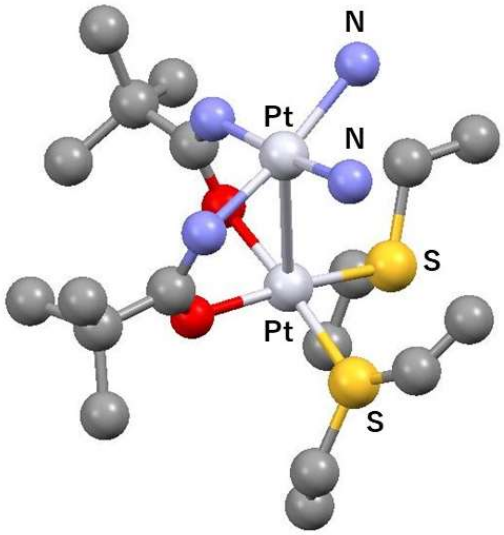

図 1 の結晶構造

1) W. Chen, K. Matsumoto, *Inorg. Chim. Acta*, **2003**, *342*, 88–96, K. Uemura, K. Yamasaki, K. Fukui, K. Matsumoto, *Inorg. Chim. Acta*, **2007**, *360*, 2623–2630.

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直座状四座ホスフィン配位子に支持された銅９核ヒドリドクラスターの合成

（奈良女子大学）○島田 円香・小村 優理花・坂部 靖奈・中島 隆行・棚瀬 知明

Synthesis of Cu9 Hydride Clusters Supported by Linear Tetraphosphine Ligand (*Nara Women's University*) ○Madoka Shimada, Yurika Komura, Seina Sakabe, Takayuki Nakajima, Tomoaki Tanase

Reaction of *meso*-**L** with Cu^{I} salts, PPh_3, and $NaBH_4$ in MeCN/MeOH gave copper hydride cluster $[Cu_9H_7(meso\text{-}\mathbf{L})_3]X_2$ (**1**). Furthermore, complex **1** reacted with $LiBH_4$ in THF to form $[Cu_9H_8(meso\text{-}\mathbf{L})_3]X$ (**2**). X-ray crystallography confirmed that complexes **1** and **2** had similar structures, and their hydride positions were determined by DFT calculations. Variable temperature NMR showed the fluxional behavior of hydride ligands only in the case of **1**.

Keywords : Copper, Hydride, Metal Cluster, Phosphine Ligand

貴金属の代替材料として安価な銅を用いた銅ヒドリドクラスターは，水素化反応，CO_2 還元反応などの触媒反応への応用や水素貯蔵材料設計への可能性から近年注目されている。

当研究室では，多座ホスフィン配位子を用いた銅ヒドリドクラスターの合成並びに，それらを触媒とするギ酸分解反応や CO_2 の水素化反応などの反応開発を行っている [1]。本研究では、四座ホスフィン配位子 *meso*-dpmppp (*meso*-**L**) を支持配位子とする２種類の銅９核ヒドリドクラスターの合成を行った (**Figure 1**)。*meso*-**L** を Cu^{I}塩, PPh_3, $NaBH_4$ と MeCN/MeOH で反応させると$[Cu_9H_7(meso\text{-}\mathbf{L})_3]X_2$ (**1**) (X = PF_6, BF_4) が生成し，**1** に THF 中 $LiBH_4$ を反応させることで$[Cu_9H_8(meso\text{-}\mathbf{L})_3]X$ (**2**) が得られた (**Scheme 1**)。X 線結晶構造解析から錯体 **1** と **2** は類似構造を有することが分かり，各々のヒドリドは DFT 計算により位置決定を行った。温度可変 NMR の測定により，錯体 **1** のヒドリドのみ動的挙動がみられた。

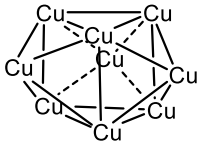
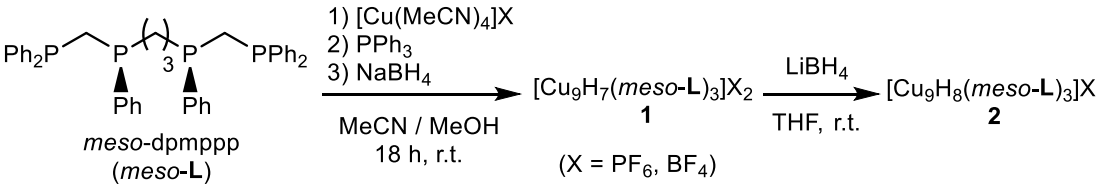


Figure 1.
Metal framework of **1** and **2**.



Scheme 1.

1) T. Nakajima, K. Nakamae, Y. Ura, and T. Tanase, *Eur. J. Inorg. Chem.* **2020**, *23*, 2211-2226.

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新規シッフ塩基型[2+2]環状体の合成と金属蛍光センサー評価

（東電大工）○松岡　みちる・宮坂　誠

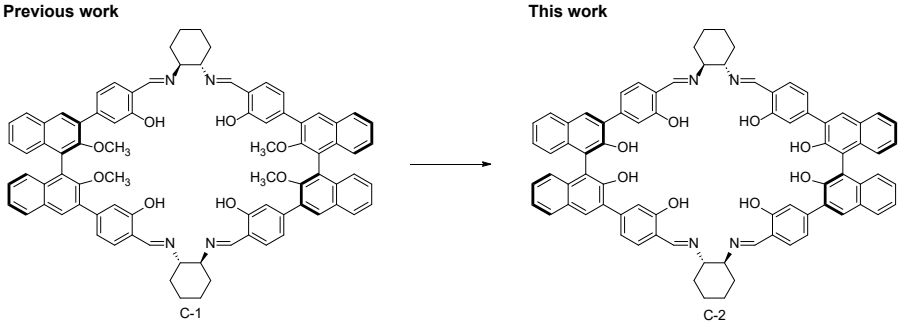
Synthesis and Evaluation as Metal Fluorescent Sensor of Novel Schiff Base [2+2] Macrocycles (*School of Engineering, Tokyo Denki University*) ○Michiru Matsuoka, Makoto Miyasaka

Schiff bases are easily synthesized by the dehydration-condensation reaction of amine and carbonyl compounds, and bind to metal ions via the nitrogen atom of the azomethine group to function as a sensor. In addition, a Schiff base cyclic compound composed of a diamine and a dicarbonyl compound forms a chelate complex with a metal ion and stabilizes it. Therefore, they have been extensively studied as fluorescent chemical sensors in recent years due to their ease of operation and high sensitivity. In our laboratory, we have synthesized Schiff base type cyclic compounds composed of 1,2-cyclohexanediamine and (*R*)-1,1'-bi-2-naphthol and evaluated their metal coordination ability. In this study, we synthesized a new cyclic compound in which the methoxy moiety of the binaphthol moiety was changed to a hydroxy moiety, and evaluated the metal coordination ability of the new cyclic compound.

Keywords; Schiff Base; Macrocyclic Compound; Complex; Fluorescence Sensor

シッフ塩基はアミンとカルボニル化合物の脱水縮合反応で容易に合成でき、アゾメチン基の窒素原子を介して金属イオンと結合しセンサーとして機能する。また、ジアミンとジカルボニル化合物で構成されるシッフ塩基型環状体は、金属イオンとキレート錯体を形成し安定化する[1]。このことから、近年操作の容易さや高感度の点で蛍光化学センサーとして幅広く研究されている[2]。

当研究室では、1,2-シクロヘキサンジアミンと(*R*)-1,1’-ビ-2-ナフトールからなるシッフ塩基型環状体 **C-1** の合成および金属配位能を評価してきた。本研究では、ビナフトール部位のメトキシ基部分をヒドロキシ基に変更した新規環状体 **C-2** の合成及び金属配位能を報告する。



1) J. K. Kapoor *et al., Inorganica Chemica Acta,* **2023***, 546*, 121300.
2) D. Ezhumalai *et al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* **2018***, 199,* 209-219.

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ターピリジン骨格により構築した鉄錯体$[Fe(tppz)_2]^{2+}$の合成と構造

（近畿大理工[1]，理工総研[2]）○木原真生[1]，Goo Zi Lang[1]，前川 雅彦[2]，黒田 孝義[1]，杉本 邦久[1]

Synthesis and structure of $[Fe(tppz)_2]^{2+}$ constructed by terpyridine moiety; ([1]*Department of Chemistry,* [2]*Science and Technology Research Institute, Kindai university*) ○Mao Kihara,[1] Zi Lang Goo,[1] Masahiko Maekawa,[2] Takayoshi Kuroda-Sowa,[1] Kunihisa Sugimoto[1]

Porous coordination polymer and metal-organic frameworks are highly pore polymeric structures composed of metal ions and organic ligands, which are reported with various applications, such as storage, separation, and catalysts. Our study aims to synthesize new multi-dimensional metal coordination polymers and characterize their structure based on a terpyridine skeleton and property. In our research, tetra-2-pyridinyl-pyrazine(tppz) with a terpyridine skeleton is selected as a bridging ligand. A single crystal was successfully obtained by reaction with $Fe(BF_4)_2$•$6H_2O$ by hydrothermal synthesis. X-ray structure analysis determined a molecular structure of $[Fe(tppz)_2](BF_4)_2$ (**1**) in Fig. 1. Furthermore, CV measurement was performed by dissolving **1** in acetonitrile and the reversible redox peak shown in Fig. 2 was observed. And, since the chloroform solution of **1** is available for NMR measurement, it is suggested that it has a low spin state that corresponds with Fe－N distance obtained from structural analysis.

Keywords: Iron; Pyridyl ligand; Crystal structure; Coordination polymer

多孔性配位高分子および金属有機構造体は、金属イオンと有機配位子からなる細孔を有する構造であり、物質の分離や貯蔵、触媒などの幅広い機能を発現することが報告されている。本研究では、ターピリジン骨格を基盤とした新規な多次元金属配位高分子の合成および構造解析を行い、その特性について明らかにすることを目的とした。合成では、ターピリジン骨格を有する配位子として tetra-2-pyridinyl-pyrazine(tppz)を用い、水熱合成によって $Fe(BF_4)_2 \cdot 6H_2O$ と反応させた後、室温になるまで放冷することにより単結晶を得た。得られた単結晶は、X 線構造解析により Fig. 1 に示す $[Fe(tppz)_2](BF_4)_2$ (**1**)の分子構造であることを決定した。さらに、電気化学的な知見を得るために **1** をアセトニトリルに溶解し CV 測定を行ったところ、Fig. 2 に示す可逆的な酸化還元波を観測した。また、**1** のクロロホルム溶液は NMR 測定が可能であることから低スピンであることが示唆され、構造解析から得られた Fe－N 間距離とも矛盾しない。

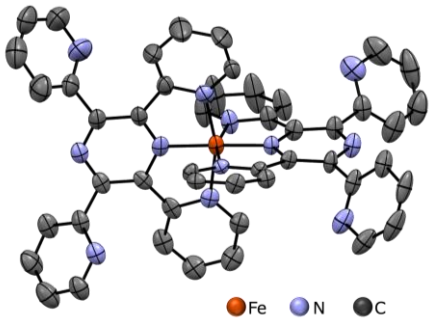

Fig. 1 Structure of $[Fe(tppz)_2](BF_4)_2$

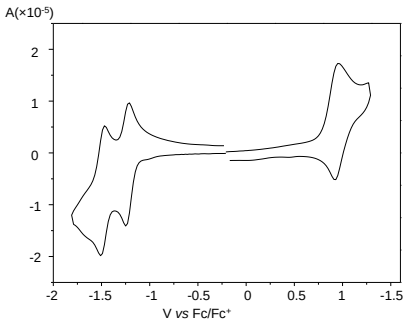

Fig. 2 CV of 1mM $[Fe(tppz)_2](BF_4)_2$

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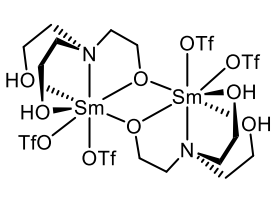
Syntheses and Structures of Aminoalcohol-ligated Mononuclear and Dinuclear Samarium Complexes

(*Graduate School of Engineering Science, Osaka University*) ○Kulsum Bano, Tetsuro Kusamoto, Hayato Tsurugi

Keywords: Samarium; Aminoalcohol; Multi-nuclear Complex

Samarium complexes with aminoalcohol ligands have been explored as versatile reductants in organic transformations *via* proton-coupled electron transfer (PCET) process.[1] Utilization of the bifunctional characteristics of amino (-NH_2) and hydroxy (-OH) groups for the aminoalcohols results in a diverse range of coordination fashion to the central metal, and the protons at the hydroxy groups play an important role for the reduction of unsaturated organic compounds. Herein, we report on the synthesis and structures of samarium(III) complexes having aminoalcohol ligands, and we evaluated the reactivity toward decamethylcobaltocene (Cp^*_2Co) as a reductant for the samarium(III) center.

We first treated $Sm(OTf)_3$ with triethanolamine ($H_3\mathbf{L^1}$) in THF at room temperature for 24 h, and two $H_3\mathbf{L^1}$-ligated samarium(III) complex, $[Sm(H_3\mathbf{L^1})_2(THF)][OTf]_3$ (**1**) was isolated as colorless microcrystals; overall structure of **1** was clarified by the X-ray diffraction study, revealing that two $H_3\mathbf{L^1}$ ligands coordinate to the samarium(III) center as a tetradentate fashion with dissociating three triflate anions from the metal center. In sharp contrast, longer reaction time (over 3 days) at 60 °C gave a dimeric samarium(III) complex **2** containing two singly deprotonated ligands $H_2\mathbf{L^1}$, which was characterized by the ESI-MS analysis. Reactions of $Sm(OTf)_3$ with other aminoalcohol ligands such as $PhN(CH_2CH_2OH)_2$ ($H_2\mathbf{L^2}$) and $(HOCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2OH)_2$ ($H_4\mathbf{L^3}$) produced dimeric samarium complexes $Sm_2(H\mathbf{L^2})_2(OTf)_4$ (**3**) and $[Sm_2(H_3\mathbf{L^3})_2(OTf)_2][OTf]_2$ (**4**) without forming the monomeric complexes. The dimeric structures of **3** and **4** are characterized by the X-ray diffraction study, clearly showing two bridging alkoxide ligations. Reduction of **1-4** with Cp^*_2Co rapidly formed H_2 gas along with precipitation of the samarium(III) complexes, while further addition of proton sources such as colidinium triflate to the reaction mixture regenerated the dimer species as the major products.



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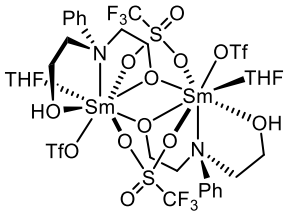

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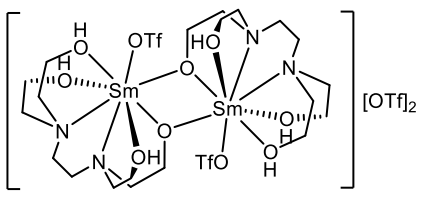

4

This paper is based on results obtained from a project, JPNP21020, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

1) Boekell, N. G.; Bartulovich, C. O.; Maity, S.; Flowers II, R. A. *Inorg. Chem.* **2023**, *62*, 5040-5045.

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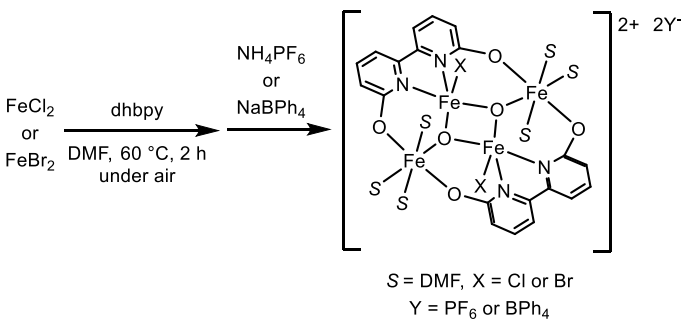
ビピリドナート配位子を有する四核鉄オキソ錯体の合成

（奈良女大理）○阪本 愛菜・浦 康之
Synthesis of Tetranuclear Iron-oxo Complexes Having Bipyridonate Ligands (*Faculty of Science, Nara Women's University*) ○Aina Sakamoto, Yasuyuki Ura

Iron is one of the most abundant, inexpensive, and low-toxicity transition metals, and multinuclear iron complexes are of interest for their reactivity and catalytic functions based on multi-electron oxidation/reduction. In this study, we found that the reaction of iron halides with 6,6'-dihydroxy-2,2'-bipyridine (dhbpy) produces novel tetranuclear iron-oxo complexes. The reaction of $FeCl_2$ or $FeBr_2$ with dhbpy in DMF at 60 °C under air was followed by anion exchange using salts such as NH_4PF_6 and $NaBPh_4$. Single crystal X-ray structure analysis revealed the formation of dicationic tetranuclear iron-oxo complexes with two bipyridonate ligands, two μ_3-oxo ligands, two halogens, and six DMF ligands. The geometric structures around the inner (Fe1, Fe1*) and outer (Fe2, Fe2*) iron atoms were tetragonal pyramidal and octahedral, respectively, and the oxygen atoms of the bipyridonate and oxo ligands coordinated meridionally to the outer iron atoms.

Keywords：*iron complex, tetranuclear complex, bipyridonate ligand, oxo ligand*

鉄は遷移金属の中でも豊富・安価・低毒性であり，多核鉄錯体では多電子酸化/還元に基づく反応性および触媒機能に興味が持たれる。本研究では，ハロゲン化鉄と 6,6'-ジヒドロキシ-2,2'-ビピリジン（dhbpy）との反応によって新規四核鉄オキソ錯体が生成することを見出した。空気下，塩化鉄(II)または臭化鉄(II)と dhbpy を DMF 溶媒中，60 °C で反応させ，NH_4PF_6 または $NaBPh_4$ などの塩を用いてアニオンを交換し，結晶化を行ったところ，いずれの場合も濃褐色結晶が得られた。単結晶 X 線構造解析によって，2 個のビピリドナート配位子，2 個の μ_3-オキソ配位子，2 個のハロゲンおよび 6 個の DMF 配位子をもつジカチオン性の四核鉄オキソ錯体が生成していることが明らかとなった。内側(Fe1, Fe1*)および外側(Fe2, Fe2*)の鉄原子周りの幾何構造はそれぞれ四角錐構造および八面体構造であり，ビピリドナート配位子およびオキソ配位子の酸素原子は外側の鉄原子に対してメリディオナルに配位座を占めていた。



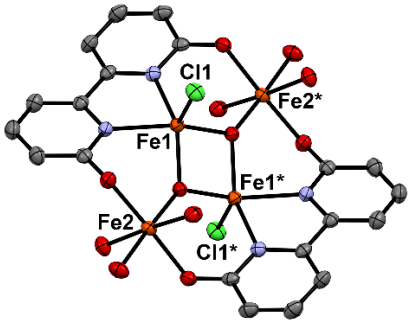


Fig. 四核鉄オキソ錯体のカチオン部分の ORTEP 図 (X＝Cl, Y＝BPh_4, DMF の O 原子以外は省略)

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酸素あるいは窒素ドナー配位子による三重架橋構造を有するコバルト二核錯体の合成

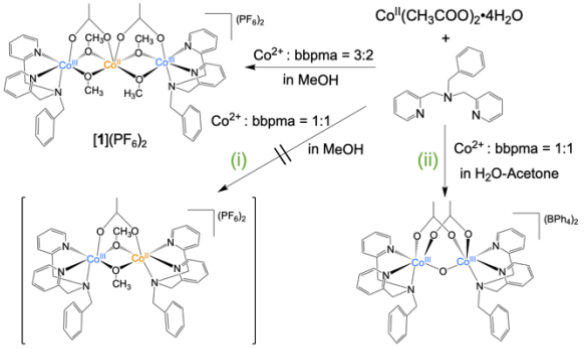
（上智大理工）伊東 稜晟・三澤 智世・長尾 宏隆
Synthesis of dinuclear cobalt complexes, triply bridged by the oxygen- or nitrogen-donor ligands (*Faculity of Science and Technology., Sophia University*) Ryosei Ito, Tomoyo Misawa, Hirotaka Nagao

Multinuclear transition metal complexes could have multiple electronic structures depending on the kind of the metal centers and the bridging structures. They are capable of multi-electron transfer and are expected to function as reaction centers for material conversion. The reaction of cobalt(II) acetate tetrahydrate and benzylbis(2-pyridylmethyl)amine (bbpma) in methanol with a 3:2 molar ratio affords a linear-type trinuclear complex bridged by two methoxido and one acetato ligands having the Co(III)-Co(II)-Co(III) centers ([**1**]$(PF_6)_2$).[1)]

In this study, we investigated the synthesis of dinuclear complexes through a reaction of cobalt(II) acetate tetrahydrate and bbpma at a 1:1 molar ratio in methanol or water (Scheme (i), (ii)). In methanol, [**1**]$(PF_6)_2$ is formed instead of a dinuclear complex bridged by two methoxido and an acetato ligands. In water, a dinuclear complex bridged by two acetato and one oxido ligands is formed. We also investigated the synthesis of dicobalt complexes having the hydroxido-bridged core by the reactions of dichloridocobalt(II) complex ([$Co^{II}Cl_2$(bbpma)]) in pH 9 ~ 11 aqueous solution, by inducing chlorido ligand dissociation.
Keywords : dinuclear complex, electrochemical behaviors, spectrochemical properties

多核遷移金属錯体は、中心金属や配位子の種類や架橋構造により複数の電子構造を取り、多電子移動反応が可能であることから、物質変換反応場として期待される。これまでに、メタノール中における酢酸コバルト四水和物とベンジルビス（2-ピリジルメチル）アミン（bbpma）の物質量比 3:2 での反応を行い、2 つのメトキシドと 1 つのアセタトが三重に架橋した Co(III)-Co(II)-Co(III)の三核錯体（[**1**]$(PF_6)_2$）を得た [1)]。

本研究では、フレームワークの異なる二核錯体を創製するため、同じ原料において物質量比 1:1 の反応をメタノールや水中で行い、コバルト二核錯体の合成を検討した（スキーム (i), (ii)）。メタノール中では、$[\mathbf{1}]^{2+}$と類似骨格の二核錯体は生成せず、[**1**]$(PF_6)_2$ を得た。水中では、2 つのアセタトと 1 つのオキシドにより三重に架橋した二核錯体の単離が示唆された。また、bbpma を有するジクロリドコバルト(II)錯体[$Co^{II}Cl_2$(bbpma)]の pH 9 ~ 11 の水溶液中での反応により、ヒドロキシド架橋構造を有する二核錯体の合成についても検討した。



スキーム． Co^{2+}とbbpmaの反応

1) 伊東、三澤、長尾 第 103 回日本化学会春季年会 P1-1am-10。

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三座アブノーマル NHC 配位子を有する Pd(II)錯体の合成と性質

（名工大院工[1]）○渡邉 愛[1]・柳生 剛義[1]

Synthesis and Characterization of Tridentate Abnormal NHC Pd(II) Complexes([1]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Ai Watanabe,[1] Takeyoshi Yagyu[1]

Pd complexes have shown high catalytic performance in organic synthesis, and complexes with *N*-heterocyclic carbene (NHC) ligands, which bind strongly to the metal center, have attracted much attention. Although NHC ligands usually coordinate to the metal center at C2 carbons, abnormal NHC complexes that are coordinated at C4 and C5 carbons with stronger electron-donating properties have also been reported. But there are a few reports of abnormal NHC complexes and the details of their catalytic activity have not been clarified.

In this laboratory, we have synthesized Pd(II) complexes with a tridentate abnormal NHC ligands, which are highly stable and active due to the chelating effect, and investigated various catalytic reactions. In this study, we synthesized new Pd(II) abnormal NHC complexes with extended chelate rings and investigated their catalytic abilities in order to clarify the steric and electronic effects.

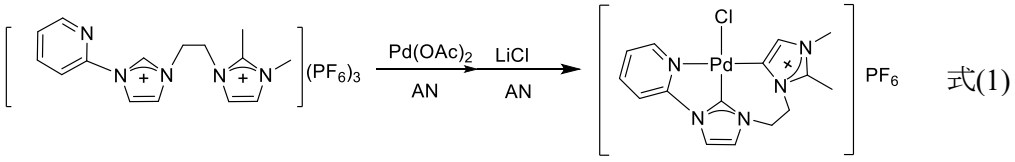
Tridentate Abnormal NHC complexes with terminal pyridyl group were synthesized using the corresponding ligand precursor and palladium(II) acetate, as shown in equation (1).

Keywords : Palladium complex; Abnormal NHC

Pd 錯体は有機合成において高い触媒性能を示しており、その中でも中心金属と強く結合する *N*-ヘテロ環カルベン(NHC)を配位子とする錯体が注目されている。NHC は通常 C2 炭素を介して金属中心に配位するが、より強い電子供与性を持つ C4 及び C5 炭素を介して配位するアブノーマル型 NHC 錯体も報告されている。このようなアブノーマル型 NHC 錯体の合成例は少なく、触媒活性への影響の詳細は明らかになっていない。

本研究室では、キレート効果により高い安定性と反応活性を兼ね備えた三座アブノーマル NHC 配位子を有する Pd(II)錯体を合成し、種々の触媒反応を検討している。本研究では、三座アブノーマル型 NHC 錯体の更なる立体的及び電子的効果の検討のために、キレート環を拡張した新規 Pd(II)錯体を合成し、その触媒能を評価することを目的とした。

ピリジル基を末端に有する三座アブノーマル型 NHC 錯体は、式(1)に示すように、対応する配位子前駆体と酢酸パラジウム(II)を用いて合成した。



式(1)

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2 つのビスイミノピロール部位からなる環状配位子を有するルテニウム錯体の合成

（上智大理工[1]・阪大院理[2]）○安江 華鈴[1]・三澤 智世[1]・舩橋 靖博[2]・長尾 宏隆[1]

Syntheses of ruthenium complexes bearing a macrocyclic ligand consisting of two bis(imino)pyrrole units ([1]*Fac. of Sci. and Tech., Sophia Univ.*, [2]*Osaka Univ.*) ○Karin Yasue,[1] Tomoyo Misawa,[1] Yasuhiro Funahashi,[2] Hirotaka Nagao[1]

A macrocyclic ligand ($H_2^{Et}L_{Pr}$; Figure) having two bis(imino)pyrrole units, that function as multiple coordination sites of *N*-donors, forms a dinuclear complex. Dinuclear metal complexes bearing $H_2^{Et}L_{Pr}$ are expected to give new insights into the metal-metal interactions. In this work, we studied the syntheses of ruthenium complexes using $Ru^{III}Cl_3 \cdot nH_2O$, Ru-Blue solution, $[RuCl_2(dmso)_4]$, or $K_2[RuX_5(NO)]$ (X = Cl, I) as starting complexes. In a reaction of $H_2^{Et}L_{Pr}$ and $[RuCl_2(dmso)_4]$ in acetone under refluxing conditions, absorption bands at 365 and 440 nm were observed by UV-vis spectroscopy, indicating the formation of a new complex. A reaction product obtained by a reaction using Ru-Blue solution in the presence of hydrochloric acid showed redox waves at 0.41 and -0.57 V, which were attributed to the redox of the Ru complex. We will also report synthetic reactions and characterization of products by spectroscopic and electrochemical methods.

Keywords : macrocyclic ligand; multinuclear complex; bis(imino)pyrrole

2 つのビスイミノピロール部位を有する環状配位子（$H_2^{Et}L_{Pr}$; Figure）は、環内の大きな空間に 6 つの窒素ドナー部位が存在するため、二核錯体の形成が期待される。2 つの金属間距離が制限された二核錯体について、金属間相互作用に関する知見が得られる。

本研究では、原料として三塩化ルテニウム、Ru-Blue 溶液、$[Ru^{II}Cl_2(dmso)_4]$、$K_2[RuX_5(NO)]$ (X = Cl, I)を用い、ルテニウム錯体の合成について検討した。$H_2^{Et}L_{Pr}$ と $[Ru^{II}Cl_2(dmso)_4]$の反応では、アセトン中で加熱還流をすることにより吸収スペクトルで 365 と 440 nm に吸収帯が観測され、錯体生成が進行していることを確認した。Ru-Blue 溶液との反応において、塩酸を加えた条件下で得られた生成物は、電気化学的測定により 0.41 と-0.57 V にルテニウム中心の酸化還元と考えられる酸化還元波が観測された。さらに、他の原料との反応および生成したルテニウム錯体の分光学的、電気化学的性質についても報告する。

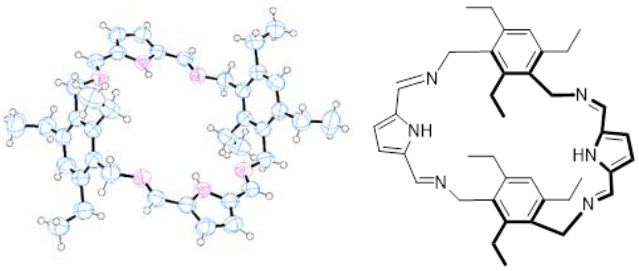

Figure　Cyclodi(*N*-dimethyl-1,3,5-triethylphenyl-2,5-bismethyliminopyrrole) ($H_2^{Et}L_{Pr}$)

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柔軟なペプチド異種環状金属錯体の選択的形成における多核化の影響

（お茶大理）○長谷川　遥香・三宅　亮介

Effect of multinuclear structures on the selective formation of heterometallic cyclic complexes using flexible tripeptides

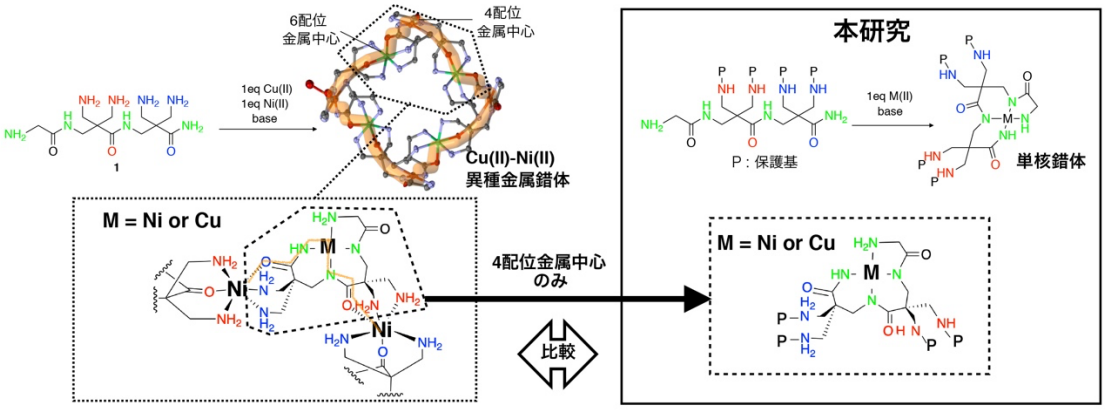
（*Ochanomizu University*）○Haruka Hasegawa, Ryosuke Miyake

We previously reported a flexible tripeptide **1**, which formed cyclic complexes possess two kinds of metal center (square-planar and octahedral) connected through its amide groups[1]. The tripeptide selectively forms heterometallic cyclic metal complexes caused by selective coordinaiton at the square planar center[2]. Herein, we discuss the effect of multinuclear structures on this selective formation of the heterometallic complexes by comparison with mononuclear complexes possessing square-planar metal center.

Keywords : multinuclear structures, selective formation, metal complex of flexible peptide

我々は、柔軟なトリペプチド **1** を用いれば、平面４配位と八面体６配位の金属中心がアミド基を介して交互に連結した環状錯体を合成できることを報告した（図左）[1]。この錯体では、柔軟な骨格を用いているにも関わらず、金属イオンの混合比によらずCu(II)-Ni(II)異種金属錯体が選択的に形成できる [2]。これは、Cu(II)イオンの平面４配位金属中心への選択的結合に起因していた。本研究では、これら異種金属錯体の選択的形成の要因を詳細に調べるため、平面４配位金属中心のみを持つ単核錯体を新規合成し、選択的形成における多核構造の影響について検討を行った。

まず、**1** の八面体６配位を形成する部分のみを保護した配位子を設計・合成し、その錯体形成挙動を調べた。UV-Vis スペクトル測定や Mass 測定から異種金属錯体の平面４配位中心と類似の構造を持つ単核錯体の形成が示唆された（図右）。一方、金属イオンの当量によっては、構造の異なる単核錯体の形成も示唆され、環状に連結することで形成可能な金属錯体を制限している可能性が明らかになった。



図：柔軟なペプチド **1** の Cu(II)-Ni(II)異種金属錯体と
本研究で合成した平面４配位金属中心のみを持つ単核金属錯体

1) Miyake, R.; Ando, A.; Ueno, M.; Muraoka, T. *J. Am. Chem. Soc.* **2019**, *141*, 8675-8679.
2) Miyake, R; Suganuma, E.; Kimura, S.; Mori, H.; Okabayashi, J.; Kusamoto, T. *Angew. Chem. Int. Ed.* **2021**, *60,* 5179-5183.

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トリメシン酸誘導体を配位子とする金属錯体菱形十二面体の合成

（京大工[1]・京大院工[2]・京大 iCeMS[3]）○吉田 亮平[1,3]・徳田 駿[2,3]・宮田 彩名[2,3]・古川 修平[2,3]

Synthesis of metal-organic rhombic dodecahedra with trimesic acid derivatives

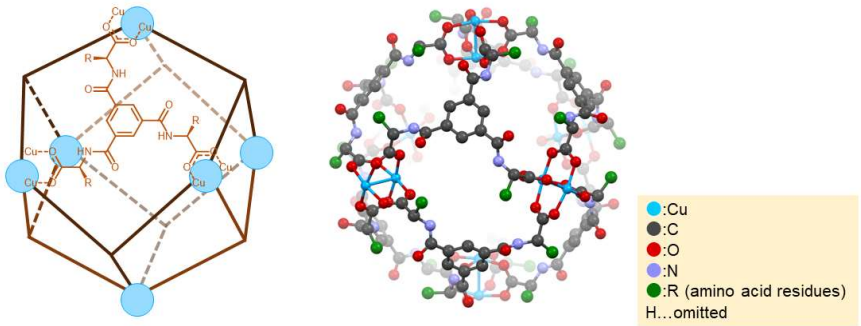
([1]*Undergraduate School of Engineering,* [2]*Graduate School of Engineering,* [3]*Institute for Integrated Cell-Material Sciences, Kyoto University*) ○Ryohei Yoshida[1,3], Shun Tokuda[2,3], Ayana Miyata[2,3], Shuhei Furukawa[2,3]

Metal-organic polyhedra (MOPs) assembled from metal ions and bidentate organic ligands have been widely investigated, thanks to their structural designability and potential microporosity. The synthesis of MOPs with tridentate ligands is still challenging due to the structural complexity. Here, we synthesized novel MOPs based on trimesic acid derivatives. The tridentate ligands were prepared by the condensation reaction between trimesoyl chloride and various L-amino acids and further reacted with copper(II) ions, leading to the formation of a series of novel MOPs. Single-crystal X-ray diffraction analysis determined the rhombic dodecahedral topology composed of six dicopper(II) paddlewheels linked with eight tricarboxylate ligands. We found that the size and shape of the pore window of the MOPs are readily altered by the choice of amino acid residues on the MOP surface. This result suggests the high potential of the rhombic dodecahedral MOP family as a new porous materials platform.

Keywords : metal-organic polyhedra; porous materials

金属錯体多面体（MOPs）は中空かご状の分子であり、多孔性材料の構成要素として注目されている。この MOPs の分子表面の修飾や幾何構造の制御は、使用される配位子設計を工夫することで実現できる。二座配位子を用いた MOPs の合成は数多く報告されている一方で、三座以上の配位点を持つ多座配位子は、異なる多くの MOP 構造を取りうるため積極的に利用されていない。

本研究では、トリメシン酸クロリドと種々の L-アミノ酸との縮合反応により合成される三座配位子と銅イオンとを反応させることで、新規の MOPs を合成した。単結晶 X 線構造解析により、これらの MOPs は 6 つの銅パドルウィール構造と 8 つの三座配位子からなる菱形十二面体構造を形成していることを確認した（下図）。加えて、MOP 表面に導入されるアミノ酸側鎖の違いが細孔窓サイズに大きな影響を与えることが明らかになった。この新規 MOP 群は、ゲスト分子拡散機能を調整可能な新しい多孔性材料のプラットフォームとなりうる。



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金属及び有機配位子の両方が水素化された Ru(II)錯体に及ぼす軸配位子の影響

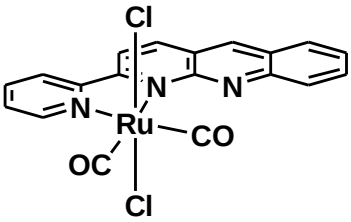
（福島大院理工）○森原 麻斗・伊藤 敬哉・高瀬 つぎ子・大山 大
Effects of axial ligand on Ru(II) complexes with both hydrogenated metal and organic ligand (*Graduate School of Science and Engineering, Fukushima University*) ○Asato Morihara, Keiya Ito, Tsugiko Takase, Dai Oyama

We have reported the synthesis and reactivity of a Ru(II) complex in which both the metal and organic ligand were hydrogenated. However, it is unclear regarding the effect of axial ligands on reactivities of the complex. To elucidate influences of axial ligands on hydrogenation, we synthesized a new complex with tricyclohexylphosphine (PCy_3) as axial ligands and compared some properties with those of the reported complex.

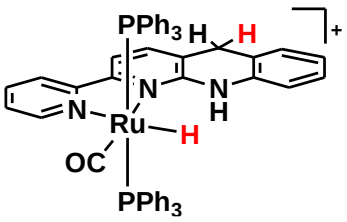
Keywords : Ruthenium Hydride complex Phosphine Axial ligand Crystal structure

我々は，金属および有機配位子の両方が水素化された Ru(II)錯体の合成および反応性について報告した [1]。しかし，錯体の反応性に及ぼす軸配位子の影響は明らかになっていない。軸配位子が水素化反応に及ぼす影響を明らかにするため，本研究ではトリシクロヘキシルホスフィン(PCy_3)を軸配位子とする新規錯体を合成し，既報のトリフェニルホスフィン(PPh_3)錯体との間で構造や反応性を比較した。

下に示す既報ヒドリド錯体(PPh_3 錯体)の合成とは異なり [1]，ギ酸ナトリウムを用いて Cl 錯体から一段階の反応で PCy_3 を軸配位子とする新規ヒドリド錯体の合成に成功した。得られた新規錯体について，分光測定(MS, IR, ^{1}H NMR)および X 線構造解析(**図 1**)により分析を行い，既報錯体の各データと比較した。Ru–H 結合長に有意な差は見られなかったが(PCy_3 錯体: 1.39(8) Å, PPh_3 錯体: 1.39(3) Å), ^{1}H NMR 測定ではルテニウムに結合したヒドリド由来のシグナルが高磁場側に観測された(PCy_3 錯体: –12.9 ppm, PPh_3 錯体: –11.8 ppm)。また, IR 測定における CO 伸縮振動は PCy_3 錯体において 1926 cm^{-1} に観測され，PPh_3 錯体と比較して約 25 cm^{-1} 低波数シフトした。これらの結果は，軸配位子の変更により中心金属の電子密度が上昇していることを示しており，PPh_3 錯体と比較して Ru–H 部位の反応性は向上していると考えられる。



Cl 錯体
$[Ru(paa)(CO)_2Cl_2]$



既報ヒドリド錯体
$[Ru(paaHH)(CO)(H)(PPh_3)_2]^+$

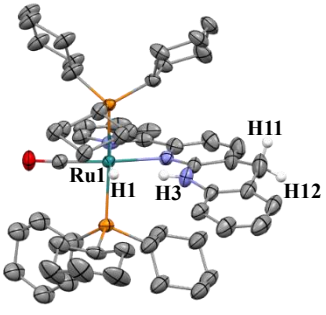


図 1. 新規ヒドリド錯体の結晶構造.

1) 伊藤ほか，錯体化学会第 68 回討論会, 2PA-009 (2018).

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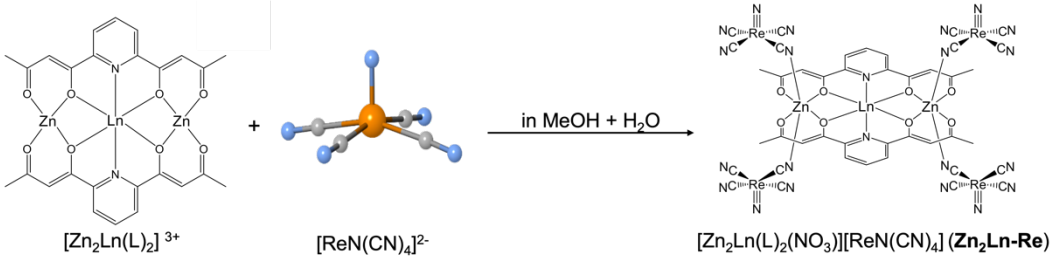
複数の発光中心を組み込んだ三元金属 MOF の開発

（九大院理 [1]）周堯 [1]・ルウェ バンジャマン [1]・大谷 亮 [1]・大場 正昭 [1]
Development of Ternary Metallic MOFs Incorporating Multiple Luminescent Centers (*Graduate School of Chemistry, Kyushu University*) Zhou Yao[1], Benjamin Le Ouay[1], Ryo Ohtani[1], Masaaki Ohba

In Metal-organic frameworks (MOFs) incorporated multiple luminescent centers, a wide range of luminescence color changes is expected; eg. guest-dependent changes in the intensity of one of the two emissions. We have symthesized MOFs with two emission centers by combining the luminescent $[ReN(CN)_4]^{2-}$, lanthanide ions and 1,10-phenanthroline as an antenna ligand. However, dual emission (DE) at room temperature could not be achieved in this system because of energy transfer between Re(V) and Ln(III). In order to suppress the energy transfer, we designed new ternary metallic MOFs consisting of a trinuclear complex with diamagnetic Zn(II) and Ln(III) (Zn_2Ln) and $[ReN(CN)_4]^{2-}$. In this system, $[ReN(CN)_4]^{2-}$ forms a network with coordinating to Zn(II) centers, which prevents the formation of bridges between Ln(III) and Re(V) and and surpresses the energy transfer. Currently, systematic synthesis of the MOF is carrying out using $[ReN(CN)_4]^{2-}$ and an analogue $[MnN(CN)_4]^{2-}$ with Zn_2Ln (Ln= Eu, Dy, Tb), in order to achieving DE and guest-responsive luminescence changes.
Keywords : Metal Organic Frameworks , Dual Emission, Luminescenc, Energy Transfer.

二種類の発光中心を組み込んだ MOF においては、二つの発光のうちの一方の発光強度がゲストに応じて変化することで、幅広い発光色変化が期待できる。当研究室では、発光性の $[Re^{V}N(CN)_4]^{2-}$ とランタノイドイオンを組合せて、1,10-phenanthroline をアンテナ配位子として導入することで、二つの発光中心を有する MOF を合成した。しかし、この系では発光中心間のエネルギー移動により、室温での Dual emission (DE) は達成できなかった。そこで本研究では、エネルギー移動を抑制するために、反磁性の Zn(II) と Ln(III) による三核錯体 (Zn_2Ln)[1)] と $[ReN(CN)_4]^{2-}$ を集積した三元金属 MOF を発案した。$[ReN(CN)_4]^{2-}$ と Zn(II) に結合させることでネットワークを形成するとともに、発光中心である Ln(III) と Re(V) 間の架橋形成を妨げてエネルギー移動を抑制し、DE およびゲスト応答的発光特性変化を示す MOF の合成を目指している。

現在は、$[ReN(CN)_4]^{2-}$ および類縁体 $[MnN(CN)_4]^{2-}$ を用いて、Zn_2Ln (Ln = Eu, Dy, Tb) との集積化、ならびに構造と発光特性の評価を進めている。



1) T. Shiga, M. Ohba, et al., *Inorg. Chem.,* **2004**, 43, 4435-4446

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ピリジルチアゾール配位子を含む新規白金(II)錯体における結晶多形と固体発光特性

(兵庫県立大院理[1]) ○橋本　廉[1]・中村瞭汰[1]・小澤芳樹[1]・阿部正明[1]

Structures and Solid-State Photoluminescence of Novel Polymorphic Platinum(II) Complexes Containing a Pyridylthiazole Ligand ([1] *Graduate School of Science, University of Hyogo*) ○Ren Hashimoto,[1] Ryota Nakamura,[1] Yoshiki Ozawa,[1] Masaaki Abe[1]

2,2'-Pyridylthiazole derivatives, which are potentially redox-active and photoluminescent, potentially form coordination compounds with transition-metal ions in a bidentate chelating mode and may also yield network structures in the solid state assisted by various intermolecular interactions. In our earlier study, we have systematically synthesized transition-metal complexes and network structures using the ligand ppt, one of the pyridylthiazole derivatives, and shown the solid-state photoluminescence (PL) tuned by external stimuli such as temperature, pressure, vapors, and mechanical grinding. Herein we have synthesized and characterized a new derivative, a mononuclear Pt(II) complex with ppt *cis*-[Pt(ppt)Cl_2] (**1**) (Fig. 1). This presentation will address the synthesis, structures of the polymorphic crystals, phase-transition behavior between the polymorphs and amorphous, and the thermochromic PL behavior including the determination of the PL lifetimes and quantum yields.

Keywords：Platinum(II) complex; Pyridylthiazole; Solid-state photoluminescence; Polymorph; Network structure

2,2’-ピリジルチアゾール誘導体[1)]は、レドックス活性能と発光特性を併せ持つ二座キレート配位子として機能するとともに、チアゾール環 S 原子および π 共役系芳香環を起点とした分子間相互作用により集積型ネットワーク錯体の構築が期待される化合物である。我々は先に、チアゾール環 4 位にフェニル基を導入した配位子 ppt を用いて遷移金属錯体の合成を系統的に行い、それらを単位とした発光性ネットワーク結晶を作製するとともに、その固体発光挙動における温度、超高圧、有機溶媒蒸気、すりつぶし等の外部刺激応答性について検討を進めてきた。本研究では新たに、単核 Pt(II)錯体 *cis*-[Pt(ppt)Cl_2] (**1**) (Fig. 1) を合成し、その結晶構造と固体発光特性について検討した。本発表では、錯体 **1** の再結晶法による多形作製とその構造解析、多形―アモルファス間のすりつぶし-蒸気曝露による相転移挙動、さらに固体発光スペクトルと発光寿命・発光量子収率などの固体発光特性に見られる多形依存性について報告する。

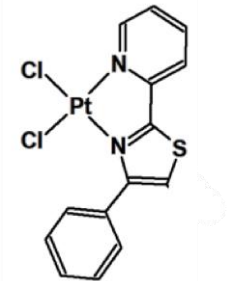

Fig. 1. 錯体**1**の構造

1) T. Murai et al., *J. Org. Chem.* **2015**, *80*, 10742-10756.

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バナジウムおよびクロムを用いた異種二核窒素錯体の構造と反応性

（東工大 ZC 研[1]・愛工大院工[2]）○小久保 佳亮[1]・梶田 裕二[2]
Structures and Reactivity of Heterogeneous Dinuclear Dinitrogen Complexes using Vanadium and Chromium Ions ([1]*Laboratory for Zero-Carbon Energy, Tokyo Institute of Technology*, [2]*Graduate School of Engineering, Aichi Institute of Technology*) ○Yoshiaki Kokubo,[1] Yuji Kajita[2]

To investigate effect of metal center in regards to protonation of dinitrogen complex, we have synthesized two heterodinuclear dinitrogen complexes bearing triamidoamine ligands which have same structure each ([MK(L^{Cy2})(N_2)(18-crown-6)(THF)], M = V, Cr). We will report the structures and reactivity in detail.
Keywords : Vanadium; Chromium; Dinitrogen Fixation; Triamidoamine Ligand

近年、多くの窒素錯体が報告されており、その反応性も検討されてきた。しかし、金属中心を変えて同様の配位子を用いても構造が異なることが多く、反応性の違いを単純に金属中心の違いとするのは難しい。我々は、以前より tren 骨格を有する配位子を用いて異種二核バナジウム窒素錯体の合成に成功している。今回、同様の配位子を用いて同様の構造を持つ異種二核クロム窒素錯体の合成に成功し、金属中心が異なる窒素錯体の構造と反応性の違いを検討した。

今回、ジシクロヘキシルメチル基を置換基として持つトリアミドアミン配位子を合成し (**L^{Cy2}**)、窒素雰囲気下で $CrCl_3$、金属カリウムおよび 18-crowon-6-ether を反応させることによって異種二核クロム窒素錯体([CrK(**L^{Cy2}**)(N_2)(18-crown-6)(THF)]) (Cr 錯体)の合成に成功した。この Cr 錯体は単結晶 X 線結晶構造解析により同定した。

今回、合成した Cr 錯体は、異種二核バナジウム窒素錯体([VK(**L^{Cy2}**)(N_2)(18-crown-6)(THF)]) (V 錯体)と同様の構造を持っていた。Cr 錯体の N≡N の結合長は 1.160(3) Å で V 錯体 (1.152(3) Å) と比べると伸長しており、逆に Cr—N_2 の結合長は 1.761(2) Å であり V 錯体 (V—N_2: 1.853(3) Å) と比べると短くなっていた。

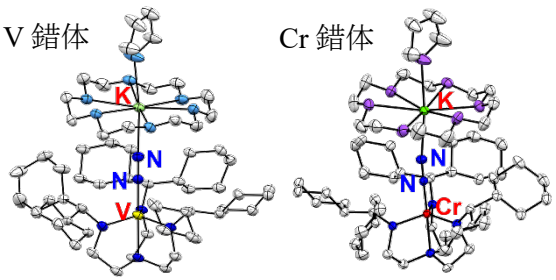

図. 窒素錯体の結晶構造

次に架橋窒素のプロトン化を窒素雰囲気下で行ったところ、V 錯体は、アンモニアが 80 % / V 得られておりヒドラジンも 7 % / V 検出したが、Cr 錯体の方は、アンモニアが検出できず、ヒドラジンのみ 4.5 % / Cr で得られた。本発表では、これらの錯体の構造と化学的諸性質について詳細に報告する。

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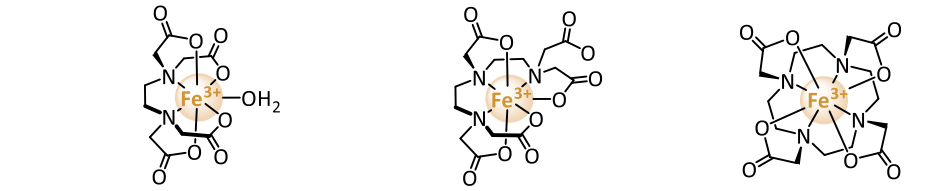
高配位鉄錯体が与えるレドックスフロー電池性能への影響

（早大先進理工）○児玉創志・岡澤 厚・川合航右、大久保將史
Effect of Highly-Coordinated Iron Complex on Redox Flow Battery Performance (*School of Advanced Science and Engineering, Waseda University*) ○Soshi Kodama, Atsushi Okazawa, Kosuke Kawai, Masashi Okubo

Redox flow batteries (RFBs) have a longer cycle life than other secondary batteries owing to their limited electrode deterioration upon charge/discharge cycling. However, commercial RFBs use vanadium, causing severe disadvantages such as high cost. Although iron-based complexes are a promising catholyte active material for RFBs in terms of cost, elemental abundance and environmental-friendliness, the formation of ferric hydroxides in aqueous media during charge/discharge should be suppressed, for example, by stabilizing the complex structure with a chelating effect. In this study, we improved the stability of iron complexes by controlling the coordination number of chelating ligands. With a DOTA iron complex of an 8-coordinated structure, we successfully achieved a higher redox potential than that of a DTPA one. The solubility and charge-discharge properties of the DOTA complex will also be discussed.

レドックスフロー電池（RFB）は酸化還元能を有する活物質が電気化学セル外のタンクに貯蔵され、リチウムイオン電池と比較してメンテナンス性に優れた蓄電デバイスである。しかし、商用の RFB は高コストで稀少なバナジウムを使用しているため、再生可能エネルギーの電力を平準化する定置用大型電池としての普及を妨げている。従って、安価で資源豊富な鉄錯体を活物質として使用した水系 RFB を開発することが喫緊の課題である。そのためには水酸化鉄を経由する鉄錯体の分解反応を抑制する必要があり、キレート配位子を活用した分子設計が不可欠である。本研究では、キレート配位子の配位数を制御し、鉄錯体の安定性を改善することを目指した。具体的には、8 配位構造を持つ DOTA 鉄錯体を用いて、7 配位 DTPA 鉄よりも高いレドックス電位を得た。当日はこれらの物質の溶解度や充放電特性についても議論する。



1) S. E. Waters, B. H. Robb, M. P. Marshak, *ACS Energy Lett.* **2020**, *5*, 1758.

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キャスト法による[NPr_4][$MnCr(C_2O_4)_3$] MOF 配向膜の作製

（東理大院理[1]）○舟橋　友紀[1]・張　啓原[1]・原口　知之[1]

Fabrication of two-dimensional oriented thin film [NPr_4][$MnCr(C_2O_4)_3$] by casting method

([1]*Graduate School of Science, Tokyo University of Science*) ○Yuki Funahashi[1], Qiyuan Zhang[1], Tomoyuki Haraguchi[1]

Recently, highly oriented crystalline thin films of Metal-Organic Frameworks (MOFs) have been intensively desired, which are expected to be applied as functional devices such as gas sensors and electrode materials. We have already succeeded in fabricating oriented crystalline MOF thin films by casting method using a colloidal solution of charge-neutral MOF nanosheets.[1)] In this study, we fabricated [NPr_4][$MnCr(C_2O_4)_3$] thin film on a substrate using the casting method. First, we synthesized [NPr_4][$MnCr(C_2O_4)_3$] MOF nanosheets with reference to a previous report.[2)] Next, we fabricated 2D MOF thin film on a substrate using the casting method. High crystallinity and orientation of the films were confirmed by X-ray diffraction measurements in both parallel (in-plane) and vertical (out-of-plane) directions to the substrate.

Keywords : interface; thin film; Metal-Organic Frameworks

近年、多孔性配位高分子(MOF)薄膜はセンサーや電極材料への応用が期待され盛んに研究されている。我々は、電荷中性の MOF ナノシートのキャスト法による MOF 配向膜の構築に既に成功しているが、本研究ではアニオン性フレームワークを有する MOF である [NPr_4][$MnCr(C_2O_4)_3$]を用いてキャスト法による MOF 配向膜の構築と評価を行った。まず、既法[2)]を参考に[NPr_4][$MnCr(C_2O_4)_3$]のナノシートを合成し、次に[NPr_4][$MnCr(C_2O_4)_3$]のコロイド溶液を用いてキャスト法により薄膜を作製した。Fig1. に示すように X 線回折(XRD)測定を行ったところ、Out-of -Plane 方向(基盤垂直方向、図左)ではレイヤー間の周期構造由来の(00*l*)の回折ピークのみが、In-plane(基盤水平方向、図右)ではレイヤー内の周期構造由来の(*hk*0)の回折ピークのみが観測され、薄膜が高い配向性を示すことが明らかになった。

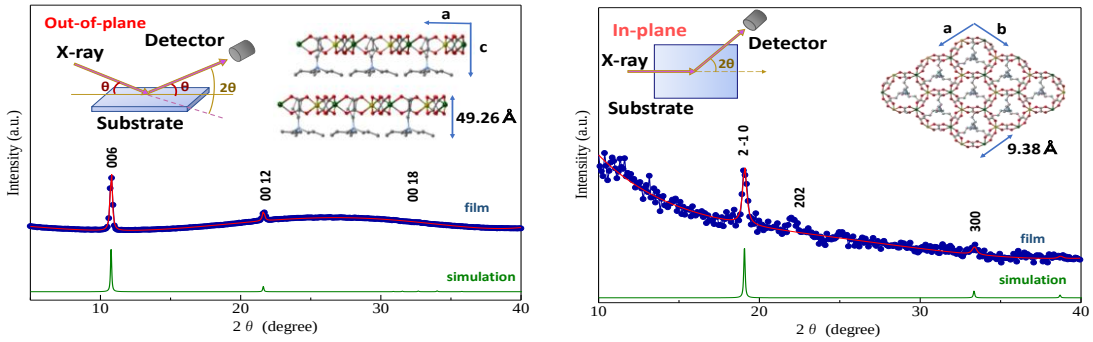

Fig1. XRD patterns of thin film : (Left) out-of-plane, (Right) in-plane

1) T. Haraguchi, et al., *The 72nd Conference of JSCC,* **3A-06** (2020).
2) Rene Pellaux et al., *Inorganic Chemistry*, 1997, 36, 2301-2308

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Synthesis and magnetic properties of cyano-bridged Fe^{II}-W^{IV} complex incorporated three-types of organic ligands

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○D. Kobayashi [1], S. Nagashima [1], J. Wang [1], S. Ohkoshi [2], H. Tokoro [1]

Keywords: Molecule-based magnets, spin crossover, cyanide complex

Introduction : Molecule-based magnets constitute an intriguing category of magnetic materials that can demonstrate various magnetic functionalities through the selection of metal ions, coordinated ligands, and other factors.[1] In this study, we synthesized a new cyanide-bridged Fe^{II}-W^{IV} complex incorporating three types of organic ligands, $[Fe^{II}(4\text{-chloropyridine})_{1.5}(4\text{-iodopyridine})_{1.5}(\text{pyrazole})]_2$-$[W^{IV}(CN)_8]$ (**FeW**) and investigated its crystal structure and magnetic properties.

Experiment : Target crystals were prepared by slow diffusion of $FeCl_2 \cdot 4H_2O$ (0.2 mmol), 4-chloropyridine hydrochloride (1.0 mmol), 4-iodopyridine (1.0 mmol) and pyrazole (1.0 mmol) aqueous solution into $K_4[W(CN)_8] \cdot 2H_2O$ (0.5 mmol) aqueous solution at room temperature for a week. The crystal structure was determined by single-crystal X-ray diffraction analysis. The physical properties were evaluated using infrared and UV-Vis spectroscopy. Magnetic properties were measured using a SQUID magnetometer.

Result : Single-crystal structural analysis revealed that **FeW** belongs to a tetragonal system (space group: $I4_122$) with a three-dimensional network structure of Fe and W connected by groups (Fig. 1a). Each Fe^{II} additionally coordinates to four organic ligands, randomly occupied by cyanide the mentioned three different types, which are statistically in the proportions of 1.5 4-iodopyridine, 1.5 4-chloropyridine and 1 pyrazole. In the IR spectrum, a peak due to the CN stretching mode of Fe^{II}-NC-W^{IV} was observed at 2118 cm^{-1}. From UV-vis spectrum, a peak due to the d-d transition of W was observed around 400 nm. The $\chi_M T$-T plot shows a value of 7.4 K cm^3 mol^{-1} at 300 K, which is in good agreement with the calculated spin-only value of 7.3 K cm^3 mol^{-1} considering Fe^{II}_{HS} (S = 2) and W^{IV} (S = 0) (Fig. 1b). As the temperature is lowered, the $\chi_M T$ value begin to decrease from around 170 K, reaching 5.1 K cm^3 mol^{-1} at 40 K. This is due to the spin crossover of Fe^{II}, suggesting that 30 % of the Fe^{II} high-spin state changed to the low-spin state Fe^{II}_{LS} (S = 0).

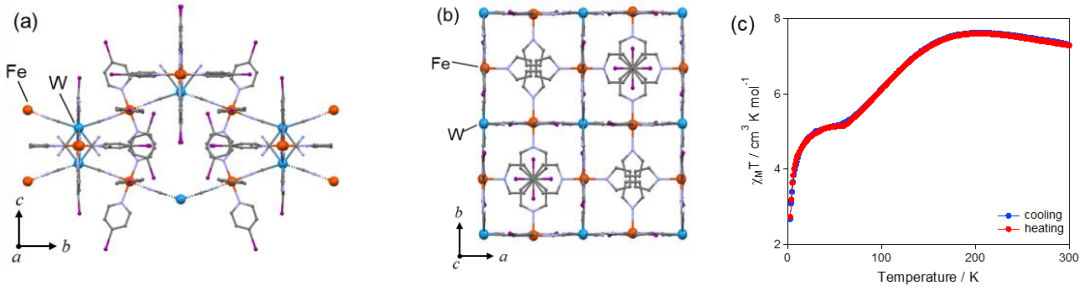

Figure 1. (a)crystal structure of **FeW** view along the *a* axis. (b) crystal structure of **FeW** view along the *c* axis. (c)$\chi_M T$-T plots of **FeW** under 5000 Oe.

Reference :1) S. Ohkoshi, A, Namai, H. Tokoro, *Coord. Chem. Rev.*, **2019**, 380, 572.

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Pt(II)Pd(II)錯体混合結晶における混合比による発光励起状態制御

(関学大院理工[1]・関学大生命環境[2])○瀬川 海斗[1]・吉田 将己[2]・加藤 昌子[2]

Control of Emission Excited States of Mixed Crystals of Platinum(II)/Palladium(II) Complexes by Mixing Ratio ([1]*Kwansei Gakuin Univ. Graduate school of Science and Technology.*, [2]*Kwansei Gakuin Univ. School of Biological and Environmental Sciences.*)○Kaito Segawa[1], Masaki Yoshida[2], Masako Kato[2]

Square-planar Pt(II) and Pd(II) complexes exhibit characteristic luminescence by assembly but quite different temperature dependence due to the different metal-metal interactions. In the present study, we have succeeded in changing the luminescence energy of mixed crystals of Pt(II)/Pd(II) complexes by controlling the excited states depending on the mixing ratio. The mixed crystals exhibited emission color changes from dark red (l_{em} = 685 nm) to yellow (l_{em} = 583 nm) depending on the Pt(II)/Pd(II) mixing ratio. The emissive excited states of mixed crystals are discussed on the basis of the variable temperature measurement.

Keywords: Cyclometalated Pt(II), Pd(II) complexes, Co-crystal, Metal-Metal interactions, Excited states, Luminescence

平面四配位型 Pt(II)錯体は集積により Pt 間相互作用に基づく特異な吸収・発光を示すことができ、温度に依存して励起の非局在化状態が変化する[1)]。一方で、Pd(II)錯体は、Pt(II)錯体と同形の結晶構造を形成しても励起状態による温度依存性が見られなかった[2)]。本研究では、温度依存性の異なる Pt(II), Pd(II)錯体を混合結晶化することにより、混合比によって発光エネルギーを変化させることに成功した。

K[Pt(CN)$_2$(dFppy)]および K[Pd(CN)$_2$(dFppy)] (dFppy = 4,6-difluorophenylpyridinate)を各比率で acetonitrile に加熱溶解させ、自然冷却することで針状結晶を得た。これらの Pt/Pd 混合結晶は混合比率に応じて 1/0.5 の暗赤色(λ_{em} = 685 nm)から 1/13 の黄色(λ_{em} = 583 nm)まで発光色が変化した。さらに、室温では単一成分の減衰曲線を持つ発光であったが、77 K では 3 成分の発光ピークに分裂した。各成分は、異なる Pt/Pd 集積ドメインの励起状態に由来していると考えられる。当日は発光スペクトルの温度変化挙動に基づいて Pt/Pd 混合結晶の発光励起状態について議論を行う。

1) S. Sakaki *et al., J. Phys. Chem. C*, **2020**, *124*, 10453.
2) T. Saito et. al, The 71st JSCC Conference, **2021**, 4Ab-05.

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2,3’－ビピリジンを有する白金錯体の合成と物性

（城西大理[1]・産総研[2]）○橋本 雅司[1]・竹本 和司[1]・今野 英雄[2]
Synthesis and Properties of Platinum Complexes with 2,3'-Bipyridine ([1]*Faculty of Science, Josai University*, [2]*National Institute of Advanced Industrial Science and Technology*)
○Masashi Hashimoto,[1] Kazushi Takemoto,[1] Hideo Konno[2]

The cyclometalated platinum(II) complex with a 2,3′-bipyridine ligand is difficult to synthesize using the general method because the 2,3′-bipyridine ligand has two coordination sites.We demonstrate a new synthetic strategy for the construction of platinum complexes with a 2,3′-bipyridine ligand by selective oxidation and reduction at 3' position nitrogen on the ligand.We synthesized the platinum complexes with a 2,3-bipyridine ligand. The platinum complexe with 2,3’-bipyridine ligand wes showed blue phosphorescence in dichloromethane solution, with an emission maximum at 462 nm.
Keywords : Platinium; Luminescent; phosphorescent

無置換の 2,3’-ビピリジンの選択的酸化により３’位の窒素を酸化することで配位サイトをブロックした Nーオキシド配位子を有する白金（Ⅱ）錯体(1)を合成した。その後、1,4-ジヒドロピリジン誘導体存在下での光反応で酸化された３’位の窒素を還元することで無置換 2,3’-ビピリジンを発光性配位子として有する白金（Ⅱ）錯体(2)を合成した。

Nーオキシド錯体(1)とビピリジン錯体(2)のジクロロメタン中の吸収スペクトルと発光スペクトルを Fig. 2 に示した。どちらの錯体も 250~300nm 付近にモル吸光係数の大きい(ε 25000) π-π*性の吸収帯が観測された。また 300~450nm 付近にモル吸光係数の小さい(ε≦5000)吸収帯が観測された。発光スペクトルでは、Nーオキシド錯体(1)は、λmax=566 nm のブロードな黄色発光を示した。一方、錯体(2)は、明確な振動構造を持つλmax=462 nm の青色発光を示した。また、ジクロロメタン中での発光収率は、Nーオキシド錯体(1)では Φ=0.22 錯体(2)では Φ=0.04 であった。

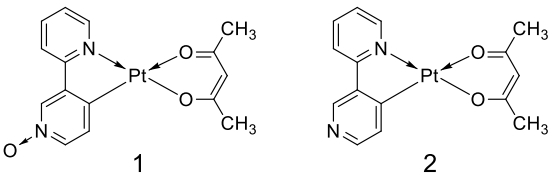

Fig. 1. Structure of Pt(II) complexes

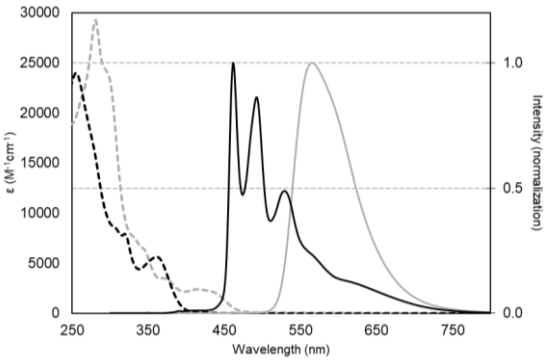

Fig. 2. Absorption and Emission spectra of 1 (▬) and 2 (▬)

Table 1. Optical physics of 1 and 2

	Abs, λ_{max} (in CH_2Cl_2)	Emission (in CH_2Cl_2)	
Complex	λ (nm) {ε($10^{-3}cm^{-1}M^{-1}$)}	λ_{max} (nm)	Φ_{PL}
1	281(29), 348(5.4), 371(2.9), 413(1.9)	566	0.22
2	255(23), 305(8.6), 316(7.7), 364(5.5)	462	0.04

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配位高分子を用いた新規カルシウムイオン伝導体の創出

（東理大 [1]）○江利川 貴大 [1]・貞清 正彰 [1]

Creation of a Novel Calcium Ion Conductor Using a Metal–Organic Framework ([1]*Tokyo University of Science*) ○Takahiro Erikawa,[1] Masaaki Sadakiyo[1]

Metal–organic frameworks (MOFs) are the crystalline porous solids showing various functionalities. In the field of ion-conductive MOFs, proton (H^+) or lithium ion (Li^+)-conductive MOFs have been widely studied. However, multivalent ion-conductive MOFs were rarely reported. We have focused on creation of divalent cation (such as magnesium ion (Mg^{2+}) or calcium ion (Ca^{2+})) conductors with MOFs. We attempted to improve the conductivity of the divalent ions by employing the optimal framework as the ion-conducting pathway. Very high conductivity of around 10^{-3} S cm^{-1} was observed in both magnesium and calcium ion-containing samples.

Keywords : Ionic conductor; Metal–organic framework; Calcium Ion

配位高分子(PCP または MOF)は、金属イオンと有機配位子が自己組織化することで形成される多孔性の結晶性固体である。配位高分子のナノ細孔に電荷担体を導入したイオン伝導体の研究は広く行われているが、我々は二価カチオンに着目して研究を行っている。これまでに先行研究として、MIL-101 を母骨格に用いたマグネシウムイオン(Mg^{2+})含有配位高分子がゲスト分子である MeCN の蒸気存在下で 1.9×10^{-3} S cm^{-1} の超イオン伝導性を示すことが報告され、細孔内の Mg^{2+}に MeCN 分子が配位した化学種が生成することで高イオン伝導性を示すことが示唆されていた [1]。本研究では、先行研究で提唱されていた配位性のイオンキャリアがより伝播しやすいと考えられる母骨格を用いることで、先行研究 [1]を上回る Mg^{2+}伝導体を創出するとともに、細孔内に導入する塩をカルシウムイオン(Ca^{2+})の塩に変更し、Ca^{2+}伝導体の創出を試みた。母骨格として MOF-808 に着目し、既報 [2]に従い合成した MOF-808 に、二価カチオンの塩である $M(TFSI)_2$ (M^{2+} = Mg^{2+}, Ca^{2+}; $TFSI^-$ = Bis(trifluoromethanesulfonyl)imide)を導入した試料 MOF-808⊃$\{M(TFSI)_2\}_x$ を合成した。種々の測定により試料の同定を行い、交流インピーダンス法によりイオン伝導度を測定した (図 1.)。

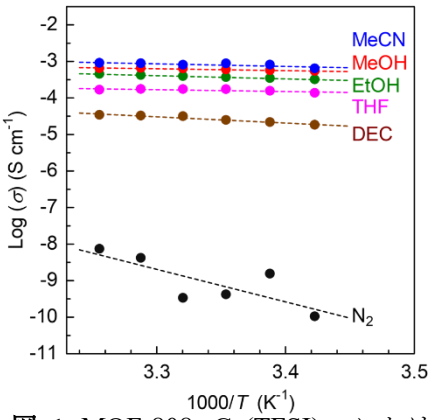

図 1. MOF-808⊃$Ca(TFSI)_{1.4}$ における各種ゲスト分子蒸気圧存在下でのイオン伝導度

Mg^{2+}塩を包接した試料においては先行研究 [1]を凌駕するイオン伝導性を発現し、Ca^{2+}塩を包接した試料においても Mg^{2+}塩を包接した試料と同等の超イオン伝導性を発現することがわかった。イオン伝導度におけるカチオンの寄与を調べるために非ブロッキング電極を用いた直流分極測定を行った結果、いずれの試料においてもカチオンの伝播が確認された。

1) Y. Yoshida, M. Sadakiyo et al., *J. Am. Chem. Soc.* **2022**, *144*, 8669–8675.

2) H. Furukawa et al., *J. Am. Chem. Soc*. **2014**, *136*, 4369–4381.

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二価カチオン含有配位高分子におけるゲスト誘起イオン伝導のカチオン種依存性

（東理大[1]）○谷口 香[1]・貞清 正彰[1]

Dependence of Guest-Induced Ionic Conductivity on Cationic Species in Divalent Ion-Containing Metal–Organic Frameworks ([1] *Tokyo University of Science*) ○Kaori Taniguchi,[1] Masaaki Sadakiyo[1]

Metal–organic frameworks (MOFs) are well known as porous materials, which are formed by self-assembly of metal ions and organic ligands. In recent years, there has been much interest in the development of ionic conductors with its nanospaces as conduction pathways. We have focused on ionic conduction of divalent ions in MOFs. We previously reported that the MOF containing $Mg(TFSI)_2$ ($TFSI^-$ = Bis(trifluoromethanesulfonyl)imide), MIL-101⊃$\{Mg(TFSI)_2\}_x$, shows high ionic conductivity of 1.9×10^{-3} S cm^{-1} at room temperature under the presence of guest vapor (acetonitrile). In this study, we aimed to compare the conductivity and conduction mechanisms of the MOF samples that includes different divalent metal ions (e.g., Ca^{2+}) in MIL-101. We measured ionic conductivity under the controlled partial pressure of guest vapors. As a result, superionic conductivity around 10^{-3} S cm^{-1} was observed in each sample.

Keywords : Ionic Conductor; Metal; Metal–organic framework; Divalent ion

配位高分子(MOF または PCP)は、金属イオンと架橋配位子が自己集積することでできる多孔質の結晶性固体である。近年、配位高分子の細孔をイオン伝導経路として応用した研究開発が盛んに行われている。我々は特に、一般に伝導が困難とされる二価金属イオンの伝導に着目して研究を行っている。先行研究として、MIL-101 と呼ばれる配位高分子の細孔内に $Mg(TFSI)_2$ ($TFSI^-$ = Bis(trifluoromethanesulfonyl)imide)) を導入した試料である、MIL-101⊃$\{Mg(TFSI)_2\}_x$が、特定の有機ゲスト分子の蒸気存在下で高いイオン伝導性を示すことが報告されている[1)]。特に、アセトニトリル蒸気下では室温で最大 1.9×10^{-3} S cm^{-1} の超イオン伝導性が観測されている。本研究では、イオンキャリアを Mg^{2+}から Ca^{2+}等の別の二価の金属イオン種に変化させた際のイオン伝導度評価し、伝導メカニズムの考察を行った。試料の同定は粉末 X 線回折測定、窒素吸着等温線測定及び ICP 発光分析によって行った。イオン伝導度の測定は交流インピーダンス法により、ゲスト蒸気の相対圧を変化させた環境で行った(図 1)。その結果、いずれの試料においても特定のゲスト蒸気下において、室温で最大 10^{-3} S cm^{-1} 程度の超イオン伝導性を示すことが明らかとなった。

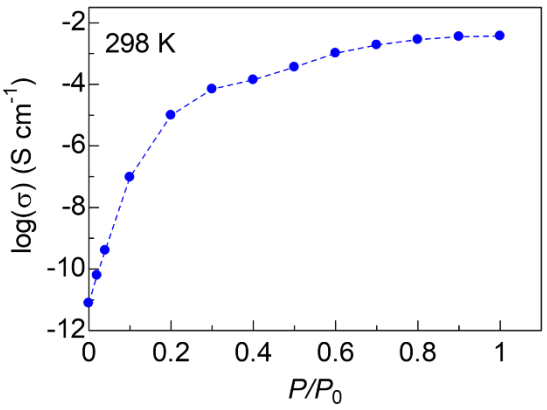

図 1　MIL-101⊃$\{Ca(TFSI)_2\}_x$のイオン伝導度

1) Y. Yoshida, M. Sadakiyo, et al., *J. Am. Chem. Soc.* **2022**, *144*, 8669–8675.

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テルピリジン部位をもつポルフィリンの金属イオンによる自己集合挙動

（日大理工[1]）大月 穣[1]・○阿部 智哉[1]・須川 晃資[1]
Self-Assembly behavior of porphyrins having terpyridine sites induced by metal ions ([1]*College of Science and Technology, Nihon University*) Joe Otsuki,[1] ○Tomoya Abe,[1] Kosuke Sugawa,[1]

Porphyrins can be organized to have new functions, and examples of porphyrins forming various assemblies with different substituents have been reported. Our laboratory found that a porphyrin with bipyridine moieties forms a face-to-face dimer with the two rings facing each other by making coordination bonds with zinc ions (Figure (a)).[1)] However, it was not clear how the structure of the coordination bonding site affected the dimer formation. In this study, we designed ZnPor(tpy)$_4$ with terpyridine moieties and achieved its synthesis. We investigated the type of porphyrin aggregates that form upon the addition of various metal ions (Figure (b)). The addition of zinc ions to ZnPor(tpy)$_4$ resulted in the formation of ranges of aggregates, which were reduced to several stable structures upon annealing. On the other hand, the addition of silver ions resulted in the formation of dimers similar to those of porphyrins with bipyridine side chains in mM-order concentrations.
Keywords : Complex Chemistry, Porphyrin Self-Assembly,

ポルフィリンは組織化することで新たな機能を発揮することができ、置換基の違いによって様々な集合体を形成する例が報告されている。当研究室でも、側鎖にビピリジンを導入したポルフィリンが、亜鉛イオンとの配位結合により、２つの環が正面で向かい合った face-to-face 二量体を形成することを見出した（Figure (a)）[1)]。しかし、配位結合部位の構造が二量体の構築にどれだけ影響するかは明らかになっていない。

本研究では、側鎖にテルピリジンを導入した ZnPor(tpy)$_4$ を設計し、その合成を達成した。その後、各種金属イオンを添加した際にどのようなポルフィリン集合体を形成するか調査した（Figure (b)）。ZnPor(tpy)$_4$ に亜鉛イオンを添加すると凝集体を形成し、加熱処理することでいくつかの安定な構造に絞られることが分かった。一方で銀イオンを添加すると mM オーダーの溶液中では側鎖にビピリジンをもつポルフィリンの場合と同様の二量体が構築されていることが示唆された。

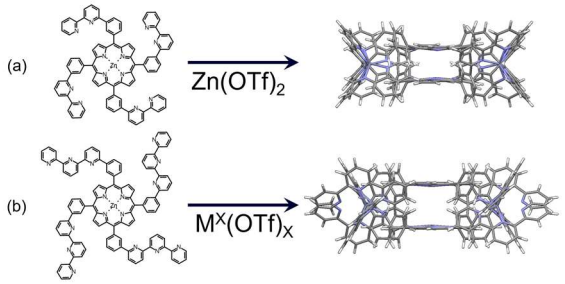

Figure. Face-to-face porphyrin dimers from (a) porphyrins with bipyridine coordination sites and (b) porphyrins with terpyridine coordination sites

1) K. Sato *et al*, *The 73rd Conference of Japan Society of Coordination Chemistry*, **2023**, 2PA-62.

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フッ素修飾された三次元多孔性金属錯体の合成とガス吸着特性

（北大院地球環境）○齋藤 結大・鄭 キン・野呂 真一郎
Synthesis and gas adsorption properties of the fluorinated three-dimensional porous coordination polymer (*Faculty of Environmental Earth Science, Hokkaido University*) ○Yuki Saito, Xin Zheng, Shin-ichiro Noro

[$Cu(SiF_6)$(bis(4-pyridinyl)acetylene)$_2$] (SIFSIX-2-Cu-i) is a porous 3D porous coordination polymer consisting of Cu ion, bis(4-pyridinyl)acetylene ligand, and SiF_6 anion, which shows remarkable CO_2 adsorption properties in practical conditions. However, there are very limited studies on introducing substituted ligands, and the effect of the surface modification on the adsorption properties has not been examined. In this work, we used bis(3-fluoro-4-pyridinyl)acetylene as a ligand to synthesize a SIFSIX-2 derivative and investigated its fluorine substitution effects on gas adsorption and separation.
Keywords : Porous coordination polymer, CO_2, Fluorine, Gas separation

金属イオンと有機配位子から構成される多孔性配位高分子（Porous Coordination Polymer, PCP）は、孔の大きさや表面の化学環境を自在に設計できることから、近年最も注目を集める材料の一つである。これまで 10 万種近い PCP が報告されており、中には非常に高選択的に二酸化炭素（CO_2）を吸着する PCP も報告されている。その一つが、Cu イオン、bis(4-pyridinyl)acetylene (bpa)、SiF_6 から成る三次元の相互貫通型 PCP である[$Cu(SiF_6)(bpa)_2$] (SIFSIX-2-Cu-i)であり、実使用条件下で高い CO_2 吸着分離特性を示すことが報告されている。[1] 本研究では、ピリジン環の三位にフッ素を導入した bis(3-fluoro-4-pyridinyl)acetylene (bfpa)を配位子に用いて SIFSIX-2-Cu-i 誘導体[$Cu(SiF_6)(bfpa)_2$] (**1**)を合成し、ガス吸着分離能に対するフッ素の効果を調べた (Figure)。その結果、**1** の CO_2 吸脱着等温線（298 K）において、わずかであるがヒステリシスが表れることがわかり、導入したフッ素と CO_2 間相互作用により構造変化している可能性が示唆された。本発表では結晶構造と吸着特性の詳細について説明する。

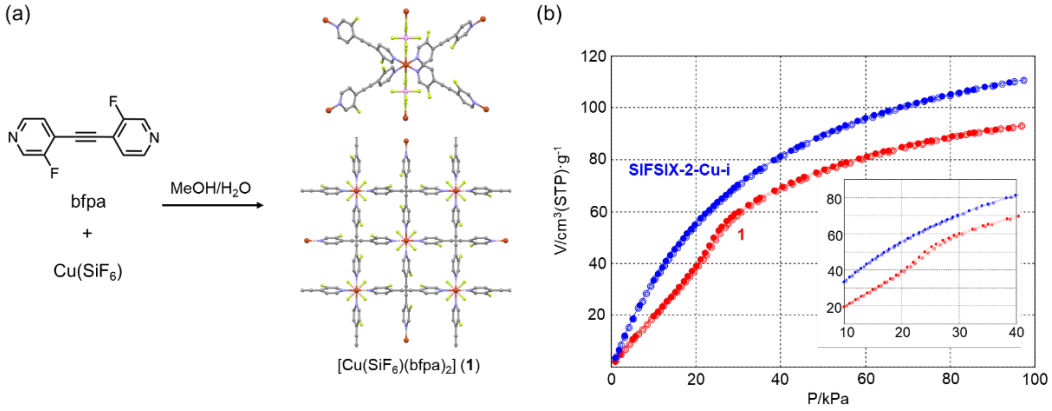

Figure. (a) Synthesis and crystal structure of **1**. (b) CO_2 sorption isotherms for SIFSIX-2-Cu-i and **1** at 298 K.

1) M. J. Zaworotko *et al., Nature* **2013**, 495, 80.

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キャスト法によるピラードレイヤー型 MOF 配向膜の作製とスピンクロスオーバー挙動の評価

（東理大院理[1]）○張　啓原[1]・原口　知之[1]

Fabrication of Oriented Crystalline Pillared-Layer-Type MOF Thin Film Using the Casting Method and Analysis of the Spin-Crossover Phenomena

([1]*Graduate School of Science, Tokyo University of Science*) ○Qiyuan Zhang[1], Tomoyuki Haraguchi[1]

Recently, significant research has focused on fabricating crystalline-oriented Metal-organic frameworks (MOFs) thin films, with potential applications as proton-conducting membranes or gas sensors. In this study, we formed oriented crystalline pillared-layer-type MOF: Fe(pz)[Pt(CN)$_4$] thin film (**Film-pz**) by the casting method. The high crystallinity and controllable orientation of **Film-pz** in both in-plane and out-of-plane directions were confirmed by thin film X-ray diffraction measurement. The magnetic susceptibility measurement was also carried out on **Film-pz**. A spin-crossover behavior accompanied by a hysteresis loop distinct from the bulk sample (**Bulk-pz**) was observed within the temperature range of 200 K to 320 K.
Keywords: Thin film; Metal-Organic Frameworks; Magnetism

近年、高配向性と結晶性を有する多孔性配位高分子（MOF）薄膜はプロトン伝導膜やセンサーとしての機能性表面材料への応用が期待されている。本研究では、キャスト法を用いてピラードレイヤー型 MOF である Fe(pz)[Pt(CN)$_4$]の結晶性配向膜(**Film-pz**)を作製した。薄膜 X 線回折測定により、**Film-pz** が面外と面内における高い結晶性と配向性を確認した。また、**Film-pz** の磁化率測定を行ったところ、200K から 320K の温度範囲において、バルクサンプルとは異なるヒステリシスループを伴うスピンクロスオーバー挙動が観測された。

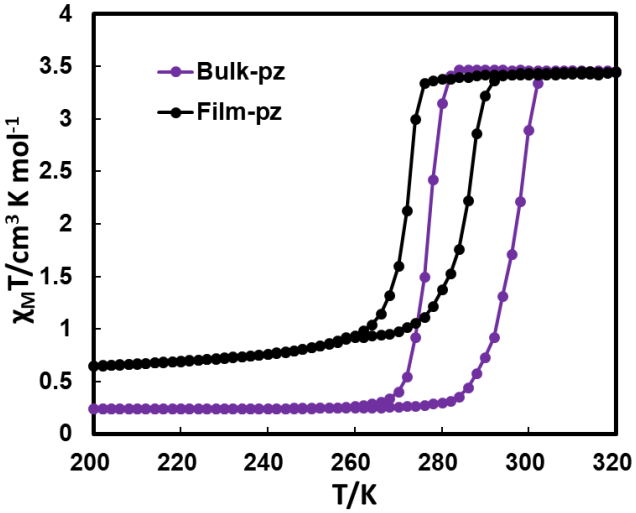

Fig.　$\chi_M{}^T$ vs T plot for **Bulk-pz** (purple line), **Film-pz** (black line) powder sample

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5 位および 15 位にフェニルビスビピリジンを導入したポルフィリンの錯形成挙動

（日大理工 [1]）大月 穣 [1]・須川 晃資 [1]・○秋冨 称李 [1]
The complex formation behavior of porphyrins with phenylbisbipyridine introduced at positions 5 and 15 ([1]*College of Science and Technology, Nihon University*) Joe Otsuki,[1] Kosuke Sugawa,[1] ○Aguri Akitomi[1]

Porphyrins exhibit distinctive optical and electronic properties, and their functionalities can be further enhanced through self-assembly. In this study, we examined the structures of aggregates of porphyrins, in which two bipyridine moieties were introduced at the trans positions, formed by coordination with zinc ions. The investigations were conducted on both solution and solid states. In the solution state, adding more than 8 μM of zinc ions to a 10 μM acetonitrile solution of porphyrin caused a red shift in the Soret band of the absorption spectrum. In the solid state, we used AFM to observe the morphology of samples on a substrate. These were prepared by dropcasting solutions with varying molar ratios of porphyrin to zinc ions (5:0, 5:4, 5:10, and 5:20) onto a mica substrate. Porphyrin alone and the 5:4 samples exhibited a particle-like morphology, while the 5:10 and 5:20 samples displayed a film-like morphology. *Keywords: Bipyridine; Porphyrin; Self assembly; Zinc Complex*

ポルフィリンは、特徴的な光・電子特性をもち、さらに自己組織化させることで新たな機能を持たせることができる。本研究ではテトラフェニルポルフィリンのトランス位に 2 つのビピリジンを導入し(Figure 1)、亜鉛イオンとの錯形成により生成する集合体の構造を溶液状態および基板上の固体状態で検討した。溶液状態では、ポルフィリン 10 μM のアセトニトリル溶液に対し亜鉛イオンを 8 μM 以上添加すると吸収スペクトルにおいて等吸収点の移動が起こり、ソーレー帯の長波長シフトが始まった。基板上の固体として、ポルフィリン単独の溶液およびポルフィリンと亜鉛イオンを 5:4、5:10、5:20 の割合で含む溶液をマイカ基板上にドロップキャストして得られた固体を AFM で観察した。ポルフィリン単独および 5:4 試料では粒子状の形状像が観察されたのに対し、5:10、5:20 の試料では層状の形状像が観察された(Figure 2)。

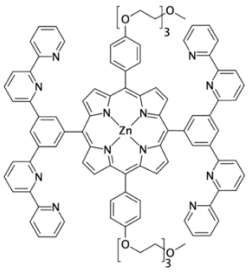

Figure 1. Molecular structure.

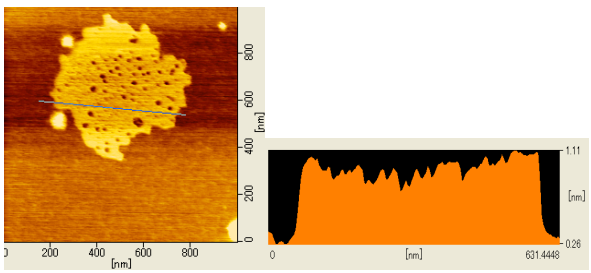

Figure 2. AFM image of porphyrin:Zn^{2+} = 5:20 on mica.

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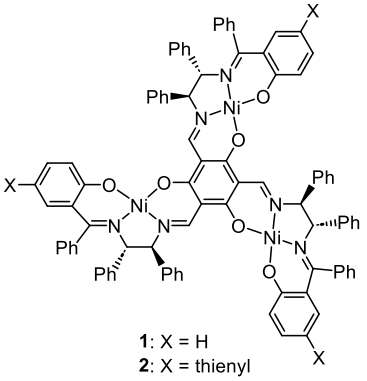
チエニル基を有する C_3 対称シッフ塩基ニッケル錯体の電気化学的性質

（神奈川大[1]・工学院大[2]）大島 百合[1]、古川 照人[1]、○桑村 直人[2]、力石 紀子[1]、廣津 昌和[1]

Electrochemical Properties of C_3-Symmetric Schiff Base Nickel Complexes with Thienyl Groups ([1]*Faculty of Science, Kanagawa University*, [2]*Center for Promotion of Higher Education, Kogakuin University*) Yuri Oshima,[1] Teruto Furukawa,[1] ○Naoto Kuwamura,[2] Noriko Chikaraishi,[1] Masakazu Hirotsu[1]

Oxidation of salen-type nickel(II) complexes leads to the formation of electroactive polymeric films. This characteristic behavior can be applied to the construction of two-dimensional (2D) polymers from C_3-symmetric complex units, as reported for 2D covalent organic frameworks (COFs) and 2D metal-organic frameworks (MOFs). In this study, we prepared trinuclear nickel(II) complexes **1** and **2** by using a C_3-symmetric Schiff base ligand and its derivative with three thienyl groups, respectively, and the formation of polymer films **poly-1** and **poly-2** was confirmed by cyclic voltammetry. The electropolymerization of **2** occurs at lower potentials than that for **1**, suggesting the intermolecular C-C bond formation between the thienyl groups, which is related to the enhanced stability of **poly-2**. The surface morphology and electrochromism of **poly-1** were also investigated.
Keywords : C_3 symmetry, Schiff base, thienyl group, nickel complex, electropolymerization

サレン配位子をもつニッケル(II)錯体は、電解酸化によりフェノール酸素のパラ位の炭素が分子間でカップリングして、電気活性ポリマーを生成することが報告されている。この特性を C_3 対称錯体に適用することで、共有結合性有機構造体（COF）や金属－有機構造体（MOF）に見られるような、２次元シート状ポリマーの構築に応用展開できることが期待される。我々は、C_3 対称シッフ塩基配位子をもつ平面型ニッケル(II)三核錯体のサイクリックボルタモグラム測定を行うと、電極表面上で電解酸化重合が進行し、ポリマーフィルムが形成することを見出している。本研究では、ポリマーフィルムの表面観察、C-C 結合形成部位へのチエニル基の導入による重合特性の向上を検討した。



C_3 対称シッフ塩基ニッケル三核錯体 **1** および 3 つのチエニル基を導入した類似錯体 **2** を合成した。いずれの錯体もサイクリックボルタンメトリーにより電極表面上で電解酸化重合が進行し、ポリマーフィルム（**poly-1**, **poly-2**）を形成することを確認した。**poly-2** は **poly-1** よりも低電位で生成することから、錯体 **2** ではチエニル基の酸化により C-C 結合が形成すると考えられる。ポリマーフィルムのサイクリックボルタモグラムでは、**poly-2** は **poly-1** よりも安定であることが示唆された。また、**poly-1** について、表面構造とエレクトロクロミズムを調査した。

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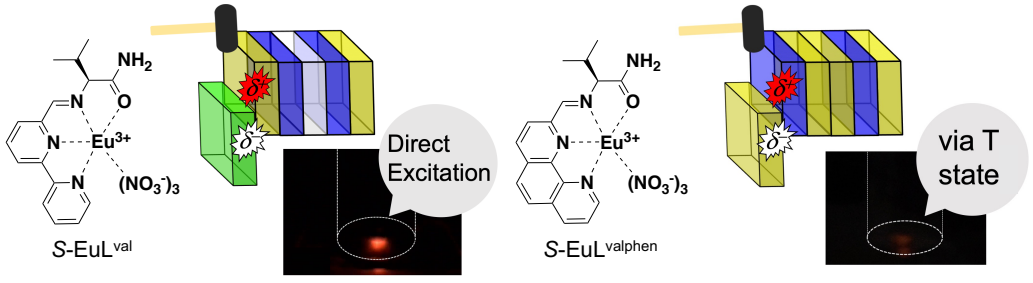
キラルな希土類錯体のトリボルミネッセンス発現とエネルギー緩和過程のπ電子系依存性

（青山学院大理工）○早内 大介・大野 礼雄・大曲 仁美・長谷川 美貴
The π-electronic system-dependence on the energy relaxation process of triboluminescence of the chiral lanthanide complexes (*Coll. Sci. & Eng, Aoyama Gakuin University*) ○Daisuke Hayauchi, Reo Ohno, Hitomi Ohmagari, Miki Hasegawa

Recently, the triboluminescence (TL) of lanthanide (Ln) complexes has attracted much attention. However, the exact principle of TL is still investigated due to the complex mechanism. The TL phenomena of LnL^{val} including bipyridine moiety were reported. In the present study, we examined TL of chiral Ln complexes, $LnL^{valphen}$, which has phenanthroline skeleton instead of bipyridine to elucidate π-electronic system-dependences in Ln complexes. For example, the intensity of TL of $EuL^{valphen}$ appears much weaker than that of EuL^{val}. Furthermore, no TL and PL in $TbL^{valphen}$ was observed. Here, we determined molecular and packing structures($P3_1$) of $LnL^{valphen}$ by single crystal X-ray structure analyses. It suggests that the TL is caused by the charge separation when the crystal was crushed. Finally, the TL of LnL^{val} is induced by the direct excitation of the ff transition, while $LnL^{valphen}$ done by the excited state of the ligand.
Keywords : Luminescence; Triboluminescence; Lanthanide complex

近年、トリボルミネッセンス(TL)を示すランタニド(Ln)錯体の報告が増えてきている [1]が、その発光の原理は不明瞭な点が多い化合物群である。本研究では TL 活性であり、π電子系の大きさが異なる 2 つのキラル Ln 錯体 LnL^{val} [2]および $LnL^{valphen}$ を用い、光学特性および構造解析から、TL におけるエネルギー緩和過程のπ電子系依存性を考察することを目的とした。以前の報告で、EuL^{val} はキラル結晶を形成しその空間群は $P6_5$ である。この錯体の TL は、ff 遷移の直接励起で起こる。

$EuL^{valphen}$ のキラル結晶が得られたので、単結晶構造解析を行ったところ、分子構造は EuL^{val} と類似しており空間群は $P3_1$ であった。$EuL^{valphen}$ は、PL と同様の位置に Eu イオン特有の TL を示し、$TbL^{valphen}$ は PL も TL も示さないことから、この系の TL は配位子の励起状態を経由して発現する。すなわち、π電子系の広がりの違いが TL 機構に影響する。なお、TL 発現の駆動力は、いずれも機械的刺激による劈開面での電荷分離状態が寄与している。



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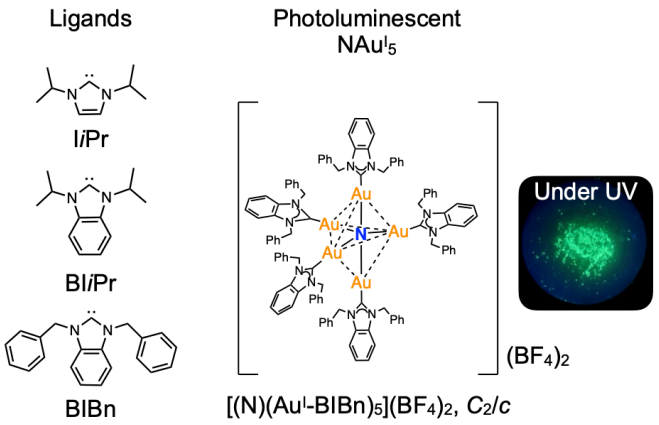
Ligand and aggregation-dependent photoluminescence in *N*-heterocyclic carbene-protected nitrogen-centered pentagold(I) clusters

([1]*The University of Tokyo,* [2]Institute for Molecular Science)
○ Leonardo Hayato Takeshige,[1] Xiao-Li Pei,[1] Pei Zhao,[2] Koichi Nagata,[1] Hitoshi Ube,[1] Zhen Lei,[1] Masahiro Ehara,[2] Mitsuhiko Shionoya[1]

Keywords: Gold clusters, *N*-Heterocyclic carbene ligands, Luminescence, Ligand effects, Aggregation state

In recent years, the chemistry of gold clusters has gained great attention due to their numerous applications in size-dependent catalysis, luminescence, and theranostics. Our group has successfully developed a series of carbon-centered hexagold(I) clusters protected by *N*-heterocyclic carbene (NHC) ligands with strong ligand dependence.[1–7] These findings provided valuable insights into the influence of external protecting ligands on the properties of gold clusters. However, the effect of doping gold(I) clusters with main group atoms remained unexplored. In contrast to the well-known *C*-centered hexagold(I) clusters, this study presents a series of nitrogen-centered pentagold(I) clusters protected by NHC ligands. The ligand-dependent photophysical properties were investigated experimentally and theoretically.

Several NHC ligands were used to synthesize nitrogen-centered pentagold(I) clusters. First, a diisopropylimidazolylidene ligand (I*i*Pr) was utilized. However, the digold(I) cluster $[(N)(Au^{I}\text{-}I\mathit{i}Pr)_2H_2](BF_4)$ was formed preferentially to the pentagold(I) cluster $[(N)(Au^{I}\text{-}I\mathit{i}Pr)_5](BF_4)_2$. Next, the diisopropylbenzimidazolylidene ligand (BI*i*Pr) gave a pentagold(I) $[(N)(Au^{I}\text{-}BI\mathit{i}Pr)_5](BF_4)_2$ cluster, which did not show photoluminescence (PL). Finally, a dibenzylbenzimidazolylidene ligand (BIBn) was used to synthesize a pentagold(I) cluster $[(N)(Au^{I}\text{-}BIBn)_5](BF_4)_2$, which crystallized in three different pseudopolymorphs, one of which showed green PL (λ_{em}^{max} = 519 nm). These results suggest that the aggregation state of nitrogen-centered gold(I) clusters plays a fundamental role in determining their photophysical properties. The origin of the photoluminescence of the cluster $[(N)(Au^{I}\text{-}BIBn)_5](BF_4)_2$ is currently under investigation.



1) H. Ube, *et al*., *Organometallics* **2018**, *37*, 2007; 2) Z. Lei *et al.*, *J. Organomet. Chem.* **2020**, *917*, 121271; 3) Z. Lei, *et al.*, *Bull. Chem. Soc. Jpn.* **2021**, *143*, 5406; 4) X.-L. Pei, *et al.*, *J. Am. Chem. Soc.* **2022**, *144*, 2156; 5) Z. Lei, *et al.*, *Nat. Commun.* **2022**, *13*, 4288; 6) Z. Lei *et al.*, *Chem. Sci.* **2023**, *14*, 6207; 7) L. H. Foianesi-Takeshige, *et al.*, *Adv. Optical Mater.* **2023**, *11*, 2301650.

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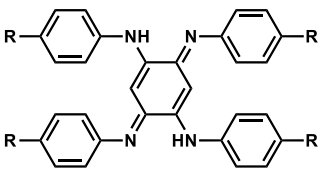
金属錯体の配位子としてのアゾフェニン類の溶液内におけるプロトン脱着挙動の研究

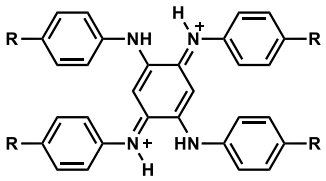
（埼玉大院理工[1]・日女大理[2]・埼玉大分セ[3]）○中丸稚也[1]・稲垣優花[1]・大野桂史[2]・藤原隆司[3]
Investigation of protonation-deprotonation behavior of azophenines as ligands for metal complexes in solution ([1]*Grad. Sch. Sci., Eng., Saitama Univ.*, [2]*Fac. Sci., Jpn. Women's Univ.*, [3]*CACS, Saitama Univ.*) ○Noriya Nakamaru,[1] Yuka Inagaki,[1] Keiji Ohno,[2] Takashi Fujihara [3]

Substances, that show remarkable color changes by protonation-deprotonation depending on the acid-base concentration in solution, are used as acid-base indicators. The acid dissociation constant (pK_a) of acid-base indicators is an important factor for determining the acid-base concentration in solution. However, there are only a few reports about pK_a values of the indicator in organic solvents such as chloroform, and accordingly, calculation of the pK_a values can lead to visualizing the acid-base concentration in organic solution. Azophenines ($RApH_2$) act as a bis(N^NH chelating) ligand. Although protonation-induced color changes in azophenines were reported, their pK_a have not been calculated yet. In this study, we synthesized azophenines with different electron-donating groups, and their pK_a in chloroform were determined by spectroscopic measurements. Electronic effects of the substituent on their pK_a were discussed. In addition, the deprotonation-induced changes in spectroscopic and structural properties of 4-EtApH_2 and its mononuclear complexes in THF were investigated.
Keywords : Complexes; ligands; Azophenines; Acid dissociation constant

酸塩基濃度に応じたプロトン化-脱プロトン化によって顕著な色変化を示す物質は，酸塩基指示薬として利用され，その酸解離定数（pK_a）は溶液中の酸塩基濃度を知る上で重要である．しかしながら，クロロホルムのような水と混和しにくい有機溶媒中における指示薬の pK_a を調査した例は少なく [1]，これを明らかにすることができれば，有機溶媒中の酸塩基濃度を直接知ることが可能になる．2 つの N^NH キレート配位部を有するアゾフェニン類（$RApH_2$，下図）は，酸によるプロトン化によって顕著な色変化を示すが，その pK_a は明らかになっていない [2]．本研究では，置換基を導入した種々の $RApH_2$ を合成し，クロロホルム中におけるそれらの pK_a を分光学的手法より明らかにし，pK_a に対する置換基の電子的な影響について検討した．また，THF 中における $RApH_2$ およびその単核錯体の脱プロトン化による分光学的性質および構造の変化についても明らかにした．



$RApH_2$



$RApH_2$ のプロトン化体

1) Agnes Kütt, *et. al*., *Tetrahedron Letters*, **2018**, *59*, 3738-3748.
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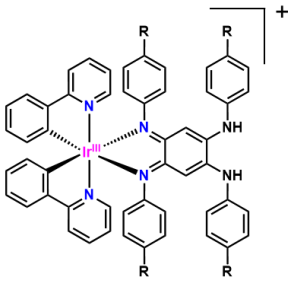

単核錯体の一例

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N-ヘテロ環状構造単位を外周部に導入したトリス(salen)型大環状配位子の合成と性質

(東大院理[1]) ○北島 拓実[1]・田代 省平[1]・塩谷 光彦[1]

Synthesis and Properties of Tris(salen)-Type Macrocyclic Ligands with *N*-Heterocyclic Building Blocks Introduced onto the Outer Periphery

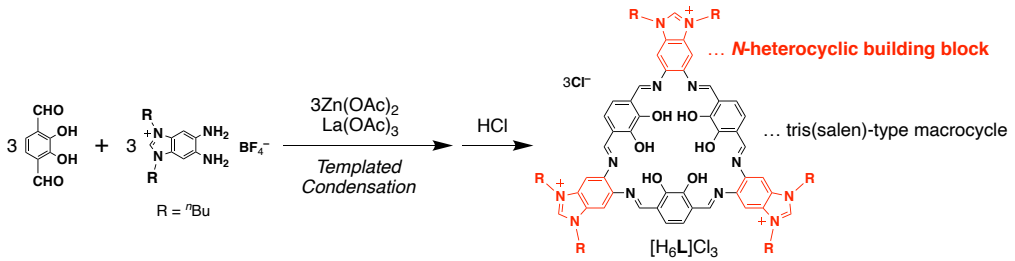
([1]*Graduate School of Science, The University of Tokyo*) ○Takumi Kitajima,[1] Shohei Tashiro,[1] Mitsuhiko Shionoya[1]

Introducing metal ion accumulation sites into a coordination network structure enables template synthesis of various metal clusters within the coordination nano-space. As a ligand for this purpose, we focused on the tris(salen)-type macrocyclic ligand developed by Nabeshima *et al.* and MacLachlan *et al*. This macrocyclic ligand has three N_2O_2-type tetradentate salen structures within the ring, so it forms various multinuclear metal complexes in the inner pore. To construct a coordination network structure composed of tris(salen)-type macrocyclic ligands, we here designed a novel ligand by introducing three *N*-heterocyclic building blocks into the outer periphery of the ring. First, dihydroxyterephthalaldehydes and diaminobenzimidazolium salt were synthesized, and then the desired compound was synthesized by dehydration condensation and cyclization using zinc(II) ions and lanthanum(III) ions as template, followed by removing the metals using hydrochloric acid. The ligand was obtained as the chloride salt in 41% yield, and its structure was identified by NMR spectroscopy and mass spectrometry. We also report the properties and coordination abilities of the ligand.

Keywords : Multinuclear metal complex; Supramolecular chemistry; Template synthesis; N-Heterocyclic ligand

金属イオン集積部位を配位ネットワーク構造に組み込むことで、配位ナノ空間内でさまざまな金属クラスターを鋳型合成できる。そのための配位子として我々は、鍋島らや MacLachlan らによって開発されたトリス(salen)型大環状配位子に注目した。この大環状配位子は、環内に三つの N_2O_2 型四座配位の salen 構造を有するため、内孔でさまざまな多核金属錯体を形成する。

本研究では、トリス(salen)型大環状配位子からなる配位ネットワーク構造を構築することを目指し、その環外周部に新たな配位部位として *N*-ヘテロ環状構造単位を三ヶ所導入した新規配位子を設計した。ジヒドロキシテレフタルアルデヒドとジアミノベンズイミダゾリウム塩をそれぞれ合成し、亜鉛(II)およびランタン(III)イオンを鋳型とした両者の脱水縮合環化反応ののち、塩酸で鋳型金属イオンを除くことにより、目的の配位子（H_6LCl_3）を収率 41%で合成した（下図）。得られた大環状配位子は、NMR および質量分析によって同定した。本発表では、同配位子の物性および金属配位能についても報告する。



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ビラジカル配位子で架橋した１次元 Cu(II)錯体の磁性

（東理大）○落合 一稀・金友 拓哉・榎本 真哉

Magnetic properties of a one-dimensional copper(II) compound bridged by a terpyridine-based biradical ligand

(*Tokyo University of science*) ○Kazuki Ochiai, Takuya Kanetomo, Masaya Enomoto

In this study, we synthesized a five-coordinate copper(II) complex $[Cu^{II}(Br)_2(5tpybNO)]$ (**1**), where 5tpybNO is 2,2':5',2"-terpyridine-5,5"-diyl bis(*t*-butyl nitroxide). In addition, the reaction between **1** and $[Gd^{III}(hfac)_3(H_2O)_2]$ resulted in the formation of a one-dimensional chain complex $[Cu^{II}(Br)(5tpybNO)][Gd^{III}(hfac)_4(H_2O)]$ (**2**) as shown in Fig. 1a. Complex **2** exhibits two different exchange coupling species between Cu and radical sites (Fig. 1b); namely, direct (J_1) and indirect (J_2) interactions between Cu and nitroxide at the axial and equatorial positions, respectively. Considering of the coordination structure and the overlap of the magnetic orbitals, the J_1 and J_2 interactions may be ferro and antiferromagnetic couplings, respectively. If $J_1 >> J_2$, **2** is expected to behave as a one-dimensional $S = 3/2$ antiferromagnetic chain. We will report on the estimated experimental and theoretical exchange coupling constants (J_1 and J_2) and the magnetic structure for **2**.

Keywords : Terpyridine; radical; molecular magnetism.

本研究では、5,5"位にニトロキシド (NO) 基を有するテルピリジン配位子 (5tpybNO) を用いて Cu^{2+}イオンとの錯形成を行った。配位子 5tpybNO と $CuCl_2$ より、5 配位の Cu 錯体 **1** が得られた。さらに、**1** と$[Gd^{III}(hfac)_3(H_2O)_2]$の反応より、NO 基が隣接する Cu イオンに配位した 1 次元鎖 Cu 錯体 **2** を形成した (図 1a)。錯体 **2** は経路が異なる 2 種類の Cu-ラジカル間相互作用が考えられる (図 1b)。すなわち、ax 位から配位する NO 基と Cu 中心の直接的な相互作用 (J_1) と eq 位の tpy 部位を介した間接的な 3d-2p 間相互作用 (J_2) である。配位構造と磁性軌道の重なり方より、J_1 は強磁性的、J_2 は反強磁性的相互作用を示すと考えられる。$J_1 >> J_2$ のとき、**2** は 1 次元 $S = 3/2$ 反強磁性鎖になる。本発表では、実験及び計算化学的に見積もられた交換相互作用定数より、**2** の磁気構造について報告する。

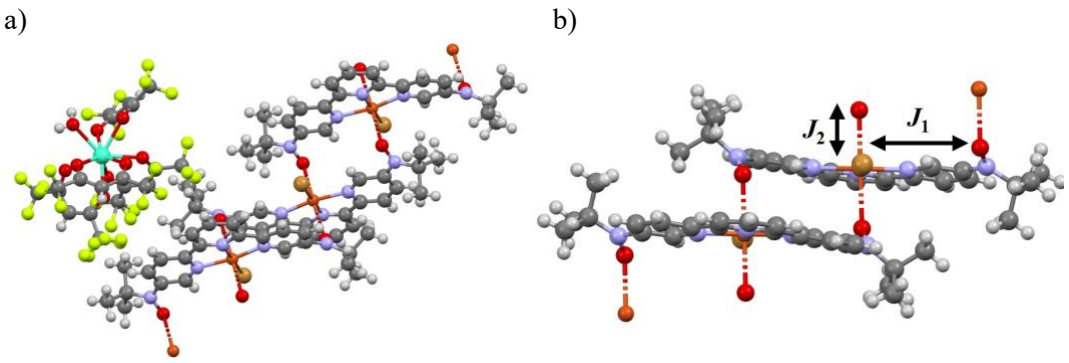

Fig 1. (a) Crystal structure of **2**. (b) the [Cu(Br)(5tpybNO)] moiety with J_1 and J_2. Gray, blue, red, yellow, and orange colors represent C, N, O, Br, and Cu atoms, respectively.

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金属–有機構造体(MOF)中における脂肪酸の相転移温度の変化

（東大院理 [1]）○吉井 嶺 [1]・畠山 元気 [1]・Kunyi Leng[1]・山田 鉄兵 [1]
The phase transition behavior of fatty acids in metal–organic frameworks ([1]*The University of Tokyo*) ○Rei Yoshii [1], Genki Hatakeyama [1], Kunyi Leng [1], Teppei Yamada [1]

Phase change materials (PCMs) can store and utilize thermal energy as latent heat during phase transitions, and attract increasing attention. Metal–organic frameworks（MOFs） with adjustable chemical compositions and tunable pore structures emerge as promising candidates for fabricating the next generation of advanced composite PCMs.[1]

In this study, we focused on incorporating various fatty acids with diverse chain lengths into the UiO-66 framework to explore their phase transition behaviors within the ordered micropores (Fig. 1a). PXRD and IR measurements revealed that the dodecanoic acid was introduced into the micropores of UiO-66. DSC measurements showed that the phase transition temperature (346 K) of dodecanoic acid (DA) in UiO-66 is elevated compared to the melting point (319 K) of bulk DA (Fig. 1b). The effect of the chain length of fatty acids on their phase transition behavior within the micropores of UiO-66 will be discussed. This research may contribute to the development of shape-stabilized PCMs with efficient thermal energy conversion and storage.

Keywords : Metal–organic Frameworks; *Phase transition Materials*; *Phase Transition*; *Fatty Acid*;

相変化時に潜熱を消費することで熱エネルギーを貯蔵・利用できる蓄熱材料が注目されている。熱材料の漏れは実用の妨げとなるため、多孔質シリカやカーボンな支持体として用いた形状安定化複合 PCM の開発されている。金属–有機構造体(MOF)は、化学組成および細孔構造を調整できるため、次世代の高度な複合 PCM を作製するための有望な候補とされる[1]。本研究ではまず、相転移潜熱が大きいドデカン酸を UiO-66 中に導入し、細孔内における相挙動を探索した（図 1a）。

XRD 測定および IR 測定により、ドデカン酸の UiO-66 への導入を確認した。DSC 測定の結果、DA@UiO-66 では、バルクのドデカン酸の融点（319 K）では吸熱ピークが観測されず、それよりも高い 346 K、364 K および 396 K で観測された（図 1b）。同様にデカン酸を UiO-66 へ導入し、DSC 測定を行ったところ、バルクのデカン酸の融点（306 K）では吸熱ピークが観測されず、333 K、356 K で観測された。ドデカン酸、デカン酸の結果から、脂肪酸を細孔に取り込んだ UiO-66 では、バルクの脂肪酸の融点より 27 K だけ高い温度において、吸熱ピークが観測されると推測される。今後、他の鎖長の脂肪酸でも同様の傾向がみられるか調査していく。この研究は、効率的な熱エネルギー変換と貯蔵を可能にする形状安定化 PCM の開発につながる可能性がある。

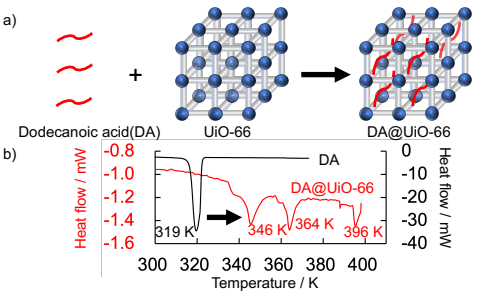

Fig. 1 a) Schematic of introducing DA into UiO-66, b) DSC of DA and DA@UiO-66.

[1] Y. Luan et al., *J. Mater. Chem. A.*, **2016**, *4*, 7641-7649

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分極性官能基を持つカチオンを挿入したジチオシュウ酸架橋鉄混合原子価錯体及び物性評価

（東理大）○大場 崇史・金友 拓哉・榎本 真哉
Structural and Physical Properties of Dto-bridged Iron Mixed Valence Complexes with Intercalation of Polarizable Cations (*Tokyo University of Science*) ○Takashi Oba, Takuya Kanetomo, Masaya Enomoto

1,2-Dithiooxalato (dto) ligand bridges between Fe^{II} and Fe^{III} and constructs a mixed valence iron complex, $((n\text{-}C_3H_7)_4N)[Fe^{II}Fe^{III}(dto)_3]$ (**1**) whose structure is 2D honeycomb layered one.[1] Complex **1** shows the charge transfer phase transition between Fe^{II}-Fe^{III} sites below 120 K. The development of this behavior depends on the intercalated cation. On the other hand, $[Fe^{II}Fe^{III}(ox)_3]$ (ox = oxalato) with $NEt_3(CH_2COOH)^+$ or $NBu_3(CH_2COOH)^+$, indicate a proton conduction behavior.[2] In this case, the carboxy groups are expected to give an internal polarization due to a proton displacement between adjacent cations. In this study, we will synthesize $[Fe^{II}Fe^{III}(dto)_3]$ complexes with $NPr(CH_2COOH)$ (**2**), $NBu(CH_2COOH)$ (**3**), $PBu(C_2H_4COOH)$ (**4**)) to investigate the effect of the proton displacement to the CTPT behavior by magnetic and dielectric measurements.

Keywords：Charge transfer phase transition; Mixed-valence complex

鉄混合原子価錯体$((n\text{-}C_3H_7)_4N)[Fe^{II}Fe^{III}(dto)_3]$ (**1**, dto = 1,2-dithiooxalato) は、非対称な配位子である dto が Fe^{II} と Fe^{III} を架橋した 2 次元ハニカム構造のアニオン層を形成し、層間にカチオンが挿入された積層構造を持つ[1]。**1** は 120 K 付近において Fe^{II}-Fe^{III} 間で電荷移動相転移 (CTPT) が生じる。この CTPT の発現は対カチオンのサイズや形状に依存する[1]。また $[Fe^{II}Fe^{III}(ox)_3]$ (ox = oxalate)層間に $NEt_3(CH_2COOH)^+$や $NBu_3(CH_2COOH)^+$を挿入した場合、プロトン伝導の発現が確認されている[2]。この時、層間のカルボキシ基は二量化によりプロトン変位に由来する内部分極が期待できる。本研究では、$[Fe^{II}Fe^{III}(dto)_3]$層間に $NPr_3(CH_2COOH)^+$, $NBu_3(CH_2COOH)^+$, $PBu_3(CH_2CH_2COOH)^+$を挿入した化合物 **NPr(MeCOOH)-dto** (**2**), **NBu(MeCOOH)-dto** (**3**), **PBu(EtCOOH)-dto** (**4**)の合成を行い、その物性を調査した。カチオン層での分極誘起や磁性層の磁気挙動に対して誘電応答や磁気測定を行うことで、内部分極やプロトン伝導が CTPT の発現に及ぼす影響を調査した。

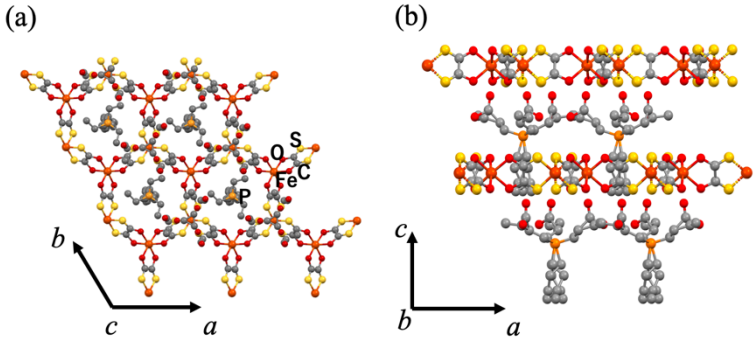

Figure 1. (a) The layered structure along the *c*-axis and (b) the honeycomb structures in the *ab*

1) Itoi, M. et al. *Solid State Commun.* **2004**, *130*, 415. 2) Okawa, H. et al. *J. Am. Chem. Soc.* **2013**, *135*, 2256.

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Synthesis and Photochemical Properties of Phthalocyanine Complexes Bearing Fluorine and Alkyl Groups

(*Institute of Industrial Science, The University of Tokyo*) ○Hongfeng Liu, Kei Murata, Kazuyuki Ishii

Keywords: Phthalocyanine; Singlet Oxygen; Photodynamic Therapy; Fluorine Group

Phthalocyanine complexes are recognized as promising photosensitizers for photodynamic therapy (PDT). Their efficacy in PDT is attributed to their photochemical properties, such as the efficient generation of singlet oxygen being a critical PDT agent and the strong absorption of red or near-infrared light which deeply penetrates human tissues. However, phthalocyanine complexes tend to be oxidized by singlet oxygen, which leads to their decompositions. The rapid decomposition of active photosensitizers decreases the treatment efficacy. Therefore, it is important to improve the tolerance toward singlet oxygen-based oxidation.

In addressing the issue of stabilizing phthalocyanine complexes against singlet oxygen-based oxidation, it is essential to lower the energy level of the highest occupied molecular orbital (HOMO).[1)] Although one approach to stabilize the HOMO energy level is the introduction of electron-withdrawing groups, such as fluorine, onto the phthalocyanine ring, the solubility of perfluorinated phthalocyanine complexes (F_{16}MPc) to various organic solvents is very low, which prevents the detailed analyses and further applications.

To overcome this problem, in this study, we rationally designed a new zinc phthalocyanine complex bearing both fluorine and alkyl groups (F_{12}(*n*-Bu)$_4$ZnPc) for stabilizing the HOMO energy level and increasing the solubility toward organic solvents, respectively (Fig. 1). The target Zn complex was successfully synthesized, which exhibited a characteristic, intense Q absorption band at around 690 nm in toluene (Fig. 2) and was soluble to various organic solvents. The details on its photochemical properties will be discussed in the poster presentation.

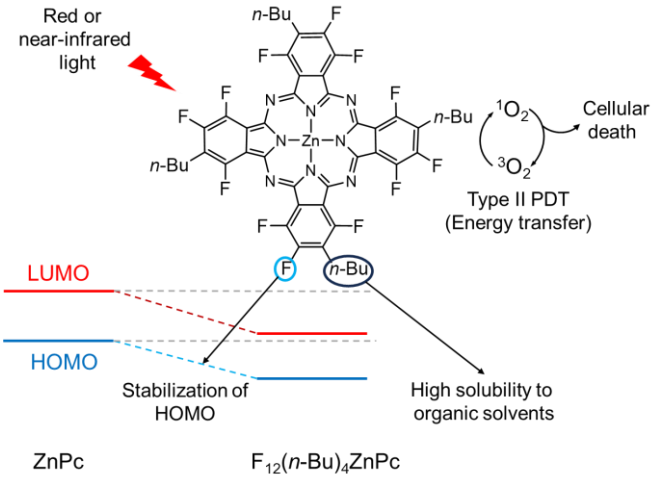

Fig. 1 Schematic representation of this study.

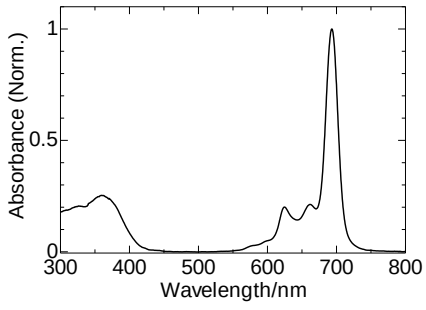

Fig. 2 An electronic absorption spectrum of F_{12}(*n*-Bu)$_4$ZnPc in toluene.

1) K. Murata, Y. Koike, K. Ishii, *Chem. Commun*. **2020**, *56*, 13760.

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リノール酸とフェナントロリン誘導体を配位子とするガラス状ユウロピウム錯体の発光スペクトル

（青山学院大理工）○力石 洸太・吉川 知輝・早内 大介・大野 礼雄・大曲 仁美・長谷川 美貴

Luminescence spectra of glassy europium complexes with linoleic acid and phenanthroline derivative (*Coll. Sci. & Eng., Aoyama Gakuin Univ.*) ○Kota Chikaraishi, Tomoki Yoshikawa, Daisuke Hayauchi, Reo Ohno, Hitomi Ohmagari, Miki Hasegawa

Luminescent lanthanide complexes have been studied mainly in the solid, solution, and thin-film. While, there are few reports of liquid state of lanthanide complexes. Hitherto, linoleic acid (LA) has been used as a ligand to control the melting point of the lanthanide complexes. Here, we will report the synthesis and aspects of a novel Eu complex with a tetradentate phenanthroline derivative ligand and LA, and their luminescence properties. The complexes luminesce at red-wavelength region originated from Eu ion under UV excitation.

Keyword : Europium Complexes; Linoleic Acid; Glassy

発光性希土類錯体は、固体、溶液あるいは薄膜に分類される系が主に研究対象とされてきている。これに対し、液体の錯体の報告はほとんど見当たらない。リノール酸(LA)は、配位子として用いると錯体の低融点化が期待される。これまで、円偏光発光(CPL)性希土類錯体 *S/R*-LnL^{val}[1]のカウンターアニオンを LA に置換した *S/R*-LnL^{val}(LA)$_3$を報告している[2]。この錯体は、アモルファス様を示す固体として得られ、LA の比率を増加させると、ガラス状および液体状態になる。発光および電子吸収スペクトルから、LA は配位子 L^{val}の一部の末端ピリジンの解離を誘起し、π電子共役長が変化した可能性が推測される。なお、この系は CPL を示さない。

本研究では、液体で CPL 性を示す希土類錯体の作成を目的としており、ここでは先の課題を凌駕するためにビピリジン部位を、フェナントロリンにした L^{valphen} を配位子に希土類錯体 *S*-EuL^{valphen}(LA)$_3$ を設計した。これにより、分子内回転が抑制されることが期待される。目的の錯体は、赤色の固体粉末として得られ、紫外線励起により赤色発光を示した。発光スペクトルを測定したところ、595 および 616 nm に Eu に特徴的な発光帯が観測され、発光量子収率は 12%であった。本系は、CPL を示すことも分かった。

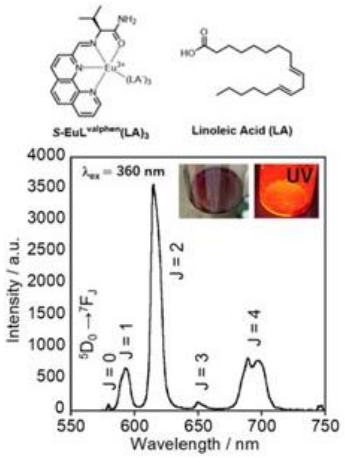

Fig. Molecular structures and luminescence spectrum.

CPL 測定は、北里大学長谷川真士先生に御助力いただきました。この場をお借りして御礼申し上げます。

1) M. Hasegawa, H. Ohmagari, M. Iwamura, K. Nozaki, et al., *ChemPlusChem*, **2020**, *85*, 294-300.
2) 吉川, 大曲, 長谷川, *錯体化学会第 72 回討論会*, **2022**.

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Identification of luminescent species contributing to induced CPL of a Eu(III) complex with Δ(Λ)-Co(III) complexes by time-resolved CPL spectroscopy

([1]*Grad. Sch. Sci. Eng., Univ. Toyama*, [2]*Seikei Univ.*) ○Juri Yamashita,[1] Munetaka Iwamura,[1] Koichi Nozaki,[1] Taro Tsubomura[2]

Keywords: Circularly Polarized Luminescence; Europium (III) Complex; Tris (ethylenediamine) Cobalt (III) ion; Time-resolved CPL Spectroscopy

Circularly polarized luminescence (CPL) from an achiral Eu(III) or Tb(III) complex interacting with chiral molecules is called induced CPL (iCPL). iCPL has been paid attention to the application of highly sensitive chiral sensing. $[Eu(pda)_2]^-$ (pda:1,10-phenanthroline-2,9-di-carboxylic acid) exhibits intense iCPL with chiral molecules such as amino acid[1)]. Recently, we found that $[Eu(pda)_2]^-$ exhibited iCPL when coexisting with Δ or Λ-$[Co(en)_3]^{3+}$. In this study, chemical species contributing to the iCPL were identified by time-resolved CPL spectroscopy (TRCPL) and, the concentration dependence of the CPL spectra and the emission lifetimes were examined to reveal the mechanism of the iCPL. Fig.1 shows TL (Total Luminescence) and g_{lum} value spectra of a $[Eu(pda)_2]^-$ solution containing 0.1 mM Δ/Λ-$[Co(en)_3]^{3+}$. The g_{lum} values of +0.11 and -0.13 were observed for Δ/Λ-Co, respectively. Fig.2 demonstrates time profiles of left and right-handed CPL (L- and R-CPL) and g_{lum} value at 590 nm obtained by TRCPL for the $[Eu(pda)_2]^-$ solution containing 0.5 mM Λ-Co. The decays of both the CPL were reproduced using to lifetimes of τ_1 (14.6 μs) and τ_2 (66.5 μs), which are shorter than that of $[Eu(pda)_2]^-$ (745 μs) due to energy transfer quenching by $[Co(en)_3]^{3+}$. The two time-components are probably assignable to associated species of $[Eu(pda)_2]^-$ and $[Co(en)_3]^{3+}$ with different structures. The g_{lum} values of τ_1 and τ_2 components calculated from eq.1 were $g_1 = 1.8\times10^{-2}$, $g_2 = -1.5\times10^{-1}$:

$$g_n(t) = \frac{2(L_n - R_n)}{L_n + R_n} \quad (n = 1, 2) \cdots (1)$$

where L_n and R_n are intensity of L- and R-CPL of each lifetime component, respectively. These results indicate τ_2-component mainly contributes to the iCPL.

1) K. Okutani *et al., Inorg. Chem.*, **2014**, 53, 5527-5537.

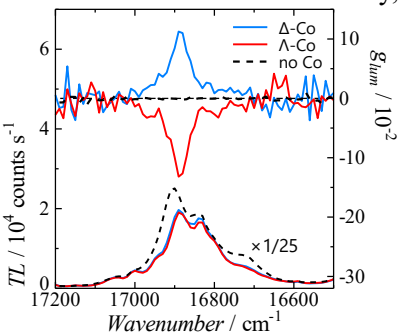

Fig.1. TL and g_{lum} value spectra of $[Eu(pda)_2]^-$ when coexisting with Δ/Λ-$[Co(en)_3]^{3+}$. (λ_{ex} = 310 nm. [Eu] = 0.1 mM, [Co] = 0.1 mM)

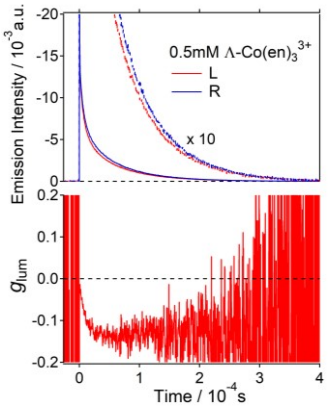

Fig.2. Temporal profiles of L- and R-CPL and g_{lum} value at 590 nm. (λ_{ex} = 355 nm. [Eu] = 0.1 mM)

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Spin state changes of luminescent cobalt(II) complexes bearing bulky substituent in the solid state and solution

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Keywords: Cobalt(II) complex; Spin crossover; Magnetic property; Luminescence

The spin-crossover (SCO) phenomenon represents a stimulus-driven spin state conversion between the low-spin (LS) and high-spin (HS) states of a metal center and is quite sensitive to structural changes that can also act as triggers for inducing the SCO behavior. Such molecular-based spin switching materials are promising candidates for next-generation molecular devices.[1] Furthermore, although SCO phenomena are based on the electronic structure of the single molecule they can be observed in solutions or soft polymer matrices. The softening of the molecular structure itself and/or the whole of molecular assemblies tuned by flexible molecular design through chemical modification offers new possibilities for tailoring the functional molecular materials.

We have investigated the spin state of cobalt(II) complexes, $[Co(\mathbf{L1})_2](X)_2$ (**1·X**; **L1** = 4'-(4-N,N'-Diphenylaminophenyl)-2,2':6',2''-terpyridine, X = PF_6, BPh_4) and $[Co(\mathbf{L2})_2](X)_2$ (**2·X**; **L2** = 4'-(4-N,N'-Dimethylaminophenyl)-2,2':6',2''-terpyridine, X = PF_6, BPh_4) in the solid state and in solution (Fig. a). In the solid state, **1·PF$_6$** and **2·PF$_6$** both containing smaller PF_6^- counter anions showed gradual spin crossover behavior (Fig. b). On the other hand, **1·BPh$_4$** and **2·BPh$_4$** both were in the high-spin state in the temperature range of 50 – 400 K due to the lower molecular cooperativity. In contrast, all the cobalt(II) complexes gave the temperature- and concentration-dependency on the absorption spectra related to the spin state (around 430 nm = 23200 cm^{-1}) in various organic solution (Fig. c). Associated to this absorption, the present cobalt(II) complexes demonstrated luminescence in the solution. Detailed spectrum discussion will be on the presentation.

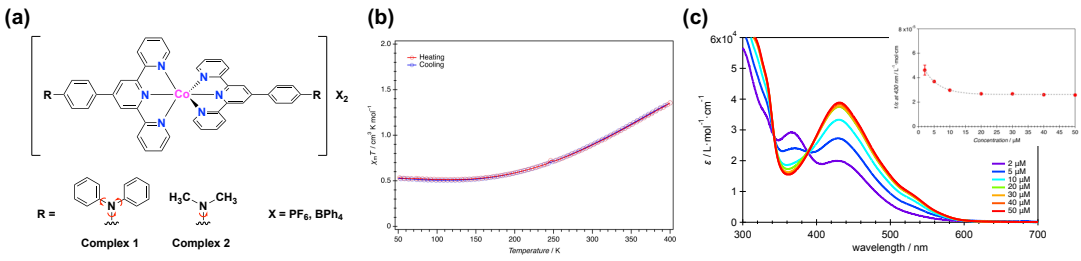

Figure (a) Molecular structures for complexes **1·X** and **2·X** (X = BPh_4 or PF_6). Red arrows indicate the rotatable bonds in the terpyridine ligand derivatives. (b) SCO behavior of **1·PF$_6$** in the solid state between 50 – 400 K. (c) The concentration dependent molar adsorption constant (ε) changes of **1·PF$_6$** in DMSO. Inset indicates the plots of $1/\varepsilon$ versus T plots at 430 nm.

1) M. Nakaya *et al*, *Eur. J. Inorg. Chem.*, **2020**, 3709–3719.

2) M. Nakaya *et al*, *Inorg. Chem. Front.*, **2021**, 8, 484–498.

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含アルキル鎖バリンアミド-ビピリジン骨格を有する希土類錯体の発光スペクトル

（青山学院大理工[1]）○大野 礼雄[1]・大曲 仁美[1]・長谷川 美貴[1]

Luminescence spectra of valinamide-bipyridine lanthanide complexes with a series of alkyl groups

([1]*Coll. Sci. & Eng., Aoyama Gakuin University*) ○Reo Ohno,[1] Hitomi Ohmagari,[1] Miki Hasegawa[1]

Alkylation affects to amphiphilic molecular design, spatial arrangement and photophysical properties. However, there are few systematic reports on the alkylated lanthanide (Ln) complexes compared to the case of organic molecules. This study aims to clarify the effect of alkylation on the luminescence properties of circularly luminescent lanthanide complexes. Eu$L^{val}C_n$ were newly synthesized which are valinamide derivatives with straight-chain alkyl group with carbon numbers, *n* of 1, 2, 3, 4, and 8. SC-XRD and synchrotron PXRD measurements of Eu$L^{val}C_n$ show that alkylation contributes to the extension of the intermolecular periodic distance while maintaining the coordination structure. This result corresponds to the luminescence properties, which are retained in the mother skeleton. Interestingly, their luminescence quantum yields and CPL properties demonstrate similarities each other.

Keywords : Lanthanide complexes; Luminescence spectra; Substituent effect

アルキル基の導入は分子の両親媒性設計等に影響する。例えば、分子間の配置、光物性等を調整できる[1]。しかし、有機分子の場合と比較し、希土類(Ln)錯体のアルキル鎖導入に関わる系統的な報告はほとんどない。本研究の目的は、円偏光発光(CPL)性 Ln 錯体[2]を、アルキル鎖の導入により拡張し、Ln 錯体の発光とアルキル鎖導入の相互関係を系統的に議論することである。

アルキル直鎖は炭素数 *n* が 1, 2, 3, 4 および 8 を用い、錯体 Eu$L^{val}C_n$ とした。Eu$L^{val}C_n$ の単結晶 X 線構造解析および放射光 XRD 測定から、アルキル化は配位回りの構造を保持しつつ、分子間の周期的距離の伸長に寄与することを見出した。このことは、発光スペクトルの挙動にも対応し EuLC_n の母骨格の錯体の発光は保持される。興味深いことに、発光量子収率が 43%で CPL 性も同程度である。これは構造からの推測を満足する。

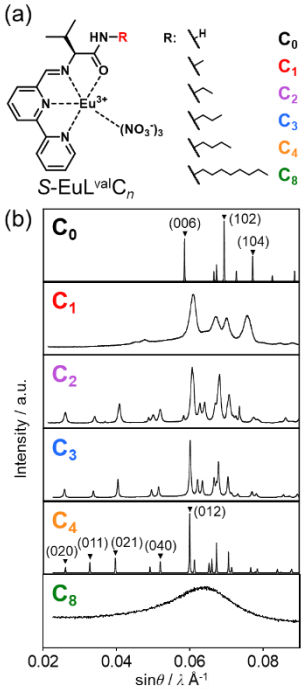

Fig. (a) Molecular structure and (b) Synchrotron PXRD patterns of *S*-Eu$L^{val}C_n$.

1) Y. Fan, *et al*., *Mater. Chem. Front*., **2021**, *5*, 1525-1540.
2) M. Hasegawa, H. Ohmagari, *et al*., *ChemPlusChem*, **2020**, *85*, 294-300.

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硫黄原子架橋型 thia-TriQuinoline (t-TQ)の合成とその錯化挙動の精査

（慶大院薬[1]・微化研[2]）○尾谷 亮[1]・小林 透威[1]・熊谷 直哉[1,2]

Design, Synthesis, and Complexation Behavior of Sulfur-Embedded TriQuinoline (t-TQ)

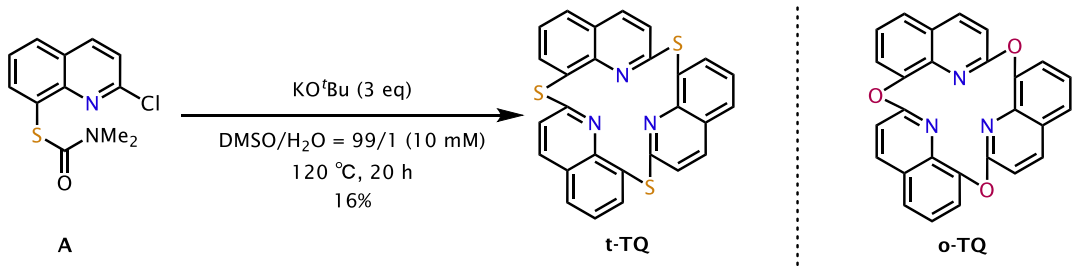
([1]*Graduate School of Pharmaceutical Sciences, Keio University* [2]*Institute of Microbial Chemistry*) ○Ryo Otani,[1] Toi Kobayashi,[1] Naoya Kumagai[1,2]

An oxygen embedded cyclic quinoline trimer concatenated at the 2- and 8-positions in a head-to-tail fashion, oxa-TriQuinoline (o-TQ), exhibits unique physicochemical properties by capturing metal cations as a semi-rigid crown molecule.[1] In the present study, we designed and synthesized its sulfur-embedded counterpart, thia-TriQuinoline (t-TQ), featuring a larger inner cavity. A Newman-Kwart rearrangement of 2-chloro-8-quinolinol allowed for the synthesis of requisite 8-thio precursor **A**, and subsequent hydrolysis/S_NAr sequence gave rise to t-TQ in a one-pot process (16% yield). X-ray crystallographic analysis of t-TQ and its metal complexes revealed distinct physicochemical behavior compared to o-TQ.

Keywords : Quinoline; Tridentate Ligand; Aggregation-Induced Emission

酸素原子架橋によって 2,8 位を逐次連結した head-to-tail 型キノリン 3 量体 oxa-TriQuinoline（o-TQ）は，半剛直性クラウン分子として種々の金属カチオンを捕捉し，多彩な物理化学的特性を示す[1]。本研究では，酸素原子を同族の硫黄原子に置換したキノリン 3 量体 thia-TriQuinoline（t-TQ）を新たにデザインした。

Newman-Kwart 転位反応により 2-chloro-8-quinolinol を 8-thio 化した **A** が得られ，**A** を環化前駆体とする加水分解/芳香族求核置換反応による t-TQ のワンポット合成法の開拓に成功した（単離収率 16%）。X 線結晶構造により，t-TQ はより拡大した中心空隙を有していることが明らかとなり，錯形成挙動についても o-TQ と異なる傾向を示した。



1) T. Kobayashi and N. Kumagai, *Angew. Chem. Int. Ed.* **2023**, e202307896.

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Synthesis and Structural Exploration of Iron(II) and Nickel(II) Complexes Bearing Unsymmetrical Azine Ligands with Heteroaromatic Moieties

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Keywords: (pyridyl)(imidazolyl)azine; (pyridyl)(oxazolyl)azine aldazines; iron(II) complexes; nickel(II) complex; crystal structures

In our concerted synthetic effort, we have selectively synthesized Fe^{II} and Ni^{II} complexes bearing unsymmetric azine ligands with heteroaromatic moieties. The iron(II) complex $[Fe(HL^{H})_2](PF_6)_2 \cdot H_2O \cdot MeCN$ (**1**), where HL^{H} is 2-pyridylmethylidenehydrazono(4-imidazolyl)methane, was exclusively obtained by reacting 2-pyridine carboxaldehyde, 4-formylimidazole, hydrazine monohydrate, and $FeCl_2 \cdot 4H_2O$ (in a molar ratio of 2:2:2:1) in methanol, followed by the addition of an aqueous NH_4PF_6 solution. Similarly, employing 2-methyl-1*H*-oxazole-4-carboxaldehyde instead of 1*H*-imidazole-4-carboxaldehyde, we obtained complexes $[Fe(L^{Me})_2](PF_6)_2 \cdot MeOH$ (**2**) and $[Ni(L^{Me})_2](PF_6)_2$ (**3**), where L^{Me} is 2-pyridylmethylidenehydrazono-4-(2-methyloxazolyl)methane. Spectroscopic measurements and elemental analysis validated the purity of bulk product, and single-crystal X-ray analyses revealed the molecular and crystal structures of both Fe^{II} and Ni^{II} complexes with unsymmetric HL^{H} and L^{Me} azines adopting a tridentate κ^3*N,N',N"* coordination mode. In complex **1**, Fe^{II} was surrounded by two HL^{H} azines with a planar *E*(py),*Z*(im) conformation, forming a monomeric six-coordinated complex (Figure 1a). The complex cations in **1** formed a 1D chain structure through intermolecular hydrogen-bonding interactions between imidazole N–H and the neighboring uncoordinated azine-N atom, linked by water molecules. Conversely, complexes **2** and **3** with respective metal ions; Fe^{II} and Ni^{II} were each ligated by two unsymmetrical L^{Me} azines in a planar *E*(py),*Z*(ox) conformation (Figure 1b). The ORTEP drawing of **3** revealed two independent structures (Figure 1c), and unlike **1**, complexes **2** and **3** displayed no intermolecular hydrogen-bonding interactions. The selective formation of these unsymmetrical azines (HL^{H} and L^{Me}) from a stoichiometric mixture arose from the steric preference of the 2-pyridyl and 4-imidazolyl/4-(2-methyloxazolyl) azine moieties, respectively, leading to the *E*(py),*Z*(im)/*Z*(ox) conformation in the five- and six-membered chelate rings.

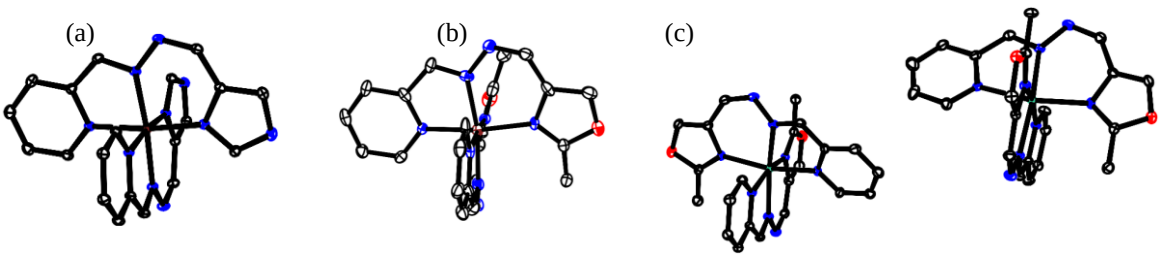

Figure 1. ORTEP drawing of cationic complexes in (a) $[Fe(HL^{H})_2]^{2+}$, (b) $[Fe(L^{Me})_2]^{2+}$, and (c) $[Ni(L^{Me})_2]^{2+}$; (ellipsoids are drawing at a 25% probability level). Color code: Fe, firebrick; Ni, green; N, blue; O, red; C, black.

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・フォトクロミズムと偏光発光を示す希土類錯体 LB 膜の開発

(青山学院大学理工) ○近藤 淳也・大曲 仁美・長谷川 美貴

Development of LB films of lanthanide complexes with photochromic and polarized luminescence properties (*Coll. Sci. & Eng., Aoyama Gakuin University*[1])

○Junya Kondo, Hitomi Ohmagari, Miki Hasegawa

The LB film technique is one of useful methods to assemble molecules periodically. Hitherto, we reported that the LB films consisting to the chiral amphiphilic compound (L) and lanthanide (Ln) ions demonstrated the linearly and circularly polarized luminescence (LPL and CPL, respectively) of Ln. In this study, we aimed to develop the LB films to induce LPL and CPL properties of Tb based on the mixing of two amphiphilic moieties, azobenzene skeleton (*trans*-AZ/*cis*-AZ) and L. Both AZ-L-Tb films demonstrate ff emission bands. The LPL of *cis*-AZ-L-Tb LB film does not appear as-deposition, but does after Vis-irradiation for 2 d. While, no LPL phenomena show in the *trans*- AZ-L-Tb LB film before/after UV irradiation. Here, we will discuss the isomer-effect on LPL of their LB films.

Keywords : Lanthanide complex; Langmuir-Blodgett film; Luminescence

ラングミュアブロジェット(LB)膜法を用い、これまでに希土類錯体の直線偏光発光(LPL)を発現している[1]。最近、更に L^{val} 基[2]に長鎖アルキル基を導入した両親媒性希土類(Ln)錯体 *S*/*R*-LnL の LB 膜が LPL だけでなく円偏光発光(CPL)も示すことを見出している[3]。アゾベンゼンの誘導体(AZ)はフォトクロミズムを示す代表的な化合物であり、*cis*-/*trans*-異性化に伴い構造が可逆的に変化する LB 膜も報告されている[4]。この際、アルキル鎖は C_9 である。本研究は、フォトクロミズムによる分子配向の変調に伴う希土類錯体の偏光発光のスイッチングを最終的な目標としている。具体的には、アルキル鎖が C_{18} の AZ を合成し[5]、先の *S*/*R*-LnL との混合 LB 膜(*cis*-/*trans*-AZ-L-Tb)を作製し,その光異性化と LPL の変調に着目し考察した。

π-A 曲線から、*cis*-AZ-L-Tb LB 膜は 15 mN m^{-1} で疎水処理を施した溶融石英基板 10 層累積させた。*trans*-体も同様に累積した。いずれの LB 膜も 315 nm で励起したところ Tb に由来する特徴的な発光帯を示した。興味深いことに *cis*-AZ-L-Tb LB 膜の LPL は累積直後にみられなかったのに対し、可視光下で 2 日間静置すると顕著に現れる。*trans* 体で製膜した場合、LB 膜は紫外光照射前後において LPL を示さなかった。ここでは、AZ の異性化による LB 膜の LPL への影響について議論する。

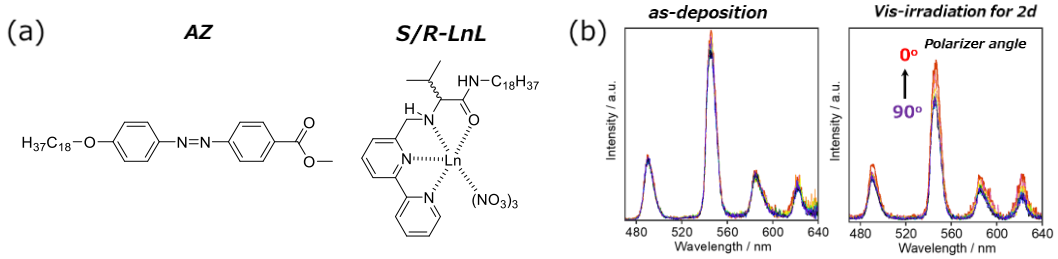

Fig.1 (a) Molecular structure of AZ and *S*/*R*-LnL and (b) LPL spectra of *cis*-AZ-L-Tb LB film. λ_{ex} = 315 nm.

1) M. Hasegawa, A. Ishii, *Coord. Chem. Rev.*, **2020**, *421*, 213458.
2) M. Hasegawa *et al*., *ChemPlusChem*, **2020**, *85*, 294-300.
3) H. Tanaka, H. Ohmagari, K. Murata, M. Iwamura, K. Ishii, K. Nozaki, M. Hasegawa, Annual Meeting on Photochemistry, **2022**, 1C06.
4) E. Piosik *et al*., *Phys. Chem. Chem. Phys*., **2017**, *19*, 23386-23396.
5) H. Mehmood *et al*., *Mol. Crist. Liq. Crist.*, **2018**, *Vol.664*, 14-23.

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Mechanism of Water Molecule Adsorption/Desorption and Phase Transition in Cobalt Terpyridine Complex Crystals

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Keywords: Cobalt Complex; Phase Transition; Terpyridine; Water Adsorption/Desorption

We found that crystals of $[Co(ttpy)_2](NO_3)_2$ (ttpy = 4'-(p-tolyl)-2,2':6',2"-terpyridine; Figure) exhibit adsorption/desorption of water molecules, as well as crystal-to-crystal phase transitions. The mechanism of these processes was elucidated through X-ray crystal structure analysis. When humidity is reduced from 90%, a half of water molecules in the crystal were cooperatively desorbed between 60% and 50% humidity, while the remaining ones desorbed continuously. In the meantime, a crystal-to-crystal phase transition was observed in DSC, characterized by an exothermic peak at -16.0 °C during cooling and an endothermic peak at -30.8 °C during heating. X-ray single crystal structure analysis confirmed that the crystal contains maximum four water molecules per Co complex. Three of these water molecules, along with three others that are crystallographically equivalent, form an interesting hexagonal structure. The water molecules forming this hexagon, along with nitrate ions, create a two-dimensional hydrogen bonding network that spreads throughout the crystal. It is likely that water molecules adsorb/desorb through channels formed by these hydrogen bonding networks. Although the remaining water molecule was isolated in the crystal, this water molecule is ultimately desorbed at low humidity. The structure of single crystals without water molecules was also analyzed, revealing that the unit cell contracts when water molecules are removed. Furthermore, the structure of single crystals containing an average of 2.8 water molecules suggests that the water molecules that exit first are those forming the two-dimensional network, and a cooperative effect appears as the hexagonal structure collapses. We also analyzed the crystal structures below and above the phase transition temperatures to address the mechanism of the phase transition.

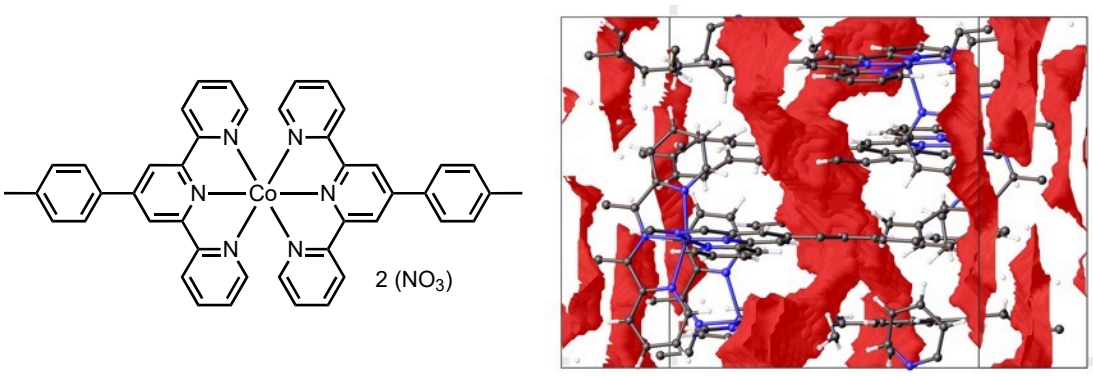

Figure. $[Co(ttpy)_2](NO_3)_2$ and water channels in the crystal.

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混合原子価クラスターを用いた可視透明—紫外および近赤外吸収色素の開発とクロミズム制御

（兵庫県大院理[1]・阪大産研[2]）○鎌田 知希[1]・森野 喬[1]・下元 直樹[1]・小阪田 泰子[2]・藤塚 守[2]・小澤 芳樹[1]・阿部 正明[1]

Development and chromism control of visible-transparent and UV/NIR-absorbing dyes based on mixed-valence clusters

([1]*Graduate School of Science, University of Hyogo*, [2]*SANKEN, Osaka University*) ○ Tomoki Kamada[1], Takashi Morino[1], Naoki Shimomoto[1], Yasuko Osakada[2], Mamoru Fujitsuka[2], Yoshiki Ozawa[1], Masaaki Abe[1]

Trinuclear ruthenium clusters formulated $[Ru_3O(RCOO)_6L_3]^{n+}$ exhibit multi-step and reversible redox behavior accompanied with multi-step electrochromic (EC) properties over a wide wavelength range from the ultraviolet (UV) to near infrared (NIR) region. In this study, we have developed new smart dyes based on the characteristics of the Ru_3 clusters. Herein, new Ru_3 derivatives bearing L with widely varying electron-donating/accepting properties have been synthesized and identified by UV-vis-NIR, ^{1}H NMR spectroscopy, elemental analysis, and single-crystal X-ray structure analysis. The multi-step redox and electrochromic properties in solution have also been investigated by cyclic voltammetry and controlled-potential UV-vis-NIR absorption spectroscopy. Effects of chemical constituents employed in the clusters, including substituent R, ligand L, and Ru valence states, on the molecular structures and EC properties will be discussed.

Keywords : Triruthenium clusters; Mixed valence; Redox; Near infrared; Electrochromism

オキソ中心を持つルテニウム三核クラスター $[Ru_3O(RCOO)_6L_3]^{n+}$ は、溶液内で多段階かつ可逆な酸化還元挙動を示す錯体であり、酸化状態のスイッチングにより紫外から近赤外領域にかけての広い波長領域において、多段階のクロミック特性を示すことが知られている。本研究では、Ru_3 クラスターの特徴を利用した新たなスマート色素の開発を目指した研究を進めている。本報告では、カルボン酸置換基 R に電子吸引基を導入し、NIR 吸収を与える混合原子価(II,III,III)状態の安定化を図ったクラスター骨格へ、電子供与性/吸引性 (pK_a 値) を広範に変えた配位子 L を導入した Ru_3 クラスター誘導体を新しく合成した。L には、従来研究が多く行われてきたピリジル系配位子に加え、ホスフィン系配位子も数種検討した。得られた新規 Ru_3 クラスターは、紫外-可視-近赤外 (UV-vis-NIR) 分光、^{1}H NMR、元素分析、単結晶 X 線構造解析により同定した。また、溶液中における各クラスターの酸化還元特性と定電位電解 UV-vis-NIR 吸収分光を調査し、多段階クロミック特性ついて明らかとした。置換基 R と配位子 L および Ru 原子価状態 (錯体の全体電荷 n) が光吸収特性に与える効果について議論する。

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希土類フタロシアニンダブルデッカー錯体の合成とそのキラル誘起

（東大生研[1]）○森 智仁[1]・村田 慧[1]・石井 和之[1]
Synthesis of Rare-Earth Phthalocyanine Double-Decker Complexes and Their Chiral Induction
([1]*IIS, The Univ. of Tokyo*) ○Tomohito Mori,[1] Kei Murata,[1] Kazuyuki Ishii[1]

In this study, we focused on rare-earth phthalocyanine double-decker complexes ($LnPc_2$), which are expected to show magneto-chiral dichroism (MChD) or chirality-induced spin selectivity (CISS) because of their electronic properties. $GdPc_2$ complexes having octyloxy or *t*-butyl groups as the side chains were synthesized, and their photophysical properties and chiral induction will be discussed in the poster presentation.
Keywords: Phthalocyanine; Chirality

キラルな物質が磁場方向によって性質を変える磁気キラル異方性として、磁気キラル二色性 (MChD) や Chirality Induced Spin Selectivity (CISS)[1] が知られている。700nm 付近に強い吸収帯を持つフタロシアニン（Pc）は、磁気円偏光二色性を示すとともに、Pc 同士が捩れて会合した場合、励起子キラリティに由来した円偏光二色性が期待できることから、Pc 多量体は MChD を調べるための良い候補と考えられる。

そこで本研究では、希土類 Pc ダブルデッカー錯体（$LnPc_2$、Figure 1a）に着目した。Pc 多量体では、キラル側鎖の導入やマクロな機械的回転[2] によるキラリティ誘起が報告されているだけでなく、この $LnPc_2$ 錯体は、HOMO から電子が抜けた分子半導体（Figure 1b）として合成されることから、CISS 発現も期待できる。そこで中心金属として Gd^{3+}、側鎖にオクチルオキシ基または *tert*-ブチル基をもつ Pc ダブルデッカー錯体を合成した。ポスター発表の際には、これらの光物性 (Figure 1c) やキラリティ誘起について報告する。

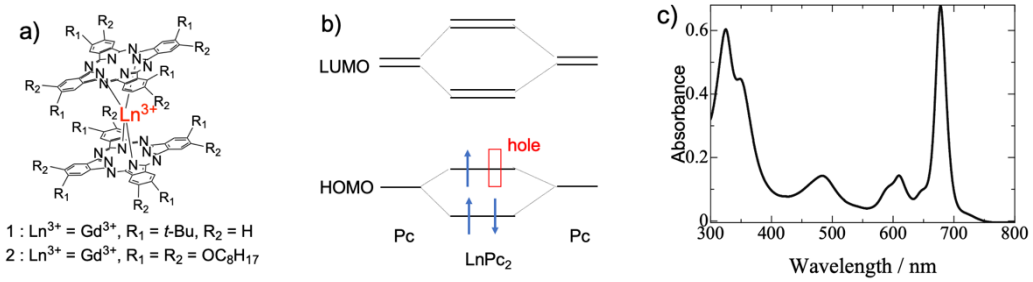

Figure 1. Molecular structure of $LnPc_2$ (a), electronic state of $LnPc_2$ (b), and an electronic absorption spectrum of **1** (c).

1) B. Gohler *et al.*, *Science,* **2011**, *331*, 894. 2) M. Kuroha *et al.*, *Angew. Chem. Int. Ed.*, **2019**, *58*, 18454.

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蒸気応答性付与を志向したFe(III)イオンを有する柔粘性イオン結晶の合成と相挙動

（金沢大ナノマリ）○重田　泰宏・水野　元博
Synthesis and phase transition behavior of Fe(III) ion-based plastic crystal aimed at endowing vapor response (*Nanomaterials Research Institute, Kanazawa University*) ○Yasuhiro Shigeta, Motohiro Mizuno

In this work, we have newly synthesized Fe(III) ion-based plastic crystals, and their phase transition behavior was examined. Candidates for plastic crystal were synthesized by combining the $Fe(III)X_3$ (X=Cl, Br) and organic cation with halogen anions in ethanol. Among them, 1-methyl-1-propylpiperidinium (Pip_{13}) as a cation, $(Pip_{13})FeCl_3Br$ showed plastic crystalline phase, because of small ΔS value (11 J/(K･mol)) at melting point confirmed by DSC measurement.
Keywords : Plastic crystal

気体分子に応答してその性質・状態を変化させる物質群は、気体の検出・分離等に役立つことから、多孔性物質や高分子膜など様々な材料が創製されている。このような性質には、気体の吸脱着能・拡散性が重要であることが知られているが、これらのパラメータは物質とその構造に固有といえる。これを外部刺激によって調整できれば、気体の吸脱着挙動を制御可能な新たな物質群の創製に繋がると期待される。そこで本研究では柔粘性結晶に着目した。柔粘性結晶相中では、分子の重心秩序が保たれている一方配向秩序は失われており、このディスオーダーが気体の拡散に影響を与えうることが報告されている[1]。柔粘性結晶相と、より低温で現れる結晶相との拡散性の差を利用すると、蒸気吸脱着挙動を能動的に制御できる系の構築が期待される。本発表では、蒸気吸着能を有する柔粘性結晶を創製すべく、Fe(III)イオンを有する柔粘性イオン結晶を創製したので、その相挙動と蒸気曝露に対する応答について報告する。

柔粘性結晶の候補となる物質群は、エタノール中で $Fe(III)X_3$ (X= Cl, Br)と、ハロゲンを対アニオンとして有する種々の有機カチオンを混合することで合成した。1-メチル-1-プロピルピペリジニウム(Pip_{13})を有する化合物$(Pip_{13})FeCl_3Br$ の DSC 曲線を図に示す。室温から 373 K の範囲において DSC 曲線は 359 K に一つの吸熱ピークを示した。加熱時の顕微鏡観察結果から、この吸熱ピークは融解に対応するものと分かった。柔粘性結晶相を示す典型的な例として、融解時のエントロピー変化ΔS が 20 J/(K･mol)以下であることが知られている。この化合物において、ΔS は 11 J/(K･mol)と算出されたことから、融点以下、すなわち室温においても柔粘性結晶相を示すことが示唆された。

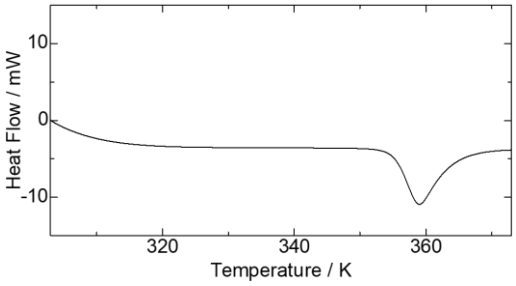

図 $(Pip_{13})FeCl_3Br$ の DSC 曲線

[1] Kandagal, V. S. *et al. J. Phys. Chem. B*, **2018**, *122*, 8274-8283.

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嵩高い配位子を持つ Rh 複核錯体を基盤とした新規ドナー-アクセプター集合体の合成

（東理大理）○木村 文紀・大坪 主弥

Synthesis of a novel doner-acceptor molecular assembly composed by Rh binuclear unit with a bulky dicarboxylic acid ligand and an electron acceptor molecule (*Faculty of Science, Tokyo University of Science*) ○Fuminori Kimura, Kazuya Otsubo

Molecular assemblies composed of electron donor and acceptor molecules are expected to show a variety of physical properties depending on the degree of charge transfer. Here, we report synthesis, crystal structure, and electronic properties of a novel molecular assembly composed of a paddle-wheel Rh binuclear complex with a bulky dicarboxylic acid ligand and electron acceptors. Single-crystal X-ray structure analysis revealed that acceptor molecules coordinate with the Rh dimer to form 2D network structure. Details are presented.

Keywords : Mixed valence state; Donor-acceptor system; Electronic state; Charge transfer; Crystal structure.

【緒言】

ドナー分子とアクセプター分子からなる分子集合体は電荷移動量に応じた多彩な物性を示す。今回我々は、構造的に嵩高いジカルボン酸配位子を用いた paddle wheel 型の Rh 複核錯体 $Rh_2(esp)_2$ (esp: *α*, *α*, *α'*, *α'*-tetramethyl-1,3-benzenedipropionic acid)とアクセプター分子を反応させることにより、新規ドナー-アクセプター集合体を得ることに成功し、構造と物性についての知見を得たので報告する。

【合成】

目的物の合成は以下の反応で行なった。

(a) $Rh_2(esp)_2$ + TCNQ → $\{Rh_2(esp)_2\}_2(TCNQ)\cdot(solvent)_n$ (**1**)

(b) $Rh_2(esp)_2$ + F_4TCNQ → $\{Rh_2(esp)_2\}_2(F_4TCNQ)\cdot(solvent)_n$ (**2**)

（TCNQ: 7,7,8,8,-tetracyanoquinodimethane）

【結果と考察】

拡散法を用いて $Rh_2(esp)_2$ のクロロホルム溶液とアクセプター分子のトルエン溶液の反応させることにより錯体**1**の緑色の針状結晶と錯体**2**の茶色のブロック状結晶を得た。単結晶 X 線構造解析により得られた 150 K における結晶 **2** の結晶構造を Figure. 1 に示す(Triclinic, *P*–1, *a* = 12.7616(2) Å, *b* = 14.7262(2) Å, *c* = 14.8140(2) Å, *α* = 85.432(1)°, *β* = 69.880(2)°, *γ* = 74.281(1)°, *V* = 2516.06(8) Å^3)。Rh 複核錯体に F_4TCNQ が配位することで二次元ネットワーク構造を形成し、溶媒分子が層間に取り込まれた構造を有していることが明らかになった。詳細は当日報告する。

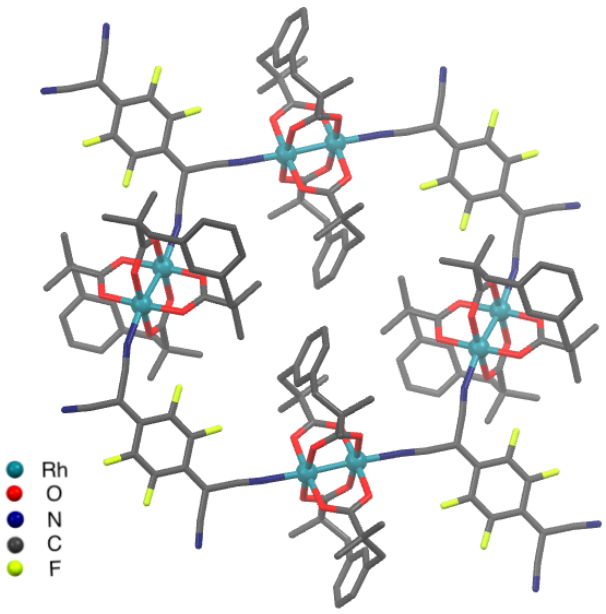

Figure 1. Crystal structure of **2** at 150 K. (Solvents are omitted.)

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磁性金属錯体鎖のキラル誘起スピン選択性(CISS)の解明

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Chiral induced spin selectivity (CISS) of magnetic coordination molecular chain ([1]*Faculty of Science, Kumamoto university* , [2]*Faculty of Advanced Science and Technology, Kumamoto university*) ○Karin Kubo,[1] Zhongyue ZHANG,[2] Yoshihiro Sekine,[2] Shinya Hayami[2]

Chiral Induced Spin Selectivity (CISS) is the phenomenon of the selective conductance of polarized spin currents within a molecule with structural chirality. Such phenomena are expected to play an important role in spintronics devices and understanding spin-selective behavior in biological processes, but its mechanism has not yet been revealed. Previous studies of CISS have focused on the spin-free chiral organic molecules, herein, we focused on magnetic chiral coordination molecular chain with the existence of large spin-orbit coupling (SOC) as chiral molecules, and attempt to reveal the mechanism of CISS from two perspectives: chirality and SOC.

In this study, we select $[Co_3(dpa)_4(NCS)_2]$ (Fig. 1, dpa^- = di(2-pyridyl)amide anion) as the target molecule. To observe the CISS effect by applying an electric current to the target molecule, we attempted to form self-assembled monolayers (SAMs) of the target molecule on a gold substrate. We use racemic monolayers to form SAMs, and AFM observations showed that the thickness of the SAMs corresponded to the length of the target molecule (Fig. 2).

Keywords : Chiral induced spin selectivity; Magnetic coordination molecular chain; Self assemble monolayer

キラル誘起スピン選択性(CISS)とは、キラル分子内で分極したスピン流が選択的に伝導する現象である。この現象はスピントロニクスデバイスや生体内のスピン選択的過程の理解において重要な役割を果たすことが期待されているが、そのメカニズムはいまだ解明されていない。従来の研究ではキラル分子として有機分子に焦点が当てられていたが、我々は大きなスピン軌道相互作用(SOC)を持つ磁性金属錯体鎖に着目し、キラリティと SOC の 2 つの観点から CISS のメカニズムの解明を試みた。

本研究では、対象分子として$[Co_3(dpa)_4(NCS)_2]$ (Fig.1, dpa^- = di(2-pyridyl)amide anion) を選択した。対象分子に電流を流して CISS 効果を観測するために、金基盤上への対象分子の自己組織化単分子膜(SAMs)の形成を試みた。ラセミ体を用いて SAMs を形成し、AFM で観察を行った結果、対象分子の長さに相当する厚みが観測された(Fig.2)。

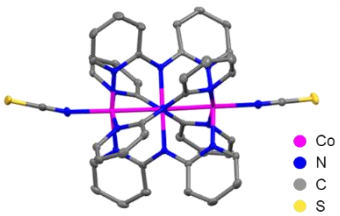

Fig. 1 Structure of $[Co_3(dpa)_4(NCS)_2]$

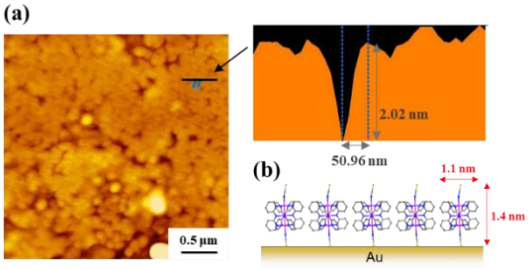

Fig. 2 (a) AFM image (b) Schematic view of SAMs

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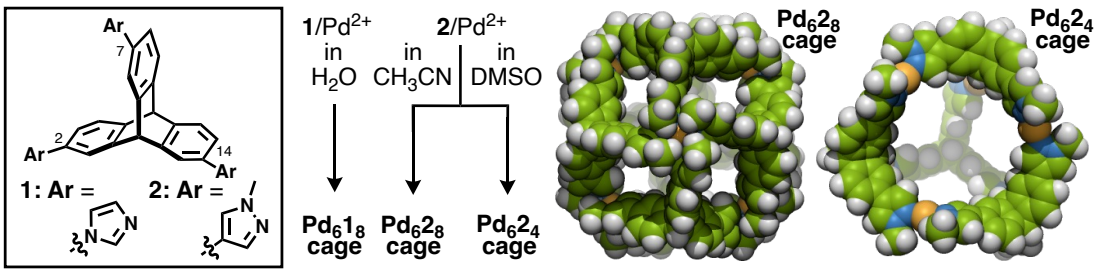
トリプチセン骨格を基盤とした三脚型配位子による Pd_6L_8 型と Pd_6L_4 型ケージの合成

（東工大理）○山本大夢・山科雅裕・豊田真司
Synthesis of Pd_6L_8 and Pd_6L_4 cages from triptycene-based tripodal shaped ligands (*School of Science, Tokyo Institute of Technology*) ○Hiromu Yamamoto, Masahiro Yamashina, Shinji Toyota

The CH-π interaction occurring between C–H bond and π-electron system plays a key role in a molecular recognition. We previously reported an organic molecular cage that can include a C_{60} guest through multiple CH–π interactions, by using selective bromination of triptycene. In order to utilize CH–π interactions, we herein synthesized two tripodal ligands based on the triptycene scaffold and constructed coordination-driven supramolecular cages. Considering the coordination angle, both imidazole-based ligand **1** and methylpyrazole-based ligand **2** were designed in this study. When Pd ions and **1** were mixed in a 6:8 ratio in water, Pd_6**1**$_8$ cage was quantitatively formed, as confirmed by ^{1}H NMR. In contrast, although ligand **2** did not form any assemblies under the same condition, it alternatively formed two types of cages, Pd_6**2**$_8$ cage in CH_3CN and Pd_6**2**$_4$ cage in DMSO.
Keyword: Self-assembly; Triptycene; Molecular cage; Solvent effect; Palladium

C–H 結合と芳香環の間に働く CH–π 相互作用は、分子認識において重要な役割を担う[1]。近年我々は、トリプチセンの 2,7,14 位への選択的臭素化を利用して有機ケージを合成し、CH–π 相互作用を駆動とした C_{60} の内包に成功した[2]。本研究では、効果的に CH–π 相互作用を活用するために、トリプチセンを基盤とした三脚形配位子を合成し、配位結合を駆動とした超分子ケージを合成した。配位部には配位角を考慮してイミダゾールとメチルピラゾールをそれぞれ有する配位子 **1** と **2** を設計した。水中で Pd(II)イオンと **1** を 6:8 の比率で混合すると、Pd_6**1**$_8$ 型ケージが定量的に形成したことが ^{1}H NMR 測定より明らかになった。一方、**2** は水中で Pd イオンと混ぜても集合体を形成しなかったが、CH_3CN 中で Pd_6**2**$_8$ 型を、DMSO 中で Pd_6**2**$_4$ 型ケージを形成することが判明した。すなわち、配位力の低い配位子では、集合体の形成時に溶媒依存性が発現した。



[1] M. Nishio, Y. Umezawa, M. Hirota, Y. Takeuchi, *Tetrahedron* **1995**, *51*, 8665–8701.
[2] T. Mitani, E. Tsurumaki, S. Toyota, *Chem. Eur. J.* **2023**, *29*, e202203462.

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Effects of cationic surfactants on the emission properties of $[Au(CN)_2]^-$ oligomers

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Keywords: Aurophilic interaction, Cationic surfactant, Excited oligomers, Exciplex tuning, Supermolecule

$[Au(CN)_2]^-$ in aqueous solutions forms emissive oligomers due to aurophilic interaction. The emission peak maxima depend on the degree of oligomerization, e.g. 330 nm (dimer), 390 nm (trimer), and 430 nm (tetramer) [1]. Additions of quaternary ammonium salts to $[Au(CN)_2]^-$ solutions promote the oligomers formation and significantly increases emission intensity [2]. Recently, we found that cationic surfactants enhance the emission intensity of $[Au(CN)_2]^-$ oligomers more efficiently than quaternary ammonium salts. In this study, we investigated the effects on the emission properties of $[Au(CN)_2]^-$ oligomers by the addition of several cationic surfactants (alkyltrimethylammonium chloride (bromide): C*n*TMAC(B) and alkyltriethylammonium bromide: C*n*TEAB, (*n* = 14, 16 and 18)). In these surfactants, trimethyl or triethylammonium acts as hydrophilic group and long alkyl chain acts hydrophobic group.

Aqueous solutions of $[Au(CN)_2]^-$ (1.0 mM) containing the cationic surfactants (1.0 mM) showed emission peaks at 450-480 nm (Table 1). These emissions are assigned to the phosphorescence of excited pentamers and/or larger oligomers. The emission peak wavelengths depended on the hydrophilic groups, not on the hydrophobic groups (Table 1, Fig.1(a)). The surfactants having trimethyl ammonium induce the formation of larger oligomers compared to the surfactants having triethylammonium. Meanwhile, the emission quantum yields and intensities were higher, as the hydrophobic groups got longer (Table 1, Fig.1(b)). Aqueous solutions containing C_{18}TMAC exhibit much higher emission intensity and longer lifetime compared to aqueous solutions containing the other surfactants. In addition, the emission of the solution containing C_{18}TMAC was not quenched by oxygen (Table 1). This suggests that C_{18}TMAC and $[Au(CN)_2]^-$ oligomers forms densely packed aggregates so that $[Au(CN)_2]^-$ oligomers are blocked from oxygen.

Table 1. Peak wavelength (λ_{ex}=290 nm), emission quantum yield (Φ_{em}), emission life time for air-saturated (τ_{air}) or Ar-saturated (τ_{Ar}) aqueous solutions of $[Au(CN)_2]^-$ (1.0 mM) containing cationic surfactants (1.0 mM).

Cationic Surfactants	λ_{em} / nm	Φ_{em}	τ_{air} / μs	τ_{Ar} / μs
C_{14}TMAC (1.0 mM)	470	0.20	0.311	0.602
C_{16}TMAC (1.0 mM)	470	0.22	0.324	0.621
C_{16}TMAB (1.0 mM)	470	-	0.351	0.714
C_{18}TMAC (1.0 mM)	**480**	**0.56**	**0.917**	**1.05**
C_{14}TEAB (1.0 mM)	450	0.12	0.337	0.596
C_{16}TEAB (1.0 mM)	450	0.17	0.388	0.729
C_{18}TEAB (1.0 mM)	450	0.21	0.380	0.838

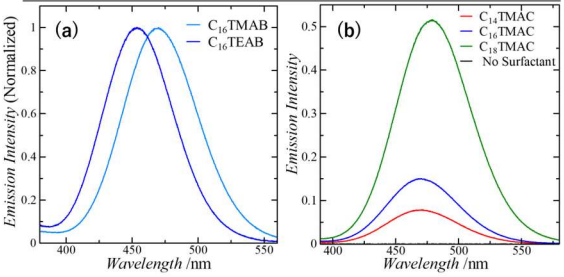

Fig.1. Emission spectra of $[Au(CN)_2]^-$ (1.0 mM) aqueous solutions containing cationic surfactants (1.0 mM, λ_{ex} = 290 nm)
(a) C_{16}TMAB and C_{16}TEAB (b) C*n*TMAC (*n* = 14,16 and 18)

[1]M. Iwamura *et al*., Phys. Chem. Chem. Phys., **2023**, 25, 966-974.[2] R. Wakabayashi *et al*., Inorg. Chem., **2016**, 55, 7739-7746.

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Optical and Magnetic Properties of Octacyanidemetalate Ionic Crystals with Alkali Cations and Glycine

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Keywords: Cyanide Complex; Paramagnetic-Antiferromagnetic Transition; Near-Infrared Emission; Second Harmonic Generation

Molecular-based materials have been studied from various perspectives because of diverse functionalities. Among them, our laboratory has developed multifunctional complexes by focusing on magnetic and optical properties, such as humidity responsive emissive single-molecule magnets[1)] and chiral crystals with photoswitchable superionic conductivity[2)].

We synthesized the ionic crystalline complex of $Cs_3[W^V(CN)_8]$(glycine) (**CsW-gly**) by mixing aqueous solutions of cesium-octacyanotungstate dihydrate ($Cs_3[W^V(CN)_8]\cdot 2H_2O$) with glycine. **CsW-gly** exhibits paramagnetic-antiferromagnetic transition at 27 K and near-infrared fluorescence originating from $[W^V(CN)_8]^{3-}$, while the precursor $Cs_3[W^V(CN)_8]\cdot 2H_2O$ exhibits paramagnetism and very weak emission. These differences could be originated from the crystal structure of **CsW-gly** in which the W (S = 1/2) sites are close each other and the coordination geometry of $[W^V(CN)_8]^{3-}$ is an ideal square antiprism. In order to tune the fluorescence and magnetic properties, we prepared the iso-structural complexes $A_3[M^V(CN)_8]$(glycine) (A = Rb, M = W (**RbW-gly**), A = Cs, M = Mo (**CsMo-gly**), A = Rb, M = Mo (**RbMo-gly**)) with the metal substitution. These complexes exhibited fluorescence peaks at 788 nm (**CsW-gly**), 800 nm (**RbW-gly**), 713 nm (**CsMo-gly**), and 734 nm (**RbMo-gly**) with 470 nm excitation light.

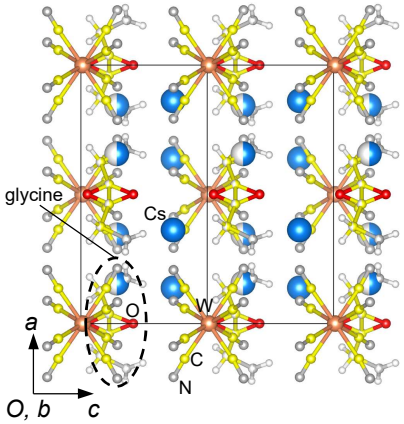

Figure 1 Crystal structure of **CsW-gly** viewed from *b*-axis.

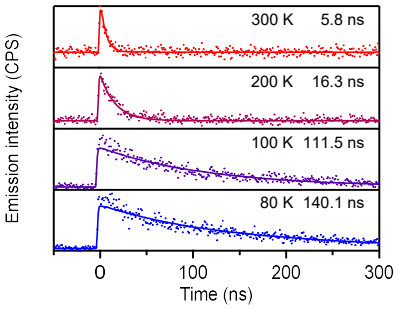

Figure 2 Emission lifetime of **CsW-gly**. $\lambda_{ex} = 470$ nm, $\lambda_{em} = 750$ nm

1) Y. Xin, J. Wang, J. M. Zychowicz, J. J. Zakrzewski, K. Nakabayashi, B. Sieklucka, S. Chorazy, S. Ohkoshi, *Journal of American Chemistry Sciety*, **2019**, *141*, 18211. 2) S. Ohkoshi, K. Nakagawa, K. Imoto, H. Tokoro, Y. Shibata, K. Okamoto, Y. Miyamoto, M. Komine, M. Yoshikiyo, and A. Namai, *Nature Chemistry*, **2020**, *12*, 338.

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配位結合によるポルフィリン二量体の形成と超分子ホスト機能

（日大院理工[1]・日大理工[2]）○宮﨑 茂樹[1]・佐藤 賢[1]・須川 晃資[2]・大月 穣[2]
Formation of porphyrin dimer by coordination bonding and supramolecular host function
([1]*Graduate School of Science and Technology, Nihon University*, [2]*College of Science and Technology, Nihon University*) ○Shigeki Miyazaki[1], Ken Sato[1], Kosuke Sugawa[2], Joe Otsuki[2]

The arrangement of porphyrin rings facing each other can provide host functions through molecular recognition and catalytic functions. In our laboratory, we have found that incorporation of bipyridine into porphyrins forms stable complexes. We have designed a porphyrin that could accommodate guest molecules when forming a dimer for application to host compounes. In this presentation, we report on the synthesis of this porphyrin, the evaluation of its self-assembly by the addition of Ag^+ and Zn^{2+} ions, and the recognition of guest molecules.

Keywords : Bipyridine; Complex; Dimer; Porphyrin; Supramolecular;

ポルフィリンは特有の分光学的性質を持っており，組織化することによりエネルギー移動や分子認識によるホスト機能などの新たな性質を示す[1]．当研究室では，ポルフィリンのメソ位にフェニル基を介し，配位結合部位としてビピリジンを導入したポルフィリンに Zn^{2+}イオンを添加すると安定な face-to-face 二量体を形成することを見出した[2]．そこで本研究では，このポルフィリン錯体をホスト分子として機能化させるために，スペーサーとしてフェニル基とビピリジンとの間にエチニレン基を導入した新規ポルフィリン(ZnPor(PhCCbpyMe)$_4$)を設計・合成し，溶媒中で金属イオン(Zn^{2+}, Ag^+)を加えた際の錯体形成についての評価を行なった(Fig. 1).

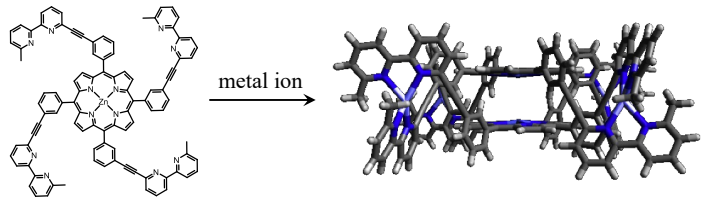

Fig. 1. Complex formation.

^{1}H NMR スペクトルにおいて, Ag(OTf)存在下では ZnPor(PhCCbpyMe)$_4$ の β 位の共鳴が 0.5 ppm 高磁場シフトした．吸収スペクトルにおいてはソーレー帯の短波長シフトや等吸収点が現れ，ESI-MS ではポルフィリン二量体 ([(ZnPor(PhCCboyMe)$_4$)$_2$Ag$_4$(OTf)$_{4-n}$]$^{n+}$ (n = 2-4))を示すピークが現れた．また, Zn(OTf)$_2$ 存在下でも同様の変化が見られた．これらのことから，ポルフィリン二量体が形成していると考えられる．

[1] J. Otsuki *et al*., *Chem. Eur. J*., **2016**, *22*, 1165-1176.
[2] 日本化学会第 104 春季年会，日大院理工， 佐藤賢.

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三核亜鉛クリプタンド錯体による迅速 CO_2 回収、及びその構造状態の解析

（豊田中央研究所）○村瀬 雅和・前川 佳史・大橋 雅卓・後藤 康友・坂本 直柔・野中 敬正・宇山 健・荒井 健男

Rapid CO_2 Fixation Using a Trinuclear Zn(II) Cryptate Complex and Analysis of its Structure State

(Toyota Central R&D Labs., Inc.) ○Masakazu Murase, Yoshifumi Maegawa, Masataka Ohashi, Yasutomo Goto, Naonari Sakamoto, Takamasa Nonaka, Takeshi Uyama, Takeo Arai

CO_2 separation and capture is one of the technologies aimed at reducing the concentration of CO_2 in the atmosphere, which is expected to contribute to suppressing the progress of global warming. A variety of material systems, including aqueous alkaline solutions, amine-based organics, porous materials such as zeolites, and metal-organic flameworks, have been reported as CO_2 fixatives with appropriate conditions for the operating environment. Then, in order to propose a more promising CO_2 fixative, we newly synthesized a trinuclear Zn(II) cryptate complex (Zn_3**L**) inspired by the function of carbonic anhydrase (**Fig.1**) [1]. The CO_2 fixative solution containing Zn_3**L** exhibited a faster CO_2 fixation rate than that of an alkaline aqueous solution (KOH(aq)) set at the same solute concentration. In addition, Zn_3**L** released CO_2 by decomposition of the complex structure through protonation of the cryptate ligand (**L**) after CO_2 fixation and also refixed CO_2 by reconstructing the complex structure through deprotonation of **L**. The structural state of Zn_3**L** during these reactions was elucidated based on spectral changes obtained from *Operando* X-ray absorption spectroscopy measurements.

Keywords : CO_2 capture; Zinc complexes; Carbonic anhydrase; X-ray absorption spectroscopy

CO_2 分離回収技術は、大気中 CO_2 濃度低減を目指す技術の一つであり、地球温暖化対策への貢献が期待されている。上記技術の中核を担う CO_2 吸収物質には、アルカリ水溶液、アミン系有機物、ゼオライトなどの多孔体、金属有機構造体（MOF）など様々な材料系が報告されている。その中で我々は、より優れた CO_2 吸収物質の創製に向け、炭酸脱水酵素の機能に着想を得た三核亜鉛クリプタンド錯体（Zn_3**L**）を新たに合成した（**Fig.1**）[1]。Zn_3**L** を含む溶液は、同濃度のアルカリ水溶液（KOH(aq)）よりも速い CO_2 吸収速度を示した。加えて、Zn_3**L** をプロトン化し錯体構造を分解させることで CO_2 を放出し、さらに脱プロトン化により錯体構造を再構築させることで CO_2 の再吸収が可能であることも確認した。これら反応中における Zn_3**L** の構造状態については、*Operando* X 線吸収分光スペクトルをもとに明らかにした。

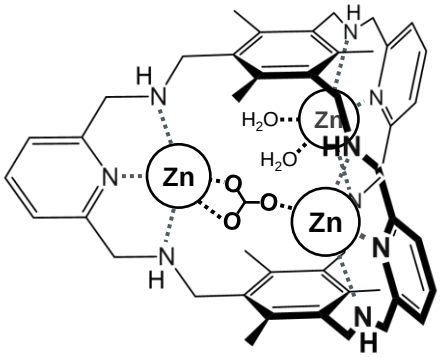

Fig.1 Chemical structure of Zn_3**L** incorporating the carbonate ion converted from CO_2.

1) M. Murase et al., ChemSusChem **2023**, *16*, e202300679.

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Heterogenized Cationic Ru(II) Polypyridine Complexes for Visible-Light Photoredox Catalysis

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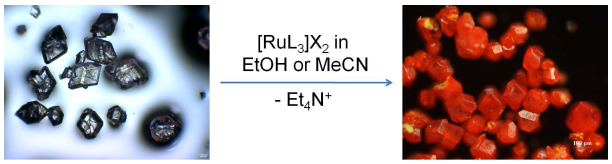
○ Seong Huh,[1] Jong-Seo Kim[1]

Keywords: Metal-Organic Framework; Ru Complexes; Photoredox Catalysis; Visible-Light Catalysis; Luminescence

Three cationic Ru(II) polypyridine complexes were successfully encapsulated into the mesoscale channels of the anionic framework of InTATB metal-organic framework (MOF) having doubly-interpenetrated channel structure to give three new RuL_3@InTATB photoredox catalytic systems (L = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2'-bipyrazine (bpz)). The counter-cations (NEt_4^+) in the as-prepared InTATB (H_3TATB = 4,4',4''-*s*-triazine-2,4,6-triyltribenzoic acid) were partially exchanged with the cationic Ru(II) polypyridine complexes in a simple cation-exchange process. The uptake amounts of $[RuL_3]^{2+}$ by InTATB ranged 0.38 – 0.55 μmol/10 mg-solid. These uptake values are slightly larger than those of previously reported RuL_3@InBTB cases.[1] The photoluminescence (PL) of RuL_3@InTATB systems were investigated by steady-state fluorescence spectroscopy. The time-resolved photoluminescence (TRPL) decay curves for the solid-state RuL_3@InTATB were also measured to compare the excited state lifetimes of the encapsulated $[RuL_3]^{2+}$ species compared to free ions. Both $Ru(bpy)_3$@InTATB and $Ru(bpz)_3$@InTATB exhibited extended PL lifetimes compared to free ions and RuL_3@InBTB.

The photoredox catalytic activities were tested using the aza-Henry reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (THIQ) under visible light at room temperature.[1,2] The photoredox catalytic reaction, aza-Henry reaction of THIQ, indeed indicated the superior catalytic activities of RuL_3@InTATB systems over RuL_3@InBTB systems. The product selectivities were also enhanced. These results clearly suggest that RuL_3@InTATB is a good visible-light photoredox catalytic system.



1) I.-H. Choi, S. Yoon, S. Huh, S.-J. Kim, Y. Kim, *Chem. Eur. J.* **2020**, *26*, 14580. 2) J. Pang, S. Yuan, J.-S. Qin, C. T. Lollar, N. Huang, J. Li, Q. Wang, M. Wu, D. Yuan, M. Hong, H.-C. Zhou, *J. Am. Chem. Soc.* **2019**, *141*, 3129.

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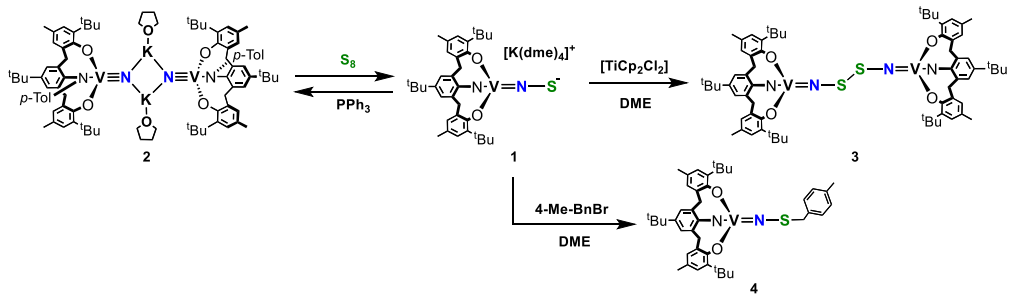
[ONO]型配位子を有するアニオン性バナジウムチオニトロシル錯体の合成と反応

（東工大理）○菅原 大地・石田　豊・川口　博之
Synthesis and Reactions of the Anionic Vanadium Thionitrosyl Complex with the [ONO] Ligand (*School of Science*, *Tokyo Institute of Technology*) ○Daichi Sugawara, Yutaka Ishida, Hiroyuki Kawaguchi

While nitrosyl complexes of transition metals are well developed, the chemistry of thionitrosyl complexes has received less attention due to the difficulty in their preparations. Here we present the synthesis and reactions of the anionic thionitrosyl vanadium complex with the [ONO] ligand. The anionic thionitrosyl complex (**1**) was prepared by treatment of **2** with S_8 in THF. The X-ray diffraction study reveals that the terminal thionitrosyl complex **1** possesses an approximately linear V-N-S linkage (174.8(4)˚) with the N–S distance of 1.614(4) Å. Addition of PPh_3 to a DME solution of **1** resulted in sulfur abstraction, regenerating the nitride complex **2**. When **1** was treated with [$TiCp_2Cl_2$], intermolecular S-S coupling took place to produce the dinuclear complex **3** with two vanadium centers linked by the N-S-S-N unit. Alkylation of **1** with 4-methyl-benzyl bromide smoothly proceeded to yield the (*p*-methyl-benzylthio)imido complex **4**. All these complexes have been characterized by single crystal-X-ray diffraction.

Keywords ： vanadium; thionitrosyl ligand; nitride complex

チオニトロシル錯体の研究は、ニトロシル錯体と比べて限られている[1]。本研究では[ONO]配位子を持つアニオン性バナジウムチオニトロシル錯体（**1**）の合成および反応について報告する。チオニトロシル錯体 **1** は、ニトリド錯体（**2**）の THF 溶液に S_8 を加えることで得た。X 線構造解析の結果、**1** の N-S 結合長は 1.614(4) Å と長く、V-N-S 結合角は 174.8(4)˚ と直線構造であることが明らかになった。錯体 **1** に PPh_3 を加えると、Ph_3PS が生成するともにニトリド錯体 **2** の再生が観測された。次に、**1** の DME 溶液に[$TiCp_2Cl_2$]を加えると二核錯体 **3** が得られた。反応過程で、チオニトロシル配位子間で S-S 結合の形成が進行し、N-S-S-N 骨格で連結された二核錯体が生成した。また、4-メチル-ベンジルブロミドを **1** に作用させると、硫黄上でアルキル化が進行し、錯体 **4** を得た。



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Re(I)単核錯体を触媒、カルバミン酸塩を CO_2 源として用いた電気化学的 CO_2 還元反応

(東工大理[1]・広島大院先進理工[2]) ○根本 賢周[1]・石谷 治[1,2]

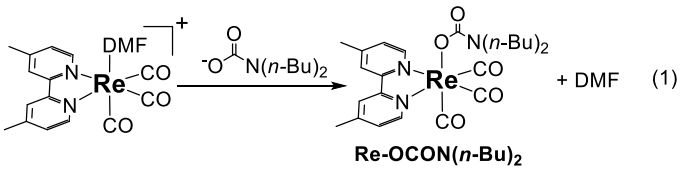
Electrochemical CO_2 reduction using a Re(I) complex catalyst and carbamate as a CO_2 source

([1]*School of Science, Tokyo Institute of Technology*, [2] *Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kenshu Nemoto,[1] Osamu Ishitani [1,2]

We successfully synthesized a carbamate Re(I) complex, *fac*-[Re(dmb)(CO)$_3$OCON(*n*-Bu)$_2$] (**Re-OCON(*n*-Bu)$_2$** : dmb = 4,4'-dimethyl-2,2'-bipyridine) (eq. 1), and obtained its single crystal x-ray structure. This Re complex electrochemically catalyzed CO_2 reduction in the presence of NH(*n*-Bu)$_2$: CO was a main product and H_2 also formed as a minor product (eq. 2). Under 10% CO_2 atmosphere, turnover number of CO formation (TON_{CO}) was 46% compared to that under pure CO_2. In the absence of NH(*n*-Bu)$_2$, on the other hand, TON_{CO} was 16% even under pure CO_2. In this presentation, we will report reactivities of the isolated **Re-OCON(*n*-Bu)$_2$** as well.

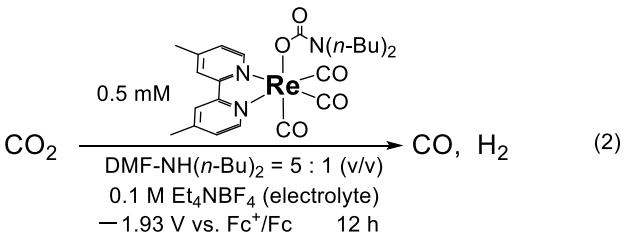
Keywords : Electrochemical reduction of CO_2; Re(I) complex catalyst; Secondary amine; Carbamate anion

2 級アミンの NH(*n*-Bu)$_2$ 溶液に CO_2 を通気することでカルバメートアニオン(N(*n*-Bu)$_2$COO$^-$)の塩を合成した。この溶液を、配位置換活性な DMF を配位させた Re(I)錯体を含む DMF 溶液に添加すると *fac*-[Re(dmb)(CO)$_3$OCON(*n*-Bu)$_2$] (**Re-OCON(*n*-Bu)$_2$**) がほぼ定量的に生成した(eq. 1)。この錯体の単離と単結晶 X 線構造解析に成功した。



Re-OCON(*n*-Bu)$_2$

Re-OCON(*n*-Bu)$_2$ を含む DMF–NH(*n*-Bu)$_2$ 混合溶液に対して、100% CO_2 雰囲気下、−1.93 V vs. Fc^+/Fc の電位をかけて 12 時間定電位電解を行うと、主生成物として CO が生成し H_2 が副生した(eq. 2)。CO_2 濃度が 10%の Ar ガスを通気して同様の電解を行ったところ、100%CO_2 を用いた時の 46%の速度で CO が生成した。一方、NH(*n*-Bu)$_2$ を含まない *fac*-[Re(dmb)(CO)$_3$DMF]$^+$を含む DMF 溶液を、100% CO_2 雰囲気下で電解すると、上述した NH(*n*-Bu)$_2$ を含む溶液で電解した結果と比べ約 16%の CO 生成速度であった。発表では、単離した **Re-OCON(*n*-Bu)$_2$** の反応性に関しても報告する。



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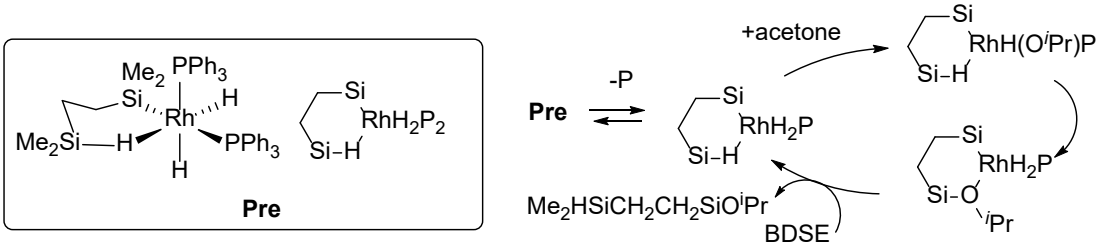
Mechanisms of hydrosilylation of carbonyl compounds catalyzed by rhodium-phosphine complexes: The rate enhancement by proximate two Si-H groups

([1]*Transdisciplinary Research and Education Center*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*) ○ Hideo Nagashima,[1] Yoshihito Shiota,[2] Kazunari Yoshizawa[2]

Keywords: Hydrosilylation; Carbonyl Comounds; Rhodium-Phosphine Complexes; Catalysts; DFT calculations

The hydrosilylation of ketones mediated by transition metal catalysts provides a practical method for reduction of carbonyl compounds by appropriate selection of the catalyst and the hydrosilane. We have found unique acceleration of the hydrosilylation of ketones, when $RhCl(PPh_3)_3$ and certain bifunctional hydrosilanes bearing closely located two Si-H groups were used as the catalyst and the hydrosilane, respectively. For instance, $Me_2HSiCH_2CH_2SiHMe_2$ (BDSE) quickly reacted with acetone to form $Me_2(^iPrO)SiCH_2CH_2SiHMe_2$ selectively. The reaction was much faster than that of the hydrosilylation with $EtMe_2SiH$ under the same conditions. The discovery led to the active use of bifunctional hydosilanes like BDSE and $Me_2HSiOSiHMe_2$ (TMDS) as reducing agents, [1] but the reaction mechanism is still unclear. [2]

We propose here a mechanism obtained by a DFT study, which reasonably explains the rate enhancement and selective formation of $Me_2(^iPrO)SiCH_2CH_2SiHMe_2$ described above. As shown below, a Rh(III) species (**Pre**) is a catalyst precursor, from which dissociation of one of the PPh_3 ligands initiates the catalytic cycle. Subsequent reactions with acetone and BDSE complete the catalytic cycle. It is important that all the intermediates and transition states have disilametallacylic structures. Although the hydrosilylation mechanisms recently summarized by Nakatani and Hasegawa,[3] this disilametalacyclic mechanism is not among them, and new.



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鉄触媒を用いた 14 族水素化物の脱水素化カップリング反応

（東大院工 [1]・東大生研 [2]）○KIM TAEWOO[1]・砂田 祐輔 [1,2]

Development of the dehydrogenation coupling reactions of group 14 hydrides mediated by iron catalyst ([1]*Graduate School of Engineering, The University of Tokyo,* [2]*Institute of Industrial Science, The University of Tokyo*) ○TAEWOO KIM,[1] Yusuke Sunada[1,2]

In conventional methods, compounds consisting of E-E bonds (E = group 14 element) are often synthesized through reductive coupling reactions using group 14 halides and strong reducing agents such as alkali metals. However, this method requires stoichiometric amounts of alkali metals, thus development of catalytic synthetic reactions that do not rely on these reagents is highly desired. Recently, our research group reported the formation of Ge-Ge bonds through the dehydrogenative coupling reaction of germanium hydrides using a catalyst composed of $[FeMes_2]_2$ (Mes = 2,4,6-Trimethylphenyl) and N-heterocyclic carbene (NHC). Based on this, the current study focuses on establishing a dehydrogenative coupling reaction using easy-to-handle precursors as catalysts.

First, the dehydrogenative coupling reaction of Ph_2GeH_2 was conducted using 5 mol% $FeBr_2$ as the iron precursor, 10 mol% MesMgBr, and 10 mol% $^{i}PrIM^{Me}$ (1,3-diisopropyl-4,5-dimethyl-2-ylidene) in THF at room temperature for 48 hours, resulting in the high-yield formation of the target product $(Ph_2Ge)_5$. Similarly, by employing $FeBr_2$ as the iron catalyst precursor and conducting the reaction in the presence of an appropriate reducing agent, we observed the efficient progress of the catalytic dehydrogenative coupling reaction of germanium hydrides, which is also reported herein.

Keywords : iron catalyst, group 14 elements, germanium, dehydrogenative coupling

従来法では、14 族間結合を持つ化合物は多くの場合、14 族ハライドとアルカリ金属などの強還元剤を用いた還元的カップリング反応により合成される。しかし本手法では、化学量論量のアルカリ金属を使用する必要があり、これらを必要としない触媒的な合成反応の開発が望まれる。一方、当研究室では最近、$[FeMes_2]_2$(Mes = 2,4,6-Trimethylphenyl)と N-ヘテロ環状カルベン(NHC)からなる触媒を用い、ゲルマニウム水素化物の脱水素化カップリング反応による Ge-Ge 結合形成反応を報告した [1)]。この知見をもとに本研究では、より調整・取り扱い容易な触媒前駆体を用いた脱水素カップリング反応の開発を行った。

まず Ph_2GeH_2 の脱水素カップリング反応を、鉄前駆体として 5 mol%の $FeBr_2$ を用い、10 mol%の MesMgBr と 10 mol%の $^{i}PrIM^{Me}$(= 1,3-diisopropyl-4,5-dimethyl-2-ylidene)の存在下、THF 中、室温下、48 時間の反応条件下で行ったところ、目的生成物である$(Ph_2Ge)_5$ を高収率で得た。同様に、$FeBr_2$ を鉄触媒前駆体として用い、適切な還元剤存在下で反応を行うことで、ゲルマニウム水素化物の触媒的な脱水素カップリング反応が高効率的に進行することを見出したので、併せて報告する。

1) Kobayashi, Y., Sunada, Y., *Chem. Sci.* **2023**, *14*, 1065-1071.

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キラル希土類リン酸錯体を用いた不斉 Friedel-Crafts アルキル化反応の開発

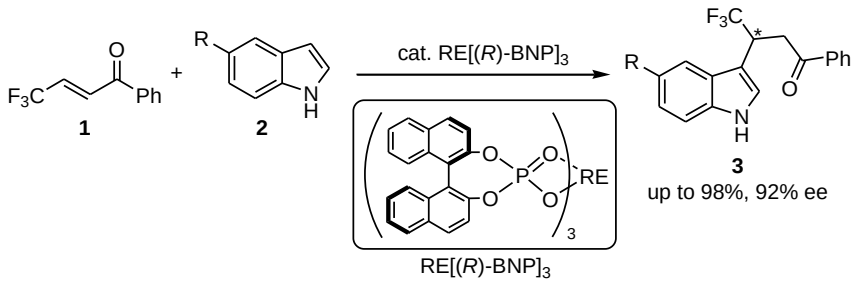
（京都教育大[1]・秋田高専[2]）○鈴木 祥子[1]・塚田 雄大[1]・大山 菜摘[1]・惣元 美咲[1]・横山 保夫[2]

Development of the Asymmetric Friedel-Crafts Alkylation Using the Chiral Rare Earth Organophosphate ([1]*Faculty of Education, The Kyoto University of Education*, [2]*National Institute of Technology, Akita College*) ○Shoko Suzuki,[1] Yudai Tsukada,[1] Natsumi Ohyama,[1] Misaki Sogen,[1] Yasuo Yokoyama[2]

We developed an asymmetric Friedel-Crafts alkylation of indoles with a fluorinated α,β-unsaturated ketone using a chiral rare earth organophosphate, RE[(*R*)-BNP]$_3$ (RE = rare earth metal, BNP = 1,1'-binaphthyl-2,2'-diyl phosphate). The reaction of β-trifluoro α,β-unsaturated ketone **1** with indole **2** in the presence of RE[(*R*)-BNP]$_3$ was carried out and it gave the corresponding product **3** in good yield. It was found that Y[(*R*)-BNP]$_3$ was most effective among these rare earth complexes and its reaction gave the products with high enantioselectivity (up to 92% ee).

Keywords : Chiral Rare Earth Organophosphate; Optically Active Organofluorine Compounds; Lewis Acid Catalyst; Asymmetric Friedel-Crafts Alkylation

光学活性な有機フッ素化合物はフッ素の物理化学的性質に起因して特異な物性や生理活性を示すことが知られており、医薬化学、農芸化学のなどの幅広い分野において注目されている。また天然に存在するものはごく少なく、有機合成化学の分野においては依然として様々な有機フッ素化合物の不斉合成法の開発に興味が持たれている。当研究室では、光学活性ビナフチルリン酸エステル配位子を有する三価の希土類錯体 RE[(*R*)-BNP]$_3$（RE＝希土類金属、BNP＝1,1'-ビナフチル-2,2'-ジイルホスフェート）を用いた触媒的不斉反応の開発を行っている。本錯体は調製が容易、かつ空気中で取扱い可能な不斉ルイス酸触媒であり、含フッ素 α,β-不飽和ケトン **1** を用いた不斉 Friedel-Crafts アルキル化反応に対して有効な触媒となるのではないかと考えた。そこで、実際に本錯体を用いた α,β-不飽和ケトン **1** とインドール **2** の Friedel-Crafts 反応を行ったところ、本錯体が触媒として有効であり、特にイットリウム錯体では高いエナンチオ選択性で目的物 **3** が得られた（最高 92% ee）。



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三座ホスフィン配位子に支持された銅四核ヒドリド錯体を触媒とした CO_2 のヒドロシリル化反応

（奈良女子大学）○馬場 好花・中島 隆行・棚瀬 知明

CO_2 Hydrosilylation Catalyzed by Tetranuclear Copper Hydride Complex Supported by Tridentate Phosphine Ligand (*Nara Women's University*) ○Konoka Baba, Takayuki Nakajima, Tomoaki Tanase

The utilization of CO_2 as valuable chemical feedstocks has received much attention. Especially, CO_2 hydrosilylation gives silyl formate, which can be converted into C_1 synthon of carbonyl compounds. Here we report that tetranuclear copper hydride complex $[Cu_4H_3(dpmp)_3]PF_6$ supported by tridentate phosphine ligand dpmp (bis(diphenylphosphinomethyl)phenylphosphine) [1] (**Figure 1**) was found to be an effective catalyst for CO_2 hydrosilylation. The reaction of CO_2 (1 atm) with tertiary silanes R_3SiH (R_3 = Me_2Ph, $MePh_2$, Et_3, Ph_3) was performed at 60 ℃ for 1 h (**Scheme 1**), and TON was determined by ^1H NMR spectroscopic analysis. As a result, Me_2PhSiH was the most optimal silane, and the catalytic activity increased considerably by adding 4 eq. of ^{t}BuNC. Also, we proposed the possible catalytically active species of this reaction.

Keywords : Carbon dioxide; Copper hydride complex; Hydrosilylation; Phosphine ligand; Silyl formate

豊富な炭素源である CO_2 を価値のある化学物質の原料として利用する反応開発が注目されている。中でも、CO_2 のヒドロシリル化によって生成するギ酸シリルは、カルボニル化合物などの化学物質に変換することができる。そこで、本研究では三座ホスフィン配位子 dpmp (bis(diphenylphosphinomethyl)phenylphosphine)に支持された銅四核ヒドリド錯体$[Cu_4H_3(dpmp)_3]PF_6$ [1] (**Figure 1**)を触媒として CO_2 のヒドロシリル化反応を検討した。1 気圧の CO_2 雰囲気下、第三級シランを 60 ℃、1 時間反応させ(**Scheme 1**)、TON は ^1H NMR 測定により算出した。結果、Me_2PhSiH を用いた時にギ酸シリルが選択的に生成し、^{t}BuNC を 4 等量添加させると、さらに活性が向上した。また、本反応における触媒活性種についても考察した。

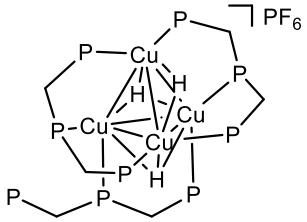
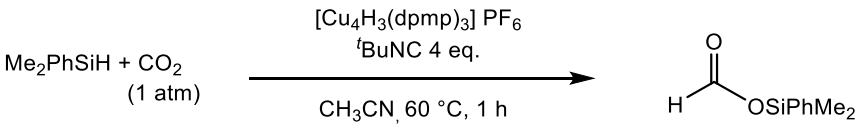


Figure 1 Structure of $[Cu_4H_3(dpmp)_3]$ PF_6



Scheme 1

[1] T. Nakajima, K. Nakamae, R. Hatano, K. Imai, M. Harada, Y. Ura, T. Tanase, *Dalton Trans.*, **2019**,*48*, 12050.

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ITO 電極上の Al 含有メソポースシリカ薄膜への Ru 錯体の固定化と光・電気化学特性

（神奈川大工 [1]）中野 成美 [1]・原田 駿平 [1]・山田 綾乃 [1]・岡村 将也 [1]・引地 史郎 [1]
Photo and electrochemical properties of Ru complexes immobilized on Al-containing mesoporous silica thin films on ITO electrodes. ([1]*Graduate School of Engineering, Kanagawa University*) Narumi Nakano[1], Shunpei Harada[1], Ayano Yamada[1], Masaya Okamura[1], Shiro Hikichi[1]

Cation-exchangeable mesoporous aluminosilicate (Al-SiO_2) thin films with vertically oriented meso-channels were prepared on ITO electrodes by the Stöber method. To the resulting aluminosilicate-ITO composite, a ruthenium complex could be immobilized through electrostatic interaction. When the ruthenium complex-immobilized electrode was irradiated with light, a photocurrent arising from the electron transfer from the photoexcited ruthenium complex was detected.

Keywords : Mesoporous silica; Metal Complexes Immobilization on Electrodes; Photo-electrochemical Reaction

光エネルギーを化学エネルギーに変換する光電気化学セルでは、金属錯体の機能性や安定性を損なうことなく錯体を電極表面に固定することが重要である。その固定場として、規則的に配向した垂直メソチャネル構造を持つシリカ薄膜の利用が期待される。しかし、これまでシリカ薄膜への機能性金属錯体の固定例はない。そこで本研究では、シリカ骨格中の Si^{4+} の一部を Al^{3+} に置換することにより発現するカチオン交換能を利用して、電極上に形成したアルミノシリケート(Al-SiO_2)薄膜に光増感機能を持つ$[Ru(bpy)3]^{2+}$(bpy = 2,2'-bipyridine)を固定し、光電気化学的性質を評価した。

電極上の Al-SiO_2 薄膜は、既報に準じ、エタノール/アンモニア水溶液中に、$Al(NO_3)_3$ を Al 源として加え、界面活性剤をテンプレートとしたシリカ前駆体の自己組織化(Stöber 法)により合成した [1,2]。垂直配向したメソチャネル構造は走査型電子顕微鏡 (SEM) によって確認した。この Al-SiO_2 薄膜上に CH_2Cl_2 に溶解した$[Ru(bpy)_3]^{2+}$を滴下して固定化し、その固定量は定電位電解により 2~4 nmol/cm^2 であると見積もった。得られた Ru 錯体固定化電極に対してリン酸緩衝液 (pH = 5.0) 中で 0.1 V (vs Ag/AgCl) を印加し光照射したところ、未修飾 ITO 電極では変化がない一方で、Ru 錯体固定化電極では光照射に伴って約 9 nA/cm^2 のカソード電流が観測された。これは光励起種に由来する電子移動であると考えられる。

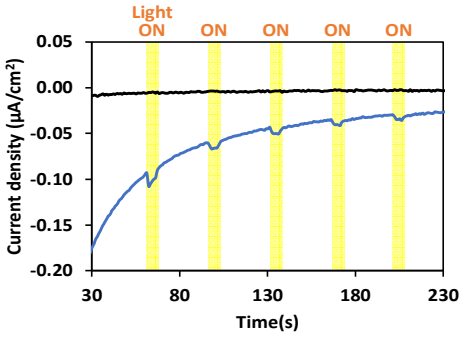

Figure1. Current response by photo irradiation (colored areas are light ON).

1) Z. Teng, *et al,Angew. Chemie Int. Ed.* **2012,** 51, 2173-2177.
2) K-C Kao, *et al, J. Am. Chem. Soc.* **2015,** 137, 3779-3782.

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アンモニア検知及び選択的な触媒反応を可能とするイリジウム錯体を内包した架橋ドメイン構造を有するハイドロゲルの合成

（京大院人環[1]・滋賀県大工[2]）○古川 翔一[1]・伊田 翔平[2]・藤田 健一[1]

Synthesis of Hydrogels with Thermoresponsive Crosslinked Domains Containing Iridium Complex for Ammonia Sensing and Selective Catalytic Reaction

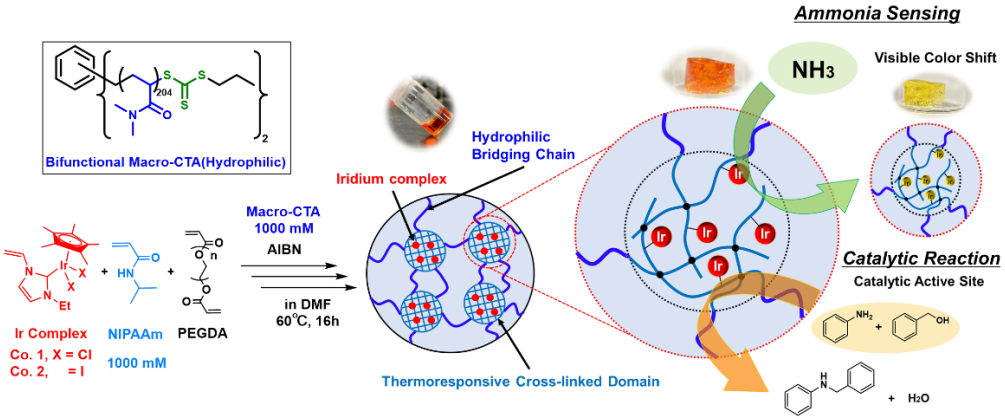
([1]*Graduate School of Human and Environmental Studies, Kyoto University*, [2]*Department of Materials Science, The University of Shiga Prefecture*) ○Shohichi Furukawa,[1] Ida Shohei,[2] Fujita Ken-ichi[1]

Novel soft materials would be potentially developed by introducing organometallic complexes with unique functions into the nanostructure inside the hydrogel. In this study, we designed a novel functional gel with crosslinked domain structure containing the iridium complex for ammonia detection material by changing the color. We synthesized iridium complex monomers and employed them for gel synthesis using reversible addition-fragmentation chain transfer (RAFT) polymerization. The product gel maintained clarity upon temperature change in water, and turned from red to pale yellow by immersion in an aqueous solution of ammonia. The gel could also perform selective N-alkylation of alcohol with amine.

Keywords : Polymer Gel, Iridium Catalyst, N-Alkylation, N-Heterocyclic Carbene, Closs-linked Domain

ハイドロゲルの高分子鎖へ有機金属錯体を導入することにより、ゲル特有の柔軟性や湿潤性に錯体特有の機能（溶媒親和性、色の変化、触媒等）を付与して幅広い展開が期待される。最近伊田らは、架橋された温度応答性高分子から成るナノドメイン（架橋ドメイン；CD)構造を有する新規ハイドロゲルについて報告している[1]。

一方、当研究室では、以前より水溶性イリジウム錯体を用いてアンモニアとアルコールを原料とするN-アルキル化を報告してきた[2]。今回、このイリジウム錯体を架橋ドメインゲルに導入することにより、色調変化を伴うアンモニア検知が可能とすることや高分子ゲルの構造を活用した反応場設計による選択的なN-アルキル化を可能とする新規機能性高分子ゲルの合成を達成した。



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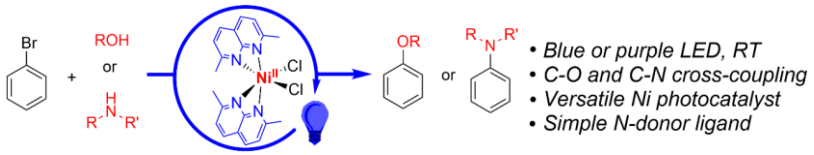
Photoinduced Carbon-Heteroatom Cross-Coupling Catalyzed by Nickel Naphthyridine Complexes

(*Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University*) ○ Pavan K. Vardhanapu, Janet Bahri, Julia R. Khusnutdinova*

Keywords: Nickel; Photocatalysis; C-N coupling; C-O coupling; Naphthyridine

C–N and C-O cross-coupling is an important class of reactions with far-reaching impacts across chemistry, biology, materials science, and medicine.[1] Using the energy provided by visible or near-UV irradiation would provide a convenient approach to facilitate cross-coupling reactions under mild conditions, and recent developments in this field include photocatalytic approaches using noble metal-based catalysts. Due to its poor natural abundance, toxicity issues, and high cost, application of earth-abundant photocatalysts would provide a significant advantage. Recently, nickel has emerged as a significantly cheaper alternative to palladium in a wide array of catalytic reactions.[2] In this regard, our group is actively working on 2,7-dimethyl-1,8-naphthyridine-based photoactive nickel complexes for C-H trifluoromethylation.[3] As further expansion of the application of naphthyridine nickel photocatalysts, herein we describe a light-driven and Ni-catalyzed C–N and C-O cross-coupling methodology.

This work will discuss the synthesis of new nickel complexes supported by 2,7-dimethyl-1,8-naphthyridine ligand. We demonstrated their catalytic activity in C-N and C-O cross-coupling of aryl bromides with amines and alcohols under blue LED (459 nm) or purple LED irradiation (399 nm) without any additional photocatalysts. These results demonstrate that Ni is a solo catalyst for photoredox catalytic activity, and naphthyridine represents a versatile ligand as an alternative to commonly used bipyridines or multidentate ligands.



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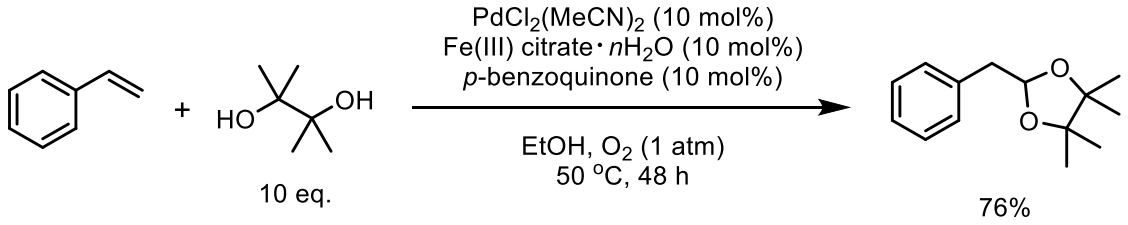
パラジウム/鉄触媒系を用いる末端アルケンからの末端アセタール合成反応

（奈良女大理）○福井 奈々子・浦 康之
Pd/Fe-catalyzed Synthesis of Terminal Acetals from Terminal Alkenes (*Faculty of Science, Nara Women's University*) ○Nanako Fukui, Yasuyuki Ura

Although palladium/copper catalysts are commonly used in conventional Wacker-type oxidation and oxidative acetalization of alkenes, it would be desirable to replace the copper complexes with less toxic co-catalysts. We have previously reported a Wacker-type oxidation of terminal and internal alkenes using iron complexes such as Fe(III) citrate as a co-catalyst. In the present study, we found that the synthesis of terminal acetals from styrenes and diols proceeds efficiently by using the palladium/iron catalyst system. A terminal acetal was obtained in high yield with high selectivity by the reaction of styrene with an excess amount of pinacol using a $PdCl_2(MeCN)_2$/Fe(III) citrate/*p*-benzoquinone catalyst system in EtOH at 50 °C for 48 h under 1 atm O_2. The reaction was applicable to styrenes with various substituents. Terminal acetals were also obtained in good yields when diols other than pinacol, such as ethylene glycol and 1,3-propanediol, were used.
Keywords：palladium catalyst; iron catalyst; terminal alkenes; terminal acetals; oxygen

従来のワッカー型酸化やアルケンの酸化的アセタール化反応ではパラジウム/銅触媒系が一般的に用いられるが，銅錯体に代えてより低毒性 [1]の助触媒を用いることができれば望ましい。当研究室ではこれまでに，助触媒として Fe(III) citrate などの鉄錯体を用いた末端および内部アルケンのワッカー型酸化を報告している [2]。本研究では，同様にパラジウム/鉄触媒系を用いることにより，スチレン類およびジオールからの末端アセタール合成反応が良好に進行することを見出した。

1 気圧の酸素下，エタノール溶媒中，スチレンおよびピナコール（10 当量）を基質として，$PdCl_2(MeCN)_2$/Fe(III) citrate/*p*-ベンゾキノン触媒系を用いて 50 °C で 48 時間反応を行ったところ，対応する末端アセタールが高選択的に高収率で得られた。本反応は種々の置換基を有するスチレン類に適用可能であった。また，ジオールとしてエチレングリコールや 1,3-プロパンジオールなど，ピナコール以外のものを用いた場合にも末端アセタールが高選択的に良好な収率で得られた。



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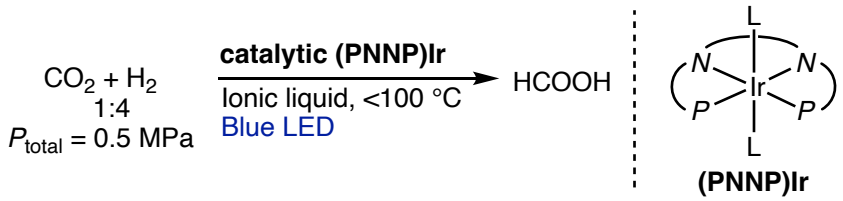
PNNP 型四座配位子を有するイリジウム錯体の光活性化による CO_2 の触媒的水素化

（名大院理[1]・IRCCS[2]）○多賀 光希[1]・Bendik Grømer[1]・Jieun Jung[1]・斎藤 進[1,2]
Catalytic Hydrogenation of CO_2 at Mild Conditions Using a Photo-activated (PNNP)Ir Complex
([1]*Graduate School of Science, Nagoya University,* [2]*IRCCS, Nagoya University*) ○Koki Taga,[1] Bendik Grømer,[1] Jieun Jung,[1] Susumu Saito [1,2]

Methanol, formic acid, and carbon monoxide are synthetically valuable carbon sources that can be utilized for pharmaceutical synthesis. Carbon dioxide (CO_2) has gained attention as a C_1-feedstock for obtaining these one-carbon compounds and conversion of CO_2 utilizing hydrogen (H_2) potentially allows for the clean generation of energy and raw material. In our laboratory, catalytic hydrogenation of CO_2 under a high temperature and pressure has been achieved using an iridium complex with a PNNP ligand ((PNNP)Ir).[1] However, the high temperature and pressure conditions have posed challenges for practical applications. We report here very mild hydrogenation of CO_2 under light irradiation with a (PNNP)Ir complex, expanding its scope to different carbonyl compounds. Efficient CO_2 hydrogenation was achieved at mild conditions (<1 MPa, <100 °C) when an ionic liquid was employed in the reaction solution, furnishing formic acid with a turnover number (TON) of approximately 17,000. Initial mechanistic studies revealed that the role of light was catalyst induction.
Keywords : Iridium complex; Photo-activation; Catalytic hydrogenation; Carbon dioxide; Formic acid

メタノールやギ酸、一酸化炭素は有機合成的に有用であり、医薬品などの資源として活用できる。これらの一炭素化合物の原料として二酸化炭素（CO_2）が注目されている。CO_2 を変換するクリーンな方法として水素化が挙げられる。当研究室では既に、PNNP 配位子をもつイリジウム錯体（(PNNP)Ir）を用いて高温・高水素圧下での CO_2 の触媒的水素化を報告した[1)]。しかし、高温・高水素圧であることが実用化に向けた課題だった。本研究では、光照射下で水素化を行うことで、低温・低圧下（<100 ℃、<1 MPa）での CO_2 およびカルボニル化合物の還元を達成した。特に反応溶液にイオン液体を使用することで、ギ酸が触媒回転数（TON）約 17,000 で得られた。光によって触媒活性種が誘導されている可能性が高いことが、初期的な反応機構研究によって明らかになった。



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β-ケトイミンホウ素錯体を光増感剤とする光触媒的二酸化炭素還元

（東京工科大院工[1]・東京工科大工[2]）○瓜田 陸[1]・久田 悠磨[2]・森本 樹[1]

Photocatalytic Reduction of Carbon Dioxide using β-Ketoimine Boron Complexes ([1]*Graduate School of Engineering, Tokyo University of Technology* [2]*School of Engineering, Tokyo University of Technology*) ○Riku Urita,[1] Yuma Hisata,[2] Tatsuki Morimoto[1]

The recycling of carbon dioxide (CO_2) into useful carbon compounds using inexhaustible solar energy is expected to be an important technology for realizing a sustainable society, but most CO_2 reduction photocatalytic systems use rare and expensive metals. Therefore, various boron complexes with β-ketoimine ligands, which are easily prepared from readily available starting materials, were synthesized and were applied to CO_2 reduction photocatalysis as photosensitizers. It was found that the photophysical and electrochemical properties as well as thermal- and photo-stability were significantly affected by the β-ketoimine ligands and supporting ligands. We also found that the CO_2 reduction photocatalyst using β-ketoimine boron complexes as photosensitizers is also greatly affected by the ligands.

Keywords : Boron complex, Photocatalyst, CO_2 reduction

無尽蔵な太陽光エネルギーを使って、二酸化炭素(CO_2)を有用な炭素化合物へ再資源化することは、サステイナブル社会の実現に向けて有望な技術の一つとして期待されている。しかし、従来の金属錯体を用いた CO_2 還元光触媒系では、希少で高価な金属が用いられることがほとんどである。本研究では、入手しやすい出発物質から容易に調製可能な β-ケトイミンを配位子とするホウ素錯体[1]を種々合成し、それらが CO_2 還元光触媒反応の光増感剤として適用可能かを検討した（図）。その結果、用いる β-ケトイミン配位子によって、光物性、電気化学的特性、さらに、熱・光安定性が大きく変化することがわかった。さらに、ホウ素錯体を光増感剤、レニウム錯体を触媒とする CO_2 還元光触媒反応を検討したところ、いくつかの系で CO_2 が CO に還元され、その効率が用いた配位子の種類に大きく左右されることも見出した。

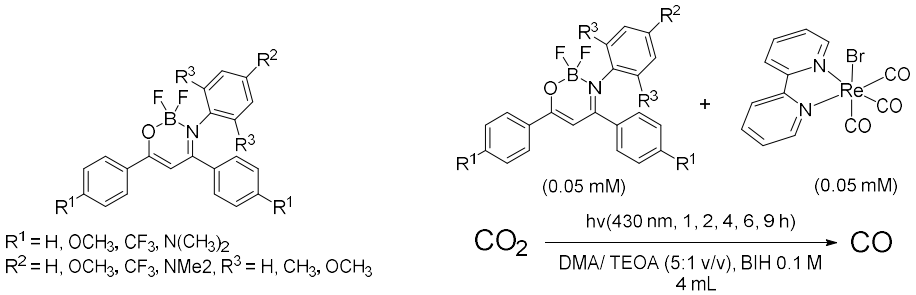

図 β-ケトイミンホウ素錯体とそれを光増感剤とする CO_2 還元光触媒反応

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日本化学会 第104春季年会 (2024)

触媒量の低減によるカップリング反応における選択性および置換基効果の発現

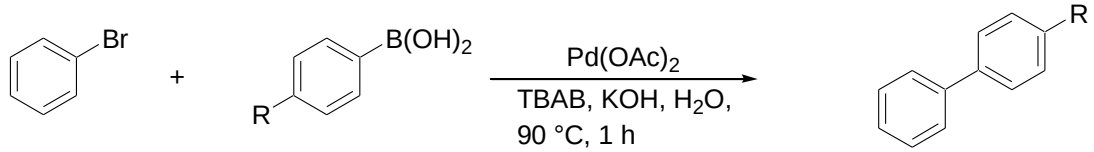
（大阪工業大学）柴田　智浩・○佐賀　皓斗・木村　花・川瀬 美沙・松村　吉将・下村 修・大高 敦

Expression of the Reaction Selectivity and the Substituent Effect in Coupling Reactions by Reducing the Catalyst Loading (*Osaka Institute of Technology*)　Tomohiro Shibata, ○Hiroto Saga, Hana Kimura, Misa Kawase, Yoshimasa Matsumura, Osamu Shimomura, Atsushi Ohtaka

The control of regio-, stereo-, and chemo-selectivity in the reaction is one of the most important topics in organic synthesis and is generally achieved by changing substrates, ligands, and metal species. For example, asymmetric reactions are controlled by the steric configuration of the ligand in many cases.[1] On the other hand, we confirmed expression of reaction selectivity and the substituent effect by changing only the amounts of catalysts.[2] For example, the Suzuki coupling reaction with arylboronic acid having an electron-withdrawing group does not proceed efficiently using 40 mol ppm of $Pd(OAc)_2$. Now we report the relationship between reducing the catalyst loading and the rate-determining step in the catalytic reaction.

Keywords : catalyst loading; selectivity; ppm.

反応における位置，立体および化学選択性の制御は，有機合成において最も重要なトピックの一つであり，一般に基質，配位子，金属種など用いる化合物を変更することにより制御されている．例えば配位子の立体配置により不斉反応は制御されている [1]．一方我々は，反応に用いる化合物を変更することなく，触媒量のみの変化で反応選択性や置換基効果の発現を確認している [2]．例えば酢酸パラジウムを触媒とする鈴木カップリング反応において触媒量を 40 mol ppm に減少させると電子求引基を有するアリールボロン酸との反応が効率よく進行しなくなる．本発表では金属量の低下と反応の律速段階との関係についても紹介する．



0.5 mmol　　0.75 mmol

Amount of Pd	R	Yield
1 mol%	Me	99%
	CF_3	99%
40 mol ppm	Me	91%
	CF_3	26%

1) Irina P. Beletskaya, Carmen Najera, and Miguel Yus, *Chem. Rev*. **2018**, 118, 5080.
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Synthesis and Characterization of UiO-67 MOFs Incorporated with Photocatalytic Components for Solar Energy Conversion

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Keywords: Metal-Organic Frameworks; Hydrogen Evolution; Ru-Pt Co-modification; Water-splitting; Photocatalysis

Metal-organic frameworks (**MOFs**), known as porous crystalline materials, represent a novel class of hybrid materials consisting of metal clusters as secondary building units (SBUs) and organic linkers. By following our previous report on the **Ru-Pt** dyads active as a single-component photocatalyst for hydrogen evolution from water,[1] some reports demonstrated that the **UiO-67**-derived **MOFs** modified with $[Ru(dcbpy)(bpy)_2]^{2+}$ (dcbpy=2,2'-bipyridyl-5,5'-dicarboxylic acid) as a photosensitizer and $Pt(dcbpy)Cl_2$ as an H_2 evolving catalyst can also serve as photocatalytic materials for visible-light-driven hydrogen evolution.[2,3] However, rational strategies to control their catalytic activities still remain unexplored. Moreover, the methodologies to finely tune the construction of multiple photocatalytic components within the **MOF** frameworks still remain unclarified. It is important to further examine the effect of varying the doping ratios of the three linkers, $[Ru(dcbpy)(bpy)_2]Cl_2$ (**Rudcbpy**), $Pt(dcbpy)Cl_2$ (**Ptdcbpy**), and biphenyl-4,4'-carboxylic acid (**bpdc**) (see **Figure 1**).

In this study, three distinct **UiO-MOFs** were synthesized: the first one modified solely with **Rudcbpy**, the second solely with **Ptdcbpy**, and the third co-modified with both Rudcbpy and Ptdcbpy. The modification patterns were controlled by varying the synthetic conditions, aiming to explore the more highly efficient **RuPt**-incorporated **MOFs** for solar-driven water splitting. The precise determination of Ru and Pt contents relative to the $Zr_6O_4(OH)_4$ cluster was achieved using ICP-MS. Subsequently, **MOFs** with different **RuPt**-doping ratios were subjected to photocatalytic experiments to assess the individual performance in H_2 production. We are hoping to settle down the structure-activity relationship useful to develop more highly efficient photocatalytic systems for solar-driven hydrogen generation from water.

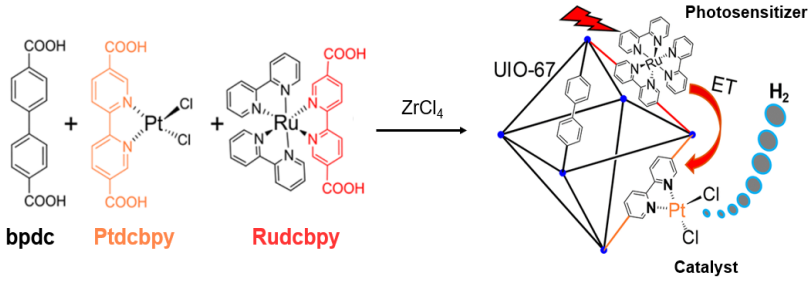

Figure 1. Synthesis Scheme of **RuPt**-modified **Uio67**.

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[2] S. Z. Yang, J. E. Huang, *et al. J. Phys. Chem. C.,* **2018**, *122*, 3305.
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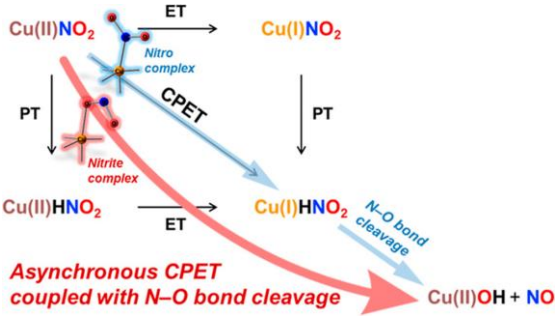
銅錯体による亜硝酸還元反応に関する理論的研究

（九大先導研）○塩田 淑仁・亀谷 陽平・吉澤 一成
Theoretical study of reduction of nitrite into NO by copper(II) complexes (*Institute for materials chemistry and engineering, Kyushu University*) ○ Yoshihito Shiota, Yohei Kametani, Kazunari Yoshizawa

Kundu and co-workers have reported nitrite reduction by a copper(II) complex.[1] In their report, the copper(II) complex reduced nitrite using a phenol derivative as a reductant, resulting in NO, a hydroxyl copper(II) complex, and the corresponding biphenol. The involvement of proton-coupled electron transfer was also proposed by mechanistic studies. Here, density functional theory calculations were performed to determine a mechanism for the reduction of nitrite by a copper(II) complex.[2] As a result of geometry optimization of an initial complex, two possible structures were obtained: Cu-ONO and Cu-NO_2. Two possible reaction pathways initiated by Cu-ONO or Cu-NO_2 were then considered. The calculation results indicated that the Cu-ONO pathway is energetically favorable. When changes in the electronic structure were considered, both pathways were found to involve concerted proton-electron transfer (CPET). In addition, an intrinsic reaction coordinate analysis revealed that the two pathways are achieved by different types of CPET.

Keywords : Cu complex, transition state, density functional theory, concerted proton-electron transfer

Kundu らは、三脚型配位子を有する銅(II)ニトリト錯体 **[LCu-NO_2]**$^+$（**L**= 配位子）と 2,4-ジ-*tert*-ブチルフェノールを反応させることで銅(II)ヒドロキシ錯体 **[LCuOH]**$^+$、一酸化窒素（NO）、ビフェノールが生成されることを報告した [1]。本研究では、この銅錯体による亜硝酸還元の反応機構を明らかにするため、DFT 計算による理論的考察を行った [2]。理論計算の結果、二つの異なる配位様式の出発錯体、ニトリト錯体 **[LCu-ONO]**およびニトロ錯体 **[LCu-NO_2]**（**L**: 配位子）が得られた。ニトリト錯体では、犠牲還元剤からの協奏的プロトン-電子移動（CPET）と N–O 結合開裂が同時に進行することで、一段階でヒドロキシル錯体 **[LCuOH]**と NO が生成する。一方、ニトロ錯体を出発点とする場合は多段階反応であり、CPET により**[LCuHNO_2]**中間体が生成したのち、N–O 結合開裂により**[LCuOH]**と NO が生成する。固有反応座標解析の結果、2 つの経路は互いに異なる様式の CPET を経て達成されることが示唆された。また、これらの銅錯体による NO 還元反応は複数ステップが同時に進行する協奏反応であることが示された。



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2) Y. Kametani, K. Ikeda, K. Yoshizawa,Y Shiota *Inorg. Chem.* **2023**, *62*, 13765–13774.

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二つの α-シアノカルボアニオン配位子を有するニッケル錯体の反応性

（阪公大院理 [1]）○野垣 夏槻 [1]・亀尾 肇 [1]・松坂 裕之 [1]

Reactivity of Nickel Complexes bearing Two α-Cyanocarboanion Ligands ([1]*Graduate School of Science, Osaka Metropolitan University*) ○Natsuki Nogaki,[1] Hajime Kameo,[1] Hiroyuki Matsuzaka[1]

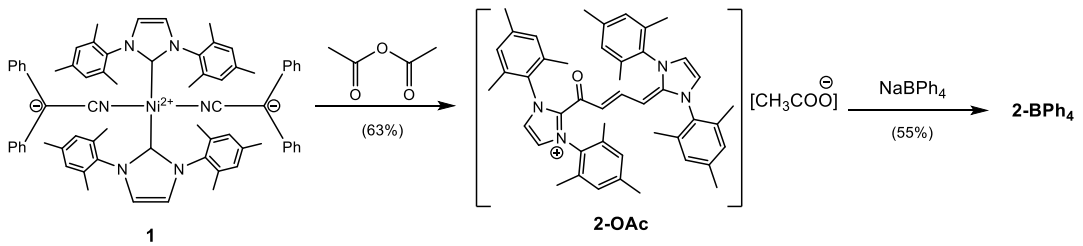
Cleavage of chemical bonds between quaternary carbons using transition metal complexes is challenging because the central metal is not accessible to such congested carbon–carbon bonds. Recently, our group has found that a zero-valent nickel complex cleaves the bond between the quaternary carbons of tetramethylsuccinonitrile via radical oxidative addition. In this contribution, the reactions of the oxidative addition product **1** with several organic substrates were investigated in order to develop the catalytic transformation of the carbon–carbon bond.

When the reaction of **1** with acetic anhydride in THF was carried out (Scheme 1), the novel product **2-OAc** was obtained. After the anion exchange of **2-OAc** with $NaBPh_4$, the structure of **2-BPh$_4$** was determined by X-ray diffraction study (Figure 1), and demonstrated the proceeding of C–C bond formation and C–O/C–H bond activation. The role of the Ni center in the reaction will be discussed.

Keywords: NHC Ligand; Bond Activation; Bond Formation; Ni complex; Acetic Anhydride

遷移金属錯体を用いた 4 級炭素間の炭素–炭素結合の切断は、中心金属がその炭素–炭素結合にアクセスしにくいことから容易ではない。我々のグループでは、0 価ニッケル錯体を用いることで、テトラフェニルスクシノニトリルの四級炭素間結合がラジカル的な酸化的付加により切断されることを見出している。本発表では、触媒的な炭素–炭素結合の変換を実現するため、その酸化的付加生成物 **1** と種々の有機基質との反応を検討した。

錯体 **1** と無水酢酸との反応で、新規化合物 **2-OAc** を得た。化合物 **2-OAc** の $NaBPh_4$ を用いたアニオン交換の後、化合物 **2-BPh$_4$** の構造を X 線構造解析によって決定した。この結果、無水酢酸との反応では、C–C 結合の形成、C–O 結合および C–H 結合の活性化が進行していることが明らかになった。発表では、本反応のおけるニッケル錯体の役割についてもディスカッションする。



Scheme 1. ニッケル錯体 **1** と無水酢酸の反応と続くアニオン交換

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単座ホスフィンを基盤とした Cu-MOF を用いた触媒反応

（青学大理工[1]・鶴岡高専[2]・島根大材エネ[3]）○油井 翔希[1]・古賀 満理奈[1]・荒船 博之[2]・澤野 卓大[3]・武内 亮[1]

Catalytic Reactions with Monodentate Phosphine-Based Cu-MOF ([1]*Department of Chemistry and Biological Science, Aoyama Gakuin University,* [2]*National Institute of Technology, Tsuruoka College,* [3]*Faculty of Materials for Energy, Shimane University*) ○ Shouki Yui,[1] Marina Koga,[1] Hiroyuki Arafune,[2] Takahiro Sawano,[3] Ryo Takeuchi[1]

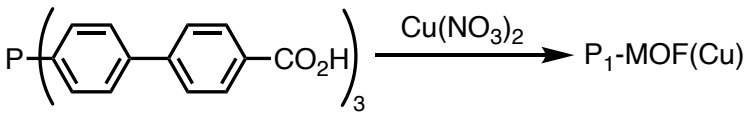
Monodentate phosphine ligands have been widely used as pivotal ligands for transition-metal catalyzed reactions, demanding the synthesis of novel monodentate phosphine ligands to provide highly active catalysts. As an emerging class of porous molecular materials, metal-organic frameworks (MOFs) synthesized from metal salts and organic linkers provide a highly tunable platform to realize highly active heterogeneous catalysts. However, the examples of monodentate phosphine-based MOF are still limited.[1,2] We have recently developed a novel MOF derived from an organic linker containing a phosphorus atom and a copper salt.

A mixture of copper nitrate and an organic linker containing a phosphorus atom formed a novel phosphine-based MOF (P_1-MOF(Cu)). The measurement of powder X-ray diffraction (PXRD) of the synthesized MOF confirmed the crystallinity of MOF. P_1-MOF(Cu) metalated with a palladium complex or a gold complex showed the excellent catalytic activity for hydrogenation of alkenes and intramolecular cyclization of amides.

Keywords :Metal-Organic Framework; Heterogeneous Catalyst; Monodentate Phosphine; Cu-MOF; Hydrogenation

単座ホスフィン配位子は遷移金属触媒を用いた反応に広く利用されてきた重要な配位子であり、より高活性な触媒を形成する新たな単座ホスフィン配位子の合成が望まれている。金属塩と有機リンカーから構成される Metal-Organic Framework (MOF)は新しい種類の多孔性分子材料であり、高い活性をもつ不均一触媒を実現するための自在に調節可能なプラットフォームを提供する。しかしながら、単座ホスフィンを基盤とした MOF の合成方法の開発は遅れている [1), 2)]。我々は最近、銅塩とホスフィンを含む有機リンカーから新たな MOF の作成を行なった。

ホスフィンを含む有機リンカーと硝酸銅を反応させたところ新たな単座ホスフィンを基盤とした MOF（P_1-MOF(Cu)）が得られた。合成した MOF の結晶性は粉末 X 線構造解析の測定によって確認された。P_1-MOF(Cu)はパラジウムや金とメタル化することが可能であり、アルケンの水素化反応やアミドの分子内環化反応に対して非常に高い活性を示した。



1) Xu, X.; Rummelt, S. M.; Morel, F. L.; Ranocchiari, M.; van Bokhoven, J. A. *Chem. Eur. J.* **2014**, *20*, 15467-15472.
2) Sawano, T.; Lin, Z.; Boures, D.; An, B.; Wang, C.; Lin, Z. *J. Am. Chem. Soc.* **2016**, *138*, 9783-9786.

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Photo-accelerated decomposition of ammonia borane with phosphine-ligated Au clusters

([1]*Graduate School of Environment Science, and* [2]*Faculty of Environment Earth Science, Hokkaido University,* [3]*Department of Chemistry, Tokyo University*) ○Shaojing Yan,[1] Tomotaka Nakajima,[1] Yukatsu Shichibu,[1,2] Haru Hirai,[3] Tatsuya Tsukuda,[3] Katsuaki Konishi,[1,2]

Keywords: Gold cluster; Ammonia borane; Photo-accelerated; Phosphine-ligated

In recent years, ammonia borane has been considered as a next-gen hydrogen storage material because of its high hydrogen mass capacity. Generally, high energy is required for the decomposition of ammonia borane due to its high stability[1]. Previously, we discovered that gold clusters protected by phosphine ligands showed unique and strong visible-light absorptions[2], which could act as catalysts for the decomposition of ammonia borane.

In this work, we investigated the catalytic activities by using various kinds of phosphine-ligated Au_n clusters ($n = 9$, 11 and 13), which were evaluated by ^{1}H-NMR measurement. Under dark condition, the strongest activity was observed in the case with Au_{13} clusters (**Figure 1**). Furthermore, we found photo-acceleration effect from the catalytic reactions under visible-light condition. From the analysis by 1H-NMR, the conversion rate of ammonia borane with a Au_{13} cluster in light condition is almost six times higher than that in dark condition within 6 h (**Figure 2**). We also examined the decomposition reaction with various types of Au_{13} clusters.

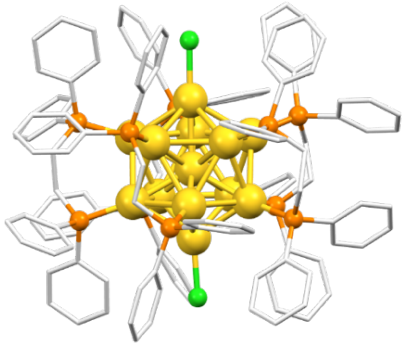

Figure 1. Structure of a Au_{13} cluster.

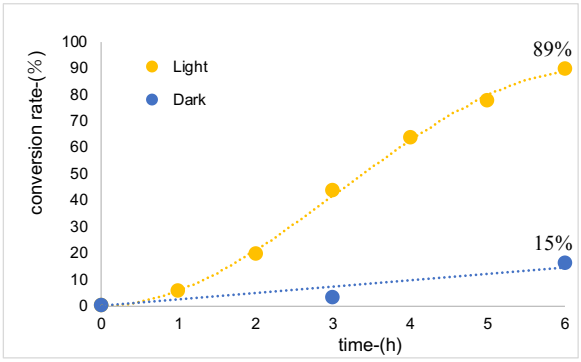

Figure 2. Conversion rate of ammonia borane with a Au_{13} cluster under light (yellow) and dark (blue) conditions.

1) A. Staubitz *et. al., Chem. Rev*. **2010**, *110*, 4079. 2) K. Konishi, *Struct. Bonding*. **2014**, *161*, 49.

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銅錯体上での分子内プロトン移動を伴う一酸化窒素還元の理論研究：DFT 計算による反応機構解析

（九大先導研）○亀谷陽平・豊嶋凌我・塩田淑仁・吉澤一成
DFT study on a reaction mechanism of nitric oxide reduction by copper complex with in-built proton-donating functional group (*IMCE, Kyushu Univ.*) ○ Yohei Kametani, Ryoga Toyoshima, Yoshihito Shiota, Kazunari Yoshizawa

Reduction of nitric oxide (NO) into nitrous oxide (N_2O) is an important chemical reaction in the nitrogen cycle, physiology, and exhaust gas purification. In the nitrogen cycle, NO reduction is accomplished by NO reductase (NOR). NOR converts NO, protons, and electrons into N_2O and water. ($2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$) Karlin and co-workers recently reported the first example of a copper-only NOR model with in-built, acidic H-bonding functionalities. However, the reaction mechanism is still unknown.[1] In this study, using DFT calculation we investigated a reaction pathway of NO reduction catalyzed by a mono-copper complex. Computed results indicated that this reaction proceeds through three steps: (1) N_2O_2 formation, (2) $H_2N_2O_2$ formation, and (3) N_2O formation. Furthermore, the surroundings of the proton-donating site, particularly a solvent and substitution of amide group, significantly play an important role in the reactivity of the NO reduction.

Keywords : Nitric Oxide Reduction; Copper Complex; DFT Calculation

一酸化窒素（NO）の亜酸化窒素（N_2O）への還元（NO 還元）は窒素循環、生理反応、排ガス浄化に関わる重要な化学反応である。窒素循環における NO 還元は NO 還元酵素（NOR）によって達成される。NOR は NO にプロトンと電子を与えることで N_2O と水を生成することが知られており、その反応機構には興味が持たれている。過去にプロトン供与能を持つ銅錯体による NO 還元が報告されているが、そのメカニズムは明らかになっていない [1]。そこで本研究では、量子化学計算を用いて銅錯体による NO 還元の反応機構を決定した。計算結果から、本反応は (1) N_2O_2 生成、(2) $H_2N_2O_2$ 生成、(3) N_2O 生成の 3 つの段階を経て進行することが示された（Figure 1）。また、溶媒や配位子置換といったプロトン供与部位の周辺環境が NO 還元の反応性に関与することも示された。

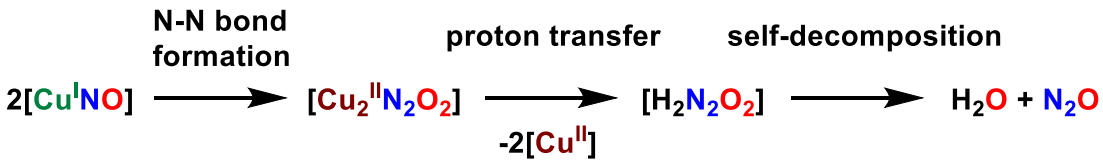

Figure 1. Calculated reaction pathway of nitric oxide reduction by the copper(I) complex.

1) G. B. Wijeratne, M. Bhadra, M. A. Siegler, and K. D. Karlin *J. Am. Chem. Soc.* **2019**, *141*, 17962-17967.

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サリチリデンアニリン配位子を有する金属錯体の抗微生物特性

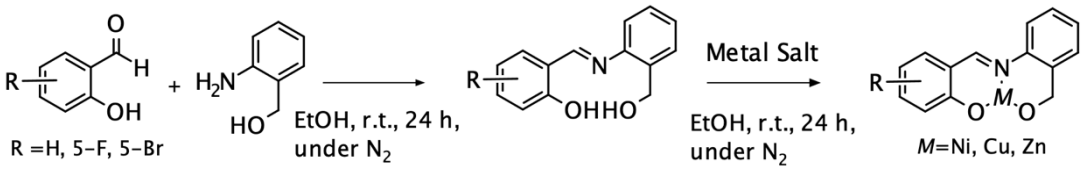
（新居浜高専生物応用化学）○新延 亜利紗・大村 聡
Antimicrobial properties of metal complexes bearing salicylideneaniline ligand (*Department of Applied Chemistry and Biotechnology, National Institute of Technology, Niihama College*)
○Arisa Niinobe, Satoshi Ohmura

Schiff base compounds are widely used as ligands for metal complexes, utilizing the coordination ability derived from the nitrogen atom in the structure. Various complex compounds with Schiff base ligands, some known to exhibit antimicrobial activity, have been studied and reported. In our group, we focused on the *N*-salicylidylideneaniline skeleton, which has a Schiff base structure and is photoresponsive, and synthesized derivatives with a 2-hydroxymethyl moiety as a ligand and examined the antimicrobial properties of the complexes obtained by interacting them with various metal salts.

The reaction of salicylaldehyde derivatives with 2-aminobenzyl alcohol synthesized salicylideneaniline derivatives with the corresponding 2-hydroxymethyl moiety. The obtained derivatives were reacted with various metal salts to obtain the corresponding metal complexes. The obtained complexes were examined for their antimicrobial properties against Bacillus and other organisms using the paper disk method.
Keywords : Schiff Base; N-Salicylideneaniline; Metal Complex; Antimicrobial Property

Schiff塩基化合物は構造中の窒素原子に由来する配位能を利用した金属錯体の配位子として広く利用されている。Schiff 塩基を配位子とした様々な錯体化合物が研究、報告されており、それらのなかには抗微生物活性を示すものも知られている。当研究室では Schiff 塩基構造を持ち、かつ光応答性を有する *N*-サリチリデンアニリン骨格に着目し、2-ヒドロキシメチル部位を導入した誘導体を配位子として合成し、種々の金属塩と作用させることで得られた錯体の抗菌特性について検討を行った。

サリチルアルデヒド誘導体と 2-アミノベンジルアルコールを反応させ、対応する2-ヒドロキシメチル部位を有するサリチリデンアニリン誘導体を合成した。得られた誘導体は種々の金属塩と作用させることで対応する金属錯体を得た(Scheme 1)。得られた錯体について、ペーパーディスク法を用いてバチルス等に対する抗菌特性の検討を行ったので詳細を報告する。



Scheme 1

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還元型酸化グラフェンに固定化した三座 *N*-ヘテロ環カルベン配位子を有する Pd(II)錯体触媒の開発

(名工大院工 [1])○山田 緋奈 [1]、柳生 剛義 [1]

Development of Pd(II) complex catalyst with a tridentate (*N*-heterocyclic carbene) ligand immobilized on reduced graphene oxide

([1]*Graduate School of Engineering, Nagoya Institute of Technology*) ○Hina Yamada,[1] Takeyoshi Yagyu[1]

Transition metal complexes catalysts are employed as high activity and high selectivity in organic synthesis reactions. However, most of them are used as homogeneous catalysts, it is difficult to reuse the catalysts. In order to reduce the environmental impact, we have to develop reusable, highly active and highly selective heterogeneous complex catalysts. In this study, a tridentate *N*-heterocarbene (NHC), which has strong σ-donating properties and forms stable complexes with late transition metals, was used as a supporting ligand. Using the tridentate ligand, we aimed to prevent dissociation of the central metal due to the chelate effect. In addition, chemically stable reduced graphene oxide (rGO) was used as a support carrier. A heterogeneous Pd(II) complex catalyst (Fig.1) was synthesized by covalently immobilizing the ligand end on rGO and using a transmetalation reaction. Its catalytic performance and recycling performance in hydroarylation was examined.

Keywords : palladium complex; heterogeneous catalyst; tridentate complex; N-heterocyclic carbene

遷移金属錯体は、有機合成反応において高活性かつ高い選択性を発現する触媒として、幅広く用いられている。しかしその多くは、均一系触媒として用いられており、触媒の再利用が困難である。環境負荷軽減のため、再利用可能な高活性かつ高選択性を有する不均一系錯体触媒の開発が求められている。本研究では、支持配位子として強いσ供与性を持ち、後周期遷移金属と安定した錯体を形成する三座 *N*-ヘテロカルベン(NHC)を用いた。この配位子の 2 つのキレート環により中心金属との解離を防ぐことを狙った。また、支持担体としては化学的に安定な還元型酸化グラフェン(rGO)を採用した。不均一系 Pd(II)錯体触媒(図 1)は rGO に配位子末端を共有結合で固定化し、トランスメタル化反応を利用して合成した。これをヒドロアリール化反応に用いて、触媒性能とリサイクル性能を検討した。

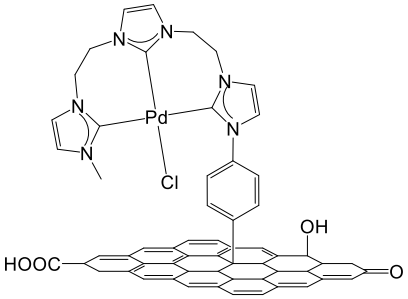

Fig.1 Heterogeneous Pd(II) complex catalyst synthesized in this study

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[Ni(dmit)$_2$]錯体とアゾベンゼン類を複合した PMMA 膜の偏光誘起光学的異方性

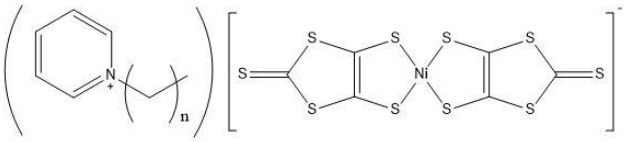
（東理大理 [1] 中大理工 [2]）○今江 太河 [1]・本田 暁紀 [2]・中根 大輔 [1]・秋津 貴城 [1]・宮村 一夫 [1]

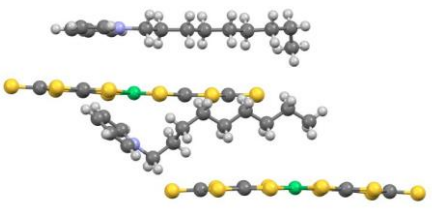
Polarized light induced optical anisotropy PMMA films of containing [Ni(dmit)2] complexes and azobenzene compound ([1]*Graduate School of Science, Tokyo University of science*, [2]*Chuo University*) ○Taiga Imae,[1] Akinori Honda,[2] Daisuke Nakane,[1] Takashiro Akitsu,[1] Kazuo Miyamura[2]

Since the exchange of the counter cation is easy, it is suitable for the study of the factors that determine the crystal structure. In this study, (C*n*Py) salts of planar [Ni(dmit)$_2$]$^-$ complex anion were synthesized. Single crystal structures were successfully analyzed for those with carbon chains of n=9 and 10. Since those cations took a specific structure, computational chemistry such as DFT calculations and Hieshfeld surface analysis were used to discuss them. In addition, polarized UV light induced optical anisotropy (so called Weigert effect) of azobenzene-containing Schiff bases with amino acids and [Ni(dmit)$_2$] salts in PMMA films was also investigated by measuring polarized IR and UV-Vis spectroscopy.

Keywords : Ni dmit complex; azobenzene PMMA film; polarized spectra; Weigert effect

[Ni(dmit)$_2$]$^-$錯体は豊富なπ電子を有する dmit 配位子がⅢ価の Ni に配位することで形成されるアニオン性錯体であり、対カチオンによって多様な結晶構造を形成する特徴がある。対カチオンの交換は容易であるため結晶構造を決定する要因を研究するのに適しているといえる。本研究では、ピリジン窒素にアルキル鎖を導入した C*n*Py を対カチオンとし、(C*n*Py)[Ni(dmit)$_2$]錯塩の合成を行った（左図）。炭素鎖 9,10 のもので単結晶構造解析に成功した（右図）。それらのカチオンが特異的な構造をとったため、DFT 計算や Hieshfeld 表面解析といった計算化学を用いて、考察を行った。さらに、この比較的剛直な平面性の[Ni(dmit)$_2$]アニオンとアゾベンゼンやそれを含むアミノ酸シッフ塩基カチオン等の PMMA 複合膜中での偏光照射による光学的異方性の誘起（ワイゲルト効果のイオン間の伝達）を、偏光 IR や UV-Vis スペクトル測定により調べた。





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オリゴエチレングリコキシ鎖を導入した新規レドックス活性白金錯体の合成とカチオン認識能

(1 中大院理工・2 中大理工・3 京大院工) ○井上 颯大 1・本田 暁紀 2・中田 明伸 2,3・張 浩徹 2

Synthesis and Cation Recognition Capacity of Novel Redox-Active Platinum Complexes with Oligoethylene Glycoxy Chains ([1]Graduate School of Science and Engineering, Chuo Univ., [2]Faculty of Science and Engineering, Chuo Univ., [3] Graduate School of Engineering, Kyoto Univ.) ○Sota INOUE,[1] Akinori HONDA,[2] Akinobu NAKADA,[2,3] Ho-Chol CHANG[2]

A novel platinum(II) complex [Pt^{II}(DEG-s-bqdi)$_2$] (**1**) with diethyleneglycoxy (DEG) chains was synthesized. ^{1}H NMR studies revealed that complex **1** interacted with $XClO_4$ (X = Li, Na, K) in solution. When complex **1** was mixed with $NaClO_4$, single crystals were obtained in which the DEG chains trapped Na ions, indicating that the complex has a cation recognition ability. In this presentation, we will report on the differences in the assembly structures and physical properties between complex **1** and cationic complex.

Keywords : Ethylene glycoxy chain; Redox-active complex; Platinum complex; Crystal stracture; Cation recognition

我々は、カテコラート等のレドックス活性配位子 (L)と長鎖アルキル基を修飾したビピリジン (C8,10 bpy)配位子を有する[Pt(L)(C8,10bpy)]が室温で安定な液晶相を示すことを報告している。[1] この様なレドックス活性分子集合体の設計においては、L種及び側鎖種により多様な機能をデザイン可能である。そこで本研究では、プロトン共役電子移動可能な配位子である *o*-phenylenediamine (opda)をコアとして有し、側鎖に Li^+などと複合化し電解質として働くことが知られているジエチレングリコキシ(DEG)鎖を導入した新規 Pt(II)錯体 [Pt^{II}(DEG-s-bqdi)$_2$] (**1**)を合成した (Figure 1)。錯体 **1** は、^{1}H NMR スペクトルにおいて $XClO_4$ (X = Li, Na, K)を共存させると 1 のシグナルの高磁場シフト及び 2-5 のシグナルの低磁場シフトを示し、カチオン種との相互作用が示唆された (Figure 1a-d)。さらに、錯体 **1** と $NaClO_4$ のアセトニトル (MeCN)/Et_2O の混合溶液から赤色針状結晶[Pt^{II}{Na(DEG-s-bqdi)$_2$($NaClO_4$)(MeCN)}] (**2**)が得られ (Figure 2)、錯体 **1** のカチオン認識能が示された。当日は錯体 **1** とカチオン複合体の物性の差異についても報告する予定である。

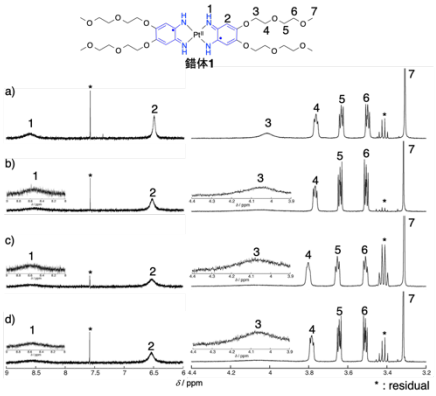

Figure 1. a) 錯体 **1** の ^{1}H NMR スペクトル、及び二当量の b) Li, c) Na, d) $KClO_4$ を共存させた場合のスペクトル変化(500 MHz, CD_3CN)

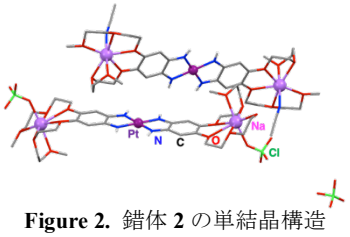

Figure 2. 錯体 **2** の単結晶構造

1) H.-C. Chang et. al., J. Mater. Chem. 2007, 17, 4105.

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Academic Program [Poster] | 10. Organic Chemistry -Organometallic Compounds-：Poster

Wed. Mar 20, 2024 1:00 PM - 2:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-3pm] 10. Organic Chemistry -Organometallic Compounds-

Japanese

[P2-3pm-01]

Synthesis of NHC-Ru and NHC-Pd Complexes form Hydroxyalkyl-substituted Azolium Salts

○Ryota Usui[1], Satoshi Sakaguchi[1] (1. Kansai Univ.)

Japanese

[P2-3pm-02]

Ruthenium Hydride-Catalyzed Oxidative Dehydrogenation of Primary and Secondary Alcohols Using Hydrogen Acceptor

○Masaki Ochi[1], Yutaro Komiya[1], Aina Fujii[1], Kosho Makino[1,2], Shunsuke Sueki[1,2], Masahiro Anada[1,2] (1. Fac. Pharm., Musashino Univ., 2. Res. Inst. Pharm. Sci., Musashino Univ.)

Japanese

[P2-3pm-03]

Enantioselective Silane Reduction of Ketones Catalyzed by Polymer-supported NHC-Ir Complex

○Masamune Koyabu[1], Satoshi Sakaguchi[1] (1. Kansai Univ.)

Japanese

[P2-3pm-04]

Synthesis of NHC-Rh Complexes from Hydroxyamide- or Hydroxyalkyl-substituted Azolium Salts and Its Application for Catalytic Reactions

○Shogo Matsuo[1], Satoshi Sakaguchi[1] (1. Kansai Univ.)

Japanese

[P2-3pm-05]

Selective Synthesis of Secondary Amines from Aqueous Ammonia and Alcohols Catalyzed by Iridium Complexes

○Ryo Sei[1], Ken-ichi Fujita[1] (1. Kyoto University)

Japanese

[P2-3pm-06]

Dehydrogenation of Alcohols Catalyzed by Iridium Complexes Bearing Functional Polymer Ligands

○Hiroki Maeda[1], Taiki Kuno[1], Jaeyoung Jeong[1], Yasuhiro Morisaki[2], Ken-ichi Fujita[1] (1. The Univ. of Kyoto, 2. The Univ. of Kwansei Gakuin)

Japanese

[P2-3pm-07]

Iridium Complex-Catalyzed Methylamination of Alcohols in Aqueous Media

○Maimi Kubo[1], Nanase Yoshida[1], Ken-ichi Fujita[1] (1. Graduate School of Human and Environmental Studies, Kyoto University)

Japanese

[P2-3pm-08]

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Platinum-Catalyzed Hydroiodination of Alkynes Using Phosphoric Acid and Sodium Iodide

○Moeka Yanagisawa[1], Hidenori Kinoshita[1], Katsukiyo Miura[1] (1. The Univ. of Saitama)

Japanese

[P2-3pm-09]

Platinum-Catalyzed anti-Markovnikov Hydrochlorination of Alkynes: Effects of Neighboring Functional Groups

○Takaki Ikeshima[1], Katsukiyo Miura[1], Hidenori Kinoshita[1] (1. Saitama University)

Japanese

[P2-3pm-10]

Platinum-Catalyzed Hydrative Dimerization of Alkynylsilanes and Its Application to Arene Synthesis

○Chinatsu Ambe[1], Katsukiyo Miura[1], Hidenori Kinoshita[1] (1. Saitama University)

Japanese

[P2-3pm-11]

Research of regioselectivity and reactivity in cross-dehydrogenative coupling reaction of disubstituted benzene with polyfluoroarene

○Tianya Xiong[1], Tomoki Iida[1], Takaki Kanbara[1], Junpei Kuwabara[1] (1. Univ. of Tsukuba)

Japanese

[P2-3pm-12]

Reactivity of Tetranuclear Nickel Sheet Sandwich Clusters Bearing Cyclooctatetraene Ligands.

○Yuji Nemoto[1], Genki Sakai[1], Tsubasa Omoda[1], Koji Yamamoto[2], Tetsuro Murahashi[1] (1. Tokyo Tech, 2. Natioal Defense Academy)

Japanese

[P2-3pm-13]

Palladium-catalyzed asymmetric allylic amination using a cinnamamide-type chiral ligand with axial chirality

○Natsume Akimoto[1], Hiroto Mizuno[1], Kaho Takaya[1], Yasushi Yoshida[1], Takashi Mino[1] (1. Chiba University)

Japanese

[P2-3pm-14]

Synthesis of Novel Phosphine Ligands Bearing Three 1-Tetralone Imine Moieties and Their Palladium(II) Complexes

○Yukiko Wakimoto[1], Hidetoshi Ohta[1], Minoru Hayashi[1] (1. Grad. Sch. Sci., Eng., Ehime Univ.)

Japanese

[P2-3pm-15]

Pd-catalyzed asymmetric allylic amination using chiral P,olefin ligand with cinnamyl group

○Hiroto Mizuno[1], Kaho Takaya[1], Yuto Toba[1], Yasushi Yoshida[1], Takashi Mino[1] (1. Chiba University)

Japanese

[P2-3pm-16]

[Withdraw] Synthesis and optical analysisof unique silver nanoparticle composites

○KAZUKI MATSUO[1], KENGO ITO[2] (1. Premier Anti-Aging Co., Ltd., 2. Ito Research Institute Co.,Ltd.)

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Japanese

[P2-3pm-17]

Benzylation of Isatinimines Using Metallic Barium

○Hiroto Sone[1], Akira Yanagisawa[1] (1. Chiba University)

Japanese

[P2-3pm-18]

Synthesis, structures and reactivity of (chloro)tetraphenylgallacyclopentadienes

Ayaka Yamauchi[1], ○Takako Muraoka[1], Haruka Katayama[1] (1. Gunma University)

Japanese

[P2-3pm-19]

Ring-opneing Reaction of Epoxide Catalyzed by Hydorosilane

○Toru Hashimoto[1], Kohei Nishikimura[1], Makoto Hojo[1] (1. Sanyo-Onoda City University)

Japanese

[P2-3pm-20]

Stereoselective Addition Reaction of Allenyl Titaniums to Nitroalkenes

○Riku Okawa[1], Sentaro Okamoto[1], Kota Ibe[1] (1. Kanagawa University)

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ヒドロキシアルキル置換アゾリウム塩からの NHC-Ru および NHC-Pd 錯体の合成

（関西大化学生命工）○臼井亮汰・坂口　聡

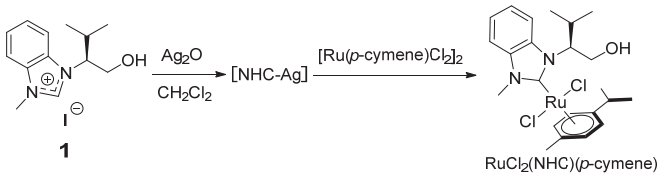
Synthesis of NHC-Ru and NHC-Pd Complexes form Hydroxyalkyl-substituted Azolium Salts

(*Faculty of Chemistry, Materials and Bioengineering, Kansai University*) ○Ryota Usui, Satoshi Sakaguchi

Recently, we reported the enantioselective Cu-catalyzed allylic substitution reaction of allyl phosphates with diethylzinc using a chiral hydroxyalkyl-substituted azolium salt **1** as a *N*-heterocyclic carbene (NHC) ligand precursor. Now, we investigated the synthesis of NHC-metal complexes from **1**. On the basis of our previously reported procedures, we employed the Ag_2O method for the preparation of NHC-metal complexes. First, treatment of **1** with Ag_2O at room temperature for 2 h to form NHC-Ag complex. Second, $[RuCl_2(p\text{-cymene})]_2$ was added to reaction vessel. After stirring the resulting reaction mixture at room temperature, the corresponding monodentate $RuCl_2(NHC)(p\text{-cymene})$ complex was obtained in good yield. The NHC-Ru complex thus obtained was fully characterized by ^{1}H- and ^{13}C-NMR as well as elemental analysis. Furthermore, the synthesis of NHC-Pd complex from **1** and $PdCl_2(CH_3CN)_2$ using the Ag_2O method was performed.

Keywords : N-Heterocyclic Carbene; Azolium ; Monodentate Ligand; Anionic Alkoxide Ligand

最近我々は、ヒドロキシアルキル置換アゾリウム塩 **1** をキラル *N*-ヘテロサイクリックカルベン(NHC)配位子前駆体として利用することで、Cu 触媒によるりん酸ジエチル(*E*)-シンナミルとジエチル亜鉛のエナンチオ選択的アリル位置換反応が生起することを報告した。[1]本研究では、この不斉触媒反応に関する知見を得ることを目的として、これまで当研究室で報告してきたヒドロキシアミド置換アゾリウム塩 **2** からの NHC-金属錯体の合成に関する研究をもとに、[2]**1** から生成する NHC-金属錯体について検討した。従来ヒドロキシアルキル置換 NHC-金属錯体の合成についての研究は数例が報告されているのみであった。**1** を Ag_2O で処理して反応系中で NHC-Ag 錯体を形成させた後、$[RuCl_2(p\text{-cymene})]_2$ と反応させることで、単座配位型の $RuCl_2(NHC)(p\text{-cymene})$が生成することがわかった。得られた NHC-Ru 錯体は、^{1}H-および ^{13}C-NMR ならびに元素分析によりその構造を決定した。特に ^{13}C-NMR 測定において C-Ru 結合に特徴的なシグナルが δ =185.3 ppm に観測された。さらに、同様に Ag_2O 法を利用し、錯体前駆体として $PdCl_2(CH_3CN)_2$ を用いた **1** からの NHC-Pd 錯体の合成についても検討した。



1) S. Sakaguchi, H. Kawashima, R. Kamisue, Y. Kashioka, Y. Nakahigashi, R. Usui, *Trends in Org, Chem*., **2024**, in press. 2) (a) S. Sakaguchi, K.S. Yoo, J. O'Neill, J.H. Lee, T. Stewart, K.W. Jung, *Angew. Chem. Int. Ed*., **2008**, *47*, 9326; (b) M. Yoshimura, R. Kamisue, S. Sakaguchi, *J. Organomet. Chem*., **2013**, *740*, 26.

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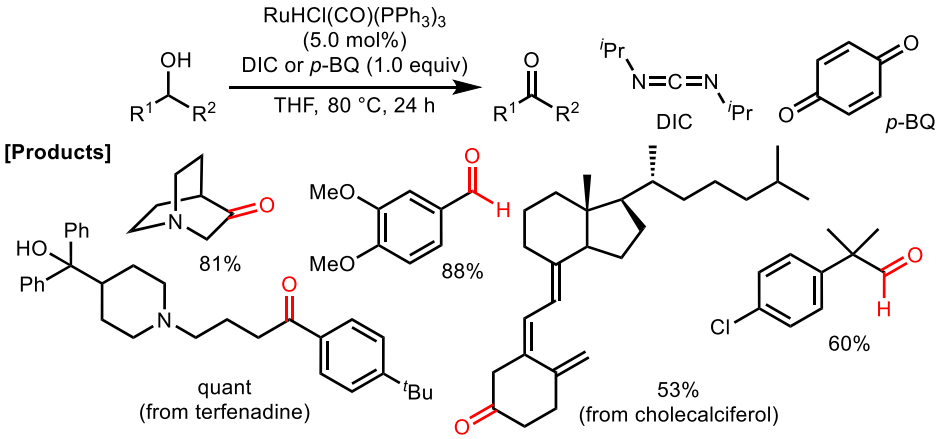
ルテニウムヒドリド錯体と水素受容体を用いたアルコールの触媒的脱水素反応の開発

(武蔵野大薬[1]・武蔵野大薬研[2]) ○越智 政希[1]・小宮 雄太朗[1]・藤井 愛奈[1]・牧野 宏章[1,2]・末木 俊輔[1,2]・穴田 仁洋[1,2]
Ruthenium Hydride-Catalyzed Oxidative Dehydrogenation of Primary and Secondary Alcohols Using Hydrogen Acceptor ([1]*Faculty of Pharmacy, Musashino University*, [2]*Research Institute of Pharmaceutical Sciences, Musashino University*) ○ Masaki Ochi,[1] Yutaro Komiya,[1] Aina Fujii,[1] Kosho Makino,[1,2] Shunsuke Sueki,[1,2] Masahiro Anada[1,2]

We have recently reported ruthenium-catalyzed oxidative dehydrogenation of alcohols using carbodiimide as a hydrogen acceptor, though the main drawbacks are that it requires higher reaction temperature and the applicable substrates are limited to secondary alcohols. We herein report that the combination of ruthenium hydride complex as a catalyst and carbodiimide or *p*-benzoquinone as hydrogen acceptor is effective for the oxidative dehydrogenation of not only secondary alcohols but also primary alcohols under mild reaction conditions to give the corresponding ketones and aldehydes, respectively, in good to high yields.
Keywords : Ruthenium Hydride; Oxidation; Carbodiimide; p-Benzoquinone; Oxidative Dehydrogenation

我々はこれまでにルテニウム錯体を触媒、カルボジイミドを水素受容体として用いるアルコールの酸化的脱水素反応を開発しているが、本法の円滑な進行には高温(120 °C)を要し、適用可能な基質は第 2 級アルコールに限られていた[1]。今回我々は、ルテニウム触媒を用いた第 1 級アルコールにも適用可能な酸化的脱水素反応の開発を目指し種々条件検討を行った。その結果、触媒としてルテニウムヒドリド錯体、水素受容体としてカルボジイミド(DIC)または *p*-ベンゾキノン(*p*-BQ)を用いると第 1 級および第 2 級アルコールの酸化的脱水素が 80 ºC で円滑に進行し、対応するケトンまたはアルデヒドを収率よく与えることを見出した。



1) Sueki, S.; Matsuyama, M.; Watanabe, A.; Kanemaki, A.; Katakawa, K.; Anada, M. *Eur. J. Org. Chem.* **2020**, 4878.

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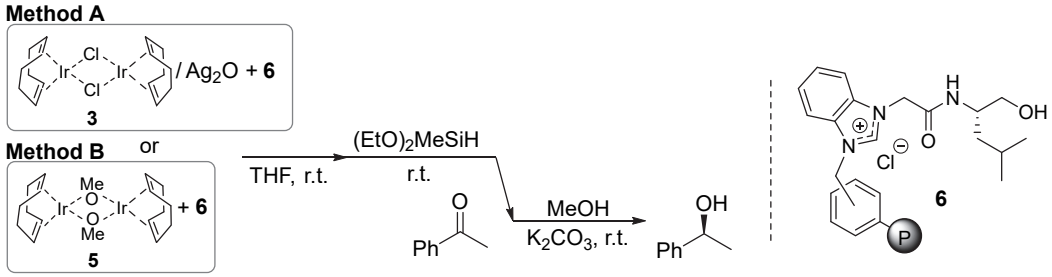
ポリマー担持 NHC-Ir 錯体を触媒とするエナンチオ選択的なケトンのシラン還元反応

（関西大化学生命工）○小薮正宗・坂口　聡
Enatioselective Silane Reduction of Ketones Catalyzed by Polymer-supported NHC-Ir Complex (*Faculty of Chemistry, Materials and Bioengineering, Kansai University*) ○ Masamune Koyabu and Satoshi Sakaguchi

In recent years, we have shown that azolium **2** prepared from coupling of hydroxyamide-substituted azole **1** and benzyl chloride promoted Ir-catalyzed enantioselective silane reduction of ketones. We have used $[IrCl(cod)]_2$ (**3**), $[Ir(cod)_2]BF_4$ (**4**) and $[Ir(OMe)(cod)]_2$ (**5**) as an iridium catalyst precursor, and the highly enantioselective catalytic reactions have been achieved by optimizing the reaction conditions for use of these Ir complexes **3**-**5**, respectively. Previously, we briefly reported the catalytic reaction using **5**.[1] Now, we investigated the asymmetric silane reduction of ketone catalyzed by polymer-supported NHC-Ir complex **7**. First, we performed coupling of **1** and chloromethyl polystyrene to produce the corresponding azolium **6**. The NHC-Ir complex **7** could be obtained by treating **6** with Ag_2O and **3** (Method A) or by treating **6** with **5** (Method B).
Keywords : N-Heterocyclic Carbene; Azolium Salt; Asymmetric Catalyst; Silane Reduction

当研究室では、天然α-アミノ酸のロイシンから誘導されるヒドロキシアミド置換ベンズイミダゾール **1** と塩化ベンジルのカップリングにより得られるアゾリウム塩 **2** をキラル配位子前駆体として利用した、Ir 触媒によるエナンチオ選択的なケトンのシラン還元反応に関する研究を行ってきた。この一連の研究において、$[IrCl(cod)]_2$ (**3**)、$[Ir(cod)_2]BF_4$ (**4**)および$[Ir(OMe)(cod)]_2$ (**5**)のそれぞれが、Ir 触媒前駆体として良好にはたらくような触媒反応系を設定することによって、高エナンチオ選択的な還元反応を達成している。先の年会において **5** を利用した不斉触媒反応について報告したが、[1] 本研究では **1** とクロロメチルポリスチレンのカップリングで調製したアゾリウム塩 **6** をキラル配位子とする不均一系での触媒反応について検討した。具体的には **6** を Ag_2O および **3** で処理する手法(Method A)、あるいは **6** を **5** で処理する手法(Method B)で得られるポリマー担持 NHC-Ir 錯体 **7** の触媒作用について検討した。その結果、Ir 錯体 **7** を用いることにより、不均一系条件下におけるケトンのエナンチオ選択的シラン還元反応が生起し、対応する光学活性アルコールが得られた。



1) 小薮, 市原, 坂口, *日本化学会第 103 春季年会*, P2-3pm-05 (2023).

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ヒドロキシアミドあるいはヒドロキシアルキル置換アゾリウム塩からの NHC-Rh 錯体の合成と触媒反応への利用

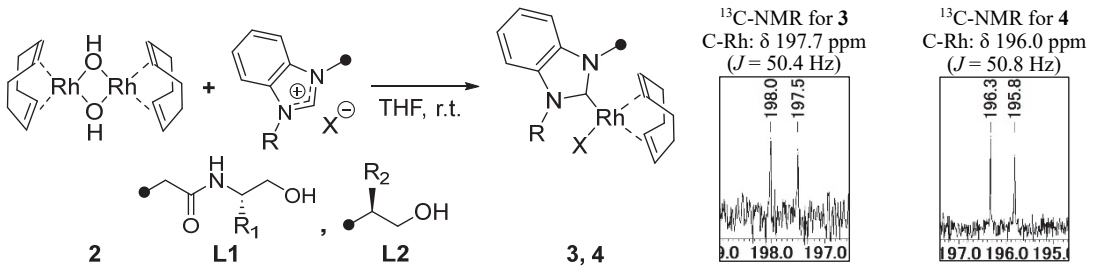
（関西大化学生命工）○松尾将吾・坂口　聡

Synthesis of NHC-Rh Complexes from Hydroxyamide- or Hydroxyalkyl-substituted Azolium Salts and Its Application for Catalytic Reactions (*Faculty of Chemistry, Materials and Bioengineering, Kansai University*) ○Shogo Matsuo and Satoshi Sakaguchi

Previously, we showed that the OMe group on of the readily available [Ir(OMe)(cod)]$_2$ (**1**) acts as an internal base for deprotonation at the C2 position of the hydroxyamide-substituted azolium salt **L1**. Thus, the corresponding NHC-Ir complex was successfully synthesized by treating **1** with **L1**. Now, we focused on commercially available and easily accessible [Rh(OH)(cod)]$_2$ (**2**). We assumed that the corresponding NHC-Rh complexes could be synthesized from the reaction of **2** with **L1** or hydroxyalkyl-substituted azolium salt **L2**, respectively. As a result, reaction of **2** with **L1** or **L2** efficiently proceeded in THF at room temperature to produce the desired NHC-Rh complex **3** or **4**. ^{13}C-NMR measurements of **3** and **4** showed the characteristic carbene signals at δ 197.7 ppm and 196.0 ppm, respectively. In addition, **3** and **4** exist as a diastereomeric mixture of two NHC-Rh complexes. Catalytic reactions using **3** and **4** were also investigated.

Keywords : N-Heterocyclic Carbene; Azolium Salt; Internal Base; Anionic Hydroxide Ligand

最近我々は、入手容易な[Ir(OMe)(cod)]$_2$ (**1**)の OMe 基が、キラルなヒドロキシアミド置換アゾリウム塩 **L1** の C2 位プロトンを引き抜く内部塩基として作用し、**1** と **L1** を反応させることで対応する NHC-Ir 錯体が得られることを報告した。[1]本研究では、**1** と同様に市販されおり入手容易な[Rh(OH)(cod)]$_2$ (**2**)に着目し、**2** を **L1** あるいはヒドロキシアルキル置換アゾリウム塩 **L2** と反応させることによって、それぞれ対応する NHC-Rh 錯体が合成できるものと考えた。結果として、**2** と **L1** あるいは **L2** との反応は、THF 中室温下で極めて効率よく進行し、目的の NHC-Rh 錯体 **3** ならびに **4** が得られた。**3** および **4** の ^{13}C-NMR 測定において、それぞれカルベン炭素に特徴的なシグナルが観測された。また、**3** および **4** は、NHC 配位子上に不斉炭素原子をもつために、ジアステレオマー混合物として存在していることが NMR 測定から示唆された。先行研究により、NHC-Ir 錯体が高収率かつ高エナンチオ選択的なケトンの不斉シラン還元反応を触媒することを明らかにしており、[1]本研究では、NHC-Rh 錯体 **3** および **4** を触媒反応へ利用する検討を行った。



1) 長尾, 市原, 坂口, *日本化学会第103 春季年会*, P2-3pm-01 (2023).

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イリジウム触媒を用いたアンモニア水とアルコールからの第二級アミンの高選択的合成

（京大院人環）○LYU JING・藤田 健一

Selective Synthesis of Secondary Amines from Aqueous Ammonia and Alcohols Catalyzed by Iridium Complexes

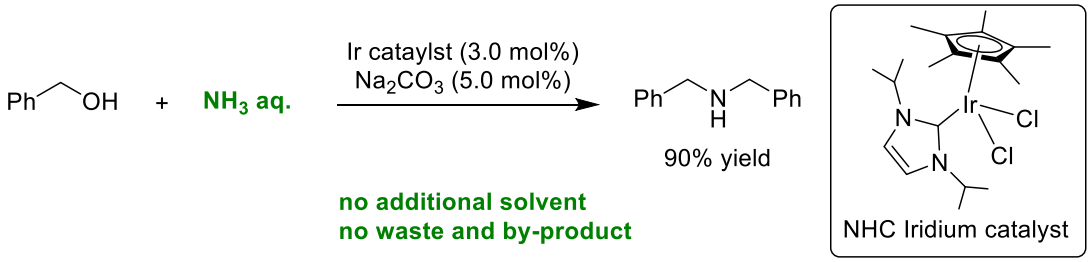
(*Graduate School of Human and Environmental Studies, Kyoto University*)
○Jing Lyu, Ken-ichi Fujita

Amines are a crucial class of organic compounds widely used as intermediates for the synthesis of pharmaceutical drugs, agrochemicals, dyes, and polymers. However, most of the conventional methods for the synthesis of amines have drawbacks, such as employment of toxic agents and low selectivity towards the desired product. Thus, it is important to develop a new method for the synthesis of amines with environmental-benignity, excellent atom-efficiency, and high selectivity. Recently, several catalytic systems for the N-alkylation of ammonia with alcohols to obtain various amines through the “borrowing hydrogen” strategy have been reported.[1-3)]

In this study, a new system for N-alkylation of aqueous ammonia with primary alcohols employing iridium complexes bearing an N-heterocyclic carbene (NHC) ligand leading to the selective formation of secondary amines has been developed.

Keywords：Iridium; N-Alkylation; Ammonia; Alcohols; Secondary amines;

アミン類は重要な有機化合物のひとつであり、医薬品、農薬、染料、ポリマーの合成のため中間原料として広く利用されている。しかし、従来のアミン合成法は有害な試薬を使いたり、目的のアミン生成物を与える選択性が低い等の問題点があった。したがって、環境調和性や原子効率に優れ、高い選択性をそなえたアミンの新規合成法を探索する必要がある。最近は、水素借用機構に基づいた、アンモニアとアルコールとの N-アルキル化による触媒的アミン合成法が報告されている [1-3)]。本研究では、第一級アルコールとアンモニア水を原料として用いることによって、第二級アミンの選択的合成を達成する新しい反応系を開発した。含窒素複素環カルベン（NHC）配位子を有するイリジウム錯体は、この反応において高い触媒性能を示した。



1) Gunanathan, C.; Milstein, D. *Angew. Chem. Int. Ed.* **2008**, *47*, 8661. 2) Kawahara, R.; Fujita, K.; Yamaguchi, R. *J. Am. Chem. Soc*. **2010**, *132*, 15108. 3) Fujita, K.; Furukawa, S.; Morishima, N.; Shimizu, M.; Yamaguchi, R. *ChemCatChem* **2018**, *10*, 1993.

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機能性高分子配位子を有するイリジウム錯体触媒を用いたアルコールの脱水素化

（京大院人環[1]・関西学院大院理工[2]）○前田 紘希[1]・久野 太希[1]・丁 在瑛[1]・森崎 泰弘[2]・藤田 健一[1]

Dehydrogenation of Alcohols Catalyzed by Iridium Complexes Bearing Functional Polymer Ligands ([1]*Graduate School of Human and Environmental Studies, Kyoto University*, [2]*Graduate School of Science and Technology, Kwansei Gakuin University*) ○Hiroki Maeda,[1] Taiki Kuno,[1] Jaeyoung Jeong,[1] Yasuhiro Morisaki,[2] Ken-ichi Fujita[1]

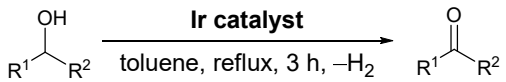
The concept of green chemistry has been incorporated into modern organic chemistry, and the development of synthetic reactions with minimal environmental impact is required. For example, catalytic reactions often have reduced environmental impact compared to conventional ones. Among catalysts containing transition metal elements, homogenous catalysts that exhibit their activity when dissolved in the reaction solvent commonly possess high activity and selectivity for various reactions. However, these catalysts are usually difficult to separate from the reaction products, and often lose catalytic activity after a single use.

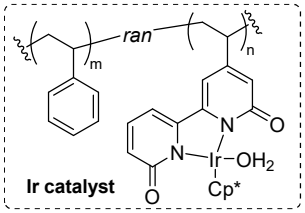
We are continuously studying the catalytic chemistry utilizing "functional ligands" which act cooperatively with transition metals. We have already reported the dehydrogenation of alcohols using such catalysts composed of functional ligand and iridium.[1)] In this study, we developed a new iridium catalyst with reusability properties by introducing a functional ligand into polymer chain.

Keywords : Iridium Catalyst; Functional Ligand; Polymer Ligand; Alcohol; Dehydrogenation

近年、有機合成化学分野にグリーンケミストリーの考え方が取り入れられるようになり、より環境に与える影響の少ない反応の開発が求められている。例えば、触媒反応は従来の反応と比べて環境への影響が小さな反応である。中でも均一系遷移金属触媒は、対象の化合物とともに反応溶媒に溶解して、高い活性・選択性を発現することがよく知られている。一方で均一系触媒の多くは、反応生成物と分離することが困難であり再利用が難しいことが課題である。

当研究室では、金属と協働して反応に寄与する「機能性配位子」を開発し、それを用いたイリジウム錯体触媒によるアルコールや環状アミンの脱水素化反応を報告してきた[1)]。本研究では、機能性配位子を高分子鎖に導入した機能性高分子配位子を新たに開発し、イリジウム錯体触媒によるアルコールの脱水素化において高い触媒活性と再利用特性を有することを見出した。





1) K. Fujita, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 344.

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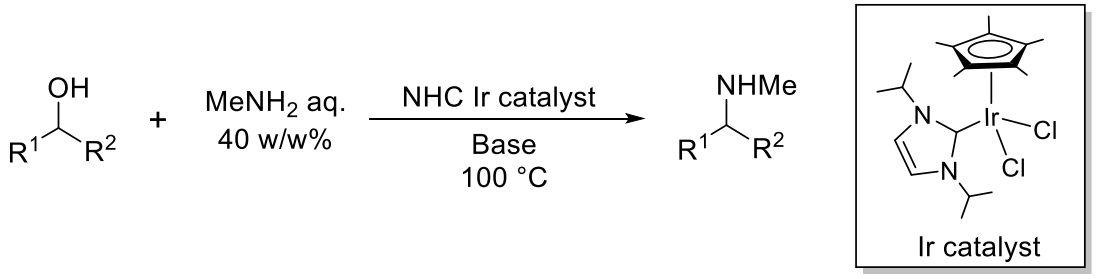
イリジウム錯体触媒を用いた水溶媒中におけるアルコールのメチルアミノ化反応

（京大院人環）○久保 舞実・吉田 七瀬・藤田 健一
Iridium Complex-Catalyzed Methylamination of Alcohols in Aqueous Media (*Graduate School of Human and Environmental Studies, Kyoto University*) ○Maimi Kubo, Nanase Yoshida, Ken-ichi Fujita

N-Methylamine derivatives are important compounds in organic synthesis because they are often recognized in natural products and bioactive substances. Synthesis of N-methylamines is conventionally performed based on reductive amination using formaldehyde and N-methylation of simple amines using methylating reagents.[1),2)] However, such methods have problems from the viewpoint of atom economy and environmental-benignity due to the use of hazardous reagents and/or the generation of byproducts. In this work, we have developed a new system for the synthesis of N-methylamine derivatives based on methylamination of alcohols using aqueous solution of methylamine catalyzed by an iridium complex bearing an N-heterocyclic carbene (NHC) ligand. For example, when benzyl alcohol was heated and stirred in methylamine solution in the presence of an iridium catalyst and base at 100 °C, N-methylbenzylamine was obtained in a good yield.
Keywords : Iridium Catalyst; Methylamination; Alcohol; Aqueous Media; Hydrogen Transfer

N-メチルアミン誘導体は、天然物や生理活性を有する物質に多く見られ、重要な有機化合物群である。従来の合成法として、ホルムアルデヒドを用いた還元的アミノ化反応やメチル化剤による N-メチル化反応が挙げられる[1),2)]。しかし、これらの手法には、有害な試薬の使用や廃棄物の副生など、原子効率や環境調和性の観点から改善すべき点があった。本研究では、含窒素複素環カルベン（NHC）配位子を有するイリジウム錯体触媒を用いるメチルアミン水溶液中でのアルコールのメチルアミノ化に基づく N-メチルアミン誘導体合成法を開発した。例えば、ベンジルアルコールをメチルアミン水溶液中でイリジウム錯体触媒と塩基の存在下、加熱撹拌（100 °C）したところ、良好な収率で N-メチルベンジルアミンが得られた。



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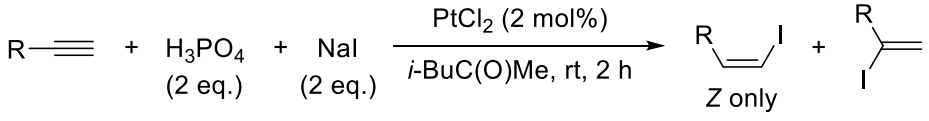
リン酸とヨウ化ナトリウムを用いる白金触媒によるアルキンのヒドロヨウ素化反応

（埼大院理工）○柳沢 萌華・木下 英典・三浦 勝清
Platinum-Catalyzed Hydroiodination of Alkynes Using Phosphoric Acid and Sodium Iodide (*Graduate School of Science and Engineering, Saitama University*) ○Moeka Yanagisawa, Hidenori Kinoshita, Katsukiyo Miura

Iodoalkenes are quite valuable for regio- and stereo-selective synthesis of multi-substituted alkenes by carbon-carbon bond-forming reaction. Since they serve not only as alkenyl electrophiles but also as precursors of alkenylmetals and alkenyl radicals, the versatility enables diverse molecular transformations. Hydroiodination of alkynes with hydrogen iodide and its equivalents provides a straightforward, atom-economical access to iodoalkenes. However, the conventional electrophilic addition of hydrogen iodide has some drawbacks in terms of regio-, stereo-, and chemo-selectivity. In this study, we found that $PtCl_2$ efficiently catalyzed hydroiodination of alkynes using phosphoric acid and NaI. The Pt(II)-catalyzed reaction of terminal alkynes afforded *anti*-Markovnikov adducts as major products with high levels of *Z*-selectivity. Particularly, the hydroiodination of propargyl esters and ethers exhibited high regio-, stereo-, and chemo-selectivity to give (*Z*)-γ-iodoallyl esters and ethers in high yield. Internal alkynes also underwent the Pt(II)-catalyzed addition in an *anti* fashion.
Keywords : Platinum Catalyst; Alkyne; Iodoalkene; Hydroiodination; anti-Markovnikov Addition

ヨードアルケンは、炭素−炭素結合生成による多置換アルケンの位置及び立体選択的合成に極めて有用である。アルケニル求電子剤としてだけでなく、アルケニル金属やアルケニルラジカルの前駆体となるため、様々な分子変換が可能である。ヨウ化水素やその等価体を用いるアルキンのヒドロヨウ素化反応は、直截的で原子効率が高いヨードアルケン合成法であるが、従来の反応には、位置、立体及び化学選択性についていくつか問題がある。本研究では、塩化白金(II) がリン酸とヨウ化ナトリウムを用いるアルキンのヒドロヨウ素化を効率よく触媒すること見出したので報告する。

塩化白金(II) を触媒とする末端アルキンのヒドロヨウ素化反応は、逆マルコフニコフ付加体を主生成物として与え、高い *Z* 選択性を示した。特に、プロパルギルエステルやエーテルの反応は高い位置、立体、化学選択性で進行し、高収率で (*Z*)-γ-ヨードアリルエステルやエーテルが得られた。白金触媒による付加反応は内部アルキンにも適用可能で、アンチ付加で進行した。



R = Ph	77%, 65:35
R = $PhCH_2OCH_2$	89%, 98:2
R = $PhCO_2CH_2$	93%, 99:1
R = (*E*)-$PhCH{=}CHCH_2OCH_2$	88%, 97:3

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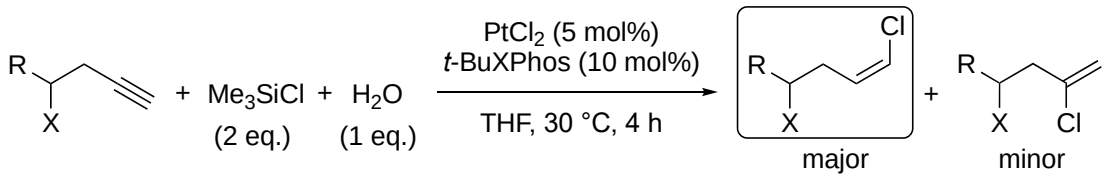
白金触媒によるアルキンの逆マルコフニコフ型ヒドロ塩素化反応：隣接官能基の効果

（埼大院理工）・○池島 崇貴・三浦 勝清・木下 英典
Platinum-Catalyzed *anti*-Markovnikov Hydrochlorination of Alkynes: Effects of Neighboring Functional Groups (*Graduate School of Science and Engineering, Saitama University*) ○ Takaki Ikeshima, Katsukiyo Miura, Hidenori Kinoshita

Since 1-haloalk-1-enes are useful intermediates for the synthesis of 1,2-disubstituted alkenes, much attention has been paid for regio- and stereoselective synthesis of 1-haloalk-1-enes. Hydrohalogenation of terminal alkynes with hydrogen halides is a potential method for simple, atom-economical synthesis of 1-haloalk-1-enes. However, the reaction of unactivated alkynes gives 2-haloalk-1-enes by Markovnikov addition. We have found that the Pt-catalyzed hydrochlorination of terminal alkynes proceeds by *anti*-Markovnikov addition. In this study, we investigated the effects of the heteroatom functional groups at the homopropargylic position on the regioselectivity and rate of the Pt-catalyzed reaction. Screening of various oxygen functionalities revealed that the hydrochlorination of terminal alkynes bearing a trifluoroacetoxy group exhibited high *anti*-Markovnikov selectivity. The reactions directed by other heteroatom functionalities also proceeded efficiently, and indicated that inductive electron-withdrawing effects are crucial for improving the regioselectivity and reaction rate.
Keywords : Platinum Catalyst; Alkyne; Chloroalkene; Hydrochlorination; anti-Markovnikov Addition

1-ハロ-1-アルケンは、1,2-二置換アルケンの合成中間体として有用で、その位置及び立体選択的合成法は活発に研究されている。ハロゲン化水素を用いる末端アルキンのヒドロハロゲン化反応は、1-ハロ-1-アルケンの簡便かつ原子効率の高い合成法になり得る。しかし、活性化されていない末端アルキンの反応は、マルコフニコフ付加により 2-ハロ-1-アルケンを与える。当研究室では、白金触媒による末端アルキンのヒドロ塩素化反応が、逆マルコフニコフ選択性を示すことを発見した [1]。本研究では、この白金触媒反応について、ホモプロパルギル位のヘテロ官能基が位置選択性や反応速度に及ぼす影響を調査した。

様々な酸素官能基を検討した結果、トリフルオロアセトキシ基を有する基質が高い位置選択性を示した。また、他のヘテロ官能基を有する末端アルキンについても検討し、本反応が高い官能基許容性を示すとともに、電子求引性の高い官能基の導入が位置選択性や反応速度の向上に有効であることがわかった。



1) 石田匠、木下英典、三浦勝清、第 10 回 JACl/GSC シンポジウム、2021、A35.

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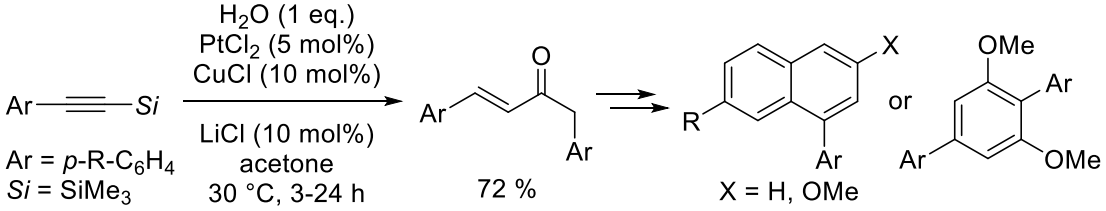
白金触媒によるアルキニルシランの水和二量化反応とアレーン合成への応用

（埼大院理工）○安倍 智夏・三浦 勝清・木下 英典
Platinum-Catalyzed Hydrative Dimerization of Alkynylsilanes and Its Application to Arene Synthesis (*Graduate School of Science and Engineering, Saitama University*) ○Chinatsu Ambe, Katsukiyo Miura, Hidenori Kinoshita

α,β-Unsaturated ketones are important synthetic intermediates because they have multiple reaction sites capable of diverse molecular transformations. For this reason, a large number of methods for preparing α,β-unsaturated ketones from various precursors have been developed so far. We have found that the $PtCl_2$-catalyzed reaction of alkynylsilanes with water forms α,β-unsaturated ketones by hydrative dimerization with elimination of the silyl group. In this study, we investigated not only the applicability of a Pt-Cu-Li catalyst system for the homo- and cross-dimerization of alkynylsilanes but also derivatization of the products to conjugated arenes. In the presence of CuCl and LiCl as cocatalysts, the homo-dimerization of (arylethynyl)silanes to 1,4-diarylbut-3-en-2-ones efficiently proceeded with a reduced loading of $PtCl_2$. The Pt-Cu-Li system promoted cross-dimerization between different alkynylsilanes but with low selectivity. The homodimer, or 1,4-diarylbut-3-en-2-ones were successfully converted into 1-arylnaphthalenes and *p*-terphenyls by intra- or intermolecular cyclization followed by aromatization.
Keywords : Platinum Catalyst; Hydrative Dimerization; Alknylsilane; Unsaturated Ketone; Arene

α,β-不飽和ケトンは、多様な分子変換を可能にする複数の反応点を持ち、合成中間体として重要である。このため、様々な前駆体を利用した数多く合成法が開発されている。当研究室では、塩化白金(II) $PtCl_2$ を触媒とするアルキニルシランと水との反応が、シリル基の脱離を伴う水和二量化によりα,β-不飽和ケトンを与えることを見出している。本研究では、Pt-Cu-Li 触媒系によるアルキニルシランのホモおよび交差二量化と、生成物の共役アレーン類への誘導体化について検討した。

助触媒として CuCl と LiCl の存在下、少ない量の $PtCl_2$ で（アリールエチニル）シランのホモ二量化が効率よく進行した。Pt-Cu-Li 触媒系は、異なるアルキニルシラン間の交差二量化にも利用できたが、交差二量体への選択性は低くかった。ホモ二量体である 1,4-ジアリール-3-ブテン-2-オンは、分子間あるいは分子内環化と芳香化により、首尾よく 1-アリールナフタレンや *p*-テルフェニルに変換できた。



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二置換ベンゼンとポリフルオロアレーンの脱水素型クロスカップリング反応における位置選択性と反応性の評価

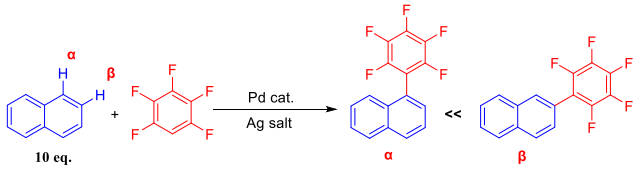
(筑波大院数理物質 [1]) ○熊 天雅 [1]・飯田 智希 [1]・神原 貴樹 [1]・桑原 純平 [1]

Research of regioselectivity and reactivity in cross-dehydrogenative coupling reaction of disubstituted benzene with polyfluoroarene ([1]Univ. of Tsukuba) ○Tianya Xiong[1], Tomoki Iida[1], Takaki Kanbara[1], Junpei Kuwabara[1]

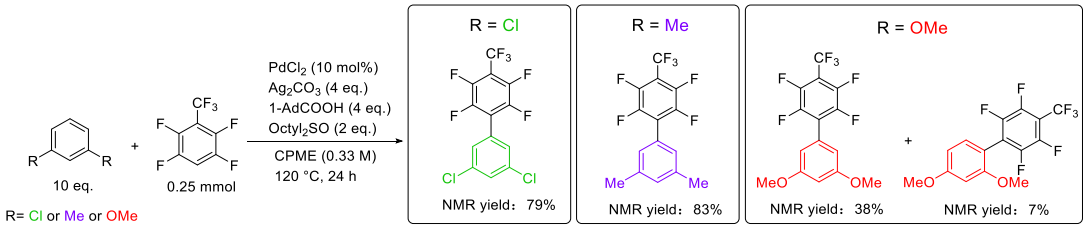
Recently we reported cross-dehydrogenative coupling (CDC) reaction of naphthalene with polyfluoroarene proceeded at the β-position where the steric hindrance is small, in contrast to the general α-position selectivity (Scheme 1).[1)] This study investigates whether disubstituted benzenes also exhibit similar regioselectivity (Scheme 2). The influence of electronic factors of substituents on reactivity was also investigated. Compared to the other disubstituted benzenes researched, the lowest reactivity and regioselectivity are observed for dimethoxybenzene (R = OMe). As the cause of the regiospecificity is associated with the difference in the reaction rate of reductive elimination, we focused on the reductive elimination step and revealed that the reductive elimination also proceeded at the sterically hindered 4-position.

Keywords : Regiospecificity; Cross-Dehydrogenative Coupling; Reductive elimination

我々が以前に報告した acene 類と polyfluoroarene の脱水素型クロスカップリング(CDC)反応は、一般的なα位選択性とは異なり、立体障害が小さなβ位に polyfluoroarene が導入される (Scheme 1)。[1)] 本研究では acene 類だけでなく、ベンゼン誘導体も同様の位置選択性が発現するのかを調べると共に、置換基の電子的な要因が反応性に及ぼす影響を調査した (Scheme 2)。検討した他の二置換ベンゼンと比べて、ジメトキシベンゼン (R = OMe) の場合には、反応性と位置選択性が一番低いことが明らかとなった。位置特異性が発現する要因が還元的脱離の反応速度の差にあることから、還元的脱離の段階の錯体化学的な検討も行ったところ、ジメトキシベンゼンでは立体障害の大きな 4 位でも還元的脱離が進行することを明らかにした。



Scheme 1. Naphthalene と polyfluoroarene の CDC 反応 [1)]



Scheme 2. 二置換ベンゼンと heptafluorotoluene (HFT)の CDC 反応の位置選択性と収率

1) R. Sato; T. Iida; T. Kanbara; J. Kuwabara, *Chem. Commun*. **2022**, *58*, 11511-11514.

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シクロオクタテトラエン配位子を有するニッケル 4 核サンドイッチ錯体の反応性調査

（東工大物質理工 [1]・防衛大応化 [2]）○根本 悠史 [1]・酒井 元気 [1]・重田 翼 [1]・山本 浩二 [2]・村橋 哲郎 [1]

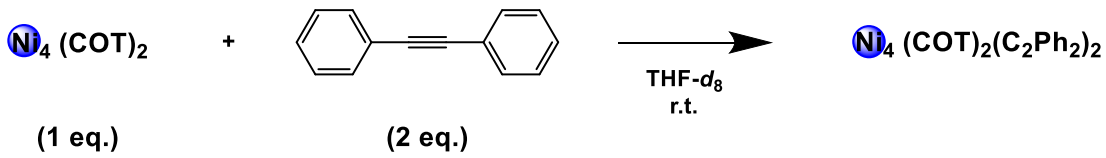
Reactivity of Tetranuclear Nickel Sheet Sandwich Clusters Bearing Cyclooctatetraene Ligands

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Department of Applied Chemistry, National Defense Academy*) ○Yuji Nemoto,[1] Genki Sakai,[1] Tsubasa Omoda,[1] Koji Yamamoto,[2] Tetsuro Murahashi [1]

Since the report of nickelocene, Ni sandwich complexes have attracted great interest. However, it has been difficult to synthesize multinuclear Ni sandwich complexes by assembling Ni atoms between unsaturated hydrocarbon ligands. We have reported the synthesis of tetranuclear Ni sheet sandwich clusters with Ni-Ni bonds by using cyclooctatetraene (COT) ligands. Here, we investigated the reaction of the clusters with alkynes.

Keywords : Nickel; Multinuclear Sandwich Complexes; Cyclooctatetraene

1952 年にニッケロセンが報告されて以来、ニッケルサンドイッチ錯体に興味がもたれている。しかし、低原子価 Ni 種の強い還元力のために、不飽和炭化水素が酸化的π付加し、Ni(Ⅱ)になりやすい傾向があり、不飽和炭化水素間に安定に多数の低原子価 Ni 種を集合させて多核サンドイッチ錯体を合成することは難しいとされてきた。我々は 8 員環シクロオクタテトラエン(COT)を配位子として用いることで、Ni-Ni 結合を有する 4 核サンドイッチクラスターが合成可能であることを見出している。今回我々は、Ni4 核サンドイッチクラスターとアルキンの反応を調査したので報告する。



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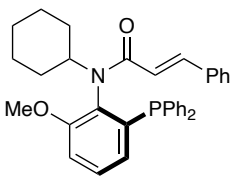
軸不斉を有するシンナムアミド型不斉配位子を用いたパラジウム触媒による不斉アリル位アミノ化反応

（千葉大学[1]）○秋本 南椰[1]・水野 広登[1]・髙谷 香帆[1]・吉田 泰志[1]・三野 孝[1]
Palladium-catalyzed asymmetric allylic amination using a cinnamamide-type chiral ligand with axial chirality ([1]*Chiba University*) ○Natsume Akimoto,[1] Hiroto Mizuno,[1] Kaho Takaya,[1] Yasushi Yoshida,[1] Takashi Mino[1]

We have been developing chiral compounds with axial chirality between carbon-nitrogen bonds that can be used as chiral ligands for catalytic asymmetric reactions. Recently, we have developed P,olefin-type ligands with a cinnamamide group. These ligands were found to be applicable to Pd-catalyzed asymmetric allylic reactions using indole derivatives as nucleophiles. In this study, aiming to further investigate the scope of nucleophile application, we sought to apply this ligand to the Pd-catalyzed asymmetric allylic amination of isatins.

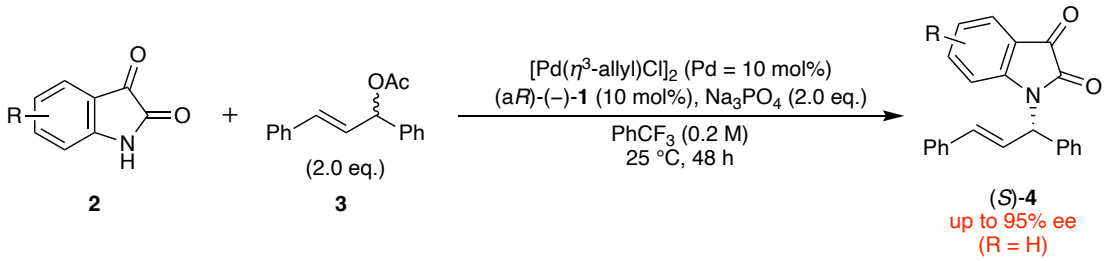
Keywords : Pd; P,Olefin Type Ligand; Isatin; Asymmetric Allylic Amination

当研究室では以前より、触媒的不斉反応に利用可能な炭素−窒素結合間に軸不斉を有する不斉配位子の開発を行ってきた。近年、シンナモイル基が窒素原子上に置換されたリン, オレフィン型アミドホスフィン配位子 **1** を開発したところ、インドール誘導体を求核剤として用いた不斉反応に適用可能なことが明らかとなった[1)]。そこで本研究では、**1** のさらなる基質適用範囲を調査するため、パラジウム触媒によるイサチンの不斉アリル位アミノ化反応への応用を目的として研究を行った。実際に、**1** を不斉アリル位アミノ化反応に適用したところ *S* 体の目的生成物が優先して生成し不斉配位子として働くことが明らかとなった。反応条件の最適化を行ったところ塩基として Na_3PO_4、溶媒として $PhCF_3$ を用いた場合に 95% ee と高い選択性で目的物が得られた。



1

続いて、最適条件の下、基質検討を行った。求核試薬として様々な電子求引性および電子供与性の置換基をもつイサチンを検討したところ、ほとんどの基質において良好な不斉収率で反応が進行した。



2 **3** (*S*)-**4**
up to 95% ee
(R = H)

Scheme 1. Asymmetric Allylic Amination of Isatin

1) T. Mino *et al.*, *Org. Biomol. Chem.*, **2023**, *21*, 2775.

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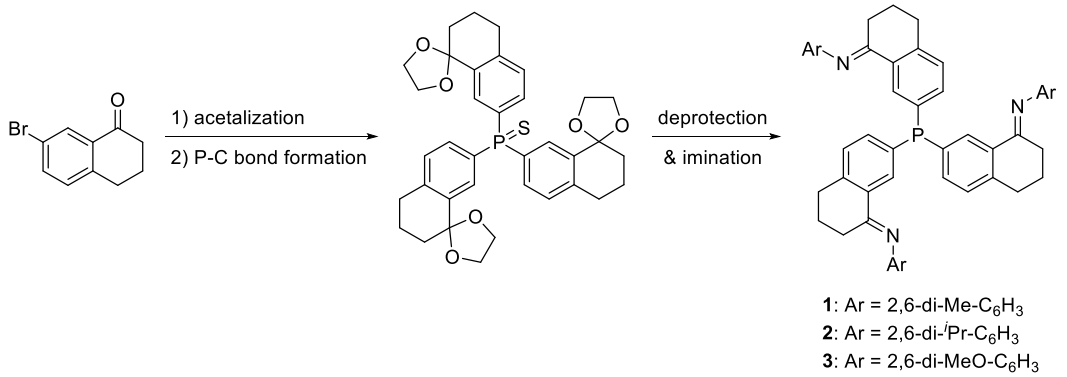
３つの 1-テトラロンイミン部位を有する新規ホスフィン配位子とそのパラジウム錯体の合成

（愛媛大院理工）○脇本 有紀子・太田 英俊・林 実
Synthesis of Novel Phosphine Ligands Bearing Three 1-Tetralone Imine Moieties and Their Palladium(II) Complexes (*Grad. Sch. Sci., Eng., Ehime Univ.*) ○Yukiko Wakimoto, Hidetoshi Ohta, Minoru Hayashi

Multinuclear metal complexes are capable of efficient trapping and activation of reaction substrates by utilizing multiple metal centers in a cooperative manner, thereby often exhibiting distinctive catalytic behaviors in comparison to mononuclear metal complexes. Organic ligands play an important role in controlling the structure and electronic state of multinuclear metal complexes. Therefore, much effort has been devoted to the synthesis of various organic ligands for the creation of high-performance multinuclear metal complex catalysts. Here, we developed novel phosphine ligands **1-3** bearing three 1-tetralone imine moieties. These ligands were prepared via the acetalization of 7-bromo-1-tetralone followed by a P-C bond formation, deprotection, and imination. The complexation behaviors of **1-3** with palladium(II) species were investigated.

Keywords : Phosphine, 1-Tetralone Imine, Palladium, Multinuclear Metal Complex

多核金属錯体は複数の金属中心の協同作用による効率的な反応基質の捕捉や活性化が可能であり、単核金属錯体とは異なる触媒作用を示すことがある。有機配位子は多核金属錯体の構造と電子状態を制御するために重要であり、高性能な多核金属錯体触媒の創製を目的として様々な有機配位子が開発されている。今回我々は３つの 1-テトラロンイミン部位を有する新規ホスフィン配位子 **1-3** を設計し、これらを 7-ブロモ-1-テトラロンのアセタール化と P-C 結合形成、脱保護、イミノ化を経て合成した。さらに、配位子 **1-3** とパラジウム(II)種の錯化挙動について調査したので報告する。



1: Ar = 2,6-di-Me-C_6H_3
2: Ar = 2,6-di-^{i}Pr-C_6H_3
3: Ar = 2,6-di-MeO-C_6H_3

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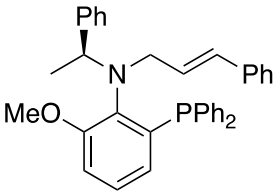
シンナミル基を有するP,オレフィン型不斉配位子を用いたPd触媒による不斉アリル位アミノ化反応

（千葉大学[1]）○水野 広登[1]・髙谷 香帆[1]・鳥羽 結斗[1]・吉田 泰志[1]・三野 孝[1]
Pd-catalyzed asymmetric allylic amination using chiral P,olefin ligand with cinnamyl group
([1]*Chiba University*) ○Hiroto Mizuno,[1] Kaho Takaya,[1] Yuto Toba,[1] Yasushi Yoshida,[1] Takashi Mino[1]

We have previously reported that a chiral ligand with cinnamyl group derived from optically active phenethylamine works effectively in Pd-catalyzed asymmetric allylic substitution. In this study, we report that this ligand is also effective in Pd-catalyzed asymmetric allylic amination using phthalimide as a nucleophilic reagent.

Keywords : Chiral Ligand; Pd; Asymmetric Allylic Amination; Phthalimide

触媒的不斉合成において高純度の光学活性化合物を得るためには、不斉配位子により中心金属の周辺に不斉環境が構築される必要があり、配位子の開発は重要である。当研究室では以前より、触媒的不斉反応に利用可能な中心不斉および軸不斉を有する不斉配位子の開発を行ってきた。近年、光学活性なフェニチルアミンから誘導した、シンナミル骨格を有する不斉配位子 **1** が、インドールを求核剤とする Pd 触媒による不斉アリル位置換反応において、有効に作用することを報告している [1)]。そこで本研究では、**1** のさらなる基質適用範囲を調査するため、パラジウム触媒によるフタルイミドの不斉アリル位アミノ化反応への応用を目的として研究を行った。実際に、**1** を不斉アリル位アミノ化反応に適用したところ *R* 体の目的生成物が優先して生成し不斉配位子として働くことが明らかとなった。そこで反応条件の最適化を行ったところ塩基として Na_3PO_4、溶媒として THF を用いた場合に 92%、不斉収率 98% ee と高い選択性で目的物が得られた。



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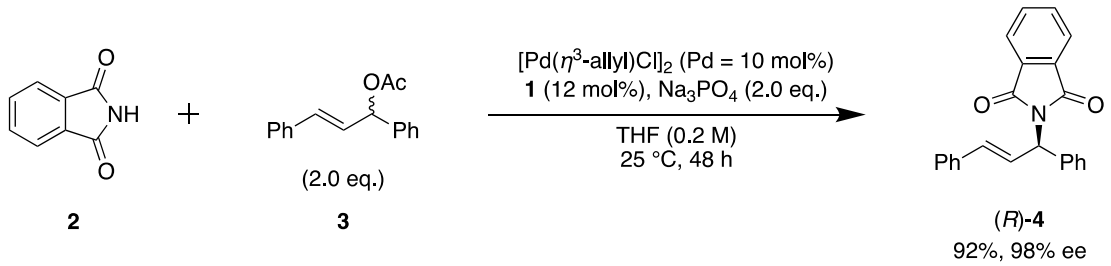

2 **3** (*R*)-**4**
92%, 98% ee

Scheme 1. Asymmetric Allylic Substitution of Phthalimide

1) T. Mino *et al.*, *Synlettl*, **2021**, 532-538.

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新規銀ナノ粒子複合体の合成と光遮蔽効果

(プレミアアンチエイジング株式会社[1]・株式会社伊都研究所[2])
○松尾　一貴[1]・伊東　謙吾[2]

Synthesis and optical analysis of unique silver nanoparticle composites

([1] *Premier Anti-Aging Co., Ltd*, [2] *Ito Research Institute Co., Ltd.*)
○Kazuki Matsuo,[1] Kengo Ito [2]

Metal nanoparticles such as silver has been reported that resonate strongly thorough the interaction between these nanoparticles and light. Near-infrared reflective materials using the enhancement of the photoelectric field associated with resonance has been actively developed. However, conventional wavelength of the targeted near-infrared light was mainly at ~1000 nm. Calcium carbonate is well known to have scattering effects on mid- to far-infrared radiation.

In this study, we synthesized a composite of calcium carbonate and silver nanoparticles with a binder of clays. It was revealed that this composite has strongly scatter near-infrared light up to ~ 1900 nm and confirmed that its spectral property changes depending on the amount of the moisture in the film (Fig.1). ***Keywords : Silver, Light, Complex, Near-IR***

銀などの金属ナノ粒子は、光との相互作用により強く共鳴することが報告されている[1)]。共鳴に伴う光電場の増強を利用した近赤外光反射材料の開発が盛んに行われている[2)]。しかし従来、対象となる近赤外光の波長は～1000nm であった。一方、炭酸カルシウムは、中赤外光から遠赤外光に対して散乱効果があることが知られている。

そこで本研究では、バインダーとして粘土鉱物を用いて、炭酸カルシウムと銀ナノ粒子の複合体を合成した。複合体は～1900 nm までの近赤外光を散乱し、そのスペクトル特性は塗膜中の水分量に応じて変化することがわかった（図 1）。

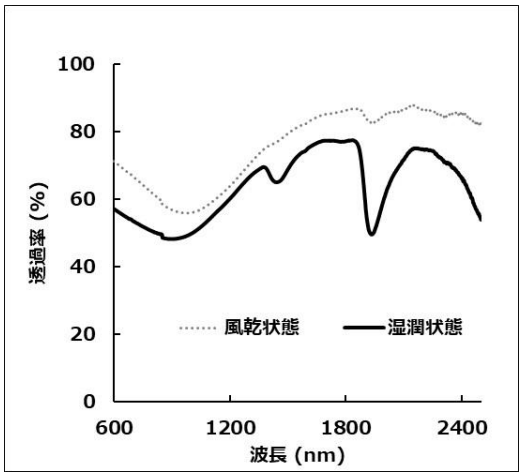

Fig.1 Transmission spectrum properties in response to moisture.

1) I M. I. Stockman. *Opt. Express*, 19 (2011) 22029―22106.
2) S. Yamazoe, M. Naya, M. Shiota, T. Morikawa, A. Kubo, T. Tani, T. Hishiki, T. Horiuchi, M. Suematsu and M. Kajimura. *ACS Nano*, 8 (2014) 5622―5632.

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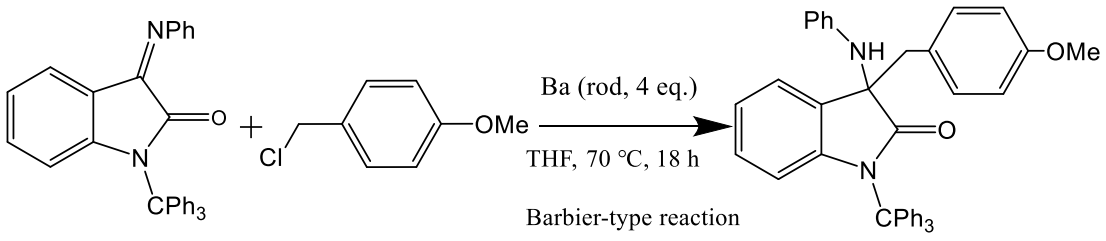
金属バリウムを用いたイサチンイミン類のベンジル化反応

（千葉大院融合理工[1]・千葉大院理[2]）○曾根 洸人[1]・柳澤 章[2]
Benzylation of Isatin Imines Using Metallic Barium
(Chiba University) ○Hiroto Sone, Akira Yanagisawa

We have reported that a benzylic barium reagent, generated from metallic barium and a benzylic chloride, was added to isatin imines under Barbier-type reaction conditions to afford 3-amino-2-oxindoles efficiently in the 103rd annual meeting of the Chemical Society of Japan. Here, we report that we attempted to react various isatin imines with benzylic chlorides using similar reaction conditions, and as a result, desired benzylated products were obtained in good yields.
Keywords : Barium; Benzylation; Isatin Imines; Benzylic Chloride

当研究室では昨年の第 103 春季年会で、金属バリウムと塩化ベンジル型化合物から発生させたベンジル型バリウム反応剤が、Barbier 型反応条件でイサチンイミン類に付加し、3-アミノ-2-オキシインドール化合物を効率的に与えることを発表している[1]。今回、同様な反応条件を用いて様々なイサチンイミン類と塩化ベンジル型化合物との反応を試みた結果、目的とする各種ベンジル化生成物が良好な収率で得られたので報告する。イサチンイミン **1** と塩化 4-メトキシベンジル**(2)**の 1:3 混合物に金属バリウムを 70 ℃で作用させたところ、目的とするベンジル化生成物 **3** が 72%の収率で得られた。



1 (1 eq.)　　**2** (3 eq.)　　**3,** 72% yield

1) 曾根洸人、柳澤章、日本化学会第 103 春季年会、P2-3pm-19.

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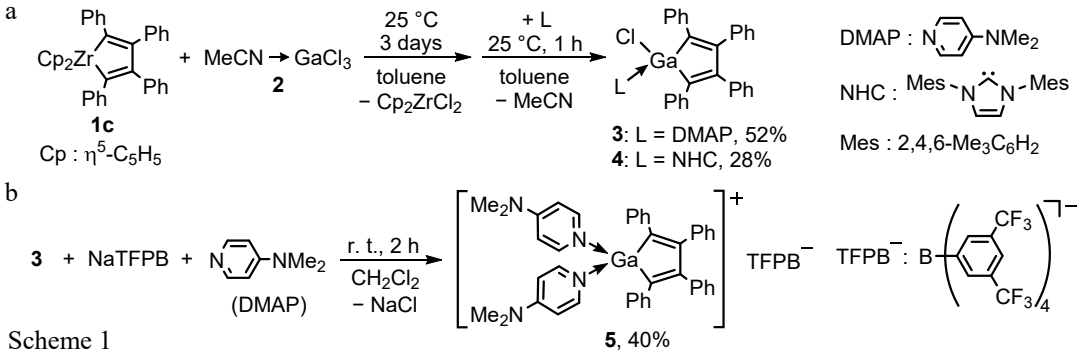
ルイス塩基が配位した（クロロ）テトラフェニルガラシクロペンタジエンの合成，構造および反応性

（群馬大院理工）山内 彩花・○村岡 貴子・片山 晴留香
Synthesis, Structures and Reactivity of (Chloro)tetraphenylgallacyclopentadienes (*Graduate School of Science and Technology, Gunma University*) Ayaka Yamauchi, ○Takako Muraoka, Haruka Katayama

Synthesis, structures, and properties of boracyclopentadiene derivatives $RBC_4R'_4$ have attracted significant attention, however, those of gallacyclopentadiene derivatives $RGaC_4R'_4$ have remained unexplored. In this paper, we report synthesis and structures of Lewis base-stabilized gallacyclopentadienes (L)$ClGaC_4Ph_4$ (L = DMAP (**3**), NHC (**4**)) and transformation of **3** to the first cationic gallacyclopentadiene derivative $[(DMAP)_2GaC_4Ph_4][TFPB]$ (**5**) (Scheme 1).
Keywords : Gallacyclopentadiene; Cationic Gallacyclopentadiene; Gallium; Lewis Base

ボラシクロペンタジエン誘導体 $R'BC_4R_4$ はシクロペンタジエニルカチオンと等電子構造であり，その合成，構造および性質は活発に研究されている．一方，$R'BC_4R_4$ の高周期類縁体であるガラシクロペンタジエン誘導体 $R'GaC_4R_4$ は 16 例報告されているが，反応性はほとんど検討されていない．最近我々は，$Cp_2ZrC_4R_4$ (R = Me (**1a**), Et (**1b**), Cp: η^5-C_5H_5)と $GaCl_3$ との反応により $ClGaC_4R_4$ (**A**)の合成を試みたが，**A** は得られず，10 員環テトラエン誘導体 $ClGaC_8R_8GaCl$ が得られることを見出した [1]．本研究では，フェニル基を有する **1c** と $GaCl_3$ および$(MeCN)GaCl_3$ (**2**)との反応を検討した．

$Cp_2ZrC_4Ph_4$ (**1c**)と $GaCl_3$ を C_6D_6 中，室温から 60 ºC で 2 日間反応させたところ，複雑な混合物が得られた．次に **1c** と **2** をトルエン中 25 ºC で 3 日間反応させた後，反応混合物にルイス塩基 L を加えると，ルイス塩基付加体(L)$ClGaC_4Ph_4$ (L = DMAP (**3**), NHC (**4**))が生成した(Scheme 1a)．**3** と DMAP の混合物に 1 当量の NaTFPB を反応させたところ，**3** から Cl^-が引き抜かれて，初めての陽イオン性ガラシクロペンタジエン誘導体$[(DMAP)_2GaC_4Ph_4][TFPB]$ (**5**)が得られた(Scheme 1b).



Scheme 1

1) T. Muraoka, et al. *Organometallics* **2023**, *42*, 982.

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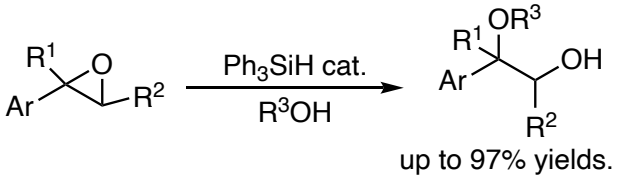
ヒドロシランを触媒としたエポキシドの開環反応

（東理大工[1]）○橋本 徹[1]・錦村 康平[1]・北條 信[1]
Ring-opening Reaction of Epoxide Catalyzed by Hydorosilane ([1]*Department of Applied Chemistry, Faculty of Engineering, Sanyo-Onoda City University*) ○Toru Hashimoto,[1] Kohei Nishikimura,[1] Makoto Hojo[1]

Neutral silicon compounds exhibit weak to moderate Lewis acidity, and these compounds have been utilized as Lewis-acid catalysts in organic reactions. To enhance the Lewis acidity of silicon-based catalysts for organic reactions, many research groups have developed organosilicon compounds ligated with electron-deficient substituents. In contrast, we were interested in the Lewis-acidity of organosilicon compounds ligated with alkyl, aryl, and/or hydride groups, and whether these organosilicon compounds can serve as a Lewis-acidic catalyst in organic reactions. Herein, we present that Ph_3SiH work as Lewis-acidic catalysts for the ring-opening reaction of di- and tri-substituted epoxides and alcohols to furnish β-alkoxy alcohols. These reactions proceed under transition-metal-free conditions to afford the corresponding β-alkoxy alcohols in good-to-very-high yield with excellent regioselectivity.
Keywords : Ring-opening Reaction; Epoxide; Hydrosilane

有機ケイ素化合物は、アルコールの保護基や、クロスカップリング反応やヒドロシリル化反応などの反応剤、還元反応のヒドリド源として広く利用されている。また不安定化学種である 3 配位カチオン性ケイ素化合物はルイス酸触媒としても利用され、その高い酸素親和性やフッ素親和性を生かした分子変換反応が報告されている。しかし 4 配位ケイ素化学種をルイス酸触媒として利用している例は少ない。最近、電子不足な 4 配位ケイ素化学種のルイス酸性を利用することで炭素−フッ素結合や炭素−酸素結合などの反応不活性な結合の官能基化反応が報告されている。そのような背景のもと、本研究では、電子豊富なケイ素化合物であるトリフェニルシランを触媒として用いるとエポキシドの開環反応が進行し、生成するカルボカチオン中間体がアルコール溶媒と反応することでβ-アルコキシアルコールが高収率で得られることを明らかにした。[1)]



1) T. Hashimoto, K. Nishikimura, M. Hojo, *ChemistrySelect*. **2023**, *8*, e202303292.

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二価チタン反応剤を用いて発生するアレニルチタンのニトロアルケンへの立体選択的付加反応

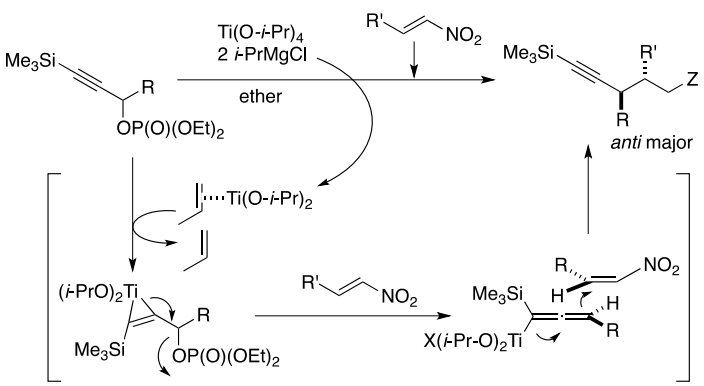
（神奈川大学）○大川理玖・伊部公太・岡本専太郎

Stereoselective Addition Reaction of Allenyl Titaniums to Nitroalkenes

(*Kanagawa University*)○Riku Okawa, Kouta Ibe, and Sentaro Okamoto

アレニル金属反応材剤の多くは求核的プロパルジル化あるいはアレニル化反応剤として有用である。我々は二価チタン反応剤[Ti(O-*i*-Pr)$_4$/2*i*-PrMgCl]を用いるプロパルギルアルコール誘導体からのアレニルチタン反応剤の発生法およびその反応性や利用法の開発を行ってきている。その中で，二価チタン反応剤とプロパルジル化合物から発生するアレニルチタンがアルキリデンマロン酸エステル類と高立体選択的に 1,4-付加反応することを見いだしている。さらに，光学活性な基質を用いると高い不斉転写立で光学活性な生成物を与えることを明らかにしている。本発表では，さらに求電子剤として幾つかの求電子アルケン類との反応を検討したところ，ニトロアルケン類との 1,4-付加反応が容易に進行し，連続する三級炭素を含む付加体としてδ-アルキニル-β，γ-ジ置換ニトロ化合物を立体選択的に与えることを見出した。現在，光学活性基質での反応について検討している。

Allenyl metal agents are useful as nucleophilic propargylation or allenylation reactants. We have developed a method for generating allenyl titanium reactants from propargyl alcohol derivatives using a divalent titanium reactant [Ti(O-i-Pr)4/2i-PrMgCl] and their reactivities and application.[1] Among them, we found that allenyl titanium generated from the divalent titanium reactant and a propardyl compound undergoes a highly stereoselective 1,4-addition reaction with alkylidene malonic acid esters.[2] In addition, it has been revealed that the reaction using an optically active substrate produces an optically active product with a high level of chirality transfer. In this presentation, we further investigated reactions with several electrophilic alkenes as electrophiles, and found that 1,4-addition reactions with nitroalkenes proceeded smoothly and stereoselectively produce δ-alkynyl-β,γ-disubstituted nitro compounds that contain consecutive tertiary carbons. We are now investigating reactions using optically active substrates.



1) F. Sato, H. Urabe, S. Okamoto, *Chemical Reviews* **2000**, 100, 2835-2886.

2) Y. Song, S. Okamoto, F. Sato, *Organic Letters* **2001**, *3*, 3543-3545.

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Academic Program [Poster] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Poster

Wed. Mar 20, 2024 10:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:00 AM - 2:30 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-3am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Japanese

[P2-3am-01]

Elucidation of a formation mechanism of hollow structures on spherulites in photochromic diarylethene thin films

○Mami Isobe[1], Daichi Kitagawa[1,2], Seiya Kobatake[1,2] (1. Grad. Sch. of Eng., Osaka Metropolitan Univ., 2. Grad. Sch. of Eng., Osaka City Univ.)

Japanese

[P2-3am-02]

Construction and structural analysis of a heterocycle containing benzene-1,3-disulfonamide using double Mitsunobu annulation

○Kyosuke Kaneda[1,2], Takato Koideya[1], Ryuji Toshima[1], Yoshiki Konno[1], Takehiro Yamagishi[1,2] (1. Hokkaido University of Science, 2. CRILS)

Japanese

[P2-3am-03]

Synthesis of trispap, a macrocyclic ligand with three *N*,*N*,*O* tridentate chelating units in close proximity

○Jia Chen Zhao[1], Nadiia Varzhel[2], Yuya Hokimoto[1], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Taras Shevchenko Natl. Univ. of Kyiv)

Japanese

[P2-3am-04]

Construction of electroconductive elastic crystal based on phthalocyanine

○Chiharu Watanabe[1], Yoji Horii[1], Takashi Kajiwara[1] (1. Nara Women's University)

Japanese

[P2-3am-05]

Mechanofluorochromic properties of boronic acid derivatives having anthracene unit

○Natsuki Kataoka[1], Manato Nishimura[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

[P2-3am-06]

Synthesis of multinuclear lanthanoid complexes with structural changes in salen macrocyclic ligand

○Yi-Fu Liu[1], Guzman Gil-Ramirez[2], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Univ. of Lincoln)

Japanese

[P2-3am-07]

Synthesis of a luminescent chiral bis(oxazoline) ligand

○Kei Shimada[1], Junpei Yuasa[1] (1. Tokyo University of Science)

Japanese

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[P2-3am-08]

Molecular design of pyrene derivatives to make microcrystalline films with silver luster effect using drop-casting method

○Tatsuya Maeda[1], Yuuma Nakagawa[2], Ryou Nshimura[3], Masakazu Morimoto[3], Satoshi Yokojima[4], Nakamura Shinitirou[5], Kingo Uchida[1] (1. Ryukoku University, 2. Molecular Engineering Institute, Shiga University of Medical Science, 3. Rikkyo University, 4. Tokyo University of Pharmacy and Life Sciences, 5. Kumamoto University)

English

[P2-3am-09]

Synthesis of azobenzene-containing salen-based macrocycle

○Mads Nybo Sørensen[1], Masaru Kondo[2], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Univ. of Shizuoka)

Japanese

[P2-3am-10]

Crystal Structures of Quinophthalone Compounds with an Ether Bond at 8 Position

○Kento Nakamura[1], Reo Hasegawa[2], Motohiro Akazome[2], Rihito Ito[3], Joji Mikami[3], Hiroyuki Yanai[3], Shoji Matsumoto[2] (1. Faculty of Engineering, Chiba University, 2. Graduate School of Engineering, Chiba University, 3. TOYOCOLOR CO., LTD.)

Japanese

[P2-3am-11]

Synthesis of Cyclic Composites of Nickel Porphyrins and Bipyridines Having Hydrophylic Groups, and Their Conformational Changes in Solution.

○Kenta Suzuki[1], Yusuke KuramochiKuramochi[1], Akiharu Satake[1] (1. Tokyo University of Science)

Japanese

[P2-3am-12]

Phase transition and changes in chromism of halosalicylidene alkylamine crystals

○Shunji Miyazato[1], Ryo Koibuchi[1], Isao Yoshikawa[1], Hirohiko Houjou[1] (1. The University of Tokyo)

Japanese

[P2-3am-13]

Synthesis of Azaylide-Based Amphiphile with a Phosphine Coordination Site and Evaluation of its Assembling Behaviors

○Sho Naito[1], Yoshimori Akiyama[2], Masahiro Yamashina[2], Shinji Toyota[2], Tomohito Ide[1] (1. National Institute of Technology, Tokyo College, 2. Tokyo Institute of Technology)

Japanese

[P2-3am-14]

Synthesis of macrocyclic ligand hexasap that assembles *O*,*N*,*O* tridentate chelating units in the cavity

○Mamoru Kamisaka[1], Sara Machleit[1,2], Takashi Nakamura[1] (1. Univ. of Tsukuba, 2. Free Univ. of Berlin)

Japanese

[P2-3am-15]

Variety and Systematics in Crystal Structure of Organic Semiconductors with Substituents

○Hiromi Minemawari[1] (1. AIST)

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Japanese

[P2-3am-16]

Synthesis and solvent adsorption/desorption behavior of porous coordination polymers with heterocycles inside one-dimensional channels

○Tatsuya Okuyama[1], motoko akita[1] (1. Josai University)

Japanese

[P2-3am-17]

X-ray structure study of co-crystals with tropolone and hydrogen-bond donor and acceptor molecules

○Hiromu Nomura[1], Hideki Saitoh[1] (1. Saitama University)

Japanese

[P2-3am-18]

Evaluation of inclusion behavior and optical properties of a host-guest conjugate with an environmentally responsive fluorescent dye

○Taiyou Tsutsumi[1], Takaaki Miyazaki[1], Osamu Hayashida[1] (1. Graduate School of Science, Fukuoka University)

Japanese

[P2-3am-19]

Synthesis of Dihydrophenazine Cationic Radical Derivative Fused by Spin Localized Nitroxyl Radical Unit and Their Physicochemical Properties

○Ryo Ohtaka[1], Shigeyuki Oba[1], Yohei Miura[1], Naoki Yoshioka[1] (1. Keio University)

Japanese

[P2-3am-20]

Synthesis of Benzodithiophenone and its Application to Stimuli Responsive Molecular Crystals

○Masahiro Ikeda[1], Tomohiro Seki[1] (1. Department of Chemistry, Faculty of Science, Shizuoka University)

Japanese

[P2-3am-21]

Complexation behavior of metalloporphyrins with bipyridyl-type ligand

○Ken Sato[1], Shigeki Miyazaki[1], Kosuke Sugawa[1], Joe Otsuki[1] (1. Nihon Univ.)

English

[P2-3am-22]

PEGylated porphyrin without phenyl groups

○Yuri Oie[1], Daiki Hirota[1], Kosuke Sugawa[1], Joe Otsuki[1] (1. Nihon Univ.)

Japanese

[P2-3am-23]

Construction of Cationic Molecular Cages Composed of Tetra(N-alkylpyridinium)porphyrins and Their Two-dimensional Assembly

○Daisuke Hayashi[1], Toshio Nishino[1], Gwénaël Rapenne[1,2] (1. Nara Institute of Science and Technology, 2. University of Toulouse)

Japanese

[P2-3am-24]

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Inclusion of Iodine and halide ions in hydrogen-bonded organic frameworks composed of fused-ring pyrazine derivatives

○Moka Tabata[1], Yuto Suzuki[2], Ryusei Oketani[2], Ichiro Hisaki[2] (1. School of Engineering Science, Osaka University, 2. Graduate School of Engineering Science, Osaka University)

Japanese

[P2-3am-25]

Crystal Structures and Fluorescence Properties of Methyl-substituted Organoboron Complexes

○Fuko Matsumoto[1], Takuya Ogaki[1], Shiori Miyazaki[2], Kiyoshi Miyata[2], Ken Onda[2], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ., 2. Kyushu Univ.)

Japanese

[P2-3am-26]

Cocrystallization of hinokitiol with hydroquinone and its physical properties

Kanji Takeuchi[1], Kyoka Taketazu[1], Junki Tomita[2], Yutaka Inoue[3], ○Mitsuaki Suzuki[1] (1. Faculty of Science, Josai University, 2. Instrumental Analysis Center, Josai University, 3. Faculty of Pharmacy and Pharmaceutical Sciences, Josai University)

Japanese

[P2-3am-27]

Synthesis, crystal structure and luminescence behavior of chrysene derivatives with butadiyne

○Ryoya Kamiyama[1], Ryusei Oketani[1], Ichiro Hisaki[1] (1. The Univ. of Osaka)

Japanese

[P2-3am-28]

Carboxylic acid recognition of a diamidine having a tetraarylethylene unit with an extended π-conjugation

○Suzu Uetani[1], Akane NAKAJIMA[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

[P2-3am-29]

Carboxylic Acid Recognition of a Diamidine Having a Tetraphenylethylene Unit

○Ryo Watanabe[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

[P2-3am-30]

Synthesis of water-soluble cyclophanes having multiple cationic side chains and a pyrene moiety

○Haruna Okuma[1], Takaaki Miyazaki[1], Osamu Hayashida[1] (1. Fukuoka University)

Japanese

[P2-3am-31]

Synthetic Study of Amide Cyclodextrin Oligomers Utilizing Imine Bonds

○Tomoya Endo[1], Takashi Nakamura[1] (1. Univ. of Tsukuba)

Japanese

[P2-3am-32]

Synthesis and STM Observation of Dissymmetric Star-shaped Molecules

○Sota Seki[1], Gwenael Rapenne[1,4], Shigeki Kawai[2], Kenichiro Omoto[3] (1. Nara Institute of Science and Technology, 2. National Institute for Materials Science, 3. Nagasaki University, 4.

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University of Toulouse)

Japanese

[P2-3am-33]

Self-Assembled Structures Formed by Triphenylene Derivatives with the Different Substitution Patterns of Alkoxy and Hydroxy Groups at the Liquid/Solid Interfaces.

○Wangjie Pan[1], Matsuhiro Maeda[1], Kazukuni Tahara[2] (1. Graduate School of Science and Technology, Meiji University , 2. School of Science and Technology, Meiji University)

Japanese

[P2-3am-34]

Preparation and applications of supramolecular structures from dimethylated α-cyclodextrin

○Momoka Miyasaka[1], Haruya Isida[1], Hajime Shigemitsu[1], Toshiyuki Kida[1] (1. Osaka University)

Japanese

[P2-3am-35]

Stimuli-responsive solid-state chlorophyll derivatives possessing esterified alkyl chains at the 3- and 17-positions

○Koki Yamada[1], Tomohiro Miyatake[1] (1. Faculty of Advanced Science and Technology, Ryukoku Univ.)

Japanese

[P2-3am-36]

Coordination Self-Assembly of Triarylmethanes Modified with Their Arm Moieties

○Masaya Kobayashi[1], Yosuke Nakamura[1], Domoto Yuya[1] (1. Gunma Univ.)

Japanese

[P2-3am-37]

Steric Control over Self-Assembly of Highly Entangled Polyhedral Complexes via Acetylene Coordination

○Ren Nakabayashi[1], Yosuke Nakamura[1], Yuya Domoto[1] (1. The Univ. of Gunma)

Japanese

[P2-3am-38]

Synthesis and Properties of a Rotaxane Composed of a Redox-responsive Macrocyclic Crown Ether and a Diammonium Cation

Kabeya Natsuki[1], ○Akira Ohta[1] (1. Shinshu Univ.)

Japanese

[P2-3am-39]

Development and functions of supramolecular photocatalyst formed by self-assembly of stable carbocation molecules

○Yuya Imuro[1], Hajime Shigemitsu[1], Sakura Yamamoto[1], Toshiyuki Kida[1] (1. Osaka University)

Japanese

[P2-3am-40]

Mechanochromic Luminescence Properties of Benzothienylbenzothiadiazole Derivatives

○Haruto Furukawa[1], Suguru Ito[1,2] (1. Yokohama Natl. Univ., 2. PRESTO, JST)

Japanese

[P2-3am-41]

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Crystal Structure and Luminescence Properties of Perylene-Substituted Binaphthol Derivatives

○Riko Yano[1], Suguru Ito[1,2] (1. Yokohama Natl. Univ., 2. PRESTO, JST)

Japanese

[P2-3am-42]

Circularly polarized electroluminescence (CPEL) from phthalocyanine and porphyrin luminescent materials

Seika Suzuki[1], Yuta Yamamoto[1], Shikura Ryuta[2], Satoko Suzuki[3], Shigeyuki Yagi[2], ○Yoshitane Imai[1] (1. Kindai University, 2. Osaka metropolitan University, 3. JASCO)

Japanese

[P2-3am-43]

Synthesis and Photophysical Properties of Diarylethene containing Thienothiophene Rings with Extended π-Conjugation.

○Manami Furusen[1], Hibiki Naneko[1], Ryo Nishimura[1], Masakazu Morimoto[1] (1. Rikkyo university)

Japanese

[P2-3am-44]

Synthetic Study of a Cage-Type Molecule Undergoing Fluid Bond Shifting

○Hiromichi Yokoyama[1], Reo Kayama[1], Atsuko Kosaka[1], Yoshiaki Shoji[1], Takanori Fukushima[1] (1. CLS, Tokyo Tech.)

Japanese

[P2-3am-45]

stimuli responsive properties of rotaxane-based supramolecular mechanophores having a long rod molecule

○Riku Yamamoto[1], Yoshimitsu Sagara[1] (1. Tokyo institute of technology)

Japanese

[P2-3am-46]

Mechanism of Photo-Induced Crawling Motion of Azobenzene Crystals

○Makoto Saikawa[1,2], Keegan McGehee[1,2], Kengo Manabe[2], Koichiro Saito[2], Yoshihiro Kikkawa[2], Yasuo Norikane[2,1] (1. Univ. of Tsukuba, 2. AIST)

Japanese

[P2-3am-47]

Acridine-based 1D double-wall nanotubes as a scaffold for solid-state electron transfer

○Hiroyuki Kishi[1], Daiji Ogata[1], Junpei Yuasa[1] (1. Tokyo University of Science)

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フォトクロミックジアリールエテン薄膜の球晶における中空ロッド結晶の生成機構の解明

（阪公大院工[1]・阪市大院工[2]）○磯辺 茉実[1]・北川 大地[1,2]・小畠 誠也[1,2]
Elucidation of a Formation Mechanism of Hollow Structures on Spherulites in Photochromic Diarylethene Thin Films ([1]*Graduate School of Engineering, Osaka Metropolitan University*, [2]*Graduate School of Engineering, Osaka City University*) ○Mami Isobe,[1] Daichi Kitagawa,[1,2] Seiya Kobatake[1,2]

The hollow rod crystal of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**)[1,2] and 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**2a**) can be generated by the sublimation on the glass substrates. In this work, we focused on spherulites formed in the polycrystalline thin films of **1a** and **2a** with the different surface morphology on sapphire substrates washed with concentrated sulfuric acid. In addition, the effect of the weight ratio of **1a** and **2a** in their mixed powder crystals on the growth of spherulites in the sublimation process was investigated. As the result, it was indicated that hollow structures formed on these spherulites were influenced by the weight ratio of the mixed powder crystals.
Keywords : Diarylethene; Vapor Phase Crystal Growth; Hollow Rod Crystal; Thin Film

1a および **2a** の粉末結晶をそれぞれ加熱し昇華すると、濃硫酸洗浄後のガラス基板上において中空ロッド結晶を生成する。濃硫酸洗浄後のサファイア基板を用いると、それぞれの昇華過程で生成する薄膜においてより鮮明な球晶の表面形態が観測され、**1a** および **2a** は異なる球晶構造を形成することがわかった。そこで、**1a** と **2a** の粉末結晶の重量比を変えて混合し、昇華した場合に生成する球晶の表面形態の分類をおこない、**1a** と **2a** の混合比率が球晶成長へ及ぼす影響、またそれらの上に生成する中空構造の生成機構について検討した。

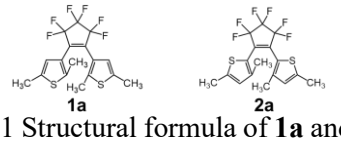

Fig. 1 Structural formula of **1a** and **2a**.

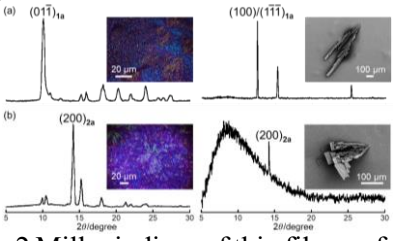

Fig. 2 Miller indices of thin film surfaces and side faces of hollow crystals prepared by sublimation at **1a**/**2a** of (a) 7.0 and (b) 0.14. POM and SEM images represent surface morphology of spherulites and crystal morphology of hollow crystals, respectively.

まず、濃硫酸で洗浄後、真空乾燥したサファイア基板を氷冷し、3 mg の **1a**、**2a** の粉末結晶および **1a** と **2a** の異なる重量比（**1a**/**2a**: 7.0, 0.14）の混合粉末結晶を、それぞれ 95℃に加熱し 2 時間昇華をおこなった。図 2 のように、薄膜表面とロッド結晶の形態を偏光顕微鏡（POM）、走査型電子顕微鏡（SEM）で観察し、X 線回折測定により指数付けをした。**1a** の粉末結晶および **1a**/**2a** が 7.0 の混合粉末結晶を用いた場合、薄膜表面から(01$\bar{1}$)$_{1a}$、ロッド結晶側面から(100)/(1$\bar{1}\bar{1}$)$_{1a}$ の回折ピークが検出され、薄膜中に非バンド球晶模様が見られた一方、**2a** の粉末結晶および **1a**/**2a** が 0.14 の混合粉末結晶を用いた場合、薄膜表面とロッド結晶側面の両方から(200)$_{2a}$ の回折ピークが検出され、薄膜中にバンド球晶模様が表れた。即ち、高い **1a**/**2a** 比率で昇華されると、放射状に広がる繊維状組織の薄膜表面から垂直下方に(01$\bar{1}$)$_{1a}$ 面を断面、(100)/(1$\bar{1}\bar{1}$)$_{1a}$ 面を側面にもつ細長い中空ロッド結晶が成長するが、低い **1a**/**2a** 比率で昇華されると、ラメラの捻れを伴いながら薄膜が形成され、その表面から斜め下方に(200)$_{2a}$ 面を側面にもつ扁平な中空ロッド結晶が生じることが明らかとなった。

1) M. Isobe, D. Kitagawa, S. Kobatake, *Cryst. Growth Des.* **2022**, *22,* 5489. 2) M. Isobe, D. Kitagawa, S. Kobatake, *ChemPlusChem,* **2023**, *88,* e2023004.

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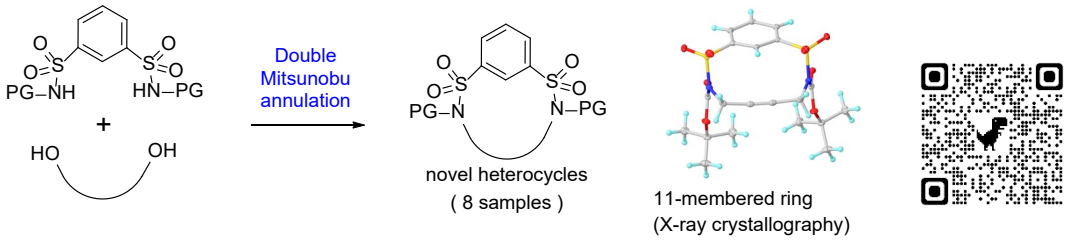
ダブル光延環化反応を用いたベンゼン-1,3-ジスルホンアミドを含有する複素環の構築と構造解析

（北海道科学大薬[1]・CRILS[2]）○金田 京介[1,2]・小出谷 貴登[1]・戸島 竜二[1]・今野 良季[1]・山岸 丈洋[1,2]

Construction and Structural Analysis of Heterocycles Containing Benzene-1,3-disulfonamide Using Double Mitsunobu Annulation ([1]*Department of Medicinal Chemistry, Hokkaido University of Science,* [2]*Creation Research of Life Science in KITA-no-DAICHI, Hokkaido University of Science*) ○Kyosuke Kaneda,[1,2] Takato Koideya,[1] Ryuji Toshima,[1] Yoshiki Konno,[1] and Takehiro Yamagishi[1,2]

The sulfonamide structure is a group contained in pharmaceuticals such as sulfa drugs and is very important in terms of medicinal chemical function due to its pharmacological activity expression mechanism. Here, we synthesized a new 11- to 13-membered heterocyclic compound containing benzene-1,3-disulfonamide using a double Mitsunobu annulation reaction. Comparing parameters in several crystal structures, it was found that there is a margin in the distance between the two nitrogen atoms in the ring and the bond angle of the sulfonamide moiety. These findings expand the possibilities of sulfonamide structures in medicinal chemistry. We hope that this will be useful for molecular design in drug discovery.
Keywords : Sulfonamide; Mitsunobu Reaction; Crystal Structure Analysis; Heterocycles

スルホンアミド構造はサルファ剤等の医薬品に含まれる官能基で、その薬理活性発現機構から医薬化学的に大変興味深い。我々はスルホンアミドの有機化学的反応性やその結晶立体配座の特性について言及している。今回、ベンゼン-1,3-ジスルホンアミドを含有する新規な 11 員環から 13 員環の複素環化合物を、ダブル光延環化反応を利用して合成した。更に、得られた化合物を結晶化し、単結晶 X 線結晶構造解析によって構造の特性を調査した。いくつかの結晶構造にあるパラメータを比較すると、環内にある 2 つの窒素原子間の距離やスルホンアミド部位の結合角度に差異が見られ、スルホンアミド構造の柔軟性や多様性が示唆された。これらの知見は、医薬化学におけるスルホンアミド構造の可能性を拡げるもので、創薬における分子設計に役立つことを期待する [1]。



1) Synthesis and Structural Characterization of Benzene-1,3-disulfonamide-containing 11- to 13-membered Heterocycles via Double Mitsunobu Annulation, K. Kaneda, T. Koideya, R. Toshima, Y. Konno, T. Yamagishi, *Chemistry Letters*, **2023**, upad 016, https://doi.org/10.1093/chemle/upad016

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接近した３つの *N*,*N*,*O* 三座キレート配位部位をもつ大環状配位子 trispap の合成

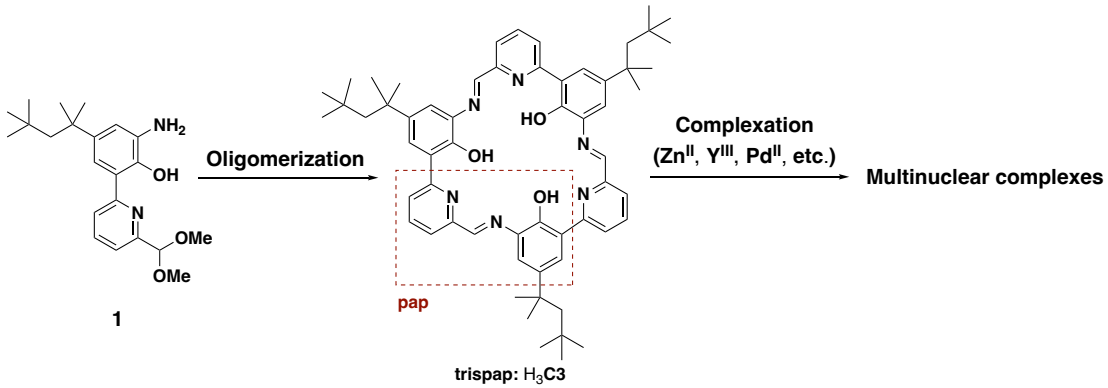
（筑波大院数理物質[1]・キーウ大[2]・筑波大数理物質[3]）○趙 佳晨[1]・Nadiia Varzhel[2]・岩本 優也[1]・中村 貴志[3]

Synthesis of Trispap, A Macrocyclic Ligand with Three *N*,*N*,*O* Tridentate Chelating Units in Close Proximity ([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, [2]*Taras Shevchenko National University of Kyiv*, [3]*Institute of Pure and Applied Sciences, University of Tsukuba*) ○ Jia Chen Zhao,[1] Nadiia Varzhel,[2] Yuya Hokimoto,[1] Takashi Nakamura[3]

Macrocyclic complexes whose coordination sites of multiple metals are in proximity are expected to exhibit characteristic molecular recognition and catalytic properties. Here we synthesized trispap H_3**C3**, a cyclic trimer in which *N*,*N*,*O* tridentate chelating units pap are arranged close together, by the oligomerization of the bifunctional monomer **1** with an *o*-aminophenol moiety and a 2-pyridyl moiety with an acetal-protected formyl group at 6 position. Complexation of this macrocyclic ligand with metals such as Zn^{II}, Y^{III}, and Pd^{II} resulted in the formation of interesting multinuclear complexes that reflect the coordination numbers and geometry structures of each metal.

Keywords : Supramolecular Chemistry; Oligomers; Macrocycles; Imine Bonds; Multinuclear Complexes

複数の金属の配位サイトが接近した大環状錯体は、特徴的な分子認識能や触媒能を発揮すると期待される。我々は、6位にアセタール保護されたホルミル基をもつ2-ピリジル部位と*o*-アミノフェノール部位とをもつ両官能性単量体 **1** の多量化反応により、*N*,*N*,*O*三座キレート配位部位であるpapが3つ接近して配置された環状3量体trispap H_3**C3**を合成した。この大環状配位子をZn^{II}, Y^{III}, Pd^{II}などの金属と錯形成したところ、それぞれの金属の配位数と幾何構造を反映した興味深い多核錯体を形成することが明らかになった。



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フタロシアニンからなる導電性弾性結晶の構築

（奈良女大理 [1]）○渡邉 千遥 [1]・堀井 洋司 [1]・梶原 孝志 [1]

Electroconductive elastic crystal based on phthalocyanine

([1]Nara Women's University) ○Chiharu Watanabe,[1] Yoji Horii,[1] Takashi Kajiwara[1]

Elastic crystals that show reversible bending have attracted a great attention due to application possibility for functional materials that are responsive to external force.[1)] Especially, electroconductive elastic crystals can be applied to highly sensitive mechanical sensors due to their ability to change conductivity in response to external forces.[2)] Recently, we have reported the elastic crystals that consist of porphyrin involving long alkyl chains. Single-crystal X-ray diffraction analysis revealed that thermal motion of the alkyl chains contributes to the elastic behavior.

In this study, we succeeded in constructing electroconductive elastic crystals by iodine oxidation of alkoxy substituted phthalocyanine, that is beneficial to construct a π-stacked column structure due to high planarity. The crystals ware reversibly bended and exhibited semiconducting properties with an activation energy of 0.033 eV.

Keywords : elastic crystal, conductivity

近年結晶でありながら可逆的な屈曲と伸展を示す弾性結晶が注目を集めており、弾性と他の物性を複合化した例も報告されている [1)]。特に電気伝導性と弾性を複合化した導電性弾性結晶は、外力に応じて導電性が変化するため高感度な力学センサーなどへの応用が期待される [2)]。我々は最近、アルキル鎖を導入したポルフィリンによる弾性結晶の構築に成功した。アルキル鎖の熱運動によって弾性が生じることが単結晶 X 線構造解析より示唆されており、柔軟な置換基の導入が弾性結晶の形成に有効であることが示唆された。ポルフィリンに比べて平面性の高いフタロシアニンを弾性結晶の構成要素として用いることができれば、分子間の π-π スタックによって 1 次元カラム構造を構築することができ、導電性弾性結晶の構築に有利である。

本研究では、ブトキシ基を導入したフタロシアニンをヨウ素酸化することで、弾性と電気伝導性を複合化した導電性弾性結晶 **1** の構築に成功した (図 1)。この結晶は可逆的な屈曲と伸展を示し、電気伝導度測定から活性化エネルギー 0.033 eV の半導体的性質を示すことが明らかになった (図 2)。

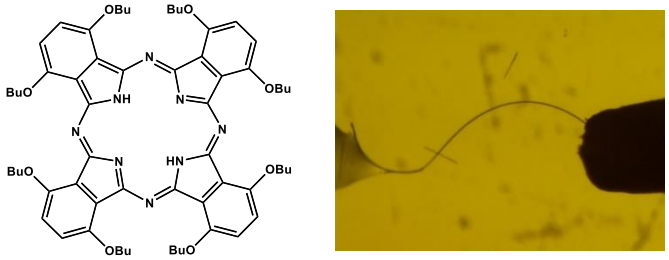

図 1 アルキル鎖を導入したフタロシアニンと結晶の屈曲の様子

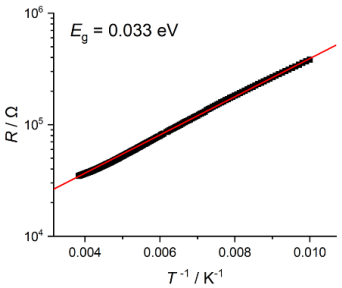

図 2 **1** における電気伝導性

1) S. Ghosh *et al*., *Cryst. Growth Des.* **2021**, *21*, 2566-2580
2) T. Kwon *et al*., *Angew. Chem. Int. Ed.* **2020**, *59*, 16436-16439

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アントラセン骨格を有するボロン酸誘導体のメカノクロミズム特性

（京工繊大・工芸）○片岡 捺貴・西村 愛翔・楠川 隆博

Mechanofluorochromic properties of boronic acid derivatives having anthracene unit (Kyoto Institute of Technology) Natsuki Kataoka, Manato Nishimura, Takahiro Kusukawa

Mechanofluorochromism, which is emission color change phenomenon under mechanical stimulation, has attracted much attentions. In this study, we observed the mechano-fluorochromic properties of boronic acid derivatives having an anthracene unit. In the case of derivative **1**, light-blue emission turned to the blue-green emission (λ_{max} = 489 nm) after grinding. These phenomena indicate the formation of excimer emission due to the formation of π–π stacking of **1** after grinding.

Keywords: Anthracene; Fluorescence; Mechanochromism

近年、機械的刺激によって蛍光発光色が変化する、メカノクロミズムが注目されている。当研究室では、単純な構造の 1,8-ジフェニルアントラセン誘導体をすりつぶすことで、発光色が青色から緑色に変化することを明らかにしている [1)]。このメカノクロミズムは、CN 基が置換した場合に顕著に観測されるため、水素結合(Ar-CN•••H-Ar)の関与が重要であると考えられる。

本研究では、メカノクロミズム特性への水素結合の関与を調査するために、水素結合を形成するボロン酸をアントラセン骨格の 2 位と 9 位に置換したアントラセン誘導体のメカノクロミズム特性について調査した。誘導体 **1**, **2** ともに固体状態で水色の発光を示し、すりつぶし後には発光色が青緑色へと変化するメカノクロミズムを示すことを見出した (Figure 1)。さらに、**1** のすりつぶし後には、蛍光寿命が長くなり、蛍光量子収率が向上した(Figure 1)。これらの発光色変化は、アントラセン環のモノマー発光から、アントラセン環同士のπ–πスタッキングによるエキシマー発光へと変化したことに由来すると考えられる。発表では誘導体 **1** の単結晶構造解析の結果を含めて議論する予定である。

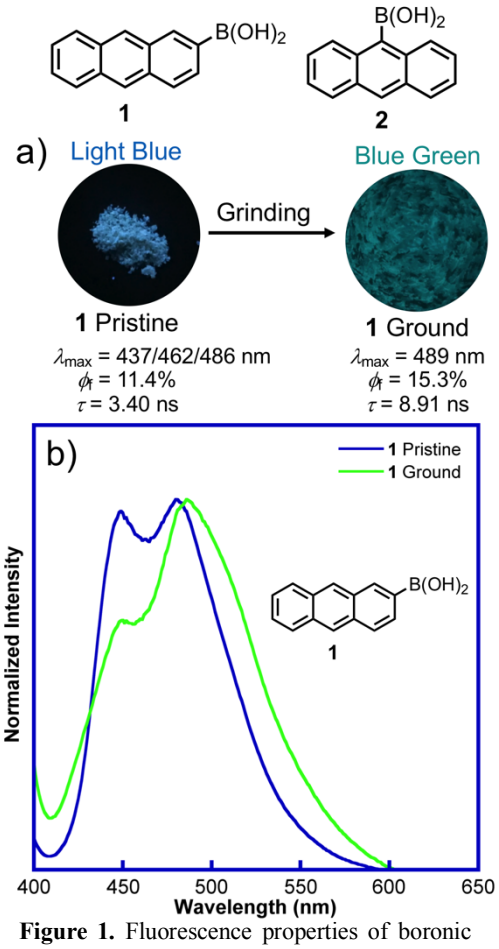

Figure 1. Fluorescence properties of boronic acid **1** before and after grinding, a) fluorescence images and photophysical properties, b) fluorescence spectra (λ_{ex}=365 nm).

1) T. Kusukawa *et al.*, *Chem. Lett.* **2019**, *48*, 1213.

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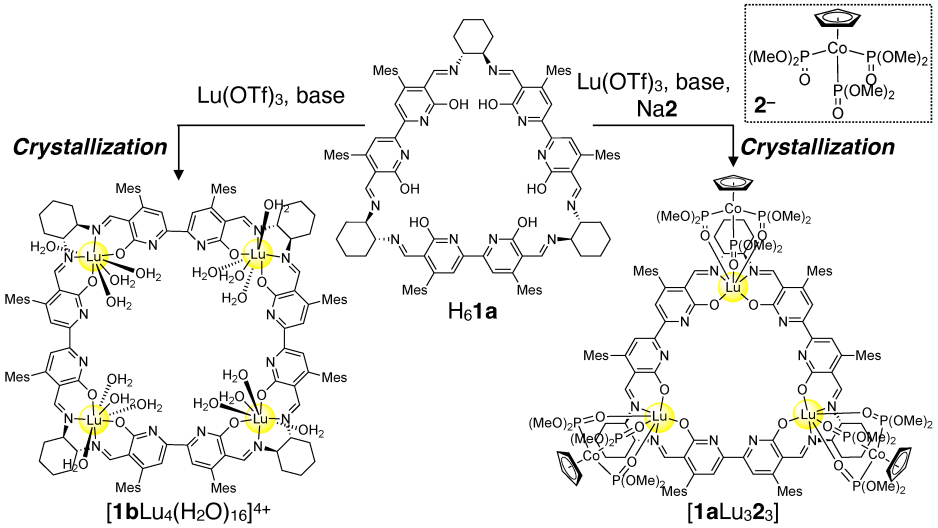
サレン大環状配位子の構造変化を伴うランタノイド多核錯体の合成

（筑波大院数理物質[1]・リンカーン大[2]・筑波大数理物質[3]）○劉 譯夫[1]・Guzman Gil-Ramirez[2]・中村 貴志[3]

Synthesis of Multinuclear Lanthanoid Complexes with Structural Changes in Salen Macrocyclic Ligand ([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, [2]*School of Chemistry, University of Lincoln*, [3]*Institute of Pure and Applied Sciences, University of Tsukuba*) ○Yi-Fu Liu,[1] Guzman Gil-Ramirez,[2] Takashi Nakamura[3]

Lanthanoid complexes take high coordination number with 7 and more, thus are used to form unique multinuclear complex structures. Although the coordination structure of lanthanoids is flexible, control of the coordination environment with appropriate ligands allows the regulation of overall structural frameworks. In this study, we have found that the complexation of $Lu(OTf)_3$ and bpytrisalen[1] H_6**1a**, a triangular macrocycle composed of reversible imine bonds, followed by crystallization, yielded a cyclic tetramer of Lu-salen accompanied by a structural change in the macrocyclic ligand. Furthermore, crystallization with a tripodal chelating ligand, the Kläui ligand[2] Na**2**, gave a cyclic trimer of Lu-salen coordinated by **2**$^-$, thus resulting in the formation of different oligomers depending on the presence and absence of the capping ligand.
Keywords : Supramolecular Chemistry, Oligomer, Macrocycle, Lanthanoid, Salen

ランタノイド錯体は 7 配位以上の高配位数をとることから、ユニークな多核錯体構造の形成に利用される。また、ランタノイドの配位構造は柔軟であるが、適切な配位子によって配位環境を制御することで、錯体全体の構造制御が可能となる。今回我々は、可逆なイミン結合でつくられた三角形大環状分子 bpytrisalen[1] H_6**1a** に対して、$Lu(OTf)_3$ を錯形成して結晶化すると、大環状配位子の構造変化を伴い、Lu-salen の環状 4 量体が得られることを見出した。また、3 脚型キレート配位子である Kläui 配位子[2] Na**2** とともに結晶化すると、**2**$^-$が Lu-salen に配位した環状 3 量体が得られ、キャッピング配位子の有無により環状多量体を作り分けることができた。



1) T. Nakamura, Y. Kawashima, E. Nishibori, T. Nabeshima, *Inorg. Chem.* **2019**, *58*, 7863–7872.
2) J.-L. Zhang et al. *Inorg. Chem.* **2019**, *58*, 1806–1814.

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発光性キラルビスオキサゾリン配位子の合成と特性評価

（東理大理）○島田 渓・湯浅 順平
Synthesis of a luminescent chiral bis(oxazoline) ligand
(*Fac. Sci., TUS*) ○Kei Shimada, Junpei Yuasa

Here, we demonstrated a chiral ligand with photoluminescent properties. The newly synthesized ligand was capable of dissolving in various organic solvents and exhibited strong emission under UV light irradiation. The observed emission maxima shifted depending on the solvent polarity, indicating the charge-transfer emission.
Keywords : chiral ligand; bis(oxazoline); Pybox; luminescence; solvatochromism

ビス(オキサゾリニル)ピリジン(Pybox)配位子は、不斉触媒反応に用いられる汎用的な不斉配位子の一つであり、多くの不斉触媒反応において高いエナンチオ選択性を示す。一方で、Pybox は熱的な基底状態での反応に利用が限定されており、光反応としての応用はほとんど知られていない。これは、Pybox がピリジン環と２つのオキサゾリン環の窒素原子の非共有電子対の影響から発光性を示さないことが要因として考えられる。Pybox に対して発光性を付与することができれば、その励起状態を利用した新たな光不斉触媒反応への応用展開が期待される。

本研究では、Pybox に発光性を付与した新規キラル配位子、Pybox 誘導体(L)を合成し、その発光特性について検討をおこなった。

合成した Pybox 誘導体(L)は ^{1}H NMR および精密質量分析から生成を確認した。Pybox 誘導体(L)は、ヘキサン、クロロホルム等の有機溶媒に対して高い溶解性を示した。また、Pybox 誘導体(L)は紫外光照射下で強い発光を示した。そこで、異なる誘電率をもつ溶媒中に Pybox 誘導体(L)を溶解させ発光スペクトルを測定した。観測された Pybox 誘導体(L)の発光極大は溶媒極性の増大とともに連続的に長波長へとシフトした。このことから、Pybox 誘導体(L)の発光が電荷移動発光に由来することが示唆された。

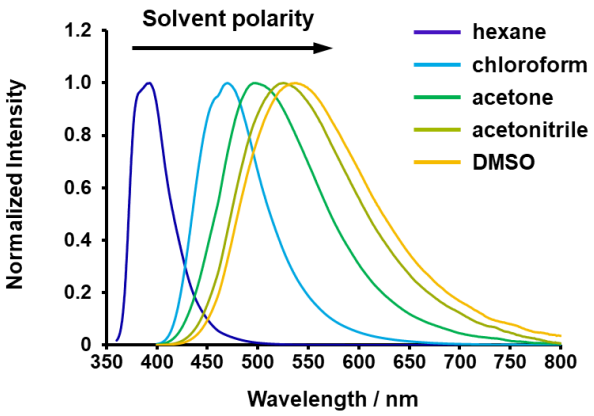

Figure 1. Normalized emission spectra of L (5.0×10^{-5} M) in different solvents (hexane: λ_{ex} = 352.8 nm, chloroform: λ_{ex} = 377.2 nm, acetone: λ_{ex} = 366.8 nm, acetonitrile: λ_{ex} = 370.0 nm, DMSO: λ_{ex} = 377.2 nm).

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ドロップキャスト法を用いた銀色光沢効果を有する微結晶膜の作製を可能とするピレン誘導体の分子設計

(龍谷大先端理工[1]・滋賀医大分子研[2]・立教大院理[3]・東薬大薬[4]・熊本大院先導機構[5]) ○前田 龍治[1]・中川 優磨[2]・西村 涼[3]・森本 正和[3]・横島 智[4]・中村 振一郎[5]・内田 欣吾[1]

Molecular design of pyrene derivatives to make microcrystalline films with silver luster effect using drop-casting method ([1]*Fac. Sci. Tech., Ryukoku Univ.*, [2]*Mol. Eng. Inst., SUMS*, [3]*Coll. Sci., Rikkyo Univ.* [4]*Sch. Pharm., TUPLS*, [5]*POIE, Kumamoto Univ.*) ○Tatsuya Maeda,[1] Yuma Nakagawa,[2] Ryo Nishimura,[3] Masakazu Morimoto,[3] Satoshi Yokojima,[4] Shinichiro Nakamura,[5] Kingo Uchida[1]

The development of metallic-appearing luster materials using metal-free organic compounds is an important issue from the viewpoint of environmental pollution. We present here a silver luster microcrystalline film based on pyrene derivative (**2**) having *tert*-butyl group. This luster film was easily fabricated on a glass substrate by drop-casting an *n*-hexane solution of the compound. The film was formed by the stacking of very thin, flat, and small platelet-shaped crystals. The luster effect of crystal films was evaluated by focusing on their molecular structure and on the associated molecular packing in the crystalline state as well as their crystal shape.

Keywords : Silver luster; Pyrene; Drop-casting method; Crystal; tert-Butyl group

金属を含まない有機化合物を用いた金属調光沢材料の開発は、環境汚染の観点から重要な課題となっている。本研究では、*tert*-ブチル基をもつピレン誘導体 **2** を用いた銀色光沢を示す微結晶膜を報告する (Fig. 1)。この光沢膜は、化合物の *n*-ヘキサン溶液をガラス基板にドロップキャストすることで容易に作製でき、非常に薄く、平らで、小さな板状の結晶の積み重ねによって形成されていた。結晶膜の光沢効果について、その分子構造と結晶状態での分子パッキング、及び結晶形状に焦点を当てることによって評価した。

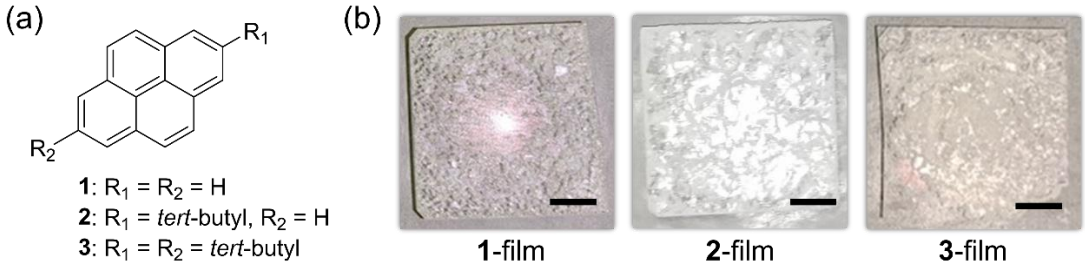

Figure 1. (a) Molecular structures of pyrene derivatives. (b) Photographs of crystal films of **1**, **2**, and **3**.

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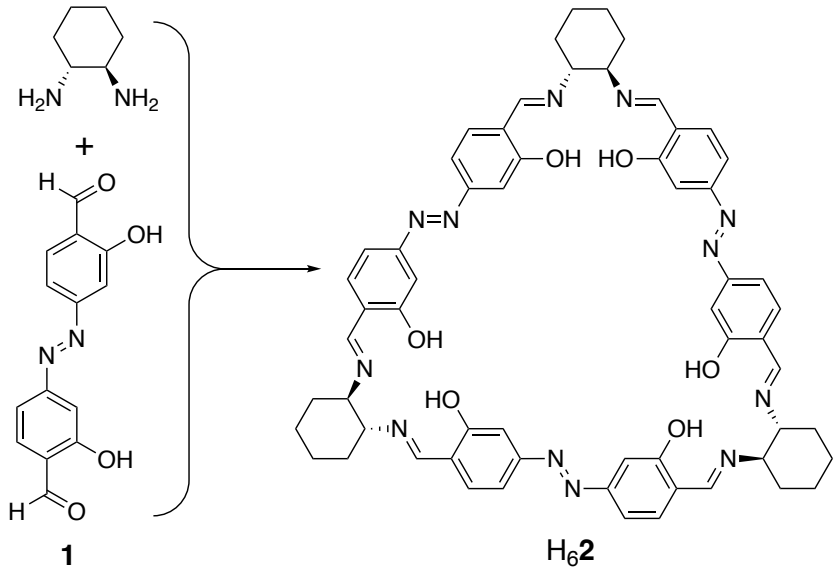
Synthesis of Azobenzene-Containing Salen-Based Macrocycle

([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, [2]*School of Pharmaceutical Sciences, University of Shizuoka*, [3]*Institute of Pure and Applied Sciences, University of Tsukuba*) ○Mads Nybo Sørensen,[1] Masaru Kondo,[2] Takashi Nakamura[3]
Keywords: Salen; Macrocycle; Azobenzene; Responsive Materials; Supramolecule

Macrocyclic receptors are capable of strongly binding guests, but for some applications such as sensors and catalysts, it is desirable for the binding to be reversible. The binding can often be reversed through heating, adding competing ligands, or changing solvents. These methods are not always repetitive or practical, so we set out to design a receptor that could bind guests with binding affinities that can be regulated with irradiation of light.

It is known that the reaction of a diamine and a bis-salicylaldehyde linker with its formyl group in the 180° position yields a triangular cyclic trimer with salen units at its vertexes.[1] Salen complexes can act as recognition sites that can bind guests through coordination in the axial site.[2] As a light-responsive unit, we chose azobenzene[3] that provides the ability to switch its backbone based on photoisomerization. In this work, a new azobenzene derivative **1**, whose two salicylaldehyde units are directly connected by the azo group, was designed and synthesized. The azobenzene bis-salicylaldehyde **1** was reacted with (1*R*,2*R*)-cyclohexanediamine to form azobenzene-containing salen-based macrocycle H_6**2**. Characterization of H_6**2**, macrocyclization trials with different diamines, metal complexation, and the photochemical properties including photoisomerization will be discussed in the presentation.



1) S. Akine, T. Taniguchi, T. Nabeshima, *Tetrahedron Lett.* **2001**, *42*, 8861. 2) T. Nakamura, Y. Kawashima, E. Nishibori, T. Nabeshima, *Inorg. Chem.* **2019**, *58*, 7863. 3) J. Vapaavuori, C. G. Bazuin, A. Priimagi, *J. Mater. Chem. C* **2018**, *6*, 2168.

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8 位にエーテル結合を有するキノフタロン化合物の結晶構造

（千葉大工[1]・千葉大院工[2]・トーヨーカラー株式会社[3]）○中村 建斗[1]・長谷川 怜勇[2]・赤染 元浩[2]・伊藤 理人[3]・三上 譲司[3]・矢内 宏幸[3]・松本 祥治[2]
Crystal Structures of Quinophthalone Compounds with an Ether Bond at 8 Position ([1]*Faculty of Engineering, Chiba University*, [2]*Graduate School of Engineering, Chiba University*, [3]*TOYOCOLOR CO., LTD.*) ○Kento Nakamura,[1] Reo Hasegawa,[2] Motohiro Akazome,[2] Rihito Ito,[3] Joji Mikami,[3] Hiroyuki Yanai,[3] Shoji Matsumoto[2]

Quinophthalone compounds have long played an important role as dyes and pigments because of their bright yellow color. However, the reports about their crystal structures are very rare.[1~3] In this study, we report the crystal structures of quinophthalone compounds with an ether bond at 8 position. All quinophthalone moiety showed NH-type tautomer and we found to be highly planer structurer with NH···O intramolecular hydorogen bonds. π-Stack was also found in all crystal structures. But the stacking mode were different from the parallel (**1b**) and the anti-parallel (**1a**, **1c** and **1d**) motifs. In addition, we found that the distance between the π-stacks was shortest in **1a**.
Keywords : Quinophthalone; Ether Bond; Crystal Structure; Tautomerism; π-Stack Structure

キノフタロン化合物は鮮明な黄色を呈するため古くから染料や顔料として重要な役割を担っており，今まで数多くの類似化合物が合成されてきた。しかし，その結晶構造に関する報告はほとんどされていない[1~3]。本研究では，8 位にエーテル結合を持つキノフタロン化合物(**1a~1d**)の結晶構造を明らかにした。**1a~1d** はいずれも NH 型の互変異性体であり，インダンジオン部位やエーテルとの NH···O 分子内水素結合を形成し，高い平面性を有していることが明らかとなった。さらに，いずれの結晶構造でも，キノフタロン骨格は π-スタック構造を形成していたが，**1b** は順平行，その他の **1a**, **1c**, **1d** は逆平行といった違いが見られた。また，π-スタック間の距離は **1a** が最も短くなっていた。

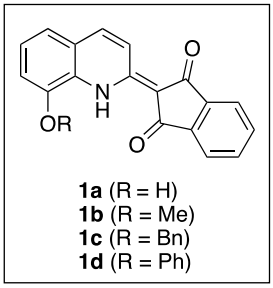

Table 1. The difference of π -stack

compound	stacking mode	π-stack distance [Å]
1a	anti-parallel	3.217, 3.363
1b	parallel	3.380
1c	anti-parallel	3.350, 3.371, 3.388
1d	anti-parallel	3.368, 3.409

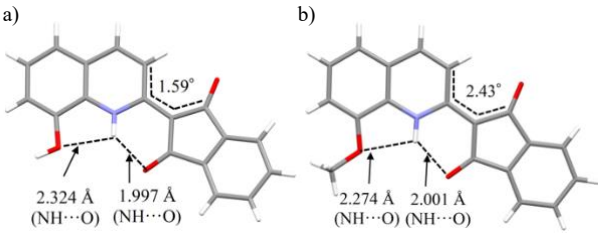

Figure 1. Single crystal structures of a) **1a** and b) **1b**.

1) I. Fujii, T. Kodama, N. Yanagihara, N. Hirayama, *Anal. Sci.* **2004**, *20*, x35.
2) S. D. Gumbert, M. Körbitzer, E. Alig, M. U. Schmidt, M. R. Chierotti, R. Gobetto, X. Li, J. van de Streek, *Dyes Pigm.* **2016**, *131*, 364.
3) B. Ding, Y. Jiang, Y. Zhang, R. Ye, J. Sun, C. Yan, *Chinese J. Org. Chem*. **2020**, *40*, 1003.

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周囲に親水性基を有する Ni ポルフィリンービピリジン直交型環状化合物の合成と溶液中でのコンフォメーション変化

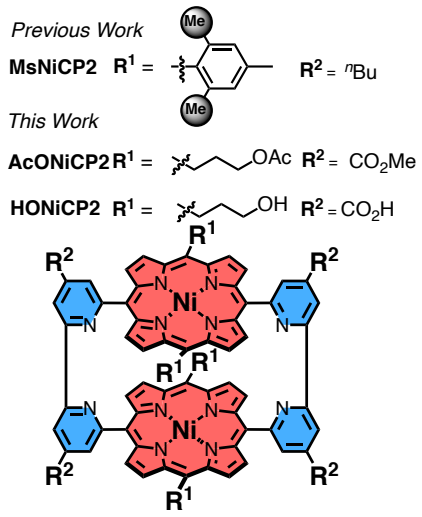
（東理大院理 [1]）○鈴木 健太 [1]・倉持 悠輔 [1]・佐竹彰治 [1]
Synthesis of Cyclic Composites of Nickel Porphyrins and Bipyridines having Hydrophlic Groups, and Their Conformational Changes in Solution ([1] *Graduate School of Science, Tokyo University of Science*)○Kenta Suzuki,[1] Yusuke Kuramochi,[1] Akiharu Satake[1]

We have previously reported that **MsNiCP2** with mesityl groups at the *meso* positions has a rigid structure due to the steric hindrance between the mesityl groups.[1)] Here, **AcONiCP2** having acetoxypropyl groups instead of mesityl groups at the *meso* positions was newly synthesized. A ^{1}H NMR spectrum of **AcONiCP2** was D_{2h} symmetry even at high concentrations in pyridine-d_5. In above 12 mM $CDCl_3$ solutions, however, ^{1}H NMR signals on the acetoxypropyl side chains were inequivalently observed, whereas D_{2h} symmetry in 3 mM $CDCl_3$ solution, suggesting formation of self-assembled **AcONiCP2** in the concentrated $CDCl_3$ solution. **AcONiCP2** was hydrolyzed with aqueous KOH to give **HONiCP2**. A UV-vis absorption spectrum of **HONiCP2** in 3M KOH solution showed characteristic split Soret band at 384 and 450 nm. The characteristic spectra were observed even in 7×10^{-6} ~ 8×10^{-7} M concentration, suggesting that **HONiCP2** were strongly interacted one another to give J-type supramolecular polymer in the KOH solution.

Keywords: nickel porphyrin, J-aggregate, self-organization, supramolecular polymer, solvent effect

これまでにメソ位にメシチル基を有する Ni ポルフィリン環状二量体 **MsNiCP2** を合成し、溶液中 ^{1}H NMR 測定および単結晶の X 線構造解析を行っている。[1)] その結果、**MsNiCP2** は対面するメシチル基同士の立体障害のためにポルフィリンとビピリジンを結ぶ炭素—炭素結合周りの回転が抑制されていることが分かった。本研究ではメソ位置換基に鎖状のアセトキシプロピル基を導入し、さらに周囲に親水性基を付与した **AcONiCP2** を新規に設計・合成した。この誘導体について、水を含む各種溶媒中における配座変化や自己集合形態を調査することを目的とした。

AcONiCP2 の ^{1}H NMR 測定において、pyridine-d_5 中では高濃度でも D_{2h} 対称性のスペクトルを示したが、$CDCl_3$ 中では 12 mM 以上ではアセトキシプロピル側鎖上の各信号が 4 種類非等価に観測された。一方 3 mM 以下では D_{2h} 対称性を示したことから、$CDCl_3$ 中高濃度では **AcONiCP2** が異方的に自己集合を起こしていると考えられる。次に、Ac 基とエステル基を KOH 中で加水分解した **HONiCP2** を合成し、3 M KOH 水溶液中で UV-vis 吸収スペクトルを測定したところ、単量体では 420 nm 付近に現れていたポルフィリンの Soret 帯が 384 nm と 450 nm に大きく分裂した。この特徴的なスペクトルは 7×10^{-6}～8×10^{-7} M の低濃度でも変化しなかったことから、水中で **HONiCP2** 同士が強く相互作用し、J-型の超分子ポリマーを形成していると考えられる。



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ハロサリチリデンアルキルアミン結晶の相転移とクロミズム特性の変化

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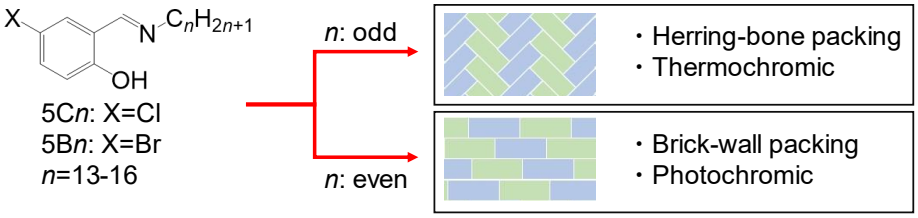
Phase transition and changes in chromism of halosalicylidene alkylamine crystals ([1]*Institute of Industrial Science, The University of Tokyo,* [2]*Environmental Science Center, The University of Tokyo*) ○Shunji Miyazato[1], Ryo Koibuchi[1], Isao Yoshikawa[1], Hirohiko Houjou[1,2]

Abstract: We have studied on *N*-(5-halosalicylidene) alkylamine (5X*n*), focusing on the relation between crystal structures and chromic properties depending on alkyl chain length *n*. In this study, using solid-state microspectroscopy, we investigate the changes in chromism and crystal structures of 5X*n* accompanied by the phase transition. Based on the analysis, the influence of solid-to-solid phase transition on the chromic properties is discussed.

Keywords: Schiff base, crystal engineering, UV-Vis absorption spectra, photo luminescence, polymorphism

1. 緒言 我々はこれまでに 5-ハロサリチリデンアルキルアミン (5X*n*, Fig. 1) が直鎖アルキル基の炭素数 (*n*) の違いにより異なるクロミズム特性(サーモクロミズム:TC, フォトクロミズム: PC)を示すことを見出し、結晶構造との関係に着目して研究を行ってきた[1)]。昨年の発表では、5B*n* (*n* = 6–12) の相転移に伴うクロミズム特性変化に規則性があることを報告した[2)]。本研究では、5X*n* (*n* = 13–16) の加熱・冷却により生じた結晶相のクロミズム特性を 5B*n* (*n* = 6–12) で得られた知見と比較し、解析することを試みた。

Fig. 1



2. 実験・結果・考察 5X*n* (*n* = 13–16) を合成し、結晶試料の相転移挙動を温度制御下での顕微鏡観察により調べた。相転移により生じた結晶相のクロミズム特性は、顕微 UV-Vis 吸収スペクトル測定により調べた。

5B*n* (*n* = 13–15) では温度変化の過程で TC 相と PC 相の両方が見られたが、5B16 では TC 相は見られなかった。また、5B13 と 5B15 では 5B11 までに見られた TC2 相は見られなかったことから、*n*≧13 では TC2 相は熱力学的安定相ではなくなることが示唆された。5B14 と 5B16 では既知の相と挙動が異なる PC 相が見られたため、それらを定量的に判別するために退色過程の減衰曲線を測定し、速度論解析[3)]を行った。PC 相の退色挙動については発表にて詳しく報告する。

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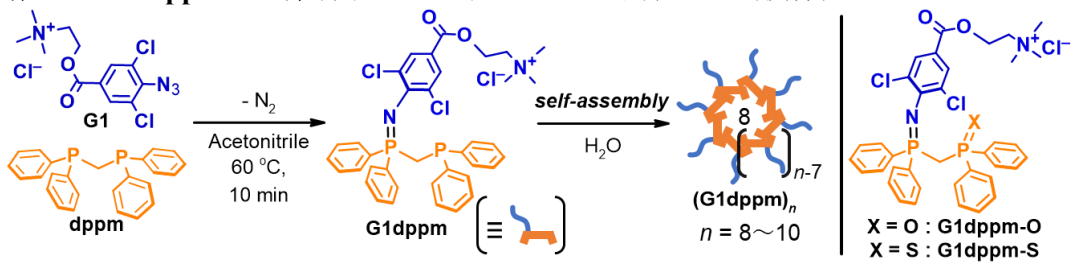
アザイリド形成によるホスフィン配位サイトを持つ両親媒性分子の合成と集合能評価

（東京高専[1]・東工大理[2]）○内藤 翔[1]・秋山 善守[2]・山科 雅裕[2]・豊田 真司[2]・井手 智仁[1]

Synthesis of Azaylide-based Amphiphile with a Phosphine Coordination Site and Evaluation of its Assembling Behavior ([1]*National Institute of Technology, Tokyo College*, [2]*School of Science, Tokyo Institute of Technology*) ○ Sho Naito,[1] Yoshimori Akiyama,[2] Masahiro Yamashina,[2] Shinji Toyota,[2] Tomohito Ide[1]

Amphiphilic phosphines are attractive molecules that possess the reactivities of phosphorus. However, their synthesis usually requires the use of highly reactive reagents.[1] We previously reported a facile synthetic method for amphiphiles by using azaylide (N=P bond) formation.[2] Herein, we successfully synthesized an amphiphile with a phosphine coordination site (**G1dppm**) by introducing hydrophilic azide (**G1**) into one of the phosphine moieties of bis(diphenylphosphino)methane (**dppm**). NMR and DLS measurements revealed that **G1dppm** formed spherical micelles with a diameter of ca. 2 nm in water, which corresponds to aggregates of 8–10 **G1dppm**. The critical micelle concentration of **G1dppm** was estimated to be ca. 0.45 mM by concentration-dependent ^{1}H NMR analysis. Furthermore, hydrophobic dyes (e.g., Nile Red) were encapsulated within the micelles in water. In addition, we will discuss the aggregation behavior and guest uptake capabilities of **G1dppm-O** and **G1dppm-S**.
Keyword: Amphiphile; Staudinger reaction; Bidentate Phosphine; Phosphine coordination site

ホスフィン配位サイトを有する両親媒性分子は，リンの反応性を備えた魅力的な分子であるが，その合成には高反応性試薬を必要とする[1]．近年我々は，アザイリド(N=P結合)形成を用いた簡便な両親媒性分子の合成法を報告した[2]．そこで本研究では，bis(diphenylphosphino)methane (**dppm**)の片側のリンにアザイリド形成を介して親水基(**G1**)を導入し，もう一方のホスフィン部位を残した両親媒性分子(**G1dppm**)を合成した．NMR と DLS 測定より，**G1dppm** は水中で直径約 2 nm の球状ミセルを形成することが判明した．その会合数は分子力場計算より 8–10 分子と見積もられた．濃度依存 ^{1}H NMR 測定より，**G1dppm** の臨界ミセル濃度は約 0.45 mM であることが分かった．また，**G1dppm** は水中で Nile Red などの疎水性色素分子を内包できることを明らかにした．本発表では **G1dppm** に加え，過酸化水素で酸化した **G1dppm-O** と S_8 で硫黄化した **G1dppm-S** の集合能と内包能についても合わせて議論する．



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O,*N*,*O* 型三座キレート配位部位を内孔に集積した大環状配位子 hexasap の合成

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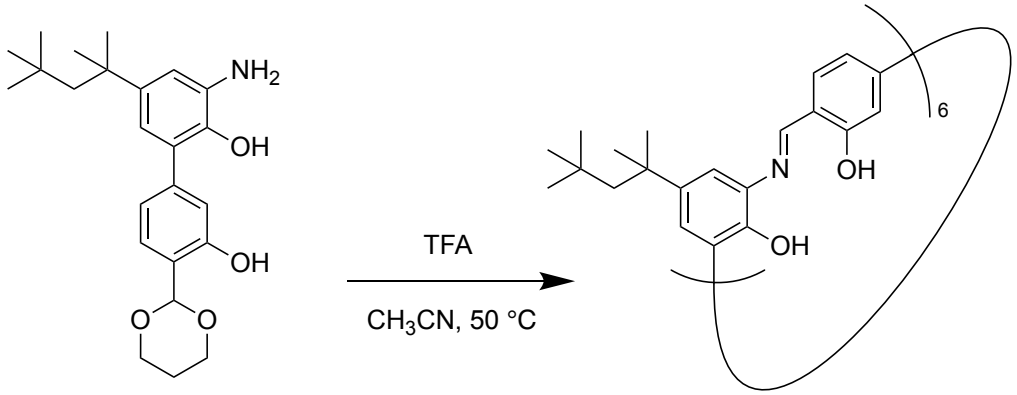
Synthesis of Macrocyclic Ligand Hexasap That Assembles *O*,*N*,*O* Tridentate Chelating Units in the Cavity ([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, [2]Freie Universität Berlin, [3]*Institute of Pure and Applied Sciences, University of Tsukuba*) ○Mamoru Kamisaka,[1] Sara Machleit,[1,2] Takashi Nakamura[3]

Macrocyclic ligands with chelating coordination units assembled in the cavity can be used to synthesize multinuclear complexes that capture molecules through multipoint coordination bonds. We have previously reported hexapap, a cyclic hexamer of *N*,*N*,*O* tridentate chelating unit pap (pyridylmethylene-aminophenol).[1–4] In this work, we have designed hexasap, a cyclic hexamer of *O*,*N*,*O* tridentate chelating unit sap (salicylidene-aminophenol), which forms electrically neutral complexes with divalent positively charged metal ions. Selective synthesis of hexasap H_{12}**1** has been achieved by heating bifunctional monomer **2** bearing *o*-aminophenol unit and acetal-protected salicylaldehyde unit under acidic condition.

Keywords : Supramolecule Chemistry; Oligomer; Macrocycles; Tridentate Chelates; Sap

キレート配位部位を内孔に集積した大環状配位子は、多点配位結合による分子捕捉能を持つ多核錯体の合成に用いることができる。我々は以前、*N*,*N*,*O* 三座キレート配位部位であるピリジルメチレンアミノフェノール（pap）の環状 6 量体 hexapap とその多核錯体を報告している[1–4]。本研究では、2 価の正電荷を持つ金属イオンと電気的中性の錯体を作る *O*,*N*,*O* 型三座キレート配位部位であるサリチリデンアミノフェノール（sap）の環状 6 量体 hexasap を設計した。*o*-アミノフェノール部位とアセタール保護されたサリチルアルデヒド部位をもつ両官能性単量体 **2** を酸性条件下で加熱することで、hexasap H_{12}**1** の選択的合成に成功した。



2 H_{12}**1**

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置換基を有する低分子有機半導体の結晶構造多様性と系統性

（産総研）○峯廻 洋美
Variety and Systematics in Crystal Structure of Organic Semiconductors with Substituents
(AIST) ○Hiromi Minemawari

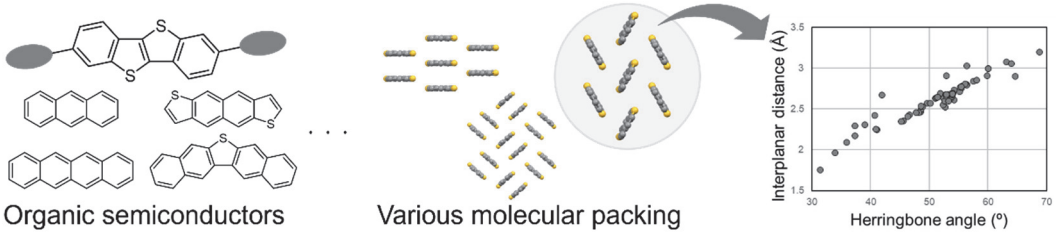
Chemical substitution to the π-skeletons of organic semiconductors (OSCs) is a common molecular design for control of material properties. However, minor differences in substituent size or structure can often cause dramatic changes in crystal structure. Therefore, a comprehensive understanding of substituent effects is essential to develop OSCs with excellent processability, thermal properties, and device characteristics.

In this study, crystal structures, intermolecular interactions and transfer integrals of acene and thienoacene-based OSCs were analyzed. Molecular packing varied dramatically or systematically depending on the substituents. Particularly in the layered herringbone-type arrangement, which is advantageous for achieving high-performance thin-film transistors [1, 2], calculated intermolecular interactions and transfer integrals systematically changed along the linear correlation between the face-to-edge dihedral angles and the interplanar distances of the slipped-parallel arrangement. Based on the results, the impact of substituent effects on crystal structure is discussed.

Keywords : Organic Semiconductor; Crystal Structure; Molecular Packing; Substituent effect

有機半導体材料ではπ電子骨格への置換基導入が一般に行われているが、置換基のサイズや構造のわずかな違いにより結晶構造は劇的に変化するため、優れた製膜性や熱物性・デバイス特性を実現するにはその効果についての理解が不可欠である。

本研究では、報告例が多い炭素鎖や環構造などの置換基が導入されたアセン・チエノアセン系低分子有機半導体について、結晶構造および DFT 計算による分子間相互作用・移動積分の評価を実施した。置換基に応じて分子パッキングが多様に、あるいは系統的に変化する系がそれぞれ見出され、特に、薄膜トランジスタ作製に有利とされる層状ヘリンボーン型配列 [1, 2] においては、*face-to-edge* 型配置の二面角および *slipped-parallel* 型配置の面間距離に線形の相関がみられ、これに沿って分子間相互作用および移動積分が系統的に変化することがわかった。得られた結果に基づき、置換基導入が結晶構造に及ぼす影響の体系的理解と高性能材料開発に向けた分子設計について議論する。



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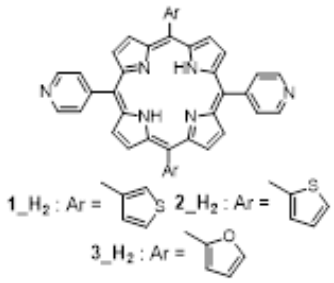
一次元細孔内部に複素環をもつ多孔性配位高分子の合成と溶媒の吸脱着挙動

（城西大院理）○奥山 達也・秋田 素子

Synthesis and Solvent Adsorption/desorption Behavior of Porous Coordination Polymers with Heterocycles inside One-dimensional Channels (*Graduate School of Science, Josai University*)
○Tatsuya Okuyama and Motoko Akita

Porous coordination polymers (PCPs) are attractive new materials because the size and properties of pores can be controlled by selecting appropriate organic ligands and transition metal ions. We have synthesized 5,15-bis(aryl)-10,20-bis(4-pyridyl)porphyrins as building block of PCPs possessing one-dimensional channel structure. We present here solvothermal synthesis, crystal structures and inclusion properties of PCPs composed of 5,15-bis(aryl)-10,20-bis(4-pyridyl)porphyrins with manganese(II) ions (aryl = 2-thienyl, 3-thienyl, 2-fulyl and 3-fulyl) . In all or the samples after synthesis, the solvent water molecules were included in the channel. Thermogravimetric analysis revealed that the water molecules liberated below 120 °C. Single X-ray structure analysis showed that the porous frameworks were retained after the loss of water molecules on heating. Immersion of the crystals in organic solvents resulted in the inclusion of cyclohexane and fluorocyclohexane.
Keywords : Porphyrin, Porous Coordination Polymers, Inclusion Compound

多孔性配位高分子(PCPs)は分子設計により細孔径や内部環境、特性を付加、制御できる次世代の多孔質材料である。我々は、これまでに 5,15 位にアリール基をもつ 10,20-*bis*(4-pyridyl)porphyrin を配位子とする一次元細孔を有する PCP を作製してきた。その中で、メソ位に 3-チエニル基を導入した PCP はフルオロシクロヘキサンを包接し、その包接体が強誘電的挙動を示すことを明らかにした [1)]。本研究では更なる強誘電体のホストとなる PCP を得るために、ポルフィリンと Mn^{2+}から成る一次元細孔内部に複素環が向く PCP をソルボサーマル条件下で作製した。この PCP は合成時包接された水分子が加熱により脱離し、室温で再吸着する。また、脱離後も細孔が安定に存在している。この結晶に加熱及び減圧により水を取り除き、有機溶媒に浸漬または曝露による分子吸着で細孔内に有機分子を取り込むことを明らかにした。



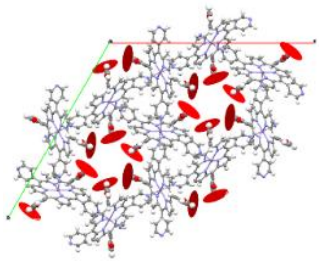


Fig. 1 一次元細孔構造(*c* 軸投影)

1) 永山早伽, 秋田素子, 第 20 回ホスト-ゲスト・超分子化学シンポジウム, 1B03, 2023 年(東京).

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トロポロンと水素結合ドナーおよびアクセプター分子を用いた共結晶の X 線構造解析

(埼玉大学 [1]) ○野村 拓夢・齋藤英樹

X-ray structure study of co-crystals with tropolone and hydrogen-bond donor and acceptor molecules

(Saitama university [1]) ○Hiromu Nomura[1], Hideki Saitoh[1]

Tropolone is one of the non-benzene aromatic compounds with 7-membered ring and is widely used as a chelating ligand and antibacterial agent together with the natural product hinokitiol. In this study, five co-crystals (I) to (V) of tropolone (Tr), two hydrogen-bond donor molecules, hydroquinone (Hq) and naphthalene-2,6-diol (N26), and three hydrogen-bond acceptor molecules, 1,4-diazabicyclo[2.2.2]octane (DABCO), phenazine (Phz) and tetramethylpyrazine (TMPy), were prepared by a solvent evaporation method and X-ray structure analyses were performed. The results of the X-ray structural analysis are shown in the table attached at the bottom. All the co-crystals were monoclinic, and the space groups were $P2_1/c$ or $P2_1/n$. Typical intermolecular hydrogen bonds, such as O-H···O and N-H···O, were observed in all the co-crystals. In the co-crystals (I) and (II), Tr and Hq , Tr and N26 formed hydrogen bond networks. In the co-crystal (III), H_2O molecules formed a hydrogen bond network to fill the gap between Tr and DABCO. Co-crystals (IV) and (V) formed hydrogen-bond, but not chain networks. The details of each co-crystal will be discussed on the same day.

Keywords : co-crystals, X-ray structure analysis, tropolone

トロポロンは 7 員環を持つ非ベンゼン系芳香族化合物の 1 つであり,キレート配位子や抗菌剤として天然物であるヒノキチオールと共に広く用いられている.本研究ではトロポロン(Tr)と水素結合ドナー分子のヒドロキノン(Hq),ナフタレン-2,6-ジオール(N26)の 2 種および水素結合アクセプター分子の 1,4-ジアザビシクロ[2.2.2]オクタン(DABCO),フェナジン(Phz),テトラメチルピラジン(TMPy)の 3 種,計 5 種類の共結晶(I)～(V)を溶媒蒸発法で作成し,X 線構造解析を行った.X 線構造解析の結果は下部に添付した表の通りである.いずれの共結晶も単斜晶で,空間群は $P2_1/c$ または $P2_1/n$ だった.いずれも分子間に代表的な水素結合である O-H···O や N-H···O 結合が見られた.共結晶(I),(II)では Tr と Hq, Tr と N26 が水素結合ネットワークを形成していた.共結晶(III)では Tr と DABCO の隙間を埋めるように H_2O 分子がネットワークを形成していた.共結晶(IV),(V)は水素結合による複合体を形成していたが,連鎖ネットワークは形成していなかった.各共結晶の詳細は当日に述べる.

table. トロポロンを含む5種の共結晶の構造解析の結果

	Tr-Hq (2:1) (I)	Tr-N26 (2:1) (II)	Tr-DABCO-H_2O (1:1:2) (III)	Tr-Phz (2:1) (IV)	Tr-TMPy (3:2) (V)
測定温度(K)	250	295	250	150	150
晶系	単斜晶	単斜晶	単斜晶	単斜晶	単斜晶
空間群	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	9.3254(8)	10.6495(10)	9.1162(2)	5.4263(2)	9.0888(2)
b/Å	10.7786(10)	5.8176(6)	20.4966(4)	16.1910(5)	17.2533(4)
c/Å	8.9070(8)	16.1864(15)	15.2553(3)	11.7024(4)	11.3925(3)
β/°	104.4600(20)	103.1420(14)	90.8898(4)	102.3510(10)	95.1640(10)
V/Å^3	866.92(13)	976.56(16)	2850.13(10)	1004.34(6)	1779.23(7)
Z	2	2	8	2	2
R/wR	0.040 / 0.102	0.044 / 0.133	0.060 / 0.176	0.041 / 0.108	0.042 / 0.121

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日本化学会 第104春季年会 (2024)

環境応答性蛍光色素を有するホスト-ゲストコンジュゲートの包接挙動および光学特性の評価

（福岡大院理 [1]）○堤 大洋 [1]・宮﨑 隆聡 [1]・林田 修 [1]

Evaluation of inclusion behavior of host-guest conjugate with environmentally responsive fluorescent dye ([1] *Graduate School of Science, Fukuoka University*)

○Taiyou Tsutsumi,[1] Takaaki Miyazaki,[1] Osamu Hayashida[1]

Host-guest conjugates, consisting of a host molecule and a guest one with an appropriate linker, have attracted much attention due to a promising strategy to design a functional molecule based on weak non-covalent interactions. In this study, we designed a host-guest conjugate **1** (Fig.1.), with a hydrophilic tetraazacyclophane **CPX$_2$** and a fluorophore **G1** as host and guest moieties, respectively. **CPX$_2$** has a hydrophobic cavity for guest-binding and hydrophilic side chains for water-solubility. **G1** exhibits an environment-dependent fluorescence; for instance, yellow-orange fluorescence in polar solvents and blue in non-polar solvents[1)]. Therefore, **1** is expected to show fluorescence spectral changes, depending on the formation of the intramolecular self-inclusion host-guest complex. According to a time-dependency of the fluorescence spectra of **1** in an aqueous solvent and methanol, the reversible fluorescence change was observed, suggesting that **G1** unit is in and out of **CPX$_2$** unit, depending on the surrounding micro environments. In this presentation, the synthesis and optical properties of **1** and its self-inclusion behavior by NMR will be discussed.

Keywords : Host-guest conjugate; Cyclophane; Environmentally responsive fluorescent; Inclusion complex; Fluorescence

ホスト分子とゲスト分子が適切なリンカーで連結させたホストーゲストコンジュゲートは, 非共有結合的な弱い相互作用を利用した機能性分子を構築するための優れた分子設計戦略として注目されている．今回我々は，疎水性空洞を有する親水性テトラアザシクロファン **CPX$_2$** と蛍光分子 **G1** をそれぞれホストとゲストとした，ホスト-ゲストコンジュゲート **1** を設計した (Fig. 1.). **CPX$_2$** はカチオン性の側鎖によって親水性を有し，水系溶媒中でゲスト分子を包接することが出来る．また，**G1** は極性環境では黄橙蛍光, 非極性環境では青色蛍光を示す環境応答性蛍光分子である [1)]. そのため, **CPX$_2$** と **G1** を適切なリンカーで連結させた **1** は，分子内ホスト-ゲスト複合体の形成挙動に応じた蛍光色変化を示すと期待できる．**1** の蛍光の時間変化を水系溶媒やメタノール中で測定したところ，可逆的な蛍光変化が観測された．これは，微視的環境に応じた **CPX$_2$** と **G1** 間での包接体形成挙動を反映させたものと考えられる．本発表では，**1** の合成および光学特性と NMR による評価について議論する．

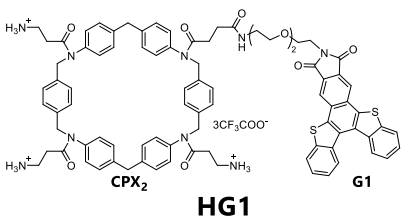

Fig. 1. Host-guest conjugate **1**.

1) T. Miyazaki, T. Tsutsumi, O. Hayashida. *ChemistrySelect.* **2023**, *8*, e202301421.

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スピン局在型ニトロキシラジカルを縮環導入したジヒドロフェナジンカチオンラジカル誘導体の合成と物理化学的性質

（慶大理工）○大髙 遼・大場 重幸・三浦 洋平・吉岡 直樹

Synthesis of Dihydrophenazine Cationic Radical Derivative Fused by Spin Localized Nitroxyl Radical Unit and Their Physicochemical Properties (*Faculty of Science and Technology, Keio University*) ○Ryo Ohtaka, Shigeyuki Oba, Youhei Miura, Naoki Yoshioka

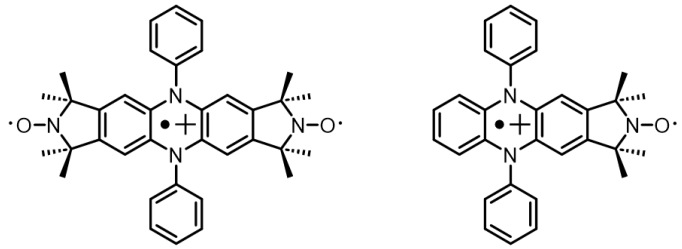
We have reported moderate intramolecular magnetic interaction in a diradical molecule fused with delocalized benzotriazinyl and localized pyrroline oxyl through nonconjugated framework. Because the interaction is different from the conventional spin-alignment rule for organic molecular system, further exploration is needed to develop a method for magnetic interaction without π-conjugated system.

In the present study, we designed the hetero-triradical and diradical systems containing dihydrophenazine cationic radical derivative fused by one or two spin localized nitroxyl radical units and investigated their physicochemical properties.

Keywords : Organic Radical; Nitroxyl Radical; Molecule-based Magnetism; Organic Crystal; Magnetic Property

当研究室では、局在型ラジカルであるピロリンオキシルと非局在型ラジカルであるベンゾトリアジニル（BT）を、非共役骨格を介して縮環したジラジカル分子の構造-磁性相関から、分子内に中程度の反強磁性的相互作用の発現を報告している。[1)] これは、2 つのラジカルの SOMO が縮環部位で空間的に接近したことに起因すると推察されたが、有機分子に磁性を発現させる手法としてはπ共役系を用いた従来のスピン整列則と異なるためさらなる探索が必要である。

本研究では、非局在型ラジカルとして、SOMO の位相およびスピン密度の広がりが BT と類似しているイオンラジカルに着目し、中でも固体状態で二量化に伴う反強磁性的相互作用を示さなかったジヒドロフェナジンカチオンラジカルを選択した。これと非共役骨格を介してスピン局在型ニトロキシラジカルを配置した分子 **1**$^{\bullet+}$および**2**$^{\bullet+}$（**Scheme 1**）を設計し、磁気的相互作用と電子状態の変化について検討した結果を報告する。



1$^{\bullet+}$　　**2**$^{\bullet+}$

Scheme 1

1) Y. Takahashi, R. Matsuhashi, Y. Miura, N. Yoshioka, *Chem. Eur. J.* **2018**, *24*, 7939-7948.

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日本化学会 第104春季年会 (2024)

ベンゾジチオフェノン分子の合成と刺激応答性分子結晶への展開

（静大理）○池田 昌弘・関 朋宏

Synthesis of Benzodithiophenone and its Application to Stimuli Responsive Molecular Crystals

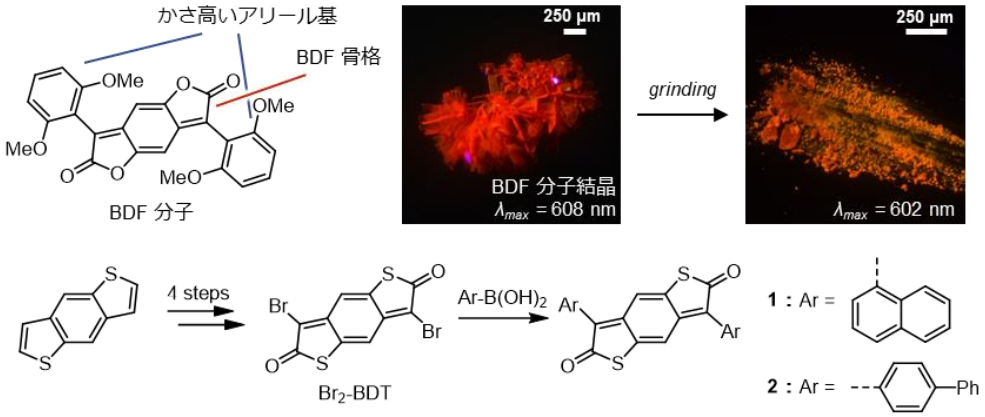
(*Faculty of Science, Shizuoka University*) ○Masahiro Ikeda, Tomohiro Seki

We have found that benzodifuranone (BDF), which has originally been developed as a pigment, exhibited solid-state photoluminescence and stimuli-responsiveness by introducing bulky aryl groups[1]. Here, we attempted to develop benzodithiophenone (BDT), in which the oxygen atoms of BDF were replaced by sulfur atoms, to impart phosphorescent properties. Here, we successfully prepared dibrominated BDT (Br_2-BDT) and introduced bulky aryl groups to it via coupling reactions to give novel BDTs **1** and **2**. From commercially available benzodithiophene, Br_2-BDT was prepared in 4 steps. We have introduced bulky aryl groups, naphthyl and biphenyl groups. We will report the crystal structures and photophysical properties of BDTs **1** and **2** and those of other BDTs bearing different aryl groups.

Keywords : Molecular Crystal; Pigment; Phosphorescence; Stimuli Response

我々は、顔料として開発されたベンゾジフラノン（BDF）にかさ高いアリール基を導入することで、BDF からなる分子結晶として初めて固体発光や刺激応答性を示すことを見出した[1]。本研究では、BDF 類縁骨格に対しリン光発光特性を付与するべく、BDF の酸素を硫黄に置き換えたベンゾジチオフェノン（BDT）の開発を試みた。本研究では、既知化合物であるジブロモ化 BDT（Br_2-BDT）の新たな合成経路を開発し、クロスカップリング反応によって新規 BDT **1**、**2** の合成に成功した。

市販のベンゾジチオフェンの α 位を、リチオ化を経由してホウ素化した。続いて過酸化水素による酸化でホウ素部位をケトンに変換し、NBS と AIBN により臭素化した。ヨウ化ナトリウムを用いて共役化することで、Br_2-BDT を 4 ステップで合成した。BDF 分子では、BDF 骨格間の積層の抑制が固体発光や刺激応答性の発現の起源であることを見出している。そこで、クロスカップリング反応によって BDT 骨格に、積層の抑制が期待できる芳香環を導入した。得られた BDT **1**、**2** の結晶構造や物性、その他のアリール基を導入した BDT 誘導体に関して報告する。



1) *manuscript under preparation*.

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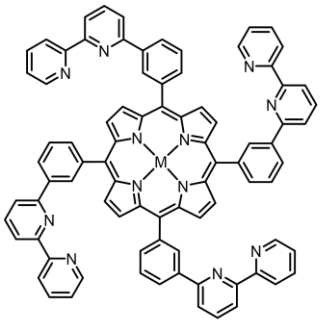
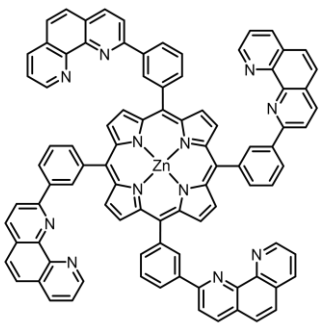
ビピリジン類を配位子として持つ金属ポルフィリンの錯形成挙動

（日大院理工[1]・日大理工[2]）○佐藤 賢[1]・宮﨑 茂樹[1]・須川 晃資[2]・大月 穣[2]
Complexation behavior of metalloporphyrins with bipyridyl-type ligand ([1]*Graduate School of Science and Technology, Nihon University*, [2]*Science and Technology, Nihon University*)
○Ken Sato,[1] Shigeki Miyazaki,[1] Kousuke Sugawa,[2] Joe Otsuki[2]

Porphyrin molecules possess unique optical and electrochemical properties, and they can exhibit even more novel functionalities through organization. Recently, we synthesized a novel porphyrin derivative ($ZnPor(bpy)_4$) and found that upon the addition of zinc ions, it forms a dimeric structure where the porphyrin rings face each other, as evidenced by absorption spectra, ^{1}H-NMR, and ESI-MS.[1)] In this study, we investigated the complexation behavior, with metal ions, of a porphyrin derivative having Co(II) at its center ($Co^{II}Por(bpy)_4$) and a porphyrin derivative with phenanthroline moieties as the ligand ($ZnPor(phen)_4$). The addition of zinc ions resulted in a blue shift of the Soret band for both porphyrins. The changes in the spectral shape ceased at two equivalents of zinc ion with respect to the porphyrin. This behavior is consistent with the formation of dimers, which are similar to the dimer of $ZnPor(bpy)_4$.
Keywords： Bipyridine; Molecular Organization; Porphyrin; Ring Current Effect; Synergistic Association

ポルフィリン分子は特徴的な光学的、電気化学的特性を有しており、組織化することでさらに新しい機能を持たせることができる。当研究室では、新規のポルフィリン誘導体 ($ZnPor(bpy)_4$)を合成し、亜鉛イオンを加えると、吸収スペクトル、^{1}H-NMR、ESI-MS から、ポルフィリン環が正面に向き合う二量体を形成することを見出した[1)]。本研究では、ポルフィリンの中心を Co (II)にした誘導体 ($Co^{II}Por(bpy)_4$)、並びに配位子をフェナントロリンにしたポルフィリン ($ZnPor(phen)_4$)に対して金属イオンを添加し、錯体の形成挙動を調査した。吸収スペクトルでは、どちらのポルフィリンでも亜鉛イオンを添加すると、Soret 帯がブルーシフトし、このスペクトル形状の変化はポルフィリン濃度に対して二倍の金属イオン濃度で完了した。これらの変化は $ZnPor(bpy)_4$ の場合と同様で、二量体を形成しているものと考えられる。





1) ホスト-ゲスト・超分子化学シンポジウム, 都立大, 2023 年 6 月.

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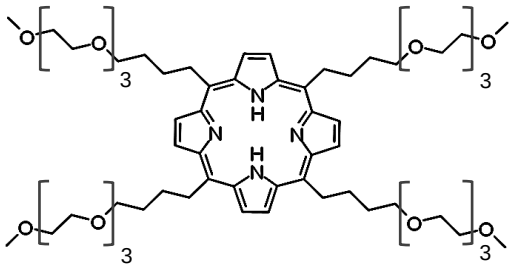
フェニル基を介さない PEG 化ポルフィリン

（日大理工[1]）○追榮 優里[1]・廣田 大樹[1]・須川 晃資[1]・大月 穣[1]
PEGylated porphyrin without phenyl groups([1]*College of Science and Technology, Nihon University*) ○Yuri Oie,[1] Daiki Hirota,[1] Kosuke Sugawa,[1] Joe Otsuki[1]

Water solubility of porphyrins is crucial for biological and ‘green’ applications. As a neutral functional group, poly(oligo)ethylene glycol (PEG) excels in ensuring biocompatibility and minimal impact on porphyrins' optical properties. While it is known that PEGylated tetraphenyl porphyrins aggregate in water,[1)] we synthesized PEGylated porphyrins without the phenyl moieties for reducing potential steric hinderance and investigated their water solubility and aggregation behavior. While synthetic attempts via a *meso*-CH_2OTs-porphyrin was unsuccessful due to low reactivity, we have achieved the synthesis starting from a monomethylated PEG, via tosylation, ether formation with 1,5-pentanediol, oxidation into aldehyde, and condensation with pyrrole under the Lindsay conditions. The porphyrin showed a 3-nm blue-shift of the Soret band and a reduction in absorbance approximately in half in water compared from features in organic solvents, which suggest aggregate formation in aqueous environments.
Keywords : Aggregates; Porphyrin; Water Solubility

ポルフィリンへ水溶性を付与することは応用上重要であり，中性のポリ(オリゴ)エチレングリコール(PEG)は，生物学や医学的な応用における生体適合性を確保できる点や，ポルフィリンの光学特性にほとんど影響を与えない点で，水溶性置換基として優れている．PEG 化ポルフィリンは水中で凝集することが知られているが，これらの多くはメソ位にフェニル基を介して PEG 鎖が導入されているポルフィリンについての結果である [1)]．本研究では，潜在的に立体障害となり得るフェニル基を介さずに PEG 鎖を導入したポルフィリンを新規に合成し(図)，それらの水溶性や凝集性を検討した．メソ位に CH_2OH 基を導入したポルフィリンを合成してから，OH 基をトシル化し，エーテル化により PEG 鎖を導入することは反応性の低さから困難であった．そこで，片側がメチル基の PEG 鎖をトシル化し，1,5-ペンタンジオールの片側にエーテルとして結合し，もう一方の OH 基を酸化してアルデヒドにし，ピロールと Lindsay 法で縮合することによって，フェニル基を介さない PEG 化ポルフィリンを合成することに成功した．有機溶媒中と水中における吸収スペクトルでは，後者の Soret 帯が 3 nm 短波長シフトし，吸光度は約半分に減少したことから，水中では分子間相互作用が働いていることが示唆された．



1) Valentina Villari *et al*. *Topics in Current Chemistry*, **2021**, 35, 379.

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テトラ(*N*-アルキルピリジニウム)ポルフィリンからなるカチオン性分子ケージの構築とその２次元配列化

(奈良先端科学技術大学院大学[1]・トゥールーズ大学[2]) ○林　大輔[1]・西野　智雄[1]・ラッペン　ゲナエル[1,2]

Construction of Cationic Molecular Cages Composed of Tetra(*N*-alkylpyridinium)porphyrins and Their Two-dimensional Assembly ([1]*Nara Institute of Science and Technology*, [2]*University of Toulouse*) ○Daisuke Hayashi,[1] Toshio Nishino,[1] Gwénaël Rapenne[1,2]

Molecular cages have the potential to encapsulate guest molecules depending on the size, shape, and environment of their internal nanospace. The regular arrangement of molecular cages can be expected to the arrangement of the encapsulated guest molecules. In this study, we have designed and synthesized a cationic molecular cage for the construction of a two-dimensional assembly of the molecular cage onto the anionic inorganic nanosheets through the electrostatic interaction. Molecular cage **3**·8PF_6^- was synthesized by the Huisgen cycloaddition of **1**·4PF_6^- with **2**·4PF_6^- (**Figure (a)**). ESI-TOF MS spectrum showed a molecular ion peak corresponding to **3**, which was consistent with the calculated isotopic pattern (**Figure (b)**).

Keywords : Molecular Cage; Porphyrin; Self assembly; Clay material

分子ケージは、その内部空孔のサイズ、形状、環境に応じたゲスト分子の包摂能を持つ。そのため、分子ケージを規則的に配列することができれば、内包されたゲスト分子の配列化につながると考えられる。本研究では、静電相互作用を用いたアニオン性無機ナノシート上への分子ケージの配列化を指向して、テトラ(*N*-アルキルピリジニウム)ポルフィリンが共有結合で連結されたカチオン性分子ケージを合成した。

アジド末端を有する **1**·4PF_6^-と、アルキン末端を有する **2**·4PF_6^-を高希釈条件下、銅触媒を作用させることで、分子ケージ **3**·8PF_6^-を合成した **(図(a))**。ESI-TOF MS 測定から、**3** に対応する分子イオンピークが観測され、計算値の同位体分裂パターンと良い一致を示した **(図(b))**。発表では、分子ケージ合成の詳細に加えて、静電相互作用を用いた分子ケージの二次元配列化について述べる。

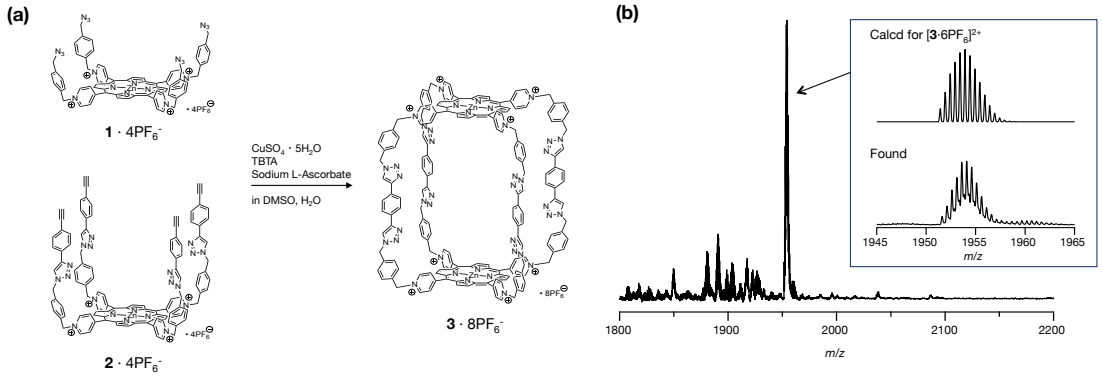

図 (a) 分子ケージの合成スキーム、(b) ESI-TOF MS スペクトル

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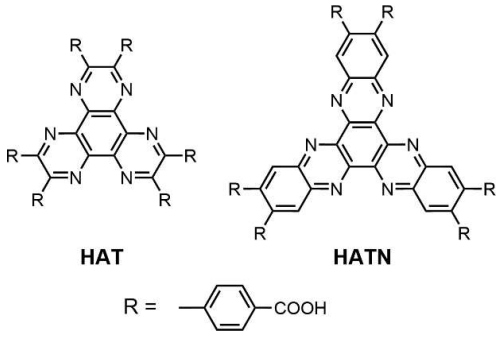
ピラジン縮環分子で構成される水素結合性有機フレームワークへのヨウ素およびハロゲン化物イオンの導入

（阪大基礎工[1]・阪大院基礎工[2]）○田畑 萌花[1]・鈴木 悠斗[2]・桶谷 龍成[2]・久木 一朗[2]
Inclusion of Iodine and halide ions in hydrogen-bonded organic frameworks composed of fused-ring pyrazine derivatives ([1]*School of Engineering Science, Osaka University*, [2]*Graduate School of Engineering Science, Osaka University*) ○Moka Tabata[1], Yuto Suzuki[2], Ryusei Oketani[2], Ichiro Hisaki[2]

Hydrogen-bonded Organic Frameworks (HOFs) containing charge carriers in their vacancies have the potential for applying to electrode materials. Iodine doping is particularly interesting in terms of ionic conductivity and nonlinear optical properties. In this work, we planned to form materials with such properties by encapsulating iodine and iodide ions in the inner space of HOFs composed of hexaazatriphenylene (HAT) and hexaazatrinaphthylene (HATN) derivatives, which are pi electron systems consisting of fused pyrazine rings with lone electron-pair. According to the literature, solvated crystals of HAT and HATN derivatives incorporating trichlorobenzene were prepared.[1,2] These were activated by heating, followed by exposure to iodine vapor. The resulting iodine-included crystals retained the original framework structure. We also attempted to include iodide ions in the HOFs. In this presentation, we will report on these crystal structures.
Keywords: Hydrogen bonds; Iodine; Iodide ion; Supramolecular chemistry; Self-assembly

水素結合性有機フレームワーク (Hydrogen-bonded Organic Frameworks, HOF) は、空孔に電荷キャリアを導入することにより、電極材料などへの応用が期待できる。特にヨウ素の導入は、イオン伝導性や非線形光学特性の発現の観点から興味がもたれる。本研究では、孤立電子対を有するピラジン環が縮環したπ電子系であるヘキサアザトリフェニレン誘導体 (HAT) およびヘキサアザトリナフチレン誘導体 (HATN) で構成された HOF の内部空間に、ヨウ素およびヨウ化物イオンを包接させることにより先述の物性を示す超分子ネットワークの形成を目指した。

既報に従って、トリクロロベンゼンを包む HAT および HATN 誘導体の溶媒和結晶を調製した[1,2]。これを加熱により脱溶媒した後、ヨウ素蒸気に暴露した。得られたヨウ素包接結晶は、ヨウ素吸着前のフレームワークを維持していた。また、ヨウ化水素酸に浸漬させることによりヨウ化物イオンの導入を試みたので、これらの詳細な結晶構造を報告する。



1) Hisaki, I.; Ikenaka, N.; Gomez, E.; Cohen, B.; Tohnai, N.; Douhal, A. *Chem. Eur. J.* **2017**, 23, 11611. 2) Hisaki, I.; Suzuki, Y.; Gomez, E.; Ji, Q.; Tohnai, N.; Nakamura, T.; Douhal, A. *J. Am. Chem. Soc.* **2019**, 141, 2111.

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メチル置換有機ホウ素錯体の結晶構造と蛍光特性

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Crystal Structures and Fluorescence Properties of Methyl-substituted Organoboron Complexes

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We previously proposed that crystals of organoboron complex **1a** (Fig. 1a) with methyl groups at the *p*-positions of phenyl groups exhibit "excited multimer luminescence" which is the luminescence from the multiple molecules with the interaction in the excited state.[1] To gain further insights into the proposal, in this work, we synthesized some organoboron complexes **1a**–**e** with methyl groups at various positions.

Two crystal polymorphs were obtained for complex **1b** (*m*-Me), and crystals **1b-B** and **-Y** exhibited blue (λ_{FL} = 460 nm) and yellow (536 nm) luminescence (Fig. 1b,c), respectively. The long-wavelength luminescence of **1b-Y** was assigned to an excimer from two facts: 1) π-stacked dimers exist in the crystal, and 2) time-resolved photoluminescence spectroscopy of the crystal showed-a rise of a *ca.* 550-nm component associated with a decay of a *ca.* 400-nm component attributable to the excited monomer luminescence. In the presentation, we will discuss new findings on "excited multimer luminescence" based on the results of **1a** and **1c**–**e**.

Keywords: Organoboron Complex; Organic Crystal; Fluorescence; X-ray Crystallographic Analysis; Time-resolved Photoluminescence Spectroscopy

我々は以前，フェニル基の *p* 位にメチル基をもつ有機ホウ素錯体 **1a**（Fig. 1a）の結晶が，励起状態で複数分子が相互作用した発光である“励起マルチマー発光”を示すことを提唱した[1]．さらなる知見を得るべく，本研究ではメチル基を種々の位置にもつ有機ホウ素錯体 **1b**–**e** を合成し，結晶構造と発光特性の関係を調べた．

錯体 **1b**（*m*-Me）では 2 種の結晶多形，結晶 **1b-B**，**-Y** が得られ，それぞれ青色（λ_{FL} = 460 nm），黄色（536 nm）の発光を示した（Fig. 1b,c）．結晶 **1b-Y** の発光については，1）結晶中に積層二量体が存在すること，2）時間分解発光分光で励起モノマーに帰属可能な短波長（*ca.* 400 nm）発光成分の減衰に伴う長波長（*ca.* 550 nm）発光成分の増加が観測されたことの 2 点から，エキシマー発光と帰属した．発表では，他の誘導体（**1a**，**1c**–**e**）の結果も含め，“励起マルチマー発光”の新しい知見について議論する．

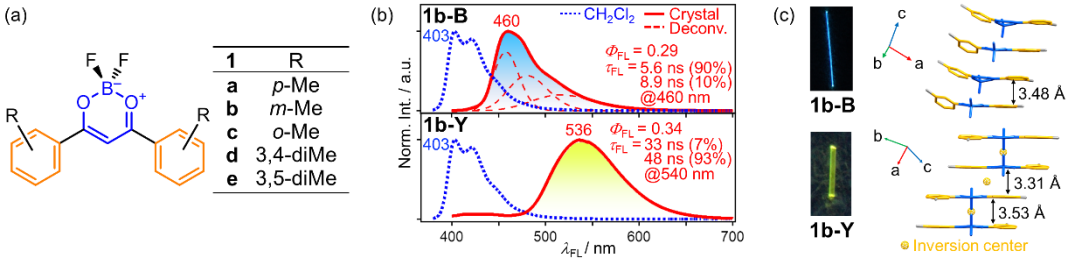

Fig. 1. (a) Molecular structures of **1a**–**e**. (b) Fluorescence spectra of **1b-B** and **1b-Y** in CH_2Cl_2 (*ca.* 1 × 10^{-5} M, λ_{EX} = $\lambda_{AB,max}$) and crystal (λ_{EX} = 365 nm). (c) Crystal structures of **1b-B** and **1b-Y**.

1) Sakai, A.; Tanaka, M.; Matsui, Y.; Ikeda, H. *et al. Chem. Eur. J.* **2015**, *21*, 18128–18137.

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ヒノキチオールとヒドロキノンの共結晶化とその物性

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Co-crystallization of hinokitiol with hydroquinone and its physical properties ([1]*Faculty of Science, Josai University*, [2]*Instrumental Analysis Center, Josai University*, [3]*Faculty of Pharmacy and Pharmaceutical Sciences, Josai University*) Kanji Takeuchi,[1] Kyoka Taketazu,[1] Junki Tomita,[2] Yutaka Inoue,[3] ○Mitsuaki Suzuki[1]

Active pharmaceutical ingredients (API) and their candidates often have solubility and permeability issues. The solubility and dissolution rates of API are important in drug development. Co-crystallization is a known solution to these issues. Co-crystallization can improve the physical properties of API by simply adding a co-crystallization agent without chemically modifying the API. Hinokitiol (HT) has been extensively studied in pharmaceuticals and quasi-drugs, and its sublimation and poor solubility in water have been problematic in applied research. In this study, we investigated the co-crystallization of HT with hydroquinone (HQ), which is known as a co-crystallization agent, and its effect on HT's thermal stability and solubility. For co-crystallization, 1 mmol each of HT and HQ were measured, and the mixture was mixed and ground using a ball mill. The obtained physical mixture (PM) was crystallized. IR measurement, powder X-ray diffraction, and thermal analysis were performed on the PM and the obtained single-crystal. For the obtained single-crystal, single-crystal X-ray structural analysis was also performed. Based on these results, the co-crystal of HT with HQ was evaluated.
Keywords : Hinokitiol; Hidroquinone; Co-crystallization; Single-crystal X-ray structural analysis

医薬品成分は、溶解性、浸透性等の課題があることが多い。医薬品の開発において、医薬品成分の溶解性や溶出速度は重要である。これらの課題の解決方法として、共結晶化が知られている。共結晶化は、医薬品成分を化学修飾することなく共結晶化剤を添加するだけで、医薬品成分の物性の改善が狙える。

ヒノキチオール（HT）は医薬品および医薬部外品の分野で幅広く研究されており、その昇華性や水への溶解性の低さは、応用研究において問題となっている。本研究では、HT と共結晶化剤として知られているヒドロキノン（HQ）との共結晶化を検討することで、HT の熱的安定性、溶解性や溶解度への影響を検討した。

HT と HQ の共結晶化は、それぞれ 1 mmol ずつ測りとり、ボールミルを用いて混合粉砕した。得られた物理的混合物 (PM) を結晶化した。PM と得られた単結晶について、IR 測定、粉末 X 線回折、熱分析を行った。得られた単結晶については単結晶 X 線構造解析も行った。これらの結果より、HT と HQ の共結晶について評価した。

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ブタジインを側鎖にもつクリセン誘導体の合成と結晶構造および蛍光挙動

(阪大基礎工[1]・阪大院基礎工[2]) ○神山凌弥[1]・桶谷龍成[2]・久木一朗[2]
Synthesis, crystal structure and luminescence behavior of chrysene derivatives with butadiyne
([1]*Faculty of Engineering Science, Osaka University*, [2]*Graduate School of Engineering Science, Osaka University*) ○Ryoya Kamiyama,[1] Ryusei Oketani,[2] Ichiro Hisaki[2]

By applying high pressure to the crystals composed of π-conjugated molecules, expansion or shrinkage of intermolecular distances occurs and their physical properties could be tuned or enhanced. For example, electron conductivity increases due to an increase in interorbital interactions. However, it is challenging to maintain these physical properties under ambient pressure because these changes are reversible with respect to pressure. In this study, we designed chrysene derivative **1** which possesses reactive butadiyne side chains for topochemical polymerization under high pressure. Single crystal X-ray structure analysis of **1** revealed that the chrysene skeleton and TIPS groups are arranged adjacent to each other. The CH_2Cl_2 solution of **1** showed fluorescence at 406 nm and its quantum yield was 65%. In this presentation, we will discuss the synthesis, crystal structure, and luminescence behavior in detail.
Keywords : π-conjugated molecules, topochemical polymerization

π 共役系化合物の結晶に圧力を印加すると、分子間空隙の収縮に伴い物性が変化することが知られている。例えば軌道間相互作用の増加による導電性の増加が挙げられる[1]。しかし、この変化は圧力に対して可逆的であるため、高圧下での密な構造を常圧に戻した際に保持することは困難である。そこで本研究は高圧下でのトポケミカル反応による集積構造の固定化を志向し、クリセンを基盤にジイン骨格を導入した誘導体 **1** (Figure 1a)を設計、合成した。**1** の単結晶を X 線構造解析すると、この結晶の空間群は *P*−1 であり、クリセン骨格同士および TIPS 基同士が隣接するように配列していることがわかった (Figure 1b)。また、**1** のジクロロメタン溶液は、406 nm に発光極大をもつ比較的強い蛍光発光 ($\Phi_F = 0.65$) を示すことがわかった (Figure 1c)。本発表では **1** の合成、結晶構造および蛍光特性について詳細に報告する。

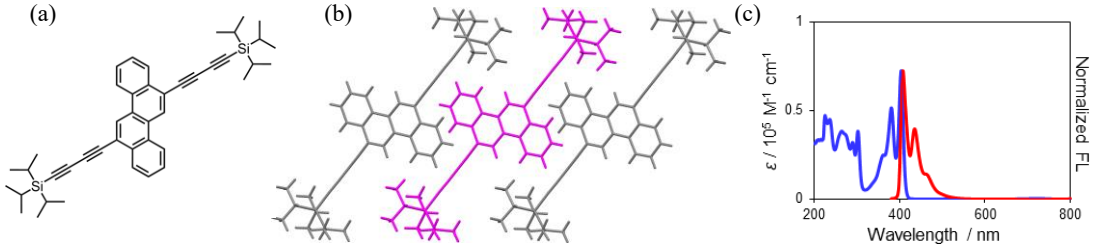

Figure 1. (a) Chemical structure of **1**. (b) Crystal structure of **1**. (c) Absorption (blue line) and fluorescence (red line) spectra of **1** in CH_2Cl_2.

1) Rang, Z. *et al. Appl. Phys. Lett.* **2011**, *79*, 2731.

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π共役拡張型テトラアリールエチレンを基本骨格とするジアミジンのカルボン酸認識

(京工繊大・工芸科学) ○上谷 涼・中島 茜音・楠川 隆博
Carboxylic acid recognition of a diamidine having a tetraarylethylene unit with an extended π-conjugation (Kyoto Institute of Technology) Suzu Uetani, Akane Nakajima, Takahiro Kusukawa

Previously, we synthesized tetraphenylethylene-based diamidine **1b** for the detection of dicarboxylic acid **2**. After the formation of 1:1 complex **1b**・**2** and its aggregate, blue fluorescence was observed in DMSO/MeCN mixed solvents. Therefore, we extended the π-conjugation and investigated its effect on fluorescence color before and after the formation of an aggregate with dicarboxylic acid **2**. Diamidine **1a** showed blue fluorescence in DMSO/MeCN mixed solvents, but when mixed with dicarboxylic acid **2**, it showed blue-green and light blue fluorescence depending on the chain length of **2**. Therefore, dicarboxylic acids of specific chain lengths can be detected by the differences in fluorescence color.
Keywords: diamidine; fluorescence; dicarboxylic acid

ジカルボン酸を選択的に認識する蛍光発光センサーの開発は、医療診断において重要である。蛍光発光性分子として知られているテトラフェニルエチレンは、溶媒中では、それぞれのフェニル基の自由回転により無放射失活するため蛍光発光を示さないが、固体状態や貧溶媒中では、フェニル基の回転が抑制され、凝集誘起発光を示す。当研究室では、テトラフェニルエチレンを基本骨格とするジアミジン **1b** がジカルボン酸 **2** と安定な会合体および凝集体を形成し、DMSO/MeCN 混合溶媒中で青色の凝集誘起発光を示すことを明らかにしている[1]。

そこで本研究では、テトラアリールエチレンを基本骨格とするジアミジン **1a** を新たに合成し、π 共役を拡張することにより会合体形成後に、より長波長の蛍光発光を示すことを期待して検討を行った。

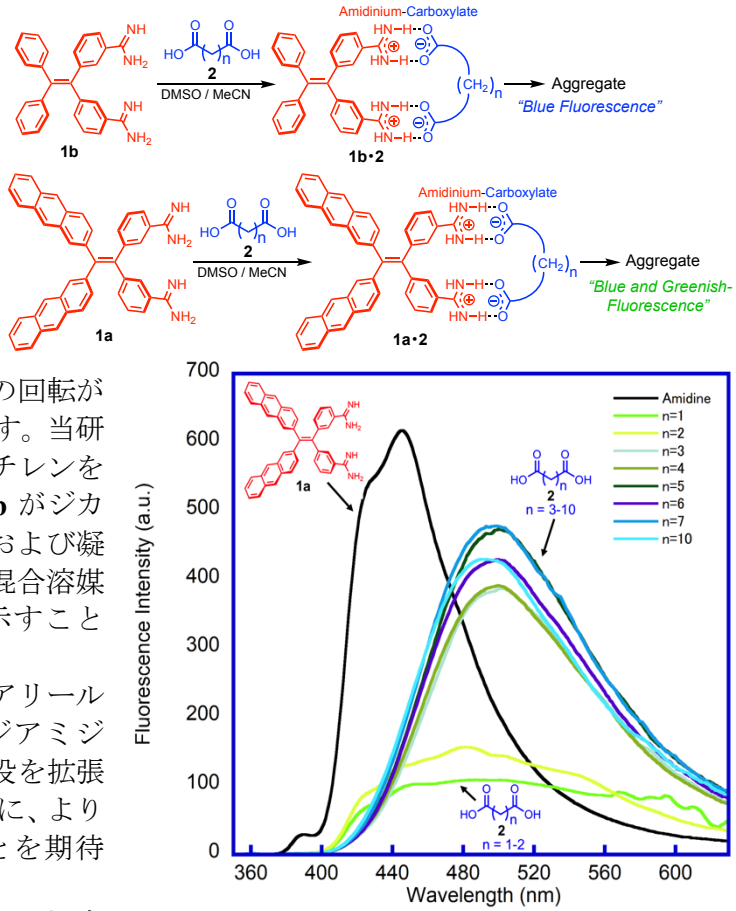

Figure 1. Fluorescence spectra of diamidine **1a** upon the addition of dicarboxylic acids **2** (50 mM, DMSO/MeCN =1:6, λ_{ex}=326 nm).

ジアミジン **1a** は DMSO/MeCN 混合溶媒中で青色の蛍光発光を示したが、ジカルボン酸 **2** と混合したところ、メチレン鎖長 n=1-2 では薄い青緑色、メチレン鎖長 n=3-10 では水色の蛍光発光を示した。このことから、発光色の違いにより特定の鎖長のジカルボン酸が検出可能となった。

1) T. Kusukawa *et al.*, *Chem. Lett.* **2018**, 47, 1395.

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テトラフェニルエチレン骨格を有するジアミジンのカルボン酸認識

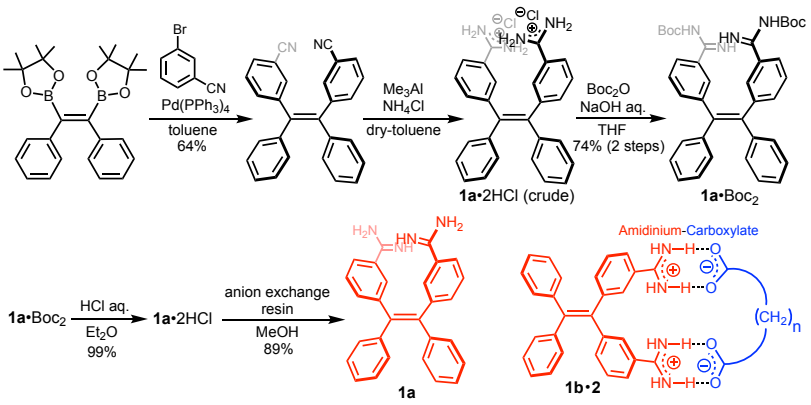
(京工繊大・工芸科学)　○渡辺 亮・楠川 隆博

Carboxylic acid recognition of a diamidine having a tetraphenylethylene unit (Kyoto Institute of Technology) Ryo Watanabe and Takahiro Kusukawa

The design and synthesis of fluorescent chemosensors for the selective recognition of dicarboxylic acids is of great importance. Recently we reported the fluorescent detection of dicarboxylic acids **2** using tetraphenylethylene-based diamidine **1b** in a DMSO/CH_3CN mixed solvent. In this study, a new diamidine **1a** was synthesized by changing the substitution position of the amidino group, and studied the fluorescence detection of dicarboxylic acids **2**. In this presentation, we will discuss fluorescence phenomena in the recognition of dicarboxylic acids **2** using diamidine **1a**.

Keywords : Diamidine; Fluorescence; Dicarboxylic acids

当研究室ではテトラフェニルエチレン骨格を有するジアミジン **1b** が DMSO/ CH_3CN (1:6) 混合溶媒中で、ジカルボン酸 **2** と安定な 1:1 会合体 **1b•2** を形成し、その会合体が凝集することにより凝集誘起発光を示すことを明らかにしている [1]。



Scheme 1. Synthetic route of diamidine **1a** and structure of **1b•2**.

本研究では、アミジノ基の置換位置の違いにより、ジカルボン酸 **2** との会合体の形成後におけるフェニル基の回転抑制および凝集体形成に違いが生じることを期待して、**1b** とは異なる位置にアミジノ基が置換したジアミジン **1a** を新たに合成した(Scheme 1)。

ジアミジン **1a** 単独では溶液中では蛍光発光を示さず、ジアミジン **1b** で用いていた DMSO/MeCN 混合溶媒中で、ジカルボン酸 **2** と混合しても蛍光発光は観測されなかった。しかしながら、溶媒に THF を用いると、ジカルボン酸 **2** との混合により青色の蛍光発光が観測され、ジアミジン **1a** が turn-on 型のセンサーとして利用可能であることが明らかになった。さらに、**1b** が中程度の鎖長(n = 3~8)のジカルボン酸 **2** を認識して蛍光発光を示すのに対し、ジアミジン **1a** はより短い鎖長のジカルボン酸 **2** (n = 1~3)についても蛍光発光を示した。

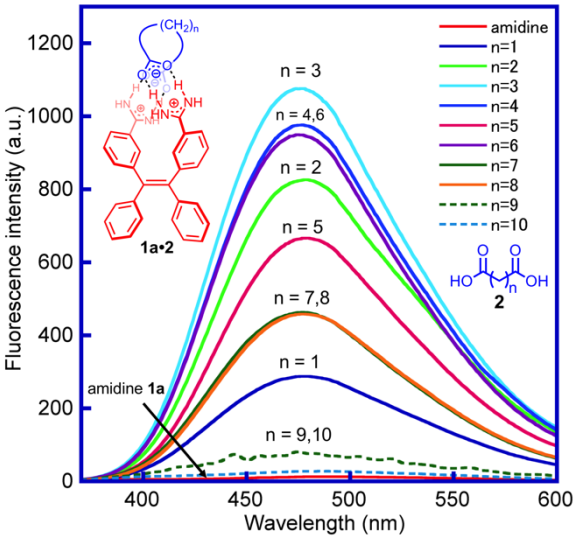


Figure 1. Fluorescence spectra of diamidine **1a** upon the addition of dicarboxylic acids **2** (50 μM in THF, λ_{ex} = 326 nm).

1) T. Kusukawa *et al.*, *Chem. Lett.* **2018**, *47*, 1395-1398.

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複数のカチオン性側鎖と蛍光性のピレン部位を有する水溶性シクロファンの合成

（福岡大院理[1]）○大熊 春菜[1]・宮﨑 隆聡[1]・林田 修[1]
Synthesis of water-soluble cyclophanes having multiple cationic side chains and a pyrene moiety ([1]*Graduate School of Science, Fukuoka University*) ○Haruna Okuma,[1] Takaaki Miyazaki,[1] Osamu Hayashida[1]

Water-soluble cyclophanes are typical host molecules capable of providing hydrophobic binding sites for guest-binding. On the other hand, guanidyl groups of arginine residues play an important role in molecular recognition of both naturally occurring enzymes and receptors. On these grounds, we have prepared a water-soluble cyclophane by introducing three ammonium and guanidyl groups as polar side chains as well as a fluorescent pyrene moiety into a rigid cyclophane skeleton (**N3** and **G3**, respectively). In addition, an analogous pyrene-appended cyclophane having six ammonium groups (**N6**) was designed and prepared. Guest-binding affinities of the hosts toward anionic fluorescent guests will be also discussed.
Keywords : Water-soluble host; Cyclophane; Guanidyl group; Pyrene

大環状シクロファンは、ゲスト捕捉能をもつ人工ホストとして知られている。その中でもアザシクロファンは、窒素原子を介して様々な機能性側鎖を分子外部に導入できることから、ゲストに対する分子認識や保護、可溶化、薬物ターゲティングなどに利用されている。我々は分子外部にカチオン性側鎖であるアンモニウム基と蛍光基であるピレン部位を導入したシクロファン（**N3**）を開発している。今回は酵素や受容体などの結合部位において重要な役割を担っているアルギニン側鎖のグアニジル基に着目して、複数のグアニジル基による分子認識が可能な蛍光性シクロファンを開発することにした。具体的には、**N3** に対してグアニジニル化剤である 1-アミジノピラゾール塩酸塩を作用させてグアニジル基を 3 箇所に導入した蛍光性シクロファン（**G3**）を合成した（Fig.1）。同定は ^{1}H および ^{13}C NMR、MALDI-TOF MS で行った。さらに、**N3** の側鎖を分岐化して 6 つの末端アンモニウム基を有する蛍光性シクロファン（**N6**）の合成も試みた。これらの合成と複数のカチオン性基とピレン基を有する水溶性シクロファンのゲスト分子に対する分子認識や捕捉挙動などについて報告する。

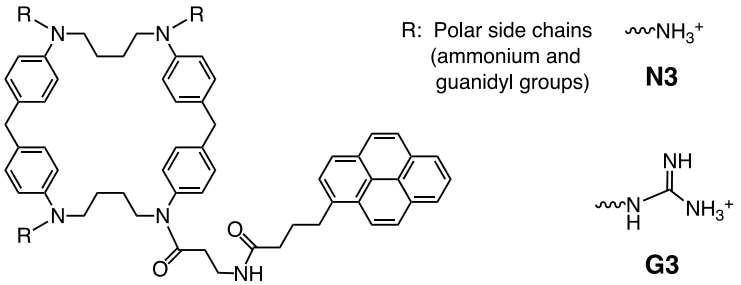

Fig. 1 Molecular design of cationic and water-soluble cyclophanes having a pyrene moiety.

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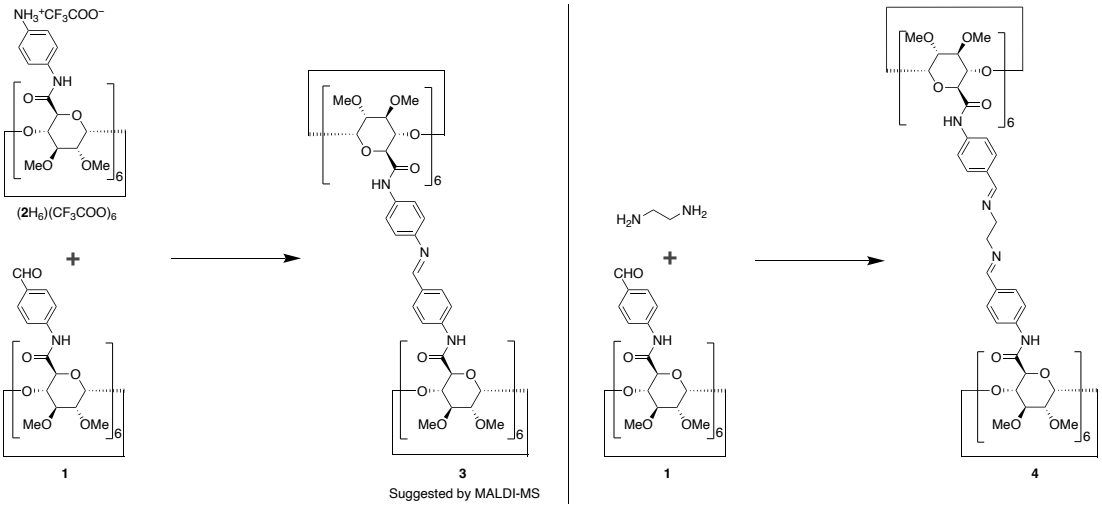
イミン結合を利用したアミドシクロデキストリン多量体の合成検討

(筑波大理工[1]・筑波大数理物質[2]) ○遠藤 智也[1]、中村 貴志[2]
Synthetic Study of Amide Cyclodextrin Oligomers Utilizing Imine Bonds ([1]*School of Science and Engineering*, *University of Tsukuba*, [2]*Institute of Pure and Applied Sciences*, *University of Tsukuba*) ○Tomoya Endo,[1] Takashi Nakamura[2]

Amide cyclodextrins (amide CDs) are cyclodextrin derivatives whose amide groups are connected to 5 position of pyranose rings, and they recognize anions by multipoint hydrogen bonds with amides. Aiming at creating functional molecules that exhibit recognition property utilizing multiple amide CD units, we have investigated the synthesis of amide cyclodextrin oligomers in this study, which are formed by linking an amide CD with 4-formylphenyl group **1** and that with 4-aminophenyl group **2**, via imine bonds as dynamic covalent bonds. As a result, a dimer **3** was observed in MALDI TOF-MS. Moreover, we succeeded in the synthesis of a homo dimer **4** of amide CD by the reaction of formyl derivative **1** and ethylenediamine.
Keywords : Supramolecular Chemistry, Oligomers, Cyclodextrins, Imine Bonds, Amides

アミドシクロデキストリン (アミド CD) は、ピラノース環の 5 位にアミド基が結合した CD 誘導体であり、アミド基との多点水素結合でアニオンを認識する [1–3]。本研究で我々は、複数のアミド CD 部位を活かした認識能を示す機能性分子の創出を目指し、4-ホルミルフェニル基をもつアミド CD **1** と 4-アミノフェニル基をもつアミド CD **2** を動的共有結合であるイミン結合で連結した多量体の合成を検討した。結果として、MALDI TOF-MS で二量体 **3** に帰属される化合物が観測された。また、ホルミル体 **1** とエチレンジアミンを反応させることで、アミド CD のホモ二量体 **4** の合成に成功した。



1) T. Nakamura, S. Yonemura, T. Nabeshima, *Chem. Commun*. **2019**, *55*, 3872.
2) S. Yonemura, T. Nakamura, T. Nabeshima, *Chem*. *Lett*. **2020**, *49,* 493.
3) T. Nakamura, S. Yonemura, S. Akatsuka, T. Nabeshima, *Angew. Chem*. *Int. Ed.* **2021**, *60*, 3080.

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非対称星型分子の合成と STM による測定

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Synthesis and STM Observation of Dissymmetric Star-shaped Molecules (Nara Institute of Science and Technology[1], National Institute for Materials Science[2], Nagasaki University[3], University of Toulouse[4]) ○ Sota Seki[1], Kenichiro Omoto[3], Shigeki Kawai[2], Gwénaël Rapenne[1,4]

Pentaphenylcyclopentadienyl derivatives have been reported to act as molecular gears on metal substrates for propagating rotational motion up to three consecutive molecules[1)]. Optimization of the intermolecular distance and orientation of molecular assemblies will affect the efficiency of molecular gears, however the relationship between the molecular structure and its supramolecular arrangement on the surface is not clear, especially for pentagonal molecules due to their symmetry.

In this study, methyl and fluoro groups were introduced at the *m*-position to clarify how the size and polarity of the functional groups at this unconventional substitution position affect the molecular assembly. STM showed that the monolayer arrangement depends on the substrates and the deposition conditions. Molecule with methyl group (**1**) formed a periodical structure but orientationally permuted 2D crystal（**Figure 1**）. In this presentation, the various 2D assemblies formed by molecules **1** and **2** will be discussed in detail based on STM images.

Keywords : Two-dimensional crystal; Cyclopentadienyl derivatives; Scanning Tunneling Microscope

シクロペンタジエニル誘導体は金属基板上において整列することで最大 3 分子の分子歯車として運動を伝搬した例が報告されている [1)]。集合体中の分子間距離や配向は分子歯車としての効率に影響を与えると考えられるが、シクロペンタジエニル誘導体のような 5 回対称分子においては分子構造と集合体構造の相関は明らかではない。

本研究では先行例とは異なる置換位置における官能基のサイズや極性の違いが集合体構造にどのような影響を与えるかを明らかにすることを目的とし、メタ位にメチル基(**1**)およびフルオロ基(**2**)を導入したシクロペンタジエニル誘導体を合成した。STM 観察より、導入された置換基の種類や蒸着条件によって異なる集合構造を形成することが分かった。特に分子 **1** では Ag(111)上で分子の中心位置が周期的である一方、分子の配向の乱れた二次元結晶が形成された(**Figure 1**)。本発表では分子 **1** および **2** が示す多様な二次元集合体について STM 像を元に詳しく議論する。

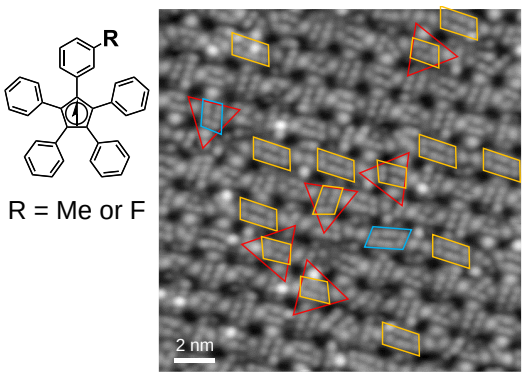

Figure 1. Molecular structure (**1**: R = Me, **2**: R = F) and 2D assembly formed by **1** on Ag(111) surface

1) a) F. Moresco et.al., *J. Phys. Chem. Lett.* **2020**, *11*, 6892-6899, b) G. Rapenne et.al., *Chem. Eur. J.* **2021**, *27*, 12019-12031.

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アルコキシ基とヒドロキシ基の置換パターンが異なるトリフェニレン誘導体の固液界面における自己集合構造

(明大院理工[1]・明大理工[2]) ○潘 王杰[1]・前田 松祐[1]・田原 一邦[2]

Self-Assembled Structures Formed by Triphenylene Derivatives with the Different Substitution Patterns of Alkoxy and Hydroxy Groups at the Liquid/Solid Interfaces.

([1]*Graduate School of Science and Technology, Meiji University,* [2]*School of Science and Technology, Meiji University*) ○Wangjie Pan,[1] Matsuhiro Maeda,[1] Kazukuni Tahara[2]

Construction and structural control of self-assembled molecular networks (SAMNs) at the liquid/solid interface are subject of intense interest because of perspective applications in the field of nanotechnology and nanoscience. In this context, SAMN formed by a triphenylene derivative having six long alkoxy groups on graphite was reported. We herein investigated the self-assembly of four triphenylene derivatives **1**–**4** having different numbers and positions of long-chain alkoxy groups and hydroxy groups at the interfaces between the organic solvent and graphite using scanning tunneling microscopy. Moreover, we investigated the effect of the sort of the solvent and a solute concentration on the self-assembled structures. As a result, various structures were formed depending on the differences in molecular structural features.

Keywords : Self-assembled molecular networks; Scanning tunneling microscopy; Liquid/solid interfaces

近年、固液界面での自己集合分子ネットワーク (SAMN) の構築と構造制御は、ナノテクノロジーやナノサイエンス分野での応用の潜在性から興味を集めている[1)]。その一環として、過去に、グラファイト上で六つの長鎖アルコキシ基をもつトリフェニレンが形成する SAMN が報告されている[2)]。今回、我々は置換する長鎖アルコキシ基とヒドロキシ基の数と位置が異なる四つのトリフェニレン誘導体 (Figure 1a) のそれぞれについて、溶媒の種類と溶質濃度が固液界面での SAMN 構造に与える影響を走査型トンネル顕微鏡 (STM) により調査した (Figure 1b)。その結果、アルコキシ基とヒドロキシ基の数と位置により分子間の相互作用が変化して、多様な構造が形成されることが分かった。

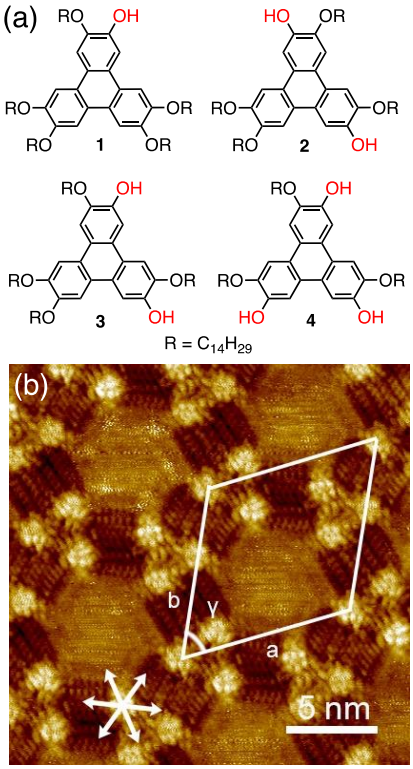

Figure 1. (a) Four triphenylene derivatives **1**–**4**. (b) STM image of SAMN formed by compound **4**.

1) Goronzy, D. P. et al. *ACS Nano* **2018**, *12*, 7445.
2) Bai, C.-L. et al. *ChemPhysChem* **2001**, *12*, 750.

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日本化学会 第104春季年会 (2024)

２位及び６位修飾 α-CD による超分子構造体の作製とその利用

（阪大院工 [1]）○宮坂萌々香 [1]・石田遥也 [1]・重光孟 [1]・木田敏之 [1]

Preparation and Applications of Supramolecular Structures from Dimethylated α-Cyclodextrin

([1]*Graduate School of Engineering, Osaka University*) ○Momoka Miyasaka,[1] Haruya Ishida,[1] Hajime Shigemitsu,[1] Toshiyuki Kida[1]

Cyclodextrins (CDs) can incorporate guest molecules of the appropriate size and shape. CDs can also regularly assemble intermolecularly through hydrogen bonding between hydroxyl groups on the upper and lower rims of their rings. Supramolecular structures consisting of channel-type assemblies of CD molecules that can selectively incorporate specific molecules into their cavities have attracted much research interest in their fabrication and use. We present here various supramolecular structures formed from 2,6-*O*-dimethylated α-CD. The morphology of the supramolecular structures varied with changes in the concentration of 2,6-*O*-dimethylated α-CD solution and the presence of the guest molecules.

Keywords : Cyclodextrin; Methylation; Channel-type Assembly; Supramolecular Structures; Guest Inclusion

シクロデキストリン (CD) は空孔の形と大きさに合う分子を取り込む性質を持つ。また、環骨格の上下に多数の水酸基を持ち、それら水酸基同士の水素結合を利用して分子間で規則的に集合することができる。特に、CD 分子が一直線上に並んだチャンネル型集合体はその貫通孔に特定の分子を選択的に取り込むことができることから、それらから構成される超分子構造体の作製とその利用についての研究が注目を集めている [1)]。本研究では、2 位と 6 位をメチル化した 2,6-*O*-ジメチル化 α-CD から形成される様々な超分子構造体の形態及びそれを構成する CD 分子の集合様式について明らかにした。

種々の濃度の 2,6-*O*-ジメチル化 α-CD のクロロホルム溶液を室温でヘキサン中に滴下後 24 時間静置した時、ロッド状あるいは六角形プレート状のマイクロ構造体が形成されることがわかった。これらの構造体の形態は 2,6-*O*-ジメチル化 α-CD/クロロホルム溶液の濃度に依存し、75 mg/mL 以上の濃度ではロッド状構造体が、50 mg/mL 以下の濃度では六角形プレート状構造体が選択的に生成した (Figure 1)。XRD 測定により、これらの構造体はいずれも 2,6-*O*-ジメチル化 α-CD 分子の head-to-tail 型集合体から構成されていることが明らかになった。本系に脂肪酸エステルゲストを共存させた時に形成される超分子構造体の形態ならびに CD 分子の集合様式についても検討した。

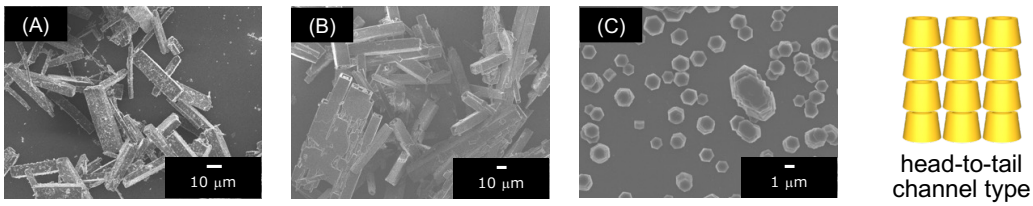

Figure 1. SEM images of supramolecular structures formed by mixing a 2,6-*O*-dimethyl α-CD/chloroform solution of various concentrations and hexane: (A) 200 mg/mL, (B) 75 mg/mL, and (C) 50 mg/mL.

1) H. Shigemitsu, T. Kida, *Polym. J.*, **2018**, *50*, 541–550.

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3 位と 17 位に様々なアルキルエステルを有するクロロフィル誘導体の固体状態ならびに物理的刺激下における集積挙動の変化

(龍谷大先端理工) ○山田 皓貴・宮武 智弘

Synthesis and optical properties of chlorophyll derivatives possessing esterified long alkyl chains at the 3- and 17-positions (*Faculty of Advanced Science and Technology, Ryukoku University*) ○Koki Yamada, Tomohiro Miyatake

Chlorophylls are found in photosynthetic organisms and play important roles in the early events of photosynthesis. Many kinds of chlorophyll derivatives have been prepared and they often exhibit specific optical properties especially in their aggregated state. Here we prepared chlorophyll derivatives possessing esterified long alkyl chains at the 3- and 17-positions, and their optical properties were examined in neat conditions.

Keywords : Chlorophyll, Self-Aggregation, Optical Properties

クロロフィル類は天然に存在するテトラピロール色素であり、生体内では多くのクロロフィル分子が組織化され、色素間相互作用を発現して特異的な光吸収特性を示している。また一般にアルキル鎖を有する環状 π 共役分子は分子間の π—π 相互作用を利用しながら安定な分子集積体を構築する。本研究では天然より抽出したクロロフィル-*a* を改変し、2 本のアルキル鎖を導入した誘導体について、その色素間相互作用ならびに分光学的特性について検討した。

まず、クロロフィル-*a* を原料として 3 位と 17 位の側鎖にドコシルエステルを有するクロロフィル誘導体 **1**(図 1)を合成した。誘導体 **1** の固体粉末は DSC 測定において 47℃に融解ピークを示し、50～70℃の間に相転移に伴う複数のピークを与えた。粉末状態の **1** をガラス板で挟み、加温により融解させた後に、冷却させることによりフィルムを作成した。クロロホルム溶液中で **1** は 685 nm に Qy 吸収帯を示すのに対して、フィルム状態の **1** は色素間相互作用により 700 nm に長波長シフトした Qy 帯を示し、その波長領域に S 字型の CD シグナルを与えた。このフィルムを 75℃まで加温して融解させると **1** は長波長シフトした吸収帯を示しながら、その CD シグナルを消失させた。つぎに 66℃にて、**1** を挟んだ 2 枚のガラス板をこすり合わせると再び S 字型の CD シグナルを示すことがわかった。以上のことから、クロロフィル誘導体 **1** は外部からの刺激に応答してその分光学的な特性を変化させることがわかった。

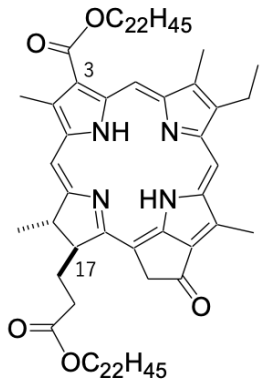

図 1. クロロフィル誘導体 **1** の構造

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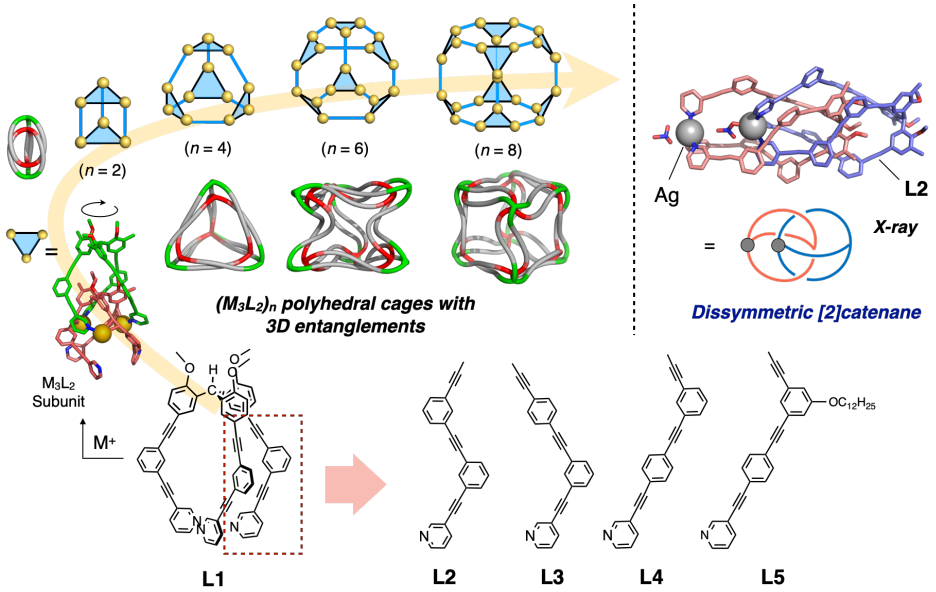
腕部分を種々改変したトリアリールメタンの配位自己集合

（群馬大理工[1]・群馬大院理工[2]）○小林 将也[1]・中村 洋介[2]・堂本 悠也[2]
Coordination Self-Assembly of Triarylmethanes Modified with Their Arm Moieties ([1]*School of Science and Technology, Gunma University*, [2]*Graduate School of Science and Technology, Gunma University*) ○Masaya Kobayashi,[1] Yosuke Nakamura,[2] Yuya Domoto[2]

We have recently developed the construction of highly entangled 3D polyhedral cages utilizing the cooperative acetylene π-coordination[1,2]. Here, we will present the synthesis of novel triarylmethane ligands with modified arm moieties and their self-assembly with Ag(I) ions targeting at the unexplored 3D topologies.
Keywords : Acetylene; Supramolecule; Self-assembly; Interlocked compound; Porous complex

複雑な 3 次元分子骨格の自在構築に向けて、共有結合に基づく有機合成を補完する手法として、金属配位に駆動された自己集合技術が開拓されてきた。我々は最近、アセチレン･･･金属間のπ配位が他種配位結合と柔軟に協働することを利用した、サブユニットのオリゴマーからなる 3 次元空孔分子群の構築を開拓している [1)]。一連の $(M_3(\mathbf{L1})_2)_n$ 組成(M = Ag(I), Cu(I))の空孔分子群における多面体骨格が、3 次元的な「絡まった」構造を有することを明らかとするとともに、対アニオン交換による構造の巨大化や分子絡まり構造の部分的な改変も達成している [2)]。本研究では、ナノ空孔分子のさらなる 3 次元トポロジー改変を目指し、トリアリールメタン型配位子 **L1** の腕部分を種々改変した新規配位子 **L2–L5** を設計、合成した。これら配位子群と銀(I)イオンの配位自己集合について検討を行ったところ、例えば **L2** からは非対称構造を示す [2]カテナン$(\mathrm{Ag}\mathbf{L2})_2$ が形成された。また、**L3** および **L4** においては錯形成時の沈殿が問題となったが、溶解性を改善した **L5** においては銀塩との自己集合による新規ディスクリート錯体の形成が ^{1}H NMR より示唆された。



1) Y. Domoto, M. Fujita, *Coord. Chem. Rev.* **2022**, *466*, 214605.
2) Y. Domoto, M. Abe, G. R. Genov, Z. Yu, M. Fujita, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303714.

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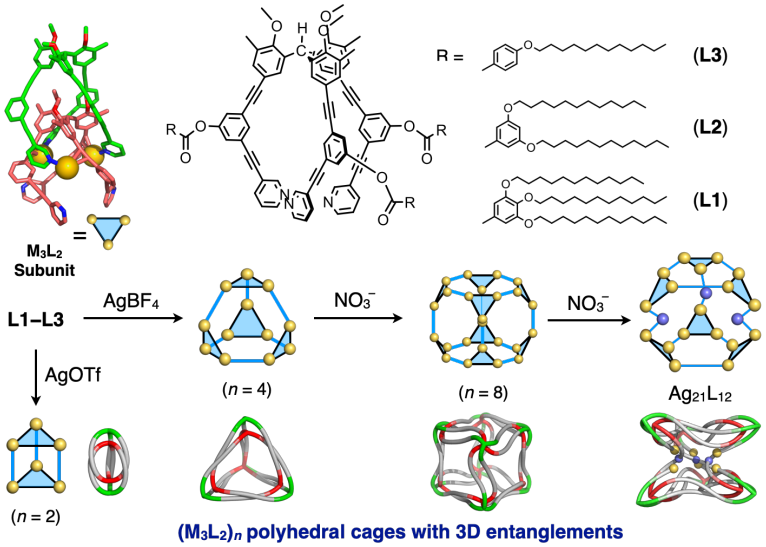
高度に絡まったアセチレン配位型多面体構築の立体効果による制御

(群馬大理工[1]・群馬大院理工[2]) ○中林 蓮[1]・中村 洋介[2]・堂本 悠也[2]
Steric Control over Self-Assembly of Highly Entangled Polyhedral Complexes via Acetylene Coordination ([1]*School of Science and Technology, Gunma University*, [2]*Graduate School of Science and Technology, Gunma University*) ○Ren Nakabayashi,[1] Yosuke Nakamura,[2] Yuya Domoto[2]

We have recently investigated the construction of highly entangled 3D coordination cages utilizing the cooperative acetylene π-coordination. In this presentation, we will discuss the steric control over their self-assembly processes by changing steric bulkiness of the triarylmethane ligands equipped with linear or branched side chains.
Keywords : Acetylene; Supramolecule; Self-assembly; Molecular entanglement; Steric effect

我々は最近、アセチレン･･･金属間のπ配位が他種配位結合と柔軟に協働することを利用した 3 次元空孔分子群の構築を開拓している[1]。今回、高度に絡まった構造を有するナノ空孔の自己集合における、配位子のかさ高さによる制御を目的として、種々の直鎖あるいは枝分かれ側鎖を導入したトリアリールメタン型配位子 **L1–L3** を合成した。**L1–L3** と AgOTf の自己集合では$(Ag_3L_2)_2$ 錯体が生じたのに対し、$AgBF_4$ を用いた場合は **L2**, **L3** については$(Ag_3L_2)_4$ が形成し、さらに硝酸イオンへのアニオン交換[2]を行うことで$(Ag_3L_2)_8$ および $Ag_{21}L_{12}$ へと段階的に変換が進行した。一方で **L1** では高次の多面体錯体は形成されなかった。本発表では、一連の自己集合過程における中間体形成などに対する立体効果について議論するとともに、**L1–L3** を混合することで立体効果を微細調節する試みについても報告する。



1) Y. Domoto, M. Fujita, *Coord. Chem. Rev.* **2022**, *466*, 214605.
2) Y. Domoto, M. Abe, G. R. Genov, Z. Yu, M. Fujita, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303714.

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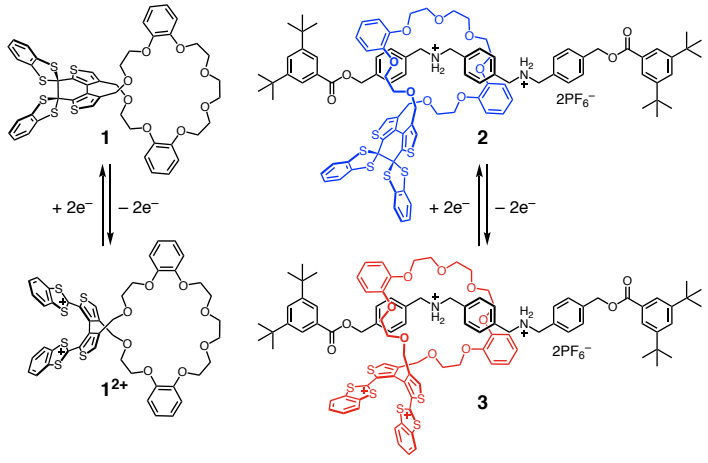
酸化還元応答性大環状クラウンエーテルとジアンモニウムカチオンからなるロタキサンの合成と性質

（信州大理）壁谷 菜月・○太田 哲
Synthesis and Properties of a Rotaxane Composed of a Redox-responsive Macrocyclic Crown Ether and a Diammonium Cation (*Faculty of Science, Shinshu University*) Natsuki Kabeya, ○Akira Ohta

We previously reported the synthesis and redox properties of a rotaxane composed of redox-responsive macrocyclic crown ether **1**/**1**$^{2+}$ and a secondary ammonium cation. In the present work we designed and synthesized a rotaxane consisting of a diammonium axle and **1**/**1**$^{2+}$. It is expected that the translational motion of the ring on the axle can be controlled by the change in the effective cavity size of the crown ether ring upon redox reactions. Rotaxane **2** was synthesized by an end-capping method. The cyclic voltammogram of **2** indicated that the interconversion between **2** and **3** undergoes reversibly. Chemical oxidation of **2** gave the oxidized form **3** in 89% yield. VT NMR measurements for **2** and **3** suggested that there is no significant difference in the shuttling rate of the ring component between them.
Keywords : Rotaxane; Crown Ether; 1,3-Benzodithiole; Redox Property

我々は以前、酸化還元応答性大環状クラウンエーテル **1**/**1**$^{2+}$ と第二級アンモニウムカチオンからなるロタキサンの合成と酸化還元挙動について報告した[1]。今回、2つのアンモニウムカチオン部位を有する軸状分子と **1**/**1**$^{2+}$ からなるロタキサン **2**/**3** を設計した。ロタキサン **2**/**3** では、酸化還元に伴う環状分子の実効的な空孔径の変化によって、軸上における環成分の並進運動を制御できると期待される。本発表では、ロタキサン **2**/**3** の合成、酸化還元挙動およびシャトリング挙動について報告する。

ロタキサン **2** の合成は末端封止法によって行った。**2** のサイクリックボルタモグラムは **2** と **3** の間での相互変換が可能であることを示した。また、**2** を 2当量のアミニウム塩で酸化すると **3** が収率 89%で得られた。ロタキサン **2** と **3** のシャトリング挙動を温度可変NMRで調べた結果、両者間で有意な差は認められなかった。これは、シャトリングにおいて軸状分子中央のベンゼン環による立体障害が小さいためと考えられる。



1) 壁谷菜月, 太田 哲, 日本化学会第 102 春季年会, **2022**, P2-1vn-14.

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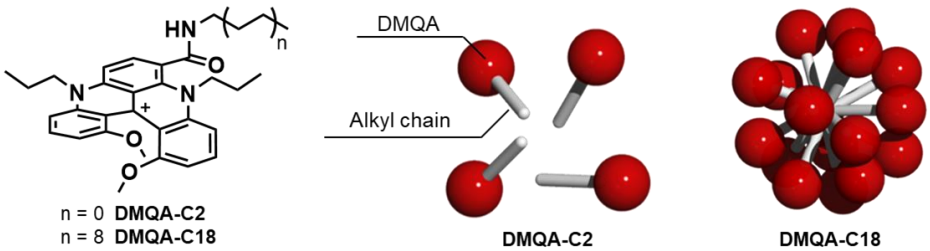
安定カルボカチオン分子の自己集合による超分子光触媒の創製と機能

（阪大院工）○飯室 祐也・重光 孟・山本 紗玖楽・木田 敏之
Development and functions of supramolecular photocatalysts formed by self-assembly of stable carbocation molecules (*Graduate School of Engineering, Osaka University*) ○Yuya Imuro, Hajime Shigemitsu, Sakura Yamamoto, Toshiyuki Kida

Photocatalysts have attracted much attention as an important material for clean energy generation. We have discovered that non-photocatalytic dye molecules acquire photocatalytic activity *via* self-assembly. Supramolecular photocatalysts employing xanthene and cyanine dyes have successfully demonstrated hydrogen evolution and organic oxidation reactions in water. However, their photo-durability and catalytic activity remain low. In this study, we report a supramolecular photocatalyst based on dimethoxyquinacridine (**DMQA**), a stable carbocation molecule. The **DMQA** supramolecular photocatalyst is anticipated to produce stable radical species after photoirradiation, and its stability and catalytic ability is expected to be quite high. In this presentation, we discuss the photophysical properties and catalytic activity of the supramolecular assemblies formed by the **DMQA** derivatives.
Keywords : Supramolecular assembly; Self-assembly; Photocatalyst; Carbocation; Quinacridine

光触媒は、クリーンなエネルギー創出のための重要なマテリアルとして注目を集めている。我々はモノマー状態では光触媒活性を有していない色素分子が、自己集合することで活性を獲得することを見出し、これを超分子光触媒と称して研究を行っている。[1] これまでにキサンテンやシアニン色素を利用した超分子光触媒を創製し、水中における水素発生や有機酸化反応に成功してきたが、耐久性および触媒能が低いことが課題であった。本研究では、安定なカルボカチオン分子であるジメトキシキナクリジン（**DMQA**）による超分子光触媒の創製を行った。**DMQA** は、光照射後に安定なラジカル種が発生すると期待され、その超分子光触媒は優れた耐久性と触媒能が見込まれる。本発表では、**DMQA** 誘導体が水中で形成される超分子集合体の光物性と触媒活性について報告する。



1) H. Shigemitsu, Y. Tani, T. Tamemoto, T. Mori, X. Li, Y. Osakada, M. Fujitsuka, T. Kida, *Chem. Sci.* **2020**, *11*, 11843.

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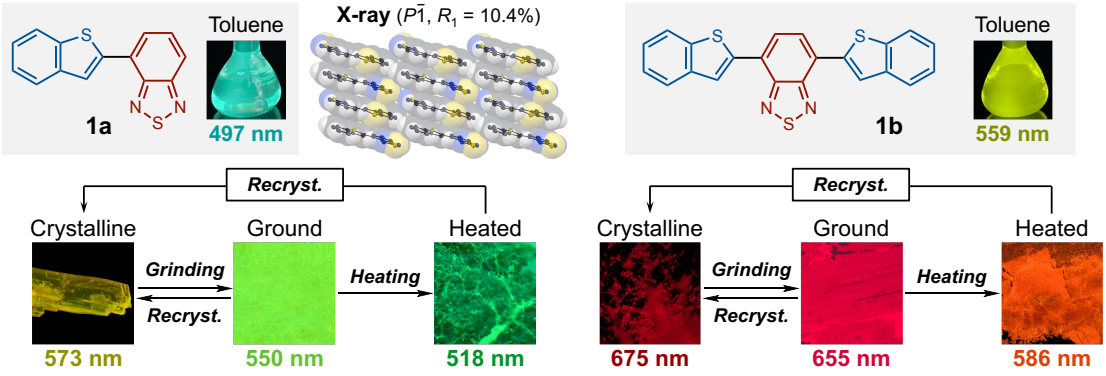
ベンゾチエニルベンゾチアジアゾール誘導体のメカノクロミック発光特性

(横浜国大理工[1]・JST さきがけ[2]) ○古川 陽斗[1]・伊藤 傑[1,2]
Mechanochromic Luminescence Properties of Benzothienylbenzothiadiazole Derivatives ([1]*College of Engineering Science, YOKOHAMA National University*, [2]*PRESTO, JST*) ○Haruto Furukawa,[1] Suguru Ito[1,2]

We have reported versatile mechanochromic luminescence based on a molecular design where an electron-donating heteroaromatic ring is directly substituted for an electron-accepting benzothiadiazole ring. In this study, benzothiophene-substituted benzothiadiazole derivatives have exhibited hypsochromic luminescence shifts in response to mechanical stimuli and heating. The emission color of yellow-emissive crystals of monosubstituted **1a** changed to yellowish green upon grinding, and then to green upon heating. Disubstituted **1b** also changed its luminescence color from deep red to red upon grinding, and to orange upon heating.
Keywords: *Organic Crystal; Solid-State Luminescence; Fluorescent Molecule; Mechanochromic Luminescence; Intramolecular Charge Transfer*

我々は、種々のドナー性複素環をアクセプター性ベンゾチアジアゾール環に直接置換する分子設計に基づき、機械的刺激に応答して多彩に発光色が変化するメカノクロミック発光(MCL)を実現している[1)]。今回、ベンゾチオフェン環をドナーとするベンゾチアジアゾール誘導体 **1** の発光色が、機械的刺激と加熱に応答して段階的に短波長化することを見出した。一置換体 **1a** は、トルエン溶液中で水色(λ_{em} = 497 nm)に発光したが、結晶状態では平面配座の分子が head-to-tail 型でスタッキングしており、黄色(λ_{em} = 573 nm)に発光した。結晶状態の **1a** をすり潰すと、発光色は黄緑色(λ_{em} = 550 nm)に変化し、さらに加熱すると緑色(λ_{em} = 518 nm)に変化した。二置換体 **1b** も同様に、溶液中(λ_{em} = 559 nm)よりも長波長の深赤色発光(λ_{em} = 675 nm)を示す結晶をすり潰して加熱すると、発光色は赤色(λ_{em} = 655 nm)、橙色(λ_{em} = 586 nm)へと順次変化した。



1) S. Ito, *Chem. Lett.* **2021**, *50*, 649 (review).

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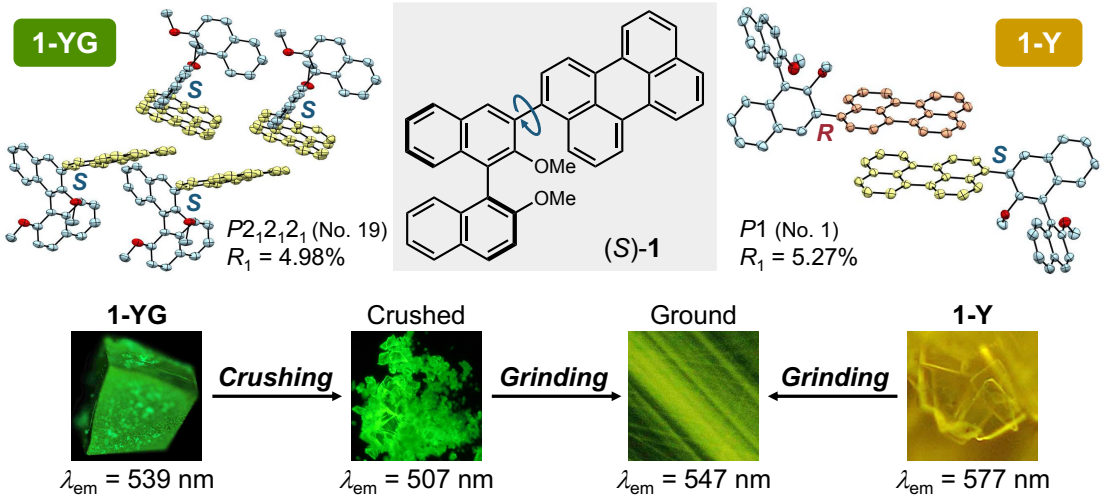
ペリレン置換ビナフトール誘導体の結晶構造と発光特性

（横浜国大院理工[1]・JST さきがけ[2]）○矢野 理子[1]・伊藤 傑[1,2]
Crystal Structure and Luminescence Properties of Perylene-Substituted Binaphthol Derivatives
([1]*Graduate School of Engineering Science, YOKOHAMA National University*, [2]*PRESTO, JST*)
○Riko Yano,[1] Suguru Ito[1,2]

Controlling the formation of polymorph is important because the luminescence color of organic molecular crystals varies significantly depending on the molecular conformation and intermolecular interactions. Herein, we synthesized a binaphthol derivative (*S*)-**1** substituted with perylene ring at the 3-position. After examining the crystallization of (*S*)-**1** using various solvents, two polymorphic crystals were obtained. Solvate crystals **1-YG** containing MeCN showed yellow-green emission, whereas solvate-free crystals **1-Y** showed yellow emission. In both cases, mechanical stimuli induced a transition to a yellow-green-emissive state.
Keywords : Solid-State Luminescence; Organic Crystals; Polymorphism

有機分子結晶の発光色は、分子の立体配座や分子間相互作用に応じて大きく変化するため、結晶多形の生成を制御することは重要である[1)]。今回、ペリレン環を 3 位に置換したビナフトール誘導体(*S*)-**1** を合成し、種々の溶媒を用いて結晶化することで、発光色の異なる 2 種類の結晶を得た。アセトニトリルを等モル量含む結晶 **1-YG**(空間群 $P2_12_12_1$)は、ペリレン環とナフタレン環との間のキラル軸が *S* の立体配置となるジアステレオマーのみから構成されており、黄緑色(λ_{em} = 539 nm)に発光した。一方、溶媒分子を含まない結晶 **1-Y**(空間群 *P*1)では、キラル軸が *S* と *R* のジアステレオマーがペリレン環同士で積層しており、黄色(λ_{em} = 577 nm)に発光した。結晶 **1-YG** に機械的刺激を加えると、発光波長は短波長化した後に長波長化した。すなわち、**1-YG** を粉砕すると発光色は緑色(λ_{em} = 507 nm)になり、強く擦ると発光色は黄緑色(λ_{em} = 547 nm)に変化した。結晶 **1-Y** も同様に、強く擦ると発光色は黄緑色になった。



1) Ito, S. *CrystEngComm* **2022**, *24*, 1112 (review).

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フタロシアニン・ポルフィリン発光体からの円偏光電界発光 (CPEL)

（近畿大学[1]・大阪公立大学[2]・日本分光株式会社[3]）鈴木 聖香[1]・山本 優太[1]・志倉 瑠太[2]・鈴木 仁子[3]・八木 繁幸[2]・○今井 喜胤[1]
Circularly polarized electroluminescence (CPEL) from phthalocyanine and porphyrin luminescent materials ([1]*Graduate school of science and engineering. Kindai University*, [2]*Graduate school of engineering, Osaka Metropolitan University*, [3]*JASCO*) Seika Suzuki,[1] Yuta Yamamoto,[1] Ryuta Shikura,[2] Satoko Suzuki,[3] Shigeyuki Yagi,[2] ○Yoshitane Imai[1]

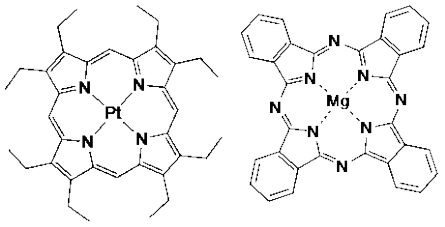
Circularly polarized organic light-emitting diodes (CP-OLEDs) were prepared using achiral phthalocyanine and porphyrin luminophores. By applying an external magnetic field and voltage to these CP-OLEDs, magnetic circularly polarized electroluminescence (MCPEL) from these CP-OLEDs was successfully extracted.

Keywords : Circularly polarized electroluminescence (CPEL), *Circularly polarized luminescence (CPL), CP-OLED*, *Phthalocyanine, Porphyrin*

円偏光発光(Circularly polarized luminescence: CPL)は、基本的に、キラルな発光体から取り出すことができるが、外部磁場を印加することによっても、円偏光発光を生じさせることが可能である。これを磁気円偏光発光(Magnetic circularly polarized luminescence: MCPL)という。MCPL の大きな特徴は、外部磁場という物理的刺激を用いるため、発光体にキラリティーが無くても CPL を生み出すことができきる点である

当研究室では、有機 EL ディスプレイ用の燐光材料として利用可能なイリジウム錯体、白金錯体、TADF 発光体に注目し、外部磁場を印加することで、RGBY のマルチカラーMCPL の発現に成功している。[1)]

本研究では、Platinum octaethylporphyrin (**Pt-OEP**)を発光層に組み込み込んだ磁気円偏光有機発光ダイオード(MCP-OLED)と、Magnesium phthalocyanine(**Pc-Mg**) を発光層に組み込み込んだ MCP-OLED を作成した。続いて、電圧と外部磁場を印加することで、それらデバイスの磁気円偏光電界発光(MCPEL)特性について検討した。Pt-OEP を発光層に含む MCP-OLED からは、$|g_{MCPEL}|10^{-3}$ オーダーで、赤色の MCPEL を取り出すことに成功した。さらに、Pc-Mg を発光層に含む MCP-OLED からは、$|g_{MCPEL}|10^{-3}$ オーダーで、近赤外の MCPEL を取り出すことに成功した。



Pt-OEP **Pc-Mg**

以上、Pt-OEP および Pc-Mg を発光層に組み込んだ MCP-OLED の開発に成功した。

1) *ChemPhotoChem.,* **5** (2021) 969. *ChemPhotoChem.*, **6** (2022) e202100253. *Org Electron.*, **119** (2023) 106814. *Org Electron.*, **122** (2023) 106893. *Front. Chem. Nanoscience.* **11** (2023) 1281168.

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π共役を拡張したチエノチオフェン環を有するジアリールエテンの合成と光物性

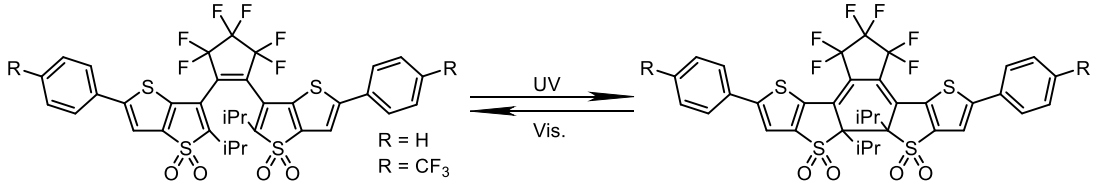
（立教大学[1]）○古仙 愛美[1]・金子 響[1]・西村 涼[1]・森本 正和[1]

Synthesis and Photophysical Properties of Diarylethene having Thienothiophene Rings with Extended π-Conjugation. ([1]*Rikkyo University*) ○Manami Furusen,[1] Hibiki Kaneko,[1] Ryo Nishimura,[1] Masakazu Morimoto[1]

When the diarylethene (DAE) molecules are packed in the antiparallel conformation and have the short distance between the reactive carbon atoms (< 4.2 Å) in crystal, the photocyclization reaction in the single-crystalline phase can proceed. However, there are few reported examples of Turn-on mode fluorescent DAE single crystals. In this study, we found that DAEs having benzothiophene dioxide, which are known to exhibit Turn-on mode fluorescence switching in solution, have the distance around 4.2 Å between the reactive carbon atoms in the stable structure due to the steric hindrance between the hydrogen atom at 4-position of the benzothiophene ring and the fluorine atom of the hexafluorocyclopentene ring by quantum chemical calculations. Therefore, we think that by introducing a thienothiophene ring at the aryl position, which has a smaller ring size than benzothiophene and has no hydrogen atom to induce steric hindrance with the fluorine atom, the steric hindrance can be avoided. Hence, we tried to synthesize a photochromic DAE having thienothiophene rings, which is expected to undergo photochromism with Turn-on mode fluorescence switching ability in the crystalline state.

Keywords: photochromism; diarylethene; thienothiophene

結晶状態でアンチパラレル体でパッキングされ、反応点炭素原子間距離が 4.2 Å 以内であるときジアリールエテンは結晶状態でフォトクロミズムを示す[1]が、ジアリールエテン自身の蛍光特性を開環・閉環異性化で変化させる Turn-on 型の蛍光性ジアリールエテン結晶の例は極めて少ない。本研究では、溶液中で Turn-on 型の蛍光スイッチングを示すことで知られるベンゾチオフェンジオキシド骨格をもつジアリールエテンが、ベンゾチオフェン環の 4 位の水素原子とヘキサフルオロシクロペンテン環のフッ素原子の立体障害が原因で、安定構造の反応点炭素原子間距離が 4.2 Å 前後になりやすくなることを量子化学計算により突き止め、それが原因で結晶中でフォトクロミズムを示さないことを見出した。そこで、ベンゾチオフェンよりも環のサイズが小さく、フッ素原子と立体反発を生じうる位置に水素原子を持たないチエノチオフェン環をアリール位に導入することで、立体反発を緩和し、結晶状態でフォトクロミズムを示すパッキングを取りやすくなると考え、以下に示す分子の合成を進めた。



1) S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem Commun.* **2002**, 2804

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化学結合が流動的に変化する新規カゴ型分子の合成検討

（東工大化生研[1]）○横山寛義[1]・嘉山怜央[1]・小阪敦子[1]・庄子良晃[1]・福島孝典[1]
Synthetic Study of a Cage-Type Molecule Undergoing Fluid Bond Shifting ([1]*Lab. Chem. Life Sci., Tokyo Tech.*) ○Hiromichi Yokoyama[1], Reo Kayama[1], Atsuko Kosaka[1], Yoshiaki Shoji[1], Takanori Fukushima[1]

Molecules that exhibit “fluid” structural changes such as bullvalene are called “shape-shifting” molecules. We designed a new molecular system in which the constituent chemical bonds change fluidly while maintaining the molecular shape. The required design to achieve such particular dynamic behavior is a cage-type molecule in which two seven-membered rings are linked together. In this presentation, we will report synthetic approaches toward the target molecule.
Keywords : Shape-Shifting; Degenerated Cope Rearrangement; Bullvalene; Cage Compound

一般的な分子では、骨格を形成する化学結合の組み替えは自発的には起こらない。対照的に、ブルバレンのように化学結合が流動的に変化するような分子は Shape-Shifting 分子と呼ばれる[1)]。ブルバレンは縮退 Cope 転位によって炭素原子の位置が組み替わった等価な構造を生じる。複数の置換基をもつブルバレン誘導体は、溶液中で Shape-Shifting により置換基どうしの相対位置が柔軟に変化するため、ゲスト認識や刺激応答機能の観点から最近注目を集めている[1)]。一方、このような Shape-Shifting は分子骨格の変化を伴うため、分子が緊密にパッキングした凝集状態では起こらない。それに対して本研究では、分子形状を保ちつつ、分子を構成する化学結合のみが流動的に変化する新しい動的分子システムの構築を目指し、縮退 Cope 転位を示すカゴ型構造からなる炭化水素分子の合成に取り組んでいる[2)]。本発表では、新規カゴ型分子の合成検討について報告する。

1) (a) G. Schröder, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 481. (b) J. F. Teichert, D. Mazunin, J. W. Bode, *J. Am. Chem. Soc.* **2013**, *135*, 11314.
2) 嘉山怜央, 菓子田惇輝, 庄子良晃, 福島孝典, 第 32 回基礎有機化学討論会, 1P073.

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長い軸分子を導入したロタキサン型超分子メカノフォアの刺激応答特性

（東工大物質理工）○山本 陸・相良 剛光

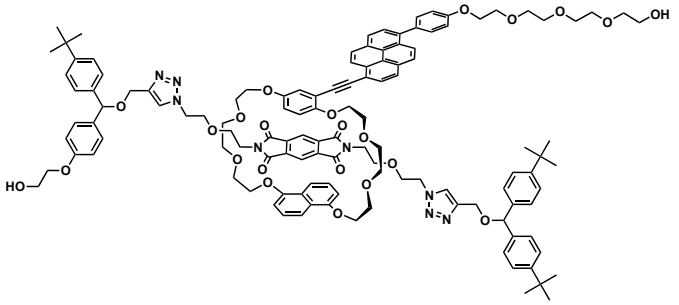
Stimuli-responsive properties of rotaxane-based supramolecular mechanophores having a long rod molecule

(*Department of Materials Science and Engineering, Tokyo Institute of Technology*) ○Riku Yamamoto, Yoshimitsu Sagara

Mechanochromic mechanophores are molecular structures that change absorption and fluorescence properties in response to mechanical stimuli. Rotaxane-based supramolecular mechanophores show rapid and reversible changes in fluorescence intensity.[1] The polyurethane elastomer films into which the mechanophores are covalently introduced change their fluorescence intensity when the films are deformed. The emission color can be adjusted by replacing the luminophore introduced into the cyclic molecule.[2] In this study, we synthesized rotaxane-based supramolecular mechanophores having a pyrene group varying the length of the rod molecule. We investigated how extending the length of the rod molecule affects the fluorescence properties of the mechanophores.

Keywords: Mechanophore, Rotaxane, Supramolecular mechanophore, Mechanoresponsive luminescent material

機械的刺激に応答して吸収・蛍光特性変化を示す分子骨格は、メカノクロミックメカノフォアと呼ばれる。ロタキサン型超分子メカノフォアは、機械的刺激に応じて迅速かつ可逆的に蛍光特性変化を示すメカノフォアである[1]。このメカノフォアが導入されたポリウレタンエラストマーは、延伸すると内部のメカノフォアに力が伝達され、蛍光強度が変化する。また、このロタキサン型超分子メカノフォアでは環状分子に導入する蛍光団を変更することによって、蛍光色を調整できる[2]。本研究では、蛍光団としてπ共役が拡張されたピレンを導入したロタキサンと、さらにその軸分子の長さを延長したロタキサンを合成した。軸分子の長さが異なるロタキサンの刺激応答特性を比較し、軸分子の長さがどのように刺激応答特性に影響を及ぼすかを調べた。



1) Y. Sagara, M. Karman, E. Verde-Sesto, K. Matsuo, Y. Kim, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2018**, *140*, 1584.
2) Y. Sagara, M. Karman, A. Seki, M. Pannipara, N. Tamaoki, C. Weder, *ACS Cent. Sci.* **2019**, *5*, 874.

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アゾベンゼン結晶が示す光誘起移動のメカニズム

（筑波大院数理[1]・産総研電子光[2]）○齊川 誠[1,2]・キーガン マギー[1,2]・真部 研吾[2]・齋藤 滉一郎[2]・吉川 佳広[2]・則包 恭央[2,1]

Mechanism of Photo-Induced Crawling Motion of Azobenzene Crystals ([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*National Institute of Advanced Industrial Science and Technology (AIST)*) ○Makoto Saikawa,[1,2] Keegan McGehee,[1,2] Kengo Manabe,[2] Koichiro Saito,[2] Yoshihiro Kikkawa,[2] Yasuo Norikane[2,1]

A Crystal of 3,3’-dimethylazobenzene exhibits photo-induced crawling motion upon exposure to UV and visible light on solid surface. The photo-induced crawling motion of DMAB analogues has rarely been investigated, and no guidelines for appropriate molecular design to induce the crawling motion have been obtained. In this presentation, we will discuss the mechanism to further understand the crawling motion by comparing the photoresponses of crystals of DMAB and its analogue.

Keywords : Azobenzene; Organic Crystal; Photomechanical Effect; Photomelting; Crystal Crawling

3,3’-ジメチルアゾベンゼン (3,3’-DMAB, Figure 1a) の結晶は、紫外光及び可視光を同時に照射することで基板表面上を移動する (Figure 1b)[1]。我々はこれまでに、基板の表面特性を利用することで結晶の移動速度や形状を制御することに成功した[2]。一方で、3,3’-DMAB 類縁体の光誘起移動はほとんど検討されておらず、光誘起移動を起こすための適切な分子設計の指針は得られていない。今回新たに 4,4’-ジエチルアゾベンゼン (4,4’-DEAB, Figure 1a) の結晶の光誘起移動を試みた。その結果、現行の実験条件において、3,3’-DMAB と比較して移動現象が観察されにくいことがわかった (Figure 1c)。本発表では、これらの結晶の光応答性を比較し、光誘起移動の理解を深めるためのメカニズムを議論する。

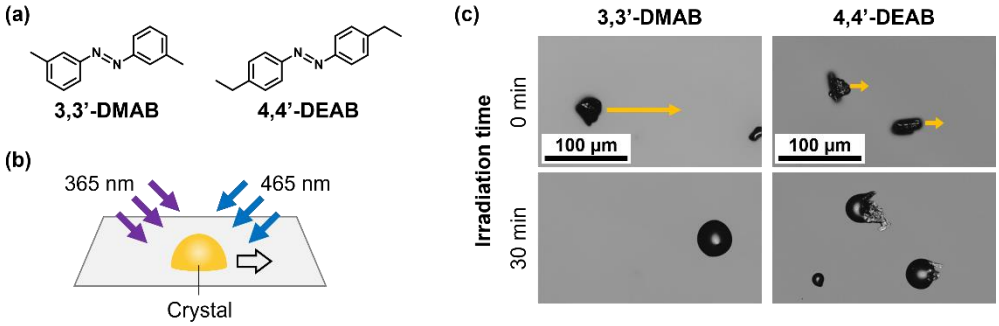

Figure 1. (a) Chemical structure of 3,3’-DMAB and 4,4’-DEAB, (b) Schematic illustration of the crawling motion of the crystal, and (c) Photomicrographs of the crawling motion of the crystals.

1) E. Uchida, R. Azumi, Y. Norikane, *Nat. Commun.* **2015**, *6*, 7310.

2) (a) Y. Norikane, M. Hayashino, M. Ohnuma, K. Abe, Y. Kikkawa, K. Saito, K. Manabe, K. Miyake, M. Nakano, N. Takada, *Front. Chem.* **2021**, *9*, 684767. (b) M. Saikawa, M. Ohnuma, K. Manabe, K. Saito, Y. Kikkawa, Y. Norikane, *to be submitted*.

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アクリジン骨格を基盤とした一次元性ダブルウォールナノチューブの構築と固体電子移動反応場としての応用

（東理大理）○岸 寛之・緒方 大二・湯浅 順平

Acridine-based 1D double-wall nanotubes as a scaffold for solid-state electron transfer

(*Fac. Sci., TUS*) ○Hiroyuki Kishi, Daiji Ogata, Junpei Yuasa

In this study, novel supramolecular Zn^{2+} complexes (**1**) were synthesized from bridging ligands ($\mathbf{L_A}$). Crystal structure analysis revealed that **1** are multinuclear double-walled macrocyclic complexes and have a one-dimensional aligned nanotube structure. The structure is rigid and robust, and $\mathbf{L_A}$ has an acridine backbone with excellent electron-accepting ability, which enables the inclusion of electron-donor guest molecules. When carbazole was encapsulated and brought into contact with the solid oxidant $Fe(ClO_4)_3$, the color changed, suggesting that the carbazole was oxidized. Therefore, we considered that this structure could be applied as a solid-state electron transfer reaction field.

Keywords : Supramolecular complex, Acridine, Zinc, Solid-state electron transfer

固体内でのナノスケールの電子移動（ET）は、機能性ナノ材料の設計において重要な要素の一つである。ナノ材料の中でもユニークな構造であるナノチューブは、電子と正孔をナノチューブ内に蓄積させることによって、固有の電子状態を提供する実用的なナノ材料である。しかし、カーボンベースのナノチューブ材料は、アーク放電法や高温などの苛烈な条件で反応させるため、サイズや形状の制御が困難である。そこで、有機分子または金属大環状分子を柱状に配置し、非共有結合を用いてボトムアップ的に合成することで、サイズや形状の制御が容易な結晶系ナノチューブ材料を作製することができる。こうした考えから、現在、ナノチューブを形成する超分子金属錯体の研究が盛んに行われている。[1)]

本研究では、新規架橋配位子 $\mathbf{L_A}$ と Zn^{2+}から新規大環状金属錯体を合成した(**Figure. a**)。単結晶 X 線構造解析から、これらは多核のダブルウォール大環状錯体 **1** を形成し、一次元状に配列したナノチューブ構造を持つことを明らかにした。この構造は一般的な環状錯体と比べて剛直かつ堅牢であり、また $\mathbf{L_A}$ は電子受容能に優れたアクリジン骨格をもつため、電子ドナーゲスト分子($\mathbf{D_G}$)を包摂できる。実際にカルバゾール(**Cz**)をゲストとして包摂させ、固体酸化剤である $Fe(ClO_4)_3$ を接触させると **Cz** が酸化されて黒褐色に変化した(**Figure. b**)。このことから、固体状で電子移動反応が行われたことが示唆された。

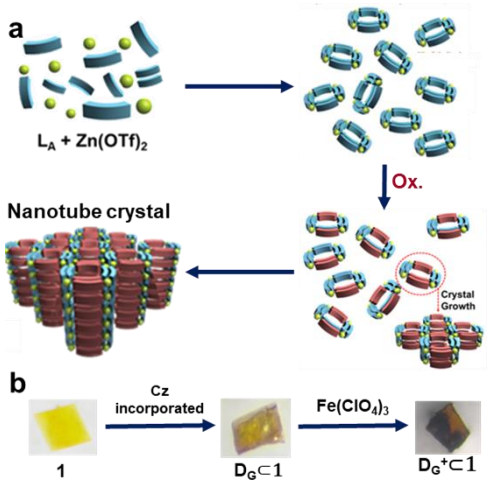

Figure. a) Synthesis of double wall nanotube crystal **1**. b) Change of crystal color.

1) Otsubo, K. Wakabayashi, Y. Ohara, J. Kitagawa, H. et al. *Nat. Mater.* **2011**, *10*, 291–295.

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Academic Program [Poster] | 16. Natural Products Chemistry, Chemical Biology：Poster

Wed. Mar 20, 2024 10:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:00 AM - 2:30 AM UTC Poster Site 3(理工スポーツホール [1階] アリーナ)

[P3-3am] 16. Natural Products Chemistry, Chemical Biology

Japanese

[P3-3am-01]

Chemical degradation of poecillastrins for structural analysis

Raku Irie[1], Zian Han[1], ○Masato Oikawa[1] (1. Yokohama City University)

Japanese

[P3-3am-02]

Functional analysis of putative isomerases in the biosynthesis of macrolactam antibiotic hitachimycin

○Kazuma Tsuboi[1], Ikezaki Mutsumi[1], Koichi Kawamura[1], Tadashi Eguchi[1], Fumitaka Kudo[1] (1. Tokyo Institute of Technology)

Japanese

[P3-3am-03]

Directed Evolution of Product Specificity of 4-hydroxy-3-methyl-2-butenyl diphosphate reductase IspH Using Novel Screening Method for Cellular IPP/DMAPP Ratio

○Aya Nagashima[1], Daichi Ishihara[1], Daisuke Umeno[1] (1. Waseda University)

Japanese

[P3-3am-04]

Effect of various aroma glycosides on glycosidase activity

○Shiori Miyako[1], Yasushi Kawai[1] (1. Nagahama Institute of Bio-Science and Technology)

Japanese

[P3-3am-05]

Synthetic Studies of Interleukin-8 Analog Having High Mannose-type N-glycan

○Taito Akayama[1], Haruna Kanno[1], Masayuki Izumi[1] (1. Kochi University)

Japanese

[P3-3am-06]

Preparation of desmosine-carrier protein conjugated antigen

○Mika Ryu[1], Toyonobu Usuki[1], Mayu Kodaka[1], Reiko Yoko (1. Sophia Univ)

Japanese

[P3-3am-07]

Synthesis of desmosine/isodesmosine-$^{13}C_3$,$^{15}N_1$

○Saki Kondo[1], Mika Hirose, Takahiro Tanigawa, Toyonobu Usuki[1] (1. Sophia University)

Japanese

[P3-3am-08]

Construction of β-hairpin peptides based on dynamic imine bonds

○Harunori Honda[1], Takahiro Nakama[1], Makoto Fujita[1,2,3] (1. Grad. School of Engineering, The Univ. of Tokyo, 2. UTIAS, The Univ. of Tokyo, 3. IMS)

Japanese

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[P3-3am-09]

One-pot Synthesis of Peptide Thiolactone from Hydrazide via Peptide Thioester or Selenoester

○Yuki Funyu[1], Sayaka Sasaki[1], Masayuki Izumi[1] (1. Kochi University)

Japanese

[P3-3am-10]

Fabrication of beta-barrel peptide nanopores using peptide-immobilized beads with photocleavable linkers

○Takuto Kariya[1], Fumihiro Kayamori[1], Ryuji Kawano[2], Kenji Usui[1] (1. Konan University, 2. Tokyo University of Agriculture and technology)

Japanese

[P3-3am-11]

Synthetic Studies on Cyclic Oligosaccharides Using Multivalent Linkers

○Hikari Nishida[1], Tohru Taniguchi[2], Kenji Monde[2] (1. Grad. School of Life Sci., Hokkaido Univ., 2. Grad. School of Advanced Life Sci., Hokkaido Univ.)

Japanese

[P3-3am-12]

Analysis of the main component in the periostracum of the green mussel (*Perna viridis* L.)

○Rena Ikeya[1] (1. Keio University)

Japanese

[P3-3am-13]

Development of a near-infrared fluorescence probe for hROS based on the TICT mechanism.

○Hisashi Ohno[1], Takuya Myochin[2], Shun Sumitani[3], Kenjiro Hanaoka[1,3] (1. Grad. Sch. Pharm. Sci. Keio Univ., 2. Grad. Sch. Pharm. Sci. The Univ. of Tokyo, 3. Fac. Pharm. Keio Univ.)

English

[P3-3am-14]

Development of a natural product-functionalized gold-nanoparticle photoaffinity probe for target analysis

○Masaki ONO[1], Koutharou Abe[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P3-3am-15]

In vivo synthesis of anticancer compounds from acetaldehyde

○Koichi Ishida[1], Ren Kumakura[1], Yudai Ode[1], Ambara Rachmat Pradipta[1], Tsung-che Chang[1], Katsunori Tanaka[1,2] (1. Tokyo Institute of Technology, School of Materials and Chemical Technology, Department of Chemical Science and Engineering, 2. RIKEN Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory)

Japanese

[P3-3am-16]

Photo-chemical control of anticancer activity by novel photo-triggered cyclization reaction

○Hidenori Okamura[1,2], Arisa Kawamori[1,2], Momoka Iida[1,2], Yui Kaneyama[1,2], Mamiko Ozawa[1], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku Univ., 2. Grad. Sch. Sci., Tohoku Univ.)

Japanese

[P3-3am-17]

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Synthesis and biological functions of microbial 6-position-modified glucosyl acylglycerols and their analogues

○Shingo Mochizuki[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Fac. Sci. Tech., Keio Univ.)

Japanese

[P3-3am-18]

Synthetic studies of GlcNCer derivatives with modifying acyl groups

○Ken Shirasaka[1], Kodai Sueyoshi[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Fac. Sci. Tech., Keio Univ.)

Japanese

[P3-3am-19]

Synthesis of novel glycolipids containing cyclopentanetetraol structure for immunomodulatory molecules

○Yuto Aoki[1], Hiroki Sekita[1], Takanori Matsumaru[1], Yukari Fujimoto[1] (1. Fac. Sci. Tech., Keio Univ.)

English

[P3-3am-20]

Improvement of a direct response version of near-infrared genetically encoded Ca^{2+} indicator, dNIR-GECO

○Takumi Kobayashi[1], Rina Hashizume[1], Yong Qian[2], Yusuke Nasu[1], Takuya Terai[1], Robert E. Campbell[1,2] (1. Sch. of Science, The Univ. of Tokyo, 2. Dept. of Chemistry, The Univ. of Alberta)

Japanese

[P3-3am-21]

Unique NMR sampling method controlling water amounts in organic solvent

○Yasuhiro Kajihara[1,2], Tatsuya Moriguchi[1], Yuta Maki[1,2], Ryo Okamoto[1,2] (1. Schl. Sci. Osaka University,, 2. FRC, Grad. Schl. Sci. Osaka university)

Japanese

[P3-3am-22]

Antimutagenic Activity of Fatty Acid Esters from *Pyrus communis*

○Yuki Kakinuma[1], Nozomi Tomaru[1], Atsushi Ogashiwa[1], Kairi Miyashita[1], Hideyuki Tomosaka[1] (1. Nat Inst Tech (KOSEN), Gunma Coll)

Japanese

[P3-3am-23]

Investigation of the photolysis reaction of pyridinium salts

○Kazuma Hiasa[1], Tomohiro Sugiyama[1], Rintaro Gemma[1], Hajime Sato[1,2,3] (1. The Univ. of Yamanashi, 2. Precursory Research for Embryonic Science and Technology, 3. Leading Initiative for Excellent Young Researchers)

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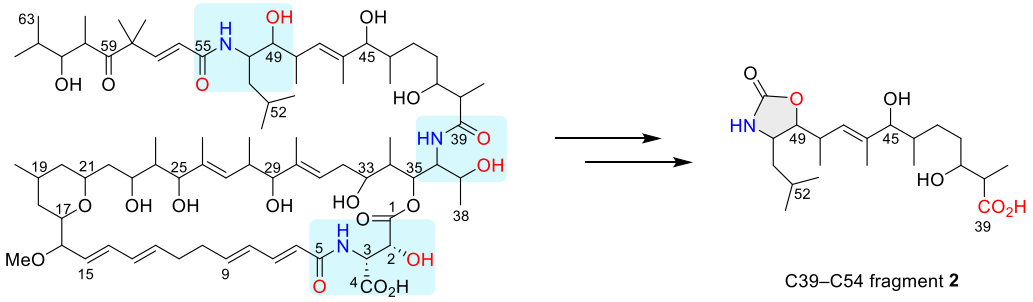
Poecillastrin 類の構造解析に向けた分解反応の試み

（横市大院生命ナノ）入江 樂・韓 子安・○及川 雅人
Chemical degradation of poecillastrins for structural analysis
(*Yokohama City University*) Raku Irie, Zian Han,○Masato Oikawa

Poecillastrins are structurally complex marine natural products with multiple unassigned stereogenic centers. In this study, we aimed to chemically degrade poecillastrins into smaller fragments for structural analysis. We attempted to cleave the *N*-(2-hydroxyalkyl)amide moieties of poecillastrins through oxazolidinone formation at a nanomolar scale, and successfully detected several fragments including its side chain in LC-MS analysis.
Keywords : marine natural product; structural analysis; chemical degradation; amide bond; LC-MS

Poecillastrin 類は化学構造の複雑さと試料の稀少性から、立体化学を含む完全な構造決定がなされていない海洋天然物である。演者らは主成分 poecillastrin C（**1**）の基本骨格を化学的に分解し、天然物に 25 個含まれる不斉炭素原子の数を減らしたフラグメントへと導いたうえで構造解析する方針を立てた。本研究では分子内に 3 箇所存在する「水酸基が隣接したアミド結合」に着目し、ここでの選択的な切断反応によって側鎖がマクロ環から切り離されたフラグメント **2** を得ることに成功したので、モデル化合物を用いた検討とあわせて報告する。



1) Takada, K.; Choi, B. W.; Rashid, M. A.; Gamble, W. R.; Cardellina, J. H., II; Van, Q. N.; Lloyd, J. R.; McMahon, J. B.; Gustafson, K. R. *J. Nat. Prod.* **2007,** *70*, 428.
2) Irie, R.; Takada, K.; Ise, Y.; Ohtsuka, S.; Okada, S.; Gustafson, K. R.; Matsunaga, S. *Org. Lett.* **2017,** *19*, 5395.

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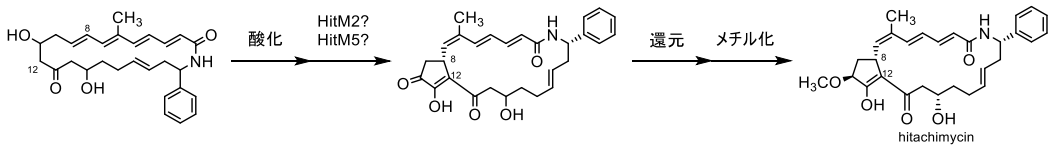
マクロラクタム抗生物質ヒタチマイシン生合成における推定異性化酵素の機能解析

（東工大理[1]）○坪井 一馬[1]・池崎 睦実[1]・川村 紘一[1]・江口 正[1]・工藤 史貴[1]
Functional analysis of putative isomerases in the biosynthesis of macrolactam antibiotic hitachimycin ([1]*Department of Chemistry, Tokyo Institute of Technology*) ○Kazuma Tsuboi,[1] Mutsumi Ikezaki,[1] Koichi Kawamura,[1] Tadashi Eguchi,[1] Fumitaka Kudo[1]

Hitachimycin is a macrolactam antibiotic with a unique bicycle polyketide skeleton produced by *Streptomyces scabrisporus*. This study focuses on the functional analysis of two putative isomerases, HitM2 and HitM5, which appear to facilitate the carbon-carbon bond formation between C8 and C12 within hitachimycin's distinctive bicyclic polyketide structure. Initially, we supplemented two putative biosynthetic intermediates, derived from disruption mutants, to the *hitM2* and *hitM5* gene disruption mutants to confirm the involvement of the *hitM5* gene in the post-PKS modification reaction. Subsequently, we conducted in vitro functional analysis of HitM2 and HitM5 using these biosynthetic intermediates.
Keywords : hitachimycin; macrolactam antibiotic; biosynthesis; polyketide; post-PKS

ヒタチマイシンは、放線菌 *Streptomyces scabrisporus* が生産するマクロラクタム抗生物質であり、ポリケチド骨格の C8 位と C12 位が結合した特徴的な二環式ポリケチド構造を有している。ポリケチド合成酵素（PKS）によって形成される生合成中間体が修飾反応を受けて生合成されると考えられ、ポスト PKS 修飾反応に関わると推定された酵素の遺伝子破壊実験については既に報告している。本研究では、C8 位と C12 位の炭素–炭素結合形成に関わると推定された異性化酵素 HitM2 と HitM5 の機能解析を行った。まずこれら酵素の遺伝子破壊株に別の破壊株が蓄積する推定生合成中間体を投与して、少なくとも HitM5 はポスト PKS 修飾反応に関わることを確認した。現在、これら生合成中間体を用いて、大腸菌にて異種発現させ調製した HitM2 と HitM5 の in vitro での機能解析を進めており、合わせて報告する。



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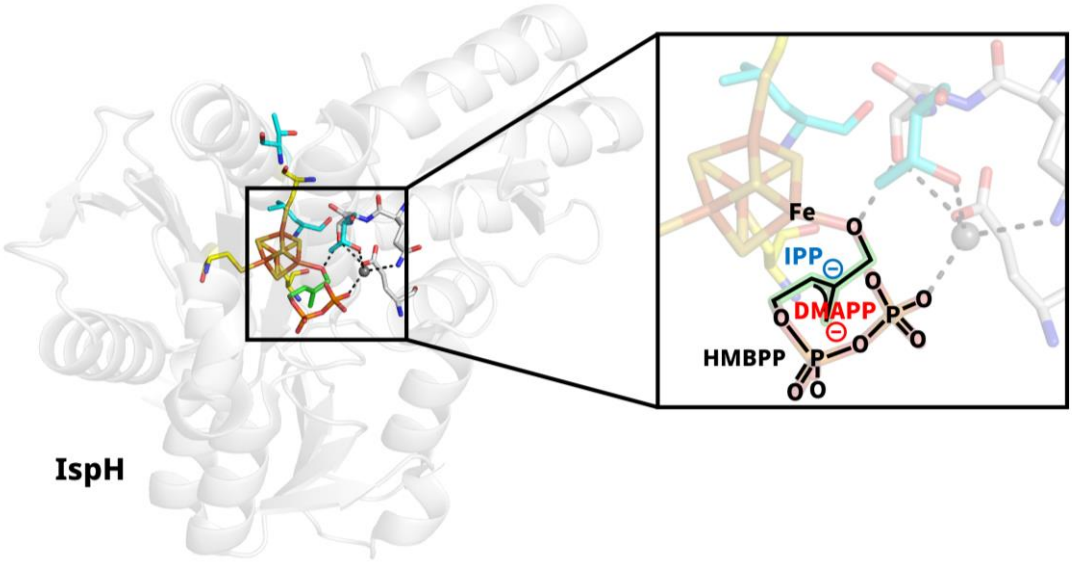
新規 IPP/DMAPP 比スクリーニング法を用いた 4-ヒドロキシ-3-メチル-2-ブテニルニリン酸レダクターゼ IspH の生産物特異性の改変

（早稲田大先進理工[1]）○長島 綾[1]・石原 大地[1]・梅野 太輔[1]

Directed evolution of product specificity of 4-hydroxy-3-methyl-2-butenyl diphosphate reductase IspH using novel screening method for cellular IPP/DMAPP ratio ([1]*Department of Applied Chemistry, Waseda University*) ○ Aya Nagashima,[1] Daichi Ishihara,[1] Daisuke Umeno[1]

Isoprenoids are a class of compounds with commercial value such as fragrances, drugs, and pigments. They all are synthesized by the stepwise addition of IPPs (elongation units) to DMAPP (starter unit). We discovered that some of the nonnatural carotenoid pathways we previously created exhibit significant change in their product size speciticities, reflecting the change in intracellular ratio of IPP and DMAPP. This phenomenon was used for isolating IspH mutants with altered product specificity (IPP/DMAPP production ratio) from random libraires.
Keywords : Synthetic Biology; Directed Evolution; Metabolic Engineering; Isoprenoids; Carotenoids

イソプレノイド類は，香料や医薬品，色素など多様な用途を持ち，産業的に有用な化合物群である．イソプレノイド骨格は全て，ジメチルアリル二リン酸（DMAPP）へのイソペンテニル二リン酸（IPP）の逐次付加によって合成される．我々は，以前作成したサイズ特異性の低い人工カロテノイド経路が，細胞内の IPP/DMAPP 比の変化を反映して著しく生産物を変化させることを発見した．この現象を利用したスクリーニング系によって大腸菌のイソプレノイド前駆体供給経路の最終ステップを担う 4-ヒドロキシ-3-メチル-2-ブテニル二リン酸レダクターゼ（IspH）変異体のプロダクト特異性（IPP/DMAPP 産生比）を決定づける残基の組織的な探索を行った．



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様々な香気成分配糖体がグリコシダーゼ活性に与える影響

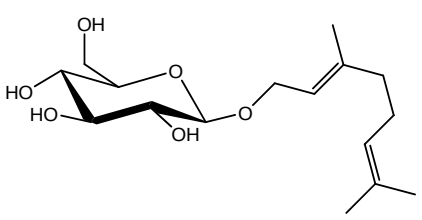
(長浜バイオ大院バイオサイエンス)○都詞織、河合靖

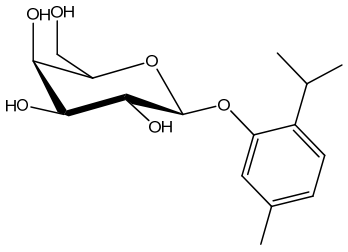
Effect of various aroma glycosides on glycosidase activity. (*Graduate School of Bioscience, Nagahama Institute of Bio-Science and Technology*)○Shiori Miyako, Yasushi Kawai

While the bioactivity of aroma compounds has been studied extensively, little has done on their glycosides, which are structures that allow plants to stably store these aroma compounds. Because of their structural diversity, some of them are expected to be used as drugs in the future. Therefore, we have synthesized about 10 glycosides (glucopyranoside, galactopyranoside, *etc*.) of several aroma compounds having hydroxyl group such as geraniol and menthol, and investigated their effects on various glycosidase activities. These glycosides did not have such a strong effect with IC_{50} values of about 2 mM, but the inhibition efficiency differed greatly among the mirror isomers of aroma components and among the different sugar structures. The results of systematic evaluation of these inhibitory activities will be reported.

Keywords : Aroma glycosides, Glycosidases, Inhibitory effects

現在までに香気成分の生理活性に関する多くの研究が行われてきたが、植物がこれらの香気成分を安定的に貯蔵するための構造である香気成分配糖体の生理活性に関する研究はほとんどなされていない。これらには構造の多様性があるので、その中には将来的に医薬品として利用可能な生理活性分子があると期待される。そこで水酸基を持つゲラニオールやチモールなどの複数の香気成分の配糖体(グルコピラノシドやガラクトピラノシドなど)を 10 種類ほど合成し、それらが種々のグリコシダーゼ活性に与える影響を検討した。最も顕著な阻害効果を示した香気成分配糖体の IC_{50} 値は 2 mM 程度とそれ程強い効果は無かったが、香気成分の鏡像異性体間や糖の構造の違いだけで阻害の傾向が大きく異なることが示された。本講演では、これらの阻害活性を系統的に評価した結果について報告する。





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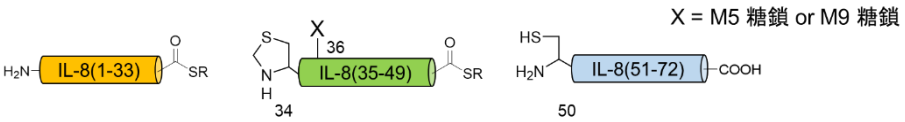
ハイマンノース型糖鎖を有するインターロイキン-8 アナログの合成研究

（高知大理工）○赤山 泰斗・菅野 遥南・和泉 雅之
Synthetic Studies of Interleukin-8 Analog Having High Mannose-Type N-glycan (*Faculty of Science and Technology, Kochi University*) ○Taito Akayama, Haruna Kanno, Masayuki Izumi

During the biosynthesis of glycoproteins in the endoplasmic reticulum, the high mannose-type glycan structure acts as a tag. Glycoproteins folded in a native form bearing M9 glycan proceed to the secretory pathway, whereas M9 glycan on misfolded glycoproteins is hydrolyzed to M5 glycan and proceed to the degradation pathway. To examine the effect of glycan size on the folding of glycoproteins, we decided to synthesize interleukin-8 (IL-8) analogs bearing M9 or M5 glycan at Asn36.[1] Fmoc-Asn(M9) and Fmoc-Asn(M5) required for the synthesis of glycopeptides were prepared from delipidated hen egg yolk.[2] Because of the relatively small amount of M5 glycan compared to M9 glycan, we examined a three-segment coupling strategy, employing IL-8 (1–33), M9/M5-IL-8 (34–49), and IL-8 (50–72).[3] In this presentation, we report glycopeptide synthesis and ligation of the three (glycol)peptide segments.
Keywords : high mannose-type glycan, M9 glycan, M5 glycan, chemical protein synthesis, protein folding

小胞体内での糖タンパク質の生合成過程において、ハイマンノース型糖鎖の構造が、分泌経路に進むか、分解経路に進むかを区別するタグとなっている。天然型にフォールディングした M9 糖鎖をもつ糖タンパク質は分泌経路へと進み、ミスフォールドした糖タンパク質の糖鎖は M5 までトリミングされて分解経路へと進む。本研究では、糖鎖の大きさが糖タンパク質のフォールディングに与える影響を調べる目的で、Asn36 に M9 または M5 糖鎖を有する IL-8 アナログ [1]の化学合成を検討した。

糖ペプチドの合成に必要な Fmoc-Asn(M9)と Fmoc-Asn(M5)は、脱脂卵黄から既知の方法で単離した [2]。M9 糖鎖に比べて M5 糖鎖の収量が少ないため、合成する糖ペプチドセグメントの鎖長を短くし、72 残基の全長ポリペプチド鎖を 1–33, 糖鎖を有する 34–49, 50–72 の 3 つの（糖）ペプチドセグメントに分割するストラテジーで合成することとした [3]。現在、1–33 と 50–72 ペプチドセグメントの合成を完了し、糖鎖を有する 34–49 ペプチドの合成を検討している。



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Desmosine-キャリアタンパク質複合体抗原の作製

（上智大理工）〇劉 美佳・小高 愛悠・横尾 玲子・臼杵 豊展

Preparation of desmosine-carrier protein conjugated antigen (*Faculty of Science and Technology, Sophia University*) 〇Mika Ryu, Mayu Kodaka, Reiko Yokoo, Toyonobu Usuki

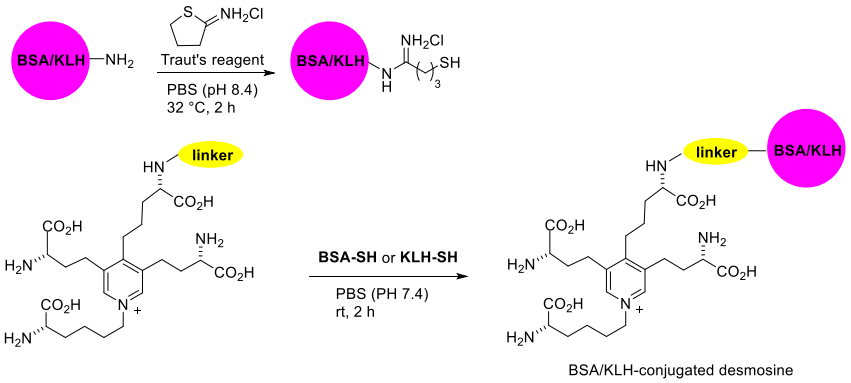
Desmosine is a major crosslinking amino acid in elastic fiber elastin. Our laboratory has succeeded in quantitative analysis of desmosine using LC-MS/MS, but this measurement method requires advanced technology, high cost and sample pretreatment. In this study, we aimed to establish a simpler and more versatile ELISA method. Since desmosine is too small to have immunogenicity, we need to create desmosine-protein complex antigen which a carrier protein BSA/KLH is linked and impart immunogenicity to desmosine.

Synthesis of desmosine along with the linkers was achieved by Sonogashira and Negishi cross-coupling and amidation. Michale addition with thiolated carrier protein (BSA/KLH) was then conducted and desmosine-BSA/KLH conjugates was obtained.

Keywords : Desmosine; ELISA ;cross-coupling reaction; antigen; carrier protein

Desmosine は、皮膚や肺胞などに含まれる弾性線維エラスチンの主要な架橋アミノ酸である。当研究室では LC-MS/MS による desmosine の定量分析に成功した [1]。一方、本測定法では高度な技術、高価な機器や試料への前処理が必要なため、大量分析や診断法としての活用は現実的ではない。本研究では、より簡便で汎用性のある ELISA 法の確立を目指し、desmosine の抗体作製を目的とした。分子量が小さく抗原単体では免疫原生をもたない desmosine (MW: 526)に免疫原生を付与するため、マレイミドリンカーでキャリアタンパク質 BSA/KLH を結合させた desmosine-BSA/KLH 複合体抗原の作製に着手した [2]。

菌頭および根岸クロスカップリング、縮合反応によってリンカーを結合させた desmosine を合成した後、トラウト試薬を用いてチオール化したキャリアタンパク質とのマイケル付加反応により desmosine-BSA/KLH 複合体抗原の作製を達成した。



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Desmosine/isodesmosine-$^{13}C_3$,$^{15}N_1$ の Chichibabin ピリジニウム合成

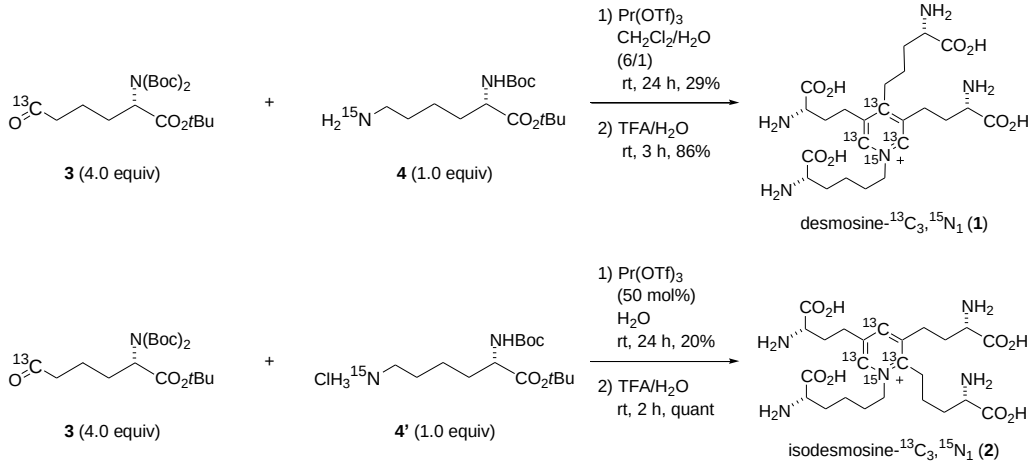
（上智大理工）○近藤 沙季・広瀬 美香・谷川 貴寛・臼杵 豊展
Synthesis of desmosine/isodesmosine-$^{13}C_3$,$^{15}N_1$ (*Faculty of Science and Technology, Sophia University*) ○Saki Kondo, Mika Hirose, Takahiro Tanigawa, Toyonobu Usuki

Desmosine and isodesmosine are crosslinking amino acids of elastin that contribute to elasticity of ligaments, skin, etc. They are expected to be biomarkers for diseases associated with elastin degradation. In this study, syntheses of internal standards desmosine-$^{13}C_3$,$^{15}N_1$ (**1**) and isodesmosine-$^{13}C_3$,$^{15}N_1$ (**2**) for quantitative LC-MS/MS analysis of desmosine and isodesmosine were targeted.

Starting from commercially available protected glutamic acid, **3** was obtained via introduction of Wittig reaction to incorporate ^{13}C atom. **4** and **4'** was obtained via S_N2 reaction using K^{15}N to insert ^{15}N atom. Synthesis of **1** and **2** were then achieved by removing all protecting groups after Chichibabin pyridinium synthesis using **3** and **4**[1] or **4'**[2].

Desmosine および isodesmosine は、靭帯や皮膚などの弾性・伸縮性に寄与する弾性線維エラスチンの架橋アミノ酸である。これらはエラスチンの分解に伴う疾患のバイオマーカーとして期待されている。本研究では、desmosine および isodesmosine の厳密な LC-MS/MS 定量分析に用いる内部標準物質として desmosine-$^{13}C_3$,$^{15}N_1$ (**1**)および isodesmosine-$^{13}C_3$,$^{15}N_1$ (**2**)の合成を目指した。

購入可能なグルタミン酸保護体を出発物質とし、Wittig 反応により ^{13}C を導入して **3** を合成した。また、K^{15}N を用いた S_N2 反応により ^{15}N を導入し、**4** および **4'**を得た。**3** と **4** もしくは **4'**を用いて Chichibabin ピリジニウム合成を行った後に、全ての保護基を除去することによって **1** および **2** の合成を達成した[1, 2]。



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動的イミン結合を用いたβ-ヘアピンペプチドの構築

（東大院工[1]・東大国際高等研[2]・分子研[3]）○本田 陽紀[1]・中間 貴寛[1]・藤田 誠[1,2,3]
Construction of β-hairpin peptides based on dynamic imine bonds ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*UTIAS, The University of Tokyo,* [3]*Institute for Molecular Science*) ○Harunori Honda,[1] Takahiro Nakama,[1] Makoto Fujita[1,2,3]

Because of their uncontrolled folding, it has been challenging to construct high-order protein structures with their functions from chemically synthesized peptides. We have previously shown that the folding and assembly of short peptides through dynamic metal coordination bonding allow for the construction of a variety of high-ordered structures[1)]. In this study, we aimed to construct protein-like structures from short peptides using dynamic covalent imine bonds, which have a chemical structure similar to peptide bonds.

We here discuss the synthesis of β-hairpin using dynamic imine bonding. A β-hairpin is composed of a turn unit containing D-proline (DPro) and hydrophobic β-strands. We introduced a formyl group at the C-terminus of the turn moiety DPro-Gly to construct a β-hairpin structure by imine bond formation (**Fig. 1**). A five-residue peptide modified with a formyl group was synthesized by solid-phase synthesis. It was conjugated with a short peptide chain by imine bonding, and the structure of the product was evaluated.

Keywords : Peptide; β-hairpin; Imine bond; Dynamic covalent chemistry; Self-assembly

化学合成した長鎖ペプチドの折りたたみを制御し、タンパク質の高次構造・機能を再現することは困難である。当研究室では、動的な金属配位結合を活用して短鎖ペプチド鎖の集合と折りたたみを誘起し、多様な高次構造の構築を示してきた[1)]。本研究では、イミン結合のペプチド結合との類似性に着目し、イミンの動的共有結合を用いて短鎖ペプチド鎖からタンパク質様の高次構造を構築することを目的とする。

本発表では、イミン結合を用いたβ-ヘアピン構造の構築を議論する。β-ヘアピンは、D-プロリン(DPro)を含むターン部分と疎水性残基からなるβ-ストランドで構成される。ターン部分 DPro-Gly の C 末端にホルミル基を導入し、イミン結合形成に伴うβ-ヘアピンの構築を目指した(**Fig. 1**)。ホルミル基で修飾した 5 残基ペプチド鎖を固相合成法により合成した。これと短鎖ペプチドとのイミン縮合を行い、その構造を評価した。

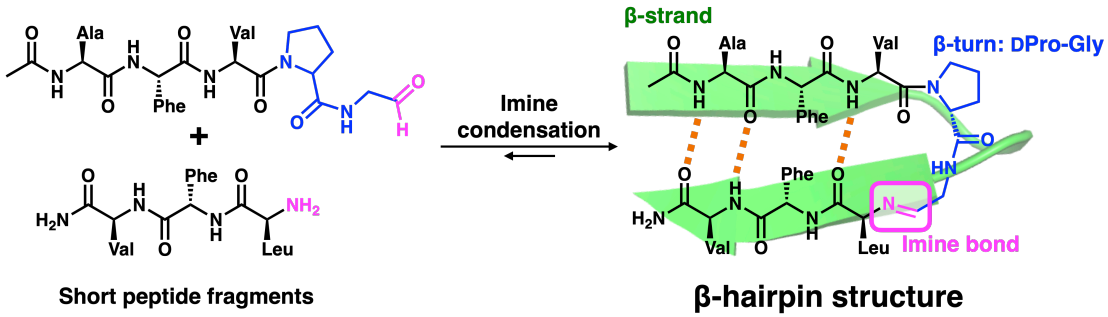

Fig. 1 Synthesis of β-hairpin structures by imine bond formation from short peptide fragments.

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チオエステルまたはセレノエステルを経由するペプチドヒドラジドのチオラクトンへのワンポット変換反応

（高知大理工）○船生 悠貴・佐々木 沙也佳・和泉 雅之

One-pot Synthesis of Peptide Thiolactone from Hydrazide via Peptide Thioester or Selenoester

(*Faculty of Science and Technology, Kochi University*) ○ Yuki Funyu, Sayaka Sasaki, Masayuki Izumi

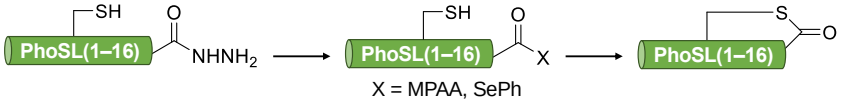
Native chemical ligation (NCL), which involves the chemoselective coupling of a peptide thioester with a cysteinyl peptide, is commonly used in chemical protein synthesis. We have been studying the use of peptide thiolactone as a thioester surrogate because free thiols are not released after the ligation, which simplifies the purification of ligated peptides and is also advantageous for an NCL-desulfurization protocol to convert cysteine to alanine. Here, we report a one-pot conversion of peptide hydrazide to thiolactone via thioester of selenoester.

PhoSL (1–16) peptide [APVPVTKLVCDGDTYK] was synthesized as hydrazide by Fmoc solid phase peptide synthesis. Then, hydrazide was converted to thioester by treatment with acetylacetone and 4-mercaptophenylacetic acid (MPAA) at pH 3.[1] Subsequently, the pH of the reaction was adjusted to 6 to yield thiolactone in one pot. Thiolactone was also obtained using diphenyl diselenide[2] instead of MPAA at pH 3.5 via selenoester without changing the pH.

Keywords: Native chemical ligation; peptide thiolactone; thioester; selenoester; one-pot reaction

ネイティブケミカルライゲーション(NCL)法は、C 末端がチオエステルのペプチドと N 末端がシステインのペプチドとの化学選択的な連結反応であり、タンパク質化学合成に汎用されている。当研究室では、反応後に遊離のチオールが生成しないチオラクトンを利用した NCL を検討しており、一昨年の年会で報告した。遊離のチオールが生成しない利点は、反応後の連結されたポリペプチドの精製が容易であることと、連結部位のシステインをアラニンに変換する NCL-脱硫化を精製なしに行えることである。本研究では、チオラクトンのワンポット合成法を確立したので報告する。

チオラクトンへのワンポット変換反応は、PhoSL (1–16) [APVPVTKLVCDGDTYK] ペプチドヒドラジドを利用して検討した。まず、ペプチドヒドラジドを pH 3 でアセチルアセトンと MPAA と反応させることでチオエステルへと変換し [1]、その反応液の pH を 6 に調整することでチオラクトンを得た。同様の条件でペプチドヒドラジドをセレノエステルに変換する反応 [2]を各種の pH で検討したところ、pH 3.5 でセレノエステルを経由してそのままチオラクトンに変換されることを見出した。



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光開裂リンカー固定化ビーズを用いたβバレル型ペプチドナノポアの作製

(甲南大 FIRST[1]・東京農工大工[2]) ○仮屋 拓斗[1]・栢森 史浩[1]・川野 竜司[2]・臼井 健二[1]

Fabrication of beta-barrel peptide nanopores using peptide-immobilized beads with photocleavable linkers ([1]*Faculty of Frontiers of Innovative Research and Technology (FIRST), Konan University*, [2]*Department of Biotechnology, Tokyo University of Agriculture and Technology*), ○Takuto Kariya,[1] Fumihiro Kayamori,[1] Ryuji Kawano,[2] Kenji Usui[1]

Nanopores are used for various applications such as sequencing of DNA, RNA, and proteins. Recently, peptide-based nanopores including beta-strand peptides have attract much attention. We have developed a simple method of the beta-strand peptide synthesis that enables comprehensive analysis to investigate the correlation between peptide sequences and structures of nanopores. However, using *O*-acyl isopeptide method to suppress the aggregation of the peptides, it limited the design of peptide sequences. Therefore, we linked peptides to microbeads via a photocleavable moiety, and then could cleave the peptides from the microbeads by light irradiation immediately before nanopore-formation of the peptides were analyzed.

Keywords : peptide nanopore; photocleavable linker; beta-strand peptide; aggregation; solid-phase peptide synthesis

ナノポアとは数 nm の細孔であり、核酸やタンパク質のシーケンシングなどに用いられている[1)]。ナノポアの分子選択性は、設計されたナノポアの構造やサイズに依存するが、現状のナノポア作製法ではそれらの制御、また機能の付加についても難しい。近年、ペプチドを用いたナノポアが注目されている。ペプチドを使用する利点として、合成が簡便である、二次構造を設計できる、自己集合により安定な機能性ナノ構造体を作製できるなどの点が挙げられる。そこで我々は以前、βシートペプチドから成るβ-バレル型ナノポアを開発した[2)]。このβシートペプチドの合成では、*O*-アシルイソペプチド法を用い、合成や精製時に問題となるペプチドの凝集の抑制に成功している[3)]。しかし、多数のペプチド配列とナノポアの立体構造との相関を網羅的に解析するためには、より簡便かつ効率的な合成法が必要となる。そこで本研究では *O*-アシルイソペプチド法を使用しないペプチドの合成法を検討した。樹脂には PEGA、光開裂リンカーとして *O*-フェニルプロピオニルリンカーを用いて、固相合成により樹脂に担持された SVG28 を得た。SVG28 担持樹脂への光照射後、得られた SVG28 について各種分析を行ったところ、*O*-アシルイソペプチド法により合成した SVG28 と同等の結果が得られた。本手法を用いることにより、従来では不可能であった SVG28 の高純度合成とナノポア解析が可能であることが示唆された。

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多価リンカーを用いた環状オリゴ糖の合成研究

(北大院生命[1]・北大院先端生命[2]) ○西田ひかり[1]・谷口透[2]・門出健次[2]

Synthetic Studies on Cyclic Oligosaccharides Using Multivalent Linkers

(Grad. School of Life Sci., Hokkaido Univ[1], Grad. School of Advanced Life Sci., Hokkaido Univ.[2]) ○Hikari Nishida[1], Tohru Taniguchi[2], Kenji Monde[2] (1. Grad. School of Life Sci., Hokkaido Univ., 2. Grad. School of Advanced Life Sci., Hokkaido Univ.)

Cyclic oligosaccharides other than cyclodextrin have rarely been studied because of difficulties in their synthesis. In this study, we aim to develop a new synthetic method for cyclic oligosaccharides using multivalent linkers. The linkers were designed to display several mono- or disaccharide molecules with their glycosidation reaction points located in a close vicinity to produce cyclic oligosaccharides. In this presentation, we show the synthesis of a glucose octamer using a tetravalent linker toward preparation of a cyclic glucose octasaccharide.

Keywords : cyclic oligosaccharide, glucose, multivalent linker

環状オリゴ糖は複数の糖分子が環状に連なっている分子の総称であり、代表的なシクロデキストリン以外にもシクロアワオドリンやシクロデキストランなど様々な分子が存在する。環状オリゴ糖はシクロデキストリンのみが広く利用されている一方で、その他の環状オリゴ糖やその構造類縁体などは、合成の困難さのため機能解明や利用が進んでいない。本研究では、環化前の糖同士の反応点が近くなるように設計した多価リンカーを用いた環状オリゴ糖の新規合成法の開発を目指す。具体的な戦略として、中心にコア分子を含む多価リンカーに短い糖鎖を組み合わせ、糖同士を円状に配置する。これにより、環化の際の反応点が近くなること、また任意の長さの環状糖鎖を比較的単純な二糖類や三糖類から、リンカーの価数の組み合わせによって合成することが可能となると考えられる。本発表では４価リンカーを用いた環状グルコース８糖の合成研究について紹介する。

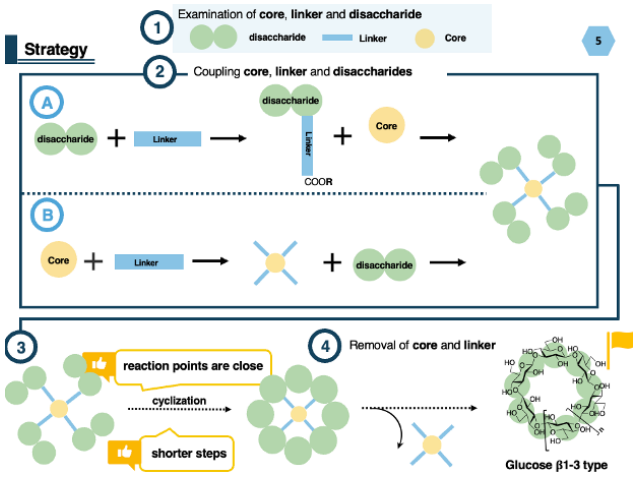

Fig. 合成の戦略

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ミドリイガイ殻皮主成分の解析

（慶大理工）○池谷 玲奈・佐藤 未歩・川本 瑛・中谷 優梨香・森 信之介・犀川 陽子
Analysis of the main component in the periostracum of the green mussel (*Perna viridis* L.)
(*Faculty of Science and Technology, Keio University*) ○ Rena Ikeya, Miho Sato, Aki Kawamoto, Yurika Nakatani, Shinnosuke Mori, Yoko Saikawa

The green mussel (*Perna viridis* L.) is a bivalve with a green shell, composed of a calcareous ostracum and organic periostracum covering the outer surface. In the course of investigations into the pigments in periostraca, the ^{1}H NMR spectrum of HCl extract from the periostraca predominantly exhibited signals attributed to glycine and tyrosine, with a ratio of 2:1[1)], suggesting that the periostraca consist of glycine and tyrosine. Here, we isolated the main component from the HCl extract and identified it with a tripeptide, glycine-tyrosine-glycine, based on the ^{1}H and ^{13}C NMR spectral data. The absolute configuration of the tyrosine was determined to be L-configuration by the advanced Marfey's method. Subsequently, glycine-L-tyrosine-glycine was chemically synthesized; its NMR spectra were identical to those of the isolated natural product, confirming that the main component of the extract is glycine-L-tyrosine-glycine. In addition, the retrieved transcriptome profiles of the mantle, the secretory organ of the periostracum, revealed a significant number of sequences encoding glycine-L-tyrosine-glycine repeats. These findings suggest that the periostraca are composed mainly of polypeptides containing glycine-L-tyrosine-glycine.
Keywords : Perna viridis L.; Peptide; Periostracum

ミドリイガイ (*Perna viridis* L.) は緑色の貝殻をもつ二枚貝で、その貝殻は炭酸カルシウムからなる殻質層とその表面を覆う殻皮から構成される。この殻皮に含まれる色素を調べるため、塩酸で抽出すると、粗抽出物の ^{1}H NMR スペクトルはグリシンとチロシンに由来するシグナルを主に示し、その比は 2:1 であった [1)]。このことから殻皮主成分がグリシンとチロシンから構成されると予想し、主成分の単離・構造決定を行なった。殻皮が完全に溶解するまで塩酸にて抽出し、得られた粗抽出物を各種クロマトグラフィーによって精製し、主成分を単離した。その ^{1}H および ^{13}C NMR スペクトル解析より、主成分はグリシン-チロシン-グリシンのトリペプチドであると推定した。また、改良 Marfey 法によりチロシンは L 体であると決定した。グリシン-L-チロシン-グリシンを化学合成し、天然物の NMR スペクトルと比較すると、良い一致を示し、抽出物の主成分はグリシン-L-チロシン-グリシンであると決定した。また殻皮の分泌器官である外套膜のトランスクリプトームデータを公共データベースから取得して解析したところ、グリシン-L-チロシン-グリシンの繰り返し配列が多く認められた。以上のことから、殻皮は主にグリシン-L-チロシン-グリシンのポリペプチドから構成されていることが示唆された。

1. 森信之介、川本暎、宮澤史明、木内達也、佐藤未歩、池谷玲奈、宮崎翔、中田雅也、犀川陽子、ミドリイガイに含まれる色素ならびにペプチド、日本化学会第 103 春季年会 (2023)、P2-1vn-39

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TICT 機構に基づいた hROS 検出近赤外蛍光プローブの開発

(1. 慶應大院薬、2. 東大院薬、3. 慶應大薬) ○大野 久史[1]、明珍 琢也[2]、炭谷 峻[3]、花岡 健二郎[1,3]

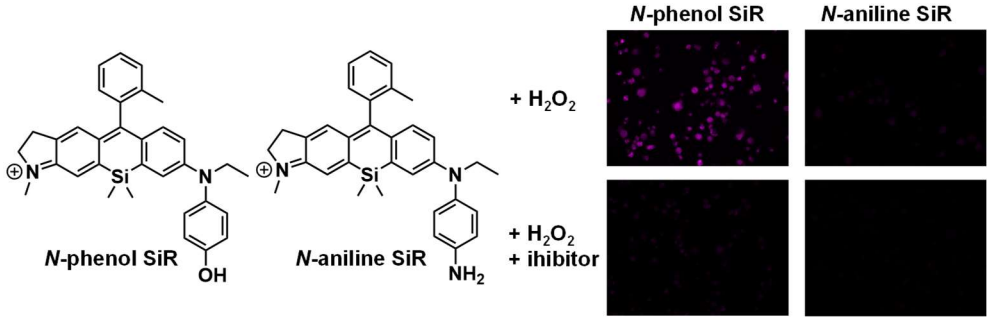
Development of a near-infrared fluorescence probe for hROS based on the TICT mechanism

(1. Grad. Sch. Pharm. Sci., Keio Univ., 2. Grad. Sch. Pharm. Sci., The Univ. of Tokyo, 3. Fac. Pharm., Keio Univ.) ○Hisashi Ohno[1], Takuya Myochin[2], Shun Sumitani[3], Kenjiro Hanaoka[1,3]

Highly reactive oxygen species (hROS) such as HOCl are important biomolecules in life science, because they are involved in redox biosystems and mediate various biological phenomena. We have previously reported that the fluorescence on/off change of rhodamines with a phenyl group on the N atom can be controlled by the twisted intramolecular charge transfer (TICT) process.[1] In this study, we developed fluorescence probes, in which phenol and aniline groups were introduced to the N atom of Si-rhodamines, and these probes showed a rapid fluorescence increase upon reaction with HOCl. Further, when HL60 cells expressing myeloperoxidase (MPO) were incubated with *N*-phenol SiR or *N*-aniline SiR followed by the addition of H_2O_2, *N*-phenol SiR reacted with intracellularly produced HOCl and showed a large fluorescence increase, while *N*-aniline SiR showed almost no fluorescence increase.

Keywords: Fluorescent probe, Reactive oxygen species, Near-infrared fluorescence

HOCl などの反応性の高い活性酸素種(hROS)は、様々な生命現象に関わることから生命科学研究において重要な生体分子である。我々はこれまでに N 原子上にフェニル基を導入した rhodamine 類がねじれ型分子内電荷移動(TICT)によって蛍光の on-off を制御可能であることを報告している。本研究では、近赤外蛍光を有する Si-rhodamine 類の N 原子上に phenol 基または aniline 基を導入した *N*-phenol SiR および *N*-aniline SiR を開発した。*In vitro* において、何れのプローブも HOCl との反応により速やかな蛍光上昇を示した。さらに、HOCl 産生酵素である myeloperoxidase (MPO)が発現している HL60 細胞に対して *N*-phenol SiR または *N*-aniline SiR を加えてインキュベートした後に MPO の基質である H_2O_2 を添加したところ、細胞内で産生する HOCl と反応して *N*-phenol SiR は大きな蛍光上昇を示したのに対し、*N*-aniline SiR はほとんど蛍光上昇を示さなかった。



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Development of gold-nanoparticle photoaffinity probes for target identification of natural products

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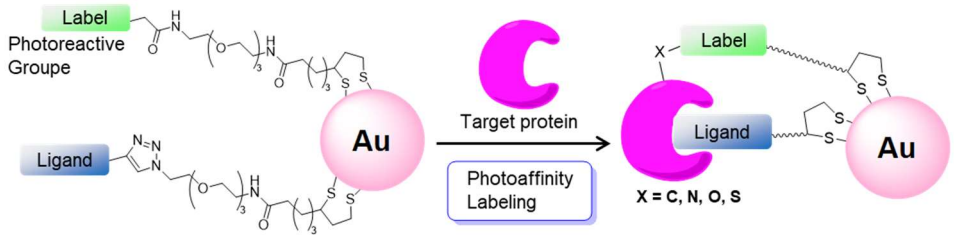
Keywords: Natural products; Photoaffinity labeling; Photoreactive group; Target identification; Gold nanoparticles.

Photoaffinity labeling is a powerful target identification method because it can covalently capture direct target proteins. To facilitate the probe synthesis and design optimization, we developed gold-nanoparticle probes that can be rapidly assembled with a carbohydrate ligand and a photoreactive group.[1-3] However, it is challenging to maintain the colloidal stability of functionalized nanoparticles and the scope of the applications of the gold-nanoparticle probes to various types of ligands remains to be explored. In this presentation, we have designed and synthesized new gold nanoparticle-based photoaffinity probes bearing a hydrophobic and medium-sized natural product ligand.

Based on our previous studies, we designed and synthesized two building blocks composed of lipoic acid moiety and either a natural product ligand or a photoreactive group conjugated with a triethylene glycol (PEG3) linker. Selective acylation method[4] was employed to install hexynoyl moiety to a ligand, which then was conjugated to azide-terminated PEG linker by click chemistry. Several photoreactive groups were employed to optimize the outcome of photoaffinity labeling. Two building blocks and a spacer bearing PEG3 were functionalized to gold nanoparticles with various ratios by ligand exchange reaction to provide photoaffinity probes with different compositions.



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アセトアルデヒドを用いた生体内合成化学治療

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In vivo synthesis of anticancer compounds from acetaldehyde ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Biofunctional Synthetic Chemistry Laboratory*, *Cluster for Pioneering Research, RIKEN*) ○Koichi Ishida,[1] Ren Kumakura,[1] Yudai Ode,[1] Ambara R. Pradipta,[1] Tsung-Che Chang,[1] Katsunori Tanaka[1,2]

Previously, we developed an innovative approach that uses an artificial metalloenzyme to protect a transition metal catalyst within a hydrophobic pocket of albumin.[1)] Furthermore, by manipulating the glycans present on the albumin surface, we effectively targeted cancer cells.[2)] We also utilized a Lewis acid as an artificial metalloenzyme with the transition metal catalyst. In this research, we focus on synthesizing anti-cancer compounds using acetaldehyde, a byproduct of alcohol consumption, as a non-toxic raw material. By reacting with acetaldehyde in vivo, we investigated the synthesis of the anti-cancer active molecules locally at the cancer using a metal catalyst. This approach is expected to be highly effective in eradicating side effects as the reaction targets the cancer cells.

Keywords: In vivo synthesis; Cancer therapy; Lewis acid catalyst; Artificial metalloenzyme; Acetaldehyde

現在のがん治療において、抗がん剤が正常細胞にもダメージを与えることによる副作用が課題となっている。そのため、我々の研究室では疾患部位現地で薬剤分子を合成する生体内現地合成を目標とした技術を開発している。最近では遷移金属触媒をアルブミンの疎水性ポケット内に保護した人工金属酵素を開発した[1)]。また、アルブミン表面の糖鎖を修飾することで、糖鎖のパターン認識によってがんを標的化できることを実証した[2)]。さらに、人工金属酵素にスカンジウム触媒を用いたルイス酸触媒を開発した。

本研究では、アルコールが代謝されたときに体内に生じるアセトアルデヒドを原料とした抗がん活性分子の現地合成を考案した。本研究では、毒性の低い原料化合物を投与し、生体内のアセトアルデヒドと反応させた。その後、がん細胞に結合させた金属触媒による反応によって、肝臓がん現地で抗がん活性分子を合成することを試みたので、これらの経緯について報告する。

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新規光誘起型環化反応の開発に基づく抗腫瘍活性の光化学制御

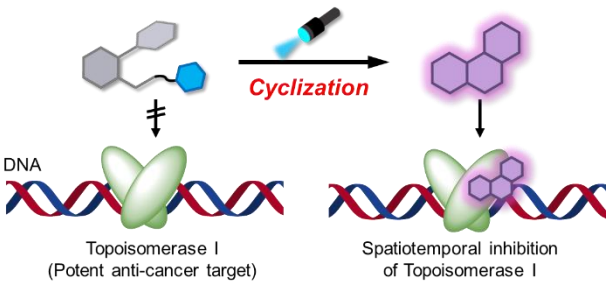
（東北大多元研 [1]・東北大院理 [2]）○岡村 秀紀 [1,2]・川森 有沙 [1,2]・飯田 百香 [1,2]・金山 唯 [1,2]・小澤 眞美子 [1]・永次 史 [1,2]

Photo-chemical control of anticancer activity by novel photo-triggered cyclization reaction ([1]*Institute of Multidisciplinary Research for Advanced Materials*, *Tohoku University*, [2]*Department of Chemistry, Graduate School of Science*, *Tohoku University*) ○Hidenori Okamura,[1,2] Arisa Kawamori,[1,2] Momoka Iida,[1,2] Yui Kaneyama,[1,2] Mamiko Ozawa,[1] Fumi Nagatsugi[1,2]

Photochemical control of drug activity has been attracting considerable attention as a method to suppress adverse effect. Very recently, our group discovered a unique photo-reactivity of *o*-nitrobenzyl oxime ethers and developed an intramolecular cyclization reaction that provides *N*-centered aromatic compounds under physiological conditions.[1] By utilizing this reaction, in the present study, we investigated the drug activity control based on the photo-triggered construction of the molecular structure. As a result, we demonstrated the photo-chemical control of anticancer activity of the drug molecules with highly efficient OFF-ON switching.
Keywords : Photochemistry, Photocontrol, N-centered aromatic compound, Anticancer activity

薬理活性の光制御は、副作用の少ない薬効発現につながるため、近年大きな注目を集めている。その一つとして、薬物分子に光切断性保護基を導入し、光照射で活性を OFF-ON 制御する光ケージド法が活発に研究されている。しかし、本法では、光切断性保護基を導入しても薬理活性が完全に消失しない場合があること、また、光切断性保護基を導入できる置換基が限られるといった問題点がある。そのため、生体応用可能な光化学反応のレパートリーの拡張が必要である。

我々はごく最近、*o*-ニトロベンジルオキシムエーテルの特異な光反応性を発見し、光照射するだけで含窒素芳香環を与える分子内環化反応を開発した [1]。本光反応は、細胞内でも進行することを確認している。そこで本研究では、新規光誘起型環化反応を用いて、薬物分子の骨格構築に基づく活性制御を検討した。具体的には、光照射によってトポイソメラーゼ I 阻害剤の誘導体を与える光環化前駆体を設計・合成した。合成した前駆体の溶液に光照射したところ、環化反応が進行し、目的の薬物分子が得られることを確認した。次に、この光環化前駆体を Hela 細胞に添加し、光照射に基づく活性制御を検証した。その結果、未照射の場合には細胞毒性を示さないのに対し、光照射した場合には強力な細胞毒性を示すことを見出した。以上より、光による分子骨格の構築が、薬理活性の制御に有用であることが示唆された。



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微生物由来糖 6 位修飾型グリセロ糖脂質および類縁化合物の合成と機能

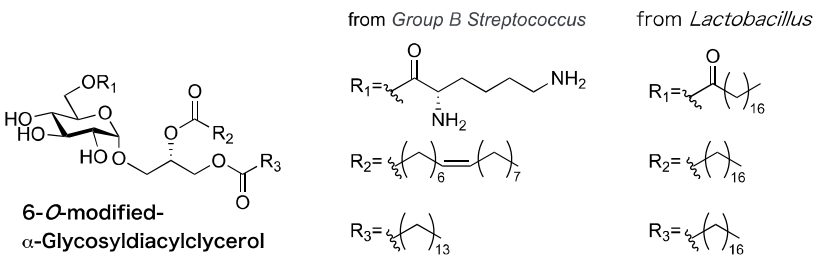
（慶大理工）○望月 慎吾・松丸 尊紀・藤本 ゆかり

Synthesis and biological functions of microbial 6-position-modified glucosyl acylglycerols and their analogues (*Faculty of Science and Technology, Keio University*) ○Shingo Mochizuki, Takanori Matsumaru, Yukari Fujimoto

Glucosyldiacylglycerol functions as a key anchor structure of lipoteichoic acid, a principal constituent of bacterial cell walls, and exhibits a variety of structures depending on the species. In this study, we focused on the glucose-6-*O*-modified glucosyldiacylglycerol structures found in several microbial species and established a simple method to synthesize various 6-*O*-modified glucosyl diacylglycerols, including a variety of the lipid structures. We applied the established synthetic method to the synthesis of microbial 6-*O*-modified glucosyl diacylglycerols. We also synthesized various derivatives and evaluated their biological activities.

Keywords : Glycolipid; lipoteichoic acid; glycerolipid; immunomodulatory activity

グルコシルジアシルグリセロールは、細菌細胞壁を構成する主要成分であるリポタイコ酸のアンカー構造であり、生物種によって様々な構造を有するとともに一部の分子は免疫調節活性を示す。本研究では、細菌より見出されたグルコース 6 位修飾型α-グルコシルアシルグリセロール構造を合成するため、脂質やアミノ酸等の多様な構造をグルコース 6 位に導入可能とする、グルコース 6 位修飾型類縁体の合成法を確立した。特にα-グリコシド構造を効率的に得るため立体選択的グリコシル化を行うとともに、グルコース 6 位およびグリセロール部位へ不飽和脂肪酸等の多様な脂肪酸の選択的導入を可能とする保護基戦略とした。確立した合成法を応用し、グルコース 6 位にリシン残基が結合した B 型レンサ球菌型 6 位修飾α-グルコシルジアシルグリセロール[1]の初の合成を達成するとともに、グルコース 6 位およびグリセロール部位に脂肪酸が結合した乳酸菌型α-グルコシルトリアシルグリセロール構造の他、種々の類縁体合成に展開した。また合成化合物について免疫調節活性評価を行った結果についても報告する。



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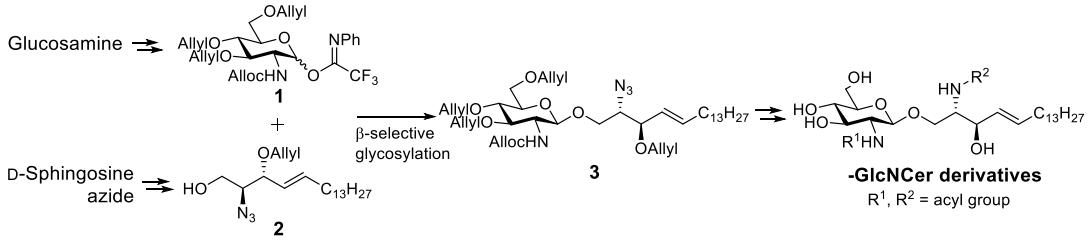
アシル化部位構造制御を志向した糖脂質 GlcNCer 合成法の開発

（慶大理工）○白坂 謙・末吉 耕大・松丸 尊紀・藤本 ゆかり
Synthetic studies of GlcNCer derivatives with modifying acyl groups (*Faculty of Science and Technology, Keio University*) ○Ken Shirasaka, Kodai Sueyoshi, Takanori Matsumaru, Yukari Fujimoto

Glycolipids play a crucial role not only in contributing to membrane stabilization as components of cell membranes but also in exhibiting a variety of biofunctions, including immunomodulatory activity. Sphingoglycolipids display various natural lipid structures, and the modification of acyl moieties affects their immunomodulatory activities. In this study, we utilized GlcNCer backbone structures, which are not abundant as natural sphingoglycolipids, or easier modification of the sugar component. Namely, we established a synthetic method for β-GlcNCer derivatives by introducing various substituent groups into the amino group or acyl groups into the ceramide in GlcNCer structures with using allyl protecting group strategy.[1)]
Keywords : Glycolipids; Ceramide; GlcNCer

糖脂質は、細胞膜等の膜構成成分として膜の安定化に寄与するほか、細胞間相互作用に関与し免疫調節活性をはじめとした多様な機能を示す。特に糖にセラミドが結合したスフィンゴ糖脂質においては、生体内において多様な脂質構造を有する一方、スフィンゴ糖脂質のアシル基部位の構造の差異は、免疫調節能にも大きな影響を与えることを示す結果が最近種々報告されている。

本研究では、糖修飾を容易とする糖脂質骨格として天然にはあまり存在しない GlcNCer 構造を利用して誘導体合成を行うこととした。すなわち、GlcN のアミノ基およびセラミド部位に種々の置換基あるいはアシル基の導入を可能とする多様な β-GlcNCer 類縁体構造の合成法を確立した。合成に際しては、allyl 型の保護基戦略を利用した手法を用いるとともに [1)]、グルコサミンより調製した糖ドナー**1** とスフィンゴシン誘導体 **2** による隣接基関与を利用した β 選択的グリコシル化により基幹中間体 **3** を得た後、糖 2 位のアミノ基の置換基およびセラミド部位のアシル基の選択的導入を行うことで、目的の β-GlcNCer 誘導体を合成する方法の確立に成功した。



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免疫調節性分子創製を志向したシクロペンタンテトラオール構造を含む新規糖脂質分子の合成

（慶大理工）○青木 優人・関田 大輝・松丸 尊紀・藤本 ゆかり

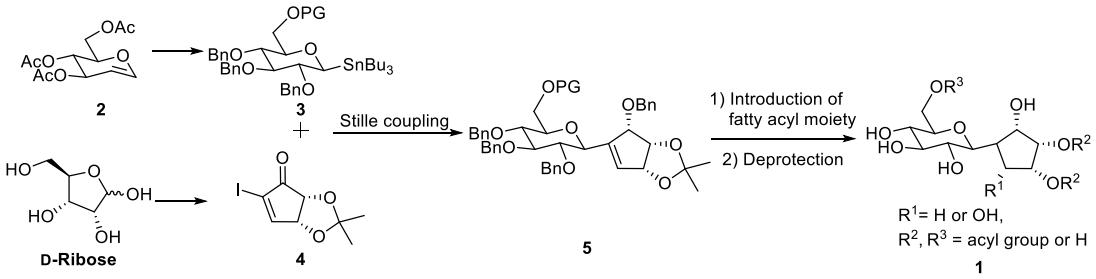
Synthesis of novel glycolipids containing cyclopentanetetraol structure for immunomodulatory molecules (*Faculty of Science and Technology, Keio University*) ○Yuto Aoki, Hiroki Sekita, Takanori Matsumaru, Yukari Fujimoto

The all-*syn*-cyclopentane tetraol structure found in natural products is one of cyclitol-related structures having a five-membered ring with four hydroxy groups in the *syn* configuration. In this study, based on the disaccharide-containing glycolipid structures exhibiting immunomodulatory activity, we designed novel glycolipid molecules **1**, which have a disaccharide-like backbone containing cyclopentanetetraol. In order to synthesize the novel glycolipids, the glycosyl stannane **3** synthesized from acetylglucal **2** and the cyclopentane-ol moiety **4** derived from D-ribose were combined using the C(sp^2)-C(sp^3) Stille coupling reaction to construct a disaccharide-like structure **5**. The novel glycolipid structures were successfully synthesized by the subsequent introduction of the lipid moieties.

Keywords : glycolipid; cross-coupling reaction; cyclopentanetetraol

天然物由来構造として見出される all-*syn*-シクロペンタンテトラオール構造[1]は、*syn* 配置のヒドロキシ基を有する 5 員環をもつ糖類似シクリトール関連構造である。本研究では免疫調節活性を示す二糖含有糖脂質構造に基づき、シクロペンタンテトラオールおよび関連構造を用いた二糖構造類似骨格を含有する糖脂質 **1** を設計し、その合成を行った。

新規糖脂質分子の合成においては、糖骨格とシクロペンタノール構造を結合させた後、脂質部位を導入することとし、種々の脂肪酸を有する誘導体の容易な合成を可能とした。まずアセチルグルカール **2** より調製可能なスズ化合物 **3** を得るとともに D-ribose から閉環メタセシスを含む 7 工程でビニルヨード体 **4**[2]を得た。化合物 **3** および **4** を用いた sp^2-sp^3 炭素間の Stille カップリング反応により、二糖類似構造中間体 **5** を構築した。続けて脂質部位の導入および脱保護を行うことで新規糖脂質構造の合成法確立を行った。



1) Ando, K.; Suzuki, S.; Saeki, T.; Tamura, G.; Arima, K. *J. Antibiot.* **1969**, *22*, 189.

2) Inuki, S.; Sato, K.; Zui, N.; Yamaguchi, R.; Matsumaru, T.; Fujimoto, Y. *J. Org. Chem.* **2019**, *84*, 12680.

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Improvement of a direct response version of near-infrared genetically encoded Ca^{2+} indicator, dNIR-GECO

([1]*Graduate School of Science, The University of Tokyo*, [2]*Department of Chemistry, The University of Alberta*) ○Takumi Kobayashi,[1] Rina Hashizume,[1] Yong Qian,[2] Yusuke Nasu,[1] Takuya Terai,[1] Robert E. Campbell[1,2]

Keywords: Calcium Ion; Biosensor; Protein Engineering; Fluorescence Imaging

Calcium ion (Ca^{2+}) is a second messenger in many biological processes including neuronal signal transduction. For example, the ion has an important role in regulation of neurotransmitter release through the function of voltage-gated Ca^{2+} channels. Visualization of the spatiotemporal dynamics of intracellular Ca^{2+} will enhance our understanding of the mechanisms of various biological phenomena that involve the ion. In our group, Dr. Qian and other previously developed a series of near-infrared genetically encoded Ca^{2+} indicator (NIR-GECI) proteins based on the near-infrared fluorescent monomeric protein mIFP and a calcium sensing domain CaM/RS20. Although the published NIR-GECIs show inverse response to Ca^{2+},[1,2] we have also identified a mutant called dNIR-GECO0.5 that exhibited a direct response to Ca^{2+} (**Figure 1A**). Such sensors should have advantages in terms of reducing background signal and photobleaching during experiments. However, dNIR-GECO0.5 and other known dNIR-GECO derivatives had a large room for improvement of brightness in living cells.[3] Therefore, the aim of this study was to search for novel dNIR-GECO mutants with superior fluorescence intensity in living cells compared with the existing dNIR-GECO derivatives based on further protein engineering.

A total of seven rounds of directed evolution, including improved screening methods, resulted in a promising variant (dNIR-GECO-v7) that was superior to the original template of dNIR-GECO0.5 in terms of $\Delta F/F_0$ and fluorescence intensity in vitro (**Figure 1B**). The v7 mutant was also characterized in HeLa cell imaging.

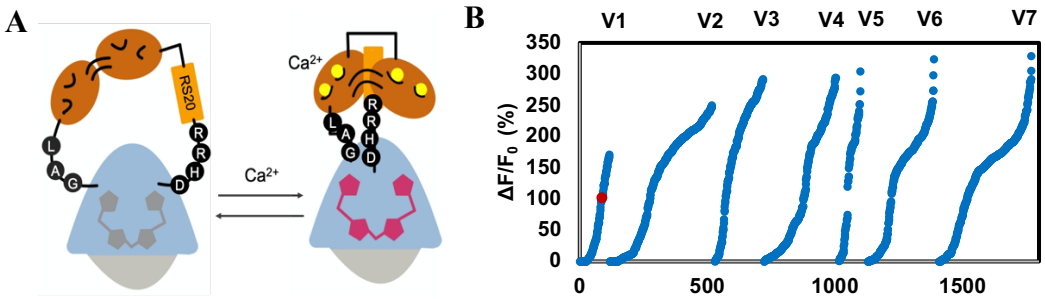

Figure 1. A) The schematic representation of the variant dNIR-GECO0.5. **B)** Directed evolution of dNIR-GECO. A red dot represents dNIR-GECO0.5.

1) Qian et al. *Nat. Methods*, **2019**, 16, 171–174. 2) Qian et al. *PLoS Biol*. **2020**, 18, e30000965. 3) 橋爪里奈　東京大学大学院理学系研究科化学専攻修士論文 2021.

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有機溶媒中の水分量を簡便に制御する核磁気共鳴法のための新規サンプリング法

（阪大院理[1]・阪大院理 FRC[2]）○梶原 康宏[1,2]、森口 達也[1]、真木 勇太[1,2]、岡本 亮[1,2]

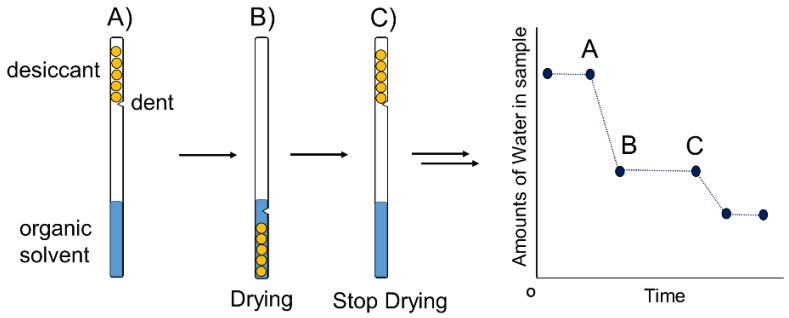
Unique NMR sampling method controlling water amounts in organic solvent

(*[1]Graduate School of Science, and [2]FRC, Graduate School of Science, Osaka University*) ○ Yasuhiro Kajihara[1,2], Tatsuya Moriguchi[1], Yuta Maki[1,2], Ryo Okamoto[1,2]

Nuclear magnetic resonance spectroscopy can analyze molecular structure and dynamics. However, contamination of a small amount of water in the NMR sample often interferes with the analysis of molecules. In order to remove a small amount of water molecules, an elaborate drying system is frequently needed for deuterated organic solvents, material of interest, and glass sample tubes. In this presentation, we will introduce a very efficient method to remove almost all water molecules from a sample solution including a tiny amount of material of interest.

Keywords : NMR; natural compound

NMR によって分子の構造解析が行えるが、少量の水の混入によって天然物などの貴重な目的物の測定が干渉されることがある。そこで、少量の水分子を重水素有機溶媒から除く手法が必要となる。これまで、有機溶媒から水を除くためガスクロマトグラフィーシステムを利用し溶媒を加熱しながら乾燥する方法が報告されている[1]。しかしながら、この方法では水を除くのに手間がかかる。そこで、我々は NMR 測定のためのサンプリングにおいて簡便な水の除去法を検討した。



我々は、図 A のような NMR チューブの上部に窪みを持ち、球状の乾燥剤が入った NMR チューブを作った。このサンプルを上下反転させることで、有機溶媒が移動し乾燥剤と接触することで乾燥が始まる(図 B)。さらに上下反転させることで乾燥剤を除き、水を減らした状態での NMR 測定が可能になる(図 C)。

本発表では、このサンプリング法の実例や応用例について述べる。

1)Joseph B. Alper, *Analytical Chemistry,* **1978**, *50*, 2, 381-382.

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Pyrus communis 由来の脂肪酸エステルの抗変異活性

（群馬高専専攻科環境工学専攻[1]・群馬高専物質工学科[2]）○柿沼 勇輝[1]・都丸 望[1]・小柏 敦詩[2]・宮下 海光[2]・友坂 秀之[2]
Antimutagenic Activity of Fatty Acid Esters from *Pyrus communis* ([1]*Advanced Environmental Engineering Course, National Institute of Technology (KOSEN), Gunma College,* [2]*Department of Chemistry and Materials Science, National Institute of Technology (KOSEN), Gunma College*) ○ Yuki Kakinuma,[1] Nozomi Tomaru,[1] Atsushi Ogashiwa,[2] Kairi Miyashita[2], Hideyuki Tomosaka[2]

Antimutagens inhibit the mutation able to cause cancer. Active consumption of antimutagens present in vegetables and fruits through eating and drinking is expected to lead to cancer prevention in everyday life. We have previously isolated four fatty acid esters (compounds **1–4**) as antimutagens from the fruit of *Pyrus communis* (cv. Le Lectier). In this study, the antimutagenic activity of these esters was evaluated in a modified method of a mutation assay, Ames test using *Salmonella typhimurium* TA98. In the antimutation assay, IQ (2-amino-3-methylimidazo[4,5-*f*]quinoline, 0.05 nmol/plate) and Trp-P-1 (3-amino-1,4-dimethyl-5*H*-pyrido[4,3-*b*]indole, 0.20 nmol/plate) found in burned meat and fish were used as mutagens.

Compound **4** at a concentration of 0.05 μmol/plate showed inhibition of mutagenic activity of 53% against IQ. At the same concentration, compound **3** inhibited the mutagenicity of IQ by 51%, and inhibitions of mutagenic activity against IQ for compounds **1** and **2** were less than 40%. Against Trp-P-1, compound **4** exhibited antimutagenic activity with 47% inhibition and compounds **1–3** with less than 40% at a concentration of 0.10 μmol/plate, respectively. Therefore, antimutagenic activity of compound **4** was higher than those of other tested compounds.

Keywords：Antimutagenic Activity; Pyrus communis; Fatty Acid Ester; TA98

抗変異原物質は、がんの原因の一つである DNA の突然変異を抑制する。飲食を通し、野菜や果物に含まれる抗変異原物質を積極的に摂取することは、がんの予防につながると期待される。これまでに我々は、抗変異原物質として、果物の *Pyrus communis*（cv. Le Lectier）から四つの脂肪酸エステル（化合物 **1–4**）を単離している。本研究では、これらの脂肪酸エステルについて、変異原性試験の Ames test に用いられる *Salmonella typhimurium* 変異株の TA98 を使用し、抗変異活性の評価を行った。このとき、変異原物質として、肉や魚のこげに含まれる変異原物質である IQ（2-amino-3-methylimidazo[4,5-*f*]quinoline, 0.05 nmol /plate）および Trp-P-1（3-amino-1,4-dimethyl-5*H*-pyrido[4,3-*b*]indole, 0.20 nmol/plate）を用いた。

化合物 **4** では、変異原物質 IQ に対する抗変異活性（変異の抑制率）は、濃度 0.05 μmol/plate において 53%であった。また、同濃度において、化合物 **3** では 51%であり、化合物 **1** と **2** ではいずれも 40%未満であった。変異原物質 Trp-P-1 に対する抗変異活性は、化合物 **4** では濃度 0.10 μmol/plate において 47%であり、化合物 **1–3** では同濃度においていずれも 40%未満であった。よって、四つの脂肪酸エステルのうち化合物 **4** に、比較的高い抗変異活性が認められた。

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ピリジニウム塩の光分解反応の検討

（山梨大院総合 [1]・JST さきがけ [2]・MEXT 卓越研究員 [3]）○日浅 和馬 [1]・杉山 朋寛 [1]・弦間 麟太郎 [1]・佐藤 玄 [1, 2, 3]
Investigation of the photolysis reaction of pyridinium salts ([1]*Integrated Graduate School of Medicine, Engineering, and Agricultural Sciences School of Engineering, Yamanashi University*, [2]*Precursory Research for Embryonic Science and Technology,* [3]*Leading Initiative for Excellent Young Researchers*) ○Kazuma Hiasa,[1] Tomohiro Sugiyama,[1] Rintaro Gemma,[1] Hajime Sato[1, 2, 3]

The degradation of lignin is an area of intense research, and in recent years, photoredox degradation reactions using visible light and photocatalysis have been reported. The problem with this reaction is that it requires expensive precious metal catalysts such as ruthenium (Ru). Therefore, we started to develop a visible light reaction that does not require a precious metal catalyst, referring to the photoredox decomposition reaction of the β-O-4 bond in the lignin basic skeleton. In this study, various substituents were introduced based on the lignin basic skeleton, and combinations of R_1 and hydroxypyridine were investigated. When the model substrates were irradiated with blue visible light in the presence of $Ru(bpy)_3$ catalyst or in the absence of the catalyst, photolysis reaction was observed to proceed in several model substrates.
Keywords : Lignin; Precious Metal Free; photoredox decomposition reaction

リグニンの分解は研究が盛んに行われている分野であり、近年では可視光と光触媒を利用した光レドックス分解反応の研究も報告されている [1)]。この反応は、ルテニウム（Ru）等の高価な貴金属触媒が必要であるが、昨今の国際情勢から、貴金属の継続した安定供給は難しく、その代替方法の開発は喫緊の課題である。 そこで、リグニン基本骨格に含まれる β-O-4 結合の光レドックス分解反応を参考に貴金属触媒を必要としない可視光反応の開発に着手した。

本研究ではリグニン基本骨格を基にして各種置換基 R_1 を導入し、ヒドロキシピリジンと組み合わせることにより、数種類のモデル基質を合成した。合成したモデル基質の UV スペクトルの測定を行い、光学的特性を明らかにするとともに、光分解反応における置換基の影響を精査した。モデル基質を $Ru(bpy)_3$ 触媒存在下、または触媒が存在しない条件下で青色可視光を照射し、いくつかのモデル基質において光分解が進行することを確認した。本発表では、光分解反応の実験結果の詳細について議論を行う。



1) Nguyen, J. D.; Matsuura, B. S.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2014**, 136, 1218–1221.

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Academic Program [Poster] | 18. Polymer：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 2 (理工スポーツホール [1階] アリーナ)

[P2-3vn] 18. Polymer

Japanese

[P2-3vn-01]

Synthesis and properties of copolymers of trimethylene carbonate and 4-substituted trimethylene carbonate derivatives

○Ai Teranishi[1], Koji Nakano[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P2-3vn-02]

Oxidatively degradable polyesters using diol with thioacetal structure

○Miho Homma[1], Nobuhiro Kihara[1] (1. The Univ. of Kanagawa)

Japanese

[P2-3vn-03]

Identification of impure structure in the polymer obtained by oxidative polymerization of 5-cyano -2-methoxyphenol oxidizing polymer

○Shimon Takechi Takechi[1], Akiyuki Nakano[1], Takahiro Oshima[2], Hideyuki Higashimura[1,2] (1. Grad. Sch. of Sci., Okayama Univ. of Sci., 2. Grad. Sch. of Sci and Eng., Okayama Univ. of Sci.)

Japanese

[P2-3vn-04]

Synthesis and depolymerization of recyclable polymers using bifunctional aromatic molecular LEGO blocks having lophine moiety

○Wataru Morishita[1], Ryuhei Taguchi[2], Kaoru Adachi[3], Masashi Shiotsuki[1,2], Takeru Iwamura[1,2] (1. Graduate School of Integrative Science and Engineering, Tokyo City University, 2. Faculty of Science and Technology, Tokyo City University, 3. Faculty of Molecular Applied Chemistry and Engineering, Kyoto Institute of Technology)

Japanese

[P2-3vn-05]

Chain end modification of polylactide copolymers and homopolymers by isocyanates and their stereocomplex formation

○Jaeyeong Choi[1], Hiroharu Ajiro[2] (1. Sangpaedong Community Service Center, 2. NAIST)

Japanese

[P2-3vn-06]

Machine Learning-assisted Prediction of Chemical Resistance of Resin Materials for Semiconductor Manufacturing Equipment

○Shogo Kunieda[1], Mitsuru Yambe[1], Yosuke Hanawa[1], Hitoshi Kamijima[2], Toshiaki Shintani[2], Takuo Okude[2], Yoshihiro Hayashi[3], Ryo Yoshida[3] (1. SCREEN Holdings Co., Ltd., 2. Research Institute of Systems Planning, Inc., 3. The Institute of Statistical Mathematics)

Japanese

[P2-3vn-07]

The effect of side chains terminal functional group on physical properties of functional polymer hydrogels

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○Riku Fukuoka[1], Yuka Wakayama[1], Takuma Kureha[1] (1. The Univ of Hirosaki)

Japanese

[P2-3vn-08]

Structural changes of water in hydrogels of carboxymethyl cellulose nanofiber during vapor swelling and drying

○Yuta Takahara[1], Yurina Sekine[2], Takuya Nankawa[2], Tomoko Ikeda-Fukazawa[1] (1. Department of Applied Chemistry, Meiji University, 2. Materials Sciences Research Center, Japan Atomic Energy Agency)

Japanese

[P2-3vn-09]

The effect of different lengths of cross-linkers in hydrogels

○Yuki Hatakeyama[1], Takuto Hirayama[1], Takuma Kureha[1] (1. The Univ. of Hirosaki)

Japanese

[P2-3vn-10]

Effects of block copolymers on properties of aliphatic polycarbonate/vinyl polymer blends

○Mai Nakamura[1], Kousuke Sugeno[1], Hiromu Saito[1], Koji Nakano[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P2-3vn-11]

Unique temperature dependence of aqueous solutions of lactic acid oligomers

○KATSUYUKI NAMAI[1], SHIN-ICHIRO SATO[1] (1. The Univ. of Hokkaido)

Japanese

[P2-3vn-12]

Structure of water in carboxymethyl cellulose nanofiber hydrogel

○Yusuke Beni[1], Yurina Sekine[2], Takuya Nankawa[2], Tomoko Ikeda-Fukazawa[1] (1. Meiji University, 2. Materials Sciences Research Center, Japan Atomic Energy Agency (JAEA))

Japanese

[P2-3vn-13]

Effect of Carbonyl Groups in aromatic Polyimides on Optical Properties.

○Taichi Hirasima[1], Tomoyuki Hirayama[1], Hiroki Miyauchi[1] (1. Graduate School of Engineering Kyushu Sangyo University)

Japanese

[P2-3vn-14]

Ordered Structures of Liquid Crystalline Polyurethanes with Bis (benzylidene) phenylenediamine Group in the Skeletal Main-Chain

○Aya Seike[1], Ryoga Nishimura[2], Masanori Nata[3], Seiji Ujiie[3] (1. Division of Applied Chemistry, Faculty of Science and Technology, Oita University, 2. Division of Applied Chemistry,Graduate School of Engineering, Oita University, 3. Biological and Material Chemistry Program, Faculty of Science and Technology, Oita University)

Japanese

[P2-3vn-15]

Liquid Crystalline and Orientational Properties of Mesogenic Diol Compounds and Their Polyaddition Polymers

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○Kanoko Miyawaki[1], Masanori Nata[2], Seiji Ujiie[2] (1. Division of Applied Chemistry, Faculty of Science and Technology, Oita University, 2. Biological and Material Chemistry Program, Faculty of Science and Technology, Oita University)

Japanese

[P2-3vn-16]

Properties and Cross-Linked Structure of Allyl-Containing Benzoxazine–Maleimide Thermosetting Resins

○Shuichi Nakao[1], Toshiyuki Iwai[1], Masatoshi Mihara[1], Keiko Ohtsuka[1], Junichi Takashiro[2], Shimpei Obata[2], Hirosuke Saito[2] (1. Osaka Research Institute of Industrial Science and Technology, 2. Panasonic Industry Co., Ltd.)

Japanese

[P2-3vn-17]

Improvement of gel-state NMR spectroscopy to investigate the adsorption property of π-conjugated molecules onto cellulose nanofiber

○Mashu Hirogari[1], Yasuko Saito[2], Yoshiharu Mitoma[1], Keita Sakakibara[2] (1. Prefectural University of Hiroshima, 2. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese

[P2-3vn-18]

Development and biodegradability of wood adhesive polyesters composed of lignin-derived 2-pyrone-4,6-dicarboxylic acid (PDC)

○Yijie Jin[1], Takuma Araki[2], Naofumi Kamimura[3], Eiji Masai[3], Masaya Nakamura[3], Tsuyoshi Michinobu[1] (1. Tokyo Institute of Technology, 2. Forestry and Forest Products Research Institute, 3. Nagaoka University of Technology)

English

[P2-3vn-19]

Obtain thermal responsive star-shaped copolymer gel with homogeneous network containing gold nanoparticles

○YIAN WANG[1], Yukikazu Takeoka[1] (1. The Univ. of Nagoya)

Japanese

[P2-3vn-20]

Preparation and properties of indroquinoxailine-containing polymer

○Hideki Hayashi[1], Oda Mitsuo[1], Take-aki Koizumi[2] (1. Nagoya Municipal Industrial Research Institute, 2. Advanced Instrumental Analysis Center, Shizuoka Institute of Science and Technology)

Japanese

[P2-3vn-21]

Design of wireless electrochemical gel actuators

○Soma Hodono[1], Keiichi Imato[1], Taichi Hino[1], Ichiro Imae[1], Yousuke Ooyama[1] (1. Hiroshima university)

English

[P2-3vn-22]

Supramolecular Assembly of Biodegradable Amphiphilic Block Copolymers Built through Biomolecule Folic Acid as a Hydrogen Bonding Moiety

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○Rongjian Lang[1], Yusuke Miyazaki[1], Masaki Nakahata[2], Kazuki Fukushima[1], Takashi Kato[1] (1. The University of Tokyo, 2. Osaka University)

Japanese

[P2-3vn-23]

Polymer matrix effects on photoinduced electron transfer

Yilin Cao[1], Hikaru Soutome[2], Syoji Ito[2], ○Hiroyasu Yamaguchi[1] (1. Graduate School of Science, Osaka Univ., 2. Graduate School of Engineering Science, Osaka Univ.)

Japanese

[P2-3vn-24]

Polymerization of 3,5-dihydroxymethylphenylacetylene with oligophenylene at position 4 and properties of the resulting polymer

○Yuki Taguchi[1], Toshiki aoki[1], Takashi Kaneko[1], Masahiro Teraguchi[1] (1. The Univ. of Niigata)

Japanese

[P2-3vn-25]

A design of lithium-ion conductive electrolytes based on alignment of zwitterions

○Satomi Yokoyama[1] (1. Tokyo University of Agriculture and Technology)

Japanese

[P2-3vn-26]

Synthesis of silicone-based multiblock copolymers and additive effects on epoxy resins

○Hirokazu Iwata[1], Itaru Asano[1] (1. Toray Industries, Inc.)

Japanese

[P2-3vn-27]

Triple helix formation and properties of modified ß-glucan derivatives

○masami okue[1] (1. Graduate school of Engineering, Sojo University)

Japanese

[P2-3vn-28]

Preparation of polyion complex microparticles composed of salmon milt DNA and cationic lipids having a disulfide bond

○Kota Ohmukai[1], Mituhiro Shibata[1], Naozumi Teramoto[1] (1. Chiba Inst. Technol)

Japanese

[P2-3vn-29]

Effect of degree of acetylation and molecular weight on solubility of chitosans

○Miho Araki[1], Hironori Izawa[1] (1. University of Miyazaki)

Japanese

[P2-3vn-30]

Development of casein-based materials

○Hirotaka Nakashima[1], Hironori Izawa[1] (1. University of Miyazaki)

Japanese

[P2-3vn-31]

Synthesis and characterization of surface-modified nanofibrillated bacterial cellulose by EDTA for the adsorption of heavy metal ions

○Ryosui Sasa[1], Nanami Kinoshita[1], Ryota Kishimoto[1], Sayaka Fujita[1], Hiroyuki Kono[1], Kenji Tajima[2] (1. Natl. of Tech, Tomakomai Col., 2. Hokkaido Univ.)

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Japanese

[P2-3vn-32]

Thermal degradation behavior of polystyrene confined in MOF pores

○Haruma Tatsumi[1], Ami Nishijima[2], Yuki Kametani[2], Takashi Uemura[2] (1. School of Engineering, The Univ. of Tokyo, 2. Graduate School of Engineering, The Univ. of Tokyo)

Japanese

[P2-3vn-33]

Aggregation behavior and molecular recognition by the thermoresponsive block polymers having optically active acrylamide units in the presence of organic substrates.

○Keisuke Takamure[1], Manabu Ishihune[1] (1. Kindaiuniversity)

English

[P2-3vn-34]

Non-catalytic Hydrothermal Dechlorination Kinetics of Polyvinyl chloride

○Douglas Hungwe[1], Satomi Hosokawa[1], Yuki Yamasaki[1] (1. Hosei University)

Japanese

[P2-3vn-35]

Aldol reactions in water by using optically active thermoresponsive polymers having glutamic acid derived side chains – Sc (III) complexes

○Hikaru Aoyagi[1], Manabu Ishifune[1] (1. Kindai University)

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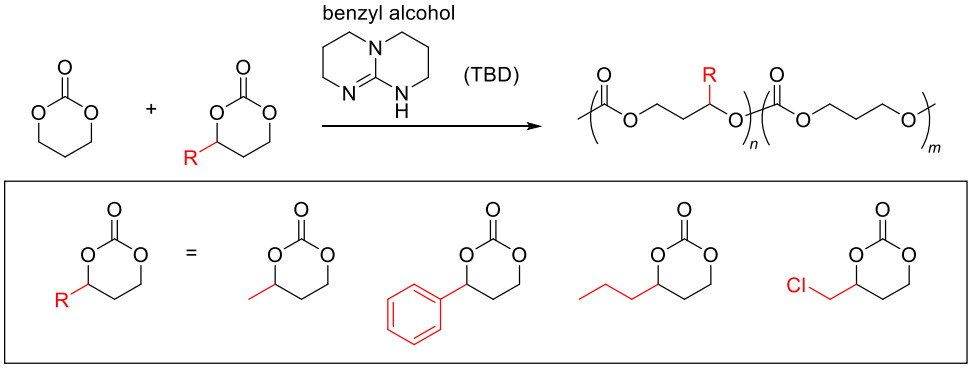
トリメチレンカルボナートと 4 位に置換基を有するトリメチレンカルボナート誘導体との共重合体の合成と物性

（東農工大院工）○寺西 愛・中野 幸司
Synthesis and Properties of Copolymers of Trimethylene Carbonate and 4-Substituted Trimethylene Carbonate Derivatives (*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Ai Teranishi, Koji Nakano

Poly(trimethylene carbonate)s (PTMCs) have widely been investigated for biological applications because of their biocompatibility and biodegradability. Most of them are obtained by ring-opening polymerization of unsubstituted and/or 5-substituted TMCs.[1)] On the other hand, the copolymerization with substituted TMCs at other position(s) has rarely been investigated. In this study, we focus on TMC derivatives with a substituent at the 4-position and investigate the copolymerization of them with unsubstituted TMC. The TMC derivatives with methyl, phenyl, propyl, and chloromethyl groups at the 4-position were copolymerized with unsubstituted TMC. The reactivity of each monomer was found to depend on the substituent. In addition, the substituents have great impact on the thermal and degradation properties of the resulting PTMC copolymers.
Keywords : Aliphatic Polycarbonate; Trimethylene Carbonate; Ring-Opening Polymerization

ポリトリメチレンカルボナート（PTMC）は生体適合性や生分解性などの特徴をもつことから，生体材料として盛んに研究が進められている．その多くは無置換トリメチレンカルボナート（TMC）や 5 位に置換基を有する TMC の開環重合により得られたものである．一方，その他の位置に置換基をもつ TMC と無置換 TMC との共重合の検討例は極めて限定的である．本研究では，これまでほとんど検討されていない 4 位に置換基を有する TMC 誘導体に着目し，無置換 TMC との共重合を検討した．

4 位にメチル基，フェニル基，プロピル基，クロロメチル基を有する TMC 誘導体を無置換 TMC と共重合させた．各モノマーの反応性は置換基の種類により大きく異なることが分かった．また，置換基の効果により，得られる共重合体の熱的性質や熱分解特性が大きく異なることが分かった．



(1) Poly(trimethylene carbonate)-based polymers engineered for biodegradable functional biomaterials Fukushima, K. *Biomater. Sci.* **2016**, *4*, 9.

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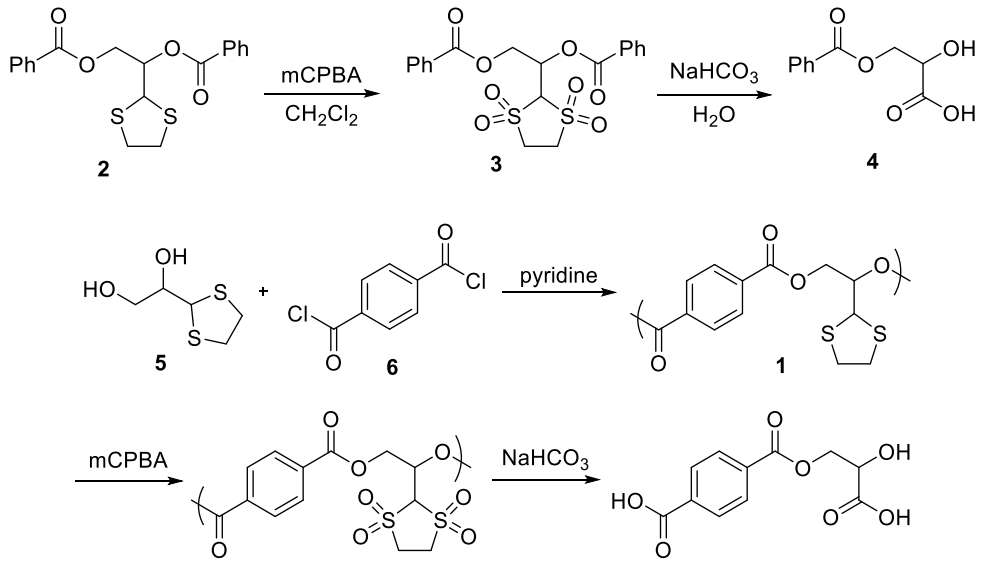
チオアセタール構造を有するジオールを用いた酸化分解性ポリエステル

（神奈川大理 [1]）○本間 美帆 [1]・木原 伸浩 [1]
Oxidatively degradable polyesters using diol with thioacetal structure ([1]*Kanagawa University*)
○Miho Homma[1], Nobuhiro Kihara [1]

2-Thioethyl ester undergoes facile β-elimination with a mild base such as potassium carbonate after oxidation because of the high acidity of a hydrogen at the α-position of the sulfone group. Moreover, ester with a thioacetal group at β-position undergoes rapid β-elimination even under almost neutral conditions after oxidation because of the double effect of the sulfone groups. In this study, polyester **1** bearing the thioacetal moiety was synthesized, and its oxidative degradation behavior was investigated. Oxidation of **2** with mCPBA followed by the treatment with aqueous sodium bicarbonate resulted in the immediate decomposition to yield a complex mixture containing **4** as a main product. Polycondensation of **5** and **6** was performed to synthesize **1**. The oxidative degradation of **1** is in progress.
Keywords : oxidative degradation, thioacetal, 2-thioethyl ester, sulfone

2-チオエチルエステルは、スルホンに酸化されるとスルホンのα-位の水素の酸性が高くなるため、炭酸カリウムなどの穏やかな塩基でもβ-脱離を起こす。2 位にチオアセタールをもつエステルでは、スルホンの効果が重なるため、中性に近い条件下でも速やかにβ-脱離する[1)]。そこで本研究では、チオアセタール構造を組み込んだポリエステル **1** の合成とその酸化分解挙動を検討した。チオアセタール構造を有する **2** を mCPBA で酸化してから炭酸水素ナトリウム水溶液で処理したところ、直ちに分解が起こり、**4** を主生成物とする複雑な混合物が得られた。**5** と **6** の重縮合により **1** を合成し、**2** と同様に **1** の酸化分解を検討した。



1) H. Kunz, H. Waldmann, *Angew. Chem. Int. Ed.*, **1983**, *22*, 62.

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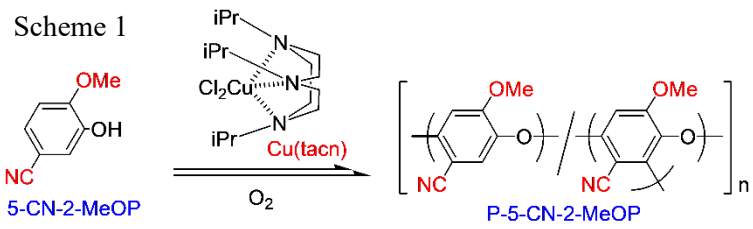
5-シアノ-2-メトキシフェノール酸化重合体の不純構造同定

（岡山理大院理[1]・岡山理大院理工[2]）○武智 士門[1]・中野 晟志[1]・大島 貴宏[2]・東村 秀之[1,2]

Identification of Impure Structure in the Polymer Obtained by Oxidative Polymerization of 5-Cyano-2-methoxyphenol ([1]*Graduate School of Science, Okayama University of Science*, [2]*Graduate School of Science and Engineering, Okayama University of Science*) ○Shimon Takechi,[1] Akiyuki Nakano,[1] Takahiro Oshima,[2] Hideyuki Higashimura[1,2]

We found that enzyme model-catalyzed oxidative polymerization of 5-cyano-2-methoxyphenol (5-CN-2-MeOP) produced a new C–O coupling polymer (P-5-CN-2-MeOP).[1] The 5-CN and 2-MeO groups cancel the mutual defect, resulting in the first example for oxidative polymerization of a cyano-substituted phenol. From the FT-IR spectrum of P-5-CN-2-MeOP, a small peak at 1,741 cm^{-1} was detected and considered to be a C=O stretching. In this work, identification of the impure C=O structure was tried by experiment and calculation.

Scheme 1



The component containing the C=O structure was insoluble in acetone, and thereby, the component was condensed and analyzed with FT-IR, showing it was not a carboxylic acid. Thus, the C=O structure was considered to be one of benzoquinone- or diphenoquinone-structures from the previous findings, and therefor, DFT calculation (B3LYP/6-311+G(d,p)) on two benzoquinones and three diphenoquinones of 5-CN-2-MeOP was performed. From the results, the *o*-benzoquinone structure was estimated to have a C=O stretching peak at 1,723 cm^{-1} and could be the most possible structure as the C=O impure structure at the present.

Keywords : Enzyme Model-Catalyst; Oxidative Polymerization; 5-Cyano-2-Methoxyphenol; Impure Structure Analysis; C=O Stretching Calculation

酵素モデル触媒 (Cu(tacn)) を用いた 5-シアノ-2-メトキシフェノール (5-CN-2-MeOP) の酸化重合 (Scheme 1) により、新規な C–O 結合ポリマー (P-5-CN-2-MeOP) が得られることを見出している[1]。シアノ基はフェノールモノマーの酸化電位を高めて酸化重合を困難にし、*o*-位のメトキシ基は Cu へキレート配位を形成して C–O 結合を阻害する。そこで、これらを互いに *p*-位に置換させることで双方の欠点を相殺させ、シアノ置換フェノールとしては初めて酸化重合を可能にした。本ポリマーは FT-IR から 1,741 cm^{-1} に C=O 結合と考えられる微小ピークが検出されており、今回はこの不純構造の同定を実験と計算の両面から検討した。

P-5-CN-2-MeOP 中の C=O 含有成分はアセトンに不溶なことが分かり、本成分を約 10 倍以上に濃縮することができた。FT-IR にて O–H 伸縮ピークは検出されなかったことから、シアノ基が加水分解されたカルボン酸ではないことが確認できた。一方、これまでの知見からベンゾキノン構造又はジフェノキノン構造の可能性が考えられ、5-CN-2-MeOP の前者 2 種及び後者 3 種につき、DFT 計算 (B3LYP/6-311+G(d,p)) に基づく振動解析を行った。その結果、*o*-ベンゾキノン構造が 1,723 cm^{-1} に C=O 伸縮ピークを持ち、現時点では最も可能性が高いと考えている。詳細は当日報告する。

1) 武智士門, 中野晟志, 東村秀之, 日本化学会第 103 春季年会, P1-2pm-03 (2023).

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ロフィン部位を有する 2 官能性芳香族分子レゴブロックを用いたリサイクル性ポリマーの合成と解重合

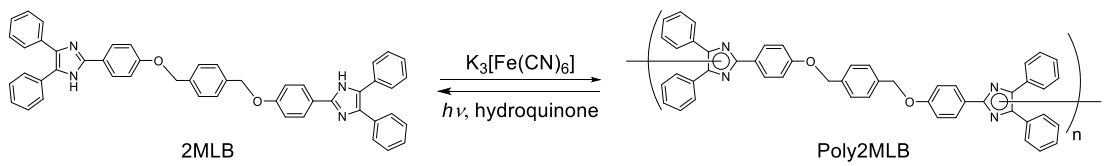
(都市大院総合理工[1]・都市大理工[2]・京工繊大工芸科学[3])
○森下　航[1]・田口　竜平[1]・足立　馨[3]・塩月　雅士,[1,2]・岩村　武[1,2]

Synthesis and depolymerization of recyclable polymers using bifunctional aromatic molecular LEGO blocks having lophine moiety ([1]*Graduate School of Integrative Science and Engineering*, *Tokyo City University*, [2]*Faculty of Science and Technology*, *Tokyo City University*, [3]*Faculty of Molecular Chemistry and Engineering*, *Kyoto Institute of Technology*)
○ Wataru Morishita,[1] Ryuhei Taguchi,[2] Kaoru Adachi,[3] Masashi Shiotsuki,[1,2] Takeru Iwamura[1,2]

A cold 2% aqueous solution of potassium ferricyanide was slowly added dropwise to a solution of bifunctional molecular LEGO block dissolved in a mixed solvent of ethanol and THF containing potassium hydroxide. During addition the reaction mixture was maintained at 0°C and vigorously stirred. The reaction mixture after the dropping was further stirred for 3 h to obtain the corresponding polymer (yield 47%). The obtained polymer was dissolved in chloroform with the addition of hydroquinone and depolymerized by light irradiation. As a result, it was clarified that 60% of the bifunctional aromatic LEGO block was obtained by depolymerization.

Keywords : recyclable; molecular LEGO block; polymerization; depolymerization; lophine

持続可能な社会の実現に向けて、近年様々な取り組みが行われている。廃プラスチック類もその一つでプラスチックの排出抑制、再利用、リサイクルの 3R の推進がなされている。しかしながら、廃プラスチックのおよそ 60%が熱としてリサイクルされ、結果的に CO_2 を排出している。これまでに我々の研究グループでは、玩具のレゴブロックのように必要に応じて、付け外しができるような仕組みをモノマーに付与することによりリサイクル性の高い高分子の合成を試みてきた。今回はリンカー部位に芳香族を有する 2 官能性芳香族分子レゴブロックポリマーを合成し、その解重合を評価した。モノマーである 2MLB に、水酸化カリウムの THF/エタノール中、フェリシアン化カリウム水溶液を滴下することで重合を行い、メタノールで再沈殿することにより収率 47%の poly2MLB を得た。得られた poly2MLB をヒドロキノン存在下、クロロホルム中で 48 時間光照射を行うことにより 2MLB を 60%回収した。一方、得られた poly2MLB (M_n=3,940)のクロロホルム溶液に光照射し解重合を行った後、暗所で 24 時間以上静置した。その後、溶媒を留去し GPC 測定を行った。その結果、poly2MLB の濃度が高いほど、光照射前の poly2MLB の分子量に回復する傾向が認められた。



Scheme 1

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イソシアネートによるポリ乳酸共重合体および ホモポリマーの末端制御とステレオコンプレックス化

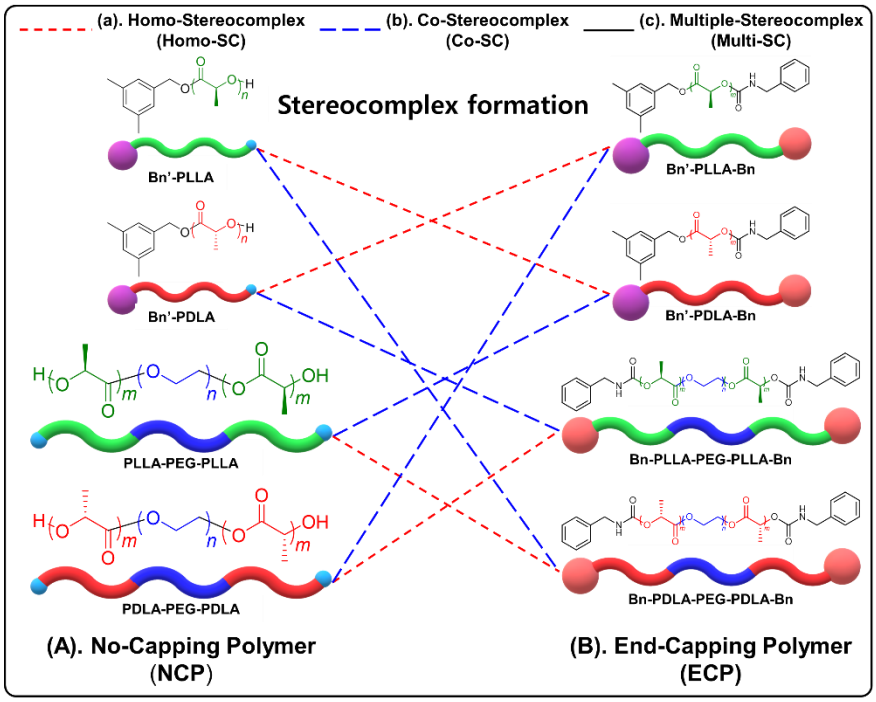
サンパドン注民センター[1]、奈良先端大物質[2] ○チェ ジェヨン[1]、網代 広治[2]

Chain end modification of polylactide copolymers and homopolymers by isocyanates and their stereocomplex formation ([1]*Sangpaedong Community Service Center*, [2]*Division of Materials Science, Nara Institute of Science and Technology*) ○Jaeyeong Choi[1], Ajiro Hiroharu[2]

In this study, homopolymers were obtained by ring-opening polymerization of lactide with low molecular weight compound as an initiator, and copolymers were also obtained by the same polymerization method with poly(ethylene glycol) as an initiator. The hydroxyl groups at chain end of these polymers were reacted with isocyanate, to obtain end-capping polymers. Furthermore, we investigate and analyze their stereocomplex formation with L-isomers and D-isomers of polylactides.

Keywords: Polylactide, Stereocomplex, Linear polymer, End-capping polymer, Thermal property

本研究では、まず開始剤としてポリエチレングリコールと低分子化合物を用い、ラクチドを開環重合させることで、リニア構造を持つポリ乳酸の共重合体とホモポリマーを得た。次に得られたポリマーの末端をイソシアネートと反応させることで、末端封鎖ポリマーを得た。得られたそれぞれのポリマーの構造解析とL体およびD体から成るポリ乳酸同士を混合して得られるステレオコンプレックスについて分析したので報告する。



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半導体製造装置への利用に向けた機械学習による樹脂材料の耐薬性予測

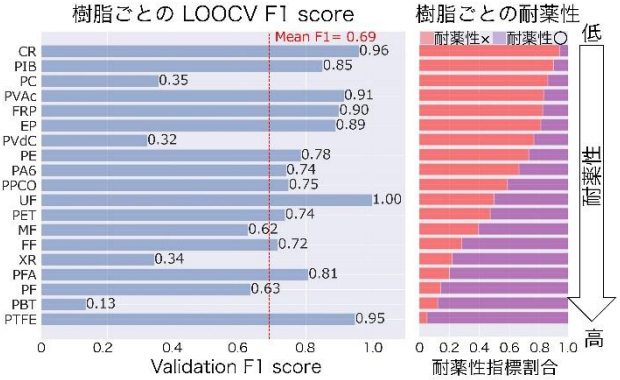
(株式会社 SCREEN ホールディングス[1]・株式会社システム計画研究所[2]・統計数理研究所[3]) ○國枝 省吾[1]・山家 暢[1]・塙 洋祐[1]・上島 仁[2]・新谷 俊了[2]・奥出 拓生[2]・林 慶浩[3]・吉田 亮[3]

Machine Learning-assisted Prediction of Chemical Resistance of Resin Materials for Semiconductor Manufacturing Equipment ([1]*SCREEN Holdings. Co. Ltd.*, [2]*Research Institute of Systems Planning. Inc.,* [3]*The Institute of Statistical Mathematics*) ○ Shogo Kunieda,[1] Mitsuru Yambe,[1] Yosuke Hanawa,[1] Hitoshi Kamijima,[2] Toshiaki Shintani,[2] Takuo Okude,[2] Yoshihiro Hayashi,[3] Ryo Yoshida[3]

In semiconductor manufacturing equipment, resin materials used in pipes and other components are constantly in contact with solvents, and therefore, the assurance of long-term chemical resistance of the resin materials is of great importance. However, testing for chemical resistance lifespan is time and cost consuming. In this study, with the goal of predicting the chemical resistance lifespan of resin materials, we first developed a machine learning model to distinguish between good and poor chemical resistance based on combinations of resin materials and organic solvents, and then verified its classification accuracy.
A total of 4,144 data with labels of good or poor chemical resistance from 39 polymers and 220 solvents were collected from public datasets and used as a binary classification task. The features of resin materials and solvents were calculated from SMILES using the Force Field Descriptor.[1)] The classification accuracy was verified using Leave-One-Group-Out Cross Validation for 39 types of resin materials, resulting in an average F1 score of 0.69.
Keywords : Resin Materials; Organic Solvent; Chemical Resistance; Machine Learning

半導体製造装置では配管等の樹脂材料と溶媒が常時接液するため、溶媒に対する樹脂材料の長期的な耐薬性を担保することが求められる。しかし、耐薬寿命を試験するには時間とコストがかかる。そこで本研究では、溶媒に対する樹脂材料の耐薬寿命を予測することを見据え、その前段階として、樹脂材料と有機溶媒の組み合わせから耐薬性良好・不良を判別するための機械学習モデルを作成し、分類精度を検証した。

樹脂材料 39 種と溶媒 220 種から耐薬性良好・不良のラベルを持つ合計 4,144 データを収集し 2 値分類タスクとした。樹脂材料および溶媒の特徴量には Force Field Descriptor を用いた[1)]。39 種の樹脂材料に対する Leave-One-group-Out Cross Validation による平均 F1 は 0.69 となった。



1) Representation of materials by kernel mean embedding. M. Kusaba, Y. Hayashi, C. Liu, A. Wakiuchi, R. Yoshida, *Phys. Rev. B.* **2023**, *108*, 134107.

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機能性高分子ハイドロゲルにおける側鎖末端官能基による物性への影響

（弘前大理工 [1]）○福岡 陸 [1]・若山 佑香 [1]・呉羽 拓真 [1]

The effect of side chains terminal functional group on physical properties of functional polymer hydrogels ([1]*Faculty of science and technology, Hirosaki University*) ○Riku Fukuoka[1], Yuka Wakayama[1], Takuma Kureha[1]

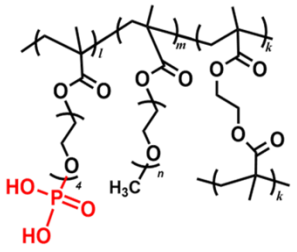
Poly(oligo ethylene glycol methyl ether methacrylate) (pOEGm) has the ethylene glycol side chains. The side chain lengths of pOEGm can be changed and the physical properties of pOEGm based gels are controlled by side chain lengths. To improve the functionality of such gel, we focused on the terminal functional group of side chains. In this study, the poly(tetraethylene glycol methacrylate phosphate) (pOEGp) was applied and copolymerized with pOEGm (Scheme 1). The effect of the terminal functional group was investigated by mechanical tests and swelling tests on these gels.

Fig. 1 shows the stress-strain curves obtained from the compression tests. The compressive modulus was improved by changing the end of the side chain from methyl groups to phosphate groups. Furthermore, the addition of a small amount of pOEGp rapidly increased the compressive modulus. It suggested that the electrostatic interaction between phosphate groups occurred in the gel network. In this presentation, the mechanical tests and swelling behavior will be used to discuss the effect of the charge at the end of the side chain on gel properties.

Keywords : Side Chain Termination ; gelatinization ; polyelectrolyte

ポリ(オリゴエチレングリコールメチルエーテルメタクリレート)(pOEGm)は、側鎖の長さを変化させることで、力学物性を制御することが可能である[1]。我々は、このゲルのさらなる機能向上のために、ポリマー側鎖末端の電荷の有無に着目した。Scheme.1 に示すように、側鎖末端官能基にリン酸基を有する、ポリ(テトラエチレングリコールメタクリレートフォスフェイト)(pOEGp)と pOEGm を任意の比で共重合されたゲルを合成し、力学試験により評価することで、側鎖の末端官能基の効果を調査した。

Fig1 に圧縮試験により得られた応力−ひずみ曲線を示す。側鎖末端がリン酸基に変化することで、弾性率の向上がみられ、さらに pOEGm に対して少量の pOEGp を加えることで弾性率が急激に向上した。これは、静電相互作用によるものだと考察する。当日は、力学試験と膨潤挙動から、側鎖末端の電荷の有無が与えるゲル物性への影響を議論する。



Scheme 1. (a) Chemical structures of p(OEGm-co-OEGp) gels.

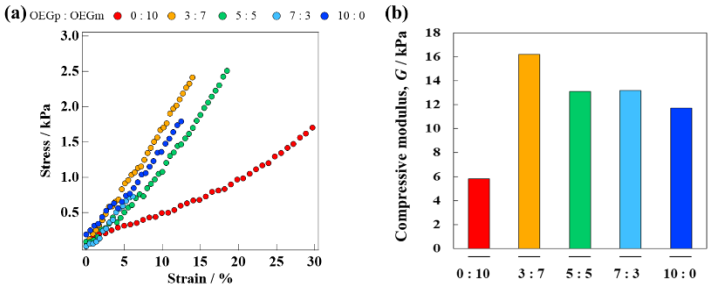


Figure.1 (a) Stress-strain curves of p(OEGm-co-OEGp). (b) compressive modulus, *G,* of each gel.

1) T. Kureha, K. Takahashi, M. Kino, H. Kida, T. Hirayama, *Soft Matter* **2023**, *19*, 2878.

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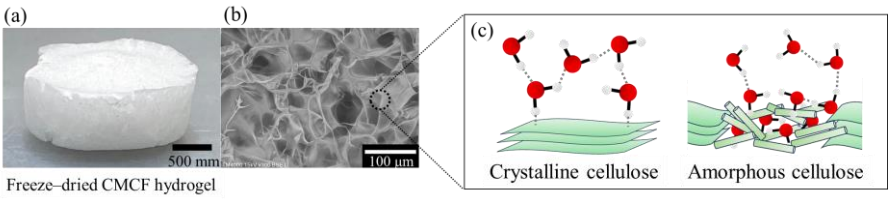
水蒸気膨潤・乾燥に伴うカルボキシメチルセルロースナノファイバーゲル中の水の構造変化

（明治理工[1]・JAEA[2]）○髙原 裕大[1]・関根 由莉奈[2]・南川 卓也[2]・深澤 倫子[1]
Structural changes of water in hydrogels of carboxymethyl cellulose nanofiber during vapor swelling and drying ([1] *Department of Applied Chemistry, Meiji University*, [2]*Japan Atomic Energy Agency*) ○ Yuta Takahara,[1] Yurina Sekine,[2] Takuya Nankawa,[2] Tomoko Ikeda-Fukazawa[1]

Carboxymethyl cellulose nanofiber (CMCF) forms mechanically strong hydrogels with freeze cross-linking.[1)] The result of X-ray diffraction measurements showed that CMCF forms cellulose type-II crystal and amorphous in hydrogel.[2)] In order to investigate the structure of water in CMCF hydrogel, we measured IR spectra during vapor swelling and drying. The results show that the wavenumbers of the bending mode and O–H stretching modes of water, and C=O stretching mode of CMCF decrease as the water content increases. These results suggest that an interstitial water exists within the amorphous region due to formation of hydrogen bonds with carboxymethyl groups in the side chain of CMCF, where no water exists in the inside of the crystal region. The results indicate that the structural changes of water and CMCF in hydrogel result from their interactions and water has a critical role in properties of hydrogel.
Keywords : Hydrogel; Cellulose nanofiber; Water; Amorphous

カルボキシメチルセルロースナノファイバー（CMCF）は、凍結架橋によりセルロース II 型結晶と非晶質が共存した高強度なハイドロゲルを生成する[1,2)]。本研究では赤外分光法を用いて、CMCF ゲルの水蒸気膨潤および乾燥過程の水の構造変化を解析した。この結果、含水率の増加に伴い、水の変角振動および O–H 伸縮振動の波数が減少することが明らかになった。これらの波数変化は、結晶近傍と非晶質近傍の水の構造の違いに起因したものであると考えられる。本研究の結果は、非晶質 CMCF の場合には CMCF 分子間隙に入り込んでカルボキシメチル基と水素結合を形成した束縛水が存在することを示す。一方、結晶については内部には水分子が存在せず、水分子が水素結合を形成するのは結晶表面のカルボキシメチル基のみであることが分かった。本講演では、水と CMCF の相互作用のメカニズムについて議論する。



(a) Photograph and (b) SEM image of freeze-dried CMCF hydrogels. (c) shows the schematics of structures of water around crystalline and amorphous cellulose.

1) Y. Sekine, T. Nankawa, S. Yunoki, T. Sugita, H. Nakagawa, T. Yamada, *ACS Appl. Polym. Mater.* **2020**, *2*, 5482.
2) D. Miura, Y. Sekine, T. Nankawa, T. Sugita, Y. Oba, K. Hiroi, T. Ohzawa, *Carbohyd. Polym. Technol. Appl.* **2022**, *4*, 100251.

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架橋点間の長さがハイドロゲルの力学特性に与える効果

(弘前大理工[1]) ○畠山 優騎[1]・平山 拓杜[1]・呉羽拓真[1]
The effect of different lengths of cross-linkers in hydrogels ([1]*Faculty of Science and Technology, Hirosaki University*)○Yuki Hatakeyama[1], Takuto Hirayama[1], Takuma Kureha[1]

Hydrogels are soft and brittle due to the high-water content and inhomogeneous network structures. We focus on poly(oligo(ethylene glycol) methyl ether methacrylate), (pOEG, Fig.1), which have ethylene glycol side-chains. So far, pOEG gels with long side chains exhibited good mechanical properties, such as elastic modulus, due to the steric hindrance of side chains. However, the crosslinking agent, ethylene glycol dimethacrylate (EGD), was not effectively incorporated in the gel network as a crosslinking point because the size of EGD was smaller than that of OEG with a long side chain. Thus, in this study, EGD with a long ethylene glycol segment was applied to pOEG gels to improve toughness.

As a result, the compressive modulus was increased by increasing ethylene glycol segments of EGD (Fig. 2). It indicated that the segment length of the crosslinker contributed to the effective crosslink density. In the presentation, we will further discuss the changes in physical properties as a function of crosslinker length based on the results of swelling tests.

Keywords : Hydrogel, Length of Cross-linker, Mechanical Property, Swelling Ratio

ハイドロゲルは、高い生体適合性と柔らかさを活かしたバイオ工学等で応用が期待される一方で、高い含水率と網目構造の不均一性から壊れやすく脆いことが欠点である。この課題を解決する鍵となるポリマーとしてポリ(オリゴエチレングリコール)メチルエーテルメタクリレート(pOEG, Fig.1)に着目し、pOEG のエチレングリコール側鎖が長いほど強靭になることを発見した[1]。しかし、側鎖が長い pOEG ゲルの場合、架橋剤であるエチレングリコールジメタクリレート(EGD)が架橋点として有効に組み込まれていないことがわかった。そこで本研究では、架橋剤の長さ(エチレングリコールユニット数, *n*)に着目し、OEG 側鎖長に応じた適切な長さの EGD を用いることで力学特性の制御ができると考案し、架橋剤の長さがゲル物性に与える影響を調査した。

Fig.2a に圧縮試験により得られた応力-ひずみ曲線、Fig.2b に算出した弾性率を示す。同モノマー濃度、架橋剤濃度において、EGD の長さが長くなるほど弾性率が向上した。このことより、架橋剤が長いほど架橋点として pOEG ゲルネットワークに組み込まれやすいことがわかった。当日は、膨潤試験による結果も踏まえて架橋剤の長さによる物性の変化について議論する。

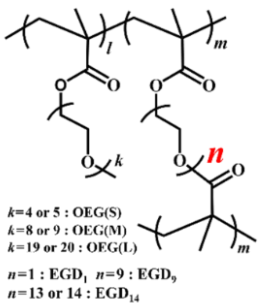

Figure 1. Chemical structure of pOEG gel.

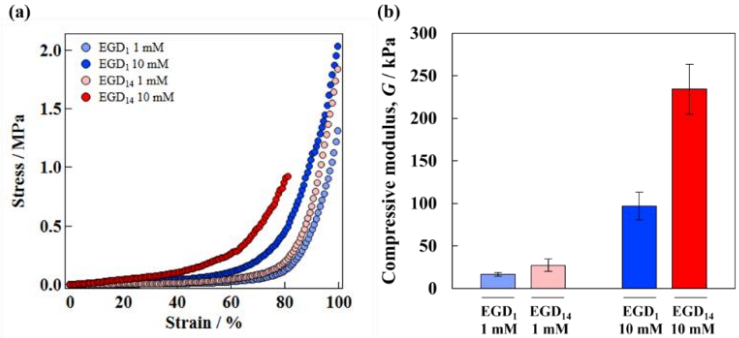

Figure 2. (a) Stress-strain curves of pOEG gels. (b) Compressive modulus of each gel.

1)T. Kureha, K. Takahashi, M. Kino, H. Kida, T. Hirayama, *Soft Matter* **2023**, *19*, 2878.

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脂肪族ポリカルボナートとビニルポリマーとのブレンド系の物性に及ぼすブロック共重合体の添加効果

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Effects of block copolymers on properties of aliphatic polycarbonate/vinyl polymer blends

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○Mai Nakamura, Kousuke Sugeno, Hiromu Saito, Koji Nakano

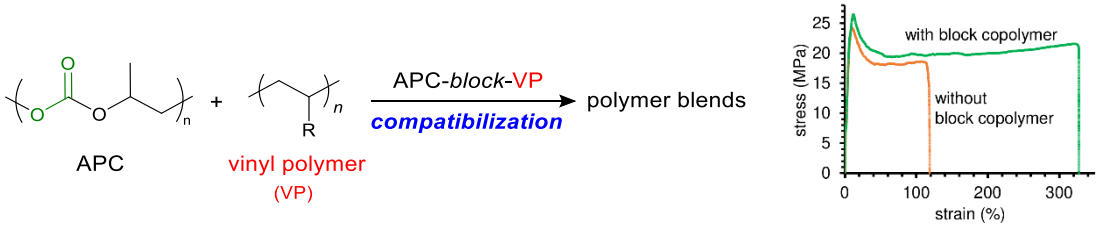
Aliphatic polycarbonates (APCs) obtained by the alternating copolymerization of epoxides with carbon dioxide (CO_2) are promising polymer materials with attractive properties such as biodegradability, gas barrier properties, and ionic conductivity.[1] Recently, polymer blend approach has attracted growing attention to tailor their properties and to apply them as value-added polymer materials. Herein, we report polymer blends of APCs with vinyl polymers, such as poly(methyl methacrylate) and polystyrene, which exhibit improved mechanical properties.

In order to achieve a high degree of compatibility between APCs and vinyl polymers, block copolymers of APCs and vinyl polymers, which have been developed previously by our group,[2] were used as compatibilizers. Tensile tests of the polymer blends containing APCs, vinyl polymers, and the corresponding block copolymers revealed that the addition of block copolymers improves the breaking stress and elongation at break.

Keywords : Polymer Blend, Block Copolymer, Compatibilization, Aliphatic Polycarbonate, Vinyl Polymer

二酸化炭素 (CO_2) とエポキシドとの交互共重合により得られる脂肪族ポリカルボナート (APC) は，生分解性やガスバリア性，イオン伝導性などの特性を示す高分子材料である [1]． 近年，APC を基盤とする高分子材料の物性を制御し，高分子材料として応用することを目指して，ポリマーブレンドが検討されている．本研究では，APC と優れた機械的性質を有するポリメタクリル酸メチルやポリスチレンといったビニルポリマーとのポリマーブレンドに着目した．

APC とビニルポリマーとの混和性を向上させるために，われわれがこれまでに開発した APC とビニルポリマーとのブロック共重合体を相容化剤として用い，ポリマーブレンドを調製した [2]． APC，ビニルポリマー，および対応するブロック共重合体を混合して得られたポリマーブレンドの引張試験をおこなったところ，ブロック共重合体の添加によって破断応力や破断伸びが向上することが分かった．



1) Taherimehr, M.; Pescarmona, P. P. *J. Appl. Polym. Sci.* **2014**, *131*, 41141. 2) Mizuno, Y.; Nakano, K. *Chem. Lett*. **2018**, *47*, 580.

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乳酸オリゴマーの水溶液の特異な温度依存性

（北大院総合化学[1]・ 北大院工[2]）○生井 克幸[1]・佐藤 信一郎[2]

Unique temperature dependence of aqueous solutions of lactic acid oligomers

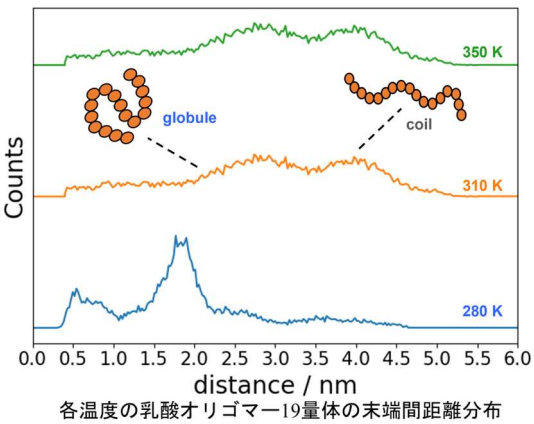
([1] *Graduate School of Chemical Science and Engineering*, *Hokkaido University*, [2]*Graduate School of Engineering, Hokkaido University*, ○NAMAI KATSUYUKI [1], SATO SHIN-ICHIRO[2]

Polylactic acid (PLA) is known as a biodegradable plastic and has been applied as a useful material in various fields. According to previous research, the 17-lactamers of PLA showed Large Amplitude Coil-Globule Fluctuation at 300 K, violently moving between the coil state and the globule state.[1] It is expected that there is a temperature dependence to this large amplitude motion. In this study, we investigated the temperature dependence of lactic acid oligomers using molecular dynamics simulations. Simulations were performed for different degrees of polymerization of lactic acid oligomers at various temperatures, and comparisons were made focusing on the Tail-Tail distance. All lactic acids used in the simulations were D-body.

The simulation results suggest that the temperature dependence of lactic acid oligomers varies with the degree of polymerization.

Keywords : MD simulation; Temperature-responsive polymer; Lactide acid oligomer

乳酸は生分解性プラスチックとして知られ注目されている素材である。我々の先行研究においてポリ乳酸の 17 量体が 300 K において coil 状態と globule 状態を激しく行き来する大振幅揺らぎ運動が確認された。[1] この大振幅運動は温度依存性があることを期待される。しかし、ポリ乳酸の温度依存性は不明である。本研究では分子動力学シミュレーションを用いて乳酸オリゴマーの温度依存性について調査した。乳酸オリゴマーの重合度や温度を変えてシミュレーションをし、末端間距離に注目して比較した。シミュレーションで使用した乳酸は全て D 体を使用した。



各温度の乳酸オリゴマー19量体の末端間距離分布

シミュレーションの結果、乳酸オリゴマー水溶液には UCST 型の温度依存性があることが示唆された。

1 C. Hori, T. Sugiyama, K. Watanabe, J. Sun, Y. Kamada, T. Ooi, T. Isono, T. Satoh, S.-I. Sato, S. Taguchi and K. Matsumoto, *Polym Degrad Stab*, 2020, **179**, 109231.

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カルボキシメチルセルロースナノファイバーハイドロゲル中の水の構造

(明治大学理工学部応用化学科 [1]・日本原子力研究開発機構物質科学研究センター[2])
○紅 裕介[1]・関根 由莉奈[2]・南川 卓也[2]・深澤 倫子[1]

Structure of water in carboxymethyl cellulose nanofiber hydrogel ([1]*Department of Applied Chemistry, Meiji University,* [2]*Material Research Center, Japan Atomic Energy Agency* (*JAEA*))

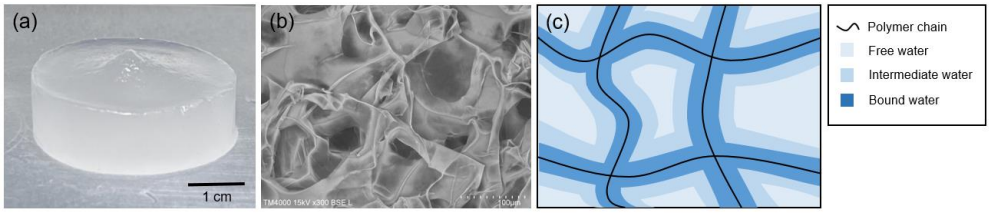
Yusuke Beni,[1] Yurina Sekine,[2] Takuya Nankawa,[2] Tomoko Ikeda-Fukazawa[1]

Carboxymethyl cellulose nanofiber (CMCF) forms a hydrogel with a high mechanical strength by a freeze cross-linking method.[1)] Water in hydrogels can be classified into three types depending on strength of hydrogen bonds: free, intermediate, and bound waters.[2)] Using differential scanning calorimetry (DSC), we investigated the dependence on the water content of melting point and relative amounts of three types of water. From the DSC heating curves, an endothermic peak, which is assigned to the melting of intermediate water, was found at temperatures below 273 K. The melting point of intermediate water decreased with decreasing of the water content. In addition, the result shows that the relative amount of intermediate water increases as the water content decreases. The results suggest that the hydrogen bonds of intermediate water in CMCF hydrogels are weaker than that of ordinary water.

Keywords : Hydrogel; Cellulose nanofiber; Water; Differential scanning calorimetry

カルボキシメチルセルロースナノファイバー (CMCF) は、凍結架橋法により強固なハイドロゲルを生成する[1)]。一般に、親水性の高分子から成るハイドゲル中の水は自由水、中間水、束縛水に分類されるが[2)]、CMCF ハイドロゲルにおける三種の水の存在やその構成は明らかではない。本研究では、示差走査熱量 (DSC) 法を用いて CMCF ゲル中の水の融点および三種の水の相対量の含水率依存性を解析した。

DSC 昇温曲線の測定により、273 K 以下に中間水の融解に帰属される吸熱ピークが存在することが確認された。解析の結果、含水率の減少とともに中間水の融点が低下し、ゲル中に存在する中間水の割合が増加することが分かった。このことから、CMCF ゲル中には通常の水と比べて水分子間の水素結合が弱い中間水が存在することが明らかとなった。講演では、水の構造変化のメカニズムについて議論する。



(a) Photograph of swollen CMCF hydrogel, (b) SEM image of freeze-dried CMCF hydrogel, and (c) schematic representation of three types of water in hydrogel

1) Y. Sekine, T. Nankawa, S. Yunoki, T. Sugita, H. Nakagawa, T. Yamada, *ACS Appl. Polym. Mater.* **2020**, *2*, 5482.
2) R. Naohara, S. Namai, J. Kamiyama, T. Ikeda-Fukazawa, *J. Phys. Chem. B* **2022**, *126*, 7992.

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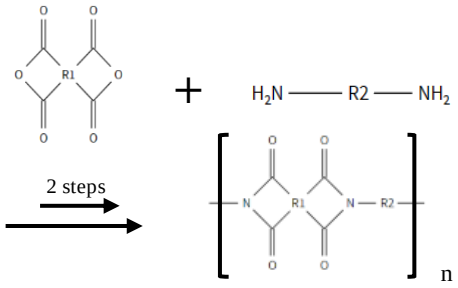
部分フッ素化ポリイミドにおける含有カルボニル基が及ぼす光学特性への影響

(九産大院工) ○平島大地・宮内大樹・平山智之
Effect of Carbonyl Groups in Partially Fluorinated Polyimides on Optical Properties
(*Graduate School of Engineering, Kyusyu Sangyo University*)○Taichi Hirashima, Hiroki Miyauchi, Tomoyuki Hirayama

In recent years, polymer optical waveguides have attracted focus as a high-speed communication medium. In polymeric materials, attention has been focused on the reduction of C-H in the structure as a measure to reduce loss at 1310 nm, the main wavelength band. The effects of carbonyl (C=O) bonds that exist in the vicinity of this wavelength are required to be studied. Therefore synthesized 12 types of polyimides carbonyl groups per unit molecular weight (carbonyl equivalent) and evaluated their Optical properties. The results showed that there is a correlation between the carbonyl equivalent of polyimides and the optical properties at 1310 nm.
Keywords: Polymeric materials; carbonyl bonds; optical properties

近年、高度情報化が進み高速通信媒体として、ポリマー光導波路が注目されている。現在の主な通信波長帯である 1310 nm に対するポリマー材料低損失化の施策として、分子構造中 C-H 結合の低減に主眼が置かれているが、同様に、当波長の吸収損失因子として懸念されるカルボニル（C=O）基が及ぼす光学特性への影響に関する報告は見受けられない。そこで本研究では、カルボニル基による伝搬損失の影響を確認することを目的として、単位構造分子量当たりのカルボニル基数（カルボニル当量）の異なる 12 種ポリイミドを合成し、それらの光学特性を評価した。その結果、ポリイミドのカルボニル等量と 1310 nm 光伝搬損失に相関関係を見出したので報告する。



Scheme 1 Polyimide Synthesis

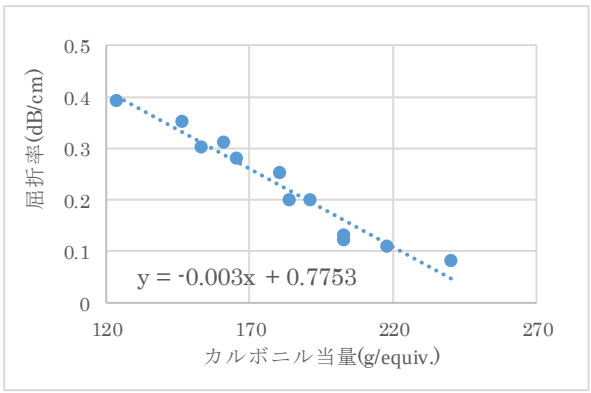


Figure 1 Relationship between carbonyl equivalent

Junya Kobayashi: Trends in polymer optical waveguide material technology. Journal of the Society of Electronics and Decorative Arts Vol.5 No.5 (2002)

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ビス（ベンジリデン）フェニレンジアミン基を主鎖骨格中に有する液晶ポリウレタンの熱的性質と配向秩序

(大分大学理工学部応用科学コース[1]・大分大学大学院工学研究科[2]・大分大学理工学部生命・物質化学プログラム[3])
○清家 綾[1]・西村 諒雅[2]・那谷 雅則[3]・氏家 誠司[3]

Thermal Properties and Orientational Orders of Liquid Crystalline Polyurethanes with Bis(benzylidene)phenylenediamine Group in the Skeletal Main-Chain ([1]*Division of Applied Chemistry, Faculty of Science and Technology, Oita University*, [2]*Graduate School of Engineering, Oita University*,[3]*Biological and Material Chemistry Program, Faculty of Science and Technology, Oita University*) ○Aya Seike,[1] Ryoga Nishimura,[2] Masanori Nata,[3] Seiji Ujiie[3]

The liquid crystal formation of liquid crystalline polyurethanes is influenced by interactions between mesogens and hydrogen bonds between urethane linkages. In this study, novel liquid crystalline polyurethanes, having bis(benzylidene)phenylenediamine skeleton, were synthesized by the reaction of phenylene diamine derivatives and diurethane compounds with formyl groups. The liquid crystalline polyurethane (P1) with bis(benzylidene) *p*-phenylene diamine (BBPD) and toluene-2, 4-diurethane (TDU) groups exhibited nematic and smetic F phases. However, the liquid crystalline polyurethane (P2) in which BBPD replaced with bis(benzylidene) 2-methyl-*p*-phenylenediamine, formed a nematic phase. A nematic-isotropic phase transition temperature of P2 was lower than that of Pl. The liquid crystalline polyurethane with TDU of P1 replaced by *m*-xylylene diurethane revealed a nematic phase.

Keywords : Liquid Crystalline Polyurethane; Phase Transition; Orientational Behavior; Nematic; Smectic

液晶ポリウレタンは，芳香族原子団であるメンゲンとジウレタンコアを屈曲鎖で連結した構造をもち，その配向形成は，メンゲン間の相互作用とウレタン結合間の水素結合に強く影響される．また，液晶相の秩序はメンゲンの構造に強く依存する．本研究では，高い秩序性をもつ液晶相の形成に有利なビス（ベンジリデン）フェニレンジアミン骨格をもつ原子団をメンゲンとして導入した液晶ポリウレタンを合成し，熱的性質および配向特性について検討した．

ホルミル基を分子鎖の両端に有するジウレタン誘導体とフェニレンジアミン誘導体との反応によって，ビス（ベンジリデン）フェニレンジアミン骨格をメンゲンにもつ主鎖型液晶ポリウレタンを得た．メンゲンの中央ベンゼン環の側方にメチル基あるいはニトロ基を置換基として有し，ジウレタン骨格に 2,4-トルエンジウレタンをもつ主鎖型液晶ポリウレタンは，メンゲンを無置換基のメンゲン（ビス（ベンジリデン）*p*-フェニレンジアミン）に代えた主鎖型液晶ポリウレタン（P1）よりも液晶形成能が低下した．また，P1 はビフェニルやアゾベンゼンなどのメンゲンをもつ場合に比べ，液晶温度範囲も広く，ネマチック相（配向秩序のみを有する）と層内長距離秩序を有するスメクチック F 相（配向秩序と位置秩序を有する）を形成した．メンゲンにメチル側方置換基をもつ主鎖型高分子液晶（P2）はネマチック相を形成し，スメクチック相は形成しなかった．これは，P2 ではメチル基によってメンゲンの分子幅が拡張され，メンゲン間相互作用が低下したことに起因する．P1 のジウレタン骨格を *m*-キシリレンジウレタンに置き換えた主鎖型液晶ポリウレタンはネマチック相を形成した，これはジウレタン骨格も液晶形成に強く影響することを示唆する．

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メソゲン基を有するジオールとそれらの重付加ポリマーの液晶性と配向挙動

(大分大学理工学部応用科化学コース[1]・大分大学理工学部生命・物質化学プログラム[2])
○宮脇 香乃子[1]・那谷 雅則[2]・氏家 誠司[2]

Liquid Crystalline and Orientational Properties of Mesogenic Diol Compounds and Their Polyaddition Polymers

([1]*Division of Applied Chemistry, Faculty of Science and Technology, Oita University,* [2]*Biological and Material Chemistry Program, Faculty of Science and Technology, Oita University*), ○ Kanoko Miyawaki,[1] Masanori Nata,[2] Seiji Ujiie[2]

In liquid crystalline compounds, the liquid crystal formation mainly depends on interactions between mesogenic groups. Furthermore, the liquid crystalline properties are influenced by alkyl chain length and structures of terminal groups. In the case of liquid crystalline polymers, the polymer backbone also plays an important role for the liquid crystal formation. In this work, novel mesogenic diols and liquid crystalline polyurethanes were synthesized. Their thermal and orientational properties were examined.

The mesogenic diol (A6B) with a butylazobenzene group did not exhibit a liquid crystalline phase. However, the mesogenic diol dimer (DA6B) having two butylazobenzene groups formed a smectic C phase. The nitroazobenzene containing mesogenic diols (A6N, DA6N) formed a smectic A phase. The smectic A-isotropic phase transition temperature of DA6N was 74.1 °C higher than that of A6N. Liquid crystalline polyurethanes (LCPUs) were obtained by the polyaddition reaction of mesogenic diols and TDI. LCPUs exhibited a nematic phase.

Keywords: Liquid Crystal; Polyurethane; Phase Transition; Smectic A; X-Ray

低分子化合物の液晶形成は，液晶分子の形状，メソゲン基や屈曲鎖の組み合わせ，原子団の連結順序，ミクロ相分離構造の形成，非共有結合相互作用などに依存する．また，高分子液晶では，これらに加え高分子効果が液晶形成に重要な役割を果たす．本研究では，両親媒性構造をもつ 2 種類のメソゲンジオールを用いて，新規の液晶ポリウレタンを得ることを目的に研究を行った．最初に Fig. 1 に示すニトロアゾベンゼン基あるいはブチルアゾベンゼン基をもつジオール化合物（X=NO_2 : A6N，DA6N ; X=C_4H_9 : A6B，DA6B）を合成した． A6N および DA6N はスメクチック A 相を形成した．DA6N は，A6N に比べ， スメクチック A－等方相転移温度が 74.1 ℃高く，液晶配向の熱安定性が向上した．A6B は液晶を形成しなかったが，2 つのメソゲン側方基をもつ DA6B はスメクチック C 相を形成した．メソゲンジオールと TDI の重付加反応によって得られた液晶ポリウレタンは，ネマチック相を形成し，液晶ポリウレタンの液晶配向の熱安定性は，原料であるメソゲンジオールの熱的性質に依存した．ポリウレタン高分子骨格主鎖にメソゲン基をもち，側鎖にニトロアゾベンゼン基を導入した液晶ポリウレタンではスメクチック A 相が形成された．このスメクチック A 相の形成は，ニトロアゾベンゼン基と高分子骨格主鎖中のメソゲン基間の相互作用によるものと考えられる．このほか，メソゲンジオールのアミノ基をイオン化したイオン化したイオン性メソゲンジオールを用いた液晶ポリウレタンについての検討も行った．

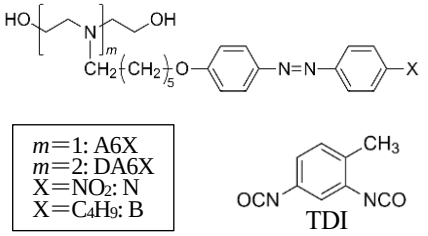

Fig. 1. Structures of mesogenic diols (A6X, DA6X) and diisocyanate (TDI).

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アリル基含有ベンゾオキサジン/マレイミド硬化物の物性と架橋構造の解明

（大阪産業技術研究所[1]・パナソニック インダストリー株式会社[2]）○中尾 秀一[1]・岩井 利之[1]・三原 正稔[1]・大塚 恵子[1]・高城 順一[2]・小畑 心平[2]・齋藤 宏典[2]

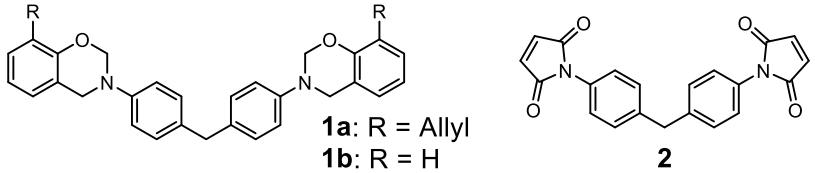
Properties and Cross-Linked Structure of Allyl-Containing Benzoxazine–Maleimide Thermosetting Resins ([1]*Osaka Research Institute of Industrial Science and Technology*, [2]*Panasonic Industry Co., Ltd.*) ○Shuichi Nakao[1], Iwai Toshiyuki[1], Masatoshi Mihara[1], Keiko Ohtsuka[1], Junichi Takashiro[2], Shimpei Obata[2], Hirosuke Saito[2]

Maleimide resins have been utilized for electronic materials because of their high thermal stability and low thermal expansion. Improving the cross-linking density by introducing other functional groups reacting with maleimide is a way for enhancing the properties. In this work, allyl-containing benzoxazine improved thermal stability and thermal expansion of benzoxazine–maleimide thermosetting resins. The cross-linked structure of the resins was elucidated by model reactions. The thermosetting resins were prepared from benzoxazine **1** and maleimide **2** in the presence of a catalyst. The cured resin containing allyl group showed higher glass transition temperature and lower coefficient of thermal expansion than that without allyl group. Model reactions showed that allyl group changed the ring-opening mechanism of benzoxazine and the reaction occurred between the degradation product of benzoxazine and maleimide. In addition, a radical initiator increased consumption of allyl group.

Keywords: Benzoxazine; Maleimide; Thermosetting Resin; Cross-Linked Structure

マレイミド樹脂は耐熱性や低熱膨張性に優れており、主に電子材料に利用されている。本研究では、物性のさらなる向上のため、マレイミド二重結合と反応する官能基の導入による架橋ネットワークの緻密化を検討した。ベンゾオキサジンへのアリル基の導入により、ベンゾオキサジン/マレイミド硬化物の耐熱性と熱膨張性が向上することを確認した[1)]。またモデル化合物を用いた反応機構解明によって、硬化物中の架橋構造を明らかにした。

ベンゾオキサジン **1**、およびマレイミド **2** から硬化物を作製した。アリル基を有するベンゾオキサジン **1a** から作製した硬化物はアリル基を持たない **1b** から作製したものと比べ、高耐熱性と低熱膨張性を示した。またモデル反応において、アリル基の導入によってオキサジン環の開環機構が変化すること、およびベンゾオキサジン分解物とマレイミド二重結合が反応することを明らかにした。さらにアリル基とマレイミド二重結合間の反応が触媒によって変化することが示唆された。



1a: R = Allyl
1b: R = H

2

1) Properties and the curing mechanism of cured blends of diallyl bisphenol A-based benzoxazine and bismaleimide have been reported. Z. Wang, J. Zhao, Q. Ran, R. Zhu, Y. Gu, *React. Funct. Polym.* **2013**, *73*, 668–673.

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セルロースナノファイバーの π 吸着特性解明に向けた gel-state NMR 分析法の改良

（県立広島大学[1]・国立研究開発法人産業技術総合研究所[2]）◯広狩 摩周[1]・齋藤 靖子[2]・三苫 好治[1]・榊原 圭太[2]

Improvement of gel-state NMR spectroscopy to investigate the adsorption property of π-conjugated molecules onto cellulose nanofiber ([1]*Prefectural University of Hiroshima,* [2]*National Institute of Advanced Industrial Science and Technology (AIST)*)

◯Mashu Hirogari,[1] Yasuko Saito,[2] Yoshiharu Mitoma,[1] Keita Sakaibara[2]

Curcumin is expected to have antioxidant and anti-inflammatory effects and has been actively studied. However, since curcumin is insoluble in water and expresses low bioactivity when ingested, its solubility needs to be improved to obtain its medicinal effects. On the other hand, cellulose nanofibers (CNFs) have been known to adsorb π-conjugated compounds such as curcumin well. As the results, the absorption peak at 1512 cm^{-1} of curcumin and CNF in FT-IR spectrum shifted to the higher wavenumber side. However, it was found that the gel-state NMR signal of cellulose was not sufficiently detectable to evaluate the intermolecular interaction of adsorption behavior in the presence of deuterated water. Therefore, we also attempted to optimize the NMR measurement conditions so that cellulose-derived signals can be detected even in the presence of deuterated water.

Keywords : Curcumin; Cellulose nanofiber; NMR

クルクミンには、抗酸化作用、抗炎症作用などの効果が期待され、応用研究が進んでいる。しかしながら、クルクミンは水に難溶であり、摂取時の生理活性が低いため、薬効を得るには溶解性の向上が必要である。一方、セルロースナノファイバー（CNF）はクルクミンなどのπ共役化合物を良好に吸着することが見出されている[1)]。CNF 含有量の増加に伴い、クルクミンの C=O に由来する吸収ピーク[2)]が 1512 cm^{-1} まで高波数シフトした。（fig. 1）吸着メカニズム解明のため gel-state NMR 法を用いて重水分散中での分子間相互作用の解析を試みたが、重水存在下ではセルロース由来の NMR シグナルが十分に検出できず、水中での吸着挙動を評価できないことがわかった。そこで、重水存在下でもセルロース由来のシグナルが検出できるような NMR 測定条件の最適化も試みたので、併せて報告する。

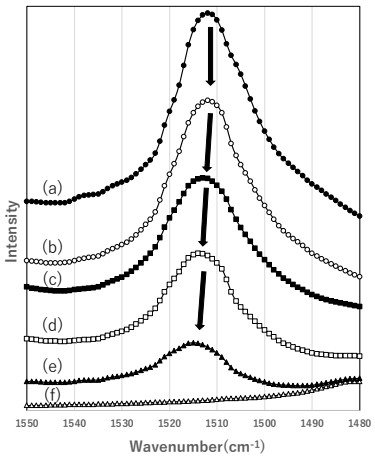

Fig. 1 FT-IR spectra of **a** curcumin, the curcumin-CNF mixtures **b** 1:9, **c** 1:4, **d** 1:2, **e** 1:1 (w/w), and **f** CNFs

1) Dispersion of quinacridone pigments using cellulose nanofibers promoted by CH-π interactions and hydrogen bonds. Y. Saito, S. Iwamoto, N. Hontama, Y. Tanaka, T. Endo, *Cellulose*. **2020**, *27*, 3153.

2) DFT and Experimental Studies of the Structure and Vibrational Spectra of Curcumin, T.M. Kolev, E.A. Velcheva, B.A. Stamboliyska, M. Spiteller, Int. J. Quantum Chem. 102 (6) (2005) 1069–1079.

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リグニン由来 2-ピロン-4,6-ジカルボン酸（PDC）から成る木材接着剤ポリエステルの開発と生分解性評価

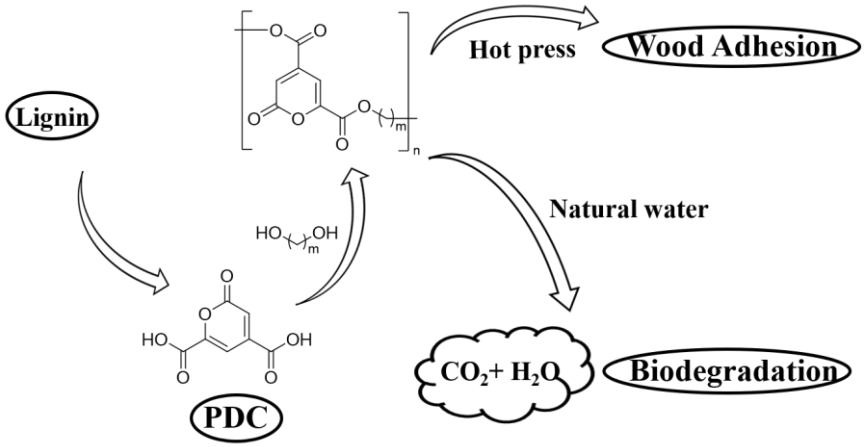
(東京工業大学[1]・森林総合研究所[2]・長岡技術科学大学[3]) ○金 易介[1]・荒木 拓馬[2]・上村 直史[3]・政井 英司[3]・中村 雅哉[2]・道信 剛志[1]

Development and biodegradability of wood adhesive polyesters composed of lignin-derived 2-pyrone-4,6-dicarboxylic acid (PDC) ([1]*Department of Materials Science and Engineering, Tokyo Institute of Technology*, [2]*Forestry and Forest Products Research Institute*, [3]*Nagaoka University of Technology*) ○Yijie Jin,[1] Takuma Araki,[2] Naofumi Kamimura,[3] Eiji Masai,[3] Masaya Nakamura,[2] and Tsuyoshi Michinobu[*1]

2-Pyrone-4,6-dicarboxylic acid (PDC) is a chemically stable metabolic intermediate of lignin, and its condensation polymers can be synthesized by utilizing the functionality of two carboxylic acids.[1] In this study, PDC-based polyesters named P(PDC2) and P(PDC3) were synthesized, and they showed strong adhesive strengths to wood with the highest adhesion of 6.40 MPa, which usually causes wood failure. The adhesive strength of 3.13 MPa remained even after immersion in hot water at 60 °C for 4 h, demonstrating the excellent adhesive strength and water resistivity of the PDC-based polyesters. The PDC polymers biodegraded after 180 days of incubation in a natural pond water environment and reached a biodegradation rate of about 15%.

Keywords : Adhesive; Biomass; Biodegradation; Lignin; Polyester

リグニン代謝中間体由来の 2-ピロン-4,6-ジカルボン酸（PDC）は二つのカルボン酸を有するため、ジオールと共重合して対応するポリエステルを合成した。得られた PDC ポリエステル（P(PDC2)および P(PDC3)）は木材への強い接着性を示し、最大接着力は 6.40 MPa であった。60℃の温水中に 4 時間浸した後でも 3.13MPa の接着力を示し、PDC ポリエステルの強い耐水性と接着性を明らかにした。また、PDC ポリエステルは池水中で生分解し、分解度は 180 日後に約 15%であった。



1) T. Michinobu, M. Hishida, M. Sato, Y. Katayama, E. Masai, M. Nakamura, Y. Otsuka, S. Ohara, K. Shigehara, *Polym. J*. **2008**, *40*, 68.

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Obtain thermal responsive star-shaped copolymer gel with homogeneous network containing gold nanoparticles

([1] *Graduate School of Engineering, Nagoya University*) ○ Yian WANG[1],, Yukikazu TAKEOKA[1]

Keywords: Gold Nanoparticle, Controlled polymerization, Thermal-responsive hydrogel, Homogeneous network.

Gold nanoparticles (AuNPs) are particles smaller than 100 nm which can change optical properties dependent on factors such as size, shape, dielectric distance. However, AuNPs are prone to aggregation due to their high surface energy, resulting in the loss of unique properties [1]. Therefore, stabilizing agent is typically required during the synthesis of AuNPs. Recently, hydrogels have been employed to support the synthesis [2]. Among these, thermoresponsive gels (*N*-isopropylacrylamide (NIPA) gel) can undergo a phase transition in responsive to heat. When AuNPs are loaded into these gels, a rise of temperature causes gels to shrink, altering the electron distance between AuNPs, consequently, changing their optical properties. As a result, the hybrid material exhibits thermoresponsive optical properties. However, traditional gels have the problem of inhomogeneity and low shrinkage rate which impair the control of AuNPs' properties and limit application.

In this study, star-shaped block-copolymers gels with homogeneous network composed by NIPA and *N,N*-dimethylacrylamide (DMA) were prepared. DMA, a hydrophilic monomer, is used as comonomer to increase shrinkage rate. Pentaerythritol tetra (2-chloropropionate) (PETCP) and *N,N'*-methylenebisacrylamide (MBAA) were used as initiator and crosslinker respectively. The entire process is illustrated in Figure1. Au ions were firstly introduced into gels and then reduced into AuNPs. Results showed that particles prepared in gels with homogeneous network were proved to be less aggregated and ultra small with sizes below 10 nm comparing to the particles prepared in traditional gels.

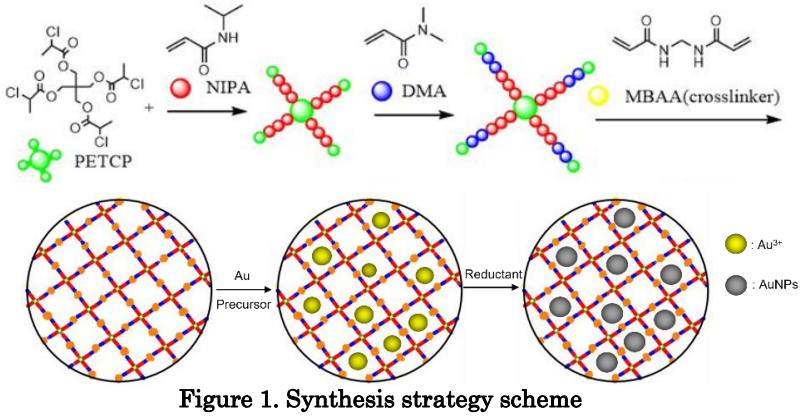

Figure 1. Synthesis strategy scheme

1) Gibson, M. I.; O'Reilly, R. K. *Chem. Soc. Rev.* **2013**, 42 (17). 2) Palmese, L. L.; Thapa, R. K.; Sullivan, M. O.; Kiick, K. L. *Current Opinion in Chemical Engineering* **2019**, 24, 143–157.

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主鎖にインドロキノキサリンを持つポリマーの合成と性質

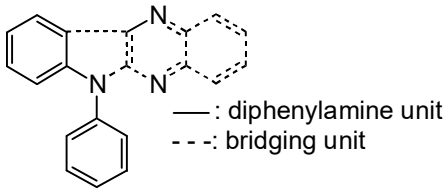
(名市工研[1]・静岡理工科大先端機器分析セ[2]) ○林 英樹[1]・小田 三都郎[1]・小泉 武昭[2]

Preparation and Properties of Indroquinoxailine-containing Polymer ([1]*Nagoya Municipal Industrial Research Institute*, [2]*Advanced Instrumental Analysis Center, Shizuoka Institute of Science and Technology*) ○Hideki Hayashi,[1] Mitsuo Oda,[1] Take-aki Koizumi[2]

Indroquinoxaline-containing polymers were prepared and their properties were investigated. Each polymer was prepared by dehalogenative polymerization of corresponding dihalogenoindoroquinoxaline, which was prepared from dehydrative condensation of the phenylenediamine derivative and the isatin derivatives. Electrochemical measurements of the polymers indicated the usability of the compounds as n-type semiconductors.

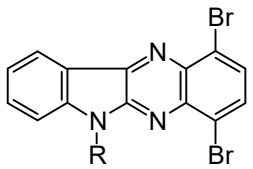
Keywords : Indroquinoxaline; π-Conjugated Polymer; Electrochemical Properties; Optical Properties

発表者は、n-型半導体特性を示すジフェニルアミン化合物として、*N*-フェニルインドロキノキサリン (Scheme 1) およびその関連化合物の合成を行い、それらの特性評価を行っている[1)]。Scheme 1 に示すとおり、この化合物は、実線で示したジフェニルアミンユニットのベンゼン環の一つが、点線で示した N-上の置換基によって架橋されており、かつ架橋ユニットがキノキサリンユニットである。さらに、このインドロキノキサリンユニットに着目し、二量体の合成および特性評価も行っている[2)]。今回は、インドロキノキサリン含有ポリマーの合成および特性評価を行った結果について報告する。



Scheme 1. Chemical structure of *N*-phenylindroquinoxaline.

インドロキノキサリン含有ポリマーは、Scheme 2 に示したジブロモインドロキノキサリンをモノマーとして、遷移金属錯体を用いるカップリング反応により合成した。ポリマーの吸収極大波長は、モノマーユニットのそれよりも長波長側にシフトしており、重合によるπ共役の広がりが示唆された。このポリマーの CV 測定を行ったところ、還元側に活性を示したことから、このポリマーが n-型半導体特性を持つことが示唆された。



Scheme 2. Chemical structure of dibromoindroquinoxaline.

1) H. Hayashi, E. Tsuda, T.-a. Koizumi, *ChemistrySelect,* **2021**, *6*, 5441. 2) H. Hayashi, M. Oda, T.-a. Koizumi, *ChemistrySelect*, **2023**, *8*, e202302569.

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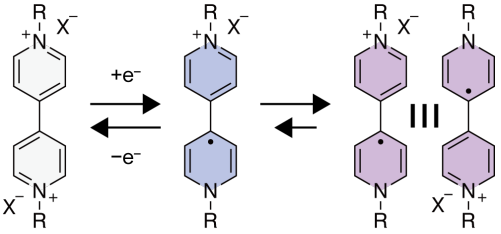
ワイヤレスな電気化学ゲルアクチュエーターの設計

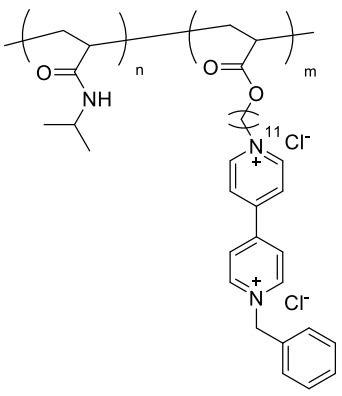
（広島大工[1]・広島大院先進理工[2]）○程野 颯真[1]・今任 景一[2]・日野 太一[2]・今榮 一郎[2]・大山 陽介[2]
Design of Wireless Electrochemical Gel Actuators ([1]*School of Engineering*, *Hiroshima University*, [2]*Graduate School of Advanced Science and Engineering*, *Hiroshima University*)
○Soma Hodono,[1] Keiichi Imato,[2] Taichi Hino,[2] Ichiro Imae,[2] Yousuke Ooyama[2]

Soft actuators that convert external stimuli into macroscopic motion as artificial muscles have attracted much attention in a wide range of fields. Electric stimulation is suitable and desired particularly for the application in soft robotics to control actuation. However, the shapes of previous electric actuators are limited to thin films, and the movement is limited to bending and extension, narrowing their applications. In our previous study, we developed electrochemical gel actuators that contracted and swelled like a muscle without any tethered connection to a power supply by combination of hydrogels with viologen, which reversibly forms a π-dimer by redox, in the side chains and bipolar electrochemistry, which works wirelessly in a dilute supporting electrolyte solution.[1)] However, the gel actuators showed low strength, response speed, and reversibility.

In this study, to improve them, we changed the substituent of viologen and the main chain to poly(*N*-isopropyl acrylamide) (PNIPAAm), which has a lower critical solution temperature (LCST), and used living radical polymerization.
Keywords: Soft actuators; Viologen; Bipolar electrochemistry; Poly(N-isopropylacrylamide); Hydrogels



外部刺激で駆動する柔軟なアクチュエーターはソフトロボティクスなどへの応用が期待され、特に電気刺激は応答速度や制御性の観点からその応用に適する。しかし、これまでの電気駆動ソフトアクチュエーターの形状は薄膜に限られ、動作も簡単な屈曲や伸展程度で、用途は限られた。そこで当研究室では、酸化還元によって可逆的に二量体を形成するビオロゲンを側鎖に有するヒドロゲルと、希薄な電解質溶液中でワイヤレスに駆動するバイポーラ電極を組み合わせ、外部電源との直接の接続なしに筋肉のように伸縮する電気化学ゲルアクチュエーターを開発した[1)]。しかし、このゲルアクチュエーターの強度や応答速度、可逆性は低かった。



今回、これらの改善を目指して、ビオロゲンの置換基の変更や主鎖骨格の下限臨界溶液温度（LCST）を示すポリ（*N*-イソプロピルアクリルアミド）（PNIPAAm）への変更、リビングラジカル重合の適用などを検討した。

1) K. Imato, T. Hino, N. Kaneda, I. Imae, N. Shida, S. Inagi, Y. Ooyama, ***Small*** **2024**, 2305067, in press.

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Supramolecular Assembly of Biodegradable Amphiphilic Block Copolymers Built through Biomolecule Folic Acid as a Hydrogen Bonding Moiety

([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering, Osaka University*) ○Rongjian Lang,[1] Yusuke Miyazaki,[1] Masaki Nakahata,[2] Kazuki Fukushima,[1] Takashi Kato[1]

Keywords: Self-organization; Amphiphilic Block Copolymer; Hydrogen Bond; Molecular Assembly

Amphiphilic diblock copolymers, consisting of hydrophilic and hydrophobic segments, are known to self-assemble into a variety of nanostructures in aqueous solution[1]. Various dimensions and morphologies of polymeric micelles are achieved by tuning the chemical structure and amphiphilic balance of the component polymers[1]. Hydrogen-bonding motif is a valuable option for polymeric micelles to change the morphology and enhance interactions with drugs and aggregation force in the hydrophobic core[2]. In this study, V-shaped block copolymers **1** were designed and synthesized, conjugating two chains of poly(ε-caprolactone)-*b*-poly(ethylene glycol) (PCL-*b*-PEG) with folic acid as a hydrogen bonding moiety[3].

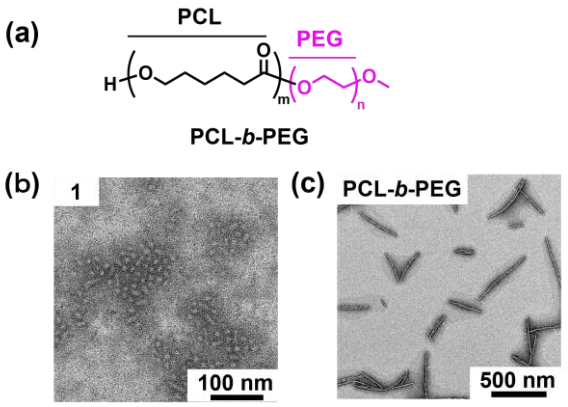

Figure 1. Molecular structure of PCL-*b*-PEG (a). TEM images of self-assemblies of **1** (b) and PCL-*b*-PEG (c) in water.

Diblock copolymers PCL-*b*-PEG (Figure 1a) were prepared by ring-opening polymerization with different block ratios. The chains of PCL-*b*-PEG were then conjugated with folic acid to form **1**. In aquatic solution, the assemblies of **1** showed small dots with diameters less than 20 nm in the transmittance electron microscope image (Figure 1b). In contrast, the assemblies of PCL-*b*-PEG formed larger dimensions of needle-like and fibrous structures with lengths over 500 nm (Figure 1c). Therefore, the hydrogen-bonding unit folic acid conjugated to two PCL-*b*-PEG chains could alter the self-assembled structures and contribute to the formation of uniform discrete nanospheres.

1) Y. Mai, A. Eisenberg, *Chem. Soc. Rev.,* **2012**, *41*, 5969.
2) T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem., Int. Ed.* **2006**, *45*, 38.
3) T. Kato, *Science*. **2002**, *295*, 2414.

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Polymer matrix effects on photoinduced electron transfer

([1]Graduate School of Science, Osaka University, [2]Graduate School of Engineering Science, Osaka University)
Yilin Cao[1], Hikaru Sotome[2], Syoji Ito[2], ○Hiroyasu Yamaguchi[1]
Keywords: Photoinduced Electron Transfer, Porphyrin, Electron Acceptor, Polymer, Supramolecular Complex

To transfer electrons efficiently from electron donors to electron acceptors, the distance between the two must be maintained appropriately to prevent reverse electron transfer. In this study, we report our finding that the amount of electron transfer products can be increased by adding polymers that can specifically form complexes with electron donors through various types of non-covalent bonds.

Polyvinylpyrrolidone (PVP) was found to form complex with pigments 5,10,15,20-tetrakis-(4-sulfonatophenyl) porphyrin (TPPS) and its zinc complex (ZnTPPS) quantitatively through different interactions (hydrogen bonds and coordination bonds, respectively). These complex formations hinder the interaction between ground-state TPPS or ZnTPPS and an electron acceptor (methyl viologen, MV^{2+}) and could control the photoinduce electron transfer from TPPS or ZnTPPS to MV^{2+}, giving more electron transfer products methyl viologen cationic radical ($MV^{+\bullet}$) (**Figure 1a**).

An artificial photoinduced electron transfer system within a poly(N-methyl-4-vinylpyridinium) (P4VPMe) polymer matrix was also developed. In the presence of an excess of P4VPMe, ZnTPPS exists as individual molecules rather than self-aggregating, favoring photoinduced electron transfer. Under these conditions, P4VPMe inhibits the formation of ground-state charge-transfer complex between ZnTPPS and MV^{2+}. This shifts the main electron transfer process from singlet to triplet states. ZnTPPS with an excess of P4VPMe increased the catalytic activity of photoinduced oxidation of MV^{2+} more than 10-fold compared to ZnTPPS alone (**Figure 1b**).

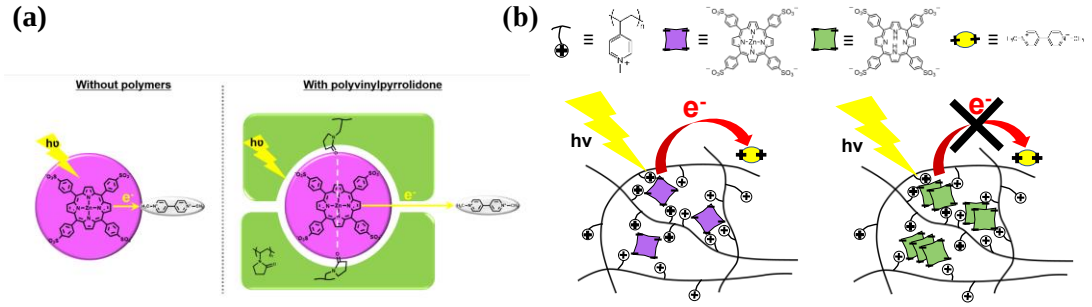

Figure 1. Complex formation of **(a)** PVP with ZnTPPS and **(b)** P4VPMe with ZnTPPS (left) and TPPS (right). Corresponding photoinduced electron transfer behaviors of the complexes are also shown in each figure.

1) Y. Cao, T. Takasaki, S. Yamashita, Y. Mizutani, A. Harada, H. Yamaguchi, *Polymers* **2022**, 14, 1191. 2) Y. Cao, H. Sotome, Y. Kobayashi, S. Ito, H. Yamaguchi, H. *Submitted*.

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4 位にオリゴフェニレンを有する 3,5-ジヒドロキシメチルフェニルアセチレンの重合と生成ポリマーの性質

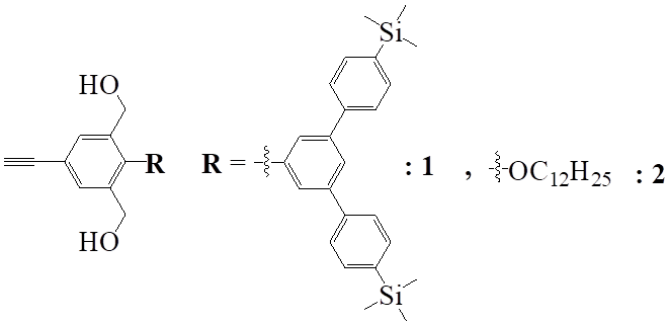
（新潟大院自然）○田口 裕規・金子 隆司・青木 俊樹・寺口 昌宏

Polymerization of 3,5-dihydroxymethylphenylacetylene having oligophenylene moiety at 4 - position and properties of the resulting polymers

(*Graduate School of Scienece and Technology, Niigata University*)○Yuki Taguchi, Toshiki Aoki, Takashi Kaneko, Masahiro Teraguchi

We previously reported that polymerization of phenylacetylene monomers with two hydroxymethyl groups at 3- and 5- positions using a rhodium catalyst system afforded polymers consisting of a tight helical main chain with a cis-cisoidal structure, and that the helical structure was maintained by intramolecular hydrogen bonds between hydroxymethyl groups in the side chains[1]. In this study, we synthesized and polymerized a 3,5-bis(hydroxymethyl) phenylacetylene having a bulky terphenyl derivative at 4- position**(1)**, and investigated the properties of the resulting polymers. **1** was polymerized by a rhodium catalyst system to give poly**1**, which was partially soluble in THF and $CHCl_3$. On the other hand, copolymerization with **2** afforded the corresponding copolymers with number-average molecular weights (M_n) ranging from 2.0~3.0×10^5, which were completely soluble in THF and $CHCl_3$.

Keywords: *Polyphenylacetylene; Helical polymer; Terphenyl group; Fluorescence; cis-cisoidal structure*



我々は、以前に 3，5 位に 2 つのヒドロキシメチル基, 4 位にドデシルオキシ基を有するフェニルアセチレンモノマー**(2)**が、ロジウム触媒系を用いた重合によりシスシソイダル構造のタイトならせん主鎖からなるポリマーを与えること、およびそのらせん構造が 2 つの水酸基による分子内水素結合により維持されていることを報告した [1]。本研究では、新しく 4 位にターフェニル誘導体を導入したフェニルアセチレン**(1)**の合成と重合を行い、生成ポリマーの構造および性質を明らかにした。

ターフェニル誘導体を有するフェニルアセチレン**(1)**はロジウム触媒系により重合し、THF、$CHCl_3$ に一部可溶なポリ**(1)**を生成した。一方、**2** との共重合では数平均分子量(M_n)が 2.0~3.0×10^5 で、THF や $CHCl_3$ に完全に可溶な高重合体が得られた。当日は生成ポリマーの側鎖置換基の積層構造や蛍光特性についても報告する。

1) T. Aoki *et al., J. Am. Chem. Soc.* **2003***, 125,* 6346-6347.

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Zwitterion の配列制御を利用したリチウムイオン伝導性電解質の開発

（東京農工大）○横山智美・一川尚広
A design of lithium-ion conductive electrolytes based on alignment of zwitterions
(*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Satomi Yokoyama, Takahiro Ichikawa

Development of polymer electrolytes with excellent lithium-ion conductivity is important to further improve the performance of lithium-ion batteries. Zwitterion is an ion with cation and anion in the same molecule. It is characterized by high ion density and the ability to transport the target ions selectively. For example, the zwitterion shown in Figure 1 was found to contribute to improved lithium-ion conductivity because of the delocalization of electrons in its anionic moiety.

We have developed amphiphilic molecules with zwitterions as hydrophilic moieties. These amphiphilic zwitterions self-organize by the phase separation of the hydrophilic and hydrophobic moieties. In this study, we expected that the regular arrangement of such zwitterions could yield a new material conducting lithium-ions selectively. New amphiphilic zwitterions were designed based on zwitterions with excellent lithium-ion conductive ability. Their physicochemical properties and self-organizing behavior were investigated.
Keywords : Zwitterion; Self-organization; Amphiphilic molecule; Lithium-ion conduction

リチウムイオン電池の更なる高性能化のためには、優れたリチウムイオン伝導性を有する高分子電解質の開発が重要である。Zwitterion は同一分子内にカチオンとアニオンが存在するイオンであり、イオン密度が高く、目的イオンのみ輸送することが出来ることが特徴である[1]。例えば、Figure 1 に示した Zwitterion は、そのアニオン部位の電子が非局在化しているため、リチウムイオン伝導度の向上に寄与することが分かっている。

これまで当研究室では、Zwitterion を親水部として有する種々の両親媒性分子を開発してきた[2]。分子内に疎水部位と親水性の Zwitterion 部位を併せ持つ両親媒性分子は、親水部位と疎水部位の相分離を駆動力として自己組織化する。我々は、自己組織化を駆使して Zwitterion を規則的に配列させることでリチウムイオンを高速かつ選択的に伝導することが出来るのではないかと考えた。本研究では、リチウムイオン伝導性に優れた Zwitterion を用い、新たに両親媒性 Zwitterion を設計し、その自己組織化挙動について調べた。

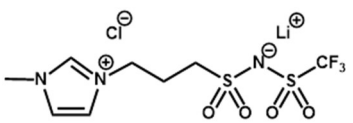

Figure 1 リチウムイオン伝導性 Zwitterion.

[1] A. Narita, W. Shibayama and H. Ohno, *J. Mater. Chem.*, **2006,** *16*, 1475.
[2] T. Ichikawa, T. Kato and H. Ohno, *J. Am. Chem. Soc.*, **2012**, *134*, 11354.

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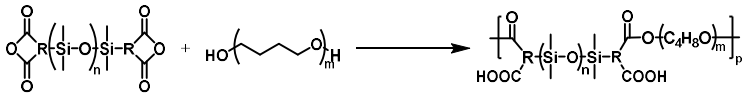
シリコーン系マルチブロック共重合体の合成とエポキシ樹脂の改質効果

（東レ株式会社）○岩田 寛和・浅野 到
Synthesis of silicone-based multiblock copolymers and additive effects on epoxy resins (*Toray Industries, Inc.*) ○Hirokazu Iwata, Itaru Asano

Silicone additives are often used to make hard and brittle epoxy resins less elastic. However, since silicones aggregate in epoxy resins due to have a dissimilar solubility parameter (SP) from epoxy resins, concern such as deterioration of appearance and decrease in mechanical properties remain. To develop silicone additives that disperse well in epoxy resins, we design and synthesize silicone-based multiblock copolymers by copolymerizing components that have close SP value to epoxy resin. In practice, we confirmed that the multiblock copolymer obtained by copolymerizing poly(tetramethylene ether)glycol with polydimethylsiloxane indeed nano-disperses within epoxy resin matrices. Furthermore, epoxy resins with this multiblock copolymer exhibited both reduced elasticity and enhanced toughness compared to epoxy resins without them.
Keywords : multiblock copolymers; silicone; nanophase separation; epoxy resin composition

硬く脆いエポキシ樹脂を低弾性率化する際、シリコーン系添加剤がしばしば使用される。しかし、シリコーンはエポキシ樹脂と SP 値が離れているため、エポキシ樹脂中で凝集し、外観の悪化、機械特性の低下などを引き起こす懸念がある。そこで、エポキシ樹脂に良分散するシリコーン系添加剤を開発するため、シリコーンに対し、エポキシ樹脂と SP 値が近い成分を共重合させたシリコーン系マルチブロック共重合体を設計・合成した。

実際に、末端酸無水物変性ポリシロキサンに対し、ポリ(テトラメチレンエーテル)グリコールを共重合し得られたマルチブロック共重合体は、狙い通りエポキシ樹脂硬化物中でナノ分散化することを確認した。また、マルチブロック共重合体を配合したエポキシ樹脂硬化物は、非配合のエポキシ樹脂硬化物と比較し、低弾性率化するとともに高靭性化した。



Scheme 1. Synthesis of multiblock copolymer

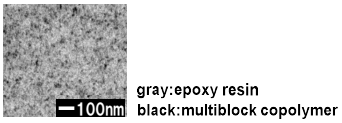


Figure 1. TEM images of epoxy resin with multiblock copolymer

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β-1, 3-グルカン誘導体の三重らせん構造形成に基づく機能発現

（崇城大院 工）○奥江　眞海, 田丸　俊一
Triple helix formation and properties of modified ß-glucan derivatives , (*Graduate School of Engineering, Sojo University*) ○Masami Okue, Shun-ichi Tamaru

β-glucans are natural polysaccharides forming a triple-helical structure. Owing to the reversible helix formation ability, we have utilized these polysaccharides as one-dimensional host materials and reported various application studies. In this study, we investigated the establishment of the formation of hetero-triple-helix composed of different β-glucans by using amphoteric curdlans, with the aim of developing the advanced functional molecular system based on the assembling of several functional molecules. In addition, the water solubilization of single-walled carbon nanotubes by yeast-derived *β*-glucans had been studied.
Keywords : *Helical structure, polysaccharides, supramolecular chemistry, stimuli responsiveness, self-assmbly*

β-グルカン（**BG**）は、免疫賦活効果などの有用な生理活性を有している。可逆的ならせん構造形成能を持つことから高分子ホスト材料として活用でき、他の天然または合成らせん性高分子とは大きく異なる特徴を有する天然のらせん性高分子の一つである。当研究室ではこれまでにさまざまな **BG** 誘導体を開発し、三重らせん構造形成能に基づく機能発現を実現してきた。本研究では、より複雑な分子集積に基づく高度な機能の実現を期待して、両性カードラン（**AC**）[1]を母体とした側鎖修飾カードランを調製し、異なる **BG** 誘導体からなるヘテロ三重鎖の形成法の確立について検討した。天然由来の水溶性 **BG** であるシゾフィラン（**SPG**）と蛍光色素との錯形成は、定量的に進行することが確認され、最大包接量はグルコースユニットに対して 5 mol%程度であることが確認された。以上の結果を基準として、本発表では色素修飾 **AC** の 3 重らせん形成能および、異なる **AC** からなるヘテロ 3 重らせん形成に関する検討結果について発表する。

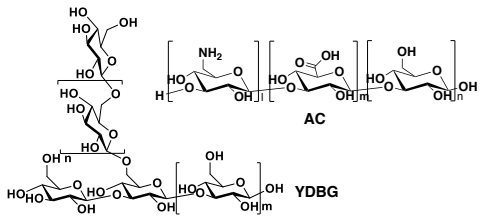

Fig. 1, Structure of **AC** and **YDBG**.

さらに、酵母由来 *β*-1,3-1,6-グルカン（**YDBG**）による単層カーボンナノチューブの単分子的可溶化に関する検討を行った。酵母を次亜塩素酸処理する事で、側鎖/主鎖のグルコース残基比などの構造特性の異なる **YDBG** を調製した。いずれも三重らせんを形成し、物質包摂能を持つことが確認されたが、主鎖の β グルカン鎖の鎖長が短くなるほど、三重らせん形成能は損なわれた。いずれの **YDBG** を用いても **SWCNT** との単分子的可溶化に成功したが、特に比較的主鎖の鎖長が長い **YDBG** が、**SWCNT** との錯形成に有利であることが示唆された。この錯形成過程には **SWCNT** 上のカイラリティーに対してある程度の選択性を示すことが見出された。

[1] Tamaru, S. -I.; et al., *Org. Bromol. Chem.,* **2014**, *12,* 815; *Chem. Asian J.* **2019**, *14*, 2102.

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サケ白子由来 DNA とジスルフィド結合を有するカチオン性脂質からなるポリイオンコンプレックス微粒子の作製

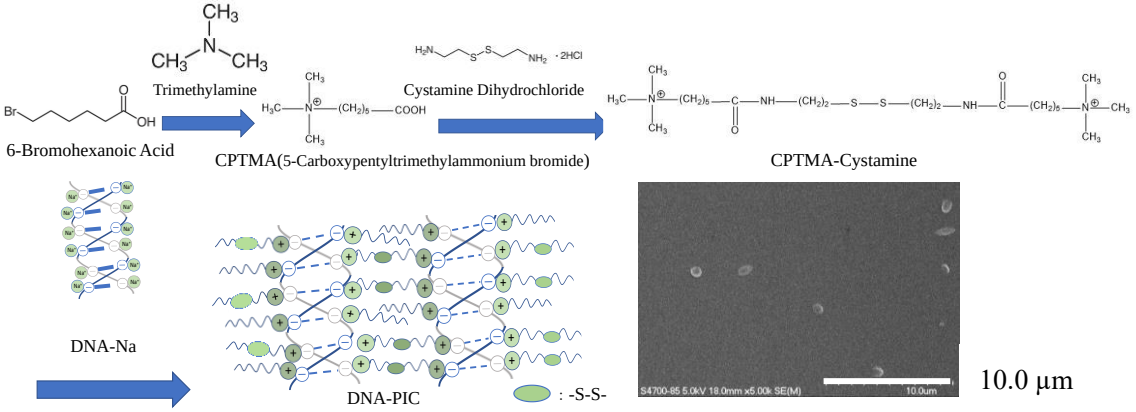
(千葉工大院工[1])○大向 康太[1]・柴田充弘[1]・寺本直純[1]

Preparation of polyion complex microparticles composed of salmon milt DNA and cationic lipids having a disulfide bond ([1]Chiba Inst. Technol.) ○Kota Ohmukai, Mitsuhiro Shibata, Naozumi Teramoto

DNA attracts interest as a biofunctional material due to its biodegradability, double helical structure, high molecular weight and hydrophilicity. Salmon milt contains high content of DNA, but most of salmon milt is not utilized effectively.[1)] Therefore, we intend to develop the application of DNA derived from salmon milt as a biodegradable drug carrier accompanied by stimulus-responsive properties. In this study, we decided to prepare DNA-based polyion complexes (DNA-PIC) using a dicationic lipid having a disulfide bond for its redox responsiveness. A cationic lipid was synthesized as follows: 6-bromohexanoic acid was reacted with trimethylamine to prepare a cationic aliphatic acid molecule, 5-carboxypentyltrimethylammonium bromide (CPTMA). CPTMA was reacted with cystamine dihydrochloride using *N,N'*-diisopropylcarbodiimide (DIPC) as a condensation reagent to yield a dicationic molecule CPTMA-cystamine containing a disulfide bond. The product was dissolved in pure water and added to a DNA-Na aqueous solution. The mixture was then centrifuged, washed, and lyophilized to form DNA-PIC powder. The DNA-PIC powder was easily dispersed in water. The resulting dispersion was dropped onto a cover slip and dried in air. The SEM microphotographs revealed that microparticles with a diameter of approximately 1 μm were obtained.

Keywords: DNA, Microparticles, Dicationic molecule

DNA は、生分解性、二重らせん構造、高い分子量、親水性などの特徴を持ち、生体機能性材料としての応用が期待されている。サケ白子は多量の DNA を含んでいるが、そのほとんどが有効に利用されていない。[1)] そのためサケ白子由来の DNA を生分解性の薬物担体として応用すること、また、これに刺激応答性を持たせることを考えた。そこで、酸化還元に対する応答性官能基として、ジスルフィド結合を有するジカチオン性脂質と DNA のポリイオンコンプレックス(DNA-PIC)を作製することとした。本研究では 6-bromohexanoic acid を trimethylamine と反応することでアルキル基含有カチオン性分子 CPTMA (5-carboxypentyltrimethylammonium bromide)を合成した。その後縮合剤として *N,N'*-diisopropylcarbodiimide を使用し、cystamine 塩酸塩と反応させることで、ジスルフィド結合含有ジカチオン性分子 CPTMA-cystamine を合成した。これを純水に溶解させ、DNA-Na 水溶液に加えて撹拌した後、遠心分離、洗浄、凍結乾燥の工程を経て DNA-PIC を得た。この DNA-PIC を水に分散させることで、その分散液を得た。これをカバーガラス上に滴下して乾燥した後、SEM で観察したところ、直径が約 1 μm の微粒子が確認された。



1) 西則雄, 北村秀光, 素材としての DNA, 高分子, **47**, 398-401 (1998)

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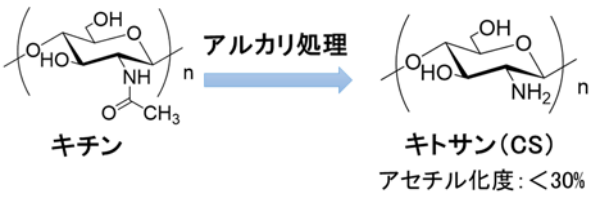
分子量とアセチル化度がキトサンの溶解性に与える影響

（宮崎大工[1]）○荒木　美穂[1]・井澤　浩則[1]
Effect of Degree of Acetylation and Molecular Weight on Solubility of Chitosans (Faculty of Engineering, University of Miyazaki)○Miho Araki, Hironori Izawa

Chitosan (CS) is an amino-polysaccharide produced by deacetylation of chitin. CS is widely used in various fields. Although common CSs are only soluble in acidic aqueous solutions, CS with the degree of acetylation (DA) of 50% is soluble in water. Namely, the solubility of CS is highly dependent on DA. However, the reports concerning the relationship between DA and solubility are very old. In addition, it is unclear whether the state in water is dissolved or dispersed. In this study, solubility of CSs with different DA and/or molecular weights was investigated. The 30 mg/mL low molecular weight CS lactate (DA11%, 23%, and 32%) solutions were prepared with water and pH values were adjusted to 7 by adding 1 mol/L NaOH. In the case of DA11% and DA23%, visible precipitation was appeared when pH value was adjusted to 7. In contrast, DA32% did not show visible precipitation, suggesting solubility increased with DA increases. Indeed, transmittance of DA32% was higher than those of DA11% and DA23%. We additionally investigated solubility of acetylated CSs prepared from the above CS lactate with DA11% and higher molecular weight acetylated CSs.
Keywords : Chitosans; Degree of Acetylation; Solubility; Water Soluble Chitosan



キトサン（CS）は、キチンの脱アセチル化により得られるアミノ多糖である（右図）。CS には、加水分解されなかったキチン構造が含まれており、その量はアセチル化度（DA）として表される。CS は、酸性水溶液にしか溶解しないが、DA が 50%の CS は水に溶解することが知られている。この DA50%の CS は水溶性 CS と呼ばれているが、その水溶性を報告した例は非常に古く、分子レベルで溶解しているのか、分散状態なのかどうかが曖昧である。水溶性 CS の溶解性を再検証し、水溶性 CS の組成（DA 及び分子量）を明確に提示すれば、CS 材料に新展開が期待できる。そこで本研究では DA の異なる CS の溶解性を評価した。

DA11%、DA23%、DA32%の低分子量 CS 乳酸塩を用いた。30 mg/mL CS 乳酸塩水溶液に、1 mol/L の NaOH を加えて pH を 7 に調整した。この際、DA11%及び DA23%では CS の析出が観察された。DA11%、DA23%、DA32%の 700 nm における透過率は、それぞれ、7.2%、49.0%、80.6%であり、DA が上がるにつれて透過率が向上することが確認された。透過率の低下は CS の析出による散乱に起因することから、DA が 50%に近づくほど、溶解性が上がることが示唆された。

一般の CS と同様な溶解性を示す DA11%の CS 乳酸塩を無水酢酸でアセチル化することで DA を制御したアセチル化 CS（DA32%、DA45%、DA55%）を合成した。合成したアセチル化 CS の酢酸水溶液と水への溶解性試験を行った。いずれのアセチル化 CS も酢酸水溶液に溶解した。一方、DA55%と DA45%のアセチル化 CS は水に溶解したが、DA32%は水に溶解しなかった。このことから、DA を 50%に近づけることで、水溶性 CS が得られることが確認された。異なる分子量のアセチル化 CS を合成し、同様に溶解性を検証した。

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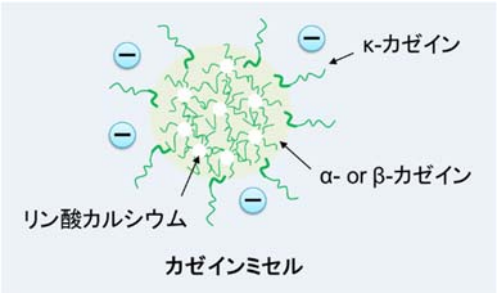
カゼインベース材料の開発

（宮崎大工）・○中島 弘貴・井澤 浩則
Development of Casein-Based Materials (*Faculty of Engineering, University of Miyazaki*) ○ Hirotaka Nakashima, Hironori Izawa

Casein is a protein presented in Milks. In the late 1800s, casein was used as a plastic material, so called casein plastic. However, the casein plastic was replaced by oil-based plastics. Recently, casein plastic has attracted much attention because of worldwide interest in carbon neutral. Here we investigated preparation of casein-based materials. Casein films were prepared with a casein solution made by dissolution of a casein in alkaline aqueous solution or additionally neutralized casein solution with HCl aqueous solution. The mechanical property of the casein films was investigated. The casein film made by the neutralized solution showed significantly higher strength than that made without the neutralized. In addition, the casein film was enhanced by adding glycerol as a plasticizer.
Keywords：Casein; Film material; Bioplastic; Milk



カゼインは、牛乳にカゼインミセルとして含まれるタンパク質であり（右図）、食品、医薬品、化粧品素材として利用されている。一方、1800 年代後半から 1900 年代中盤にかけてカゼインをホルムアルデヒドで架橋したカゼインプラスチックがボタンや装飾品、繊維として利用されていたが [1]、石油由来ポリマーが開発されたことで、カゼインプラスチックは利用されなくなった。しかし、近年のカーボンニュートラルへの機運の高まりや廃棄牛乳問題を背景にカゼインの材料利用に再び注目が集まっている。高強度化や熱可塑性の付与など、従来のカゼインプラスチックには無い特性を付与できれば、新規なバイオプラスチックとしての利用拡大が期待される。そこで、本研究では基礎的知見の収集を目的にカゼイン水溶液から得られるフィルムの創製及び物性評価を行った。

カゼインに水を加えた後に、1.0 M NaOH を加え、1 時間撹拌することでカゼイン溶液とした。得られたカゼイン溶液に、1.0 M HCl を加え、中和した後、一晩撹拌することで、中性カゼイン溶液とした。カゼイン溶液及び中性カゼイン溶液からキャストフィルムの引張試験を行った。カゼイン溶液から得られたフィルムの破断応力及び破断歪み率は、5.9±0.5 MPa 及び 1.1±0.3 %であった。一方、中和したカゼイン溶液から得られたフィルムでは、11.9±1.5 MPa 及び 2.1±0.2 %であり、中和により強度が上がることが分かった。また、可塑剤としてグリセロールを添加することで、強度がさらに向上することがわかった。

1) E. O. Whittier, S. P. Gould, *Ind. Eng. Chem.*,32, 906-907. (1940).

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EDTA グラフト化によるセルロースナノファイバー表層改質と金属吸着性評価

（苫高専[1]・北大院工[2]）○佐々 涼水[1]・木下 七海[1]・岸本 亮太[1]・藤田 彩華[1]・甲野 裕之[1] 田島 健次[2]

Synthesis and characterization of surface-modified nanofibrillated bacterial cellulose by EDTA for the adsorption of heavy metal ions ([1]*National Institute of Technology, Tomakomai College,* [2]*Faculty of Engineering, Hokkaido University*) ○Ryosui sasa,[1] Nanami Kinoshita,[1] Ryota Kishimoto,[1] Sayaka Fujita,[1] Hiroyuki Kono,[1] Kenji Tajima[2]

Nano-fibrillated bacterial cellulose (NFBC) with a diameter of 20–30 nm has very long fibers and, that is, it has a very high aspect ratio as well as large surface area. In this study, EDTA grafting was performed on the NFBC surface using EDTA monoanhydride to convert NFBC into an efficient metal adsorbent. The EDTA-grafted NFBC preferentially adsorbed transition metals in aqueous solutions such as Cu(II) and Pb(II), but almost no Mg(II). Its adsorption was extremely fast, and the adsorption equilibrium was reached within 5 min. Moreover, no significant loss in the adsorption efficiency even after five continuous adsorption–desorption cycles confirmed the good stability. From these results, the EDTA-grafted NFBC are expected to be applied to the fields of remediation and treatment of wastewater contained heavy metal ions.

Keywords : cellulose nanofiber, surface modification, EDTA, adsorption of heavy metal ion

ナノフィブリル化バクテリアセルロース（NFBC）は水溶性多糖を含む培地中で酢酸菌を通気撹拌培養することで得られる[1]。一般にセルロースナノファイバーは木材を機械解繊し調製するため、不均一な繊維形態で繊維長は短いが、NFBC は均一かつ 15 μm 以上の繊維長を持つ。そこで、表層水酸基を EDTA で置換し、NFBC の超比表面積効果を発揮した吸着効率が高い重金属吸着材の合成を試みた。本研究では NFBC 表層水酸基への EDTA グラフト化を確立し、金属吸着性を持ったナノ繊維材料（ED-NFBC）の合成と金属吸着性評価を目的とした。

ED-NFBC は NFBC の持つ高い表面積から、水中で三次元的なネットワーク構造を示し、極めて短時間での金属吸着が達成された。金属吸着性は EDTA の安定度定数に従い、遷移金属である銅と鉛に対して選択的に吸着した（Fig. 1）。また、希酸で処理することで金属イオンを脱着可能で、5 回繰り返し使用しても吸着能は 10% 程度しか低下せず、反復使用が期待できる。

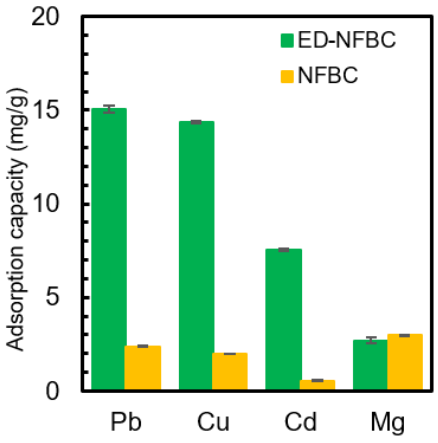

Fig. 1 The adsorption capacities of various metal ions of ED-NFBC and NFBC. The initial concentration each metal ions 25 mg/L, dosage of sample 0.5 g/ml, pH 5, contact time 5 min.

1) Kose, R., *et al.*, *Cellulose*, **20**, 2971 (2013).

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MOF 細孔内に閉じ込められたポリスチレンの熱分解挙動

（東大工[1]・東大院工[2]）○辰巳 遥真[1]・西島 杏実[2]・亀谷 優樹[2]・植村 卓史[2]

Thermal degradation behavior of polystyrene confined in MOF pores

([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering, The University of Tokyo*) ○Haruma Tatsumi,[1] Ami Nishijima,[2] Yuki Kametani,[2] Takashi Uemura[2]

Nanosized polymeric materials often exhibit thermal properties distinguished from those in the bulk state due to drastic increase in the surfaces/interfaces.[1) 2)] In this study, we prepared nanocomposites between a Metal−Organic Framework (MOF) and polystyrene to investigate the thermal decomposition behaviors of the polymer. As the addition of inorganic fillers in polymeric materials often leads to an increase in thermal decomposition temperature, formation of the MOF−polymer nanocomposites resulted in the significant changes of the polymer thermal decomposition behavior (Figure 1). In particular, thermal decomposition temperature of single polystyrene chains accommodated in the MOF nanopores[3)] was 60 °C higher than that in the bulk state, showing the specific nanoconfinement effect of MOF nanopores on polymer properties.

Keywords : Vinyl polymers, metal-organic frameworks, polymer decomposition, composite material, thermogravimetric analysis

高分子材料をナノサイズまでスケールダウンすると、材料全体に対する表面・界面の割合が増加し、バルク状態とは異なる熱的性質を示すことがある[1)2)]。本研究では、ポリスチレンと多孔性金属錯体 (MOF)を混合したナノ複合体を形成し、高分子の熱分解挙動を調べた。一般的に、高分子材料に無機フィラーなどを分散させることで、その熱分解温度が上昇することはよく知られるが、ここでは、MOF-ポリスチレン複合体の形成方法によって、熱分解挙動に大きな違いが出ることが分かった（Figure 1）。特に、MOF 細孔に単分子鎖の状態で吸着させたポリスチレン[3)]は通常のバルク状態のポリスチレンに比べて 60℃以上も高い温度から分解がはじまることが分かり、MOF 空間による特異なナノ拘束効果が示された。

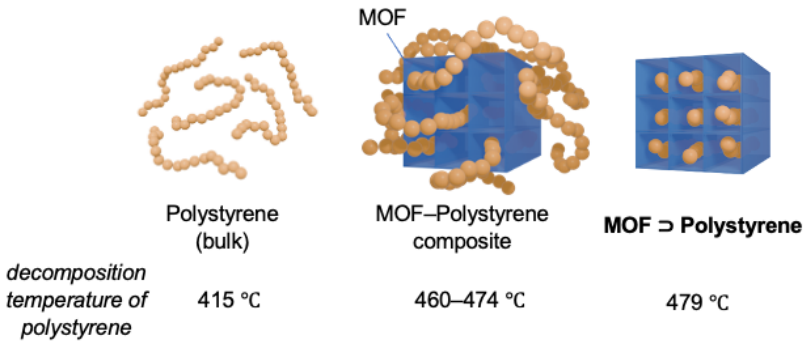

Figure 1. Thermal decomposition temperatures of polystyrene in the bulk, the nanocomposite with a MOF, and the MOF-mediated single chain states.

1) K. Chrissafis, D. Bikiaris, *Thermochim. Acta* **2011**, 523, 1-24.
2) L. S. Schadler et al., *Nat. Mater.* **2005**, 4, 693-698.
3) T. Uemura et al., *Chem. Commun.* **2005**, 5968-5970.

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光学活性アクリルアミド連鎖を有する熱応答性ブロックポリマーの有機基質存在下における会合挙動と分子認識への利用

（近畿大院総理工）○高群 佳佑・石船 学

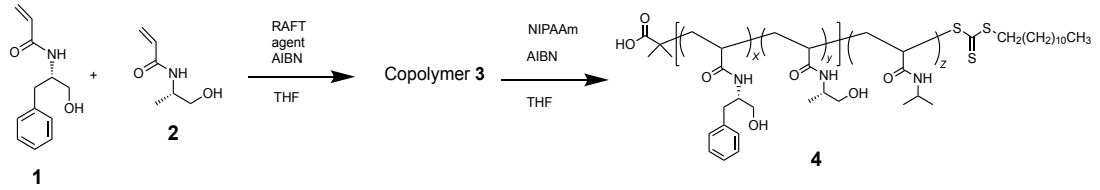
Aggregation behavior and molecular recognition by the thermoresponsive block polymers having optically active acrylamides units in the presence of organic substrates

(*Graduate School of Science and Engineering, Kindai University*)
○Keisuke Takamure, Manabu Ishifune

Copolymerization of optically active monomers, *N*-acryloyl-(S)-phenylalaninol and *N*-acryloyl-(S)alaninol, with *N*-isopropylacrylamide which provides the thermoresponsive moieties, was performed to synthesize thermoresponsive block copolymers by using RAFT polymerization technique. Thermoresponsive aggregation of the resulting copolymers, including polymeric micelle formation, was observed in water containing various amino acids. Thermoresponsivity, particle size distribution, and stereoselectivity were evaluated during the incorporation of the amino acids into the aggregated polymers.

Keywords : Block copolymer; Thermoresponsivity; Optical activity; Molecular recognition; Polymer micelle

意図的に水中で疎水空間を出現させることは、基質の分子認識や有機合成反応への展開が可能である点において興味がもたれる。これに対して当研究室では、Poly(*N*-isopropylacrylamide)(PNIPAAm)に光学活性部位を導入した新規熱応答性高分子を種々合成している[1)]。本研究では、アラニンおよびフェニルアラニン由来の光学活性モノマーを熱応答性部位を提供する NIPAAm と共重合させ、熱応答性を有するブロックポリマーを合成した。モノマー共重合比、ポリマー鎖長を変化させ、温度変化にともなう会合状態の変化を観察するとともに、種々のアミノ酸存在下における熱応答性、粒子径分布の変化や取り込まれるアミノ酸の立体選択性を評価した。



1)高群 佳佑,石船 学,日本化学会第 103 春季年会 K304-1am-13 (2013).

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Non-catalytic Hydrothermal Dechlorination Kinetics of Polyvinyl chloride

([1]*Research and Development, Hosei University*, [2]*Department of economics, Hosei University*)
○Douglas Hungwe,[1] Satomi Hosokawa,[1] Yuki Yamasaki[2]
Keywords: Hydrothermal dechlorination; Polyvinyl chloride, Multi-stage, Autocatalysis

The conversion of polyvinyl chloride to environmentally friendly and water-soluble polyvinyl alcohol is a subject of interest that seems far from realization. Controlled hydrothermal treatment is a promising method to achieve the aforementioned, however, only about 25% of nucleophilic substitution can be achieved.[1] In order to understand this limitation of the process, reaction kinetics are revisited because literature data[2,3] is not adequately supported by the prevailing mechanistic understanding of the dechlorination process.[4] Unlike published data which suggested that dechlorination is a one-stage process, this contribution shows from a kinetic viewpoint that it is a multi-stage process marked with the autocatalytic effect at the tail of the reaction. Autocatalysis is observed at a dechlorination degree of about 50 – 56% depending on the concerted reaction temperature (230- 250°C) and polymer polymerization degree. Therefore, to maximize hydroxyl nucleophilic substitution methods of limiting autocatalysis are currently under consideration.

1) Y. Yamasaki, S. Hosokawa, D. Hungwe. *J. Japan Soc. Mater. Cycles Waste Manag.* **2023**, 34, 30–43. 2) Z. Li, S. Niu, J. Liu, Y. Wang. *Sci. Total Environ.* **2022,** 843,157082. 3) M. Yang, P. Zhao, X. Cui, F. Geng, Q. Guo. *Environ. Technol. Innov*. **2021**, 23, 101703. 4) D. Hungwe, S. Hosokawa, H. Xu, L. Ding, Y. Yamasaki. *Process Saf. Environ. Prot.* **2023**, 177 (December 2022), 202–211

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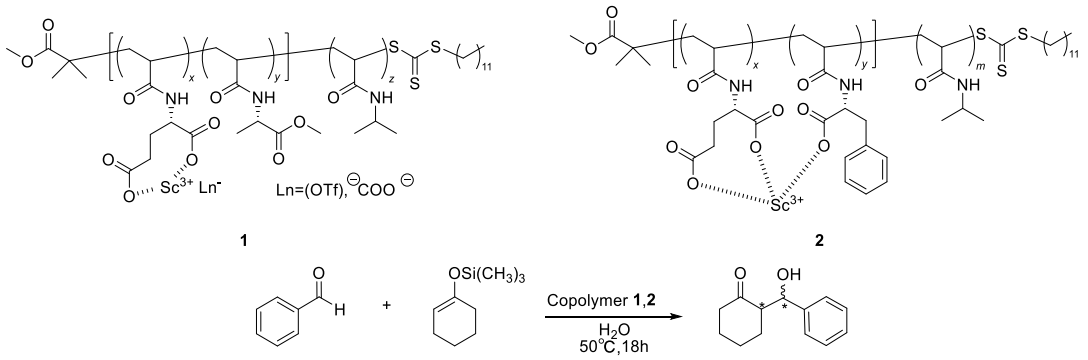
グルタミン酸由来側鎖－Sc(III)錯体構造を有する光学活性熱応答性高分子を用いた水中アルドール反応

（近畿大院総理工）○青柳 光瑠・石船 学
Aldol reactions in water by using optically active thermoresponsive polymers having glutamic acid derived side chains – Sc (III) complexes (*Graduate School of Science and Engineering, Kindai University*) ○Hikaru Aoyagi, Manabu Ishifune

By utilizing RAFT polymerization method were synthesized the diblock copolymers consisting of the poly (*N*-isopropylacrylamide) (PNIPAAm) as a thermoresponsive polymer chain and the poly(*N*-acryloyl-(*S*)-glutamic acid-*co*-*N*-acryloyl-(*S*)-alanine methyl ester) as an optically active polymer chain containing chiral ligands. Scandium (III) ions were then introduced by complexation with the glutamic acid side chains to provide Lewis acid centers. Aldol reactions of benzaldehyde with 1-(Trimethylsilyloxy)cyclohexene in the polymer fields generated by aggregation of the resulting polymers showed higher *syn* form than that in water. Poly(*N*-acryloyl-(*S*)-glutamic acid-*co*-*N*-acryloyl-(*S*)-phenyl alanine)-*block*-PNIPAAm, which provides three carboxy groups for complexation with Sc (III) ions, was also synthesized.
Keywords : Thermoresponsive polymer; Optically active polymer; Block copolymer; Hydrophobic polymer field; Lewis acid center

当研究室では、熱応答性高分子の疎水場内の水中での反応への応用を目指し[1]光学活性点とルイス酸点を有する新たな熱応答性高分子の合成を検討している。本研究では RAFT 法により Poly(*N*-acryloyl-(*S*)-glutamic acid-*co*-*N*-acryloyl-(*S*)-alanine methyl ester)-*block*-PNIPAAm **(1)** を合成し、この共重合体に Sc(Ⅲ)を錯化させた。これをルイス酸点としたアルドール反応**(Scheme)**を実施した結果、水中での反応に比べ *syn* 体の割合が増加することが確認された。さらに Sc(III)イオンとのイオン対形成を安定化させるため 3 つのカルボキシ基を提供する Poly(*N*-acryloyl-(*S*)-glutamic acid-*co*-*N*-acryloyl-(*S*)-phenyl alanine)-*block*-PNIPAAm **(2)**も新たに合成したのでその結果についても報告する。



1　　2

Scheme

[1]Uemukai, T.; Ishifune, M. *J. Apply. Polym. Sci.* **2013**, *129*, 2554-2560.

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Academic Program [Poster] | 19. Colloid and Interface Chemistry：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 3(理工スポーツホール [1階] アリーナ)

[P3-3vn] 19. Colloid and Interface Chemistry

English

[P3-3vn-01]

Circularly polarized luminescence chiral inversion of monodisperse structural colored particles

○Jialei He[1], Yukikazu Takeoka[1] (1. Nagoya University)

Japanese

[P3-3vn-02]

Synthesis and localized surface plasmon resonance properties of PtSn nanoparticles

○HYUNJI LEE[1], Haruka TAKEKUMA[1,2], Ryota SATO[2], Kenji IIDA[3], Toshiharu TERANISHI[1,2] (1. Grad. Sch. of Fac. of Sci., Kyoto Univ., 2. ICR, Kyoto Univ., 3. ICAT, Hokkaido Univ.)

Japanese

[P3-3vn-03]

Preparation and catalytic performance of supported gold nanoflowers prepared by 3-morpholinopropanesulfonic Acid

○Yuki Ishii[1], Yshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-04]

Changing color of gold nanoflower supported on alumina by addition of solvent

○Minoru Kuge[1], Asuka Kasuga[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-05]

Improving catalytic activity of supported small-size gold nanoflower by UV-ozone treatment

○Shogo Sasaki[1], Asuka Kasuga[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-06]

Water and organic solvent dispersible gold and silver nanoparticles capped with long-chain amine

○Koshi Okada[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-07]

Effective Drying Methods for Colloidal Magnetic Iron Oxide Nanoparticles Utilizing Micro Powder Drying Technique

○Satoshi Seino Seino[1], Kota Nishigaki[1], Takashi Nakagawa[1] (1. Osaka University)

Japanese

[P3-3vn-08]

Supported anisotropic Au nanocrystals prepared by seed growth method using gold nanoparticles supported on modified silica

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○Riko Kawahara[1], Yoshiro Imura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-09]

Synthesis of poly(*N*-isopropylacrylamide-*co*-2-carboxyisopropylacrylamide) gel particles for tumor-selective delivery of cisplatin

○Yoshiki Tajima[1], Yukiya Kitayama[1], Eiji Yuba[1], Atsushi Harada[1] (1. Osaka Metropolitan University Graduate School)

Japanese

[P3-3vn-10]

Stability of three-phase emulsion under hydrothermal conditions

○Masashi Takahashi[1], Riina Kimura[1], Kazuki Imaida[1], Koshiro Toyokawa[1], Kana Miyasaka[2], Yoko Imai[2], Kazuo Tajima[2] (1. Tokyo City University, 2. Kanagawa University)

Japanese

[P3-3vn-11]

Adsorption of Neutral Compounds on Clay Nanosheet

○Yuki Fukasawa[1], Nanako Nishida[2], Tetsuya Shimada[2], Tamao Ishida[2,3], Shinsuke Takagi[2,3] (1. Fac. of Urb. Env. Sci., Tokyo Metropolitan Univ., 2. Grad. Sch. of Urb. Env. Sci., Tokyo Metropolitan Univ., 3. ReHES, Tokyo Metropolitan Univ.)

Japanese

[P3-3vn-12]

Structural Analysis of Aggregates Formed by Cationic Gemini Surfactants Using Small-Angle X-ray Scattering and Rheology

○Tsukasa Morita[1], Shiho Yada[2], Tomokazu Yoshimura[1] (1. Nara Women's Univ., 2. Tokyo University of Science)

Japanese

[P3-3vn-13]

Wettability of Solid Surface and Antibacterial Properties of Cationic Gemini and Trimeric Surfactants

○Risa Kawai[1,2], Hideyuki Kanematsu[1], Shiho Yada[3], Tomokazu Yoshimura[2] (1. National Institute of Technology, Suzuka College, 2. Nara Women's University, 3. Tokyo University of Science)

Japanese

[P3-3vn-14]

Foam characteristics in mixed aqueous solutions of homogeneous polyoxyethylene alkyl ether sulfate-type anionic and acetic acid betaine-type zwitterionic surfactants.

○Yuta Matsumoto[1], Yukishige Kondo[1], Shiho Yada[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-15]

Organic dye-induced sol-gel transition of zwitterionic surfactants

○Nozomi Katsurai[1], Clara Imura[1] (1. Ochanomizu University)

Japanese

[P3-3vn-16]

Effect of amino acid addition on the gelation of amidoamine-derivative surfactant

○Haruka Tsurui[1], Clara Imura[1] (1. Ochanomizu University)

Japanese

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[P3-3vn-17]

Gelation property of Rice Bran Wax and the aplication as a separation agent

○Kazuaki Ito[1], Asuka Takahashi[1], Sayaka Yamada[1], Takanori Inoue[2] (1. Yamagata University, 2. Sanwa Yushi Co. Ltd.)

Japanese

[P3-3vn-18]

Effect for Thermodynamic Behaviors of Organogels with the Terminal Alkyl Chain Length in Phenyl 4-(Tridecafluorohexyl)ethylthiobenzoates

○Soma Mutaguchi[1], Junya Yamaguchi[1], Takumi Sugiura[1], Kenta Matsumoto[1], Yuki Morita[1], Hiroaki Okamoto[1] (1. Yamaguchi University)

Japanese

[P3-3vn-19]

Correlation between Thermal Properties and A Terminal Alkyl Chain Length of Organogels Formed by 4-(Semi-fluoroalkyl)thiophenyl 4-Alkoxybenzoates

○Yosei Suzuki[1], Kotaro Kanatada[1], Daiki Kajiyama[1], Kenta Matumoto[1], Yuki Morita[1], Hiroaki Okamoto[1] (1. Yamaguchi University)

Japanese

[P3-3vn-20]

Thermal and Rheological Properties of Organogels Formed by Benzoate and Biphenylcarboxylate Derivatives Having Fluoroalkyl Groups at Both Terminal Positions

○Atsuki Kojo[1], Ryotaro Takenaka[1], Sota Kanemitsu[1], Kenta Matsumoto[1], Yuki Morita[1], Hiroaki Okamoto[1] (1. Yamaguchi University)

Japanese

[P3-3vn-21]

Monolayer Formation of Quaternary-Ammonium-Salt-Type Amphiphilic Gemini Ionic Liquids at Air/Water Interface

○Yasuharu Domoto[1], Risa Kawai[1,2], Shiho Yada[3], Tomokazu Yoshimura[2] (1. National Institute of Technology, Suzuka College, 2. Nara Women's University, 3. Tokyo University of Science)

Japanese

[P3-3vn-22]

Localized formation of MOFs induced by near-infrared light irradiation on plasmonic metal nanoparticles

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Japanese

[P3-3vn-23]

Preparation and Morphology Control of Silver Nanoparticles via Electrochemical Deposition on a Transparent Electrode

○Hiroyasu Nishi[1], Nozomi Yamamoto[1] (1. Univ. of Toyama)

Japanese

[P3-3vn-24]

Singlet oxygen generation by near-infrared light for metal nanoparticle/metal porphyrin MOF hybrids

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Japanese

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[P3-3vn-25]

Effect of liposome and solute composition on the kinetics of insulin amyloid fibrillation

○Satoru Goto[1], Shingo Tsurumoto[1], Yusuke Horizumi[1], Tomohiro Tsuchida[1], Kanji Hasegawa[1], Ryotaro Koga[1], Yuta Okumura[1] (1. Tokyo University of Science)

Japanese

[P3-3vn-26]

In situ microscopic measurements of stability of surfactin emulsion

○Chisato Kondo[1,2], Satoshi Tsukahara[3] (1. Osaka Prefectural Toyonaka High School, 2. Osaka Univ. SEEDS program, 3. Graduate School of Science, Osaka Univ.)

Japanese

[P3-3vn-27]

Microcontact Printing of Semiconductor Nanocrystals by Chemical Functionalization

○Takuya Okamoto[1], Vasudevanpillai Biju[1] (1. Hokkaido University)

Japanese

[P3-3vn-28]

Observation of structure formation process via structural color in spherical colloidal clusters

○Ryosuke Ohnuki[1], Yukikazu Takeoka[2], Shinya Yoshioka[1] (1. Tokyo University of Science, 2. Nagoya University)

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Circularly polarized luminescence chiral inversion of monodisperse structural colored particles

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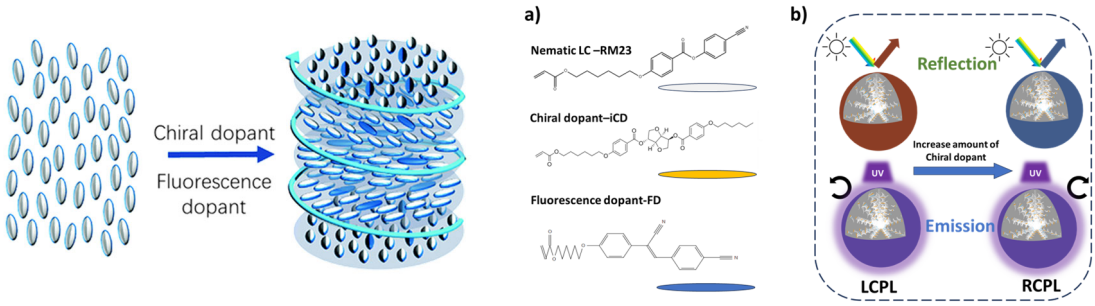
Keywords: circularly polarized luminescence, chirality inversion, cholesteric liquid crystals particles, structural color, chiral structural colors

The development of materials with novel optical properties, especially those with unique circularly polarized luminescence (CPL) properties, is a challenging but promising area in advanced materials science. These materials are central to high-tech applications and are of great interest because of their chirality. Recent research has focused on CPL materials capable of chirality inversion modulated by internal or external environmental changes, thereby expanding the application possibilities. Studies have included the control of the chirality of chiral polymers by varying the chiral dopant concentration. However, chirality inversion of CPL of fluorescent liquid crystal particles by chiral dopant concentration has not been reported. This paper focuses on the self-assembly of liquid crystals within monodisperse fluorescent cholesteric liquid crystals particles that exhibit high luminescence asymmetry (g_{lum}) and CPL inversion properties. This study confirms the key role of twisted grain boundary phase formation in the CPL chirality inversion process.



1) Longhi, G.; Castiglioni, E.; Koshoubu, J.; Mazzeo, G.; Abbate, S. *Chirality* 2016, 28 (10), 696–707.
(2) Yao, K.; Liu, Z.; Li, H.; Xu, D.; Zheng, W.-H.; Quan, Y.-W.; Cheng, Y.-X. *Sci. China Chem*. 2022, 65 (10), 1945–1952.
3) He, J.; Liu, S.; Gao, G.; Sakai, M.; Hara, M.; Nakamura, Y.; Kishida, H.; Seki, T.; Takeoka, Y. *Adv. Opt. Mater*. 2300296.

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PtSn ナノ粒子の合成と可視局在表面プラズモン共鳴特性評価

（京大院理[1]・京大化研[2]・北大触媒研[3]）○Hyunji Lee[1]・竹熊 晴香[1,2]・佐藤 良太[2]・飯田 健二[3]・寺西 利治[1,2]
Synthesis and Localized Surface Plasmon Resonance Properties of PtSn Nanoparticles ([1]*Graduate School of Science, Kyoto University*, [2]*ICR, Kyoto University,* [3]*ICAT, Hokkaido University*)
○Hyunji Lee,[1] Haruka Takekuma,[1,2] Ryota Sato,[2] Kenji Iida,[3] Toshiharu Teranishi[1,2]

Localized surface plasmon resonance (LSPR) of nanoparticles (NPs) has been vigorously investigated and applied to biosensors and solar cells. Spherical NPs of group 11 elements (Au, Ag, and Cu) are commonly used as plasmonic materials in visible region. Recently, we discovered that *C*1 (CaF_2-type) structured $PtIn_2$ NPs exhibited LSPR in visible region. In this study, PtSn NPs were synthesized to demonstrate the structure-specific LSPR properties. An injection of an oleylamine solution of $SnCl_2$ into the size-controlled Pt NPs dispersion gave sphere NPs. The XRD pattern indicated that the NPs were $B8_1$ (NiAs-type) structured PtSn NPs. PtSn NPs showed two characteristic peaks at ca. 380 nm and ca. 850 nm in extinction spectrum, which were found to be derived from LSPR.
Keywords : Localized Surface Plasmon Resonance; Inorganic Nanoparticles; Intermetallic Compound; Ordered Alloy

金属ナノ粒子の局在表面プラズモン共鳴（LSPR）は太陽電池などで応用され、現在も注目を集めている。可視領域に LSPR を示す球状金属ナノ粒子としては 11 族元素（Au、Ag、Cu）が代表的であり、これらを含むナノ粒子を中心に研究が進められてきた。我々の研究室では最近、11 族元素を含まない合金ナノ粒子である *C*1（CaF_2 型）構造の $PtIn_2$ ナノ粒子が可視域に LSPR を示すことを発見した[1]。本研究では、11 族元素を含まない $B8_1$（NiAs 型）構造の PtSn ナノ粒子の合成と局在表面プラズモン共鳴特性について検討した。Pt 種ナノ粒子合成後 $SnCl_2$ と反応させ、球状ナノ粒子を得た。ナノ粒子の XRD パターンは、$B8_1$-PtSn 相と一致し（Fig. 1a）、TEM の測定からは薄いシェル構造も確認された（Fig. 1b）。吸収スペクトル測定では、約 380 nm と約 850 nm に二つのピークが観測され、プラズモン特有の挙動を示した。

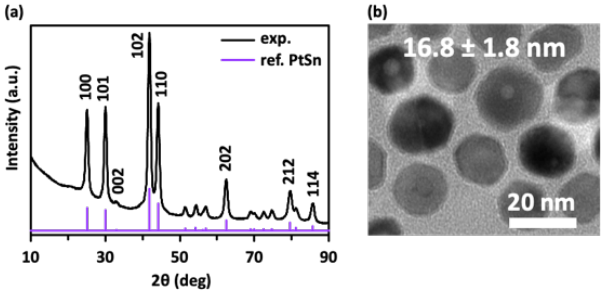

Fig. 1 (a) XRD pattern and (b) TEM image of PtSn NPs.

1) H. Takekuma, R. Sato, T. Teranishi *et al*., *Adv. Sci.*, in press

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3-モルホリノプロパンスルホン酸を保護剤に用いた金ナノワイヤーの合成とアルコール酸化反応に対する触媒特性

（東京理科大学）○石井 勇輝・伊村 芳郎

Preparation and catalytic performance of supported gold nanoflowers prepared by 3-morpholinopropanesulfonic acid (*Tokyo University of Science*) ○Yuki Ishii, Yoshiro Imura

The catalytic properties of Au nanocrystals were changed by morphology.[1)] Anisotropic Au nanocrystals such as nanowires are easily prepared with liquid methods using capping agents.[1)] However, catalytic activity is limited due to capping agents adsorbed on the Au surface. Therefore, the use of capping agents with weak adsorption properties on Au surface is effective for catalytic application. Previously, we reported that Au nanowires with high catalytic activity were prepared by using 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) as a capping agent. In this study, we conducted the preparation of Au nanowires by using 3-morpholinopropanesulfonic acid (MOPS) with a similar structure to HEPES and the examination of catalytic performance for oxidation reaction from 1-phenylethyl alcohol to acetophenone.

Keywords : Nanowire; Gold; Alcohol oxidation reaction; Nanocrystal

金ナノ結晶の触媒特性は、形状により大きく変化することが知られている[1)]。金ナノワイヤーのような異方形態金ナノ結晶は、保護剤を含む溶液中で金イオンを還元することにより容易に得ることができる[1)]。しかし、ナノ結晶の合成時に用いた保護剤が、触媒活性能を低下させるといった欠点がある。触媒利用を考えると、合成後に除去が容易な金表面への吸着力が弱い保護剤を使用することが効果的とされる。これまでに、金表面に吸着力が弱い HEPES を用いて、アルコール酸化反応に対して高い触媒活性能を持つ金ナノワイヤーの合成を行った[1)]。本研究では、HEPES と類似した構造を持つ 3-モルホリノプロパンスルホン酸（MOPS）を保護剤に用いて金ナノワイヤーの合成を行い、アルコール酸化反応に対する触媒特性を評価した。

金ナノワイヤーは、MOPS 水溶液に塩化金酸を加えた後水素化ホウ素ナトリウムを添加して合成した（Fig. 1）。TEM 観察の結果、保護剤として MOPS を用いた時の方が、HEPES を使用したときよりも細いこともわかった。この金ナノワイヤーをアルミナ上に担持した後に、遠心分離を用いた洗浄操作を行い MOPS の除去を行った。その後、アルミナ担持金ナノワイヤーの触媒特性を 1-フェニルエチルエチルアルコールからアセトフェノンを生成する酸化反応を用いて評価した。その結果、HEPES を用いて調製した金ナノワイヤーと同様に高いアセトフェノン生成速度を示すことがわかった。

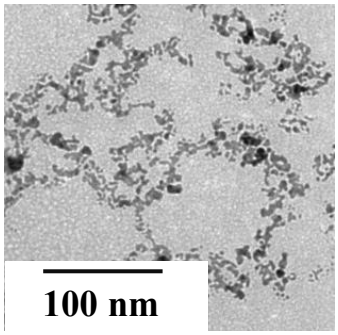

Fig. 1 TEM image of Au nanowires prepared by using MOPS.

1) Y. Imura, M. Maniwa, K. Iida, H. Saito, C. Morita-Imura, T. Kawai, *ACS Omega*, **2021**, *6*, 16043-16048.

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溶媒添加によるアルミナ担持金ナノフラワーの色調への影響

（東京理科大学）○久下 稔・春日 あすか・伊村 芳郎

Changing color of gold nanoflower supported on alumina by addition of solvent

(*Tokyo University of Science*) ○Minoru Kuge, Asuka Kasuga, Yoshiro Imura

The optical properties of Au nanocrystals depend on their size, shape, and refractive index of solvent. Previously, we reported the absorption peak of unsupported Au nanoflowers was changed by dispersion solvent. In the case of unsupported Au nanocrystals, the centrifugation method is effective for repeated use. However, the centrifugation method often results in aggregating the nanocrystals. In this study, we prepared Au nanoflowers supported on alumina to inhibit aggregation and examined their optical properties before and after the addition of solvent. Au nanoflowers were obtained by reducing the metal ions in melamine and ascorbic acid aqueous solution. Supported nanoflowers were prepared by adding Al_2O_3 as support to nanoflower dispersion. The color of supported Au nanoflowers was reversibly controlled by the addition and removal of the solution.

Keywords : Gold; Nanoflower; Nanocrystal; Optical property

金ナノ結晶の光学特性は、サイズや形状、周囲の屈折率により異なる[1)]。これまでに、非担持金ナノフラワーの分散溶媒を変えることで、ナノフラワー周囲の屈折率が変化し、それにより光吸収波長を制御できることを報告した。非担持金ナノ結晶の場合、繰り返し使用するためには、遠心分離操作などの回収作業が必要となるが、ナノ結晶が凝集融合するといった問題点がある。そこで本研究では、アルミナ上に金ナノフラワーを担持したアルミナ担持金ナノフラワーを調製し、溶媒添加による色調変化と、その繰り返し利用について検討した。

金ナノフラワーは、保護剤であるメラミンを含む水溶液に、塩化金酸とアスコルビン酸を加えて調製した[1)]。金ナノフラワー分散溶液にアルミナを加えることで、薄紫色のアルミナ担持金ナノフラワー粉体を得た（Figure 1a）[1)]。担持金ナノフラワー粉体にトルエンを加えると、粉体の色調は紺色へと変化した（Figure 1b）。これは、金ナノフラワーの周囲の屈折率が増加したためである。さらに、この紺色粉体を加熱乾燥することで薄紫色となり、回収再利用が可能であることがわかった。また、添加溶媒をトルエンから水に変化しても、可逆的な色調変化が確認された。

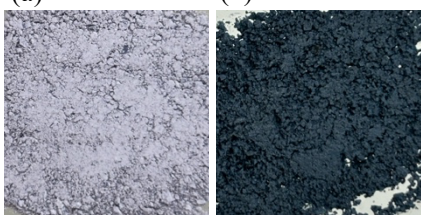

Figure 1. Photographic images of Au nanoflowers supported on alumina (a) before and (b) after addition of toluene.

1) Y. Imura, S. Koizumi, R. Akiyama, C. Morita-Imura, T. Kawai, *Langmuir*, **2017**, *33*, 4313.

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UV オゾン処理による担持小型金ナノフラワーの触媒活性向上

（東京理科大学）○佐々木 省吾・春日 あすか・伊村 芳郎

Improving catalytic activity of supported small-size gold nanoflower by UV-ozone treatment

(*Tokyo University of Science*) ○Shogo Sasaki, Asuka Kasuga, Yoshiro Imura

Shape-controlled Au nanocrystals such as nanoflowers are attractive due to their potential novel catalytic properties. Previously, we reported the preparation and high catalytic performance of Al_2O_3-supported Au nanoflowers with an average size of 75 nm.[1)] In addition, the average size of Au nanoflowers was decreased by using 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) as a capping agent. However, catalytic activity is limited due to capping agents adsorbed on Au surface.[1)] Therefore, it is necessary to remove the capping agent from Au nanocrystals without morphological change. In this study, we conducted the removal of HEPES as a capping agent from small-size Au nanoflowers by UV-ozone treatment.

Au nanoflowers were prepared by adding $HAuCl_4$ aqueous solution to HEPES aqueous solution. Alumina-supported small-size Au nanoflowers were obtained by adding alumina to the nanoflower dispersion. We examined the catalytic performance of the oxidation reaction from 1-phenylethy alcohol to acetophenone. The catalytic activity of supported Au nanoflowers after UV-ozone treatment was higher than that before UV-ozone treatment.

Keywords : Gold; Nanoflower; Capping agent; UV-ozone; Alcohol oxidation reaction

異方性金ナノ結晶は、球状金ナノ粒子とは異なる触媒特性を示すことが知られている[1)]。これまでに、平均サイズ 75 nm の金ナノフラワーが、同程度のサイズの球状金ナノ粒子よりも高い触媒活性能を持つことを報告した[1)]。さらに、保護剤に 2-[4-(2-ヒドロキシエチル)-1-ピペラジニル]エタンスルホン酸（HEPES）を用いたナノフラワーの小型化と、それによる触媒性能の向上も行った。しかしながら、保護剤がナノ結晶表面に残存すると触媒活性能は減少する[1)]。そこで本研究では、アルミナ担持小型金ナノフラワーに UV オゾン処理を行い、触媒能の向上に取り組んだ。

小型金ナノフラワーは HEPES 水溶液に塩化金酸水溶液を加えて調製した。保護剤である HEPES の濃度を変えることで約 28 nm、50 nm の二種類のサイズのナノフラワーを作製した。アルミナ担持小型金ナノフラワーは、金ナノフラワー分散溶液に担持金ナノフラワー分散溶液を加えて得た。触媒特性は 1-フェニルエチルアルコールからアセトフェノンを生成する酸化反応により評価した(Figure 1)。その結果、二種類のサイズの金ナノフラワーに UV オゾン処理を行うことで、触媒活性能が向上することが示された。

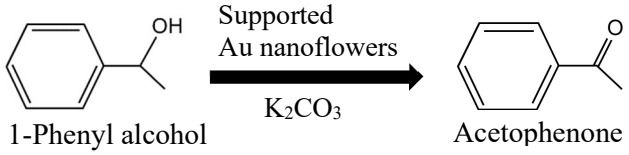

Figure 1. Catalytic reaction of 1-phenyl alcohol to acetophenone.

1) Y. Imura, S. Furukawa, K. Ozawa, C. Morita-Imura, T. Kawai, T. Komatsu, *RSC advances*, **2016**, 6, 17222-17227.

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長鎖アミンによる水と有機溶媒に分散性を持つ金および銀ナノ粒子

(東京理科大学) ○岡田 昂士・伊村 芳郎
Water and organic solvent dispersible gold and silver nanoparticles capped with long-chain amine (*Tokyo University of Science*) ○Koshi Okada, Yoshiro Imura

Capping agents are necessary to disperse the nanocrystals in solvents. However, the dispersion solvent is generally either water or an organic solvent. Previously, we reported dispersing spherical Au nanoparticles and Au nanorods to both the water phase and chloroform phase by using long-chain amine C18AA (Figure 1a) as a capping agent.[1,2] In this study, we obtained water and organic solvent dispersible Au and Ag nanoparticles by using C18AA as a capping agent. Au nanoparticles and Ag nanoparticles were prepared by citric acid as a capping agent. Then, their nanoparticles conducted ligand exchange to C18AA and examined dispersion properties in water and organic solvent. As a result, Ag nanoparticles were dispersed in water and chloroform (Figure 1b). In addition, we also obtained water and chloroform containing Au nanoparticles and Ag nanoparticles.
Keywords : Gold; Silver; Nanocrystal; Capping agent

金や銀はナノサイズまで小さくすることで、特異的な光学特性を示す[1,2]。ナノ結晶の分散性は保護剤による影響を受けるが、水と有機溶媒の両方に対して分散性を持つナノ結晶は少ない[1,2]。これまでに、長鎖アミン C18AA (Figure 1a) を保護剤に用いることで、水とクロロホルムに分散性を示す球状金ナノ粒子と金ナノロッドが調製できることを報告した[1,2]。本研究では、C18AA を保護剤として用いることで、水と有機溶媒に分散した銀ナノ粒子、金と銀ナノ粒子が得られたので報告する。

金ナノ粒子および銀ナノ粒子は、水溶液中で保護剤としてクエン酸ナトリウムを用いて合成した。その後、C18AA に配位子交換を行い水と有機溶媒での分散能について評価した。その結果、銀ナノ粒子のみの場合では、クロロホルムと水に高い分散性を示したが、アセトンやメタノールにはほとんど分散しなかった (Figure 1b)。さらに、金と銀ナノ粒子の混合溶液においても、同様の分散能を示した。

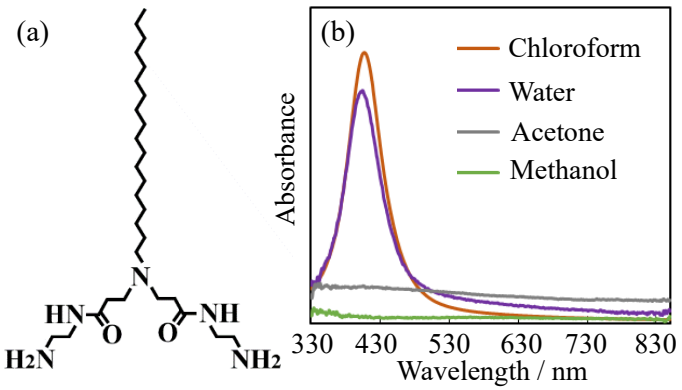

Figure 1. (a) Molecular structure of C18AA. (b) UV-vis spectra of Ag nanoparticles in various solvents.

1) Y. Imura, K. Fukuda, C. Morita-Imura, T. Kawai, *ChemistrySelect*, **2016**, *1*, 5404-5408.
2) Y. Imura, C. Morita, H. Endo, T. Kondo, T. Kawai, *Chem. Commun.*, **2010**, *46*, 9206-9208.

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マイクロパウダードライ法を活用したコロイド状磁性酸化鉄ナノ粒子の乾燥技術の研究

（阪大院工[1]）○清野 智史[1]・西垣 紘汰[1]・中川 貴[1]

Effective Drying Methods for Colloidal Magnetic Iron Oxide Nanoparticles Utilizing Micro Powder Drying Technique

([1]*Graduate School of Engineering, Osaka University*)
○Satoshi Seino,[1] Kota Nishigaki,[1] Takashi Nakagawa,[1]

The study examines the drying technique of colloidal iron oxide nanoparticle dispersion using a method referred to as "micro-powder drying." Dry powders obtained through this method were found to maintain a similar dispersion state to that before processing when mixed with a buffer solution simulating blood. Additionally, it was confirmed that the magnetic properties of iron oxide nanoparticles remain unchanged before and after the drying process. The correlation between processing conditions and redispersibility is reported.

Keywords : Micro-Powder Drying, Iron Oxide; Nanoparticles; ABS; redispersion

磁性ナノ粒子は、外部から与える磁場によりその機能を発現させることが可能であり、医療・バイオ分野において様々な応用研究が展開されている。中でも、MRIやMPI の造影剤や、磁気ハイパーサーミア療法における発熱体などの *in-vivo*（生体内）用途が注目されている。*In-vivo*応用では、生体内に投与された磁性ナノ粒子が標的部位まで適切に送達されるための粒子設計が求められる。中でも、血液中等の生体内環境において凝集せず、良好な分散性を維持することが最も重要である。

本研究では、生体内投与用に設計されたコロイド状磁性酸化鉄ナノ粒子の乾燥技術について検討を行った。水溶液や体液と接触するだけで従前の分散状態へと再分散する乾燥粉末が得られれば、極めて優秀な保存技術となるだけでなく、生体への投与量の向上も期待される。乾燥技術として、真空中に直接液体を噴射し、水分の蒸発による自己凍結で凍結粒子を生成させ凍結乾燥するマイクロパウダードライ法（μPD 法）に着目した。磁性ナノ粒子として、生体内投与の実績があること、また市販品で安定に入手可能という観点から、肝臓用 MRI 磁気造影剤として実用化されているFerucarbotran（カルボキシデキストランで保護された超常磁性酸化鉄ナノ粒子の分散液）を使用した。

μPD法で得られた乾燥試料に超純水およびPBSバッファー液を加え再懸濁させたところ、超音波処理を行っていないにも関わらず、ほぼ従前と同様の液中分散径を示すことを確認した。また乾燥処理の前後において、磁気的性能がほぼ変化しないことも確認した。SEM観察を行ったところ、乾燥試料は微細化したカルボキシデキストランの粉体として存在していることが分かった。水溶液への再溶解が容易となり、結果として良好な再分散性が得られたものと推測される。発表では、乾燥処理条件と、得られた粉末試料の再分散性との関係について議論する。

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表面改質シリカ上の金ナノ粒子をシードに用いた担持異方形態ナノ結晶の調製

（東京理科大学）○河原 莉子・伊村 芳郎

Supported anisotropic Au nanocrystals prepared by seed growth method using gold nanoparticles supported on modified silica (*Tokyo University of Science*) ○Riko Kawahara, Yoshiro Imura

Anisotropic Au nanocrystals are attractive due to their novel optical and catalytic properties. The seed growth method is known to easily obtain unsupported anisotropic Au nanocrystals. However, it is few reports to prepare supported anisotropic Au nanocrystals by seed growth method using supported spherical Au nanoparticles as seed. In this study, we prepared SiO_2-supported anisotropic Au nanocrystals by using spherical Au nanoparticles supported on modified SiO_2 and examined the effect on the morphology of Au nanocrystals by changing the pH of the solvent. The spherical Au nanoparticles supported on modified SiO_2 were obtained by adsorbing spherical Au nanoparticles to SiO_2 after modifying the SiO_2 surface with 3-aminopropyltriethoxysilane (Figure 1a). The growth reaction was conducted by using 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) as a capping agent under conditions at pH 5.3, 8.0, and 11. The supported Au nanocrystals prepared in 200 mM HEPES solution at pH 8.0 had the highest anisotropy (Figure 1b).

Keywords : Gold; Nanocrystal; Silica; Seed growth method

異方形態金ナノ結晶は、球状金ナノ粒子とは異なる光学特性や触媒特性を持つため注目を集めている。シード成長法は、異方形態金ナノ結晶の合成手法として非常に有用であるが、担体上の金ナノ結晶をシードとして用いた成長法に関しては報告が少ない。そこで本研究では、表面改質シリカ上の金ナノ粒子をシードして用いた異方形態金ナノ結晶の調製を行い、pH 変化がもたらす形状への影響について検討した。

表面改質シリカ粒子は、ストーバー法 [1] で作製したシリカ粒子分散溶液に、3-アミノプロピルトリエトキシシランを加えて得た。クエン酸還元法 [2] により合成した平均直径~10 nm の金ナノ粒子分散液に、表面改質シリカ粒子を加えて、表面改質シリカ担持金ナノ粒子を調製した(Figure 1a)。形態制御剤として機能する HEPES 溶液（pH5.3, 8.0, 11）に、シードとして担持金ナノ粒子を添加後、塩化金酸を加えて成長反応を行った。その結果、200 mM HEPES 水溶液中で pH を 8 としたときに、最も異方成長することがわかった（Figure 1b）。

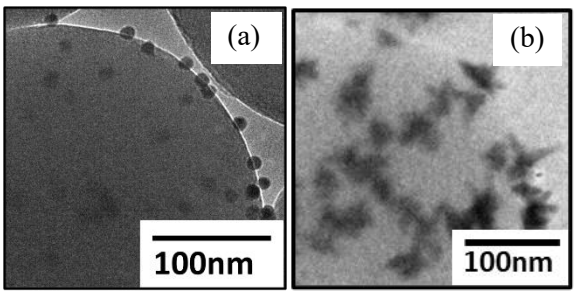

Figure 1. TEM images of (a) supported spherical Au nanoparticles and (b) supported anisotropic Au nanoparticles.

1) Y. Imura, Y. So, C. Morita-Imura, T. Kawai, *ChemistrySelect*, **2017**, *2*, 5695-5700.
2) Y. Imura, C. Morita, H. Endo, T. Kondo, T. Kawai, *Chem. Commun.*, **2010**, *46*, 9206-9208.

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シスプラチンの腫瘍選択的送達を指向した poly(*N*-isopropylacrylamide-*co*-2-carboxyisopropylacrylamide)ゲル微粒子の合成

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Synthesis of poly(*N*-isopropylacrylamide-*co*-2-carboxyisopropylacrylamide) gel particles for tumor-selective delivery of cisplatin (*Graduate School of Engineering, Osaka Metropolitan University*) ○Yoshiki Tajima, Yukiya Kitayama, Eiji Yuba, Atsushi Harada

Delivery of cisplatin (CP) and other platinum drugs to tumor tissues by drug delivery systems (DDS) is important to reduce side effects against the normal tissues and to improve the therapeutic effect. Poly(*N*-isopropylacrylamide) (PNIPAm) gel particles have been developed as a nanocarrier platform for DDS because of their capability of the functionalization by copolymerization with functional molecules of various kinds. Previously, 2-carboxyisopropylacrylamide (CIPAm), which has both carboxy and isopropylamide groups, was developed as a functional monomer to introduce carboxy groups with maintaining thermoresponsiveness [1]. In this study, we prepared PNIPAm-based gel particles with various molar ratios of CIPAm towards cisplatin delivery.

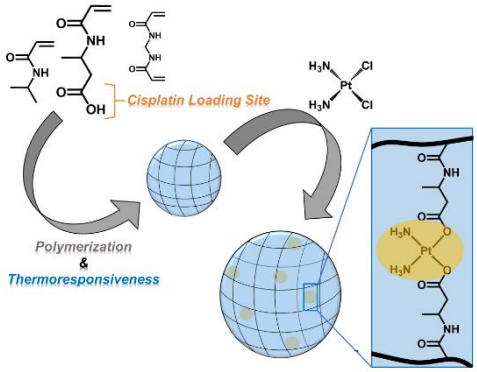

Fig. 1. Preparation of cisplatin (CP)-encapsulated polymer gel particles via copolymerization of *N*-isopropylacrylamide (NIPAm), 2-carboxyisopropylacrylamide (CIPAm) and *N,N'*-methylenebisacrylamide (MBAA).

Keywords : Thermoresponsiveness; Dispersion polymerization; Gel particle

ドラッグデリバリーシステム（DDS）による腫瘍組織へのシスプラチン（CP）をはじめとした白金製剤の送達は、CP 由来の副作用の低減と薬効の増強が期待できるため注目されている。ここで、poly(*N*-isopropylacrylamide) (PNIPAm)は、その温度応答性を利用した分散重合あるいは沈殿重合によりゲル微粒子化でき、様々なモノマーを共重合することによる機能化が可能であることから、DDS 用ナノキャリアとしての開発が進められてきた。そのような中、既報においてカルボキシ基とイソプロピルアミド基を併せ持つ 2-carboxyisopropylacrylamide (CIPAm)が、温度応答性を保ちながらカルボキシ基を導入できる機能性モノマーとして開発された[1]。本研究では、CP の腫瘍選択的送達キャリアとして、NIPAm, *N,N'*-methylenebisacrylamide (MBAA)に加え、種々のモル濃度で CIPAm を混合したモノマー溶液から分散重合することで、CIPAm 導入量の異なる P(NIPAm-CIPAm-MBAA)ゲル微粒子を作製し、その分散安定性、温度応答性を調査し、カルボキシ基を利用した CP 担持能を評価した。

[1] Aoyagi, T.; Ebara, M.; Sakai, K.; Sakurai, Y.; Okano, T., *J. Biomater. Sci., Polym. Ed.* **2000**, 11, 101-110.

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水熱条件における三相乳化エマルションの安定性の検討

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Stability of Three-phase Emulsion under Hydrothermal Conditions ([1]*Faculty of Science and Engineering, Tokyo City University*, [2]*Research Promotion Division, Kanagawa University*) ○ Masashi Takahashi,[1] Riina Kimura,[1] Kazuki Imaida,[1] Koshiro Toyokawa,[1] Kana Miyasaka,[2] Yoko Imai,[2] Kazuo Tajima[2]

Since three-phase emulsions are stabilized by the irreversible attachment of hydrophilic nanoparticles to the surface of dispersed droplets, they are expected to have high stability at high temperatures in principle. Therefore, in this study, we verified the stability of three-phase O/W emulsions using various emulsifiers under hydrothermal environment. As a result, it was confirmed that the emulsion using polyglycerol fatty acid ester is more stable than the emulsions using surfactants, maintaining its emulsified state even after heating at 170 ℃ for 1.5 hours.
Keywords : Three-phase Emulsification Technique; O/W Emulsion; Thermal Stability; Polyglycerol Fatty Acid Ester

三相乳化は親水性のナノ粒子によって油脂を乳化する方法で、エマルションの安定化は油/水界面への親水性ナノ粒子の不可逆的な付着に基づくことから、原理的に高温でも良好な安定性を示すことが期待される。そこで本研究では、様々な乳化剤による O/W エマルションの水熱環境下での状態を調べることで、三相乳化の高温領域での特性を検証した。

三相乳化の乳化剤としてポリオキシエチレン(40)硬化ひまし油（HCO-40）とミリスチン酸デカグリセリル-10（1M10G）を用いた。油相は流動パラフィンまたはドデカンとし、乳化剤 1 wt%、油相 50 wt%で O/W エマルションを調製した。耐圧容器を用いてエマルションを 70～170℃で 1.5 時間加熱し、冷却後の状態観察から高温での安定性を評価した。Fig. 1 より、1M10G のエマルションは 170 ℃加熱でもエマルションが保持されることが確認された。HCO-40 では 150 ℃以上で乳化剤分子の加水分解が促進されて油滴サイズが増大したが、エマルション状態は 170 ℃の加熱でも維持されていた。一方、界面活性剤乳化では、170 ℃でドデシル硫酸ナトリウムのエマルションは水相と油相に完全分離し、臭化ヘキサデシルトリメチルアンモニウムのエマルションでは油相の分離が認められた。これらの結果は分子の分解や吸着状態の変化が安定性に直接影響したためと考えられ、これに対して三相乳化では水熱条件下でもエマルションの破壊が起こりにくいことが確認された。



Fig. 1. Photo of the three-phase emulsions prepared with 1 wt% 1M10G after 1.5 h of solvothermal treatment. From left: room temperature, 70, 90, 110, 130, 150, 170 ˚C.

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中性化合物の粘土ナノシートへの吸着

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Adsorption of Neutral Compounds on Clay Nanosheet ([1]*Fac. of Urb. Env. Sci., Tokyo Metropolitan Univ.*, [2]*Grad. Sch. of Urb. Env. Sci., Tokyo Metropolitan Univ.*, [3]*ReHES, Tokyo Metropolitan Univ.*) ○Yuki Fukasawa,[1] Nanako Nishida,[2] Tetsuya Shimada,[2] Tamao Ishida,[2,3] Shinsuke Takagi[2,3]

Clay nanosheet is useful in analyzing the adsorption behavior of guest molecules because they are dispersible in water and its surface is flat and uniform, allowing for clear analysis. Clay nanosheet can be dispersed homogeneously in water and the solution is a transparent in the UV-visible range. Our laboratory has reported unique photochemical properties of a “dye-nanosheet complex” in which dyes are adsorbed on an anionic nanosheet. However, since the clay nanosheet used is anionic, the dyes combined with the nanosheet were limited to cationic dyes. Therefore, in this study, we focused on electrically neutral compounds in order to develop an understanding of the “dye-nanosheet complex” and extend its universality.

Neutral compounds generally have low solubility in water compared to ionic compounds. In this study, we succeeded in remarkably increasing the solubility of neutral compounds in water by adsorbing them on clay nanosheet. For example, the saturation solubility of pyrene in water is 0.14 mg/L,[1)] but due to the coexistence of clay nanosheet, dissolution up to 2.3 mg/L was observed (Fig. (a)). As the concentration of clay nanosheet increased, the solubility of pyrene increased (Fig. (b)). In the presentation, adsorption isotherms for neutral compounds on clay nanosheet will be discussed to clarify their adsorption behavior in detail.
Keywords: Clay Nanosheet; Neutral Compounds; Adsorption; Solubilization; Aqueous System

粘土ナノシートは、その表面が平滑で均一であるため、ゲスト分子の吸着挙動を解析するうえで、明瞭な解析ができる点で有用である。粘土ナノシートは、水中で均一分散が可能で、紫外可視域で透明な溶液を与える。当研究室では、粘土ナノシートに色素を吸着させた「色素-ナノシート複合体」の優れた光化学特性を報告してきた。しかし、用いている粘土ナノシートはアニオン性であることから、これまで組み合わせる色素はカチオン性のものに限られてきた。そこで、本研究ではさらに「色素-ナノシート複合体」の理解、および、汎用性を深めるため、電気的に中性な化合物（中性化合物）に着目した。

イオン性化合物と比較したとき、一般に、中性化合物は水への溶解度が低い。本研究では、粘土ナノシートに中性化合物を吸着させることで中性化合物の水への溶解性を大幅に高めることに成功した。例えば、ピレンの水への飽和溶解度は、0.14 mg/L[1)]であるが、粘土ナノシートの共存により、2.3 mg/Lまでの溶解が観察された（図(a)）。ピレンの溶解度は、粘土ナノシートの濃度が上がるほど増大した（図(b)）。発表では、粘土ナノシートに対する中性化合物の吸着等温線を作成し、その吸着挙動について詳細に考察する。

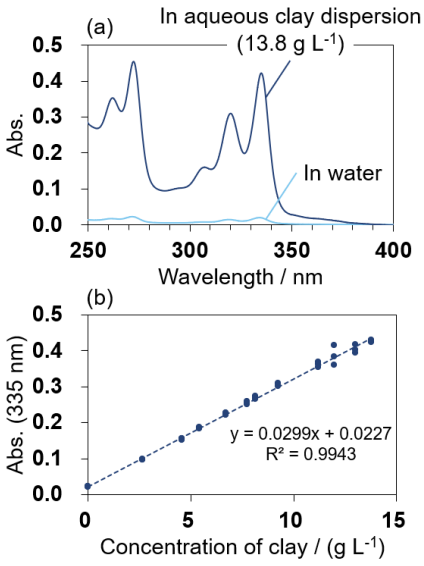

図. ピレンを過剰量添加した際の
(a)吸収スペクトル、
(b)335 nm における吸光度

1) Yalkowsky, S. H.; He, Y.; Jain, P. *Handbook of Aqueous Solubility Data*, 2nd ed.; Taylor & Francis, 2010.

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X 線小角散乱とレオロジーを用いたジェミニ型カチオン界面活性剤が形成する会合体の構造解析

（奈良女大院[1]・東理大[2]）○守田 つかさ[1]・矢田 詩歩[2]・吉村 倫一[1]
Structural Analysis of Aggregates Formed by Cationic Gemini Surfactants Using Small-Angle X-ray Scattering and Rheology ([1] *Department of Chemistry, Faculty of Science, Nara Women's University*, [2] *Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science*) ○Tsukasa Morita,[1] Shiho Yada,[2] Tomokazu Yoshimura[1]

Structures of aggregates formed by cationic gemini surfactants ($2C_{12}$(Spacer)) with spacers having cyclic structures such as diethylene and triethylene chains, and atoms such as nitrogen and oxygen were investigated using small-angle X-ray scattering, rheology and dynamic light scattering. The gemini surfactants with cyclic structures in spacer formed small micelles with several nanometers in size at low concentrations in aqueous solution. On the other hand, the gemini surfactants with oxygen and nitrogen atoms in spacer formed ellipsoidal micelles at low concentrations, and became highly viscous solutions with increasing surfactant concentrations.
Keywords : Gemini Surfactant; Spacer Structure; Micelle; Small-Angle X-ray Scattering; Rheology

従来の単鎖型界面活性剤の物性の向上や機能性の発現を目指して、新しい構造のジェミニ型界面活性剤の研究が行われている。本研究では、Fig. 1 に示すようなスペーサーにジエチレン鎖とトリエチレン鎖の環状構造、窒素および酸素原子を有するジェミニ型カチオン界面活性剤（$2C_{12}$(Spacer)）を用いて、水中での会合体の構造を調べ、スペーサー構造と界面活性剤の濃度が会合挙動に与える影響を検討した。

ジェミニ型界面活性剤 $2C_{12}$(Spacer)が形成する会合体の構造は、X 線小角散乱（SAXS）、レオロジー、動的光散乱（DLS）の測定により 25 ºC で調べた。

スペーサーに環状構造を有する $2C_{12}$(2/2)、$2C_{12}$(2/2-N-2)および $2C_{12}$(2/2/2)-1-OH は、水とほぼ同じ粘度を示し、DLS から得られる拡散係数より、低濃度で数 nm のサイズのミセルを形成した。$2C_{12}$(2-N-2)および $2C_{12}$(2-O-2)は、低濃度で水とほぼ同じ粘度を示し、SAXS のフィッティングによるモデル解析より楕円体ミセルの形成が認められた。楕円状ミセルの短軸と長軸のコアの半径、シェルの厚み、軸比などを見積もることができ、コアの半径は、濃度の増加とともに小さくなった。$2C_{12}$(2-N-2)と $2C_{12}$(2-O-2)の濃度がさらに増加すると粘度の増大が見られた。$2C_{12}$(2-N-2)および $2C_{12}$(2-O-2)は、長く剛直なスペーサーを有するために、ミセル形成の際に密にパッキングしにくいことが考えられる。

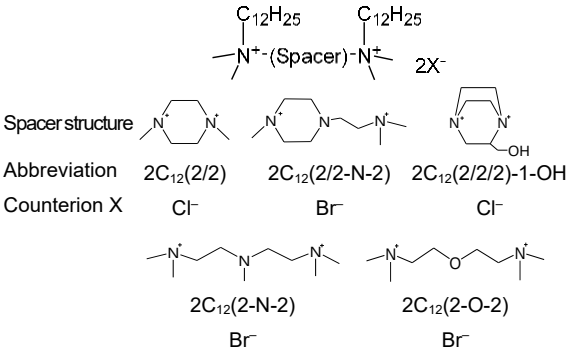

Fig. 1 Structures and abbreviations of quaternary ammonium salt-based gemini surfactants with various spacer structures.

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ジェミニ型およびトリメリック型カチオン界面活性剤による固体表面の濡れ性と抗菌性

（鈴鹿高専 [1]・奈良女大 [2]・東理大工 [3]）○河合 里紗 [1,2]・兼松 秀行 [1]・矢田 詩歩 [3]・吉村 倫一 [2]）

Wettability of Solid Surface and Antibacterial Properties of Cationic Gemini and Trimeric Surfactants ([1]*National Institute of Technology, Suzuka College*, [2]*Nara Women's University*, [3]*Tokyo University of Science*) ○Risa Kawai,[1,2] Hideyuki Kanematsu,[1] Shiho Yada,[3] Tomokazu Yoshimura[2]

Wettability on various solid surfaces of quaternary-ammonium-salt-type gemini and trimeric surfactants was evaluated by measuring contact angle using sessile drop method, and their antibacterial properties against *Staphylococcus epidermidis* and *Escherichia coli* were investigated by agar plate culture method and turbidity measurement. The relationship between wettability and antibacterial properties, and the effects of the structures of the cationic surfactants on these properties were discussed. The gemini surfactants showed higher wettability on hydrophobic surfaces, and inhibited bacterial growth at lower concentration than the corresponding monomeric and trimeric surfactants.

Keywords : Quaternary Ammonium Salt; Amphiphilic Gemini Surfactant; Trimeric Surfactant; Contact angle; Antibacterial Property

四級アンモニウム塩系界面活性剤は、細菌や真菌に対して高い抗菌・殺菌性を示す。2 疎水鎖 2 親水基構造のジェミニ型界面活性剤は、対応する単鎖型よりも低い臨界ミセル濃度（CMC）や高い表面張力低下能などの優れた性質を示す。四級アンモニウム塩タイプのジェミニ型界面活性剤は高い抗菌性が認められるものの、ジェミニ型を延長した 3 疎水鎖 3 親水基構造のトリメリック型界面活性剤の抗菌性については明らかではない。本研究では、四級アンモニウム塩系ジェミニ型およびトリメリック型界面活性剤のポリエチレンテレフタラート（PET）表面における濡れ性を接触角測定により調べ、表皮ブドウ球菌および大腸菌に対する抗菌性を寒天平板培養法と濁度法により評価し、濡れ性と抗菌性の関係およびこれらに及ぼすカチオン界面活性剤の構造の影響について検討した。

ジェミニ型界面活性剤（$2C_{12}$-2）とトリメリック型界面活性剤（星状 $3C_{12}$tris-*s*-Q、*s* は連結鎖長で *s* = 2、3、直鎖状 $3C_{12}$lin-3-Q）の PET 表面における滴下 60 秒後の接触角と濃度の関係を Fig. 1 に示す。1.0 mmol dm^{-3} における接触角はトリメリック型（星状 > 直鎖状）> ジェミニ型の順に低下し、ジェミニ型構造のときに最も優れた濡れ性を示した。これらの界面活性剤は 2 種類の細菌に対して高い抗菌活性を示し、表皮ブドウ球菌に対する最小発育阻止濃度は、$2C_{12}$-2（0.020 mmol dm^{-3}）< $3C_{12}$lin-3-Q（0.040 mmol dm^{-3}）< $3C_{12}$tris-3-Q（0.080 mmol dm^{-3}）の順に増加した。これより、疎水基板上での濡れ性の高い界面活性剤ほど低濃度で菌の増殖を抑制できることが明らかとなった。

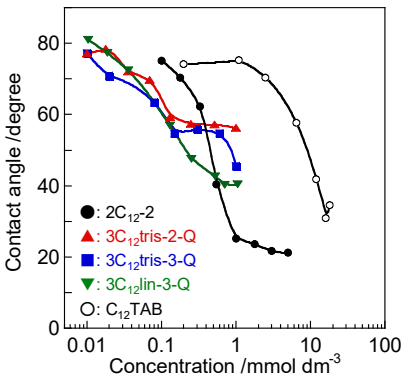

Fig. 1 Variation in contact angle of cationic surfactants with concentration after 60 s dripping on PET surface at 25 °C.

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単一鎖長ポリオキシエチレンアルキルエーテル硫酸エステル塩系アニオン界面活性剤 / 酢酸ベタイン型両性界面活性剤混合系における泡沫特性

（東理大工 [1]）○松本 悠汰 [1]・近藤 行成 [1]・矢田 詩歩 [1]
Foam Characteristics in Mixed Aqueous Solutions of Homogeneous Polyoxyethylene Alkyl Ether Sulfate-type Anionic and Acetic Acid Betaine-type Zwitterionic Surfactants. ([1]*Faculty of Engineering, Tokyo University of Science*) ○Yuta Matsumoto,[1] Yukishige Kondo,[1] Shiho Yada[1]

Foam characteristics in homogeneous polyoxyethylene (EO) alkyl ether sulfate anionic surfactant / acetic acid betaine-type zwitterionic surfactant mixtures were investigated by changing the mixing ratio, molecular structure, etc., and the relationship between the aggregate structure and foam characteristics. Foam stability was increased by mixing zwitterionic surfactants with an anionic surfactant with an EO chain of 8. The higher the ratio of zwitterionic surfactants, the higher the foam stability. A similar trend was also observed for other EO chain lengths.
Keywords : Homogeneous Polyoxyethylene Alkyl Ether Sulfate-Type Anionic Surfactant; Acetic Acid Betaine-Type Zwitterionic Surfactant; Mixture System; Micelle; Form Characteristics

アニオン / 両性界面活性剤混合系は、臨界ミセル濃度の低下や混合比に応じて分子集合体の形状が変化するなど、単独系ではみられない優れた機能や相乗効果が発現する [1, 2]。ポリオキシエチレン (EO) アルキルエーテル硫酸エステルナトリウム（$C_nEO_xSO_4Na$）のアニオン界面活性剤 / 酢酸ベタイン型両性界面活性剤（$C_{12}CB$, $C_{12}ACB$, Fig. 1）混合系はシャンプーなどに用いられるが、$C_nEO_xSO_4Na$ は EO 鎖長に分布を有するものがほとんどである。本研究では正確な物性の把握を目指し、鎖長分布をもたない単一鎖長 $C_{12}EO_xSO_4Na$ ($x = 0, 2, 4, 6, 8$) / $C_{12}ACB$, $C_{12}CB$ 混合系における泡沫特性を調べた。

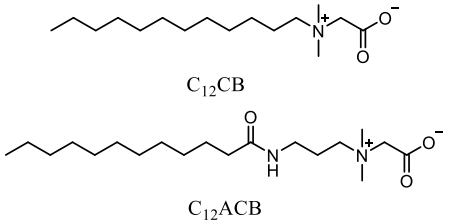

Fig. 1 Structures of acetic acid betaine-type type zwitterionic surfactant ($C_{12}CB$ and $C_{12}ACB$).

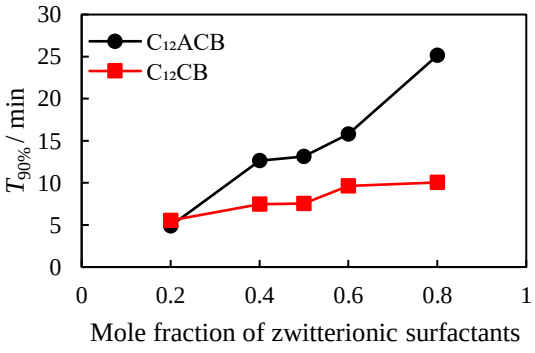

Fig. 2 Relationship between foam stability $T_{90\%}$ and mole fraction of zwitterionic surfactants for $C_{12}EO_8SO_4Na$ / $C_{12}ACB$, $C_{12}CB$ mixture.

$C_{12}EO_8SO_4Na$ / $C_{12}ACB$, $C_{12}CB$ 混合系 10 mmol dm^{-3} における泡沫安定性 $T_{90\%}$ と両性界面活性剤のモル分率の関係を Fig. 2 に示す。ここで $T_{90\%}$ は起泡直後に対して泡沫の割合が 90 %になる時間を示す。泡沫安定性は、両性界面活性剤のモル分率の増加に伴い向上した。また、両性界面活性剤にアミド基を導入することで泡沫安定性は高くなった。これは、分子間の水素結合により界面活性剤が気/液界面に密に吸着・配向できるためと考えられる。

1) Iwasaki, T. et al., *Langmuir* **1991**, 7, 30–35. 2) Christov, N. C. et al., *Langmuir* **2004**, 20, 565–571.

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有機色素の添加で誘起される両イオン性界面活性剤のゲル形成

（お茶の水女子大学）○桂井 望・伊村 くらら
Organic dye-induced sol-gel transition of zwitterionic surfactants (*Ochanomizu University*)
○Nozomi Katsurai, Clara Imura

Surfactants are self-assembled in various shapes affected by the change in pH, temperature, concentration and additives. One of the properties of surfactant aggregates is molecular inclusion, which is important for the use of surfactants as molecular carriers. It has been known that the function of surfactants depends on the aggregate state of them. Therefore, it is necessary to investigate the relations between the molecular inclusion and the surfactant aggregates. Previously, our group reported the molecular inclusion of organic dyes using a gel of zwitterionic surfactant C16CA (Fig.1). In this study, we aimed to control the sol-gel transition induced by the addition of dyes. C16CA aggregates solubilized fluorescein or methyl red at 30°C. ^{1}H-NMR measurements revealed that the dyes were included in the C16CA aggregates. We also found that C16CA undergoes gelation by the addition of the dyes below ~20°C (Fig.2). XRD measurements showed that C16CA/dye gels were lamellar structure, and the concentration of dyes didn't affect them.
Keywords : zwitterionic surfactant; dye; gel; sol-gel transition;

界面活性剤は外部環境の影響を受けて、多様な会合体を形成する。界面活性剤の会合体の多くは分子包接作用を示し、これは界面活性剤を分子キャリアとして利用するにあたって有用な特性である。界面活性剤の分子包接機能はその会合状態に依存するため、分子包接と会合形態変化の関係を明らかにすることは重要である。当研究室ではこれまでに、pH に応答する両イオン性界面活性剤 C16CA（Fig. 1）のゲル状会合体を用い、水溶性有機色素分子の包接を試みてきた。本研究では新たに油溶性色素を添加し、可溶化と分子包接が引き起こす C16CA の会合状態の変化について検討した。

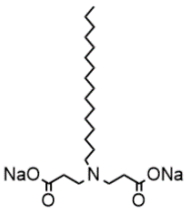

Fig. 1 C16CA の分子構造

30°C 条件において、C16CA は Fluorescein や Methyl Red といった油溶性の色素を可溶化した。^{1}H-NMR 測定からも、これらの色素は C16CA 会合体内部に取り込まれていることが確認された。 さらに、Fluorescein ならびに Methyl Red を包接した C16CA/色素混合系では、C16CA はおよそ 20°C 以下でゲル化することも見いだされた（Fig. 2)。いずれの系でも、C16CA 量のおよそ 0.25 倍量の色素を添加したときに最も効率的にゲル化した。XRD 測定から、C16CA/色素混合系でのゲルはラメラ構造を持ち、その面間隔は色素添加量の影響をほとんど受けないことがわかった。 しかし、色素添加量をさらに増していくとゲル形成は阻害された。これらの結果から、添加色素が C16CA の会合体内部に取り込まれ、会合形態に影響をおよぼすことでゲル形成を引き起こす促進することが明らかになった。一方で、過剰量の色素包接では会合数の低下がもたらされ、ゲル化を抑制することが示唆された。



Fig. 2 色素添加によって誘起されたゲル形成

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アミドアミン型界面活性剤を用いた低分子ゲルへのアミノ酸添加の効果

（お茶の水女子大学）敦井　晴香・伊村　くらら
Effect of amino acid addition on the gelation of amidoamine-derivative surfactant
(*Department of Chemistry, Ochanomizu University*) Haruka Tsurui, Clara Imura

Low molecular-weight gels are expected to be used in many fields as functional substances. Among them, the gels formed by an amidoamine derivative C18AOH, cause gelation by intermolecular hydrogen bonds. In this study, we aimed to control the gels by focusing on amino acids that form intermolecular hydrogen bonds. The addition of amino acids decreased the minimum gelation concentration of C18AOH hydrogels. In particular, the arginine-added system showed a significant decrease. Also, it was found that the gel-to-sol transition temperature increased when amino acids were added. Furthermore, XRD measurements showed that amino acids shortened the lamellar spacing of the C18AOH hydrogel. These results revealed that the addition of amino acids promoted gel formation.
Keywords :　amino acid, surfactant, low molecular-weight gel, hydrogen bond

機能性物質として塗料や増粘剤、薬物送達など多くの分野での利用が見込まれる低分子ゲルは、その用途に応じたゲル物性の制御が求められる。特に、界面活性剤を用いた低分子ゲルは疎水性相互作用や水素結合を駆動力としているため、温度や添加物などの因子を調節することでゲル物性の制御が可能である。本研究では、アミド基の分子間水素結合によって低分子ゲルを形成するアミドアミン型界面活性剤 C18OAH[1]（図 1）について、水素結合をもたらす低分子化合物の添加を試み、分子間相互作用の変化によるゲル物性の制御を試みた。

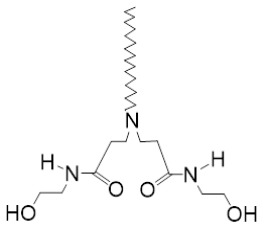

図 1　C18AOH の分子構造

C18AOH にアミノ酸を加えたところ、非添加系と同様にゲルを形成することが確認された。XRD 測定からいずれのゲルにおいてもラメラ構造が確認され、面間隔はアミノ酸添加系でわずかに減少していた。最低ゲル化濃度はアミノ酸を加えることで低下し、アルギニンを添加した系では C18AOH 単独での 0.75 wt%から 0.35 wt%まで著しく低下した（図 2）。またアミノ酸添加によってゲルーゾル転移温度は C18AOH 単独での 52 ℃ から上昇する傾向を示した。これらの結果から、アミノ酸の添加が C18AOH のゲル形成を促進し、特にアルギニンといった直鎖型に近い分子構造の両端に極性官能基をもつ分子では効果的にゲル物性に影響をおよぼす可能性が示唆された。

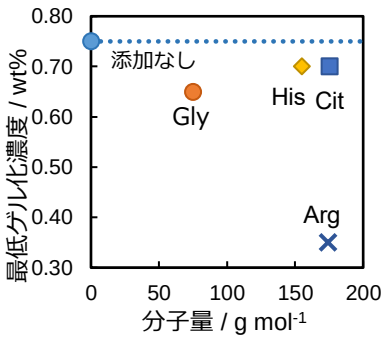

図 2　アミノ酸添加系での最低ゲル化濃度の変化.（アミノ酸濃度はいずれも 10 mM.）

1)　Yoshiro I. *et al*, *Chem. Lett.* 38, 778-779 (**2009**)

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ライスブランワックスのゲル化能評価と分離剤への応用

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Gelation Properties of Rice Bran Wax and the Application as a Separation Agent ([1]*Graduate School of Science and Engineering, Yamagata University*, [2]*Sanwa Yushi Co.*) ○Kazuaki Ito,[1] Asuka Takahashi,[1] Sayaka Yamada,[1] Takanori Inoue[2]

The rice bran produced during the rice milling process is pressed to give rice bran oil. Rice bran wax (RBW) is produced by purifying the crude residue obtained during this pressing process. RBW is one of the unused natural resources. In this study, we investigated the gelation properties of RBW using organic solvents and elucidated the gelation mechanism of RBW using Hanson solubility parameters (HSP). RBW formed gels with long-chain alcohols such as 1-hexanol, 1-heptanol, 1-octanol, 1-nonaol, and 1-decanol. The analysis of gelation of RBW using HSPiP program showed that the main driving force for gel formation of RBW is van der Waals forces between RBWs due to moderate solvophobic effects from the gelling solvents. FT-IR spectra and powder XRD measurements of xerogels of RBW prepared from long-chain alcohols indicated that the alkyl chains of RBW were arranged in *trans*-form and had a close-packed structure. Gel melting point measurements indicated that the gelation of RBW was characteristic of supramolecular gels in which entropy loss was compensated by enthalpy. We further investigated the application of the RBW gel as a separation agent. The conducted organic dye removal experiments employing organogels of RBW showed the separation of organic dyes from the aqueous solutions according to their Clog P values.

Keywords : Rice Bran Wax; Organogel; Separation Agent;

米の精米過程で生じる米糠は、圧搾によりこめ油を与える。この圧搾過程で得られる粗漏の精製によりライスブランワックス(RBW)を生じる。RBW は、天然由来の未利用資源の一つである。本研究では、RBW のゲル形成について有機溶媒を用いて検討し，得られたゲル化試験の結果について Hansen 溶解度パラメータ(HSP)を用い解析を行った。その結果，ゲル化はゲル化溶媒からの疎溶媒効果と RBW 間に働く van der Waals 力によるものと推測された。また，RBW ゲルの構造は，IR および XRD から RBW の長鎖アルキル基間が細密に充填した構造であることが示された。ゲル融解点測定から，ゲル形成過程はエントロピー損失をエンタルピー補う超分子ゲルの特徴を示したら。また RBW ゲルを用いた水溶液中に溶解した有機色素の除去実験では，色素の ClogP 値に応じた分離能を示したことから，混合物に対する分離能を示すことが期待できる。

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Effect for Thermodynamic Behaviors of Organogels with the Terminal Alkyl Chain Length in Phenyl 4-(Tridecafluorohexyl)-ethylthiobenzoates

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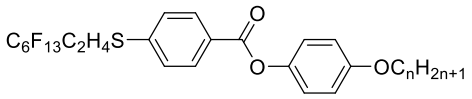
Keywords: Low-molecular Gels; Organogels; Phenyl Benzoates; Fluoroalkyl Group; Even-odd Effect

In our previous works[1], it was found that some low molecular weight compounds having fluoroalkyl groups can gelate various organic solvents. However, correlation between molecular structures and gelation properties is not elucidated.

In this work, 4-alkoxyphenyl 4-(tri-decafluorohexyl)ethylthiobenzoates (Figure 1) were synthesized and evaluated gelation properties of organogels.



Compounds **1**-n (n = 4-12)

Figure 1. Chemical structures of compounds **1**-n.

Critical gel concentration of compounds **1**-n, which is one of the results of gelation tests, are shown in Table 1. When its value is smaller, it can be said that it behaves a better gelator, since it can be gelated with smaller addition. It was confirmed that compounds **1**-n were able to gelate n-octane, dimethyl sulfoxide (DMSO), and propylene carbonate (PC) in added amont of 5wt% or less.

Table 1 Critical gel concentration in each solvent

Solvents	Concentration (wt%)								
	1-4	**1**-5	**1**-6	**1**-7	**1**-8	**1**-9	**1**-10	**1**-11	**1**-12
n-Octane	G(1.0)	S(5.0)	G(3.0)	S(5.0)	G(1.0)	G(3.0)	G(1.0)	S(5.0)	G(2.0)
DMSO	G(0.8)	S(5.0)	G(5.0)	S(5.0)	G(0.4)	G(2.0)	G(0.4)	G(3.0)	G(0.6)
PC	G(0.8)	G(5.0)	G(0.6)	G(2.0)	G(0.3)	G(2.0)	G(0.4)	G(4.0)	G(0.6)

G = Gel, S = Sol

DMSO = Dimethyl sulfoxide, PC = Propylene carbonate

In the PC gels, the compounds having the even number of the terminal carbon chains tend to gelate in smaller addition following elongation of the terminal alkyl chains, whereas the odd tend to with gelate in larger addition following elongation of the terminal alkyl chains. It is suggested that critical gel concentrations in PC are affected by the elongation of the terminal alkyl chains and the even-odd effect.

In this presentation, the effect of the terminal alkyl chains on the thermodynamic behavior of gelation in organic solvents will be reported.

1) T. Yoshida *et al*, *Mol. Crysts. Liq. Crysts.* **2017**, *647*, 299.

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Correlation between Thermal Properties and A Terminal Alkyl Chain Length of Organogels Formed by 4-(Semi-fluoroalkyl)thiophenyl 4-Alkoxybenzoates

(*[1]Faculty of Engineering, Yamaguchi University, [2]Graduate School of Sciences and Technology for Innovation, Yamaguchi University, [3]Advanced Technology Institute, Yamaguchi University)* ○ Yosei Suzuki,[1] Kotaro Kanetada,[2] Daiki Kajiyama,[2] Kenta Matsumoto,[2] Yuki Morita,[3] Hiroaki Okamoto[2]

Keywords: Low Molecular Weight Gelators; Fluoroalkyl Groups; Thermal Properties; Gelation Properties; Organogels

In our previous work[1)], it has been found that some liquid crystal compounds with fluoroalkyl groups at a terminal position can gelate several organic solvents by heating and dissolving then cooling.

In this work, 4-(semi-fluoroalkyl) thiophenyl 4-alkoxybenzoates (Figure 1, Compounds **1**-n) with different lengths of the terminal alkyl chain were synthesized and their gelation properties were evaluated by critical gelation concentration and gel-sol transition temperatures ($T_{gel\text{-}sol}$).

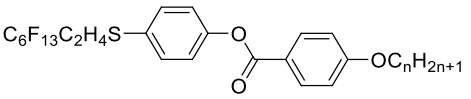

Figure 1. Chemical structures of compounds **1**-n (n=3,5,7,9,11)

Compound **1**-3 in bulk state showed polarized optical microscope (POM), a typical focal conic fan texture at 101℃ on a cooling process, under POM observation (Figure 2). It can assign to be a smectic A (SmA) phase. Compound **1**-5, **1**-7, **1**-9, and **1**-11 also exhibited a SmA phase.

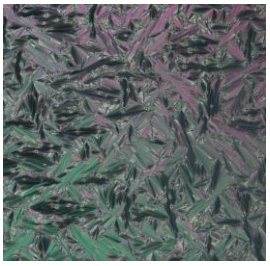

Figure 2. A POM image of compound **1**-3 at 101℃.

$T_{gel\text{-}sol}$ of propylene carbonate (PC) gels are shown in Figure 3. Compounds **1**-n were able to gelate PC in added of 5wt% or less. In particular, compounds **1**-9 and **1**-11 were able to gelate in 0.9wt% addition.

In addition, $T_{gel\text{-}sol}$ of 5wt% PC gels were increased with elongation of the terminal alkyl chain since hydrophobic interaction were increased.

In this presentation, effect of elongation of the alkyl chain of the compounds **1**-n on thermo-dynamic properties of the gels will be reported.

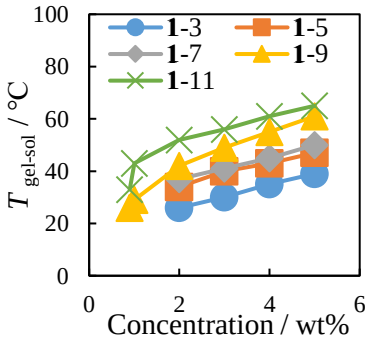

Figure 3. Gel-sol transition temperatures of PC gels.

1) B-P. Cao *et al*, *Liquid Crystals* **2023**, *50*, 1162.

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Thermal and Rheological Properties of Organogels Formed by Benzoate and Biphenylcarboxylate Derivatives Having Fluoroalkyl Groups at Both Terminal Positions

(*[1]Faculty of Engineering, Yamaguchi University, [2]Graduate School of Sciences and Technology for Innovation, Yamaguchi University, [3]Advanced Technology Institute, Yamaguchi University*)
○ Atsuki Kojo,[1] Ryotaro Takenaka,[2] Sota Kanemitsu,[2] Kenta Matsumoto,[2] Yuki Morita,[3] Hiroaki Okamoto[2]

Keywords: Fluoroalkyl group; Low Molecular Weight Organic Gelators; Thermal Properties; Gelation Properties; Rheological Properties

In our previous works, it has been found that low molecular weight compounds having fluoroalkyl groups at both terminal positions formed organogels by heating and dissolving in various organic solvents then cooling. However, correlation between molecular structures and gelation properties has been not elucidated.

In this work, physicochemical properties of silicone oil gels formed by benzoate and biphenylcarboxlate derivatives having fluoroalkyl groups at both terminal positions (Figure 1, Compounds **1**–**3**) were evaluated by critical gel concentration and gel-sol transition temperatures.

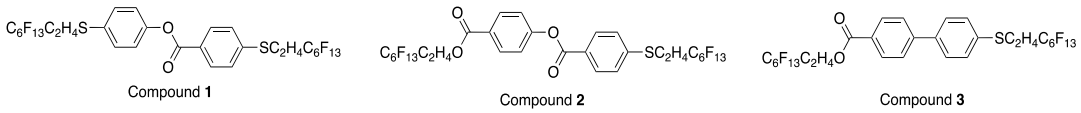

Figure 1. Chemical structures of compounds **1**–**3**.

Gel-sol transition temperatures of poly(methylphenylsiloxane) gels formed by compounds **1**–**3** is shown in Figure 2. The compounds which added in amount of 5wt% were able to gelate. As noteworthy point, compound **2** were able to gelate with 1wt% addition. It can be said that compound **2** is a better gelator than compounds **1** and **3**.

In addition, gel-sol transition temperature of 5wt% poly(methylphenylsiloxane) gel formed by compounds **2** were 20–30 ºC higher than the gels formed by compound **1** and **3**. It is considered that the structures of gelator may not need only rigid units but also a flexible unit.

In this presentation, thermal and rheological properties of poly(methylhydrosiloxane) gels and poly(dimethylsiloxane) gels will be reported.

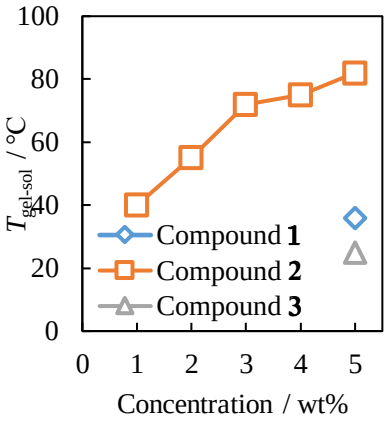

Figure 2. Gel-sol transition temperatures of poly(methylphenyl-siloxane) gels

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四級アンモニウム塩系ジェミニ型両親媒性イオン液体の気/水界面における単分子膜形成

（鈴鹿高専 [1]・奈良女大 [2]・東理大工 [3]）○堂本 泰晴 [1]・河合 里紗 [1,2]・矢田 詩歩 [3]・吉村 倫一 [2]

Monolayer Formation of Quaternary-Ammonium-Salt-Type Amphiphilic Gemini Ionic Liquids at Air/Water Interface ([1]*National Institute of Technology, Suzuka College*, [2]*Nara Women's University*, [3]*Tokyo University of Science*) ○Yasuharu Domoto,[1] Risa Kawai,[1,2] Shiho Yada,[3] Tomokazu Yoshimura[2]

It is known that amphiphilic ionic liquids containing long alkyl chains in the molecules show surface activities. Gemini surfactants, in which two conventional monomeric surfactants are connected by a spacer, show excellent surface-active properties, such as lower critical micelle concentrations and a greater ability to low the surface tension than the corresponding monomeric surfactants. In this study, the monolayer formation of quaternary-ammonium-salt-type amphiphilic gemini ionic liquids containing various spacer structures at air/water interface was investigated by Langmuir-Blodgett method. The amphiphilic gemini ionic liquids with alkyl chain lengths of 12 formed monolayers at the air/water interface. It was found that the monolayer formed by the amphiphilic gemini ionic liquids containing oxygen and nitrogen atoms in the spacer oriented densely at the interface, and the state of monolayers differed by the structure of the spacer.

Keywords : Quaternary Ammonium Salt; Amphiphilic Gemini Ionic Liquid; Langmuir-Blodgett Method; Monolayer; Surface Pressure

分子内にアルキル鎖を有する両親媒性構造のイオン液体は、水溶液中で界面活性を示す。フッ素を含む対イオンを有する両親媒性イオン液体は、水溶性が低く、高濃度における水溶液物性を調べることは困難である。そこで、ジェミニ型構造の両親媒性イオン液体にすることで、気/水界面での密なパッキングや特異な分子配向が期待される。本研究では、異なるスペーサー構造を有する四級アンモニウム塩系ジェミニ型両親媒性イオン液体（$2C_n$(Spacer) NTf_2）の気/水界面における単分子膜の形成挙動をLangmuir-Blodgett 法により検討した。

ジェミニ型両親媒性イオン液体 $2C_{12}$(Spacer) NTf_2 を水面上に展開したときの表面圧（π）–面積（A）曲線を Fig. 1 に示す。表面圧はいずれも面積の減少とともに増加し、ある面積で明瞭な屈曲を示して増加が緩やかになった。この屈曲点は $2C_{12}$(Spacer) NTf_2 の分子占有面積に相当し、界面の圧縮によって単分子膜が破壊されることが示唆される。$2C_{12}$(Spacer) NTf_2 の分子占有面積は、Spacer：2-O-2-O-2 < 2-O-2 < 2-N-2 < 5 < 2/2-N-2 の順に増大した。これより、スペーサーに酸素および窒素原子を含有することで単分子膜は密に配向し、とくに柔軟なスペーサー構造により界面に密に配向した。一方、剛直な環構造を有するスペーサーでは界面に広がって配向することがわかった。

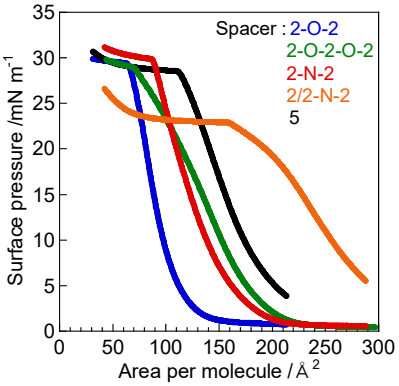

Fig. 1 Surface pressure (π)–area per molecule (A) isotherm for amphiphilic gemini ionic liquids $2C_{12}$(Spacer) NTf_2 at 25 °C.

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Localized formation of MOFs induced by near-infrared light irradiation on plasmonic metal nanoparticles

([1]*Collage of Science and Technology, Nihon University*) ○Ritsurai Tomii[1], Kosuke Sugawa[1], Joe Otsuki[1]

Keywords: Metal Organic Frameworks, Localized Surface Plasmon Resonance, Localized heat

Metal-organic frameworks (MOFs) are porous materials composed of organic ligands and metal nodes that are used for applications of molecular adsorption, storage, and catalysis.[1)] Many MOFs are synthesized by applying thermal energy to the entire system, making it challenging to selectively synthesize MOFs in specific locations. In this study, we propose a new method for synthesizing MOFs that uses local heat to control the arrangement of MOFs. We focused on the local heat generated by the localized surface plasmon (LSP) resonance of metal nanoparticles as a novel approach for synthesizing MOFs in specific locations. A sample substrate having gold nanostructures fabricated by a colloidal lithography was immersed in a precursor solution of porphyrin MOFs containing porphyrin derivatives（TCPP）and Zn nodes.[2)] The synthesis MOFs was carried out by irradiating the substrate with an 808 nm laser. The scanning electron microscopy (SEM) image shows that MOFs were synthesized locally around the gold nanostructures.（Fig.1）This is believed to be the result of the localized heat generated by the surrounding gold nanostructures upon irradiation with an 808 nm laser, which selectively enhanced the formation reaction of MOFs only within the confined microspaces.

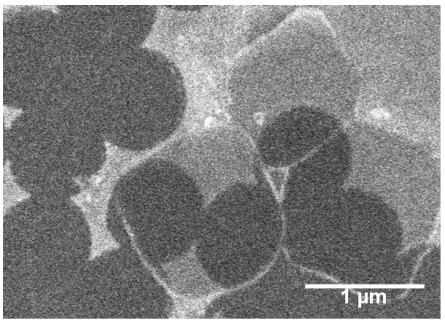

Fig.1 SEM image of porphyrin MOFs formed on the gold nanostructures using localized heat.

Reference
1) Yongteng Qian et al., *ADVANCED FUNCTIONAL MATERIALS*, **2021**, *31*, 2104231
2) Zhenyu Zhou et al., *J. Mater. Chem. A*, **2020**, 8, 25941

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電解析出法による透明電極上での銀ナノ粒子の作製と形態制御

（富山大理）○西 弘泰・山本 望弥

Preparation and Morphology Control of Silver Nanoparticles via Electrochemical Deposition on a Transparent Electrode (*School of Science, University of Toyama*) ○Hiroyasu Nishi, Nozomi Yamamoto

Silver nanoparticles are regarded as useful plasmonic materials because they absorb photons with higher energy and exhibit sharper optical spectra compared to gold nanoparticles. Although size- and shape-controlled silver nanoparticles can be prepared chemically, additional processes, such as deposition onto a substrate or an electrode and removal of protecting agents, are required for the application of plasmonic materials. In this study, we prepare size- and morphology-controlled silver nanoparticles directly onto a transparent electrode via electrochemical deposition. *Keywords : Silver Nanoparticle; Plasmon Resonance; Electrochemical Deposition*

銀ナノ粒子は金ナノ粒子よりもエネルギーの高い光を利用でき、鋭い光学スペクトルを示すため、プラズモン材料として有用である。化学合成によってサイズや形状が制御された銀ナノ粒子を合成することができるが [1]、プラズモン材料として利用するためには、基板または電極上への担持や、ナノ粒子に吸着した分子（保護剤）の除去などの操作が必要となる。本研究では、サイズや形態が制御された銀ナノ粒子を、電解析出法によって透明電極上に直接作製することを目指し、反応条件の検討を行う。

酸化インジウムスズ（ITO）電極を 1 mM の $AgNO_3$ と 0.1 M の KNO_3 を含む水溶液に浸漬し、銀塩化銀電極（飽和 KCl）に対して 0.0 V の電位を 120 s 間印加することで銀ナノ粒子を析出させた。図 1 に示す通り、プラズモン共鳴に由来する Extinction（吸収+散乱）ピークが観測されたが、電流レンジをオートレンジにした場合に、より半値幅の狭いスペクトルが得られた。そこで、ノイズに見立てて−0.3 V の電位を 50 ms 印加した後に電位を 0 V にステップし、120 s 間電析したところ、オートレンジ時と同様に明瞭なプラズモンピークが観測された。この条件は、サイズの揃った銀ナノ粒子を電析するための電位ステップ法 [2] の条件とよく似ているため、上記の実験では、電流レンジを切り替える際に生じるノイズの影響によって核形成が起こり、その後 0.0 V の電位によってナノ粒子の成長が起こったと考えられる。

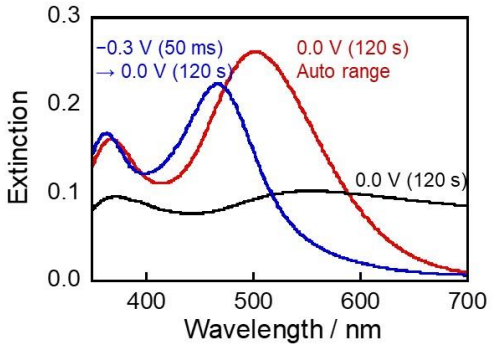

Figure 1. Extinction spectra of Ag nanoparticles prepared by electrochemical deposition on an ITO electrode.

1) B. Wiley, Y. Sun, B. Mayers, Y. Xia, *Chem. Eur. J.* **2005**, *11*, 454.
2) G. Sandmann, H. Dietz, W. Plieth, *J. Electroanal. Chem.* **2000**, *491*, 78.

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金属ナノ粒子／金属ポルフィリン MOF 複合体の近赤外光励起一重項酸素生成特性

（日大理工）○山中圭一・須川晃資・大月　穣
(College of Science and Technology, Nihon University) ○Keiichi Yamanaka, Kosuke Sugawa, Joe Otsuki

Photodynamic therapy (PDT) has gained prominence as a non-invasive cancer treatment, traditionally employing ultraviolet or visible light. Considering the applicability to deep biological tissues, it is desirable to generate singlet oxygen through highly biocompatible near-infrared light irradiation. In this study, we prepared hybrids of anisotropic gold nanoparticles and metal-organic frameworks (MOFs) consisting of palladium porphyrin derivatives. In the extinction spectrum, the localized surface plasmon resonance of gold nanoparticles was generated in the near-infrared region. In the singlet oxygen generation test under irradiation with 808 nm laser, the generation efficiency was enhanced, compared to the MOFs without any gold nanoparticles.
Keywords : Metal-organic frameworks; Localized surface plasmon resonance; singlet oxygen, anisotropic gold nanoparticles

近年、非侵襲的な癌の治療法として光線力学療法（PDT）が注目を集めている。一般的に PDT は、増感分子の光吸収波長域に制限を受けるため、紫外～可視光で駆動しうるが，人体への負荷の低減、および適用生体深度を考慮すると、生体透過性の高い近赤外光駆動できることが望ましい [1]。本研究では，ポルフィリン誘導体を用いた近赤外光による PDT の駆動を目指し、金属ナノ粒子が発現する局在型表面プラズモン共鳴（LSPR）によって生じる強い近赤外吸収を利用することを着想した。

四塩化ジルコニウム、パラジウムを中心に有するポルフィリン誘導体（PdTCPP）を DMF に溶解し、加熱することによって、PdTCPP から成る金属有機構造体（MOFs）を作製した。これを、塩化金酸を含む水溶液に分散させ、硝酸銀の存在下にて、アスコルビン酸で還元することによって、MOFs 上に金ナノ粒子（Au/MOFs）を形成させた。Fig. 1 に示した MOFs、Au/MOFs の消失スペクトルより、可視域における MOFs の吸収ピークに加え、900 nm 付近にて金ナノ粒子の LSPR バンドの発現が認められた。透過型電子顕微鏡像からは、480 nm 程度のサイズの MOFs 粒子上に、異方形状を有する金ナノ粒子の形成が認められた。DPBF の分解速度から、Au/MOFs において、808 nm レーザー照射下にて、MOFs よりも一重項酸素発生効率が高いことが示唆された。

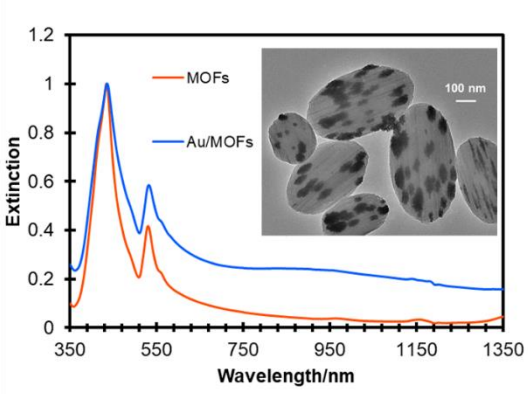

Fig. 1 Extinction spectra of MOFs and Au/MOFs and TEM images of Au/MOFs.

1) K. Deng et al. *Small* **2017**, *13*, 1702299.

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インスリンアミロイド形成速度に対する脂質膜と溶質組成の影響

（東理大薬[1]）後藤 了[1]・鶴元 辰伍[1]・堀住 祐介[1]・長谷川 寛治[1]・古賀 遼太郎[1]・奥村 勇太[1] ・槌田 智裕[1]

Effect of liposome and solute composition on the kinetics of insulin amyloid fibrillation

([1]*Faculty of Pharmacy, Tokyo University of Science*) Satoru Goto,[1] Shingo Tsurumoto,[1] Yusuke Horizumi,[1] Kanji Hasegawa,[1] Ryotaro Koga,[1] Yuta Okumura,[1] Tomohiro Tsuchida,[1]

The formation of amyloid fibrils (AF) is associated with amyloidosis, such as Alzheimer's disease and Parkinson's disease, and has been reported to be influenced by biomembranes and solutes. Here, we aim to analyze in detail the effect of these factors on the AF formation of human insulin (HI) at 65°C. HI solutions were adjusted to pH 5.5-8.0 with phosphate buffers and heated, a significantly larger amount of AF was observed at pH 7.0 compared to other pH levels through the measurement of Thioflavine T fluorescence. In contrast, using organic acid buffers, the amount of AF peaked at pH 7.5. These results suggest that the amount of AF is influenced by the charge of the protein and the ionic strength of the solution.

We also analyzed the kinetics of AF formation in HI solutions with phosphate buffers and organic acid buffers. The time before formation of AF (lag time) was 6.4 hours at pH 7.0 with phosphate buffers and 11 hours at pH 7.5 with organic acid buffers, respectively. Moreover, when small unilamellar vesicles (SUVs) prepared from egg yolk lecithin were added to these HI solutions as a model of biomembranes, the lag time decreased to 3.5 hours at pH 7.0 with phosphate buffers and 6.9 hours at pH 7.5 with organic acid buffers. In addition, the AF formation rate increased, so SUVs facilitated AF formation kinetically. Accordingly, these suggest SUVs worked as a field for AF formation by increasing the local concentration of HI on their surface.

Keywords : Amyloid fibrillation; protein; liposome; fluorescence; aggregation

アルツハイマー病やパーキンソン病などに関連するアミロイド線維(AF)の形成は生体膜や溶質組成に影響を受けることが報告されている．本研究ではヒトインスリン(HI)が 65℃で加熱されることによって誘導される AF 形成に対して，これらの要因が与える影響について詳細に解析することを目的とした．リン酸で HI 溶液を pH 5.5~8.0 に調整して加熱したところ, Thioflavive T 蛍光測定の結果から pH 7.0 でその他の pH に比べて大幅に AF 形成量が最大値を示した．一方，有機酸の緩衝液では, pH 7.5 で AF 形成量が最大に達した．このことから AF 形成量はタンパク質のもつ電荷と溶液のイオン強度の影響を受けることが示唆された．

また，リン酸と有機酸の緩衝液で種々の pH に調整した HI 溶液の AF 形成について速度論的解析を行った結果，リン酸緩衝液の pH 7.0 と有機酸緩衝液の pH 7.5 それぞれでは AF が形成し始めるまでの時間(lag time)は 6.4 時間と 11 時間だった．さらに，これらに対して，生体膜のモデルとして卵黄レシチンから調製した単層膜のリポソーム(SUVs)を添加したところ，リン酸緩衝液の pH 7.0 と有機酸緩衝液の pH 7.5 それぞれで lag time は 3.5 時間と 6.9 時間であり, lag time が減少した．加えて AF 形成速度の増大がみられたため, SUVs は AF 形成を速度論的に促進したことが分かった．このことから SUVs はその表面における局所的な HI 濃度を増大させることで AF 形成の足場として機能したと考えられる．

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サーファクチンエマルションの安定性の in situ 顕微測定

（大阪府立豊中高等学校[1]・阪大 SEEDS プログラム[2]・阪大院理[3]）○近藤千智[1,2]・塚原　聡[3]
In Situ Microscopic Measurements of Surfactin Emulsion Stability ([1]*Osaka Prefectural High School of Toyonaka,* [2]*SEEDS program, Osaka University*, [3]*Graduate School of Science, Osaka University*) ○Chisato Kondo,[1,2] Satoshi Tsukahara[3]

Emulsions are used in food and skin care products, and there are various forms of emulsions depending on the type of surfactant and the strength of its action, but all of them are required to have high stability. In the present study, we investigated the stability of O/W emulsion using surfactin, which is produced by Bacillus subtilis and is one of the natural surfactants, and squalane, which is one of the sebum components. As shown in Figure 1, we succeeded in the stable formation of squalane microdroplets in aqueous solutions using a unique method with silica capillaries (outer diameter 350 μm, inner diameter 200 μm). When the two squalane droplets were brought into contact with each other in water using a manipulator, they fused immediately. However, no fusion was observed for 5 min when an aqueous surfactin solution was used instead of water. These facts confirmed the stability of the surfactin O/W emulsion.
Keywords : O/W Emulsion; Surfactin; Oil-water Interface; Stability

エマルションは、食品やスキンケア商品などに使われており、界面活性剤の種類や働きの強さにより様々な形態のエマルションが存在するが、いずれも高い安定性が求められている。そこで本研究では、枯草菌から作られた天然界面活性剤の１種であるサーファクチンを用いた水溶液と、皮脂成分であるスクワランを用いたO／Wエマルションの安定性について検討した。図１のように、シリカキャピラリー（外直径 350 μm、内直径 200 μm）を利用した独自の方法により、水溶液中にスクワラン微小液滴を安定に形成することに成功した。形成した２つのスクワラン液滴を、マニピュレーターを用いて互いに接触させたところ、溶媒が水の場合は瞬時に融合したが、サーファクチン水溶液を用いた場合は５分間接触させても融合が見られなかった。このことから、サーファクチンO／Wエマルションの安定性を確認することができた。

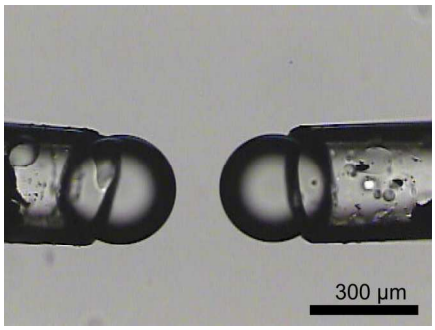

図１　サーファクチン水溶液（濃度 1.0×10^{-3} mol/L）中に形成した２つのスクワラン微小液滴（液滴の体積：左 15 nL，右 14 nL）

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化学修飾による半導体ナノ結晶のマイクロコンタクトプリンティング

(1 北大電子科学研究所) ○岡本 拓也 [1]・Biju Vasdevanpillai [1]
Microcontact Printing of Semiconductor Nanocrystals by Chemical Functionalization ([1]*RIES, Hokkaido University*)○Takuya Okamoto,[1] Biju Vasdevanpillai [1]

Nanocrystals and quantum dots of semiconductors such as lead halide perovskites show excellent optoelectronic properties. The semiconductor nanocrystal assembly shows unique collective optical properties.[1)] Also, micropatterning of semiconductor nanocrystals is important for their practical optoelectronic device fabrication. The electron-beam lithographic methods[2)] and template-assisted self-assembly methods[3)] have been studied for nanocrystal micropatterning. Although these conventional methods can precisely pattern the nanocrystals, the particle alignment in the nanocrystal patterns cannot be controlled. In this study, we report microcontact patterning of semiconductor nanocrystals by chemical functionalization of the substrate and ligand engineering of the nanocrystals.
Keywords : Halide Perovskite; Silane Coupling; Microcontact Printing; Nanocrystal; Quantum Dots

ハロゲン化鉛ペロブスカイトなどの半導体ナノ結晶は優れた光電子物性を示す。ナノ結晶を規則正しく配列し、集積させた超結晶は単一粒子とは特異な光物性を示す[1)]。半導体ナノ結晶のマイクロパターニングはナノ結晶のデバイス応用において重要であり、電子線リソグラフィ[2)]や鋳型を用いた自己組織化法などが提案されてきた[3)]。しかし、これらの手法ではパターニング内のナノ結晶の粒子配列制御は困難である。本研究では、ガラス基板の化学修飾と半導体ナノ結晶のリガンド交換による半導体ナノ結晶のマイクロコンタクトプリンティングについて検討した。Figure. (a) に示すようにポリジメチルシロキサン（PDMS）製のスタンプによってシランカップリング剤をガラス基板表面に転写し、-NH_2 基を修飾したのち-COOH 基を修飾した。このガラス基板をナノ結晶コロイド溶液に浸し、リガンド交換反応により修飾基パターン上にナノ結晶を集積させた。Figure. (b)に 50 μm の円形パターン上に配置させた $CsPbBr_3$ ナノ結晶の蛍光顕微鏡像を示す。ナノ結晶コロイド溶液の濃度や修飾基パターンのサイズ等によるナノ結晶パターンの構造への影響について検討したので報告する。

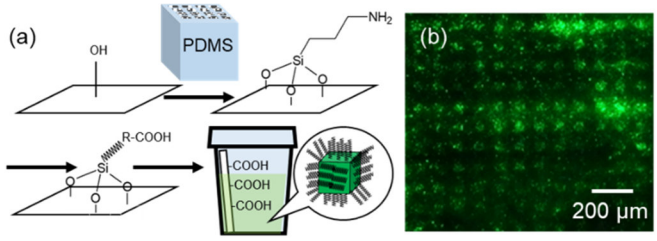

Figure. (a) Schematics of nanocrystal microcontact printing. (b) PL image of patterned $CsPbBr_3$ nanocrystals.

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球形のコロイドクラスターにおける構造色を用いた構造形成プロセスの観察

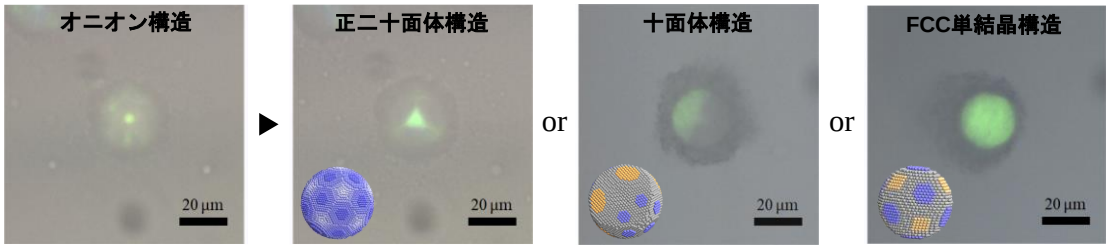
（東理大理工[1]・名大工[2]）○大貫　良輔[1]・竹岡　敬和[2]・吉岡　伸也[1]
Observation of Structure Formation Process via Structural Color in Spherical Colloidal Clusters ([1]*Faculty of Science and Technology, Tokyo University of Science*, [2]*Graduate School of Engineering, Nagoya University*) ○Ryosuke Ohnuki,[1] Yukikazu Takeoka,[2] Yoshioka Shinya[1]

Spherical colloidal clusters have recently been found to have a rich variety of crystal structures (e.g., FCC single-crystal structure, icosahedral structure), depending on the preparation conditions[1,2]. However, the crystallization process of these structures is still an open question. To elucidate the formation mechanism of clusters, it is necessary to observe the crystallization process during cluster preparation.

In this study, we directly observe the crystallization process of spherical colloidal clusters by utilizing the fact that each cluster structure shows a different structural color. The clusters with icosahedral structure have been found to exhibit a triangular reflection pattern[3,4], while the clusters with decahedral structure exhibit a half-moon shaped reflection pattern. In addition, we report that the fraction of structures formed depends on the size of the colloidal particles.
Keywords : Colloidal Cluster; Structural Color; Colloidal Crystal; Formation Process; Icosahedron

球形のコロイドクラスターは、作製条件により多種多様な結晶構造(FCC 単結晶構造や正二十面体構造など)を持つことが最近明らかになってきた[1,2]。しかし、これらの構造へどのように結晶化しているかについては未だ課題として残っている。クラスターの形成メカニズムを明らかにするためには、クラスター作製中の結晶化過程を観察する必要がある。

本研究ではクラスターの構造ごとに異なる構造色を示すことを利用して球状コロイドクラスターの結晶化過程を直接観察する(図)。正二十面体構造のクラスターは三角形の反射パターンを示し[3,4]、十面体構造のクラスターは半月状の反射パターンを示すことが分かっている。さらに、コロイド粒子のサイズに依存して、形成される構造の割合が変化することを報告する。



1) J. Wang *et al*., *Adv. Funct. Mater*., **30**, 1907730, (2020).
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Academic Program [Poster] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Poster

Wed. Mar 20, 2024 3:45 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:45 AM - 8:15 AM UTC Poster Site 4(理工スポーツホール [1階] アリーナ)

[P4-3vn] 21. Energy and Related Chemistry, Geo and Space Chemistry

Japanese

[P4-3vn-01]

Electrochemical Insertion/Deinsertion of Carbonate ions into/form Layered Double Hydroxide

○Soma Sato[1], Susumu Arai[1], Masahiro Shimizu[1] (1. Shinshu University)

Japanese

[P4-3vn-02]

Electrochemical Protonation/Deprotonation of Olivine-type $FePO_4$ in Metal-Free Aqueous Electrolytes

○Tomonori Ichikawa[1], Susumu Arai[1], Masahoro Shimizu[1] (1. Shinshu University)

Japanese

[P4-3vn-03]

Synthesis and proton conductivity of Benitoite-type phosphate, $KCa_{1-x}H_{2x}(PO_3)_3 \cdot yH_2O$

○Kou Yuuka[1], Hirose Kazuhiko[1], Matsuda Yasuaki[1] (1. Chiba Institute of Technology)

Japanese

[P4-3vn-04]

Synthesis, crystal structure and proton conductivity of the Benitoite-type phosphate, $KMg_{1-x}Li_xH_x(PO_3)_3 \cdot yH_2O$

○Kazuhiko Hirose[1], Yuuka Kou [1], Yasuaki Matsuda[1] (1. Chiba Institute of Technology)

Japanese

[P4-3vn-05]

Battery Performance of Inverse Vulcanized and Sulfurized Alcohol Composites

○Ryo matushima[1], Katsuhiro Wakamatsu[1], Hirofumi Yoshikawa[1] (1. Kwanseigakuinn university)

Japanese

[P4-3vn-06]

Effects of Structural Isomers in Hydrogen-Bonded Organic Frameworks on Battery Performance

○Soichiro Furuno[1], Katsuhiro Wakamatsu[1], Yoshihiko Yamaguchi[1], Hosei Oshima[1], Hirofumi Yoshikawa[1] (1. Kwansei Gakuin University)

Japanese

[P4-3vn-07]

Battery Performance of Two-Dimensional Layered Metal−Organic Frameworks

○Shunsuke Okata[1], Katsuhiro Wakamatsu[1], Tomoki Koyanagi[1], Takeshi Shimizu[2], Hirofumi Yoshikawa[1] (1. Kwansei Gakuin University, 2. Yonago College)

Japanese

[P4-3vn-08]

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Relationship between film thickness of organic p-n bilayer and its photocathodic activity for producing hydrogen peroxide in an acidic medium

○Yuika Sakaguchi[1], Toshiyuki Abe[1] (1. Graduate School of Science and Technology, Hirosaki University)

Japanese

[P4-3vn-09]

Synthesis of Sb_2Se_3 colloidal quantum dot and film formation using salting out for the colloidal quantum dot solar cell

○Rie Kobayashi[1], Taiga Shimizu, Toshihito Ohtake[1] (1. Prefectural University of Hiroshima)

English

[P4-3vn-10]

Short-Step Synthesized Dopant-Free Spiro-Type Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells

○Nobuko ONOZAWA-KOMATSUZAKI[1], Daisuke Tsuchiya[2], Inoue Shinichi[2], Atsushi Kogo[1], Takurou N. Murakami [1] (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Nippon Fine Chemical Co., Ltd.)

Japanese

[P4-3vn-11]

Evaluation of perovskite solar cells with potassium and thiocyanate ion.

○Hiroki Nagata[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese

[P4-3vn-12]

Fabrication and Evaluation of Dye-Sensitized Solar Cells Using Reduced Graphene Oxide as Redox material

○Mondo Nijuri[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese

[P4-3vn-13]

Development of solid-state dye-sensitized solar cells with a double-layered anatase TiO_2 electrode: effects of the sintering strategies on the electrode performance

○Satoka Wada[1], Mei Matsui[1], Shinapol Toranathumkul[1], Takashi Sugiura[1], Kazuhiro Manseki[1] (1. Gifu University)

Japanese

[P4-3vn-14]

Artificial Photosynthesis System Producing Formic Acid - Isolation of Pure Formic Acid from a Potassium Phosphate Electrolyte -

○Masahito Shiozawa[1], Yoshihiro Kikuzawa[1], Naohiko Kato[1], Yasuhiko Takeda[1] (1. Toyota Central R&D Labs., Inc.)

Japanese

[P4-3vn-15]

Emission wavelength control in dual annihilator-based triplet annihilation upconversion systems and plasmon-induced effects

○Toukichi Kusumikawa[1] (1. Nihon University)

Japanese

[P4-3vn-16]

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Trend analysis of the technologies for environment and energy by using the data of papers and patents in e-CSTI (Evidence data platform constructed by Council for Science, Technology and Innovation)

○Naoki Mimura[1], Kazumasa Omote[1], Torazo Ikeda[1], Eiko Kono[1], Hiroaki Nagai[1], Naoaki Kashiwabara[1] (1. Cabinet Office)

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層状複水酸化物へのカーボネートイオンの電気化学的挿入－脱離

（信州大工）○佐藤颯馬・新井 進・清水雅裕

Electrochemical Insertion/Deinsertion of Carbonate ions into/form Layered Double Hydroxide

(*Department of Materials Chemistry, Faculty of Engineering, Shinshu University*)
○Soma Sato, Susumu Arai, Masahiro Shimizu

There are many examples of CO_2 capture by physical adsorption on solid adsorbent, membrane separation, and chemical absorption by dissolution, followed by electrochemical reduction and conversion to secondary substances under the presence of catalysts. In this study, as the utilization of CO_2, we investigated the construction of rechargeable batteries based on the electrochemical insertion/deinsertion of carbonate ions (CO_3^{2-}), which should be one of the approaches of CO_2 capture technologies. The interlayers of layered double hydroxide (LDH) was selected as the storage and reactive sites, and the electrochemical insertion and deinsertion behavior of CO_3^{2-} was investigated. Little redox behavior was observed at MgAl-LDH, while redox currents associated with CO_3^{2-}-insertion/deinsertion ($Ni^{3+/2+}$) was detected in NiFe-LDH.
Keywords : Layered Double Hydroxide; Carbonate; Insertion

カーボンニュートラル宣言を機に, CO_2 の排出量削減に加え，吸収後の再利用や付加価値を高める資源化への注目が勢いを増している．固体吸着材に吸着させる物理吸着法, 膜分離, 吸収液に溶解させる化学吸収法などにより CO_2 を回収した後に, 電気化学的還元や触媒存在下で二次的な物質へ変換させる例が盛んに行われている．本研究では，CO_2 回収技術の 1 つである「化学吸収法」に基づき，溶液中のカーボネートイオン（CO_3^{2-}）をキャリアイオンとする炭酸イオン二次電池の構築について検討を行った．その収容サイトとして層状複水酸化物（LDH）を選択し，その層間における CO_3^{2-}の電気化学的挿入－脱離挙動について詳細を調査した．

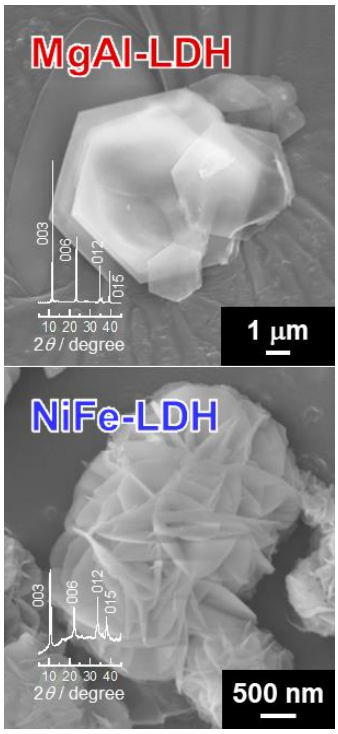

Fig. 1 SEM images and XRD patterns of MgAl-LDH and NiFe-LDH synthesized by the hydrothermal method.

水熱法により，MgAl-LDH, NiFe-LDH をそれぞれ合成し，これらを活物質として導電助剤･結着剤からなる合剤電極を作製した．任意のモル分率で混合した K_2CO_3･H_2O 水溶液（電解液）において，その電位窓範囲内で LDH の電極電位を掃引し，CO_3^{2-}の挿入－脱離挙動を検討した．LDH の構成に Mg, Al を含む系では，電位掃引に対してレドックスがあまり見られないのに対し，Ni, Fe を含有する系においては CO_3^{2-}の挿入－脱離（$Ni^{3+/2+}$）を示唆する酸化還元応答が観察された．当日は，レドックス前後での LDH の構造･層間距離および内包イオンの脱挿入について報告する．

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金属カチオンフリー水系電解質中における Olivine 型 $FePO_4$ の電気化学的プロトン挿入－脱離特性

（信州大工）○市川朋法・新井 進・清水雅裕
Electrochemical Protonation/Deprotonation of Olivine-type $FePO_4$ in Metal-Free Aqueous Electrolytes (*Department of Materials Chemistry, Faculty of Engineering, Shinshu University*)
○Tomonori Ichikawa, Susumu Arai, Masahiro Shimizu

The use of proton as a charge carrier in aqueous-based rechargeable batteries expects to achieve rapid charge/discharge performance as well as high safety. However, due to its poor electrochemical stability, irreversible H_2 or O_2 evolution reactions are caused. In this study, we focused on $FePO_4$ which has been reported as a positive electrode active material for lithium-ion batteries, and the relationship between electrochemical protonation behavior and reaction potentials was examined using metal-free aqueous electrolytes.
Keywords : Proton; Rechargeable Batteries; Metal Free; Active Materials

資源制約を受けない低コストかつ高性能な蓄電デバイスの開発を背景として，Na^+, K^+ をはじめ，様々な金属カチオンがキャリアイオンとして検討されてきている．他方，$H^+[(H_3O)(H_2O)_n]^+$ は水溶液中において金属カチオンよりも極めて高いイオン伝導性を示すことから，急速充放電特性と高い安全性とを兼ね備えた水系二次電池の構築が期待できる [1]．しかしながら，H^+ を活かす取り組みは限定的である．これは，水系電解質の電気化学的安定性の乏しさに起因し，H_2 または O_2 発生の副反応が誘発されることにある．これまでに，我々のグループでは，Rutile TiO_2 が電気化学的に H^+吸蔵-放出することを見出している．本研究では，リチウム二次電池の正極活物質として使用されている $FePO_4$ に着目し，その H^+吸蔵－放出特性について調査を行った．

HTFSA (1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide) および HOTf (trifluoromethanesulfonic acid) を酸性塩として選択し，これらを任意のモル分率で混合して電解液を調製した．定電流条件下において，$FePO_4$ への電気化学的 H^+挿入を調査した結果，酸性塩の対アニオンに依存して挿入（充電）容量および反応電位が大きく異なることが分かった．対アニオンに関わらず 1:10 (H-salt : H_2O) のモル比の電解液を用いた際にその容量は最大となった．1:2 の濃度比までは酸性塩濃度の増大にともない充電容量の増大と反応電位の正側へのシフトが見られたが 1:1 の濃度比では特異的な挙動を示した．

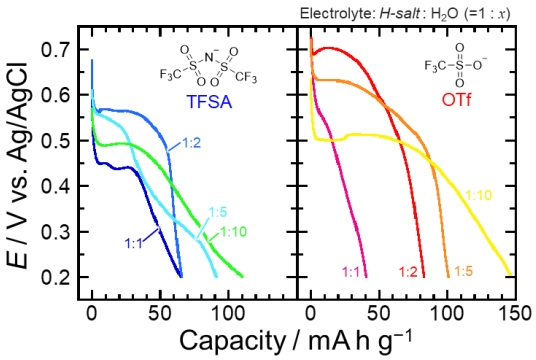

Fig. 1 Galvanostatic discharge profiles of $FePO_4$ electrodes in aqueous electrolytes with H-salt (HTFSA or HOTf) at 0.1*C*.

1) Protonation/Deprotonation of Rutile TiO_2 in Acid Aqueous Electrolytes. M. Shimizu, D. Nishida, A. Kikuchi, S. Arai, *J. Phys. Chem. C,* **2023**, *127*, 17677.

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Benitoite 型リン酸塩 $KCa_{1-x}H_{2x}(PO_3)_3{\cdot}yH_2O$ の合成とプロトン導電特性

（千葉工業大学）○黄 友香・廣瀬 和彦・松田 泰明

Synthesis and proton conductivity of Benitoite-type phosphate, $KCa_{1-x}H_{2x}(PO_3)_3{\cdot}yH_2O$

(*Chiba Institute of Technology*) ○Yuka Kou, Hirose Kazuhiko, Yasuaki Matsuda

In the present study, Benitoite-type phosphate, $KCa_{1-x}H_{2x}(PO_3)_3{\cdot}yH_2O$ was investigated as a new proton conductor operating from room temperature up to 500°C. For the sample synthesized by a coprecipitation method, a single phase was obtained from x = 0 to 0.20. In TG/DTA measurements, the desorption of water of crystallization was observed at room temperature and 150°C. The samples retained the Benitoite structure up to 500°C and the conductivity increased from x = 0 to x = 0.15, and x = 0.15 exhibited a higher conductivity than x = 0.20 from 125°C to 400°C. The sample with x = 0.15 exhibited a conductivity of 1.2×10^{-2} Scm^{-1} at 200°C, demonstrating the high potential as a proton solid electrolyte operating in the intermediate temperature.

Keywords :Proton conductor, Phosphate, Intermediate temperature

Benitoite 型リン酸塩は、室温から 500°C の温度域で高プロトン導電率を示すことから、車載用燃料電池の固体電解質として有望であるが[1]、エネルギーデバイス材料としての開発が停滞している。本研究では、$KCa(PO_3)_3{\cdot}yH_2O$ の Ca^{2+}欠損の電荷補償として H^+を導入した $KCa_{1-x}H_{2x}(PO_3)_3{\cdot}yH_2O$ を合成し、その固溶域とプロトン導電特性を評価した。試料合成は、共沈法で行なった。所定のモル比で秤量した K_2CO_3 および $CaCO_3$ を 1.0 mol dm^{-3} リン酸水溶液 15 ml に溶解し、130°C, 24 h 乾燥した。得られた前駆体を大気中、400°C, 12 - 24 h 焼成して目的物質を得た。合成した試料の X 線回折図形には、x = 0 – 0.20 の組成域で *P*-6*c*2 の Benitoite 型構造に帰属される反射が観測された。x = 0 - 0.20 の組成域で固溶体の形成に対応した *a* 軸, *c* 軸の収縮が観測された。TG/DTA 測定では、室温と 150°C から結晶水の脱離に由来する重量減少が観測された。加湿 N_2 ガス（p_{H2O} = 3 KPa）気流中で 30 min 保持後に測定した導電率は、x = 0 から x = 0.15 にかけてプロトン量の増加と共に向上し、x = 0.15 は 125°C から 400°C の温度域で x = 0.20 よりも高い導電率を示した。試料の導電率は、温度上昇に伴うプロトン拡散の向上と結晶水の脱離による導電率の低下が競合した挙動を示し、x = 0.15 は、200°C で導電率の最高値 1.2×10^{-2} Scm^{-1} が得られた。

本研究の一部は、科研費(21K05246)と電気化学会関東支部の援助を受けて実施されました。

1) Y. Matsuda, et al, *Dalton Trans.*, **50**, 7678 (2021).

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Synthesis, crystal structure and proton conductivity of the Benitoite-type phosphate, $KMg_{1-x}Li_xH_x(PO_3)_3 \cdot yH_2O$

([1]*Chiba Institute of Technology*) ○Kazuhiko Hirose,[1] Yuuka Kou,[1] Yasuyuki Matsuda,[1]
Keywords: proton conductor; phosphate

The Benitoite-type phosphate, $KMg_{1-x}H_{2x}(PO_3)_3 \cdot yH_2O$, is a promising material as a solid electrolyte for automotive fuel cells due to its high proton conductivity from room temperature to 500°C[1)]. Although this material exhibits high conductivity at the proton-rich composition, it is unstable under high humidity conditions. In this study, we aimed to develop a material exhibiting thermal stability, proton conductivity and non-deliquescent in a novel solid solution system the Benitoite-type phosphate $KMg_{1-x}Li_xH_x(PO_3)_3 \cdot yH_2O$.

In the X-ray diffraction patterns for the samples with x = 0 - 0.3, the formation of the single phase of Benitoite-type structure with the space group *P*-6c2 was confirmed. In the x = 0 - 0.3, the shrinkage of both the *a* and *c* axes due to the formation of a solid solution was confirmed. The lattice shrinkage by replacing Li^+(0.76 Å) with an ionic radius larger than Mg^{2+}(0.72 Å) is caused by the contraction between the oxygens due to the formation of hydrogen bonds with the introduction of protons and crystal water. In the FT-IR spectra, the absorption peaks corresponding to the vibrational modes of POH and OH became relatively stronger for x, suggesting an increase in the proton contents in the samples. In the TG/DTA measurement, the dehydration reactions from room temperature and 150 °C were observed, and the water content increased with increasing x. This is suggested that the acidity of the framework is enhanced by the introduced protons, water molecules tend to incorporate into the crystal structure as Lewis bases. The shape of the pellet with x > 0.1 was not retained after retained under 80% relative humidity at room temperature. Figure 1 shows the temperature dependence of the conductivity of $KMg_{1-x}Li_xH_x(PO_3)_3 \cdot yH_2O$ measured under a humidified N_2 gas flow (P_{H2O} = 3 kPa). The proton conductivity of x = 0.10 was higher than that of x = 0. x = 0.10 showed high proton conductivity exceeding 10^{-3} S cm^{-1} up to 500 °C, and the highest value of 1.9 × 10^{-2} S cm^{-1} was observed at 200°C. Proton conduction behavior and thermal stability will be discussed.

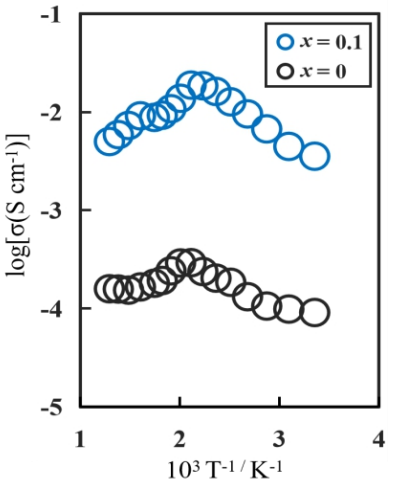

Fig 1. The temperature dependence of conductivity of $KMg_{1-x}Li_xH_x(PO_3)_3 \cdot yH_2O$ under a humidified N_2 gas flow.

This work was partially supported by Kanto Branch of the Electrochemical Society of Japan, JSPS KAKENHI Grant Number 21K05246.

1) Y. Matsuda, et al, *Dalton Trans.*, **50**, 7678 (2021).

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新規硫黄共重合体の蓄電特性

（関西学院大学大学院理工学研究科[1]・関西学院大学工学部[2]）○松島 諒[1]・若松 勝洋[2]・吉川 浩史[2]
Battery Performance of Novel Sulfur Copolymers ([1] *Graduate School of Science and Technology, Kwansei Gakuin University*, [2] *School of Engineering, Kwansei Gakuin University*) ○ Ryo Matsushima,[1] Katsuhiro Wakamatsu,[2] Hirofumi Yoshikawa[2]

Abstract: Lithium-sulfur (Li-S) batteries are expected to be a potential cathode for next-generation rechargeable batteries in terms of a superior theoretical capacity. However, the capacity decreases significantly in the cycling due to the elution of cathodes into the electrolyte solution during electrochemical reactions. Herein, we prepared vulcanized composites and sulfurized alcohol composites as cathode active material in Li-S batteries to address this problem.
***Keywords**: Lithium-sulfur batteries; Cathode active materials; Inverse vulcanized composites; Sulfurized alcohol composites; Shuttle effects*

[背景] リチウム硫黄（Li-S）電池は、その理論容量が従来のリチウムイオン電池の約 10 倍（約 1670 mAh/g）であり、硫黄が安価な材料であることから、次世代二次電池の正極材料として期待されている。しかし、電気化学反応における硫黄の電解質溶液への溶出により、サイクル安定性が低いという問題がある。本研究では、上記の問題を解決するため、逆加硫体[1)]や硫黄/アルコール複合体（SAC）[2)]の創製を試み、Li-S 電池の正極活物質としての電極特性評価を行った。ここでは、SAC についてその詳細を述べる。

[実験] 炭素鎖長や級数の異なるアルコールと硫黄を重量比 1:5 で混合し、窒素雰囲気下、400 ℃で 2 時間還流を行った。その後、未反応の硫黄を除くため、窒素雰囲気下 300 ℃で加熱した。得られた SAC を 30 wt%、トーカブラックを 50 wt%、PVDF を 20 wt%とする合材電極を作製し、Al 箔に塗工し、薄膜正極を作製した。これを用いて、0.4 M LiTFSI、0.28 M $LiNO_3$、DOL、DME からなる電解液、カーボンコートセパレーター、および Li 箔負極から成る Li-S 電池を作成し、その電池特性を計測した。

[結果・考察] 図 1 は、各種 SAC を正極とする Li-S 電池の放電容量のサイクル特性である。1-オクタノールから作製した SAC の電池特性が良好であり、電流密度 200mAh/g で初期容量は約 1660mAh/g、100 サイクル後でも約 800mAh/g を維持した。また、級数を変えたヘキサノールを用いた SAC では第 2 級が最も良好で、1-オクタノールと同等の電池特性を示した。これらより、炭素鎖長と OH 基の位置が電池特性に影響することが示唆された。逆加硫体の結果を含むその他の議論と詳細については当日の発表にて報告する。

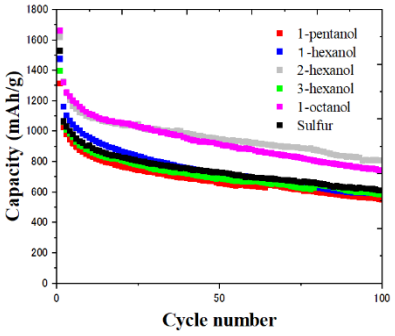

図 1 、SAC と S_8 の放電容量サイクル特性（電流密度 200 mA/g）

[文献] 1) A. G. Simmonds, J. J. Griebel, J. Park, K. R. Kim, W. J. Chung, V. P. Oleshko, J. Kim, E. T. Kim, R. S. Glass, C. L. Soles, Y.-E. Sung, K. Char, and J. Pyun, *ACS Macro Lett.* **2014**, *3*, 229−232, 2) T. Takeuchi, T. Kojima, H. Kageyama, K. Mitsuhara, M. Ogawa, K. Yamanaka, T. Ohta, H. Kobayashi, R. Nagai, and A. Ohta, *J. Electrochem. Soc.* **2017**, *164*, A6288−A6293

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水素結合性有機構造体における構造異性体の蓄電特性への影響

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○古野 壮一郎 [1]・若松 勝洋 [2]・山口 慶彦 [1]・大嶋 萌生 [3]・吉川 浩史 [2]
Effects of Structural Isomers in Hydrogen-Bonded Organic Frameworks on Battery Performance ([1] *Graduate School of Science and Technology, Kwansei Gakuin University*, [2] *School of Engineering, Kwansei Gakuin University,* [3] *School of Science and Technology, Kwansei Gakuin University*) ○ Soichiro Furuno,[1] Katsuhiro Wakamatsu,[2] Yoshihiko Yamaguchi,[1] Hosei Oshima,[3] Hirofumi Yoshikawa [2]

Abstract: We investigated the electrochemical performances of redox-active hydrogen-bonded organic frameworks (HOFs) with structural isomers as a cathode-active material in lithium-ion and sodium-ion batteries. Herein, we used tetrathiafulvalene-based HOFs and triazine-based HOFs, which have structural isomers.

Keywords: *Lithium-ion batteries (LIBs); Sodium-ion batteries (SIBs); Cathode active materials; Hydrogen-bonded organic frameworks (MOFs); Structural isomers*

[背景] 水素結合性有機構造体（HOF）は、有機分子が水素結合をすることによって形成された多孔性構造体で、分子が規則的に連結された高い結晶性材料である。特に酸化還元部位含有 HOF は、資源・環境・コストなどの視点から、次世代二次電池の新規正極材料として大変魅力的である。しかしながら、その正極活物質への応用例は限られているといっても過言ではない。本研究では、構造異性体を有するテトラチアフルバレン部位含有 HOF（PFC-77,78）（図 1）[1]とトリアジン部位含有 HOF（PFC-11,12,13）[2]に着目し、それらを正極活物質とするリチウムイオンおよびナトリウムイオン電池（LIB, SIB）特性を検討するとともに、構造異性体の電極特性への影響を調べた。

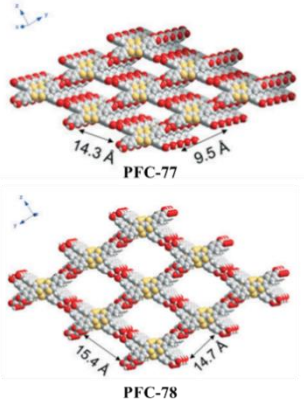

図 1、PFC-77, PFC-78 の構造

[結果・考察] ここでは、PFC-77 と PFC-78 を正極とする LIB のサイクル特性（図 2）について述べる。これより、200 サイクル後の容量保持率を考えると、それぞれの HOF の放電容量は LIB では 23～30%程度保持されており、両者に大きな違いは無かった。組成式当たり 2 電子の酸化還元反応が起きると考えた理論容量（約 78.4 mAh/g）に対して実際に得られた最大容量の比率を考えると、PFC-78 が比較的高いと分かった。SIB の結果やトリアジン部位含有 HOF を含む、その他の議論と詳細については当日の発表にて報告する。

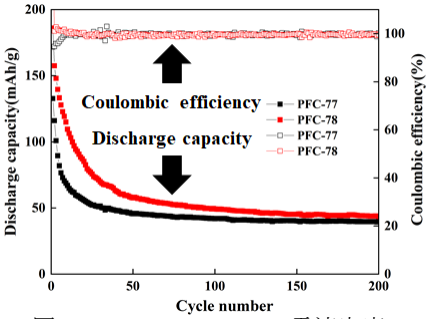

図 2、PFC-77, PFC-78 の電流密度 100 mA/g における放電容量サイクル特性とクーロン効率

[文献] 1) X.-Y. Gao, Y.-L. Li, T.-F. Liu, X.-S. Huang, and R. Cao, *CrystEngComm*, **2021**, *23*, 4743, 2) Y.-L. Li, E. V. Alexandrov, Q. Yin, L. Li, Z.-B. Fang, W. Yuan, D. M. Proserpio, T.-F. Liu, *J. Am. Chem. Soc.* **2020**, *142*, 7218-7224.

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二次元層状構造金属有機構造体の蓄電特性

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Battery Performance of Two-Dimensional Layered Metal−Organic Frameworks ([1] *Graduate School of Science and Technology, Kwansei Gakuin University*, [2] *School of Engineering, Kwansei Gakuin University,* [3] *School of Science and Technology, Kwansei Gakuin University,* [4] *Department of Materials Science, Yonago National College of Technology*) ○ Shunsuke Okata,[1] Katsuhiro Wakamatsu,[2] Tomoki Koyanagi,[3] Takeshi Shimizu,[4] Hirofumi Yoshikawa [2]

Abstract: Herein, we investigated the electrochemical performances of $Cu_3(HXTP)_2$, which consists of copper ions and organic ligands HXTP (X=N, O, S) with different coordination atoms, as a cathode active material in lithium-ion, sodium-ion, and calcium-ion batteries.

Keywords: *Lithium-ion batteries (LIBs); Sodium-ion batteries (SIBs); Calcium-ion batteries (CIBs); Cathode active materials; Two-dimensional layered metal−organic frameworks (2D-MOFs)*

[背景] 近年、金属有機構造体（MOF）は、その酸化還元特性と多孔性から、二次電池電極材料として非常に注目を集めている。一方で、同一構造を有する MOF について、配位部位の原子の違いや脱挿入するイオンの違いにより電池特性がどのように変化するかに関する系統的な研究はあまり例がない。本研究では、配位子 HXTP (X = N, O, S) と銅イオンから成る MOF（$Cu_3(HXTP)_2$）が同一の二次元層状構造を有することに着目し、それらを正極活物質とするリチウムイオン、ナトリウムイオン、およびカルシウムイオン電池（LIB, SIB, CIB）特性を検討するとともに、配位原子 X による各電池特性の違いを調べた。

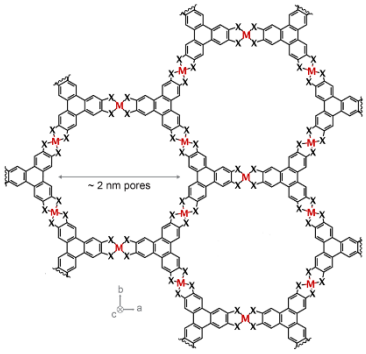

図 1、 $M_3(HXTP)_2$(M=Cu, X= O, N, S)の構造図 [2)]

[結果・考察] 文献 [1-3)]に従い、$Cu_3(HXTP)_2$(X= O, N, S) を作製し、これらを正極とする LIB, SIB, CIB 特性を計測した。図 2 に、LIB のサイクル特性を示す。100 サイクル後の容量保持率は、3 種の MOF で 40～50%で、配位原子による大きな違いは観測されなかった。一方、組成式当たり 6 電子の酸化還元反応が起きると考えた理論容量（X=O, N, S に対して約 194, 197, 158 mAh/g）に対して実際に得られた最大容量の比率を考えると、$Cu_3(HOTP)_2$ が比較的高いと分かった。これは構造的耐久性や電荷移動抵抗の違いに起因するものと思われる。SIB や CIB 特性など詳細については当日報告する。

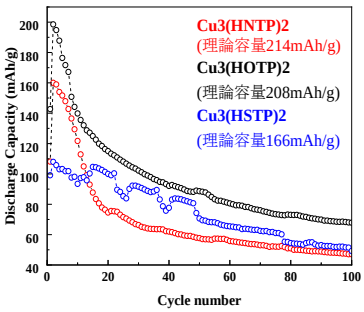

図 2、 $Cu_3(HXTP)_2$(X= O, N, S) の LIB サイクル特性
(電流密度 100 mA/g)

[文献] 1) M. G. Campbell, D. Sheberla, S. F. Liu, T. M. Swager, and M. Dincă, *Angew. Chem. Int. Ed.* **2015**, *54*, 4349−4352, 2) R. W. Day, D. K. Bediako, M. Rezaee, L. R. Parent, G. Skorupskii, M. Q. Arguilla, C. H. Hendon, I. Stassen, N. C. Gianneschi, P. Kim, and M. Dincă, *ACS Cent. Sci.* **2019**, *5*, 1959−1964, 3) L. Mendecki, M. Ko, X. Zhang, Z. Meng, and K. A. Mirica, *J. Am. Chem. Soc.* **2017**, *139,* 17229−17232

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過酸化水素酸性溶液製造のための有機 p-n 接合体系光カソードのフィルム厚と活性の関係

（弘前大院理工）○坂口 唯香・阿部 敏之
Relationship between film thickness of organic p-n bilayer and its photocathodic activity for producing hydrogen peroxide in an acidic medium (*Graduate School of Science and Technology, Hirosaki University*) ○Yuika Sakaguchi, Toshiyuki Abe

Establishing a clean procedure for the formation of hydrogen peroxide (H_2O_2) is desired. We have reported that an artificial photosynthetic reaction for H_2O_2 formation occur to apply the photocathode of organic p-n bilayer comprising p-type zinc phthalocyanine (ZnPc) and n-type fullerene (C_{60}). In that occasion, the reduction of O_2 to H_2O_2 by the ZnPc/C_{60} photocathode was confirmed to be the rate-limiting step in the overall reaction. In the present study, the organo-photocathode was examined particularly in terms of the thickness of C_{60} layer. When loading Au catalyst on the C_{60} surface, the organo-photocathode can show the activity for the H_2O_2 formation. This work presents that, when employing the extremely thin layer of C_{60} in the organic bilayer, the O_2 reduction can efficiently occur by enhancing the surface concentration of electrons available to H_2O_2 formation.
Keywords: Artificial photosynthesis; Hydrogen peroxide; Organic p-n bilayer; Photocathode

現在、H_2O_2 は工業的にはアントラキノン法により製造されている。しかし、その製造過程において大量のエネルギーや化学物質の投入が必要であり、大量の廃棄物が発生する等の問題もあり、H_2O_2 の新規でかつクリーンな製造法の確立が求められている。当研究室では、最近、有機 p-n 接合体系光カソード(ITO/ZnPc/C_{60}-Au)と可視域酸化物半導体系光アノードを組み合わせた系で人工光合成型反応による H_2O_2 の生成 ($2H_2O + O_2 \rightarrow 2H_2O_2$)を報告した[1]。しかし、光エネルギー変換効率が<0.01%と低く、律速段階である酸素還元過程の動的な向上が課題となっている。これまでに、Pt を担持した ITO/ZnPc/C_{60} 系光カソードが H_2 発生に対して活性であることを明らかにし[2]、ZnPc = 75 nm、C_{60} = 125 nm の厚さ条件が最適であることを報告している。ITO/ZnPc/C_{60}-Au 系でも同様の厚さ条件を適用して H_2O_2 生成反応を行ってきたが[1]、上述の条件よりも特に C_{60} の厚さを極端に薄くした場合(C_{60} = 2.75 nm)、酸素還元活性が大幅に向上することを見いだした（図 1 参照）。また、光電流の作用スペクトルを測定した結果から、C_{60} を薄層化しても ZnPc と C_{60} の両者の光吸収により酸素還元が誘起されていることを確認した。光カソード活性が向上した要因としては、C_{60} を薄層化したことで C_{60} 表面の電子濃度が高まった可能性が考えられる。

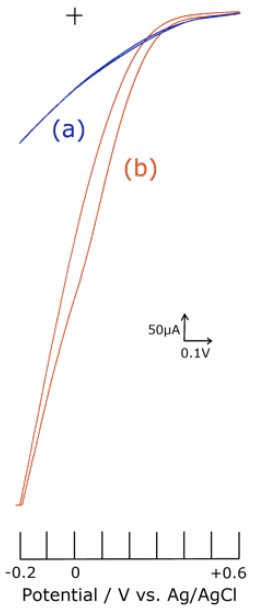

図 1　O_2 雰囲気下における ITO/ZnPc/C_{60}-Au の CV
厚さ条件：(a) ZnPc = 70 nm, C_{60} = 123 nm, (b) ZnPc = 84 nm, C_{60} = 2.8 nm

1) K. Ikezoi, M. Chisaka, T. Abe, *Int. J. Electrochem. Sci.*, 17, 221143 (2022).
2) T. Abe, Y. Hiyama, K. Fukui, K. Sahashi, K. Nagai, *Int. J. Hydrogen Energy*, 40, 9165 (2015).

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コロイド量子ドット太陽電池作製に向けた Sb_2Se_3 コロイド量子ドット合成と塩析を用いた製膜法の確立

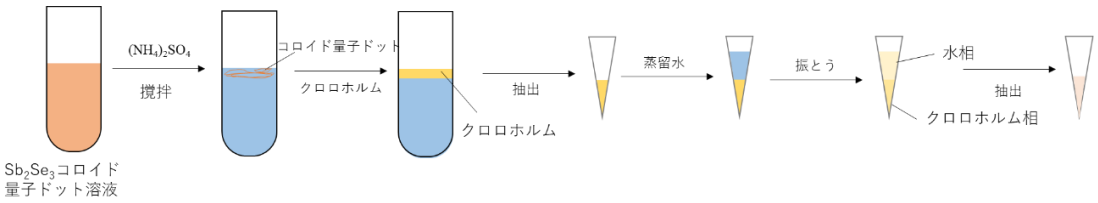
（県広大院生命 [1]）○小林 莉詠 [1]・清水 大雅 [1]・大竹 才人 [1]

Establishment of a film forming method using Sb_2Se_3 colloidal quantum dot synthesis and salting out for the fabrication of colloidal quantum dot solar cells ([1]*Graduate School of Life Science, Prefectural University of Hiroshima*) ○Rie Kobayashi[1], Taiga Shimizu[1], Toshihito Ohtake[1]

Solar cells using quantum dots have researched as next-generation highly efficient solar cells. We have noticed Sb_2Se_3 with a variety of properties and investigated colloidal quantum dots solar cells. Sb_2Se_3 colloidal quantum dots were synthesized by hydrothermal synthesis and attempt to fabricate a solar cell using the obtained Sb_2Se_3 colloidal quantum dots[1)]. The Sb_2Se_3 colloidal quantum dots aqueous solution was separated, purified, and extracted by salting out using $(NH_4)_2SO_4$. This was dispersed in distilled water and a mixed solvent of hexane, acetone, and chloroform to prepare a colloidal solution for film forming. After coating it on a substrate, it was evaporated in a vacuum atmosphere to fabricate a uniform Sb_2Se_3 thin film. The obtained thin film was evaluated about various optical properties and surface and cross-sectional observation by SEM. In addition, solar cells were fabricated and evaluated about power generation characteristics.

Keywords ：Quantum dot solar cells; Antimony selenide; Salting out; Hydrothermal synthesis; film-forming method

次世代の高効率な太陽電池として、量子ドットを活用した太陽電池が研究されている。我々は、特徴的な性質を持つ Sb_2Se_3 に着目し、コロイド量子ドット太陽電池を検討している。Sb_2Se_3 コロイド量子ドットは、水熱合成法により合成され [1)]、得られた Sb_2Se_3 コロイド量子ドット水溶液を用いて、太陽電池の作製を試みた。この Sb_2Se_3 コロイド量子ドット水溶液は、下記に示した様に$(NH_4)_2SO_4$ を用いた塩析によって、分離、精製、抽出した。これを水及びヘキサン、アセトン、クロロホルムの混合溶媒に分散させ、製膜用のコロイド溶液として調製した。これを基板上に塗布後、真空雰囲気下で蒸発させることで、均一な Sb_2Se_3 薄膜を作製した。得られた薄膜は、各種光特性、SEM による表面と断面観察で評価した。また、太陽電池セルを作製して発電特性を評価した。



1) Highly stable ethylene glycol-capped blue-emitting antimony selenide quantum dots via hydrothermal approach. D. M. Vidyadharan, N. Pullanjiyot, B. N. Meethal, S. S. Kanakkillam, S. Sadasivan, S. Swaminathan, *Applied Nanoscience* **2019**, 9, 435.

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Short-Step Synthesized Dopant-Free Spiro-Type Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells

([1]*National Institute of Advanced Industrial Science and Technology (AIST),* [2]*Nippon Fine Chemical Co., Ltd.*) ○Nobuko Onozawa-Komatsuzaki,[1] Daisuke Tsuchiya,[2] Shinichi Inoue,[2] Atsushi Kogo,[1] Takurou N. Murakami[1]

Keywords: Perovskite solar cell; hole-transporting material; dopant free; short-step synthesis

Hole-transporting materials (HTMs) play an important role in charge extraction, interfacial recombination, and device stability in perovskite solar cells (PSCs). For example, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (**Spiro-OMeTAD**) is one of the most frequently used HTMs. However, dopants such as lithium bis(trifluoromethylsulfonyl)imide are required to achieve high power-conversion efficiencies (PCEs), and these dopants have been speculated to cause severe instability issues in PSCs.[1] Recently, dopant-free organic HTMs have emerged as highly desirable materials for stable and efficient n–i–p-type perovskite solar cells (PSCs); however, the literature contains relatively few reports of such dopant-free organic HTMs. In addition, the synthesis of dopant-free organic HTMs often leads to further complications. Herein, we newly synthesized spiro-type hole-transporting materials (HTMs) **SF67** and **SF71**, which are nondoped spiro-type HTMs with both halogen and *N*,*N*-dimethylamino substituents as electron-withdrawing and electron-donating groups, respectively. The advantage of **SF67** and **SF71** is that they are easy to synthesize because of their two-step synthesis starting from commercially available precursors. Compared with **Spiro-OMeTAD**, they also exhibit superior hole extraction ability. Consequently, the PCEs of devices based on **SF67** and **SF71** were 19.6% and 19.5%, respectively (Figure 1). In addition, the thermal stability of the PSCs based on nondoped **SF67** and **SF71** at 85 °C in ambient air was superior to that of a PSC based on nondoped **Spiro-OMeTAD**. Therefore, both **SF67** and **SF71** are expected to be effective as high-performance dopant-free HTMs for PSCs.

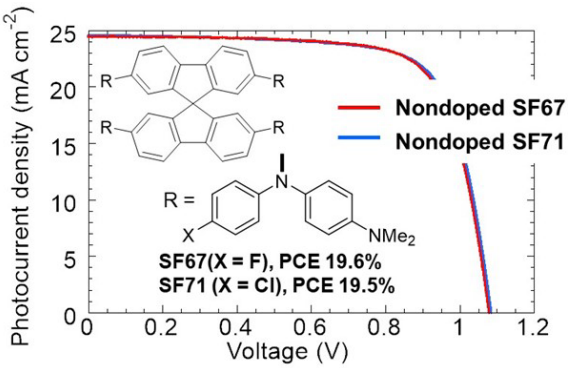

Figure1. *J-V* curves for PSCs based on nondoped **SF67** and **SF71**, recorded using backward scan.

1) P. Murugan, T. Hu, X. Hu and Y. Chene, *J. Mater. Chem. A,* **2022**, *10*, 5044.

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ペロブスカイト太陽電池におけるカリウム・チオシアン酸イオン添加の影響評価

（東京理科大工 [1]）○永田 裕樹 [1]・永田 衞男 [1]
Evaluation of the Effect of Potassium and Thiocyanate Ion Addition in Perovskite Solar Cells
([1]*Tokyo University of Science*) Hiroki Nagata,[1] Morio Nagata[1]

Perovskite solar cells can be made thinner and lighter than conventional silicon solar cells, and are attracting attention as a next-generation solar cell. On the other hand, there are still issues with power generation performance. There are reports of improving the crystal structure and stabilizing the output current by adding potassium iodide to perovskite crystals.[1)]. Here, on the subject of potassium addition, we added thiocyanate anions and other potassium compounds for comparison.
As a result, the noise in the IV curve obtained when potassium bromide was added was suppressed. Regarding the addition of bromine anions, the addition of inexpensive potassium-derived bromine is considered to be a useful tool, since the addition of lead bromide resulted in a lower efficiency.
Keywords : Perovskite Solar Cells; Additives; Doping; Renewable energy

ペロブスカイト太陽電池は、従来のシリコン型太陽電池と比較し薄膜かつ軽量に作成することが可能であり、次世代の太陽電池として注目されている。一方で発電性能にいまだ課題がある。ペロブスカイト結晶にヨウ化カリウムを添加することで、結晶構造の改善および出力電流の安定化を達成した報告がある [1)]。ここで、カリウム添加を軸にチオシアン酸アニオンや他のカリウム化合物を添加し比較検討を行った。

結果として、臭化カリウムを添加した際に得られた IV 曲線のノイズが抑制された。臭素アニオンの添加について、臭化鉛を加えた際は効率が低くなった結果を得ていることから、安価なカリウム由来の臭素添加は有用な手段であると考えられる。

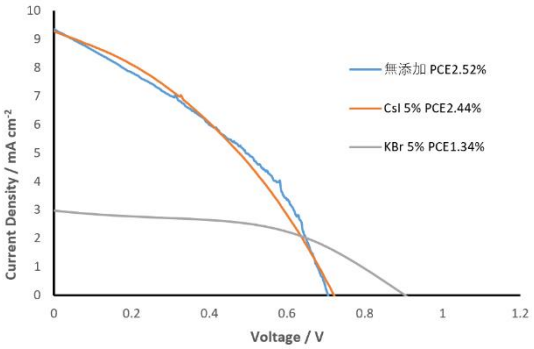

fig. 1 各サンプルの IV 曲線比較

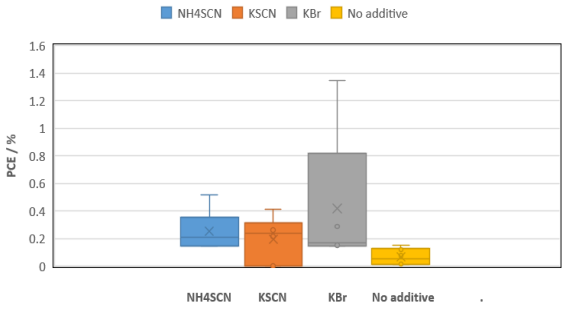

fig. 2 添加物ごとの発電効率比較

1) Tang, Z., Bessho, T., Awai, F. *et al. Sci Rep* **7**, 12183 (2017).

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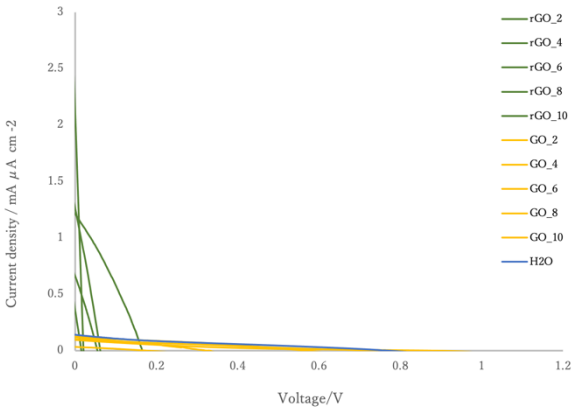
・還元型酸化グラフェンを酸化還元体に用いた色素増感型太陽電池の作製および検討

（東理大工[1]）◯二十里 文人 [1]・永田 衞男 [1]
Fabrication and Evaluation of Dye-Sensitized Solar Cells Using Reduced Graphene Oxide as Redox material([1]*Tokyo University of Science*) ◯Mondo Nijuri[1], Morio Nagata[1]

Graphene oxide (GO) is a material produced by oxidation and exfoliation of graphite, but its low electrical conductivity due to plenty oxygen-containing functional groups has been a problem. However, reduced graphene oxide (rGO), which is partially reduced from GO, improves the low electrical conductivity by decreasing the ratio of oxygen-containing groups through reduction, and the properties of GO can also be functionalized. Based on this property, we hypothesized that rGO could be optimized for the electrolytic layer of any dye-sensitized solar cell (DSSC) by controlling the redox potential (ORP) with the degree of reduction of rGO. In this study, five kinds of GO with different oxidation degree were prepared by the modified Hummers method and thermally reduced at a certain standard. Ten types of DSSC were prepared and I-V measurements were performed (Figure 2). In addition, the I-V curve of rGO depended on the degree of reduction, indicating the usefulness of controlling the degree of reduction.

Keywords: Dye Sensitized Solar Cells, Reduced Graphene Oxide, solid electrolyte, redox

酸化グラフェン(GO)は、グラファイトが酸化、剥離することによって生じる物質であるが、酸素含有基が多いことによる電気伝導率の低さが課題であった。しかし GO を部分還元した還元型酸化グラフェン(rGO)は、還元により酸素含有基の割合が低下することで低い電気伝導率が改善され、GO の性質も機能化できる。この性質から、rGO の還元度で酸化還元電位(ORP)を制御することで任意の色素増感太陽電池(DSSC)の電解層に最適な rGO を作製することが出来るのではないかと考えた。本研究では、酸化度の異なる GO を改良 Hummers 法を用いて 5 種作製し、一定基準で熱還元した。そして 10 種の DSSC を作製して I-V 測定をしたところ、電解層に rGO を導入したものは全体的に性能が向上した。また、rGO は還元度によって異なる I-V 曲線が描けたため、還元度の制御の有用性が示せた。



[1]Alvira Ayoub Arbab, Mumtaz Ali et al., Journal of Colloid and Interface Science Volume 569, **2020**,6,386-401

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固体型色素増感太陽電池における二層アナターゼ TiO_2 電極の熱処理効果

（岐阜大工）○和田諭佳・松井芽以・Shinapol Toranathumkul・杉浦隆・萬関一広
Solid-state dye-sensitized solar cells with a double-layered anatase TiO_2 electrode: effects of the sintering strategies on the electrode performance (*Faculty of Engineering, Gifu University*)
○Satoka Wada, Mei Matsui, Shinapol Toranathumkul, Takashi Sugiura, Kazuhiro Manseki

Nanostructured porous TiO_2 thin-films are promising materials owing to their potential use for the development of versatile sun-light energy conversion devices. Here we report on solid-state dye-sensitized solar cells (ss-DSSCs) using a double-layered anatase TiO_2/Z907 photoelectrode in combination with poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole-transport material. By using the integrated TiO_2 photoanode, the PEDOT was electrochemically polymerized as a hole conductor under visible-light irradiation in a way that the PEDOT is placed adjacent to the dye molecules. We focus on the effect of sintering strategies of the TiO_2 layers on the performance of ss-DSSCs.
Keywords : TiO_2 electrodes, Solid-state dye sensitized solar cells, Sintering, Conductive polymers

多孔質のナノ構造酸化チタン薄膜は、太陽光エネルギー変換デバイスの基盤的材料として設計自由度が高く興味深い。本研究では、二種のアナターゼ酸化チタン微粒子膜を積層し、熱処理後、Z907 色素、正孔輸送層のポリ（3,4-エチレンジオキシチオフェン）（PEDOT）を組み合わせ、固体型色素増感太陽電池（ss-DSSCs）を作製した。平均結晶子サイズが 4 nm (A)および 18 nm (B)の二種のアナターゼ型酸化チタンナノ粒子を FTO 基板上に A、B の順で段階的に塗布して積層膜を作製した。次のように酸化チタン層の焼結条件を 2 通り変化させた。(i)酸化チタン A、B の塗布後、両方で 500℃の熱処理を行う条件、(ii)二層目の塗布後に一度のみ 500℃の熱処理を行う条件に着目した（A の塗布後は 150℃以下の低温製膜）。Figure 1 に(ii)で作製した酸化チタン基板の SEM 像の一例を示す。酸化チタン A 層では、ナノ粒子が高密度に製膜されていることが分かった。酸化チタン/Z907 色素分子基板を用いて、光照射下で PEDOT の定電流重合を行い、金対極を形成して ss-DSSC を作製した [1]。

酸化チタン積層膜のナノ構造解析、素子の電気化学インピーダンス測定等をもとに、ss-DSSCs の高性能因子の解明を目指した。特に、焼結条件の差が発電機能に及ぼす影響について調べた。重合時間を変化させ、(ii)の光電極の素子において、フィルファクターの増大（光電変換効率の向上）につながる結果を見出した。

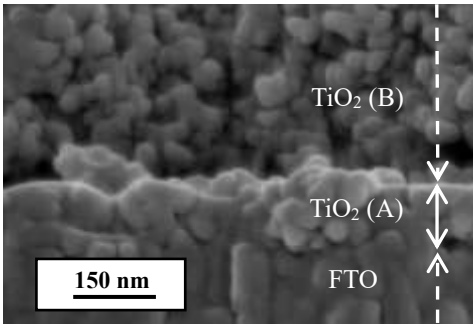

Figure 1. TiO_2 基板の断面 SEM

1) 萬関一広, 表面技術, **2015**, 66, 141

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ギ酸を生成する人工光合成システム　－リン酸カリウム電解液からのギ酸の単離－

（豊田中研）○塩澤 真人・菊澤 良弘・加藤 直彦・竹田 康彦
Artificial Photosynthesis System Producing Formic Acid - Isolation of Pure Formic Acid from a Potassium Phosphate Electrolyte - (*Toyota Central R&D Labs., Inc.*) ○Masahito Shiozawa, Yoshihiro Kikuzawa, Naohiko Kato, Yasuhiko Takeda

We are developing highly efficient large-sized artificial photosynthetic cells that reduce CO_2 to organic valuables. The newest 1 m^2-sized cell composed of an electrochemical reactor and crystalline silicon solar cells converted CO_2 to formic acid with a high solar-to-chemical energy conversion efficiency of 10.5%[1,2]. Thus, the next challenges are isolation of the produced formic acid. Figure 1 illustrates the newly developed isolation process combined with the artificial photosynthetic reaction process. Formic acid (0.02 M) dissolved in the electrolyte of 0.4 M KH_2PO_4 aqueous solution was first extracted to a mixture of tri-*n*-octylamine (TOA) and dichloromethane (DCM) by reactive extraction using a triple-series small-sized mixer-settler. Formation of a complex salt of the formic acid and TOA realized a high extraction yield of 96%. Then, the DCM was evaporated followed by distillation of the formic acid, achieving an over 90% isolation yield. The great feature of the artificial photosynthetic system is no consumption of chemicals other than the raw materials of CO_2 and water along with no generation of wastes, which is realized by cyclic use of the electrolyte, TOA, and DCM.
Keywords : Formic acid, Artificial photosynthesis, Isolation, Reactive extraction

我々は、CO_2 を還元してギ酸に変換する人工光合成セルの高効率化と大型化の両立に取り組んできた。電気化学リアクターと結晶シリコン太陽電池を組み合わせた最新の 1 m^2 サイズのセルは、10.5%の高いエネルギー変換効率でギ酸を生成した[1,2]。次の課題は、生成したギ酸の単離と、これと人工光合成セルを組み合わせたシステム化である。新たに開発した単離プロセスを Fig. 1 に示す。電解液（0.4 M KH_2PO_4 水溶液）中のギ酸（0.02 M）を、先ず、小型の三連ミキサーセトラーを用いて反応抽出した。有機塩基の一種であるトリオクチルアミン（TOA）とジクロロメタン（DCM）の混合物を抽出剤に用いることにより、ギ酸-TOA 塩が形成され、その結果 96%の高効率で抽出された。次いで、DCM を留去後、ギ酸を蒸留することにより、90%以上の収率でギ酸が単離された。この人工光合成システムの特長は、電解液、TOA、DCM を循環使用することにより、原料である CO_2 と水以外の化学物質を消費せずに、更に廃棄物なしで純粋なギ酸が生成されることである。

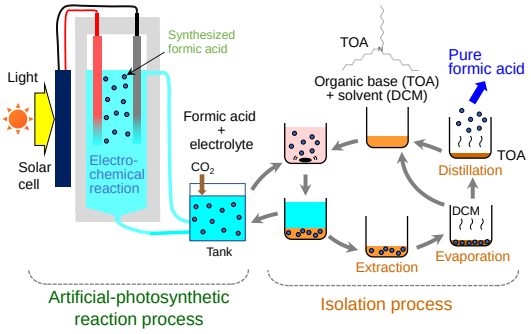

Fig.1 Pure-formic-acid-producing system consisting of an artificial-photosynthetic reaction process and an isolation process.

1) N. Kato, et al., *Joule* **2021**, *5*, 687.　2) N. Kato, et al., *ACS Sustain. Chem. Eng.* **2021**, *9*, 16031.

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デュアルアニヒレーター三重項対消滅型アップコンバージョン系の発光波長制御とプラズモン誘起効果

（日大理工）○久住川 東吉・須川晃資・大月穣
Emission wavelength control in dual annihilator-based triplet annihilation upconversion systems and plasmon-induced effects (*Collage of Science and Technology, Nihon University*)
○Tokichi Kusumikawa, Kosuke Sugawa, Joe Otsuki

Triplet-triplet annihilation-based upconversion (TTA-UC), which responds to external stimuli, including temperature, has been developed for the clinical tumor diagnosis. In this study, we have developed thin films based on dual annihilators (DPA and BPEA) for TTA-UC in which the emissive mode undergoes changes in response to the excitation light intensity. In the upconverted emission spectra sensitized by Pt porphyrin derivative (Fig. 1), BPEA fluorescence dominates under lower excitation intensity. Conversely, as the excitation intensity increases, DPA emission became more prominent, ultimately resulting in the dominance of DPA fluorescence. In the presentation, we will discuss the changes in emission behavior by hybridizing plasmonic metal nanoparticles with the TTA-UC thin films.

Keywords : Photon Upconversion; Triplet-triplet Annihilation; Localized Surface Plasmon Resonance

温度など外的刺激に応答する三重項対消滅型アップコンバージョン（TTA-UC）系は、悪性腫瘍などの疾患診断への応用が期待されている[1)2)]。 本発表では、2 種類の発光分子に特徴づけられる TTA-UC 薄膜を開発し、励起光強度に応答して発光種のスイッチングが誘起される新規機能を見出したので報告する。増感分子として Pt ポルフィリン誘導体（PtOEP）、発光分子として 2 種のアントラセン誘導体（DPA、BPEA）を採用した薄膜を、ポリマーをマトリックスとして作製した。Fig. 1 に示されたように、アップコンバージョン発光スペクトル（λ_{ex} = 532 nm）は、励起光強度 200 mW cm-2 時では BPEA の蛍光に支配された一方、強度の上昇と共に DPA の蛍光に由来する発光が顕在化し、16000 mW cm-2 時ではほぼ DPA の蛍光に支配された。発表では、この発光機構の詳細を述べると共に、当該 TTA-UC 薄膜にプラズモニック金属ナノ粒子を組み込んだ際の発光挙動についても言及する。

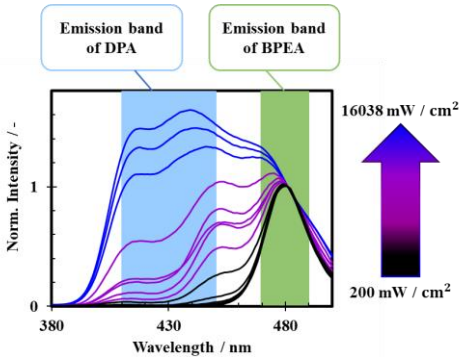

Fig. 1 Excitation power dependence of normalized upoconverted emission spectra.

1) N. Yanai *et al*., *Angew. Chem. Int. Ed.* **2020**, *59*, 10252.
2) Y. Wei *et al*., *Mater. Horizons,* **2021**, *8*, 606.

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内閣府エビデンスシステム（e-CSTI）の論文・特許情報を活用した環境・エネルギー関連技術の分析

（内閣府[1]）○三村 直樹[1]、面 和成[1]、池田 虎三[1]、河野 英子[1]、永井 博昭[1]、柏原 直明[1]

Trend analysis of the technologies for environment and energy by using the data of papers and patents in e-CSTI (Evidence data platform constructed by Council for Science, Technology and Innovation)

([1]Cabinet Office) ○Naoki Mimura[1], Kazumasa Omote[1], Torazo Ikeda[1], Eiko Kono[1], Hiroaki Nagai[1], Naoaki Kashiwabara[1]

In order to support the formulation of effective evidence-based science and technology policies, the Cabinet Office has been analyzing research capabilities using bibliographic information on papers and patents. In this presentation, as a specific case of analysis, we took up "perovskite solar cell," an environment- and energy-related technology, and attempted to clarify the current status of Japan's research capabilities.

Data of papers (2013-2021, 23,844,251 papers) were vectorized based on citation relationships and natural language processing of titles and abstracts. We used the K-means method to group items with close distances into 1000 clusters based on similarity in meaning and content. Furthermore, we subdivided each cluster into 10 using the same method, creating subclusters. Fig. 1 shows the yearly trends in the number of all papers in clusters that are strongly related to perovskite solar cell. At the time of our presentation, we will report on the trends of country-specific comparisons and others, based on the bibliographic information from the papers and patents.

Keywords : Big-data analysis, Data of papers, Data of patents, Technology for environment and energy

内閣府では、エビデンスに基づいた効果的な科学技術政策の立案に資するため、論文・特許の書誌情報を用いて研究力の分析を行っている。本発表では、具体的な分析事例として、環境・エネルギー関連技術である「ペロブスカイト太陽電池」を取り上げ、日本の研究力の現状を明らかにすることを試みた。

論文情報（2013 年～2021 年、23,844,251 件）は、引用関係とタイトル及びアブストラクトの意味的近接性による情報を基にベクトル化した。K-means 法を用いて距離が近いもの（内容が近いもの）同士が同じクラスタになるように、1000 個のクラスタに分割し、さらに一つのクラスタ内を同様の方法で 10 分割してサブクラスタとした。Fig.1 に、ペロブスカイト太陽電池に関連の強いクラスタ内に存在する総論文数の年毎推移を示す。発表時には、論文・特許等の書誌情報を基にした国別の時系列推移等の分析結果について報告する。

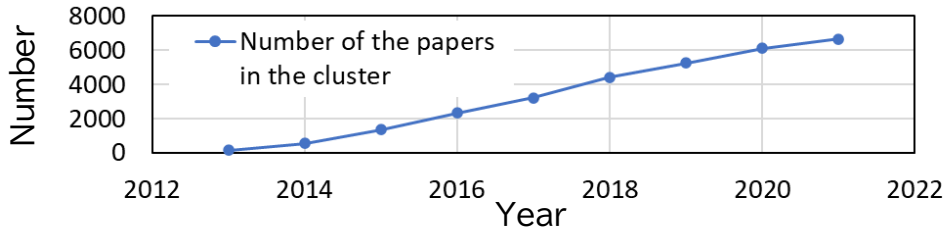

Fig.1 Time course of number of papers in the cluster involved in "perovskite solar cell"

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