Thu. Mar 21, 2024

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

Thu. Mar 21, 2024 9:30 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:20 AM UTC H937(937, Bldg. 9 [3F])

[H937-4am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Hiromasa Kaneko, Junji Seino

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H937-4am-01]
Design of ethylbenzene production process using machine learning and Bayesian optimization

○Eri Ishikawa[1], Hiromasa Kaneko[1] (1. Meiji University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H937-4am-02]
Model construction and improvement of the model for blood glucose monitoring using mid-infrared rays

○Yuta Takami[1], Keita Miyagawa[2], Yuki Tsuda[2], Koichi Akiyama[2], Ruka Ando[1], Hiromasa Kaneko[1] (1. Meiji University, 2. Mitsubishi Electric)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H937-4am-03]
Improving molecular design with direct inverse analysis of QSAR/QSPR model

○Yuto Shino[1], Hiromasa Kaneko[1] (1. Meiji University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H937-4am-04]
Development of applicability domain considering stability of molecular structures

○Soma Kosakai[1], Hiromasa Kaneko[1] (1. The Univ. of Meiji)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H937-4am-05]
Development of a Cloud Point Prediction Model for a Polyvinyl Alcohol Production Plant

○Ayami Ohkuma[1], Yoshihito Yamauchi[2], Nobuhito Yamada[2], Satoshi Ooyama[2], Hiromasa Kaneko[1] (1. Meiji University, 2. Mitsubishi Chemical Corporation)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[H937-4am-06]
Ligands' Electronic structure informatics for separative extraction of minor actinides

○Tsuyoshi Sumiyoshi[1], Nahoko Kuroki[1,2], Hirotoshi Mori[1] (1. The Univ. of Chuo , 2. JST ACT-X)

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Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H937-4am-07]

Complete enumeration and classification of polymer structural isomers with $C_6H_{11}NO$ and one amide group

○Gikyo Usuki[1], Tsutsumi Takuro[1,3], Hasebe Kohei[1], Kobayashi Masato[1,3,4], Shitamiti Mio[2], Matsuoka Keitaro[1,3], Taketsugu Tetsuya[1,3,4], Sada Kazuki[1,3] (1. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ., 2. Sch. of Sci., Hokkaido Univ., 3. Fac. of Sci., Hokkaido Univ., 4. WPI-ICReDD, Hokkaido Univ.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H937-4am-08]

Decomposition of spectrum in mixed compounds using machine learning and multivariate curve resolution

○Keitatsu Sekiya[1], Takumi Kumagai[1], Junji Seino[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Waseda Research Institute for Science and Engineering)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H937-4am-09]

Development of a Dialogic Information Retrieval System Utilizing Large Language Models for Electronic Lab Notebooks

○Nanako Unagami[1], Masahiko Nakano[2,3], Junji Seino[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Waseda Research Institute for Science and Engineering, 3. Mitsubishi Chemical Group)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H937-4am-10]

Mechanistic analysis of oxygen evolution reaction electrodes by machine-learning analysis

○Shinji Yoneyama[1], Motoki Fukasawa[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. School of Science, Hokkaido University, 3. Faculty of Science, Hokkaido University)

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

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC H937(937, Bldg. 9 [3F])

[H937-4pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Takuro Tsutsumi, Yuki Mitsuta

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H937-4pm-01]

Development of a Nudged Elastic Stiffness Band Method by Adding Stiffness Force to Improve the Nudged Elastic Band Method

○Yuki Mitsuta[1,2], Toshio Asada[1,2] (1. Graduate School of Science, Osaka Metropolitan Univ., 2. RIMED, Osaka Metropolitan Univ.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H937-4pm-02]

Towards a Post-Sabatier Theory of Electrocatalysis: Realizing Activity and Stability

○Hideshi Ooka[1], Ryuhei Nakamura[1,2] (1. RIKEN CSRS, 2. Tokyo Inst. Technol. ELSI)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H937-4pm-03]

Extrapolation Prediction of Properties of Sol-Gel Anti-Reflection Coating with Various Silicon Alkoxides as Precursors by Machine Learning

○Takuma Kurakami[1], Koichi Shiraki[1], Mizuho Matsuda[1] (1. NIPPON SHEET GLASS CO., LTD.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H937-4pm-04]

Crystal structure prediction based on heterogeneous metric learning

○Minoru Kusaba[1], Chang Liu[1], Ryo Yoshida[1,2,3] (1. The Institute of Statistical Mathematics, 2. SOKENDAI, 3. National Institute for Materials Science)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H937-4pm-05]

Exploration of alloy catalyst with highly reactive atomic configuration using a universal neural network potential and a generative model

○Kaoru Hisama[1], Atsushi Ishikawa[2], Susan Menez Aspera[1], Michihisa Koyama[1] (1. Shinshu Univ., 2. Tokyo Tech.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[H937-4pm-06]

Can LLMs be Lab Assistants?

○Gergely Juhasz[1] (1. Tokyo Institute of Technology)

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

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1441(1441, Bldg. 14 [4F])

[A1441-4pm] 04. Physical Chemistry -Properties-

Chair: Tomoyuki Mochida, Yoshiki Ishii

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1441-4pm-01]

Thermal phase transition behaviors of two-dimensional perovskite microcrystals as studied by low-frequency Raman microspectroscopy

○Ryuto Yumiba[1], Shinsuke Shigeto[1], Eric Wei-Guang Diau[2] (1. The Univ. of Kwanseigakuin, 2. National Yang Ming Chiao Tung Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1441-4pm-02]

Ionic conductivity modulation induced by the hydration structural change under vibrational strong coupling

○Hirotaka Motokawa[1], Tomohiro Fukushima[2], Kei Murakoshi[2] (1. School of Science, Hokkaido University, 2. Faculty of Science, Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1441-4pm-03]

Investigation of the optical properties of micro-structured electrodes and effects of vibrational polaritons with water molecules

○Yui Itakura[1], Hirotaka Motokawa[1], Daiki Ashizawa[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. Schoolof Science, Hokkaido University, 2. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 3. Faculty of Science, Hokkaido University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1441-4pm-04]

Structures and Phase Behaviors of Organometallic Ionic Plastic Crystals with Cyanoborate Anions

○Ryota Inoue[1], Shimada Masato[1], Tomoyuki Mochida[1,2] (1. Graduate School of Science, Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University)

English
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1441-4pm-05]

Counting the microscopic states of molecular specimens using electron diffraction

○Jiarui Fu[1], Dongxin Liu[1], Masaya Sakakibara[1], Takayuki Nakamuro[1], Eiichi Nakamura[1] (1. The Univ. of Tokyo)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1441-4pm-06]

How dose the methylation of the hydrogen atom at C2-position of imidazolium ring affect the high-pressure phase transition behavior of imidazolium-based ionic liquids?

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○Hiroki Wakatsuki[1], Atsushi Yamada[1], Takahiro Takekiyo[1], Yukihiro Yoshimura[1] (1. National Defense Academy)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[A1441-4pm-07]

Potential of Ionic Liquids for the Temporary Cell Preservation Solvent at Room Temperature

○Masaharu Nakayama[1], Atsushi Yamada[1], Takamasa Uekita[1], Hiromi Miyazaki[2], Shingo Nakamura[2], Masami Yamada[1], Takahiro Takekiyo[1], Yukihiro Yoshimura[1] (1. National Defense Academy, 2. National Defense Medical College)

English
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1441-4pm-08]

Synthesis and heat-storage property of Zr substituted λ-Ti_3O_5

○Tomu Otake[1], Lidong Wang[1], Marie Yoshikiyo[1], Fangda Jia[1], Shin-ichi Ohkoshi[1] (1. The Univ. of Tokyo)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1441-4pm-09]

Preparation of Nb-Fe alloy nanoparticles and application to electroluminescence devices

○Akito Mizobata[1], Moegi Nomura[1], Syohei Murotani[2], Honami Iguchi[1], Takeyuki Suzuki[3], Kazuki Tabaru[1], Duotian Chen[4], Takashi Toyao[4], Ken-ichi Shimizu[4], Mitsuru Inada[2], Yasushi Obora[1] (1. Fac. Chem. Matl. & Bioeng., Kansai Univ., 2. Fac. Eng. Sci., Kansai Univ., 3. SANKEN, Osaka Univ., 4. Institute for Catalysis, Hokkaido Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1441-4pm-10]

Optical Characterization of Single Hollow Silver Nanoshell Using Dark Field Microscopy

○Koki Deguchi[1], Shinpei Kado[1], Setsuko Yajima[1] (1. The Univ. of Wakayama)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[A1441-4pm-11]

Computational chemistry study on characterization of organic solvent separation using MoS_2 containing nanofiltration membrane

○Ryo Arii[1], Hayato Higuchi[1], Masaya Miyagawa[1], Hiromitsu Takaba[1] (1. Kogakuin University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[A1441-4pm-12]

Pressure-dependent Elementary Exciton Processes of CdSe-based Core Shell Quantum Dots

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

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[A1441-4pm-13]

Effects of Interfacial Potential on Electron Transfer Dynamics in InP-based Core/Shell Quantum Dots

○Kotaro Moriyama[1], Kazuki Inada[1], Daichi Eguchi[1], Naoto Tamai[1] (1. The Univ. of Kwansei Gakuin)

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English
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[A1441-4pm-14]
Adsorption properties of NH_3 on hydrogen boride sheets

○Kosei Fukuda[1], Shin-ichi Ito[1], Miwa Hikichi[1], Iwao Matsuda[2], Takahiro Kondo[1,3] (1. University of Tsukuba, 2. The University of Tokyo, 3. Tohoku University)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[A1441-4pm-15]
Discriminating Positional Isomers of Volatile Organic Compounds by Metal Oxide QCM sensor.

○Kenta Tanaka[1], Poom Jirayupat[1], Hosomi Takuro[1], Yanagida Takeshi[1,2], Takahasi Tsunaki[1], Tanaka Wataru[1], Jiangyang Liu[1] (1. The Univ. of Tokyo, 2. Kyusyu University)

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

Thu. Mar 21, 2024 11:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 2:00 AM - 2:40 AM UTC
A1441(1441, Bldg. 14 [4F])

[A1441-4am] 04. Physical Chemistry -Properties-

Chair: Takahiro Takekiyo, Yoichi Sasaki

Japanese
11:00 AM - 11:20 AM JST | 2:00 AM - 2:20 AM UTC
[A1441-4am-01]
All-atomic Analyses on the Properties of Hydrogen Bonds and Infrared Vibrational Bands in the Vicinity of Polymer Interfaces

○Yoshiki Ishii[1], Hajime Torii[2], Yuka Ikemoto[3], Hitoshi Washizu[4] (1. Kitasato University, 2. Shizuoka University, 3. JASRI, 4. University of Hyogo)

English
11:20 AM - 11:40 AM JST | 2:20 AM - 2:40 AM UTC
[A1441-4am-02]
The Influence of Alkyl Chain Length on Carboxylic Acid Molecule Adsorption onto Various Metal Oxide Surfaces.

○Wenjin Lei[1], Takuro Hosomi[1], Jianyang Liu[1], Wataru Tanaka[1], Tsunaki Takahashi[1], Takeshi Yanagida[1,2] (1. School of Engineering, The Univ. of Tokyo, 2. IMCE, Kyushu Univ.)

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Academic Program [Oral A] | 07. Inorganic Chemistry : Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1444(1444, Bldg. 14 [4F])

[A1444-4am] 07. Inorganic Chemistry

Chair: Naoki Ogiwara, Yuji Kikukawa

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1444-4am-01]

Encapsulation and stabilization of inorganic clusters in a cavity of coordination cage

○Naoki Kimura[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The Univ. of Tokyo, 2. Institute for Molecular Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1444-4am-02]

Syntheses of porous ionic crystals based on organically- decorated polyoxometalates

○Mochizuki Shunsuke[1], Zhewei Weng[1], Naoki Ogiwara[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1444-4am-03]

Methylene blue capture with polyoxometalate encapsulated metal–organic frameworks

○Naoki Ogiwara[1], Shotaro Miyazaki[1], Sayaka Uchida[1] (1. School of Arts and Sciences, The Univ. of Tokyo)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1444-4am-04]

High-Performance Solid Proton Conductors: Sodium-Centered Preyssler-Type Polyoxometalate and Urea-Modified Polyallylamine Crystalline Composites

○Linshu Zhang[1], Tsukasa Iwano[1], Sayaka Uchida[1] (1. The University of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1444-4am-05]

Synthesis and Structural Characterization of Trimethylammonium Heptamolybdate and Octamolybdate

○Rie Ishida[1], Ndaru Candra Sukmana[1], Sugiarto Sugiarto[1], Masahiro Sadakane[1] (1. Hiroshima Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1444-4am-06]

Synthesis of inorganic materials with titanium-substituted polyoxovanadate and inorganic high valent cation.

○Kai Matsumura[1], Yuji Kikukawa[1], Yoshihito Hayashi[1] (1. Kanazawa Univ.)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1444-4am-07]

Oxidate state control and catalytic property of nitrate-containing vanadium-oxo clusters

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○Isshin Yoshida[1], Yuji Kikukawa[1], Yoshihito Hayashi[1] (1. Kanazawa Univ.)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1444-4am-08]

Physical Properties of Organic-Inorganic Hybrid Polyoxometalates with Host-Guest Characteristics

○Hiroto Kaitori[1], Chiasto Kato[1], Goulven Goulven[2,3], Masaru Fujibayashi[4], Kastuya Inoue[1,2,3,5], Sadafumi Nishihara[1,3,5,6] (1. Graduate School of Advanced Science and Engineering, 2. International Institute for Sustainability with Knotted Chiral Meta Matter, Hiroshima University Japan, 3. Chirality Research Center, Hiroshima University, Japan, 4. National Institude of Technology, Ube College, Japan, 5. Institute for Advanced Materials Research, Hiroshima University, Japan, 6. Precurspry Research for Embryonic Science and Technology, Japan Science and Technology Agency, Japan)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1444-4am-09]

Dielectric Properties of Dawson like Polyoxometalates Including Iodine

○Minami Tsuruda[1], Chisato Kato[2], Cosquer Goulven[3,4], Katsuya Inoue[2,3,4,5], Sadafumi Nishihara[2,4,5,6] (1. School of Science, Hiroshima University, 2. Graduate School of Advanced Science and Engineering, Hiroshima University, Japan, 3. International Institute for Sustainability with Knotted Chiral Meta Matter, Hiroshima University, Japan, 4. Chirality Research Center (CResCent), Hiroshima University, Japan, 5. Institute for Advanced Materials Research, Hiroshima University, Japan, 6. Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency, Japan)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1444-4am-10]

Synthesis and catalysis of an organic solvent-soluble ε-Keggin type $[Al_{13}O_4(OH)_{24}(ligand)_{12}]^{7+}$

○Ayano Umakoshi[1], Takuo Minato[1], Masahiro Sadakane[1] (1. Hiroshima University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1444-4am-11]

Dielectric properties of a wheel-shape polyoxometalate with potassium ions at high temperature

○Yuma Takemoto[1], Chisato Kato[1], Masaru Fujibayashi[2], Goulven Couquer[3,4], Katsuya Inoue[1,3,4,5], Sadafumi Nishihara[1,4,5,6] (1. Grad.Sch.Adv.Sci.Eng.,Hiroshima,Univ, 2. NIT, Ube College, 3. SKCM2,Hiroshima.Univ, 4. CResCent,Hiroshima.Univ, 5. IAMR,Hiroshima.Univ, 6. PRESTO, JST)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1444-4am-12]

Physical properties of the thin films of single-molecule electret $(NH_4)_xH_{12-x}[Tb^{3+}\subset P_5W_{30}O_{110}]$

○Masaki Arima[1], Kazushi Takeda[1], Rikuto tamatani[1], Yuki Nakano[1], Chisatoisato Kato[1], Goulven Cosquer[2], Masaru Fujibayashi[3], Katuya Inoue[1,2,4,5], Sadafumi Nishihara[1,4,5,6] (1. Grad. Sch. Adv. Sci. Eng. Hiroshima Univ., 2. SKCM, Hiroshima Univ., 3. NIT, Ube College, 4. CResCent , Hiroshima Univ., 5. IAMR, Hiroshima Univ., 6. PRESTO, JST)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

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[A1444-4am-13]

Precise synthesis of Pt alloy clusters for electrochemical catalysts and evaluation of their functions

○Takuto NAKAMURA[1], Tatsuya MORIAI[1,2], Tetsuya KAMBE[1,2], Takane IMAOKA[1,2], Kimihisa YAMAMOTO[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. JST-ERATO)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[A1444-4am-14]

Synthesis of ultra small bismuth particles and evaluation of their magnetic function

○Ryotaro Hashimoto[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST ERATO)

Academic Program [Oral B] | 07. Inorganic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 2:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:00 AM UTC A1444(1444, Bldg. 14 [4F])

[A1444-4pm] 07. Inorganic Chemistry

Chair: Takayuki Nakamuro, Takuro Hosomi

English

1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC

[A1444-4pm-01]

Multi-step Mechanism of Carbonation Reaction Analysed by Atomic-resolution Electron Microscopy

○Miyuki Hanazawa[1], Xin Li[1], Takayuki Nakamuro[1], Eiichi Nakamura[1] (1. The University of Tokyo)

Japanese

1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC

[A1444-4pm-02]

Local structure analysis of near-infrared reflective black $Ca_2(Mn,Ti)O_4$ pigments using synchrotron radiation X-ray

○Ryohei Oka[1], Tomokatsu Hayakawa[1] (1. Nagoya Institute of Technology)

English

1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC

[A1444-4pm-03]

Growth-traceable fully vapour-phase organic-inorganic atomic layer deposition system

○Hideaki Matsuo[1], Takuro Hosomi[1], Jiangyang Liu[1], Wataru Tanaka[1], Tsunaki Takahashi[1], Takeshi Yanagida[1,2] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. IMCE, Kyushu Univ.)

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Academic Program [Oral A] | 08. Catalysts and Catalysis：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
A1456(1456, Bldg. 14 [5F])

[A1456-4am] 08. Catalysts and Catalysis

Chair: Akinobu Nakada, Shimpei Naniwa

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1456-4am-01]

CO_2 photoreduction by first-row transition metal loaded-Al_2O_3

○Daehyeon An[1], Megumi Okazaki[1], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1456-4am-02]

Light-intensity dependence of CO_2 reduction over Ru-complex/polymeric carbon nitride hybrid photocatalysts

○Ryuichi Nakada[1], Megumi Okazaki[1], Kazuhiko Maeda[1] (1. Tokyo Institute of Tecnology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1456-4am-03]

Improvement in a Z-schematic CO_2 reduction activity under visible light irradiation utilizing a long wavelength visible light-responsive metal sulfide photocatalyst prepared by a flux method

○Sota Arai[1], Kotaro Wada[1], Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1456-4am-04]

Single particulate CO_2 reduction under visible light irradiation over various cocatalysts-loaded a $SrTiO_3$:Ir,Sb photocatalyst using water as an electron donor

○Hana Ito[1], Yoshiya Ueki[1], Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1456-4am-05]

Consecutive photoreduction of carbon dioxide using Fe and Cu nanoparticles supported on zirconium dioxide and its mechanistic analysis

○Tomoki Oyumi[1], Keisuke Hara[1], Yasuo Izumi[1] (1. Chiba University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1456-4am-06]

Conversion of carbon dioxide to C_1-C_3 hydrocarbon compounds by titanium dioxide photocatalyst loaded with nickel metal nanoparticles

○Yuta Sekine[1], Tomoki Oyumi[1], Yasuo Izumi[1] (1. Chiba university)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1456-4am-07]
Photo-excited carrier dynamics during the photoreduction of CO_2 on transition metal oxide surfaces

○Keisuke Hara[1], Ayaka Hasegawa[1], Ayana Omata[1], Kaori Niki[1], Yasuo Izumi[1] (1. Chiba University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1456-4am-08]
Enhancement of Activity of Pt/MoO_3 Catalysts for Photo-Assisted RWGS Reaction by Supporting on Various Metal Oxide

○Daichi Takami[1], Yasutaka Kuwahara[1], Hiromi Yamashita[1] (1. Osaka Univ.)

English
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1456-4am-09]
Development of Re complexes bearing various bipyridine-derived ligands for visible-light-driven carboxylation of organic molecules with CO_2

○Phurinat Lorwongkamol[1], Masaki Kitada[1], Taito Watanabe[1], Yutaka Saga[1], Tetsuya Kambe[1], Mio Kondo[2,1,3], Shigeyuki Masaoka[1] (1. Osaka University, 2. Tokyo Institute of Technology, 3. JST PRESTO)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1456-4am-10]
Catalytic properties of delafossite-type Cu oxides for electrochemical CO_2 reduction reaction

○Takahiro Matsuu[1], Akihiko Anzai[2], Masaki Donoshita[2], Hirokazu Kobayashi[3], Miho Yamauchi[2,3,4,5] (1. Dep. Chem., Sch. Sci., Kyushu Univ., 2. IMCE, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ., 5. WPI-I2CNER, Kyushu Univ.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1456-4am-11]
Production of high value-added chemicals by the CO_2 electroreduction with copper-based electrocatalysts

○Junya Yamaguchi[1], Xiaofan Hou[1], Kenji Kamiya[1], Eika Qian[1] (1. Tokyo University of Agriculture and Technology)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1456-4am-12]
DFT Study of the Catalytic Active Site of CoN_4C_x on KB for Electroreduction of CO_2 to CO

○Sarinya Hadsadee[1], Manussada Ratanasak[1], Kiyotaka Asakura[1], Hitoshi Ogihara[3], Ichiro Yamanaka[2], Jun-ya Hasegawa[1] (1. Hokkaido University, 2. Tokyo Institute for Technology, 3. Saitama University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1456-4am-13]
Study on Electrochemical CO Reduction in Acidic Environments for the Development of Solid Polymer Electrolyte Systems Utilizing Cation Exchange Membranes

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○Ryo Kurihara[1], Kaito Nagita[1], Shotaro Ito[1], Shintaro Kato[1], Ohashi Keitaro[1], Yoshiharu Mukouyama[1,2], Takashi Harada[1], Shuji Nakanishi[1], Kazuhide Kamiya[1] (1. Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University, 2. Tokyo Denki University)

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Academic Program [Oral A] | 08. Catalysts and Catalysis：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
A1458(1458, Bldg. 14 [5F])

[A1458-4am] 08. Catalysts and Catalysis

Chair: Osamu Tomita, Yuichi Yamaguchi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1458-4am-01]

Visible-Light Driven Gas Phase Hydrogen Sulfide Photodegeneration using CdS/g-C_3N_4 Hybrid Photocatalyst

○Tomofumi Katayama[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1458-4am-02]

Photocatalytic reduction of nitrobenzene under irradiation of visible light with Ru-complex modified TiO_2.

○Shoya Oda[1], Atsuhiro Tanaka[1], Hiroshi Kominami[1] (1. Faculty of Science & Engineering, Kindai University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1458-4am-03]

Photocatalytic hydrogen peroxide production using porphyrin-based hydrophobic Zr-MOFs

○Shiori Mizutani[1], Yoshifumi Kondo[1], Yasutaka Kuwahara[1], Kohsuke Mori[1], Hiromi Yamashita[1] (1. Grad. Sch. of Eng., Osaka Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1458-4am-04]

Anionic polymer modification of dye-sensitized photocatalysts to improve activity of Z-scheme water splitting

○Haruka Yamamoto[1], Shunta Nishioka[1], Yugo Miseki[2], Kazuhiro Sayama[2], Thomas E. Mallouk[3], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology, 3. University of Pennsylvania)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1458-4am-05]

Improved photocatalytic activity of $Pb_2Ti_2O_{5.4}F_{1.2}$ nanoparticles

○Hiroto Ueki[1], Kenta Aihara[1], Megumi Okazaki[1], Fumitaka Ishiwari[2], Akinori Saeki[2], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. OSAKA UNIVERSITY)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1458-4am-06]

Effects of Ru cocatalyst loading on photocatalytic water oxidation over $Pb_2Ti_2O_{5.4}F_{1.2}$

○Megumi Okazaki[1], Yoshitaka Tamura[1], Hiroto Ueki[1], Fumitaka Ishiwari[2], Kunihisa Sugimoto[3], Akinori Saeki[2], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. Osaka University, 3. Kindai University)

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English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1458-4am-07]
Photocatalytic activity of cation-doped layered perovskite oxynitride $K_2LaTa_2O_6N$

○Hideya Tsuchikado[1], Yuta Shiroma[1], Dongxiao FAN[2], Megumi Okazaki[1], Shunsuke Nozawa[2], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. High Energy Accelerator Research Organization)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1458-4am-08]
Development of New Visible-Light-Driven Sulfide Photocatalysts by Machine Learning

○Fuga Kakami[1], Ryuto Baba[2], Yoshiya Ueki[1], Yosuke Harashima[2,3], Yuichi Yamaguchi[1,4], Mikiya Fujii[2,3], Akihiko Kudo[1,4] (1. Tokyo Univ. of Science, 2. NAIST, Material Science, 3. NAIST, DSC, 4. CVRC, RIST TUS)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1458-4am-09]
Development of Z-scheme Systems for Water Splitting using Various Long Wavelength Visible Light-Responsive Metal Sulfide Photocatalysts Prepared by a Flux Method

○Riku Nakao[1], Kotaro Wada[1], Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1458-4am-10]
Overall water splitting under visible light irradiation over single particulate $ANbO_3$:Ir,Zr (A = K, Na) photocatalysts

○Natsuki Suto[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1458-4am-11]
Temperature dependence of photocatalytic water splitting over $SrTiO_3$:Al doped with transition metals under visible light irradiation

○Erika Kikuchi[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1458-4am-12]
The specific behavior of O_2 storage on water splitting over metal oxide photocatalysts loaded with dual cocatalysts

○Kyoko Adachi[1], Natsuki Suto[1], Suguru Yagihashi[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1458-4am-13]
Study of co-catalyst for Ir and Sb co-doped $SrTiO_3$ photocatalyst

○TEPPEI YAKUBO[1], Yuichi Yamaguchi[2,3], Akihiko Kudo[2,3] (1. SUMITOMO OSAKA CEMENT CO.,LTD., 2. Tokyo Univ. of Science, 3. CVRC, RIST TUS)

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Academic Program [Oral A] | 08. Catalysts and Catalysis：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC A1457(1457, Bldg. 14 [5F])

[A1457-4pm] 08. Catalysts and Catalysis

Chair: Takayoshi Hara, Tatsuya Moriai

English
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1457-4pm-01]

Preparation and Evaluation of Redox Performances of Chromium and Rhodium Incorporated Ceria at Micrometer Size

○Wenjun LI[1,2], Chaoqi CHEN[1], Satoshi Muratsugu[1], Mizuki Tada[1,2] (1. Nagoya Univ., 2. RCMS, Nagoya Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1457-4pm-02]

Sintering suppression and catalysis of ceria nanoparticle embedded in silica-nanoparticle assemblies

○Miho Nishida[1], Takashi Nakazono[2], Yusuke Yamada[1,2] (1. Graduate School of Engineering, Osaka Metropolitan University, 2. Research Center of Artificial Photosynthesis, Osaka Metropolitan University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1457-4pm-03]

Preparation of zeolite-supported Ru catalysts and their ammonia synthesis properties

○Mahiru Umeno[1], Tomohiro Noguchi[2], Hirokazu kobayashi[3], Miho Ymauchi[1,2,3,4,5] (1. Graduate School of Science, Kyushu Univ., 2. IMCE, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ., 5. WPI-I2CNER, Kyushu Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1457-4pm-04]

Investigation of factors for improving ammonium ion selectivity in nitrate reduction using Pd-Ag catalyst with formic acid as reductant.

○Tetsuya Takeda[1], Ikko Mikami[1] (1. Tokai University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1457-4pm-05]

Selective Oxidation of Methane over Supported Iron Phosphate Catalysts Prepared Using Phosphonic Acid

○Kazuma Furuya[1], Aoi Matsuda[1], Michikazu Hara[1], Keigo Kamata[1] (1. MLS, Tokyo Tech)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[A1457-4pm-06]

Selective Oxidation of Methane into Formaldehyde over Copper Phosphate Catalysts

○Aoi Matsuda[1], Takeshi Aihara[1], Michikazu Hara[1], Keigo Kamata[1] (1. MLS, Tokyo Tech)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

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[A1457-4pm-07]

Precision synthesis of nickel clusters and methane activation

○Yuma Kikuchi[1], Tatsuya Moriai[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. JST-ERATO)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[A1457-4pm-08]

Application of valence controlled copper oxide nanocluster catalysts for aromatic alcohol oxidation reactions.

○Koki Hoshino[1], Takayoshi Hara[1], Nobuyuki Ichikuni[1] (1. Chiba University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[A1457-4pm-09]

[Withdraw] Substitution of Co into $SrTiO_3$ using hydrothermal synthesis method and its catalytic activity for alcohol oxidation reaction

○Masahiro Aoyama[1], Takayoshi Hara[1], Nobuyuki Ichikuni[1] (1. Chiba University)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[A1457-4pm-10]

Effect of zeolite pore size on product selectivity and coke formation in MTO reaction

○Itsuki Matsushita[1], Masaru Ogura[1], Takahiko Moteki[2] (1. The Univ. of Tokyo, 2. Shizuoka University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[A1457-4pm-11]

Conversion of polycyclic aromatics to monocyclic aromatics by catalysts with selective hydrogenation and dealkylation ability

○Ryoto Mori[1], Yuta Saga[2], Kenji Kamiya[1], Eika Qian[1] (1. Tokyo University of Agrigulture and Technology, 2. Maruzen Petrochemical CO,LTD.)

Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[A1457-4pm-12]

Study of pressure dependence and characterization of active Mo species for methane dehyroaromatization over Mo/H-MFI catalysts

Airi Kosuge[1], Yuya Sonobe[1], Kenta Kuramochi[1], ○Hirofumi Aritani[1] (1. Saitama Institute of Technology)

Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[A1457-4pm-13]

Creation of Cross-Coupling Catalysts by Photodecarbonylation of Iron Complexes

○Koki Yamama[1], Yuta Nishina[1] (1. Okayama University)

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Academic Program [Oral B] | 08. Catalysts and Catalysis：Oral B

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
A1457(1457, Bldg. 14 [5F])

[A1457-4am] 08. Catalysts and Catalysis

Chair: Kohsuke Mori, Takafumi Yatabe

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[A1457-4am-01]

Elucidation of the mechanism of melamine adsorption on Pt(111) surface via density functional theory calculations

○Kohei Tada[1], Shin-ichi Yamazaki[1], Masafumi Asahi[1], Tsutomu Ioroi[1] (1. National Institute of Advanced Industrial Science and Technology (AIST))

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[A1457-4am-02]

Hydrogen Spillover on a Non-reducible Metal Oxide by a Heteroatom Doping and its Diffusion Pathways

○Kazuki Shun[1], Kohsuke Mori[1], Takumi Kidawara[1], Hiromi Yamashita[1] (1. Graduate School of Engineering, Osaka University)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[A1457-4am-03]

Formal 1,2-Diketone Decarbonylation Enabled by Synergistic Catalysis of Lewis Acid-Base Sites and Redox Properties in CeO_2

○Takehiro Matsuyama[1], Yatabe Takafumi[1], Yamaguchi Kazuya[1] (1. The University of Tokyo)

Japanese
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC
[A1457-4am-04]

Subnanometer Copper Nanoparticles for Oxidative Catalysis

○Makoto Tanabe[1], Kazutaka Sonobe[2], Kimihisa Yamamoto[2] (1. Fukushima Medical Univ., 2. Tokyo Inst. of Tech., Lab. Chem. Life Sci.)

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[A1457-4am-05]

Structural Characterization during the Low Temperature Redox Reaction of Copper and Ruthenium Incorporated Ceria for Ammoxidation

○Chaoqi CHEN[1], Satoshi Muratsugu[1], Mizuki Tada[1,2] (1. Nagoya Univ., 2. RCMS, Nagoya Univ.)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[A1457-4am-06]

Analysis of factors affecting the NH_3 synthesis activity of Ru-Ce based catalysts

○Yoshihiro Goto[1], Masashi Kikugawa[1], Kiyoshi Yamazaki[1], Akinori Sato[2], Yuichi Manaka[3], Tetsuya Nanba[3], Hideyuki Matsumoto[4], Shinichi Ookawara[4] (1. Toyota central R&D labs., Inc., 2. Toyota Motor Corporation, 3. National Institute of Advanced Industrial Science and Technology, 4. Tokyo Institute of Technology)

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English

11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[A1457-4am-07]

Size-controlled synthesis of CuFe, CuRu alloy nanoparticle catalysts for electrochemical nitrogen reduction reaction

○Kaichao Zhang[1], Takehiko Sasaki[1] (1. Graduate School of Science, The University of Tokyo)

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Academic Program [Oral B] | 08. Catalysts and Catalysis：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC A1458(1458, Bldg. 14 [5F])

[A1458-4pm] 08. Catalysts and Catalysis

Chair: Hajime Suzuki, Tsuyoshi Takata

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[A1458-4pm-01]

Development of a Photoelectrochemical Cell Utilizing a Sulvanite-type Black Metal Sulfide Photocathode for Solar CO_2 Reduction to Produce a Green Syngas

○Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[A1458-4pm-02]

Addition effect of Os(II) complex photosensitizers on hybrid CO2 reduction photocatalysts of Ru(II)-Re(I) and C3N4

○Toshiya Tanaka[1], Yusuke Tamaki[2], Kazuhiko Maeda[1], Osamu Ishitani[1,3] (1. Tokyo Institute of technology, 2. National Institute of Advanced Industrial Science and Technology, 3. Grad. Sch. of Adv. Sci. and Eng., Hiroshima Univ.)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[A1458-4pm-03]

Hybrid photocatalyst prepared via photo-reductive polymerization for site-selective introduction of CO_2 reduction active sites onto a semiconductor

○Noritaka Sakakibara[1], Ewan McQueen[2], Reiner Sebastian Sprick[2], Osamu Ishitani[1,3] (1. Tokyo Tech., 2. Univ. of Strathclyde, 3. Hiroshima Univ.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[A1458-4pm-04]

CO_2 electrochemical reduction over thermal non-equilibrium intermetallic compounds synthesized by electrolysis

○Tatsuya Koubayashi[1], Soichi Kikkawa[1], tsuyashi watanabe[2], tetsuo honma[2], seiji yamazoe[1] (1. Tokyo Metropolitan University, 2. JASRI)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[A1458-4pm-05]

High-Rate CO_2 Reduction Reactions with a Current Density Exceeding 1 A/cm^2

○Kazuhide Kamiya[1], Asato Inoue[1], Tengyi Liu[1], Takashi Harada[1], Shuji Nakanishi[1] (1. Osaka Univ.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[A1458-4pm-06]

Systematic Control of Electrochemical CO_2 Reduction Reaction Performances on Cu Nanocube by Surface Alloying with M (M=Pd, Pt, Ir, Ru)

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○Hirokazu Kobayashi[1], Sachie Hikino[1], Miho Yamauchi[1,2,3,4] (1. K-NETs, Kyushu Univ., 2. IMCE, Kyushu Univ., 3. WPI-I2CNER, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ.)

English

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[A1458-4pm-07]

Highly durable Ni-based self-catalytic reactor for CO_2 methanation designed by metal 3D printing combined and selective electrochemical dissolution

○HYOJIN KIM[1], Kohsuke Mori[1], Takayoshi Nakano[1], Hiromi Yamashita[1] (1. Osaka University)

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
F1231(1231, Bldg. 12 [3F])

[F1231-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Hiroki Takezawa, Kazuhiro Uemura

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1231-4am-01]

Synthesis and Photoreaction of Metal-organic Polyhedra Bearing Anthracene Moieties

○Ryoga Umemura[1], Jenny Pirillo[2], Qu Liyuan[2], Kusaka Shinpei[2], Hijikata Yuh[2], Iguchi Hiroaki[2], Matsuda Ryotaro[2] (1. Nagoya Univ., 2. Nagoya Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1231-4am-02]

Synthesis and Photophysical Properties of Metal Complexes Bearing Phenylethenylpyrene Moieties

○Ryoto Katagiri[1], Jenny Pirillo[1], Liyuan Qu[1], Shinpei Kusaka[1], Yuh Hijikata[1], Hiroaki Iguchi[1], Ryotaro Matsuda[1] (1. Nagoya Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1231-4am-03]

Acceleration of ligand-dioxygenation of chromium(V) complexes in the presence of a platinum(II) complex and formation of chromium-platinum mixed-metallic octanuclear complexes

○Hikaru Yabe[1], Mikoto Negishi[1], Hideki Ohtsu[1], Kiyoshi Tsuge[1] (1. University of Toyama)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1231-4am-04]

Interfacial synthesis of a transparent redox-active 2D bis(terpyridine)nickel(II) complex polymer

○Kenji Takada[1], Hiroaki Maeda[1], Hiroshi Nishihara[1] (1. Tokyo University of Science)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1231-4am-05]

Reduction and ligand reactions of mononuclear nitrosylruthenium complex having acetonitrile as coexisting ligands

○Sota Fujikawa[1], Tomoyo Misawa[1], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1231-4am-06]

Redox reactions of a dinuclear ruthenium(III) complex having one oxido- and two acetato-bridged structure

○Masahiro Hayashi[1], Tomoyo Misawa[1], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

English

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10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[F1231-4am-07]

Synthesis and Properties of Iridium Dinuclear Complexes with Oxysulfur Ligands

○Shinji Suzuki[1], Hidetaka Nakai[1] (1. Grad. Sch. Sci. Eng. Kindai Univ.)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[F1231-4am-08]

Synthesis and Luminescence Properties of Samarium and Dysprosium Complexes with a Chiral 1,4,7,10-Tetraazacyclododecane Skeleton

○Kazuhiro Harada[1], Hisaki Matsui[1], Hidetaka Nakai[1] (1. Grad. Sch. Sci. Eng. Kindai Univ.)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[F1231-4am-09]

Synthesis of PdAu24 Nanoclusters Protected by Alkylthiolates Bearing Fmoc-amino Groups

○Soshi TAKEUCHI[1], Ryohei SAITO[1], Katsuhiro ISOZAKI[1], Masaharu NAKAMURA[1] (1. Kyoto University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[F1231-4am-10]

Transmetallation of Nickelladithiolene Nanosheet and Its Reaction Mechanism and Kinetics Analysis

○Ziheng Yu[1], Kenji Takada[1], Hiroaki Maeda[1], Naoya Fukui[1], Hiroshi Nishihara[1] (1. Tokyo University of Science)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[F1231-4am-11]

Adsorption behavior of a homochiral metal-organic framework (MOF) consisting of a figure-eight-shaped cyclobisbiphenylenecarbonyl ligand.

○Daisuke Owase[1], Shinpei KUSAKA[1], Ryotaro MATSUDA[1], Hiroshi SHINOKUBO[1], Norihito FUKUI[1,2] (1. Nagoya university, 2. JST PRESTO)

English

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[F1231-4am-12]

Electrochemical oxidation synthesis of oriented bis(diimino)metal coordinaion nanosheets on gold electrodes.

○Hiroaki Maeda[1], Kenji Takada[1], Naoya Fukui[1], Hiroyasu Masunaga[2], Sono Sasaki[3,4], Kazuhito Tsukagoshi[5], Hiroshi Nishihara[1] (1. Tokyo University of Science, 2. Japan Synchrotron Radiation Research Institute (JASRI), 3. Kyoto Institute of Technology, 4. SPring-8, 5. National Institute for Materials Science (NIMS))

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[F1231-4am-13]

Creation of coordination nanosheet with a triptycene-skeleton ligand and its application to electrocatalyst for hydrogen evolution reaction

○Yuta Sudo[1], Hiroaki Maeda[1], Sayoko Nagashima[1], Kenji Takada[1], Naoya Fukui[1], Hiroshi Nishihara[1] (1. Tokyo University of Science)

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
F1232(1232, Bldg. 12 [3F])

[F1232-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Hiroaki Kotani, Takahiro Iwamoto

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1232-4am-01]

Regioselective Insertion of an Alkyne into a Ruthenium-Phosphine Coordination Bond.

○Haruki Horinouchi[1], Yusuke Kimura, Yousuke Ikeda, Yuichiro Mutoh[2], Takahiro Iwamoto[1], Youichi Ishii[1] (1. Chuo University, 2. RIKEN CSRS)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1232-4am-02]

Alkyne Insertion and Cycloisomerization of Cyclometalated Complexes Derived from Biphenylphosphine

○Kentaro Shinya[1], Koki Tagai, Sae Handa, Takahiro Iwamoto[1], Youichi Ishii[1] (1. Chuo University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1232-4am-03]

Development of Hydride Substitution Reactions of Cinnamyl Alcohol Derivatives via Rhodium Catalysis

○Hokuto Kimura[1], Ken Yamanomoto[1], Kohei Endo[1] (1. Department of Chemistry, Faculty of Science, Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1232-4am-04]

Highly Efficient Mixed-Ligand Catalysts for Direct Arylation of Heteroarenes with Aryl Chlorides

○Masayuki Wakioka[1], Shunta Sakai[1,2], Keisuke Hatakeyama[1,2], Ken-ichi Tada[1], Yooichiroh Maruyama[3] (1. Sagami Chemical Research Institute, 2. Kitasato Univ., 3. JSR)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1232-4am-05]

Visible Light-promoted Oxygenation of a Mononuclear NNP(O)-Benzylpalladium Complex

○Risa Shibai[1], Yuma Shigehiro[1], Yasuyuki Ura[1] (1. Nara Women's University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1232-4am-06]

Synthesis of Novel Polypyridyl Ru Photosensitized Complex with Phenylpyridinato Ligand and Application to CO_2 Reduction Photocathode

○Yuya Tomita[1], Hironobu Ozawa[1], Ken Sakai[1] (1. Kyushu Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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[F1232-4am-07]

Development of asymmetric allylic alkylation by assembly Cu/Pd catalysts using π-donor-acceptor interaction

○Aoto Shimozaki[1], Yuichi Kominato, Tatushi Imahori[1] (1. Tokyo University of Science)

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[F1232-4am-08]

Development of Assembly Lewis acid / Crown ether combined catalyst reaction using π-Donor-Acceptor Interaction

○Rikuta Kozuka[1], Kousuke Tsunogaya, Tatsushi Imahori[1] (1. Tokyo university of science)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[F1232-4am-09]

Dihydrogen Activation by a Stannacyclopentadienylidene

○Kazuki Wada[1], Shunsuke Kudo[1], Shunsuke Furukawa[1], Taku Murata[2], Minori Abe[2], Masaichi Saito[1] (1. Department of Chemistry, Graduate School of Science and Engineering, Saitama University , 2. Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[F1232-4am-10]

Palladium-Catalyzed Synthesis of Alkoxyallenes and Their Application in Stereoselective Transformations

○Yuuki Mori[1], Tsukasa Hitomi[1], Masamichi Ogasawara[1] (1. The Univ. of Tokushima)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[F1232-4am-11]

Clarification of factors behind kinetics of CO_2 capturing reactions by Re(I)-complex catalysts

○Yuto Abiru[1], Kei Kamogawa[2], Manabu Abe[1], Osamu Ishitani[1,2] (1. Hiroshima Univ. , 2. Tokyo Tech.)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[F1232-4am-12]

Development of depolymerization systems catalyzed by an iridium complex bearing hydroxyl groups

○Chihaya Murata[1], Naoki Noto[2], Mineto Uchiyama[3], Masami Kamigaito[3], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. IRCCS, Nagoya Univ., 3. Grad. Sch. Eng., Nagoya Univ.)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[F1232-4am-13]

Synthesis and Photocatalytic Property of Water-Soluble Tris(phenylpyridinato)iridium(III) Derivatives

○Taiki Noma[1], Kosei Yamauchi[1], Ken Sakai[1] (1. Kyushu Univ.)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[F1232-4am-14]

Selective Photoreactions Based on Confinement Effects with a Visible-Light-Active Pt(II)-Cornered Hollow Cage

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○Rikuya Tanaka[1], Hiroki Takezawa[1], Makoto Fujita[2,3] (1. The University of Tokyo, 2. Institute for Molecular Science, 3. The University of Tokyo Institutes for Advanced Study Tokyo College)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[F1232-4am-15]

Mechanistic studies on cyclization of alkynoic acids catalyzed by Au_{25} nanoclusters bearing supramolecular reaction fields

○Kyosuke UEDA[1], Kenta ISERI[1], Ryohei SAITO[1], Katsuhiro ISOZAKI[1], Masaharu NAKAMURA[1] (1. Kyoto University)

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:00 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:00 AM UTC
F1234(1234, Bldg. 12 [3F])

[F1234-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Keishiro Tahara, Yoshiaki Shoji

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1234-4am-01]

Synthesis and cancer-cell selective cytotoxicity of a dicopper complex with *p*-cresol-amide-tether-tacn ligand having a porphyrin DNA target

○Riko Yamamoto[1], Machi Hata[1], Masato Kodera[1], Ami Kodama[1] (1. Doshisha university)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1234-4am-02]

Synthesis and cancer-cell selective cytotoxicity of dicopper(II) complexes with p-cresol-2,6-amide-tether-cyclen derivative having triphenylphosphine mitochondria target

○Hayato Takai[1], Machi Hata[1], Masato Kodera[1] (1. Doshisha university)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1234-4am-03]

Synthesis and cancer-cell selective cytotoxicity of a dicopper complex with cyclen per-methyl derivative of 4-phenanthrene introduced phenol-2,6-amide-tether-cyclen ligand

○Kenshiro Fujioka[1], Machi Hata[2], Masahito Kodera[2] (1. Doshisha Univ., 2. Grad. Sch. of Sci. and Eng., Doshisha Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1234-4am-04]

Cancer-Cell-Selective Cytotoxicity by Dicopper Complexes with p-Cresol-Amide-Tether-Cyclen Ligands: DNA-Targeting Effect

○Kobashi Hiroto[1], Hata Machi[1], Kodera Masahito[1] (1. Doshisha University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1234-4am-05]

Development of artificial allosteric enzyme using complex formation

○Chieon Park[1], Takaaki Mitsuhashi[2], Makoto Fujita[1,2,3] (1. Graduate School of Engineering, The University of Tokyo, 2. Institue for Molecular Science, 3. Institutes for Advanced Study (UTIAS), Tokyo College, The University of Tokyo))

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1234-4am-06]

Structural Analysis of Guest Molecules by Using Several Micro Crystalline Sponge in a Glass Capillary

○Ryo Yakushiji[1], Satoshi Yoshida[1], Sota Sato[1,3], Makoto Fujita[1,2,3] (1. Grad. School of Engineering, The Univ. of Tokyo , 2. UTIAS, The Univ. of Tokyo, 3. IMS)

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Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1234-4am-07]
Radical Addition of an Isolable Phosphinyl Radical to Unsaturated Hydrocarbons

○Yasuhiro Katayama[1], Shintaro Ishida[1], Takeaki Iwamoto[1] (1. Tohoku University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[F1234-4am-08]
Coupling reaction of cyclopentadienyl ligand with alkene in titanacyclopentene complex

Tamotsu Takahashi[2,1], Masayoshi Bando[1], Hirotaka Nakada[1], ○zhiyi song[1] (1. Hokkaido University, 2. Institute of Chemistry Co Ltd Henan Academy of Sciences)

English
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[F1234-4am-09]
Thin Film Formation of Ru Dinuclear Complex Forming Covalent Networks Based on LbL Method

○Takumi Nakanishi[1], Chisa Itoh[2], Hitoshi Miyasaka[1] (1. Institute for Materials Research, Tohoku University, 2. Department of Chemistry, Tohoku University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1234-4am-10]
Concentration-Dependent Valence Tautomerism Exhibited by Cobalt Dioxolene Complexes

○Yuki Koyama[1], Ryunosuke Konishi[1], Akinori Honda[2], Akinobu Nakada[3,2], 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.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1234-4am-11]
Control of Condensed Phases and External Stimuli Responsiveness of Redox-active Pyrazinedithiolato Platinum(II) Complexes

○Tatsuya Tamura[1], Akira Imaizumi[1], Akinori Honda[2], Ho-Chol Chang[2] (1. Graduate school of science and engineering, Chuo univ., 2. Faculty of science and engineering, Chuo univ.)

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:30 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:40 AM UTC
F1233(1233, Bldg. 12 [3F])

[F1233-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Manabu Nakaya, Yoshihiro Sekine

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1233-4am-01]

Construction and Characterization of Hydrogen-Bonded Honeycomb Networks Using Trinuclear Chromium(III) Complexes

○Shun Sumikawa[1], Shoki Ikeda[1], Yoshiki Ozawa[1], Akira Yamaguchi[1], Yu Yamane[1], Akihiko Sumiyama[1], Masaaki Abe[1] (1. University of Hyogo)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1233-4am-02]

Metamagnetism in Nickel–octacyanotungstate 2D magnet

○Shintaro Akagi[1], Junhao Wang[1], Kenta Imoto[2], Kunal Kumar[2], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. The University of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1233-4am-03]

Cooperative vapochromism and spin-state switching of discrete Ni(II) complex in response to various coordinating solvents

○Sotaro Kusumoto[1], Kento Takei[1], Yoshihiro Koide[1] (1. Kanagawa University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1233-4am-04]

Development of paramagnetic spin-crossover ligands

○Yoshimasa Noguchi[1], Satomi Watanabe[2], Takayuki Ishida[1] (1. The University of Electro-Communications, 2. Kitasato University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1233-4am-05]

Elucidation of Intermolecular Interactions of SCO Complexes by Metal Dilution

○Kanta Miyake[1], Zhongyue ZHANG[1], Yoshihiro Sekine[1], Shinya Hayami[1] (1. Kumamoto university)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[F1233-4am-06]

Adsorption Heat Control of Nanoporous Cobalt Complexes Using Spin Transition

○Kako Ohno[1], Jenny Pirillo, Liyuan Qu, Shinpei Kusaka, Yuh Hijikata, Hiroaki Iguchi, Ryotaro Matsuda (1. Nagoya Univ.)

English
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1233-4am-07]

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Investigation of Structural and Magnetic Properties of Dinuclear Fe(II) Complexes with Bridging-ligand whose Linkage Isomerization is Restricted

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

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1233-4am-08]

Cyanido-Bridged Fe(II)-Nb(IV) assemblies with Fe(II)-Fe(II)-Bridging Ligands

○Itsuki Fukagawa[1], Takefumi Kanno[1], Koji Nakabayashi[1], Kenta Imoto[1], Kazuki Nakamura[1], Yuuki Mineo[1], Shota Kobayashi[1], Yoshinori Tanaka[1], Shin-ichi Ohkoshi[1] (1. The Univ. of Tokyo)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1233-4am-09]

Magnetic and electrochemical properties of trinuclear copper complexes formed from cyclohexane-1,3-dione dioxime and copper(II) nitrate

○Yosuke Hosoya[1], Hanaka Kinjo[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
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1233-4am-10]

Substituent effects of 3d-2p heterospin coupling in copper(II) and nickel(II) nitroxide complexes

○Daichi Iida[1], Masataka Mitsui[1], Takayuki Ishida[1] (1. The University of Electro-Communications)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[F1233-4am-11]

Heterometallic chain complexes bridged with a ground-triplet 5-adamantyl-1,3-phenylene bis(*t*-butyl nitroxide)

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

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[F1233-4am-12]

Theoretical study on magnetic properties of lanthanide complexes with nitroxide radicals as ligands

○Kaito Taka[1], Ren Inoue[1], Koki Masuda[2], Ryohei Kishi[2,3,4,5], Takayuki Ishida[6], Yasutaka Kitagawa[2,3,4,5,7] (1. Faculty of Engineering Science, Osaka University, 2. Graduate School of Engineering Science, Osaka University, 3. QIQB, Osaka University, 4. Osaka University RCSEC, 5. ICS Osaka University, 6. Graduate School of Informatics and Engineering, 7. SRN, OSaka University)

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC F1231(1231, Bldg. 12 [3F])

[F1231-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kazuki Tanifuji, Tomoya Fukui

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1231-4pm-01]

Synthesis of a Phosphine-protected $Pd_2Au_{17}(PR_3)_{10}Cl_7$ Nanocluster with N_2-type Electronic Configuration

○Ryohei Saito[1], Yoshiyuki Mizuhata[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto university)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1231-4pm-02]

Properties of Diruthenium Complexes Having a Hydrogenphosphato Ligand Bridged on the $\{Ru_2(\mu\text{-}O(H))_2\}$ Core

○Tomoyo Misawa-Suzuki[1], Nagao Hirotaka[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1231-4pm-03]

The synthesis of rotaxanes consisting of α-cyclodextrin (CDX) threaded by 1,12-diaminododecane (don) bearing two different cobalt(III) complexes as stoppers

○Hiroshi Ogino[1], Shinji Inomata[2], Kayoko Kasai[3] (1. Tohoku University, 2. Fukushima University, 3. Miyagi University of Education)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[F1231-4pm-04]

Synthesis and reactivity of group 10 transition metal complexes bearing a NHC/Pyridyl hybrid ligand.

○Masaya Okamura[1], Saki Kobana[1], Kota Imaizumi[1], Misa Kitahara[1], Rena Suzuki[1], Shiro Hikichi[1] (1. Kanagawa University)

Japanese
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[F1231-4pm-05]

Preparation, Reactions, and Structure of Boron-substituted Silyllithium

Yuta Kowada[1], ○Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[F1231-4pm-06]

Formations of Al-Al Bonds by a Reaction of Nucleophilic and Electrophilic Aluminum Species

○Ryotaro Yamanashi[1], Kanata Mizutani[1], Makoto Yamashita[1] (1. Nagoya University)

English

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3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC

[F1231-4pm-07]

Construction of Expanded Hollow Cages by Templated Self-assembly in the Solid State for Conformation Control of Organic Macrocycles

○Kenta Iizuka[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The Univ. of Tokyo, 2. Institute for Molecular Science)

English

3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC

[F1231-4pm-08]

Synthesis and Structural Analysis of Metal Complexes with Azulene Derivatives as Ligands

○Tatsuya Iwashina[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Tokyo University of Science)

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC F1232(1232, Bldg. 12 [3F])

[F1232-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Yasuyuki Ura, Yumiko Nakajima

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1232-4pm-01]

Effects of the Reduction Potential of the Ru(II) Redox Photosensitizer Unit in Ru(II)-Re(I) Supramolecular Photocatalysts on their Photocatalysis for CO_2 Reduction

○Kei Kamogawa[1], Osamu Ishitani[1,2] (1. Tokyo Tech., 2. Hiroshima Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1232-4pm-02]

Electrocatalytic Reduction of Low Concentration CO_2 to CO Using Phenol and a Re(I) complex

○Siby Mathew[1], Osamu Ishitani [1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1232-4pm-03]

Iridium Catalyzed Intermolecular Silylene Transfer Reaction Utilizing Silylene Generated from Triorganohydrosilanes

○Yunhao Song[1], Michinori Suginome[1] (1. Kyoto University)

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[F1232-4pm-04]

Weakly Coordinating Anions bearing Lewis Acidic Tri-coordinated Borons Induced Selectivity Control on Iridium Catalysis

○Ryo Mandai[1], Takanori Iwasaki[1], Kyoko Nozaki[1] (1. The Univ. of Tokyo)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[F1232-4pm-05]

Electrochemical Homogeneous CO_2 Reduction Catalyzed by N-Heterocyclic Carbene Stabilized Au-Nanoclusters

○Samuel Jacob[1], Joey DeJesus[1], Masakazu Nambo[1,2], Cathleen Crudden[1,3,4] (1. Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya, Aichi, Japan, 2. Department of Chemistry, Graduate School of Science, Nagoya University; Furo, Chikusa, Nagoya, Aichi, Japan, 3. Department of Chemistry, Queen's University, Chernoff Hall, Kingston Ontario, Canada, 4. Carbon to Metal Coating Institute, Queen's University, Kingston, Ontario, K7L 3N6, Canada)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[F1232-4pm-06]

Catalytic Transformation of Alkynes Enabled by Gold Nanocluster Bearing Supramolecular Reaction Field

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○Kenta Iseri[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto University)

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC F1233(1233, Bldg. 12 [3F])

[F1233-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaya Enomoto, Takuya Shiga

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1233-4pm-01]

CO_2-Sensitive Porous Magnet: Antiferromagnet Creation from a Paramagnetic Charge-Transfer Layered Coordination Framework

○Wataru Kosaka[1,2], Jun Zhang[3], Qingxin Liu[1,2], Naoka Amamizu[4], Yasukaka Kitagawa[4] (1. IMR, Tohoku University, 2. Grad. Sch. Sci., Tohoku Univ., 3. Col. Chem. Mol. Sci., Wuhan Univ., 4. Grad. Sch. Eng. Sci., Osaka Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1233-4pm-02]

Photoinduced magnetization in organometallic and organic compounds

○Verner Saeaesk[1] (1. Kyushu Universtiy)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1233-4pm-03]

Thermal and Light-induced Switching Effects Based on Fe(II)-Hg(II) Spin-crossover Networks

○Guanping Li[1], Olaf Stefanczyk[1], Kunal Kumar[1], Koji Nakabayashi[1], Kenta Imoto[1], Guillaume Chastanet[2], Shin-ichi Ohkoshi[1] (1. Department of Chemistry, School of Science, University of Tokyo, 2. Université de Bordeaux, ICMCB)

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[F1233-4pm-04]

Proton Conductive Hydrogen-Bonded Architectures Constructed by Cobalt(II) Spin Crossover Complexes

○Fumiya Kobayashi[1], Makoto Tadokoro[1] (1. Tokyo Univ. of Sci.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[F1233-4pm-05]

Relationship between the stacking structure and magnetic behavior for two-dimensional mixed-valence iron(II,III) layered compounds bridged by a 1,2-dithiooxlate ligand

○Takuya Kanetomo[1], Yuki Sawayanagi[1], Tsubasa Endo[1], Atsushi Okazawa[2], Masaya Enomoto[1] (1. Tokyo Univ. of Sci., 2. Waseda Univ.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[F1233-4pm-06]

Spin-lattice relaxation behavior of an *S*=1/2 copper(II)-substituted Keggin-type sulfotungstate

○Toshiharu Ishizaki[1], Tomoji Ozeki[1] (1. Nihon Univ.)

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC F1234(1234, Bldg. 12 [3F])

[F1234-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryota Matsuoka, Souichirou Kawamorita

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1234-4pm-01]

Multimetalic co-accumulation of precious and base metals in phenylazomethine dendrimer

○Tadatoshi Iitsuka[1], Tatsuya Moriai[1], Takamasa Tsukamoto[2], Akiyoshi Kuzume[3], Takane Imaoka[1], Kimihisa Yamamoto[1] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. Institute of Industrial Science, University of Tokyo, 3. Clean Energy Research Center, University of Yamanashi)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1234-4pm-02]

Observation of vapochromic phase transition and micro motions in molecular crystals using confocal laser microscopy

○XIAO MA[1], Kyoko Enomoto[1], Kazuyuki Ishii[1], Yuki Matsuda[2], Masaaki Abe[2] (1. IIS, The Univ. of Tokyo, 2. Graduate School of Science, University of Hyogo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1234-4pm-03]

Vapor-Induced Structural Transformation Dynamics of Photoluminescent Coordination Network Crystals

○Yuki Matsuda[1], Ryota Nakamura[1], Yoshiki Ozawa[1], Keishiro Tahara[1], Toshikazu Ono[2], Nobuto Yoshinari[3], Takumi Konno[3], Kunihisa Sugimoto[4], Shintaro Kobayashi[5], Shogo Kawaguchi[5], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo, 2. Graduate School of Engineering, Kyushu University, 3. Graduate School of Science, Osaka University, 4. Department of Chemistry, Faculty of Science and Engineering, Kindai University, 5. SPring-8/JASRI)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[F1234-4pm-04]

Correlation Between Metal-metal Distance and Assembly-induced Luminescence of One-dimensional d^8 Metal Complexes Based on Temperature and Pressure Effects

○Masaki Yoshida[1], Kai Mitani[1], Kaito Segawa[1], Daichi Eguchi[1], Naoto Tamai[1], Masako Kato[1] (1. Kwansei Gakuin Univ.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[F1234-4pm-05]

Self-assembly of N^C^N-coordinated platinum(II) complex assisted by carbon dioxide in basic aqueous solution

○Shingo Hattori[1], Hiroyuki Mita[1], Kazuteru Shinozaki[1] (1. Yokohama City Univerisity)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[F1234-4pm-06]

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Crystal-downsizing Effect on Dual-emission Behavior in an Au(I)-based Coordination Polymer

○Haruka Yoshino[1], Takumi Ehara[2], Kiyoshi Miyata[2], Ken Onda[2], Hitoshi Miyasaka[1] (1. IMR, Tohoku University, 2. Graduate School of Science, Kyushu University)

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Academic Program [Oral A] | 10. Organic Chemistry -Organometallic Compounds-：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:00 AM UTC E1111(1111, Bldg. 11 [1F])

[E1111-4pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Masaaki Namamoto, Takashi Kurogi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1111-4pm-01]

Reductive *anti*-Dimetalation of Alkynes

○Haruka Yamaguchi[1], Fumiya Takahashi, Takashi Kurogi[1], Hideki Yorimitsu[1] (1. Kyoto University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1111-4pm-02]

Calcium-Mediated Mechanochemical Birch Reduction

○Yamato Fukuzawa[1], Keisuke Kondo[1], Yunpeng Gao[1], Kouji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1111-4pm-03]

Reduction of amide compounds to aldehydes using strontium metal

○Tatuya Watanabe[1], Masaharu Ueno[1], Norikazu Miyoshi[1] (1. Faculty of Science and Technology, Tokushima University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1111-4pm-04]

Development of a convenient and useful transesterification reaction using a catalytic amount of strontium alkoxide

○Chisato Kamada[1], Ryosuke Shimoda, Masaharu Ueno[1], Norikazu Miyoshi[1] (1. Tokushima University)

English
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1111-4pm-05]

Reactivity of Germanium Enolates Generated from Allenylesters with Ge(II) Salts

○Taishi Nojima[1], Akihito Konishi[1], Makoto Yasuda[1] (1. Graduate School of Engineering Osaka University)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1111-4pm-06]

Defluoroborylation of *gem*-difluoroalkenes with borylstannane reagents via radical chain mechanism

Yoshihiro Nishimoto[1], ○Naoya Ito[1], Makoto Yasuda[1] (1. Graduate School of Engineering, Osaka University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1111-4pm-07]

Reactivity of Germapyramidane Towards Organolithium Reagents

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○Junkang Wang[1], Vladimir Ya. Lee[2], Katsuhiko Takeuchi[3], Norihisa Fukaya[3], Takahiro Sasamori[2,4] (1. Graduate School of Science and Technology, University of Tsukuba, 2. Institute of Pure and Applied Sciences, University of Tsukuba, 3. National Institute of Advanced Industrial Science and Technology, 4. TREMS, University of Tsukuba)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[E1111-4pm-08]

Studies for Silylene Generation Using Silylboranes with Leaving Group

○Rikuro Takahashi[1], Hajime Ito[2,3] (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University, 3. WPI-ICReDD, Hokkaido University)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[E1111-4pm-09]

Synthesis of *gem*-difluoro allyl compounds from trifluoromethyl alkenes via the defluorination process

○Harue Kinoshita[1], Itaru Suzuki[2], Ikuya Shibata[2] (1. Graduate School of Engineering Osaka University, 2. Research Center for Environmental Preservatior, Osaka University)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[E1111-4pm-10]

Synthesis of 2-Iodoarylstannanes by Iodostannylation of Arynes

○Taiga Obayashi[1], Masaaki Nakamoto[1], Takumi Tsushima[1], Hiroto Yoshida[1] (1. Hiroshima University)

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Academic Program [Oral A] | 10. Organic Chemistry -Organometallic Compounds-：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:20 AM UTC E1112(1112, Bldg. 11 [1F])

[E1112-4pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takuya Kochi, Takuya Shinbayashi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1112-4pm-01]

Rhodium(III)-Catalyzed Arylation of Itaconic Acid Derivatives

○Yuito Takatsuji[1], Yoshinosuke Usuki[1], Tetsuya Satoh[1] (1. Osaka Metropolitan University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1112-4pm-02]

Synthesis of cyclopentanes by reductive coupling of benzoylalkenes in the presence of rhodium/isocyanide catalyst and diboron

○Yuji Nakamuta[1], Ken-ichi Fujita[1], Takuya Shimbayashi[1] (1. Kyoto University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1112-4pm-03]

Rhodium-catalyzed Exchange Reaction between Peptide Trisulfide and Disulfides/Diselenides

Masana Yazaki[1], ○Wataru Sonoda[2], Mieko Arisawa[3] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Fac. Sch. Agric., Kyushu Univ., 3. Grad. Agric., Kyushu Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1112-4pm-04]

Rhodium-catalyzed Insertion Reaction of Arylarsines into Peptide Disulfides in Water

○Masana Yazaki[1], Mieko Arisawa[2] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Fac. Agric., Kyushu Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1112-4pm-05]

Rhodium-catalyzed chain-walking hydrothiolation of *N*-allylamides

○Naoki Hikida[1], Hirotsugu Suzuki[1] (1. University of Fukui)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1112-4pm-06]

Synthesis of Naphthalene Derivatives by Rhodium-Catalyzed Hydroaminative Cyclization of 1,5-Diynes

○Hibiki Goto[1], Takuya Kochi[1], Fumitoshi Kakiuchi[1] (1. Keio University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1112-4pm-07]

Rhodium-catalyzed Synthesis of Selenoisocyanates Using Isocyanides and Selenium.

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Masana Yazaki[1], ○Takahiro Goto[2], Mieko Arisawa[3] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Grad. Sch. Agric., Kyushu Univ., 3. Fac. Agric., Kyushu Univ.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1112-4pm-08]

Synthesis of Triarsoles by Rhodium-catalyzed *cyclo*-$(PhAs)_6$ Addition Reaction to Alkynes

○Hiiro Otsuka[1], Mieko Arisawa[2] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Fac. Agric., Kyushu Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1112-4pm-09]

Rhodium-catalyzed Synthesis of Carbamoylphosphine Derivatives

Kohei Fukumoto[2], ○Xiaoyi Zhang[1], Shinnya Shirakawa[2], Mieko Arisawa[3] (1. Fac. Agric. Kyushu Univ, 2. Grad. Sch. Bioenv Sci. Kyushu Univ, 3. Grad. Sch. Agric. Kyushu Univ)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[E1112-4pm-10]

Enantioselective Synthesis of Tetrahydroindole Derivatives via Rh-Catalyzed [2+2+2] Cycloaddition

○Kairi Yamashiro[1], Fujii Kohei, Koji Masutomi, Ryota Shimotsukue, Yuki Nagashima[1], Ken Tanaka[1] (1. Department of Chemical Science and Engineering, Tokyo Institute of Technology.)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1112-4pm-11]

Rhodium-Catalyzed Single Carbon Atom Doping into Acyl Chlorides Using Isocyanide Derivatives.

○Kazuya Imachi[1], Teruki Nishioka[2], Rio Nishimura[3], Hayato Fujimoto[1,4], Mamoru Tobisu[1,4] (1. Graduate School of Engineering, Osaka Univ., 2. School of Engineering, Osaka Univ., 3. Graduate School of Science, Osaka Univ., 4. ICS-OTRI)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1112-4pm-12]

Enantioselective Synthesis of Axially Chiral 1,8-Diarylnaphthalenes by Rh-Catalyzed [2+2+2] Cycloaddition

○Hinako Nikawa[1], Mamoru Ito[1], Takanori Shibata[1] (1. Waseda University)

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Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds-：Oral B

Thu. Mar 21, 2024 9:30 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:30 AM UTC
E1111(1111, Bldg. 11 [1F])

[E1111-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Akihito Konishi, Masaharu Ueno

English
9:30 AM - 9:50 AM JST | 12:30 AM - 12:50 AM UTC
[E1111-4am-01]

Synthesis of Cage-shaped Borate with Heteroaromatics for Selective Activation of Aromatic Aldehydes

○Yuya Tsutsui[1], Akihito Konishi[1,2], Makoto Yasuda[1,2] (1. Osaka University, Graduate School of Engineering, 2. ICS-OTRI)

English
9:50 AM - 10:10 AM JST | 12:50 AM - 1:10 AM UTC
[E1111-4am-02]

In-Silico-Assisted Derivatization of Triarylboranes for the Catalytic Reductive Functionalization of Amino Acids with H_2

○Yusei Hisata[1], Takashi Washio[2], Shinobu Takizawa[3], Ogoshi Sensuke[1], Yoichi Hoshimoto[1,4] (1. Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2. Department of Reasoning for Intelligence and Artificial Intelligence Research Center, SANKEN, Osaka University, 3. Department of Synthetic Organic Chemistry and Artificial Intelligence Research Center, SANKEN, Osaka University, 4. Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University)

English
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC
[E1111-4am-03]

Anti-Selective 1,2-Diboration of Alkynes by Using Potassium Reductants

○Ziwei Zhang[1], Takashi Kurogi[1], Hideki Yorimitsu[1] (1. Kyoto university)

English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[E1111-4am-04]

Stereoselective Hydroxyallylation of Cyclopropenes with Cyclopropanols via NHC Control of Enolized Zinc Homoenolate

○Kento Tsukiji[1], Kazuya Kanemoto[1], Arimasa Matsumoto[2], Yoshikai Naohiko[1] (1. Tohoku Univ, 2. Nara Women's Univ)

Japanese
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[E1111-4am-05]

Zn/F Carbenoids: Preparation, Stability, Structure, and Application to Nucleophilic Monofluoroalkylation

○Kohei Miyamoto[1], Emiko Kawaguchi[1], Kazuhiro Morisaki[1], Yoshihiro Sato[1] (1. Fac. Pharm. Sci., Hokkaido Univ.)

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Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds-：Oral B

Thu. Mar 21, 2024 9:30 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:30 AM UTC
E1112(1112, Bldg. 11 [1F])

[E1112-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Ken-Ichi Fujita, Shogo Kuriyama

Japanese
9:30 AM - 9:50 AM JST | 12:30 AM - 12:50 AM UTC
[E1112-4am-01]

Catalytic Borylation of C(sp^3)-H Bonds of Ethers by Iron Complexes with Anionic PCP-type Pincer Ligands

○Shogo Kuriyama[1], Ken Sakata[2], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo, 2. Faculty of Pharmaceutical Sciences, Toho University)

English
9:50 AM - 10:10 AM JST | 12:50 AM - 1:10 AM UTC
[E1112-4am-02]

Decarboxylative Functionalization of Carboxylic Acids with Easily Oxidizable Functional Groups Catalyzed by Iron Complexes under Photo-irradiation

○Sota Tamaki[1], Tetsuro Kusamoto[1], Hayato Tsurugi[1] (1. Graduate School of Engineering Science, Osaka Univ.)

English
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC
[E1112-4am-03]

Iron-Catalyzed C–H Functionalization of Aromatic Ketones via Enyne Cyclization

○Yoichi Kitazawa[1], Takuya Kochi[1], Fumitoshi Kakiuchi[1] (1. Keio University)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[E1112-4am-04]

Effects of chalcogen elements in the ligand on the olefin metathesis activity of Hoveyda-Grubbs-type catalysis

○Tsubasa Kinugawa[1], Shun Hirota[1], Takashi Matsuo[1] (1. Div. Mat. Sci., NAIST)

English
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[E1112-4am-05]

Ruthenabicyclic Borohydride Complexes (RUCY®-BH) for Asymmetric Hydrogenation of Ketones and Asymmetric Formal Hydroamination of Allylic Alcohols under Base-Free Conditions

○Tomohiro Ishizaka[1], Yuji Nakayama[1], Taichiro Touge[1], Yamato Yuki[1], Kazuhiko Matsumura[1], Taiga Yurino[2,3], Takeshi Ohkuma[2,3] (1. Takasago International Corporation, 2. Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center, Hokkaido University)

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1113(1113, Bldg. 11 [1F])

[E1113-4am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Fumitaka Ishiwari, Yoshihiro Miyake

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1113-4am-01]

Synthesis and properties of anthracene-fused aromatic compounds with multiple helical sites

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

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1113-4am-02]

Synthesis and Properties of Acene Derivatives by Domino Cross-Scholl Reaction

○Shuri Yamaoka[1], Haruka Nakanishi[1], Haruki Nishimura[1], Masahiro Muraoka[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1113-4am-03]

Synthesis and Properties of π-Extended Cyclobisbiphenylenecarbonyls

○Junichiro Hirano[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2] (1. Nagoya University, 2. JST PRESTO)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1113-4am-04]

Enantio- and Diastereoselective Synthesis and Spiral-Stair-Like Chiral Single Helix Assembly of Figure-Eight Cyclophenylenes

○Kohei Adachi[1], Juntaro Nogami[1], Daisuke Hashizume[2], Masashi Hasegawa[3], Yuki Nagashima[1], Ken Tanaka[1] (1. Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2. RIKEN Center for Emergent Matter Science (CEMS), 3. Graduate School of Science, Kitasato University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1113-4am-05]

Synthesis and Physical Properties of Molecular Penrose Stairs via Catalyst-Free Double Friedel-Crafts Reaction

○Zhiyan Jiang[1], Yoichiro Kuninobu[1] (1. Kyushu Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1113-4am-06]

Synthesis and Property of Dihetero[8]circulenes

○Chihiro Maeda[1], Koki Akiyama[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Tech., Okayama Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1113-4am-07]

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Effect of N-Substituents on the Azahelicene Synthesis

Chihiro Maeda[1], ○Sayaka Michishita[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Technol., Okayama Univ.)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1113-4am-08]

Synthesis of Mono-Arylated Figure-Eight Cyclobisbiphenylenecarbonyl Derivative and Its Isomerization to Non-twisted Molecule

○Hiyori Idei[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2] (1. Nagoya University, 2. JST PRESTO)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1113-4am-09]

Synthesis and chiroptical properties of highly elongated fused anthracene-type expanded helicenes

○Hiroki Fukuda[1], Eiji Tsurumaki[1], Masashi Hasegawa[2], Shinji Toyota[1] (1. Tokyo Tech, 2. Kitasato Univ.)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1113-4am-10]

Asymmetric synthesis of three-dimensionally π-extended carbohelicenesand and their circularly polarized luminescence properties

○Futo Morita[1], Yu Sato[1], Yuki Nagashima[1], Naoyuki Toriumi[2], Masanobu Uchiyama[2], Gaku Fukuhara[1], Hidehiro Uekusa[1], Ken Tanaka[2,1] (1. Tokyo Institute of Technology, 2. The University of Tokyo)

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1113-4am-11]

Synthesis and optical properties of stimuli-responsive helicene-fused xanthene dyes

○Sorachi Miwa[1], Daichi Mizutani[2], Masaki Kawamoto[2], Yuuya Nagata[3], Kiyosei Takasu[1], Hiroshi Takikawa[1] (1. Graduate School of Pharmaceutical Sciences, Kyoto University, 2. Faculty of Pharmaceutical Sciences, Kyoto University, 3. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1113-4am-12]

Stereoselective synthesis of multiple carbohelicenes via asymmetric [2+2+2] cycloaddition and Scholl reaction

○Ryota shimizu[1], Futo Morita[1], Yuko Kishida[2], Yu Sato[1], Yuki Nagashima[1], Hidehiro Uekusa[2], Ken Tanaka[1] (1. Materials and Chemical Technology Tokyo Institute of Technology, 2. Science Tokyo Institute of Technology)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1113-4am-13]

Catalytic Synthesis of Antiaromatic Norcorroles

○Satoshi Kato[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, Nagoya University, 2. Institute for Advanced Research, Nagoya University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1113-4am-14]

Functionalization of 5,15-dioxaporphyrin for elucidation of conductive properties of antiaromatic molecules

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○Yukako Kawashige[1], Soji Shimizu[1] (1. Graduate School of Engineering, Kyushu University)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1113-4am-15]

Synthesis of free-base norcorroles from borylated dipyrrins

○Shotaro Hirayama[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, 2. Institute for Advanced Research, Nagoya University)

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1121(1121, Bldg. 11 [2F])

[E1121-4am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Ryo Inoue, Yusuke Inagaki

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1121-4am-01]

Chemical Modification Using Coupling Reaction for Boron Complex Containing Imidazodiazaborole Ring and Their Emission Properties

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

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1121-4am-02]

Impact of Intramolecular Boron–Sulfur Interaction on Photophysical Properties of Stimuli-Responsive Donor–Acceptor-Type Organoboron Fluorophores

○Ryoma Yamazaki[1], Tatsuya Mori[2], Mika Sakai[1], Shigehiro Yamaguchi[3,2,1] (1. Department of Chemistry, Graduate School of Science, Nagoya University, 2. Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, 3. Institute of Transformative Bio-Molecules (ITbM), Nagoya University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1121-4am-03]

Effects of Monodentate Ligands on the Intermolecular Interactions and Photophysical Properties of 9-Hydroxyphenalenone Boron Complexes

○Yuga Tarumi[1], Yuto Aoyama[1], Shunichiro Ito[1], Kazuo Tanaka[1] (1. Grad. Sch. of Eng. Kyoto Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1121-4am-04]

Boron-Bridged Benzobisthiazole Derivatives and Their Photophysical Properties

○Ryota Uchida[1], Masashi Mamada[1], Takuji Hatakeyama[1] (1. Kyoto University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1121-4am-05]

Incorporation of reactive site to tetra-BF_2 complex with bipyrrole skeleton and creation of photofunctional materials

○Ayano Tani[1], Yu Hoshino[2,3], Toshikazu Ono[2,3] (1. Faculty of Engineering, Kyushu University, 2. Graduate School of Engineering, Kyushu University, 3. Center for Molecular Systems (CMS), Kyushu University)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1121-4am-06]

Multi-Bladed Donor-Acceptor π-Electronic Systems Exhibiting Unique Emission Properties

○Yunyi Song[1], Yoshiaki Shoji[1], Fukushima Takanori[1] (1. CLS, Tokyo Tech.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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[E1121-4am-07]

Diverse Photofunctions of tetra-BF_2 Complexes with Bipyridine Skeleton

○Ryoji Furuta[1], Luxia Cui[1], Yu Hoshino[1,2], Toshikazu Ono[1,2] (1. Graduate School of Engineering, Kyushu University, 2. Center for Molecular Systems (CMS), Kyushu University)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1121-4am-08]

Synthesis and Photophysical Properties of Boron-Containing Polycyclic Aromatic Hydrocarbons with Intramolecularly-Coordinating Phorphorus Groups

○Yoshiharu sano[1], Tatsuya Mori[4], Shigehiro Yamaguchi[3,4,2] (1. Nagoya University, Department of Chemistry, School of Science, 2. Nagoya University, Department of Chemistry, Graduate School of Science, 3. Nagoya University, Institute of Transformative Bio-Molecules (ITbM), 4. Nagoya University, Integrated Research Consortium on Chemical Sciences (IRCCS))

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1121-4am-09]

Synthesis of *B*-*O*-fused-pyrrolopyrrole aza-BODIPY toward creating its cyclic oligomers with prominent chiroptical properties

○Shuhei Fukami[1], Soji Shimizu[1] (1. The Graduate School of Engineering, Kyushu University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1121-4am-10]

Au(I)-Catalyzed Cycloisomerization for the Synthesis of Fused BODIPYs

○Fumika Ohashi[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, Nagoya University, 2. Institute for Advanced Research, Nagoya University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1121-4am-11]

Iterative synthesis of donor-acceptor-type oligosilanes

○Natsumi Hammyo[1], Mingoo Jin[2], Hajime Ito[2,3] (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. Graduate School of Engineering, Hokkaido University)

English

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1121-4am-12]

Substituent Effects on the Photophysical Properties of Disilane-Bridged Trimer Thiophenophane

○Yuya Kaneko[1], Yoshinori Yamanoi[1], Teppei Yamada[1] (1. The Univ. of Tokyo)

English

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1121-4am-13]

Synthesis and Optical Evaluation of π-Conjugated Systems Based on Hypervalent Silicon Compounds

○Ippei Kanetani[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Graduated School of Engineering, Kyoto University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

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[E1121-4am-14]

Synthesis and Properties of Aromatic-Fused Phospholes via β-Substituted Phospholes

○Riku Minobe[1], Tomohiro Higashino[1], Hiroshi Imahori[1,2,3] (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ., 3. ILAS, Kyoto Univ.)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1121-4am-15]

Synthesis and Properties of Antimony Dipyrrin Complexes

○Shunsuke Kuroiwa[1], Hiroki Fukumoto[1], Tomohiro Agou[2], Tatsuya Nabeshima[3] (1. Ibaraki University, 2. University of Hyogo, 3. University of Tsukuba)

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

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC E1113(1113, Bldg. 11 [1F])

[E1113-4pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Masatoshi Ishida, Masayoshi Takase

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1113-4pm-01]

Synthesis of Dianionic Species of Cross-Conjugated γ-Thiolactone and Evaluation of its Aromaticity

○Takumi Shiokawa[1], Aiko Fukazawa[2] (1. Graduate School of Engineering, Kyoto University, 2. WPI-iCeMS, Kyoto University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1113-4pm-02]

Synthesis and properties of metal complexes of 20π antiaromatic diazaporphyrins

○Koubei Ohtake[1], Takahiro Sakurai[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, Nagoya University, 2. Institute for Advanced Research, Nagoya University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1113-4pm-03]

Synthesis and Properties of Diphenyldiaza-*m*-benziporphyrin Derivatives

○Emi Suzuki[1], Yoshihiro Matano[2] (1. Graduate School of Science and Technology, Niigata Univ., 2. Faculty of Science, Niigata Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1113-4pm-04]

Synthesis and physical properties of metal complexes of 5,10,20-triaryl-5,15-diazaporphyrin

○Yui Murata[1], Yoshihiro Matano[1] (1. Faculty of Science, Niigata Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1113-4pm-05]

Synthesis of Tin Complexes of 5,10,15,20-Tetraaryl-5,15-diazaporphyrin

○Hiroya Suzuki[1], Yoshihiro Matano[2] (1. Graduate School of Science and Technology, Niigata Univ., 2. Faculty of Science, Niigata Univ.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1113-4pm-06]

Creation of supramolecular architectures using TTF-annulated subphthalocyanine

○Riku Kitahara[1], Soji Shimizu[1] (1. Kyushu University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1113-4pm-07]

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Phthalocyanine Near-Infrared Photocatalyst for Direct Modification on Aromatic Rings

○Tasuku Iba[1], Taniyuki Furuyama[1] (1. Kanazawa Univ.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1113-4pm-08]

Synthesis of dodeca-substituted tetrabenzoporphyrin via a coupling reaction

○Osuke Fukuda[1], Kenta Horikoshi, Makoto Roppongi[1], Satoshi Ito[1] (1. Faculty of Engineering, Utsunomiya University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1113-4pm-09]

Synthesis of stacked metal complexes with porphyrin dimer ligands

○Yusei Ohnishi[1], Shigeki Mori[2], Kan Miyamoto, Masayoshi Takase[1], Tetsuo Okujima[1], Uno Hidemitsu[1] (1. Graduate School of Science and Engineering, Ehime Univercity, 2. Advanced Research Support Center(ADRES),Ehime University ADRES)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1113-4pm-10]

Synthesis of calix[4]phyrins bearing spiro-fluorene subunits

○Masaaki Suzuki[1], Eisuke Tsurumi[2] (1. Graduate School of Natural Science and Technology, Shimane University, 2. Interdisciplinary Faculty of Science and Engineering, Shimane University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[E1113-4pm-11]

Ion-Pairing Assembly of Electron-Deficient π-Electronic Cations

○Kantaro Omine[1], Yuya Hashimoto[1], Yohei Haketa[1], Hiromitsu Maeda[1] (1. Ritsumeikan University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1113-4pm-12]

Synthesis and physicochemical properties of new π-conjugated *meso*-substituted porphycene

○Chihiro Sonoda[1], Takashi Hayashi[1] (1. Osaka university)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1113-4pm-13]

Synthesis and charge transfer properties of tetrabenzo-10-heterocorrole

○Kento Teranishi[1], Kyohei Matsuo[1], Yoshiyuki Mizuhata[1], Yamada Hiroko[1] (1. Institute for Chemical Research, Kyoto University)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[E1113-4pm-14]

Synthesis of ABCD-ABCD Cofacial Porphyrin Dimers

○Ryo Inoue[1], Mayu Kobayashi[1], Yasuhiro Morisaki[1] (1. Kwansei Gakuin University)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

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[E1113-4pm-15]

Ion-Pairing Assembly of *meso*-Oxoporphyrin Au^{III} Complexes

○Shota Seki[1], Yohei Haketa[1], Hiromitsu Maeda[1] (1. Ritsumeikan University)

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Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
E1122(1122, Bldg. 11 [2F])

[E1122-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Shunsuke Ohtani, Tomoya Fukui

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1122-4am-01]

Mechanofluorochromic properties of 1,4-diphenylanthracene derivatives exhibiting a hypsochromic shift

○Fumihiro KANNEN[1], Tadatoshi ADACHI[1], Manato Nishimura[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1122-4am-02]

Structure and inclusion ability of γ-cyclodextrin dimer linked by 1,4- and 2,3-dimethylnaphthalene

○Toru Kataoka[1], Yoshihiro Ishimaru[1] (1. Saitama University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1122-4am-03]

Inner chemical modification of an $M_{60}L_{60}$ peptide cage

○Shiori Hino[1], Michito Yoshizawa[1], Tomohisa Sawada[1,2] (1. Lab. for Chem. & Life Sci., Tokyo Tech, 2. JST-PRESTO)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1122-4am-04]

Upward vibrational frequency shift due to electron–phonon polar-coupling interaction in $C_{12}H_{17}ClN_4OS{\cdot}HCl{\cdot}H_2O$ crystals

○Masae Takahashi[1], Hiroshi Matsui[1], Eunsang Kwon[1], Yuka Ikemoto[2] (1. Tohoku Univ., 2. JASRI)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1122-4am-05]

Solid-state self-complementary assembly of anthracene-based molecular tweezers: selective construction of discrete assemblies and dynamic structural transformation

○Koki Okabe[1], Masahiro Yamashina[1], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Tech)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1122-4am-06]

Formation of an optically active micelle bearing terpene frameworks and its cavity chirality

○Yoshihisa Hashimoto[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

Japanese

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10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[E1122-4am-07]

Chiral Optical Properties of Axially Chiral Molecules within Aromatic Micelles

○Tomohiro Yasuda[1], Yoshihisa Hashimoto[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech.)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1122-4am-08]

Metal-mediated confinement of dye molecules within an acetylene-containing aromatic micelle

○Shinnosuke Hirata[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Tokyo Institute of Technology)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1122-4am-09]

Synthesis of azaylide-based gemini-amphiphiles and their unique aggregation behavior caused by alkyl linker length

○Akiyama Yoshimori[1], Yamashina Masahiro[1], Toyota Shinji[1] (1. Tokyo Tech)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1122-4am-10]

Construction of Silver Nanoclusters Driven by Cooperative Acetylene Coordination

○Tasuki Tsurumi[1], Takahiro Nakagawa[2], Yuya Domoto[1], Kiyohiro Adachi[3], Takuma Kaneko[4], Tomoya Uruga[4,5], Daisuke Hashidume[3], Yosuke Nakamura[1], Makoto Fujita[2,6] (1. Gunma Univ., 2. The Univ. of Tokyo, 3. RIKEN, 4. JASRI, 5. The Univ. of Electro-Communications, 6. IMS)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1122-4am-11]

Detection of phosphonic acids and nucleotides using aggregation-induced emission of tetraamidine

○Yusuke Yamamoto[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1122-4am-12]

Cooperative Molecular Recognition of Macrocyclic Tetrakisporphyrin

○Kouta Tanabe[1,2], Naoyuki Hisano[1], Haino Takeharu[1,2] (1. Grad. Sc. Adv. Sci. Eng., Hiroshima Univ., 2. International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM^2))

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1122-4am-13]

Supramolecular Complexes Formed by Molecular Recognition of Multi-Layered Zinc Porphyrin

○Tomoki Kodama[1,2], Naoyuki Hisano[1], Takeharu Haino[1,2] (1. Grad. Sc. Adv. Sci. Eng., Hiroshima Univ., 2. WPI-SKCM^2, Hiroshima Univ.)

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Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
E1123(1123, Bldg. 11 [2F])

[E1123-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Ayumi Imayoshi, Naoya Morohashi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1123-4am-01]

Development of Regioselective Catalyst Using Hydrogen Bonding between Amides

○Joto Yabe[1], Nobuhiro Kihara[1] (1. Kanagawa University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1123-4am-02]

Photoreduction control of anthraquinone derivatives using hydrogel

○Ayuna Nishiyama[1], Yoshinori Okayasu[1], Yuki Nagai[1], Yoichi Kobayashi[1,2] (1. Ritsumeikan University, 2. PRESTO JST)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1123-4am-03]

Development of stimuli-responsive photoluminescent liquid materials

Takumi Omura[1], Shogo Morisako[1], ○Kyosuke ISODA[1] (1. SCRI)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1123-4am-04]

Afterglow sensing for metal ions using room-temperature phosphorescence properties

○Margarita Claudya Maida[1], Satoshi Takegawa[1], Masato Ito[1], Yuji Kubo[1] (1. Tokyo Metropolitan University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1123-4am-05]

The functional evaluation of a supramolecular hydrogel formed from amphiphilic bis-urea

○Minami Ishii[1], Shinya Kimura[1], Masashi Yokoya[1], Masamichi Yamanaka[1] (1. Meiji Pharm. Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1123-4am-06]

Supramolecular Gel Formation by Ring Opening Reaction of Cyclic Monourea

○Noriaki Kimishima[1], Shinya Kimura[1], Masashi Yokoya[1], Masamichi Yamanaka[1] (1. Meiji Pharm. Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1123-4am-07]

Development of a separation method for aromatic carboxylic acid regioisomers with crystals of a tetranuclear zinc(II) complex ligated by 2,2'-thiodiphenol derivative

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○Reon Sato[1], Keisuke Hara[1], Ikuko Miyoshi[1], Naoya Morohashi[1], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1123-4am-08]

Selective solid-phase extraction of rare metal ions from water with bis(tetramethylammonium) salt crystals of *p-tert*-butylcalix[4]arene-1,3-diphosphonic acid

○Ryuki Takahashi[1], Mayu Osawa[1], Seiya Ikarashi[1], Naoya Morohashi[1], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1123-4am-09]

Synthesis and Physicochemical Properties of Diphenylquinoline *N*-oxyl Derivatives with Alkyl Substituents at 6-Position

○Jumpei Yazawa[1], Kento Morinaka[1], Masaomi Takii[1], Youhei Miura[1], Naoki Yoshioka[1] (1. keio university)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1123-4am-10]

Racemization of cross-chain bridging cryptands featuring different combination of oligo(ethylene glycol) linkers

○Taisei MARUYAMA[1], Syogo NIMI[1], Masaya NAITO[1], Shinobu MIYAGAWA[1], Yuji TOKUNAGA[1] (1. University of Fukui)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1123-4am-11]

Chiral Anion Recognition By Phosphoric Triamide

○Seiichi Yoshino[1], Shin-ichi Kondo[1] (1. Yamagata University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1123-4am-12]

Thermal isomerization behavior and metal ion response of azobenzene derivatives with crown ether structure

○Yuto Hirayama[1], Runze Lin[2], Nobuyuki Tamaoki[2], Akitaka Ito[3], Rico Tabor[4], Masayuki Izumi[1], Rika Ochi[1] (1. Kochi University, 2. Hokkaido University, 3. Kochi University of Technology, 4. Monash University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1123-4am-13]

Hydrogen-bond-directed supramolecular polymerization of a U-shaped thienoacene derivative

○Chen Liu[1], Shogo Nakajima[1], Soichiro Ogi[2], Tatsuya Mori[2], Shigehiro Yamaguchi[1,2,3] (1. Graduate School of Science, Nagoya University, 2. Integrated Research Consortium on Chemical Sciences, Nagoya University, 3. Institute of Transformative Bio-Molecules, Nagoya University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1123-4am-14]

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Aqueous nanoparticles of luminescent chromophores by using aqueous bilayer membranes and their application to photon upconversion

○Keita Kuge[1], Naoyuki Harada[1], Nobuo Kimizuka[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ.)

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Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:00 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:00 AM UTC
E1131(1131, Bldg. 11 [3F])

[E1131-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Keiichi Imato, Kazuko Nakazono

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1131-4am-01]

Photoinduced solid–liquid transitions by thermally stable molecular photoswitches

○Naoki Kaneda[1], Keiichi Imato[1], Ichiro Imae[1], Yousuke Ooyama[1] (1. Hiroshima University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1131-4am-02]

Sensing behavior of stimuli-responsive liquid materials based on pyromellitic diimide

○Takumi Omura[1], Shogo Morisako[1], Kyosuke Isoda[1] (1. Sagami Chemical Research Institute)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1131-4am-03]

Rotaxane-based Supramolecular Mechanophores Using Acenes as the Fluorophores

○Keigo Nonaka[1], Yoshimitsu Sagara[1] (1. Tokyo Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1131-4am-04]

Formation of a hetero porphyrin tetramer from a pair of carboxy and aminoquinolino porphyrins.

○Kento Otani[1], Masaki Kimura[1], Masahiro Ueda[1], Yuki Akada[1], Shinobu Miyagawa[1], Masaya Naito[1], Yuji Tokunaga[1] (1. The University of Fukui)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1131-4am-05]

Stabilization of crown/ammonium type rotaxanes through ionic interaction

○Takumi Takizawa[1], Kento OTANI[1], Masaya NAITO[1], Shinobu MIYAGAWA[1], Yuji TOKUNAGA[1] (1. University of Fukui)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1131-4am-06]

Self-assembly of Benzoxadiazole Dyad into Fluorescent Nanorings

○Hina OCHIAI[1], Natsuki SUDA[2], Hiroki HANAYAMA[1], Shiki YAGAI[3] (1. Chiba University, 2. Chiba University Graduate School of Science and engineering, 3. Institute for Advanced Academic Research)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1131-4am-07]

Self-assembly of quinazolinedione-functionalized π-conjugated molecules

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○Yuhei Yamada[1], Hiroki Hanayama[3], Shiki Yagai[2] (1. Chiba University, 2. Chiba University Institute for Advanced Academic Research, 3. Chiba University Graduate School of Engineering)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1131-4am-08]

Molecular recognition behaviors of tertiary amine-type azacyclophanes

○Takeru Okura[1], Kazuko Nakazono[1] (1. Tokyo institute of Technology)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1131-4am-09]

Preparation of planar triphenylborane nanoparticles and their application to boron neutron capture therapy

○Ikumi Koyama[1], Yuichi Kitamoto[1], Yoshitaka Koseki[2], Asuka Mizutani[2], Hitoshi Kasai[2], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1131-4am-10]

Synthesis, Structure and Fluorescent Properties of *meta*-Phenylenediamine-Based Sulfonylaniline Fluorescent Dyes

○Hiroki Sato[1], Kaito Okubo[1], Aki Sato[2], Hiroshi Katagiri[1,2] (1. Grad. Sch. of Org. Mater. Sci., Yamagata Univ., 2. Grad. Sch. of Sci. and Eng., Yamagata Univ.)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1131-4am-11]

A 1D tube structure from hexa-nuclear Europium(III) complexes

○Kotaro Yakuwa[1], Junpei Yuasa[1] (1. Tokyo University of Science)

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Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC E1122(1122, Bldg. 11 [2F])

[E1122-4pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Junpey Yuasa, Yuki Ide

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1122-4pm-01]

Design of ionic liquid crystals by integrating a mesogen core with flexible tails via a rotaxane structure

○Gosuke Washino[1], Suzushi Nishimura[2], Atsushi Shishido[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech, 2. Sch. of Mater. & Chem. Technol., Tokyo Tech)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1122-4pm-02]

Switching the Emission of Two-Dimensional COFs by Tuning Interlayer Stacking Arrangements

○SIYUAN YE[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. School of Engineering, The Univ. of Tokyo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1122-4pm-03]

Material design and condition optimization for generating higher force of photomechanical crystals by machine-learning

○Kazuki ISHIZAKI[1], Toru ASAHI[1], Takuya TANIGUCHI[1] (1. Waseda University)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[E1122-4pm-04]

Analysis of light-driven self-oscillatory crystal under polarized light irradiation from a mathematical model based on reaction velocity

○Yoshiyuki Kageyama[1], Makiko Matsuura[1] (1. Hokkaido Univ.)

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Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC E1123(1123, Bldg. 11 [2F])

[E1123-4pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Shinya Kimura, Yoshitaka Tsuchido

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1123-4pm-01]

Spatiotemporally-controlled photochromic reactions using supramolecular gel

○Yuki Nagai[1], Sota Fujisaki[1], Yoshinori Okayasu[1], Yoichi Kobayashi[1,2] (1. Ritsumeikan Univ., 2. PRESTO, JST)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1123-4pm-02]

Effect of atropisomer on the physical properties of alkylated diphenylanthracene liquids

Xiao Zheng[1,2], Kazuhiko Nagura[1], Yoshitaka Matsushita[1], ○Takashi Takashi[1,2] (1. National Institute for Materials Science, 2. Hokkaido University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1123-4pm-03]

Chirality-controlling supramolecular assemblies of acidic and basic pillar[5]arenes

○Dehui Tuo[1,2], Shixin Fa[3], Seigo Tanaka [2], Kenichi Kato[2], Tomoki Ogoshi[2,1] (1. WPI-NanoLSI, Kanazawa Univ., 2. Grad.Sch.Eng., Kyoto Univ., 3. Northwestern Polytechnical Univ.)

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1123-4pm-04]

Construction of Homochiral Hierarchical Molecular Self-Assemblies Based on Self-Sorting of a Single Molecule with a C_{3h} Symmetric Core at the Liquid/Solid Interfaces.

○Matsuhiro Maeda[1], Steven De Feyter[2], Kazukuni Tahara[3] (1. Graduate School of Science and Technology, Meiji University, 2. Department of Chemistry, KU Leuven, 3. School of Science and Technology, Meiji University)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1123-4pm-05]

Analysis of 1:1 Host-Guest Systems with Temperature-Dependent Left- and Right-Twisted Conformational Changes

○Nozomu Suzuki[1], Daisuke Taura[2], Yusuke Furuta[2] (1. Kobe Univ., 2. Meijo Univ.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[E1123-4pm-06]

Vortex flow induced chiroptical response of self-assembled supramolecular objects of isoxazole-equipped platinum(II) complex

○Masaya YOSHIDA[1,2], Takehiro HIRAO[1], Takeharu HAINO[1,2] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM², Hiroshima University)

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Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC E1131(1131, Bldg. 11 [3F])

[E1131-4pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Shotaro Hayashi, Yumi Yakiyama

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1131-4pm-01]

Triptycene Frameworks for Orientational Control over Electroactive Subunits in STM Break-Junction

○Colin John Martin[1], Tomoya Fukui[1], Ryosuke Takehara[1], Shintaro Fujii[2], Takanori Fukushima[1] (1. CLS, Tokyo Tech., 2. School of Science, Tokyo Tech.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1131-4pm-02]

Alkyl chain length-dependent polymorphism and phase transition behavior of N-shaped organic semiconducting molecules

○Masato Mitani[1], Craig P. Yu[2], Chizuru Sawabe[2], Chikahiko Mitsui[2], Takuya Seki[3], Yudai Shinozaki[3], Go Watanabe[3], Daisuke Hashizume[4], Shohei Kumagai[1], Jun Takeya[2], Toshihiro Okamoto[1] (1. Tokyo Institute of Technology, 2. The Univ. of Tokyo, 3. Kitasato University, 4. RIKEN)

English
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[E1131-4pm-03]

Solid-state magnetic properties of halogen or ethynyl substituted aromatic nitroxide with cardo structure

○Masaomi Takii[1], Youhei Miura[1], Naoki Yoshioka[1] (1. Keio University)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1131-4pm-04]

Low Dimensional Single Crystal Lasers Composed of Fumaronitrile-based π-Conjugated Molecules Exhibiting Aggregation Induced Enhanced Emission

○Takumi Matsuo[1], Shotaro Hayashi[1] (1. Kochi University of Technology)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1131-4pm-05]

Quantification of Noncovalent Arene–Fullerene Interactions Using a Molecular Torsion Balance

○Michio Yamada[1], Koki Sahara[1], Yukiyo Kurihara[1], Masaaki Koizumi[1], Kasumi Tsuji[1], Haruna Narita[1], Yutaka Maeda[1], Mitsuaki Suzuki[2] (1. Tokyo Gakugei University, 2. Josai University)

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

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
E1132(1132, Bldg. 11 [3F])

[E1132-4am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Kei Ohkubo, Koichi Mitsudo

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1132-4am-01]

Boryl radical-mediated decyanation of malononitriles using photoredox catalyst

○Yuto Yoshida[1], Daniele Leonori[2], Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology, 2. RWTH Aachen University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1132-4am-02]

Study on radical reactions of a phosphatetraphene by muon spectroscopy

○Shigekazu Ito[1], Kohei Yasuda[1], Keisuke Ishihara[1], Kenji M. Kojima[2], Iain McKenzie[2] (1. Tokyo Institute of Technology, 2. TRIUMF)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1132-4am-03]

Study on Electronic Configuration of Carbenes Embedded in Cycloparaphenylene Unit

○Ku Kajikawa[1], Ryo Murata[1], Eiichi Kayahara[2], Shigeru Yamago[2], Manabu Abe[1] (1. Hiroshima University, 2. Kyoto University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1132-4am-04]

Synthesis of Highly Dispersed Hydroxylated Carbon Nanotubes by Chlorine Dioxide

○Yuki Itabashi[1], Ai Sunami[1], Kei Ohkubo[1,2] (1. Osaka Univ., OTRI, 2. Osaka Univ., IACS)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1132-4am-05]

Development of New Radical Initiators Which Decompose by Red-Light Irradiation

○Rintaro Tanikawa[1], An Shinohara[1], Kenichi Takao[1], Akihiro Ogura[1] (1. Faculty of Science and Technology, Keio University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1132-4am-06]

Effects of Solvent and Acid Catalysis on the Photosolvolysis of 3-Methoxy-2-benzyloxy-Naphthalene

○Satoshi Usui[1], Shunsuke Koyanagi[1], Chihiro Kinugawa[1] (1. Niigata University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

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[E1132-4am-07]

Arylcarboxylation of Alkenes with Formate Salts under Photoredox/HAT Catalysis

○Yamato Ueno[1], Wataru Kanna[1], Saeesh Rajendra Mangaonkar[2,3], Yu Harabuchi[2,3], Hiroki Hayashi[2,3], Tsuyoshi Mita[2,3], Satoshi Maeda[1,2,3] (1. Fac. of Sci., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. JST-ERATO)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1132-4am-08]

Synthesis of [3.3.1]Propellanes by Cyclopropanation of Furofurans and Thienothiophenes and Their Properties

○Toki Hirano[1], Koichi Mitsudo[1], Seiji Suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1132-4am-09]

Evaluation of decarboxylation of α-substituted diarylacetic acid derivatives generated by polymeric mechanochemical reactions

○Yuto Uchida[1], Takumi Yamamoto[1], Hajime Sugita[1], Akira Takahashi[1], Hideyuki Otsuka[1] (1. Dept. of Chem. Sci. and Eng., Tokyo Tech.)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1132-4am-10]

Effect of Polycyclic Aromatic Substituents on Positive Charge Delocalization and Antiaromaticity of Fluorenyl and Benzofluorenyl Cations

○Takao Okazaki[1], Taichi Kawakami[1], Reiji Kawai[1], Toshikazu Kitagawa[1] (1. Mie University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1132-4am-11]

Development of Eco-Friendly Synthesis of Cyclic Sulfide Using Thioamide Derivatives

○Urara Masamoto[1], Yusuke Yoshinaga[1], Daisuke Kaneno[1] (1. Kochi Univ.)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1132-4am-12]

Photocatalytic Carboxylation of terminal alkynes using CO_2

○Shuhei Uno[1], Tatsushi Imahori[1] (1. Tokyo University of Science)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1132-4am-13]

Photoinduced Synthesis of α-Thiooximes by Three-Component Coupling Reaction

○Toshiki Tamura[1], Ken Yamazaki[2], Shuta Akimoto[2], Tomoya Miura[2] (1. School of Engineering, Okayama University, 2. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

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

Thu. Mar 21, 2024 1:00 PM - 2:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:00 AM UTC E1132(1132, Bldg. 11 [3F])

[E1132-4pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Akira Takahashi, Satoshi Usui

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1132-4pm-01]

Aerobic Oxygenation of Benzene Using Fluorine-Substituted Acridinium as a Photoredox Catalyst

○Yusuke Akao[1,2], Shohei Ohno[2], Yuki Itabashi[3], Haruyasu Asahara[1], Yasuaki Koizumi[1], Kuninori Tai[1], Kazumi Kondo[1], Tsuyoshi Nagase[1], Tsuyoshi Inoue[2], Kei Ohkubo[3,4] (1. Otsuka Pharmaceutical Co., Ltd., 2. Osaka Univ., 3. Osaka Univ. OTRI, 4. Osaka Univ. IACS)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1132-4pm-02]

Mechanisms and the Role of Lewis Acids in Transition Metal Catalysts for C-O, C-F, and H-H Activation

○Panida Surawatanawong[1] (1. Mahidol University, Faculty of Science)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1132-4pm-03]

Synthesis of Phosphine Ligands through Radical Diphosphination of Strained Small Molecules

○Tsuyoshi Mita[1,2], Chandu G Krishnan[1,2], Hideaki Takano[1,2], Hitomi Katsuyama[1,2], Hiroki Hayashi[1,2], Wataru Kanna[3], Satoshi Maeda[1,2,3] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1133(1132, Bldg. 11 [3F])

[E1133-4am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Jumpei Taguchi, Kosuke Yasui

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1133-4am-01]

Synthesis of polyacene derivatives via dehydrative aromatization of aromatic alcohols

○Ryota Yuasa[1], Toshiyuki Hamura[1] (1. Kwansei Gakuin University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1133-4am-02]

Synthesis of [6]helicene extensions and their properties

○Masaya Miyamoto[1], Makoto Miyamoto[1] (1. Tokyo Denki University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1133-4am-03]

Desymmetrization of Naphthalene Framework Using Bromo Rearrangement and Subsequent Regioselective Transformation

○Nana Hatayama[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1133-4am-04]

Synthesis of Internal-edge-substituted Azaoxa[6]helicenes by Intramolecular C–H Amination as a Key Reaction

○Syuji Morita[1], Song Leii[1], Kazunobu Igawa[1], Katsuhiko Tomooka[2], Ryo Irie[1] (1. The Univ. of Kumamoto, 2. The Univ. of Kyushu)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1133-4am-05]

KO^{t}Bu-Catalyzed Transformation of *N*-Benzylamides to Isoindoles via 1,2-Acyl Migration

○Ryoma Shimazumi[1], Moe Morimoto[2], Mamoru Tobisu[1,3] (1. Graduate School of Engineering, Osaka Univ., 2. School of Engineering, Osaka Univ., 3. ICS-OTRI)

English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1133-4am-06]

One-pot Synthesis of Novel Tetraaryl-Diazachrysenes via the Povarov Reaction

○YUANRONG SHAN[1], Takaki Kanbra[1], Junpei Kuwabara[1] (1. University of Tsukuba Graduate School of Pure and Applied Sciences)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

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[E1133-4am-07]

Synthesis of dibenzofulvenes containing a trifluoromethyl group based on Friedel-Crafts type cyclization

○yusei noguchi[1], motohiro yasui[1], sigeyuki yamada[1], tsutomu konno[1] (1. kyoto institute of technology)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1133-4am-08]

Carbamoylarylation of Alkynes Using *N*-Aryl Oxamic Acids as Bifunctional Reagents

○GAOFAN YUE[2], Di Wu[2], Akira Shiozuka[2], Kohei SEKINE[1,2], Yoichiro KUNINOB[1,2] (1. IMCE, Kyushu Univ., 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu Univ.)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1133-4am-09]

Mono-Selective Mechanochemical Nucleophilic Aromatic Substitution Enabled by In-situ Crystallization

○Sota Kawamura[1], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1133-4am-10]

Stereoselective Synthesis of Trisubstituted Alkenes Enabled by the Reactivity of Sulfoximine

○Kosuke Yasui[1], Yuichiro Tomishima[2], Koji Hirano[1] (1. Graduate School of Engineering, Osaka University, 2. School of Engineering, Osaka University)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1133-4am-11]

Synthesis of di(1-benzothiopheno)pyrrole *via* Cadogan reaction

○Yuma Tanioka[1], Shigeki Mori[2], Masayoshi Takase[1], Hidemitsu Uno[1] (1. Graduate school of science and engineering, Ehime University, 2. Advanced Research Support Center , Ehime University)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1133-4am-12]

Formation of 2,3-benzodiazepin from *o*-vinylbenzyldiazoacetate

○Kazuki Naoi[1], Tomoya Kuroki[1], Shinji Nagumo[1] (1. Kogakuin University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1133-4am-13]

Synthesis of Novel Heterobiaryls via Siteselective Halogenation and Crosscoupling Reactions of Naphthobenzofuranol Derivatives

○Song Lei[1], Suzuna Nakashima[1], Shuji Morita[1], Kazunobu Igawa[1], Katsuhiko Tomooka[2], Ryo Irie[1] (1. Kumamoto Univercity, 2. Kyushu University)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1133-4am-14]

Syntheses and properties of diazaperopyrenes with electron- donating groups

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Hotsuma Inada[1], Yasufumi Masani[2], Yoshimitsu Tachi[1,2], ○Masatoshi Kozaki[1,2] (1. Osaka Metropolitan University, 2. Osaka City University)

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-4am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kazuya Kanemoto, Yohei Ogiwara

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1141-4am-01]

Synthesis of Thiaphenanthridinones

○Keisuke Nakamura[1], Minori Suzuki, Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1141-4am-02]

Substituent Effects in the Synthesis of Dihydrobenzene Deriratives from Thiophene Dioxides and Styrenes

○Kayoko Ohira[1], Koyo Numata[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1141-4am-03]

C4 Arylation of Benzothiazoles via Pummerer Activation

○Ryota Wakabayashi[1], Shuo Wang[1], Takashi Kurogi[1], Hideki Yorimitsu[1] (1. Kyoto University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1141-4am-04]

Synthesis and Properties of Benzodithiophene Derivatives by π-Extension Reaction

○Yuki Takenaka[1], Hideji Osuga[1,2], Hidefumi Sakamoto[1,2] (1. Graduate School, Wakayama University, 2. Wakayama University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1141-4am-05]

Preparation of unsymmetrical aminodisulfides from *N*-dithiophthalimides with amines

○Hayato Asanuma[1], Kazuya Kanemoto[1] (1. Tohoku university)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1141-4am-06]

Development of novel sulfurizing reagents with an adamantane-like structure

○Mizuki Oyanagi[1], Tomoya Sugai[1,2], Noriki Kutsumura[1,2] (1. College of Chem., Sch. Sci. Eng., Univ. of Tsukuba, 2. WPI-IIIS, Univ. of Tsukuba)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1141-4am-07]

Development of dehydrogenative synthesis of alkenyl isothiocyanates

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○Bumpei Maeda[1], Kei Murakami[1] (1. Kwansei University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1141-4am-08]

Development of Asymmetric Synthesis of Sulfinamidines

○Kana Shigenai[1], Saori Tsuzuki[2], Taichi Kano[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2. Graduate School of Science, Kyoto University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1141-4am-09]

Fe-catalyzed synthesis of thiophenes from alkyne and elemental sulfur and its application to selenophene synthesis

○Shurika Innami[1], Kento Ishida[1], Yohei Ogiwara[1], Norio Sakai[1] (1. Tokyo University of Science)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1141-4am-10]

Synthesis of dibenzyl selenides from benzyl esters by using elemental selenium and a hydrosilane

○Yasushi Kino[1], Kento Ishida[1], Norio Sakai [1] (1. Tokyo University of Science)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1141-4am-11]

Synthesis of Selenophene Derivatives via Selenium Cation-Mediated Sequential C-Se Bond Formation

○Iwamoto Hiroki[1], Kojima Yuki[1], Yasui Kosuke[1], Hirano Koji[1] (1. The Univ. of Osaka)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1141-4am-12]

Development of nitrogen-terminated cascade cyclization reactions using a recyclable selenenyl iodide

○Jun Kikushima[1], Takaaki Nakada[1], Satoru Kuwano[1], Kei Goto[1] (1. Tokyo Institute of Technology)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1141-4am-13]

Preparation and Electrochemical Properties of Subphthalocyanine with a Diselenet Ring

○Takeshi Kimura[1] (1. Iwate University)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[E1141-4am-14]

Model study of reactive intermediates involved in selenoprotein biosynthesis using molecular cavities.

○Arashi Kudo[1], Satoru Kuwano[1], Kei Goto[1] (1. Tokyo Institue of Technology)

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

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC E1133(1132, Bldg. 11 [3F])

[E1133-4pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Koh Sugamata, Masaru Kondo

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1133-4pm-01]

Synthesis of pentaphene derivatives and their cyclotrimerization

○Hyeonju Jeong[1], Makoto Miyasaka[1] (1. Tokyo Denki University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1133-4pm-02]

Synthesis of acenophanes via cyclodimerization of isoacenofurans

○Yukino Kitamura[1], Hiroaki Yamana, Toshiyuki Hamura[1] (1. Kwansei Gakuin University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1133-4pm-03]

Construction of polysubstituted tropolone scaffold from dioxinone derivative

○Sangeun Yeom[1], Ken Ohmori[1] (1. Tokyo Inst. of Tech.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1133-4pm-04]

Synthesis and Properties of 2,3,6,7-Naphthalenetetracarboxylic Diimide Derivatives with Amino and Cyano Substituents

○Daito Nakada[1], Hideji Osuga[1,2], Hidefumi Sakamoto[1,2] (1. Graduate School, Wakayama University, 2. Wakayama University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1133-4pm-05]

Synthesis and Stereochemical Study of Naphthylisoquinoline *N*-oxide Derivatives with Axial Chirality

○Shota Kawakami[1], Damjan Trpkovski[1], Kazunobu Igawa[1], Katsuhiko Tomooka[2], Ryo Irie[1] (1. Kumamoto University, 2. Kyushu University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1133-4pm-06]

Synthesis of complexes with azaazulene derivatives as a ligand.

○Shotaro Mori[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Faculty, Tokyo University of Science)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1133-4pm-07]

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Synthesis and Characterization of 4-Pyridyl-Extended Dithieno[3,2-*b*:2',3'-*d*]arsole

○Yui Hatanaka[1], Kazuma Kikuchi[2], Hiroaki Imoto[1,2], Kensuke Naka[1,2] (1. Kyoto Institute of Technology, 2. Grad. Sch. of Sci. and Tec., Kyoto Inst. of Tech.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1133-4pm-08]

Synthesis and Gas Adsorption Properties of Metal-organic Frameworks Using Triptycene Ligands with Sulfur Functional Group at the Bridgehead Position

○Shoko Yamada[1], Koh Sugamata[1], Natsuki Amanokura[1,2], Mao Minoura[1] (1. Rikkyo University, 2. Nippon Soda Co., Ltd.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1133-4pm-09]

Synthesis and Gas Adsorption Properties of Metal-organic Frameworks with Phenothiazine Ligands

○Riko Furukawa[1], Koh Sugamata[1], Natsuki Amanokura[1,2], Mao Minoura[1] (1. Rikkyo University, 2. Nippon Soda Co., Ltd.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1133-4pm-10]

Synthesis and Property of Dibenzobarrelene-hexatriene-based O,S-Mixed Crownether

○Nanaka Umehara[1], Norio Nakata[1], Akihiko Ishii[1] (1. Graduate School of Science and Engineering, Saitama University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1133-4pm-11]

Synthesis and physical properties of 3^1-thienylated chlorophyll derivatives

Hitoshi Tamiaki[1], ○Takeru Nishikawa[1] (1. Ritsumeikan University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1133-4pm-12]

Purification of Hydrophilic Ionic Liquids for Material Application and Their Biocompatibility

○Yukino Isshiki[1], Tatsuya Kaya[2], Satoshi Kitaoka[3], Kaoru Nobuoka[4] (1. Oita University Graduated School of Engineering, 2. Kindai University Graduated School of Engineering, 3. Kindai University Faculty of Engineering, 4. Oita University Faculty of Science and Technology)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[E1133-4pm-13]

Development of donor-acceptor fluorophores with 2*H*-indazole skeleton

○Tomohiro Komuro[1], Yu Miyazaki[1], Agou Tomohiro[2], Hiroki Fukumoto[1], Masaru Kondo[3] (1. Ibaraki Univ., 2. Univ. of Hyogo, 3. Univ. of Shizuoka)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[E1133-4pm-14]

The metal complex reaction of [36]trithianonaphyrin

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○Taiki Nagatsu[1], Takashi FUJIHARA[2], Yoshihiro ISHIMARU[1] (1. Saitama University, 2. Saitama University, Comprehensive Analysis Center for Science)

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

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC E1141(1141, Bldg. 11 [4F])

[E1141-4pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Toshifumi Dohi, Yuto Sumida

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1141-4pm-01]

Synthesis of optically active delta-lactones using enzymatic reaction and evaluation of their odors

○Masashi Kawasaki[1], Takuya Okada[2], Yasuo Tanaka[3], Naoki Toyooka[2] (1. Toyama Prefectural University, 2. University of Toyama, 3. Taiyo Corporation)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1141-4pm-02]

Asymmetric Synthesis of α-Heteroatom-substituted Aminonitriles by Hydrogen-Bonding-Donor Catalysis

○Yusuke Oyamada[1], Miku Fujii[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1141-4pm-03]

Engineering the C4N4 Fluorophore to Develop Turn-On Fluorescent Probes for Heavy Metal Detection.

○Miki Kohei[1,2], Harald Gröger[2], Naoya Kumagai[1,3] (1. Graduate School of Pharmacy, Keio University, 2. Fuculty of Chemistry, Bielefeld University, 3. Institute of Microbial Chemistry)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[E1141-4pm-04]

Design and Synthesis of Self-Assembling Cyclic Trimer $[HyAl\text{-}Py]_3$ and its Strategic Applications

○Kotaro Tsuruoka[1], Naoya Kumagai[1,2] (1. Graduate School of Phramaceutical Science, Keio University, 2. Institude of Microbial Chemistry)

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1142(1142, Bldg. 11 [4F])

[E1142-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Katsuhiko Moriyama, Yoshihiro Nishimoto

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1142-4am-01]

meta-Selective Acylation of Electron-rich Arenes Using Aliphatic Carboxylic Acid Derivatives

○Yamato Goto[1], Sho Murakami[2], Yuto Sumida[3], Hirohisa Ohmiya[2] (1. Grad. Sch. Med. Sci., Kanazawa Univ., 2. ICR, Kyoto Univ., 3. IBB, Tokyo Med. & Dent. Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1142-4am-02]

A Dual Photoredox/Cobalt Catalysis Enabling Branch-Selective Hydroaminoalkylation of Alkenes

○Yunosuke Takekawa[1], Kazunori Nagao[2], Hirohisa Ohmiya[2] (1. Grad. Sch. Med. Sci., Kanazawa Univ., 2. ICR, Kyoto Univ.)

English
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1142-4am-03]

Defluoroarylation of Trifluoromethylarenes with Heteroarenes by PhotoredoxCatalysis and Tin Iodide

Naoki Sugihara[1], ○Masayuki Abe[1], Yoshihiro Nishimoto[1], Makoto Yasuda[1] (1. Graduate School of Engineering, Osaka University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1142-4am-04]

Development of Cycloaddition Reactions Using Triarylmethyl Cations as Photocatalysts

○Kazumichi Maeda[1], Tomoya Hisada[1], Yasuhiro Yamashita[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1142-4am-05]

Development of Metal Thiophenoxide Catalysts for Photoalkylation of Active Methylene Compounds

○Tomoya Hisada[1], Yuki Sato[1], Yasuhiro Yamashita[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1142-4am-06]

Photoinduced Alkylation of Stabilized Carbanions with Nonactivated Alkenes

○Yuki Sato[1], Tomoya Hisada[1], Yasuhiro Yamashita[1], Shu Kobayashi[1] (1. The Univ. of Tokyo)

Japanese

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10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

[E1142-4am-07]

Development of Photocatalytic alpha-Alkylation Reactions of Active Methine Compounds with Nonactivated Alkenes in the Presence of Lewis Acids

Yasuhiro Yamashita[1], ○Rentaro Enokijima[1], Tomoya Hisada[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[E1142-4am-08]

Development of Efficient Continuous-flow Synthetic Methods for 3-Aminochromon Scaffold Using *N*-Heterocyclic Carbene Catalysts

○Shunsuke Mouri[1], Haruro Ishitani[2], Shū Kobayashi[2] (1. NIPPON SODA CO., LTD., 2. The University of Tokyo)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1142-4am-09]

Developments and Applications of Chiral Halonium Salts with Thiourea Moieties

○Shinano Kobayashi[1], Yasushi Yoshida[1], Takashi Mino[1] (1. Chiba University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1142-4am-10]

Development of Chiral Halonium Salts with Sulfonamide Moiety and Their Catalytic Applications

○Koki Obata[1], Yasushi Yoshida[1], Takashi Mino[1], Masami Sakamoto[1] (1. CHIBA University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1142-4am-11]

Remote Iodo-Esterification of 2-Substituted indole derivatives with Iodine Reagents

○Hiroko Wasaki[1], Katsuhiko Moriyama[1] (1. The Univ. of Chiba)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1142-4am-12]

Enantioselective Oxidative Aryl Rearrangement of α-Styryl Esters with Lewis Acid Combined Hypervalent Iodine Compound

○Honoka Kasahara[1], Yuna Nishiguchi[1], Katsuhiko Moriyama[1] (1. The Univ. of Chiba)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1142-4am-13]

Photoresponsive Cross Dehydrogenative Coupling Reaction of Tetrahydroisoquinolines with Iodide Catalyst

○Hikari Kurihara[1], Katsuhiko Moriyama[1] (1. Chiba Univesity)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1142-4am-14]

Development of σ-Hole Catalyzed Iodocyanation Reactions

○Ikumi Furusawa[1], Yan Yu[1], Takayoshi Arai[1] (1. Graduate School of Science, Chiba University)

Japanese

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11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1142-4am-15]

Synthetic Study of 1′-Epi-7′-hydroxy-2-methyltanzawaic Acid B Amide

Takatsugu Murata[1], Hisazumi Tsutsui[1], Daiki Usukura[1], Fumiya Watabe[1], ○Hiroki Okano[1], Ryo Hirata[1], Ryunosuke Shiogama[1], Yamato Kanai[1], Yuki Asahara[1], Sayaka Chogi[1], Mai Amemiya[1], Airi Shiihashi[1], Motoyuki Shimonaka[1], Isamu Shiina[1] (1. Tokyo Univ. of Science)

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1143(1143, Bldg. 11 [4F])

[E1143-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Ryosuke Masuda, Yota Sakakibara

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1143-4am-01]
Synthesis of four-membered ketones via intramolecular electrophilic addition reactions.

○Hayato Taguchi[1] (1. Hokkaido Univercity)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1143-4am-02]
Chiral amplification of aminonitriles and cyanohydrins by the sublimations

○Takumi Inoue[1], Tsuneomi Kawasaki[1] (1. Tokyo University of Science)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1143-4am-03]
Chirally and Chemically Reversible Strecker Reaction in Solid-state and Following Asymmetric Amplification (2)

○Yuya Masuda[1], Kawasaki Tsuneomi[1] (1. Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1143-4am-04]
Chiral amidine catalyzed enantioselective Strecker reaction

○Kohei Igota[1], Machida Yutaro, Kawasaki Tsuneomi[1] (1. Tokyo University of Science)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1143-4am-05]
Enantioselective addition of diisopropylzinc to the chiral organic crystal of achiral pyrimidine-5-carbaldehyde followed by asymmetric autocatalysis

○Tomohiro Ogawa[1], Daisuke Tateishi[1], Kenso Soai[1], Tsuneomi Kawasaki[1] (1. Tokyo University of Science)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1143-4am-06]
Synthetic studies of microbial hormone aveolide using biocatalytic reactions

○Keigo Sugimoto[1], Keiko Hishida[1], Takashi Monna[1], Atsushi Sakurai[1], Keigo Kakumaru[1], Ken-ichi Fuhshuku[1] (1. Meisei University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1143-4am-07]

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Development of Asymmetric Fluorocyclization of Difluoroalkenes with Concomitant Formation of a Trifluoromethy Group

○Chino Igarashi[1], Tomoya Mayumi[1], Hiromiti Egami[1], Yoshitaka Hamashima[1] (1. Grad. Sch. Pharm. Sci., Univ. of Shizuoka)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1143-4am-08]

Acceptorless Dehydrogenative Cross Coupling between Two C(sp^3)–H Bonds Enabled by Reversible Hydrogen-Atom Transfer

○Hiroki Fujita[1,2], Kosuke Ohmatsu[1,2], Takashi Ooi[1,2] (1. Grad. Sch. of Eng., Nagoya Univ., 2. WPI-ITbM, Nagoya Univ.)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1143-4am-09]

Development of Chiral Iron(II) Catalysts for Enantioselective Intramolecular Fluorine Transfer of *N*-Fluoroamides

○Yanghao Zhang[1], Shuhei Ohmura[1], Kazuaki Ishihara[1] (1. Nagoya University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1143-4am-10]

γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [1]

○Takumi Kinoshita[1], Yota Sakakibara[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1143-4am-11]

Aminomethylation of unactivated alkenes enabled by α-ammonio radical

○Shumpei Nakatsuka[1], Kosuke Terada[1], Takumi Kinoshita[1], Yota Sakakibara[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1143-4am-12]

γ-Selective fluorination of tertiary amines enabled by α-ammonio radical

○Haruka Ono[1], Kazuki Hirate[1], Shoma Chiba[1], Yota Sakakibara[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1143-4am-13]

Mechanochemical C–H fluorination using generic polymers as radical initiators

○Yuri Kamakura[1], Tsubura Endo[1], Daiyo Miura[1], Satoshi Maeda[2,3], Julong Jiang[3], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. Faculty of Science, Hokkaido University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1143-4am-14]

Synthesis of Stable Tetrazene Radical Cation Salts and Their Application to Oxidation Catalysts

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○Yusuke Sasano[1], Ayari Oshiro[1], Shohei Yoshinaga[2], Eunsang Kwon[1], Shinji Kajimoto[1], Yasuyuki Araki[1], Masaya Takahashi[1], Katsuhiko Sato[3], Naoki Shida[2], Mahito Atobe[2], Yoshiharu Iwabuchi[1] (1. Tohoku Univ., 2. Yokohama National Univ., 3. Tohoku Medical and Pharmaceutical Univ.)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[E1143-4am-15]

Photoinduced Coupling Reaction of Acylsilanes with Electrophilic Selenium Compounds

○Yuki Anami[1], Taisei Kuroki[1], Ryosuke Masuda[1], Hiroyuki Kusama[1] (1. Gakushuin University)

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

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC E1142(1142, Bldg. 11 [4F])

[E1142-4pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Yuki Saito, Keisuke Asano

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1142-4pm-01]

Sequential- and continuous-flow synthesis of tetraconazole by integrating heterogeneous catalytic processes and organometallic reactions

○Masahiro Sasaya[1], Haruro Ishitani[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1142-4pm-02]

Bead Mill-Driven Acceleration of Catalytic Depolymerization Reactions of Poly(ethylene terephthalate) under Mild Reaction Conditions

○Tomoya Kawase[1], Haruro Ishitani[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1142-4pm-03]

Multi-electron Reduction of Esters by Diazabenzoacenaphthene-based Photoredox Catalysts

○Shusuke Hattori[1,2], Shintaro Okumura[1,2], Yasuhiro Uozumi[1,2] (1. Institute for Molecular Science, 2. SOKENDAI)

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1142-4pm-04]

trans-Cyclooctenes as Scavengers of Bromine Involved in Catalytic Bromination

○Ryuichi Murata[1], Kenta Shitamichi[1], Masatsugu Hiramatsu[1], Seijiro MATSUBARA[1], Daisuke URAGUCHI[2], Keisuke ASANO[2] (1. Hokkaido Univ., 2. Kyoto Univ.)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1142-4pm-05]

A Dual Cobalt and Photoredox Catalysis for Hydrohalogenation of Alkenes

○Shotaro Shibutani[1], Kazunori Nagao[1], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ.)

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

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC E1143(1143, Bldg. 11 [4F])

[E1143-4pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Manabu Hatano, Takatsugu Murata

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1143-4pm-01]

Development of Diboronic Acid Anhydride-Catalyzed Dehydrative Amidations Using Aqueous Amine Solutions

○Hinata Iwasawa[1], Naoya Takahashi[2], Naoyuki Shimada[1] (1. The Univ. of Nihon, 2. The Univ. of Kitasato)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1143-4pm-02]

Highly Chemoselective Triflation Using *N*-Trifluoromethanesulfonylimidazole

○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
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1143-4pm-03]

Experimentally Mechanistic Study of Horner–Wadsworth–Emmons(HWE) Reaction with Weinreb Amide-type HWE Reagent

Takatsugu Murata[1], ○Hisazumi Tsutsui[1], Isamu Shiina[1] (1. Tokyo University of Science)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[E1143-4pm-04]

γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [2]

○Yota Sakakibara[1], Kosuke Hamawaki[1], Kazuki Hirate[1], Shoma Chiba[1], Kosuke Terada[1], Takumi Kinoshita[1], Kei Murakami[1] (1. Kwansei Gakuin University)

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC H933(933, Bldg. 9 [3F])

[H933-4am] 16. Natural Products Chemistry, Chemical Biology

Chair: Akihiro Ogura, Keisuke Murata

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H933-4am-01]

Synthetic Studies of Sterhirsutins A and B

○Yukiko Minami[1], Ryota Nomura[1], Akihiro Ogura[1], Ken-ichi Takao[1] (1. Faculty of Science and Technology, Keio University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H933-4am-02]

Synthetic Studies of Guttiferone A

○Misato Takimoto[1], Satoshi Nanataki[1], Akihiro Ogura[1], Ken-ichi Takao[1] (1. Faculty of Science and Technology, Keio University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H933-4am-03]

[2+2] Photocyclization and the Four-membered Ring Cleavage to Construct the Skeleton of Aconitine

○Kenji Ashidate[1], Masayoshi Abe[1], Tomoaki Watanuki[1], Hazuki Kobayashi[1], Masaya Nakata[1], Yoko Saikawa[1] (1. Keio University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H933-4am-04]

Asymmetric synthetic studies of Bisleuconothine A

○Hajime Yokoyama[1], Ryosuke Imai[1], Masahiro Miyazawa[1] (1. University of Toyama)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H933-4am-05]

Synthetic Study of Taberyunine E

○Daiki Kaneko[1], Yasukazu Sugiyama[1], Yuichirou Shirakata[1], Yuya Kusagawa[1], Noritaka Chida[1], Okamura Toshitaka[1], Sato Takaaki[1] (1. Keio Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H933-4am-06]

Total Synthesis of Carbazomycins E and F

○Yunosuke Shima[1], Yuxuan Feng[1], Kentaro Okano[1], Atsunori Mori[1,2] (1. Graduate School of Engineering, Kobe University, 2. Center for Membrane and Film Technology, Kobe University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H933-4am-07]

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Tandem Reaction-Based Stereoselective Synthesis of Cyclic Ethers

○Tsubasa Kasai[1], Keisuke Murata[1], Haruhiko Fuwa[1] (1. The university of Chuo)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[H933-4am-08]

Synthesis, Conformational Analysis, and Biological Evaluation of Exiguolide Stereoisomers

○Reika Murakami[1], Tomo Mori[1], Keisuke Murata[1], Haruhiko Fuwa[1] (1. The Univ. of Chuo)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H933-4am-09]

Synthetic Studies on iriomoteolide-1a: Configuration of Side-Chain Stereogenic Centers

○Tomohiro Obana[1], Miyuu Nakajima[1], Kazuki Nakazato[1], Hayato Nakagawa[1], Keisuke Murata[1], Masashi Tsuda[2], Haruhiko Fuwa[1] (1. Chuo University, 2. Kochi University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H933-4am-10]

Synthetic Studies on the Northern Hemisphere of Amphidinolide N

○Takumi Imamura[1], Hiroaki Imamura[1], Haruhiko Fuwa[1] (1. Chuo University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H933-4am-11]

Synthetic Study on γ-Rubromycin: Late Stage Oxidation of the Naphthalene Unit

○Shuichiro Morishita[1], Yoshio Ando[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H933-4am-12]

Studies on stereoselective synthesis of the antibiotics quatromycins

○Koichi Deyama[1], Kohei Kamatani[1], Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC H935(935, Bldg. 9 [3F])

[H935-4am] 16. Natural Products Chemistry, Chemical Biology

Chair: Hiroshi Tanaka, Tomonari Tanaka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H935-4am-01]

Synthesis of 6-sulfo sialyl Lewis X through a protecting group strategy preventing substrate aggregation

○Takuya Yoshimoto[1], Kumpei YANO[1], Yoshiyuki MANABE[1,2], Koichi FUKASE[1,2] (1. Osaka University Department of Chemistry, Graduate, 2. Forefront Research Center)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H935-4am-02]

Precisely Controlled Glycosylation Using Cage-Shaped Borate Catalyst

○Yosuke Tanaka[1], Yoshiyuki Manabe[1], Yuka Yokoyama[1], Yuka Ikinaga[1], Tatsuya Nishitani[1], Akihhito Konishi[1], Makoto Yasuda[1], Koichi Fukase[1] (1. Osaka University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H935-4am-03]

Stereoselective furanosylation using glycosyl donors possessing a 1,2-diacetal protecting group.

○Reita Watanabe[1], Hiroshi Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H935-4am-04]

Stereoselective syntheses of sialoglycan via the use of 4,5:7,9- dicarbonyl-protected *N*-glycolyl sialyl donor and application for glycan probe

○Yutaka Takeuchi[1], Hiroshi Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H935-4am-05]

Development of a Reductive Deprotection Method for 1,2-Diacetal Protecting Groups with Trichloroethyl Groups and Application to Glycosylation

○Reki Fukushima[1], Kazuya Murakami[1], Hiroshi Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H935-4am-06]

Synthesis and functional analysis of NICOL with *O*-linked glycosylation

○Kenta Nagahama[1], Toshifumi Takao[1], Daiji Kiyozumi[2], Shun Ito[1], Hironobu Hojo[1] (1. Osaka University, 2. Nagoya University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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[H935-4am-07]

Synthesis of glycoalbumin libraries to realize personalized medicine

○Akito Nunome[1], Kenshiro Yamada[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)

English

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[H935-4am-08]

Chemical Modification and Functionalization of Trehalose (VI): Development to Amide Condensation Reaction

○YANG YU[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Graduate School of Science and Engineering, Saitama University, 2. Strategic Research Center, Saitama University, 3. Advanced Institute of Innovative Technology, Saitama University)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[H935-4am-09]

Investigation of glycosyl acceptors in glycosylation catalyzed by GH84 N-acetylglucosaminidase

○Shunsuke Nakada[1], Rika Okuno[1], Kisuke Tonomura[2], Takayuki Ohnuma[2], Tamonari Tanaka[1] (1. Kyoto Inst. Tech., 2. Kindai Univ.)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[H935-4am-10]

Cleavage of amide bond by Cysteine fluoro acetylation

○Yuya Matsumoto[1], Naoki Zenmyo[1], Akihiro Yasuda[1], Shohei Uchinomiya[1], Naoya Shindo[1], Kaori Tabata[1], Akio Ojida[1] (1. Pharmaceutical Science, Kyushu University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[H935-4am-11]

Synthetic Study on Lydiamycins, Cyclic Depsipeptides Containing Piperazic Acid

○Keisuke Nabata[1], Masahito Yoshida[1], Hideo Kigoshi[1] (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[H935-4am-12]

Synthetic Study of Alotamide A, a Cyclodepsipeptide

○Taishi Okamoto[1], Masahito Yoshida[1], Hideo Kigoshi[1] (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[H935-4am-13]

Total synthesis of jamaicamide B

○Ryosuke Shigeta[1], Takahiro Suzuki[1], Kazuki Kaneko[1], Hiroaki Tanaka[1], Ibuki Haishima[1], Kanata Norio[1], Ayano Yanuma[1], Toyonobu Usuki[1] (1. Sophia University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

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[H935-4am-14]

Synthesis of the side-chain unit towards total synthesis of Dentigerumycin A

○Kakeru Miyamoto[1], Taiki Morita[1,2], Hiroyuki Nakamura[1,2] (1. School of Life Science and Technology, Tokyo institute of Technology, 2. Laboratory for Chemistry and Life Science, Tokyo institute of Technology)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[H935-4am-15]

Development of target protein labeling system using gold-nanoparticle probes

○Shione Kamoshita[1], Kaori Sakurai[1] (1. Tokyo University of Agriculture and Technology)

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC H933(933, Bldg. 9 [3F])

[H933-4pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Minami Odagi, Yoshio Ando

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H933-4pm-01]

Synthetic study of Zetekitoxin AB

○Kako Maeno[1], Ayato Nureki[1], Hayate Ishizuka[1], Kanna Adachi[1], Minami Odagi[1], Kazuo Nagasawa[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H933-4pm-02]

Synthetic studies of neosaxitoxin focusing on cyclic hydroxy guanidine.

○Shuya Shinkawa[1], Toma Osawa[1], Kako Maeno[1], Minami Odagi[1], Kazuo Nagasawa[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H933-4pm-03]

Synthetic studies on the C ring spiroguanidine of the trisguanidine alkaloid KB343

○Toma Osawa[1], Daiki Watanabe[2], Minami Odagi[1], Kazuo Nagasawa[1] (1. Tokyo university of Agriculture and Technology, 2. Tokyo university of Science)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H933-4pm-04]

Synthetic studies of Serratezomine A based on oxidative dearomatization

○Rintaro Hayakawa[1], Kengo Takibuchi[1], Taisei Matoba[1], Minami Odagi[1], Kazuo Nagasawa[1] (1. Tokyo University Agriculture and Technology)

English
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H933-4pm-05]

Design, Synthesis, and Chiroptical Properties of Mid-sized Molecules Utilizing C_2 Symmetric Alkaloidal Scaffolds

○Fumi Oki[1], Tasuku Honda[1], Hiroki Oguri[1] (1. The Univ. of Tokyo)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[H933-4pm-06]

Synthetic Study on Glenthamine A: Construction of the Bicyclic Skeleton

○Sota Ajima[1], Yoshio Ando[1], Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H933-4pm-07]

Efficient synthesis of abiesanol A, C_2-symmetric flavan dimer

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○Nayuta Sonoda[1], Yusuke Kawada, Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[H933-4pm-08]

Continuous flow synthesis of flavan trimers

○Naoki Narita[1], Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[H933-4pm-09]

Au-Catalyzed Intramolecular Hydroamination of Alkynic Benzamides for the Synthesis of Pyrrolidine Derivatives

○Hayato Nakagawa[1], Akane Yamaji[1], Haruhiko Fuwa[1] (1. Chuo University)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[H933-4pm-10]

Concise Total Synthesis of Fasicularin

○Yuki Takatori[1], Haruhiko Fuwa[1] (1. Chuo University)

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Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC H935(935, Bldg. 9 [3F])

[H935-4pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Daisuke Takahashi, Kaname Sasaki

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H935-4pm-01]

N-terminal modification of polypeptides via metal-mediated aldol reaction

○Kengo Hanaya[1], Yuki Wada[2], Masaki Kawano[2], Kazuaki Taguchi[1], Kazuaki Matsumoto[1], Shuhei Higashibayashi[1], Takeshi Sugai[1] (1. Keio University, 2. Tokyo Institute of Technology)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H935-4pm-02]

In Vitro Selection of Macrocyclic Peptides Containing α-Hydrazino Acid for Exploration of Drug Candidates

○Satomi Matsumoto[1], Takayuki Katoh[1], Hiroaki Suga[1] (1. The University of Tokyo)

English
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[H935-4pm-03]

Intramolecular Hydrogen-Bonding-Accelerated 2,5-Diketopiperazine Formation for Facile Synthesis of Tag-Attached Peptide Thioester

○Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H935-4pm-04]

Mechanism of phase separation of UGGAA repeat RNA induced by photoswitchable RNA binding ligands

○Yusuke Fujiwara[1,2], Tomonori Shibata[1,2], Chikara Dohno[1,2], Kazuhiko Nakatani[1,2] (1. SANKEN, Osaka University, 2. CREST, JST)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[H935-4pm-05]

Preparation and Immunological Evaluation of Lipid Nanoparticle-based Self-adjuvanting Cancer Vaccine

○Keita Ito[1], Yoshiyuki Manabe[1,2], Shino Oshima[3], Yoshie Kametani[3], Masatoshi Maeki[4], Manabu Tokeshi[4], Koichi Fukase[1,2] (1. Osaka Univ., 2. Forefront Research Center, 3. Tokai Univ., 4. Hokkaido Univ.)

English
3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC
[H935-4pm-06]

Chemical synthesis and functional evaluation of acetic acid bacterial lipopolysaccharide partial structures

○Haruki Yamaura[1], Atsushi Shimoyama[1], Koichi Fukase[1] (1. Osaka university)

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English

3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC

[H935-4pm-07]

Chemical synthesis of tetraantennary sialyl *N*-glycans

○Kumpei Yano[1], Yoshiyuki Manabe[1,2], Koichi Fukase[1,2] (1. Graduate School of Science, Osaka University, 2. Project Research Center for Fundamental Sciences, Osaka University)

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

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC H934(934, Bldg. 9 [3F])

[H934-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Kei Nishida, Yuichiro Aiba

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H934-4am-01]

Radical ring-opening reaction of cyclic ketoxime catalyzed by aldoxime dehydratase

○Haruka Nishiwaki[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Graduate School of Engineering, Osaka University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H934-4am-02]

Photo Radical Coupling Reactions between Pyruvate and N-acyloxyphthalimide Catalyzed by FAD/ThDP-Dependent Enzymes

○Yuto Adachi[1], Shuto Fujisawa[1], Kato Shunsuke[1], Hayashi Takashi[1] (1. Osaka university)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H934-4am-03]

Photoinduced Imine Reductions Catalyzed by an Artificial Photoredox Enzyme Constructed by Incorporating an Organic Photosensitizer into a Protein Matrix

○Ryusei Kano[1], Yuki Uchida[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H934-4am-04]

Photoinduced methane oxidation using particulate methane monooxygenase and photosystem II reconstituted in liposome

○Yuta Noto[1], Hidehiro Ito[1], Toshiaki Kamachi[1] (1. Tokyo Institute of Technology)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H934-4am-05]

Structural basis for the substrate inhibition mechanism of the ciliate arginine kinase

○Chihaya Baba[1], Daichi Yano[1], Yumeto Otsuka[1], Yoshino Kojima[1], Koji Uda[1], Tomohiko Suzuki[1], Shigeru Sugiyama[1] (1. kochi university)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H934-4am-06]

Creation of artificial RNA-binding proteins

○Yasuharu Yamabe[1], Kouhei Ukida[1], Kenta Yoshioka[1], Keisuke Nagao[1], Hayata Mouri[1], Tomoaki Mori[1], Koichi Mori[1], Takashi Sera[1] (1. Okayama University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H934-4am-07]

Orthogonal DNA modification of proteins utilizing multiple replication initiator proteins

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○Chika Komatsuzaki[1], Kei Nishida[1], Eiry Kobatake[1], Masayasu Mie[1] (1. Tokyo Institute of Technology)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[H934-4am-08]

Lipidation of antibodies by microbial transglutaminase

○Mari Takahara[1], Noriho Kamiya[2] (1. National Institute of Technology, Kitakyushu College, 2. Graduate School of Engineering, Kyushu University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[H934-4am-09]

Development of Decoy Molecules Introduced Dicarboxylic Acids That Induce Oxidation of Small Molecules by Cytochrome P450BM3

○Megumi Ishigami[1], Shinya Ariyasu[1], Chie Kasai[1], Yuichiro Aiba[1], Hiroshi Sugimoto[2], Osami Shoji[1] (1. Nagoya Univ., 2. SPring-8, RIKEN)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H934-4am-10]

CO_2 Fixation Reaction With *Thermoplasma acidophilum* Malic Enzyme

○Yuri Oku[1], Tomoko Matsuda[1] (1. Tokyo Institute of Techonology)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H934-4am-11]

Development of enzymatic lactate synthesis system using acetaldehyde and CO_2 as raw materials

○Kazuma Suehiro[1], Yutaka Amao[1] (1. Osaka Metropolitan University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H934-4am-12]

Construction and characterization of a NAD-dependent dehydrogenase which was site-specifically modified with electron acceptor

○Kurea IKEGAI[1], Junko Okuda[1,2], Truc Thanh Tran[2], Mika Hatada[2], Ryutaro Asano[1], Kazunori Ikebukuro[1], Koji Sode[2], Wakako Tsugawa[1] (1. Tokyo university of agriculture and technology, 2. University of North Carolina at Chapel Hill)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H934-4am-13]

Protein-protein interaction-based function regulation for flexible proteins: Applicability of monobodies

○Ibuki Nakamura[1], Hiroshi Amesaka[2], Mizuho Hara[2], Keisuke Okamoto[2], Kento Yonezawa[1], Hironari Kamikubo[1], Shun-ichi Tanaka[2], Shun Hirota[1], Takashi Matsuo[1] (1. Div. Mat. Sci., NAIST, 2. Department of Biomolecular Chemistry, Kyoto Prefectural University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[H934-4am-14]

Discrimination of proteases with similar substrate selectivity by substrates incorporating unnatural amino acids

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○Shun Honjo[1], Yuuki Yamawaki[1], Tamaki Kato[1] (1. Kyushu Institute of Technology)

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

Thu. Mar 21, 2024 9:30 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:40 AM UTC H932(932, Bldg. 9 [3F])

[H932-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Kazumitsu Onizuka, Takanori Oyoshi

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H932-4am-01]

Synthesis of G4-PROTAC ligand for degradation of G-quadruplex binding proteins

○Yuma Tanaya[1], Rena Nohara[1], Ma Yue[2], Kazuo Nagasawa[1], Masayuki Tera[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H932-4am-02]

Degradation of intracellular G-quadruplex binding proteins by G4-PROTAC ligands

○Rena Nohara[1], Yuuma Tanaya[1], Yue Ma[2], Kazuo Nagasawa[1], Masayuki Tera[1] (1. Department of Biotechnology and Life Science, Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H932-4am-03]

Selective photo-crosslinking of G-quadruplexes by a dual-recognition ligand

○Sayuri Shimada[1], Ryo Ishikawa[1], Kazuki Yanagida[1], Yue Ma[2], Shogo Sasaki[1], Kazuo Nagasawa[1], Masayuki Tera[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H932-4am-04]

Evaluation of chemical reactions in droplets with macrocyclic hexaoxazole-type G-quadruplex ligands

○Akari Oyama[1], Shogo Sasaki[1], Masayuki Tera[1], Kazuo Nagasawa[1] (1. Tokyo University of Agriculture and Technology)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H932-4am-05]

Synthetic studies of the selective G4 ligands using click chemistry

○Yuri Shimasawa[1], Shogo Sasaki[1], Yue Ma[2], Masayuki Tera[1], Kazuo Nagasawa[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Tokyo Medical and Dental University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[H932-4am-06]

Synthesis of light-up type fluorescent ligands for topology selective and dynamic detection of G-quadruplexes

○Haruki Fujita[1], Naruyuki Watatani[1], Syogo Sasaki[1], Yue Ma[2], Masayuki Tera[1], Kazuo Nagasawa[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental

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University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H932-4am-07]

Novel macrocyclic pyridone pentamers as G-quadruplex (G4) ligands

○Emina Isobe[1], Takayoshi Arai[1], Keisuke Iida[1] (1. Chiba University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H932-4am-08]

Photo-decomposition Mechanism of Quadruplex DNA Using Anionic Phthalocyanines

○Atsuya Momotake[1], Yusuke Odahara[1], Yasuhiko Yamamoto[1] (1. Univ. of Tsukuba)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H932-4am-09]

Investigation of pull-down unit position for large-scale analysis of RNA alkylation

○Ping-Yun Lan[1,2], Kazumitsu Onizuka[1,2], Yutong Chen[1,2], Emi Miyashita[3], Kaoru R. Komatsu[3], Hirohide Saito[3], Fumi Nagatsugi[1,2] (1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Department of Chemistry, Graduate School of Science, Tohoku University, 3. CiRA, Kyoto University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H932-4am-10]

Synthesis and evaluation of a turn-on fluorescent probe targeting UGGAA repeats

○Shoei Harada[1], Tomonori Shibata[1], Kazuhiko Nakatani[1] (1. Osaka Univ., SANKEN)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[H932-4am-11]

Analysis of G-quadruplex Binding Protein if EWS for Transcriptional Regulation of TERRA

○Wakana Matsudaira[1], Luthfi Lulul Ulum[2], Akinori Ishihara[1], Takanori Oyoshi[1,2,3] (1. Graduate School of integrated Science and Technology, Shizuoka University., 2. Graduate School of Science and Technology, Shizuoka University., 3. Research Institute of Green Science and Technology, Shizuoka University.)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[H932-4am-12]

Development of the functional G4 DNA binding protein regulating transcription

○Natsuki Shibata[1], Maiko Yamanashi[2], Luthfi Lulul Ulum[3], Akinori Ishihara[2], Takanori Oyoshi[2,3,4] (1. Faculty of Science Shizuoka University, 2. Graduate School of Integrated Science and Technology, Shizuoka University, 3. Graduate School of Science and Technology, Shizuoka University, 4. Research Institute of Green Science and Technology, Shizuoka University)

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

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC H934(934, Bldg. 9 [3F])

[H934-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Shun Hirota, Teruyuki Komatsu

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H934-4pm-01]

Preparation of an amyloid fibril with norbornene-type monomers and ring-opening metathesis polymerization on the fibril

○Hiroki Uchida[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H934-4pm-02]

Genetic Engineering of Acetolactate Synthase for Radical Coupling Reaction between α-Keto acid and α-Bromo ester

○Shuto Fujisawa[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Graduate School of Engineering, Osaka University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H934-4pm-03]

Modification of Cytochrome P450 Containing Co Porphyrin with a Photosensitizer toward an Artificial Metalloenzyme Catalyzing Photoinduced Carbon Dioxide Reduction

○Taishu Kojima[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H934-4pm-04]

Genetic and chemical modifications of a hexameric hemoprotein toward an artificial light harvesting system

○Shohei Katsumoto[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H934-4pm-05]

Construction of porous crystals with supramolecular structures using heme protein cyclic trimers

○Mizuho Kinuyama[1], Kodai Fujiwara[1], Tsuyoshi Mashima[1], Naoya Kobayashi[1], Hideaki Ogata[2], Shun Hirota[1] (1. NAIST, 2. University of Hyogo)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H934-4pm-06]

Construction of human cytochrome *c* dimer by hinge loop mutation and its intracellular effect

○Kotori Ohta[1], Kodai Fuijwara[1], Tsuyoshi Mashima[1], Naoya Kobayashi[1], Kenichi Kanai[1], Takaaki Matsui[1], Yasumasa Bessho[1], Shun Hirota[1] (1. NAIST)

Japanese

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2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[H934-4pm-07]

Effects of ions on the formation and stability of cytochrome *c* dimers

○Kodai Fujiwara[1], Michiko Ryuuzaki[1], Masaru Yamanaka[1], Tsuyoshi Mashima[1], Naoya Kobayashi[1], Shun Hirota[1] (1. NAIST)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[H934-4pm-08]

Synthesis of Poly(2-alkyl-2-oxazoline)-Conjugated Serum Albumins

○Ryota Hattori[1], Junya Fujisawa[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[H934-4pm-09]

Synthesis of Poly(2-alkyl-2-oxazoline)-Conjugated Hemoglobins as an Artificial O_2 Carrier

○Ryuhei Wakabayashi[1], Kota Ishii[1], Teruyuki Komatsu[1] (1. Chuo university)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[H934-4pm-10]

Synthesis and Photosterilization Ability of Zinc-Phthalocyanine-Substituted Myoglobin-Albumin Fusion Protein

○Aoi Egawa[1], Mizuki Funamoto[1], Taiga Yamada[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[H934-4pm-11]

Synthesis of Polyoxazoline-Covered Hemoglobin Nanoparticle as an Artificial O_2 Carrier

○Tomoka Araki[1], Natsumi Kohyama[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[H934-4pm-12]

Nanopore formation and molecular transport of β-barrel porin

○Toshiyuki Tosaka[1], Koki Kamiya[1] (1. Grad. Sch. Sci. & Tech. Gunma Univ.)

Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[H934-4pm-13]

In silico panning of peptide ligands using docking simulation and molecular dynamics simulation

○Haruka Kawai[1], Daimei Miura[1], Sheng Tong[1], Ryutaro Asano[1], Tsugawa Wakako[1], Fujita Shoko[1], Ryuji Kawano[1], Takatsugu Hirokawa[2], Kaori Tsukakoshi[1], Kazunori Ikebukuro[1] (1. Tokyo University of Agriculture and Technology, 2. University of Tsukuba)

Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[H934-4pm-14]

Development of an oxidative protein folding promoter using host-guest interactions

○Koki Suzuki[1], Ryoya Nojiri[1], Tomohide Saio[2], Takahiro Muraoka[1,3] (1. Tokyo University of Agriculture and Technology, 2. Tokushima University, 3. KISTEC)

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

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC H931(931, Bldg. 9 [3F])

[H931-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Akihiro Iahiwata, Hidenori Okamura

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[H931-4am-01]

Synthesis of new compounds composed of organic acids and amines with hair treatment effects

○Kohtaro Katayama[1], Hiroyuki Miyamoto[1], Yuji Mochizuki[2], Natsumi Shin[2], Shoko Yamazaki[3], Hiroki Hotta[1,4], Yoshio Tsujino[4] (1. Graduate School of Maritime Sciences, Kobe University, 2. ROHTO Pharmaceutical Co., Ltd. , 3. Nara University of Education , 4. Graduate School of Science, Technology and innovation, Kobe University)

Japanese
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[H931-4am-02]

The thieno[2,3-*b*]pyridine derivative that is a neural differentiation inducer and a fluorescent molecule

○Kento Sonoda[1], Kazuya Asao[1,2], Shin-ichi Kawaguchi[1,2], Yoshinori Kawazoe[1,2] (1. Faculty of Agriculture, Saga University, 2. Graduate School of Advanced Health Sciences, Saga University)

Japanese
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[H931-4am-03]

Supramolecular hydrogelation triggered by gold catalysis

○Tomoya Yamamoto[1,2], Akiko Nakamura[2], Akari Mukaimine[2], Katsunori Tanaka[2,3] (1. Osaka University, Department of Engineering, 2. RIKEN, Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory, 3. Tokyo Institute of Technology, School of Materials and Chemical Technology)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[H931-4am-04]

NIR Fluorescence analysis of the trypsin enzyme using unsymmetrical squaraine dye-peptide conjugate.

○PRIYANKA Priyanka[1,2], Shekhar Gupta[1], Tamaki Kato[1] (1. Kyushu Institute of Technology,Japan, 2. Kyushu Institute of Technology, Japan)

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[H931-4am-05]

Near Infrared Fluorescent Detection of Protease Activity using Peptide-Bound Squaraine Dye

○Shekhar Gupta[1], Priyanka Balyan [1], Sai Kiran Mavileti[1], Shyam Sudhir Pandey[1], Tamaki Kato[1] (1. Kyushu Institute of Technology)

English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[H931-4am-06]

Internal radioisotope therapy utilizing [3+2] cycloaddition reaction with cancer metabolites

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○Yudai Ode[1], Akihiro Ishiwata[2], Ambara Rachmat Pradipta[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)

English

11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[H931-4am-07]

Development of a new screening system to discover RNA-binding small molecules for RNA-targeting therapeutics

○Ryosuke Nagasawa[1,2], Kazumitsu Onizuka[1,2], Ryohei Iwata[1,2], Komatsu Richard Kaoru[3,4], Emi Miyashita[3,4], Sayaka Dantsuji[4], Hirotaka Murase[1,2], Mamiko Ozawa[1], Hirohide Saito[3], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku Univ., 2. Graduate School of Science, Tohoku Univ., 3. CiRA, Kyoto Univ., 4. xFOREST Therapeutics)

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

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC H936(936, Bldg. 9 [3F])

[H936-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Nobuhiko Hosono, Norifumi Kawakami

English
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[H936-4am-01]

Characterization of protein nanocage TIP60 with pyrene-modified interior surface

○Maika Yamashita[1], Kenji Miyamoto[1], Norifumi Kawakami[1] (1. Keio University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[H936-4am-02]

Construction of histidine clusters in a ferritin cage for the oxidase-mimetic catalysis

○Jiaxin Tian Tian[1], Basudev Maity[1], Tiezheng Pan[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[H936-4am-03]

Removing Denatured Proteins by Selective Adsorption in Nanopores

○Hirotaka Taketomi[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[H936-4am-04]

Optical manipulation of microtubule structures by Tau-derived peptide-fused light-responsive tetrameric protein

○Soei Watari[1], Hiroshi Inaba[1], Takashi Iwasaki[2], Akira Kakugo[3], Kazunori Matsuura[1] (1. Grad. Sch. of Eng., Tottori Univ., 2. Grad. Sch. of Agric. Sci., Tottori Univ., 3. Grad. Sch. of Sci., Kyoto Univ.)

Japanese
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[H936-4am-05]

In-cell self-assembly of fluorescent protein-modified artificial viral capsid

○Kentarou Sakamoto[1], Yuka Yamamoto[1], Hiroshi Inaba[1], Kazunori Matsuura[1] (1. Grad. Sch. of Eng., Tottori Univ.)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[H936-4am-06]

Construction of enveloped viral replica equipped with spike protein derived from SARS-CoV-2

○Hiroto Furukawa[1], Keisuke Nakamura[2], Hiroshi Inaba[1], Yoshihiro Sasaki[2], Kazunari Akiyoshi[2], Kazunori Matsuura[1] (1. Grad. Sch. of Eng., Tottori Univ., 2. Grad. Sch. of Sci., Osaka Univ.)

English
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[H936-4am-07]

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Accurate Prediction of Protein pK_a by Geometric Deep Learning

○Shijie Xu[1], Akira Onoda[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

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

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC H931(931, Bldg. 9 [3F])

[H931-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Kunihiko Morihiro, Yukiko Kamiya

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H931-4pm-01]

Developing the intracellular FRET imaging approach to elucidate the mechanism of anti-miRNA oligonucleotides

○Hongyu Zhu[1], Yukiko Kamiya[1,2], Hiroyuki Asanuma[1] (1. Nagoya University , 2. Kobe Pharmaceutical University)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H931-4pm-02]

Development of Anti-miR-21 Oligonucleotide by Acyclic Nucleic Acids

○Yukiko Kamiya[1,2], Fuminori Sato[2], Hiroyuki Asanuma[2] (1. Kobe Pharmaceutical University, 2. Nagoya University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H931-4pm-03]

Reversible optical control of receptor activity by azobenzene base-containing DNA aptamer.

○Masahiro Wakano[1], Keiji Murayama[2], Ryosuke Ueki, Hiroyuki Asanuma[2], Shinsuke Sando[1] (1. Graduate School of Engineering, The University of Tokyo, 2. Graduate School of Engineering, Nagoya University)

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H931-4pm-04]

The influence of methylated DNA on DNA polymerase with strand displacement ability

○Mizuki Tomizawa[1], Kiwako Watanabe[1], Kaori Tsukakoshi[1], Kazunori Ikebukuro[1] (1. Tokyo University of Agriculture and Technology)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H931-4pm-05]

Vinyl-quinazolione derivatives-based RNA alkylation and the single-nucleotide resolution analysis by next generation sequencing

○Yutong Chen[1,2], Kazumitsu Onizuka[1,2], Kaoru Richard Komatsu[3], Emi Miyashita[3,4], Kaho Maeta[3], Hirohide Saito[4], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku University, 2. Department of Chemistry, Graduate school of Science, Tohoku University, 3. xFOREST Therapeutics, 4. CiRA, Kyoto University)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[H931-4pm-06]

Development of cancer-selective DNA aptamer using weakly acidic microenvironment-responsive artificial nucleobase

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○Yuyuan Chen[1], Kunihiko Morihiro[1], Yui Nemoto[1], Akito Ichimura[1], Ryosuke Ueki[1], Shinsuke Sando[1], Akimitsu Okamoto[1] (1. The University of Tokyo)

Japanese

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[H931-4pm-07]

The Impact of Linker Structure and the Number of Fluorine-containing Functional Groups of Nucleic Acids on Cellular Uptake and siRNA Knockdown Efficacy

○Masako Takatsu[1], Kunihiko Morihiro[1], Yu Ota[1,2], Kosuke Aikawa[1], Takashi Okazoe[1,2], Akimitsu Okamoto[1] (1. The Univ. of Tokyo, 2. AGC Inc.)

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

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC H932(932, Bldg. 9 [3F])

[H932-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Eiji Nakata, Tomohiro Doura

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H932-4pm-01]

Development and structural analysis of subtype-selective photoresponsive ligands for adenosine A_{2A} receptor

○Harufumi Suzuki[1], Tomohiro Doura[1], Tsuyoshi Araya[2], Hidetsugu Asada[2], So Iwata[2], Shigeki Kiyonaka[1] (1. Nagoya University, 2. Kyoto University)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H932-4pm-02]

A novel imaging probe to quantify AMPA receptors trafficking during synaptic plasticity

○Kyohei Soga[1], Akihiro Shibata[1], Hansel Adriel[2], Takaaki Fujiwara[2], Eriko Nango[2,3], Shigeki Kiyonaka[1] (1. Grad. School. Eng. Nagoya University, 2. IMRAM, Tohoku University, 3. RIKEN SPring-8)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H932-4pm-03]

Visualization of lipid droplets in cells and tissues by using red and deep-red fluorescent molecules based on BODIPYs

○Toshitada Yoshihara[1], Risa Uda[1], Suzuna Iijima[1], Mayuko Shimanuki[1], Shuichi Shiozaki[1] (1. Gunma Univ.)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[H932-4pm-04]

Small allosteric disulfide/diselenide reagents may regulate cellular redox homeostasis

○Rumi Mikaimi[1], Shingo Kanemura[2], Masaki Okumura[3], Kenta Arai[1] (1. Tokai Univ., 2. Kwansei Gakuin Univ., 3. Tohoku Univ.)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H932-4pm-05]

Monitoring of RNA motility in living cells using fluorescence/bioluminescence and "mPUM technology"

○Hideaki Yoshimura[1], Masatoshi Eguchi[1], Yoshibumi Ueda[1], Takeaki Ozawa[1] (1. The University of Tokyo)

Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[H932-4pm-06]

Distribution analysis of thiol metabolites in the frozen tissue by using fluorescent labeling reagent coated TLC plate

○Tatsuya Nishihara[1], Gaku Suzuki[1], Koki Nishida[1], Rika Tsukame[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

Japanese

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3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[H932-4pm-07]

Development of new compounds using for detecting mismatch DNA

○Fumie Takei[1], Naoki Yamada[1], Sumiyo Hiruma[1] (1. National Defence Medical Colledge)

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

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC H936(936, Bldg. 9 [3F])

[H936-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Hiroshi Nonaka, Tomonori Tamura

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H936-4pm-01]

Solid-Phase Synthesis of Diketopiperazine Thioester Peptide for High-throughput Chemical Protein Synthesis

○Yuya Nakajima[1], Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Graduate School of Engineering, Nagoya University, 2. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H936-4pm-02]

Elucidation of the association character and 3D domain-swapped structure of a tetramerizing antibody light chain

○Takahiro Sakai[1], Shohei Yamaguchi[1], Tsuyoshi Mashima[1], Naoya Kobayash[1], Lian Duan[2], Ryo Fujiki[2], Hengphasatporn Kowit[2], Yasuteru Shigeta[2], Hideaki Ogata[3], Emi Hifumi[4], Taizo Uda[5], Shun Hirota[1] (1. Grad. Sch. Sci. Tech., NAIST, 2. Cent. Comp. Sci., Univ. Tsukuba, 3. Grad. Sch. Sci., Univ. Hyogo, 4. Inst. Res. Mgmt., Oita Univ, 5. Nano-tech Lab., ISIT)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H936-4pm-03]

Development of micelles bearing thiol groups to promote oxidative protein folding under crowded environment

○Mai Kitamura[1], Takahiro Muraoka[1,2] (1. Tokyo University of Agriculture and Technology, 2. KISTEC)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H936-4pm-04]

Chemogenetic Control of the AMPA Receptor Activity Using the Moleculer Stopper Approach

○Yuta Deen Miura[1], Kento Ojima[1,2], Osamu Miyashita[3], Naotaka Tsutsumi[4], Itaru Hamachi[2], Atsuko Yamashita[4], Shigeki Kiyonaka[1] (1. Nagoya Univ., 2. Kyoto Univ., 3. RIKEN, 4. Okayama Univ.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H936-4pm-05]

Development of N-acyl-N-aryl sulfonamide warheads for covalent protein modification and inhibition

○Masaharu Kawano[1], Shunsuke Murakawa[1], Dai Sugihara[2], Tomonori Tamura[1], Itaru Hamachi[1,3] (1. Graduate School of Engineering, Kyoto University, 2. Kyoto University, 3. ERATO JST)

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Academic Program [Oral A] | 18. Polymer：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC D341(341, Bldg. 3 [4F])

[D341-4am] 18. Polymer

Chair: Masayasu Totani, Yutaka Ohsedo

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[D341-4am-01]

Identification and Classification of Water-soluble Polymers Using Fluorophore-modified Proteins

○Souki Wakabayashi[1], Shion Hasegawa[1], Toshiki Sawada[1], Takeshi Serizawa[1] (1. Sch. Mat. & Chem. Tech., Tokyo Tech)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[D341-4am-02]

Control of the Capability for the Synthesis of Silver Nanoparticles of Genetically Engineered Filamentous Viruses

○Yuta Mibe[1], Takeshi Serizawa[1], Toshiki Sawada[1] (1. Sch. Mat. & Chem. Tech., Tokyo Tech)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[D341-4am-03]

Controlled Crystal Growth of Hydroxyapatite on Oriented Collagen-Peptide Composite Films for Bone Repair Materials and Its Structural Analysis

○Aika Hashizume[1], Shogo Matsubara[1], Masahiro Higuchi[1] (1. Grad. Sch. of Eng. Nagoya Inst. of Tech.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[D341-4am-04]

Synthesis of Lysine- and Isoleucine-derived Vinyl Copolymers and their cell adhesion property

○Shoma Tsukiyama[1], Shin-nosuke Nishimura[1], Tomoyuki Koga[1] (1. doshisha University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[D341-4am-05]

Synthesis of self-assembling peptide-grafted polyester

○Miki Hasegawa[1], Shin-nosuke Nishimura[1], Tomoyuki Koga[1] (1. Doshisha University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[D341-4am-06]

Construction of Chimeric Artificial Nucleic Acids (CANA) toward Pancreatic Cancer Treatments by Inhibition of Transcription Factor BACH1 III: Construction of CANA design strategy based on *in vitro* analysis

Yuto Horiuchi[1], Yuki Igarashi[1], Masahito Inagaki[4], Kazuyo Matsumoto[1], Mika OMURA[3], Yasuyuki Araki[1], Yu Mikame[2], Masaki Nishijima[1], Asako Yamayoshi[2], Ikuhiko Nakase[3], ○Takehiko Wada[1] (1. Tohoku University, 2. Nagasaki University, 3. Osaka Metropolitan University, 4. Nagoya University)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[D341-4am-07]
Synthesis and antibacterial properties of cationic cellulose (I) −Effect of degree of substitution−

○Kohei Obuchi[1], Saito Miki[1], Saito Tamao[1], Takeoka Yuko[1], Rikukawa Masahiro[1], Fujita Masahiro[1] (1. Sophia University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[D341-4am-08]
Hydrophobization of chitin nanofibers by enzymatic grafting of partially 2-deoxygenated amyloses

○Naoki Yamamoto[1], Masayasu Totani[1], Jun-ichi Kadokawa[1] (1. Kagoshima university)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[D341-4am-09]
Synthesis of Glucosamino-2-Deoxyglucan by Enzymatic Copolymerization

○Yuta Miyahara[1], Masayasu Totani[1], Jun-ichi Kadokawa[1] (1. Kagoshima University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[D341-4am-10]
Development of cellulose materials with high strength by photopolymerization (I)- Effect of amount of ionic liquid monomer and cellulose on strength-

○Keito Matsumoto[1], Arata Matsui[1], Yuko Takeoka[1], Masahiro Rikukawa[1], Masahiro Fujita[1] (1. Sophia Univ.)

English
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[D341-4am-11]
Synthetic Studies of Zwitterionic Modified Cyclodextrins (VI)
Linker introduction for fluorescent group modification

○Kanta Koizumi[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Grad. Sci.&Engin. Saitama University, 2. Adv. Inst. Innov. Tech. Saitama University, 3. Strategic Res. Ctr. Saitama University)

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[D341-4am-12]
Synthesis of novel amylase substrates using FRET effect (VI): Synthesis of glycopolymers as amylase substrate

○Yuki Yamamoto[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Grad. Sch. Sci. & Engin., Saitama University, 2. Adv. Inst. Innov. Tech., Saitama University, 3. Strategic Res. Ctr., Saitama University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[D341-4am-13]
Construction and Evaluation of Cancer Cell Selective Drug Delivery System III: Development pancreatic cancer of a selective drug delivery system to suppress the malignant progression

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○Hirari Kato[1], Ryota Azuma, Yasuyuki Araki[2], Masaki Nishijima[2], Mitsuyo Matsumoto[3], Ikuhiko Nakase[4], Mika Oomura[4], Asako Yamayoshi[1], Kazuhiko Igarashi[1] (1. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University , 2. Grduate School of Medicine, Tohoku University, 3. Graduate School of Medicine, Dentistry and Pharmacy, Nagasaki University , 4. Graduate School of Science)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[D341-4am-14]

Dehydration Condensation of Chitin Oligosaccharides by Activated Carbon Catalysts

○Tatsuki Yasuda[1], Takuya Sagawa[1], Mineo Hashizume[1] (1. Tokyo University of Science)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[D341-4am-15]

Synthesis of polyaniline/polyelectrolyte gel composites composed and its electronic conductive properties

○Ami KANEIZUMI[1], Yutaka OHSEDO[2] (1. Grad. Sch. HCE., NWU, 2. Fac., NWU)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[D341-4am-16]

Enumerations of the structural isomers of organic commodity polymers

Gikyo Usuki[1], Takuro Tsutsumi[1,2], Kohei Hasebe[1], Masato Kobayashi[1,2,3], Keitaro Matsuoka[1,2], Tetsuya Taketsugu[1,2,3], ○Kazuki Sada[1,2] (1. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ., 2. Fac. of Sci., Hokkaido Univ., 3. WPI-ICReDD, Hokkaido Univ.)

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Academic Program [Oral B] | 18. Polymer：Oral B

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC D342(342, Bldg. 3 [4F])

[D342-4am] 18. Polymer

Chair: Hiroki Fukumoto, Masayoshi Higuchi

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[D342-4am-01]

Olefin Polymerization using Aluminum Complex Catalysts

○Nanako Kimura[1], Daisuke Takeuchi[1] (1. Hirosaki University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[D342-4am-02]

Substituent effects of ether-functionalized propylenes on scandium-catalyzed copolymerization with ethylene

○Mingjun Chi[1,2], Hao Wang[2], Masayoshi Nishiura[2], Lin Huang[2], Haoran Zhang[2], Zhaomin Hou[1,2] (1. Saitama University, 2. RIKEN)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[D342-4am-03]

Synthesis and Application of Polymers Containing Highly Alkaline-resistant Triarylsulfonium.

○Tomohiro Imai[1], Ryoyu Hifumi[1], Shinsuke Inagi[1], Ikuyoshi Tomita[1] (1. Tokyo Institute of Technology)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[D342-4am-04]

Synthesis of functional polyesters containing cleavable linkages and AIE luminogen via Passerini-type multicomponent polymerizations

○Chih-Feng HUANG[1], Li-Chieh CHOU[1], Yi-Shen HUANG[1] (1. National Chung Hsing University)

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[D342-4am-05]

One-pot synthesis of hydroquinone-polymers from benzene with hydrogen peroxide

○Hideki Sugimoto[1], Kenshin Miyata[1], Akiyuki Nakano[2], Hideyuki Higashimura[2], Shinobu Itoh (1. Osaka University, 2. Okayama University of Science)

English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[D342-4am-06]

A New Synthetic Approach of Metallosupramolecular Polymer and its Electrochromic Application

○Satya Ranjan Jena[1], Masayoshi HIGUCHI[1], Chih-Wei Hu[1] (1. National Institute for Materials Science)

Japanese
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[D342-4am-07]

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Synthesis and Optical Properties of π-Conjugated Polymers with Fluorine-containing Benzodithiophene

○Hidetoshi Okuzaki[1], Sera Sato[1], Tomohiro Agou[2], Toshio Kubota[1], Hiroki Fukumoto[1] (1. Graduate School of Science and Engineering, Ibaraki University, 2. Graduate School of Science, University of Hyogo)

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Academic Program [Oral B] | 18. Polymer：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC D341(341, Bldg. 3 [4F])

[D341-4pm] 18. Polymer

Chair: Keitaro Matsuoka, Tatsuya Nishimura

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[D341-4pm-01]

Clarification of LCST-type thermo-responsiveness based on systematically evaluation of water soluble soft nylons

○Akari Sugano[1], Keitaro Matsuoka[1,2], Kazuki Sada[1,2] (1. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ., 2. Fac. of Sci., Hokkaido Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[D341-4pm-02]

Synthesis of ZnO nanorods grafted with liquid-crystalline polymers by controlled radical polymerization and their alignment behavior

○Kaho Nakano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[D341-4pm-03]

Mechano-responsive supramolecular hydrogel driven by stretch induced phase separation

○Sooyeon Noh[1], Akihide Sugawara[1], Yoshinori Takashima[1], Hiroshi Uyama[1] (1. Osaka Univ.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[D341-4pm-04]

Establishment of Massive Fabrication of Water-Repellent Nanosheets as and Their Evaluation for Next-Generation Imaging Tools.

○Rai Uchida[1], Tatsuya Hiratsuka[2], Takuto Aoki[3], Yosuke Okamura[1,3,4] (1. Grad. Sch. of Eng., Tokai Univ., 2. Bachelor Sch. of Eng., Tokai Univ., 3. Grad. Sch. of Sci. & Tech., Tokai Univ., 4. Micro/Nano Tech. Center, Tokai Univ.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[D341-4pm-05]

Stress-strain sensing using carbon composites with movable cross-links

○Ikura Ryohei[1,2], Kota kajimoto[1], Junsu Park[1,2], Yoshinori Takashima[1,2,3] (1. Grad. Sch. of Sci., Osaka Univ., 2. FRC, Osaka Univ., 3. ICS-OTRI, Osaka Univ.)

Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[D341-4pm-06]

Triangular nanoplate formed from hybrids of Dawson-type polyoxometalates with amphiphilic diblock polypeptides and their catalytic properties.

Kai Miyamoto[1], ○Keita Kuroiwa[1] (1. Sojo University)

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Academic Program [Oral A] | 19. Colloid and Interface Chemistry：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC A1443(1443, Bldg. 14 [4F])

[A1443-4pm] 19. Colloid and Interface Chemistry

Chair: Atsuhiro Fujimori, Masaki Donoshita

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1443-4pm-01]

Effect of Hyperbranched Polymers as Additive on Lubrication Properties of Base Oil

○Yutaka Takahashi[1], Yuzhong He[2], Masatoshi Tosaka[2], Masashi Mizukami[1], Shigeru Yamago[2], Kazue Kurihara[1] (1. Tohoku Univ., 2. Kyoto Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1443-4pm-02]

Hydroxyapatite Deposition on Boron-Doped Diamond Thin Films Using Simulated Body Fluids

○Nanami Takahashi[1], Takuya Sagawa[1], Takeshi Kondo[1], Mineo Hashizume[1] (1. Tokyo University of Science)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1443-4pm-03]

Structurally controlled assembly of filamentous viruses and their characterization

○Hiroki Narita[1], Takeshi Serizawa[1], Toshiki Sawada[1] (1. Sch. Mat. & Chem. Tech., Tokyo Tech)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1443-4pm-04]

Effect of Surfactant Addition to Lipid Vesicle Dispersions including Fluorescent Probes

○Chinatsu Asaoka[1], Masaki Hanzawa[2], Taku Ogura[2], Yuna Kim[1], Ken-ichi Iimura[1] (1. Utsunomiya Univ., 2. Nikko Chemicals Co., Ltd.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1443-4pm-05]

Fabrication of metal monolayer films by suppressing pinning at the droplet contact line

○Toru Shimada[1], Mohammad Kamal Hossain[2], Kohei Shibamoto[3], Yukihiro Yonemoto[4], Tomoaki Kunugi[5], Masahiro Kitajima[6,7] (1. Hirosaki Univ., 2. KFUPM, 3. TMU, 4. Kumamoto Univ., 5. Zhejiang Univ., 6. NIMS, 7. YNU)

English
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1443-4pm-06]

Synthesis of an unsymmetrically substituted π-extended tetrathiafulvalene derivative and its immobilization onto a gold electrode

○Masaki Donoshita[1], Miho Yamauchi[1,2,3,4] (1. IMCE, Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ.)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1443-4pm-07]

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New developments in the control of phase separated morphology in mixed monolayers of non-amphiphilic fluorinated derivatives and comb copolymers

○Yoshiki Shioda[1], Itsuki Fujii[2], Atsuhiro Fujimori[1] (1. Graduate School of Science and Engineering, Saitama University, 2. Faculty of Eng., Saitama Univ.)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[A1443-4pm-08]

Characterization of 12-Hydroxystearate-Modified Nanodiamonds Using Method of Organized Molecular Films

○Yui Yamagishi[1], Shoma Sakamoto[2], Yuka Hasunuma[1], Atsuhiro Fujimori[1] (1. Graduate School of Science and Engineering, Saitama University, 2. Faculty of Engineering, Saitama University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[A1443-4pm-09]

Preparation and Evaluation of Coting Films of Thixotropic Solvent Gel Containing 12-Hydroxystearate-Modified Nanodiamonds

○Yuka Haunuma[1], Yui Yamagishi[1], Kai Xu[1], Atsuhiro Fujimori[1] (1. Saitama University)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[A1443-4pm-10]

Formation of Organized Molecular Films and Metal Scavenging Behavior of Azacalyxarene-containing Copolymers with Spherulite-Forming Ability

○Ryoma Terui[1], Yoshiki Shioda[2], Yuji Shibsaki[3], Atsuhiro Fujimori[2] (1. Faculty of Engineering, Saitama Univesity, 2. Graduate School of Science and Engineering, Saitama University, 3. Faculty of Sci. and Eng., Iwate Univ.)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[A1443-4pm-11]

Morphogenesis and Its Control of Interfacial Molecular Films Using Glycan-based Polymers

○Ryoma Nakada[1], Chisato Nara[1], Rokibul Hasan Rumon[2], Atsuhiro Fujimori[2] (1. Faculty of Engineering, Saitama Univesity, 2. Graduate School of Science and Engineering, Saitama University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[A1443-4pm-12]

Structure and properties of drawn-oriented fluorinated polymer/carbon nanotube composite film containing two types of functional organic fillers

○Pinjung Chu[1], Rokibul Hasan Rumon[1], Kai Xu[1], Atsuhiro Fujimori[1] (1. Saitama Univ.)

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Academic Program [Oral B] | 19. Colloid and Interface Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC A1442(1442, Bldg. 14 [4F])

[A1442-4pm] 19. Colloid and Interface Chemistry

Chair: Tatsuya Kameyama, Tetsuya Kambe

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[A1442-4pm-01]

Exploration of highly active catalysts for hydrogen evolution reaction in multi-element alloy nanoparticles by machine learning

○Yuto Maruta[1], Kohei Kusada[1,2], Okkyun Seo[5], Osami Sakata[5], Shogo Kawaguchi[5], Yoshiki Kubota[6], Hiromasa Kaneko[7], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. HAKUBI Centre, Kyoto Univ., 3. URC, Kyushu Univ., 4. Grad. Sch. Eng., Kyushu Univ., 5. JASRI-SPring-8, 6. Grad. Sch. Sci., Osaka Metropolitan Univ., 7. Grad. Sch. Sci. and Tech., Meiji Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[A1442-4pm-02]

Machine learning guided development of size and shape controlled inorganic nanoparticles

○Quan ZOU[1], Kiyoshi Kanie[1,2] (1. International Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai, Miyagi 980- 8577, Japan, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[A1442-4pm-03]

Element–Electronic Structure–Product Selectivity Relationship in CO_2 Hydrogenation over Multi-Element Alloy Nanoparticle Catalysts

○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Shogo Kawaguchi[5], Toshiaki Ina[5], Yoshiki Kubota[6], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. HAKUBI Center, Kyoto Univ., 3. URC, Kyushu Univ., 4. Grad. Sch. Eng., Kyushu Univ., 5. JASRI/SPring-8, 6. Grad. Sch. Sci., Osaka Metro. Univ.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[A1442-4pm-04]

Vesicle Formation via Self-Assembly of Au-Fe_3O_4 Janus Nanoparticles at a Liquid-Liquid Interface

○Takehiro Yachi[1,2], Hideyuki Mitomo[2,4], Kiyoshi Kanie[3,4], Kuniharu Ijiro[2] (1. JSPS, 2. RIES, Hokkaido Univ., 3. SRIS, Tohoku Univ., 4. IMRAM, Tohoku Univ.)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[A1442-4pm-05]

Highly ordered $L1_0$-type Pt-*M*-Zn Nanoparticles for Electrocatalysts

○Wu Tian[1], Ryota Sato[2], Yoshiharu Uchimoto[3], Toshiharu Teranishi[1,2] (1. Grad. Sch. of Sci., Kyoto Univ., 2. Inst. for Chem. Res., Kyoto Univ., 3. Grad. Sch. of Human and Environ. Stud., Kyoto Univ.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

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[A1442-4pm-06]

Synthesis of 3D Ag nanoparticle superlattices and their structure-specific functions

○ZHU LINGKAI[1], SARUYAMA MASAKI[2], TERANISHI TOSHIHARU[1,2] (1. Graduate School of Science, Kyoto University, 2. Institute for Chemical Research, Kyoto University)

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

Thu. Mar 21, 2024 10:30 AM - 11:20 AM JST | Thu. Mar 21, 2024 1:30 AM - 2:20 AM UTC C442(442, Bldg. 4 [4F])

[C442-4am] 20. Materials Chemistry -Basic and Application-

Chair: Hiroki Mori, Osamu Tsutsumi

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[C442-4am-01]

Photoresponsive behavior of oligothiophene-doped liquid crystals containing an acrylate monomer by irradiation with a circularly polarized beam

○Soichiro Koyama[1], Mirai Motoyama[1], Junki Yokota[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology, 2. PREST, JST)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[C442-4am-02]

Photoinduced molecular reorientation of liquid crystals doped with dichroic dyes toward visible light dimming

○Yuya Nakata[1], Junki Yokota[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology, 2. PRESTO, JST)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[C442-4am-03]

Controlling Helical Axis Orientation by Gradient Photopolymerization of Chiral Liquid-Crystalline Monomer

○Yuki Shikata[1], Shohei Sugiyama[1], Maki Yanagihara[1], Kohsuke Matsumoto[1], Osamu Tsutsumi[1] (1. The Univ. of Ritsumeikan)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[C442-4am-04]

Development of Semiconducting Polymers Based on Vinylene-Bridged Bisdifluoroquinoxaline and Their Application to Organic Photovoltaic Cells

○Yamane Hiroki[1], Hiroki Mori[2], Yasushi Nishihara[2] (1. Grad. Sch. of Environ. Life Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayma Univ.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[C442-4am-05]

Effect of the number of fluorine atoms on the functionalization degree and photoluminescent properties of butylated single-walled carbon nanotubes

○Yasuhiro Suzuki[1], Yui Konno[1], Nobuhiro Kikuchi, Michio Yamada[1], Yutaka Maeda[1], Pei Zhao[2], Masahiro Ehara[2], Masaya Mitsuishi[3], Anh T. N. Dao[4], Hitoshi Kasai[5] (1. Tokyo Gakugei University, 2. Institute for Molecular Science, 3. Graduate School of Engineering, Tohoku University, 4. Graduate School of Engineering, Nagasaki University, 5. Institute of Multidisciplinary Reseach for Advanced Materials, Tohoku Universityity)

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Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral A

Thu. Mar 21, 2024 9:30 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:20 AM UTC
A1454(1454, Bldg. 14 [5F])

[A1454-4am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Takeo Suga, Tatsuya Kameyama

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1454-4am-01]

Selective Generation of Gaseous Species in Water Electrolysis Using Redox Reaction of Iodine

○Asuna Kai[1], Mai Tomisaki[2], Kentaro Ogawa[1], Hiroshige Matsumoto[1,2] (1. Kyushu Univ., 2. I2CNER, Kyushu Univ.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1454-4am-02]

Synthesis of Ni-Pt-Ir composite nanoparticles by ionic liquid/metal sputtering and their electrocatalytic activity for urea oxidation

○kento hiraide[1], Liu Yixiong[1], Kazutaka Akiyoshi[1], Susumu Kuwabata[2], Tsukasa Torimoto[1] (1. The Univ. of Nagoya, 2. The Univ. of Osaka)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1454-4am-03]

Nitrogen and phosphorus co-doped carbon as an efficient electrocatalyst for oxygen reduction reaction

○Naoki Tachibana[1], Hiromasa Namiki[1], Shoichi Somekawa[1] (1. Tokyo Metropolitan Industrial Technology Research Institute)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1454-4am-04]

Effects of Carotenoid Coating on Chlorin-Modified Pt/TiO_2 Nanoparticles for Photocatalytic Hydrogen Evolution

○Shin-ichi Sasaki[1], Yanxiang Liu[2], Ritsuko Fujii[3], Xiao-Feng Wang[2] (1. Nagahama Inst. Bio-Sci. Tech., 2. Jilin Univ., 3. Osaka Metropolitan Univ.)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1454-4am-05]

Preparation of Near-IR-responsive Ag-Ge-S Quantum Dots and Enhanced Photoluminescence Property through Core-Shell Structure Formation

○Masayuki Soto[1], Kazutaka Akiyosi[1], Tatsuya Kameyama[1], Norikazu Fujihira[2], Tsukasa Torimoto[1] (1. The Univ. of Nagoya, 2. Murata Manufacturing Co., Ltd.)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1454-4am-06]

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Controlling the nano-structure in silver nano arrays for solid state Vis-to-UV photon upconversion.

○Yusei Sawada[1], Kodai Matsumoto[1], Yuya Watanabe[1], Yoichi Sasaki[1,2], Shigenori Fujikawa[1,2,3,4], Nobuo Kimizuka[1,2,3] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-I2CNER, Kyushu Univ.)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1454-4am-07]

Perovskite Solar cells Using Rhodanine Derivatives as Electron Collecting Monolayers

○Yuki Miyake[1], Tomoya Nakamura[1], Minh Anh Truong[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Kyoto university, institute for chemical research)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1454-4am-08]

Relationship between hysteresis and capacitance in Organic Lead Halide Perovskite Solar Cell

○Masumi Saito[1], Satoshi Uchida[1], Kazuteru Nonomura[1], Ajay Kumar Jena[1], Hiroshi Segawa[1] (1. The University of Tokyo)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1454-4am-09]

Enhanced Efficiency of 4-Terminal Spectral Splitting Solar Cell Utilizing Perovskite Solar Cells

○Kei Ito[1], Kazuteru Nonomura[1], Ryota Kan[1], Keishi Tada[1], Ching Chang Lin[1], Takumi Kinoshita[1], Takeru Bessho[1], Satohsi Uchida[1], Hiroshi Segawa[1] (1. The University of Tokyo)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1454-4am-10]

All Inorganic Perovskite Layer Formation and Surface Passivation by Bar-coating Method Assisted by Ink Additives.

○Rio Shimizu[1], Kota Haseyama[1], Kenichi Oyaizu[1], Hiroyuki Nishide[1], Takeo Suga (1. Waseda University, School of Advanced Science and Engineering)

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Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC A1455(1455, Bldg. 14 [5F])

[A1455-4pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Atsushi Sakuda, Yuko Takeoka

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1455-4pm-01]

Preparation of crosslinked bis(benzoquinones) and their evaluation as active cathode materials of lithium ion batteries

Tsumugi Inaba[1], Kobayashi Aoi[1], Takato Yokoji[1], Yao Masaru[2], ○Hiroshi Matsubara[1] (1. Osaka Metropolitan University, 2. AIST)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1455-4pm-02]

Synthesis of naphthoquinone dimers and their application to lithium-ion batteries

○Tsumugi Inaba[1], Hiroshi Matsubara[1], Masaru Yao[2] (1. Osaka Metropolitan University, 2. AIST)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1455-4pm-03]

Aqueous solution synthesis of Li_4SnS_4 electrolytes and its application to NMC composite positive electrode

○Takashi Hashii[1], Hayata Tanigaki[1], Takuya Kimura[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1455-4pm-04]

Synthesis of Na_5FeS_4 positive electrode active material via sodium polysulfides

○Yuta Doi[1], Tomoya Otono[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1455-4pm-05]

Preparation of amorphous MoS_4 through thermal decomposition for positive electrode active materials in all-solid-state batteries

○Keitaro Imai[1], Tatsuki Shigedomi[1], Tomohiro Furukawa[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1455-4pm-06]

Mechanochemical synthesis of solid electrolytes in the system Li_2S–P_2S_5–AlF_3.

○Sotaro Sato[1], Taichi Asakura[1], Hiroe Kowada[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1455-4pm-07]
Mechanochemical synthesis of solid electrolytes in the system $NaTaCl_6$-NaCl

○Kenta Koga[1], Eiji Kurioka[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[A1455-4pm-08]
Ionic conduction properties of $La_{0.9}Ba_{0.1}F_{2.9}B_2O_3$ composite

○Shinsuke Toyoda[1], Yuki Hayashi[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1455-4pm-09]
Development of Lithium-ion Conductors Using Ionic Plastic Crystals (I) -Effect of Li-salt Concentration on Ionic Conductivity-

○Hiroki Obuchi[1], Takuto Ootahara[1], Shuho Akakabe[1], Yuko Takeoka[1], Masahiro Rikukawa[1], Masahiro Fujita[1] (1. Sophia Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1455-4pm-10]
Development of Na-ion Conductors Using Ionic Plastic Crystals (I) -Evaluation of Pyrrolidinium-salt/Na-salt composites

○Yoshifumi Hirotsu[1], Ootahara Takuto[1], Akakabe Shuho[1], Fujita Masahiro[1], Rikukawa Masahiro[1], Takeoka Yuko[1] (1. Sophia University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[A1455-4pm-11]
Preparation and evaluation of Na-ion conductors using zwitterionic polymers (I) - Preparation of ion gels-

○Rei Doai[1], Masaya Sato[1], Mina Yamaguchi[1], Masahiro Rikukawa[1], Masahiro Fujita[1], Yuko Takeoka[1] (1. Sophia University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[A1455-4pm-12]
Electrochemical characteristics of supercapacitors using anion-conducting polymer electrolyte membranes

○Yusuke Inawashiro[1], Takahumi Uchino[1], Junji Inukai[1], Kenji Miyatake[1], Shinji Nohara[1] (1. Univ. of Yamanashi)

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Academic Program [Oral B] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral B

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
A1455(1455, Bldg. 14 [5F])

[A1455-4am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Kazuhiko Maeda, Tsukasa Torimoto

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[A1455-4am-01]

Efficient separation of HTO from H_2O by membrane distillation using gas-liquid exchange

○Hirokazu Miyoshi[1], Masahiro Fujiwara[2] (1. Tokushima University, 2. Osaka University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[A1455-4am-02]

Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

○Susmita Roy[1], Masayoshi Higuchi Higuchi[1], Sanjoy Mandal[1] (1. National Institute for Materials Science (NIMS), 1 -1 Namiki)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[A1455-4am-03]

Spontaneous-Symmetry-Breaking Charge Separation in Organic Photovoltaic Material

○Takeaki Zaima[1,2], Wataru Ota[1,2], Naoki Haruta[1,2], Motoyuki Uejima[3], Hideo Ohkita[2], Tohru Sato[1,2] (1. FIFC, Kyoto Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. MOLFEX, Inc)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[A1455-4am-04]

Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

○Wentao Zhang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[A1455-4am-05]

Electrochemical water oxidation by layered-perovskite oxyfluoride $Pb_3Fe_2O_5F_2$

○Ryusuke Mizuochi[1], Yuuki Sugawara[1], Takeo Yamaguchi[1], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[A1455-4am-06]

Improvements in long-term durability of electrochemical reactors producing formate from CO_2 and water

○Naohiko Kato[1], Yasuaki Kawai[1], Natsumi Nojiri[1], Masahito Shiozawa[1], Yoshihiro Kikuzawa[1], Nobuaki Suzuki[1], Satoru Kosaka[1], Tsuyoshi Hamaguchi[1], Yasuhiko Takeda[1] (1. TOYOTA CENTRAL R&D LABS., INC.)

Japanese

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11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[A1455-4am-07]

Photocatalytic membrane electrode assemblies with proton conductive coordination polymers

○Yuji Namiki[1,2], Hiroyasu Tabe[1], Satoshi Horike[1] (1. Kyoto Univ., 2. POLA Chemical Industries, Inc.)

Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC

B1325(1325, Bldg. 13 [2F])

[B1325-4am] Award Presentations, Special Lectures

Chair: Aritomo Yamaguchi, Kosei Ueno, Mio Ishida, Tatsuya Nishimura

Japanese CSJ Award for Young Chemists in Technical Development

9:00 AM - 9:30 AM JST | 12:00 AM - 12:30 AM UTC

[B1325-4am-01]

Development of Printed Semiconductor Devices Using Semi-conductive Carbon Nanotubes

○Kazuki Isogai[1], Shota Kawai[1] (1. Toray Industries, Inc.)

Japanese CSJ Award for Technical Development

9:30 AM - 10:00 AM JST | 12:30 AM - 1:00 AM UTC

[B1325-4am-02]

Development of Manufacturing Technology for Sustainable Surfactant “Internal Olefin Sulfonate”

○Yudai Yamada[1], Koutaku Yuasa[1], Sara Sumioka[1], Shingo Takada[1], Masato Nomura[1] (1. Kao Corporation)

Japanese CSJ Award for Technical Development

10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC

[B1325-4am-03]

Development of Unique a-Olefin Copolymer with High Stress Absorption Performance and Their Applications

○Masahiko Okamoto[1], Takayuki Uekusa[1] (1. Mitsui Chemicals, Inc.)

Japanese CSJ Award for Technical Development

10:40 AM - 11:10 AM JST | 1:40 AM - 2:10 AM UTC

[B1325-4am-04]

Development of dental restorative materials with structural color

Hironobu Akizumi[1], ○Hiroshi Morisaki[1], Takuma Matsuo[1] (1. Tokuyama Dental Corporation)

Japanese CSJ Award for Technical Development

11:10 AM - 11:40 AM JST | 2:10 AM - 2:40 AM UTC

[B1325-4am-05]

Development and Commercialization of Negative-type Photodefinable Polyimide Film for Electronic Components

○Kazuyuki Matsumura[1], Keigo Kato[1], Yoshiko Tatsuta[1], Daisuke Kanamori[1], Yuki Katsurada[1] (1. Toray Industries, Inc.)

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Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 9:00 AM - 11:10 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:10 AM UTC
B1326(1326, Bldg. 13 [2F])

[B1326-4am] Award Presentations, Special Lectures

Chair: Kosuke Suzuki, Tetsuya Taketsugu

Japanese CSJ Award for Outstanding Young Women Chemists
9:00 AM - 9:30 AM JST | 12:00 AM - 12:30 AM UTC
[B1326-4am-01]

Development of Visible/Near-Infrared Light Driven Photoreactions Using Organometallic Complexes

○Kei Murata[1] (1. IIS, The Univ. of Tokyo)

Japanese Young Scholar Lecture
9:30 AM - 10:00 AM JST | 12:30 AM - 1:00 AM UTC
[B1326-4am-02]

Synthesis and Characterization of Novel Organic Molecules Based on Spatial Arrangement of π-Conjugated Skeletons

○Kenichi Kato[1] (1. Kyoto Univ.)

Japanese Young Scholar Lecture
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[B1326-4am-03]

Development of efficient hydrogenation and dehydrogenation reactions using multifunctional solid catalysts

○Xiongjie Jin[1] (1. The University of Tokyo)

Japanese Young Scholar Lecture
10:40 AM - 11:10 AM JST | 1:40 AM - 2:10 AM UTC
[B1326-4am-04]

Topical Formulation Design using Computational Chemistry and Machine Learning Modellings

○Hiromi Baba[1] (1. Maruho Co., Ltd.)

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Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 1:00 PM - 2:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:00 AM UTC B1325(1325, Bldg. 13 [2F])

[B1325-4pm] Award Presentations, Special Lectures

Chair: Yoshihiro Nishimoto, Yuichi Negishi

Japanese Young Scholar Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[B1325-4pm-01]

Novel Transformations of Organic Molecules Based on Selectivity Control Unique to Supported Nanoparticle Catalysts

○Takafumi Yatabe[1,2] (1. The University of Tokyo, School of Engineering, 2. JST, PRESTO)

Japanese Young Scholar Lecture
1:30 PM - 2:00 PM JST | 4:30 AM - 5:00 AM UTC
[B1325-4pm-02]

Catalytic Bond Cleavage Enabled by Zirconocene and Photoredox Catalysis

○Eisuke Ota[1] (1. Waseda University)

Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC B1326(1326, Bldg. 13 [2F])

[B1326-4pm] Award Presentations, Special Lectures

Chair: Izumi Imai, Masato Ito

Japanese CSJ Award for Merits for Chemical Education
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[B1326-4pm-01]

Improvement of chemistry education through textbook authorization

○Kiyotaka Shigehara[1] (1. Tokyo University of Agriculture and Technology)

Japanese CSJ Award for Chemical Education
1:30 PM - 2:20 PM JST | 4:30 AM - 5:20 AM UTC
[B1326-4pm-02]

Outstanding education activity in analytical and inorganic chemistry

○Kazuo Miyamura[1] (1. Tokyo University of Science)

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Symposium | Co-Innovation Program (CIP) : Innovative catalysts for challenging carbon negativity

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
A1431(1431, Bldg. 14 [3F])

[A1431-4am] Innovative catalysts for challenging carbon negativity

Chair, Symposium organizer: Hideshi Sasakura, Kazuhiro Sayama, Koichi Matsushita, Yutaka Amao, Yuusuke Sunada

Japanese Invited Lecture
9:10 AM - 9:40 AM JST | 12:10 AM - 12:40 AM UTC
[A1431-4am-01]
Development of innovative catalysts for organic synthetic reactions using carbon dioxide

○Tetsuaki Fujihara[1] (1. Kyoto University)

Japanese Invited Lecture
9:40 AM - 10:10 AM JST | 12:40 AM - 1:10 AM UTC
[A1431-4am-02]
Development of CCU technologies by NIPPON STEEL CORPORATION

○Ayaka Miura[1] (1. NIPPON STEEL CORPORATION)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[4A143101-03-4add]
Incubation Time

Japanese Keynote Lecture
10:20 AM - 11:20 AM JST | 1:20 AM - 2:20 AM UTC
[A1431-4am-03]
Transitions towards carbon neutrality and the future of the energy and chemical sectors

○Yasushi Sekine[1] (1. Waseda Univ.)

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[4A143101-03-6add]
Incubation Time

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Symposium | Co-Innovation Program (CIP) : Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1432(1432, Bldg. 14 [3F])

[A1432-4am] Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Chair, Symposium organizer: Hiroaki Iino, Ryo Koga, Shunpei Hitosugi, Yasunobu Ando

Japanese Keynote Lecture
9:10 AM - 10:00 AM JST | 12:10 AM - 1:00 AM UTC
[A1432-4am-01]
Policy Development for Industrial Data Space as International Government Initiative

○Noriaki Izumi[1] (1. Ministry of Economy, Trade and Industry)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[4A143201-03-3add]
Incubation Time

Japanese Invited Lecture
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[A1432-4am-02]
Cyber-physical exploration system using powder-film-formation Process Informatics

○Keisuke Nagato[1] (1. The University of Tokyo)

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[4A143201-03-5add]
Incubation Time

Japanese Invited Lecture
10:50 AM - 11:20 AM JST | 1:50 AM - 2:20 AM UTC
[A1432-4am-03]
Acceleration in the development of materials with dipersed silver nanoparticles using multiscale optical response calculations and machine learning

○Ko Osawa[1], Tsuneo Kashiwagi[1], Shigeru Kojima[1] (1. KONICA MINOLTA, INC.)

11:20 AM - 11:40 AM JST | 2:20 AM - 2:40 AM UTC
[4A143201-03-7add]
Incubation Time

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Symposium | Co-Innovation Program (CIP) : Cutting-edge research in polymer science for a sustainable society

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1433(1433, Bldg. 14 [3F])

[A1433-4am] Cutting-edge research in polymer science for a sustainable society

Chair, Symposium organizer: Kenichi Kasuya, Kenji Hara, Ryotaro Tsuji, Yoshihiro Ikari

Japanese Keynote Lecture
9:10 AM - 10:10 AM JST | 12:10 AM - 1:10 AM UTC
[A1433-4am-01]
Development of high-performance marine biodegradable biomass plastics

○Tadahisa Iwata[1] (1. The University of Tokyo)

Japanese Invited Lecture
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[A1433-4am-02]
Practical application of Biodegradable-biopolymer

○Shunsuke Sato[1] (1. KANEKA CORPORATION)

Japanese Invited Lecture
10:40 AM - 11:10 AM JST | 1:40 AM - 2:10 AM UTC
[A1433-4am-03]
Development of bio-based bifuran moiety capable of replacing benzene ring

○Yuya Tachibana[1] (1. Gunma University)

Japanese Invited Lecture
11:10 AM - 11:40 AM JST | 2:10 AM - 2:40 AM UTC
[A1433-4am-04]
Sustainable Cross-Linked Polymer Materials Based on Radical-type Dynamic Covalent Chemistry

○Hideyuki Otsuka[1] (1. Tokyo Tech)

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Symposium | Co-Innovation Program (CIP) : Innovative catalysts for challenging carbon negativity

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC A1431(1431, Bldg. 14 [3F])

[A1431-4pm] Innovative catalysts for challenging carbon negativity

Chair, Symposium organizer: Hideshi Sasakura, Kazuhiro Sayama, Koichi Matsushita, Yutaka Amao, Yuusuke Sunada

Japanese Invited Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[A1431-4pm-01]
Heterogeneous organic synthesis contributing to carbon neutrality

○Hiroki Miura[1] (1. Tokyo Metropolitan University)

Japanese Invited Lecture
1:30 PM - 2:00 PM JST | 4:30 AM - 5:00 AM UTC
[A1431-4pm-02]
Development of CO_2 electrolysis technology towards the realization of a carbon recycling society

○Ryota Kitagawa[1] (1. Toshiba Corporation)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[4A143104-06-3add]
Incubation Time

Japanese Invited Lecture
2:10 PM - 2:40 PM JST | 5:10 AM - 5:40 AM UTC
[A1431-4pm-03]
Development of Catalytic Systems for Small Molecule Conversions based on Molecular Assembly

○Mio Kondo[1,2] (1. Tokyo Institute of Technology, 2. JST PRESTO)

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Symposium | Co-Innovation Program (CIP) : Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC A1432(1432, Bldg. 14 [3F])

[A1432-4pm] Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Chair, Symposium organizer: Hiroaki Iino, Ryo Koga, Shunpei Hitosugi, Yasunobu Ando

Japanese Invited Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[A1432-4pm-01]
Materials innovation based on polymer informatics

○Masanobu Naito[1] (1. National Institute for Materials Science)

Japanese Invited Lecture
1:30 PM - 2:00 PM JST | 4:30 AM - 5:00 AM UTC
[A1432-4pm-02]
Methane oxidation catalysts design via catalysts informatics

○Keisuke Takahashi[1] (1. Hokkaido University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[4A143204-07-3add]
Incubation Time

Japanese Invited Lecture
2:10 PM - 2:40 PM JST | 5:10 AM - 5:40 AM UTC
[A1432-4pm-03]
Simulation in the development of electronic materials

○Satoshi Yotsuhashi[1] (1. Panasonic Holdings Corporation)

Japanese Invited Lecture
2:40 PM - 3:10 PM JST | 5:40 AM - 6:10 AM UTC
[A1432-4pm-04]
Organic transistor-based chemical sensors with pattern recognition techniques

○Tsuyoshi Minami[1] (1. IIS, The Univ. of Tokyo)

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC
[4A143204-07-6add]
Incubation Time

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Symposium | Co-Innovation Program (CIP) : Cutting-edge research in polymer science for a sustainable society

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1433(1433, Bldg. 14 [3F])

[A1433-4pm] Cutting-edge research in polymer science for a sustainable society

Chair, Symposium organizer: Kenichi Kasuya, Kenji Hara, Ryotaro Tsuji, Yoshihiro Ikari

Japanese Keynote Lecture
1:00 PM - 2:00 PM JST | 4:00 AM - 5:00 AM UTC
[A1433-4pm-01]
Development of catalytic resin-degradation reactions and their application to chmical recycling

○Kyoko Nozaki[1] (1. The University of Tokyo)

Japanese Invited Lecture
2:00 PM - 2:30 PM JST | 5:00 AM - 5:30 AM UTC
[A1433-4pm-02]
Depolymerization of super engineering plastics toward chemical recycling

○Yasunori Minami[1,2] (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba, Cooperative Graduate School)

Japanese Invited Lecture
2:30 PM - 3:00 PM JST | 5:30 AM - 6:00 AM UTC
[A1433-4pm-03]
Advanced Plastic Resource Circulation Based on the Physical Degradation and Physical Regeneration Theory.

○Shigeru Yao[1] (1. Fukuoka University)

Japanese Invited Lecture
3:00 PM - 3:30 PM JST | 6:00 AM - 6:30 AM UTC
[A1433-4pm-04]
Direct Air Capture by free-standing nanomembranes

○Shigenori Fujikawa[1] (1. Kyushu University)

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Symposium | Asian International Symposium：Asian International Symposium - Colloid and Surface Chemistry -

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1422(1422, Bldg. 14 [2F])

[A1422-4am] Asian International Symposium - Colloid and Surface Chemistry -

Chair, Symposium organizer: Ryo Murakami, Syuji Fujii, Taku Iiyama, Taku Ogura

English Keynote Lecture
9:05 AM - 9:40 AM JST | 12:05 AM - 12:40 AM UTC
[A1422-4am-01]
Particle Adhesion on Thin Liquid Layer

○Sanghyuk Wooh[1] (1. Chung-Ang University)

English Invited Lecture
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[A1422-4am-02]
Solution and Foam Properties of Homogeneous Polyoxyethylene-Type Nonionic Surfactants with Multi-Branched Chains

○Shiho Yada[1] (1. Tokyo University of Science)

English Invited Lecture
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[A1422-4am-03]
Lipid Based Artificial Multicellular Systems for Compartmentalized and Stimuli-Responsive Drug Delivery

○Richard James Archer[1], Tsuyoshi Inaba[1], Shin-Ichiro M. Nomura[1] (1. Tohoku University)

English Invited Lecture
10:25 AM - 10:45 AM JST | 1:25 AM - 1:45 AM UTC
[A1422-4am-04]
Colloidal interaction-mediated wrapping of zeolite crystals with graphene oxide sheets

○Hayato Otsuka[1], Kei Kubo[1], Katsumi Kaneko[1] (1. Shinshu university)

English Invited Lecture
10:45 AM - 11:05 AM JST | 1:45 AM - 2:05 AM UTC
[A1422-4am-05]
The influence of electrostatic and hydrodynamic interactions on gelation of colloidal particles

○Joeri Opdam[1], Michio Tateno[1], Hajime Tanaka[1,2] (1. Research Center for Advanced Science and Technology, The University of Tokyo, 2. Department of Fundamental Engineering, Institute of Industrial Science, The University of Tokyo)

English Keynote Lecture
11:05 AM - 11:40 AM JST | 2:05 AM - 2:40 AM UTC
[A1422-4am-06]
Clathrate hydrates: A cool way to store carbon dioxide permanently

○Praveen Linga[1] (1. National University of Singapore)

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Symposium | Asian International Symposium：Asian International Symposium - Photochemistry -

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1422(1422, Bldg. 14 [2F])

[A1422-4pm] Asian International Symposium - Photochemistry -

Chair, Symposium organizer: Ayumi Imayoshi, Hajime Shigemitsu, Hiroshi Ikeda, Jiro Abe, Masashi Hasegawa, Shinnosuke Horiuchi, Tadashi Mori, Takashi Hirose, Takuya Nakashima, Yoichi Kobayashi

English Keynote Lecture
1:05 PM - 1:40 PM JST | 4:05 AM - 4:40 AM UTC
[A1422-4pm-01]
Coordination Assembly of Photofunctional Lanthanide-Organic Architectures

○Qing-Fu Sun[1] (1. Fujian Institute of Research on the Structure of Matter)

English Invited Lecture
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[A1422-4pm-02]
Achieving Circularly Polarized Luminescent Materials Based on Chiral Multinuclear Complexes

○Toshikazu Ono[1] (1. Kyushu University)

English Invited Lecture
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[A1422-4pm-03]
Synthesis of aza[n]helicenes (n=9-19) and systematic studies on their (chir)optical and electrochemical properties

○Takayuki Tanaka[1], Yusuke Matsuo[1], Masayuki Gon[1], Kazuo Tanaka[1], Shu Seki[1] (1. Kyoto University)

English Keynote Lecture
2:20 PM - 2:55 PM JST | 5:20 AM - 5:55 AM UTC
[A1422-4pm-04]
Helical Synthetic Nanographene with Atomic Precision

○Jiaobing Wang[1] (1. Sun Yat-Sen University)

English Invited Lecture
2:55 PM - 3:15 PM JST | 5:55 AM - 6:15 AM UTC
[A1422-4pm-05]
Vibronic analysis and design strategy for circularly polarized luminescent molecules with large dissymmetry factors

○Fumitaka Ishiwari[1,2] (1. Osaka University, 2. JST PRESTO)

English Invited Lecture
3:15 PM - 3:35 PM JST | 6:15 AM - 6:35 AM UTC
[A1422-4pm-06]
Analysis of non-radiative decay pathways using quantum chemical calculations: Application to photoredox-catalyzed radical reaction

○Yu Harabuchi[1,2] (1. WPI-ICReDD, 2. JST-ERATO)

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Symposium | Special Program：Functional Systems and Utilization Using Particle and Molecular Aggregation, Dispersion, andAssembly

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1423(1423, Bldg. 14 [2F])

[A1423-4am] Functional Systems and Utilization Using Particle and Molecular Aggregation, Dispersion, andAssembly

Chair, Symposium organizer: Shinich Takeda, Tetsu Yonezawa

Japanese
9:05 AM - 9:40 AM JST | 12:05 AM - 12:40 AM UTC
[A1423-4am-01]
Assembling and aggregation of plasmonic nanoparticles towards efficient use of photoenergy

○Tsuyoshi AKIYAMA[1] (1. The University of Shiga Prefecture)

Japanese
9:40 AM - 10:20 AM JST | 12:40 AM - 1:20 AM UTC
[A1423-4am-02]
Emulsification and dispersion in cosmetics and skin cleaning

○Yoshimune Nonomura[1] (1. Yamagata University)

Japanese
10:20 AM - 11:00 AM JST | 1:20 AM - 2:00 AM UTC
[A1423-4am-03]
Physicochemical property of emulsions stabilized with interfacial membrane generated through vesicle/disc structural transition

○Kei Watanabe[1] (1. Mukogawa Women's University)

Japanese
11:00 AM - 11:35 AM JST | 2:00 AM - 2:35 AM UTC
[A1423-4am-04]
Preparation of cosmetic emulsions and their evaluation

○Sadanori Ban

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Symposium | Special Program：Informatics and AI in Chemistry

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1423(1423, Bldg. 14 [2F])

[A1423-4pm] Informatics and AI in Chemistry

Chair, Symposium organizer: Kazue Kurihara, Kei Terayama, Mitsuru Ohno, Nobuharu Iwasawa, Norie Momiyama, Seijiro Matsubara

Japanese
1:05 PM - 1:30 PM JST | 4:05 AM - 4:30 AM UTC
[A1423-4pm-01]
History and prospects of data-driven chemistry

○Kimito Funatsu[1] (1. Nara Institute of Science and Technology)

Japanese
1:30 PM - 1:55 PM JST | 4:30 AM - 4:55 AM UTC
[A1423-4pm-02]
Opportunities and Challenges in Data-Driven Materials Research: Overcoming the Barrier of Limited Data

○Ryo Yoshida[1] (1. The Institute of Statistical Mathematics)

English
1:55 PM - 2:20 PM JST | 4:55 AM - 5:20 AM UTC
[A1423-4pm-03]
Materials Integration for inverse materials/process design from desired performance

○Masahiko Demura[1] (1. National Institute for Materials Science)

Japanese
2:30 PM - 2:45 PM JST | 5:30 AM - 5:45 AM UTC
[A1423-4pm-04]
Government initiatives based on Materials Innovation Strategy

○Hiroko Takuma[1] (1. Ministry of Education, Culture, Sports, Science and Technology)

Japanese
2:45 PM - 3:05 PM JST | 5:45 AM - 6:05 AM UTC
[A1423-4pm-05]
Integration of automated robotic experiments and artificial intelligence accelerates discovery of novel materials for advanced rechargeable batteries

○Shoichi Matsuda[1] (1. National Institute for Materials Science)

Japanese
3:05 PM - 3:20 PM JST | 6:05 AM - 6:20 AM UTC
[A1423-4pm-06]
Utilization of Batch-Type Automated Reactor and Construction of Chemical Reaction Space

○Norie MOMIYAMA[1] (1. Institute for Molecular Science · SOKENDAI)

Japanese
3:20 PM - 3:35 PM JST | 6:20 AM - 6:35 AM UTC
[A1423-4pm-07]
Function-oriented design and control of the amino acid sequence of filamentous virus through machine learning

○Toshiki Sawada[1] (1. Tokyo Institute of Technology)

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Symposium | Special Program：The next generation of medical technology innovated by analytical chemistry

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1424(1424, Bldg. 14 [2F])

[A1424-4pm] The next generation of medical technology innovated by analytical chemistry

Chair, Symposium organizer: Hiroyuki Nakamura, Hiroyuki Tani, Ichiro Okura, Satoshi Ohtsuka, Yuki Okada, Yuriko Matsumura

Japanese
1:10 PM - 1:40 PM JST | 4:10 AM - 4:40 AM UTC
[A1424-4pm-01]

Application of mass spectrometry to the elucidation of the pathogenesis of allergic diseases and their diagnosis and treatment

○Takahisa Murata[1] (1. The University of Tokyo)

Japanese
1:40 PM - 2:10 PM JST | 4:40 AM - 5:10 AM UTC
[A1424-4pm-02]

Facilitating medical research and development by global data sharing

○Makoto Suematsu[1] (1. Central Institute for Experimental Medicine and Life Science)

Japanese
2:10 PM - 2:40 PM JST | 5:10 AM - 5:40 AM UTC
[A1424-4pm-03]

Analytical measurement, automation, and AI technologies for regenerative medicine and next-generation therapeutic drug development

○Toru Ezure[1] (1. Shimadzu Corporation)

Japanese
2:40 PM - 3:10 PM JST | 5:40 AM - 6:10 AM UTC
[A1424-4pm-04]

Shimadzu Effort for Helthcare business

○Hiroki Nakajima[1] (1. Shimadzu Corporation)

Japanese
3:10 PM - 3:40 PM JST | 6:10 AM - 6:40 AM UTC
[A1424-4pm-05]

Alzheimer's disease plasma analysis by mass spectrometry

○Yoshiya Oda[1] (1. The University of Tokyo, Graduate School of Medicine)

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Co-organized Symposium | Co-organized Symposium [organized by CSJ partners] : Toward Social Implementation of Mechanochemical Organic Synthesis

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1421(1421, Bldg. 14 [2F])

[A1421-4am] Toward Social Implementation of Mechanochemical Organic Synthesis

9:00 AM - 11:40 AM JST | 12:00 AM - 2:40 AM UTC

[A1421-4am]

Toward Social Implementation of Mechanochemical Organic Synthesis

Co-organized Symposium | Co-organized Symposium [organized by CSJ partners] : Science on Process of All-solid-state Lithium Ion Batteries

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1421(1421, Bldg. 14 [2F])

[A1421-4pm] Science on Process of All-solid-state Lithium Ion Batteries

1:00 PM - 3:40 PM JST | 4:00 AM - 6:40 AM UTC

[A1421-4pm]

Science on Process of All-solid-state Lithium Ion Batteries

Event | Event : The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

Thu. Mar 21, 2024 10:00 AM - 12:00 PM JST | Thu. Mar 21, 2024 1:00 AM - 3:00 AM UTC CST MUSEUM(Technoplace 15)

[SD] The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

10:00 AM - 12:00 PM JST | 1:00 AM - 3:00 AM UTC

[SD]

The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

Event | Event : The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

Thu. Mar 21, 2024 1:00 PM - 5:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 8:00 AM UTC CST MUSEUM(Technoplace 15)

[SD] The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

1:00 PM - 5:00 PM JST | 4:00 AM - 8:00 AM UTC

[SD]

The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

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Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 1434(1434, Bldg. 14 [3F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 1437(1437, Bldg. 14 [3F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 1439(1439, Bldg. 14 [3F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 624(624, Bldg. 6 [2F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

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Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 741(741, Bldg. 7 [4F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 833(833, Bldg. 8 [3F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

Speaker Ready Room | Speaker Ready Room：Speaker Ready Room

Thu. Mar 21, 2024 8:30 AM - 1:30 PM JST | Wed. Mar 20, 2024 11:30 PM - 4:30 AM UTC 1438(1438, Bldg. 14 [3F])

[SR] Speaker Ready Room

8:30 AM - 1:30 PM JST | 11:30 PM - 4:30 AM UTC

[SR]

Speaker Ready Room

Speaker Ready Room | Speaker Ready Room：Speaker Ready Room

Thu. Mar 21, 2024 8:30 AM - 1:30 PM JST | Wed. Mar 20, 2024 11:30 PM - 4:30 AM UTC 625(625, Bldg. 6 [2F])

[SR] Speaker Ready Room

8:30 AM - 1:30 PM JST | 11:30 PM - 4:30 AM UTC

[SR]

Speaker Ready Room

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

Thu. Mar 21, 2024 9:30 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:20 AM UTC H937(937, Bldg. 9 [3F])

[H937-4am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Hiromasa Kaneko, Junji Seino

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H937-4am-01]
Design of ethylbenzene production process using machine learning and Bayesian optimization

○Eri Ishikawa[1], Hiromasa Kaneko[1] (1. Meiji University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H937-4am-02]
Model construction and improvement of the model for blood glucose monitoring using mid-infrared rays

○Yuta Takami[1], Keita Miyagawa[2], Yuki Tsuda[2], Koichi Akiyama[2], Ruka Ando[1], Hiromasa Kaneko[1] (1. Meiji University, 2. Mitsubishi Electric)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H937-4am-03]
Improving molecular design with direct inverse analysis of QSAR/QSPR model

○Yuto Shino[1], Hiromasa Kaneko[1] (1. Meiji University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H937-4am-04]
Development of applicability domain considering stability of molecular structures

○Soma Kosakai[1], Hiromasa Kaneko[1] (1. The Univ. of Meiji)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H937-4am-05]
Development of a Cloud Point Prediction Model for a Polyvinyl Alcohol Production Plant

○Ayami Ohkuma[1], Yoshihito Yamauchi[2], Nobuhito Yamada[2], Satoshi Ooyama[2], Hiromasa Kaneko[1] (1. Meiji University, 2. Mitsubishi Chemical Corporation)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
Break

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[H937-4am-06]
Ligands' Electronic structure informatics for separative extraction of minor actinides

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○Tsuyoshi Sumiyoshi[1], Nahoko Kuroki[1,2], Hirotoshi Mori[1] (1. The Univ. of Chuo , 2. JST ACT-X)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[H937-4am-07]

Complete enumeration and classification of polymer structural isomers with $C_6H_{11}NO$ and one amide group

○Gikyo Usuki[1], Tsutsumi Takuro[1,3], Hasebe Kohei[1], Kobayashi Masato[1,3,4], Shitamiti Mio[2], Matsuoka Keitaro[1,3], Taketsugu Tetsuya[1,3,4], Sada Kazuki[1,3] (1. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ., 2. Sch. of Sci., Hokkaido Univ., 3. Fac. of Sci., Hokkaido Univ., 4. WPI-ICReDD, Hokkaido Univ.)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[H937-4am-08]

Decomposition of spectrum in mixed compounds using machine learning and multivariate curve resolution

○Keitatsu Sekiya[1], Takumi Kumagai[1], Junji Seino[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Waseda Research Institute for Science and Engineering)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[H937-4am-09]

Development of a Dialogic Information Retrieval System Utilizing Large Language Models for Electronic Lab Notebooks

○Nanako Unagami[1], Masahiko Nakano[2,3], Junji Seino[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Waseda Research Institute for Science and Engineering, 3. Mitsubishi Chemical Group)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[H937-4am-10]

Mechanistic analysis of oxygen evolution reaction electrodes by machine-learning analysis

○Shinji Yoneyama[1], Motoki Fukasawa[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. School of Science, Hokkaido University, 3. Faculty of Science, Hokkaido University)

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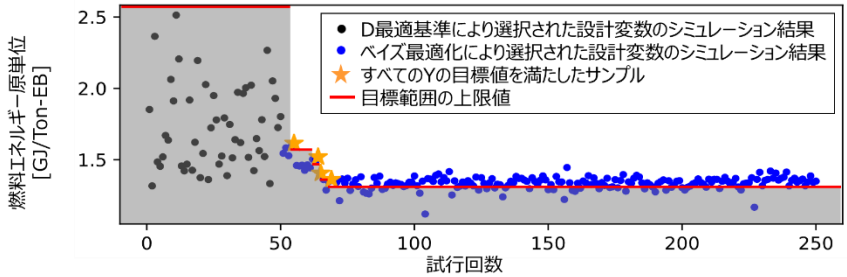
機械学習およびベイズ最適化を用いたエチルベンゼン製造プロセスの設計

(明治大学[1]) ○石川 愛理[1]・金子 弘昌[1]
Design of Ethylbenzene Production Process Using Machine Learning and Bayesian Optimization ([1]*Meiji University*) ○Eri Ishikawa,[1] Hiromasa Kaneko[1]

Ethylbenzene is a raw material for styrene monomer, which has grown into a large market. Because the current production process of ethylbenzene has a high energy load in the distillation process, and it is desired to reduce fuel consumption, the objective in this study is to design a production process that minimizes the fuel consumption required per unit production. By using machine learning, Bayesian optimization, and process simulation, the values of design variables were efficiently explored to achieve an energy-saving design of the ethylbenzene production process.
Keywords : Ethylbenzene; Process Design; Machine Learning; Process Informatics; Bayesian Optimization

エチルベンゼン (ethylbenzene, EB) は、主にプラスチックの原料として使用されるスチレンモノマーの中間原料であり、その市場は年々拡大している。商用生産が開始された当初は、塩化アルミニウム触媒を用いたプロセスによって製造されていたが、運転の容易さや環境保全性などの優位性により、ゼオライト触媒を用いた液相 EB 製造プロセスに置き換わっていった[1]。液相 EB 製造プロセスでは、反応系から出る多量の未反応ベンゼンを蒸留分離してリサイクルする必要があるが、蒸留分離工程におけるエネルギー負荷が高く多くの燃料を消費してしまう[2]。単位生産量あたり必要となる燃料消費量（燃料エネルギー原単位）の小さい新たなプロセスを設計する際、一般的にはプロセスシミュレーションをしながら化学工学の知識や知見に基づいて設計変数を最適化するが、設計変数やその候補値が多くなるほどシミュレーション回数は増え、設計にかかるコストや時間が増大してしまう。そこで本研究では、燃料エネルギー原単位が最小となる EB 製造プロセスを、プロセスシミュレーションと機械学習を組み合わせることで効率的に設計することを目的とした。設計変数の最適化にはベイズ最適化に基づく適応的実験計画法を用いた。下図のようにベイズ最適化による設計変数の候補値の提案およびプロセスシミュレーションを繰り返すことで、少ないシミュレーション回数で EB 製造プロセスの複数の条件を満たしつつ燃料エネルギー原単位を 1.3690 GJ/Ton-EB と低減させることに成功した。



1) Design and analysis of an ethyl benzene production process using conventional distillation columns and dividing-wall column for multiple objectives. Q. H. Ng, S. Sharma, G. P. Rangaiah, *Chem. Eng. Res. Des.* **2017**, *118*, 142-157.
2) Environ-economic analysis of conceptual intensification alternatives applied to the ethylbenzene production. P. G. Junqueira, I. N. Caxiano, P. V. Mangili, D. M. Prata, *Comput. Chem. Eng*. **2020**, *136*, 106783.

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中赤外光を用いた非侵襲的血糖値モニタにおける推定モデルの構築および推定精度向上の検討

(明治大学[1]・三菱電機(株)[2])○高見 優太[1]・宮川 敬太[2]・津田 祐樹[2]・秋山 浩一[2]・安藤 瑠海[1]・金子 弘昌[1]

Model construction and improvement of the model for blood glucose monitoring using mid-infrared rays

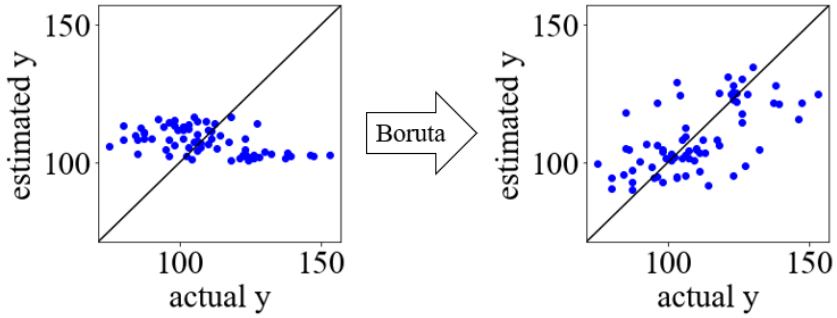
([1]*Meiji University*, [2]*Mitsubishi Electric*) ○Yuta Takami,[1] Keita Miyagawa,[2] Yuki Tsuda,[2] Koichi Akiyama,[2]Ruka Ando,[1]Hiromasa Kaneko[1]

We develop a noninvasive blood glucose monitoring system using mid-infrared rays. An estimation model is constructed with machine learning between the mid-infrared spectrum obtained by the photothermal monitoring method from several subjects as explanatory variables after pre-processing of the Savitzky-Golay (SG) method and the invasive blood glucose level as an objective variable. The parameters in the SG method were optimized and spectral wavenumbers were selected Boruta, and then, the predictive ability of the model improved for all subjects.

Keywords : Infrared rays; Noninvasive blood glucose monitoring; Photothermal monitoring method; Machine learning; Boruta

糖尿病の治療では、採血をともなう血糖値(侵襲血糖値)の測定にもとづく診断が重要である[1)]。特に自己採血は、穿刺に伴う痛みや感染症のリスク、また専用のセンサのランニングコストなど、日々の血糖値モニタとしてはいくつかの課題がある。そのため、非侵襲的な血糖値の測定法が求められている。本研究は非侵襲的血糖値モニタの開発において、中赤外光を用いた光熱モニタ法により測定される中赤外スペクトルから血糖値を推定する推定モデルの構築および推定精度向上の検討を目的とした。

光熱モニタ法で得られた複数名の被験者の中赤外スペクトルに対し、パラメータを最適化した Savitzky-Golay 法による前処理を行ったスペクトルを説明変数とした。侵襲血糖値を目的変数として機械学習により推定モデルを構築する際、Boruta によるスペクトルの波数最適化を行った。下図はある被験者を対象とした侵襲血糖値の実測値と推定値のプロットであり, Boruta を用いることにより推定精度の向上を確認した。この推定精度向上はすべての被験者において確認され、前処理と波数最適化の効果を示唆する結果となった。



1) Glycaemic control, glucose variability and the Triangle of Diabetes Care, Gerry Rayman, The British Journal of Diabetes, 2016, 16(1), S3-S6.

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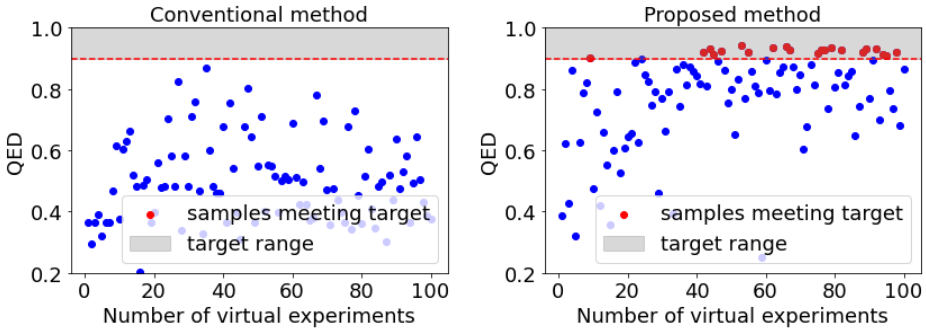
物性・活性予測モデルの直接的逆解析による分子設計における精度向上の検討

(明大理工[1]) ○紫野 優人[1]・金子 弘昌[1]
Improving Molecular Design with Direct Inverse Analysis of QSAR/QSPR Model ([1]*School of Science and Technology, Meiji University*) ○Yuto Shino,[1] Hiromasa Kaneko[1]

Molecular design by generating virtual molecules and predicting their properties and activity with machine learning models is limited in terms of the number and diversity of chemical structures to design highly functional molecules. In this study, we focused on molecular design by direct inverse analysis of models to efficiently search for target molecules. By proposing direct generation of molecules to meet target values of properties and activity and improving the molecular generation and modeling mechanism of the conventional molecular design method, in which autoencoder and Gaussian mixture regression were combined, we have achieved the generation of the molecules that could not be obtained by the conventional method.
Keywords : Molecular Design; Machine Learning; Direct Inverse Analysis; Autoencoder; Generative Model

分子設計においては実験回数にともない時間と費用が必要となるため効率的な分子の探索が課題であり、機械学習を活用した分子設計に注目が集まっている。一般的には仮想的な分子を大量に生成し、機械学習モデルによりそれらの物性・活性を予測し、良好な予測値をもつ分子を選択する。この機械学習を用いた従来の分子設計法では生成できる構造数に限りがあり構造の多様性も制限されるため、物性・活性の目標値を達成する分子が設計できるとは限らない。本研究では物性・活性の目標値からそれをもつ化学構造を直接生成する分子設計法に着目し、望ましい物性や活性を持つ分子の効率的な探索を目的とした。Chemical variational autoencoder (CVAE) と Gaussian mixture regression (GMR) を組み合わせた従来手法[1]に対し、提案手法は hierarchical variational autoencoder (HVAE) を使用する。CVAE は分子構造の表現に SMILES を利用しているのに対して HVAE は分子グラフを用いることで、連続的で滑らかな分子空間を学習でき効果的に分子を生成できると考えられる。医薬品らしさの指標である QED が 0.5 以下の少ない数の分子でモデルを構築し、100 回の仮想的な実験を実施した結果を下図に示す。従来手法では到達できなかった QED が 0.9 以上の分子を、提案手法では少ない実験回数で達成することが可能であった。



1) A molecular design method combining CVAE and GMR has been reported. K. Nemoto, H. Kaneko, J. Chem. Inf. Model. **2023**, 63, 3, 794–805.

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分子構造の安定性を考慮したモデルの適用範囲の開発

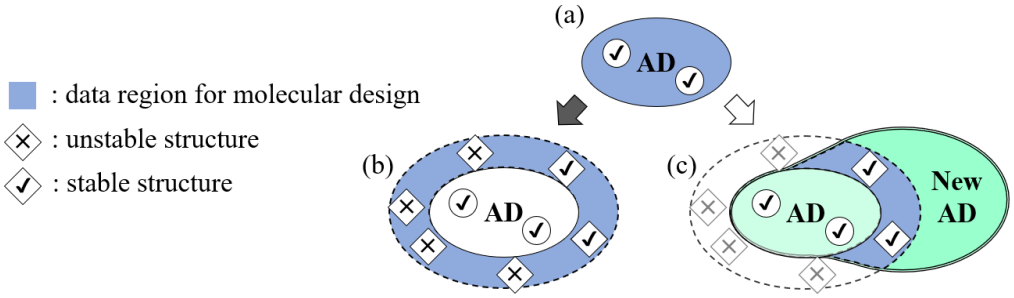
（明大理工 [1]）○小坂井 颯麻 [1]・金子 弘昌 [1]

Development of Applicability Domain Considering Stability of Molecular Structures ([1]*School of Science and Technology, Meiji University*) ○Soma Kosakai,[1] Hiromasa Kaneko[1]

An applicability domain (AD) of a mathematical model constructed with machine learning is data region of explanatory variables, and the model can achieve its original predictive performance for new candidates of explanatory variables within AD. In molecular design, when target molecular structures cannot be designed within AD, it is necessary to search for structures outside AD. However, molecular design outside AD is difficult because the predictive performance of model is not reliable and structures can be unstable. In this study, we develop a new concept of AD that defines data region where only stable structures exist, and the proposed AD is constructed with existing stable molecules. The proposed AD could judge stable and unstable structures for virtual molecules.

Keywords : Machine Learning; Applicability Domain; Inverse Analysis; Molecular Design; Stability

機械学習を用いた分子設計では、数値化した分子の構造情報を説明変数 x、分子の物性や活性を目的変数 y として構築した数理モデル y=f(x) を用いて、新たな分子構造の x の値から予測される y の値が良好な分子構造を探索する。下図の (a) のように y の予測値を信頼できるデータ領域であるモデルの適用範囲 (applicability domain, AD) [1] の内側に入る構造から探索するが、AD 内で y の予測値の良好な構造を探索できない際は (b) のように AD 外で構造を探索する必要があり、AD 外の構造は y の予測値が信頼できないだけでなく、不安定な構造であることも多い。本研究では、分子設計において安定な構造が存在する x の領域、すなわち下図の (c) を定義する新しい AD を開発することを目的とする。データベースにある安定して存在する有機分子を収集し、これらの分子から分子記述子を計算し、k 近傍法に基づいて提案する AD を設定した。安定な構造だけでなく価数が不十分な構造や環ひずみの激しい構造といった不安定な構造を含むデータセットを用いて検証したところ、提案した AD により従来の AD と比較して的確に不安定な構造を AD 外とできることを確認した。



1) Comparison of Different Approaches to Define the Applicability Domain of QSAR Models. F. Sahigara, K. Mansouri, D. Ballabio, A. Mauri, V. Consonni, R. Todeschini, Molecules. **2012**, *17(5)*, 4791-4810.

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ポリビニルアルコール製造プラントにおける曇点予測モデルの開発

(明治大学[1]・三菱ケミカル株式会社[2]) ○大熊 彩水[1]・山内 芳仁[2]・山田 信仁[2]・大山 敏[2]・金子 弘昌[1]
Development of a Cloud Point Prediction Model for a Polyvinyl Alcohol Production Plant ([1]*Meiji University*, [2]*Mitsubishi Chemical Corporation*) ○ Ayami Ohkuma,[1] Yoshihito Yamauchi,[2] Nobuhito Yamada,[2] Satoshi Ooyama,[2] Hiromasa Kaneko[1]

Although product quality must be controlled in chemical plants, it is difficult to monitor product quality in real time, which results in product loss due to delays in detecting quality deviations from target values. In this study, a soft sensor or machine learning model with high predictive ability is developed to estimate cloud point as product quality online by considering dynamics or time delays between process variables for a plant producing polyvinyl alcohol. The developed soft sensor enables real time monitoring of cloud point, which will lead to reduce product loss.
Keywords : Machine Learning; Soft Sensor; Process Control; Variable Selection; Time Delay

ポリビニルアルコール (polyvinyl alcohol; PVA) 製造プラントにおいて、製品品質の一つとして曇点を管理しているが、コストや作業負荷の影響で曇点を毎時刻分析することは難しいため、曇点が管理値を逸脱したことの検出に遅れることが問題となっている。本研究では、曇点を連続的かつリアルタイムに監視することを目的とし、温度や圧力等の測定が容易なプロセス変数から曇点を予測するソフトセンサーを機械学習により構築する。PVA 製造プラントにおけるプロセス変数は時間遅れを伴って曇点に影響を与えるため、曇点に対して影響度の大きい変数をその時間遅れを考慮した上で選択することで曇点の推定精度を向上できると考えられる。本研究では genetic algorithm-based process variables and dynamics selection (GAVDS)[1)] により重要なプロセス変数およびその時間遅れの同時選択を試みた。

PVA 製造プラントの実データを用いてソフトセンサーを構築した際の曇点の実測値と推定値の間の散布図を下図に示す。GAVDS を用いていない (a) と比較して GAVDS を用いた (b) の結果は、プロセス管理の観点から重要な曇点の値が小さい範囲のデータが対角線付近に固まっており、提案手法によるソフトセンサーの推定精度向上を確認した。



1) A method for predicting product quality using GAVDS and adaptive soft sensors has been reported. N. Yamada, H. Kaneko, Anal. Sci. Adv. **2022**, *3(5-6)*, 205-211.

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日本化学会 第104春季年会 (2024)

マイナーアクチニド分離配位子の電子状態インフォマティクス

（中大院理工[1]・JST ACT-X[2]）○住吉 剛[1]・黒木 菜保子[2]・森 寛敏[1]

Electronic structure informatics for separative extraction of minor actinides

([1]*Chuo University,* [2]*JST ACT-X*) ○Tsuyoshi Sumiyoshi,[1] Nahoko Kuroki,[1,2] Hirotoshi Mori[1]

To improve the separation performance of minor actinides (An) from lanthanides (Ln) in radioactive liquid waste, ligand design with hetero elements introduction considering the "hard & soft acids & bases (HSAB) rule" is mandatory. However, it is not appropriate to investigate all the ligand candidates by exhaustive radiochemical experiments from a risk and cost perspective. With the background, we applied materials informatics to design Ln/An extraction ligand based on electronic structure data[1)]. A database of complexation Gibbs energy was created for 336 heterosubstituted-terpyridine derivatives by B2PLYP//BP86 (Fig. 1). Then, linear multiple regression was performed with electronic state features. The coefficient of determination exceeded 0.9, *i.e.*, ΔG prediction was achieved with high accuracy (Fig. 2). The regression coefficients indicate that lone pair orbitals of the donor and the atomic charge configuration within the ligand should be important.

Keywords : f block elements; DFT; materials informatics, coordination chemistry

放射性廃液中のマイナーアクチニド（An）とランタニド（Ln）の錯形成抽出分離では、HSAB（hard & soft acids & bases）則を考慮した配位子へのヘテロ元素導入による分離能向上が試みられてきた。だが、リスクとコストの観点から、配位子構造を網羅的な放射化学実験により検討することは適切ではない。この背景下、我々は、理論的な電子状態データベースに基づく、Ln/An 抽出配位子の迅速設計に向けたマテリアルズ・インフォマティクスを行なってきた[1)]。本研究では、{Ln/An}={Eu,Gd/Am,Cm} と Terpyridine 骨格の誘導体 336 構造（Fig. 1）を対象に錯形成ギブスエネルギー（ΔG）を相対論的密度汎関数計算（B2PLYP//BP86）によりデータベース化した。次に、配位子電子状態を特徴量とした線形重回帰を実施したところ、決定係数は 0.9 を超え、化学精度での ΔG 予測を達成した（Fig. 2）。回帰係数からは、ドナー元素のローンペア軌道と配位子内の原子電荷配置の重要性が定量的に示された。詳細に関しては当日紹介する。

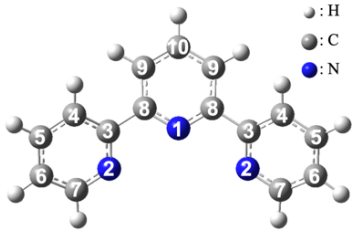

Fig. 1 Terpyridine.

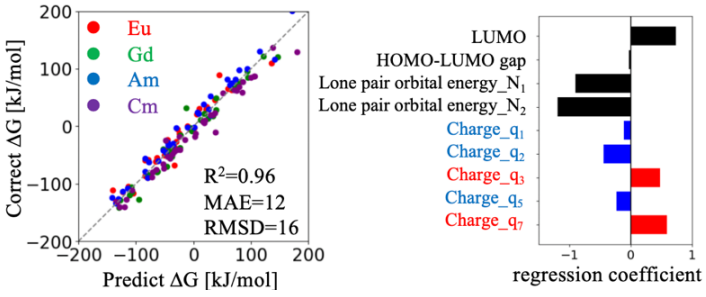

Fig. 2 Prediction ΔG (left) and regression coefficient (right).

1) 住吉剛, 黒木菜保子, 森寛敏, 放射化学会第 67 回討論会, 2023, 3A05

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アミド基を有する $C_6H_{11}NO$ 群の高分子構造異性体の全列挙とその分類

（北大院総化 [1]・北大院理 [2]・北大 WPI-ICReDD[3]・北大理 [4]）○臼杵 義亨 [1]・堤 拓朗 [1,2]・長谷部 航平 [1]・小林 正人 [1,2,3]・下道 珠緒 [4]・松岡 慶太郎 [1,2]・武次 徹也 [1,2,3]・佐田 和己 [1,2]

Complete enumeration and classification of polymer structural isomers with $C_6H_{11}NO$ and one amide group

([1] *Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2] *Graduate School of Science, Hokkaido University*, [3] *ICReDD, Hokkaido University*, [4] S*chool of Science, Hokkaido University*) ○Gikyo Usuki,[1] Takuro Tsutsumi,[1,2] Kohei Hasebe,[1] Masato Kobayashi,[1,2,3] Mio Shitamichi,[4] Keitaro Matsuoka,[1,2] Tetsuya Taketsugu,[1,2,3] Kazuki Sada,[1,2]

Thermo-responsive polymers exhibit a drastic change in solubility by changing the temperature. By evaluating the thermo-responsiveness of *N*-methylated nylon, we have previously revealed that thermo-responsiveness tends to appear when the molecular formula of the unit structure per an amide group is $C_6H_{11}NO$. However, nylon 6 does not exhibit thermo-responsiveness despite the same molecular formula. Thus, we hypothesized that the true structure-property relationship could be revealed by completely enumerating polymer structural isomers that meet the above requirements and searching their thermo-responsiveness.

First, we completely enumerated polymer structural isomers which have one amide group in unit molecular formula $C_6H_{11}NO$ by using our developed program. As a result, 387 polymer structural isomers were generated. We classified them based on the structural features such as the length of main chains and the number of NH in the amide groups. Literature research indicated that there were only 40 polymers that had already been synthesized. These findings show the existence of bias in polymer research. Clustering based on the structural properties of polymer using machine learning is ongoing in our laboratory.

Keywords : Polymer structural isomers; Complete enumeration; Thermo-responsive polymer; Polymer taxonomy

温度応答性高分子とは、周囲の温度変化に応答してその溶解性が劇的に変化する高分子である。当研究室では水中で温度応答性を発現する新たな高分子である *N*-メチル化ナイロンを開発した(1)。主鎖の炭素数を変化させて温度応答性を調査したところ、アミド基一つあたりの分子式が $C_6H_{11}NO$ である時が水中で最も温度応答性を発現しやすいことを見出した。しかし、ナイロン 6 のようにこの条件を満たしていても温度応答性を発現しない高分子も存在する。そこで、ユニット構造の分子式が $C_6H_{11}NO$ でアミド基をもつ高分子構造異性体を全て洗い出し、それらの水中における温度応答性を調査し構造との因果関係を探ることで、より詳細な構造物性相関を導けると考えた。

自作の Python プログラムを用いて分子式が $C_6H_{11}NO$ でアミド基をもつ高分子ユニット構造を全列挙したところ、387 種類の構造異性体が生成された。これらを主鎖の長さやアミド基の級数等の特徴により分類した。さらに、各構造異性体の合成例について文献調査を行ったところ、合成報告は 40 種類弱であり、構造異性体の総数に対して研究が進められている高分子の数が極めて少ないことが明らかとなった。当日は機械学習を利用した高分子の構造的特徴に基づくクラスタリングも発表する。

(1) Sugano, A.; Inaba, N.; Matsuoka, K.; Sada, K., 第 71 回高分子討論会, 2022, 2I05.

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機械学習と多変量スペクトル分解法を用いた混合物スペクトルの分解

（早大先進理工[1]・早大理工総研[2]）○関屋　鯨達[1]、熊谷　拓海[1]、清野　淳司[1,2]

Decomposition of spectrum in mixed compounds using machine learning and multivariate curve resolution

([1]School of Advanced Science and Engineering, Waseda University, [2]Waseda Research Institute for Science and Engineering) ○Keitatsu Sekiya[1], Takumi Kumagai[1], Junji Seino[1,2]

With the recent rapid technological development of automated experiments, it is important to develop a method for automatic identification of synthesized compounds. We have developed an automatic molecular identification system using machine learning and quantum chemical calculations for spectra of single compounds. In this study, we developed an additional method that can be applied to mixed compounds by using machine learning and multivariate curve resolution to decompose a spectrum of mixed compound into spectra of individual compounds.

Keywords : cheminformatics; spectrum in mixed compounds; machine learning; multivariate curve resolution

【緒言】近年、急速に技術開発が進む実験の自動化に伴い、合成した化合物を自動的に同定する手法の開発は重要である。我々はこれまで単一の化合物のスペクトルに対して、機械学習と量子化学計算を利用し化合物の自動同定を行うシステムを開発してきた[1)]。本研究では機械学習と多変量スペクトル分解（MCR）法[2)]を利用して、複数の化合物による混合物スペクトルを個々の化合物の純成分スペクトルに分解する手法を開発した。

【方法】MCR 法は、複数の成分が混合したデータから純成分を抽出する手法としてよく用いられる。この手法において、あらかじめ純成分の個数とスペクトル情報を知る必要がある。そこで本稿では、機械学習を用いて混合物スペクトルから、ある化合物が含まれるか否かを判別するモデルについて記載する。データとして、SDBS データベース[3)]から 100 個の有機化合物のスペクトルを取得し、2 種類の化合物を組み合わせて混合物スペクトルを作成した。記述子として、それぞれのスペクトルを等間隔に 150 分割し、混合物スペクトルと判別したい純成分スペクトルを合わせて使用した。各記述子の値は、その範囲内のスペクトル強度である。学習データは正解と不正解の割合を考慮し、全組み合わせの約 2%をランダムに抽出した 12,000 個を使用した。テストデータとして一部の学習データと重複した 9,900 個を用いた。機械学習手法として、ランダムフォレストを使用し、Optuna によりハイパーパラメータを最適化した。

【結果】図 1 に構築したモデルの記述子依存性を示す。記述子として、(1) ^{1}H NMR、(2) ^{13}C NMR、(3) MS を用い、それぞれの組み合わせによる精度検証を行った。一つのスペクトル情報で正解率（Accuracy）が 0.91 以上、三つのスペクトル情報で 0.98 程度となり、高い精度で該当化合物が含まれるか否かを予測できることが確認された。

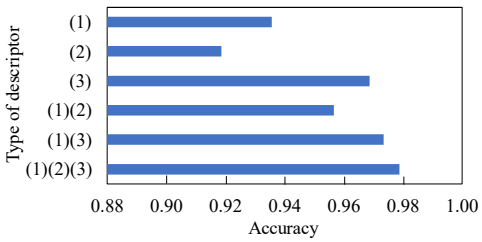

Figure 1. Prediction accuracy of presence of a reference compound using descriptors combining three types of spectral information.

1) T. Kumagai, Y. Nakajima, J. Seino, *J. Comput. Chem. Jpn.* **22**, 12 (2023). 2) E. H. Novotny, R. H. S. Garcia, E. R. deAzevedo, *J. Magn. Reson. Open*, **14–15**, 100089 (2023). 3) https://sdbs.db.aist.go.jp.

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大規模言語モデルを利用した電子実験ノート向け対話型情報検索システムの構築

(早大先進理工[1]・早大理工総研[2]・三菱ケミカルグループ[3]) ○海上 菜々子[1]、中野 匡彦[2,3]、清野 淳司[1,2]

Development of a Dialogic Information Retrieval System Utilizing Large Language Models for Electronic Lab Notebooks ([1]School of Advanced Science and Engineering, Waseda University, [2]Waseda Research Institute for Science and Engineering, [3]Mitsubishi Chemical Group) ○Nanako Unagami[1], Masahiko Nakano[2,3], Junji Seino[1,2]

Traditional paper and electronic lab notebooks present limitations in information management and sharing. This study explored the use of large language models (LLMs), recently gathering increased research interest, to redefine lab notebooks in the AI era. The presentation focuses on the development of a system that retrieves relevant information from electronic lab notebooks and leverages LLMs to generate dialogic text from this extracted information. The initial results of the performance evaluation of this system are also discussed.

Keywords: Cheminformatics, Large Language Model, Retrieval Augmented Generation, Electronic Lab Notebook

【緒言】従来の紙あるいは電子実験ノートでは、情報管理や共有に関する限界が存在する。本研究では、最近化学分野でも応用研究が盛んな大規模言語モデル (LLM) を用いて、AI 時代の実験ノートのあり方を探求する。特に本報告では、電子実験ノートから関連情報を検索し、その内容をもとに LLM を用いて対話的に文章を生成するシステムの開発について述べる。本システムの性能評価についての初期的な結果も併せて報告する。

【システム構築】本研究では、外部の知識ソースを参照することで、LLM の回答の質を向上させる retrieval augmented generation (RAG) のフレームワーク [1]に基づき、システムを構築した (Fig. 1)。本システムでは予め、読み込ませた実験ノートサンプルを embedding 変換し (❶)、ベクトルデータベースに保存した (❷)。次にユーザーが入力した実験ノートに関する質問 (①) を embedding 変換し (②③)、データベースから類似文書を検索した (④⑤)。最終的に、データベース内の関連文書に基づき作成したプロンプト (⑥) から、GPT-4 により回答を生成した (⑦⑧)。

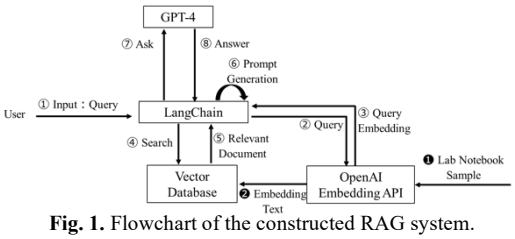

Fig. 1. Flowchart of the constructed RAG system.

【性能検証】生成した回答を評価するために、研究が先行する医療分野の特化型 LLM [2,3] の評価基準を参考に、化学分野向けの RAG システムに関する評価基準を定義した。評価基準は、14 種の評価軸から構成され、それらは 3 つの主要な評価軸 (質問への応答品質、情報ソースの活用精度、専門的な適応性) に大別できる。スコアリングには項目ごとの基準を定め、1~5 点の 5 段階で評価した。評価の結果、言葉遣いの丁寧さや簡潔性など質問への応答品質は高く (Fig. 2)、実験ノート中に記載されている基本的な質問に対して適切に回答可能であることが確認された。

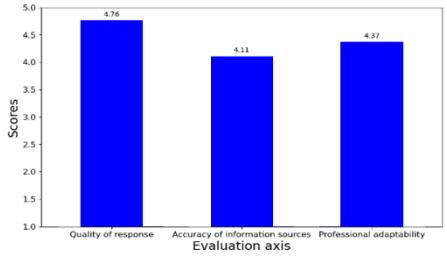

Fig. 2. Average scores of the present system on each evaluation axis.

1) P. Lewis et al. *Adv. in Neural Info. Proc. Sys.*, 33, 9459 (2020b). 2) X. Shi et al. *arXiv*, 2308.07635v1[cs.CL] (2023). 3) K. Singhal et al. *Nature*, 620, 172 (2023).

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機械学習を利用した水電解電極における酸素発生反応機構解析

(北大院総化[1]・北大理[2]・北大院理[3])
○米山 伸二[1]・深澤 元貴[2]・福島 知宏[3]・村越 敬[3]

Mechanistic analysis of oxygen evolution reaction electrodes by machine-learning analysis

(*Department of Chemistry, Faculty of Science, Hokkaido University*)
○Shinji Yoneyama, Motoki Fukasawa, Tomohiro Fukushima, Kei Murakoshi

Oxygen evolution reaction is complicated mechanism because of multi-electron transfer process. Computational analysis is demanded for the investigation of the reaction mechanism. In this study, a microkinetic model for analyzing the current-potential data of oxygen evolution reaction by assuming sequential four electron transfer reaction process at various types of electrodes. This method is applicable to the analysis of wide variety of metal catalyst electrodes.
Keywords : Electrochemistry, Machine Learning, Oxygen Evolution Reaction, Microkinetic Modeling, Genetic Algorithm

【序論】電極反応の多電子移動反応においては、一般に Tafel plot や系の pH 応答から種々の物理量が解析されている。一方で近年では機械学習を用いた手法により、反応機構解析が可能となっているが、多電子移動反応への適用は未だ難しい。本研究では 4 電子移動反応である酸素発生反応に着目し、触媒特性の定量的理解を目的として計算手法の開発およびミクロ反応速度論に基づく反応機構解析を行った。[1]
【手法】本研究では 4 電子移動逐次反応を仮定した遺伝的アルゴリズムによるミクロ反応速度論モデルを構築し、Python を利用して計算プログラムを開発した。文献データを利用することで、過去の触媒の各種酸素発生反応触媒電極の電流-電位データに対してフィッティングを行った。
【結果と考察】独立な Butler-Volmer 式を仮定したときには理論線が収束しなかったのに対して、律速段階を仮定することにより理論線が実験値に近く収束していく様子が観察された。Figure に Ni での解析の例を示す。速度論パラメータの収束具合としてはベイズ分布に従った広がりを有するエネルギー相関が観測され、中間体間の自由エネルギー関係が示された。さらには従来顕わではなかった反応ルートが観測された。本解析手法は他の電極触媒反応の解析についても応用可能であり、一般的な多電子移動系への拡張が期待される。

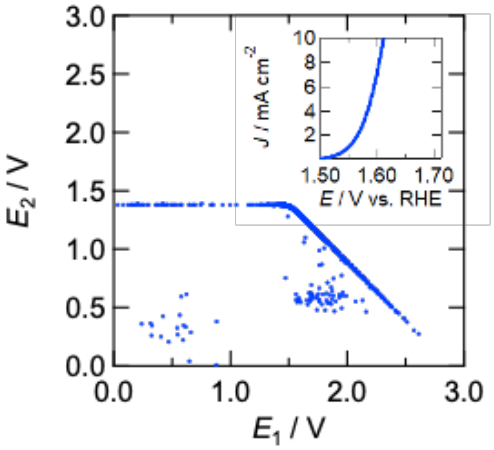

Figure. Plot of the intermediate energy from the machine-learning analysis Ni OER. Inset: linear sweep voltammogram of Ni plate in 5 M NaOH.

参考文献 1) T. Fukushima, M. Fukasawa, K. Murakoshi *J. Phys. Chem. Lett.* **2023**, *14*, 6808–6813.

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

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC H937(937, Bldg. 9 [3F])

[H937-4pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Takuro Tsutsumi, Yuki Mitsuta

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H937-4pm-01]
Development of a Nudged Elastic Stiffness Band Method by Adding Stiffness Force to Improve the Nudged Elastic Band Method

○Yuki Mitsuta[1,2], Toshio Asada[1,2] (1. Graduate School of Science, Osaka Metropolitan Univ., 2. RIMED, Osaka Metropolitan Univ.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H937-4pm-02]
Towards a Post-Sabatier Theory of Electrocatalysis: Realizing Activity and Stability

○Hideshi Ooka[1], Ryuhei Nakamura[1,2] (1. RIKEN CSRS, 2. Tokyo Inst. Technol. ELSI)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H937-4pm-03]
Extrapolation Prediction of Properties of Sol-Gel Anti-Reflection Coating with Various Silicon Alkoxides as Precursors by Machine Learning

○Takuma Kurakami[1], Koichi Shiraki[1], Mizuho Matsuda[1] (1. NIPPON SHEET GLASS CO., LTD.)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H937-4pm-04]
Crystal structure prediction based on heterogeneous metric learning

○Minoru Kusaba[1], Chang Liu[1], Ryo Yoshida[1,2,3] (1. The Institute of Statistical Mathematics, 2. SOKENDAI, 3. National Institute for Materials Science)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H937-4pm-05]
Exploration of alloy catalyst with highly reactive atomic configuration using a universal neural network potential and a generative model

○Kaoru Hisama[1], Atsushi Ishikawa[2], Susan Menez Aspera[1], Michihisa Koyama[1] (1. Shinshu Univ., 2. Tokyo Tech.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[H937-4pm-06]

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Can LLMs be Lab Assistants?

○Gergely Juhasz[1] (1. Tokyo Institute of Technology)

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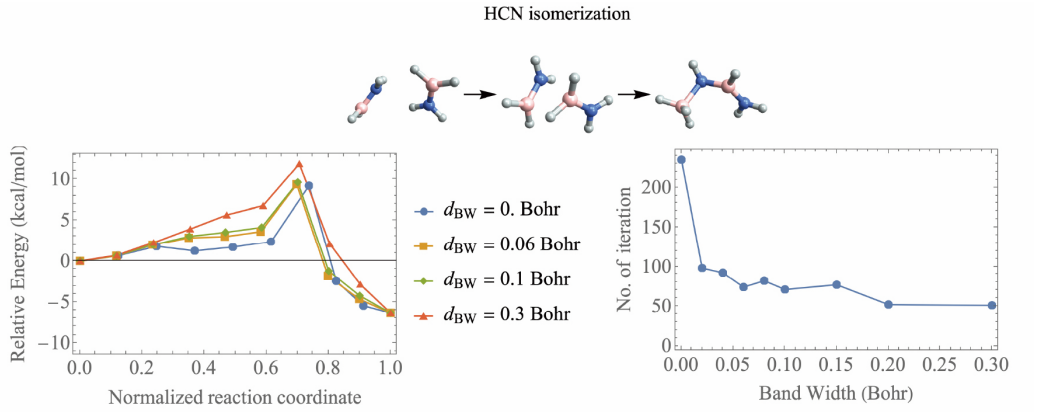
Nudged Elastic Band 法を改良するために剛性の力を加えた Nudged Elastic Stiffness Band 法の開発

（阪公大院理[1]・阪公大 RIMED[2]）○満田 祐樹[1,2]・麻田 俊雄[1,2]
Development of a Nudged Elastic Stiffness Band Method by Adding Stiffness Force to Improve the Nudged Elastic Band Method ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*RIMED, Osaka Metropolitan University*) ○Yuki Mitsuta,[1,2] Toshio Asada[1,2]

The nudged elastic band (NEB) method[1] has been used to calculate reaction paths using a single band of intermediate structures from a reactant to a product. However, the NEB method has the “kinks” problem, which is caused by the free bending of the bands. Thus, we proposed the nudged elastic stiffness band (NESB) method[2]. In this method, we applied the beam theory and added stiffness force by extending the single to double band. This additional force allowed us to prevent excessive bending of the bands. We also calculated the NESB combined with the Energy Weighted Climbing Image NEB (EW-CI-NEB)[3], and discussed the convergence of the calculations.
Keywords : Optimization; Chemical Reaction Path; Nudged Elastic Band; Quantum Chemistry

Nudged Elastic Band (NEB)法[1]は化学反応や固体の構造変化などの反応経路を計算する代表的な手法の１つである。しかしながら、系によっては経路が大きく曲がることで計算が収束しなくなる kink 問題が起こり、最適化計算が収束しない場合がある。そこで我々は、新しく Nudged Elastic Stiffness Band (NESB)法[2]を開発した。この方法では梁理論を応用することで剛性の力を計算し、経路の曲がりを補正する。梁の幅であるバンド幅 d_{BW} をコントロールすることで適切な最適化を設定し、収束性を上げることが可能となった。また、NEB 法には様々な改良手法があり、それらと NESB を組み合わせることによって収束性を上げることができる。そこで、鞍点を発見するための手法である Energy Weighted Climbing Image NEB (EW-CI-NEB)[3]と組み合わせた EW-CI-NESB を行い、収束性の向上を確認した。



1) G. Mills *et al.*, *Phys. Rev. Lett.*, **1944**, *72*, 1124–1127; G. Mills *et. al.*, *Surf. Sci.*, **1995**, *324*, 305–337; H. Jónsson *et al., Class. Quantum Dyn. Condens. Phase Simulations,* **1998**.
2) Y. Mitsuta, and T. Asada. *J. Comp. Chem.,* **2023**, *44*, 1884-1897.
3) V. Ásgeirsson et al., J. Chem. Theory Comput., **2021**, *17*, 4929-4945

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Post-Sabatier を目指した電極触媒理論の開拓：活性と安定性の両立に向けて

(理研 CSRS[1]・東工大 ELSI[2]) ○大岡英史[1]・中村龍平[1,2]

Towards a Post-Sabatier Theory of Electrocatalysis: Realizing Activity and Stability

([1]RIKEN CSRS, [2]Tokyo Inst. Tech. ELSI) ○Hideshi Ooka,[1] Ryuhei Nakamura[1,2]

Active and stable electrocatalysts are necessary to realize clean energy technology such as fuel cells or water electrolyzers. So far, the binding energy between the catalyst and the substrate has been used as a key descriptor to develop new catalysts. The Sabatier principle, which states that catalytic activity will be maximized at an intermediate binding energy, has been central to this approach. However, while the Sabatier principle provides a theoretical framework to understand catalytic activity, a similar framework for stability is lacking.

In this presentation, we will present our ongoing efforts to realize a theory which quantifies catalytic lifetime. Based on this theory, we will highlight the challenges towards realizing a catalyst which is both active and stable. Finally, we will present our ongoing efforts to verify the theory based on experimental measurements of the oxygen evolution reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) on manganese oxide.

Keywords : Electrocatalysis, Microkinetics, Applied Mathematics

水素製造や燃料電池など、今後のクリーンエネルギー技術を実現するには、高い活性と安定性を両立した電極触媒が不可欠である。これまで、触媒と反応基質の吸着エネルギーに着目した触媒開発が行われてきた。特に、適度な強さの吸着エネルギーにおいて活性が最大化される、と主張する Sabatier 則は、中心的な役割を果たしてきた。しかし、活性に関する理論的な枠組みは Sabatier 則を中心に確立されてきた一方で、触媒の寿命を定量的に議論する理論はまだ構築されていない。

そこで本発表では、触媒寿命の定式化に向けて行った数理的な検討について発表する。そして、触媒寿命を記述する数式から想定される、活性と安定性の両立に必要な条件について考察を行う。また、酸化マンガン上の酸素発生反応 ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$)をモデル系とした実験検証についても報告する。

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様々な Si アルコキシドを前駆体原料として用いたゾル-ゲル低反射膜特性の機械学習による外挿予測

（日本板硝子株式会社[1]）○倉上 拓真[1]・白木 康一[1]・松田 瑞穂[1]
Extrapolation Prediction of Properties of Sol-Gel Anti-Reflection Coating with Various Silicon Alkoxides as Precursors by Machine Learning ([1]*NIPPON SHEET GLASS CO., LTD.*) ○ Takuma Kurakami[1], Koichi Shiraki[1], Mizuho Matsuda[1]

Sol-gel method　is a process that can produce organic-inorganic hybrid materials with functionality and formability. The properties of sol-gel materials depend on many factors, for example, what kind of organic group modified precursors to use. In this study, we built machine learning models to predict sol-gel coating properties from precursors and synthesis conditions, and evaluated extrapolated prediction accuracy by predicting the properties of the coatings which contain silicon alkoxides as precursors not included in training data. The data of coating properties for training and evaluation was obtained by measuring optical property and various durability of the coatings with 8 types of silicon alkoxides as precursors. The use of molecular descriptors as explanatory variables allows the model to make extrapolated predictions, and the evaluation results confirmed good prediction accuracy.
Keywords : Sol-Gel; Machine Learning; Molecular Descriptor; Fingerprint; Materials Informatics

ゾル-ゲル法は液相合成、低温合成という特徴から、機能性・成形性に富んだ有機-無機ハイブリッド材料を作製可能な手法である。ゾル-ゲル法で得られる材料の特性を支配するパラメータは多岐にわたり、例えばどのような有機基を修飾した金属アルコキシドをゾル-ゲル前駆体原料として用いるのかによって得られる材料の特性は大きく異なる。そこで本研究ではゾル-ゲル前駆体原料および合成条件からゾル-ゲル低反射膜の特性を予測する機械学習モデルを構築し、学習データに含まれないゾル-ゲル前駆体を原料とした膜特性の予測（外挿予測）精度の評価を行った。膜特性データの収集ために、8 種類の Si アルコキシドを原料としたゾル-ゲル低反射膜をガラス基板上に成膜し、光学特性と各種耐久性を評価した。分子記述子を説明変数に用いたモデルを構築し、良好な予測結果が得られた。

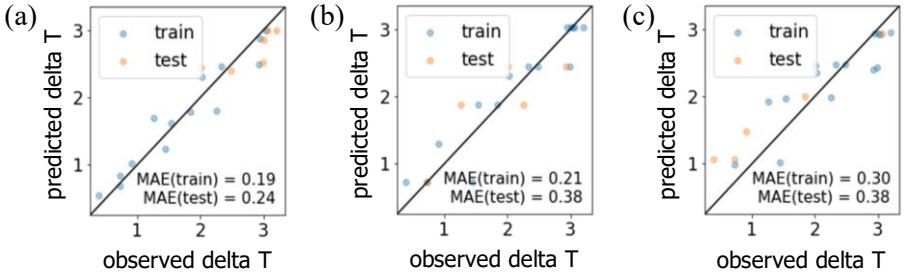

Fig. 1 Scatterplots between the observed and predicted delta Transmittance of (a) methyltriethoxysilane, (b) 3-glycidyloxypropyltriethoxysilane, and (c) phenyltriethoxysilane test data.

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Heterogeneous metric learning に基づく結晶構造予測

(統計数理研究所[1]・総合研究大学院大[2]・物質・材料研究機構[3])
○草場 穫[1]・劉 暢[1]・吉田 亮[1,2,3]
Crystal structure prediction based on heterogeneous metric learning ([1]*The Institute of Statistical Mathematics*, [2]*SOKENDAI,* [3]*National Institute for Materials Science*)
○Minoru Kusaba,[1] Chang Liu,[1] Ryo Yoshida[1,2,3]

We propose a template-based crystal structure prediction method based on heterogeneous metric learning. In this method, a function is learned from the crystal structure database to determine whether a given chemical composition and crystal structure pair is a stable structure or not. The function is used to select a template structure that has a high stability evaluation value when paired with a composition for which the stable structure is unknown, and the crystal structure of the composition is predicted by element substitution of the selected template structure.
Keywords : Crystal structure prediction; Materials informatics; Machine learning

任意の化学組成によって形成されるエネルギー的に安定した結晶構造を予測することは、固体物理学における未解決問題である。安定した原子の結晶状態は、第一原理計算によって評価されるエネルギー曲面の最適化によって決定される。しかし、この最適化問題を解くことは計算コストが高く、大規模なシステムに適用することができない。一方、エネルギー曲面の最適化に基づかない高速な手法として、既知構造の元素置き換えによって予測を行うテンプレートベースの手法が提案されている。我々は、この手法群に分類される結晶構造予測手法を2022年に発表した[1]が、以下三つの問題点が未解決であった；①準安定構造予測に対応していない ②構造から組成を探す逆向きの予測に対応していない ③データベースに無い構造を予測することができない。

そこで、本研究ではheterogeneous metric learningに基づいたテンプレートベースの新たな結晶構造予測手法の構築を目指す。本手法では、与えられた化学組成と結晶構造のペアが安定構造であるか否かを判別する関数を結晶構造データベースから学習し、その関数に基づいた結晶構造の提案によって構造予測を行う。この新しい方法論では、組成と構造を別々に扱っているため、上記三つの問題点を解決することができる。本研究では、組成と構造ともに我々が開発したカーネル平均埋め込みに基づく記述子生成手法[2]によって固定長ベクトルに変換される。発表では、幾つかのheterogeneous metric learningのモデルによる、組成と構造ペアの安定性予測性能の比較と結晶構造予測結果を紹介する。

Acknowledgment: This work was supported by JSPS KAKENHI Grant Number 22K21292.

1) Kusaba, M., Liu, C., & Yoshida, R. (2022). Crystal structure prediction with machine learning-based element substitution. *Computational Materials Science*, *211*, 111496.
2) Kusaba, M., Hayashi, Y., Liu, C., Wakiuchi, A., & Yoshida, R. (2023). Representation of materials by kernel mean embedding. *Physical Review B*, *108*(13), 134107.

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汎用ニューラルネットワークポテンシャルと生成モデルを用いた高活性合金触媒の原子配置探索

（信州大[1]・東工大[2]）○久間 馨[1], 石川 敦之[2], Aspera Susan Menez[1], 古山 通久[1]

Exploration of alloy catalyst with highly reactive atomic configuration using a universal neural network potential and a generative model ([1]*Center for Research Initiative for Supra-Materials, Shinshu University*, [2]*Department of Transdisciplinary Science and Engineering, Tokyo Institute of Technology*) ○ Kaoru Hisama[1], Atsushi Ishikawa[2], Susan Menez Aspera[1], Michihisa Koyama[1]

It is important for alloy catalyst design to reveal highly reactive atomic configurations. Therefore, we developed a fast calculation method for finding highly reactive surfaces, by generating candidates of atomic configurations with high activity using a generative adversarial networks (GAN) and evaluating the reaction energy [1], accelerated by a universal neural network potential, PFP [2]. By iterating between the generation and evaluation process, we explored atomic configurations that maximize the reactivity for ammonia synthesis of an alloy catalyst composed of Pd, Rh, and Ru elements. As a result, alloy surface structures with higher turn-over frequencies (TOF) than the monometal Ru are successfully identified [Fig. 1].
Keywords : Heterogeneous catalyst, Neural Network Potential, Generative adversarial networks, Density functional theory

合金触媒表面において，どのような元素配置や構造が高活性となるのかは触媒設計上重要である．本研究では，機械学習を用いた効率的な配置探索を行うことで，活性の高い合金配置とそのメカニズムの解明を図る．敵対的生成ネットワーク(GAN)で触媒活性の高い原子配置を模倣した構造を生成し，反応エネルギーから活性評価を繰り返し行う手法 [1]に汎用ニューラルネットワークポテンシャル PFP [2]を組み合わせることで，高活性な触媒表面を高速に自動探索する手法を開発した．アンモニア合成反応に対する Pd, Rh, Ru の三元素を組み合わせた触媒について探索を行ったところ，Fig. 1 に示すように，2 元系・3 元系合金において単体では最も活性が高い Ru を上回る触媒回転頻度(TOF)を持つ配置が見出され，本手法の有効性が示唆された．

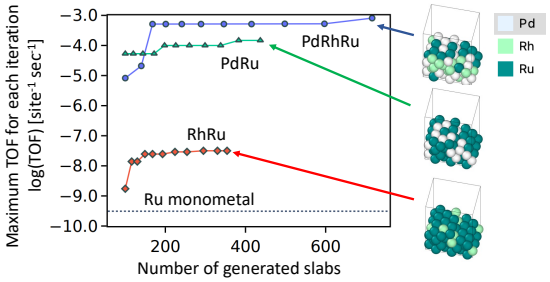

Figure 1 Maximum TOF for each alloy, as a function of the number of generated slab models.

[1] A. Ishikawa, Sci. Rep. 12, 11657 (2022). [2] S. Takamoto et al., Nat. Commun. 13, 2991 (2022).

謝辞 本研究は科研費 20H05623 の支援を受けた．また，本計算の一部は東北大学計算材料科学センターMASAMUNE-IMR を用いて行った

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Can LLMs be Lab Assistants?

([1]*Graduate School of Science, Tokyo Institute of Technology*) ○Gergely Juhasz[1]
Keywords: Chemical Literature Review, Knowledge Extraction, Automation

Scientific research has traditionally relied heavily on knowledge of relevant scientific literature, individual expertise, and know-how in the given field. This approach makes research an intellectually rewarding adventure, but also limits what individual researchers or research laboratories can achieve. The recent breakthroughs in AI, specifically in the real-world applications of large language models (LLMs), raise hopes that clever use of these tools can augment human skills and multiply what can be achieved in a laboratory. Several reports suggest that LLMs may be able to autonomously perform quantum chemical calculations,[1] answer scientific questions by performing autonomous literature reviews,[2] or run experiments autonomously.[3]

Here, we present our ongoing experiments, focusing primarily on how accurately LLMs can analyze the content of research papers and suggest calculation methods to interpret experiments. We compared the abilities of some major LLMs, including GPT-3.5 and GPT-4.0, Gemini, and open-source models. We tested the suggested input files on Orca and Gaussian software, as they are widely available and popular computational tools. We have found that careful few-shot learning prompts can significantly improve the reliability of the suggested methods. However, detailed analysis of chemical structures remains the Achilles heel of these models.

Our study reveals the immense potential of LLMs in aiding chemical research, yet also points to the necessity of further development, especially in the detailed analysis of chemical structures, to fully harness their capabilities.

1) A. D. White, et al. *Digital Discovery*, **2023**, 2-2 368–76. 2) A. M. Bran, S. Cox, A. D. White, P. Schwaller. *arXiv*, **2023**. https://doi.org/10.48550/arXiv.2304.05376. 3) Boiko, Daniil A., R. MacKnight, B. Kline, G. Gomes. *Nature* **2023**, *624*, 570–78.

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

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1441(1441, Bldg. 14 [4F])

[A1441-4pm] 04. Physical Chemistry -Properties-

Chair: Tomoyuki Mochida, Yoshiki Ishii

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1441-4pm-01]

Thermal phase transition behaviors of two-dimensional perovskite microcrystals as studied by low-frequency Raman microspectroscopy

○Ryuto Yumiba[1], Shinsuke Shigeto[1], Eric Wei-Guang Diau[2] (1. The Univ. of Kwanseigakuin, 2. National Yang Ming Chiao Tung Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1441-4pm-02]

Ionic conductivity modulation induced by the hydration structural change under vibrational strong coupling

○Hirotaka Motokawa[1], Tomohiro Fukushima[2], Kei Murakoshi[2] (1. School of Science, Hokkaido University, 2. Faculty of Science, Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1441-4pm-03]

Investigation of the optical properties of micro-structured electrodes and effects of vibrational polaritons with water molecules

○Yui Itakura[1], Hirotaka Motokawa[1], Daiki Ashizawa[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. Schoolof Science, Hokkaido University, 2. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 3. Faculty of Science, Hokkaido University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1441-4pm-04]

Structures and Phase Behaviors of Organometallic Ionic Plastic Crystals with Cyanoborate Anions

○Ryota Inoue[1], Shimada Masato[1], Tomoyuki Mochida[1,2] (1. Graduate School of Science, Kobe University, 2. Research Center for Membrane and Film Technology, Kobe University)

English
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1441-4pm-05]

Counting the microscopic states of molecular specimens using electron diffraction

○Jiarui Fu[1], Dongxin Liu[1], Masaya Sakakibara[1], Takayuki Nakamuro[1], Eiichi Nakamura[1] (1. The Univ. of Tokyo)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1441-4pm-06]

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How dose the methylation of the hydrogen atom at C2-position of imidazolium ring affect the high-pressure phase transition behavior of imidazolium-based ionic liquids?

○Hiroki Wakatsuki[1], Atsushi Yamada[1], Takahiro Takekiyo[1], Yukihiro Yoshimura[1] (1. National Defense Academy)

Japanese

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[A1441-4pm-07]

Potential of Ionic Liquids for the Temporary Cell Preservation Solvent at Room Temperature

○Masaharu Nakayama[1], Atsushi Yamada[1], Takamasa Uekita[1], Hiromi Miyazaki[2], Shingo Nakamura[2], Masami Yamada[1], Takahiro Takekiyo[1], Yukihiro Yoshimura[1] (1. National Defense Academy, 2. National Defense Medical College)

English

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[A1441-4pm-08]

Synthesis and heat-storage property of Zr substituted λ-Ti_3O_5

○Tomu Otake[1], Lidong Wang[1], Marie Yoshikiyo[1], Fangda Jia[1], Shin-ichi Ohkoshi[1] (1. The Univ. of Tokyo)

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

Break

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[A1441-4pm-09]

Preparation of Nb-Fe alloy nanoparticles and application to electroluminescence devices

○Akito Mizobata[1], Moegi Nomura[1], Syohei Murotani[2], Honami Iguchi[1], Takeyuki Suzuki[3], Kazuki Tabaru[1], Duotian Chen[4], Takashi Toyao[4], Ken-ichi Shimizu[4], Mitsuru Inada[2], Yasushi Obora[1] (1. Fac. Chem. Matl. & Bioeng., Kansai Univ., 2. Fac. Eng. Sci., Kansai Univ., 3. SANKEN, Osaka Univ., 4. Institute for Catalysis, Hokkaido Univ.)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[A1441-4pm-10]

Optical Characterization of Single Hollow Silver Nanoshell Using Dark Field Microscopy

○Koki Deguchi[1], Shinpei Kado[1], Setsuko Yajima[1] (1. The Univ. of Wakayama)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[A1441-4pm-11]

Computational chemistry study on characterization of organic solvent separation using MoS_2 containing nanofiltration membrane

○Ryo Arii[1], Hayato Higuchi[1], Masaya Miyagawa[1], Hiromitsu Takaba[1] (1. Kogakuin University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[A1441-4pm-12]

Pressure-dependent Elementary Exciton Processes of CdSe-based Core Shell Quantum Dots

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

Japanese

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3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[A1441-4pm-13]

Effects of Interfacial Potential on Electron Transfer Dynamics in InP-based Core/Shell Quantum Dots

○Kotaro Moriyama[1], Kazuki Inada[1], Daichi Eguchi[1], Naoto Tamai[1] (1. The Univ. of Kwansei Gakuin)

English

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[A1441-4pm-14]

Adsorption properties of NH_3 on hydrogen boride sheets

○Kosei Fukuda[1], Shin-ichi Ito[1], Miwa Hikichi[1], Iwao Matsuda[2], Takahiro Kondo[1,3] (1. University of Tsukuba, 2. The University of Tokyo, 3. Tohoku University)

Japanese

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

[A1441-4pm-15]

Discriminating Positional Isomers of Volatile Organic Compounds by Metal Oxide QCM sensor.

○Kenta Tanaka[1], Poom Jirayupat[1], Hosomi Takuro[1], Yanagida Takeshi[1,2], Takahasi Tsunaki[1], Tanaka Wataru[1], Jiangyang Liu[1] (1. The Univ. of Tokyo, 2. Kyusyu University)

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低振動数ラマン顕微分光を用いた２次元ペロブスカイト微結晶の熱相転移挙動の研究

（関西学院大院理工[1]・台湾国立陽明交通大[2]）○弓場 瑠人[1]・Eric Wei-Guang Diau[2]・重藤 真介[1]

Thermal phase transition behaviors of two-dimensional perovskite microcrystals as studied by low-frequency Raman microspectroscopy ([1]*Kwansei Gakuin Univ.*, [2]*National Yang Ming Chiao Tung Univ.*) ○Ryuto Yumiba,[1] Eric Wei-Guang Diau,[2] Shinsuke Shigeto[1]

Two-dimensional (2D) perovskites are expected to have various applications such as solar cells and LEDs. The thermal phase transition of 2D perovskites originating from the disordering of the organic cation chain have a significant impact on their chemical and physical properties, but the microscopic understanding of the phase transition behavior is far from complete. In this study, we observed the orthorhombic *Pbca* to *Acam* phase transition in a microcrystal of the 2D perovskite $(C_8H_{17}NH_3)_2PbI_4$ in a space-resolved manner using low-frequency Raman microspectroscopy with a high-precision temperature control stage. Using the intensity of the lattice Raman band at 22 cm^{-1} characteristic of the *Pbca* structure, we evaluated the phase transition temperature T_c at different points in the microcrystal. The resulting T_c image shows inhomogeneity within the crystal, which may be due to structural defects in the crystal.
Keywords : organic–inorganic hybrid perovskites; phase transition; lattice vibration; Raman microscope; temperature control

2 次元（2D）ペロブスカイトは太陽電池や LED など様々な応用が期待されている。有機カチオン鎖の disordering に由来する熱誘起相転移は 2D ペロブスカイトの化学的・物理的特性に大きな影響を与えるが、その制御に向けた微視的理解は不十分である。本研究では、高精度（±0.1 °C）温度制御ステージで温度を変化させながら、低振動数ラマン顕微鏡（励起波長 632.8 nm）を用いて、室温付近における 2D ペロブスカイト$(C_8H_{17}NH_3)_2PbI_4$微結晶（図 1a）の相転移挙動[1)]を空間分解して観測した。

図 1b に *Pbca* 構造（黒）および *Acam* 構造（赤）の$(C_8H_{17}NH_3)_2PbI_4$ の典型的な低振動数ラマンスペクトルを示す。*Pbca* 構造に特異的な 22 cm^{-1} の格子振動バンドの面積強度変化から転移温度 T_c を評価した（図 1c）。T_c のイメージ（図 1d）から、T_c が結晶内の場所によって異なり、最大 1.2 °C 程度の違いがあることが明らかとなった。このような同一結晶内での T_c の不均一性は 2D ペロブスカイト結晶の構造欠陥に由来する可能性が考えられる。

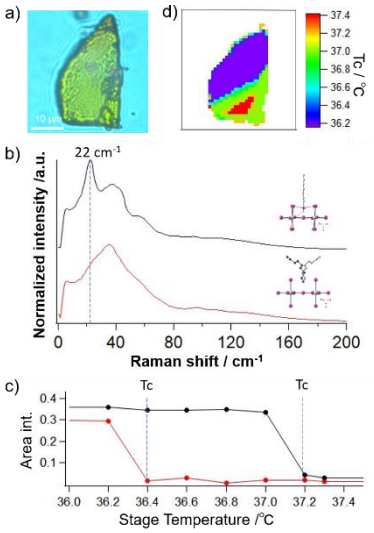

図 1. (a) $(C_8H_{17}NH_3)_2PbI_4$ 微結晶の光学顕微鏡像。(b) *Pbca*（黒）および *Acam*（赤）の典型的な低振動数ラマンスペクトル。(c) 22 cm^{-1} バンドの強度の温度依存性。(d) c から得られた T_c の空間分布。

1) A. Lemmerer and D. G. Billing, *Dalton Trans.* 2012, **41**, 1146–1157.

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振動強結合形成による水和イオン環境変化とイオン伝導度変調

（北大理[1]・北大院理[2]）○本川弘貴[1]・福島 知宏[2]・村越敬[2]
Ionic conductivity modulation induced by the hydration structural change under vibrational strong coupling (Department of Chemistry, Faculty of Science, Hokkaido University) ○Hirotaka Motokawa, Tomohiro Fukushima, Kei Murakoshi

To understand the change in hydration environment under vibrational strong coupling, ionic conductivity behavior was evaluated. The appearance of polariton peaks due to strong coupling formation was confirmed by IR spectroscopy. The relationship between cavity thickness and ionic conductivity was confirmed. The hydration environment-dependent modulation of ionic conductivity was also discussed by comparing the conductivity of concentrated aqueous solution as well as the alkali metal salt solutions.
Keywords : vibrational strong coupling; ionic conductivity; impedance spectroscopy

【序論】 分子が存在する共振器の光学モードを規定することによって、真空場が顕在化し、強結合が可能となる。我々はこれまでに Fabry-Perot 型共振器内で形成される振動強結合状態において、電解質水溶液のプロトン伝導度およびイオン伝導度が上昇する現象について報告してきた。[1] 本研究では振動強結合形成下において、水和イオンの環境変化が与えるイオン伝導度変調に関して報告する。

【実験】CaF_2 窓板上に Ti 2 nm、Au 8 nm、SiO_2 20 nm を蒸着し、2 枚の鏡面を対向させることにより、Fabry-Perot 型共振器を作成した。共振器長を調節しながら IR スペクトル計測とインピーダンス計測を繰り返し実施した。

【結果と考察】Figure に代表的な IR スペクトルを示す。水分子の有する振動子強度を反映して 3400 cm^{-1} 近傍の強い OH 伸縮が観測された。一方で共振器の厚さを 2.2 μm とすることで、2 次の共振器モードが OH 伸縮モードと結合し、760 cm^{-1} 程度の真空 Rabi 分裂が観測された。本現象は 1 M 以下の電解質水溶液において観測され、電解質水溶液に含まれる水分子を振動強結合形成が確認された。インピーダンス測定の結果から、振動強結合条件下においてイオン伝導度の向上が観測され、イオン種に従って 2-5 倍程度の増大が確認された。また、共振器長の変化に伴う伝導度変調も確認された。以上の検討から、イオンの水和環境に依存して、強結合の効果によりイオン伝導度の促進に寄与していることが明らかとなった。

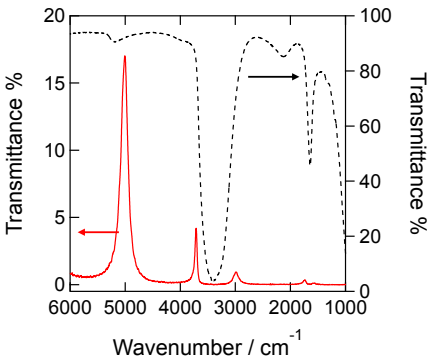

Figure. Representative IR spectra of water (black dotted line) and water in cavity (red line). Cavity thickness was 2.2 μm.

参考文献 1) T. Fukushima, S. Yoshimitsu, K. Murakoshi (a) *J. Phys. Chem. C* **2021**, *125*, 25832–25840. (b) *J. Am. Chem. Soc.* **2022**, *144*, 12177-12183. (c) *Chem. Sci.* **2023**, *14*, 11441-11446.

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マイクロ構造電極における光学特性調査と水の振動ポラリトン状態への影響

(北大理[1]・北大院総化[2]・北大院総化[3])
○板倉 由依[1]・本川 弘貴[1]・芦澤大輝[2]・福島 知宏[3]・村越敬[3]

Investigation of the optical properties of micro-structured electrodes and effects of vibrational polaritons with water molecules

(Department of Chemistry, Faculty of Science, Hokkaido University)
○Yui Itakura, Hirotaka Motokawa, Daiki Ashizawa, Tomohiro Fukushima, Kei Murakoshi

We report that the utilization of micro-structuredd electrode for the observation of vibrational polariton in cavity. Dependence of IR spectra of micro-structured electrode on the polarization angle, incident light angle, and water species are discussed for the understanding of vibrational polaritons.

Keywords : Polariton; Structured electrode; Water

【序論】物質の振動エネルギー準位と光学モードのエネルギー準位が一致するとき、振動ポラリトン状態に由来する二つのエネルギー混成準位が新たに生じる。この現象は振動強結合状態と呼ばれ、近年化学反応の設計指針として着目されている。これまでに我々は水分子の振動ポラリトン形成を利用した分光評価や電気化学評価を進めている。[1] 一方で強結合の研究においては、鏡を対向させた共振器の構造体を用いられているが、水分子の振動モードの直接観測は実現していない。本研究では、共振器配列型マイクロ構造電極を用いて、光学特性調査と水の振動ポラリトン状態への影響に関して検討を行った。

【実験】清浄ガラス基板上に共振器長が 1-5 μm の厚さで制御された、深さ 1 μm のマイクロ構造ガラス基板を作成した (Figure)。マイクロ構造ガラス基板に Ti 2 nm ,Au 8 nm, SiO_2 20 nm 蒸着し、マイクロ構造電極とした。入射光に対する基板の角度(ϕ)、偏光角(θ)を変化させて赤外分光計測を行い、基板の光学モードと水分子を導入した際の分光計測を行った (Figure)。

【結果と考察】金属を 200 nm 程度蒸着した際には、マイクロ構造電極における光学モードの存在が入射光角度依存赤外分光計測から示唆された。これは入射光に対する基板の角度(ϕ)を変化させた際に共振器への入射光が変わることにより光学モードの波数応答が見られるためである。一方で金属量が 10 nm 以下のときには明確な光学モードが観測されず、界面での反射率の重要性が示された。構造電極上に H_2O の存在有無の条件下、OH 伸縮振動モード付近のスペクトルを比較したところ、偏光方位と共振器方位に従って吸光度の変化が観測された。同一の電極における偏光異方性を D_2O 存在下との比較により、H_2O 分子集団の OH 伸縮振動モードとマイクロ構造電極の光学モードの結合の可能性を共振器長依存性から検証した。

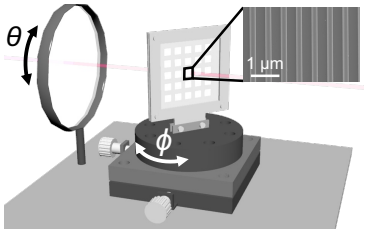

Figure. Schematic illustration of the IR measurements. SEM image of the electrode.

参考文献 1) T. Fukushima, S. Yoshimitsu, K. Murakoshi *J. Phys. Chem. C* **2021**, *125*, 25832–25840.

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日本化学会 第104春季年会 (2024)

シアノ系アニオンを有する有機金属柔粘性イオン結晶の構造および相挙動

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Structures and Phase Behaviors of Organometallic Ionic Plastic Crystals with Cyanoborate Anions ([1]*Graduate School of Science, Kobe University,* [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Ryota Inoue,[1] Masato Shimada,[1] Tomoyuki Mochida[1,2]

Most of the ionic plastic crystals reported to date are onium salts with fluorinated anions. In this study, to explore the versatility of cyanoborate anions, we synthesized organometallic salts containing several different variants of these anions (**Fig. 1**). Investigation of their thermal properties and crystal structures revealed that all the salts underwent a phase transition to an ionic plastic crystal phase. Lower-symmetry anions were found to lower the transition temperature.

Keywords : Ruthenium Complexes, Phase Transitions, Plastic Crystals, Crystal Structures

近年、固体電解質等への応用の観点から、柔粘性イオン結晶 (IPC)が注目されている。IPC相は球形に近い分子が示す固液中間相であり、分子の重心は秩序化しているが、分子配向が無秩序化している。IPC相を示す塩の多くはフッ素系アニオンを有する四級アンモニウム塩だが、当研究室ではサンドイッチ型錯体をカチオンとする多数のIPCを開発してきた[1]。ただし、これらの塩ではIPC相への転移温度が一般的に高い。

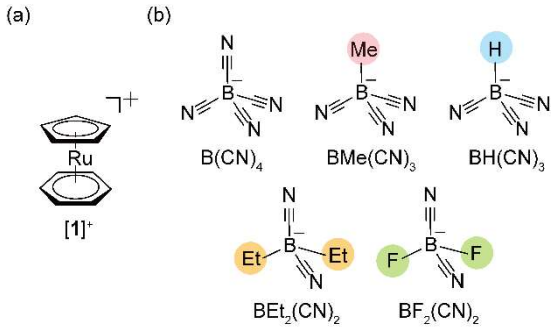

Fig. 1. Structural formulae of the (a) cation and (b) anions used in this study.

本研究では、シアノ系アニオンの有用性を探るために、サンドイッチ型錯体と種々のシアノボレートアニオンを組み合わせた塩を合成した (**Fig. 1**)。このうち[Ru(Cp)(C_6H_6)]$B(CN)_4$ ([**1**]$B(CN)_4$)は、340.3 KでIPC相に相転移するが[2]、その他の塩もすべてIPC相を発現することがわかった。なかでも[**1**]$BH(CN)_3$および[**1**]$BF_2(CN)_2$は室温付近でIPC相を発現し、アニオンの低対称化によって相転移温度が下がることが判明した。このように、IPC構築におけるシアノボレートアニオンの有用性が明らかになった。

1) T. Mochida, Y. Funasako, M. Ishida, S. Saruta, T. Kosone, T. Kitazawa, *Chem. Eur. J.*, **2016**, 22, 15725–15732.
2) T. Tominaga, T. Ueda, T. Mochida, *Phys. Chem. Chem. Phys.*, **2017**, 19, 4352–4359.

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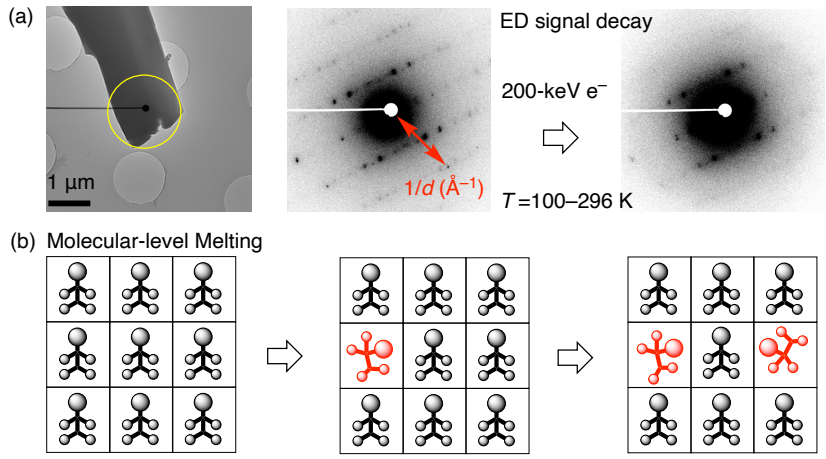
Counting the Microscopic States of Molecular Specimens Using Electron Diffraction

(*Department of Chemistry, The University of Tokyo*) ○Jiarui Fu, Dongxin Liu, Masaya Sakakibara, Takayuki Nakamuro, Eiichi Nakamura

Keywords: Microscopic States; Electron Diffraction; Molecular Crystal; Kinetics; Phase-Transition

The ensemble properties of crystals are governed by distinct microscopic states (W_d). If the value of W_d of crystals can be quantified, it becomes comparable between crystals regarding properties, stabilities, and the molecular-level understanding of phase transition. However, there is currently no direct method to count the value of W_d experimentally.

Taking advantage of the unique local interactions between fast electrons (200 keV or above) and atoms, here, we propose a straightforward method to count the W_d of molecular crystals of sub-micrometer by electron diffraction (ED). Although ED is an established method for structural analysis,[1] we exploit its potential by kinetic analysis of diffracted intensity decaying and find the disordering of crystallinity under electron beam illumination is strongly related to the melting process of the bulk crystals. Using electrons to disorder molecular crystals (more than 15 examples) at variable temperatures (4−296 K), the sample-dependent decaying rates and temperature-dependent disordering behaviors allow us to derive the frequency factors A using the Arrhenius equation. Therefore, by applying Boltzmann's entropy formula, we could measure the W_d based on an experimentally determined cross-section-related constant. The values of W_d are degenerated into the countable range of tens to thousands, which greatly facilitates the understanding of various molecular crystals.



1) C. G. Jones, *ACS Cent. Sci.* **2018**, *4,* 1587.

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２位炭素上プロトンのメチル化はイミダゾリウム系イオン液体の高圧相転移挙動にどのような影響を与えるのか

（防衛大応化）○若月 啓樹・山田 篤志・竹清 貴浩・吉村 幸浩

How Dose the Methylation of the Hydrogen Atom at C2-position of Imidazolium Ring Affect the High-pressure Phase Transition Behavior of Imidazolium-based Ionic Liquids?

(*Department of Applied Chemistry, National Defense Academy*) ○Hiroki Wakatsuki, Atsushi Yamada, Takahiro Takekiyo, Yukihiro Yoshimura

The methylation of the hydrogen atom of the C2 position (C2-H) of the imidazolium ring in the imidazolium-based ionic liquids (ILs) weakens the cation–anion interaction. However, by the methylation of C2-H group, the viscosity unexpectedly increases at room temperature and 0.1 MPa. In the present study, we have investigated the effect of methylation of C2-H group on the high pressure-phase transition behavior of imidazolium-based ILs using Raman spectroscopy. The present finding is that the methylation of C2-H group caused the increment of glass transition pressure, and there are some local structure changes up to 7.5 GPa.

Keywords : Imidazolium-based Ionic Liquids; Methylation; High-pressure Phase Behavior; Raman Spectroscopy

イオン液体は、カチオンとアニオンのみからなり、室温付近でも液体状態で存在できる塩である。不揮発性や難燃性等、従来の分子性液体には無い魅力的な性質を有している。その中でも、イミダゾリウム系イオン液体は、常温常圧下でイミダゾリウム環の C2-H 基をメチル基に置換すると、カチオンーアニオン間の水素結合が消滅するにも関わらず粘度が増加する等、興味深い物性変化を示すことが知られている [1)]。本研究では、この C2-H 基のメチル化が高圧相転移挙動にどのような影響を及ぼすか興味を抱いた。具体的には、ガラス転移圧やカチオン及びアニオンのコンフォメーション変化に着目し、7.5 GPa までの高圧ラマンスペクトル測定により調べた。その結果、ルビー蛍光線の半値幅変化 [2)]から、C2-H 基のメチル化は、予想とは逆にガラス転移圧を上昇させる効果があることが分かった。また、カチオン及びアニオンの各コンフォメーションの強度分率の圧力依存性とルビー蛍光の半値幅変化の比較から、少なくとも局所構造において何らかの構造変化が複数回あることが示唆された。従って、C2-H 基のメチル化は、高圧力下においてもイオン間の相互作用をアジャストする比較的簡単で有益な方法であると言える。

さらに、発表当日は、イミダゾリウムカチオン側鎖のアルキル鎖長及びアニオンの違いで、挙動がどのように変化するかの比較を行う予定である。

1) Why does a reduction in hydrogen bonding lead to an increase in viscosity for the 1-butyl-2,3-dimethyl-imidazolium-based ionic liquids? P. A. Hunt, *J. Phys. Chem. B* **2007**, *111*, 4844.
2) Hydrostatic limits in liquids and solids to 100 kba. G. J. Piermarini, *et al.*, *J. Appl. Phys.* **1973**, *44*, 5377.

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細胞の常温一時保存媒体としてのイオン液体の可能性

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Potential of Ionic Liquids for the Temporary Cell Preservation Solvent at Room Temperature

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Ionic liquids (ILs) containing cations and anions remain in liquid state below 100°C. Recently, ILs have been used as storage media for cells and drug delivery systems, and there have been studies examining cell toxicity of ILs[1)]. Generally, the temporary preservation of cells and tissues is performed at low temperatures using ice packs. However, if temporary storage at room temperature (RT) for these samples becomes possible, their efficiency in practical aspects such as transportation cost and time can be improved. Choline ($[Chl]^+$)-based ILs with biogenic cations have been reported to be relatively less toxic[2)]. Therefore, we investigated the solvent properties of five $[Chl]^+$-based ILs ([Chl][X]; X = Cl, I, dihydrogen phosphate (dhp), citrate (cit), and bitartrate (bit)) up to x = 5.0 mol% IL and performed a trypan blue viability tests using HEK293 cells to clarify the potential of aqueous $[Chl]^+$-based IL solutions as a RT-temporary preservation solvent for human cells. Solvent properties were investigated on the basis of electrical conductivity, pH, and osmolality. We found that [Chl][Cl] and [Chl][I] have potential application as temporary preservation solvents at RT. Furthermore, the results of trypan blue viability tests using HEK293 cells suggested that [Chl][Cl] could be most promising among the studied $[Chl]^+$-based ILs for this purpose.

Keywords：Ionic Liquid, Solvent Property, HEK293 Cell, Preservation Solvent

イオン液体(ILs)は、100℃以下で液体状態をとりうる塩である。近年、ドラッグデリバリーシステム(DDS)や細胞等の保存媒体としての利用が期待される中で、細胞毒性の研究が行われている[1)]。細胞や組織の一時保存は、一般的に氷嚢を用いた低温下での保存法が広く利用されている。一方で、常温一時保存が可能になれば、輸送のコストや時間等の実用面における効率が向上すると考えられる。ILs の中でも生体由来のカチオンを有するコリン系イオン液体([Chl]系 ILs)は比較的、低毒性であることが報告されている[2)]。そこで我々は、細胞を常温で一時保存する媒体として、5 種類の[Chl]系 ILs([Chl][X], X= Cl, I, dhp, cit, and bit)の可能性を検討するため、x = 5.0 mol% IL までの[Chl]系 ILs 水溶液の溶媒特性を、電気伝導度、pH 及び osmolality の観点から調べた。その結果、[Chl][Cl]と[Chl][I]に常温一時保存媒体としての可能性があることが分かった。次に、トリパンブルー染色によるヒト胎児腎由来の HEK293 細胞の生存率を調べたところ、[Chl][Cl]が常温一時保存媒体として利用できる可能性が最も高いことを示唆する結果を得た。

1) Biocompatible ionic liquids and their applications in pharmaceutics. R. M. Moshikur, *et al., Green Chem*. **2020**, *22*, 8116. 2) Ecotoxicity analysis of cholinium-based ionic liquids to *Vibrio fischeri* marine bacteria. S. P. M. Ventura, *et al., Ecotoxicol. Environ. Saf*. **2014**, *102*, 48.

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Synthesis and heat-storage property of Zr substituted λ-Ti_3O_5

([1]*Department of Chemistry, School of Science, The University of Tokyo*)
○Tomu Otake,[1] Lidong Wang,[1] Marie Yoshikiyo,[1] Fangda Jia,[1] Shin-ichi Ohkoshi[1]
Keywords: Phase transition; Heat-storage ceramic; Titanium oxide

Various heat-storage materials have been developed to expand the reuse of waste heat energy, although they release the stored energy as time passes. From this point of view, long-term heat-storage ceramics, lambda-trititanium-pentoxide (λ-Ti_3O_5) is drawing attention.[1] λ-Ti_3O_5 is a novel metastable phase of Ti_3O_5 discovered by our research group.[2] This material shows bistability with the energetically stable β-Ti_3O_5. Reversible phase transition between λ and β-phase can be induced by pressure and heat, and the stored heat energy can be extracted at a desired timing by applying pressure. The heat storage property can be controlled by substituting Ti with other metals such as Mg and Sc.[3-5] In this presentation, we report the synthesis of Zr-substituted λ-Ti_3O_5 and its performance as long-term heat-storage material.

Zr-substituted λ-Ti_3O_5 was obtained by reductive sintering of rutile-TiO_2 coated with $Zr(OH)_4$, which was obtained by dropping ammonia into an aqueous solution containing TiO_2 nanoparticles and zirconium oxynitrate. Elemental analysis and Powder X-ray diffraction (PXRD) measurement showed that the obtained sample is λ-$Zr_{0.06}Ti_{2.94}O_5$ (94%) and ZrO_2 (6%). Scanning electron microscopy (SEM) image showed that the sample has a coral-like morphology with secondary particle size of ca. 1 μm. The heat-storage performance was measured using differential scanning calorimetry (DSC). The phase transition temperature defined as the temperature of the endothermic peak was found to be lowered from 197℃ of λ-Ti_3O_5 to 183 ℃ of λ-$Zr_{0.06}Ti_{2.94}O_5$. Since both Zr and Ti are abundant elements, a long-term heat-storage material based on λ-$Zr_xTi_{3-x}O_5$ could rapidly accelerates the utilization of waste heat in the mid- to low-temperature range.

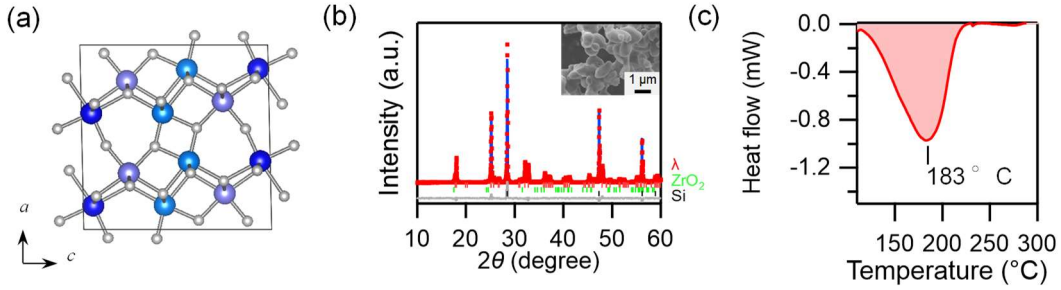

Figure 1. (a) Crystal structure of λ-$Zr_{0.06}Ti_{2.94}O_5$. (b) PXRD pattern with Rietveld analysis of $Zr_{0.06}Ti_{2.94}O_5$ and SEM image (Inset). (c) Endothermic peak of λ-$Zr_{0.06}Ti_{2.94}O_5$ observed using DSC.

[1] H. Tokoro, S. Ohkoshi, et al., *Nat. Commun.* **2015**, *6*, 7037. [2] S. Ohkoshi, et al., *Nat. Chem.* **2010**, *2*, 539-545. [3] Y. Nakamura, S. Ohkoshi, et al., *Sci. Adv.* **2020**, *6*, aaz5264. [4] S. Ohkoshi, et al., *Mater. Adv.* **2022**, *3*, 4824. [5] S. Ohkoshi, et al., *Chem. Commun.* **2023**, *59*, 7875.

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Nb-Fe 合金ナノ粒子の合成及び EL デバイス素子への応用

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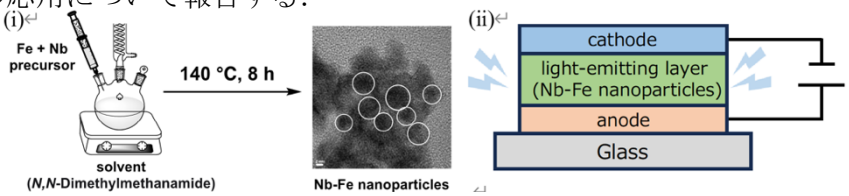
Preparation of Nb-Fe alloy nanoparticles and application to electroluminescence devices ([1] *Fac. Chem., Mater. Bioeng., Kansai univ.,* [2] *Fac.Sci., Pure. Appl. Phys. Eng., Kansai univ.,* [3]*Inst. Sci. and Industrial Research, Osaka Univ.,* [4] *Inst. for Catalysis, Hokkaido Univ.*) ○Akito Mizobata[1], Moegi Nomura[2], Shohei Murotani[3], Honami Iguchi[4], Takeyuki Suzuki[5], Kazuki Tabaru[6], Duotian Chen[7], Takashi Toyao[8], Ken-ichi Shimizu[9], Mitsuru Inada[10], Yasushi Obora[11]

Metal nanoparticles have attracted much attention as energy-efficient light emitting materials because they exhibit larger bandgap energy values than the bulk state due to the quantum dot effect[1) 2)]. We previously reported the synthesis of niobium oxide nanoparticles (NbO_x NPs) and their emission in EL devices[3)]. However, the NbO_x NPs casted on the device showed dark and red emission, suggesting that this material has low emission efficiency as an EL device material. In this study, we synthesized Nb-Fe alloy nanoparticles to improve the emission efficiency of the EL devices. We expected that the incorporation of iron oxide nanoparticles (FeO_y NPs) into the NbO_x NPs would fill defects of the NbO_x, leading to the improvement of an emitting efficiency of blue color region. We will discuss the details of the preparation and characterization of the alloy nanoparticles and their applications to the EL devises.

Keywords : Niobium; DMF-stabilized metal nanoparticles; quantum dot; electroluminescence device

金属ナノ粒子は量子ドット効果により,バルク状態と比較して大きなバンドギャップエネルギー値を示すため，エネルギー効率の良い発光材料として注目されている[1) 2)]. これまでに我々は, 酸化ニオブナノ粒子(NbO_x NPs)の合成とその EL デバイスへの応用について報告している[3)]. しかしながら，用いた NbO_x NPs のバンドギャップエネルギーは想定よりも小さく，発光効率の低い赤色発光を示した.

本研究では，発光効率の高い青色発光 EL デバイスの開発を目的とし，Nb-Fe 合金ナノ粒子の合成と特性評価を行った. 検討において我々は, 酸化鉄 (FeO_y)を混ぜ合わせることで NbO_x 中の欠陥準位が埋まることを期待し，その特性変化について種々のキャラクタリゼーションをおこなった. 講演では，合金ナノ粒子の合成法とそのＥＬデバイスへの応用について報告する.



1) P. Makkar, N. N. Ghosh, *RSC Adv.*, 2021, **11**, 27897.
2) M.Polché, B.F.José.Miguel, C.A.Guzmán.González, G.González Contreras, Romero Arellano, V.H., *Nanomaterials.,* 2023, **13**, 2480.
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暗視野顕微鏡を用いた単一中空銀ナノシェルの光学特性評価

（和歌山大システム工）○出口 航輝・門 晋平・矢嶋 摂子
Optical Characterization of Single Hollow Silver Nanoshell Using Dark-Field Microscopy (*Faculty of Systems Engineering, Wakayama University*) ○Koki Deguchi, Shinpei Kado, Setsuko Yajima

Precious metal nanoparticles exhibit localized surface plasmon resonance (LSPR), which is caused by absorbing and scattering light at specific wavelengths, and are attracting attention for their potential use in sensors and other applications. We carried out single-particle spectroscopy using a dark-field microscope, which is capable of observing the scattered light of the particles, in order to characterize optical properties of single hollow silver nanoshell. Hollow silver nanoshells were synthesized by reduction of silver thiocyanate with $NaBH_4$. As a result, the single particle scattering spectra showed different LSPR wavelengths and half-widths for different particles, which are expected to be due to the appearance of differences in particle size and shell thickness.
Keywords : Hollow Silver Nanoshell; Single Particles; Dark-Field Microscopy; Localized Surface Plasmon Resonance; Scattering

貴金属ナノ粒子は局在表面プラズモン共鳴(LSPR)を示し、特定波長の光を吸収・散乱することからセンサー等への応用が期待され、注目されている。本研究では、AgSCN の $NaBH_4$ 還元で得られる中空銀ナノシェル[1]の単一粒子の光学特性評価を目指して、粒子の散乱光を観察できる暗視野顕微鏡を用いて単一粒子分光を行った。

スライドガラス基板上に中空銀ナノシェル分散液を滴下して乾燥させ、粒子を物理的に固定させた。滴下する分散液の濃度を調整することにより基板上の粒子どうしが十分な距離をとるようにした。続いてミリ Q 水を滴下しカバーガラスで挟んで暗視野顕微鏡観察を行った。単一中空銀ナノシェルの暗視野像と対応する散乱スペクトルの例を Fig. 1 に示す。単一粒子の散乱スペクトルは、粒子によって異なる LSPR 波長を示した。また Fig.1(a)と(b)は半値幅が近い値であるのに対して、Fig.1(c)はこれらと比較すると小さい半値幅を示した。LSPR 波長および半値幅の違いは、粒子のサイズおよびシェル厚の違いが現れているためと予想される。

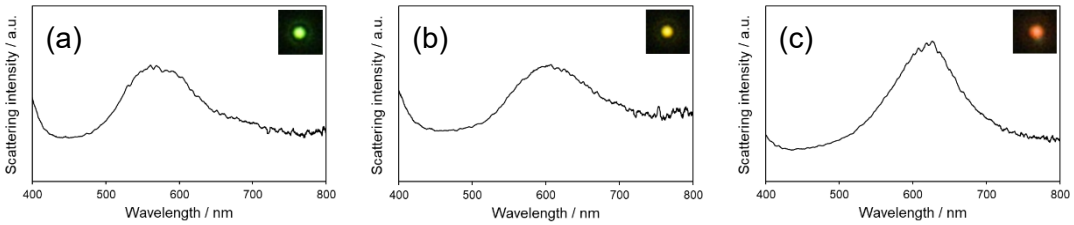

Fig.1 Typical dark-field microscopic images and corresponding scattering spectra of single hollow silver nanoshells.

[1] S. Kado, S. Yokomine, K. Kimura, *RSC Adv.*, **4**, 10830 (2014).

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日本化学会 第104春季年会 (2024)

MoS_2 含有ナノ濾過膜の有機溶媒性分離特性に関する研究

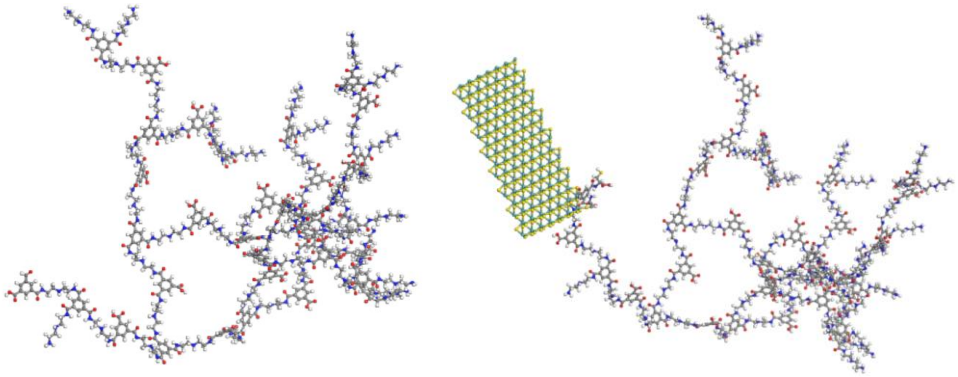
（工学院大先進工[1]・工学院大院工[2]）○有井 稜[1]・樋口 隼人[2]・宮川 雅也[1]・高羽洋充[1]

Computational chemistry study on characterization of organic solvent separation using MoS_2 containing nanofiltration membrane([1]*School of Advanced Engineering, Kogakuin University*, [2]*Graduate School of Engineering, Kogakuin University*) ○Ryo Arii,[1] Hayato Higuchi,[2] Masaya Miyagawa,[1] Hiromitsu Takaba[1]

The nanofiltration membrane composed of polymer has been used to separate organic solvents, and durability are often spoiled due to swelling. To solve this problem, the inorganic materials are added to the polymer membranes. However, it is difficult to investigate the effect of the additive experimentally, so this research builds a molecular structure of polyamide nanofiltration membrane containing MoS_2 nanosheet. As a result, through the adsorption of methanol simulation using grand canonical Montecarlo simulation of methanol, MoS_2 nanosheet controls the interaction to methanol and influence the amount of adsorption.

Keywords : Molecular Dynamics; Separation Membrane; Nanosheet; Organic solvent separation

有機溶媒をナノろ過膜を用いて分離する Organic solvent nanofiltration（OSN）が注目されている。OSN にはポリマー膜が利用されるが、溶媒膨潤による選択性や耐久性の低下が問題となっている。そこで、最近、無機材料などの添加剤をポリマー膜に含有させることで膨潤を封じ込め透過性能を向上させる試みがなされている。[1)]しかし、ナノろ過膜に含有させた添加剤がどのように分離特性に影響を与えるかについての詳細な考察は実験的に困難である。そこで本研究では、MoS_2 ナノシート含有ポリアミド系ナノろ過膜の分子構造を作成し、分子シミュレーションで MoS_2 ナノシートが吸着・拡散挙動に与える影響について考察した。グランドカノニカルモンテカルロ法と分子動力学法によるメタノールの吸着シミュレーション結果から、MoS_2 ナノシートによってメタノールとの相互作用が弱まり、吸着量に影響を与えることがわかった。



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CdSe 系コアシェル量子ドットにおける励起子素過程の圧力依存性

（関学理工）○三澤 宏介・江口 大地・玉井 尚登

Pressure-dependent Elementary Exciton Processes of CdSe-based Core Shell Quantum Dots

(*School of Science and Technology, Kwansei Gakuin University*,) ○Kosuke Misawa, Daichi Eguchi, Naoto Tamai

Core/shell quantum dots (c/s QDs) consist of the epitaxial growth of shell semiconductor layers on core QDs. While pressure-dependent steady-state physical properties have been reported, the understanding of the elementary exciton processes remains unclear. In this study, we synthesized CdSe/ZnS and CdSe/CdS c/s QDs and elucidated the pressure-dependent elementary exciton processes using fs-transient absorption spectroscopy under applied pressure.
Keywords : Elementary Exciton Process, Core/shell Quantum Dots, Diamond Anvil Cell, CdSe Quantum Dots

圧力印加に対する応答は半導体により異なり、それぞれの半導体は物質固有の体積弾性率を有している。コアシェル半導体量子ドット (c/s QDs) は、コアとシェルが異なる半導体より構成されているので圧力に対する応答はコアとシェルで異なっており、ヘテロ界面での格子不整合率は圧力により変化する。これまでに、c/s QDs の定常光を用いた光物性の圧力依存性は報告されているものの [1]、励起子素過程は未解明な点が残されている。本研究では CdSe QDs をコアとし、ZnS もしくは CdS がエピタキシャル成長した c/s QDs を合成し、ダイヤモンドアンビルセル (DAC) を用いて圧力印加を行なった。シェルの違いが及ぼす励起子素過程の圧力依存性は、フェムト秒過渡吸収分光(fs-TAS) により解析を行ったので報告する。

既報 [2, 3]を参考に CdSe/ZnS QDs と CdSe/CdS QDs を合成し、各種機器分析により構造解析を行った。透過型電子顕微鏡観察から CdSe QDs は 3.6 ± 0.2 nm、CdSe/CdS QDs と CdSe/ZnS QDs はそれぞれ 4.3 ± 0.4 nm、5.0 ± 0.4 nm であることが分かり、シェルがエピタキシャル成長していた (Figure 1)。fs-TAS の結果、CdSe/ZnS QDs では、1S 励起子吸収のブリーチ信号が観測された。DAC を用いて圧力を印加すると、このブリーチ信号は青色偏移することが分かり、これは圧力印加により電子構造が変化したためであると考えている。発表当日は、発光分光も含めシェルの違いが及ぼす励起子素過程の圧力依存性を議論する。

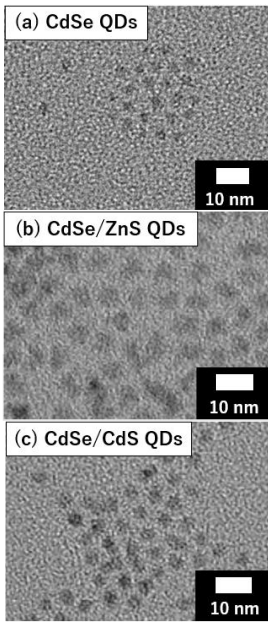

Figure 1. TEM images of (a) CdSe QDs, (b) CdSe/ZnS QDs, and (c) CdSe/CdS QDs.

1) P. Lv *et al*., *J. Phys. Chem. Lett*., **2020**, 11, 920–926. 2) L. Wang *et al*., *Nat. Commun*., **2019**, 1, 4532. 3) D. Chen *et al*., *Chem. Mater*., **2010**, 22, 1437‑1444.

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InP 系コアシェル量子ドットの界面ポテンシャル形状と電子移動ダイナミクスの研究

（（関学大理工）○森山 虎太朗・稲田 一輝・江口 大地・玉井 尚登
Effects of Interfacial Potential on Electron Transfer Dynamics in InP-based Core/Shell Quantum Dots (*School of Science and Technology, Kwansei Gakuin University*) ○Kotaro Moriyama, Kazuki Inada, Daichi Eguchi, Naoto Tamai

In hybrid systems of core/shell quantum dots (c/s QDs) and acceptor molecules, the effects of shell thickness on electron transfer processes have been investigated. However, the effects of interfacial potential shapes in c/s QDs on electron transfer dynamics remains unclear. In the present study, we synthesized InP-based c/s QDs with either steep or graded interfacial potentials and investigated their influence on the electron transfer dynamics by femtosecond transient absorption spectroscopy.
Keywords : InP Quantum Dot; Core/shell Quantum Dot; Femtosecond Transient Absorption Spectroscopy; Electron Transfer

コアシェル型半導体量子ドット (c/s QDs) は，モル吸光係数が比較的高く，コアの粒径により酸化還元電位の位置を制御可能であることから光電変換材料への応用が期待されている。光電変換においては，電荷分離過程の理解が高性能化に向けた鍵となる。これまでに，ドナーとアクセプター間距離が電荷分離過程に及ぼす影響を，シェル厚みが異なる c/s QDs を用いて明らかにした先行研究はあるものの [1]，コアシェル間の界面ポテンシャルが及ぼす影響は未解明なままである。本研究では InP QDs をコアとし，急峻もしくは滑らかな界面ポテンシャルを有する c/s QDs (InP/ZnS QDs ,InP/ZnSe$_x$ZnS$_{1-x}$/ZnS QDs) を合成し (Figure 1a)，伝導体下端からアントラキノン誘導体への電子移動過程をフェムト秒過渡吸収分光測定 (fs-TAS) で解析した。既報を参考に c/s QDs を合成し，各種機器分析により構造解析を行った [2]。定常光の吸収・発光スペクトルの結果を Figure 1b に示す。InP QDs に比べて c/s QDs では励起子吸収，極大発光波長が赤方偏移しており，発光量子収率が上昇していることから，コアに対してシェルがエピタキシャル成長したことが分かった。発表当日は，c/s QDs に配位したアントラキノン誘導体の平均分子数を 2 程度にし，fs-TAS を行い，界面ポテンシャルが及ぼす電荷分離過程の影響を議論する。

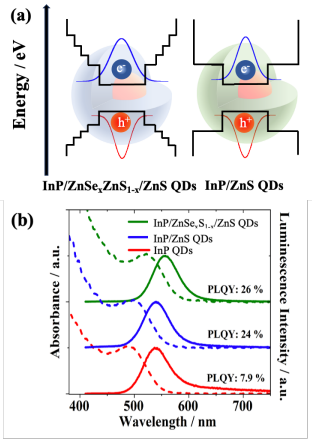

Figure 1. Steady-state absorption (dotted lines) and luminescence (solid lines) spectra of InP and c/s QDs. (λ_{ex} = 400 nm)

1) T. Lian *et al.*, *J. Am. Chem. Soc.*, **2010**, *132,* 15038-15045
2) E. Jang *et al., ACS Appl. Nano Mater.*, **2019**, *2*, 1496-1504.

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ホウ化水素シートへのアンモニア吸着特性評価

(筑波大[1]・東大[2]・東北大[3]) ○福田 弘清[1]・伊藤 伸一[1]・引地 美亜[1]・松田 巌[2]・近藤 剛弘[1,3]
Adsorption properties of NH_3 on hydrogen boride sheets ([1]*University of Tsukuba*, [2]The *University of Tokyo*, [3]*Tohoku University*) ○Kosei Fukuda,[1] Shin-ichi Ito,[1] Miwa Hikichi,[1] Iwao Matsuda,[2] Takahiro Kondo[1,3]

Hydrogen boride (HB) sheets are two-dimensional materials which consist of negatively charged hexagonal boron network and positively charged hydrogen at a molar ratio of 1:1.[1] In this study, we focused on the positively charged hydrogen and aimed to clarify whether the adsorption of NH_3 molecules occurs or not, and its mechanism. Using Fourier transformed infrared absorption spectroscopy (FT-IR), we have examined ammonia adsorption using two methods: exposure to aqueous ammonia vapor followed by heating and drying, and exposure to dry ammonia gas. In the sample exposed to dry ammonia gas, an absorption peak assigned as H-N-H vibrational mode was observed at around 1650 cm^{-1} (Fig. 1), ammonia is adsorbed on HB. On the other hand, the peak at around 2500 cm^{-1} originated from HB sheets (the terminal B-H stretching vibrational mode[2]) was found to shift about 40 cm^{-1} to lower wavenumber by ammonia adsorption, suggesting that B-H bond gets weakened by ammonia adsorption.
Keywords : Ammonia adsorption, Borophane, Hydrogen borides

ホウ化水素（HB）シートは負に帯電したホウ素原子骨格と正に帯電した水素原子によって 1:1 の原子数比で構成されている二次元物質である。[1] 本研究では HB シートの正に帯電している水素原子に注目し、HB シートへのアンモニア吸着のメカニズムを明らかにすることを目的としている。HB シート[1]に対して、アンモニア水の蒸気に曝した後に加熱乾燥する方法と真空中で乾燥アンモニアガスに曝す方法の 2 通りを用い、フーリエ変換型赤外吸収分光（FT-IR）により HB シートへのアンモニア吸着特性を評価した。アンモニア雰囲気に曝したサンプルでは H-N-H 振動に帰属される吸収ピークが 1650 cm^{-1} 付近に現れ（Fig. 1）、アンモニアが吸着していることが示された。また、HB で 2500 cm^{-1} にみられる末端 B-H 伸縮振動に起因する吸収ピーク[2]がアンモニア吸着により約 40 cm^{-1} 低波数側にシフトすることも示された。これは、アンモニア吸着により HB シートの末端 B-H 結合が弱まったことを示唆している。

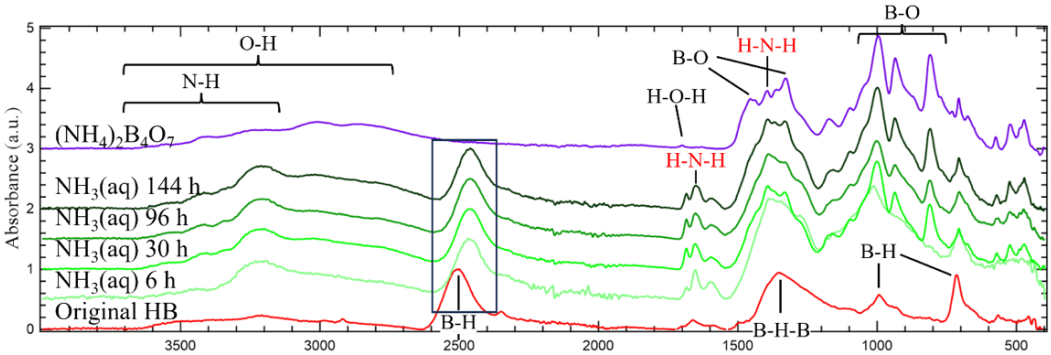

Fig. 1 FT-IR spectra of HB sheets before and after the exposure to ammonia atmosphere with 2-144 h

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金属酸化物 QCM センサを用いた揮発性有機化合物の構造異性体識別

(東大[1]・九大[2]) ○田中 健太[1]・Poom Jirayupat[1]・細見 拓郎[1]・Jiangyang Liu[1]・田中 航[1]・高橋 綱己[1]・柳田 剛[1,2]
Discriminating Positional Isomers of Volatile Organic Compounds by Metal Oxide QCM sensor. (The Univ. of Tokyo[1] ,Kyusyu University[2]) ○Kenta Tanaka[1], Poom Jirayupat[1], Hosomi Takuro[1], Yanagida Takeshi[1,2], Takahasi Tsunaki[1], Tanaka Wataru[1], Jiangyang Liu[1]

Discriminating isomers in a mixture of volatile organic compounds (VOCs) is one of the most critical issues in the field of molecular sensors. However, due to their poor differences in physical and chemical properties, expensive and large machinery such as chromatographs and spectrometers have generally been considered essential to discriminating them. On the other hand, our group has reported that molecular-specific adsorption/desorption behavior can be obtained for dilute VOCs by using QCM nanowire array structures, in which metal oxide nanomaterials are modified on quartz crystals, which are inexpensive, compact, and can operate at high speed. In this study, the molecular adsorption/desorption behavior on QCM nanowire arrays modified with various metal oxide nanomaterials was measured and evaluated. As a result, we have successfully developed a regression model to discriminate four regioisomers of C8 alcohol.
Keywords : Molecular Sensor, Metal Oxide, QCM, VOC

環境中や生体由来のガス中には脂肪族骨格を有する揮発性有機化合物（VOC）が多種類含まれており、それらの識別技術の確立は分子センサにおける重要な課題である。しかし、これらの骨格の僅かな違いによる物理的・化学的特性の違いは乏しく、一般にクロマトグラフや分光分析装置等の高価・大型の機械が必要不可欠とされてきた。一方当研究グループでは、安価・小型かつ高速動作が可能な水晶振動子（QCM）上に金属酸化物ナノ材料を修飾したQCMナノワイヤアレイ構造を用いることで、希薄なVOC分子ガスから分子固有の吸脱着挙動を測定可能なことを見出してきた。そこで本研究では、種々の金属酸化物ナノ材料で修飾したQCMナノワイヤアレイ上における分子吸脱着挙動を測定・評価し、それらを用いた分子識別を試みた。結果、特定の金属酸化物層を原子層堆積したQCMナノワイヤアレイを用いることで、オクタノールの各位置異性体を識別可能な回帰モデルの作成に成功した（図1）。

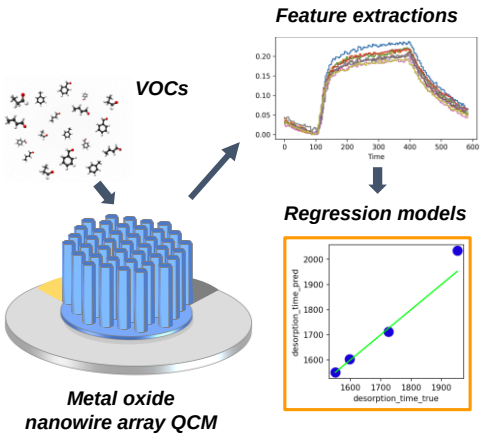

図1. ナノワイヤアレイQCMによるVOC識別モデル作製

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

Thu. Mar 21, 2024 11:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 2:00 AM - 2:40 AM UTC
A1441(1441, Bldg. 14 [4F])

[A1441-4am] 04. Physical Chemistry -Properties-

Chair: Takahiro Takekiyo, Yoichi Sasaki

Japanese
11:00 AM - 11:20 AM JST | 2:00 AM - 2:20 AM UTC
[A1441-4am-01]

All-atomic Analyses on the Properties of Hydrogen Bonds and Infrared Vibrational Bands in the Vicinity of Polymer Interfaces

○Yoshiki Ishii[1], Hajime Torii[2], Yuka Ikemoto[3], Hitoshi Washizu[4] (1. Kitasato University, 2. Shizuoka University, 3. JASRI, 4. University of Hyogo)

English
11:20 AM - 11:40 AM JST | 2:20 AM - 2:40 AM UTC
[A1441-4am-02]

The Influence of Alkyl Chain Length on Carboxylic Acid Molecule Adsorption onto Various Metal Oxide Surfaces.

○Wenjin Lei[1], Takuro Hosomi[1], Jianyang Liu[1], Wataru Tanaka[1], Tsunaki Takahashi[1], Takeshi Yanagida[1,2] (1. School of Engineering, The Univ. of Tokyo, 2. IMCE, Kyushu Univ.)

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高分子界面近傍における水素結合特性と赤外振動バンドの全原子解析

（北里大未来工[1]・静岡大工[2]・JASRI[3]・兵庫県大院情報[4]）
○石井 良樹[1]・鳥居 肇[2]・池本 夕佳[3]・鷲津 仁志[4]

All-atomic Analyses on the Properties of Hydrogen Bonds and Infrared Vibrational Bands in the Vicinity of Polymer Interfaces ([1]*School of Frontier Engineering, Kitasato University*, [2]*Faculty of Engineering, Shizuoka University,* [3]*Spectroscopy Division, JASRI,* [4]*Graduate School of Information Science, University of Hyogo*)
○Yoshiki Ishii,[1] Hajime Torii,[2] Yuka Ikemoto,[3] Hitoshi Washizu[4]

Hydrogen-bonding network of water molecules in the vicinity of polymer interfaces is considered to have a key role to avoid the adsorption of biomolecules. To clarify hydrogen-bonding structures and their functions of water molecules around the polymer-water interface, experimental measurements of infrared spectroscopy and its theoretical analysis based on molecular dynamics simulation have been widely reported to investigate specific properties of the polymer interfaces. Here we recently developed a spatially-decomposed approach of the IR band analysis, which can be adopted to nanoscopic regions in the polymer-water interface. With this theoretical approach, the modulation of OH stretching vibrational mode occurs in the region of a several nanometer space in the vicinity of polymer-water interface.
Keywords : Polymer; Hydrogen Bonds; Interface; Molecular Dynamics; Infrared Bands

高分子界面における水分子集団の水素結合は，生体分子の吸着を阻害する特性をもつことが提案され [1]，その高分子-水界面における水素結合構造と機能を解明する観点から，赤外分光スペクトルの実験測定と分子シミュレーションに基づく理論解析が進められてきた [2-4]。そこで我々は近年，高分子界面の分子動力学（MD）シミュレーションから得られた構造情報から，任意の局所空間に存在する水分子の OH 伸縮振動モードに由来する赤外（IR）スペクトルを解析可能な空間分割 IR バンド解析法を開発した [5]。この手法では，水分子の水素原子にかかる静電場と OH 伸縮振動シフトの第一原理計算に基づく関係式 [6]を基にしていることから，IR バンドのサンプリングをエネルギー座標や界面からの空間座標で分割させることが可能となる。本研究ではその空間分割法を応用して，生体適合性の優れた高分子 poly(2-methoxyethyl acrylate) (PMEA)の界面で生じる水分子の OH 伸縮振動モードを解析することで，界面近傍の数 nm 領域で IR ピークの増減が生じていることを見出した。

1) M. Tanaka, S. Kobayashi, D. Murakami, F. Aratsu, A. Kashiwazaki, T. Hoshiba, K. Fukushima, *Bull. Chem. Soc. Japan* **2019**, *92*, 2043.
2) M. Tanaka, T. Hayashi, S. Morita, *Polym. J.* **2013**, *45*, 701.
3) N. Yasoshima, T. Ishiyama, M. Gemmei-Ide, N. Matubayasi, *J. Phys. Chem. B* **2021**, *125*, 12095.
4) Y. Ikemoto, Y. Harada, M. Tanaka, S. Nishimura, D. Murakami, N. Kurahashi, T. Moriwaki, K. Yamazoe, H. Washizu, Y. Ishii, H. Torii, *J. Phys. Chem. B* **2022**, *126*, 4143.
5) Y. Ishii, H. Torii, Y. Ikemoto, H. Washizu et al., *in preparation*, **2024**.
6) H. Torii, R. Ukawa, *J. Phys. Chem. B* **2021**, *125*, 1468.

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The Influence of Alkyl Chain Length on Carboxylic Acid Molecule Adsorption onto Various Metal Oxide Surfaces

([1.] School of Engineering, The Univ. of Tokyo, [2.] IMCE, Kyushu Univ.) ○Wenjin Lei[1], Takuro Hosomi[1], Jianyang Liu[1], Wataru Tanaka[1], Tsunaki Takahashi[1], Takeshi Yanagida[1,2]
Keywords: Molecular Adsorption; Metal Oxide; VOC

The recent developments in internet-of-things have led to a growing interest in molecular sensors. However, discriminating aliphatic compounds with similar skeletons is considered one of the most challenging issues in that field. This is because these skeletons have poor interactions and reactivities with metal oxides (MOx), the most common chemical sensor materials.[1,2] This study aimed to examine the discrimination of aliphatic compounds from mixtures by utilizing various MOx species.

We first investigated the molecular adsorption behavior of various MOx surfaces by exposing them to a mixture gas of aliphatic carboxylic acids (C3-C9). As shown in **Figure 2**, the certain metal oxides exhibited unexpected selectivity toward the molecule with specific carbon chain lengths. Further investigation with molecular dynamics simulation suggested that the stronger interaction between the alkyl chain and MOx surface could deny the functional group access to the surface. These results indicated that the strength of those interactions plays a crucial role in their adsorption behaviors and may affect the molecular selectivity of the MOx surface.

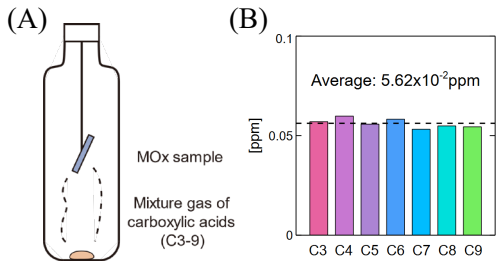

Fig 1. (A) Illustration of exposing MOx sample to the mixture gas. (B) Concentrations of C3-C9 carboxylic acids in the mixture gas.

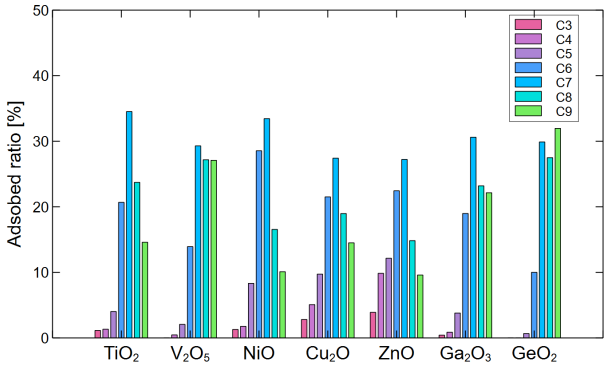

Fig 2. Relative ratios of carboxylic acids desorbed from each MOx surface after exposing the sample to the mixture gas.

1) A. Dey, *Mater. Sci. Eng. B* **2018,** 229, 206. 2) 1. R. A. Potyrailo, *Chem. Rev.* **2016**, 116, 11877.

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Academic Program [Oral A] | 07. Inorganic Chemistry : Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1444(1444, Bldg. 14 [4F])

[A1444-4am] 07. Inorganic Chemistry

Chair: Naoki Ogiwara, Yuji Kikukawa

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1444-4am-01]
Encapsulation and stabilization of inorganic clusters in a cavity of coordination cage

○Naoki Kimura[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The Univ. of Tokyo, 2. Institute for Molecular Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1444-4am-02]
Syntheses of porous ionic crystals based on organically- decorated polyoxometalates

○Mochizuki Shunsuke[1], Zhewei Weng[1], Naoki Ogiwara[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1444-4am-03]
Methylene blue capture with polyoxometalate encapsulated metal–organic frameworks

○Naoki Ogiwara[1], Shotaro Miyazaki[1], Sayaka Uchida[1] (1. School of Arts and Sciences, The Univ. of Tokyo)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1444-4am-04]
High-Performance Solid Proton Conductors: Sodium-Centered Preyssler-Type Polyoxometalate and Urea-Modified Polyallylamine Crystalline Composites

○Linshu Zhang[1], Tsukasa Iwano[1], Sayaka Uchida[1] (1. The University of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1444-4am-05]
Synthesis and Structural Characterization of Trimethylammonium Heptamolybdate and Octamolybdate

○Rie Ishida[1], Ndaru Candra Sukmana[1], Sugiarto Sugiarto[1], Masahiro Sadakane[1] (1. Hiroshima Univ.)

9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
Break

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1444-4am-06]
Synthesis of inorganic materials with titanium-substituted polyoxovanadate and inorganic high valent cation.

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○Kai Matsumura[1], Yuji Kikukawa[1], Yoshihito Hayashi[1] (1. Kanazawa Univ.)

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[A1444-4am-07]

Oxidate state control and catalytic property of nitrate-containing vanadium-oxo clusters

○Isshin Yoshida[1], Yuji Kikukawa[1], Yoshihito Hayashi[1] (1. Kanazawa Univ.)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[A1444-4am-08]

Physical Properties of Organic-Inorganic Hybrid Polyoxometalates with Host-Guest Characteristics

○Hiroto Kaitori[1], Chiasto Kato[1], Goulven Goulven[2,3], Masaru Fujibayashi[4], Kastuya Inoue[1,2,3,5], Sadafumi Nishihara[1,3,5,6] (1. Graduate School of Advanced Science and Engineering, 2. International Institute for Sustainability with Knotted Chiral Meta Matter, Hiroshima University Japan, 3. Chirality Research Center, Hiroshima University, Japan, 4. National Institude of Technology, Ube College, Japan, 5. Institute for Advanced Materials Research, Hiroshima University, Japan, 6. Precurspry Research for Embryonic Science and Technology, Japan Science and Technology Agency, Japan)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[A1444-4am-09]

Dielectric Properties of Dawson like Polyoxometalates Including Iodine

○Minami Tsuruda[1], Chisato Kato[2], Cosquer Goulven[3,4], Katsuya Inoue[2,3,4,5], Sadafumi Nishihara[2,4,5,6] (1. School of Science, Hiroshima University, 2. Graduate School of Advanced Science and Engineering, Hiroshima University, Japan, 3. International Institute for Sustainability with Knotted Chiral Meta Matter, Hiroshima University, Japan, 4. Chirality Research Center (CResCent), Hiroshima University, Japan, 5. Institute for Advanced Materials Research, Hiroshima University, Japan, 6. Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency, Japan)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[A1444-4am-10]

Synthesis and catalysis of an organic solvent-soluble ε-Keggin type $[Al_{13}O_4(OH)_{24}(ligand)_{12}]^{7+}$

○Ayano Umakoshi[1], Takuo Minato[1], Masahiro Sadakane[1] (1. Hiroshima University)

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

Break

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[A1444-4am-11]

Dielectric properties of a wheel-shape polyoxometalate with potassium ions at high temperature

○Yuma Takemoto[1], Chisato Kato[1], Masaru Fujibayashi[2], Goulven Couquer[3,4], Katsuya Inoue[1,3,4,5], Sadafumi Nishihara[1,4,5,6] (1. Grad.Sch.Adv.Sci.Eng.,Hiroshima,Univ, 2. NIT, Ube College, 3. SKCM2,Hiroshima.Univ, 4. CResCent,Hiroshima.Univ, 5. IAMR,Hiroshima.Univ, 6. PRESTO, JST)

Japanese

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11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[A1444-4am-12]

Physical properties of the thin films of single-molecule electret $(NH_4)_xH_{12-x}[Tb^{3+}\subset P_5W_{30}O_{110}]$

○Masaki Arima[1], Kazushi Takeda[1], Rikuto tamatani[1], Yuki Nakano[1], Chisatoisato Kato[1], Goulven Cosquer[2], Masaru Fujibayashi[3], Katuya Inoue[1,2,4,5], Sadafumi Nishihara[1,4,5,6] (1. Grad. Sch. Adv. Sci. Eng. Hiroshima Univ., 2. SKCM, Hiroshima Univ., 3. NIT, Ube College, 4. CResCent , Hiroshima Univ., 5. IAMR, Hiroshima Univ., 6. PRESTO, JST)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[A1444-4am-13]

Precise synthesis of Pt alloy clusters for electrochemical catalysts and evaluation of their functions

○Takuto NAKAMURA[1], Tatsuya MORIAI[1,2], Tetsuya KAMBE[1,2], Takane IMAOKA[1,2], Kimihisa YAMAMOTO[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. JST-ERATO)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[A1444-4am-14]

Synthesis of ultra small bismuth particles and evaluation of their magnetic function

○Ryotaro Hashimoto[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST ERATO)

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かご型錯体への無機クラスターの特異的包接と安定化

（東大[1]・分子研[2]）○木村　直己[1]・竹澤　浩気[1]・藤田　誠[1,2]
Encapsulation and stabilization of inorganic clusters in a cavity of a coordination cage ([1]*The University of Tokyo,* [2]*Institute for Molecular Science*) ○Naoki Kimura,[1] Hiroki Takezawa,[1] Makoto Fujita[1,2]

A self-assembled M_6L_4 cage accommodates various guest molecules in the hydrophobic cavity. Recently, we have found that the coordination cage selectively encapsulates a $Cu_4I_6^{2-}$ cluster from a bulk powder of copper(I) iodide. In this work, we evaluated the stability of the cluster inclusion complex in aqueous solution under ambient conditions. Time-course plot against the UV-Vis absorption revealed that the half-life of the cluster was about 38 h. In addition, it is suggested that this cage-cluster complex can be used as a photosensitizer that catalyzes the *cis-trans* isomerization of stilbene and azobenzene.
Keywords : Metal Cluster; Inclusion Complex; Host-Guest; self-Assembly

自己集合性かご型中空錯体は、種々のゲスト分子を内部の疎水空孔に包接することができる。最近、このかご型中空錯体は有機分子のみならずカチオン性金属錯体や無機金属化合物も包接できることが分かった。本研究では、かご型錯体へ閉じ込められた無機金属クラスターが水溶液中でも顕著な安定化を受けることを明らかにした。

自己集合性白金中空錯体 **1** は、固相中でヨウ化銅(I)、ピリジンと混合することで$Cu_4I_6^{2-}$クラスターを選択的に包接することができる。このクラスター包接錯体の水溶液中での安定性を紫外可視光吸収特性から評価したところ、室温下では半減期は約38時間であることが分かった。また、このクラスター包接錯体の光増感剤としての利用を検討したところ、スチルベンやアゾベンゼンの *cis-trans* 異性化の進行が確認され、クラスター包接錯体の光増感能が示唆された。

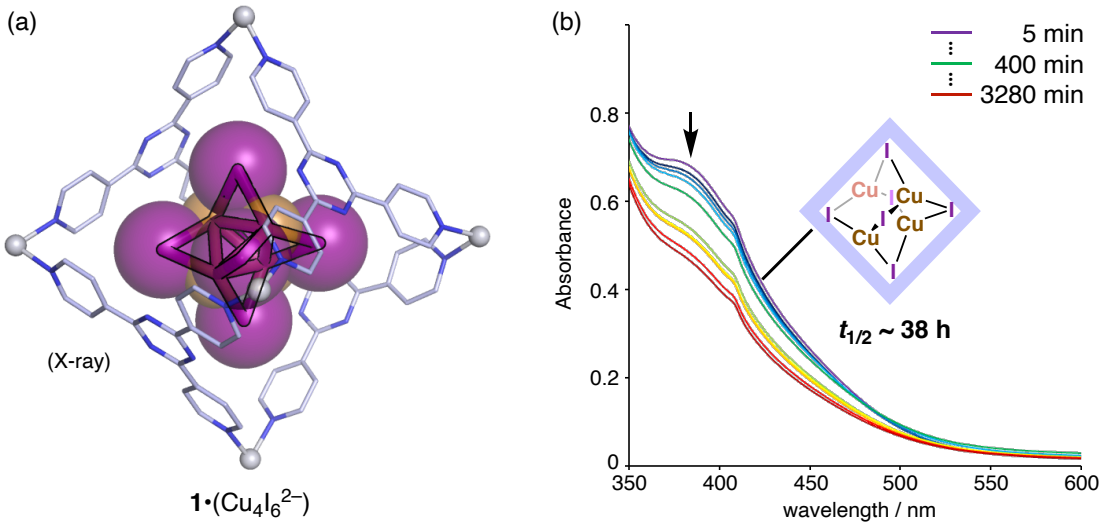

Figure. (a) Crystal structure of inclusion complex **1**•($Cu_4I_6^{2-}$) and (b) UV-Vis spectra of an aqueous solution of **1**•($Cu_4I_6^{2-}$) after standing at room temperature.

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有機修飾型ポリオキソメタレートを用いた多孔性イオン結晶の合成

（東大院総合文化[1]）○望月 舜介[1]・翁 哲偉[1]・荻原 直希[1]・内田 さやか[1]
Synthesis of porous ionic crystals based on Tris-decorated Anderson-type polyoxometalates
(1.Sch. Arts and Sci., The Univ. of Tokyo) ○Shunsuke Mochizuki[1], Zhewei Weng[1], Naoki Ogiwara[1], Sayaka Uchida[1]

Porous ionic crystals (PICs) comprising polyoxometalate (POM) anions and molecular metal complex cations have been reported for applications such as gas sorption, catalysis, and proton conductivity. In this study, we focused on Anderson-type POMs, which can be easily decorated with organic ligands and are expected to offer highly designable crystal structure, whereas only all-inorganic POMs have been used to construct conventional PICs. Anderson-type POMs decorated with tris(alkoxo) ligands ($\{[\mathbf{R}C(CH_2O)_3]_2\mathbf{M}Mo_6O_{18}\}^{3-}$, **R** = CH_3, NH_2, CH_2OH, **M** = Mn, Fe, δ/δ-isomer) and metal complex cations ($[Cr_3O(OOCH)_6(4\text{-methylpyridine})_3]^+$) were reacted in MeOH/MeCN solution to synthesize single crystals of PICs (**M-R**) with different metal and ligand species. The relationship among compositions, crystal structures, and sorption properties in **M-R** will be discussed.
Keywords : polyoxometalate; porous ionic crystal; crystal engineering

多孔性イオン結晶(PIC)はアニオン性金属酸化物クラスターであるポリオキソメタレート(POM)と金属錯体カチオンの静電相互作用により形成され、その細孔構造を生かした機能応用が報告されている[1]。しかし既報の PIC を構成する POM の種類は限られており、PIC の構造多様性は限定的である。本研究では PIC の細孔構造と付随した機能・物性を獲得する新たな手法として、POM の表面にトリヒドロキシメチル(Tris)配位子（$\mathbf{R}C(CH_2OH)_3$, (**R** = NH_2, CH_2OH 等)を導入可能な Anderson 型 POM に着目し[2]、PIC の開発を行った。Tris 修飾した Anderson 型 POM : $\{[\mathbf{R}C(CH_2O)_3]_2\mathbf{M}Mo_6O_{18}\}^{3-}$ (**R** = CH_3, CH_2OH, NH_2, **M** = Mn, Fe)と Cr 三核錯体カチオン:$[Cr_3O(OOCH)_6(4\text{-methylpyridine})_3]^+$を MeOH/MeCN 混合溶液中で、数日間静置することで、POM の金属・配位子種が異なる PIC(**M-R**)を合成した。単結晶 X 線構造解析より、PIC (**M-CH_3, CH_2OH**) はカラム構造、PIC (**M-NH_2**) は層状構造を有することがわかった(**Fig.1**)。この結晶構造の違いは、配位子が形成する水素結合ネットワークの様式変化に起因すると示唆される。当日は、PIC の蒸気吸着測定の結果に基づき、PIC における組成–結晶構造–吸着特性の相関について議論する予定である。

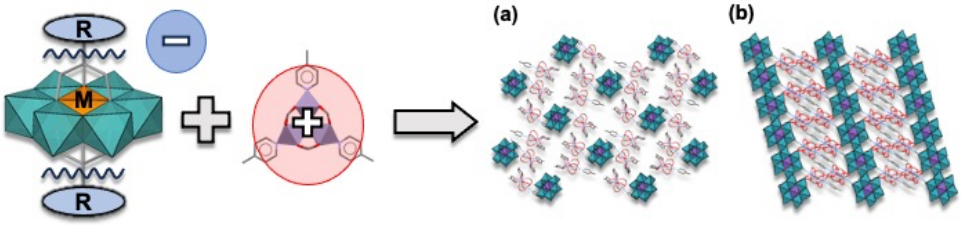

Fig.1: Syntheses of PICs with (a) columnar and (b) layer structure.

[1] Y. Shimoyama, S. Uchida, *Chem. Lett.*, 2021, **50**, 21–30.
[2] P. Wu et al., *Nanoscale*, 2021, **13**, 7119–133.

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日本化学会 第104春季年会 (2024)

ポリオキソメタレートを内包した多孔性金属錯体を利用したメチレンブルー吸着

（東大院総合[1]）○荻原 直希[1]・宮崎 翔太郎[1]・内田 さやか[1]
Methylene blue capture with polyoxometalate encapsulated metal–organic frameworks ([1]*Graduate School of Arts and Sciences, The University of Tokyo*) ○Naoki Ogiwara[1], Shotaro Miyazaki[1], Sayaka Uchida[1]

Adsorption of methylene blue (MB) from aqueous effluents is a key technique for the purification of wastewater from chemical industries. Toward MB adsorption, porous metal–organic frameworks (MOFs) have been promising owing to their high surface areas and tunable porosity. The incorporation of polyoxometalates (POMs) into MOFs facilitated MB adsorption due to electrostatic interactions between anionic POM and the cationic MB. Besides, tuning pore size and environment based on ligand engineering of the MOFs lead to an efficient MB capture, which is comparable to those of representative zeolites such as ZSM-5 and zeolite Y.
Keywords : Polyoxometalate; Metal–Organic Framework,; Ion Capture

水溶液中からのメチレンブルー（MB）吸着は水質浄化において重要である。これまで活性炭やゼオライト等の多孔性材料を用いた MB 吸着が検討されてきたが、その吸着性能は頭打ちになりつつあり、新たな吸着材料の開発が求められている。

本研究では、MB 吸着材料としてポリオキソメタレート（POM）と多孔性金属錯体（MOF）を複合化させた POM–MOF 複合体（POM@MOF）に着目した。POM@MOF を構成する MOF としては、高い構造安定性を有する[$Zr_6O_4(OH)_4(BDC)_6$ (BDC=1,4-benzenedicarboxylate)] (UiO-66)[1]、POM としては Keggin 型[α-$SiW_{12}O_{40}]^{4-}$ (SiW_{12})を選定した。SiW_{12}@UiO-66 複合体の合成は SiW_{12} の存在下で UiO-66 の前駆体を液相中で反応させることで行った。水溶液中からの MB 吸着特性を評価したところ、SiW_{12}@UiO-66 は UiO-66 単体を凌駕する吸着特性を示した。これは、アニオン性の SiW_{12} とカチオン性の MB の間に静電相互作用が発現したためだと示唆された。さらに UiO-66 の配位子の設計により、細孔サイズ・細孔環境を制御すると(Figure 1)、SiW_{12}@UiO-66 の MB 吸着特性はさらに向上し、ZSM-5 や Y 型ゼオライトに比肩する吸着機能を示すことがわかった。

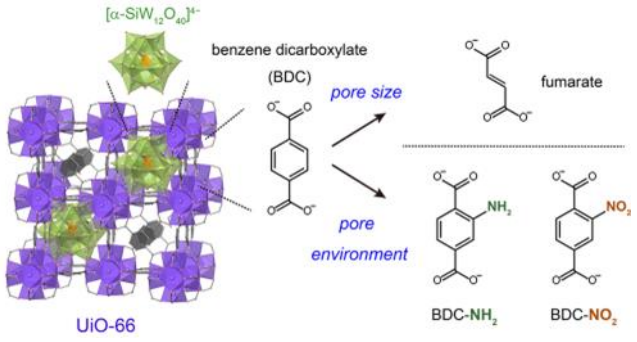

Figure 1. SiW_{12}@UiO-66 における細孔サイズ・細孔環境の制御。

1) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P., A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008,** *130* (42), 13850–13851.

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High-Performance Solid Proton Conductors: Sodium-Centered Preyssler-Type Polyoxometalate and Urea-Modified Polyallylamine Crystalline Composites

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Keywords: Polyoxometalate; Polymer; Proton Conductivity; Urea; Ammonium Ion

Fuel cells are considered to be a potential solution for global warming. Reported solid-state electrolytes for fuel cells can be categorized into organic materials, such as polymers, and inorganic materials, represented by polyoxometalates (POMs). Polymers, modifiable at the molecular level with various functional groups, enable control over carrier density which in turn affects proton mobility. Additionally, concomitant hydrogen-bonding capabilities of polymers contribute to structural stability and creation of a proton-conducting pathway.[1] POMs, anions formed by transition metal-oxygen clusters, also show potential as proton conductors due to their negatively charged molecular surface which facilitates the mobility of counter cations (H^+ ions, etc.).[2] However, POMs tend to dissolve easily, struggling to maintain solid forms under high humidity conditions.

Thus, regarding that rational functionality for electrolytes demands both designability and structural stability, this work focuses on hybrid materials merging POM and polymers. Here, three POM-polymer composites (NaPU25/50/75) are successfully synthesized by combining sodium-centered Preyssler-type POM[2] ($K_{14}[Na(H_2O)P_5W_{30}O_{110}]$) and urea-modified polyallylamine (UPAA) with modification ratio of 0.25, 0.50 and 0.75, respectively. Proton conductivity performance of the composites is evaluated by electrical impedance methods, and all samples demonstrate high performance. In particular, NaPU50 reaches 1.85×10^{-2} S cm^{-1} at 75 °C and 75% relative humidity (RH). Additionally, multiple spectroscopic studies, such as IR, Raman, solid-state MASNMR, are conducted to characterize the composites and establish the correlation between proton conductivity and urea modification ratio. Preliminary results suggest that ammonium ions produced during the combination process serve as crucial proton carriers.

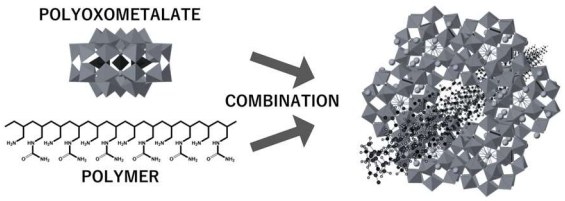

Figure. Molecular structure of Preyssler-type POM and UPAA and schematic procedure of synthesis of the crystalline composite

1) S. J. D. Lugger *et al.*, *Chem. Rev.* **2022**, 122, 5, 4946–4975.

2) K. Takahashi *et al.*, *Z. Anorg. Allg. Chem.* **2014**, 640, 1314– 1321.

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日本化学会 第104春季年会 (2024)

トリメチルアンモニウムヘプタモリブデートおよびオクタモリブデートの合成と構造解析

（広島大工[1]・広島大院先進理工[2]）○石田 理恵[1]・Ndaru Candra Sukmana[2]・Sugiarto[2]・定金 正洋[2]

Synthesis and Structural Characterization of Trimethylammonium Heptamolybdate and Octamolybdate ([1]*School of Engineering, Hiroshima University*, [2]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Rie Ishida,[1] Ndaru Candra Sukmana,[2] Sugiarto,[2] Masahiro Sadakane[2]

Polyoxomolybdates, molybdenum oxide clusters, are important compounds with a variety of applications, such as staining reagent[1)] and raw materials for catalysts[2)]. It is necessary to understand the exact structure and the effect of heating temperature on the structure, as the optimal structure depends on the application. In this study, we attempted to control the structure of trimethylammonium polyoxomolybdates depending on the temperature.

After dissolving molybdenum oxide in an aqueous solution of trimethylamine, trimethylammonium heptamolybdate was obtained by adding solvents such as DMF. Furthermore, it was found that trimethylammonium octamolybdate was obtained by heating this trimethylammonium heptamolybdate. All structures were characterized by single-crystal X-ray structure analysis, X-ray powder diffraction, infrared absorption spectrometry and Thermo Gravimetry.

Keywords : Molybdenum; Polyoxomolybdate; Thermal Transformation

モリブデンの酸化物クラスターであるポリオキソモリブデートは、染色剤[1)]、触媒の原料[2)]など様々な用途をもつ重要な化合物であり、用途ごとに最適なモリブデートの構造は異なる。したがって、応用に際して正確な構造と加熱温度が構造に与える影響を理解する必要がある。本研究ではトリメチルアンモニウムポリオキソモリブデートを合成し加熱温度を変化させた時の構造変化を解析した。

酸化モリブデンをトリメチルアミン水溶液中で溶解させた後、DMF 等の有機溶媒を加えるとトリメチルアンモニウムヘプタモリブデートが得られた。更にこのトリメチルアンモニウムヘプタモリブデートを加熱するとトリメチルアンモニウムオクタモリブデートが得られた。各構造は単結晶X線構造解析、X 線粉末回折、IR、TG により分析した。

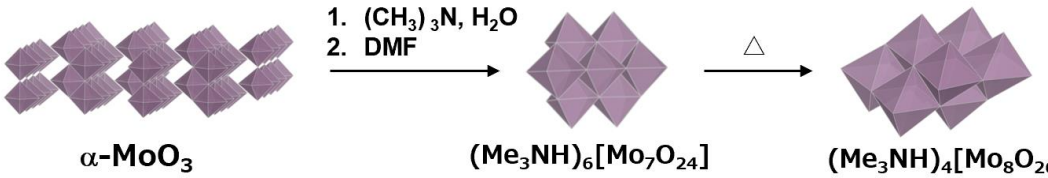

図 1. トリメチルアンモニウムヘプタモリブデート及びオクタモリブデートの合成

1) N. C. Sukmana, Sugiarto, J. Shinogi, T. Kojima, A. Higashiura, A. Yamamoto, T. Sakaguchi, M. Sadakane, *Chem. Lett*. **2023**, *52*, 167–171.
2) I. A. De Castro, R. S. Datta, J. Z. Ou, A. Castellanos-gomez, S. Sriram, T. Daeneke, K. Kalantar-zadeh, *Adv. Mater*. **2017**, *29*, 1701619.

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チタン置換型ポリオキソバナデートと無機多価カチオンの複合化

（金沢大院自然[1]）○松村 開[1]・菊川 雄司[1]・林 宜仁[1]
Synthesis of an inorganic material with titanium substituted polyoxovanadate and inorganic high valent cation (*Graduate School of Natural Science and Technology, Kanazawa University*)
○Kai Matsumura, Yuji Kikukawa, Yoshihito Hayashi

Polyoxovanadate (POV) is a vanadium-based oxide anion cluster. By the reaction of half spherical polyoxovandate $[V_{12}O_{32}]^{4-}$ and titanium source, titanovanadate $[TiV_{12}O_{34}]^{4-}$ (TiV12) is synthesized. TiV12 shows the unique acid-base property. The added proton easily moved on the surface of the anion with maintaining the structure. The aluminum cluster $[Al_{13}O_{40}H_{48}]^{7+}$ (Al13) is a cationic cluster with a structural similarity to TiV12. The each terminal oxygen atom is deprotonated and each μ_2-bridging oxygen atom is monoprotonated, showing that the surface of Al13 is covered by proton. By the reaction of salts of TiV12 and salts of Al13, an ionic material consist of TiV12 and Al13 is synthesized. From the solid state NMR spectra, the structures of TiV12 and Al13 are maintained. It shows proton conductivity of 1.2×10^{-2} S/cm at 85°C under relative humidity 90%. This value is a highest level among POM materials.
Keywords : Polyoxometalate; Vanadium; Aluminum; proton conduction

ポリオキソメタレートは、高いプロトンキャリア密度やプロトン移動性の観点からプロトン伝導材料として注目されている[1]。ポリオキソバナデート (POV)はバナジウムを基盤とするアニオン性金属酸化物クラスターである。チタノバナデート$[TiV_{12}O_{34}]^{4-}$ (TiV12)は半球状の POV $[V_{12}O_{32}]^{4-}$とチタン原料を反応させることで合成される (Figure 1)。TiV12 は POV の中でも特異な酸性質を示し、プロトンが構造表面の酸素上を移動することが明らかとなっている。アルミニウムクラスター$[Al_{13}O_{40}H_{48}]^{7+}$ (Al13)は POV と類似した構造をもつ、カチオン性クラスターである (Figure 1)。Al13 の末端酸素種は水、架橋酸素種は水酸基であり、表面がプロトンで覆われたイオンである。TiV12 と Al13 から構成される無機材料を合成し、そのプロトン伝導度の調査を行った。85℃、相対湿度 90%の条件で交流インピーダンス測定を行ったところ、1.2×10^{-2} S/cm という値が得られた。POV を基盤とした無機化合物のプロトン伝導体として、実用可能な値を示した。

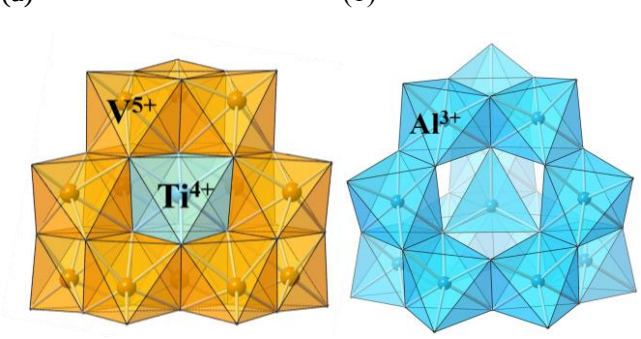

Figure 1. (a) TiV12, (b) Al13 の構造

1) N. Ogiwara, T. Iwano, T. Ito, S. Uchida, *Coordin. Chem. Rev*. **2022**, *462*, 214524.

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硝酸イオン内包バナジウムオキソクラスターの酸化数制御と触媒特性

（金沢大院自然[1]）○吉田一心[1], 菊川雄司[1], 林宜仁[1]
Oxidate state control and catalytic property of nitrate-containing vanadium-oxo clusters ([1]*Graduate School of Natural Science and Technology, Kanazawa University*) ○Isshin Yoshida[1], Yuji Kikukawa[1], Yoshihito Hayashi[1]

Polyoxovanadates show the structure versatility and the correlation between the structure and property has been discussed. The local structure control among the related polyoxovanadates leads to understand the reactivity of the specific sites. Nitrate-incorporated octadecavanadate (V18) is one of the stable polyoxovanadates with the defined oxidation state of each vanadium atom. In the previous reports, V18 was synthesized via complicated redox process. Avoiding the reductive condition gave one-electron oxidized V18 (V18ox) with maintaining the polyoxovanadate structure. The comparison of the oxidation catalysis of sulfides between V18 and V18ox was investigated. As an oxidant, *tert*-butyl hydroperoxide (TBHP) was used because the structures and oxidation states of V18 and V18ox is maintained with TBHP. The reaction rate for the oxidation of thioanisole and derivatives with V18ox was larger than that with V18. The only difference between V18 and V18ox was oxidation state of the one of the cap part of the ellipsoidal structure, showing the active site of the V18ox is the oxidized cap part.
Keywords : Polyoxometalates, Vanadium, Oxidation Catalyst

アニオン性バナジウムオキソクラスターであるポリオキソバナデートは構造多様性を示し、構造と機能の相関が議論されてきた。部分構造のみが異なる類縁構造間で機能を比較することで、特定の部位の反応性を解明することが可能である。硝酸イオンを含有したポリオキソバナデート(V18)は安定なポリオキソバナデートの一つであり、すべてのバナジウムの酸化数が明らかとなっている化合物である。[1)] この化合物は上下 2 個のバナジウムが 4 価であり、その他 16 個のバナジウムが 5 価である(Figure 1)。V18 の合成には複雑な酸化還元反応が含まれているが、合成時に還元反応を抑えることで、2 個ある 4 価のバナジウムのうち 1 つが酸化された化合物(V18ox)を単離することに成功した。V18ox の分子構造は単結晶 X 線構造解析により明らかとなった。反応性の違いを比較するために、スルフィドの酸化触媒特性を比較した。酸化剤には V18 と V18ox がともに構造、酸化数を保持することが可能な *tert*-ブチルヒドロペルオキシド(TBHP)を用いた。種々のスルフィドの酸化反応において、V18ox は V18 よりも高い触媒活性を示した。V18ox と V18 の違いは V^{4+}の数だけであるため、触媒の高い活性はもともと V^{4+}だった部位が V^{5+}になることで発現したと考えられ、新たに V^{5+}となった部位周辺が活性サイトであることが明らかとなった。

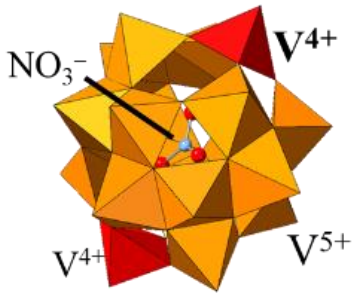

Figure 1. 硝酸イオン内包ポリオキソバナデートの構造

1) Y. Koyama, Y. Hayashi, K. Isobe, *Chem. Lett.* **2008**, *37*, 578.

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ホストゲスト特性を有する有機-無機ハイブリッド型ポリオキソメタレートの物性評価

（広島大院先進理工[1]・広島大キラルノット超物質拠点[2]・広島大キラル国際拠点[3]・宇部高専[4]・広島大先進セ[5]・JST さきがけ[6]）○飼鳥 弘人[1]・加藤 智佐都[1]・Goulven Cosquer[2,3]・藤林 将[4]・井上 克也[1,2,3,5]・西原 禎文[1,3,5,6]
Physical Properties of Organic-Inorganic Hybrid Polyoxometalates with Host-Guest Characteristics (*[1]Grad. Sch. Adv. Sci. Eng.; [2]SKCM[2]; [3]CResCent.; Hiroshima Univ.,[4]NIT, Ube College, [5]IAMR, Hiroshima Univ., [6]PRESTRO, JST*) ○Hiroto Kaitori,[1] Chisato Kato,[1] Goulven Cosquer,[2,3]Masaru Fujibayashi,[4] Katsuya Inoue,[1,2,3,5] Sadafumi Nishihara[1,3,5,6]

Polyoxometalates (POM) are molecular metal oxides with unique physical properties derived from their diverse structures and multi-electron reversible redox capabilities. We aim to develop hybrid molecules by combining POM with organic compounds such as phosphonic acids. However, the synthetic reaction of POM is difficult to control because of some unclear aspects, and no intramolecular cyclization reaction using POM has been reported. In this study, we synthesised two types of POM / crownether hybrid compounds by intramolecular cyclization reactions between a phosphonic acid derivative POM and a polyether molecule. These POM compounds with cyclic structures exhibit host-guest properties with cations such as K^+, NH_4^+, and $MeNH_3^+$ as guests.
Keywords : Crown Ether; Polyoxometalate; Hust-Guest Chemistry; organic-inorganic hybrid materials

ポリオキソメタレート（POM）は分子性金属酸化物の総称であり、多彩な構造と多段の酸化還元能に由来して特異な物性を発現する。さらに、ホスホン酸などの有機物と縮合することで有機-無機ハイブリッド分子を形成できる[1)]。そのため、POM 骨格の特性をベースとして構造の細かな設計や機能の付与ができると考えられる。しかし、POM の合成反応は不明瞭な点が多く、環化反応のような難易度の高い分子設計は達成されておらず、機能の拡張に制限があるといえる。

そこで本研究では、POM における環状化合物の合成を行い、その環状構造に由来したホストゲスト特性を調査した。具体的には、ポリエーテルをもつホスホン酸誘導体を POM 分子と分子内環化反応させることにより、クラウンエーテルに類似した構造を有する 2 種類の POM の合成に成功した（図. 1）。これらは、それぞれ UV-vis 滴定実験により、K^+や NH_4^+、$MeNH_3^+$などのカチオンをゲストとしたホストゲスト特性を発現することが明らかになった。本発表ではこれらの POM の構造およびホストゲスト特性の詳細を報告する。

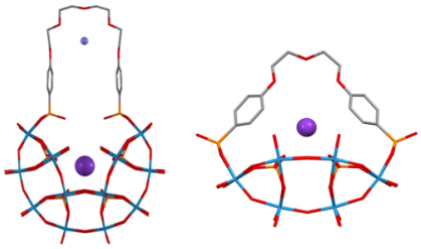

図 1. 環化合成物の構造

1) Xiaofeng Yi, *et al*., *Chem. Commun.,* **2018**, *54*, 2216-2219.

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ヨウ素を包接した Dawson 類似ポリオキソメタレートの合成と誘電率評価

(広島大理[1]・広島大院先進理工[2]・広島大キラルノット超物質拠点[3]・広島大キラル国際拠点[4]・広島大先進セ[5]・JST さきがけ[6]) ○鶴田 みなみ[1]・加藤 智佐都[2]・Goulven Cosquer[3,4]・井上 克也[2,3,4,5]・西原 禎文[2,4,5,6]
Dielectric Properties of Dawson like Polyoxometalates Including Iodine ([1]Science of school, [2]*Grad. Sch. Adv. Sci. Eng.*, [3]SKCM[2], [4]CResCent, [5]IAMR Hiroshima Univ., [6]PRESTO, JST) ○ Minami Tsuruda,[1] Chisato Kato,[2] Goulven Cosquer,[3,4] Katsuya Inoue,[2,3,4,5] Sadafumi Nishihara,[2,4,5,6]

Ferroelectric behavior is caused by long-range order of dipole-dipole interactions. However, we reported single-molecule electret (SME) which behaves like ferroelectric preyssler type polyoxometalate(POM) without long-range order.[1)2)] This molecule incorporates one metal ion inside molecular framework in cage type. There is an energy barrier because there are two stable sites inside the molecule. It shows molecular polarization depending on the position of incorporates ions. In my research, we tried to develop new SME and focused on Dawson-like POM which incorporates one iodine and two stable sites (Fig.2). Moreover, there are high spontaneous polarization because valence of incorporates ion is bigger than preyssler type POM. As the first stage of the research, from the results of depending electric field of polarization measurements was polarization hysteresis characteristic of ferroelectrics observed.
Keywords : Polyoxometalates; Ferroelectrics; Dielectrics; Single-molecule electret;

強誘電体は、外部電場により反転可能な自発分極を有する。強誘電性を発現する為には、双極子-双極子相互作用の長距離秩序が必要であり、単一分子での強誘電性の発現は不可能だと考えられていた。その様な背景の中、当研究室はプレイスラー型ポリオキソメタレート(POM)が、単一分子で恰も強誘電体の様に振る舞う事を見出し、これを単分子誘電体[1), 2)]として報告した。この分子は、籠型の分子骨格内部に１つの金属イオンを内包しており、内包イオンは分子内部に２つの安定サイトを有している。安定サイト間にはエネルギー障壁(U_E)が存在し、エネルギー障壁よりも低い温度域において内包イオンは片側の安定サイトに局在する為、内包イオンの位置に応じた分子分極を示す(Fig.1)。本研究では、新規単分子誘電体の開発を目指して Dawson 類似 POM[3)]に着目した(Fig.2)。この分子は既報の単分子誘電体と同様に１つの内包イオンと２つのイオン安定サイトを有している為、単分子誘電体であると考えた。更に内包イオンの価数が大きいため、より大きな自発分極をもつ事が期待できる。初段階として、分極の電場依存性測定を行った結果、強誘電体に特徴的な分極ヒステリシスを観測した。

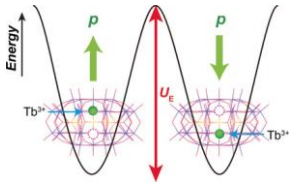

Fig.1 Double-well potential

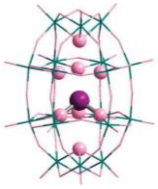
Fig.2 Structure of Dawson-like POM

1)C. Kato, S. Nishihara, *et. al*., *Angew. Chem. Int. Ed.,* **2018**, *57*, 13429-13432. 2)S. Nishihara, Nat. *Nanotechnol.*, **2020**, *15,* 966-967. 3)D. -L, Long, *et. al*., *Chem. Commun.,* **2013**, *49*, 9731-*9733*.

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有機溶媒に可溶なε-Keggin型$[Al_{13}O_4(OH)_{24}(ligand)_{12}]^{7+}$の合成と触媒特性

(広大院先進理工[1]) ○馬越 彩乃[1]・湊 拓生[1]・定金 正洋[1]

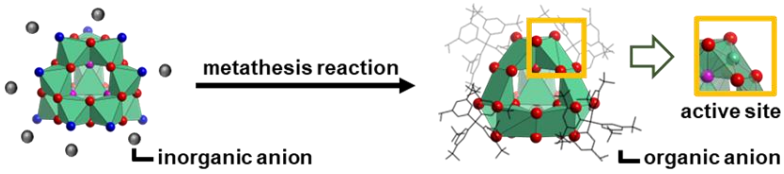
Synthesis and catalysis of an organic solvent-soluble ε-Keggin type $[Al_{13}O_4(OH)_{24}(ligand)_{12}]^{7+}$

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Ayano Umakoshi,[1] Takuo Minato,[1] Masahiro Sadakane[1]

Aluminum oxide (alumina) is widely used as a catalyst because of its heat resistance, high specific surface area, and Lewis acidity.[1)] Since catalytic active sites of Al are thought to be five coordination geometries, precise structural control of Al is quite important. However, surface structure of bulk alumina is unclear, thus making it difficult to control the structure of active sites at an atomic level. Molecular alumina clusters are cationic oxo-hydroxo clusters formed by the condensation of aluminum hydroxide and possess the similar surface structures to those of alumina. Since the molecular structures of these clusters can be finely tailored at an atomic level, they are expected to exhibit excellent catalytic activity. However, molecular aluminum clusters have not been studied as catalysts presumably because they tend to be gelatinized or isomerized in water. Therefore, we focused on stable $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ **(Al_{13})** and envisaged that development of an organic solvent-soluble **Al_{13}** could achieve unique homogeneous catalyst in organic media by mimicking the surface structure of bulk alumina. In this study, we synthesized and characterized new arylborate salts of **Al_{13}** which was synthesized by metathesis reactions.

Keywords : alumina; aluminum oxo-hydroxo clusters; catalyst

酸化アルミニウム (アルミナ)は耐熱性が高く高比表面積を有しておりルイス酸性を有しているため触媒材料として幅広く利用されている[1)]。Al の触媒活性点は 5 配位の構造であると考えられているため Al の精密な構造制御は非常に重要であるが、バルク状アルミナの表面構造は不明瞭であるため原子レベルでの活性点構造制御は困難である。分子状アルミナクラスターはバルク状アルミナの表面構造に類似した構造を有しており、分子状であるため原子レベルでの構造設計が可能であることから優れた触媒活性を示すことが期待される。しかし、分子状アルミナクラスターは水中ではゲル化や異性化によって構造変化してしまう傾向があるため触媒としての利用は進んでいない。そこで我々は、安定な$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$(**$Al_{13}$**)に着目し、有機溶媒に可溶な **$Al_{13}$** を開発することでバルクアルミナの表面構造を模倣し有機媒体中でユニークな均一系触媒として利用することを考えた。本発表では、有機溶媒に可溶な分子状アルミナクラスターの合成とキャラクタリゼーションについて報告する。



1) I. Bezverkhy P. Afanasiev, C. Geantet, M. Lacroix, *J. Catal.* **2001**, *204*, 495–497.

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カリウムイオンを内包した環状ポリオキソメタレートの高温域における誘電物性評価

(広島大院先進理工[1]・宇部高専[2]・広島大キラルノット超物質拠点[3]・広島大キラル国際拠点[4]・広島大先進セ[5]・JST さきがけ[6]) ○竹本 悠真[1]・加藤 智佐都[1]・藤林 将[2]・Cosquer Goulven[3,4]・井上 克也[1,3,4,5]・西原 禎文[1,4,5,6]

Evaluate dielectric properties of wheel-shape polyoxometalate which incorporates potassium ions at high temperature ([1]*Grad. Sch. Adv. Sci. Eng. Hiroshima Univ.*, [2]*NIT, Ube college*, [3]*SKCM*[2], [4]*CResCent*, [5]*IAMR*, *Hiroshima Univ.*, [6]*PRESTO, JST*) ○Yuma Takemoto,[1] Chisato kato,[1] Masaru Fujibayashi,[2] Goulven Cosquer,[3,4] Katsuya Inoue,[1,3,4,5] Sadafumi Nishihara,[1,4,5,6]

In our previous work, we reported single-molecule electret (SME) which behaves like ferroelectric materials as single molecule.[1] This polyoxometalate (POM) incorporates one terbium cation (Tb^{3+}), and this cation has two stable sites in the cavity so molecular polarization is occurred depending on the position. In this work, we focused on a wheel-shaped POM (Fig.1), which incorporates eight potassium cations (K^+) in the cavity. As four of them are delocalized between two stable sites in the cavity so this molecule will behave as new SME. In addition, P-E hysteresis will be observed at higher temperature than SME because the temperature of SME increased as radius of inner ion became larger and K^+ is larger than Tb^{3+}. As a result, P-E hysteresis was observed from 300 K to 440 K so this molecule behaves as new high tolerance SME (Fig.2).

Keywords : Polyoxometalates; Ferroelectrics; Dielectrics; Single-molecule electret

当研究室は， Preyssler 型ポリオキソメタレート(POM)が単一分子で強誘電体のように振る舞うことを見出し，これを「単分子誘電体」と名付けた。[1)]Preyssler 型 POM は籠型の分子骨格内に 1 つの Tb^{3+}を内包しており，その Tb^{3+}は分子内に２つの安定サイトを有している。この分子は，内包イオンの位置に応じた分子分極を示すことに加え，外部電場の印加により内包イオンが分子内を移動し，分子分極が反転する為，強誘電体に特徴的な分極ヒステリシスを発現する。

本研究では，Preyssler 型 POM の単分子誘電体特性の出現機構を継承した、分子内に複数の移動可能な内包イオンを有する環状 POM，$\mathbf{K^+\subset W_{48}}$ [2)] (Fig.1) に着目した。この分子は 8 つの K^+を内包しており，そのうち 4 つが空洞内に極座していた。一方，他の４つの各 K^+は 2 つの安定サイトを有しており、単分子誘電体特性の出現が期待される（Fig.1，紫球）。実際に $\mathbf{K^+\subset W_{48}}$ について分極の電場依存性測定を行った結果，300K から 440K の温度範囲で，強誘電体に特徴的な分極ヒステリシスが観測された。この結果から $\mathbf{K^+\subset W_{48}}$ は，熱耐久性が優れた新規「単分子誘電体」であることが示唆された(Fig.2)。

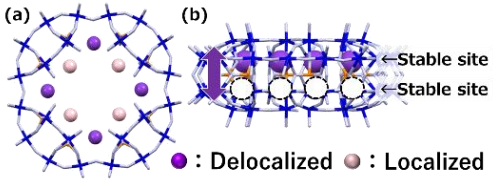

Fig.1 (a)Top and (b)side view of $\mathbf{K^+_8\subset W_{48}}$.

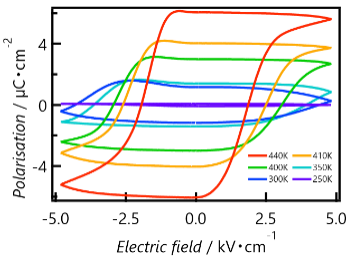

Fig.2 *P-E* loops of $\mathbf{K^+\subset W_{48}}$.

1) C. Kato, S. Nishihara, *et. al., Angew. Chem. Int. Ed.*, **2018**, *57*, 13429-13432.
2) S.Nishihara, *Nat. Nanotech.*, **2020**, *15*, 1065. 3) R. Contant, *et. al., Inorg. Chem.*, **1985**, *24*, 4610-4614.

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単分子誘電体$(NH_4)_xH_{12-x}[Tb^{3+}\subset P_5W_{30}O_{110}]$薄膜の物性評価

（広島大院先進理工[1]・広島大キラルノット超物質拠点[2]・宇部高専[3]・広島大キラル国際研究拠点[4]・広島大先進セ[5]・JST さきがけ[6]）○有馬 將稀[1]・竹田 一志[1]・玉谷 陸翔[1]・中野 佑紀[1]・加藤 智佐都[1]・Goulven Cosquer[2]・藤林 将[3]・井上 克也[1,2,4,5]・西原 禎文[1,4,5,6]

Physical properties of thin films of single-molecule electret $(NH_4)_xH_{12-x}[Tb^{3+}\subset P_5W_{30}O_{110}]$ ([1]*Grad. Sch. Adv. Sci. Eng., Hiroshima Univ.*, [2]*SKCM², Hiroshima Univ.*, [3]*NIT, Ube college,* [4]*CResCent, Hiroshima Univ.,* [5]*IAMR, Hiroshima Univ.,* [6]*PRESTO, JST*) ○[1]Masaki Arima, [1]Kazushi Takeda, [1]Rikuto Tamatani, [1]Yuki Nakano, [1]Chisato Kato, [2]Goulven Cosquer, [3]Masaru Fujibayashi, [1,2,4,5]Katsuya Inoue, [1,4,5,6]Sadafumi Nishihara

Ferroelectricity is a physical property which derives from crystal structure, and it has been believed that it is not expressed by a single molecule. However, we reported that single molecule of Preyssler-type polyoxometalate behaves like a ferroelectric and named it Single-molecule electret (SME). At the same time, thin-film state of SME has not been evaluated. In this study, we measured microscopic electrical properties of SME thin-film using a piezo-response force microscopy, one of atomic force microscope's modes.

Keywords : Single-molecule electret; Ferroelectric; Atomic Force microscope; Thin film; Polyoxometalate

強誘電性は双極子-双極子相互作用の長距離秩序に由来する物性であり、単一分子では発現しないと考えられていた。その様な背景の中、当研究室ではプレイスラー型ポリオキソメタレート（POM）が単一分子で恰も強誘電体のように振る舞うことを報告し、これを「単分子誘電体」と名付けた[1]。この分子は籠型骨格内部に一つの金属イオンを内包することができる。空洞内には結晶学的に等価な二つの安定サイトが存在しており、内包イオンが片方の安定サイトに局在化することで、イオンの位置に応じた分子分極が生じる（Fig. 1）。POM に外部電場を印加すると内包イオンがもう一方の安定サイトに移動し、分子分極が反転する。よって、POM は長距離秩序に由来せずとも、単一分子で強誘電的な分極ヒステリシスを示す（Fig. 2）。本研究では、これまでペレット試料でのみ行われていた物性測定を単分子状態でより詳細に評価するため薄膜状態で行った。具体的には，原子間力顕微鏡の測定モードの 1 つである圧電応答力顕微鏡を用いて、薄膜状態の単分子誘電体物性を評価した。

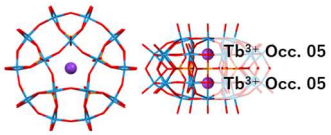

Fig. 1　プレイスラー型 POM の構造

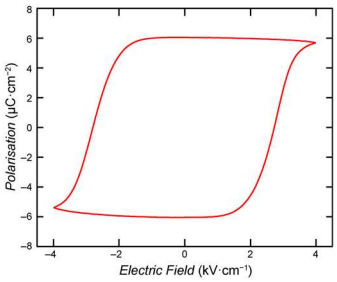

Fig. 2　プレイスラー型 POM における分極ヒステリシス

[1] C. Kato, S. Nishihara, *et al.*, *Angew. Chem. Int. Ed.*, **2018**, *57*, 13429–13432.

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電気化学触媒に向けた Pt 合金クラスターの精密合成と機能評価

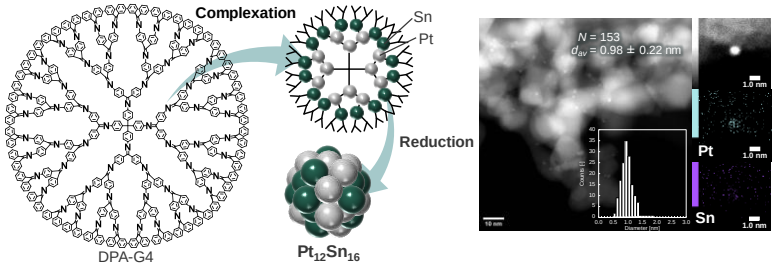
（東工大化生研[1]・JST-ERATO[2]）○中村 拓篤[1]・森合 達也[1,2]・神戸 徹也[1,2]・今岡 享稔[1,2]・山元 公寿[1,2]

Precise synthesis of Pt alloy clusters for electrochemical catalysts and evaluation of their functions ([1]*Lab. Chem. Life Sci., Tokyo Tech*, [2]*JST-ERATO*) Takuto Nakamura,[1] Tatsuya Moriai,[1,2] Tetsuya Kambe,[1,2] Takane Imaoka,[1,2] Kimihisa Yamamoto[1,2]

Metal clusters can be alloyed with different metal species in any composition, and the alloy clusters exhibit high catalytic activity[1]. We have found that carbon-loaded platinum (Pt) clusters synthesized by the template method using dendrimers show high ORR activity in comparison to conventional nanoparticles[2]. However, there were obstacles from a viewpoint of catalytic durability, such as the decay of carbon and the aggregation and leeching of clusters. Therefore, in this study, we used tin oxide and titanium oxide as supports and blended these metal elements (Sn and Ti) with Pt clusters to enhance the particle-support interaction. Here, $Pt_{12}Sn_{16}$ alloy clusters containing 12 Pt atoms and 16 Sn atoms were synthesized by this method. STEM observations and EDX analysis confirmed that the size and composition of the clusters were precisely controlled. Furthermore, their functions as catalysts were evaluated from XPS and electrochemical measurements.

Keywords : Cluster; Platinum; Dendrimer; Catalyst; Electrochemistry

金属クラスターは異なる金属種を任意の組成で合金化することができ、合金化したクラスターは高い触媒活性を示す[1]。我々の研究室では、独自に開発したデンドリマーを用いた鋳型法合成した炭素担持白金(Pt)クラスターが Pt ナノ粒子よりも優れた酸素還元反応(ORR)活性を示すことを見出している[2]。一方で、反応に伴う炭素担体の酸化被毒や、粒子の凝集・リーチングなど触媒としての耐久性に課題が残されていた。そこで、本研究では担体として酸化スズや酸化チタンを採用し、さらにこれらの金属元素(Sn、Ti)を Pt クラスターに配合させることで粒子ー担体間における相互作用の増幅を図った。ここでは、本手法により Pt 12 原子と Sn 16 原子を含む $Pt_{12}Sn_{16}$ 合金クラスターを合成した。STEM 観察や EDX 分析からクラスターの粒径や組成が精密に制御されていることを確認した。さらに、XPS 測定や電気化学測定から合金クラスターの物性や電気化学触媒としての機能を評価した。



1) T. Moriai *et al.*, *Angew. Chem. Int. Ed.*, **2020**, 59, 23051-23055.
2) K. Yamamoto *et al.*, *Acc. Chem. Res.,***2017**, 47, 4, 1127-1136.

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微小ビスマス粒子の合成と磁気機能評価

（東工大化生研[1]、JST ERATO[2]）○橋本遼太郎[1]・神戸徹也[1,2]・塚本孝政[1,2]・今岡享稔[1,2]・山元公寿[1,2]

Synthesis of ultra small bismuth particles and evaluation of their magnetic function

（[1]*Lab. Chem. Life Sci., Tokyo Tech.,* [2]*JST ERATO*）○Ryotaro Hashimoto[1], Tetsuya Kambe[1,2], Takamasa Tsukamoto[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2]

While the synthesis of bismuth nanoparticles has been reported to exhibit special magnetic properties such as superconducting behavior, sub-nanoparticles, which are smaller than nanoparticles, have been little studied. On the other hand, sub-nanoparticles smaller than nanoparticles have not been studied. In this study, we investigated the synthesis of bismuth sub-nanoparticles and their magnetic functions.

The synthesis was carried out using the dendrimer template reduction method. The number of atoms can be controlled by adjusting the equivalent amount of metal salts (Fig. 1). Bismuth particles with a particle diameter of about 1 nm were synthesized under conditions of loading of 4 wt% or less (Fig. 2). In addition, we report on the magnetic behavior of the bismuth particles depending on their particle size and valence.

Keyword : Nanoparticles; Bismuth; magnetism

ビスマスナノ粒子の合成により超伝導挙動といった特殊な磁気特性の発現が報告されているが、一方でナノ粒子より微小化したサブナノ粒子については殆ど研究されていない。また、粒径 1 nm 程度のサブナノ粒子はバルクやナノ粒子とは異なり構成原子数に依存した性質を示すことが知られている。そこで、本研究ではビスマスサブナノ粒子の合成と磁気機能の解明を目的に研究した。

合成はデンドリマー鋳型還元法を用いて行った。分子の内層に向けて電子密度が高くなる性質を有するデンドリマーを鋳型とし、金属塩を錯形成・還元することで合成する手法であり、金属塩の当量を調整することで原子数を制御できるものである（Fig.1）。担持量 4wt%以下の条件において、粒径 1 nm 程度のビスマス粒子を合成した（Fig.2）。併せて、ビスマス粒子の粒径や価数の違いによる磁性挙動を示したので報告する。

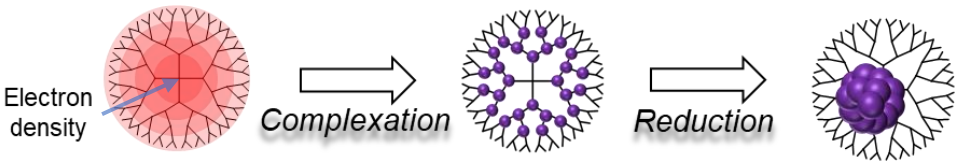

Fig1. Synthesis by template reduction method.

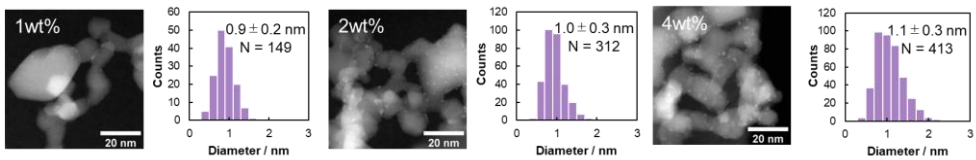

Fig2. TEM image and size distribution of Bi particles (1wt%, 2wt% and 4wt%) supported on TiO_2.

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Academic Program [Oral B] | 07. Inorganic Chemistry : Oral B

Thu. Mar 21, 2024 1:00 PM - 2:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:00 AM UTC A1444(1444, Bldg. 14 [4F])

[A1444-4pm] 07. Inorganic Chemistry

Chair: Takayuki Nakamuro, Takuro Hosomi

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[A1444-4pm-01]
Multi-step Mechanism of Carbonation Reaction Analysed by Atomic-resolution Electron Microscopy

○Miyuki Hanazawa[1], Xin Li[1], Takayuki Nakamuro[1], Eiichi Nakamura[1] (1. The University of Tokyo)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[A1444-4pm-02]
Local structure analysis of near-infrared reflective black $Ca_2(Mn,Ti)O_4$ pigments using synchrotron radiation X-ray

○Ryohei Oka[1], Tomokatsu Hayakawa[1] (1. Nagoya Institute of Technology)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[A1444-4pm-03]
Growth-traceable fully vapour-phase organic-inorganic atomic layer deposition system

○Hideaki Matsuo[1], Takuro Hosomi[1], Jiangyang Liu[1], Wataru Tanaka[1], Tsunaki Takahashi[1], Takeshi Yanagida[1,2] (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. IMCE, Kyushu Univ.)

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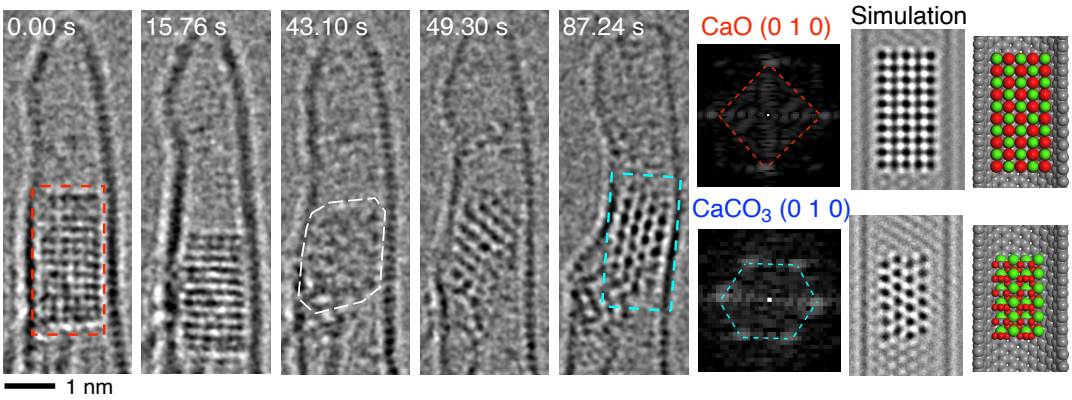
Multi-step Mechanism of Carbonation Reaction Analysed by Atomic-resolution Electron Microscopy

(*Department of Chemistry, The University of Tokyo*)
○Miyuki Hanazawa, Xin Li, Takayuki Nakamuro, Eiichi Nakamura
Keywords: Intermolecular Reaction; In-situ Observation; Transmission Electron Microscopy; Calcium Carbonate; Atomic-resolution

Calcium carbonate ($CaCO_3$) plays an important role in biology and materials engineering.[1] In recent years, the application of biomineralization, which is typical of $CaCO_3$-based biomaterials, has attracted attention in the development of new materials, and an understanding of the formation mechanism is required to control their structures and properties. However, the dynamic behavior at the atomic level is not well understood due to difficulties in experimental observation of the process with high spatial and temporal resolutions. Based on this background, here we demonstrate in-situ observation of a $CaCO_3$ formation process through an intermolecular reaction of calcium oxide (CaO) and carbon dioxide (CO_2) inside a conical-shaped carbon nanotube (CNT) by single-molecule atomic-resolution time-resolved electron microscopy (SMART-EM).[2]

Under SMART-EM observation, a CaO nanocrystal was detected at the initial state (0.00 s, red dashed line). The crystal structure began to fluctuate and decreased in size layer-by-layer from the surface by CO_2 supply to the CaO crystal (15.76 s). At a certain size, the entire cluster transformed into an amorphous structure (43.10 s, white dashed line), and a periodic structure different from the initial one was formed (49.30 s). The structural analysis revealed that the nanocrystal obtained by the gas-solid reaction was reasonably matched to the bulk crystal of aragonite structure, which is a metastable polymorph of $CaCO_3$ at ambient conditions (87.24 s, blue dashed line).[3] In the presentation, detailed analyses of local structures transiently formed on the surface and reaction mechanism will be discussed.



1) T. Akiyama *et al.*, *Phys. Rev. B*, **2011**, *84*, 085428. 2) T. Nakamuro *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 1763. 3) S. Sovova *et al.*, *J. Mater. Chem. B*, **2021**, *9*, 8308.

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放射光 X 線を用いた $Ca_2(Mn,Ti)O_4$ 黒色遮熱顔料の局所構造解析

（名工大院工）○岡 亮平・早川 知克

Local structure analysis of near-infrared reflective black $Ca_2(Mn.Ti)O_4$ pigments using synchrotron radiation X-ray (*Graduate School of Engineering, Nagoya Institute of Technology*)
○Ryohei Oka, Tomokatsu Hayakawa

Local structures of NIR-reflective black $Ca_2(Mn,Ti)O_4$ pigments were analyzed by using X-ray synchrotron radiation. A comparison of the atomic distances estimated from the Rietveld analysis and radial distribution function (RDF) revealed that there were large differences between the M–M distances (M = Mn, Ti). Therefore, XANES simulations were carried out to obtain models of the local structure. The experimental and theoretical data indicate that the Mn atoms were configured in a zigzagging arrangement, and the distortion of the MnO_6 octahedra increased with the increase in the degree of Ti^{4+} doping.

Keywords : Inorganic pigments; NIR-reflective properties; Synchrotron radiation X-ray; Local structures; First-principles calculations

近年，熱を吸収しない（遮熱）顔料の要求が高まっており，特に黒色の遮熱顔料の開発が望まれている．これまでに Ti を固溶させた $Ca_2(Mn,Ti)O_4$ が黒色遮熱顔料として高い性能を有することを明らかにした [1]．また，結晶格子内に，ある一定の相関距離をもつ Ti–Ti 配列が存在することを報告した [2]．しかしながら，Ti の固溶状態や価数変化などについては未解明な部分があり，$Ca_2(Mn,Ti)O_4$ がもつ特性をより理解するためには，構成元素の価数や局所構造，電子状態などの情報が不可欠である．そこで本研究では，放射光 X 線を用いた粉末 X 線回折（XRD）及び X 線吸収微細構造分光（XAFS）測定により，平均および局所構造を解析するとともに，第一原理計算により XANES スペクトルのシミュレーションを行った [3]．

XANES スペクトルより，Mn^{4+}及び Ti^{4+}の割合を見積もった結果，いずれの試料においてもそれぞれ約 82%及び約 95%で，Mn 及び Ti の価数は 4+が支配的であり，これらの価数は Ti の固溶によって変化しないことがわかった．また，Mn-XANES スペクトルにおいて 2 つの pre-edge ピークが観測され，Ti^{4+}の固溶によりピーク位置･強度が変化していたことから，MnO_6 八面体の対称性が変化していると考えられる．Rietveld 及び RDF 解析より M–O, M–Ca, M–M（M = Mn,Ti）原子間距離を算出したところ，M–M 間では両者に大きな差があることがわかった．以上の結果を踏まえ，**Figure 1** に示すような構造モデルを構築し XANES シミュレーションを行った．その結果，Mn^{4+} を a 軸方向に沿ってジグザグ配列させた局所構造モデルにおいて，実測スペクトルの変化をよく再現し，Ti^{4+}固溶により Mn^{4+}の c 軸方向への変位すなわち MnO_6 八面体の歪みが大きくなることがわかった．

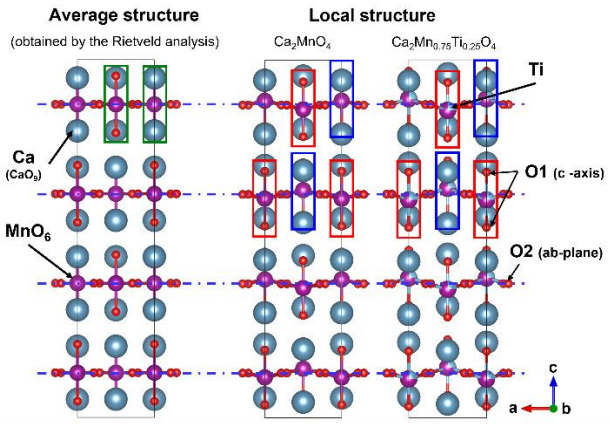

Figure 1 Average and local structure models of $Ca_2(Mn,Ti)O_4$. The green/red/blue frames indicate O–Mn/Ti–O bond unit in the c-axis direction.

1) R. Oka, T. Masui, *RSC Adv.* **2016**, *6*, 90952. 2) R. Oka, T. Hayakawa, *Inorg. Chem.* **2022**, *61*, 6500. 3) R. Oka, T. Hayakawa, *Inorg. Chem.* **2023**, *62*, 14647.

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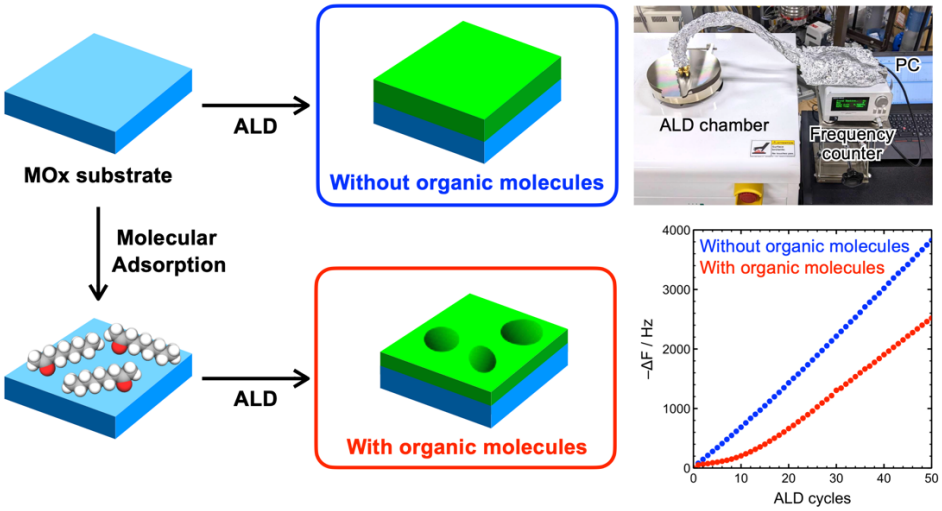
Growth-Traceable Fully Vapor-Phase Organic-Inorganic Atomic Layer Deposition System

([1]*Graduate School of Engineering, University of Tokyo*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*) ○ Hideaki Matsuo,[1] Takuro Hosomi,[1] Jiangyang Liu,[1] Wataru Tanaka,[1] Tsunaki Takahashi,[1] Takeshi Yanagida[1,2]

Keywords: Atomic Layer Deposition; Quartz Crystal Microbalance

Various methods have been developed to create nanoscale structures by growing metal oxide structures in the presence of organic molecules. Thin-film deposition of inorganic materials on organic molecules dispersed on a surface has attracted particular attention in recent years, as it is considered possible to design inorganic thin-film structures that reflect the structural features of the organic molecules.[1–3] Although monomolecular dispersion of organic molecules is essential for this method, conventional solution phase adsorption cannot avoid aggregation between molecules. In addition, the state of both organic and inorganic materials during growth is in the almost black box.

In this research, we designed a device that not only deposits metal oxides but also adsorbs target organic molecules in the gas phase using atomic layer deposition (ALD), a thin film formation method that can be controlled at the atomic layer level. In addition, by introducing quartz crystal microbalance (QCM) method and tracking mass changes on the substrate surface in real time, we were able to track the adsorption process of organic molecules and the subsequent deposition process of metal oxides. As a result, it was confirmed that there were differences in the deposition behavior of metal oxides depending on whether or not organic molecules were adsorbed, so the physical properties of both were also evaluated.



1) C. P. Canlas *et al.*, *Nature Chem.* **2012**, *4*, 1030–1036. 2) P. Ruff *et al.*, *Microporous Mesoporous Mater.* **2016**, *235*, 160–169. 3) N. Sobel and C. Hess, *Angew. Chem. Int. Ed.* **2015**, *54*, 15014–15021.

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Academic Program [Oral A] | 08. Catalysts and Catalysis：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
A1456(1456, Bldg. 14 [5F])

[A1456-4am] 08. Catalysts and Catalysis

Chair: Akinobu Nakada, Shimpei Naniwa

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1456-4am-01]

CO_2 photoreduction by first-row transition metal loaded-Al_2O_3

○Daehyeon An[1], Megumi Okazaki[1], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1456-4am-02]

Light-intensity dependence of CO_2 reduction over Ru-complex/polymeric carbon nitride hybrid photocatalysts

○Ryuichi Nakada[1], Megumi Okazaki[1], Kazuhiko Maeda[1] (1. Tokyo Institute of Tecnology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1456-4am-03]

Improvement in a Z-schematic CO_2 reduction activity under visible light irradiation utilizing a long wavelength visible light-responsive metal sulfide photocatalyst prepared by a flux method

○Sota Arai[1], Kotaro Wada[1], Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1456-4am-04]

Single particulate CO_2 reduction under visible light irradiation over various cocatalysts-loaded a $SrTiO_3$:Ir,Sb photocatalyst using water as an electron donor

○Hana Ito[1], Yoshiya Ueki[1], Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1456-4am-05]

Consecutive photoreduction of carbon dioxide using Fe and Cu nanoparticles supported on zirconium dioxide and its mechanistic analysis

○Tomoki Oyumi[1], Keisuke Hara[1], Yasuo Izumi[1] (1. Chiba University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1456-4am-06]

Conversion of carbon dioxide to C_1-C_3 hydrocarbon compounds by titanium dioxide photocatalyst loaded with nickel metal nanoparticles

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○Yuta Sekine[1], Tomoki Oyumi[1], Yasuo Izumi[1] (1. Chiba university)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1456-4am-07]

Photo-excited carrier dynamics during the photoreduction of CO_2 on transition metal oxide surfaces

○Keisuke Hara[1], Ayaka Hasegawa[1], Ayana Omata[1], Kaori Niki[1], Yasuo Izumi[1] (1. Chiba University)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1456-4am-08]

Enhancement of Activity of Pt/MoO_3 Catalysts for Photo-Assisted RWGS Reaction by Supporting on Various Metal Oxide

○Daichi Takami[1], Yasutaka Kuwahara[1], Hiromi Yamashita[1] (1. Osaka Univ.)

English
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1456-4am-09]

Development of Re complexes bearing various bipyridine-derived ligands for visible-light-driven carboxylation of organic molecules with CO_2

○Phurinat Lorwongkamol[1], Masaki Kitada[1], Taito Watanabe[1], Yutaka Saga[1], Tetsuya Kambe[1], Mio Kondo[2,1,3], Shigeyuki Masaoka[1] (1. Osaka University, 2. Tokyo Institute of Technology, 3. JST PRESTO)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1456-4am-10]

Catalytic properties of delafossite-type Cu oxides for electrochemical CO_2 reduction reaction

○Takahiro Matsuu[1], Akihiko Anzai[2], Masaki Donoshita[2], Hirokazu Kobayashi[3], Miho Yamauchi[2,3,4,5] (1. Dep. Chem., Sch. Sci., Kyushu Univ., 2. IMCE, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ., 5. WPI-I2CNER, Kyushu Univ.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1456-4am-11]

Production of high value-added chemicals by the CO_2 electroreduction with copper-based electrocatalysts

○Junya Yamaguchi[1], Xiaofan Hou[1], Kenji Kamiya[1], Eika Qian[1] (1. Tokyo University of Agriculture and Technology)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1456-4am-12]

DFT Study of the Catalytic Active Site of CoN_4C_x on KB for Electroreduction of CO_2 to CO

○Sarinya Hadsadee[1], Manussada Ratanasak[1], Kiyotaka Asakura[1], Hitoshi Ogihara[3], Ichiro Yamanaka[2], Jun-ya Hasegawa[1] (1. Hokkaido University, 2. Tokyo Institute for Technology, 3.

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Saitama University)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[A1456-4am-13]

Study on Electrochemical CO Reduction in Acidic Environments for the Development of Solid Polymer Electrolyte Systems Utilizing Cation Exchange Membranes

○Ryo Kurihara[1], Kaito Nagita[1], Shotaro Ito[1], Shintaro Kato[1], Ohashi Keitaro[1], Yoshiharu Mukouyama[1,2], Takashi Harada[1], Shuji Nakanishi[1], Kazuhide Kamiya[1] (1. Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University, 2. Tokyo Denki University)

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第一遷移金属担持アルミナを触媒とした CO_2 光還元反応

（東工大）○安 大賢・岡崎 めぐみ・前田 和彦
CO_2 photoreduction by first-row transition metal loaded-Al_2O_3 (*Tokyo Institute of Technology*)
○Daehyeon An, Megumi Okazaki, Kazuhiko Maeda

We have reported that an Fe oxyhydroxide (FeOOH) loaded onto the Al_2O_3 surface acted as a catalyst for the generation of HCOOH from CO_2 with a Ru(II) photosensitizer and 1-benzyl-1,4-dihydro-nicotinamide as an electron donor under visible light.[1)] This work suggests that other first-row transition metals also work as catalysts for the same reaction. In this work, we found that Zn showed the highest performance with ~90% CO_2 reduction selectivity, among the first-row metals examined. XRD measurement identified the loaded Zn species on Al_2O_3 to be $Zn(OH)(NO_3)(H_2O)$, which appeared to be active species for the HCOOH generation. In this presentation, the effects of preparation conditions for the Zn/Al_2O_3 catalysts on the CO_2 reduction activity will be given.
Keywords : Photocatalyst; CO_2 reduction; First-row transition metal

我々は Fe 酸水酸化物(FeOOH)を Al_2O_3 表面に担持したものが、Ru(II)光増感剤と電子供与体として 1,4-ジヒドロ-1-ベンジルニコチンアミドを用いて CO_2 から HCOOH を生成する触媒として作用することを報告した[1)]。この結果は、他の第一遷移金属も同様の反応の触媒として機能することを示唆している。調査した第一遷移金属の中で、Zn が CO_2 還元選択率 90%に達する高い性能を見せることがわかった。XRD 測定では、Al_2O_3 に担持された Zn 種は $Zn(OH)(NO_3)(H_2O)$であることが確認され、これが HCOOH 生成の活性種であると推定された。本発表では、Zn/Al_2O_3 の作成条件が CO_2 還元活性に及ぼす影響について説明する。

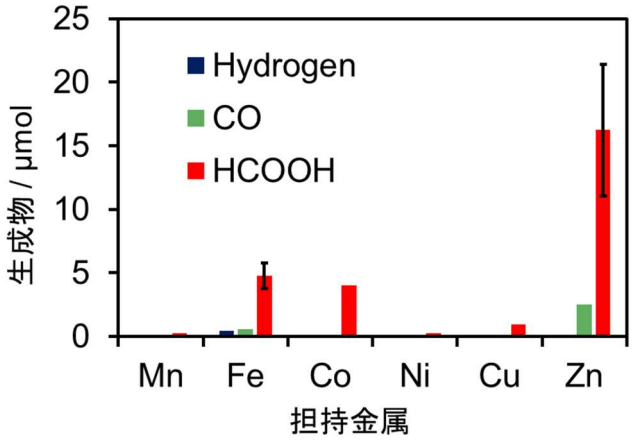

Figure 1. 第一遷移金属担持アルミナを用いた CO_2 光還元反応生成物分布

1) D. An, S. Nishioka, S. Yasuda, T. Kanazawa, Y. Kamakura, T. Yokoi, S. Nozawa, K. Maeda, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202204948

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Ru 錯体/窒化炭素ポリマー複合光触媒上での CO_2 還元反応に対する光強度依存性

（東工大理 [1]）○仲田 竜一 [1]・岡崎 めぐみ [1]・前田 和彦 [1]

Light-intensity dependence of CO_2 reduction over Ru-complex/polymeric carbon nitride hybrid photocatalysts

([1]*School of Science, Tokyo Institute of Technology*) ○ Ryuichi Nakada,[1] Megumi Okazaki,[1] Kazuhiko Maeda[1]

Polymeric carbon nitride (PCN) is known to be a visible-light-driven photocatalyst for hydrogen production. A hybrid photocatalyst of PCN and a Ru(II) mono-nuclear complex (*trans*-(Cl)-Ru[$(PO_3H_2)_2$bpy$(CO)_2Cl_2$]; **RuP**) is active for visible-light CO_2 reduction reaction[1)]. Previously, this system has been studied with respect to Ru complexes and metal nanoparticle additives,[2)] which work as catalytic active sites[1)] and charge separators on the PCN surface, respectively. However, no study has been done on how the incident light intensity affects the CO_2 reduction activity. In this study, the light intensity dependence of the **RuP**/Ag/PCN hybrid photocatalyst was investigated to determine the factors contributing to the rate of CO_2 reduction reaction.

It was found that the rate of HCOOH production over the **RuP**/Ag/PCN photocatalyst increased linearly with increasing light intensity up to 5.0 mW cm $^{-2}$, indicating light absorption PCN governs the HCOOH production rate in this region. Above 5.0 mW cm $^{-2}$, the HCOOH production rate did not increase proportionally to the light intensity, suggesting that electron-hole recombination became dominant.

Keywords : Artificial photosynthesis, Hydrogen carrier, Formic acid

有機半導体のポリマー状窒化炭素(PCN)は水素生成に有用な可視光応答型光触媒として知られている。Ru(II)単核錯体触媒(*trans*-(Cl)-Ru[$(PO_3H_2)_2$bpy$(CO)_2Cl_2$]; **RuP**)と PCN 複合光触媒は、可視光照射下で CO_2 還元反応に活性を示すことが報告されている [1)]。これまでに CO_2 還元反応の活性点となる Ru 金属錯体 [1)]の種類や、電荷分離に寄与する金属ナノ粒子 [2)]の検討が行われてきたが、光強度が **RuP**/Ag/PCN 複合光触媒の CO_2 還元反応に対してどのような影響を及ぼすのかは明らかにされていない。本研究では **RuP**/Ag/PCN 複合光触媒の光強度依存性を調べ、CO_2 還元反応速度に寄与する要素を調べた。

5.0 mW cm $^{-2}$ 以下の光強度ではギ酸の生成速度が光強度の増加に対して、線形的に増加することが確認され、この領域ではギ酸生成速度は PCN の光吸収によって支配されていることがわかった。一方で、5.0 mW cm $^{-2}$ 以上の領域ではギ酸生成速度は光強度に対して線形的に増加せず、電子・ホール再結合の寄与が全反応速度に影響することが示唆された。

1) R. Kuriki, *et al.*, Visible-Light-Driven CO_2 Reduction with Carbon Nitride: Enhancing the Activity of Ruthenium Catalysts. *Angew. Chem. Int. Ed.* **2015**, *54*, 2406-2409.

2) K. Maeda, *et al.*, Visible-light CO_2 reduction over a ruthenium(II)-complex/C_3N_4 hybrid photocatalyst: the promotional effect of silver species. *J. Mater. Chem. A* **2018**, *6*, 9708-9715.

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長波長光に応答する金属硫化物光触媒を用いた Z スキーム型可視光 CO_2 還元のフラックス合成による高活性化

（東理大理[1]・東理大総研カーボンバリュー[2]）○荒井 創大[1]・和田 浩太郎[1]・永塚 健悟[1]・山口 友一[1,2]・工藤 昭彦[1,2]

Improvement in a Z-schematic CO_2 Reduction Activity under Visible Light Irradiation Utilizing a Long Wavelength Visible Light-Responsive Metal Sulfide Photocatalyst Prepared by a Flux Method

([1]*Faculty of Science, Tokyo University of Science*, [2]*Research Institute for Science and Technology, Tokyo University of Science*) ○Sota Arai,[1] Kotaro Wada,[1] Kengo Nagatsuka,[1] Yuichi Yamaguchi,[1,2] Akihiko Kudo[1,2]

We have reported Z-schematic CO_2 reduction under visible light irradiation using $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ (BG: 2.1 eV) prepared by a solid-state reaction (SSR) as a reducing photocatalyst and reduced graphene oxide (RGO)-composited $CoO_x/BiVO_4$ as an O_2-evolving photocatalyst.[1)] However, a CO_2 reduction activity of the Z-scheme system is low at the present stage. In this study, we demonstrated Z-schematic CO_2 reduction under visible light irradiation employing fine $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ particles prepared by a LiCl-CsCl flux method[2)] as a reducing photocatalyst.

SEM images of the obtained metal sulfide photocatalyst powders revealed that the ratio of fine particles increased in the flux-prepared samples compared with the SSR-prepared samples. Sacrificial CO_2 reduction under visible light was carried out over the metal sulfide photocatalyst. As the results, the amount of CO formation of the flux-prepared sample was about thirty times higher than that of the SSR-prepared sample. Furthermore, Z-schematic CO_2 reduction activity under visible light to form CO was significantly improved by applying the flux-prepared sample, giving 9.0% of a selectivity for CO evolution. In conclusion, we successfully developed the efficient Z-schematic CO_2 reduction system under visible light by using fine $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ particles prepared by a flux method.

Keywords : Metal sulfide, CO_2 reduction, Visible light, Z-scheme, Flux method

当研究室では，固相法により調製した $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ (BG: 2.1 eV)および RGO-($CoO_x/BiVO_4$)を組み合わせた Z スキーム系による可視光 CO_2 還元を報告している[1)]．しかし，本 Z スキーム系を用いた可視光 CO_2 還元の活性は低く，さらなる高活性化が求められる．そこで本研究では，LiCl-CsCl フラックス法[2)]により調製した本金属硫化物光触媒微粒子を用いることにより，Z スキーム型可視光 CO_2 還元を高活性化することを目的とした．

調製した光触媒粉末の SEM 像を観察したところ，フラックス法で調製した試料において微粒子の割合が固相法よりも多いことがわかった．次に，本金属硫化物光触媒を用いて犠牲試薬を含む水溶液からの可視光 CO_2 還元半反応を行ったところ，固相法のものと比べて CO 生成量が約 30 倍に向上した．フラックス法で調製した高性能な本光触媒と RGO-($CoO_x/BiVO_4$)を組み合わせた Z スキーム系を用いて可視光 CO_2 還元を行った結果，CO 生成量および選択率がそれぞれ 3 倍以上に向上した．以上のように，フラックス法により調製した $Cu_{0.8}Ag_{0.2}Ga_{0.8}In_{0.2}S_2$ 微粒子粉末を用いることで，従来の固相法のものを用いた場合よりも高活性な可視光 CO_2 還元を達成した．

1)S. Yoshino, *Doctoral dissertation of science at Tokyo University of Science*, **2021**.

2)S. Yoshino, A. Iwase, Y. Yamaguchi, T. M. Suzuki, T. Morikawa, A. Kudo, *J. Am. Chem. Soc.* **2022**, *144*, 2323.

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様々な助触媒を担持した $SrTiO_3$:Ir,Sb 光触媒による可視光照射下での水を電子源とした単一粒子型 CO_2 還元

（東理大理[1]・東理大総研カーボンバリュー[2]）○伊藤 端菜[1]・植木 義也[1]・永塚 健悟[1]・山口 友一[1,2]・工藤 昭彦[1,2]

Single particulate CO_2 reduction under visible light irradiation over various cocatalysts-loaded a $SrTiO_3$:Ir,Sb photocatalyst using water as an electron donor

([1]*Faculty of Science, Tokyo University of Science,* [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*)○Hana Ito,[1] Yoshiya Ueki,[1] Kengo Nagatsuka,[1] Yuichi Yamaguchi,[1,2] Akihiko Kudo[1,2]

We have reported that a $SrTiO_3$:Al photocatalyst doped with small amounts of Ir and Sb ($SrTiO_3$:Ir,Sb,Al) exhibited a high water splitting activity under visible light irradiation.[1)] It has also been reported that a $SrTiO_3$:Al loading of Ag and Co cocatalysts was active for CO_2 reduction under UV light irradiation.[2)] Therefore, CO_2 reduction under visible light irradiation as a single particle is expected to be achieved by loading of various cocatalysts on a $SrTiO_3$:Ir,Sb,Al photocatalyst. In this study, we demonstrated CO_2 reduction under visible light irradiation over a various cocatalysts-loaded $SrTiO_3$:Ir,Sb,Al photocatalyst using water as an electron donor.

CO_2 reduction over a $SrTiO_3$:Ir,Sb,Al photocatalyst loaded with various cocatalysts by a liquid phase reduction method was carried out under visible light irradiation. Notably, CO_2 reduction proceeded under visible light irradiation when Ag/Co and Au/Co cocatalysts were loaded, and H_2 and CO were obtained as the reduction products. Especially, the photocatalyst loaded with Au/Co cocatalysts showed a stable CO_2 reduction activity accompanied by O_2 evolution by water oxidation, giving 4% of the selectivity for CO evolution. Furthermore, the ratio of reacted electrons to holes was almost unity, indicating that CO_2 reduction proceeded using water as an electron donor. In conclusion, CO_2 reduction under visible light irradiation using water as an electron doner as a single particle was successfully achieved by loading of appropriate cocatalysts on the $SrTiO_3$:Ir,Sb,Al photocatalyst.

Keywords : CO_2 reduction; metal oxide; cocatalyst; transition metal-doping; visible light

当研究室では，Ir および Sb を微量ドーピングした $SrTiO_3$:Al（$SrTiO_3$:Ir,Sb,Al）光触媒による高効率な可視光水分解を達成している [1)]．ここで，Ir, Sb 未ドープ体の $SrTiO_3$:Al 光触媒は，Ag/Co 助触媒を担持することで紫外光照射下における水を電子源とした CO_2 還元に活性を示す [2)]．このことから，$SrTiO_3$:Ir,Sb 光触媒に適切な助触媒を担持することで，可視光照射下での CO_2 還元の駆動が期待できる．そこで本研究では，様々な助触媒を担持した $SrTiO_3$:Ir,Sb,Al 光触媒による可視光照射下での単一粒子型 CO_2 還元を目的とした．

液相還元法により種々の二元複合助触媒を担持した $SrTiO_3$:Ir,Sb,Al 光触媒を $NaHCO_{3\,(aq.)}$中に懸濁させ，CO_2 雰囲気下で可視光（$\lambda > 440$ nm）を照射した．その結果，Ag/Co および Au/Co 助触媒を担持した場合に可視光照射下で CO_2 還元反応が進行し，還元生成物として H_2 および CO が得られた．特に，Au/Co 助触媒を担持した場合，本反応は定常的に進行し，CO 生成選択率は最大 4%に達した．さらに，このときの電子正孔比はおおよそ 1 となり，本反応は水を電子源とした CO_2 還元であることがわかった．以上より，$SrTiO_3$:Ir,Sb,Al 光触媒に適切な助触媒を担持することにより，可視光照射下における水を電子源とした単一粒子型 CO_2 還元を初めて達成した．

1）海谷, 渡邊, 吉野, 山口, 工藤，第 126 回触媒討論会，P058 (2020).
2）S. Wang, K. Teramura, T. Tanaka *et al.*, *ACS Appl. Energy Mater*. **2020**, *3*, 1468.

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日本化学会 第104春季年会 (2024)

Fe，Cu 金属ナノ粒子を担持した ZrO_2 光触媒による CO_2 の逐次的光還元反応とその機構解析

（千葉大院理）○大弓 知輝・原 慶輔・泉　康雄

Consecutive photoreduction of carbon dioxide using Fe and Cu nanoparticles supported on zirconium dioxide and the mechanistic analyses (*Graduate School of Science, Chiba University*) ○Tomoki Oyumi, Keisuke Hara, Yasuo Izumi

In this research, Fe and Cu metal nanoparticle-supported ZrO_2 photocatalysts were prepared using liquid-phase reduction and then treated under an H_2 atmosphere for zero-valent metal sites. Photocatalytic reactions were conducted under $^{13}CO_2$ and H_2, and the products were analyzed using GC-MS. For the Cu–ZrO_2 photocatalyst, the major product was ^{13}CO accompanied by $^{13}CH_4$ and $^{12}CH_4$, suggesting consecutive reaction steps. The Fe–ZrO_2 photocatalyst primarily produced $^{13}CH_4$, with a notable decrease in photo-production rate after 10 h of reaction. Additionally, EXAFS analysis showed that Cu sites on ZrO_2 were reduced to zero-valent metals, whereas Fe sites on ZrO_2 retained some oxides. Furthermore, Fe sites on ZrO_2 were effectively reduced by photoexcited electrons at the conduction band of ZrO_2 during photocatalysis.

Keywords : Photoreduction, carbon dioxide, Iron, Cupper, ZrO_2

本研究では、液相還元法により合成した Fe，Cu 金属ナノ粒子担持 ZrO_2 光触媒を，H_2 雰囲気下で高温還元処理してから同位体標識した $^{13}CO_2$（2.3 kPa）と H_2（21.7 kPa）中で光反応試験を行い，生成物変化を追跡した。その結果，Cu-ZrO_2 触媒では主生成物の ^{13}CO が 15.6 μmol h^{-1} g_{cat}^{-1} の速度で生成し，副生成物として $^{13}CH_4$，$^{12}CH_4$，$^{13}C_2H_6$ が生成する逐次的反応ステップが示された。また Fe-ZrO_2 触媒では，主生成物の $^{13}CH_4$ が 7.9 μmol h^{-1} g_{cat}^{-1} の速度で生成し，^{13}CO，$^{12}CH_4$，$^{13}C_2H_6$，$^{13}C_3H_8$ が副生したが，反応開始 10 時間で光生成速度が約 10%に落ちた。さらに Fe，Cu K 吸収端 EXAFS を追跡した結果，光反応試験開始時に Cu-ZrO_2 触媒の Cu サイトは H_2 処理後に 0 価になっていたが（Figure 1A），Fe-ZrO_2 触媒では酸化物が残っていた（Figure 1B）。しかし，光反応試験開始すると直ぐに，Fe-ZrO_2 触媒は光励起により ZrO_2 伝導体に励起された電子が Fe サイトを 0 価まで還元し（Figure 1B），$^{13}CH_4$ 生成を可能にした。

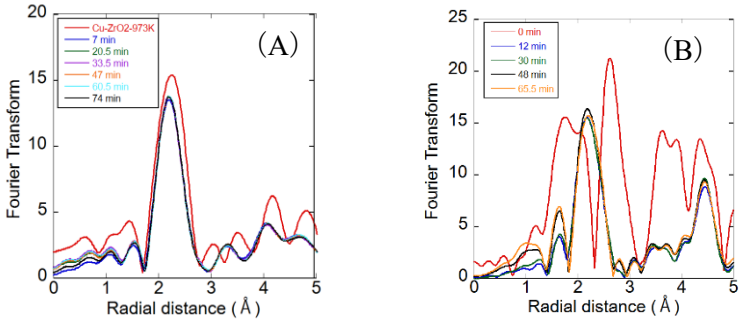

Figure 1. Cu K 吸収端 EXAFS（A）および Fe K 吸収端 EXAFS（B）の光照射中の経時変化。

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ニッケル金属ナノ粒子を担持させた酸化チタン光触媒による二酸化炭素から C_1~C_3 炭化水素化合物への変換

（千葉大）○関根 悠太・大弓 知輝・泉 康雄

Conversion of carbon dioxide into C_1–C_3 hydrocarbon compounds using titanium dioxide photocatalysts loaded with nickel metal nanoparticles (*Chiba University*) ○Yuta Sekine・Tomoki Oyumi・Yasuo Izumi

Photoreaction experiments were conducted using a TiO_2 photocatalyst loaded with Ni metal nanoparticles and $^{13}CO_2$ to examine how Ni nanoparticles and TiO_2 contribute to the CO_2 reduction reaction and how the difference in crystal structure and particle size of TiO_2 is reflected in the selectivity of the products. Ni–TiO_2 was synthesized by liquid-phase reduction, and then reduced under hydrogen at high temperatures for photoreaction experiments in $^{13}CO_2$ and H_2. The products were monitored by online GC-MS. Using rutile support, twice amount of $^{13}CH_4$ of that using the anatase support, and the subsequent reduction of ^{13}CO to $^{13}CH_4$ were found using anatase support (Figure 1A, B). These results with the time-course changes in the Debye–Waller factor and the number of oxygen defect sites on the TiO_2 surface based on $^{13}CO_2$ exchange reactions were correlated to photocatalysis.

Keywords: CO_2 photoreduction · TiO_2 · Ni · Oxygen vacancy · Hydrocarbon formation

Ni 金属ナノ粒子を担持させた TiO_2 光触媒と、$^{13}CO_2$ を用いた光反応実験を行い、Ni ナノ粒子、TiO_2 がどのように CO_2 還元反応に寄与しているか、TiO_2 の結晶構造や粒径の違いがどのように生成物の選択性に反映されるか考察した。液相還元法により Ni–TiO_2 を合成し、水素下で高温還元して $^{13}CO_2$ と H_2 中での光反応試験に供し、生成物変化を追跡した。ルチル担体の場合、アナターゼ担体の場合より 2 倍の $^{13}CH_4$ 生成を示したが、アナターゼ担体の場合 ^{13}CO から $^{13}CH_4$ への逐次還元が読み取れる (Figure 1A, B)。また、副生成物ながらアナターゼ担体の方が $^{13}C_2H_6$, $^{13}C_3H_8$ 生成が比較的多く、CO_2 から CH_x への還元過程と、CH_x から CH_4 あるいは C_2H_6, C_3H_8 生成へは別の表面サイトで独立に律されて進むことが分かった。Ni K 吸収端 XAFS に基づく局所構造および Debye-Waller 因子の経時変化や $^{13}CO_2$ 交換反応に基づく TiO_2 表面酸素欠陥サイト数との関連付けを進めている。

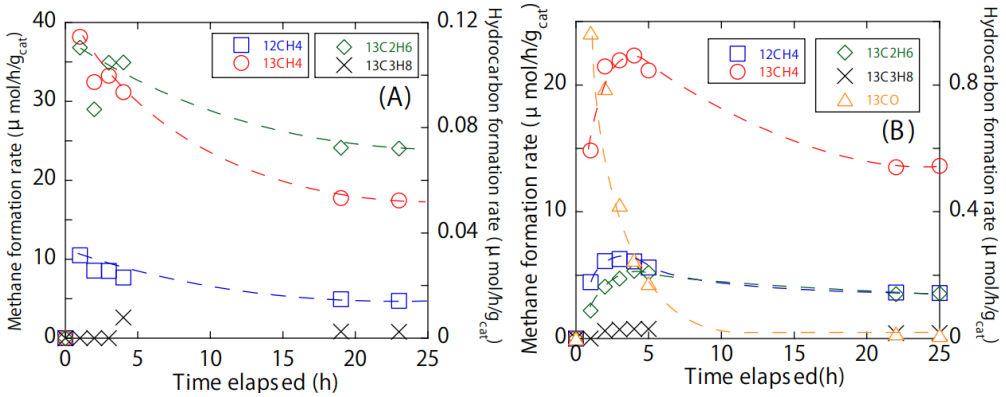

Figure 1. (A) Ni-JRC-TIO-6(ルチル型)および(B) Ni-JRC-TIO-14(アナターゼ型)を用いた CO_2 光還元試験の経時変化。$^{13}CO_2$ 2.3 kPa, H_2 21.7 kPa, 光触媒 20 mg。

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遷移金属酸化物表面での CO_2 光還元における光励起キャリアダイナミクス

（千葉大学[1]）○原 慶輔[1]・長谷川 綾香[1]・尾亦 彩奈[1]・二木 かおり[1]・泉 康雄[1]
Photo-excited carrier dynamics during the photoreduction of CO_2 on transition metal oxide surfaces ([1]*Graduate School of Science, Chiba University*) Keisuke Hara[1], Ayaka Hasegawa[1], Ayana Omata[1], Kaori Niki[1], Yasuo Izumi[1]

Transition metal oxides (TiO_2, ZrO_2) containing surface oxygen vacancies (Vo) can be divided into two groups when conducting CO_2 photoreduction reactions using H_2O or H_2 as reductants, based on whether they show activity with CO as the main product or not. To understand the factors controlling this activity, the adsorption structure of CO_2 and the electronic structure during CO_2 adsorption were studied using DFT calculations with VASP. Additionally, the dynamics of photoexcited carriers were tracked using Non-Adiabatic Molecular Dynamics. The activity correlates with CO_2 adsorption energy to Vo. In most oxides, except Rutile-TiO_2, CO_2 levels within the band gap influence the relaxation of excited electrons, essential for the reaction. Monoclinic-ZrO_2, with the fastest electron relaxation to CO_2 levels, showed the highest activity. Thus, CO_2 photoreduction activity depends on adsorption energy, the presence of CO_2 unoccupied levels in the band gap, and the speed of electron relaxation to these levels.

Keywords : CO_2 photoreduction, Photo excited carrier dynamics, Non Adiabatic Molecular Dynamics

表面酸素欠陥(Vo)を含む遷移金属酸化物(TiO_2, ZrO_2)単独で、H_2O 又は H_2 を還元剤として CO_2 光還元反応を行うと、主生成物を CO として、活性を示すものと示さないものに二分される。この活性を二分している因子を知るために、VASP による DFT 計算で CO_2 の吸着構造及び CO_2 吸着時の電子構造を、さらに Non Adiabatic Molecular Dynamics により光励起キャリアのダイナミクスを追跡した。各遷移金属酸化物の活性と Vo への CO_2 吸着エネルギーは Table 1 の通りであり、吸着エネルギーと CO_2 光還元活性は相関していることがわかる。CO_2 吸着時の状態密度を見ると、Rutile-TiO_2 以外ではバンドギャップ内に CO_2 の LUMO や LUMO+1 といった準位が現れ、その準位は励起電子の緩和先となる。最も活性の良い Monoclinic-ZrO_2 では約 500 fs で励起電子の半数が CO_2 の LUMO+1 へ緩和し、最終的に CO_2 アニオンラジカルへと還元され、反応が進行していくことが明らかとなった。これらから、CO_2 光還元活性は、CO_2 吸着エネルギー、CO_2 吸着時に非占有準位がバンドギャップ内に現れるかどうか、またその準位への励起電子緩和速度が支配していると考えられる。

Table 1. Kinetic Data on Photoreduction of CO_2 Using Transition Metal Oxide Photocatalysts and CO_2 Adsorption Energy on Transition Metal Oxide Vo Site.

Photocatalyst	^{13}CO production rate (μ mol/h/g)	CO_2 adsorption energy (eV)
Rutile-TiO_2	inactive	−0.39
Anatase-TiO_2	0.024	−1.41
Monoclinic-ZrO_2	1.8	−3.90
Tetragonal-ZrO_2	0.74	−3.08

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光アシスト RWGS 反応における Pt/MoO_3 触媒の酸化物担持による高活性化

（阪大院工）○高見 大地・桑原 泰隆・山下 弘巳
Enhancement of Activity of Pt/MoO_3 Catalysts for Photo-Assisted RWGS Reaction by Supporting on Various Metal Oxide (*Graduate School of Engineering, Osaka University*) ○ Daichi Takami, Yasutaka Kuwahara, Hiromi Yamashita

Photo-assisted reverse water gas shift (RWGS, $CO_2 + H_2 \rightarrow CO + H_2O$) reaction at low temperatures (around 473 K) have attracted much attention, aiming to utilize solar energy and waste heat. We have previously reported that RWGS reactions proceeded over Pt/MoO_3 catalysts below 473 K in the dark and that visible and near-infrared light irradiation enhanced the CO formation rate due to the photothermal effect of reduced MoO_3.[1)] In this study, the effects of supports on the catalytic activity were investigated by loading Pt and MoO_3 on various metal oxides. The activities and the surface temperature of catalysts are shown in Figure 1. ZrO_2-supported Pt/MoO_3 catalysts showed the highest catalytic activity. This enhancement would be attributed to the high dispersion of MoO_3 and the high surface temperature derived from the low thermal conductivity of ZrO_2 support.

Keywords : Reverse Water Gas Shift; Solar Light Utilization; Photothermal Effect; Oxygen Vacancy; Hydrogen Spillover

太陽光及び廃熱の利用を指向し，低温条件下での光アシスト逆水性ガスシフト (RWGS, $CO_2 + H_2 \rightarrow CO + H_2O$)反応が注目を集めている．当研究室ではこれまでに白金担持モリブデン酸化物(Pt/MoO_3)触媒が暗中低温(~473 K)条件下においてRWGSを進行させたこと，また還元型モリブデン酸化物の可視・近赤外光吸収特性を利用することで光照射によって触媒の表面温度が上昇し CO 生成速度が向上したことを報告した．[1)] 本研究では様々な金属酸化物に Pt 及び MoO_3 を担持させ，担体による触媒活性への影響を検討した．その結果，ZrO_2 に担持した触媒が光照射下で最も高い CO 生成速度を示した (Figure 1)．これは ZrO_2 に担持したことで，MoO_3 の分散性が高くなったこと，および触媒の熱伝導率の低下により熱拡散が抑制されたためであると考えられる．

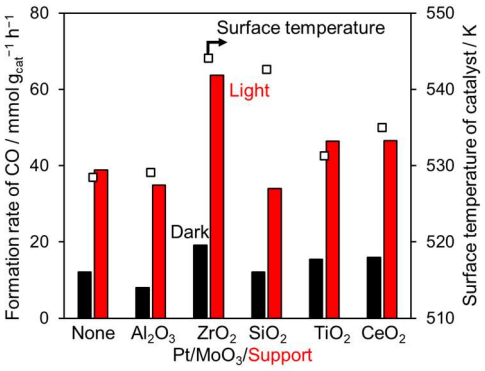

Figure 1. The CO formation rates and the surface temperature of the catalysts during RWGS reaction in the dark and under visible and near-infrared light irradiation.

1) H. Ge, Y. Kuwahara, K. Kusu, and H. Yamashita, *J. Mater. Chem. A* **2021**, 9, 13898–13907

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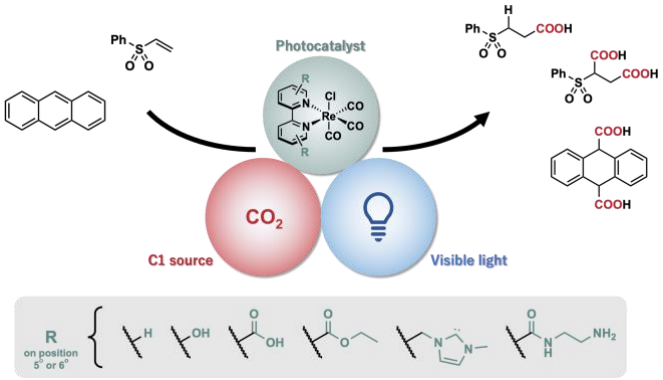
Development of Re Complexes Bearing Various Bipyridine-derived Ligands for Visible-light-driven Carboxylation of Organic Molecules with CO_2

([1]*Graduate School of Engineering, Osaka University*, [2]*School of Science, Tokyo Institute of Technology,* [3]*JST PRESTO*) ○Phurinat Lorwongkamol,[1] Masaki Kitada,[1] Taito Watanabe,[1] Yutaka Saga,[1] Tetsuya Kambe,[1] Mio Kondo,[1,2,3] Shigeyuki Masaoka[1]

Keywords: visible light; photocatalysis; carboxylation; Re complex

Carboxylic acid moieties are one of the most important structural motifs in numerous bioactive molecules, pharmaceuticals, and functional materials. A carboxylic acid group can be directly installed using CO_2 as an abundant and non-toxic C1 resource. However, the use of this highly stable molecule is challenging, and conventional methods for installing CO_2 into organic molecules require strong nucleophilic reagents or harsh conditions. In this work, we aim to develop the photochemical carboxylation of organic molecules with CO_2 using metal-complex-based catalysts under mild conditions. We employed *fac*-[Re(2,2'-bipyridine)$(CO)_3$Cl], which has been widely known to promote CO_2 reduction[1,2]. Our photocatalytic system achieved the dicarboxylation reaction of phenyl vinyl sulfone in 86% yield with 2.4/1 selectivity of di- and mono-carboxylation products at room temperature and visible-light irradiation conditions. This is a rare example of the dicarboxylation of organic molecules with CO_2.[3] Furthermore, we accomplished the control of selectivity for mono- and di-carboxylation products simply by changing the reaction solvents. Collectively, this study demonstrates a new and unique property of the Re catalyst for the carboxylation of organic molecules with CO_2 by using the Re complex as a catalyst. Development of a series of Re complex derivatives for improving the reactivity is ongoing, and the details will be given in the presentation.



1) J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc., Chem. Commun.*, **1983**, *286*, 536. 2) Y. Yamazaki, M. Miyaji, O. Ishitani, *J. Am. Chem. Soc.*, **2022**, *144*, 6640. 3) T. Ju, Y.-Q. Zhou, K.-G. Cao, Q. Fu, J.-H. Ye, G.-Q. Sun, X.-F. Liu, L. Chen, L.-L. Liao, D.-G. Yu, *Nat. Catal.*, **2021**, *4*, 304.

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デラフォサイト型 Cu 酸化物の電気化学的二酸化炭素還元特性

(九大理化[1]・九大先導研[2]・九大 K-NETs[3]・東北大 AIMR[4]・九大 I²CNER[5])
○松鵜恭弘[1]・安齊亮彦[2]・堂ノ下将希[2]・小林浩和[3]・山内美穂[1,2,3,4,5]

Catalytic properties of delafossite-type Cu oxides for electrochemical CO_2 reduction reaction

(*[1]Department of Chemistry, School of Science, Kyushu University*, *[2]Institute for Materials Chemistry and Engineering, Kyushu University,* *[3]Research Center for Negative Emissions Technologies, Kyushu University*, *[4]Advanced Institute for Materials Research, Tohoku University,* *[5]International Institute for Carbon-Neutral Energy Research, Kyushu University*)
○ Takahiro Matsuu,[1] Akihiko Anzai,[2] Masaki Donoshita,[2] Hirokazu Kobayashi,[3] Miho Yamauchi[1,2,3,4,5]

Cu catalysts are known to produce hydrocarbons such as methane and ethylene in electrochemical CO_2 reduction (eCO_2R) [1-3]. To control the product selectivity in eCO_2R, we focus on delafossite-type oxides ($CuMO_2$, M=Al, Fe, etc.) which contain a unique layered structure of monovalent Cu ions (Fig. 1). The cation substitution of M sites can modulate both the geometric (Cu–Cu distance) and band structures of the Cu oxides. In this study, we have prepared $CuAlO_2$ and investigated its catalytic property.

The catalyst was synthesized by the Pechini method and characterized by X-ray diffraction measurement which showed that the catalyst was attributable to 3R type delafossite with a space group of $R\bar{3}m$ (Fig. 1). The catalytic property was evaluated using a flow–type cell[4]. Several products from eCO_2R were obtained.

Keywords: *Electrochemical CO_2 reduction; Delafossite*

銅触媒は、電気化学的な二酸化炭素還元（eCO_2R）においてメタンやエチレン等の有用な炭化水素化合物を与えることが知られている[1-3]。我々は、1 価の銅イオンからなる層状構造を有するデラフォサイト型酸化物 $CuMO_2$（M=Al, Fe など）に着目する (Fig. 1)。この酸化物は M サイトを異なる金属カチオンで置換することにより、銅イオン間の距離およびバンド構造を制御することが可能である。本研究では、M サイトに Al が導入された $CuAlO_2$ を合成し、その eCO_2R 特性を調べることを目的とした。

試料は錯体重合法により合成した。粉末 X 線回折測定により空間群 $R\bar{3}m$ の三方晶の結晶構造を確認し、3R 型のデラフォサイト構造を有することを明らかにした (Fig. 1)。フローセル [4]を用いて eCO_2R 特性を評価したところ、種々の eCO_2R 生成物が得られた。当日は、$CuMO_2$ の eCO_2R 特性について詳細な議論を行う。

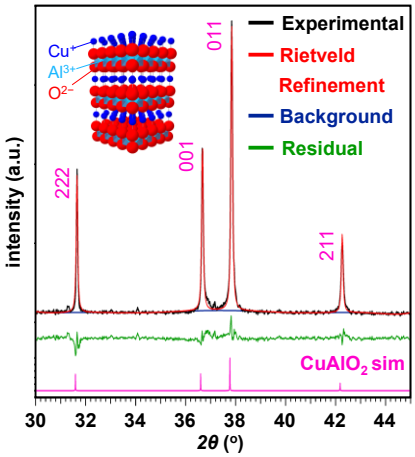

Fig. 1 $CuAlO_2$ の結晶構造と粉末 X 線回折パターン

1) Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim. Acta.*, 39, 1833–1839 (1994).
2) A. Anzai, M. Liu, K. Ura, T. G. Noguchi, A. Yoshizawa, K. Kato, T. Sugiyama, M. Yamauchi, *Catalysts*, 12, 478 (2022).
3) M. Sun, J. Cheng, M. Yamauchi, *Nat. Commun.*, in press.
4) S. Ma, M. Sadakiyo,M. Heima, R. Luo, R. Haasch, J. Gold, M. Yamauchi, P. Kenis, *J. Am. Chem. Soc.*, 139, 47-50 (2017).

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Production of High Value-added Chemicals by the CO_2 Electroreduction with Copper-based Electrocatalysts

(*Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology*) ○Xiaofan Hou, Junya Yamaguchi, Kenji Kamiya, Eika W. Qian

Keywords: Copper-based electrocatalysts, CO_2RR, High value-added, High selectivity

Recycling CO_2 to carbonaceous feedstock via CO_2 electrochemical reduction reaction (CO_2RR) is a feasible solution for environmental problems caused by gradually increased CO_2 content in the atmosphere.[1] As a reliable CO_2RR electrode material, Cu-based catalysts have received particular attention on account of its unique properties toward C_{2+} products and cost-effectiveness.[2] Unfortunately, when using Cu as catalysts, products such as a certain amount of H_2 or other unintended products are also produced with the high value-added C_{2+} molecules simultaneously.[3] Herein, we suggested using Co to improve C_{2+} selectivity, and synthesized a reasonably designed CuCo catalysts with better balance of high selectivity and high overpotential for the practical application of CO_2RR.

The CuCo was formed first through electrodeposition method and then oxidation process. It showed exceptional activity and achieved about 48% selectivity toward ethanol at -1.3 V vs. Ag/AgCl, superior to other electrolysis potential in CO_2-saturated $KHCO_3$ electrolyte (Figure 1). CO_2RR selectivity decreased with increased electrolysis potential. H_2 obtained during the electrolysis process was also detected and present in all samples regardless of the electrolysis potential. And when ionic liquid was substituted for $KHCO_3$ aqueous electrolyte, the H_2 evolution can be dramatically suppressed. It can be attributed to that, positively charged cations may interact strongly with the electrode, preventing proton diffusion to the electrode surface and reducing the number of active sites for hydrogen evolution.

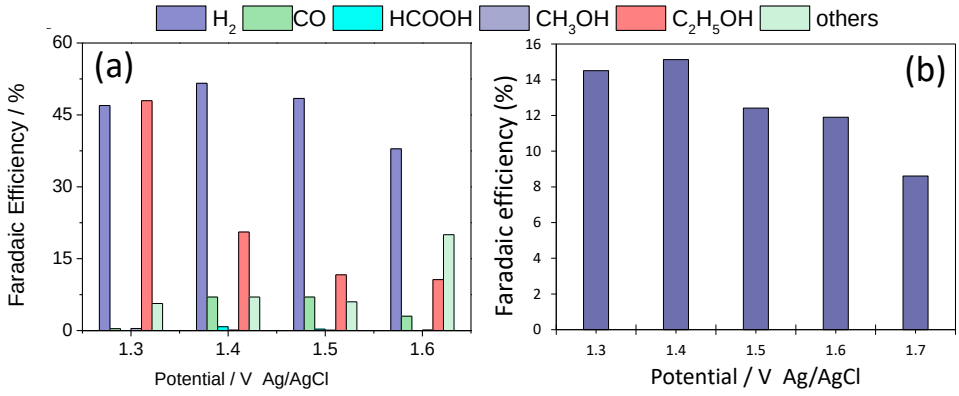

Fig. 1. Faradaic efficiency of products at different applied potentials for CuCo in (a) $KHCO_3$ electrolyte, (b) ionic liquid.

1) S. Popovic, *Angew. Chem., Int. Ed.* **2020**, *59*, 14736.
2) F. Yang, *Nat. Commun.* **2020**, *11*, 1088. 3) D. Ren, *ACS Catal.* **2016**, *6*, 8239.

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DFT Study of the Catalytic Active Site of CoN_4C_x on KB for Electroreduction of CO_2 to CO

([1]*Hokkaido University,* [2]*Tokyo Institute for Technology,* [3]*Saitama University*) ○ Sarinya Hadsadee,[1] Manussada Ratanasak,[1] Kiyotaka Asakura,[1] Hitoshi Ogihara,[3] Ichiro Yamanaka,[2] Jun-ya Hasegawa[1]

Keywords: Density Functional Theory; Co-N-C catalysis; Electrocatalysis; CO_2; CO

A novel electrocatalyst, CoN_4C_x on Ketjenblack (KB), has been reported to exhibit high performance in CO formation during the CO_2 reduction reaction (CO_2RR).[1] However, the structure of CoN_4C_x on KB and its CO_2RR activity remain unclear. Therefore, theoretical research using density functional theory has been conducted to further explore the electrolytic reduction mechanism of CO_2 using KB-supported Co-N-C catalysts. Based on the previous experimental data, various Co-N-C catalyst models were constructed to represent the coordination number of Co-N bonds and the distances of Co-N bonds. To determine the structure of CoN_4C_x on KB, the interaction between the Co atom in the CoN_4C_x molecule and the underlying pyridinic N-doped defect graphene results in the formation of a Co-coordinated five N atoms (CoN_5) active site. Additionally, the different graphene supports significantly influence the stability of the active site. Focusing on the reactivity of CO_2RR, we discovered that the adsorption energy of CO depends on the spin state of the Co center and Co-N bonds in CoN_4C_x/KB. As shown in Figure, the model catalysts in our study were classified into two groups with different reactivity against hydrogenation of CO_2. Detailed explanation will be given in the presentation. Our results highlight the crucial role of KB-supported Co-N-C catalysts for further design and development of efficient CO_2RR.

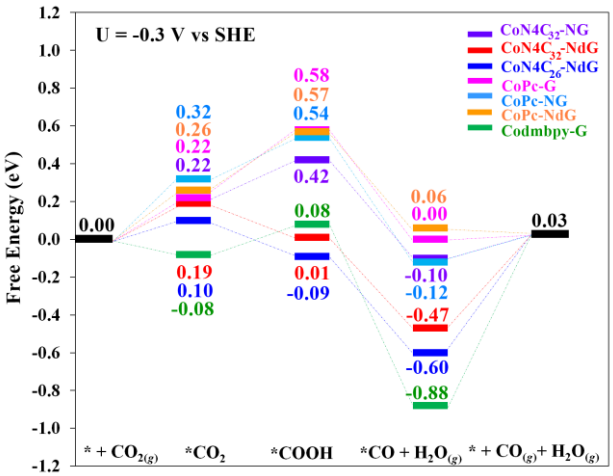

Figure Free energy profile of CO_2RR catalyzed by various Co–N–C/KB. Electrode potential with −0.3 V (vs SHE) is applied with the hydrogen electrode model.[2]

1) S. Iguchi, S. Jia, Y. Ogishima, Y. Senba, H. Ogihara, and I. Yamanaka, *Energy Fuels*. **2022**, *36*, 2300.
2) J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, and H. Jónsson, *J. Phys. Chem. B* **2004**, *108*, 17886.

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酸性電解質中での CO 還元反応特性の解析とその固体高分子型セルへの展開

（阪大院基礎工太陽エネルギー化学研究センター[1]・東京電機大学 [2]）○栗原 諒 [1]・名木田 海都 [1]・伊藤 翔太朗 [1]・加藤 慎太郎 [1]・大橋 圭太郎 [1]・向山 義治 [1,2]・原田 隆史 [1]・中西 周次 [1]・神谷 和秀 [1]

Study on Electrochemical CO Reduction in Acidic Environments for the Development of Solid Polymer Electrolyte Systems Utilizing Cation Exchange Membranes ([1]*Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University*, [2]*Tokyo Denki University*) ○Ryo Kurihara,[1] Kaito Nagita,[1] Shotaro Ito,[1] Shintaro Kato,[1] Keitaro Ohashi,[1] Yoshiharu Mukouyama,[1,2] Takashi Harada,[1] Shuji Nakanishi,[1] Kazuhide Kamiya[1]

Electrochemical CO_2 reduction is gaining attention for achieving a carbon neutral society. In the acidic electrolytes, the dissolution of CO_2 gas can be suppressed, enhancing CO_2 utilization efficiency. However, the hydrogen evolution reaction would be dominant under acidic condition. In this study, to establish guidelines for a solid polymer electrolyte system using an acidic cation exchange membrane, we focused on the electrochemical reduction of CO (an intermediate of C_{2+} compounds) in acidic solutions. The aim of this study to explore the necessary conditions for selectively producing C_{2+} compounds.

Keywords : Electrochemical CO_2 reduction, Acidic electrolyte, Cation exchange membrane

カーボンニュートラルの実現に向けて CO_2 電解還元が大きな注目を集めている。酸性電解質を用いた CO_2 電解は、CO_2 ガスが溶解しないため、基質ガスの利用効率向上が見込める。特に堅牢でイオン伝導度の高いカチオン交換膜(CEM)を搭載した固体高分子型セルによる高効率な CO_2 電解の実現が望まれる。しかし、CEM などの酸性電解質では競合反応である水素発生反応が優先的に進行することが課題である。

本研究は CEM を搭載した固体高分子型セルでの電解系構築の指針を得るために、酸性液体電解質中で C_{2+}化合物の中間体である CO を還元した。これにより酸性条件下で C_{2+}の選択的生成に必要な条件を検討した。その結果、電流密度の増加とともに水素の選択性が抑制され、C_{2+}の選択性が向上した(図 1 (a))。有限要素法を用いた電極表面 pH のシミュレーション結果を図 1 (b)に示す。この結果から、C_{2+}の選択性と電極表面 pH に相関があることが確認された [1]。発表では CEM を搭載した固体高分子型セルでの CORR の結果についても紹介する。

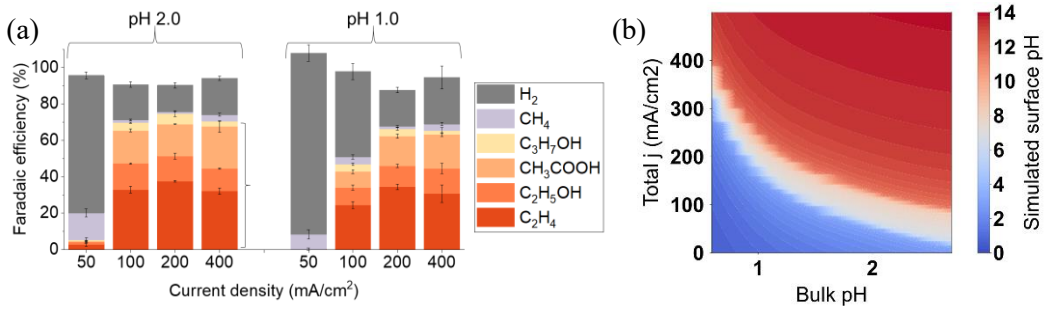

図 1(a)酸性電解液による CO 電解生成物の選択性 (b)電極表面 pH シミュレーション結果

[1] R. Kurihara *et al*. *Adv. Mater. Interfaces*, 2023, 2300731

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Academic Program [Oral A] | 08. Catalysts and Catalysis：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
A1458(1458, Bldg. 14 [5F])

[A1458-4am] 08. Catalysts and Catalysis

Chair: Osamu Tomita, Yuichi Yamaguchi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1458-4am-01]

Visible-Light Driven Gas Phase Hydrogen Sulfide Photodegeneration using CdS/g-C_3N_4 Hybrid Photocatalyst

○Tomofumi Katayama[1], Morio Nagata[1] (1. Tokyo University of Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1458-4am-02]

Photocatalytic reduction of nitrobenzene under irradiation of visible light with Ru-complex modified TiO_2.

○Shoya Oda[1], Atsuhiro Tanaka[1], Hiroshi Kominami[1] (1. Faculty of Science & Engineering, Kindai University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1458-4am-03]

Photocatalytic hydrogen peroxide production using porphyrin-based hydrophobic Zr-MOFs

○Shiori Mizutani[1], Yoshifumi Kondo[1], Yasutaka Kuwahara[1], Kohsuke Mori[1], Hiromi Yamashita[1] (1. Grad. Sch. of Eng., Osaka Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1458-4am-04]

Anionic polymer modification of dye-sensitized photocatalysts to improve activity of Z-scheme water splitting

○Haruka Yamamoto[1], Shunta Nishioka[1], Yugo Miseki[2], Kazuhiro Sayama[2], Thomas E. Mallouk[3], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology, 3. University of Pennsylvania)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1458-4am-05]

Improved photocatalytic activity of $Pb_2Ti_2O_{5.4}F_{1.2}$ nanoparticles

○Hiroto Ueki[1], Kenta Aihara[1], Megumi Okazaki[1], Fumitaka Ishiwari[2], Akinori Saeki[2], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. OSAKA UNIVERSITY)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1458-4am-06]

Effects of Ru cocatalyst loading on photocatalytic water oxidation over $Pb_2Ti_2O_{5.4}F_{1.2}$

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○Megumi Okazaki[1], Yoshitaka Tamura[1], Hiroto Ueki[1], Fumitaka Ishiwari[2], Kunihisa Sugimoto[3], Akinori Saeki[2], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. Osaka University, 3. Kindai University)

English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1458-4am-07]

Photocatalytic activity of cation-doped layered perovskite oxynitride $K_2LaTa_2O_6N$

○Hideya Tsuchikado[1], Yuta Shiroma[1], Dongxiao FAN[2], Megumi Okazaki[1], Shunsuke Nozawa[2], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology, 2. High Energy Accelerator Research Organization)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1458-4am-08]

Development of New Visible-Light-Driven Sulfide Photocatalysts by Machine Learning

○Fuga Kakami[1], Ryuto Baba[2], Yoshiya Ueki[1], Yosuke Harashima[2,3], Yuichi Yamaguchi[1,4], Mikiya Fujii[2,3], Akihiko Kudo[1,4] (1. Tokyo Univ. of Science, 2. NAIST, Material Science, 3. NAIST, DSC, 4. CVRC, RIST TUS)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1458-4am-09]

Development of Z-scheme Systems for Water Splitting using Various Long Wavelength Visible Light-Responsive Metal Sulfide Photocatalysts Prepared by a Flux Method

○Riku Nakao[1], Kotaro Wada[1], Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1458-4am-10]

Overall water splitting under visible light irradiation over single particulate $ANbO_3$:Ir,Zr (A = K, Na) photocatalysts

○Natsuki Suto[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1458-4am-11]

Temperature dependence of photocatalytic water splitting over $SrTiO_3$:Al doped with transition metals under visible light irradiation

○Erika Kikuchi[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1458-4am-12]

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The specific behavior of O_2 storage on water splitting over metal oxide photocatalysts loaded with dual cocatalysts

○Kyoko Adachi[1], Natsuki Suto[1], Suguru Yagihashi[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1458-4am-13]

Study of co-catalyst for Ir and Sb co-doped $SrTiO_3$ photocatalyst

○TEPPEI YAKUBO[1], Yuichi Yamaguchi[2,3], Akihiko Kudo[2,3] (1. SUMITOMO OSAKA CEMENT CO.,LTD., 2. Tokyo Univ. of Science, 3. CVRC, RIST TUS)

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CdS/g-C_3N_4 複合光触媒を用いた可視光・気相での硫化水素分解性能向上の検討

（東京理科大院工 [1]）○片山 智文 [1]・永田 衞男 [1]

Visible-Light Driven Gas Phase Hydrogen Sulfide Photodegeneration using CdS/g-C3N4 Hybrid Photocatalyst ([1]*Department of Industrial Chemistry, Graduate School of Engineering., Tokyo University of Science*) ○Tomofumi Katayama,[1] Morio Nagata[1]

Hydrogen sulfide is a toxic and bad-odor gas emitted from factories and power plants. It is difficult to decompose hydrogen sulfide to a completely odorless concentration using current industrial methods. In this study, we succeeded in decomposing hydrogen sulfide to almost 0 ppm using a photocatalyst. In addition, we found that the degradation of the catalyst over time was caused by sulfate ions adhering to the catalyst surface and investigated regeneration methods by washing and photoirradiating the catalyst.

Keywords : Photocatalyst; Visible-Light Driven; Hydrogen Sulfide; Carbon Nitride

硫化水素は有毒・悪臭のある気体であり、化学工場や地熱発電所等から発生する。硫化水素分解に関して、工業的手法や光触媒を用いた先行研究は 100-1000 ppm 程度の高濃度のものや純硫化水素などを対象にしており [1]、低濃度のものを高度に分解する研究は少ない。光触媒を用いた硫化水素分解は液相吸着を行い犠牲剤として利用するものが多く、本研究では気相での直接分解を試みて実験を行った。

実際に、可視光応答性光触媒 2 種を複合したものを用い、10 ppm H_2S 通気を光照射下で行うことで H_2S をほぼ 0 ppm まで分解することに成功した。加えて、先に報告していた [2]触媒の経時劣化に関して、硫酸イオンの触媒表面への付着によるものである事がわかり、触媒の洗浄及び光照射による再生法を検討した。

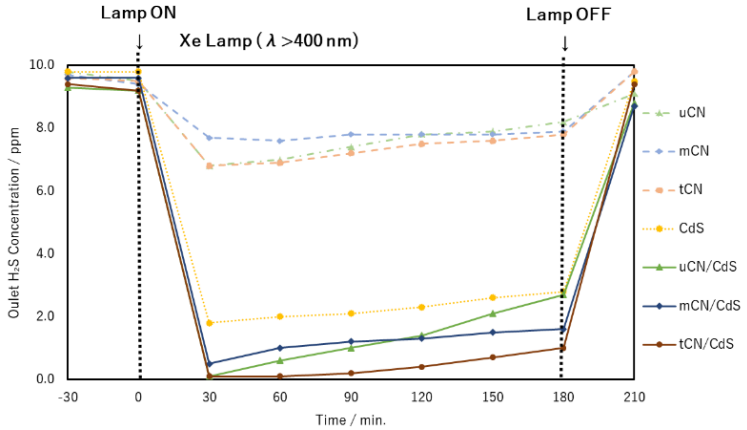

Figure 1. 可視光照射による硫化水素の光触媒分解

1) M. Dan, S. Yu, Y Li, et al, *Journal of Photochemistry and Photobiology C*, **2020**, 42, 100339.
2) Tomofumi Katayama, Morio Nagata, *ChemistrySelect*, **2023**, 8, 40, e202302709.

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日本化学会 第104春季年会 (2024)

Ru 錯体修飾 TiO_2 を用いたニトロベンゼンの可視光光触媒還元

（近畿大理工）・○小田 翔也・田中 淳皓・古南 博
Photocatalytic reduction of nitrobenzene under irradiation of visible light with Ru-complex modified TiO_2. (*Faculty of Science & Engineering, Kindai University*)○Shoya Oda, Atsuhiro Tanaka, Hiroshi Kominami

Titanium dioxide (TiO_2) is the representative semiconductor that exhibits a photocatalytic activity in the hydrogenation of nitro groups to amino groups under UV light irradiation. To make TiO_2 responsive to visible light, various methods have been proposed, including hetero atom doping, inorganic complex modification, and nanoparticle modification. Sensitization with dyes that absorb visible light is also effective. Ru complexes are commonly utilized as dyes for solar cells due to their stable electronic excitation states and absorption in the visible light region.

In this study, TiO_2 was modified with Ru complexes by impregnation. As expected, the modified TiO_2 samples exhibited absorption in the visible light region. The modified TiO_2 samples were used for the hydrogenation of nitrobenzene (NB) to aniline (AN) under visible light irradiation. A high yield of AN (95%) was achieved with an apparent quantum efficiency of 13.6%.

Keywords : photocatalyst; Ruthenium dyes; nitrobenzene

酸化チタン（TiO_2）はニトロ基からアミノ基への変換反応などにおいて優れた光触媒作用を示す [1]。紫外光応答型光触媒である TiO_2 を可視光に応答させる方法として、異元素ドープ、無機錯体修飾、金属ナノ粒子修飾などが提案されている。また、可視領域に吸収帯をもつ色素を TiO_2 上に修飾する色素増感も有力である。Ru 錯体は電子励起状態が安定であり可視光領域に幅広い吸収をもつため、太陽電池の色素増感剤として利用されている [2]。

本研究では、可視領域に幅広い吸収帯をもつ Ru 錯体を TiO_2 表面に含浸法にて修飾した。期待通り、調製した Ru 錯体修飾 TiO_2 は可視光領域に吸収を示した。つぎに、これを用いた可視光照射下における物質変換反応を検討した結果、ニトロベンゼン（NB）が高い収率（約 95%）でアニリン（AN）へと還元されることがわかった（Fig. 1）。また、可視領域における見かけの量子効率は最大 13.6%に達成した。各種調製条件や反応条件の影響についても報告する。

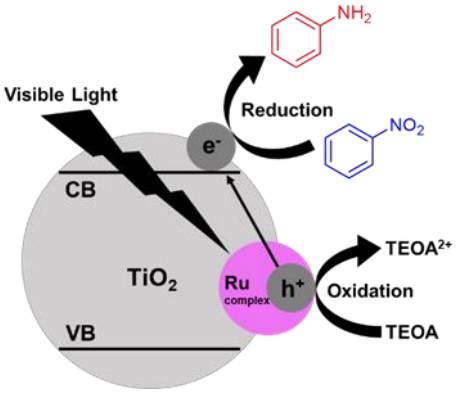

Fig. 1 Reduction of NB to AN under irradiation of visible light over $Ru_{complex}/TiO_2$.

1) Imamura *et al*., *Chem. Commun*., **48**, 4356 (2012).
2) B. O'Regan, M. Grätzel, *Nature*, **353**, 737 (1991).

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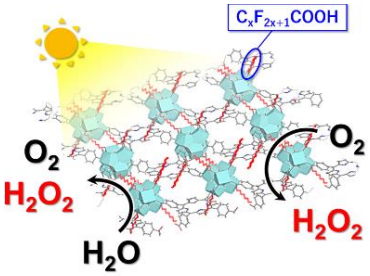
ポルフィリン含有疎水性 Zr-MOF を用いた光触媒的過酸化水素生成

（阪大院工）○水谷 志穂理・近藤 吉史・桑原 泰隆・森 浩亮・山下 弘巳
Photocatalytic hydrogen peroxide production using porphyrin-based hydrophobic Zr-MOFs (*Graduate School of Engineering, Osaka University*) ○Shiori Mizutani, Yoshifumi Kondo, Yasutaka Kuwahara, Kohsuke Mori, Hiromi Yamashita

Hydrogen peroxide (H_2O_2) has attracted much attention as not only an eco-friendly oxidant but also a promising liquid fuel alternative to fossil fuels. We have focused on metal-organic frameworks (MOFs) as photocatalysts for H_2O_2 production. MOFs are coordination compounds composed of metal oxide clusters and organic linkers. MOFs have great potential as photocatalysts due to their inherent structural characteristics, porosity, high surface area, and versatile modularity. In this work, we performed photocatalytic H_2O_2 production from dioxygen and water using porphyrin-based Zr-MOFs under visible-light (λ > 420 nm) irradiation and investigated effects of hydrophobicity of Zr-MOFs in H_2O_2 production. Perfluoroalkyl carboxylic acids were modified on Zr-MOFs to make them hydrophobic. Photocatalytic H_2O_2 production was significantly enhanced by hydrophobization of Zr-MOFs.
Keywords : Metal-Organic Framework; Hydrogen peroxide; Hydrophobicity

過酸化水素(H_2O_2)は低環境負荷な酸化剤として広く用いられており、近年、燃料電池の燃料としても注目されている。光を駆動力として酸素と水からH_2O_2を製造する光触媒的手法はクリーンな製造方法として期待されている[1)]。我々は本反応を駆動する光触媒材料としてMetal-Organic Framework(MOF)に着目した[1,2)]。MOFは金属酸化物クラスターと有機リンカーで構築される無機有機ハイブリット材料であり、クラスターやリンカーを適切に組み合わせることでMOFの細孔構造や物理化学的特性を容易に制御することができる。本研究グループにおいて、ポルフィリン環を有するTetrakis(4-carboxyphenyl)porphyrin(TCPP)をリンカーとしたMOFを光触媒として用いることで、純水中で水と酸素からH_2O_2が生成することを見出している[3)]。一方、純水中における酸素と水からのH_2O_2生成反応での課題点として、①水中で酸素濃度が希薄であることによる酸素との低い反応性と②MOFのクラスター上でのH_2O_2の分解が挙げられる。

本研究では、これらの課題を克服するためにZr-MOF光触媒を疎水化し、H_2O_2生成量の向上を試みた。ソルボサーマル法によってZr-MOFを調製し、パーフルオロカルボン酸を用いてZr-MOFの疎水化を行った。調製したZr-MOFを用いて純水中でのH_2O_2生成反応を行ったところ、可視光照射下でH_2O_2が生成し、Zr-MOFの疎水化によりH_2O_2生成量が大幅に向上することを見出した。



1) Y. Kondo, Y. Kuwahara, K. Mori, H. Yamashita, *Chem* **2022**, *8*, 2924.
2) Y. Kondo, K. Honda, Y. Kuwahara, K. Mori, H. Kobayashi, H. Yamashita, *ACS Catal.* **2022**, *12*, 14825.
3) Y. Kondo, K. Hino, Y. Kuwahara, K. Mori, H. Yamashita, *J. Mater. Chem. A* **2023**, *11*, 9530.

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アニオン性ポリマー修飾による色素増感型光触媒を用いた Z-scheme 水分解の活性向上

（東工大理[1]・産総研[2]・ペンシルベニア大[3]）○山本 悠可[1]・西岡 駿太[1]・三石 雄悟[2]・佐山 和弘[2]・Thomas Mallouk[3]・前田 和彦[1]
Anionic polymer modification of dye-sensitized photocatalysts to improve activity of Z-scheme water splitting ([1]*School of Science, Tokyo Institute of Technology,* [2]*National Institute of Advanced Industrial Science and Technology* [3]*University of Pennsylvania*) ○Haruka Yamamoto,[1] Shunta Nishioka,[1] Yugo Miseki,[2] Kazuhiro Sayama,[2] Thomas E. Mallouk,[3] Kazuhiko Maeda[1]

Dye sensitization is one of the methods to make semiconductor photocatalysts with a large band gap responsive to visible light. In Z-scheme water splitting using Ru(II) complex-modified $Pt/HCa_2Nb_3O_{10}$ nanosheets as a hydrogen-producing photocatalyst in the presence of I_3^-/I^- redox, the activity of water splitting was improved by modifying the photocatalyst surface with an anionic polymer, sodium polystyrenesulfonate (PSS).[1)] This is due to the electrostatic repulsion between PSS and I_3^- in the solution, which inhibits the back electron transfer reaction, the reduction of I_3^-. In this study, we attempted to improve the activity by modifying sodium polymethacrylate (PMA) instead of PSS as an anionic polymer. As a result, we respectively obtained a solar-to-hydrogen energy conversion efficiency of 0.12%, and an apparent quantum yield of 5.1% based on the O_2-evolution rate at 420 nm.[2)] These are highest values among the dye-sensitized water splitting systems reported so far.[2)] The suppression of the back electron transfer reaction was observed by transient absorption measurements, and it was found that the suppression effect differed between PSS and PMA.
Keywords : Dye-sensitized photocatalyst; Water splitting; Surface modification

バンドギャップの大きな半導体光触媒を可視光応答させる方法の一つとして色素増感がある。Ru(II)錯体修飾 $Pt/HCa_2Nb_3O_{10}$ ナノシートを水素生成光触媒とし、ヨウ素レドックスを用いた Z-scheme 水分解において、光触媒表面にアニオン性ポリマーのポリスチレンスルホン酸ナトリウム(PSS)を修飾することにより、水分解の活性が向上することが報告されている[1)]。これは、溶液中の I_3^- と PSS が静電反発を起こし、逆反応である I_3^- の還元反応が抑制されるためである。本研究では、PSS の代わりにポリメタクリル酸ナトリウム(PMA)を修飾することで活性向上を試みた。その結果、PtO_x/H-Cs-WO_3 と組み合わせた Z-scheme 水分解において太陽光エネルギーの水素への変換効率 0.12%、420 nm における見かけの量子収率 5.1%と色素増感型光触媒を用いた水分解において最高値を達成した[2)]。また、過渡吸収測定を行うことで逆電子移動反応の抑制効果を観測し、PSS と PMA で抑制効果が異なることがわかった。

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$Pb_2Ti_2O_{5.4}F_{1.2}$ のナノ粒子化と光触媒活性の向上

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Improved photocatalytic activity of $Pb_2Ti_2O_{5.4}F_{1.2}$ nanoparticles ([1]*School of Science, Tokyo Institute of Technology*, [2]*Graduate School of Engineering, Osaka University*) ○Hiroto Ueki,[1] Kenta Aihara,[1] Megumi Okazaki,[1] Fumitaka ishiwari,[2] Akinori Saeki,[2] Kazuhiko Maeda[1]

An oxyfluoride $Pb_2Ti_2O_{5.4}F_{1.2}$ (PTOF) is a promising photocatalyst that can reduce and oxidize water stably under visible light irradiation in the presence of the appropriate electron donor and acceptor, respectively.[1)] A microwave-assisted hydrothermal (MHT) method is a superior synthesis method to a solid-state reaction method for PTOF. By using $TiCl_4$ as a raw material, it has been reported that PTOF (chl-PTOF) with 0.5–1 μm particle sizes were obtained.[2)] However, the $TiCl_4$ precursor is not completely stable in the aqueous solution and produces an insoluble precipitate and hydrogen chloride gas. In this study, titanium citrate complex, which is a water-soluble titanium complex, was used as an alternative precursor for PTOF. The as-synthesized cit-PTOF exhibited approximately 7 times greater hydrogen evolution activity in EDTA aqueous solution. The particle sizes of cit-PTOF were 50–100 nm, with a much larger specific surface area and hydrophilicity. These are thought to be the origin of the improved photocatalytic activity.

Keywords : Artificial photosynthesis; Hydrogen evolution; Mixed-anion compounds

酸フッ化物 $Pb_2Ti_2O_{5.4}F_{1.2}$ (PTOF)は適当な電子受容剤あるいは供与剤の存在下、可視光で水を酸化または還元することが可能であり、光腐食への耐性も有する有望な光触媒である[1)]。マイクロ波支援水熱合成(MHT)法は従来の固相法よりも PTOF の合成法として有用で、チタン前駆体として四塩化チタンを用いることで粒径が 0.5–1 μm の PTOF (chl-PTOF)が得られることが報告されている[2)]。しかし、四塩化チタンは反応溶液中での安定性に問題を抱えており、沈殿と塩化水素ガスを生じる。本研究では水溶性チタン錯体の一種であるチタンクエン酸錯体をチタン前駆体に用いた PTOF (cit-PTOF)の合成に成功し、EDTA 水溶液中で chl-PTOF の約 7 倍の水素生成活性を示した。cit-PTOF の粒径は 50–100 nm であり、ガス・蒸気吸着測定の結果、比表面積と親水性が chl-PTOF と比較して著しく向上していた。したがって、これらが活性向上の起源だと考えられる。

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2) Low-Temperature Microwave-Assisted Hydrothermal Synthesis of $Pb_2Ti_2O_{5.4}F_{1.2}$ Photocatalyst for Improved H_2 Evolution under Visible Light. K. Aihara, R. Mizuochi, M. Okazaki, S. Nishioka, S. Yasuda, T. Yokoi, F. Ishiwari, A. Saeki, M. Inada, K. Maeda, *ACS Materials Lett.* **2023**, *5*, 2355-2360.

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$Pb_2Ti_2O_{5.4}F_{1.2}$ を光触媒として用いた水の酸化反応におけるルテニウム助触媒の担持効果

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Effects of Ru cocatalyst loading on photocatalytic water oxidation over $Pb_2Ti_2O_{5.4}F_{1.2}$

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$Pb_2Ti_2O_{5.4}F_{1.2}$ is a semiconductor photocatalyst that can proceed water oxidation with a suitable electron acceptor. It is necessary to load a cocatalyst for $Pb_2Ti_2O_{5.4}F_{1.2}$ because it hardly produces oxygen from water. Hence, looking for the suitable method of cocatalyst modification should be a key to enhance photocatalytic activity for water oxidation.

In this work, we have revealed that Ru loading gave the best photocatalytic activity among the transition metals examined (Figure 1). Moreover, additional heating treatment under H_2 atmosphere at 523 K for 1 hour showed at least 4 times higher activity compared to the specimen without the H_2 treatment. Furthermore, Z-scheme water splitting has successfully proceeded with the aid of $FeCl_3$ redox mediator with the optimized $Ru/Pb_2Ti_2O_{5.4}F_{1.2}$ as an O_2 evolution photocatalyst and $Ru/SrTiO_3$:Rh as a H_2 evolution photocatalyst.

Keywords : Semiconductor photocatalyst; Water oxidation; Ruthenium cocatalyst; Pb–Ti oxyfluoride; visible light

$Pb_2Ti_2O_{5.4}F_{1.2}$ は適切な電子受容体存在下にて水の酸化反応を進行させることが可能な半導体光触媒として知られている。$Pb_2Ti_2O_{5.4}F_{1.2}$ は単独で水の酸化反応を進行させることが難しく、助触媒を担持することが必須である。したがって、助触媒の担持手法の詳細な検討により、水の酸化光触媒反応に対する高活性化が期待される。

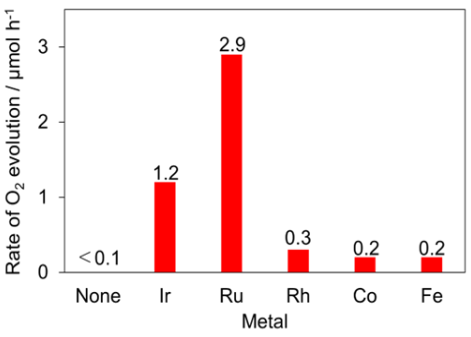

Figure 1. 各種金属助触媒を担持した $Pb_2Ti_2O_{5.4}F_{1.2}$ による酸素生成活性。反応条件: 10 mM $AgNO_3$ 水溶液 140 mL、触媒量: 50 mg、La_2O_3 200 mg、光源: 300 W Xe ランプ ($\lambda > 350$ nm)

本研究では、複数の遷移金属元素を用いた助触媒検討を行った結果、Ru が最も高活性を示すことを明らかとした(Figure 1)。Ru 助触媒の担持方法を詳細に調査したところ、含浸法で担持した Ru に対し、523 K、1 h の H_2 還元処理を施すことにより、酸素生成速度が 4 倍以上向上することが確認された。さらに、最高活性を示した $Ru/Pb_2Ti_2O_{5.4}F_{1.2}$ を酸素生成光触媒として用い、$Ru/SrTiO_3$:Rh を水素生成光触媒、$FeCl_3$ メディエータ存在下での Z スキーム反応を試みたところ、水分解反応の進行が認められた。

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カチオンをドープした層状ペロブスカイト型酸窒化物 $K_2LaTa_2O_6N$ の光触媒活性

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Photocatalytic activity of cation-doped layered perovskite oxynitride $K_2LaTa_2O_6N$ ([1]*School of Science, Tokyo Institute of Technology,* [2]*High Energy Accelerator Research Organization*) ○Hideya Tsuchikado[1], Yuta Shiroma[1], Fan Dongxiao[2], Megumi Okazaki[1], Shunsuke Nozawa[2], Kazuhiko Maeda[1]

Photocatalytic solar water splitting is one of the ideal ways to generate hydrogen energy. Although it has been reported that layered perovskite oxide photocatalysts exhibited higher water splitting activity due to their unique structure[1)], the oxide materials cannot respond to visible light, which is disadvantageous toward the effective utilization of solar energy. Our group has succeeded in synthesizing a new oxynitride photocatalyst, $K_2LaTa_2O_6N$, which has a layered perovskite structure. $K_2LaTa_2O_6N$ exhibited stable hydrogen evolution activity in an aqueous solution with the aid of a reversible electron donor under visible light irradiation[2)]. Although there have been many reports on doping with different elements as a strategy for improving photocatalytic activity, there have been no report on layered oxynitrides. In this study, doping various metal cations (e.g., Mg^{2+}, Ga^{3+}, Al^{3+}, Zr^{4+}, W^{6+}, Mo^{6+}) into $K_2LaTa_2O_6N$ was attempted. The 1 mol% M-doped $K_2LaTa_2O_6N$, where M is Mg^{2+}, Ga^{3+}, or Al^{3+} exhibited higher activity than undoped $K_2LaTa_2O_6N$. Moreover, the increase of the amount of Ga doped into $K_2LaTa_2O_6N$ was found to improve the hydrogen evolution activity of the oxynitride photocatalyst.

Keywords： Photocatalyst, hydrogen evolution, layered perovskite, oxynitride, doping

太陽光と光触媒による水分解はクリーンな水素製造法の１つである。層状ペロブスカイト構造を有する酸化物光触媒は、その構造に由来する特性によって、酸化チタンのようなバルク型の光触媒と比較して高い活性を示す[1)]。しかしこれらは紫外光しか吸収できないため、太陽光の利用効率が低い。当研究室では、層状ペロブスカイト構造を有する可視光応答性の酸窒化物 $K_2LaTa_2O_6N$ 光触媒を新規に合成し、可逆性電子ドナーが存在する水溶液中で、安定な水素生成を実現した[2)]。光触媒活性向上の戦略として、異元素ドーピングが数多く報告されてきたが、層状酸窒化物に対しては報告例がない。本研究では、層状酸窒化物 $K_2LaTa_2O_6N$ に対して６種のカチオン(Mg^{2+}、Ga^{3+}、Al^{3+}、Zr^{4+}、W^{6+}、Mo^{6+})をドープすることを新規に試みた。Ta^{5+}に比べて低原子価カチオン（Mg^{2+}、Ga^{3+}、Al^{3+}など）を 1 mol%ドープすると、未ドープのサンプルに比べて可視光照射下における水素生成活性が向上した。さらに Ga^{3+}のドープ濃度を増加させることで、酸窒化物光触媒の水素生成活性が一層向上することが明らかになった。

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機械学習による新規可視光応答性金属硫化物光触媒の開発

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Development of New Visible-Light-Driven Sulfide Photocatalysts by Machine Learning ([1]*Faculty of Science, Tokyo University of Science*, [2]*NAIST, Material Science*, [3]*NAIST, DSC*, [4]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Fuga Kakami,[1] Ryuto Baba,[2] Yoshiya Ueki,[1] Yosuke Harashima,[2,3] Yuichi Yamaguchi,[1,4] Mikiya Fujii,[2,3] Akihiko Kudo[1,4]

We have reported various visible-light-driven metal sulfide photocatalysts such as $(CuGa)_{1-x}Zn_{2x}S_2$ and Cu_3VS_4.[1,2] However, these photocatalytic activities are still low. Therefore, further development of novel photocatalyst materials is important. We have developed various photocatalysts by experimental approaches so far. In recent years, the development of materials using artificial intelligence has been paid much attention.[3] In the present study, we aimed to develop new visible-light-driven metal sulfide photocatalysts by machine learning using the data of metal sulfide photocatalysts developed in our group and ICSD.

Cu_2CdSnS_4 and Cu_2CdGeS_4 suggested by machine learning as a new photocatalyst were successfully synthesized in an almost single phase and possessed 1.3 and 1.9 eV of the band gap, respectively. These photocatalysts showed the sacrificial H_2 evolution activity under visible light irradiation. In conclusion, we successfully developed new visible-light-driven metal sulfide photocatalysts using machine learning.

Keywords : materials informatics; machine learning; metal sulfide; new material; visible light

当研究室では，これまでに$(CuGa)_{1-x}Zn_{2x}S_2$，Cu_3VS_4 などの種々の可視光応答性金属硫化物光触媒を開発してきた[1,2]．しかし，未だ活性は低く，さらなる新規光触媒材料の開発が重要である．当研究室ではこれまで実験的アプローチにより光触媒開発を行ってきた．近年では人工知能を活用した材料開発が大きな注目を集めており，光触媒分野においてもその応用が期待される[3]．そこで本研究では，当研究室の金属硫化物光触媒データを基に機械学習を行い，ICSD に収録された材料群から有望な光触媒の候補を選び出すことで，新規可視光応答性金属硫化物光触媒の開発を目指した．

機械学習により新たな光触媒として提案された Cu_2CdSnS_4 および Cu_2CdGeS_4 を合成したところ，ほぼ単一相の目的物を得ることに成功した．これらの材料はそれぞれ 1.3 eV, 1.9 eV のバンドギャップを有していた．また，いずれの光触媒においても可視光照射下での犠牲試薬を含む水溶液からの水素生成に活性を示した．以上のことから，機械学習を用いた新規可視光応答性金属硫化物光触媒を開発に成功した．

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フラックス法により調製した種々の長波長応答性金属硫化物光触媒を用いた可視光水分解用 Z スキーム系の開発

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Development of Z-scheme Systems for Water Splitting using Various Long Wavelength Visible Light-Responsive Metal Sulfide Photocatalysts Prepared by a Flux Method ([1]*Faculty of Science, Tokyo University of Science*, [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Riku Nakao,[1] Kotaro Wada,[1] Kengo Nagatsuka,[1] Yuichi Yamaguchi,[1,2] Akihiko Kudo[1,2]

We have reported Z-schematic water splitting under visible light irradiation using various long wavelength visible light-responsive metal sulfide photocatalysts prepared by a solid-state reaction.[1,2] However, these activities were low, so to develop efficient Z-scheme systems is still challenging. In the present study, we applied $Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ (BG: 1.9 eV)[3], $Cu_2ZnGe_{0.5}Sn_{0.5}S_4$ (BG: 1.8 eV), and $Cu_3Nb_{0.9}V_{0.1}S_4$ (BG: 1.7 eV)[4] prepared by a LiCl-KCl flux method to Z-scheme systems for efficient water splitting under visible light irradiation.

Water splitting under visible light irradiation was carried out using Z-scheme systems combined with these metal sulfides of H_2-evolving photocatalysts, $BiVO_4$ of an O_2-evolivng photocatalyst and $[Co(bpy)_3]^{3+/2+}$ of an electron mediator. As the results, all the Z-scheme systems using the metal sulfide photocatalysts prepared by a flux method showed higher water splitting activities than those prepared by a solid-state reaction. In conclusion, we have successfully developed Z-scheme water splitting systems by using long wavelength visible light-responsive metal sulfides prepared by the flux method.

Keywords : Z-schematic Water splitting; Metal Sulfide; Flux Method; Visible Light; Long Wavelength

当研究室では，固相法で調製した種々の長波長応答性金属硫化物を水素生成光触媒として用いた Z スキーム型可視光水分解を報告している[1,2]．しかし，これらの水分解活性はいまだ低く改善の余地がある．本研究では，金属硫化物光触媒をフラックス法で調製することによる高活性な可視光水分解用 Z スキーム系の開発を目的とした．

$Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ (BG: 1.9 eV)[3]，$Cu_2ZnGe_{0.5}Sn_{0.5}S_4$ (BG: 1.8 eV)および $Cu_3Nb_{0.9}V_{0.1}S_4$ (1.7 eV)[4]を LiCl-KCl フラックス法で調製した．これら水素生成光触媒と，$BiVO_4$ 酸素生成光触媒および$[Co(bpy)_3]^{3+/2+}$電子伝達剤を組み合わせた Z スキーム系による可視光水分解を行った結果，いずれも従来の固相法のものを用いた場合よりも高い水分解活性を示した．特に，$Cu_{0.8}Ga_{0.4}In_{0.4}Zn_{0.4}S_2$ を用いたときにもっとも高い可視光水分解活性を示した．以上より，種々の長波長応答性金属硫化物光触媒をフラックス法で調製することで，従来よりも高活性な可視光水分解用 Z スキーム系の開発に成功した．

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$ANbO_3$:Ir,Zr (A = K, Na)光触媒を用いた単一粒子型可視光水分解

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Water splitting under visible light irradiation over single particulate $ANbO_3$:Ir,Zr (A = K, Na) photocatalysts

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○Natsuki Suto[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2]

The development of visible-light-driven photocatalysts for water splitting is an important research topic for realization of green hydrogen production. We have achieved water splitting under visible light irradiation over single particulate $ANbO_3$:Ir,Zr (A = K, Na) photocatalysts[1]. However, there is an issue that the activity is low. One of the factors on the low activity is that the particle size of the photocatalyst is large. It was reported that the polymerizable complex method is a promising method to obtain fine particles[2]. In the present study, we prepared a $KNbO_3$:Ir,Zr photocatalyst with small particles prepared by various methods and investigated water splitting over the photocatalyst.

It was revealed by SEM images that fine $KNbO_3$:Ir,Zr particles with 100 nm of particle size were successfully prepared. Water splitting over the $KNbO_3$:Ir,Zr photocatalyst proceeded under visible light irradiation by loading of a $RhCrO_x$ cocatalyst[3] by an impregnation method. We successfully developed a $KNbO_3$:Ir,Zr photocatalyst with fine particles for water splitting under visible light irradiation.

Keywords：*Photocatalyst; Nb-based metal oxide; Ir doping; Water splitting; visible light*

光触媒を用いたソーラー水分解によるグリーン水素製造の社会実装に向けて，可視光応答性光触媒の開発は重要な研究課題である．当研究室では，固相法によって合成した Ir,Zr 共ドープ $ANbO_3$ (A = K, Na)光触媒を用いた単一粒子型可視光水分解を報告してきた[1]．しかし，本光触媒において水分解活性が低いという課題がある．その原因の 1 つとして光触媒粒子の粒径が大きいことが挙げられる．ここで，錯体重合法は微粒子を得る合成法として有用であることが報告されている[2]．そこで本研究では，種々の合成法によって調製した $KNbO_3$:Ir,Zr 光触媒微粒子を用いた可視光水分解を調べた．

錯体重合法によって合成した $KNbO_3$:Ir,Zr の SEM 像を観察したところ，約 100 nm の微細な粒子が得られたことがわかった．本光触媒に対して含浸法によって $RhCrO_x$ 助触媒[3]を担持したところ，可視光水分解が進行した．以上のことから，可視光水分解に活性な $KNbO_3$:Ir,Zr 光触媒微粒子の合成に成功した．

1) 須藤，山口，工藤，第 42 回光がかかわる触媒化学シンポジウム，P15 (2023).
2) M. Kakihana, K. Domen, *MRS Bull.* **2000**, *25*, 27.
3) K. Maeda, K. Domen *et al.*, *Chem. Eur. J.* **2010**, *16*, 7750.

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遷移金属をドーピングした $SrTiO_3$:Al 光触媒を用いた可視光水分解における反応温度依存性

（東理大理[1]・東理大総研カーボンバリュー[2]）○菊地 恵理佳[1]・山口 友一[1,2]・工藤 昭彦[1,2]

Temperature dependence of photocatalytic water splitting under visible light irradiation over $SrTiO_3$:Al doped with transition metal ([1]*Faculty of Science, Tokyo University of Science*, [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Erika Kikuchi,[1] Yuichi Yamaguchi,[1,2] Akihiko Kudo[1,2]

We have reported that $SrTiO_3$:Ir,Sb,Al is highly active for photocatalytic water splitting under visible light irradiation.[1)] We have also reported that the activity is improved with decreasing reaction temperature.[2)] However, the insufficient activity and unclear reaction mechanism are still issues. Here, doping amounts of Ir and Sb are one of the important factors on water splitting over the photocatalyst. In the present study, we investigated the effect of the reaction temperatures on water splitting under visible light irradiation over the $SrTiO_3$:Al photocatalyst with various doping amounts of Ir and Sb, aiming at improving the activity and finding the reaction mechanism of water splitting over a $SrTiO_3$:Ir,Sb,Al photocatalyst.

When tiny amounts of Ir were doped, 4 of the ratio of Sb/Ir was the best for efficient water splitting at 280, 290, 320, and 340 K. Even though the ratio of Sb/Ir was changed, the activity was improved comparably with a decrease of reaction temperature. On the other hand, when large amounts of Ir were doped, $SrTiO_3$:Ir,Al without Sb codoping showed the highest activity at each reaction temperature. The activities of the sample doped with small amounts of Sb were enhanced remarkably with a decrease of reaction temperature. The reason of these difference was investigated. Therefore, temperature dependence of photocatalytic water splitting under visible light irradiation over $SrTiO_3$:Ir,Sb,Al was changed with doping amounts of Ir and Sb.

Keywords：Photocatalyst; Temperature dependence; Water splitting; Transition metal doping; Visible light

当研究室では，$SrTiO_3$:Ir,Sb,Al 光触媒が可視光水分解に高い活性を示すことを報告してきた[1)]．さらに，可視光水分解における反応温度を低下させると，活性が向上することも見いだしてきた[2)]．しかし，その活性には改善の余地がある．また，反応メカニズムがいまだ不明瞭である．ここで，Ir および Sb ドープ量は本光触媒を用いた可視光水分解における重要な要因のひとつである．そこで，活性の向上や反応メカニズムの解明の手がかりを見いだすために，種々の量で Ir および Sb を共ドーピングした $SrTiO_3$:Al を用いた可視光水分解における反応温度依存性を調べた．

Ir ドープ量が少ないサンプルでは，280, 290, 320, 340 K のいずれの反応温度においても，Sb/Ir の比が 4 のときにもっとも高い活性を示した．また，Sb/Ir の比が変化しても，反応温度低下による活性向上は同程度だった．一方で，Ir ドープ量が多い場合は，どの反応温度においても Sb 未ドープ体がもっとも高い活性を示した．さらに，Sb 共ドープ量が少ないほど反応温度低下による活性の向上が顕著だった．そこでこれらの違いを考察した．このように，$SrTiO_3$:Ir,Sb,Al を用いた可視光水分解における反応温度依存性は，Ir および Sb の共ドーピング量により変化することがわかった．

1) 海谷，渡邊，吉野，山口，工藤，第 126 回触媒討論会，P058（2020）．
2) 菊地，山口，工藤，第 132 回触媒討論会，2C11（2023）．

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複合助触媒を担持した金属酸化物光触媒を用いた水分解における特異的な O_2 貯蔵

(東理大理[1]・東理大総研カーボンバリュー[2]) ○足立 響子[1]・須藤 夏希[1]・八木橋 克[1]・山口 友一[1,2]・工藤 昭彦[1,2]

The specific behavior of O_2 storage on water splitting over metal oxide photocatalysts loaded with dual cocatalysts

([1]*Faculty of Science, Tokyo University of Science*, [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Kyoko Adachi[1], Natsuki Suto[1], Suguru Yagihashi[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2]

We have reported that a specific phenomenon of O_2 storage occurs on water splitting over a $NaTaO_3$:Sr photocatalyst loaded with a Rh-Ru dual cocatalyst.[1)] The phenomenon of O_2 storage is that O_2 is released after the light is turned off. However, the mechanism of this phenomenon has not been clarified yet. In this study, we investigated the phenomenon O_2 storage on water splitting over various metal oxide photocatalysts loaded with a Pd-Ru dual cocatalyst[2)] which showed O_2 storage being similar to a Rh-Ru dual cocatalyst.

Water splitting under UV irradiation over various metal oxide photocatalysts loaded with a Pd-Ru dual cocatalyst by liquid phase reduction was carried out. Pd-Ru-loaded $NaTaO_3$:Sr showed the specific behavior of O_2 storage. Next, effect of a doping amount of Sr on O_2 storage of $NaTaO_3$ was investigated. A Sr-doped sample showed the behavior of O_2 storage whereas a non-doped sample did not. It was reported that the nano-step structure was formed on a particle by Sr doping.[3)] Therefore, it was suggested that the specific phenomenon of O_2 storage occurred by nano-step structure and a Pd-Ru dual cocatalyst.

Keywords : Water splitting; Metal oxide; Dual cocatalyst; O_2 storage; Hydrogen peroxide

当研究室では，Rh-Ru 複合助触媒を担持した $NaTaO_3$:Sr 光触媒を用いて水分解を行った際，特異的な O_2 貯蔵現象が起こることを報告してきた [1)]．本現象は光消灯後に O_2 が過剰に放出される現象である．Rh および Ru 単独担持ではほとんど本現象が起こらないため，Rh-Ru 複合助触媒が O_2 貯蔵現象を引き起こす重要な要因の一つだと考えられる．しかし，本現象のメカニズムはいまだ解明されていない．そこで本研究では，同様の現象が確認されている Pd-Ru 複合助触媒 [2)]を種々の金属酸化物光触媒に担持し，水分解における O_2 貯蔵現象の調査を目的とした．

Pd-Ru 複合助触媒を液相還元法により担持した種々の金属酸化物光触媒を用いた水分解を行ったところ, $NaTaO_3$:Sr 光触媒を用いた際に O_2 貯蔵現象が顕著に確認された．さらに，$NaTaO_3$:Sr 光触媒に着目して本現象における Sr ドープ量依存性を調べた．その結果，未ドープ体では O_2 貯蔵現象がほとんどみられず，Sr ドープ体では O_2 貯蔵現象がみられた. 既報より Sr をドープすると $NaTaO_3$ 表面にナノステップ構造が形成されることが知られている [3)]．以上より，本現象は $NaTaO_3$:Sr 光触媒の表面に形成されたナノステップ構造および Pd-Ru 複合助触媒が関係していると示唆された．

1) W. Soontornchaiyakul, A. Kudo *et al*., *J. Am. Chem. Soc*. **2023**, *145*, 20485.
2) 八木橋，吉野，山口，工藤，日本化学会第 102 春季年会，B304-4-pm-07 (2022).
3) A. Iwase, H. Kato, A. Kudo, *ChemSusChem*, **2009**, *2*, 873.

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Ir,Sb 共ドープ $SrTiO_3$ 光触媒に担持する助触媒の検討

（住友大阪セメント㈱[1]・東理大理 [2]・東理大理総研カーボンバリュー[3]）○八久保 鉄平[1]・山口 友一[2,3]・工藤 昭彦[2,3]

Study of co-catalyst for Ir and Sb co-doped $SrTiO_3$ photocatalyst ([1]*SUMITOMO OSAKA CEMENT CO., LTD.,* [2]*Tokyo Univ. of Science,* [3]*CVRC. RIST TUS*) ○Teppei Yakubo[1], Yuichi Yamaguchi[2,3], Akihiko Kudo[2,3]

Iridium and antimony- codoped strontium titanate ($SrTiO_3$:Ir,Sb) photocatalyst has been reported as a photocatalyst that exhibits water-splitting even in visible light[1]. A photocatalyst in which shape-controlled $SrTiO_3$:Ir,Sb particles synthesized by hydrothermal reaction, treated with $SrCl_2$ flux and loaded with co-catalysts, showed solar hydrogen energy conversion efficiency (STH) of 0.3%[2]. However, the STH value for social implementation of water-splitting photocatalysts has been shown to be over 5%[3], and it is necessary to improve the quantum efficiency of $SrTiO_3$:Ir,Sb photocatalysts.

In this study, we measured the irradiation wavelength dependence of the hydrogen and oxygen generation rate in a sacrificial reagent aqueous solution using a flux-treated photocatalyst of $SrTiO_3$:Ir,Sb particles synthesized by hydrothermal reaction and found the rate of oxygen evolution was significantly reduced under visible light irradiation. Based on this result, we investigated the co-catalyst for oxygen generation on $SrTiO_3$:Ir,Sb photocatalyst synthesized by hydrothermal reaction. As the result, the quantum efficiency for water splitting under visible light irradiation was improved and the STH increased to 0.52%.

Keywords : photocatalyst; co-catalyst; water-splitting

Ir,Sb 共ドープチタン酸ストロンチウム ($SrTiO_3$:Ir,Sb) 光触媒は、可視光でも水分解活性を示す光触媒として知られている [1]。水熱反応により合成した形状制御 $SrTiO_3$:Ir,Sb 粒子を $SrCl_2$ フラックス中で処理し、助触媒を担持した光触媒では、太陽光水素エネルギー変換効率 (STH) が 0.3%を超える水分解活性を示すことがわかっている [2]。水分解用光触媒の社会実装のための目安となる STH として 5%が示されており [3]、$SrTiO_3$:Ir,Sb 光触媒の量子効率の向上が課題である。

本研究では、水熱反応により合成した $SrTiO_3$:Ir,Sb 粒子をフラックス処理した光触媒による犠牲試薬水溶液中での水素、酸素発生速度の照射光波長依存性を測定し、可視光照射下では酸素発生速度が顕著に低下することを見出した。このことから、水熱合成 $SrTiO_3$:Ir,Sb 光触媒に担持する酸素発生助触媒を検討した。その結果、水分解において STH が 0.52%に向上した。

1) 海谷恭平, 渡邊健太, 吉野隼矢, 山口友一, 工藤昭彦, 第 126 回触媒討論会, P058 (2020).
2) 八久保鉄平, 山口友一, 工藤昭彦, 日本化学会第 103 回春季年会予稿集, 446 (2023).
3) 新エネルギー・産業技術総合開発機構, 「人工光合成プロジェクトの成果と社会実装に向けた課題と展望」(2022)

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Academic Program [Oral A] | 08. Catalysts and Catalysis：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC A1457(1457, Bldg. 14 [5F])

[A1457-4pm] 08. Catalysts and Catalysis

Chair: Takayoshi Hara, Tatsuya Moriai

English
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1457-4pm-01]
Preparation and Evaluation of Redox Performances of Chromium and Rhodium Incorporated Ceria at Micrometer Size

○Wenjun LI[1,2], Chaoqi CHEN[1], Satoshi Muratsugu[1], Mizuki Tada[1,2] (1. Nagoya Univ., 2. RCMS, Nagoya Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1457-4pm-02]
Sintering suppression and catalysis of ceria nanoparticle embedded in silica-nanoparticle assemblies

○Miho Nishida[1], Takashi Nakazono[2], Yusuke Yamada[1,2] (1. Graduate School of Engineering, Osaka Metropolitan University, 2. Research Center of Artificial Photosynthesis, Osaka Metropolitan University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1457-4pm-03]
Preparation of zeolite-supported Ru catalysts and their ammonia synthesis properties

○Mahiru Umeno[1], Tomohiro Noguchi[2], Hirokazu kobayashi[3], Miho Ymauchi[1,2,3,4,5] (1. Graduate School of Science, Kyushu Univ., 2. IMCE, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ., 5. WPI-I2CNER, Kyushu Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1457-4pm-04]
Investigation of factors for improving ammonium ion selectivity in nitrate reduction using Pd-Ag catalyst with formic acid as reductant.

○Tetsuya Takeda[1], Ikko Mikami[1] (1. Tokai University)

1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
Break

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1457-4pm-05]
Selective Oxidation of Methane over Supported Iron Phosphate Catalysts Prepared Using Phosphonic Acid

○Kazuma Furuya[1], Aoi Matsuda[1], Michikazu Hara[1], Keigo Kamata[1] (1. MLS, Tokyo Tech)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

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[A1457-4pm-06]

Selective Oxidation of Methane into Formaldehyde over Copper Phosphate Catalysts

○Aoi Matsuda[1], Takeshi Aihara[1], Michikazu Hara[1], Keigo Kamata[1] (1. MLS, Tokyo Tech)

Japanese

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[A1457-4pm-07]

Precision synthesis of nickel clusters and methane activation

○Yuma Kikuchi[1], Tatsuya Moriai[1,2], Takane Imaoka[1,2], Kimihisa Yamamoto[1,2] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. JST-ERATO)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[A1457-4pm-08]

Application of valence controlled copper oxide nanocluster catalysts for aromatic alcohol oxidation reactions.

○Koki Hoshino[1], Takayoshi Hara[1], Nobuyuki Ichikuni[1] (1. Chiba University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[A1457-4pm-09]

[Withdraw] Substitution of Co into $SrTiO_3$ using hydrothermal synthesis method and its catalytic activity for alcohol oxidation reaction

○Masahiro Aoyama[1], Takayoshi Hara[1], Nobuyuki Ichikuni[1] (1. Chiba University)

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

Break

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[A1457-4pm-10]

Effect of zeolite pore size on product selectivity and coke formation in MTO reaction

○Itsuki Matsushita[1], Masaru Ogura[1], Takahiko Moteki[2] (1. The Univ. of Tokyo, 2. Shizuoka University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[A1457-4pm-11]

Conversion of polycyclic aromatics to monocyclic aromatics by catalysts with selective hydrogenation and dealkylation ability

○Ryoto Mori[1], Yuta Saga[2], Kenji Kamiya[1], Eika Qian[1] (1. Tokyo University of Agrigulture and Technology, 2. Maruzen Petrochemical CO,LTD.)

Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[A1457-4pm-12]

Study of pressure dependence and characterization of active Mo species for methane dehyroaromatization over Mo/H-MFI catalysts

Airi Kosuge[1], Yuya Sonobe[1], Kenta Kuramochi[1], ○Hirofumi Aritani[1] (1. Saitama Institute of Technology)

Japanese

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3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[A1457-4pm-13]

Creation of Cross-Coupling Catalysts by Photodecarbonylation of Iron Complexes

○Koki Yamama[1], Yuta Nishina[1] (1. Okayama University)

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Preparation and Evaluation of Redox Performances for Chromium and Rhodium Incorporated Ceria at Micrometer Size

([1]*Research Center for Materials Science, Nagoya University*, [2] *Graduate School of Science, Nagoya University*) ○Wenjun Li,[1] Chaoqi Chen,[2] Satoshi Muratsugu,[2] Mizuki Tada[1,2]

Keywords: Mixed Metal Oxide; Ceria; Redox Property; Chromium; Rhodium

CeO_2 has unique redox properties that make it an indispensable material for a variety of catalytic processes. However, the redox property of pure CeO_2 was limited and combination with other metals provides remarkable improvements of the redox property and catalytic performances in a wide range of chemical reactions. Our group reported the synthesis and catalytic properties of mixed metal oxide catalysts $Cr_{0.19}Rh_{0.06}CeO_z$, which consists of cerium oxide incorporated with Cr and a small amount of Rh, and exhibited reversible redox activity at less than 373 K.[1] We previously demonstrated the redox behavior of a single $Pt/Ce_2Zr_2O_x$ ($7<x<8$) mixed oxide particle by hard X-ray spectroptychography[2], and we investigated the preparation of Cr and Rh-incorporated ceria at micrometer size for the visualization of the redox behavior of the Cr and Rh-incorporated ceria.

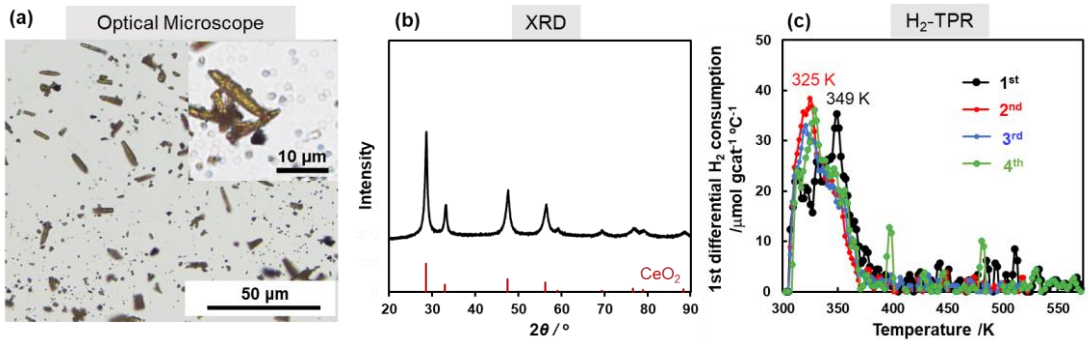

Figure 1 (a) Optical microscope of the prepared $CrRhCeO_x$, (b) XRD pattern, and (c) the profiles of TPR with H_2 for four cycles.

The Cr and Rh-incorporated ceria were prepared by a hydrothermal method with the addition of Cr and Rh sources.[3] Micro-rod shaped $CrRhCeO_x$ with 5-20 μm size, was prepared (Fig. 1 (a)). The XRD pattern of the prepared $CrRhCeO_x$ (Fig. 1 (b)) matched with that of CeO_2 (No. 01-075-0076) and peaks attributed to CrO_x or Rh were negligible, indicating the rod body was composed of CeO_2 without the aggregation of CrO_x and Rh. Temperature-programmed reduction (TPR) with H_2 suggested that the $CrRhCeO_x$ rods show remarkable reduction property at around 325 K (Fig. 1 (c)), whose behavior was reversible. The structures and redox performances of the micro-sized $CrRhCeO_x$ rods will be presented.

1) S. Ikemoto, M. Tada, *et al*., *Phys. Chem. Chem. Phys.* **2019**, *21*, 20868. 2) H. Matsui, M. Tada, Y. Takahashi, *et al*., *Commun. Chem*. **2019**, *2*, 50. 3) H. Wang, C. Lu, *Mater. Res. Bull*. **2002**, *37*, 783.

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シリカナノ粒子集合体内部へのセリアナノ粒子の分散担持による焼結抑制と触媒特性

（阪公大院工[1]・阪公大人工光合成セ[2]）○西田 美穂[1]・中薗 孝志[2]・山田 裕介[1,2]
Sintering Suppression of Ceria Nanoparticles by Immobilization in Silica-Nanoparticle Assemblies for High Catalytic Activity ([1]*Graduate School of Engineering, Osaka Metropolitan University*, [2]*Research Center of Artificial Photosynthesis (ReCAP), Osaka Metropolitan University*)○Miho Nishida,[1] Takashi Nakazono,[2] Yusuke Yamada[1,2]

Nanoparticles catalysts in solution are prone to form aggregates, which may result in deactivation. In this work, a series of ceria nanoparticles (CeO_2NPs) with various dispersion degrees were immobilized in silica-nanoparticle assemblies (SiO_2NPA) to examine catalytic activity for *p*-nitrophenyl phosphate hydrolysis in aqueous solution. CeO_2NPs/SiO_2NPA with different dispersion degree showed similar catalytic activity when uncalcined or calcined at lower than 500 °C. However, catalytic activity of CeO_2NPs/SiO_2NPA with high dispersion degree calcined at 800°C showed higher catalytic activity than that with low dispersion degree due to suppression of sintering as evidenced by TEM observation.
Keywords : Aggregation; Calcination Temperature; Nanoparticles Assembly; Dispersion Degree

溶液中での触媒反応に用いられるナノ粒子は、反応中に凝集体を形成することで活性が低下すると考えられている。シリカナノ粒子集合体（SiO_2NPA）の内部に、分散度が異なる状態でセリアナノ粒子（CeO_2NPs）を固定化することで、触媒反応中でも CeO_2NPs の分散度が変化しない CeO_2NPs/SiO_2NPA を調製した。これらの触媒を種々の温度で焼成した後、水中でのパラニトロフェニルリン酸 (*p*-NPP) の加水分解反応に対する触媒活性を調べることで、CeO_2NPs の凝集や焼結が触媒活性に与える影響を明らかにした。

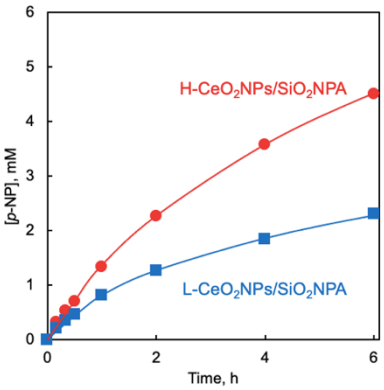

Fig. 1 Time courses of *p*-nitrophenol (*p*-NP) formation by catalytic hydrolysis of *p*-NPP (8.0 mM) in a HEPES buffer (1.0 mL, 200 mM, pH 6, 60 ºC) containing H-CeO_2NPs/SiO_2NPA (●, red) and L-CeO_2NPs/SiO_2NPA (■, blue).

未焼成または焼成温度が 500 ºC 以下の場合は、凝集度の違いによる触媒活性の差は見られなかった。しかし、800℃で焼成した場合には分散度が高い H-CeO_2NPs/SiO_2NPA は、分散度が低い L-CeO_2NPs/SiO_2NPA より高い活性を示した（Figure 1）。TEM 観察の結果、H-CeO_2NPs/SiO_2NPA では CeO_2 ナノ粒子の形状は焼成前と同様であったのに対し、L-CeO_2NPs/SiO_2NPA では CeO_2NPs どうしが焼結し、一塊となっていた。以上の結果より、CeO_2 ナノ粒子触媒における触媒活性低下の原因は、凝集体の形成ではなく、凝集体が一塊の焼結体を形成することであることが明らかとなった。

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Ru 担持ゼオライト触媒の調整とアンモニア合成特性

（九大理[1]・九大先導研[2]・九大 K-NETs[3]・東北大 AIMR[4]・九大 I[2]CNER[5]）
○梅野磨比流[1]・野口朋寛[2]・小林浩和[3]・山内美穂[1,2,3,4,5]

Synthesize of zeolite-supported Ru catalysts and their ammonia synthesis properties

([1]*School of Science, Kyushu University*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University,* [3]*Research Center for Negative Emissions Technologies, Kyushu University*, [4]*International Institute for Carbon-Neutral Energy Research, Kyushu University*, [5]*Advanced Institute for Materials Research, Tohoku University*) ○Mahiru Umeno,[1] Tomohiro Noguchi,[2] Hirokazu Kobayashi,[3] Miho Yamauchi,[1,2,3,4,5]

Ru nanoparticles supported on an alkaline MgO (Ru/MgO) are known to exhibit high activity for ammonia synthesis [1]. For further functionalization of ammonia synthesis catalysts, we focus on zeolites as a new support due to their catalytic tunability based on the pore size, component cations, degree of aluminum substitution of zeolites. In this study, we investigate the catalytic performance of ZSM-5 zeolite supported Ru nanoparticle catalyst (Ru/ZSM-5) for the ammonia synthesis reaction.

ZSM-5 was prepared by hydrothermal synthesis from a mixture containing aluminum chloride hexahydrate, tetraethyl orthosilicate, and tetrapropylammonium hydroxide as an organic structure directing agent, and Ru/ZSM-5 was prepared by an impregnation method. Transmission electron microscopy (TEM) observation and powder X-ray diffraction measurements revealed that Ru nanoparticles were supported on the ZSM-5 skeleton (Figure 1). We found that Ru/ZSM-5 shows ammonia synthesis activity. Details of the catalytic performance will be discussed in the presentation.

Keywords : ZSM-5 zeolite, ammonia synthesis

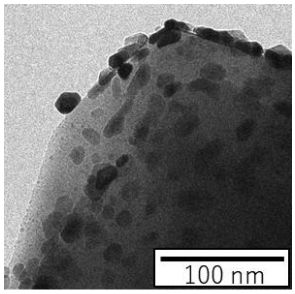

図 1 Ru/ZSM-5 の TEM 像

アルカリ性の担体である MgO に担持された Ru ナノ粒子（Ru/MgO）はアンモニア合成触媒として高い活性を示すことが知られている [1]。我々は、アンモニア合成触媒の更なる機構向上を目指し、新規担体として細孔径、カチオン、アルミニウムの置換量などにより反応特性を制御できるゼオライトに着目した。本研究では、10 員環細孔のみを有する中細孔ゼオライトである ZSM-5 に担持された Ru ナノ粒子触媒（Ru/ZSM-5）を作製し、アンモニア合成特性を調べることを目的とする。

塩化アルミニウム六水和物、オルトケイ酸テトラエチルおよび有機構造規定剤であるテトラプロピルアンモニウムヒドロキシドを含む混合物から水熱合成法により ZSM-5 を作製し、含浸法により Ru ナノ粒子を担持することで Ru/ZSM-5 を調製した。透過型電子顕微鏡（TEM）観察（図１）と粉末 X 線回折測定から ZSM-5 骨格を維持したまま Ru ナノ粒子が担持されていることがわかった。また、流通式触媒反応装置を用いた、アンモニア合成試験により、Ru/ZSM-5 はアンモニア合成活性を示すことが明らかとなった。詳細については当日議論する。

1) F. Rosowski, A. Hornung, O. Hinrichsen, D. Herein, M. Muhler, *Appl. Catal.* 1997, 151, 443-460.

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ギ酸を還元剤とし Pd-Ag 触媒を用いた硝酸イオン還元反応におけるアンモニア選択率向上因子の調査

（東海大院理）○武田徹也・三上一行

Investigation of factors for improving ammonium ion selectivity in nitrate reduction using Pd-Ag catalyst with formic acid as reductant（*Graduate School of Science, Tokai University*）○Tetsuya Takeda, Ikko Mikami

Nitrate is a causative agent of eutrophication, for which effluent standards have been established. We have been studying the treatment of wastewater containing nitrate and have found that a system using formic acid as the reductant and a Pd-Ag catalyst can be used to treat wastewater at a high reaction rate. In this system, we aim to convert NO_3^- to NH_3 for resource recovery. In this study, we examined the effects of catalyst composition and reaction conditions on selectivity. Regarding the influence of the second metal species, Ag reduced NO_3^- faster and with higher NH_4^+ selectivity than other metals under constant pH 6 conditions. The decomposition of NO_2^- proceeded rapidly on Ag surfaces, while it did not progress as much on other metals. Regarding the coating effect of Ag on the Pd surface, it became highly selective for NH_4^+ when the coverage rate was high. These results suggest that NH_4^+ selectivity improves as the reduction of NO_2^- proceeds on Ag. As for the influence of the $HCOOH/NO_3^-$ ratio, an increase in the ratio resulted in a higher reaction rate and NH_4^+ selectivity. Thus, it was also found that the selectivity varied with the amount of reducing agent added.

Keywords : Nitrate ion; Ammonia; Pd catalyst; Water treatment

硝酸塩は、富栄養化の原因物質であるため排水基準が設定されている。本研究室では、硝酸イオンを含む排水の処理について研究しており、これまでに還元剤をギ酸とし Pd-Ag 触媒を用いた系で高速で処理できることを見出している。この系では、NO_3^- の NH_3 への変換による資源化を目指しており、本研究では触媒組成や反応条件が選択率に与える影響について pH6 一定条件下で検討した。

Pd に添加する第二金属種を比較したところ、Ag が他の金属よりも高速かつ高 NH_4^+ 選択的に NO_3^- を還元した。また、NO_2^- の分解では、他の金属上では分解が進行しにくいが、Ag では高速で分解された。さらに、Ag/Pd 比の異なる試料を用いて NO_3^- 還元反応を行ったところ、Pd の Ag による表面被覆率が高い場合に高 NH_4^+ 選択的になった。これらのことから、NO_3^- 還元の中間生成物である NO_2^- の還元が Ag 上で反応が進むことで NH_4^+ 選択性が向上すると考えられる。$HCOOH/NO_3^-$ 比の影響については、その比の値が増加すると、より高速かつ高 NH_4^+ 選択的になり、還元剤の添加量によっても選択性が変動することも分かった。

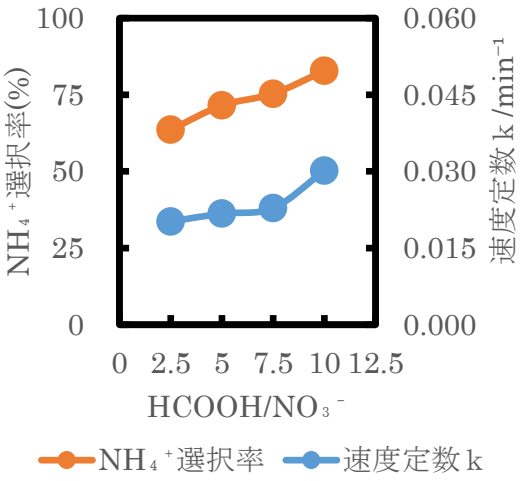

図 1 NH_4^+ 選択率および NO_3^- 還元速度に対する $HCOOH/NO_3^-$ 比の影響

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ホスホン酸を用いた担持リン酸鉄触媒によるメタンの選択酸化

（東工大フロンティア材料研）○古谷 一眞・松田 蒼依・原 亨和・鎌田 慶吾

Selective Oxidation of Methane over Supported Iron Phosphate Catalysts Prepared Using Phosphonic Acid (*Laboratory for Materials and Structures, Tokyo Instituted of Technology*)

○Kazuma Furuya, Aoi Matsuda, Michikazu Hara, Keigo Kamata

Methane has attracted attention as an important molecule due to its abundance around the world as a main source of natural gas. However, it is difficult to activate methane, which has strong C–H bonds and suppress sequential oxidation into CO_x for selective oxidation of methane. We have focused on metal phosphates with redox-active Lewis acidic and weakly basic sites as heterogeneous catalysts for selective oxidation of methane into formaldehyde, which is an important raw material for resins and paints. In this study, we investigated the effect of phosphorous source on supported iron phosphate catalysts to improve formaldehyde yield. We prepared supported iron phosphate catalyst using methylphosphonic acid as a phosphorous source by impregnation method (5 wt%$FePO_4$(MeP)/SBA-15). No diffraction peaks of iron phosphate were observed in the XRD pattern of the catalyst and the band corresponding to the P–O stretching vibration of $FePO_4$ was observed by Raman spectroscopy, suggesting that $FePO_4$ nanoparticles are highly dispersed on SBA-15. The present catalyst showed higher formaldehyde yield than previously reported iron phosphate nanoparticles ($FePO_4$-NP) and supported iron phosphate catalysts using ammonium dihydrogen phosphate (5 wt%$FePO_4$(NHP)/SBA-15).

Keywords : Phosphonic acid; Iron phosphate; Methane; Selective oxidation;

天然ガスの主成分であるメタンは世界中に豊富に存在するため、重要な化学原料として注目されている。しかし、メタンの選択酸化ではメタンの C–H 結合の活性化や逐次酸化の抑制が困難である。このような背景の下、我々は、金属リン酸塩の逐次酸化の抑制効果に着目し、メタンから樹脂や塗料の原料であるホルムアルデヒドへの選択酸化触媒を開発してきた[1,2]。本研究では、ホルムアルデヒド収率の向上を目的とし、担持リン酸鉄触媒のリン源の効果を検討した。含浸法によりメチルホスホン酸をリン源とした担持リン酸鉄触媒(5 wt%$FePO_4$(MeP)/SBA-15)を合成した。本触媒の XRD パターンではリン酸鉄に由来する回折ピークを確認できず、ラマン分光測定より $FePO_4$ の P–O 伸縮振動に由来する吸収帯が観測されたため、$FePO_4$ ナノ粒子の高分散担持が示唆された。本触媒は、既報のリン酸鉄ナノ粒子触媒 ($FePO_4$-NP)[1] やリン酸二水素アンモニウムを用いた担持リン酸鉄触媒 (5 wt%$FePO_4$(NHP)/SBA-15) よりも高いホルムアルデヒド収率を示した。

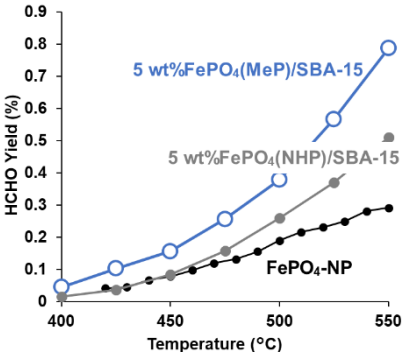

図. 担持リン酸鉄触媒によるホルムアルデヒド収率. 反応条件 : 触媒 (50 mg), $CH_4/N_2/O_2$ = 7/8/1 sccm.

1) A. Matsuda, H. Tateno, K. Kamata, M. Hara, *Catal. Sci. Technol.* **2021**, *11*, 6987.
2) A. Matsuda, K. Obara, A. Ishikawa, M.-H. Tsai, C.-H. Wang, Y.-C. Lin, M. Hara, K. Kamata, *Catal. Sci. Technol.* **2023**, *13*, 5180.

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リン酸銅触媒によるメタンからホルムアルデヒドの直接合成

（東工大　フロンティア材料研）○松田 蒼依・相原 健司・原 亨和・鎌田 慶吾
Selective Oxidation of Methane into Formaldehyde over Copper Phosphate Catalysts (MLS, Tokyo Tech) ○Aoi Matsuda, Takeshi Aihara, Michikazu Hara, Keigo Kamata

Methane is a main component of natural gas and has attracted much attention as a feedstock for the manufacture of chemicals and fuels. Since direct oxidation of methane to formaldehyde can be a low energy process without syngas production, the development of superior catalytic systems is strongly demanded. Among various Cu-based catalysts and metal phosphate nanoparticles[1, 2] ($FePO_4$ and $BiPO_4$), $Cu_2P_2O_7$-NO_3 prepared with $Cu(NO_3)_2 \cdot 3H_2O$ as the copper source exhibited the highest HCHO yield. Mechanistic studies including the catalyst effect, kinetics, isotope-labelling and pulse-reaction experiments, and IR spectroscopy for adsorbed probe molecules, indicated that (i) surface lattice oxygen species of $Cu_2P_2O_7$ possibly react with CH_4 to give HCHO as the primary product and (ii) the surface Cu^{2+} sites and weakly-basic phosphate units on $Cu_2P_2O_7$ would be important in the C–H activation and the suppression of overoxidation into CO_2, respectively.
Keywords : copper phosphate; methane; selective oxidation

メタンは天然ガスの主成分であり、化学物質や燃料の原料として注目されている。メタンからホルムアルデヒドへの直接酸化は合成ガスを経由しない低エネルギープロセスであるため、優れた触媒システムの開発が強く求められている。検討した種々の銅系触媒およびリン酸金属ナノ粒子[1, 2] ($FePO_4$ および $BiPO_4$) の中で、$Cu(NO_3)_2 \cdot 3H_2O$ を Cu 源として調製した $Cu_2P_2O_7$-NO_3 が最も高い HCHO 収率を示した (図 1)。触媒比較、速度論解析、同位体標識実験、パルス反応実験、吸着したプローブ分子の IR 分光分析などのメカニズム検討から、(i)$Cu_2P_2O_7$ の表面格子酸素種が CH_4 と反応して HCHO を一次生成物として形成すること、(ii)$Cu_2P_2O_7$ の表面 Cu^{2+}サイトと弱塩基性リン酸ユニットが、それぞれ C–H の活性化と CO_2 への過剰酸化の抑制に重要な役割を果たすことが示唆された。

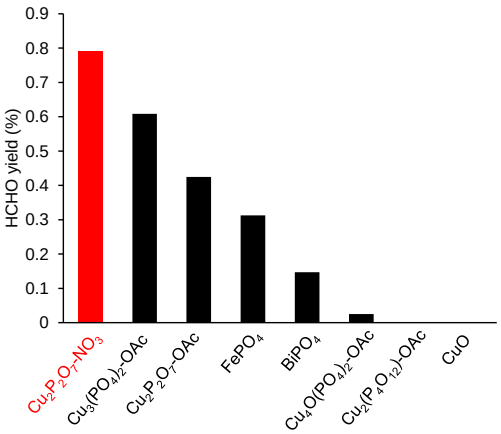

図 1　銅系触媒と各種金属リン酸塩の HCHO 収率．反応条件：50 mg, $CH_4/O_2/N_2$ (7/1/8 sccm), 550 ºC.

1) A. Matsuda, H. Tateno, K. Kamata, M. Hara, *Catal. Sci. Technol*. **2021**, *11*, 6987.
2) A. Matsuda, K. Obara, A. Ishikawa, M.-H. Tsai, C.-H Wang, Y.-C. Lin, M. Hara, K. Kamata, *Catal. Sci. Technol.* **2023**, *13*, 5180.

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ニッケルクラスターの精密合成とメタン活性化

(東工大化生研[1]・JST-ERATO[2]) ○菊地 優真[1]・森合 達也[1,2]・今岡 享稔[1,2]・山元 公寿[1,2]
Precision synthesis of nickel clusters and methane activation ([1]*Lab. Chem. Life Sci., Tokyo Tech*, [2]*JST-ERATO*) ○Yuma Kikuchi,[1] Tatsuya Moriai,[1,2] Takane Imaoka,[1,2] Kimihisa Yamamoto[1,2]

Metal clusters with a diameter of about 1 nm have unique properties such as geometric structures and reactivity depending on the atomicity due to their extremely small number of constituent atoms. However, it has been difficult to synthesize clusters precisely in large quantities using conventional gas- and liquid-phase methods. In this study, we succeeded in the precise synthesis of Ni clusters with different atomicity by the template method using the dendrimer originally developed in our laboratory. We subsequently applied the Ni clusters as the catalysts in the non-oxidation coupling reaction of methane, resulting that they demonstrated high catalytic performance due to their smallness compared to that of Ni bulk and Ni nanoparticles. Furthermore, these clusters showed the reactivity depending on the atomicity, and among them, Ni_{60} showed the lowest reaction initiation temperature.
Keywords : Clusters; Dendrimer; Catalyst; Methane; Non-Oxidative Coupling

粒径約 1 nm 程度の金属クラスターは、その構成原子数が極めて少ないことから、構成原子数に依存して幾何構造や反応性を変化させるといった特異的な性質を示す。しかしながら、クラスターを精密かつ大量に合成することは、従来の気相・液相法では困難とされてきた。そこで本研究では、当研究室が独自に開発したデンドリマーを鋳型とする手法[1)]を採用することで、核数の異なる複数の Ni クラスターの精密合成に成功した。また、これらの Ni クラスターをメタンの非酸化カップリング反応に触媒として応用したところ、Ni バルク体や Ni ナノ粒子と比較して、非常に高い活性を示した。さらに、クラスターの中でも反応性に対する核数依存性が確認され、とくに Ni_{60} では、その反応開始温度が最も低温となることが示された。

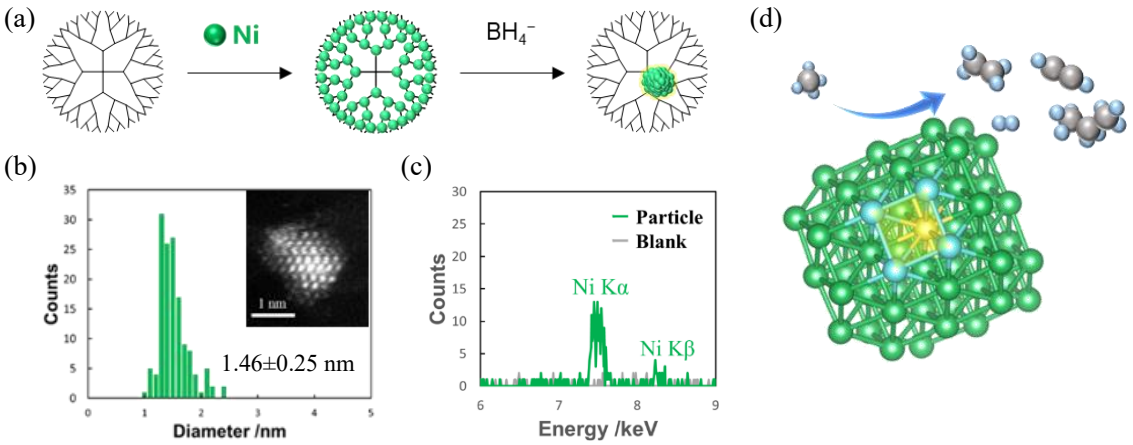

Fig. 1. (a) Synthesis scheme of Ni_{60} using the dendrimer template. (b) The histogram of a diameter of Ni_{60} on graphene. (c) EDS spectra of the sample using Ni_{60} on carbon. (d) Non-oxidation coupling reaction of methane on Ni_{60}.

1) T. Moriai et al, Angew. Chem. Int. Ed. 2020, 59, 23051-23055.

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酸化銅ナノクラスター触媒の価数制御と芳香族アルコール酸化反応への応用

（千葉大院工）○星野 航輝・原 孝佳・一國 伸之

Application of valence controlled copper oxide nanocluster catalysts for aromatic alcohol oxidation reactions. (*Chiba University*) ○Koki Hoshino, Takayoshi Hara, Nobuyuki Ichikuni

Copper, one of the base metal elements, is an attractive catalytic material from the viewpoint of abundance. Not only the nanoclusterization but also the control of the oxidation state of copper oxide is considered to be important to improve the catalysis. In this study, we attempted to control the oxidation state of copper nanocluster. Copper colloids were synthesized using PVA (polyvinyl alcohol) and hydrazine hydrate as a stabilizer and reductant, respectively. Obtained colloid was supported on SiO_2 supports, followed by washing and drying to convert into copper oxide nanocluster catalysts. The catalyst was denoted with the N_2H_4-H_2O/Cu molar ratio in parentheses as col CuO_x/SiO_2 (0.5).

XAFS analysis showed that main component of the catalyst is Cu_2O and Cu in the col CuO_x/SiO_2 (0.5) and col CuO_x/SiO_2 (5), respectively (Table 1). The acetophenone yield of 1-phenylethanol oxidation reaction on col CuO_x/SiO_2 (0.5) was the higher compared to that on col CuO_x/SiO_2 (5). Cu species in col CuO_x/SiO_2 (0.5) was oxidized into CuO during the reaction. This Cu(II) species showed less activity toward the reaction. In this reaction Cu_2O was an active species and the importance of creating Cu(I) species on the support was presented.
Keywords: Copper oxide nanocluster catalysts, Colloidal method, 1-phenylethanol oxidation reaction, XAFS

卑金属元素である銅は埋蔵量などの観点から魅力的な触媒材料である。酸化銅触媒の活性向上のため、コロイド法による銅のナノクラスター化に取り組んだが、銅の酸化状態も触媒性能に大きく影響することが知られている。本研究ではコロイド調製時の還元剤量を変えることで銅種の酸化状態制御を試みた。PVA (polyvinyl alcohol)を保護剤とし、$N_2H_4{\cdot}H_2O$ を還元剤として銅コロイドを合成し、これを SiO_2 担体に担持させ、洗浄、乾燥により酸化銅ナノクラスター触媒とした。得られた触媒は col CuO_x/SiO_2 (0.5)のように $N_2H_4{\cdot}H_2O$/Cu 比を括弧内に表記した。

col CuO_x/SiO_2 (0.5)は Cu_2O が、col CuO_x/SiO_2 (5)は Cu が主な化学種となることが XAFS 解析から明らかとなった(Table 1)。2 つの触媒を 1-フェニルエタノール酸化反応に用いた結果、col CuO_x/SiO_2 (0.5)の方が高い活性を示した。また、触媒反応後の col CuO_x/SiO_2 (0.5)は CuO へと酸化されることがわかった。この状態ではほとんど活性が見られなかった(収率 2.6 %)ことから、本反応では Cu_2O が活性種となっており、触媒上に Cu(I) を構築することの重要性が示された。

Table 1 Chemical composition and result of 1-phenylethanol oxidation.

Catalyst	Composition[a] (%)			Yield[b]
	Cu	Cu_2O	CuO	(%)
col CuO_x/SiO_2 (0.5)	0	98.7	1.3	29.4
col CuO_x/SiO_2 (5)	72.6	20.6	6.8	5.3
col CuO_x/SiO_2 (0.5)_reuse	0	13.9	86.1	2.6

a: Determined by XANES pattern fitting analysis. (Fitting range: 8970-9020 eV). b: acetophenone yield, catalyst (0.1 g), 1-phenylethanol (0.5 mmol), mesitylene (5 mL), 423 K, 6 h, O_2 atmosphere.

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水熱合成法を用いた $SrTiO_3$ への Co の組み込みとアルコール酸化反応に対する触媒活性

（千葉大院工）○青山 将大・原 孝佳・一國 伸之

Substitution of Co into $SrTiO_3$ using hydrothermal synthesis method and its catalytic activity for alcohol oxidation reaction (*Chiba University*) ○Masahiro Aoyama, Takayoshi Hara, Nobuyuki Ichikuni

In perovskite type oxides, both A and B sites can be substituted for other elements, allowing high dispersion of chemical species. Additionally, this substitution leads to unique catalytic activities such as the creation of oxygen vacancy by introducing other elements. we synthesized a catalyst in which Co is partially introduced into a perovskite type oxide, $SrTiO_3$ (STO) , by a hydrothermal method and investigated the catalytic activity of Co-STO.

Co-STO was synthesized with reference to the report by Yu et al.[1]. In 3 wt% Co-STO, XAFS analysis confirmed that all of the added Co species was doped into the B site of STO. On the other hand, in the 10 wt% Co-STO, some of the added Co was doped into the STO, but the non-doped Co species precipitated on the STO as $Co(OH)_2$, which was confirmed to be Co_3O_4 after calcination treatment. Non-doped catalysts and 3 wt% Co-STO_cal calcined at 573 K were not active in the oxidation reaction of 1-phenylethanol (Table; entries 1-3), while 10 wt% Co-STO_cal was highly active. Since imp Co/STO calcined at the same temperature showed low activity at both 3 wt% and 10 wt%, it is considered that the coexistence of Co incorporated in STO and Co_3O_4 was highly active in that reaction.

Keywords : Perovskite type oxide; Alcohol oxidation reaction; Hydrothermal synthesis method; XAFS; Cobalt oxide

ペロブスカイト型酸化物は、A, B 両サイトが他の金属と置換可能であり、高分散した化学種の設計が可能なだけでなく、価数の異なる元素の導入による酸素空孔の生成など、特異な触媒作用の発現が期待できる。本研究では、ペロブスカイト型酸化物である $SrTiO_3$ (STO)へ Co を部分的に組み込んだ触媒(Co-STO)を水熱法により合成し、その触媒作用について検討した。

Co-STO は Yu らの報告[1]を参考にして合成した。3 wt% Co-STO は、添加した Co が全て STO の B サイトに組み込まれていることが XAFS 解析から確認できた。一方 10 wt% Co-STO では、添加した一部の Co は STO 中に組み込まれているがそれ以外の Co は、$Co(OH)_2$ として STO 上に析出し、焼成処理により Co_3O_4 となることが確認された。未焼成の組み込み触媒と 3 wt% Co-STO を 573 K で焼成した 3 wt% Co-STO_cal は 1-phenylethanol の酸化反応に活性を示さなかった（Table; entries 1-3）が、10 wt% Co-STO_cal は高い活性を示した。同温度で焼成している imp Co/STO は担持量によらず活性が低いため STO 中に組み込まれた Co と、Co_3O_4 の共構造が本反応に高い活性を示したと考えられる。

Table Acetophenone yield of 1-phenylethanol oxidation reaction [a]

Entry	Catalyst	Yield (%)
1	3 wt% Co-STO	1.7
2	3 wt% Co-STO_cal	1.9
3	10 wt% Co-STO	2.8
4	10 wt% Co-STO_cal	29.7
5	imp 3 wt% Co/STO	3.2
6	imp 10 wt% Co/STO	4.4

[a] Catalyst 0.10 g, 1-phenylethanol (0.05 mmol), *p*-xylene (5 mL), O_2 atmosphere, 373 K, 6 h.

1) H. Yu, S. Ouyang, S. Yan, Z. Li, T. Yu, Z. Zou, *J. Mater. Chem.* **2011**, *21*, 11347.

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MTO 反応においてゼオライトの細孔サイズが生成物選択性およびコーク形成に及ぼす影響

(東大院工[1]・東大生研[2]・静大院工[3]) ○松下一輝[1]・小倉賢[2]・茂木堯彦[2,3]
Effect of zeolite pore size on product selectivity and coke formation in MTO reaction ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute of Industrial Science, The University of Tokyo*, [3]*Graduate School of Engineering, Shizuoka University*) ○Itsuki Matsushita,[1] Masaru Ogura,[2] Takahiko Moteki[3]

Methanol-to-olefins (MTO) reaction catalyzed by zeolite currently attracts attention as an alternative to naphtha cracking for olefin production. ZSM-5, widely used as the MTO catalyst, mainly produces propylene and other lower olefins, but also aromatic compounds as a by-product. Such aromatic by-products react up to polycyclic aromatic compounds and precipitate as coke, causing catalyst deactivation[1)]. Therefore, understanding of the coke formation mechanism over zeolite framework is critical to prolong the catalyst lifetime. In this study, the effects of zeolite pore size on product selectivity and coke formation in the MTO reaction were investigated over four types of zeolites (ZSM-5, ZSM-11, ITQ-13, and SUZ-4). Although SUZ-4 was expected to show the period of high activity among the four zeolites due to its small inner space that hinders aromatics formation, it deactivated rapidly in a short time. On the other hand, the other zeolites with a larger internal space than SUZ-4 had a better space time yield.
Keywords : Zeolite; MTO reaction; Crystal structure

固体酸として働くゼオライトを触媒とするメタノール転換オレフィン合成反応(MTO 反応)は、エネルギー消費の大きいナフサクラッキングに代わるオレフィン製造方法として現在注目を集めている。MTO 触媒として広く用いられる ZSM-5 は、プロピレンを主とする低級オレフィンを生成するが、同時に芳香族化合物を副生する。芳香族化合物は多環芳香族化合物にまで至り、コークとして析出することで触媒の失活を引き起こす[1)]。よって、触媒寿命延伸のためには、芳香族種生成を抑制するゼオライト触媒の開発が有望である。本研究では、細孔サイズの異なる 4 種類のゼオライト(ZSM-5, ZSM-11, ITQ-13, SUZ-4)を用いて触媒反応を行うことで、細孔サイズが生成物選択性およびコーク形成に及ぼす影響について調査した。

図 1 に 4 種類のゼオライト(ZSM-5, ZSM-11, ITQ-13, SUZ-4)の MTO 反応に対するメタノール転化率の経時変化を示す。内部空間が最も小さい SUZ-4 では、芳香族形成が抑制され寿命が最も長くなると予測していたが、短時間で急激に失活した。一方、内部空間が SUZ-4 よりも大きい他のゼオライトでは、いずれも空時収量が SUZ-4 より大きく優れていた。

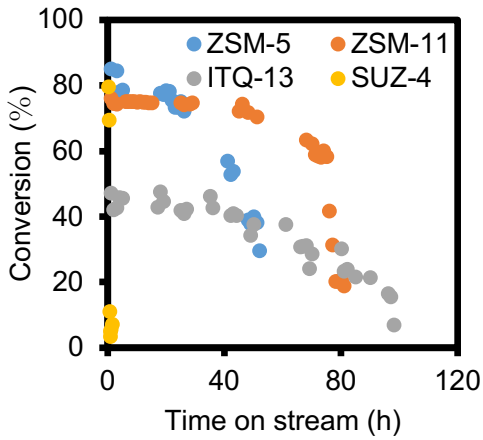

図 1　4 種類のゼオライト(ZSM-5, ZSM-11, ITQ-13, SUZ-4)の MTO 反応に対するメタノール転化率の経時変化

1) J. F. Haw et. al., *Acc. Chem. Res.*, **36**, 317 (2003)

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選択的水素化及び脱アルキル能を有する触媒による多環芳香族の単環芳香族への転換

(農工大院 BASE[1]・丸善石油化学[2])○森 涼斗[1]・佐賀 勇太[2]・神谷 憲児[1]・銭 衛華[1]

Conversion of polycyclic aromatics to monocyclic aromatics by catalysts with selective hydrogenation and dealkylation ability

([1]*Tokyo University of Agriculture and Technology*, [2]*Maruzen Petrochemical CO,LTD.*) ○Ryoto Mori,[1] Yuta Saga,[2] Kenji Kamiya,[1] Eika W. Qian[1]

The demand for petrochemical products has been increasing year by year, and the production of light cycle oil (LCO), a byproduct of petroleum refining, has also been increasing. Therefore, we aim to make effective use of LCO by converting it to monocyclic aromatics, mainly benzene, toluene, and xylene (BTX), which are basic raw materials for chemical products. The conversion to monocyclic aromatics requires three reactions: selective dearomatization, ring-opening, and dealkylation, and no catalyst has yet been developed to simultaneously satisfy these requirements in a single step[1)]. Therefore, using 1-methylnaphthalene (1-MN), a model feedstock for bicyclic aromatics, we aimed to develop functional catalysts with aromatic hydrogenation, ring-opening, and dealkylation capabilities.

Transition metal-supported catalysts were prepared on zeolite supports, and the effects of the Si/Al ratio of the zeolite, the amount of transition metal loaded, and the pretreatment method were investigated. The dispersion of metal species was improved by the addition of chelating agents. Experiments were conducted at a hydrogen pressure of 5 MPa and WHSV = 20 h^{-1}, with a conversion of 62% and BTX selectivity of 13% at 430 °C.

Keywords : Hydrogenation : Hydrocracking ; Light Cycle Oil ; BTX production ; Polycyclic aromatics

近年、石油化学製品の需要は年々増加し、石油精製での副生成物であるライトサイクルオイル(LCO)の生成も増加している。LCO は多環芳香族を多く含むため、有用な利用法が確立されていない。そこで化学製品の基礎原料である単環芳香族、主にベンゼン、トルエン、キシレン(BTX)に変換することで、LCO の有効活用を目指す。単環芳香族への変換は、多環芳香族の選択的な水素化脱芳香族、さらに開環・脱アルキル等の複数の工程が必要となり、同時に満たす触媒は未だ開発されていない[1)]。そこで、二環芳香族のモデル原料である 1-メチルナフタレン(1-MN)を用い、芳香族の水素化，開環・脱アルキル能を有する機能触媒の開発を目指した。

ゼオライト担体に、遷移金属を担持した触媒を調製し、ゼオライトの Si/Al 比、遷移金属の担持量、前処理方法の影響を検討した。また、キレート剤添加による金属種の分散度を向上させた。実験は水素圧力 5 MPa、WHSV = 20 h^{-1} で行い、430 °C では転化率 62%、BTX 選択率は 13%であった。

Table 1 キレート剤添加触媒の転化率及び選択率

反応温度［℃］	転化率［%］	BTX選択率［%］
340	34.3	1.3
370	45.5	3.8
400	53.1	7.5
430	62.4	13.3

1) Jaeuk Shin, *et al*, *Applied Catalysis A*, *General* **2017**, *547*, 12–21

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Mo/H-MFI 触媒のメタン芳香族化活性の圧力依存性と活性種の検討

（埼玉工業大）小菅 愛理・園部 裕也・倉持 健太・○有谷 博文
Study of Pressure Dependence and Characterization of Active Mo Species for Methane Dehyroaromatization over Mo/H-MFI Catalysts (*Saitama Institute of Technology*) Airi Kosuge, Yuya Sonobe, Kenta Kuramochi, ○Hirofumi Aritani

Methane dehydroaromatization is an extremely important process for direct GTL, but deactivation due to carbon precipitation on the catalyst cannot be avoided. Suppressing acid strength and/or adding a small amount of H_2 during the reaction have been studied as effective methods to suppress deactivation. In this study, the pressure dependence on reactivity for methane aromatization was evaluated to elucidate the high and durable activity on Mo/H-MFI catalysts. A relationship between effective conditions for suppressing deactivation and the active species formed was also investigated. The catalytic activity over Mo(5wt%)/H-MFI catalysts, pre-reduced with CO(2%)+Ar, was evaluated at 750°C using CH_4(20%)+H_2(2%)-Ar under 0.1 - 0.2 MPa. It is shown that both initial reactivity and suppression of deactivation were simultaneously observed with an increase in the reaction pressure. The Mo species after the reaction at 0.1 MPa was similar to α-Mo_2C. In contrast, β-Mo_2C like reductive Mo species was shown after the reaction under 0.15 MPa. It is inferred that the formation of reductive Mo species at high pressure, can be associated with high activity and high durability.
Keywords : Methane Aromatization; Mo/H-MFI; β-Mo_2C Species; Mo L-edge XANES

メタン脱水素芳香族化は極めて重要な直接 GTL プロセスであるが、炭素析出による失活が不可避であり、その抑制策が本触媒の高活性化と同時に求められる。失活抑制として酸強度抑制や反応時 H_2 微量添加等が有効であるが、本研究では反応活性の圧力依存性を検討するとともに、各圧力下での触媒活性種となる炭化モリブデン種の局所構造を Mo の L 殻 XANES より検討し、失活抑制に有効な条件と形成活性種との関連性を検討した。Mo(5wt%)/H-MFI 触媒は H-MFI(Si/Al_2=23)に MoO_2(acac)$_2$非水含浸後乾燥、600℃焼成し得た。活性評価は CO(2%)+Ar 前還元処理後、CH_4(20%)+H_2(2%)-Ar を反応ガスとした 750℃にて各圧力下での定温活性から行った。その結果、0.1~0.2 MPa 下では圧力の増大に従って初期活性の増大と失活の抑制が同時に認められた。また反応後の Mo 種は 0.1 MPa 反応後はα-Mo_2C 類似種であったのに対し、高圧側ではβ-Mo_2C へ還元的に変化した。以上より H_2 共存と併せて高圧時の還元的活性種の形成が高活性および高耐久性と関連することが推論された。

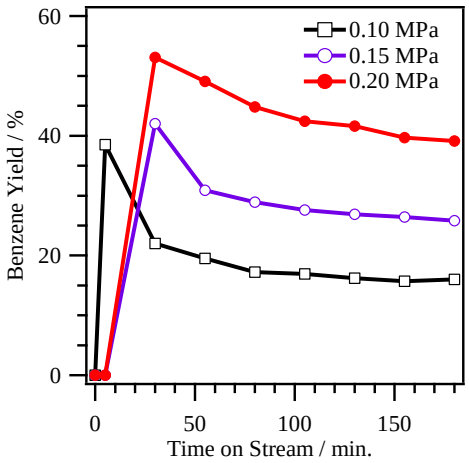

Fig. 1 Methane aromatization activity over Mo(5wt%)/H-MFI(Si/Al_2=23) at 750°C under various pressures.

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鉄錯体の光脱カルボニルによるクロスカップリング触媒の創出

（岡大院自然[1]）○山間 巧貴[1]・仁科 勇太[1]

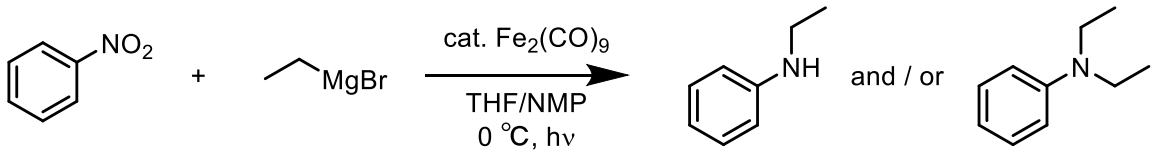
Creation of Cross-Coupling Catalysts by Photodecarbonylation of Iron Complexes

([1]*Graduate School of Natural Science and Technology, Okayama University*) ○Koki Yamama[1], Yuta Nishina[1]

Cross-coupling reactions are important reactions to form C-C, C-N, and C-O bonds, and catalysts using precious metals such as palladium are generally used. Currently, rare metal-free catalysts are required from the viewpoints of resources and safety. Therefore, we focused on iron, a transition metal with abundant resources and low toxicity. The synthesis of secondary and tertiary amines was achieved by cross coupling reactions of nitrobenzene and its derivatives with Grignard reagents through the activation of $Fe_2(CO)_9$. In addition, carbon supports with high specific surface area were investigated for the fixation of iron catalysts for recycling.

Keywords: Cross-coupling reactions, Iron catalysts, Nanocarbon materials

クロスカップリング反応は、C-C、C-N、C-O 結合を形成する重要な反応であり、一般的にパラジウムなどの貴金属を使用した触媒が用いられている。現在は、貴金属の資源問題や毒性といった観点から，レアメタルフリーな触媒が求められている。そこで，資源が豊富で毒性の低い遷移金属である鉄に着目した。光分解により配位座を空けることが可能な鉄錯体であるノナカルボニル二鉄（$Fe_2(CO)_9$）に対して LED 光を照射することで CO を脱離させて活性化し、ニトロベンゼンおよびその誘導体と Grignard 反応剤のクロスカップリング反応によって第２級および第３級アミンの合成を達成した。また、鉄触媒の固定化[1)]を目指し、高比表面積の炭素担体を検討した。



1) F. Matthew, D. Gerd, W. Wolfgang, Nano Lett. **2012**, 12, 4651

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Academic Program [Oral B] | 08. Catalysts and Catalysis：Oral B

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
A1457(1457, Bldg. 14 [5F])

[A1457-4am] 08. Catalysts and Catalysis

Chair: Kohsuke Mori, Takafumi Yatabe

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[A1457-4am-01]

Elucidation of the mechanism of melamine adsorption on Pt(111) surface via density functional theory calculations

○Kohei Tada[1], Shin-ichi Yamazaki[1], Masafumi Asahi[1], Tsutomu Ioroi[1] (1. National Institute of Advanced Industrial Science and Technology (AIST))

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[A1457-4am-02]

Hydrogen Spillover on a Non-reducible Metal Oxide by a Heteroatom Doping and its Diffusion Pathways

○Kazuki Shun[1], Kohsuke Mori[1], Takumi Kidawara[1], Hiromi Yamashita[1] (1. Graduate School of Engineering, Osaka University)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[A1457-4am-03]

Formal 1,2-Diketone Decarbonylation Enabled by Synergistic Catalysis of Lewis Acid-Base Sites and Redox Properties in CeO_2

○Takehiro Matsuyama[1], Yatabe Takafumi[1], Yamaguchi Kazuya[1] (1. The University of Tokyo)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

Break

Japanese
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC
[A1457-4am-04]

Subnanometer Copper Nanoparticles for Oxidative Catalysis

○Makoto Tanabe[1], Kazutaka Sonobe[2], Kimihisa Yamamoto[2] (1. Fukushima Medical Univ., 2. Tokyo Inst. of Tech., Lab. Chem. Life Sci.)

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[A1457-4am-05]

Structural Characterization during the Low Temperature Redox Reaction of Copper and Ruthenium Incorporated Ceria for Ammoxidation

○Chaoqi CHEN[1], Satoshi Muratsugu[1], Mizuki Tada[1,2] (1. Nagoya Univ., 2. RCMS, Nagoya Univ.)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[A1457-4am-06]

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Analysis of factors affecting the NH_3 synthesis activity of Ru-Ce based catalysts

○Yoshihiro Goto[1], Masashi Kikugawa[1], Kiyoshi Yamazaki[1], Akinori Sato[2], Yuichi Manaka[3], Tetsuya Nanba[3], Hideyuki Matsumoto[4], Shinichi Ookawara[4] (1. Toyota central R&D labs., Inc., 2. Toyota Motor Corporation, 3. National Institute of Advanced Industrial Science and Technology, 4. Tokyo Institute of Technology)

English

11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[A1457-4am-07]

Size-controlled synthesis of CuFe, CuRu alloy nanoparticle catalysts for electrochemical nitrogen reduction reaction

○Kaichao Zhang[1], Takehiko Sasaki[1] (1. Graduate School of Science, The University of Tokyo)

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本講演の予稿原稿は、当日の発表内容と異なることが判明したため、講演発表後に差し替えを行いました（2024年10月8日）。

なお差し替え前の原稿は、次の通りです。
「表面場を用いた開殻分子のジラジカル性変調に関する理論検討　○多田 幸平[1]、川上 貴資[2]、日沼 洋陽[1] (1.産総研、2.大阪大理)」

密度汎関数理論計算を用いた白金(111)によるメラミン吸着機構の解明

（産総研 [1]）○多田 幸平 [1]・山崎 眞一 [1]・朝日 将史 [1]・五百蔵 勉 [1]

Elucidation of the mechanism of melamine adsorption on Pt(111) surface via density functional theory calculations ([1]*AIST*) ○Kohei Tada,[1] Shin-ichi Yamazaki,[1] Masafumi Asahi,[1] Tsutomu Ioroi[1]

Improving the oxygen reduction reaction activity (ORR activity) of Pt catalysts in polymer electrolyte fuel cells (PEFCs) is important to reduce the amount of Pt used. It has been found that the ORR activity is improved by adsorption of molecules such as melamine and tetraazaporphyrins on the Pt surface. However, in the enhancement of ORR activity using such molecules, over-adsorption of the molecules by the Pt surface significantly reduces the ORR activity. Therefore, it is important to adjust the amount of adsorbed molecules, but it is unclear how the molecules with the ORR activity enhancing effect are adsorbed on the Pt surface. We then performed density functional theory (DFT) calculations using more than 10,000 adsorption models and elucidated the adsorption mechanism of melamine/Pt (111).
Keywords :　PEFC; ORR activity; Pt catalyst; Melamine; DFT calculation

固体高分子形燃料電池（PEFC）における白金触媒の酸素還元反応活性（ORR 活性）の向上は、白金使用量を減らすうえで重要である。メラミンやテトラアザポルフィリンといった分子を白金表面へ吸着させることで ORR 活性が向上することが見出された [1,2]。一方で、このような分子を用いた ORR 活性向上においては、触媒である白金表面による分子の過剰吸着が ORR 活性を著しく低下させる。そのため、吸着量や溶液中の分子濃度の調整が重要となるが、ORR 活性向上効果を持つ分子が白金表面にどのように吸着されるかはわかっていなかった。

我々は１万構造を超える吸着モデルに対して密度汎関数理論計算（DFT 計算）を実行し、メラミン/白金(111)の吸着メカニズムを解明した [3]。メラミンは 2 つの N で白金に配位する形で傾いて吸着され、吸着構造の安定性は共鳴構造によって説明された。この結果は、「トリアジン環に対して、電子供与性の置換基が複数ついた分子」に ORR 活性向上効果があり、「置換基の電子供与性の強弱で吸着力を制御可能」であることを示すものである。実際に、アミノ基をより電子供与性の低い置換基にすることで ORR 活性向上効果が得られる濃度範囲が拡張した [4]。

1) S. Yamazaki, M. Asahi, T. Ioroi, *Electrochim. Acta*, **2019**, *297*, 725
2) M. Asahi, S. Yamazaki, N. Taguchi, T. Ioroi, *J. Electrochem. Soc.*, **2019**, *166*, F498
3) K. Tada, S. Yamazaki, M. Asahi, T. Ioroi, *Phys. Chem. Chem. Phys.*, **2023**, *25*, 23047
4) S. Yamazaki, M. Asahi, N. Taguchi, T. Ioroi, *Electrochimica Acta*, **2023**, *472*, 143417

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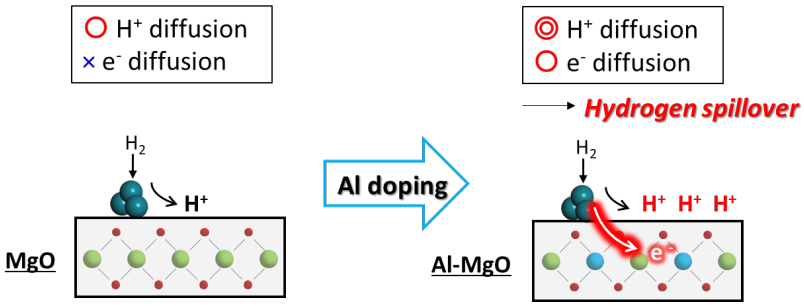
Hydrogen Spillover on a Non-reducible Metal Oxide by a Heteroatom Doping and its Diffusion Pathways

([1]*Graduate School of Engineering, Osaka University*)
○Kazuki Shun,[1] Kohsuke Mori,[1] Takumi Kidawara,[1] Hiromi Yamashita[1]
Keywords: Hydrogen Spillover; Non-reducible Metal Oxide; Heteroatom Doping

The hydrogen spillover, a concomitant diffusion of proton (H^+) and electron (e^-), is a phenomenon enabling the solidification of gaseous H_2 into dynamic and reactive hydrogen species and expected to be a new hydrogen handling technology.[1] It is known that its occurrence requires the redox of cations and therefore is limited to on reducible metal oxides composed of rare elements, which prevents the development of technologies using hydrogen spillover.[2] Based on this consideration, non-reducible metal oxides, such as MgO and Al_2O_3, are suitable platforms because their components are only ubiquitous elements. However, only H^+ can diffuse over such metal oxides because their metal cations prohibit the conduction of e^- due to low reducibility, which significantly decreases migration distance and reactivity of spilled hydrogen.[3] Stated differently, the creation of materials with such ubiquitous elements that displays superior hydrogen spillover ability will provide a new way of handing hydrogen.

In the present work, we firstly report that Al doped MgO (Al-MgO) composed of only ubiquitous elements exhibits excellent hydrogen spillover performance. Al-MgO stored a 0.29 wt% of H^+, which was more than 3.1 times higher than not only MgO but also a number of typical reducible metal oxides composed of rare elements. Surprisingly, Al-MgO allowed concurrent H^+ and e^- diffusion as hydrogen spillover on reducible metal oxides even though Mg^{2+} and Al^{3+} are both originally irreducible. The diffusion pathways of H^+ and e^- evolved within Al-MgO were comprehensively studied by the systematic characterizations, thermodynamical analysis, and theorical calculations. Furthermore, hydrogen spillover on Al-MgO significantly accelerated the catalysis of Ni during CO_2 hydrogenation reaction.



1) K. Shun, K. Mori, S. Masuda, N. Hashimoto, Y. Hinuma, H. Kobayashi, H. Yamashita, *Chem. Sci.* **2022**, 13, 8137. 2) R. Prins, *Chem. Rev.* **2012**, 112, 2714. 3) W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, J. Bokhoven, *Nature*, **2017**, 541, 68.

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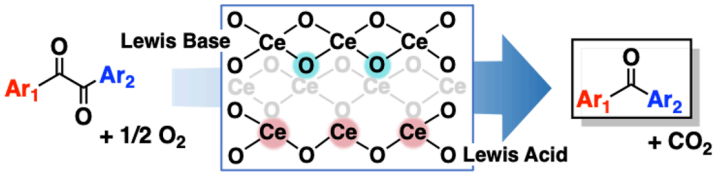
Formal 1,2-Diketone Decarbonylation Enabled by Synergistic Catalysis of Lewis Acid-Base Sites and Redox Properties in CeO_2

([1]*School of Engineering, The University of Tokyo*) ○Takehiro Matsuyama,[1] Takafumi Yatabe,[1] Kazuya Yamaguchi[1]

Keywords: Ceria; Formal Decarbonylation; 1,2-Diketones; Heterogeneous Catalysts; Synergistic Catalysis

Diaryl ketone is an essential moiety widely seen in various chemistry fields.[1)] In recent years, diaryl ketone synthesis via 1,2-diketones has attracted much attention because 1,2-diketones can be synthesized from various starting materials including ketones, aldehydes, alkynes, and alkenes. However, there are some problems in reported diaryl ketone synthesis via 1,2-diketones; decarbonylation of 1,2-diketones via oxidative addition have difficulty in selectivity control due to double-decarbonylation to afford biaryls,[2)] and formal decarbonylation via benzilic acid rearrangement, which enables highly selective molecular transformations, required stoichiometric amounts of bases and anilines.[3)]

In this study, we have developed CeO_2-catalyzed formal decarbonylation of different diaryl 1,2-diketones to afford diaryl ketones with no additives by using O_2 as the terminal oxidant. A series of control experiments combined with catalyst characterization revealed that the present formal decarbonylation was achieved by the synergistic catalysis of CeO_2: Lewis acid–base pairs synergistically catalyzed efficient benzilic acid rearrangement followed by aerobic oxidative decarboxylation via redox of CeO_2. This system exhibited wide substrate scope and was applicable to the decarbonylation of *ortho*-substituted and halogenated 1,2-diketones, which could not be performed using our previous decarbonylation via oxidative addition.[2)] The catalyst proved to function as a heterogeneous catalyst and could be reused several times. In this presentation, we will discuss the synergistic catalysis of CeO_2 for the formal 1,2-diketone decarbonylation in detail based on the thorough catalyst characterization and control experiments.



✓ formal diaryl 1,2-diketone decarbonylation catalyzed by CeO_2
✓ synergistic Lewis acid–base and redox properties

1) M. L. N. Rao, B. S. Ramakrishna, *Eur. J. Org. Chem*. **2017**, *2017*, 5080. 2) T. Matsuyama, T. Yatabe, T. Yabe, K. Yamaguchi, *ACS Catal.* **2022**, *12*, 13600. 3) a) A. Maji, S. Rana, Akanksha, D. Maiti, *Angew. Chem. Int. Ed*. **2014**, *53*, 2428. b) X. Wang, R.-X. Chen, Z.-F. Wei, C.-Y. Zhang, H.-Y. Tu, A.-D. Zhang, *J. Org. Chem.* **2016**, *81*, 238. c) X. Li, W. Huang, D. Liang, L. Yuan, Y. Ma, L. Gu, *Tetrahedron* **2015**, *71*, 1045. d) L. Gu, H. Zhang, *RSC Adv*. **2015**, *5*, 690.

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酸化銅サブナノ粒子の酸化触媒機能

(福島県医大[1]・東工大化生研[2]) ○田辺 真[1]・園部 量崇[2]・山元 公寿[2]
Subnanometer Copper Nanoparticles for Oxidative Catalysis ([1]*Fukushima Medical University,* [2]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○Makoto Tanabe,[1] Kazutaka Sonobe,[2] Kimihisa Yamamoto[2]

Subnanoparticles (SNPs) with sizes of ~1 nm are attractive for enhancing the catalytic performance of transition metals and their oxides. Copper-based SNPs particularly have been focused on activating hydrocarbons at low temperatures. However, the electronic states and the geometric structures of copper oxide SNPs are still a subject of debate in terms of their redox properties during oxidation reactions for hydrocarbons. Herein, *in situ* X-ray absorption fine structure (XAFS) measurements of $Cu_{28}O_x$ SNPs, which were prepared using a dendritic phenylazomethine template, during temperature-programmed reduction (TPR) with H_2 achieved lowering of the temperature reported thus far for the Cu(II)→Cu(I) reduction reaction because of Cu–O bond elongation in the ultrasmall copper oxide particles. Methane activation was also achieved by $Cu_{28}O_x$ SNPs under mild conditions. These results highlight the mineralized local structures in the copper oxide SNPs induce the generation of active oxygen species by their atomic configurations.

Keywords: Nanoparticles, Copper, H_2 reduction, Methane activation, Dendrimer

約 1 nm サイズのサブナノ粒子は、ナノ粒子とは異なる幾何構造や電子状態を示すため、それらを活かした触媒反応が注目されている。近年では、元素代替の概念から貴金属より安価な銅を用いた触媒開発が注目されている。しかしながら、サブナノ粒子の反応性が向上する構造的要因は議論されている。本研究では、XAFS 法を用いて酸化銅サブナノ粒子 $Cu_{28}O_x$ の構造解析をおこない、その知見を基に酸素分子を酸化剤とするメタン酸化反応を検討した。既報に応じて、フェニルアゾメチンデンドリマーDPA を鋳型とし、原子数が規定された不均一系触媒 $Cu_{28}O_x/SiO_2$ を合成した[1]。$Cu_{28}O_x/SiO_2$ の H_2 TPR における *in situ* XAFS 測定結果、Cu(II)→Cu(I)への還元温度の低下が観察された (図 1 左)[2]。$Cu_{28}O_x/SiO_2$ に対して CH_4 と O_2 の混合ガス雰囲気下 (1.8 MPa)、110 °C で MeOH と HCO_2H を生成する低温メタン酸化が達成された (図 1 右)[3]。

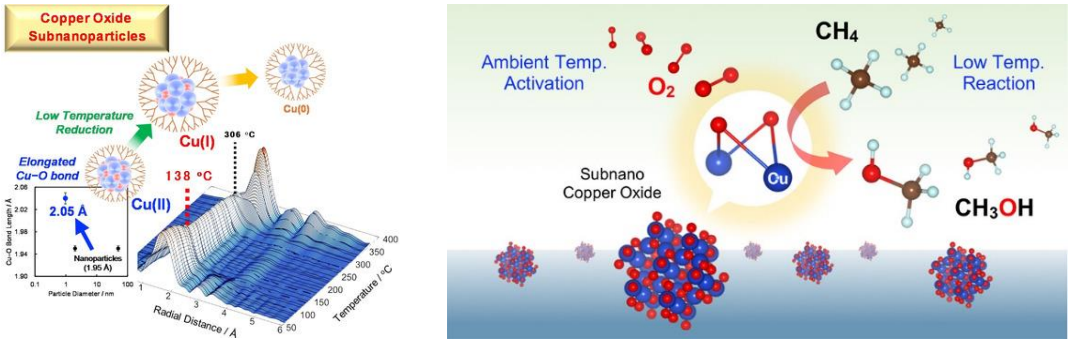

図 1 $Cu_{28}O_x/SiO_2$ による水素還元反応(左)およびメタン酸化反応(右)の概念図

1) Sonobe, K.; Tanabe, M.; Yamamoto, K. *ACS Nano* **2020**, *14*, 1804. 2) Sonobe, K.; Tanabe, M.; Imaoka, T.; Chun, W.-J.; Yamamoto, K. *Chem. Eur. J.* **2021**, *27*, 8452. 3) Sonobe, K.; Tanabe, M.; Imaoka, T.; Chun, W.-J.; Ida, Y.; Kuzume, A.; Yamamoto, K. *ACS Appl. Nano Mater.* **2023**, *in press.*

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Structural Characterization during the Low Temperature Redox Reaction of Copper and Ruthenium Incorporated Ceria for Ammoxidation

([1]*Graduate School of Science, Nagoya University*, [2]*Research Center for Materials Science (RCMS), Nagoya University*) ○Chaoqi Chen,[1] Satoshi Muratsugu,[1] Mizuki Tada[1,2]

Keywords: Mixed metal ceria; Redox property; Ammoxidation; Copper, Ruthenium

We reported mixed metal ceria with the incorporation of Cu and the trace amount of Ru (denoted as $Cu_{0.18}Ru_{0.05}CeO_z$) with remarkable redox property and catalytic performances toward the ammoxidation of benzyl alcohol.[1] The structural characterization of $Cu_{0.18}Ru_{0.05}CeO_z$ was fully investigated during the redox process and the catalysis to clarify the structural changes in each metal species in the mixed oxide catalyst.

$Cu_{0.18}Ru_{0.05}CeO_z$ was prepared by a hydrothermal method, and its structure was characterized by XRD, TEM, XAFS and XPS; the Cu^{2+} oxide and Ru^{n+} ($4 < n < 6$) oxide nanodomains were found to be finely dispersed over the bulk ceria. $Cu_{0.18}Ru_{0.05}CeO_z$ showed remarkable redox performance below 523 K (**Figure 1(A)**) with 2.38 mmol g^{-1} H_2 consumption. Ru *K*-edge, Cu *K*-edge and Ce L_{III}-edge XANES during H_2 TPR clearly showed that all the metal species were reduced; Ru species was initially reduced and after that both Cu and Ce species were subsequently reduced (**Figure 1(B,C,D)**). In addition, the Ru *K*-edge and Cu *K*-edge EXAFS of $Cu_{0.18}Ru_{0.05}CeO_z$ after the reduction with H_2 newly showed Ru-Ru and Cu-Cu bonds, respectively, indicating the formation of both Ru and Cu nanoclusters on the reduced ceria surface. When reduced $Cu_{0.18}Ru_{0.05}CeO_z$ was reacted with O_2, the average oxidation states of all metal species were almost recovered to the original values, and Ru-O and Cu-O bonds regenerated after the oxidation with O_2. It is to be noted that the reduction temperature of $Cu_{0.18}Ru_{0.05}CeO_z$ was slightly decreased from the 2nd redox cycles, and it became steady up to 4th redox cycle below 523 K. The onset temperature of the oxidation state changes in the XANES spectra was also decreased. The detailed relationship between the catalyst structure and the redox and catalytic ammoxidation performances of $Cu_{0.18}Ru_{0.05}CeO_z$ after H_2 reduction and O_2 oxidation will also be discussed.

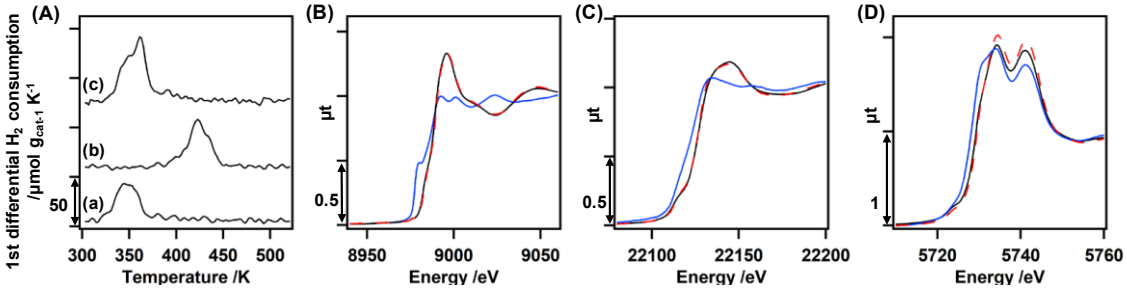

Figure 1. (A) The redox performances of (a) $Ru_{0.04}CeO_z$ (b)$Cu_{0.18}CeO_z$ and (c) $Cu_{0.18}Ru_{0.05}CeO_z$ below 523 K. XANES spectra of (B) Cu *K*-edge (C) Ru *K*-edge and (D) Ce L_{III}-edge. Black line: as-prepared $Cu_{0.18}Ru_{0.05}CeO_z$, blue line: after temperature programmed reduction with H_2, red dash line: after temperature programmed oxidation with O_2.

[1] Chen, C. et al. The 102nd CSJ Annual Meeting, **2022**, B304-1am-02.

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Ru-Ce 系触媒の NH_3 合成活性に影響を与える因子の解明

(豊田中研[1]・トヨタ自動車[2]・産総研[3]・東工大[4]) ○後藤 能宏[1]・菊川 将嗣[1]・山崎 清[1]・佐藤 彰倫[2]・眞中 雄一[3]・難波 哲哉[3]・松本 秀行[4]・大川原 真一[4]

Analysis of factors affecting the NH_3 synthesis activity of Ru-Ce based catalysts ([1] *Toyota Central R&D Labs., Inc.*, [2] *Toyota Motor Corporation*, [3] *Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology*, [4] *Chemical Science and Engineering, Tokyo Institute of Technology*) ○Yoshihiro Goto,[1] Masashi Kikugawa,[1] Kiyoshi Yamazaki,[1] Akinori Sato,[2] Yuichi Manaka,[3] Tetsuya Nanba,[3] Hideyuki Matsumoto,[4] Shinichi Ookawara[4]

Ammonia (NH_3) has recently attracted attention owing to its applicability as a H_2 carrier or fuel; thus, the development of both catalysts and reaction systems that allow the synthesis of NH_3 under mild conditions is desired. Although Ru-Ce catalysts[1)] are reported to show high NH_3 synthesis activity at lower pressure, the factors affecting their activity require further discussion (Fig. 1). We present here the investigation of $Ru/Ce_{1-x}Pr_xO_\delta$[2)], $Ru/Ce_{0.5}La_{0.5-x}A_xO_\delta$ (A = Ti, Si)[3)], and $Ru/BO_x/CeO_2$ (B = Si, Zr, Mg) catalysts. The valence of Ru and the pore volumes of the support oxides dominantly affected the NH_3 synthesis activity. Moreover, controlling H/N ratios in feed gases was effective in suppressing hydrogen poisoning that inhibits the activity of Ru catalysts.

Keywords : Ammonia synthesis; Ru catalyst; Ceria; H/N ratio control; Hydrogen carrier

アンモニア(NH_3)は農業用肥料や化成品の合成に必須な原料であり、工業的には Fe 系触媒を用いたハーバーボッシュ法により高圧下(20–30 MPa)で合成される。近年は水素キャリアや燃料としての利用に注目が集まっており、より低圧で NH_3 を合成できる触媒の開発と触媒の特性を活かした反応システムの構築の両方が望まれる。

低圧(10 MPa 以下)で高い NH_3 合成活性を示しかつ安定性の高い触媒として、Ce 系酸化物に Ru を担持した Ru-Ce 触媒[1)]が報告されているが、その活性に寄与する要因は不明な部分が多い(Fig. 1)。本研究では、Ru-Ce 触媒として開発した $Ru/Ce_{1-x}Pr_xO_\delta$[2)]、$Ru/Ce_{0.5}La_{0.5-x}A_xO_\delta$ (A = Ti, Si)[3)]、および $Ru/BO_x/CeO_2$ (B = Si, Zr, Mg)の状態解析から、NH_3 合成活性には Ce 還元状態よりも Ru 還元状態および担体の細孔構造が大きく寄与することが分かった。また反応ガス中の H/N 比制御により、Ru 触媒に固有な水素被毒という活性低下現象を抑制でき、NH_3 合成活性を向上できた。これらの観点から開発した触媒と反応システムにより、我々は低圧での NH_3 合成（8 MPa, 1 kg day^{-1}）をデモプラントで実証した。当日の発表では、検討触媒の in-situ 状態解析、並びに反応条件が NH_3 合成活性に与える影響を中心に、Ru-Ce 触媒の性質について報告する。

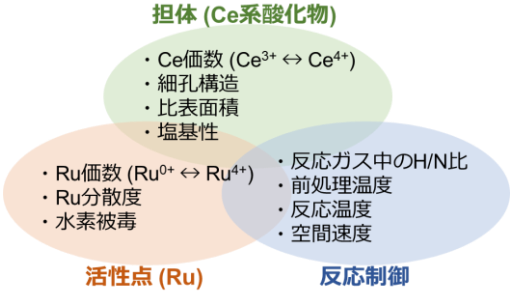

Fig. 1 Ru-Ce 触媒の NH_3 合成活性に影響を与える因子

1) Y. Ogura, et al., *Chem. Sci.*, **2018**, *9*, 2230; 2) M. Kikugawa, et al., *J. Catal.*, **2022**, *413*, 934. 3) Y. Goto, et al. *Chem. Commun.*, 2022, *58*, 3210.

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Size-controlled synthesis of CuFe, CuRu alloy nanoparticle catalysts for electrochemical nitrogen reduction reaction

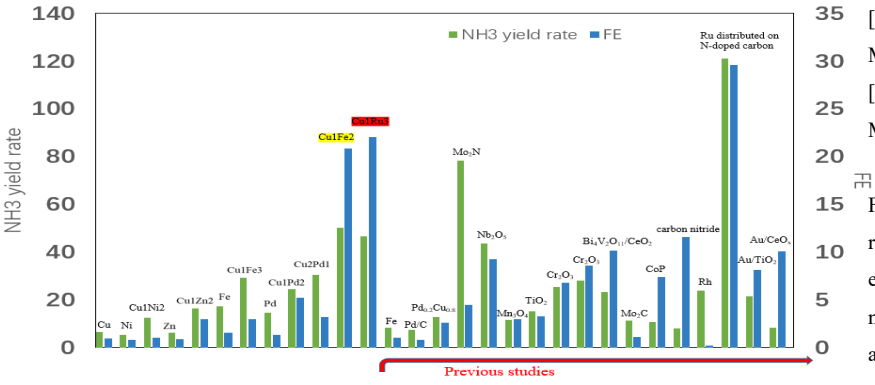
([1]*Graduate School of Science, The University of Tokyo*) ○Kaichao Zhang[1], Takehiko Sasaki[1]

Keywords: alloy nanoparticle, ammonia synthesis, N_2RR, Faradaic efficiency

To enhance catalytic activity and selectivity and investigate the effect of nanoparticle size on catalytic performance, in this study, CuFe, CuRu alloy nanoparticles were synthesized and used for electrochemical nitrogen reduction reaction. As to synthesis of alloy nanoparticles, a typical precursor solution was prepared by mixing metal chlorides in deionized water. Surfactant CTAB was added at different concentrations to control nanoparticle size. PH of the solution was adjusted with NaOH. Then, $N_2H_4 \cdot H_2O$ was added slowly with stirring. The obtained solution was transferred into Teflon autoclave and heated. After cooling down to room temperature, the solid product was filtered, washed and dried to yield a powder. Synthesized catalyst and Nafion solution were dispersed in a solution containing ethanol and water. After forming a homogeneous ink through sonicating, catalyst ink was loaded onto a carbon paper and dried under ambient condition.

A three-electrode configuration (working electrode: prepared catalyst electrode; counter electrode: Pt wire; reference electrode: Ag/AgCl) was used in an H-type electrochemical cell. Each compartment was filled with 0.1 M Na_2SO_4 aqueous solution. N_2 gas was bubbled into the chamber before and during the measurement. LSV (linear sweep voltammetry), CA (Chronoamperometry) and CV (cyclic voltammetry) were tested. After reduction, working electrode-side electrolyte was collected for the indophenol blue method with UV-Vis measurements for determination of produced ammonia. Catalysts were characterized with EXAFS, XRD and TEM.

Compared with previous studies, as shown in Fig.1, Cu_1Fe_2 achieved the Faradaic efficiency (20.81%) and the ammonia yield rate (50.18 μg $mg^{-1}cat.\ h^{-1}$), which is better than the previous study (2.94% and 29.13 μg $mg^{-1}cat.\ h^{-1}$). [1] With Cu_1Ru_3, the Faradaic efficiency (22.06%) and the ammonia yield rate (46.52 μg $mg^{-1}cat.\ h^{-1}$) were obtained, which are also superior to the previous study. [2] It was also discovered that the smaller alloy nanoparticles exhibited better catalytic performances.



[1] X. Wang et al., Adv. Mater., 2020, 32, 2004382.
[2] C. Kim et al., Adv. Mater., 2022, 34, 2205270.

Fig1. Ammonia formation rate and Faradaic efficiency for synthesized nanoalloy catalysts in this and previous research

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Academic Program [Oral B] | 08. Catalysts and Catalysis：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC A1458(1458, Bldg. 14 [5F])

[A1458-4pm] 08. Catalysts and Catalysis

Chair: Hajime Suzuki, Tsuyoshi Takata

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[A1458-4pm-01]

Development of a Photoelectrochemical Cell Utilizing a Sulvanite-type Black Metal Sulfide Photocathode for Solar CO_2 Reduction to Produce a Green Syngas

○Kengo Nagatsuka[1], Yuichi Yamaguchi[1,2], Akihiko Kudo[1,2] (1. Tokyo Univ. of Science, 2. CVRC, RIST TUS)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[A1458-4pm-02]

Addition effect of Os(II) complex photosensitizers on hybrid CO2 reduction photocatalysts of Ru(II)-Re(I) and C3N4

○Toshiya Tanaka[1], Yusuke Tamaki[2], Kazuhiko Maeda[1], Osamu Ishitani[1,3] (1. Tokyo Institute of technology, 2. National Institute of Advanced Industrial Science and Technology, 3. Grad. Sch. of Adv. Sci. and Eng., Hiroshima Univ.)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[A1458-4pm-03]

Hybrid photocatalyst prepared via photo-reductive polymerization for site-selective introduction of CO_2 reduction active sites onto a semiconductor

○Noritaka Sakakibara[1], Ewan McQueen[2], Reiner Sebastian Sprick[2], Osamu Ishitani[1,3] (1. Tokyo Tech., 2. Univ. of Strathclyde, 3. Hiroshima Univ.)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[A1458-4pm-04]

CO_2 electrochemical reduction over thermal non-equilibrium intermetallic compounds synthesized by electrolysis

○Tatsuya Koubayashi[1], Soichi Kikkawa[1], tsuyashi watanabe[2], tetsuo honma[2], seiji yamazoe[1] (1. Tokyo Metropolitan University, 2. JASRI)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[A1458-4pm-05]

High-Rate CO_2 Reduction Reactions with a Current Density Exceeding 1 A/cm^2

○Kazuhide Kamiya[1], Asato Inoue[1], Tengyi Liu[1], Takashi Harada[1], Shuji Nakanishi[1] (1. Osaka Univ.)

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English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[A1458-4pm-06]
Systematic Control of Electrochemical CO_2 Reduction Reaction Performances on Cu Nanocube by Surface Alloying with M (M=Pd, Pt, Ir, Ru)
○Hirokazu Kobayashi[1], Sachie Hikino[1], Miho Yamauchi[1,2,3,4] (1. K-NETs, Kyushu Univ., 2. IMCE, Kyushu Univ., 3. WPI-I2CNER, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ.)

English
3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC
[A1458-4pm-07]
Highly durable Ni-based self-catalytic reactor for CO_2 methanation designed by metal 3D printing combined and selective electrochemical dissolution
○HYOJIN KIM[1], Kohsuke Mori[1], Takayoshi Nakano[1], Hiromi Yamashita[1] (1. Osaka University)

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Development of a Photoelectrochemical Cell Utilizing a Sulvanite-type Black Metal Sulfide Photocathode for CO_2 Reduction to Produce a Green Syngas

([1]*Faculty of Science, Tokyo University of Science*, [2]*Carbon Value Research Center, Research Institute for Science and Technology, Tokyo University of Science*) ○Kengo Nagatsuka,[1] Yuichi Yamaguchi,[1,2] Akihiko Kudo[1,2]

Keywords: Metal Sulfide; Photocathode; CO_2 Reduction; Water as an Electron Donor; Whole Range of Visible Light

Photoelectrochemical solar CO_2 reduction in water is a worthwhile CCU technology because this reaction produces a mixture of H_2 and CO gases, so called "green syngas." We have reported a variety of visible light-driven Cu(I)-containing metal sulfide photocathodes which directly reduce CO_2 to form CO.[1] Additionally, we have reported that a powder-based Cu_3VS_4 photocathode with a sulvanite structure was active for solar hydrogen production.[2] This material is a Cu(I)-containing black metal sulfide which can utilize the whole range of visible light. Therefore, the photocathode is expected to be also active for CO_2 reduction. In the present study, we demonstrated photoelectrochemical CO_2 reduction under visible light and simulated sunlight using a Cu_3VS_4 black photocathode to form a green syngas.

A powder-based Cu_3VS_4 photocathode was fabricated by a particle transfer method deposited with an Au layer[1, 3], and an Au cocatalyst was loaded on the photocathode. Fisrt, photoelectrochemical CO_2 reduction under visible light irradiation using the black photocathode was carried out. As a result, a green syngas evolved, giving almost 100% of total faraday efficiency (Fig. 1). During the reaction, 24% of a selectivity was obtained for CO formation from an aqueous $KHCO_3$ solution without any organic solvents. Notably, it was revealed by an action spectrum that the black metal sulfide photocathode utilized visible light up to 820 nm. Furthermore, solar CO_2 reduction utilizing a photoelectrochemical cell consisting of the Cu_3VS_4 photocathode and a $BiVO_4$:Mo photoanode was successfully achieved under simulated sunlight irradiation at 1.0 V. This reaction proceeded even without a pH adjustment at ambient conditions. The ratio of reacted electrons to holes was unity, indicating that the CO_2 reduction reaction proceeded using water as an electron donor.

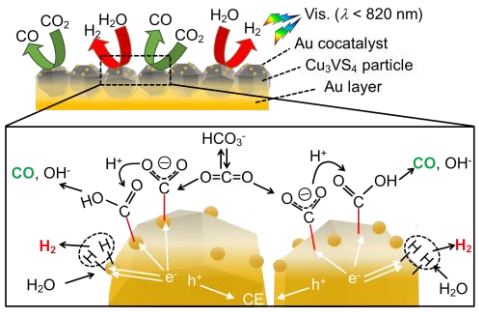

Fig. 1 Schematic illustration of photoelectrochemical CO_2 reduction using a powder-based Cu_3VS_4 photocathode.

1) S. Yoshino, T. Takayama, Y. Yamaguchi, A. Iwase, A. Kudo, *Acc. Chem. Res.* **2022**, *55*, 966. 2) H. Fukai, K. Nagatsuka, Y. Yamaguchi, A. Iwase, A. Kudo, *ECS J. Solid State Sci. Technol.* **2022**, *11*, 063002. 3) T. Minegishi, N. Nishimura. J. Kubota, K. Domen, *Chem. Sci.* **2013**, *4*, 1120.

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Addition effect of Os(II) complex photosensitizers on hybrid CO_2 reduction photocatalysts of Ru(II)-Re(I) and C_3N_4

([1] *School of Science, Tokyo Institute of Technology*, [2] *National Institute of Advanced Industrial Science and Technology,* [3] *Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Toshiya Tanaka,[1] Yusuke Tamaki,[2] Kazuhiko Maeda,[1] Osamu Ishitani[1, 3]

Keywords: hybrid photocatalyst, CO_2 reduction, Os(II) complex photosensitizer

The supramolecular photocatalyst (**RuRe** of Figure 1) consisting of photosensitizer of Ru tris-diimine complex and $[Re(CO)_3(dmb)(L)]^{n+}$ of CO_2 reduction catalyst can reduce CO_2 to CO with high selectively (dmb = dimethylbipyridine). The hybrid photocatalyst of **RuRe**/TiO_2/C_3N_4 which constructed with this supramolecular photocatalyst and semiconductor of TiO_2/C_3N_4 with strong photo-oxidative power can reduce CO_2 by triethanolamine (TEOA) as a reductant.[1] However, this hybrid photocatalyst had a problem of low durability.

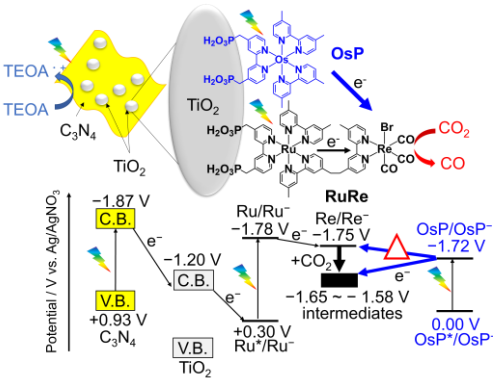

Figure 1 the structure of **OsP**+**RuRe**/TiO_2/C_3N_4 and predicted photo-electron transfer.

Therefore, in this study, we developed a new system that Os(II) complex photosensitizers (**OsP**), which absorb longer wavelength photons than Ru(II) photosensitizers, additionally introduced around **RuRe** in **RuRe**/TiO_2/C_3N_4 (Figure 1). It is reported that Re(I) catalyst becomes intermediates by reaction with CO_2 after receiving an electron.[2] Therefore, the **OsP** can supply the second electron to these intermediates. The durability of photocatalytic reaction in **OsP**+**RuRe**/TiO_2/C_3N_4 was improved, compared with that of **RuRe**/TiO_2/C_3N_4 (Figure 2), and the turnover number (TON) of evolved CO was increased from 120±26 to 223±30 after irradiating 48 h (TON was calculated based on adsorbed **RuRe**). The addition effects of irradiation of longer wavelength will be also reported in this presentation.

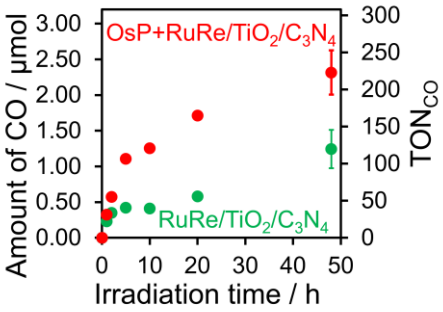

Figure 2 Time course of CO formation during the photocatalytic reduction under CO_2 in **RuRe**/TiO_2/C_3N_4 and **OsP**+**RuRe**/TiO_2/C_3N_4.

1) M. Shizuno, K. Kato, S. Nishioka, T. Kanazawa, D. Saito, S. Nozawa, A. Yamakata, O. Ishitani, K. Maeda, *ACS Appl. Energy Mater*. **2022**, *5*, 9479. 2) M. Takahashi, T. Asatani, T. Morimoto, Y. Kamakura, K. Fujii, M. Yashima, N. Hosokawa, Y. Tamaki, O. Ishitani, *Chem. Sci.* **2023**, *14*, 691.

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半導体表面への位置選択的な CO_2 還元反応活性点の設計を指向した、光還元重合によるハイブリッド光触媒の開発

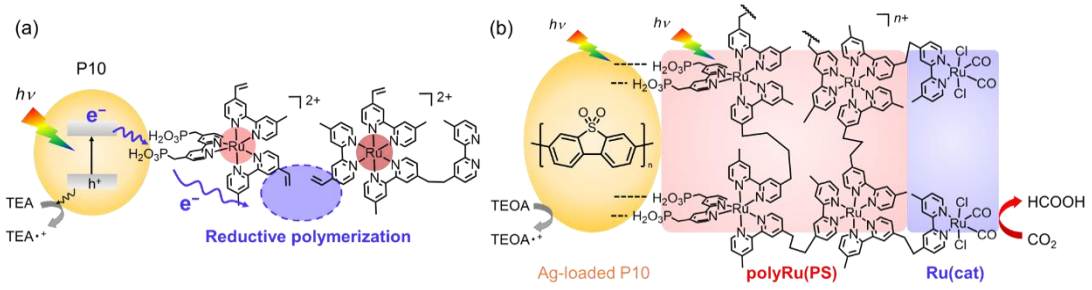
（東工大理 [1]・ストラスクライド大 [2]・広島大院先進理工 [3]）○榊原 教貴 [1]・Ewan McQueen[2]・Sebastian Sprick[2]・石谷 治 [1, 3]

Hybrid photocatalyst prepared via photo-reductive polymerization for site-selective introduction of CO_2 reduction active sites onto a semiconductor ([1]*Tokyo Tech.*, [2]*Univ. of Strathclyde*, [3]*Hiroshima Univ.*) ○Noritaka Sakakibara,[1] Ewan McQueen,[2] Sebastian Sprick,[2] Osamu Ishitani[1, 3]

In the development of highly efficient hybrid photocatalysts for CO_2 reduction, separation of active sites for CO_2 reduction and oxidation of reductant is of paramount importance. In this study, we have developed a new methodology to prepare hybrid photocatalyst. Ru(II) photosensitizing polymer was formed onto the semiconductor surface via photo-reductive polymerization, and then Ru(II) catalysts were coordinated onto the Ru(II) photosensitizing polymer. When poly(dibenzo[*b*,*d*]thiophene sulfone) was used as a semiconductor, the hybrid photocatalyst reduced CO_2 to formate almost quantitatively under visible light irradiation with maintaining high selectivity (> 85%) for CO_2 reduction.
Keywords：Conjugated polymer; Supramolecular photocatalyst; CO_2 reduction

半導体と超分子光触媒からなるハイブリッド光触媒は、可視光を有効利用し CO_2 を有用資源へと変換する高性能なシステムの構築に向けて大変有望である [1]。本研究では、CO_2 還元反応活性点と、対をなす酸化反応活性点の分離を目的として、光増感錯体の光還元重合を用いた、新たなハイブリッド光触媒作製法を開発した。

共役ポリマー半導体であるポリジベンゾ[*b*,*d*]チオフェンスルホン（P10）を還元剤共存下で光励起し、Ru(II)光増感錯体のビニル基を還元的にラジカル重合することで、P10 表面に Ru(II)光増感ポリマー層（**polyRu(PS)**）を形成した（図 a）。その後、ポリマー層へ Ru(II)触媒（**Ru(cat)**）を配位させることでハイブリッド光触媒を得た。CO_2 で飽和させた *N,N'*-ジメチルアセトアミド／トリエタノールアミン（TEOA）中にハイブリッド光触媒を懸濁させ、可視光（$\lambda = 460$ nm）を照射したところ、ギ酸と少量の CO、および副生成物の H_2 を生成した（図 b）。光照射 144 時間にて、高い CO_2 還元反応の選択率（> 85%）を維持しながら、系中に存在する CO_2 がほぼすべて還元された。



1) H. Kumagai, Y. Tamaki, O. Ishitani, *Acc. Chem. Res.* **2022**, *55*, 978-990.

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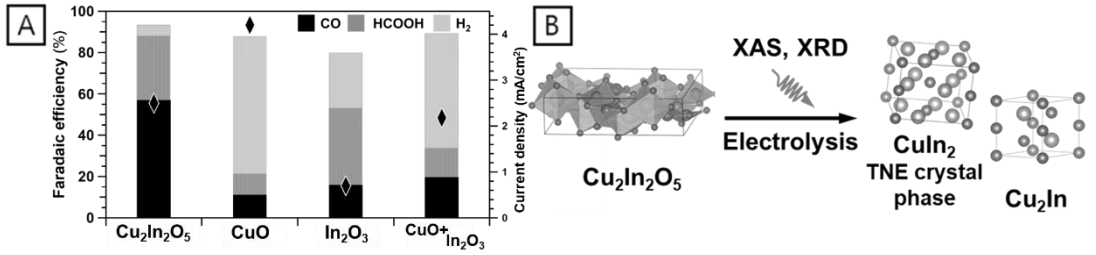
電解合成した熱非平衡金属間化合物による CO_2 電解還元

（都立大院理[1]・JASRI[2]）○幸林竜也[1]・吉川聡一[1]・渡辺剛[2]・本間徹生[2]・山添誠司[1]
CO_2 electrochemical reduction over thermal non-equilibrium intermetallic compounds synthesized by electrolysis ([1]*Graduate School of Science, Tokyo Metropolitan University*, [2]*JASRI*) ○Tatsuya Koubayashi,[1] Soichi Kikkawa,[1] Tsuyoshi Watanabe,[2] Tetsuo Honma[2], Seiji Yamazoe[1]

Electrochemical conversion of CO_2 has attracted much attention from the viewpoint of effective utilization of carbon resources and surplus electricity. It is important to design an electrode that selectively reduces CO_2 while suppressing H_2 generation in aqueous solution. For example, it has been reported that Cu-based alloy electrode with the second metal species improved CO_2 reduction selectivity[1)]. In this study, we focused on Cu–In thermal non-equilibrium (TNE) intermetallic compound formed by electrochemical reduction of $Cu_2In_2O_5$, a Cu–In composite metal oxide, and applied to electroreduction of CO_2. The electrode after the reaction showed diffraction patterns of a TNE crystal phase, $CuIn_2$, with high crystallinity, and promoted highly selective CO_2 reduction with suppressing H_2 production. We caried out *in situ* observation of the structural change of electrode with XAS and XRD, and revealed that the preferential reduction of In species in $Cu_2In_2O_5$ was important to form the TNE phase $CuIn_2$.
Keywords : Electrochemical CO_2 reduction; intermetallic compound; thermal non-equilibrium crystal phase

CO_2 の電気化学変換は、炭素資源の有効利用と余剰電力の活用の観点から注目されている。水溶液中では H_2 生成を抑制しながら CO_2 を選択的に還元する電極設計が重要である。例えば、Cu 系電極と第二金属種との合金化により CO_2 還元選択性が向上することが報告されている[1)]。本研究では、Cu と In の複合金属酸化物 $Cu_2In_2O_5$ を電気化学的に還元して生成した Cu-In 非平衡金属間化合物に着目し、CO_2 電解還元特性を評価した。複合金属酸化物の還元により得られた電極は熱非平衡結晶相である $CuIn_2$ を高い結晶性で含んでおり、図のように H_2 生成を抑制し高選択的に CO_2 還元が進行した。還元に伴う電極構造の変化を X 線吸収分光と X 線回折の同時計測により *in situ* 観察したところ、複合金属酸化物中の In 種が優先的に還元されることが熱非平衡結晶相の $CuIn_2$ の生成に重要であることが示唆された。



図(A) 種々の酸化物電極の CO_2 電解活性. (B) 還元に伴う $Cu_2In_2O_5$ の構造変化.

1) S. Rasul *et al*, *Angew. Chem. Int. Ed.* **2015**, 54, 2146.

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1 A/cm^2 を超える電流密度での CO_2 電解還元反応

（阪大院基礎工 [1]）○神谷和秀 [1]・井上明哲 [1]・Tengyi Liu[1]・原田隆史 [1]・中西周次 [1]

High-Rate CO_2 Reduction Reactions with a Current Density Exceeding 1 A/cm^2

([1]*Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University*) ○Kazuhide Kamiya,[1] Asato Inoue,[1] Tengyi Liu,[1] Takashi Harada,[1] Shuji Nakanishi[1]

Excessive emissions of carbon dioxide (CO_2) from the use of fossil fuels are becoming a serious obstacle to the sustainable development of society. Electrochemical CO_2 reduction (CO_2RR) into value-added products using solar electricity is a promising technology to close the carbon cycle and sequester anthropogenic CO_2 into chemical feedstocks[1)]. The practical implementation of CO_2RR requires a high current density, as the current density for CO_2RR is directly correlated to the capital cost of the electrodes and electrochemical cells. In the present work, we sophisticatedly fabricated a triple-phase interface composed of solid electrocatalysts, liquid electrolytes and gaseous CO_2 to achieve record current densities of over 1 A/cm^2 to produce multicarbon products (C_{2+}) and formic acid[2,3)].

Keywords：CO_2 electrolysis; Multicarbon Products; High Current Density; A Triple-Phase Interface

カーボンニュートラルの実現に向けて，再生可能エネルギー由来の電力を用いた CO_2 電解が大きな注目を集めている [1)]。特に近年、ガス拡散電極(GDE)を用いて基質 CO_2 をガス状のまま反応界面に供給することで、CO_2 電解を高電流化しようとする試みが活発になりつつある。これまでこのガス状 CO_2 電解の高活性化に向けては、触媒などの各構成要素を個別に設計・開発する研究が主流であった。

我々は分子スケールでの材料設計と、マクロスケールでの界面設計を組み合わせることで、材料のポテンシャルを最大限に発揮させるといった思想に基づき研究を行ってきた。その結果、最も標準的な触媒である金属銅ナノ粒子を用いて、その触媒層の厚みや多孔性を精密に制御することで、世界最高の電流密度で駆動する超高電流密度 CO_2 電解系（C2 以上の化合物の生成電流密度 j_{C2+} = 1.7 A/cm^2）の立ち上げに成功した [2)]。さらに、我々は金属ナノフォームとカーボンナノ粒子をハイブリッドすることで、親/疎水界面を厚み方向に増加させることで、反応面である三相界面の面積を大幅に増加させた。その結果、水素キャリアとして期待されるギ酸の生成電流密度を 1 A/cm^2 を超えるまでに増大させることに成功した [3)]。

1) CO_2 electrolysis in integrated artificial photosynthesis systems. K. Kamiya, K. Fujii, M. Sugiyama, S. Nakanishi *Chem. Lett*. **2021**, *50*, 166-179.
2) Ultra-high-rate CO_2 reduction reactions to multicarbon products with a current density of 1.7 A cm^{-2} in neutral electrolytes A. Inoue, T. Harada, S. Nakanishi, K. Kamiya *EES Catal.* **2023***, 1,* 9-16.
3) A tin oxide-coated copper foam hybridized with a gas diffusion electrode for efficient CO_2 reduction to formate with a current density exceeding 1 A cm^{-2} T. Liu, K. Ohashi, K. Nagita, T. Harada, S. Nakanishi, K. Kamiya *Small* **2022***, 18,* 2205323.

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Systematic Control of Electrochemical CO_2 Reduction Reaction Performances on Cu Nanocube by Surface Alloying with M (M=Pd, Pt, Ir, Ru)

([1]*Research Center for Negative Emissions Technologies, Kyushu University*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*, [3]*International Institute for Carbon-Neutral Energy Research, Kyushu University*, [4]*Advanced Institute for Materials Research, Tohoku University*)
○Hirokazu Kobayashi,[1] Sachie Hikino,[1] Miho Yamauchi[1,2,3,4]
Keywords: Copper; Nanocubes; Electrochemistry; Carbon Dioxide Reduction

Converting carbon dioxide (CO_2) into valuable chemicals through an electrochemical process holds great promise for establishing a carbon-neutral cycle. Among monometallic catalysts, copper (Cu) has shown particular potential for the electrochemical reduction of CO_2 into C_2 chemicals including ethylene (C_2H_4) and ethanol (C_2H_5OH). The formation of C_2 products is believed to involve the dimerization of intermediate CO* species, which plays a crucial role in the process.[1, 2)] In order to control a selectivity for the production of C_2 chemicals, we have paid attention to alloying Cu nanocubes with a metal (such as Pd, Pt, Ru or Ir) that exhibits different CO adsorption properties compared to Cu, although H_2 evolution reaction (HER) facilely occurs on their metals.

We have synthesized Cu-M core-shell surface alloy nanocrystals (Cu-M NCs, M=Pd, Pt, Ru and Ir), where a shell part of Cu NCs is alloyed with M by a galvanic replacement reaction. To characterize the shape and structure of the synthesized nanocrystals, we conducted scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and powder X-ray diffraction (XRD) measurements. The electrochemical CO_2 reduction performance was investigated using a gas diffusion cell.

TEM images shown in Fig. 1 revealed that the synthesized Cu-M NCs have cubic shapes similar to Cu NCs. The STEM and energy-dispersive X-ray (EDX) mappings demonstrated that the M element (Pd, Pt, Ru or Ir) was uniformly distributed around the surface of Cu NCs, forming a core/shell surface alloy structure. From the results of CO_2 reduction performance of Cu-Pd NCs, the selectivity for C_2H_4 decreased with increasing Pd content, whereas the selectivity for H_2 increased. This suggests that the alloying with Pd promotes HER. Interestingly, Cu-Pt and Cu-Ir NCs exhibited high selectivity, approximately 40% and 70%, respectively, for the production of formic acid (HCOOH). Cu NCs exhibit low selectivity (< 5%) for HCOOH, and Pt or Ir predominantly produces H_2, indicating the emergence of novel catalytic properties of Cu-Pt and Cu-Ir nanoalloys, which are completely distinct from those in their monometallic counterparts.

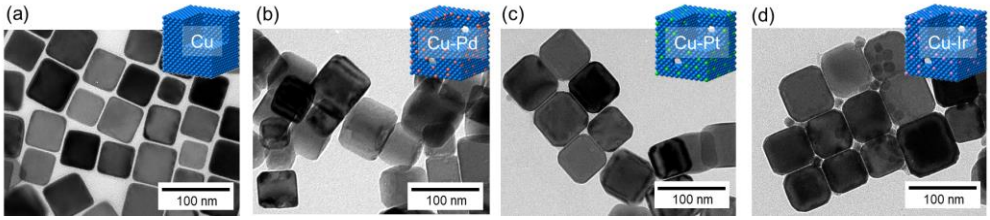

Fig. 1 TEM images of (a) Cu cubes, (b) Cu-Pd, (c) Cu-Pt and (d) Cu-Ir NCs.

1) S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. Haasch, J. Gold, M. Yamauchi, P. Kenis, *J. Am. Chem. Soc*., **2017**, *139*, 47.
2) M. Sun, A. Staykov, M. Yamauchi, *ACS Catal*., **2022**, *12*, 14856.

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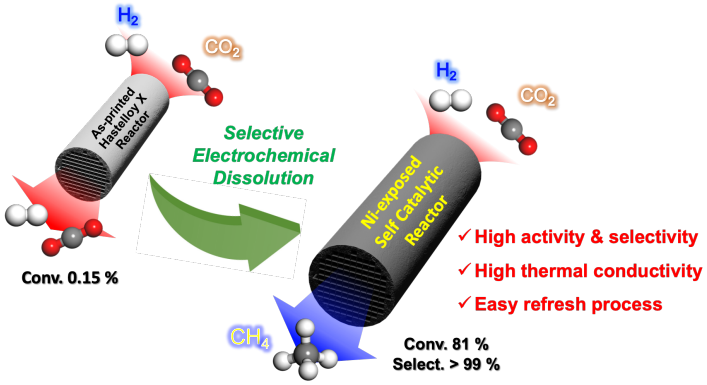
Highly durable Ni-based self-catalytic reactor for CO_2 methanation designed by metal 3D printing combined and selective electrochemical dissolution

([1]*Division of Materials and Manufacturing Science, Osaka University*, [2]*Anisotropic Design & Additive Manufacturing Research Center, Osaka University*, [3]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University*) ○ Hyo-Jin Kim,[1] Kohsuke Mori,[1,2,3] Takayoshi Nakano,[1,2] Hiromi Yamashita,[1,3]
Keywords: CO_2 methanation, Metal 3D printing, Self-catalytic reactor, Selective electrochemical dissolution

CO_2 methanation ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is anticipated to play a pivotal role in future energy scenarios, owing to its high energy density and the accessibility of a well-established infrastructure. However, the commercial availability of catalysts is limited due to the intricacies involved in the catalyst development process. A recent breakthrough in addressing these challenges is the emergence of self-catalytic reactors (SCR). This innovative technology combines metal 3D printing with catalysis, integrating the functions of a catalyst and reactor into a single entity and simplifying the development process. Metal 3D printing technology has significantly facilitated the design of complex geometries for SCR, offering substantial benefits to catalytic performance.[1] In this study, we present the fabrication of a practical Ni self-catalytic reactor for CO_2 methanation using the selective laser melting (SLM) technique and electrochemical selective dissolution method.[2]



The as-printed Ni-SCR, treated at 50 $mV_{vsHg/HgO}$, exhibited the highest CO_2 conversion rate of 60% with > 99% CH_4 selectivity at 350 °C. This represents a 400-fold increase compared to the as-printed reactor. Analysis using SEM/EDS, XRD, and XPS indicated that the reactor surface treated at 50 $mV_{vsHg/HgO}$ transformed into β-$Ni(OH)_2$, characterized by a dark-green color, with a significant enrichment of nickel. Geometrically, an increase in the cell density of reactors was found to enhance the CO_2 conversion rate. The self-dissolution refresh process of the SCR proved to be a simple and effective method for regenerating active sites. This process resulted in overperformance, correlating with the number of refresh cycles undertaken.

1) Wei, Q, *Nat Commun* **11**, 1–8 (2020). 2) Kim, H. J., *Adv Funct Mater* **2303994**, 1–11 (2023).

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
F1231(1231, Bldg. 12 [3F])

[F1231-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Hiroki Takezawa, Kazuhiro Uemura

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1231-4am-01]
Synthesis and Photoreaction of Metal-organic Polyhedra Bearing Anthracene Moieties

○Ryoga Umemura[1], Jenny Pirillo[2], Qu Liyuan[2], Kusaka Shinpei[2], Hijikata Yuh[2], Iguchi Hiroaki[2], Matsuda Ryotaro[2] (1. Nagoya Univ., 2. Nagoya Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1231-4am-02]
Synthesis and Photophysical Properties of Metal Complexes Bearing Phenylethenylpyrene Moieties

○Ryoto Katagiri[1], Jenny Pirillo[1], Liyuan Qu[1], Shinpei Kusaka[1], Yuh Hijikata[1], Hiroaki Iguchi[1], Ryotaro Matsuda[1] (1. Nagoya Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1231-4am-03]
Acceleration of ligand-dioxygenation of chromium(V) complexes in the presence of a platinum(II) complex and formation of chromium-platinum mixed-metallic octanuclear complexes

○Hikaru Yabe[1], Mikoto Negishi[1], Hideki Ohtsu[1], Kiyoshi Tsuge[1] (1. University of Toyama)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1231-4am-04]
Interfacial synthesis of a transparent redox-active 2D bis(terpyridine)nickel(II) complex polymer

○Kenji Takada[1], Hiroaki Maeda[1], Hiroshi Nishihara[1] (1. Tokyo University of Science)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1231-4am-05]
Reduction and ligand reactions of mononuclear nitrosylruthenium complex having acetonitrile as coexisting ligands

○Sota Fujikawa[1], Tomoyo Misawa[1], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1231-4am-06]
Redox reactions of a dinuclear ruthenium(III) complex having one oxido- and two acetato-bridged structure

○Masahiro Hayashi[1], Tomoyo Misawa[1], Hirotaka Nagao[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

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10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

Break

English

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[F1231-4am-07]

Synthesis and Properties of Iridium Dinuclear Complexes with Oxysulfur Ligands

○Shinji Suzuki[1], Hidetaka Nakai[1] (1. Grad. Sch. Sci. Eng. Kindai Univ.)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[F1231-4am-08]

Synthesis and Luminescence Properties of Samarium and Dysprosium Complexes with a Chiral 1,4,7,10-Tetraazacyclododecane Skeleton

○Kazuhiro Harada[1], Hisaki Matsui[1], Hidetaka Nakai[1] (1. Grad. Sch. Sci. Eng. Kindai Univ.)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[F1231-4am-09]

Synthesis of PdAu24 Nanoclusters Protected by Alkylthiolates Bearing Fmoc-amino Groups

○Soshi TAKEUCHI[1], Ryohei SAITO[1], Katsuhiro ISOZAKI[1], Masaharu NAKAMURA[1] (1. Kyoto University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[F1231-4am-10]

Transmetallation of Nickelladithiolene Nanosheet and Its Reaction Mechanism and Kinetics Analysis

○Ziheng Yu[1], Kenji Takada[1], Hiroaki Maeda[1], Naoya Fukui[1], Hiroshi Nishihara[1] (1. Tokyo University of Science)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[F1231-4am-11]

Adsorption behavior of a homochiral metal-organic framework (MOF) consisting of a figure-eight-shaped cyclobisbiphenylenecarbonyl ligand.

○Daisuke Owase[1], Shinpei KUSAKA[1], Ryotaro MATSUDA[1], Hiroshi SHINOKUBO[1], Norihito FUKUI[1,2] (1. Nagoya university, 2. JST PRESTO)

English

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[F1231-4am-12]

Electrochemical oxidation synthesis of oriented bis(diimino)metal coordinaion nanosheets on gold electrodes.

○Hiroaki Maeda[1], Kenji Takada[1], Naoya Fukui[1], Hiroyasu Masunaga[2], Sono Sasaki[3,4], Kazuhito Tsukagoshi[5], Hiroshi Nishihara[1] (1. Tokyo University of Science, 2. Japan Synchrotron Radiation Research Institute (JASRI), 3. Kyoto Institute of Technology, 4. SPring-8, 5. National Institute for Materials Science (NIMS))

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[F1231-4am-13]

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Creation of coordination nanosheet with a triptycene-skeleton ligand and its application to electrocatalyst for hydrogen evolution reaction

○Yuta Sudo[1], Hiroaki Maeda[1], Sayoko Nagashima[1], Kenji Takada[1], Naoya Fukui[1], Hiroshi Nishihara[1] (1. Tokyo University of Science)

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アントラセン部位を有する金属有機多面体の合成と光反応

（名大工[1]・名大院工[2]）○梅村 凌我[1]・Jenny Pirillo[2]・Qu Liyuan[2]・日下 心平[2]・土方 優[2]・井口 弘章[2]・松田 亮太郎[2]

Synthesis and Photoreaction of Metal-organic Polyhedra Bearing Anthracene Moieties

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Nanoporous metal complexes are materials formed by the self-assembly of metal ions and organic linkers, which have uniform nanospaces within their structures, allowing the reversible inclusion and release of small molecules. Among them, metal-organic polyhedra (MOP) is a discrete molecule that can quantitatively modify the boundary between nanospace and outer space through organic synthesis. This has led to active research on the development of MOPs whose structure and function can be controlled by external stimuli.

In this study, we focused on anthracene, which is capable of reversible structural change with endoperoxide via the addition and dissociation of singlet oxygen resulting in the interconversion of carbon atoms at 1- and 9- positions between sp^2 and sp^3. We expected that the structural change of anthracene could be utilized for on-demand trapping and release of guest molecules. In this study, a MOP was synthesized using ligands with an anthracene moiety and a zirconium(IV) ion. Single crystal X-ray diffraction measurements revealed that the obtained MOP is a tetrahedral complex with a zirconium trinuclear cluster at the top. The obtained MOP was reacted with singlet oxygen by photoirradiation, which was observed by UV-Vis absorption spectroscopy and other techniques.

Keywords : Metal-organic polyhedra; photoreaction; anthracene

ナノポーラス金属錯体は金属イオンと架橋有機配位子の自己集合により形成される材料であり、その構造内に均一なナノ空間を有するため、小分子を可逆に包摂・放出させることができる。ナノポーラス金属錯体の中でも Metal-Organic Polyhedra (MOP) はディスクリートな分子であり、有機合成によってナノ空間と外部空間の境界を定量的に修飾できる。これを活用した、外部刺激により構造や機能を制御できる MOP の開発が盛んに研究されている。

本研究で我々はアントラセンに着目した。アントラセンは一重項酸素の付加と脱離によりアントラセンエンドペルオキシドと可逆に変化し、1,9 位の炭素原子が sp^2 と sp^3 の間で相互変換する。この構造変化を活用して、ゲスト分子のオンデマンドな捕捉と放出が可能になるのではないかと考えた。本研究では、アントラセン部位を有する配位子とジルコニウム(IV)イオンを用いて MOP の合成を行った。単結晶 X 線回折測定により、得られた MOP がジルコニウム 3 核クラスターを頂点とする正四面体型の錯体であることを明らかにした。得られた MOP に対して光照射をすることによって一重項酸素との反応を行い、その光反応による変化を紫外可視吸光スペクトルなどを用いて確認した。

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フェニルエテニルピレン部位を有する金属錯体の合成と光物性

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Synthesis and photophysical properties of metal complexes with phenylethenylpyrene moieties(*Graduate School of Engineering, Nagoya University*) ○Ryoto Katagiri, Pirillo Jenny, Qu Liyuan, Shinpei Kusaka, Yuh Hijikata, Hiroaki Iguchi, Ryotaro Matsuda

Nanoporous metal complexes (NMCs) are crystalline solids obtained by bridging metal ions with organic ligands and have nanometer-sized internal pores. Recently, many studies have been reported on MOFs whose structures and properties can be changed by light. For example, a two-dimensional sheet-like NMC was converted to a three-dimensional structure NMC by bonding of olefin moieties upon light irradiation.

Phenylethenylpyrene is known to form a dimer by [2+2] photocyclization of two carbon-carbon double bond sites when irradiated with 400-500 nm visible light. In turn, photocleavage of the dimer by UV light with 340 nm light gives back to the monomer. We hypothesized that introducing phenylethenylpyrene as a substituent into NMCs would enable NMCs to undergo reversible structural transformation upon irradiation using light with different wavelengths. In this study, we synthesized phenylethenylpyrene derivatives with a carboxylic acid moiety as a metal coordinating site and investigated the synthesis of NMCs using these derivatives.

Keywords : Nanoporous metal complex; Phenylethenylpyrene; [2+2] photocyclization

多孔性金属錯体（NMC）は金属イオンを有機配位子が架橋することによって得られる結晶性固体であり、内部にナノメートルサイズの空孔を有する。近年、光により構造や物性を変化させられる NMC の研究が盛んに行われており、二次元のシート状の構造を有する NMC を、光照射によるオレフィン部位同士の結合生成により三次元の構造に転換するといった例が報告されている。

フェニルエテニルピレンは、400～500 nm の波長を持つ可視光を照射すると、炭素-炭素二重結合部位二つが[2+2]光環化反応を起こすことで二量体を形成し、逆に二量体に対して 340 nm の波長を持つ紫外光を照射すると光開裂により単量体に戻ることが知られている。我々はこのフェニルエテニルピレンを置換基として NMC に導入すると、異なる波長の光照射により可逆的な構造変換が可能な NMC が得られるのではないかと考えた。本研究では、金属配位部位としてカルボン酸部位を有するフェニルエテニルピレン誘導体を合成し、それを用いた NMC の合成を検討した。

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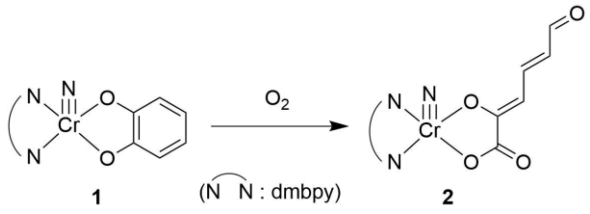
白金(Ⅱ)錯体添加によるクロム(V)錯体上での配位子酸素化反応の加速とクロム-白金混合八核錯体の生成

（富山大理[1]・富大院理工[2]）○矢部 輝[1]・根岸 海琴[2]・大津 英揮[1,2]・柘植 清志[1,2]
Acceleration of ligand-dioxygenation of chromium(V) complexes in the presence of a platinum(II) complex and formation of chromium-platinum mixed-metallic octanuclear complexes ([1]*University of Toyama*, [2]*Graduate School of Science and Engineering, University of Toyama*) ○Hikaru Yabe,[1] Mikoto Negishi,[2] Hideki Ohtsu,[1,2] Kiyoshi Tsuge[1,2]

We have reported that a catecholato-nitirido-chromium(V) complex [Cr(N)(dmbpy)(Cat)] was converted to an HMS complex [Cr(N)(dmbpy)(HMS)] (H_2HMS: 2-hydroxymuconic semialdehyde) by ring-opening dioxygenation. Here, we report that the addition of [$PtCl_2(DMSO)_2$] to the reaction solution accelerated the oxygenation to yield an eight-nuclear platinum(II)-chromium(V) mixed-metal complex bridged by nitrido and HMS^{2-}.
Keywords : chromium(V), nitrido complex, catecholate complex, dioxygenation, octanuclear complex

我々はカテコラト配位子(Cat^{2-})を持つクロム(V)ニトリド錯体[Cr(N)-(dmbpy)(Cat)] (**1**)が、アセトニトリル溶液中で酸素化され、2-ヒドロキシムコン酸セミアルデヒダト配位子(HMS^{2-})を持つ錯体[Cr(N)(dmbpy)-(HMS)] (**2**)に変換されることを報告してきた（スキーム 1。dmbpy: 4,4′-ジメチル-2,2′-ビピリジン）[1]。この反応は、ニトリド錯体上でのカテコラト二酸素付加開環反応の最初の例である。最近、可視紫外吸収スペクトルの測定により、[$PtCl_2(DMSO)_2$] (**3**)が共存すると錯体 **1** の酸素化反応が加速されることが示唆された[2]。今回、この反応についてさらに検討を行い、その生成物の単離を行った。



スキーム 1．カテコラト錯体 **1** の二酸素付加開環反応

室温・空気中で **1** の橙赤色のアセトニトリル溶液に、2 当量の白金錯体 **2** を加えると、溶液の色が速やかに褐色に変化した。この溶液を一晩放置すると黒色結晶が析出した（収率 44%）。単結晶構造解析によりこの化合物は、クロム―白金混合八核錯体[{Cl_2(DMSO)Pt(μ-N)Cr(dmbpy)}$_4$(μ-HMS)$_4$] (**4**)であることが分かった（図 1）。この錯体中で Pt^{II} イオンは 2 つの Cl^- と DMSO に加え、N^{3-}が配位した平面 4 配位構造をとっている。また各 Cr^V イオンは、N^{3-}, dmbpy, HMS^{2-}による八面体型 6 配位構造をとった。それぞれの HMS 配位子はさらにもう一つの Cr^V に配位し、環状八核錯体を形成している。

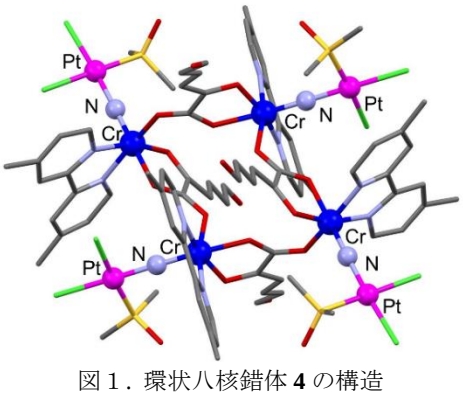


図 1．環状八核錯体 **4** の構造

1 から **2** への変換は約 30 日かかるが[1]，白金錯体 **3** を共存させると 1 日で **4** へ変換された。**4** は HMS 配位子を持つ錯体であることから、白金錯体 **3** を加えることにより **1** の酸素化が加速されることが明らかとなった。

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Interfacial synthesis of a transparent redox-active 2D bis(terpyridine)nickel(II) complex polymer

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○Kenji Takada,[1] Hiroaki Maeda,[1] Hiroshi Nishihara[1]
Keywords: Coordination Polymers; Electrochemistry; Terpyridine Complexes; Interfacial Synthesis

Coordination nanosheets (CONASHs) are emerging two-dimensional materials prepared in bottom-up ways via coordination bonds. Rich varieties of the combinations between metal ions and organic ligands endow various functionalities to CONASHs.[1]

Bis(terpyridine)metal(II) complexes are one of the most fundamental coordination compounds. When redox-active metal ions are employed as metal centers in bis(terpyridine)metal(II)-based CONASHs, they exhibit rich electrochemical properties such as electrochromism and electrical conductivity based on redox-conduction mechanism.[2,3] While Fe and Co are mainly used as metal centers in the conventional terpyridine-based CONASHs, Ni ions are not familiarly used in spite of rich electrochemistry of bis(terpyridine)nickel(II) complexes.

Herein, we introduce a redox bis(terpyridine)nickel(II)-based CONASHs (**1-Ni**) as a colorless and transparent redox-active material (**Fig. 1**).[4] **1-Ni** was prepared by the method of liquid-liquid interfacial coordination reaction of a three-armed terpyridine ligand **1** and nickel ion. **1-Ni** shows a reversible redox behavior based on the $[Ni(tpy)_2]^{3+/2+}$ redox couple. The redox reaction of **1-Ni** does not accompany distinct color change while the Fe and Co counterparts demonstrate electrochromism. Thus, **1-Ni** has a great potential to transparent electronic materials.

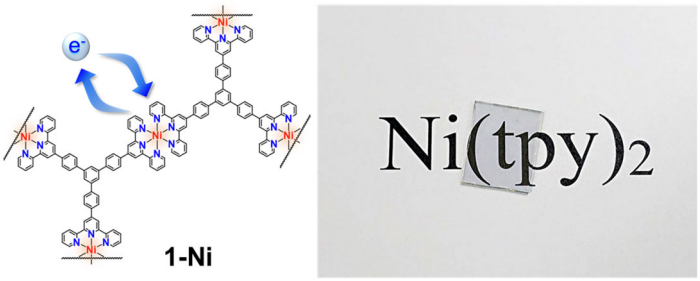

Fig. 1. Chemical structure and appearance of redox-active **1-Ni**.

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アセトニトリルを共存配位子とするニトロシルルテニウム単核錯体の還元および配位子反応

（上智大理工）藤川　壮太・三澤　智世・長尾　宏隆

Reduction and ligand reactions of mononuclear nitrosylruthenium complex having acetonitrile as coexisting ligands.

([1]*Fac.of Sci. and Tech., Sophia University*) Sota Fujikawa, Tomoyo Misawa, Hirotaka Nagao

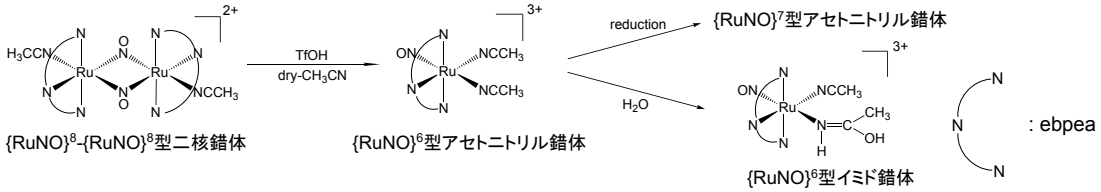
The nitrosyl (NO) ligand is a "non-innocent" ligand. In a nitrosylruthenium complex, a notation of $\{RuNO\}^n$ is used, where n is the sum of the number of electron in the dπ orbitals of the Ru center and the π^* orbital of the nitrosyl ligand.[1)] A diacetonitrilenitrosylruthenium complex ($\{RuNO\}^6$-type) bearing ethylbis(2-pyridylethyl)amine (ebpea) as a supporting ligand ($[Ru(NO)(NCCH_3)_2(ebpea)]^{3+}$), which shows the reduction waves in a high potential regions, has been synthesized.

In this study, we investigated a reduction reaction of the $\{RuNO\}^6$-type complex and a reaction with H_2O affording a $\{RuNO\}^6$-type imide complex by the addition of an nucleophilic attack to the N-C triple bond of the acetonitrile ligand activated by the strong electron-withdrawing property of the nitrosyl ligand via the ruthenium center. We will report a function as a catalyst for acrylonitrile polymerization reactions that occur without a polymerization initiator or promoter.

Keywords : nitrosyl ligand; redox reactions; electrochemistry

ニトロシル（NO）配位子はノンイノセントな配位子であり、ニトロシルルテニウム錯体の電子状態は、中心金属 Ru の dπ軌道とニトロシル配位子のπ*軌道の電子数の総和 *n* を用いて$\{RuNO\}^n$と表す[1)]。これまでにエチルビス（2-ピリジルエチル）アミン（ebpea）を支持配位子とする$\{RuNO\}^8$-$\{RuNO\}^8$型ニトロシル二重架橋ルテニウム二核錯体から高電位に還元波を示す$\{RuNO\}^6$型アセトニトリルニトロシルルテニウム錯体（$[Ru(NO)(NCCH_3)_2(ebpea)]^{3+}$）を合成した[2)]。

本研究では、$\{RuNO\}^7$型錯体を合成するため、$\{RuNO\}^6$型錯体について様々な条件下で還元反応およびルテニウム中心を介したニトロシル配位子の強い電子吸引性により活性化されたアセトニトリル配位子の N-C 三重結合への水の付加による$\{RuNO\}^6$型イミド錯体の生成反応について検討した。重合開始剤や助触媒なしに起こるアクリロニトリルの重合反応[3)]の触媒としての機能についても発表する。



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一つのオキシドと二つのアセタトによる架橋構造を有するルテニウム（III）二核錯体の酸化還元反応

（上智大理工）○林 昌弘・三澤 智世・長尾 宏隆

Redox reactions of a dinuclear ruthenium(III) complex having one oxido- and two acetato-bridged structure (*Faculity of Science and Technology, Sophia University*) ○ Masahiro Hayashi, Tomoyo Misawa, Hirotaka Nagao

We have synthesized a dinuclear ruthenium(III) complex bearing a tridentate ligand, ethylbis(2-pyridylmethyl)amine (ebpma), $[\{Ru^{III,III}(ebpma)\}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}$ ($[\mathbf{1(III,III)}]^{2+}$), as a dinuclear reaction model for natural iron-containing enzymes, that perform multi-electron reactions. For $[\mathbf{1(III,III)}]^{2+}$, a reversible oxidation wave at +0.5 V and an irreversible reduction wave at -1.0 V were observed in cyclic voltammetry. The irreversibility of the reduction wave suggests a structural change upon a reduction reaction.

In this study, the oxidation and reduction reactions of $[\mathbf{1(III,III)}]^{2+}$ were investigated. The one-electron oxidized species, $[\mathbf{1(III,IV)}]^{3+}$, was synthesized by using a molar equivalent of cerium(IV) ammonium nitrate as an oxidant. In consideration of the protonation to the bridging oxido ligand associated with reduction reactions, the reduction reactions were studied in aqueous solution, in which the pH was adjusted to around pH 3.0 and pH 9.0. Reduction reactions were studied in organic solvents as well. Since each reaction solution showed different color, isolation of the product was attempted and the electrochemical and spectrochemical behaviors of each product were studied.

Keywords : dinuclear complex, oxido-bridge, acetato-bridge, electrochemical behaviors, redox reactions

これまでに、多電子反応を行う天然の鉄含有酵素の二核反応点モデルとして、一つのオキシドと二つのアセタト配位子が架橋した構造を有するルテニウム（III）二核錯体 $[\{Ru^{III,III}(ebpma)\}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}$（$[\mathbf{1(III,III)}]^{2+}$, ebpma; エチルビス（2-ピリジルメチル）アミン）を合成した[1]。$[\mathbf{1(III,III)}]^{2+}$は+0.5 V に可逆な酸化波を、-1.0 V に非可逆な還元波を示す。これより、還元反応に伴う構造変化が示唆された。

本研究では、$[\mathbf{1(III,III)}]^{2+}$の酸化還元反応について検討した。$[\mathbf{1(III,III)}]^{2+}$（図 1. 実線）と等量の硝酸二アンモニウムセリウム（IV）を酸化剤として用いることで、一電子酸化体である$[\mathbf{1(III,IV)}]^{3+}$（図 1. 点線）を合成し、単離した。還元反応は、亜鉛粉末を用いて行った。還元に伴うオキシド架橋配位子へのプロトンの付加を考慮し、pH 3.0 付近と pH 9.0 付近に調整した水溶液中で還元反応を検討した。また、有機溶媒中での還元反応では、水溶液中での還元反応後と溶液の色が異なったため、単離を試み、生成物の電気化学的および分光化学的挙動を検討した。

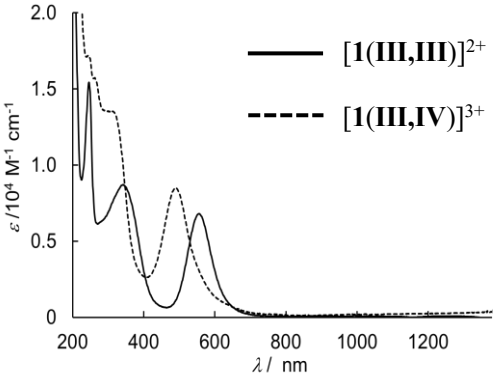

図 1. 一電子酸化前後の UV-vis-NIR

[1] 林、三澤、長尾 第 103 日本化学会春季年会 K503-1vn-10。

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Synthesis and Properties of Iridium Dinuclear Complexes with Oxysulfur Ligands

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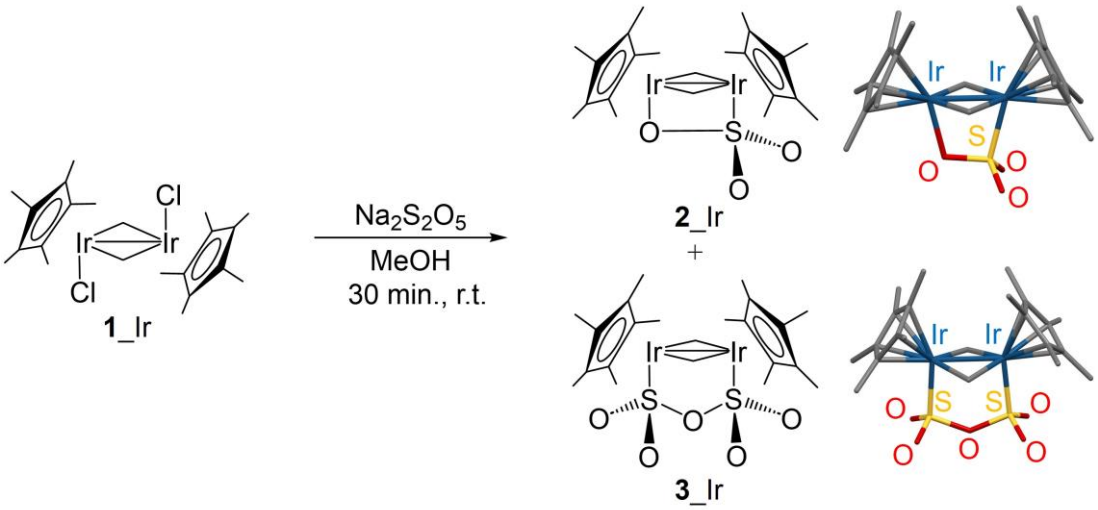
Keywords: Iridium Complex; Dinuclear Complex; Oxysulfur Ligand

Metal dinuclear complexes with oxysulfur ligands are appealing for stabilizing oxysulfur species, which are unstable as organic compounds, and for developing new properties and functions of oxysulfur species.[1] In this context, we have demonstrated that a rhodium dinuclear complex, *trans*-[Cp*M(μ-CH_2)Cl]$_2$ (**1**_M, Cp* = η^5-C_5Me_5, M = Rh), reacts with sodium dithionite ($Na_2S_2O_4$) to produce an "O_2SSO_2" complex, [(Cp*Rh)$_2$(μ-CH_2)$_2$(μ-O_2SSO_2)], with unprecedented photo-responsive propertoes.[2]

To explore new functional metal complexes with oxysulfur ligands, we are synthesizing iridium dinuclear complexes with various oxysulfur ligands. Now, we found that various oxysulfur complexes, an "OSO_2" complex [(Cp*Ir)$_2$(μ-CH_2)$_2$(μ-OSO_2)] (**2**_Ir) and an "O_2SOSO_2" complex [(Cp*Ir)$_2$(μ-CH_2)$_2$(μ-O_2SOSO_2)] (**3**_Ir), can be synthesized and isolated by the reaction of **1**_Ir with sodium disulfite ($Na_2S_2O_5$) in MeOH for 30 minutes at room temperature. This is in contrast to the reaction of **1**_Rh with $Na_2S_2O_5$ in MeOH for 30 minutes at room temperature, which only isolates the corresponding "OSO_2" complex (**2**_Rh). Here, we report on the structure and properties of the successfully isolated **2**_Ir and **3**_Ir, comparing them with **2**_Rh. Intriguingly, **3**_Ir contains a new type of oxysulfur species, O_2SOSO_2, in which an oxygen atom bridges two sulfur atoms.



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キラルな 1,4,7,10-テトラアザシクロドデカン骨格を有するサマリウムおよびジスプロシウム錯体の合成と発光特性

（近畿大院総理工 [1]）○原田 和海 [1]・松井 久宜 [1]・中井 英隆 [1]

Synthesis and Luminescence Properties of Samarium and Dysprosium Complexes with a Chiral 1,4,7,10-Tetraazacyclododecane Skeleton

([1]*Graduate School of Science and Engineering*, *Kindai University*) ○Kazuhiro Harada,[1] Hisaki Matsui,[1] Hidetaka Nakai[1]

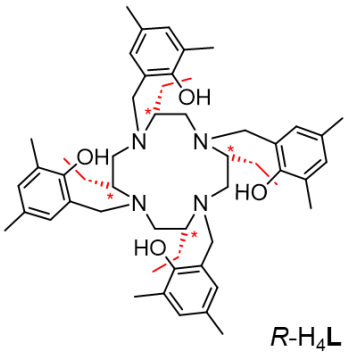
In our development of luminescent lanthanide(III) complexes with tris-/tetrakis-aryloxide ligands, we have successfully synthesized a highly luminescent samarium(III) complex as well as the first dysprosium(III) complex that shows oxygen-sensitive luminescence.[1,2]

We have very recently developed a tetrakis-phenol with a “chiral” 1,4,7,10-tetraazacyclododecane skeleton $H_4\{(^{MeMe}ArO)_4$*R/S*-Et-cyclen$\}$ (*R/S*-H_4**L**, ^{MeMe}ArO = $CH_2C_8H_8O$, *R/S*-Et-cyclen = $(C_2H_5)_4C_8H_{12}N_4$), and have successfully synthesized an oxygen-sensitive luminescent terbium(III) complex with chirality.[3] In this presentation, we report the synthesis and luminescence properties of “chiral” samarium(III) and dysprosium(III) complexes with *R/S*-**L**, $[H\{(^{MeMe}ArO)_4$*R/S*-Et-cyclen$\}Ln^{III}]$ (*R/S*-$\mathbf{1}^{Ln}$, Ln = Sm and Dy).

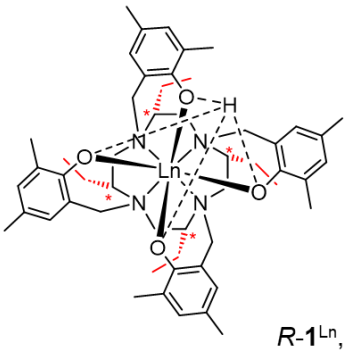
Keywords : Samarium Complex; Dysprosium Complex; Luminescence

我々は、トリス-/テトラキス-アリールオキシドを配位子とする発光性ランタニド(III)錯体の開発において、強発光性のサマリウム(III)錯体や酸素に敏感な発光を示す初めてのジスプロシウム(III)錯体の合成に成功している [1,2]。

最近、我々は、「キラル」な 1, 4, 7, 10-テトラアザシクロドデカン骨格を有するテトラキスフェノール $H_4\{(^{MeMe}ArO)_4$*R/S*-Et-cyclen$\}$ (*R/S*-H_4**L**, ^{MeMe}ArO = $CH_2C_8H_8O$, *R/S*-Et-cyclen = $(C_2H_5)_4C_8H_{12}N_4$)を開発し、キラリティーを有する酸素応答性の発光性テルビウム(III)錯体の合成に成功している [3]。本発表では、*R/S*-**L** を有する「キラル」なサマリウム(III)およびジスプロシウム(III)錯体$[H\{(^{MeMe}ArO)_4$*R/S*-Et-cyclen$\}Ln^{III}]$ (*R/S*-$\mathbf{1}^{Ln}$, Ln = Sm and Dy)の合成および発光特性を報告する。



R-H_4**L**



R-$\mathbf{1}^{Ln}$, Ln = Sm and Dy

1) H. Nakai et al., *Dalton Trans*. **2017**, *46*, 9126. 2) H. Nakai et al., *Dalton Trans*. **2016**, *45*, 9492. 3) H. Matsui, S. Suga, H. Nakai, *the 103rd Annual meeting of CSJ* **2023**, K504-2pm-06

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Fmocアミノ基を有するアルキルチオラートにより保護された $PdAu_{24}$ クラスターの合成

（京大化研・京大院工）○竹内 創史・齋藤 亮平・磯﨑 勝弘・中村 正治

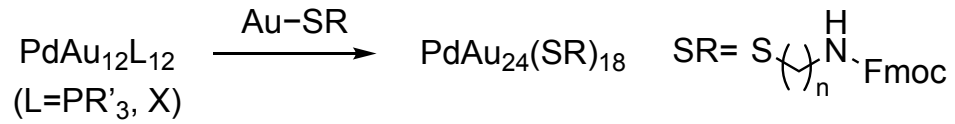
Synthesis of $PdAu_{24}$ Nanoclusters Protected by Alkylthiolates Bearing Fmoc-amino Groups

(*Institute for Chemical Research, Kyoto University, Graduate School of Engineering, Kyoto University*) ○Soshi Takeuchi, Ryohei Saito, Katsuhiro Isozaki, Masaharu Nakamura

Thiolate-protected gold nanoclusters have been widely studied due to their unique physical properties and catalytic activity. However, the low synthetic yield with the conventional reduction methods has hampered the practical application of these nanoclusters. Recently, we developed a facile synthesis of $MAu_{24}(SR)_{18}$ nanoclusters by the reaction between MAu_{12} nanoclusters and gold–alkyl thiolate compounds bearing hydrogen bonding moieties. In this presentation, we will report the efficient synthesis of $PdAu_{24}(SR)_{18}$ nanoclusters by introducing Fmoc-amino groups to the terminal of alkylthiolate ligands.

Keywords : Metallic Nanocluster; Facile Synthesis; Superatom; Thiolate ligand; Fmoc Protecting Group

チオラートを配位子とする $Au_{25}(SR)_{18}$ ナノクラスター，及び異種金属により置換された $MAu_{24}(SR)_{18}$ ナノクラスターは高い熱力学的安定性と特異な電子構造に基づく様々な物性を示すことから，盛んに研究が行われている。一般的にこれらのクラスターは金属塩を還元することで合成されるが，低収率であることが課題とされてきた。この課題を解決する新たな合成法として，ホスフィン保護 Au_{13} ナノクラスターに金ーチオラート化合物を反応させることで，高収率で $Au_{25}(SR)_{18}$ ナノクラスターを得る手法が報告されたが，芳香族チオラートしか適用できないという制限があった [1]。これに対し，我々は MAu_{12} (M＝Au, Pd, Pt)クラスターに水素結合部位を有する金—チオラート化合物を反応させることで脂肪族チオラートを用いても $MAu_{24}(SR)_{18}$ が得られることを見出した。本研究では，水素結合部位に加えてπースタッキングが期待される芳香族官能基を導入することで， $MAu_{24}(SR)_{18}$ ナノクラスターの更なる高収率合成が可能と考えて研究を行った。具体的には 9-Fluorenylmethyloxycarbonyl(Fmoc)アミノ基を末端に有するアルキルチオールから合成した金ーチオラート化合物を用い，$PdAu_{12}$ クラスターとの反応により $PdAu_{24}(SR)_{18}$ クラスターを合成する手法について検討した。本講演では，この新規の $PdAu_{24}(SR)_{18}$ クラスターの合成と分子・電子構造について報告する。



1. Lei, Z.; Wang, Q.-M. et al. *Angew. Chem. Int. Ed.* **2021**, *60,* 14415–14419.

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ニッケラジチオレンナノシートのトランスメタル化と反応機構・速度論解析

（東理大創域理工 [1]・東理大総研 [2]）○蔚 子恒 [1]・高田 健司 [2]・前田 啓明 [2]・福居 直哉 [2]・西原 寛 [1,2]

Transmetallation of Nickelladithiolene Nanosheet and Its Reaction Mechanism & Kinetics Analysis

([1]*Faculty of Science and Technology, Tokyo University of Science,* [2]*Research Institute for Science and Technology, Tokyo University of Science*)○Ziheng Yu[1], Kenji Takada[2], Hiroaki Maeda[2], Naoya Fukui[2], Hiroshi Nishihara[1,2]

Coordination nanosheets (CONASHs) are two-dimensional coordination polymers consisting of metal ions and planar organic molecules. Their structure and properties are tunable by metal ions and ligands. In recent years, heterometallic coordination nanosheets have attracted significant attention due to the enhancement of properties from monometallic.[1)] They represent an important advancement in the field of coordination nanosheets. Transmetallation reactions[2)] offer a new avenue for synthesizing heterometallic coordination nanosheets. In the current study, we found that a nickelladithiolene nanosheet Ni_3BHT, using benzenehexathiol (BHT) as a ligand, is transformed into Cu_3BHT through a transmetallation reaction with Cu^{2+}, involving an intermediate heterometallic nanosheet Ni_xCu_{1-x}BHT. Kinetic analysis clarified that the reaction is a two-step reaction and identified a metastable phase of Ni_1Cu_2BHT that contains both Ni and Cu metals.

Keywords : Coordination Chemistry; Coordination Nanosheet; Transmetallation Reactions

配位ナノシート（CONASHs）は、金属イオンと平面形の有機配位子の配位結合により形成される二次元物質である。金属イオンと配位子の組み合わせを変えることにより、構造や性質が変化する。近年、金属配位ナノシートのヘテロメタル化により、性能向上が進められている。[1)] また、トランスメタル化反応[2)]は、ヘテロ金属配位ナノシートの新たな合成手法として報告されている。本研究では、配位子としてベンゼンヘキサチオール（BHT）を用いた Ni_3BHT が Cu^{2+} とのトランスメタル化反応を示し、ヘテロ金属ナノシート Ni_xCu_{1-x}BHT を経て、Cu_3BHT を形成することを見出した。反応速度解析の結果、Ni と Cu の両金属を含む準安定相 Ni_1Cu_2BHT が存在することを明らかにした。

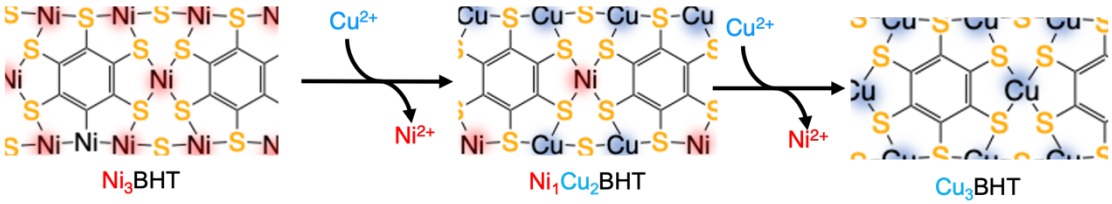

図 1. Ni_3BHT のトランスメタル化反応

1) R. Toyoda *et al*. *Adv. Mater.* **2022**, *34*, 2106204.
2) C. M. Tan, N. Fukui *et al*. *Angew. Chem. Int. Ed.* **2024**, e202318181.

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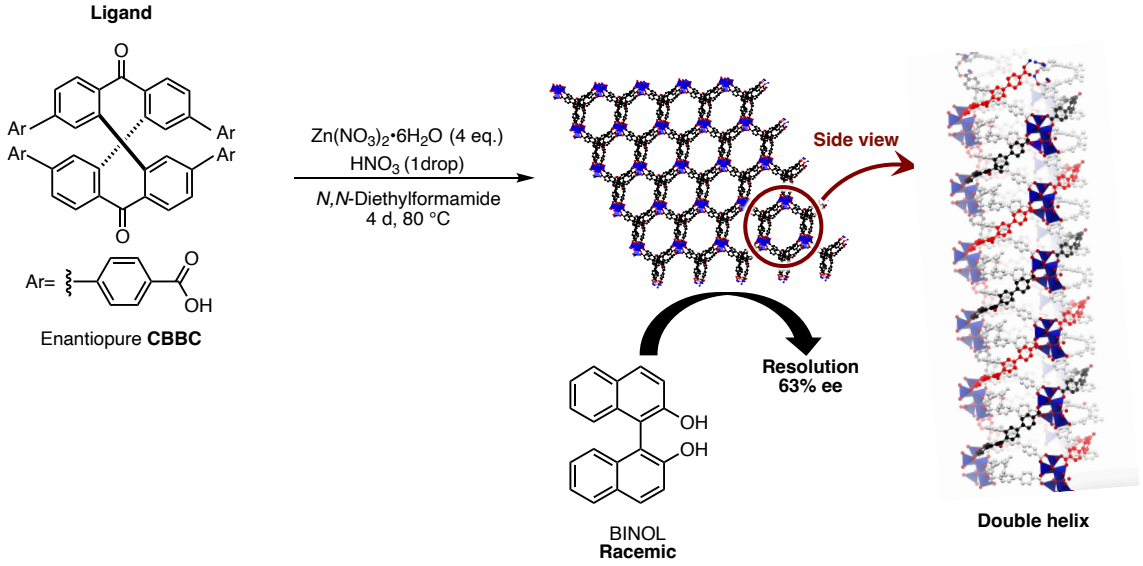
８の字型分子シクロビスビフェニレンカルボニルを配位子とするホモキラル金属有機構造体(MOF)への分子吸着

(名大院工[1]・JST さきがけ[2])○尾初瀬 大祐[1]・日下 心平[1]・松田 亮太郎[1]・忍久保 洋[1]・福井 識人[1,2]
Adsorption behavior of a homochiral metal-organic framework (MOF) consisting of a figure-eight-shaped cyclobisbiphenylenecarbonyl ligand ([1]*Graduate School of Engineering, Nagoya University*, [2]*JST PRESTO*)○Daisuke Owase,[1] Shinpei Kusaka,[1] Ryotaro Matsuda,[1] Hiroshi Shinokubo,[1] Norihito Fukui[1,2]

Homochiral metal–organic frameworks (MOFs) have been actively explored due to their potential applications for chiral stationary phases and asymmetric catalysts. We have recently synthesized a homochiral MOF consisting of a figure-eight macrocycle, cyclobisbiphenylenecarbonyl (CBBC), as a ligand. In this MOF, the ligands assemble with a double helical manner, forming one-dimensional cavity with a diameter of approximately 20 Å. In this study, we have investigated the adsorption of organic molecules into this homochiral MOF. The adsorption of racemic binaphthol resulted in preferential inclusion of one enantiomer with 63% ee.
Keywords: Figure-eight molecule: Metal-organic-frameworks: Chirality

新規ホモキラル金属有機構造体(MOF)の創出は、光学分割用充填剤や不斉触媒の開発につながるため精力的に研究されている。我々は最近シクロビスビフェニレンカルボニル(CBBC)というキラルな８の字型分子を配位子とする MOF を合成した。この MOF において、配位子は２重らせん状に配列しており、これにより直径約 20 Å の一次元空孔が与えられる。今回我々はこの新規ホモキラル MOF に対するゲスト分子の吸着を調査した。その結果、ラセミ体のビナフトールを吸着させた場合、63% ee で片方の光学異性体が優先的に吸着されることを見いだした。



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Electrochemical oxidation synthesis of oriented bis(diimino)metal coordination nanosheets on gold electrodes

([1]*Tokyo University of Science*, [2]*Japan Synchrotron Radiation Research Institute (JASRI)*, [3]*Kyoto Institute of Technology*, [4]*SPring-8*, [5]*National Institute for Materials Science (NIMS)*)
○Hiroaki Maeda[1], Kenji Takada[1], Naoya Fukui[1], Hiroyasu Masunaga[2], Sono Sasaki[3,4], Kazuhito Tsukagoshi[5], Hiroshi Nishihara[1]

Keywords: Coordination nanosheet, Bis(diimino)metal, Electrochemical oxidation method

Various synthetic methods to produce highly crystalline coordination nanosheets have been developed to clarify their inherent physical and chemical properties. Bis(diimino)metal coordination nanosheets consisting of metal ions and hexaaminobenzene (MHABs) are attractive functional materials because their electrical conductivities, redox properties, and porosities are useful for the applications in cathode materials in secondary batteries, supercapacitors, chemiresistive sensors, and electrocatalysts.[1)] Our group previously reported the facile and rapid synthesis of MHABs (M = Co, Ni, Cu) on electrodes by an electrochemical oxidation method.[2, 3)] However, the rough morphologies and low crystallinities of prepared MHABs are issues to be improved. Recently, we succeeded in controlling the crystallinity of CuHAB by modulating the reaction conditions of the liquid-liquid interfacial synthesis.[4)] Hence, optimizing synthesis conditions in the electrochemical oxidation method is expected to produce crystalline MHABs on electrodes.

In this study, we investigated the optimum synthesis conditions for crystalline MHABs on gold electrodes by an electrochemical oxidation method. Microscopic, spectroscopic, and diffraction measurements revealed the anisotropic and uniformed formation of NiHAB and CuHAB with a face-on orientation on electrodes in the optimized condition. A possible mechanism of the oriented MHAB formation will also be discussed in the presentation.

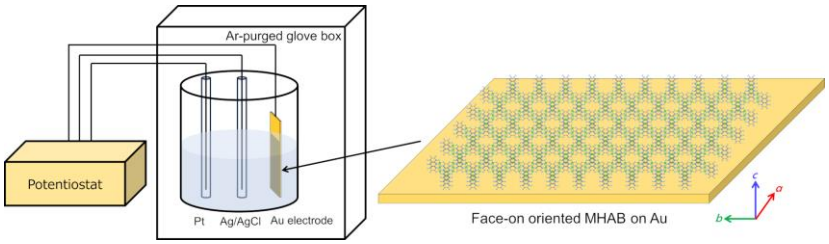

Fig. Schematic illustration of the electrochemical oxidation synthesis of MHABs and the prepared MHAB on an Au electrode in the face-on orientation.

1) H. Maeda *et al.*, *Coord. Chem. Rev.*, **2022**, *470*, 214693. 2) E. J. H. Phua *et al.*, *Chem. Lett.*, **2018**, *47*, 126. 3) K.-H. Wu *et al.*, *ACS Appl. Energy Mater.*, **2021**, *4*, 5403. 4) H. Maeda, *et al.*, *J. Inorg. Organomet. Polym.*, **2023**, in press, DOI: 10.1007/s10904-023-02920-5.

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トリプチセン骨格を有する配位ナノシートの創製と水素発生反応電極触媒への応用

（東理大創域理工[1]・東理大総研[2]）○須藤 裕太[1]・前田 啓明[2]・長島 佐代子[2]・福居 直哉[2]・高田 健司[2]・西原 寛[1,2]
Creation of coordination nanosheet with a triptycene-skeleton ligand and its application to electrocatalyst for hydrogen evolution reaction ([1]*Graduate School of Science and Technology, Tokyo University of Science,* [2]*Research Institute for Science and Technology, Tokyo University of Science*) ○Yuta Sudo,[1] Hiroaki Maeda,[2] Sayoko Nagashima,[2] Naoya Fukui,[2] Kenji Takada,[2] Hiroshi Nishihara[1,2]

Coordination nanosheets (CONASHs), which are two-dimensional materials composed of organic ligands and metal ions, have been applied as electrode materials by utilizing their variations of chemical structure designs and functionalities[1)]. Conventional CONASHs composed of π-conjugated planar ligands easily form multilayered films due to the strong interlayer π-π interaction. Hence, the stacked neighboring layers shield the metal complex sites and may depress the performance as electrode materials. To overcome this issue, we newly synthesized a Ni-HATT CONASH using a triptycene-skeleton ligand instead of conventional π-conjugated planar ligands (Fig. 1). This approach enabled metal complexes in Ni-HATT to expose the axial positions to pores. Furthermore, we investigated the catalytic activity of Ni-HATT for hydrogen evolution reaction and found it to exhibit superior catalytic performance.

Keywords : Coordination Nanosheet; Triptycene; Hydrogen Evolution Reaction; Electrocatalyst

配位ナノシートは、金属イオンと有機配位子から形成される二次元物質であり、化学構造の設計自由度の高さや金属錯体由来の機能性を利用した電極材料への応用展開が行われてきている[1)]。従来の配位ナノシートでは電気伝導性獲得のため、π共役系平面配位子が用いられてきたが、強いπ-π層間相互作用により~~容易に~~多層膜を形成しやすい。そのため、機能性発現の活性点となる金属錯体部位が遮蔽され、材料としての性能が低下しうることが課題となる。本研究では、従来のπ共役系平面配位子に代わり、トリプチセン骨格配位子を用いて、錯体部位がナノシート平面に対し直立することによりアキシアル位が空孔方向に開放される配位ナノシート(Ni-HATT)を創製した(Fig. 1)。さらに、Ni-HATT の水素発生反応(HER)に対する触媒特性を調べたところ、優れた触媒活性を示すことを見出した。

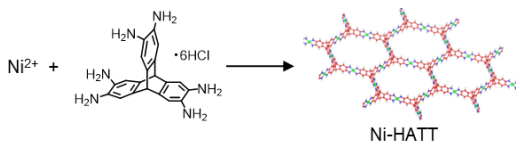

Fig. 1. Chemical structure of Ni-HATT.

1) H. Maeda, K. Takada, N. Fukui, S. Nagashima, H. Nishihara, Coord. Chem. Rev., **2022**, 470, 214693.

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
F1232(1232, Bldg. 12 [3F])

[F1232-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Hiroaki Kotani, Takahiro Iwamoto

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1232-4am-01]
Regioselective Insertion of an Alkyne into a Ruthenium-Phosphine Coordination Bond.

○Haruki Horinouchi[1], Yusuke Kimura, Yousuke Ikeda, Yuichiro Mutoh[2], Takahiro Iwamoto[1], Youichi Ishii[1] (1. Chuo University, 2. RIKEN CSRS)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1232-4am-02]
Alkyne Insertion and Cycloisomerization of Cyclometalated Complexes Derived from Biphenylphosphine

○Kentaro Shinya[1], Koki Tagai, Sae Handa, Takahiro Iwamoto[1], Youichi Ishii[1] (1. Chuo University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1232-4am-03]
Development of Hydride Substitution Reactions of Cinnamyl Alcohol Derivatives via Rhodium Catalysis

○Hokuto Kimura[1], Ken Yamanomoto[1], Kohei Endo[1] (1. Department of Chemistry, Faculty of Science, Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1232-4am-04]
Highly Efficient Mixed-Ligand Catalysts for Direct Arylation of Heteroarenes with Aryl Chlorides

○Masayuki Wakioka[1], Shunta Sakai[1,2], Keisuke Hatakeyama[1,2], Ken-ichi Tada[1], Yooichiroh Maruyama[3] (1. Sagami Chemical Research Institute, 2. Kitasato Univ., 3. JSR)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1232-4am-05]
Visible Light-promoted Oxygenation of a Mononuclear NNP(O)-Benzylpalladium Complex

○Risa Shibai[1], Yuma Shigehiro[1], Yasuyuki Ura[1] (1. Nara Women's University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1232-4am-06]
Synthesis of Novel Polypyridyl Ru Photosensitized Complex with Phenylpyridinato Ligand and Application to CO_2 Reduction Photocathode

○Yuya Tomita[1], Hironobu Ozawa[1], Ken Sakai[1] (1. Kyushu Univ.)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1232-4am-07]
Development of asymmetric allylic alkylation by assembly Cu/Pd catalysts using π-donor-acceptor interaction

○Aoto Shimozaki[1], Yuichi Kominato, Tatushi Imahori[1] (1. Tokyo University of Science)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1232-4am-08]
Development of Assembly Lewis acid / Crown ether combined catalyst reaction using π-Donor-Acceptor Interaction

○Rikuta Kozuka[1], Kousuke Tsunogaya, Tatsushi Imahori[1] (1. Tokyo university of science)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
Break

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[F1232-4am-09]
Dihydrogen Activation by a Stannacyclopentadienylidene

○Kazuki Wada[1], Shunsuke Kudo[1], Shunsuke Furukawa[1], Taku Murata[2], Minori Abe[2], Masaichi Saito[1] (1. Department of Chemistry, Graduate School of Science and Engineering, Saitama University , 2. Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1232-4am-10]
Palladium-Catalyzed Synthesis of Alkoxyallenes and Their Application in Stereoselective Transformations

○Yuuki Mori[1], Tsukasa Hitomi[1], Masamichi Ogasawara[1] (1. The Univ. of Tokushima)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1232-4am-11]
Clarification of factors behind kinetics of CO_2 capturing reactions by Re(I)-complex catalysts

○Yuto Abiru[1], Kei Kamogawa[2], Manabu Abe[1], Osamu Ishitani[1,2] (1. Hiroshima Univ. , 2. Tokyo Tech.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1232-4am-12]
Development of depolymerization systems catalyzed by an iridium complex bearing hydroxyl groups

○Chihaya Murata[1], Naoki Noto[2], Mineto Uchiyama[3], Masami Kamigaito[3], Susumu Saito[1,2] (1. Grad. Sch. Sci., Nagoya Univ., 2. IRCCS, Nagoya Univ., 3. Grad. Sch. Eng., Nagoya Univ.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1232-4am-13]

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Synthesis and Photocatalytic Property of Water-Soluble Tris(phenylpyridinato)iridium(III) Derivatives

○Taiki Noma[1], Kosei Yamauchi[1], Ken Sakai[1] (1. Kyushu Univ.)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[F1232-4am-14]

Selective Photoreactions Based on Confinement Effects with a Visible-Light-Active Pt(II)-Cornered Hollow Cage

○Rikuya Tanaka[1], Hiroki Takezawa[1], Makoto Fujita[2,3] (1. The University of Tokyo, 2. Institute for Molecular Science, 3. The University of Tokyo Institutes for Advanced Study Tokyo College)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[F1232-4am-15]

Mechanistic studies on cyclization of alkynoic acids catalyzed by Au_{25} nanoclusters bearing supramolecular reaction fields

○Kyosuke UEDA[1], Kenta ISERI[1], Ryohei SAITO[1], Katsuhiro ISOZAKI[1], Masaharu NAKAMURA[1] (1. Kyoto University)

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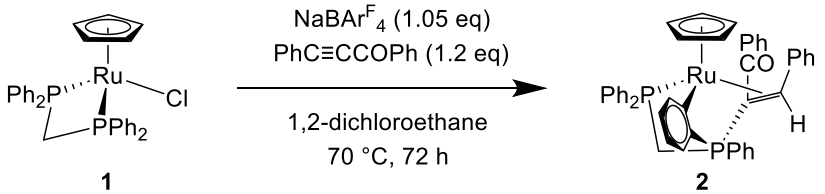
ルテニウム–dppm 錯体の Ru–P 結合への位置選択的アルキン挿入反応

（中央大学[1]・理研 CSRS[2]）○堀之内 陽樹[1]・木村 祐介・池田 洋輔・武藤 雄一郎[2]・岩本 貴寛[1]・石井 洋一[1]
Regioselective Insertion of an Alkyne into a Ruthenium–Phosphine Coordination Bond ([1]*Chuo University,* [2]*RIKEN CSRS*) ○Haruki Horinouchi,[1] Yusuke Kimura, Yousuke Ikeda, Yuichiro Mutoh,[2] Takahiro Iwamoto,[1] Youichi Ishii[1]

Although alkyne insertion represents a fundamental elementary step in transition metal chemistry, alkyne insertion toward a metal-phosphine coordination bond remains elusive. We here report a unique transformation induced by regio- and syn-selective alkyne insertion toward a ruthenium-phosphine coordination bond in a reaction of a cationic $[CpRu(dppm)]^+$ complex with an alkyne. The observed selectivity suggested that the insertion process is not a simple nucleophilic attack of a dissociated phosphorous atom toward the coordinated alkyne. Effects of substituents in unsymmetrical alkynes on the regioselectivity of the insertion reaction will be discussed.
Keywords： Regioselective; Alkyne Insertion; Unsymmetrical Alkyne; Ruthenium

不飽和化合物の挿入反応は有機金属化学における重要な素反応であるが、金属–リン配位結合への挿入反応は限られている。[1,2] 一方、当研究室では $[CpRu(dppm)]^+$ と内部アルキンとの反応において、金属–リン配位結合への挿入反応が進行することを見出している。[3] 本研究では、この挿入反応における非対称アルキンの挙動を検討することにより挿入機構に関する知見を得ることを目指した。

既法に倣い、[3] $[CpRu(dppm)]^+$ と非対称アルキンを反応させたところ、金属–リン配位結合への挿入と引き続く異性化反応が進行することが分かった。この際、挿入反応は完全に位置選択的に進行し、カルボニル基やホスホリル基などの電子求引性置換基を持つ非対称アルキンではリン原子が電子求引性置換基を持つ炭素上に導入されることを見出した。従来、金属–リン配位結合への形式的な挿入反応の多くは解離したリン原子の求核付加により進行すると提唱されていたが、上述の位置選択性は単純な求核付加型の反応から予想されるものと異なる。よって、本反応が協奏的な挿入過程で進行していることが示唆された。発表では、理論計算を用いた反応機構に関する考察についても報告する。



1 **2**

(1) Kambe, N. *et al*. *Organometallics* **2015**, *34,* 1373−1376. (2) Allen, A.; Lin, W. *Organometallics* **1999**, *18*, 2922−2925. (3) Ishii, Y. *et al*. *Organometallics* **2012**, *31,* 5150−5158.

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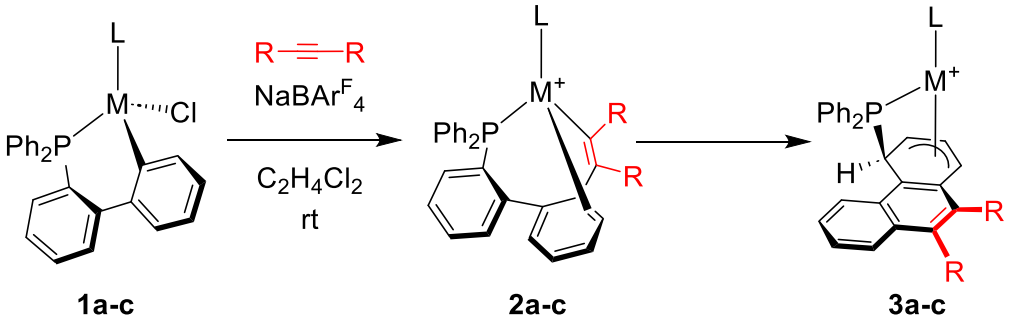
ビフェニルホスフィンから誘導されるシクロメタレート錯体のアルキン挿入と環化異性化反応

（中大理工）○新谷健太郎・互井孔貴・半田彩恵・岩本貴寛・石井洋一
Alkyne Insertion and Cycloisomerization of Cyclometalated Complexes Derived from Biphenylphosphine (*Faculty of Science and Engineering, Chuo University*) ○Kentaro Shinya, Koki Tagai, Sae Handa, Takahiro Iwamoto, Youichi Ishii

We have examined reactions of 6-membered metallacycles (Ir, Rh, Ru) derived from a biphenyl ligand with diaryl alkynes. A novel cyclo-isomerization was found to proceed with all three metals through an 8-membered metallacycle intermediate formed by the initial alkyne insertion. Of interest, this reaction includes dissociation of phosphine ligand, which is facilitated by the rotation of the biphenyl unit, and the subsequent dearomatization coupled with C-C bond formation and H-migration to afford a unique chelate structure. In addition, the isomerization rate depends strongly on the central metal. In the presentation, substituent effects of alkynes will also be discussed.
Keywords : Isomerization; Cyclometalated Complex; Ruthenium; Iridium; Rhodium

遷移金属化学において、シクロメタレート錯体は古くから研究されており、その特異なキレート効果に由来した反応性が明らかにされてきた。最近我々はナフチルホスフィンから誘導されたシクロメタレート錯体とアルキンの反応において、P-C 還元的脱離や[1]、アルキン挿入錯体からの β 炭素脱離を見出している[2]。今回は、回転自由度を持つビフェニルホスフィンから誘導されるシクロメタレート錯体 **1a-c** を用いて、ジアリールアルキンとの反応性を検討した。

6 員環シクロメタレート錯体に対してアルキンを作用させたところ、いずれの場合も 8 員環メタラサイクル **2** を経由し、ホスフィンの解離とビフェニル部位の脱芳香化を伴う新奇異性化反応が進行することを見出した。本異性化の速度は金属中心の性質に大きく依存し、イリジウム錯体では当初室温で比較的安定な **2a** が生成するが[3]70°C で 18 時間反応させることで **3** が得られるのに対して、ルテニウム錯体では室温で容易に異性化が完結することが分かった。発表では、アルキン上の置換基が異性加速度に及ぼす効果についても議論する。



1a-c **2a-c** **3a-c**

Ar^F = 3,5-$(CF_3)_2C_6H_3$, LM=Cp*Ir (**a**), Cp*Rh (**b**), (η^6-C_6Me_6)Ru (**c**)

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2) Ishii, Y. *et al*. *Organometallics* **2022**, *41*, 182–186.
3) Zhu B. *et al*. *Eur. J. Inorg. Chem.* **2018**, 3195–3202.

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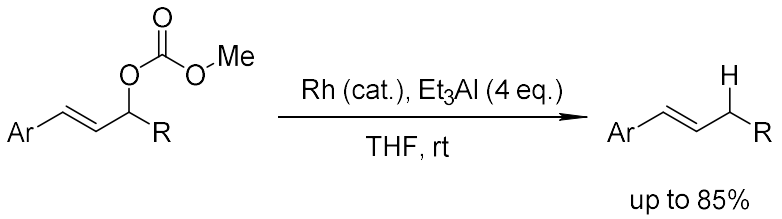
ロジウム触媒によるシンナミルアルコール誘導体のヒドリド置換反応の開発

（東理大院化学）○木村 北斗・山野本 健・遠藤 恆平
Development of Hydride Substitution Reactions in Cinnamyl Alcohol Derivatives via Rhodium Catalysis (*Department of Chemistry, Graduate School of Science, Tokyo University of Science*)
○Hokuto Kimura,[1] Ken Yamanomoto,[1] Kohei Endo[1]

Metal hydride complexes serve as essential reaction intermediates in organic synthesis. In our previous research, we explored the use of rhodium catalysts for efficient hydroboration reactions.[1] This study focuses on the hydride substitution reaction of cinnamyl alcohol derivatives. We discovered that this reaction proceeds with high regioselectivity and yield. Our approach involves using triethylaluminum as a reducing agent, coupled with a rhodium catalyst. The reaction occurs efficiently without the reduction of a carbon-carbon double bond. Furthermore, the primary cinnamyl alcohol derivatives can participate in the present reaction via the direct hydride-substitution of a hydroxyl group.
Keywords : Metal Hydride; Hydride Substitution; Rhodium

金属ヒドリド錯体は有機合成化学における重要な反応中間体である. 我々は過去にロジウム触媒を用いるヒドロホウ素化反応においてロジウムヒドリド錯体の制御に基づく高効率的な触媒設計に取り組んだ[1]. 今回, エチルロジウム錯体の β-ヒドリド脱離を経由するエチレンの発生を伴うロジウムヒドリド錯体の調製を試みた. 金属ヒドリド中間体を経由する過去の反応例では, ヒドリド置換やヒドリド付加反応と不飽和結合の還元反応が競合することが多い. 一方で本研究では, トリエチルアルミニウムを還元剤とすることでロジウム触媒を用いるシンナミルアルコール誘導体のヒドリド置換反応が, 炭素—炭素二重結合部位の還元を抑制しながら選択的に進行することを見出した.

今回我々は, 第一級および第二級のシンナミルアルコール誘導体のヒドリド置換反応が, ロジウム触媒, ノルボルナジエン, トリエチルアルミニウムのテトラヒドロフラン溶媒下で進行することを確認した. 第二級のシンナミルアルコール誘導体では, 反応の効率的な進行に水酸基の炭酸エステル誘導体を用いる必要がある. 一方, 第一級シンナミルアルコールにおいては, 水酸基のヒドリド置換反応が効率よく進行する.



1) Kohei Endo *et al.*, *Organometallics,* **2008**, *27*, 5390–5393.

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塩化アリールによるヘテロアレーン類の直接的アリール化のための高効率混合配位子触媒

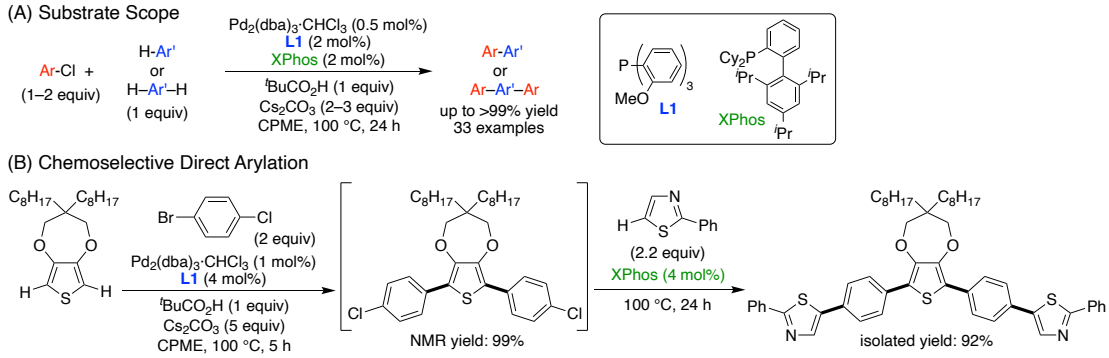
（相模中研[1]・北里大[2]・JSR[3]）○脇岡正幸[1]・坂井駿太[2]・畠山啓介[2]・多田賢一[1]・丸山洋一郎[3]

Highly Efficient Mixed-Ligand Catalysts for Direct Arylation of Heteroarenes with Aryl Chlorides ([1]*Sagami Chemical Research Institute*, [2]*Kitasato University*, [3]*JSR Corporation*) ○ Masayuki Wakioka,[1] Shunta Sakai,[2] Keisuke Hatakeyama,[2] Ken-ichi Tada,[1] Yooichiroh Maruyama[3]

We have reported that the combined use of XPhos and P(2-MeOC$_6$H$_4$)$_3$ (**L1**) enhances the efficiency in the palladium-catalyzed direct arylation of heteroarenes with aryl chlorides. In this study, we have investigated the substrate scope of this mixed-ligand catalyst. Moreover, we have found that the catalyst enables sequential reactions that leverage the differential reactivity between C–Cl and C–Br bonds, producing π-extended small molecules in a one-pot synthesis.

Keywords: Direct Arylation, Palladium Catalyst, Mixed-Ligand Catalyst, C–Cl Bond Activation, C–H Bond Activation

最近我々は、塩化アリールによるヘテロアレーン類のパラジウム触媒直接的アリール化において、２種類の配位子（XPhos と P(2-MeOC$_6$H$_4$)$_3$ (**L1**)）を同時に用いると反応が高効率化することを見出している[1]。高効率化の鍵は、XPhos と **L1** を有する錯体がそれぞれ、C–Cl 結合と C–H 結合を優先的に活性化することにある。本研究では、この混合配位子触媒の基質適応範囲を詳しく調査し、様々な基質に適応可能であること見出した（下図 A）。さらに、この触媒を用いてπ拡張型低分子化合物の合成を検討した（下図 B）。XPhos と **L1** を用いる混合配位子触媒は、C–Cl 結合活性化に有効である一方、Pd/**L1** 触媒は C–Cl 結合を活性化できないものの、C–Br 結合を活性化が可能である[2]。これらの知見に基づき、C–Cl 結合と C–Br 結合の反応性の違いを利用した逐次反応により、π拡張型低分子化合物のワンポット合成が可能であることを明らかにした（下図 B）。



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可視光が促進する単核 NNP(O)-ベンジルパラジウム錯体の酸素化

（奈良女大理）○芝井 理紗・重弘 悠真・浦 康之

Visible Light–promoted Oxygenation of a Mononuclear NNP(O)–benzylpalladium Complex

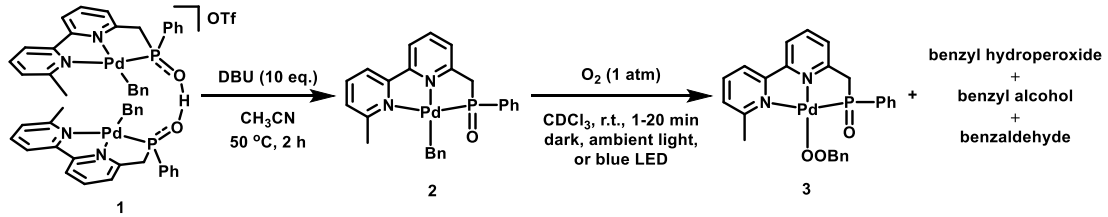
(*Faculty of Science, Nara Women's University*) ○Risa Shibai, Yuma Shigehiro, Yasuyuki Ura

Transition-metal complexes with a phosphoryl moiety are expected to exhibit characteristic reactivity and catalytic functions due to the cooperative effect of the phosphoryl moiety and a metal atom. In our laboratory, a dinuclear benzylpalladium complex containing a phosphoryl moiety, [{PdBn(MeNNP(O))}$_2$H][OTf] (**1**), has been previously synthesized. In the present study, a mononuclear benzyl complex was synthesized from the dinuclear complex **1** and the reaction with O_2 under various conditions was investigated. The mononuclear benzyl complex with a phosphoryl moiety, [PdBn(MeNNP(O))] (**2**), was obtained in high yield by adding 10 eq. of DBU to **1**. The reaction of **2** with 1 atm O_2 in $CDCl_3$ at room temperature afforded complex **3**, in which O_2 was inserted into the Pd–C(sp^3) bond of **2**, and oxygenated products derived from the benzyl ligand. The oxygenation of **2** was further examined under various conditions and was found to be promoted under visible light irradiation such as ambient light or blue LED, or in the presence of HCl.

Keywords : palladium complex; benzyl ligand; oxygen; visible light; phosphoryl ligand

ホスホリル部位をもつ遷移金属錯体では，ホスホリル部位と金属原子との協同効果による特徴的な反応性や触媒機能の発現が期待される。当研究室では，ホスホリル部位を含む二核ベンジルパラジウム錯体[{PdBn(MeNNP(O))}$_2$H][OTf] (**1**)を以前に合成している [1]。本研究では，二核錯体 **1** から単核ベンジル錯体を合成し，種々の条件下での酸素との反応について検討した。

錯体 **1** に対して 10 当量の DBU を加えることにより，ホスホリル部位をもつ単核ベンジル錯体[PdBn(MeNNP(O))] (**2**)が高収率で得られた。重クロロホルム溶媒中，**2** を室温下で 1 気圧の酸素と反応させることで，**2** の Pd–C(sp^3)結合に酸素分子が挿入した錯体 **3** およびベンジル配位子由来の酸素化生成物が得られた。錯体 **2** の酸素化反応をさらに種々の条件下で検討したところ，周辺光または青色 LED などの可視光照射下，または HCl 存在下で促進されることがわかった。



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2-フェニルピリジナート配位子を有する新規ポリピリジルルテニウム光増感剤の合成と CO_2 還元 TiO_2 フォトカソードへの応用

（九大[1]）○富田 悠也[1]・酒井 健[1]・小澤 弘宜[1]

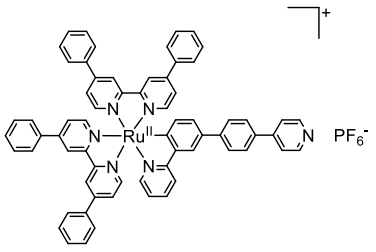
Synthesis of a Novel Polypyridyl Ruthenium Photosensitizer with 2- Phenylpyridinato Ligand and Its Application to the TiO_2 Photocathode for CO_2 Reduction

([1]*Kyushu Univ.*) ○Yuya Tomita,[1] Ken Sakai,[1] Hironobu Ozawa[1]

Recently, we have achieved CO_2-to-CO conversion with a relatively higher selectivity even in aqueous media by using the TiO_2 electrode modified with a Co porphyrin molecular catalyst having a pyridyl anchor (i.e., FTO/TiO_2/CoP-py cathode). In this study, in order to achieve the TiO_2 photocathode for solar-driven CO_2-to-CO conversion, a novel polypyridyl ruthenium complex with 2-phenylpyridinato derivative (Ru(ppy)-py) has been designed and synthesized as a photosensitizer for the FTO/TiO_2/CoP-py cathode. Synthesis, characterization, and photo- and electrochemical properties of Ru(ppy)-py will be presented. Moreover, photoinduced electron transfer over the Ru(ppy)-py-modified TiO_2 electrode will be also discussed.

Keywords : Polypyridyl Ruthenium Photosensitizer; Cyclometalated Complexes; Photoelectrochemical CO_2 Reduction; TiO_2 Photocathode

最近我々は、ピリジルアンカーを有する Co ポルフィリン触媒(CoP-py)を修飾した TiO_2 電極(FTO/TiO_2/CoP-py カソード)を用いることによって、水溶液中においても比較的高選択的に CO_2 を CO に還元できることを報告した。[1] 本研究では、太陽光によって CO_2 還元反応を駆動できる CO_2 還元 TiO_2 フォトカソードの開発に向けて、FTO/TiO_2/CoP-py カソード用の新規光増感剤の開発を目的とした。CoP-py による CO_2 還元反応は-1.25 V vs. SCE よりも負の印加電圧下において効率良く進行することが明らかとなっていることから[1]、CoP-py を触媒とした CO_2 還元 TiO_2 フォトカソード用の光増感剤においては、TiO_2 伝導帯の励起電子によって還元的消光が効率良く進行すること、およびその結果生じた一電子還元体が-1.25 V よりも強い還元力を持つことが必要不可欠であると考えられる。そこで本研究では、2-フェニルピリジナートにピリジルアンカーを導入した新規ポリピリジルルテニウム光増感剤(Ru(ppy)-py、右図)を設計し、その合成を行った。講演では Ru(ppy)-py の合成と性質、およびこれを修飾した TiO_2 電極上における光電子移動反応に関して報告する予定である。



[1] H. Ozawa, R. Kikunaga, H. Suzuki, R. Abe, K. Sakai, *Sustain. Energy Fuels*, **2023**, *7*, 1627.

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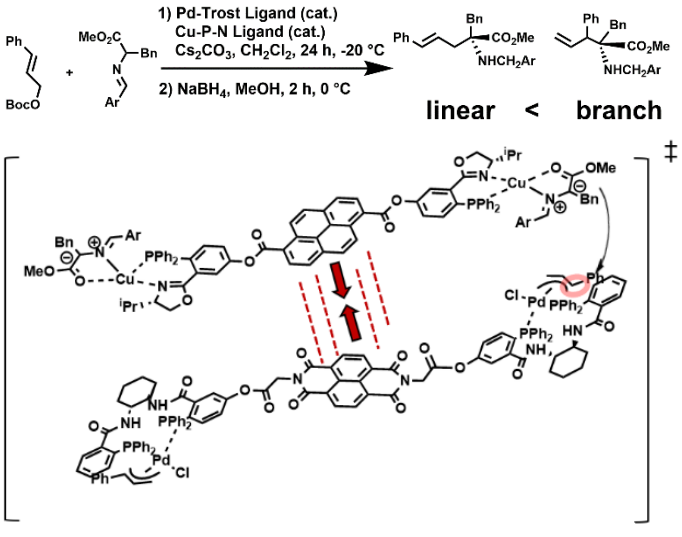
π-ドナー–アクセプター相互作用を活用した集積型 Cu/Pd 複合触媒システムによる不斉アリル位アルキル化反応の開発

(東理大院工)○霜崎 碧人・今堀 龍志・小湊 雄一

Asymmetric allylic alkylation with assembly Cu/Pd catalyst system using π-donor-acceptor interaction (*Graduate School of Engineering, Tokyo University of Science*), ○Aoto Shimozaki, Tatsushi Imahori, Yuichi Kominato

Bimetallic catalyst system can demonstrate sophisticated catalysis through the dual activation and multiple regulations of the different type of catalyst.[1)] The key for the successful bimetallic catalyst system is efficient induction of the cooperative functions of the different catalysts. Then our group has designed and developed a hetero-bimetallic catalyst system using π-donor-acceptor interaction that would efficiently induce the cooperative functions through assembly.[2)] In this study, we developed a new assembly hetero-bimetallic catalyst system for asymmetric allylic alkylation with Cu-*P*,*N*-ligand catalyst and Pd catalyst[1)] by introducing π-donor-acceptor interaction units. We envisioned that the bimetallic transition state would be efficiently constructed by the assembled catalysts, and the catalysis would be selectively promoted. In addition, we expected branch-selective reaction by using the assembly Pd-Trost-ligand catalyst.
Keywords：Asymmetric catalysis; Supramolecular catalyst; Asymmetric allylic alkylation

異なる金属触媒を 2 種類用いた異種金属触媒反応は、異なる金属触媒が協同的に機能することで高度な化学変換を実現できる [1)]。異種金属触媒反応を円滑に進行させるためには、異なる金属触媒を効率的にかつ協同的に機能させることが重要であり、我々のグループは、π-ドナー-アクセプター相互作用によって異なる金属触媒を集積させ、効率的にかつ協同的に機能させる集積性異種金属触媒システムの開発を行ってきた [2)]。本研究では、新たな集積性異種金属触媒システムとして、不斉アリル位アルキル化反応に用いる Cu-*P,N* 配位子触媒と Pd 触媒 [1)] の集積触媒システムの開発を行った。Cu-*P,N*配位子触媒と Pd 触媒が集積して協同的に機能することで、二核型遷移状態を効率的に構築し、より円滑な触媒反応が進行することを想定した(右図)。また、Pd 触媒の配位子に Trost 配位子を用いることで、分岐型生成物の生成を期待した。



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2) 角ケ谷幸佑, 今堀龍志, 日本化学会 第 98 春季年会(2018), 1A8-35

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π-ドナー・アクセプター相互作用を活用した集積性ルイス酸/クラウンエーテル複合触媒の開発

（東理大院工）○小塚 陸太・角ケ谷 幸佑・今堀 龍志

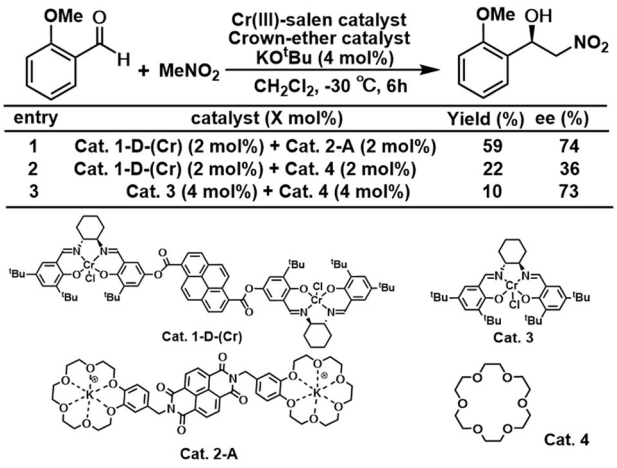
Development of Assembly Lewis acid / Crown ether combined catalyst system using π-Donor-Acceptor Interaction (*Graduate School of Engineering, Tokyo University of Science*)

○Rikuta Kozuka[1], Kosuke Tsunogaya, Tatsushi Imahori[1]

To smoothly promote bimetallic cooperative catalysis, efficient construction of the bimetallic transition state is important. Then our group has designed and developed a new hetero-bimetallic catalysts system using π-donor-acceptor interaction.[1)] By introducing the π-interaction units into different two metal catalyst each, assembly of the different catalysts would be induced, and hetero-bimetallic catalysis with the assembled two different catalysts would be selectively promoted. In this study, we developed an assembly Crown-ether/Cr-salen catalyst system using π-donor-acceptor interaction. The Crown-ether unit would bring a nucleophile through capturing the counter cation, and the Cr-salen complex would activate an electrophile as a Lewis acid, which would assembly and cooperatively function to induce catalysis. The designed assembly catalyst system showed higher catalytic activity and stereoselectivity than non-assembled catalyst system in Henry reaction (Figure 1). This result would arise from the efficient construction of the transition state through assembly.

Keywords : Asymmetric catalyst; Supramolecular catalyst; Henry reaction;

異なる金属触媒を 2 種類用いた異種金属触媒反応を円滑に進行させるためには、異なる金属触媒が協同的に機能する二核型遷移状態を効率的に構築することが重要である。我々の研究室では、π−ドナー・アクセプター相互作用を利用して異なる 2 種類の金属触媒を集積させ、効率的に協同的に機能させる集積性異種金属触媒システムの開発を行ってきた[1)]。本研究では、アニオン性求核剤の対カチオンを捕捉するクラウンエーテルと親電子剤を Lewis 酸として活性化する Cr-salen 錯体をπ−ドナー・アクセプター相互作用によって集積させた新たな集積性異種金属触媒システムの開発を行った。設計した触媒を合成し、Henry 反応に適用したところ（Figure 1）、非集積性触媒（Cat.3, Cat.4）を用いた時に比べて、収率・立体選択性が大きく向上した。触媒の集積によって、求核剤であるニトロナートイオンと親電子剤であるアルデヒドが適切に配置され、効率的な遷移状態形成が行われたと推定される。集積性の柔軟な反応空間によって広い基質適用性が期待され、今後、基質適用性の検討を行う。



entry	catalyst (X mol%)	Yield (%)	ee (%)
1	Cat. 1-D-(Cr) (2 mol%) + Cat. 2-A (2 mol%)	59	74
2	Cat. 1-D-(Cr) (2 mol%) + Cat. 4 (2 mol%)	22	36
3	Cat. 3 (4 mol%) + Cat. 4 (4 mol%)	10	73

Figure 1. Evaluation of Catalyst

1) 角ケ谷幸佑，今堀龍志，東京理科大学大学院，第 98 回春季年会(2018)，1A8-35

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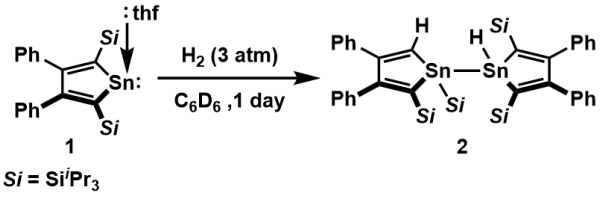
スタンナシクロペンタジエニリデンを用いた水素分子の活性化

(埼玉大院理工[1]・広島大院先進理工[2]) ○和田 一樹[1]・工藤 俊輔[1]・古川 俊輔[1]・村田 拓[2]・阿部 穣里[2]・斎藤 雅一[1]
Dihydrogen Activation by a Stannacyclopentadienylidene ([1]*Department of Chemistry, Graduate School of Science and Engineering, Saitama University*, [2]*Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kazuki Wada,[1] Shunsuke Kudo,[1] Shunsuke Furukawa,[1] Taku Murata,[2] Minori Abe,[2] Masaichi Saito[1]

Activation of small molecules by main group compounds is of current interest in terms of no need of less abundant transition metals. In particular, group 14 divalent species have received considerable attention as alternatives of transition-metal compounds. For example, a boryl-substituted stannylene undergoes a 1,1-addition reaction with dihydrogen, which is generally unreactive toward main group compounds. The unique reactivity is ascribed to increase in an energy level of the lone pair electrons on tin because of the electro-positive boryl groups. On the other hand, we have designed stannacyclopentadienylidene **1**, which possesses a low-lying LUMO, and synthesized its Lewis-base adducts. We now demonstrate the reaction of **1** with dihydrogen to afford compound **2** through the reaction pathway different from that of the known 1,1-addition reaction and its reaction mechanism is elucidated by quantum-chemical calculations.
Keywords: metallylene; stannacyclopentadienylidene; small molecule activation; tin

地球上に豊富に存在する典型元素を希少な遷移金属の代わりに用いる化学の開拓は、省資源の観点から重要な研究課題である。中でも、近年、14 族元素二価化学種を用いて遷移金属では容易に起こる小分子活性化を達成しようという試みが盛んである。例えば、スズ上にホウ素官能基を有するスタンニレンは、通常典型元素化学種に対して不活性な水素分子を活性化できることが知られている[1)]。これはホウ素官能基の電子供与効果によりスズ上の孤立電子対の反応性が増加したため、と解釈できる[2)]。一方当研究室はスタンニレンの反応性を高める方法として、スズ二価中心をブタジエン骨格に組み込むことにより LUMO を下降させることを考案し[3)]、スタンナシクロペンタジエニリデン **1** を設計・合成した（Scheme 1）[4)]。今回、化合物 **1** の高い反応性を活かして水素との反応を検討した。化合物 **1** に水素を作用させたところ、予想した 1, 1−付加反応[1)]とは異なる反応経路を経て化合物 **2** が生成することを見いだした（Scheme 1）。その反応機構を量子化学計算より明らかにしたので、併せて報告する。

Scheme 1. Reactions of stannacyclopentadienydene **1** with dihydrogen.



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パラジウム触媒を用いたアルコキシアレンの合成と立体選択的分子変換への応用

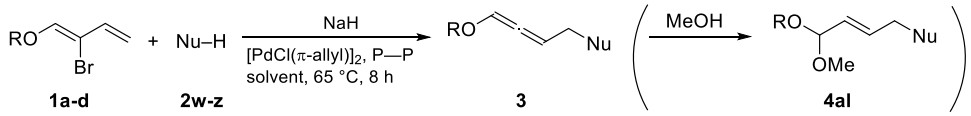
（徳島大院理工）○森　勇綺・人見　牧・小笠原正道

Palladium-Catalyzed Synthesis of Alkoxyallenes and Their Application in Stereoselective Transformations ([1]*Department of Natural Science, Graduate School of Science and Technology, Tokushima University*) ○Yuuki Mori,[1] Tsukasa Hitomi,[1] and Masamichi Ogasawara[1]

Allenes are unique compounds with characteristic reactivity and steric properties. Although allenes have gained much attention as synthetic intermediates lately, their applications in organic synthesis are still relatively unexplored compared to those of alkenes and alkynes. In this presentation, we would like to report a palladium-catalyzed reaction giving a variety of alkoxyallenes **3** and their applications. It was found that a series of alkoxyallenes **3** could be prepared and isolated in good yields under the optimized conditions. The results of the Pd-catalyzed reaction are summarized in Table 1. For the success of the reaction, the use of an appropriate polar solvent is crucial. When the reaction of **1a** with **2w** was conducted in THF, no allenic product was obtained and the substrate was recovered intact (entry 1). The reaction in dioxane/methanol consumed **1a** completely, but the product was acetal **4al** in 60% instead of allene **3aw** (entry 2). It was found that the same reaction in dioxane/DMSO provided expected allene **3aw** in 66% isolated yield (entry 3).

アレンは特徴的な反応性と立体的性質を持つユニークな化合物である。近年、アレンは合成中間体として注目されているが、有機合成における応用はアルケンやアルキンに比べて未開拓である。本発表では、Pd 触媒を用いたアルコキシアレンの合成反応とその応用について報告する。一連のアルコキシアレン **3** は、下図に示す反応により良好な収率で合成できることがわかった。この反応が進行するには、適切な極性溶媒を使用することが重要である。**1a** と **2w** の反応を THF 中で行った場合、目的とするアレンは全く得られず未反応基質がそのまま回収された (entry 1)。dioxane/MeOH を溶媒として用いると **1a** は完全に消費されたが、目的とするアレン **3aw** の代わりに 60%収率でアセタール **4al** が生じた (entry 2)。一方、dioxane/DMSO 中で同じ反応を行うと、**3aw** が単離収率 66%で得られた (entry 3)。

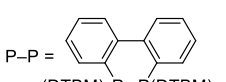
Table 1. Palladium-Catalyzed Synthesis of Alkoxyallenes **3** from (*Z*)-1-Alkoxy-2-bromo-1,3-butadienes **1** and Malonates **2**[a]



1a-d **2w-z** **3** **4al**

R = Me (**a**), Et (**b**), Ph (**c**), -C_6H_3-2,6-Me_2 (**d**)

Nu = $CMe(CO_2Me)_2$ (**w**)
$CEt(CO_2Et)_2$ (**x**)
$CPh(CO_2Et)_2$ (**y**)
$C(NHAc)(CO_2Et)_2$ (**z**)



entry	**1**	Nu-H **2**	solvent	yield(%)[b]
1	**1a**	**2w**	THF	0[c]
2	**1a**	**2w**	dioxane/MeOH	0[d]
3	**1a**	**2w**	dioxane/DMSO	66(**3aw**)

[a]The reaction was carried out with **1** (ca. 1 mmol), **2** (2.0 equiv. to **1**) and NaH (1.8 equiv. to **1**) in the presence of a palladium-catalyst (5.0 mol %) generated in situ from $[PdCl(\pi\text{-allyl})]_2$ and the bisphosphine ligand in the given solvents. [b]Isolated yield by silica gel chromatography. [c]Unreacted **1a** was recovered. [d]Substrate **1a** was completely consumed and **4al** was obtained in 60% yield.

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Re(I)錯体触媒による CO_2 捕集反応速度の測定と影響因子の解明

(広島大院先進理工[1]・東工大理[2]) ○阿比留 悠斗[1]、鴨川 径[2]、安倍 学[1]、石谷 治[1,2]

Clarification of factors behind kinetics of CO_2 capturing reactions by Re(I)-complex catalysts

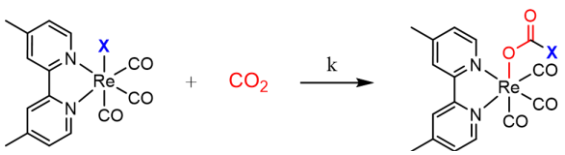
(*Hiroshima Univ.*[1], *Tokyo Tech.*[2]) ○Yuto Abiru[1], Kei Kamogawa[2], Manabu Abe[1], Osamu Ishitani[1,2]

Catalytic reduction reactions of low concentration CO_2 are attracting attention as important technology for solving global warming and shortage of carbon and energy resources because the high energy and additional cost are required for concentration of CO_2 in exhaust gas. We already reported that Re(I) complexes coordinated with deprotonated triethanolamine efficiently capture CO_2 from 10% CO_2 and the captured CO_2 can be directly reduced.[1,2] However, its activity decreases under lower concentrations of CO_2 such as 1%. In this study, for clarifying origins of this CO_2 capturing reactions, the rates and activation parameters of the CO_2 capture reactions using various alcohols were investigated by using the stopped-flow method.

Keywords : CO_2 capture reaction, Kinetics, Re(I) complex catalyst

CO_2 還元触媒反応は、地球温暖化や化石資源枯渇の問題を一挙に解決する可能性のある技術として注目されている。これまでの研究では、純粋な CO_2 を用いて触媒活性が評価されてきた。しかし、排ガス中の CO_2 を濃縮するためには高いエネルギーと追加コストが必要となることを考慮すると、低濃度 CO_2 を光化学的・電気化学的に直接還元する触媒システムの開発が望ましい。

我々は、脱プロトン化したトリエタノールアミン(TEOA)が酸素原子で配位した Re(I)錯体は CO_2 を効率よく捕集することを見出した。この捕集反応により、Re(I)触媒は、10%の CO_2 雰囲気下においても純粋な CO_2 雰囲気下での還元触媒活性を維持する。[1][2]しかし、より低濃度の CO_2 例えば 1%CO_2 雰囲気下ではその触媒活性が低下した。このような極低濃度 CO_2 を効率よく還元する光触媒を開発するためには、CO_2 捕集反応の性能をさらに向上させなければならない。本研究では、ストップトフロー法を用いて、様々なアルコールによる Re(I)錯体触媒の CO_2 捕集反応（式 1）の速度、活性化パラメーターを詳細に調べ、この反応の速度を決定する因子の解明を試みた。



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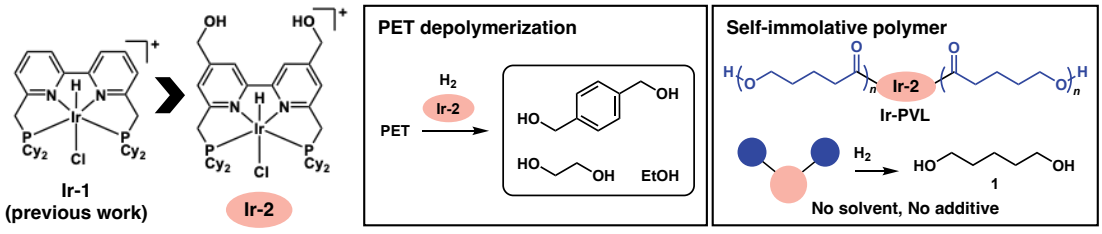
ヒドロキシ基を含有する新規 Ir 錯体を触媒とするポリマー解重合法の開発

（名大院理[1]・名大 IRCCS[2]・名大院工[3]）○村田 知隼[1]・納戸 直木[2]・内山 峰人[3]・上垣外 正己[3]・斎藤 進[1,2]
Development of depolymerization systems catalyzed by an iridium complex bearing hydroxyl groups ([1]*Grad. Sch. Sci., Nagoya Univ.* [2]*IRCCS, Nagoya Univ.*, [3]*Grad. Sch. Eng., Nagoya Univ.*) ○Chihaya Murata,[1] Naoki Noto,[2] Mineto Uchiyama,[3] Masami Kamigaito,[3] Susumu Saito[1,2]

In recent years, wasteful plastics disposed of in nature have become a serious problem because microplastics are harmful to human health and can deteriorate marine ecosystems. The development of methods for depolymerization, which contributes to polymer upcycling, plays a crucial role in addressing this challenge. We have developed an iridium complex bearing two hydroxyl groups that can efficiently promote the hydrogenative degradation of polyesters, affording monomeric alcohols which are valuable as fuels and synthetic building blocks. In addition, we have synthesized a self-immolative polymer by incorporating this iridium complex into the polyester main chain. This polymer could be easily decomposed under a hydrogen atmosphere, resulting in the production of the corresponding monomeric alcohol.
Keywords : Iridium, Catalytic hydrogenation, Metal complex, Depolymerization

高分子材料のリサイクルを可能とする化学分解性ポリマーの開発は、海洋プラスチック等の課題に対処する上で重要である[1)]。当研究室では、独自に開発したイリジウム錯体 **Ir-1** が、触媒的水素化によるエステルからアルコールへの変換に有効であることを既に報告している[2)]。本研究では、**Ir-1** に 2 つのヒドロキシメチル基を導入することで、エステルの触媒的水素化反応においてより有効性の高いイリジウム錯体 **Ir-2** を新たに開発した。この **Ir-2** は、小分子のエステルだけでなく、ポリエチレンテレフタラート（PET）等のポリエステルの水素化にも有効であった。さらに、ポリマーの設計と合成の段階から化学分解性を付与するために、イリジウム錯体をポリマーの主鎖に組み込んだ自己分解可能なポリマー**Ir-PVL** の開発にも取り組んだ。このポリマーを高圧水素に高温で付したところ、**Ir-PVL** は容易に解重合し、生成物としてアルコール **1** が得られた。



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水溶性トリス(フェニルピリジナト)イリジウム誘導体の合成と光触媒機能

（九大理化）○野間 大暉、山内 幸正、酒井 健
Synthesis and Photocatalytic Property of Water-Soluble Tris(phenylpyridinato)iridium(III) Derivatives (*Dept. Chem., Kyushu Univ.*) ○Taiki Noma, Kosei Yamauchi, Ken Sakai

Recently, catalytic CO_2 reduction into value-added chemicals has been actively explored in order to establish a carbon-neutral energy society. In line with this direction, one of our recent interests has concentrated on the development of environmentally friendly photocatalytic CO_2 reduction systems which are operatable in fully aqueous media by avoiding the use of any organic solvents causing a risk of pollution by their emission to the environment. In this context, a water-soluble diimine-diphosphine copper(I) photosensitizer was proven to be quite excellent in promoting aqueous-based photocatalysis.[1,2] Nevertheless, the copper(I) complex was found to suffer from its instability due to the ligand dissociation when it is oxidized into the copper(II) species. In order to achieve more highly robust water-soluble photosensitizers, the present study attempts to synthesize and characterize water-soluble tris(phenylpyridinato)iridium(III) derivatives having a water-solubilizing carboxyl group on each phenylpyridinate ligand. With this aim, we have chosen 3-methoxycarbonyl-6-phenylpridine to prepare a precursor complex having methoxycarbonyl residues. After obtaining the tris(3-methoxycarbonyl-6-phenylpyridinato)iridium(III), the water-soluble photosensitizer designed in this study is expected to be yielded by the simple hydrolysis of the methoxycarbonyl group into the carboxyl group. The synthetic strategy is shown in the figure.

Keywords : Photocatalysis, Water-soluble Iridium Photosensitizer, CO_2 Reduction

近年、カーボンニュートラル社会の実現のため CO_2 還元反応が盛んに研究されている。我々のグループでは水溶液中での光エネルギー変換反応の研究を重点的に推進しており、水溶性 Cu 錯体を光増感剤として用いた水中での CO_2 還元反応に成功している。[1,2]しかしながら、銅(I)錯体は光反応中に中心金属の酸化を受け、分解する点が問題視されてきた。そこで本研究では、より強固な配位構造を有する $Ir(ppy)_3^+$ (ppy = phenylpyridinate)に水溶性置換基としてカルボキシル基を導入した水溶性 Ir 光増感剤の合成と性質について検討したので報告する。本研究では、カルボン酸のメチルエステルを置換基に有する配位子を用い、まずエステル化した錯体を合成し、その後けん化することにより、目的化合物の合成を試みている。得られる錯体については、分光学的特性ならびに光触媒特性について検討し、報告する予定である。

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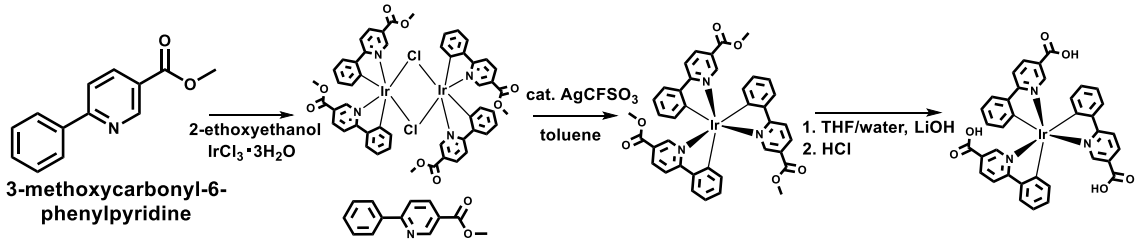

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可視光応答性 Pt(II)中空錯体による基質の包接状態制御に基づく選択的光反応

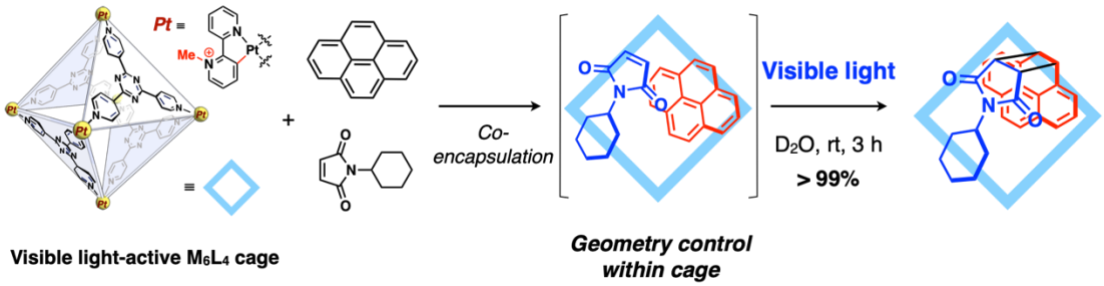
（東大院工[1]・分子科学研究所[2]・東大 UTIAS[3]）○田中 陸也[1]・竹澤 浩気[1]・藤田 誠[1,2,3]
Selective Photoreactions Based on Confinement Effects with a Visible-Light-Active Pt(II)-Cornered Hollow Cage ([1]*Graduate School of Engineering, University of Tokyo*, [2]*Institute for Molecular Science*,[3]*UTIAS, The University of Tokyo*) ○Rikuya Tanaka[1], Hiroki Takezawa[1], Makoto Fujita[1,2,3]

Photoreactions within a cage compound enable unique molecular transformations based on confinement effects.[1] Most of them require UV light, which limits substrate scope and selectivity. Recently, we reported a visible light-active M_6L_4 cage constructed from a cyclometalated Pt(II) complex. Herein, we report a selective and efficient visible-light-induced [2+2] reaction using the cage. The cycloaddition proceeded quantitatively under blue-light irradiation via a ternary complex with well-defined geometry. The mechanistic study revealed that the reaction proceeded through an energy transfer process, and the cyclometalated Pt(II) vertex contributed to the improved reactivity.
Keywords: Self-Assembly, Host-Guest, Photochemistry, Photoredox Catalyst, Visible-Light-Induced Reactions

かご型分子に包接された基質は，その配座や立体環境が強く制限される。この包接状態制御に基づき，ケージ内での光反応は特異な反応性・選択性などバルク溶液中では不可能な分子変換を可能にする[1]。しかし，その多くが紫外光照射を必要とし，反応基質の制限や選択性低下などの問題があった。最近我々は，優れた分子認識・配座制御能を有する M_6L_4 中空錯体の骨格をもとに，シクロメタル化白金(II)錯体を頂点とすることで包接能力と可視光応答性を兼ね揃えた中空錯体を構築できることを報告している(第103春季年会)。本研究では，可視光応答性 M_6L_4 ケージを用いると，芳香族炭化水素とマレイミドの立体選択的クロス[2+2]環化付加反応が可視光照射で進行することを見出した。

中空錯体と基質を水中で撹拌すると，空孔内で基質配座と位置関係が明確に定まった三元系包接錯体を形成した。これに青色 LED 光を室温で 3 時間照射すると，定量的に環化付加生成物(*syn* 体)が得られた。可視光応答性を持たない従来の M_6L_4 ケージを用いた場合と比較して収率は向上し，可視光応答性シクロメタル化白金(II)頂点の導入が，反応性向上に寄与していることがわかった。反応機構に関する研究から，反応はケージから基質へのエネルギー移動を経て進行することがわかった。

***Syn*-selective and reactivity-enhanced [2+2] cycloaddition**



1) M. Fujita *et al. J. Am. Chem. Soc*. **2007**, *129*, 7000.; K. Raymond *et al. J. Am. Chem. Soc.* **2015**, *137*, 10128.; M. Fujita *et al. Bull. Chem. Soc. Jpn.* **2021**, *94*, 2351.

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超分子反応場を有する Au_{25} ナノクラスターによるアルキン酸の触媒的環化の反応機構研究

（京大化研・京大院工）○上田 恭輔・齋藤 亮平・井芹 建太・磯﨑 勝弘・中村 正治

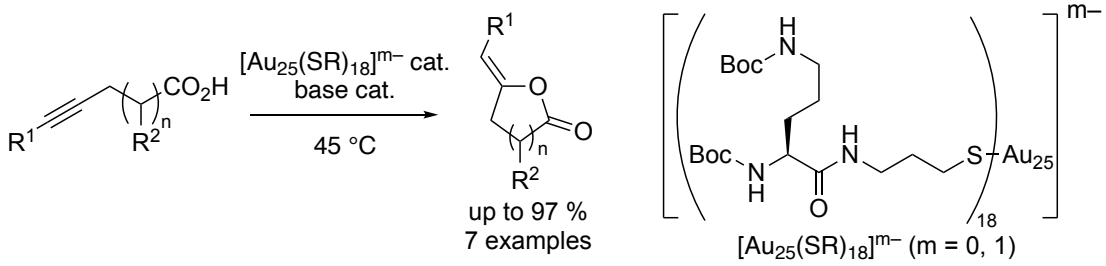
Mechanistic Studies on Cyclization of Alkynoic Acids Catalyzed by Au_{25} Nanoclusters Bearing Supramolecular Reaction Fields. *(Institute for Chemical Research, Kyoto University, Graduate School of Engineering, Kyoto University)* ○Kyosuke Ueda, Ryohei Saito, Kenta Iseri, Katsuhiro Isozaki, Masaharu Nakamura

Peptide dendron thiolate ligands act as a hydrogen bonding supramolecular reaction field to accelerate the cyclization reaction of alkynoic acids catalyzed by $[Au_{25}(SR)_{18}]^-$ nanoclusters: In the presence of the gold nanocluster (AuNC) catalysts, alkynoic acids were smoothly cyclized to afford corresponding alkylidene lactones. We herein report elucidating the catalytically active species, the reaction mechanism, and the reaction acceleration effect of the hydrogen bonding reaction field.

Keywords: Gold Nanocluster; Catalyst; Supramolecular Reaction Fields; Cyclization Reaction; Reaction Field.

チオラート保護金ナノクラスターは単一組成の分子として単離可能であることから，触媒利用研究が盛んに行われてきた。しかし，強固な金－チオラート結合が触媒毒となるため，触媒活性が低いことが課題とされてきた。我々は多数の水素結合点を有するペプチドデンドロンチオラート配位子を用いることで，Au_{25}ナノクラスター（Au_{25}NC）上に水素結合性超分子反応場が構築され，Au_{13}超原子コアの光増感作用に基づく光触媒反応[1]や，アルキン酸の触媒的環化反応[2]が効率よく進行することを見出している。本研究ではアルキン酸の触媒的環化反応における反応機構解明を目的として，触媒活性種の同定および超分子反応場の作用検証を行った。

4-ペンチン酸のクロロホルム溶液に対しそれぞれ触媒量の塩基およびAu_{25}NCを添加し，各種スペクトルによる経時変化を追跡した。紫外可視吸収スペクトルから反応系中においてAu_{25}NCが酸化されていること，NMRスペクトルからはこの酸化体が活性種として作用していることが明らかとなった。更にAu_{25}NCとアルキン酸の会合実験により，配位子－基質間の水素結合が反応速度向上に寄与していることが強く示唆された。本講演では，酸化数の異なるAu_{25}NCの触媒活性の比較，ならびに，水素結合超分子反応場の効果について報告する。



1. (a) Isozaki, K.; Nakamura, M. et al. *ACS Catal.* **2021,** *11,* 13180–13187. (b) Isozaki, K.; Nakamura, M. et al. *Angew. Chem. Int. Ed.* **2024,** *63,* e202312135.
2. Ueda, K.Iseri, K.; Isozaki, K. Nakamura, M. *The 103st CSJ Annual Meeting,* **2023,** K502-3pm-09.

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:00 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:00 AM UTC
F1234(1234, Bldg. 12 [3F])

[F1234-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Keishiro Tahara, Yoshiaki Shoji

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1234-4am-01]
Synthesis and cancer-cell selective cytotoxicity of a dicopper complex with *p*-cresol-amide-tether-tacn ligand having a porphyrin DNA target

○Riko Yamamoto[1], Machi Hata[1], Masato Kodera[1], Ami Kodama[1] (1. Doshisha university)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1234-4am-02]
Synthesis and cancer-cell selective cytotoxicity of dicopper(II) complexes with p-cresol-2,6-amide-tether-cyclen derivative having triphenylphosphine mitochondria target

○Hayato Takai[1], Machi Hata[1], Masato Kodera[1] (1. Doshisha university)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1234-4am-03]
Synthesis and cancer-cell selective cytotoxicity of a dicopper complex with cyclen per-methyl derivative of 4-phenanthrene introduced phenol-2,6-amide-tether-cyclen ligand

○Kenshiro Fujioka[1], Machi Hata[2], Masahito Kodera[2] (1. Doshisha Univ., 2. Grad. Sch. of Sci. and Eng., Doshisha Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1234-4am-04]
Cancer-Cell-Selective Cytotoxicity by Dicopper Complexes with p-Cresol-Amide-Tether-Cyclen Ligands: DNA-Targeting Effect

○Kobashi Hiroto[1], Hata Machi[1], Kodera Masahito[1] (1. Doshisha University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1234-4am-05]
Development of artificial allosteric enzyme using complex formation

○Chieon Park[1], Takaaki Mitsuhashi[2], Makoto Fujita[1,2,3] (1. Graduate School of Engineering, The University of Tokyo, 2. Institue for Molecular Science, 3. Institutes for Advanced Study (UTIAS), Tokyo College, The University of Tokyo))

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1234-4am-06]
Structural Analysis of Guest Molecules by Using Several Micro Crystalline Sponge in a Glass Capillary

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○Ryo Yakushiji[1], Satoshi Yoshida[1], Sota Sato[1,3], Makoto Fujita[1,2,3] (1. Grad. School of Engineering, The Univ. of Tokyo , 2. UTIAS, The Univ. of Tokyo, 3. IMS)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

Break

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[F1234-4am-07]

Radical Addition of an Isolable Phosphinyl Radical to Unsaturated Hydrocarbons

○Yasuhiro Katayama[1], Shintaro Ishida[1], Takeaki Iwamoto[1] (1. Tohoku University)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[F1234-4am-08]

Coupling reaction of cyclopentadienyl ligand with alkene in titanacyclopentene complex

Tamotsu Takahashi[2,1], Masayoshi Bando[1], Hirotaka Nakada[1], ○zhiyi song[1] (1. Hokkaido University, 2. Institute of Chemistry Co Ltd Henan Academy of Sciences)

English

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[F1234-4am-09]

Thin Film Formation of Ru Dinuclear Complex Forming Covalent Networks Based on LbL Method

○Takumi Nakanishi[1], Chisa Itoh[2], Hitoshi Miyasaka[1] (1. Institute for Materials Research, Tohoku University, 2. Department of Chemistry, Tohoku University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[F1234-4am-10]

Concentration-Dependent Valence Tautomerism Exhibited by Cobalt Dioxolene Complexes

○Yuki Koyama[1], Ryunosuke Konishi[1], Akinori Honda[2], Akinobu Nakada[3,2], 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.)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[F1234-4am-11]

Control of Condensed Phases and External Stimuli Responsiveness of Redox-active Pyrazinedithiolato Platinum(II) Complexes

○Tatsuya Tamura[1], Akira Imaizumi[1], Akinori Honda[2], Ho-Chol Chang[2] (1. Graduate school of science and engineering, Chuo univ., 2. Faculty of science and engineering, Chuo univ.)

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日本化学会 第104春季年会 (2024)

ポルフィリン DNA 標的を持つ *p*-cresol-2,6-amide-tether-tacn 配位子とその二核銅錯体の合成とがん細胞選択的毒性

（同志社大理工）○山本 莉子・児玉 愛実・畑 真知・小寺 政人

Synthesis and cancer-cell selective cytotoxicity of a dicopper complex with *p*-cresol-amide-tether-tacn ligand having a porphyrin DNA target (*Doshisha University*) ○Riko Yamamoto, Ami Kodama, Machi Hata, Masahito Kodera

A clinically used cisplatin Pt complex exerts high anticancer activity but has strong side effects due to no selectivity between normal cells and cancer cells. Compared with metal complexes of extrinsic Pt, Rh, and Ru not existing in the body naturally, complexes of intrinsic Cu is attracting attention because they reduce the side effects and are effective against Pt-resistant cancers. These complexes cause oxidative stress by binding to glutathione (GSH) to increase ROS level, which induces cell death via DNA cleavage and organelles disruption. Moreover, copper complexes directly generate hydroxy radical HO• by Fenton-type reactions via reductive O_2-activation with mM level existing ascorbate (AscNa) and GSH in cells. We synthesized *p*-cresol-amide-tether-tacn ligand and its dicopper complex **1** (Fig. 1). **1** formed a relatively stable peroxo intermediate and produced HO• via reductive O_2-activation efficiently. **1** generated HO• selectively in cancer cells and enhanced the cancer-cell selective cytotoxicity. It is known that cancer-cell selective cytotoxicity of metal complexes is enhanced by targeting DNA, mitochondria, and endoplasmic reticulum. Thus, *p*-cresol-amide-tether-tacn having a cationic porphyrin and its dicopper complex **2** (Fig. 1) were newly synthesized to enhance the cancer cell-selective cytotoxicity of **1**.

Keywords: dicopper complex; oxidative stress; cytotoxicity; targeting DNA and organelles

臨床利用されている Pt 錯体である cisplatin は高い抗がん活性を示すが，正常細胞とがん細胞の選択性がないために強い副作用を示す．生体内に本来存在しない外来性の Pt, Rh, Ru などの錯体に比べ，内在性の Cu の錯体は副作用を軽減し，白金耐性がんに有効なために注目されている．これらの錯体はグルタチオン(GSH)と結合して酸化ストレスを起こし，ROS レベルを増加させる．ROS は DNA 切断や細胞小器官の損傷を通して細胞死を誘導する．また銅錯体は細胞内に mM レベルで存在するアスコルビン酸(AscNa)や GSH を電子源として O_2 を還元的に活性化し，Fenton type の反応で直接的にヒドロキシラジカル(HO•)を生成する．我々は，*p*-cresol-amide-tether-tacn 配位子を開発し，その二核銅錯体 **1** (Fig 1) を合成した．**1** は，tacn の配位で分光学的に検出可能な程度に安定なペルオキソ中間体を生成し，O_2 の還元的活性化で効率的に HO•を生成した．**1** は，がん細胞選択的に HO•を生成し，比較的高いがん細胞選択的毒性を示した．DNA，ミトコンドリア，小胞体などの標的で，錯体のがん細胞選択的毒性が大きく向上することが知られている．そこで，**1** のがん細胞選択的毒性をさらに向上させるため，*p*-cresol-amide-tether-tacn にカチオン性ポルフィリンを導入した配位子とその二核銅錯体 **2** (Fig 1)を合成した．

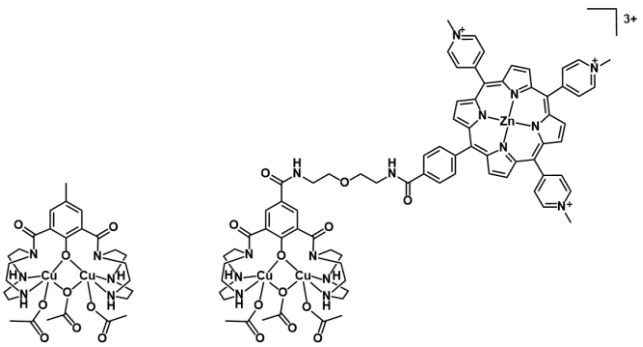

Fig 1. Chemical structures of **1** (left) and **2** (right).

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トリフェニルホスフィンをミトコンドリア標的とする *p*-cresol-2,6-amide-tether-cyclen 誘導体とその二核銅錯体の合成及びがん細胞選択的毒性の評価

(同志社大理工) ○高井 隼人・畑 真知・小寺 政人
Synthesis and cancer-cell selective cytotoxicity of dicopper(II) complexes with *p*-cresol-2,6-amide-tether-cyclen derivative having triphenylphosphine mitochondria target (*Molecular Chemistry and Biochemistry, Doshisha univ*) ○Hayato Takai, Machi Hata, Masahito Kodera

Cisplatin and oxaliplatin are Pt complexes clinically used anticancer agents to show high effecacy against various cancers, but there are problems of the strong side-effects. Therefore, instead of complexes of extrinsic metals such as Pt, As, Rh, and Ru, complexes of intrinsic copper have been widely investigated as anticancer agents to suppress the side-effects. Previously, we have developed various dicopper complexes to exert cancer-cell selective cytotoxicity. Especially, a dicopper complex **2** (Fig 1) having a phenanthrenyl DNA intercalator induced mitochondrial apoptosis by accelerating double strand breaks of mitochondrial DNA to exert cancer-cell selective cytotoxicity.[1,2] In this study, we synthesized a new dicopper complex **3** (Fig 1) having triphenylphosphonium group, which has both cationic and hydrophobic properties and is known to specifically accumulate within mitochondria, to localize **3** to mitochondria.
Keywords: dicopper complex, cancer cell selectivity, DNA cleavage activity, cytotoxicity, triphenylphosphine

現在抗がん剤として臨床利用されているシスプラチンやオキサリプラチンなどの白金製剤は，様々ながんに対して高い抗がん作用を示す一方で，強い副作用を示すことが問題である．そこで，Pt などの重金属に代わる，内在性の金属である銅錯体を用いた副作用の少ない抗がん剤の開発が注目されている．我々は，正常細胞に比べ，がん細胞に選択的に高い細胞毒性を示す二核銅錯体を開発してきた．その中でも，DNA intercalator である phenanthrene を持つ二核銅錯体 **2** (Fig 1)は，phenanthrene が DNA 標的としてミトコンドリア DNA の二本鎖切断を加速し，ミトコンドリア経由のアポトーシスを誘導することでがん細胞選択的細胞毒性を大きく向上することを見出した [1,2]．本研究では，ミトコンドリアへの局在を目的として，カチオン性と疎水性の両方の性質をもち，ミトコンドリアに特異的に局在するトリフェニルホスフォニウム基を導入した，ミトコンドリア標的を持つ二核銅錯体 **3** を合成し，**2** の活性と比較したので報告する．

[1] M. Hata, M. Kodera, et.al., Dalton Trans, **2022**, *51*, 4720.
[2] M. Hata, M. Kodera, et.al., *ACS Omega*, **2023**, *8*, 28690.

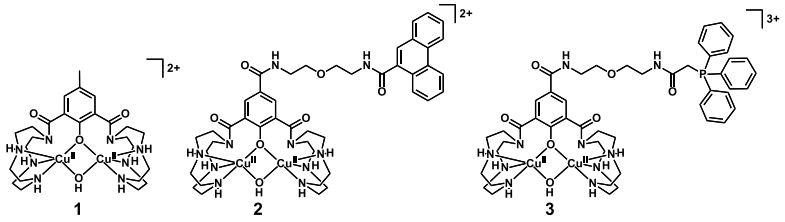

Fig 1. Chemical structures of **1**, **2**, and **3**.

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Cyclen をパーメチル化した phenanthrene introduced phenol-2,6-amide-tether-cyclen 配位子の二核銅錯体の合成とがん細胞選択性

（同志社大理工[1]・同志社大院理工[2]）○藤岡賢志郎[1]・畑真知[2]・小寺政人[1,2]

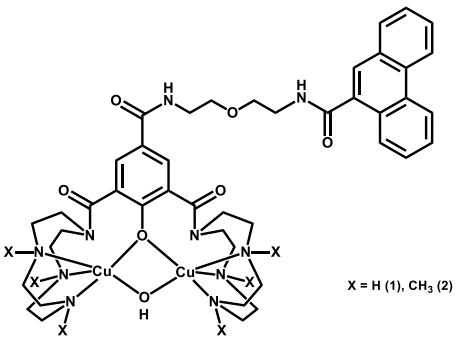
Synthesis and cancer-cell selective cytotoxicity of a dicopper complex with cyclen per-methyl derivative of 4-phenanthrene introduced phenol-2,6-amide-tether-cyclen ligand

(*Doshisha University*) ○Kenshiro Fujioka, Machi Hata, Masahito Kodera

Clinically used anticancer agents such as cisplatin and related platinum complexes show high efficacy to various cancers, but their strong side effects are problematic. Cancer cells have higher H_2O_2 concentrations than normal cells due to mitochondrial dysfunction. We found that a dicopper complex (**1**) of an amide-tether cyclen-type ligand having phenanthrene, shown in the figure below, forms a hydroperoxo complex that cleaves mitochondrial DNA and shows cancer cell-selective cytotoxicity.[1] However, the cellular uptake of **1** is low, and if this point can be improved, even higher cancer cell-selective cytotoxicity can be expected. Therefore, in this study, we synthesized a dicopper complex (**2**) by permethylating cyclen moiety of **1** in order to increase the cellular uptake by increasing its lipophilicity. Here, we report the synthesis and cancer cell-selective cytotoxicity of **2**.

Keywords : dicopper complex; cancer cell selectivity; cytotoxicity; cellular uptake; intercalator

がん治療で臨床利用されているシスプラチンや関連する白金錯体などの抗がん剤は高い活性を示すが、強い副作用を示すことが問題である。がん細胞は、ミトコンドリア不全を起こしているために正常細胞に比べて H_2O_2 濃度が高い。我々は、下図に示す phenanthrene を持つ amide-tether cyclen 型配位子の二核銅錯体(**1**)が、H_2O_2 を利用してヒドロペルオキソ錯体を形成し、ミトコンドリア DNA を切断してがん細胞選択的毒性を示すことを見出した[1]。しかし、錯体 **1** の細胞取込率は低く、この点を改善できれば、さらに高いがん細胞選択的毒性の発現が期待できる。そこで、本研究では脂溶性を増大させて細胞取込を高めるため、**1** の cyclen をパーメチル化した二核銅錯体(**2**)を合成した。今回は、**2** の合成とがん細胞選択的毒性について報告する。



[1] “Roles of DNA Target in Cancer Cell-Selective Cytotoxicity by Dicopper Complexes with DNA Target/Ligand Conjugates”, Machi Hata, Jin Ueno, Yutaka Hitomi, and Masahito Kodera, *ACS Omega* 2023, 8, 31, 28690–28701

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p-Cresol-Amide-Tether-Cyclen 配位子の二核銅錯体によるがん細胞選択的毒性：DNA 標的の効果

（同志社大理工[1]・同志社大院理工[2]）○小橋 寛人[1]・畑 真知[2]・小寺 政人[1,2]
Cancer-Cell-Selective Cytotoxicity by Dicopper Complexes with *p*-Cresol-Amide-Tether-Cyclen Ligands: DNA-Targeting Effect (*Doshisha Universit*) ○Hiroto Kobashi, Machi Hata, Masahito Kodera

Cisplatin is a clinically used anticancer agent to show high efficacy to various cancers, but there are problems of the strong side-effects. Therefore, in place of complexes of exogenous metals such as Pt, As, Rh, and Ru, complexes of endogenous copper have been widely studied as anticancer agents to suppress the side-effects. We have developed various dicopper complexes to exert cancer-cell selective cytotoxicity. Especially, a dicopper complex $\mathbf{2^P}$ (Fig 1) having a phenanthrenyl group (P) as a DNA intercalator showed cancer-cell selective high cytotoxicity by inducing mitochondrial apoptosis via accelerating double strand breaks of mitochondrial DNA.[1,2] In this study, we synthesized new dicopper complexes $\mathbf{2^A}$ and $\mathbf{2^N}$ (Fig 1) having acridinyl (A) and 1,8-naphthalimid (N) as DNA intercalators to optimize the DNA target and found that A and N enhance cancer-cell selective cytotoxicity similarly to P.
Keywords: Anticancer agent; Cancer cell selectivity; Copper complex; DNA binding; DNA cleavage

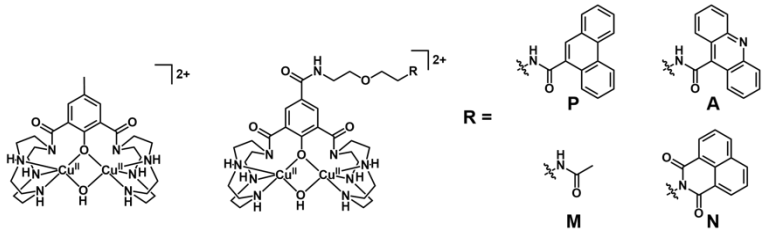

Fig 1. Chemical structures of **1** (left) and $\mathbf{2^R}$ (R = P, M, A, N) (right).

シスプラチンなどの臨床利用される細胞障害性の抗がん剤は高い抗がん活性を示すが，強い副作用を伴うことが問題である．そこで，Pt などの重金属に代わる内在性の金属である銅錯体による副作用の少ない新たな抗がん剤の開発が注目されている．我々は，正常細胞に比べ，がん細胞に選択的に高い細胞毒性を示す二核銅錯体を開発してきた．その中で DNA intercalator である phenanthrene (P) を持つ二核銅錯体 $\mathbf{2^P}$ (Fig 1)では，P が DNA 標的としてミトコンドリア DNA の二本鎖切断を加速し，ミトコンドリア経由のアポトーシスを通してがん細胞選択的毒性を大きく向上できることを見出した[1,2]．$\mathbf{2^P}$ は膵臓のがん細胞と正常細胞に対する細胞毒性で，がん細胞に対して約 12 倍高い細胞毒性を示した[2]．そこで，DNA 標的の最適化を目指し，DNA intercalator として acridinyl (A)や 1,8-naphthalimid (N)を導入した二核銅錯体 $\mathbf{2^A}$, $\mathbf{2^N}$ (Fig 1)を合成し，DNA 切断活性と細胞毒性を測定した． A, N は，P と同様に $\mathbf{2^R}$ のがん細胞選択的毒性を向上させることを見出した．

[1] M. Hata, M. Kodera, et.al., Dalton Trans, **2022**, *51*, 4720.
[2] M. Hata, M. Kodera, et.al., *ACS Omega*, **2023**, *8*, 28690.

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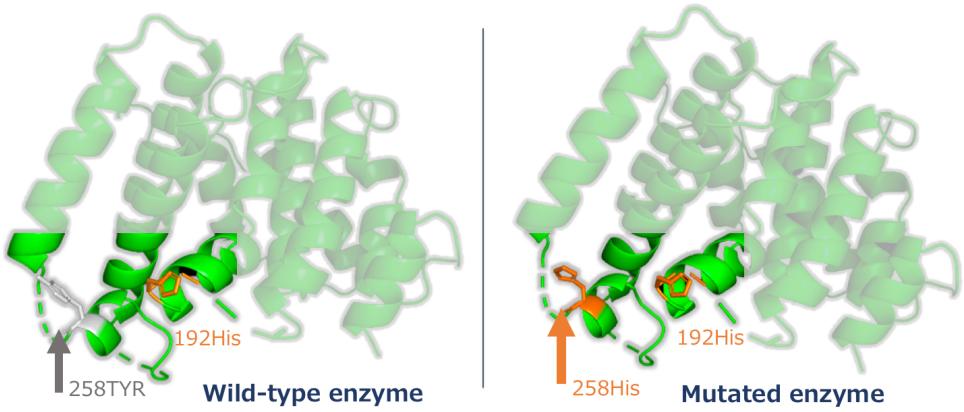
錯体形成を利用した人工アロステリック酵素の開発

（東大院工[1]・分子研[2]・東大国際高等研[3]）○朴 治彦[1]・三橋 隆章[2]・藤田 誠[1,2,3]
Development of artificial allosteric enzyme using complex formation ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute for Molecular Science*, [3]*Institutes for Advanced Study, The University of Tokyo*) ○Chieon Park,[1] Takaaki Mitsuhashi,[2] Makoto Fujita[1,2,3]

Allosteric enzymes are enzymes whose activities are regulated by effector molecules binding to sites other than the active site of the enzymes. In this study, we aimed to engineer non-allosteric enzyme and develop an artificial allosteric enzyme. As the target enzyme, OILTS, a terpene synthetase derived from a giant virus, was used[1)]. The histidine residue was placed on the enzyme by site-directed mutagenesis so that it could form a complex with metals away from the active site. We expect that the complex formation would change the structure of the enzyme slightly. When we used a palladium complex as a molecule to modulate the activity of the enzyme, it was confirmed that the activity of the mutant enzyme was significantly reduced only in the existence of the effector molecule, suggesting the successful development of the artificial allosteric enzyme.
Keywords : Allosteric enzyme; Complex formation

アロステリック酵素とは、活性部位以外の位置に分子が結合することで機能が調節される酵素である。本研究では、アロステリック酵素ではない酵素をアロステリック酵素へと改変することを目指した。対象の酵素としては、巨大ウイルス由来のテルペン合成酵素 OILTS を用いた[1)]。OILTS への変異導入により、活性部位から離れた位置にヒスチジン残基を金属と錯形成できるように配置し、錯形成に応じて酵素の構造に微細な変化が引き起こされることを期待した。また、酵素の活性を調節する分子として、パラジウム錯体を使用した。その結果、パラジウム錯体存在下においてのみ、酵素の活性が著しく低下することが確認され、アロステリック酵素への改変の成功が示唆された。



1) Y. Jung, T. Mitsuhashi, S. Sato, M. Senda, T. Senda, M. Fujita, *J. Am. Chem. Soc* **2023**, *145*, 25966–25970.

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キャピラリー内壁に固定化した複数個のマイクロ結晶スポンジを用いたゲスト分子の構造解析

（東大院工[1]・分子研[2]・東大 UTIAS[3]）○薬師寺 諒[1]・吉田 知史[1]・佐藤 宗太[1,2]・藤田 誠[1,2,3])

Structural analysis of Guest Molecules by Using Several Micro Crystalline Sponges Fixed on an Inner Wall of Capillary ([1]*School of Engineering, The Univ. of Tokyo,* [2]*IMS,* [3]*UTIAS, The Univ. of Tokyo*) ○Ryo Yakushiji[1], Satoshi Yoshida[1], Sota Sato[1,2], Makoto Fujita[1,2,3]

The crystalline sponge (CS) method is the powerful method which enables the X-ray crystallographic analysis of small organic compounds. In this work, aiming for direct connection of GC and CS method, the model compounds were searched at first. Then, the synchrotron X-ray diffraction measurements were performed for micro CS fixed on an inner wall of a capillary. Several partial data were obtained and by merging these partial data using the KAMO software[1], the structural analysis of carvacrol was achieved.

Keywords: Crystalline Sponge Method, Capillary Containment, X-ray Structural Analysis

結晶スポンジ(CS)法は、細孔内に分子を周期配列させることで単結晶 X 線結晶構造解析を可能とする手法であり、気体試料や液体試料などの結晶化不可能な分子にも適用可能である。しかし、試料量が μg を下回るほど微量である場合、200 μm 程度の大きい CS を用いる従来法では包接率が低下し、また、取り扱い上のコンタミにより構造解析ができなくなる問題が生じる。これまでに、包接量を減らすことができる微小なマイクロ CS を、キャピラリー内壁上に固定する試料調製法を見出した。本研究では、この固定化された CS の応用として、コンタミを避けるためにガスクロマトグラフィー（GC）装置への直結に向けた検討を進めた。はじめに、GC 分離でき、CS 解析に適するモデル化合物を選定した。50 μm 程度の CS を 1.1mL バイアル瓶に封入し、30 °C でゲスト分子の気相ソーキングを行った。12 種類のゲスト分子を検討し、カルバクロール、(-)-メントール、(-)-カンファーキノンが構造解析できることを見出した（図 1 (a)）。次に、キャピラリー内壁に固定した CS に対して放射光 X 線回折測定及び解析を行った。初めに、マイクロ CS に対して 1 粒ずつ放射光 X 線を照射し、得られた部分データを KAMO ソフトウェア[1]を用いて統合した。その結果、カルバクロールの構造解析を達成した（図 1 (b)）。より幅広いゲスト分子包接に向けて、CS 骨格中の Zn イオンのカウンターアニオンとして Cl イオンに加えて、I イオンを用いた CS 試料調製にも成功した。本手法を GC 装置からの直接分取に展開することで、手作業では不可能な痕跡量試料の構造解析の達成を目指す。

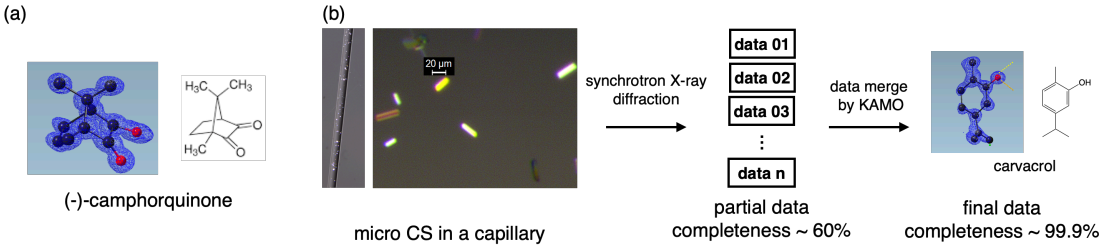

図 1 (a)気相ソーキングで構造解析された(-)-カンファーキノン　(b)キャピラリー内壁上に固定化された CS の測定から構造解析までの流れ

[1]Yamashita et al. **2018** *Acta Cryst. D***74**, 441-449

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単離可能なリン中心ラジカルと不飽和炭化水素とのラジカル付加反応

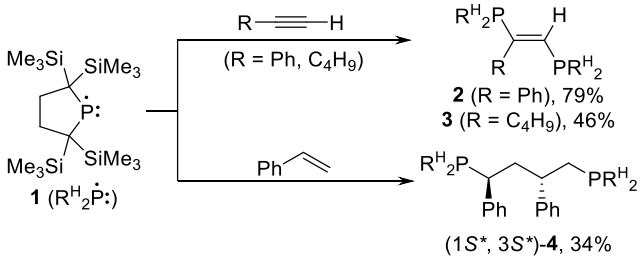
（東北大院理[1]）○片山 泰宏[1]・石田 真太郎[1]・岩本 武明[1]
Radical Addition of an Isolable Phosphinyl Radical to Unsaturated Hydrocarbons ([1]*Graduate School of Science, Tohoku University*) ○Yasuhiro Katayama,[1] Shintaro Ishida,[1] Takeaki Iwamoto[1]

Radical addition across C–C multiple bonds is an important step in radical polymerization and 1,2-addition. Herein, we report the addition reactions of isolable phosphinyl radical **1** with various unsaturated hydrocarbons.

Two equivalents of **1** reacted with terminal alkynes to afford the corresponding 1,2-adducts **2** and **3**. The pyramidal inversion at the phosphorous centers of **2** was observed at room temperature, which would be due to the high planarity of the geometry around the phosphorus atom and the effective π-conjugation between the lone-pair orbital on the phosphorus atoms and the π-orbital of the C=C bond. The reaction of **1** with styrene afforded 2:2 adduct (1*S**, 3*S**)**-4**. Higher oligomers were also detected by MS.
Keywords : Conjugated System; Phosphine; Radical; Radical Addition

単離可能なホスフィニルラジカル **1** は、嵩高い置換基によって速度論的に安定化されているにも関わらず、炭化水素の水素や塩素引き抜き反応など、ラジカルとしての高い反応性を有する[1]。一方で、重合反応などの素反応として重要な炭素－炭素多重結合に対する **1** のラジカル付加は未解明であった。今回、ラジカル **1** と種々の不飽和炭化水素との付加反応を報告する。

ラジカル **1** と末端アルキンとの反応では、二分子の **1** がアルキンに対してトランス付加した生成物 **2** および **3** が得られた。フェニルアセチレンと **1** との生成物 **2** は、リン原子周りの立体反転が室温で容易に起こることがわかった。以上の生成物の特徴は、リン原子周りの平面性が高くなっていることと、リンの非共有電子対と炭素－炭素二重結合のπ軌道が共役できる配座をとるためと推定される。アルケンであるスチレンに対しては **1** とスチレンが 2 対 2 で反応した生成物(1*S**, 3*S**)**-4** が主生成物として得られた。



1) S. Ishida, F. Hirakawa, T. Iwamoto, *J. Am. Chem. Soc.* **2011**, *133*, 12968.

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チタナシクロペンテンにおけるシクロペンタジエニル配位子とアルケニル炭素とのカップリング反応

（河南化学研[1]・北大触媒研[2]）高橋 保[1,2]・坂東 正佳[2]・中田 啓貴[2]・○宋 志毅[2]

Coupling Reaction of Cyclopentadienyl Ligand with Alkene in Titanacyclopentene Complex

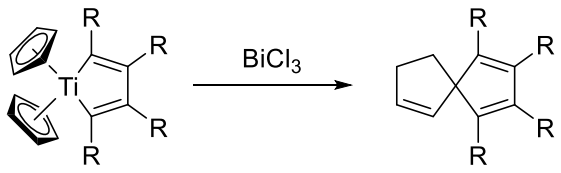
([1]*Institute of Chemistry, Henan Academy of Sciences,* [2]*Institute for Catalysis Hokkaido University*) Tamotsu Takahashi,[1,2] Masayoshi Bando,[2] Hirotaka Nakada,[2] ○Zhiyi Song [2]

A cyclopentadienyl ligand on titanacyclopentene complexes reacted with alkenyl carbons of titanacyclepentenes in the presence of BiI_3 to give cyclopropylmethylenecyclopentene derivatives. It is in sharp contrast to the reaction of titanacyclopentadienes with $BiCl_3$ which afforded spiro[4.4]nonatriene compounds.

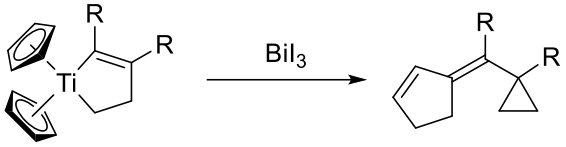
Keywords : Titanacyclopentene; Cyclopentadiene; Cyclopropylmethylenecyclopentene; Coupling

チタノセンジクロリドを THF に溶かし、－７８℃で２等量のエチルグリニャールと反応させ、１等量のアルキンと反応させるとチタナシクロペンテン誘導体を収率よく得ることができる。このチタナシクロペンテン誘導体にヨウ化ビスマスを１等量加えて加熱すると、シクロプロピルメチレンシクロペンテン誘導体を２重結合の位置異性体の混合物として、５０－６０％の収率で得た。これはこれまでに報告してきたスピロ誘導体スピロ[4.4]ノナトリエン誘導体を与えたチタナシクロペンタジエン誘導体と塩化ビスマスとの反応と大きく異なっており、興味深い。本反応ではシクロプロパン化を経て、錯体のシクロペンタジエニル配位子が、同じチタンシクロペンテン上のアルケニル炭素と反応している。

Perious Work



This Work



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Thin Film Formation of Ru Dinuclear Complex Forming Covalent Networks Based on LbL Method

([1]*Institute for Materials Research, Tohoku University,* [2]*Department of Chemistry, Tohoku University*) ○Takumi Nakanishi[1], Chisa Itoh[2], Hitoshi Miyasaka[1]

Keywords: *Thin film, Paddlewheel-type [Ru_2] complex, Metal–covalent organic frameworks, Layer-by-layer method*

Paddlewheel-type [Ru_2] complexes are an attractive group of materials that exhibit a wide range of interesting functions due to the diversity of valence of ruthenium ions, ease of substituent modification, and structural stability. For example, metal organic framework (MOF) materials based on dinuclear ruthenium complexes with electron acceptor ligands have been applied to the development of functional materials whose magnetism can be controlled by external fields or by absorption and desorption of guest molecules. Furthermore, paddlewheel-type dinuclear ruthenium complexes with open metal sites have also attracted much attention as catalytic materials.

An important and challenging approach to explore further functionalities of such materials is the fabrication of thin films that allow the construction of arbitrary structures and functional sites. Thin film fabrication methods that allow precise design of space size, growth direction of network structures and active sites is expected to provide the novel properties and catalytic activities based on the paddlewheel-type [Ru_2] complex. Furthermore, the thin films fabricated on functional substrate such as conductive substrate is expected to expand in new directions, such as electrocatalytic activity.

In this study, we aim to develop the thin films of paddlewheel-type [Ru_2] complexes, especially based on covalent bond-based network structures (metal-covalent organic framework, MCOF). Recently, our group reported the paddlewheel-type [Ru_2] complexes with a formyl group at the end of the ligand (Fig. 1)[1], which can construct the covalent network structure by the reaction with molecules containing amine group. In this presentation, we will report on the characterization of thin films obtained by layer-by-layer and electrochemical methods based on the formation of covalent bonds of terminal substituents of [Ru_2] complexes.

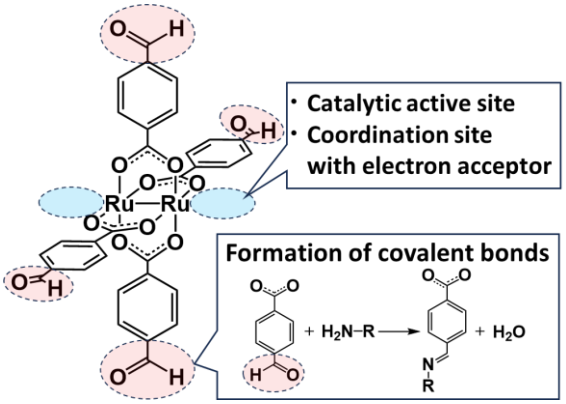

Figure 1. Schematic illustration of paddlewheel-type [Ru_2] complex with formyl group at the end of ligand.

1) Chisa Itoh, Haruka Yoshino, Taku Kitayama, Wataru Kosaka and Hitoshi Miyasaka, *Dalton. Trans*. **2024**, *53*, 444-448.

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コバルトジオキソレン錯体が示す濃度依存型原子価互変異性

（中大院理工[1]・中大理工[2]・京大院工[3]）○古山 雄貴[1]・小西 龍之助[1]・本田 暁紀[2]・中田 明伸[2,3]・張 浩徹[2]
Concentration-Dependent Valence Tautomerism Exhibited by Cobalt Dioxolene Complexes ([1]*Graduate School of Science and Engineering, Chuo University*, [2]*Faculty of Science and Engineering, Chuo University,* [3]*Graduate School of Engineering, Kyoto University*) ○Yuki Koyama,[1] Ryunosuke Konishi,[1] Akinori Honda,[2] Akinobu Nakada,[2,3] Ho-Chol Chang[2]

Valence tautomeric (VT) complexes show a molecular bistability induced by heat, high pressure, and photoirradiation. We found that the concentration-dependent VT phenomenon at room temperature exhibited by the highly symmetric [Co(3,6-DTBQ)$_2$(R-py)$_2$] (**36CoR**) (R = CN, H, Me) for the first time. The influence of molecular symmetry and substituents of pyridine derivatives on the VT equilibrium was clarified. Herein, we will present the substituent dependence of the concentration-dependent VT of **36CoR** in solution.
Keywords : Valence tautomerism; Concentration dependence; Cobalt dioxolene complex; Substituent dependent; Molecular magnetism

原子価互変異性(VT)錯体は、溶液中で分子内における電荷移動により、分子内電荷分布の異なる低スピン型 (*ls*-[Co(III)])および高スピン型 (*hs*-[Co(II)])の二つの互変異性体間の双安定性を発現することが知られている (Figure a)。[1] このような VT 錯体は、熱、光及び圧力などの外部刺激により誘起され、磁化率変化や色の変化などの興味深い性質を示す。[2] 一方、我々は高対称性コバルトジオキソレン錯体[Co(3,6-DTBQ)$_2$(R-py)$_2$] (**36CoR**) (R = CN, H, Me) がトルエン中、室温において、低濃度下では *hs*-[Co(II)]を高濃度下では *ls*-[Co(III)]を形成する濃度依存型 VT 現象を初めて報告した。[3] 当日は、コバルトジオキソレン錯体のジオキソレン配位子上の置換基の位置及びピリジン上の置換基が、濃度依存 VT に及ぼす影響ついて発表する (Figure b)。

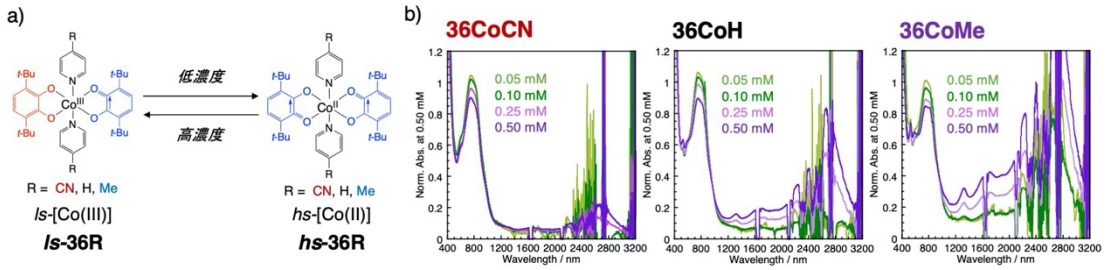

Figure a) **36CoR** の濃度依存型 VT, b) **36CoR** (R = CN, H, Me)のトルエン中における濃度依存 UV-vis-NIR スペクトル (R.T., N_2)

1) C. G. Pierpont *et al*., *J. Am. Chem. Soc*. **1980**, *102*, 4951. 2) D. Kiriya, H.-C. Chang, S. Kitagawa, *J. Am. Chem. Soc.*, **2008**, 130, 5515-5522. 3) 日本化学会第 100 回春季年会, 小西ら, 2F3-06, **2020**.

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レドックス活性ピラジンジチオラート白金(II)錯体の凝集相制御と外場応答性

（中大院理工[1]・中大理工[2]）○田村 竜也[1]・今泉 暁[1]・本田 暁紀[2]・張 浩徹[2]

Control of Condensed Phases and External Stimuli Responsiveness of Redox-active Pyrazinedithiolato Platinum(II) Complexes ([1]*Graduate School of Science and Engineering, Chuo University,* [2]*Faculty of Science and Engineering, Chuo University*) ○Tatsuya Tamura,[1] Akira Imaizumi,[1] Akinori Honda,[2] Ho-Chol Chang[2]

In our earlier research, we identified that platinum complexes featuring redox-active benzene dithiolato ligands form a Col_{ho} phase at room temperature, displaying distinctive redox properties. [1] Building upon this, our current study focuses on the synthesis of a novel platinum complex incorporating a pyrazineditiolato derivative with a proton-accepting N atom in the complex core. Our investigation aims to explore the control of aggregation phases and external field responsiveness, aiming to create a novel molecular assembly.

Keywords : Liquid crystal; Redox-active ligand; Platinum (II) complex; Acid-base properties; Proton-coupled electron transfer

我々は、レドックス活性ベンゼンジチオラート配位子を有する白金錯体が室温下で Col_{ho} 相を形成し、可逆的なレドックス特性を発現することを報告している。[1] 本研究では、錯体コアに H^+受容性 N 原子を有する pyrazineditiolato (pdt)誘導体を導入した [Pt(pdt)(Rbpy)] (Rbpy = 4,4’-di-*tert*-butyl (**1**) or 4,4’-di-nonyl (**2**) or 4, 4’-di-(3-octyltridecyl) (**3**) -2, 2’-bipyridine)を合成し、凝集相制御及び外場応答性を検討することで、新たな分子集合体の創製を目的とした (Fig. 1a)。

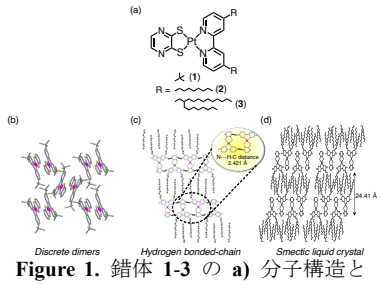

Figure 1. 錯体 **1-3** の **a)** 分子構造と **b)-d)** 凝集相

錯体 **1** 及び **2** は室温で結晶として得られ、その単結晶構造から **1** は錯体分子の二量体が離散した集積構造を形成する一方 (Fig. 1b)、**2** は分子間で水素結合とアルキル間相互作用を有する集積構造を形成した (Fig. 1c)。また、**3** は室温で粘性物質として得られ、そのXRDパターンより、スメクチック液晶相の形成が示唆された (Fig. 1d)。これらの結果は、アルキル種により様々な相の誘起が可能であることを示唆している。さらに、錯体 **3** は溶液中で 530 nm に吸収極大を示すが、HCl 添加に伴いその吸収が減衰し、470 nm に新たな吸収を示した (Fig. 2a)。また、Et_3N を添加することで初期状態に戻ることは、錯体と H^+の可逆的な相互作用を示唆している。さらに、溶液中で HCl 添加に伴う電気化学応答を測定すると、HCl 添加に伴い 0.46 V の応答が減少し、0.49, 0.8 V の応答が増加し、–1.1 V に新たな応答が発現することから、錯体 **3** は H^+移動が関与したレドックス特性を示すことが示唆された (Fig. 2b)。当日は、凝集相での外場応答性について議論する。

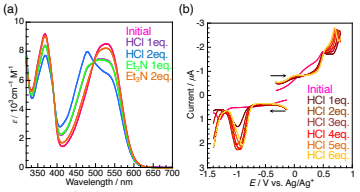

Figure 2. 錯体 **3** の **a)** HCl 及び Et_3N 添加時の吸収スペクトル (0.1 mM THF)と **b)** HCl 添加時の DPV (N_2, 0.1 M $TBAPF_6$, 0.1 mM THF solution, GC (W), Pt (C), Ag/Ag^+ (R))

1) H.-C. Chang, *et al.*, *Inorg. Chem.*, **2011**, *50*, 4279-4288.

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Academic Program [Oral A] | 09. Coordination Chemistry, Organometallic Chemistry：Oral A

Thu. Mar 21, 2024 9:30 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:40 AM UTC
F1233(1233, Bldg. 12 [3F])

[F1233-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Manabu Nakaya, Yoshihiro Sekine

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1233-4am-01]
Construction and Characterization of Hydrogen-Bonded Honeycomb Networks Using Trinuclear Chromium(III) Complexes

○Shun Sumikawa[1], Shoki Ikeda[1], Yoshiki Ozawa[1], Akira Yamaguchi[1], Yu Yamane[1], Akihiko Sumiyama[1], Masaaki Abe[1] (1. University of Hyogo)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1233-4am-02]
Metamagnetism in Nickel–octacyanotungstate 2D magnet

○Shintaro Akagi[1], Junhao Wang[1], Kenta Imoto[2], Kunal Kumar[2], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. University of Tsukuba, 2. The University of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1233-4am-03]
Cooperative vapochromism and spin-state switching of discrete Ni(II) complex in response to various coordinating solvents

○Sotaro Kusumoto[1], Kento Takei[1], Yoshihiro Koide[1] (1. Kanagawa University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1233-4am-04]
Development of paramagnetic spin-crossover ligands

○Yoshimasa Noguchi[1], Satomi Watanabe[2], Takayuki Ishida[1] (1. The University of Electro-Communications, 2. Kitasato University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1233-4am-05]
Elucidation of Intermolecular Interactions of SCO Complexes by Metal Dilution

○Kanta Miyake[1], Zhongyue ZHANG[1], Yoshihiro Sekine[1], Shinya Hayami[1] (1. Kumamoto university)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[F1233-4am-06]
Adsorption Heat Control of Nanoporous Cobalt Complexes Using Spin Transition

○Kako Ohno[1], Jenny Pirillo, Liyuan Qu, Shinpei Kusaka, Yuh Hijikata, Hiroaki Iguchi, Ryotaro Matsuda (1. Nagoya Univ.)

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

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Break

English
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1233-4am-07]
Investigation of Structural and Magnetic Properties of Dinuclear Fe(II) Complexes with Bridging-ligand whose Linkage Isomerization is Restricted

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

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1233-4am-08]
Cyanido-Bridged Fe(II)-Nb(IV) assemblies with Fe(II)-Fe(II)-Bridging Ligands

○Itsuki Fukagawa[1], Takefumi Kanno[1], Koji Nakabayashi[1], Kenta Imoto[1], Kazuki Nakamura[1], Yuuki Mineo[1], Shota Kobayashi[1], Yoshinori Tanaka[1], Shin-ichi Ohkoshi[1] (1. The Univ. of Tokyo)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1233-4am-09]
Magnetic and electrochemical properties of trinuclear copper complexes formed from cyclohexane-1,3-dione dioxime and copper(II) nitrate

○Yosuke Hosoya[1], Hanaka Kinjo[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
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1233-4am-10]
Substituent effects of 3d-2p heterospin coupling in copper(II) and nickel(II) nitroxide complexes

○Daichi Iida[1], Masataka Mitsui[1], Takayuki Ishida[1] (1. The University of Electro-Communications)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[F1233-4am-11]
Heterometallic chain complexes bridged with a ground-triplet 5-adamantyl-1,3-phenylene bis(*t*-butyl nitroxide)

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

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[F1233-4am-12]
Theoretical study on magnetic properties of lanthanide complexes with nitroxide radicals as ligands

○Kaito Taka[1], Ren Inoue[1], Koki Masuda[2], Ryohei Kishi[2,3,4,5], Takayuki Ishida[6], Yasutaka Kitagawa[2,3,4,5,7] (1. Faculty of Engineering Science, Osaka University, 2. Graduate School of Engineering Science, Osaka University, 3. QIQB, Osaka University, 4. Osaka University RCSEC, 5. ICS Osaka University, 6. Graduate School of Informatics and Engineering, 7. SRN, OSaka University)

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クロム(III)三核錯体を利用した水素結合型ハニカムネットワークの構築とその物性評価

（兵庫県立大院理[1]）○住川 舜[1]・池田 祥貴[1]・小澤 芳樹[1]・山口 明[1]・山根 悠[1]・住山 昭彦[1]・阿部 正明[1]

Construction and Characterization of Hydrogen-bonded Honeycomb Networks Using Trinuclear Chromium(III) Complexes

([1]*Graduate School of Science, University of Hyogo*)
○Shun Sumikawa,[1] Shoki Ikeda,[1] Yoshiki Ozawa,[1] Akira Yamaguchi,[1] Yu Yamane,[1] Akihiko Sumiyama,[1] Masaaki Abe[1]

In our laboratory, we have found that Ru(III) trinuclear complexes with isonicotinamide (ina) ligands form honeycomb network structures through intermolecular N-H•••O hydrogen bonds. In this study, we focused on the use of trichromium(III) complexes (Fig. 1), having the same type of core structure as triruthenium(III), to prepare 3d-transition-metal-based honeycomb networks. In this presentation, we report on the preparation of Cr(III) trinuclear honeycomb network crystals and their structural changes by changing the counter anions; for the PF_6^- salt, the crystals obtained by the liquid/liquid diffusion method were identified as having a wave-shaped honeycomb structure isomorphic to the Ru(III) complex by X-ray structural analysis. On the other hand, a novel network structure encompassing Na^+ was isolated as the BPh_4^- salt. Crystalline powders were also obtained by spontaneous evaporation and agitated precipitation, both of which showed, based on PXRD measurements, the same honeycomb structure as the single crystal; the Cr(III)-wave honeycomb crystals were amorphized by mechanical grindings and recovered crystallinity by exposure to soluble solvent vapor. The temperature dependence of the magnetic susceptibility using the SQUID method and the redox behavior of honeycomb crystal-modified electrodes fabricated by the drop-casting method will also be discussed.

Keywords : Chromium; Trinuclear Complex; Hydrogen-Bonded Honeycomb Networks; Magnetic Properties; Redox Behavior

我々の研究室では、イソニコチンアミド(ina)を配位子に持つ Ru(III)三核錯体が、分子間 N-H･･･O 水素結合によりハニカムネットワーク構造を形成することを見出している。本研究では、Ru ハニカム構造の 3d 遷移金属への拡張化と一般化を目指し、Ru(III)三核錯体と同型の骨格構造を持つ Cr(III)錯体に着目し、その ina 配位錯体を合成した(Fig. 1)。本発表では、Cr(III)三核ハニカムネットワーク結晶の作製と対アニオンを変えることによる構造変化について報告する。PF_6^-塩では液/液拡散法で得た結晶を X 線構造解析することで Ru(III)錯体と同型の波型ハニカム構造であると同定した。一方で BPh_4^-塩では Na^+を包摂した新規ネットワーク構造が単離された。自然蒸発法および攪拌沈殿法によっても結晶性粉末が得られたが、PXRD 測定よりいずれも単結晶と同じハニカム構造であった。Cr(III)波型ハニカム結晶は、機械的すりつぶしによりアモルファス化し、溶解性溶媒蒸気にさらすことで結晶性が回復した。本発表では、SQUID 法を用いた磁化率の温度依存性およびドロップキャスト法で作製したハニカム結晶修飾電極の酸化還元挙動についても議論する。

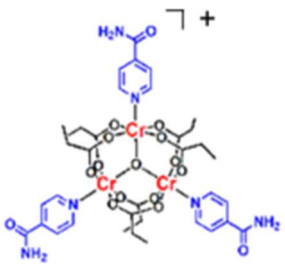

Fig. 1. Cr(III)三核錯体の構造

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Metamagnetism in Nickel–octacyanotungstate 2D magnet

([1]*Department of Materials Science, Faculty of Pure and Applied Science, University of Tsukuba,* [2]*Department of Chemistry, School of Science, The University of Tokyo*)
○Shintaro Akagi,[1] Junhao Wang,[1] Kenta Imoto,[2] Kunal Kumar[2],Shin-ichi Ohkoshi,[2] Hiroko Tokoro[1]
Keywords: Cyano-bridged assembly, Molecule-based magnet, Metamagnetic transition

Introduction: Crystal engineering of molecular magnetic materials can facilitate development of novel magnetic functionalities, such as photomagnetism and gas-sensitive magnets.[1)] In this study, we synthesized a $[Ni^{II}(pyrazole)_4]\{[Ni^{II}(pyrazole)_3][W^{V}(CN)_8]\}_2\cdot 3.5H_2O$ (**NiW**) layered magnet and report its crystal structure and magnetic properties. [2)]
Experiment: Target crystals were prepared by slow diffusion of $NiCl_2\cdot 6H_2O$ (0.4 mmol) and pyrazole (0.8 mmol) aqueous solution into $Cs_3[W^{V}(CN)_8]\cdot 2H_2O$ (0.2 mmol) aqueous solution at room temperature for two weeks. The crystal structure was determined using single-crystal X-ray diffraction analysis. Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer.
Results and Discussion: Single-crystal X-ray diffraction analysis revealed that the chemical formula of **NiW** was $[Ni^{II}(pyrazole)_4]\{[Ni^{II}(pyrazole)_3][W^{V}(CN)_8]\}_2\cdot 3.5H_2O$. **NiW** crystallizes in an orthorhombic *Pbcn* space group, which has wavy coordination layers made up of two differently sized molecular squares with ladder-shaped topologies (Figure 1a). **NiW** exhibits ferromagnetic interactions between Ni^{II} ($S = 1$) and W^{V} ($S = 1/2$) within the layers via cyanide groups; however, owing to the relatively short interlayer distance (ca. 10.4 Å), spontaneous ordering was found to be antiferromagnetic with a Néel temperature of 21 K (Figure 1b). Such interlayer antiferromagnetic interactions can be overcome by external magnetic fields above 400 Oe, indicating the metamagnetic behavior of **NiW** (Figure 1c).

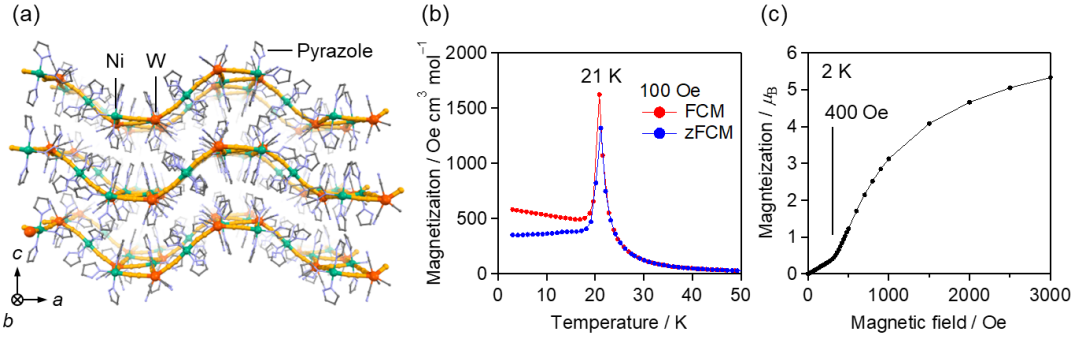

Figure 1. (a) Crystal structure of **NiW** view along the *b* axis, (b) magnetization curves of **NiW**, magnetic-field dependence of magnetization at 2 K **NiW**.

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nat. Photonics* **8**, 65 (**2014**).
2) S. Akagi, J. Wang, K. Imoto, K. Kumar, S. Ohkoshi, H. Tokoro, *Pure Appl. Chem.,* **9**, 701 (**2023**).

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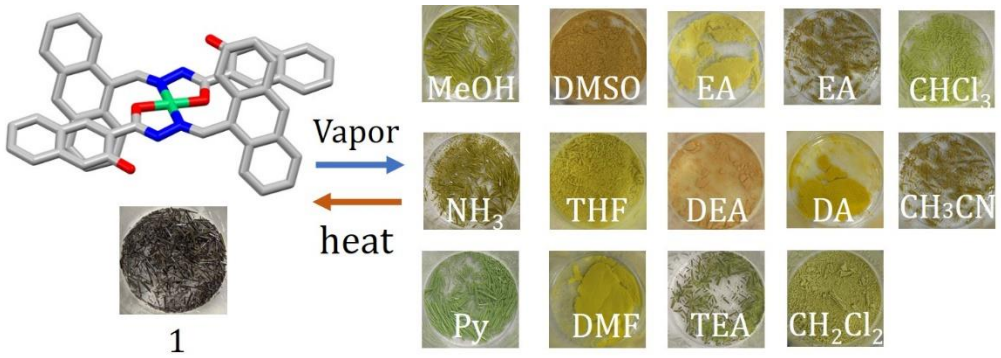
様々な配位性溶媒に色と磁性で応答可能な Ni 錯体の開発

（神奈川大学[1]）○楠本 壮太郎[1]・竹井 健人[1]・小出 芳弘[1]
Cooperative vapochromism and spin-state switching of discrete Ni(II) complex in response to various coordinating solvents ([1] *Department of Applied Chemistry, Faculty of Chemistry and Biochemistry, Kanagawa University*) ○Sotaro Kusumoto,[1] Kento Takei,[1] Yoshihiro Koide[1]

The development of systems capable of detecting different coordinating solvents has received considerable attention in the field of chemical sensing and storage. Ni complexes have proven to be well suited for such advancements due to their ability to undergo color and magnetic changes based on coordination numbers. In previous studies, Ni complexes typically responded only to a specific type of solvent vapor. In this research, however, we have successfully developed Ni complexes that respond to multiple types of coordinating solvent vapors.
Keywords : Nickel complex, vapochromism, magnetic switching

様々な配位性溶媒を検知可能なシステムの開発は化学センサーや貯蔵の観点から注目を集めている。Ni 錯体は、配位数の違いにより色と磁性を変換可能なため上記のシステムの開発に好都合である。これまで報告されている Ni 錯体は、1 種類の溶媒蒸気にしか応答しなかった[1]。この要因として平面四配位 Ni 錯体の集積構造の高い安定性が要因の一つであると考えた。そこで本研究では、かさ高い置換基であるアントラセンを導入した配位子を用いて、集積構造の安定性を低下させた平面四配位ニッケル錯体を合成し、その溶媒蒸気応答性を調査した。

単結晶構造解析の結果、メタノール中で合成した Ni 錯体はメタノールが 2 分子配位した六配位八面体構造(**1_MeOH**)であった。**1_MeOH** を加熱すると、黄緑色の粉末色が黒赤色に変化した(1)。この粉末に様々な蒸気を曝すと、NH_3 やメタノール、アセトニトリル、ピリジンなど様々な有機溶媒蒸気に応答し、粉末色が変化した。更に磁化率測定の結果、反磁性から常磁性へと変化が確認された。従って、様々な溶媒蒸気に応答して色と磁性を変換可能な単核 Ni 錯体の合成に成功した。



1) S. Kusumoto, K. Inaba, H. Suda, M. Nakaya, R. Tokunaga, P. Thuery, R. Haruki, T. Kanazawa, S. Nozawa, Y. Kim, S. Hayami, Y. Koide, *Inorg. Chem.* 2023, 62, 39, 16222–16227.

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常磁性スピンクロスオーバー配位子の開発

（電通大院情報理工[1]・北里大理[2]）○野口 義正[1]・渡辺 聡美[2]・石田 尚行[1]
Development of paramagnetic spin-crossover ligands ([1]*The University of Electro-Communications*, [2]*Kitasato University*) ○Yoshimasa Noguchi,[1] Satomi Watanabe,[2] Takayuki Ishida[1]

We attempted to synthesize paramagnetic SCO ligands based on 2,6-bis(pyrazol-1-yl)pyridine (1-bpp) and 2,6-bis(oxazol-2-yl)pyridine (pybox). The first target is a 1-bpp biradical ligand having nitroxide groups at the pyrazole 5,5' positions. The X-ray crystal structure analysis clarified that the N-O bond distance is 1.27 Å, being shorter than normal nitroxide N-O distance (Figure 1). Moreover, the $\chi_m T$ value was far lower than the theoretical value in the magnetic susceptibility measurement (Figure 2). It is suggested that the nitroxide radical was decomposed. The stabilization effect of five-membered arromatic ring seems to be insufficient. Other radical ligands and their iron(II) complexes will be developed.
Keywords: spin crossover; nitroxide; aminoxyl; iron(II); 1-bpp; pybox

常磁性スピンクロスオーバー(SCO)配位子は、それらの Fe^{2+}錯体が SCO を引き起こすだけでなく、SCO 特有の構造変化を利用した新たなスイッチングデバイスへの応用が期待できる。本研究では、2,6-bis(pyrazol-1-yl)pyridine (1-bpp) と 2,6-bis(oxazol-2-yl)pyridine (pybox)にニトロキシドラジカルを導入した常時性 SCO 配位子の合成を目指す。現在 1-bpp の pyrazole 5,5'位にニトロキシドラジカルを導入した配位子及び錯体の合成を行った。この配位子の X 線結晶構造解析の結果、NO 結合長が 1.27 Å とニトロキシドラジカルの一般的な NO 結合長よりも短いことがわかった(図 1)。さらに、磁化率測定においても理論値よりも大幅に低い $\chi_m T$ 値が得られた(図 2)。これらの結果からニトロキシドラジカルが分解してしまったことが示唆される。五員環を用いたニトロキシドラジカルの安定性は低く、報告例が少ないため慎重な操作が必要になる。また、他の常磁性 SCO 配位子として 1-bpp と pybox の pyridine 4 位にニトロキシドラジカルを導入したモノラジカル配位子の合成を行っている。

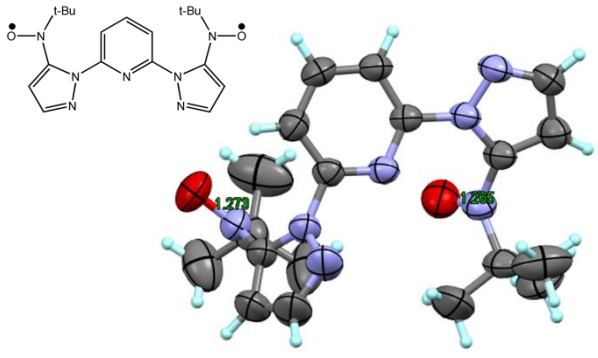

図 1　標的分子の構造式と合成した配位子の ORTEP 図.

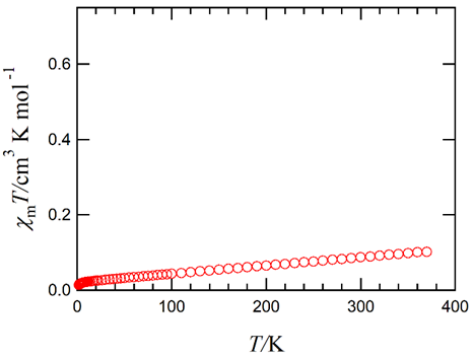

図 2 合成した配位子の $\chi_m T$ vs T プロット

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金属希釈による SCO 錯体の分子間相互作用に関する理論的解釈

(熊大理[1]・熊大院先端[2]) ○三宅 貫太[1]・張 中岳[2]・関根 良博[2]・速水 真也[2]
Theoretical interpretation of the intermolecular interactions of SCO complexes by metal dilution of iron(III) complexes ([1]Faculty of Science, *Kumamoto University*, [2] Faculty of Advanced Science and Technology, *Kumamoto University*) ○Kanta Miyake,[1] Zhongyue ZHANG,[2] Yoshihiro Sekine,[2] Shinya Hayami[2]

The spin crossover (SCO) behavior has attracted attention as a bistable material that can be applied to switching materials, and it has been reported that its behavior strongly depends on not only ligand field strength but intermolecular interactions. In particular, the metal dilution experiments for Fe(II) complexes have been systematically investigated in the view point of the interactions. However, the investigation of the interactions by dilution effect in Fe(III) complexes affects the SCO behavior is still unclear.

In this study, we have focused on the effect of the metal dilution by Al^{3+} or Ga^{3+} ions, and researched on the diluted effect in spin crossover Fe(III) complexes. As a result, it was found that the SCO traces changes depending on diluted ratio. In this presentation, we would like to discuss about the intermolecular interactions in SCO iron(III) systems based on dilution effect.
Keywords : Metal complex; Molecular magnetism; Spin crossover; Intermolecular interaction

スピンクロスオーバー現象はスイッチング材料などに応用可能な双安定性を示す物質として注目されており、その挙動が分子間相互作用に強く依存するということが報告されてきた。これまでに Fe(II)錯体に関して金属希釈によってスピン転移温度の変化や、相互作用の抑制による協同性の変化が報告されている[1]。一方で Fe(III)錯体に関しては金属希釈に伴う系統的研究がほとんど行われておらず Fe(III)錯体における希釈効果がスピンクロスオーバー挙動に如何に作用するかは未開拓の領域である。

本研究では既報の鉄(III)錯体[2]において Al^{3+}と Ga^{3+}を用いた金属希釈によって磁気挙動にどのような影響を与えるか明らかにすることを目的とした。その結果、希釈金属イオンの種類によって希釈試料の SCO 挙動が大きく異なるということがわかった(Figure)。当日は希釈に伴う磁気挙動変化について、分子間相互作用変化と併せて報告する。

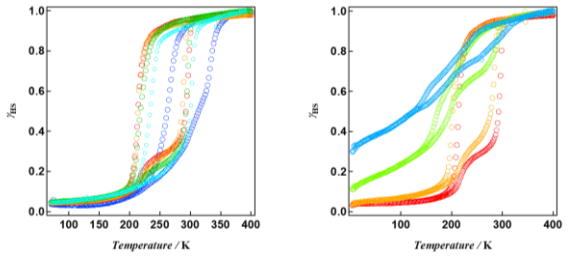

Figure [Fe(qsal)$_2$NCSe]の Al^{3+}希釈(左)と Ga^{3+}希釈(右)の温度依存磁化率

Ref. 1. Philipp, G., Andres, H., and Hartmut S., Angew. Chem. Int. Ed, 33, 2024-2054, (1994)
Ref. 2. Hayami, S., Gu, Z. Z., Yoshiki, H., Fujishima, A., and Sato, O., J. Am. Chem. Sc.123, 11644-11650 (2001).

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吸着誘起スピン転移を利用したナノポーラスコバルト錯体の吸着熱制御

（名大院工）○大野華子・Jenny Pirillo・Liyuan Qu・日下心平・土方優・井口弘章・松田亮太郎

Adsorption Heat Control of Nanoporous Cobalt Complexes Using Spin Transition (*Graduate School of Engineering, Nagoya University*) ○Kako Ohno, Jenny Pirillo, Liyuan Qu, Shinpei Kusaka, Yuh Hijikata, Hiroaki Iguchi, Ryotaro Matsuda

Porous materials such as activated carbons, zeolites, and nanoporous metal complexes (NMCs) are used as adsorbents. In general, the adsorption of gas molecules into adsorbents generates heat. Although adsorption heat is useful in a heat pump, in gas storage and separation application, it is problematic that adsorption performance decreases due to the temperature rising of the adsorbent. Recently, NMCs that exhibit phase changes are gained attention for controlling the adsorption heat. We focused on spin crossover (SCO), a reversible transition between high-spin (HS) and low-spin (LS) electronic states of transition metal ions, as an effective phase change for controlling heat of adsorption. SCO metal complexes have long been studied as magnetic materials for switches and memories, but recently they are attracting attention again because of their proposed potential application as thermal management materials by taking advantage of their latent heat. In this study, to demonstrate the control of adsorption heat by SCO induced by gas adsorption, we observed gas adsorption and heat of adsorption simultaneously for NMC showing gas adsorption-induced SCO.

Keywords : Nanoporous Metal Complex; Adsorption Heat; Spin crossover

私たちの身の回りで吸着材料として用いられる多孔性材料には、活性炭やゼオライト、有機配位子と金属イオンの自己集合により形成されるナノポーラス金属錯体(NMC)などがあげられる。一般に吸着材へのガス分子の吸着は発熱過程であることが知られている。この吸着熱はエアコンや冷蔵庫などのヒートポンプへと応用できるが、ガス分子の吸着・貯蔵への応用においては、温度上昇により吸着材の吸着量を減少させてしまうという問題がある。最近、この問題を解決可能な物質として相変化を起こすNMCが注目されている。我々は吸着熱の制御に有効な相変化として、遷移金属イオンの電子状態が高スピン(HS)と低スピン(LS)の間で可逆的に転移する現象であるスピンクロスオーバー(SCO)に注目した。SCO金属錯体はスイッチやメモリなどの磁性材料として古くから研究されてきたが、最近になって、その潜熱を生かした熱管理材料への応用の可能性が提案され、再び注目されつつある。本研究では、SCO現象による吸着熱制御の実証を目的とし、ガス吸着に伴ってSCOを示すNMCのガス吸着と吸着熱の同時観測を行った。

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Investigation of Structural and Magnetic Properties of Dinuclear Fe(II) Complexes with Bridging-ligand whose Linkage Isomerization is Restricted

(*Graduate School of Science, Tokyo University of Science*) ○Ryosuke Taniai, Takuya Kanetomo, Masaya Enomoto

Keywords: Spin Transition; Iron Complex

A dithiooxalato-bridged (μ-dto, Fig. 1a) dinuclear iron(II) complex terminated with tris(2-pyridylmethyl)amine (TPA) as a capping ligand exhibits an N_4OS coordination environment around the Fe centers. Interestingly, a linkage isomer (N_4O_2 and N_4S_2) and a diastereomer (N_4SO) exist within the same crystal, due to the rotational degree of freedom of the dto ligand. This complex shows an irreversible and a multi-step spin crossover behavior in the temperature dependence of the magnetic moment.[1] The former is considered to be caused by an irreversible structural change of the molecular arrangement, because the compound has no solvent. On the other hand, the coexistence of these mixed coordination states gives rise to the different spin-transition temperatures, resulting in the multi-step transition.

In this study, we have attempted to synthesize new dinuclear iron(II) complexes using 1,2- and 1,3-dithiosquarato (1,2-dts and 1,3-dts, respectively, as shown in Figs. 1b and c) as the bridging ligands. The use of 1,2-/1,3-dts bridging ligands allows to separate the contribution of several components for the coordination environments, because the rotation of the *O*,*S* coordination sites of these ligands is not considered. Here, we will introduce the dts ligands as selective coordination environments for the iron(II) sites to allow the deconvolution of multiple components of spin crossover states.

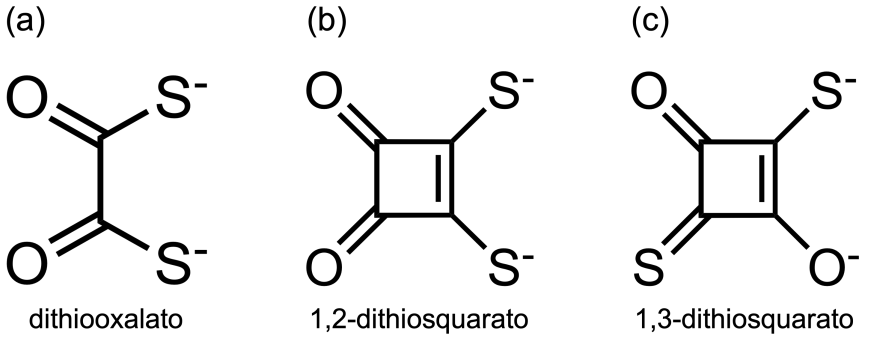

Figure 1. Chemical structures of the bridging ligands, (a) dto, (b) 1,2-dts, and (c) 1,3-dts.

1) T. Kanetomo, et al. *Dalton Trans.* **2023**, *52*, 12496.

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Cyanido-Bridged Fe^{II}-Nb^{IV} assemblies with Fe^{II}-Fe^{II}-Bridging Ligands

([1]*School of Science, The University of Tokyo*) ○Itsuki Fukagawa,[1] Takefumi Kanno,[1] Koji Nakabayashi,[1] Kenta Imoto,[1] Kazuki Nakamura,[1] Yuuki Mineo,[1] Shota Kobayashi,[1] Yoshinori Tanaka,[1] Shin-ichi Ohkoshi,[1]

Keywords: *Spin crossover; Photomagnetism*

Spin crossover (SCO), the transition between two different electronic configurations of high spin(HS) state and low spin(LS) state, is attracting attention in many fields such as photo-chemistry and molecular magnets[1, 2]. SCO properties are sensitive not only to the ligand field but also to intermolecular interactions in the crystal. It was reported that $Fe^{II}_2[Nb^{IV}(CN)_8](dpds)_4 \cdot 6H_2O$ (dpds = 4,4'-dipyridyl disulfide, **FeNb-dpds**) shows gradual and incomplete SCO where only 22 % of Fe^{II}_{HS} turns into Fe^{II}_{LS} possibly due to the negative cooperative effect provided by the additional bridging ligand[(3)]. In addition, assemblies with metals bridged by cyanides exhibit a parallel or anti-parallel order of spins because superexchange interactions work between metals through cyanides. Iron(II) octacyanidoniobate(IV) complexes are well-studied as ferrimagnetic assemblies with SCO.

In this work, we synthesized an Iron(II) octacyanidoniobate(IV) complex with 1,3-di(4-pyridyl)propane (dpp), $Fe^{II}_2[Nb^{IV}(CN)_8](dpp)_4 \cdot 6H_2O$ (**FeNb-dpp**). The Fe sites and Nb sites in the crystal structure are connected through cyanides and Fe-sites are additionally bridged by dpp, which forms a 3D network structure in the $I4_1/a$ space group (Figure 1.). The product of magnetic susceptibility χ_M and temperature T decreased around 120 K, $\chi_M T$ = 7.50 K cm^3 mol^{-1} at 300 K and $\chi_M T$ = 2.64 K cm^3 mol^{-1} at 50 K (Figure 2.), inducing SCO in which about 70 % of Fe^{II}_{HS} sites changed into Fe^{II}_{LS} sites on the basis of paramagnetic Fe^{II}_{HS} (g = 2.2, S = 2) and Nb^{IV} (g = 2, S = 1/2). The transition was more drastic than **FeNb-dpds**. Moreover, the magnetization of **FeNb-dpp** increased at 3 K by irradiating 473 nm light. suggesting light-induced excited spin-state trapping (LIESST).

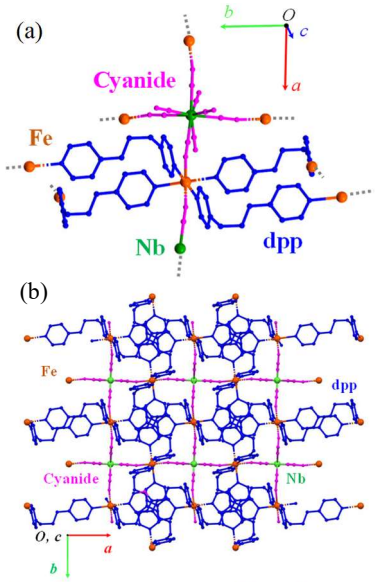

Figure 1. (a) Coordination environment of **FeNb-dpp** (b) The crystal structure viewed along the c-axis.

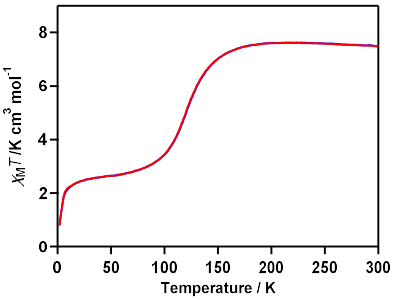

Figure 2. $\chi_M T$-T plot of **FeNb-dpp** under external magnetic field of 5000 Oe.

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nature Photon.*, **2014**, 8, 65-71.
2) S. Ohkoshi, K. Imoto, Y. Tsunobuchi, S. Takano, H. Tokoro, *Nature Chem.*, **2011**, 3, 564-569.
3) T. Kanno, K. Nakabayashi, K. Imoto, Y. Tanaka, S. Ohkoshi, *Inorg. Chim. Acta.*, **2024**, 559, 121769.

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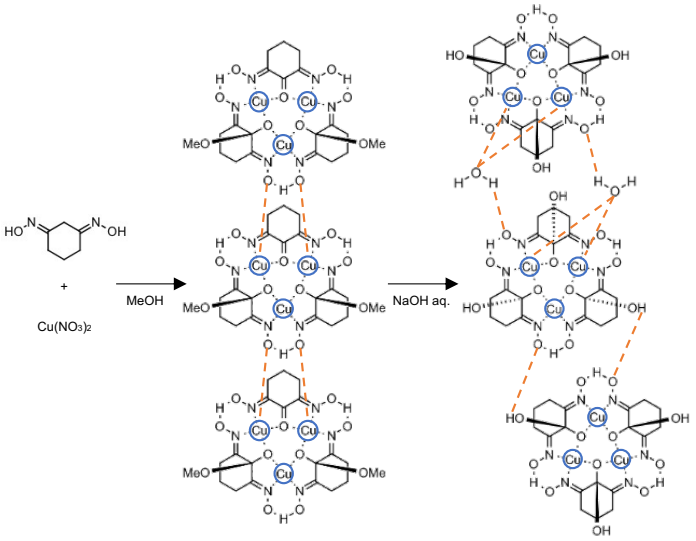
シクロヘキサン-1,3-ジオンジオキシムと硝酸銅(II)から形成した三核銅錯体の磁気特性と電気化学特性

（日大院理工[1]・日大理工[2]）○細谷 遥佑[1]・金城 はなか[1]・須川 晃資[2]・大月 穣[2]

Magnetic and electrochemical properties of trinuclear copper complexes formed from cyclohexane-1,3-dione dioxime and copper(II) nitrate ([1]*Graduate School of Science and Technology, Nihon University*, [2]*College of Science and Technology, Nihon University*)
○Yosuke Hosoya,[1] Hanaka Kinjo,[1] Kosuke Sugawa,[2] Joe Otsuki[2]

We obtained a trinuclear copper complex formed from cyclohexane-1,3-dione dioxime and copper(II) nitrate.[1)] The molecular arrangement of the complexes changes drastically when the recrystallization conditions are changed, although the structure of the complexes is almost the same. In one crystal, the oxime groups in the complex also coordinate to the copper ions in the neighboring complex, forming a one-dimensional chain (Figure, center), whereas in the other crystal, the complex is isolated without forming a network (Figure, right). The magnetic properties of the two complexes are different, and *inter*-complex copper(II) ions displays weak ferromagnetic interactions in the former crystals, whereas no interaction is observed in the latter crystals. We also report the electrochemical properties of the complex, as electrochemical measurements suggested that the complex could work as a water reduction catalyst.
Keywords : Electrochemical Properties; Magnetic Properties; Molecular Arrangement; Multinuclear Copper Complexes

当研究室では，シクロヘキサン-1,3-ジオンジオキシムと硝酸銅(II)から三核銅錯体が形成することを見出した[1)]．この錯体は，再結晶条件を変えると，ほぼ同じ錯体構造でありながらも，分子配列が大きく変化する．一方の結晶では，錯体中のオキシム基が隣の錯体の銅イオンにも配位することで 1 次元鎖を形成するのに対し（図中央），他方では，ネットワークを形成せず孤立している（図右）．これらの分子配列の変化に伴い，磁気特性にも違いが見られ，錯体間には，前者では弱い強磁性相互作用があるのに対し，後者では相互作用は見られなかった．また，この錯体は水中で還元触媒として機能することが示唆されたので，この錯体の電気化学特性についても合わせて報告する．



1) Y. Hosoya, S. Kobori, Y. Kojima, K. Sugawa, J. Otsuki, *J. Indian Chem. Soc.*, **2021**, *98*, 100110.

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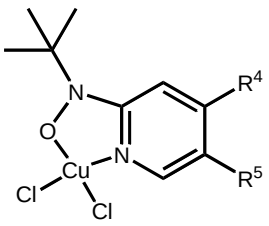
銅(II)やニッケル(II)のニトロキシド錯体における 3d–2p ヘテロスピンカップリングの置換基効果

（電通大院情報理工[1]・電通大情報理工[2]）○飯田大智[1]・三井允嵩[2]・石田尚行[1]
Substituent effects of 3d-2p heterospin coupling in copper(II) and nickel(II) nitroxide complexes (*Graduate School of Informatics and Engineering, The University of Electro-Communications*) ○Daichi Iida,[1] Masataka Mitsui,[2] Takayuki Ishida[1]

We have reported the preparation of various Cu^{2+} and Ni^{2+} complexes having a paramagnetic ligand and their spin-transition behavior. The torsion angle M-O-N-C in the chelate plane is a useful parameter for evaluating orbital orthogonality. When the torsion is large, 3d-2p coupling becomes antiferromagnetic, and when small it becomes ferromagnetic. Now we have prepared CH_3-, CF_3- and Ph-substituted ligands and their complexes with MX_2 (M = Cu, Ni; X = Cl, Br, ClO_4, BF_4). Their crystallographic analysis, SQUID measurements, and DFT calculations suggested the possibility of spin-transition originating in the 3d-2p coupling switch. The substituent effects on the nitroxide-Cu and -Ni interactions will be discussed.
Keywords : radical , molecular magnetism, complex, spin transition

我々はこれまでに比較的強い3d-2pカップリングを有する金属錯体を合成してきた。その中で $[Ni(phpyNO)_2X_2]$ の X = Cl[1], Br[2] は $S_{total} = 0$ と 2 の間のスピン転移を示した。この転移はスピン間の相互作用が低温領域では反強磁性的に、高温領域では強磁性的になるために起こり、キレート構造の平面性が高いときは強磁性的に、平面性が低いときは反強磁性的になる。今回、同様なスピン転移挙動が期待される錯体を開発するためにピリジン環上に置換基を導入した。

ピリジン環にメチル、トリフルオロメチル、またはフェニル基を有する誘導体を合成した。銅錯体の例を図1に示す。それぞれの配位子に対してMX_2 (M = Cu, Ni; X = Cl, Br, ClO_4 , BF_4) との錯形成を行った。磁化率測定の結果（図２）、高温側で $\chi_m T$ の上昇が見られ、配位構造に変化がなければ二重項-四重項モデルで解析し、変化が認められればファントホッフ式で解析することになる。本発表では、磁化率測定、X線結晶構造解析、DFT計算をもとにスピン転移の有無と同時に、置換基が今回の機構に対して与える影響を議論する。



R^4, R^5 =
Me, H: **4mepyNO**
Ph, H: **4phpyNO**
H, Me: **5mepyNO**
H, CF_3: **5cf3pyNO**

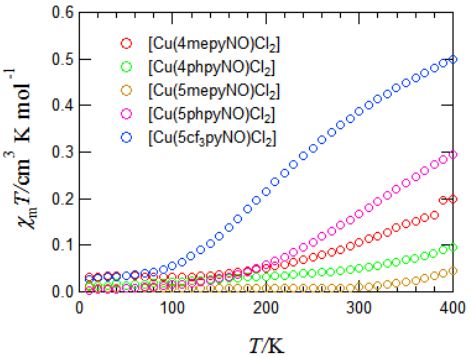


図 1 .[Cu(RpyNO)Cl_2](R= H, Ph, Me, CF_3)の構造. 図 2.[Cu(RpyNO)Cl_2]の$\chi_m T$ vs T プロット

Ref. 1) Y. Homma et al. *Chem. Mater.* **2018**, *30*, 1835. 2) Y. Kyoden, et al. *Inorg. Chem.* **2019,** *58*, 10743.

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基底三重項 5-アダマンチル-1,3-フェニレンビスニトロキシドを架橋配位子に用いたヘテロ金属鎖状錯体

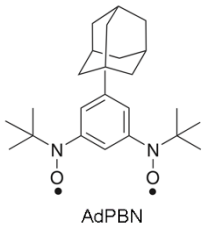
（電通大院情報理工）○上野隼弥・石田尚行

Heterometallic chain complexes bridged with a ground-triplet 5-adamantyl-1,3-phenylene bis(*t*-butyl nitroxide) (*Graduate School of Informatics and Engineering, The University of Electro-Communications*) ○Shunya Ueno, Takayuki Ishida

We have been working on lanthanide-bisnitroxide one-dimensional complexes toward development of novel single-chain magnets. 5-(1-Adamantyl)-1,3-phenylene bis(*tert*-butyl nitroxide) (abbreviated as AdPBN) was prepared and applied to complexation with rare-earth metal ions. During this study, novel heterometallic chain complexes [-M-AdPBN-RE-AdPBN-]$_n$ were isolated and structurally characterized. Here, the M ion is divalent, and accordingly further various complexes involving heterospins from nitroxide, transition metal ion, and lanthanide ion can be developed. Their magnetic properties will be presented.

Keywords : Nitroxide radical, Rareearth complex, Heterometaric complex, Aminoxyl

当研究室では単鎖磁石として希土類-ビスニトロキシドラジカル RE-tBuPBN を得ている[1]。本研究では、より嵩高いアルキル置換基であるアダマンチル基を持つビラジカル(AdPBN)と希土類金属イオンの錯形成を行った。その際、[-M-AdPBN-RE-AdPBN-]$_n$ の鎖状錯体が得られた（Fig. 1 left）。ここで M は２価の金属陽イオン、RE 希土類陽イオンは Y^{3+}と Gd^{3+}であり、補助配位子は hfac である。鎖の中では M と RE は AdPBN の架橋を挟んで交互に配置されており、M/RE/AdPBN 比は 1/1/2 である。AdPBN は直接ニトロキシド酸素原子による直接配位結合を有し、同様に RE と AdPBN も直接結合を有する。また、Ba^{2+}イオン 2 つを AdPBN 架橋で安定化するような鎖状錯体[-Ba-Ba-AdPBN-]$_n$ ([Y(hfac)$_4$])$_n$ も得た（Fig. 1 right）。講演では種々の M と RE を用いた錯体の合成および磁性を報告する。



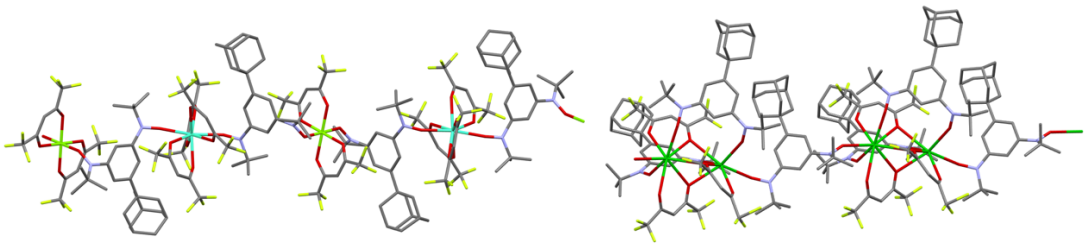


Fig. 1. (left) X-ray crystallography result of polymeric $M_1RE_1AdPBN_2$. (right) Polymeric $Ba_2AdPBN_3^+$ with a counteranion $[Y(hfac)_4]^-$ omitted.

Ref. 1) S. Ito et al., *Inorg. Chem.* **2022**, *61*, 10619−10623.

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配位子にニトロキシドラジカルを有するランタノイド錯体の磁気特性に関する理論研究

(阪大基礎工[1]・阪大院基礎工[2]・阪大 QIQB[3]・阪大 RCSEC[4]・阪大 ICS[5]・電通大院情報理工[6]・阪大 SRN[7])
○高海斗[1]・井上廉[1]・益田晃希[2]・岸亮平[2,3,4,5]・石田尚行[6]・北河康隆[2,3,4,5,7]
Theoretical study on magnetic properties of lanthanide complexes with nitroxide radicals as ligands ([1] *Faculty of Engineering Science, Osaka University,*[2] *Graduate School of Engineering Science, Osaka University,* [3]*QIQB, Osaka University* [4]*RCSEC, Osaka University,* [5]*ICS Osaka University,* [6]*Graduate School of Informatics and Engineering, The University of Electro-Communications,* [7]*SRN, Osaka University)*
○Kaito Taka,[1] Ren Inoue[1], Koki Masuda,[2] Ryohei Kishi,[2,3,4,5] Takayuki Ishida,[6] Yasutaka Kitagawa,[2,3,4,5,6]

Single-molecule magnets based on lanthanide (Ln) complexes have been actively investigated in recent years. Our group has found that orbital interactions between 4f and 2p orbitals affect the magnetic anisotropy of the complex.[1)] It suggests that the magnetic anisotropy can be controlled by orbital interactions between the metal ion and ligands. On the other hand, there are several reports about the Ln complexes with radicals on coordinating ligands.[2)] There is little information about the relationship between f-p orbital interactions and the magnetic properties of those complexes. In this study, therefore, we focus on Ln-NO radical complexes and elucidate the magnetic exchange coupling between 4f and 2p spins by quantum chemical calculations. And we also discussed how the interaction affects to the magnetic anisotropy of the Ln ion.
Keywords : single-molecule magnets, quantum chemical calculation, magnetic property, electronic structure.

現在、ランタノイド（Ln）錯体を用いた単分子磁石（SMMs）が盛んに研究されている。これまでに我々の研究グループでは、配位子の 2p 軌道と 4f 軌道との相互作用が、磁気異方性に影響を与えることを見出した[1)]。これは、金属イオンと配位子との配置関係や軌道エネルギー差などから軌道相互作用をうまく設計することにより、磁気異方性を制御できる可能性を示唆している。他方、配位子にラジカルを有する Ln 錯体の報告がある[2)]。しかし、このような錯体において、f-p 間の軌道相互作用と磁気異方性の関係に関する情報は極めて少ない。そこで本研究では、Fig.1 に示したような、配位子に NO ラジカルを有する Ln-NO ラジカル錯体に着目し、4f-2p 間の磁気的相互作用を量子化学計算を用いて明らかにするとともに、配位子の NO ラジカルが Ln の磁気異方性にどのような影響を与えるかを議論した。

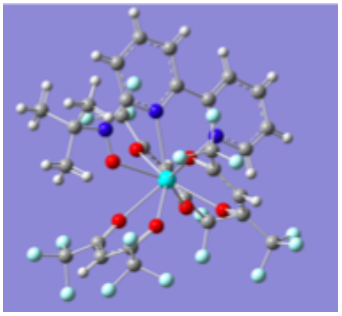
Fig.1 Example of the Ln-NO radical complex

1) 長奎吾 他, 日本化学会 第 102 回春季年会, 口頭発表（J202-4pm-13）, **2022**.
2) R. Murakami, T. Nakamura, T. Ishida, *Dalton Trans*. **2014**, *43*, 5893-5898.

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC F1231(1231, Bldg. 12 [3F])

[F1231-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kazuki Tanifuji, Tomoya Fukui

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1231-4pm-01]

Synthesis of a Phosphine-protected $Pd_2Au_{17}(PR_3)_{10}Cl_7$ Nanocluster with N_2-type Electronic Configuration

○Ryohei Saito[1], Yoshiyuki Mizuhata[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto university)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1231-4pm-02]

Properties of Diruthenium Complexes Having a Hydrogenphosphato Ligand Bridged on the $\{Ru_2(\mu\text{-}O(H))_2\}$ Core

○Tomoyo Misawa-Suzuki[1], Nagao Hirotaka[1] (1. Fac. of Sci. and Tech., Sophia Univ.)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1231-4pm-03]

The synthesis of rotaxanes consisting of α-cyclodextrin (CDX) threaded by 1,12-diaminododecane (don) bearing two different cobalt(III) complexes as stoppers

○Hiroshi Ogino[1], Shinji Inomata[2], Kayoko Kasai[3] (1. Tohoku University, 2. Fukushima University, 3. Miyagi University of Education)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[F1231-4pm-04]

Synthesis and reactivity of group 10 transition metal complexes bearing a NHC/Pyridyl hybrid ligand.

○Masaya Okamura[1], Saki Kobana[1], Kota Imaizumi[1], Misa Kitahara[1], Rena Suzuki[1], Shiro Hikichi[1] (1. Kanagawa University)

Japanese
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[F1231-4pm-05]

Preparation, Reactions, and Structure of Boron-substituted Silyllithium

Yuta Kowada[1], ○Atsushi Kawachi[2] (1. Graduate School of Science and Engineering, Hosei University, 2. Faculty of Bioscience and Applied Chemistry, Hosei University)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[F1231-4pm-06]

Formations of Al-Al Bonds by a Reaction of Nucleophilic and Electrophilic Aluminum Species

○Ryotaro Yamanashi[1], Kanata Mizutani[1], Makoto Yamashita[1] (1. Nagoya University)

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English
3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC
[F1231-4pm-07]
Construction of Expanded Hollow Cages by Templated Self-assembly in the Solid State for Conformation Control of Organic Macrocycles

○Kenta Iizuka[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The Univ. of Tokyo, 2. Institute for Molecular Science)

English
3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC
[F1231-4pm-08]
Synthesis and Structural Analysis of Metal Complexes with Azulene Derivatives as Ligands

○Tatsuya Iwashina[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Tokyo University of Science)

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N_2型の電子配置を有する$Pd_2Au_{17}(PR_3)_{10}Cl_7$クラスターの合成

（京大院工・京大化研）○齋藤　亮平[1,2]・水畑　吉行[2]・磯﨑　勝弘[1,2]・中村　正治[1,2]
Synthesis of a Phosphine-protected $Pd_2Au_{17}(PR_3)_{10}Cl_7$ Nanocluster with N_2-type Electron Configuration ([1]*Graduate School of Engineering, Kyoto University,* [2]*Institute for Chemical Research, Kyoto University*) ○ Ryohei Saito, Yoshiyuki Mizuhata, Katsuhiro Isozaki, Masaharu Nakamura

Metal nanoclusters often have an electronic structure resembling small molecules due to the formation of superatomic molecular orbitals originating from the linear combination of superatomic orbitals. In this study, we successfully synthesized novel $Pd_2Au_{17}(depp)_{10}Cl_7$ (depp = diethylphenylphosphine) by visible light irradiating to $PdAu_{12}(depp)_8Cl_4$. Single crystal X-ray diffraction revealed that this new cluster has a Pd_2Au_{17} core composed of two $PdAu_{12}$ units sharing an Au_5 facet. Density-functional theory (DFT) calculations reveal that superatomic orbitals of the two icosahedrons construct dinitrogen (N_2)-type superatomic molecular orbitals having the electron configuration of $(1\Sigma_s)^2(1\Sigma_s^*)^2(1\Pi_{px,\,py})^4(1\Sigma_{pz})^2$.

Keywords : Gold Nanocluster; Superatom; Superatomic molecule; Electron Configuration

正二十面体形のM_{13}コアを有する金属ナノクラスターは，8つの価電子を1S, 1P超原子軌道に収容したNe型の閉殻電子配置を取る際に安定化される。さらにM_{13}超原子がそれぞれの頂点や面の金原子を共有したコア構造を有する金属ナノクラスターでは，複数のM_{13}コアの超原子軌道同士が線形結合し超原子分子軌道を形成し，結合性軌道に価電子を収容するために安定化すると考えられている。例として，2つのAu_{13}超原子が3つの金原子を面共有して結合したコア構造を持つ$Au_{38}(SR)_{24}$クラスターは安定であるが，これは F_2分子様の閉殻電子配置をとるためと考えられている[1]。しかしながら，このような小分子と類似した超原子分子軌道を有するクラスターの合成例は少なく，超原子軌道間の相互作用や，それにより発現する機能は未解明である。

今回我々は，中心にPdを有する正二十面体形の$PdAu_{12}(depp)_8Cl_4$ (depp = diethylphenylphosphine) を前駆体とし，可視光を照射することで，新規の組成と構造を有する$Pd_2Au_{17}(depp)_{10}Cl_7$の合成に成功した(Figure 1)。単結晶構造解析から，得られた新規クラスターは二つのMAu_{12}超原子が5つの金原子を面共有したコアを有することが明らかとなった。DFT計算からは，M_2Au_{17}クラスターは，2つのMAu_{12}超原子の超原子軌道が線型結合することで，10個の価電子が窒素分子と同様の電子配置 $(1\Sigma_s)^2(1\Sigma_s^*)^2(1\Pi_{px,\,py})^4(1\Pi_{pz})^2$ をとることが示唆された。本発表では，クラスターの合成法や構造，計算により得られた結果の詳細について報告する。

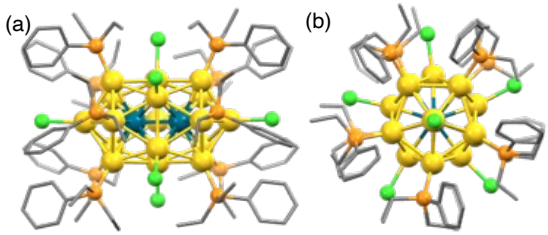

Figure 1. Crystal structure of $Pd_2Au_{17}(depp)_{10}Cl_7$: (a) front and (b) side view.

1. Jin, R. *et al. J. Am. Chem. Soc.* **2010,** *132*, 8280–8281.

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Properties of Diruthenium Complexes Having a Hydrogenphosphato Ligand Bridged on the {$Ru_2(\mu\text{-}O(H))_2$} Core

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Keywords: *Dinuclear Complex, Doubly Oxido-Bridge, Redox Behaviors, Spectroscopic Behaviors*

For the development of model compounds of natural metalloenzymes having diiron centers, we have been studying a series of diruthenium complexes having the doubly oxido-/hydroxido-bridged core, {$Ru_2(\mu\text{-}O(H))_n$} (n = 1, 2).[1,2] The electronic structures of the complexes range from Ru(IV)-Ru(IV),[1] Ru(III)-Ru(IV),[2] to Ru(III)-Ru(III),[3] in the same tridentate ligand (ethylbis(2-pyridylmethyl)amine; ebpma) system.

In this work, a HPO_4^{2-}-bridged Ru(III)-Ru(IV) complex having the {$Ru_2(\mu\text{-}O)_2$} core, [{$Ru^{III,IV}$(ebpma)}$_2$(μ-O)$_2$(μ-O_2PO_2H)]ClO_4 ([**III,IV(HPO$_4$)**]ClO_4), was synthesized in water-acetone (pH of around 8) at room temperature, showing the S = 1/2 state (μ_{eff} / μ_B = 1.70 at 297 K). The electronic structures and electrochemical and spectroscopic properties of [**III,IV(HPO$_4$)**]$^+$ were investigated and the comparisons were made with a series of Ru(III)-Ru(IV) complexes having the μ-O_2XY^{m-} ligand (**Table**). The redox potentials ($E_{1/2}$) of the Ru^{IV}-Ru^{IV}/Ru^{III}-Ru^{IV} couple and the maximum absorption bands (λ_{max}) of the {$Ru_2(\mu\text{-}O)_2$}-{$Ru_2(\mu\text{-}O)_2$}* transitions in CH_3CN showed correlations, indicating that the stronger electron-donating characters of the μ-O_2XY^{m-} ligand on the {$Ru_2(\mu\text{-}O)_2$} core destabilize the SOMO energy levels.

The pK_as were observed at 8.8 for the equilibrium between [**III,IV(HPO$_4$)**]$^+$ and [**III,IV(PO$_4$)**], and 3.5 for that between {$Ru_2(\mu\text{-}O)(\mu\text{-}OH)$} ([**III,IV(HPO$_4$)_1H**]$^{2+}$) and {$Ru_2(\mu\text{-}O)_2$} ([**III,IV(HPO$_4$)**]$^+$) by the spectroscopic studies in water at 298 K. The redox behaviors in water and the one-electron oxidation of [**III,IV(HPO$_4$)**]$^+$ will be reported as well.

Table. Properties of Ru(III)-Ru(IV) complexes with the {$Ru_2(\mu\text{-}O)_2$} core bridged by the O_2XY^{m-} ligand at 298 K.

μ-O_2XY^{m-}	μ_{eff} / μ_B (295 ~ 298 K)	pK_a *	$E_{1/2}$** (Ru^{IV}-Ru^{IV}/ Ru^{III}-Ru^{IV}) / V	E_{pa}** (Ru^{IV}-Ru^{V}/ Ru^{IV}-Ru^{IV}) / V	λ_{max} (ε) / nm (M^{-1} cm^{-1})
CO_3^{2-} [1,2a]	2.01	†	0.15	†	1067 (660)
HPO_4^{2-}	**1.70**	**3.5**	**0.22**	**2.22**	**1016 (1020)**
SO_4^{2-}	1.79	2.1	0.31	2.02	945 (1440)
$CH_3CO_2^-$ [2b]	2.19	1.5	0.57	†	977 (1440)
HCO_3^- [1,2a]		2.4	0.60	†	972 (1490)
NO_3^- [2b]	2.17	†	0.93	†	762 (1300)

*between {$Ru_2(\mu\text{-}O)(\mu\text{-}OH)$} and {$Ru_2(\mu\text{-}O)_2$}. **$vs$. Ag|0.01 M $AgNO_3$(CH_3CN), 100 mV s^{-1}. † not observable.

1) T. Misawa-Suzuki, H. Nagao, *Dalton Trans*. **2023**, *52*, 2863.

2) a) T. Misawa-Suzuki, H. Nagao *et al*., *Inorg. Chem*. **2021**, *60*, 9996. b) T. Misawa-Suzuki, H. Nagao *et al*., *Inorg. Chem*. **2020**, *59*, 612. c) T. Suzuki, H. Nagao *et al*., *Inorg. Chem*. **2016**, *55*, 6830.

3) T. Misawa-Suzuki *et al*., 10th Asian Biological Inorganic Chemistry Conference, **2022**.

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α-シクロデキストリン（CDX）に糸通しした 1,12-ジアミノドデカン（don）の両末端に異なるコバルト(III)錯体をもつロタキサンの合成

(東北大院理[1]・福島大共生システム理工[2]・宮教大教育[3])
○荻野 博[1]・猪俣慎二[2]・笠井香代子[3]

The Synthesis of Rotaxanes Consisting of α-Cyclodextrin (CDX) Threaded by 1,12-Diaminododecane (don) Bearing Two Different Cobalt(III) Complexes as Stoppers

([1]Tohoku University, [2]Fukushima University, [3]Miyagi University of Education)

○Hiroshi Ogino[1], Shinji Inomata[2], Kayoko Kasai[3]

The title rotaxanes were synthesized by the following two routes:
Route 1: $[CoCl(en)_2(\text{monodentate don})]^{2+} + [Co(H_2O)(NH_3)_5]^{3+} + CDX \rightarrow$
[2]-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane A)
Route 2: $[Co(\text{monodentate don})(NH_3)_5]^{3+} + [CoCl_2(en)_2]^{+} + CDX \rightarrow$
[2]-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane B)
Where en denotes 1,2-diaminoethane. ^{13}C-NMR spectra of the rotaxanes indicate that those of A and B are largely different. It is suggested that the direction of CDX in the rotaxane A is opposite to that in the rotaxane B.

Keywords : Synthesis of Rotaxanes; Cyclodextrin Rotaxane; Cobalt(III) Complexes

CDX はバケツの底を抜いた形の筒状の分子である。本研究の発表者(H.O.)は 1979 年に CDX に糸通しした don (1,12-diaminododecane)の両末端に$[CoCl(en)_2]^{2+}$を結合させたロタキサンを合成し、発表した。[1, 2] 両末端に異なる錯体をもつロタキサンを合成すると、CDX の向きの違いによる異性体が生成するはずである。本研究では、次の２つのルートでロタキサンを合成した（溶媒は DMSO）。

ルート１：$[CoCl(en)_2(\text{monodentate don})]^{2+} + [Co(H_2O)(NH_3)_5]^{3+} + CDX \rightarrow$
[2]-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane A)

ルート２：$[Co(\text{monodentate don})(NH_3)_5]^{3+} + [CoCl_2(en)_2]^{+} + CDX \rightarrow$
[2]-$[CoCl(en)_2donCo(NH_3)_5]^{5+}$-[CDX] rotaxane (rotaxane B)

ロタキサン A と B の ^{13}C-NMR スペクトルは大きく異なっており、ロタキサンに取り込まれた CDX の向きは A と B とで逆向きであることを示唆している。

1) 荻野博、第 29 回錯体化学討論会(1979).
2) H. Ogino, *J.Am.Chem.Soc*., **23**, 1303-1304(1981).

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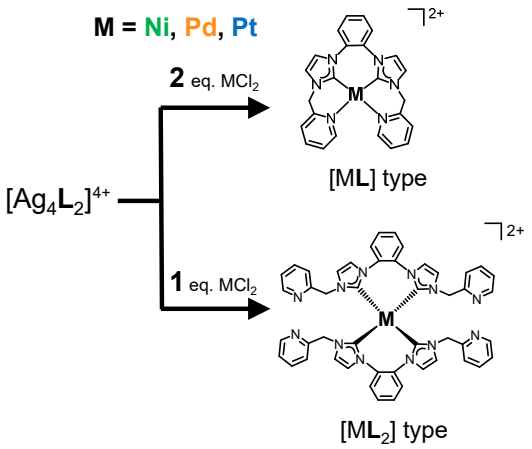
Synthesis and reactivity of group 10 transition metal complexes bearing a NHC/Pyridyl hybrid ligand.

([1]*Faculty of Chemistry and Biochemistry, Kanagawa University*) ○Masaya Okamura[1], Saki Kobana[1], Kota Imaizumi[1], Misa Kitahara[1], Rena Suzuki[1], Shiro Hikichi[1]

Keywords: N-Heterocyclic Carbene; Chelating Ligand; Catalyst; CO_2 Reduction

Recently, transition metal complexes bearing NHC/Pyridyl hybrid ligands, which have electron-donating NHCs with π-electron accepting pyridyl sites, have attracted attention for their excellent catalytic activity in a variety of reactions. In such mixed system ligands, it is known that the length and flexibility of the linker moiety connecting each functional group significantly affect their steric structure and catalytic activity. In this study, a hybrid chelating ligand, **L** was developed by connecting two NHC groups with a rigid phenylene linker and introducing a pyridyl group via a methylene spacer to provide flexibility in the coordination mode, and group 10 transition metal complexes with **L** as the ligand were synthesized and characterized.



Scheme 1. Synthesis of the complexes.

The imidazolium precursor, $H_2\mathbf{L}^{2+}$ was synthesized according to the procedure reported for a similar compound. The Br^- salt of $H_2\mathbf{L}^{2+}$ was then treated with an excess of Ag_2O at 80° in CH_3CN to form an Ag-**L** intermediate. X-ray structural analysis of this crystal revealed a $[Ag_4\mathbf{L}_2]^{4+}$ structure consisting of linear Ag_4 chains. Next, the reaction of the BF_4^- or ClO_4^- salts of the $Ag_4\mathbf{L}_2$ complex with metal-halides ($NiCl_2$, $PdCl_2$, K_2PtCl_4) in CH_3CN at 80°C led to the formation of two types of complexes depending on the equivalent amount of metal ions (Scheme 1). Upon the reaction of $[Ag_4\mathbf{L}_2]^{4+}$ complexes with two equivalents of metal ions, complexes with [M**L**]-type compositions were formed. Single crystal X-ray analysis revealed a distorted square planar structure with a tetradentate coordination of **L**. On the other hand, $[M\mathbf{L}_2]$-type complexes were obtained when one equivalent of the metal ion was used. The crystal structures showed that the two **L** ligands were bidentate to the metal center via NHC moieties, while the four pyridine moieties were free without coordination. Due to the different orientations of the phenylene groups, the Ni(II) and Pd(II) complexes form an almost perfect square planar structure, while the Pt(II) complex has a distorted square planar structure. The electrochemical properties of the obtained complexes were evaluated by cyclic voltammetry, and a large increase in cathodic current was observed in the [M**L**]-type complexes upon reductive scanning in a CO_2 atmosphere, suggesting their catalytic activity.

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ホウ素置換シリルリチウムの合成，反応および構造

(法政大院理工[1]・法政大生命[2])小和田 雄太[1]・○河内 敦[2]

Preparation, Reactions, and Structure of Boron-substituted Silyllithium

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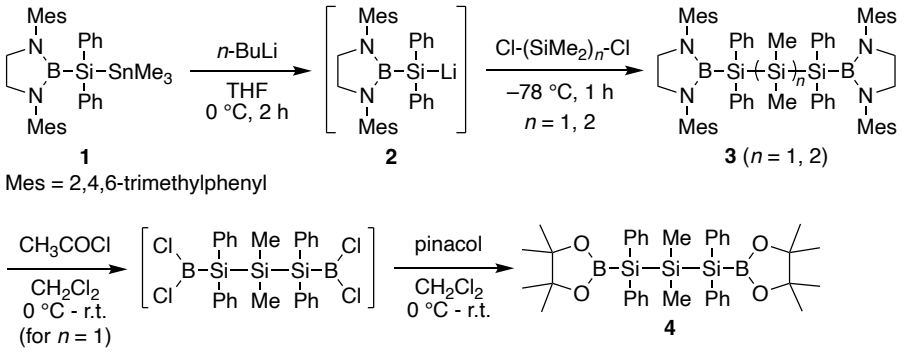
We previously reported the preparation of boron-substituted silyllithium **2** via the Sn-Li exchange reaction between silylstannane **1** and *n*-BuLi and the preparation of boron-substituted oligosilanes **3** by the reaction of **2** with dichlorosilanes. Herein, we report the structural analysis of oligosilanes **3** and the transformation of the substituents on the boron atoms in oligosilanes **3**. Some findings about the preparation of **2** and the structural study on silyllithium **2** in THF solution by NMR spectroscopies are also reported.

Keywords: Borylsilane, Silylstannane, Silyllithium, Oligosilane, Silane, Borane

当研究室ではすでに，ボリルシリルスタンナン **1** と *n*-ブチルリチウムとの Sn-Li 交換反応によるホウ素置換シリルリチウム **2** の合成とそれを用いたホウ素置換オリゴシラン **3** の合成について報告している[1)]。本発表では，オリゴシラン **3** の詳細な構造解析およびオリゴシランのホウ素原子上の置換基変換反応によるオリゴシラン **4** の合成について報告する。また，ホウ素置換シリルリチウム合成におけるホウ素原子上の置換基についての知見および各種 NMR スペクトル測定による THF 中でのシリルリチウム **2** の構造解析についても報告する。

Scheme 1



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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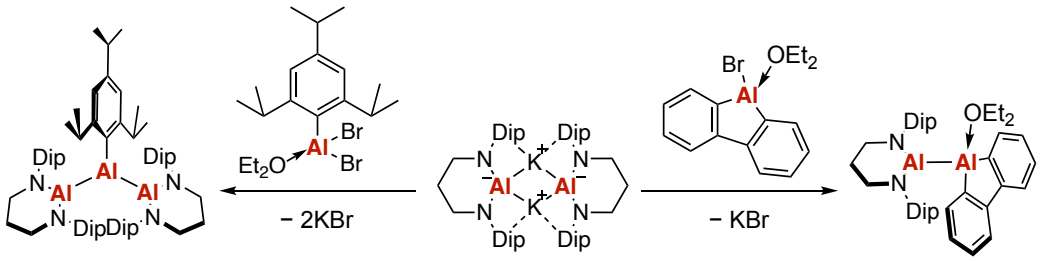
Synthesis of linear trialumane and unsymmetrical dialumane using Al anion

([1]*Graduate School of Engineering, Nagoya University*) ○Ryotaro Yamanashi,[1] Kanata Mizutani,[1] Makoto Yamashita[1]

Keywords: Aluminum; Dialumane; Trialumane; Catenation

Catenation is a term that refers to a property of an element to form the linear linkage of bonds between identical elements. It is a common phenomenon for group 14 elements as found in polyolefins and polysilanes. In contrast, no linear aluminum linkage with three or more aluminum atoms has been reported. In molecular chemistry of aluminum, three methods have been known to construct Al-Al bonds: (1) reduction of Al-H or -halogen bonds;[1] (2) insertion of alumylene, neutral Al(I) species, into the Al-halogen bond;[2] and (3) generation of neutral CpAl species and its spontaneous oligomerization to form Al clusters.[3] Recently, the first nucleophilic Al anion was reported to initiate a rapid advance in chemistry of Al nucleophiles.[4] Herein, we report the synthesis of dialumane and trialumane using our newly reported amino-substituted Al anion[5] and electrophilic aluminum reagents.

A linear trialumane was synthesized by reaction of our amino-substituted Al anion with $TipAlBr_2{\cdot}OEt_2$ (Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) (Scheme 1, left). Following the same strategy, we synthesized an unsymmetrical dialumane by reaction of the Al anion with *Al*-bromoaluminafluorene-ether complex (Scheme 1, right). In the presentation, the synthesis, structure, and reactivity of the resulting alkyl-, aryl substituted trialumanes and the unsymmetrical dialumane will be discussed.



Scheme 1. left: Synthesis of trialumane, right: Synthesis of unsymmetrical dialumane

1) A) Uhl, W. Z. *Naturforsch. B* **1988**, *43b*, 1113. B) Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nat. Chem.* **2010**, *2*, 865. 2) A) Li, B.; Kundu, S.; Zhu, H.; Keil, H.; Herbst-Irmer, R.; Stalke, D.; Frenking, G.; Andradac, D. A.; Roesky, H. W. *Chem. Commun.* **2017**, *53*, 2543. B) Hofmann, A.; Tröster, T.; Kupfer, T.; Braunschweig, H. *Chem. Sci.* **2019**, *10*, 3421. 3) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem. Int. Ed.* **1991**, *30*, 564. 4) A) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Nature 2018, 557, 92. B) Hobson, K.; Carmalt, C. J.; Bakewell, C. Chem. Sci. 2020, 11, 6942. C) Zhang, X.; Mei, Y.; Liu, L. L. *Chem. Eur. J.* **2022**, *28*, e202202102. 5) Feng, G.; Chan, K.L.; Lin, Z.; Yamashita, M. *J. Am. Chem. Soc.* **2022**, *144*, 22662.

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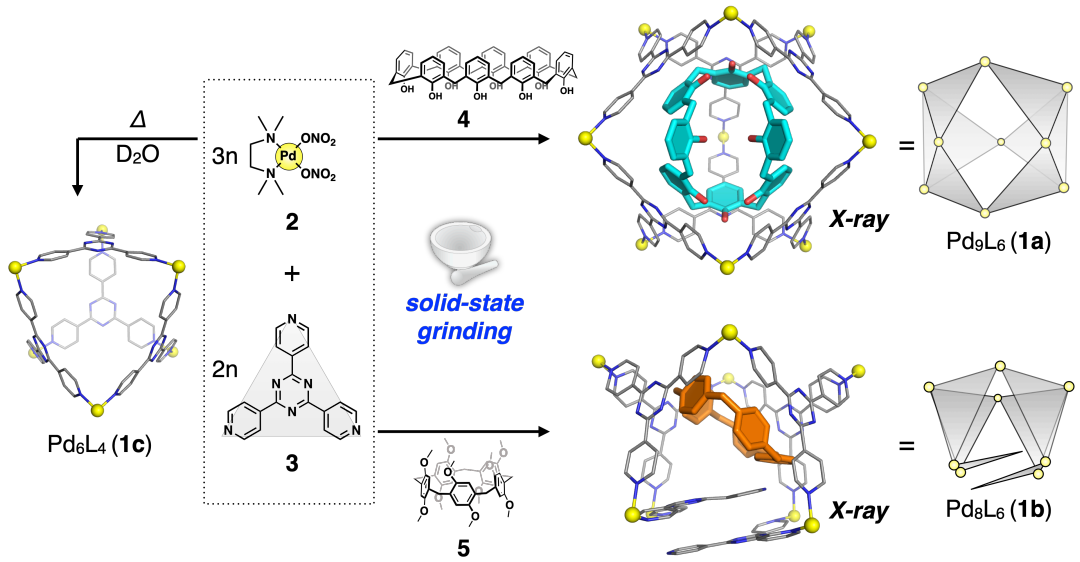
Construction of Expanded Hollow Cages by Templated Self-assembly in the Solid State for Conformation Control of Organic Macrocycles

([1]*School of Engineering, The University of Tokyo*, [2]*Division of Advanced Molecular Science, Institute for Molecular Science,* [3]*UTIAS, The University of Tokyo*)
○Kenta Iizuka,[1] Hiroki Takezawa,[1] Makoto Fujita[1,2,3]
Keywords: Self-assembly; Hollow cage; Conformational manipulation; Macrocycle; Solid-state reaction

Conformational manipulation by inclusion in host molecules is effective for controlling reactivities and properties of the guest molecule. However, the conformation fixing of middle molecules in a confined cavity has not been explored because of the absence of a suitable artificial host that has a large enough hydrophobic cavity. In this work, we achieved the construction of two types of expanded hollow cages **1** for conformational fixation of middle molecules by templated self-assembly in a solid state.

Powders of palladium complex **2**, tripodal ligand **3**, and macrocycle **4** were ground in a mortar with a pestle, and the resulting solid was suspended in D_2O and heated for several minutes. NMR and single-crystal X-ray diffraction studies revealed the formation of an inclusion complex of **4** with novel Pd_9L_6 cage **1a** in 46 % yield. The symmetry of **4** was degraded from apparent D_{8h} to C_{2v}, which reflects the conformational fixation of flexible macrocycle **4** by confinement. When **2**, **3**, and **4** were heated in D_2O without grinding, known M_6L_4 cage **1c** was solely obtained, suggesting no template effect of **4** in the solution state. When macrocycle **5** was used instead of **4**, Pd_8L_6 cage **1b** was formed with a similar protocol. In this case, D_5 symmetry of **5** was completely degraded to C_1 by inclusion.



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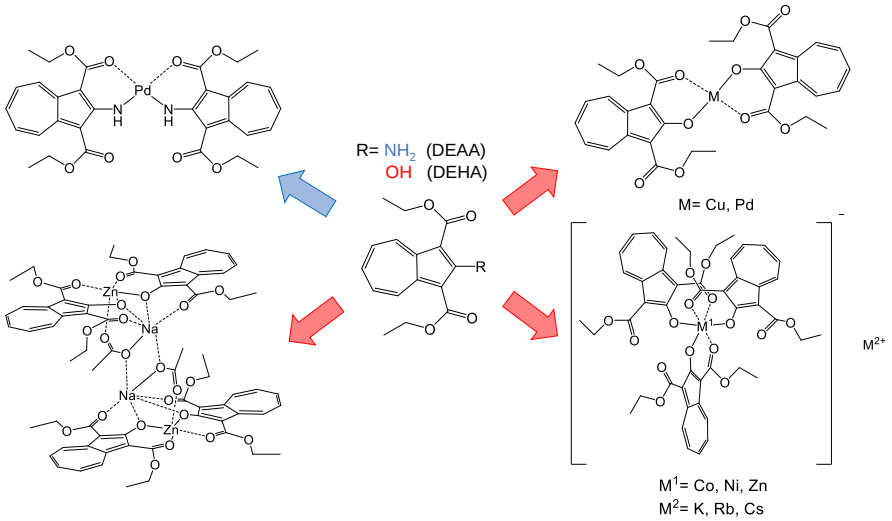
Synthesis and Structural Analysis of Metal Complexes with Azulene Derivatives as Ligands

([1]*Tokyo University of Science*) ○Tatsuya Iwashina,[1] Kazuki Yamamoto,[1] Takahiro Gunji[1]
Keywords: Azulene; Metal complexes; Coordination polymer; Double salt; Complexation reaction

Azulene is a structural isomer of naphthalene and is known as a unique compound that exhibits blue coloration with a simple structure. Azulene and its derivatives have attracted attention in the fields of organic synthesis and photochemistry because of their unique reactivity derived from their electronic states and optical properties [1), 2)]. However, there are few reports on metal complexes with azulene derivatives as ligands, and their structures and properties are of great interest. Therefore, we investigated the synthesis of metal complexes with azulene derivatives, diethyl 2-aminoazulene-1,3-dicarboxylate (**DEAA**) and diethyl 2-hydroxyazulene-1,3-dicarboxylate (**DEHA**), as ligands.

When **DEAA**, an azulene derivative with nitrogen, was used as a ligand, stable complexes were formed only with Pd. On the other hand, stable complexes with Co, Ni, Cu, Zn, and Pd were formed when **DEHA**, an azulene derivative with oxygen, was used as a ligand. In the Pd complexes, a change in coordination structure was observed between DEAA and DEHA as ligands. In the Co, Ni, and Zn complexes, hetero-complexes with Cs^+ used as a base were formed. In the synthesis of Zn complexes, when the base was changed from Cs_2CO_3 to Rb_2CO_3, K_2CO_3, Na_2CO_3, coordination polymers were formed for Cs, Rb, and K, but in the case of Na, the complexes had a cluster structure. Identification was performed by ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometries, elemental analysis, single crystal X-ray structure analysis, and UV-Vis spectra.



1) A. C. Razus, *Symmetry*. **2023**, *15*, 1391. 2) D. Dunlop, L. Ludviková, A. Banerjee, H. Ottosson, T. Slanina, *J. Am. Chem. Sos*. **2023**, *145*, 21569-21575.

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC F1232(1232, Bldg. 12 [3F])

[F1232-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Yasuyuki Ura, Yumiko Nakajima

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1232-4pm-01]
Effects of the Reduction Potential of the Ru(II) Redox Photosensitizer Unit in Ru(II)-Re(I) Supramolecular Photocatalysts on their Photocatalysis for CO_2 Reduction

○Kei Kamogawa[1], Osamu Ishitani[1,2] (1. Tokyo Tech., 2. Hiroshima Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1232-4pm-02]
Electrocatalytic Reduction of Low Concentration CO_2 to CO Using Phenol and a Re(I) complex

○Siby Mathew[1], Osamu Ishitani [1,2] (1. Tokyo Institute of Technology, 2. Hiroshima University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1232-4pm-03]
Iridium Catalyzed Intermolecular Silylene Transfer Reaction Utilizing Silylene Generated from Triorganohydrosilanes

○Yunhao Song[1], Michinori Suginome[1] (1. Kyoto University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[F1232-4pm-04]
Weakly Coordinating Anions bearing Lewis Acidic Tri-coordinated Borons Induced Selectivity Control on Iridium Catalysis

○Ryo Mandai[1], Takanori Iwasaki[1], Kyoko Nozaki[1] (1. The Univ. of Tokyo)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[F1232-4pm-05]
Electrochemical Homogeneous CO_2 Reduction Catalyzed by N-Heterocyclic Carbene Stabilized Au-Nanoclusters

○Samuel Jacob[1], Joey DeJesus[1], Masakazu Nambo[1,2], Cathleen Crudden[1,3,4] (1. Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya, Aichi, Japan, 2. Department of Chemistry, Graduate School of Science, Nagoya University; Furo, Chikusa, Nagoya, Aichi, Japan, 3. Department of Chemistry, Queen's University, Chernoff Hall, Kingston Ontario, Canada, 4. Carbon to Metal Coating Institute, Queen's University, Kingston, Ontario, K7L 3N6, Canada)

English

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2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[F1232-4pm-06]

Catalytic Transformation of Alkynes Enabled by Gold Nanocluster Bearing Supramolecular Reaction Field

○Kenta Iseri[1], Katsuhiro Isozaki[1], Masaharu Nakamura[1] (1. Kyoto University)

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Effects of the Reduction Potential of the Ru(II) Redox Photosensitizer Unit in Ru(II)-Re(I) Supramolecular Photocatalysts on their Photocatalysis for CO_2 Reduction

([1]*School of Science, Tokyo Institute of Technology*, [2]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kei Kamogawa,[1] Osamu Ishitani[1,2]

Keywords: *Carbon dioxide reduction, Photocatalyst, Metal Complex*

A Ru(II)-Re(I) supramolecular photocatalyst (**1**) consisting of the $[Ru(diimine)_3]^{2+}$ redox photosensitizer and *fac*-$[Re(diimine)(CO)_3(OC(O)OC_2H_4N(CH_2CH_2OH)_2]$ as a catalyst can efficiently reduce CO_2 to CO with high selectivity, which has been applied to various combined systems with solid materials.[1] Recently, we fully clarified the photocatalytic CO_2 reduction mechanism by **1** detecting the reaction intermediates using various techniques such as time-resolved spectroscopy and liquid chromatography.[2,3] This mechanistic study suggests some important points for improving the photocatalysis of **1**. Two electron reduced intermediates of **1** which have carboxylic acid ligand (-COOH) or carboxylate ester ligand ($-COOCH_2CH_2N(CH_2CH_2OH)_2$) at axial position of Re catalyst unit show relatively low reactivity and are accumulated during the photocatalytic reaction. Importantly, reduction of the intermediates increases release of CO from the intermediates. Since, however, the Re units of these intermediates have a ~100 mV more negative reduction potential compared with the Ru photosensitizer unit, the accumulation of these intermediates causes the accumulation of one-electron reduced species (OERS) of Ru unit of which excitation induces ligand substation,[4] resulting in the decomposition of the photosensitizer unit.

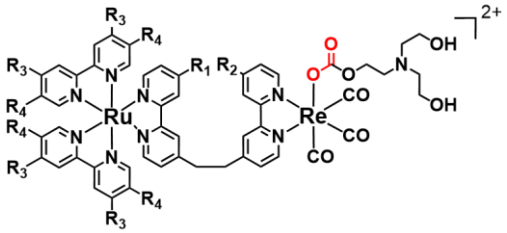

Fig. 1 Structure of photocatalysts

To suppress the accumulation of the intermediates and accelerates the CO release from the intermediates, novel photocatalysts (**2-4**) of which the reduction potentials of the Ru and Re centers shift to negative and positive, respectively. By this adjustment of the potentials, the accumulation of OERS in the Ru unit was clearly suppressed, and the photocatalytic reaction speed increased. However, these structure changes of the photocatalysts induces another decomposition process. In this presentation, we will provide detailed insights into the photocatalytic activity of these photocatalysts.

[1] T. Nakajima, O. Ishitani, *et. al.*, *J. Am. Chem. Soc.*, 2016, **138**, 13818. [2] K. Kamogawa, O. Ishitani, *et. al., Chem. Sci.*, 2021, **12**, 9682. [3] K. Kamogawa, O. Ishitani, *et. al.*, *Chem. Sci.*, 2024 in press. [4] J. M. Lehn, *et. al.*, *J. Organomet. Chem.* 1990, **382**, 157.

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Electrocatalytic Reduction of Low Concentration CO_2 to CO Using Phenol and a Re(I) Complex

([1]*Department of Chemistry, Tokyo Institute of Technology;* [1]*Department of Chemistry, Hiroshima University*) ○Mathew Siby,[1] Ishitani Osamu [1,2]

Keywords: CO_2 reduction; Electrocatalyst; Phenol; Low concentration CO_2; Re-complex catalyst

The electrocatalytic reduction of CO_2 into energy-rich chemicals is a pivotal strategy in the pursuit of sustainable energy solution. Although extensive efforts have been dedicated to the photo- and electro-catalytic reduction of pure CO_2, the reduction of low-concentration CO_2 remains a significant challenge, primarily due to the inefficient CO_2 capturing under these conditions. Our previous investigations on the Re(I) complex have unveiled a plausible approach for the capture of low concentration CO_2 using an axially ligated triethanolamine (TEOA) and its selective electrolytical reduction into CO.[1] In this presentation, we report the electrocatalytic reduction of CO_2 by fac-$[Re(bhmb)(CO)_3(H_2O)]^+$ (**Re(bhmb)**, bhmb = 4,4'-bis(hydroxymethyl)-2,2'-bipyridine), with the assistance of phenol in the absence and presence of water.

In a DMSO-PhOH (3M) mixed solution, **Re(bhmb)** selectively produces CO with a very high Faradic efficiency in 100% CO_2 atmosphere (Figure 1a). This electrocatalysis could be kept even under Ar containing 10% CO_2 (Figure 1b). In the case using 1% CO_2, formation speed of CO decreased (Figure 1c). The deprotonated phenol, i.e., the phenoxide anion was coordinated to the Re complex, forming Re(bhmb)-OPh complex and serving as CO_2 capturing ligand. The resulting CO_2 inserted complex Re(bhmb)-CO_2-OPh liberates CO. This transformation proceeds very efficiently, at a similar rate, even in the presence of water (5% v/v).

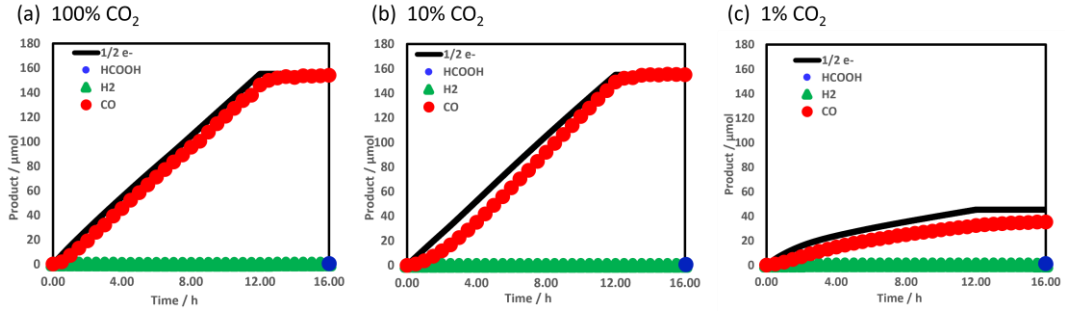

Figure 1 Time courses of generation of CO (red data point), H_2 (green triangle), and formic acid (blue data point) with half of the electrons flowing (line) during bulk electrolysis using the Re(bhmb) (0.5 mM) at -1.71 V vs $Ag/AgNO_3$ in a DMSO–PhOH (3M) solution containing Et_4NBF_4 (0.1 M) under (a) 1%, (b) 10% and (c) 100% CO_2 atmospheres.

1) Kumagai, H. and Ishitani, O. *et al.*, *Chem. Sci*. **2019**, *10*, 1597.

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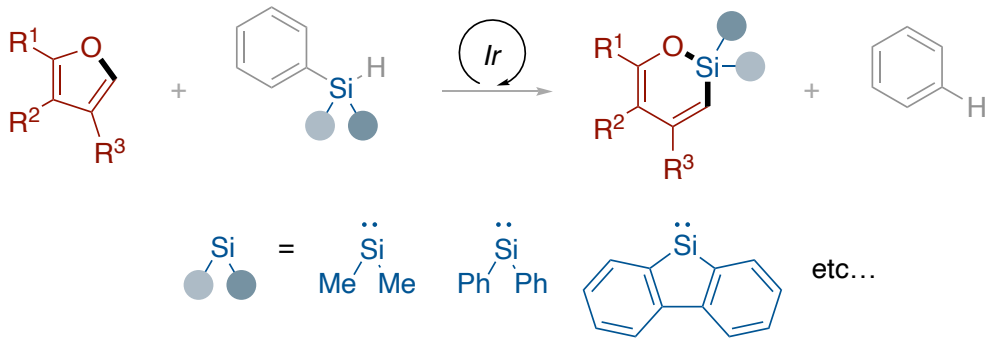
Iridium-Catalyzed Intermolecular Silylene Transfer Reaction Utilizing Silylene Generated from Triorganohydrosilanes

(*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University*) ○Yunhao Song, Michinori Suginome

Keywords: Silylene; Iridium Catalyst; Hydrosilane; Insertion Reaction; C-O Bond Cleavage

Silylene transfer reactions (STR) have attracted much attention in synthetic organosilicon chemistry, because two silicon-containing σ-bonds are formed in a single transformation either via insertion into σ-bonds or via cycloaddition to unsaturated bonds.[1,2] While a variety of silylene precursors for STR under catalytic and thermal reaction conditions have been developed, they are in most cases poorly handleable, less accessible, or requiring too harsh reaction conditions, hampering wide utilization of STR in the synthesis of organosilicon compounds. It is therefore highly desirable to explore new silylene precursors for more practical synthesis of organosilicon compounds and for the development of new STR. We herein report use of aryldiorganohydrosilanes as easily available and stable silylene precursors in the presence of iridium catalysts, leading to new STR in which diorganosilylene is inserted into the C–O bond of furan rings.

Furan derivatives and PhR_2SiH were heated in the presence of an iridium catalyst, affording 1,2-oxasiline derivatives via insertion of diorganosilylene (R_2Si:) into the C(sp^2)–O bond in the furan rings. It should be noted that formation of benzene was confirmed as a single byproduct in this intermolecular STR, indicating α-elimination of the phenyl group and the hydride on the silicon atom took place with cleavage of the Si-Ph bond.[3] Using this reaction protocol, a wide range of acyclic and cyclic diorganosilylenes including dimethylsilylene (Me_2Si:), diphenylsilylene (Ph_2Si:) and 9-silafluoren-9-ylidene were successfully generated.



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Weakly Coordinating Anions bearing Lewis Acidic Tri-coordinated Borons Induced Selectivity Control on Iridium Catalysis

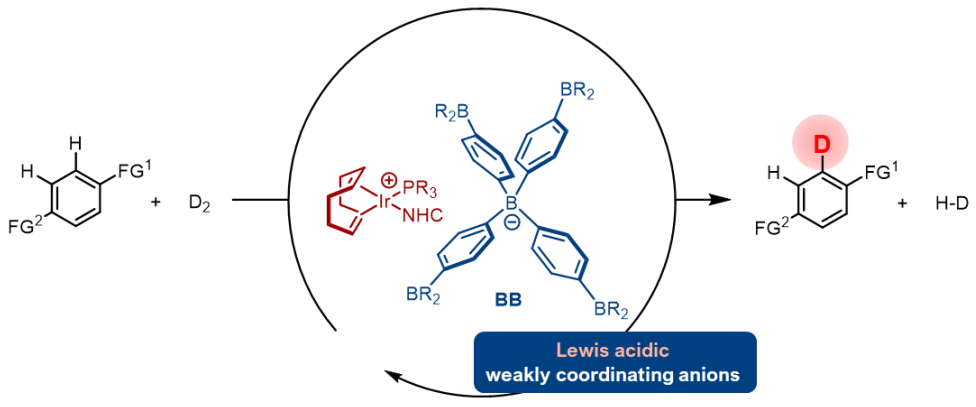
(*Graduate School of Engineering, The University of Tokyo*) ○Ryo Mandai, Takanori Iwasaki, and Kyoko Nozaki

Keywords: Cooperative Catalysts, Weakly Coordinating Anions, Catalytic C-H Bond Cleavage, Borates, Lewis acid

New class of transition metal catalysts owing activation sites in the second coordination sphere is drawing attractions with expectation that they enable challenging transformations by precise control of the molecular orientation by the acid/base residues incorporated in the ligands.[1] Realization of this concept, however, requires complicated design and synthesis to arrange activation sites in an appropriate location with a covalent and rigid linkage.

We envisioned that a novel weakly coordinating anion (WCA) endowed with Lewis acidic property would serve as a sterically flexible multi-activation site catalyst when combined with a cationic transition metal catalyst. A Lewis acidic WCA recognizes polar functional groups in substrates, such as halogens, carbonyls, and nitriles, by acid-base interaction to control orientation of the substrates. The electrostatic interaction between the ion pair approximates the captured substrate to the metal center and achieves unique chemo-, stereo- and regio-selectivity.

We newly synthesized tetraarylborates **BB**s featuring tri-coordinated boryl moieties. NMR analysis with the addition of $Et_3P{=}O$ to their tetrabutylammonium salts proved their Lewis acidity despite their anionic property. The mixture of $[Ir(cod)Cl]_2$, a phosphine ligand, and borate **BB** afforded the corresponding ion pair, where cationic Ir complex and anion BB separately exist but locates in the neighborhood of each other in DCM. When the ion pair was employed to hydrogen isotope exchange (HIE) of 1,4-difunctionalized arenes,[2] a unique regioselectivity was observed, being not observed with a commonly-employed WCA, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **BAr^F** under the same condition. This result may have demonstrated the concept of Lewis acidic WCA controlling selectivity.



1) H. J. Davis, R. J. Phipps, *Chem. Sci.* **2017**, 8, 864. 2) J. Atzrodt, V. Derdau, W. J. Kerr, M. Reid, P. Rojahn, R. Weck, *Tetrahedron* **2015**, *71*, 1924.

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Electrochemical Homogeneous CO_2 Reduction Catalyzed by N-Heterocyclic Carbene Stabilized Au-Nanoclusters

([1]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya Unveristy*, [2]*Graduate School of Science, Nagoya University*, [3]*Department of Chemistry, Queen's University*) ○Samuel Jacob,[1] Joey DeJesus,[1] Masakazu Nambo,[1,2] Cathleen Crudden[1,3]

Keywords: Gold Nanocluster, Electrocatalyst, CO2 Reduction, Homogeneous, Carbene

Gold nanoclusters (AuNC) are well-studied and reputable for their ability to electrochemically catalyze several reactions of energy importance such as CO_2 reduction reaction (CO_2RR). Typically, AuNCs are stabilized by either phosphine or thiol-based ligands, however, our lab has focused on the synthesis and characterization of several new AuNCs stabilized by N-heterocyclic carbenes (NHC).[1-6] Due to their promising stability and facile means of structural modification, N-heterocyclic carbene (NHC) stabilized gold nanoclusters (AuNC) are a growing field of interest. Furthermore, their activity for electrocatalytic reduction of CO_2 to CO is notable compared to analogous thiol and phosphine supported AuNCs.[5,6] However, reaction mechanisms and means of catalyst optimization remain understudied. Herein, we present the homogeneous electrocatalytic CO_2 reduction activity of NHC stabilized AuNCs in nonaqueous solution. For this investigation we studied a family of AuNCs with varied ligand functionality and cluster sizes. Furthermore, the effect of solvent as well as protic and aprotic reaction conditions were explored. These studies provide insight for the structural optimization and mechanism for CO_2RR reactivity for AuNCs.

(1) Kawawaki, T.; Negishi, Y. Gold Nanoclusters as Electrocatalysts for Energy Conversion. *Nanomaterials (Basel)* **2020**, *10* (2). (2) Yi, H.; Osten, K. M.; Levchenko, T. I.; Veinot, A. J.; Aramaki, Y.; Ooi, T.; Nambo, M.; Crudden, C. M. Synthesis and enantioseparation of chiral Au13 nanoclusters protected by bis-N-heterocyclic carbene ligands. *Chem Sci* **2021**, *12* (31), 10436-10440. (3) Man, R. W. Y.; Yi, H.; Malola, S.; Takano, S.; Tsukuda, T.; Hakkinen, H.; Nambo, M.; Crudden, C. M. Synthesis and Characterization of Enantiopure Chiral Bis NHC-Stabilized Edge-Shared Au10 Nanocluster with Unique Prolate Shape. *J Am Chem Soc* **2022**, *144* (5), 2056-2061. (4) Lummis, P. A.; Osten, K. M.; Levchenko, T. I.; Sabooni Asre Hazer, M.; Malola, S.; Owens-Baird, B.; Veinot, A. J.; Albright, E. L.; Schatte, G.; Takano, S.; et al. NHC-Stabilized Au10 Nanoclusters and Their Conversion to Au25 Nanoclusters. *JACS Au* **2022**, *2* (4), 875-885. (5) Kulkarni, V. K.; Khiarak, B. N.; Takano, S.; Malola, S.; Albright, E. L.; Levchenko, T. I.; Aloisio, M. D.; Dinh, C. T.; Tsukuda, T.; Hakkinen, H.; et al. N-Heterocyclic Carbene-Stabilized Hydrido Au24 Nanoclusters: Synthesis, Structure, and Electrocatalytic Reduction of CO2. *J Am Chem Soc* **2022** *144* (20), 9000-9006. (6) Yang, D.; Wang, J.; Wang, Q.; Yuan, Z.; Dai, Y.; Zhou, C.; Wan, X.; Zhang, Q.; Yang, Y. Electrocatalytic CO2 Reduction over Atomically Precise Metal Nanoclusters Protected by Organic Ligands. *ACS Nano* **2022** *16* (10), 15681-15704.

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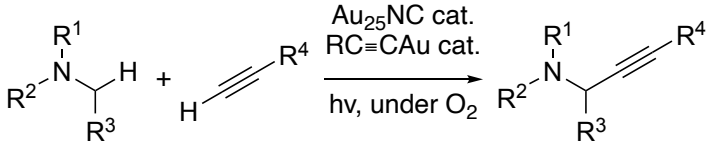
Catalytic Transformation of Alkynes Enabled by Gold Nanocluster Bearing Supramolecular Reaction Field

(*Institute for Chemical Research, Kyoto University*, *Graduate School of Engineering, Kyoto University*) ○Kenta Iseri, Katsuhiro Isozaki, Masaharu Nakamura

Keywords *: Gold Nanocluster, Catalyst, Supramolecular Reaction Field, Hydrogen Bond, Alkyne*

Thiolate-protected gold nanoclusters (AuNCs) consist of a superatomic core composed of tens of gold atoms and gold–thiolate staple motifs surrounding the core. Such AuNCs show photosensitization properties based on the superatomic core and catalytic activities based on the reactivity of gold–thiolate moieties. Although the strong gold–thiolate bond contributes to stabilizing the cluster structure, it tends to lower the catalytic activity of AuNCs. Our group has reported that the installation of peptide dendron thiolate ligands to Au_{25} nanoclusters (Au_{25}NCs) enables the construction of supramolecular reaction field, accelerating photocatalytic oxidation[1] and catalytic cyclization reactions.[2] Recently, we reported that the two structural components of AuNCs, the superatomic core and gold–thiolate staples, cooperatively participate in photooxidative alkynylation of amines to show unprecedented dual catalysis of AuNCs.[3] This reaction showed a long induction period due to the sluggish generation of catalytically active species, which bear σ,π-coordinated alkynyl ligands through ligand exchange between gold–thiolate staples and alkyne substrates. Herein, we report a new catalyst system for efficient catalytic transformation of alkynes enabled by mixing gold–alkynyl compounds with Au_{25}NCs bearing supramolecular reaction field.

Typically, aliphatic tertiary amines and terminal alkynes are oxidatively cross-coupled by the irradiation of visible light in the presence of Au_{25}NC and gold–alkynyl compounds under oxygen atmosphere, providing the corresponding propargylamine products regioselectively. The scope of substituent on gold–alkynyl compounds revealed the impact of electron-withdrawing groups on the rapid generation of catalytically active species. This presentation will also report screening of reaction conditions, scope of substrates, and applicability to other catalytic transformation of alkynes.



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2) Ueda, K.; Iseri, K.; Isozaki, K.; Nakamura, M. *The 103rd CSJ Annual Meeting,* **2023,** K502-3pm-13.

3) Isozaki, K.; Iseri, K.; Saito, R.; Ueda, K.; Nakamura, M. *Angew. Chem. Int. Ed.* **2024**, 63, e202312135.

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC F1233(1233, Bldg. 12 [3F])

[F1233-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaya Enomoto, Takuya Shiga

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1233-4pm-01]

CO_2-Sensitive Porous Magnet: Antiferromagnet Creation from a Paramagnetic Charge-Transfer Layered Coordination Framework

○Wataru Kosaka[1,2], Jun Zhang[3], Qingxin Liu[1,2], Naoka Amamizu[4], Yasukaka Kitagawa[4] (1. IMR, Tohoku University, 2. Grad. Sch. Sci., Tohoku Univ., 3. Col. Chem. Mol. Sci., Wuhan Univ., 4. Grad. Sch. Eng. Sci., Osaka Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1233-4pm-02]

Photoinduced magnetization in organometallic and organic compounds

○Verner Saeaesk[1] (1. Kyushu Universtiy)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1233-4pm-03]

Thermal and Light-induced Switching Effects Based on Fe(II)-Hg(II) Spin-crossover Networks

○Guanping Li[1], Olaf Stefanczyk[1], Kunal Kumar[1], Koji Nakabayashi[1], Kenta Imoto[1], Guillaume Chastanet[2], Shin-ichi Ohkoshi[1] (1. Department of Chemistry, School of Science, University of Tokyo, 2. Université de Bordeaux, ICMCB)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[F1233-4pm-04]

Proton Conductive Hydrogen-Bonded Architectures Constructed by Cobalt(II) Spin Crossover Complexes

○Fumiya Kobayashi[1], Makoto Tadokoro[1] (1. Tokyo Univ. of Sci.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[F1233-4pm-05]

Relationship between the stacking structure and magnetic behavior for two-dimensional mixed-valence iron(II,III) layered compounds bridged by a 1,2-dithiooxlate ligand

○Takuya Kanetomo[1], Yuki Sawayanagi[1], Tsubasa Endo[1], Atsushi Okazawa[2], Masaya Enomoto[1] (1. Tokyo Univ. of Sci., 2. Waseda Univ.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[F1233-4pm-06]

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Spin-lattice relaxation behavior of an *S*=1/2 copper(II)-substituted Keggin-type sulfotungstate

○Toshiharu Ishizaki[1], Tomoji Ozeki[1] (1. Nihon Univ.)

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CO_2-Sensitive Porous Magnet: Antiferromagnet Creation from a Paramagnetic Charge-Transfer Layered Coordination Framework

([1]*Institute for Materials Research, Tohoku University*, [2]*Graduate School of Science, Tohoku University,* [3]*Collage of Chemistry and Molecular Science, Wuhan University,* [4]*Graduate School of Engineering Science, Osaka University*) ○Wataru Kosaka,[1,2] Jun Zhang,[3] Qingxin Liu,[1,2] Naoka Amamizu,[4] Yasutaka Kitagawa,[4] Hitoshi Miyasaka[1,2]

Keywords: Metal−organic Framework; Charge-transfer complex; Gas-responsive magnetic property; Porous magnet; Antiferromagnet

Porous magnets that undergo a magnetic phase transition in response to gaseous adsorbates are desirable for the development of sustainable sensing and memory devices. However, a strong magnetic response to ubiquitous gases, such as O_2 and CO_2, is still rare and remains a significant challenge.[1,2,3] Especially, the creation of a magnet, meaning the change from a nonmagnet to a magnet by gas adsorption, has not yet been explored. Here, we demonstrate reversible control of the magnetic phase by cooperative CO_2 adsorption/desorption, which was achieved in a donor/acceptor metal-organic framework (D/A-MOF) [{Ru_2(2,4-F_2PhCO_2)$_4$}$_2$TCNQ(OEt)$_2$] (**1**; 2,4-$F_2PhCO_2^-$ = 2,4-difluorobenzoate; TCNQ(OEt)$_2$ = 2,5-diethoxy-7,7,8,8-tetracyanoquinodimethane).[4]

Compound **1** (Fig. 1a), which consists of two [Ru_2(2,4-F_2PhCO_2)$_4$] units (abbreviated as [Ru_2]) and one TCNQ(OEt)$_2$ moiety, shows a two-electron transferred ionic state represented as [{$Ru_2^{II,III}$}$^+$–TCNQ(OEt)$_2^{2-}$–{$Ru_2^{II,III}$}$^+$] below room temperature, resulting in the paramagnetic behavior (Fig. 1b). Meanwhile, **1** adsorbed three molar equivalents of CO_2, which is accompanied by the electronic state change into a one-electron transferred ionic state represented as [{$Ru_2^{II,II}$}–TCNQ(OEt)$_2^{\bullet-}$–{$Ru_2^{II,III}$}$^+$]. Strong intra-layer antiferromagnetic coupling between [$Ru_2^{II,II}$] (S = 1) or [$Ru_2^{II,III}$]$^+$ (S = 3/2) and TCNQ(OEt)$_2^{\bullet-}$ (S = 1/2), as well as interlayer antiferromagnetic interaction, induced the onset of long-range antiferromagnetic ordering at T_N = 62 K (Fig. 1b). This is the first example of the creation of a CO_2-responsive magnet, which is promising for novel molecular multifunctional devices.[5]

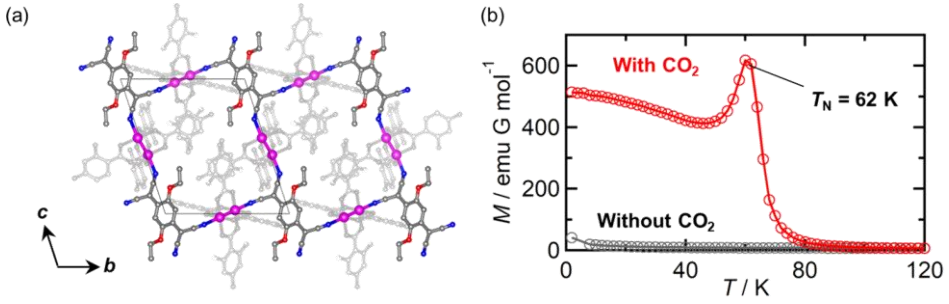

Fig. 1 (a) Crystal structure of **1**. (b) Temperature dependence of magnetization (100 Oe).

1) W. Kosaka et al., *Nat. Commun.* **2018**, *9*, 5420. 2) J. Zhang et al., *Nat. Chem.* **2021**, *13*, 191. 3) W. Kosaka et al., *Chem. Sci.* **2023**, *14*, 791. 4) J. Zhang et al., *J. Am. Chem. Soc.* **2021**, *143*, 7021. 5) J. Zhang et al., *J. Am. Chem. Soc.* **2023**, *145*, 26179.

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Photoinduced magnetization in organometallic and organic compounds

([1]*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Verner Sääsk,[1] Shengqun Su,[1] Osamu Sato[1]

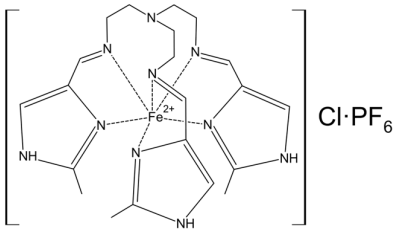
Keywords: Photoinduced magnetization, Soft crystals, Organometallics, Ultralong organic phosphorescence, Molecular crystals

Achievement of photoinduced magnetization phenomenon in two different molecular systems is reported.

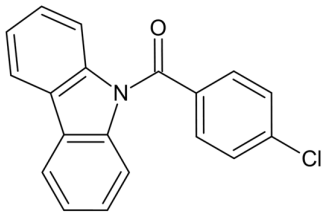
In system 1, photoinduced magnetization is achieved by exploiting a spin-crossover phenomenon in an iron complex $[Fe^{II}H_3L^{Me}]Cl{\cdot}PF_6$ (where H_3L^{Me} stands for tris[2-{[(2-methylimidazol-4-yl)methylidene]amino}ethyl]amine), first reported by Yamada *et al*. in 2006.[1] When this complex is irradiated with a 532 nm laser at a temperature of 5 K it undergoes a spin-crossover from a low-spin state to a high-spin state, resulting in a drastic change in its magnetic susceptibility. It was demonstrated that this metastable high-spin state can be trapped for hours at 5 K or reverted to the low-spin state by raising the temperature to 75 K. Moreover, the transition between low-spin and high-spin states of this iron complex also induces a change of polarity in its crystal lattice, which, in principle, should allow the realization of pyroelectric and photoelectric currents in this system.

In system 2, photoinduced magnetization is achieved in a purely organic molecule, 9H-carbazol-9-yl)(4-chlorophenyl)methanone (CPhCz), which was first described by Cai *et al*. in 2017.[2] A sufficient amount of triplet states to detect a change in the magnetic susceptibility of CPhCz was accumulated by exploiting the unique ability of this molecule to stabilize excited triplet states for a long time through H-aggregation.

Finally, structures of excited states and molecular mechanisms behind the photoinduced magnetization phenomenon in those two systems are compared and possible applications of such systems are suggested.



$[Fe^{II}H_3L^{Me}]Cl{\cdot}PF_6$



CPhCz

1. Yamada, M. et al. *Chem. – Eur. J.* **12**, 4536–4549 (2006).
2. Cai, S. et al. *Adv. Mater.* **29**, 1701244 (2017).

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Thermal and Light-induced Switching Effects Based on Fe(II)-Hg(II) Spin-crossover Networks

([1]*Department of Chemistry, School of Science, University of Tokyo,* [2]*Université de Bordeaux, ICMCB*) ○Guanping Li,[1] Olaf Stefanczyk,[1] Kunal Kumar,[1] Koji Nakabayashi,[1] Kenta Imoto, Guillaume Chastanet,[2] Shin-ichi Ohkoshi[1]

Keywords: Fe(II) Complexes, Hg(II) Complexes, Terahertz spectroscopy, Spin-crossover

The pursuit of molecular switches with adjustable properties has been an ongoing objective of research for several decades.[1,2] In this context, a novel spin-crossover (SCO) compound (**1**) was synthesized, based on iron(II) complexes incorporating 4-acetylpyridine (4-acpy) and $[Hg(SCN)_4]^{2-}$ anions, and denoted as $[Fe(4\text{-acpy})_2][Hg(\mu\text{-}SCN)_4]$ (**Figure 1**). Compound **1** is crystallized in a three-dimensional (3D) network in the non-centrosymmetric orthorhombic space group $Pna2_1$ with two distinct Fe centers (Fe1 and Fe2) and two tetrahedral $[Hg(SCN)_4]$ units. Moreover, magnetic measurements revealed an incomplete SCO exclusively at the Fe2 centers, with a transition temperature ($T_{1/2}$) of approximately 102 K. Photomagnetic studies conducted at 10 K, employing twelve lasers ranging from 405 to 1310 nm, elucidated both the light-induced excited spin-state trapping (LIESST) phenomenon with $T_{LIESST} \approx 74$ K and the reverse-LIESST effect. Notably, a distinctive and highly responsive LIESST effect was observed under near-infrared light (1064 and 1310 nm). Optical and vibrational properties consistently supported the results from magnetic and photomagnetic studies. Additionally, the temperature and light-dependent terahertz (THz) absorption were associated with phonon vibrations around Fe2 centers, corroborating with the spin-crossover behavior, as confirmed by *ab initio* calculations. The Fe(II)-Hg(II) systems thus emerge as promising benchmarks for exploring synergistic switching effects across magnetic, photomagnetic, and spectroscopic properties.

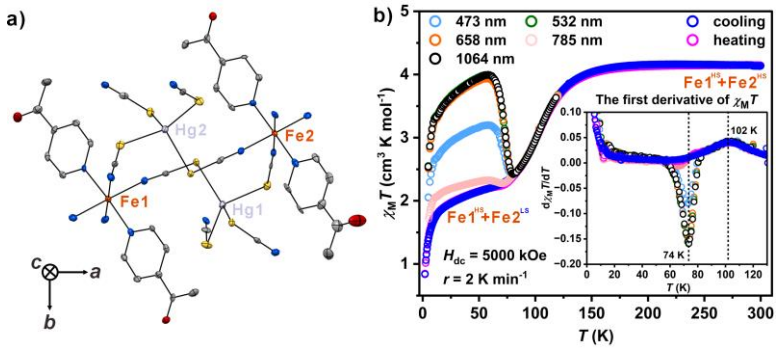

Figure 1. (a) Structural unit of **1** at 90 K. (b) Temperature dependences of $\chi_M T$ before and after photoirradiation with selected lasers. The inset contains the first derivatives of the $\chi_M T$ *vs*. *T* plots.

1) G. Li, O. Stefanczyk, K. Kumar, Y. Mineo, K. Nakabayashi, S. Ohkoshi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214673. 2) G. Li, O. Stefanczyk, K. Kumar, K. Imoto, K. Nakabayashi, S. Ohkoshi, *Chem. Mater.* **2023**, *35(22)*, 9613.

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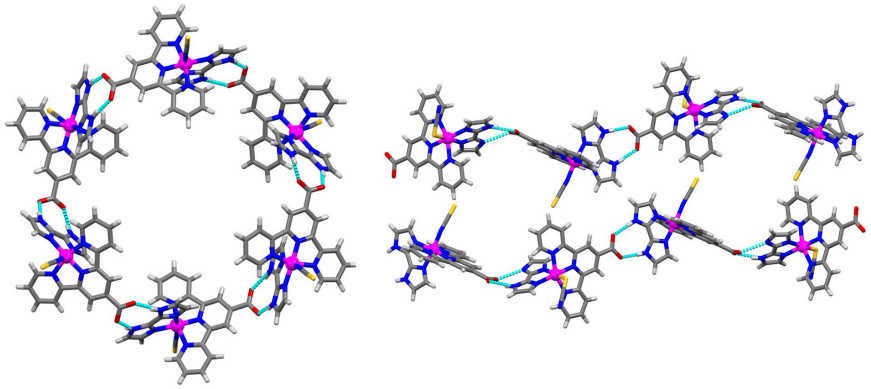
Proton Conductive Hydrogen-Bonded Architectures Constructed by Cobalt(II) Spin Crossover Complexes

(*Department of Chemistry, Faculty of Science, Tokyo University of Science*) ○Fumiya Kobayashi, Makoto Tadokoro

Keywords: Cobalt(II) Complex, Spin Crossover, Proton Conduction, Hydrogen Bonding

The development of molecule-based switchable multifunctional materials remains an important challenge in the field of molecular science. Achievement of a high proton conduction in spin crossover (SCO) compounds is of significant interest because of the possibility that the spin state can be controlled via proton transfer induced by an electric field, leading to the magnetoelectric effects, molecular spintronics and spin-protonics. However, there are few reports of proton conductive SCO molecules. Constructing hydrogen-bonding networks for efficient proton transport is important for achieving a high proton conductivity in such molecular compounds. To that end, high proton conductivities can be achieved via proton hopping along hydrogen-bonding networks. Controlling the molecular arrangement using hydrogen-bonding could also aid in the construction of advanced structures such as hydrogen-bonded organic frameworks (HOFs). In the present study, $[Co(COOH\text{-}terpy)_2]^{2+}$ (COOH-terpy = 4′-carboxyl-2,2′:6′,2″-terpyridine) was chosen as a hydrogen-bonded molecular unit since in prior studies several examples of SCO behavior involving $[Co(terpy)_2]^{2+}$ cation have been reported.[1] Herein, we report the spin transition and proton conduction behaviors for hydrogen-bonded cobalt(II) SCO compounds $[Co(COOH\text{-}terpy)_2](ClO_4)_2\cdot 4H_2O$ (**1**)[2] and $[Co(COO\text{-}terpy)(COOH\text{-}terpy)](ClO_4)\cdot 10H_2O$ (**2**). We also report the syntheses of hydrogen-bonded architectures of hydrogen-bonded hexamer $\{[Co(COO\text{-}terpy)(H_2bim)(SCN)](ClO_4)\cdot 6H_2O\}_6$ ($[\mathbf{3}]_6$; H_2bim = 2,2′-biimidazole) and hydrogen-bonded mixed-valence 1D chain $\{[Co^{II/III}(COO\text{-}terpy)(H_2bim)(SCN)](ClO_4)\}_n$ ($[\mathbf{4}]_n$).



1) F. Kobayashi, Y. Komatsumaru, R. Akiyoshi, M. Nakamura, Y. Zhang, L. F. Lindoy, S. Hayami, *Inorg. Chem.*, **2020**, 59, 16843–16852. 2) F. Kobayashi, T. Hiramatsu, K. Sueyasu, M. Tadokoro, *Cryst. Growth Des.*, **2023**, 23, 1633–1640.

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1,2-ジチオシュウ酸配位子が架橋する 2 次元鉄混合原子価錯体における積層構造と磁気挙動の相関

（東理大[1]・早大[2]）○金友 拓哉[1]・澤柳 佑希[1]・遠藤 翼[1]・岡澤 厚[2]・榎本 真哉[1]
Relationship between the stacking structure and magnetic behavior for two-dimensional mixed-valence iron(II,III) layered compounds bridged by a 1,2-dithiooxlate ligand ([1]*Tokyo University of Science*, [2]*Waseda University*) ○Takuya Kanetomo,[1] Yuki Sawayanagi,[1] Tsubasa Endo,[1] Atsushi Okazawa,[2] Masaya Enomoto[1]

1,2-Dithiooxalato (dto)-bridged mixed-valence iron complexes (cation)[$Fe^{II}Fe^{III}(dto)_3$] exhibit an alternating stacking structure with anionic layers and cations. Compound ($^{n}Pr_4N$)[$Fe^{II}Fe^{III}(dto)_3$] (**1**; $^{n}Pr_4N$ = tetra-*n*-propylammonium) displays a staggered stacking form and undergoes a charge-transfer phase transition (CTPT) behavior accompanied with electron transfer between the Fe centers.[1] Recently, our research revealed that (Ph_4P)[$Fe^{II}Fe^{III}(dto)_3$] (**2-Ph**; Ph_4P = tetraphenylphosphonium) and its derivatives adopt an eclipsed stacking form, demonstrating non-CTPT under ambient pressure.[2,3] In this study, we synthesized (A)[$Fe^{II}Fe^{III}(dto)_3$] (**2-Me**, A = methyltriphenylphosphonium ($MePh_3P$); **3**, A = triphenylsulfonium (Ph_3S)) and investigated crystal structures and cation-dependent magnetic behavior (Fig. 1). We will discuss a relationship between their stacking manners and CTPT.

Keywords : Molecular magnetism; Layered compounds; Magnetic phase transition; Mixed-valence iron complexes

鉄混合原子価錯体(cation)[$Fe^{II}Fe^{III}(dto)_3$]はアニオン性ハニカム層とカチオンの交互積層構造を示す。$^{n}Pr_4N$ を用いた系 (**1**) は半周期ずれた staggered 積層を形成し、隣接する Fe 中心間の電荷移動による相転移 (CTPT) を示す[1]。一方、Ph_4P を用いた系 (**2-Ph**) とその類縁体は同周期で重なる eclipsed 積層を示し、常圧下で CTPT を示さない[2,3]。本研究では、積層様式と CTPT の相関を解明するため、$MePh_3P$ と Ph_3S を用いた錯体 (**2-Me** と **3**) を合成し、構造及び物性を調べた。これらカチオンはハニカム環内へ貫入する置換基の立体が小さい/無いため、従来の系に比べて積層様式に自由度がある。実際、この特異性は結晶構造に反映されており、両物質共に eclipsed 積層でありながら常圧下で CTPT 由来の磁気挙動を示した (Fig. 1)。本発表では、対カチオンの分子構造がもたらす積層様式の変調と磁気挙動との相関について報告する。

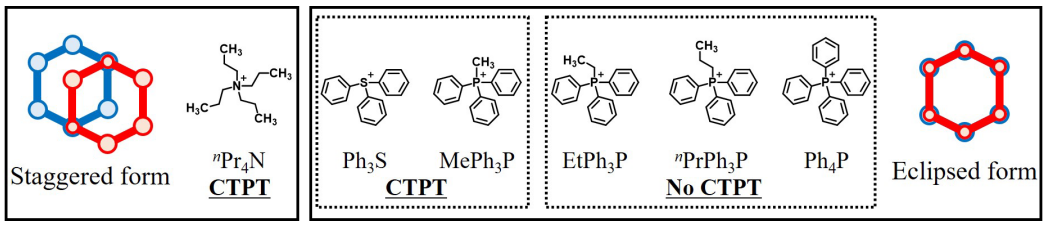

Fig. 1. Overview diagram illustrating the stacking forms and magnetic behaviors for **1**, **2**, and **3**.

1) M. Itoi et al. *Eur. J. Inorg. Chem.* **2006**, *2006*, 1198; 2) K. Nomura et al. *Cryst. Growth Des.* **2022**, *22*, 2139; 3) R. Taniai et al. *Dalton Trans*. **2023**, *52*, 8368.

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Spin-lattice relaxation behavior of an *S*=1/2 copper(II)-substituted Keggin-type sulfotungstate

([1]*College of Humanities and Sciences, Nihon University*) ○Toshiharu Ishizaki,[1] Tomoji Ozeki[1]

Keywords: Molecular magnetism; Polyoxometalate; Copper(II); *S*=1/2; Magnetic relaxation

In terms of quantum bit (qubit) for quantum computation, *S*=1/2 mononuclear transition metal complexes have recently drawn much attention due to the long spin-lattice relaxation time and quantum coherent phenomena at even elevated temperatures.[1] Recently, we have revealed that the tetrabutylammonium salt of *S*=1/2 copper(II)-substituted Keggin-type silicotungstate $[(n\text{-}C_4H_9)_4N]_4H_2[SiW_{11}O_{39}Cu]$ and phosphotungstate $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}O_{39}Cu]$ exhibit slow magnetic relaxations in applied static magnetic field (H_{dc}).[2] The phosphorous(V) analogue showed significantly longer relaxation times at low temperature compared with the silicon(IV) analogue. In this presentation, magnetic properties of a tetrabutylammonium salt of copper(II)-substituted Keggin-type sulfotungstate[3] $[(n\text{-}C_4H_9)_4N]_4[SW_{11}O_{39}Cu]$ was investigated.

AC magnetic susceptibility measurements for **1** revealed that out-of-phase (χ'') signals were successfully observed in an applied static magnetic field (H_{dc}) at low temperatures (Figure). This indicates that slow magnetic relaxation of **1**. The fitting using generalized Debye model showed that relaxation time up to 35.2 ms (1.8 K and H_{dc}=5000 Oe). The relaxation times were significantly elongated compared with the copper(II)-substituted silicon(IV) and phosphorous(V) analogues. In addition, the fitting parameter α that indicates dispersion of relaxation time is small (α≤0.16) compared with the copper(II)-substituted silicon(IV) and phosphorous(V) analogues. The small α indicates that magnetic relaxation of **1** has purer single relaxation phenomena compared with our previous results. The magnetic relaxation behavior of magnetically diluted **1** and discussion for the relaxation mechanism will be also reported.

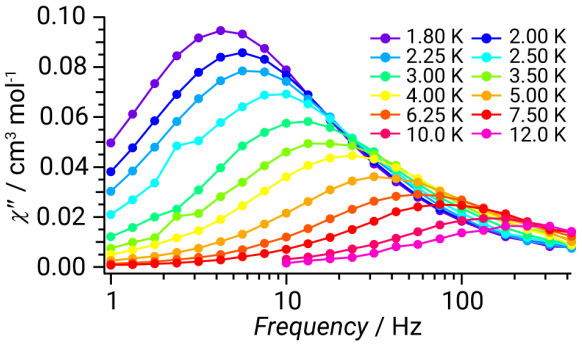

Figure The out-of-phase (χ'') signals measured in an applied static magnetic field (H_{dc}) of 3000 Oe at indicated temperatures.

1) M. Atzori, E. Morra, L. Tesi, A. Albino, M. Chiesa, L. Sorace, R. Sessoli, *J. Am. Chem. Soc.* **2016**, *138*, 11234. 2) T. Ishizaki, T. Ozeki, *Dalton Trans.* **2023**, *52*, 4678. 3). S. Azuma, T. Kadoguchi, Y. Eguchi, H. Hirabaru, H. Ota, M. Sadakane, K. Yanagisawa, T. Hasegawa, T. Ueda, *Dalton Trans.* **2020**. *49*, 2766.

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Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC F1234(1234, Bldg. 12 [3F])

[F1234-4pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryota Matsuoka, Souichirou Kawamorita

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[F1234-4pm-01]
Multimetalic co-accumulation of precious and base metals in phenylazomethine dendrimer

○Tadatoshi Iitsuka[1], Tatsuya Moriai[1], Takamasa Tsukamoto[2], Akiyoshi Kuzume[3], Takane Imaoka[1], Kimihisa Yamamoto[1] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. Institute of Industrial Science, University of Tokyo, 3. Clean Energy Research Center, University of Yamanashi)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[F1234-4pm-02]
Observation of vapochromic phase transition and micro motions in molecular crystals using confocal laser microscopy

○XIAO MA[1], Kyoko Enomoto[1], Kazuyuki Ishii[1], Yuki Matsuda[2], Masaaki Abe[2] (1. IIS, The Univ. of Tokyo, 2. Graduate School of Science, University of Hyogo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[F1234-4pm-03]
Vapor-Induced Structural Transformation Dynamics of Photoluminescent Coordination Network Crystals

○Yuki Matsuda[1], Ryota Nakamura[1], Yoshiki Ozawa[1], Keishiro Tahara[1], Toshikazu Ono[2], Nobuto Yoshinari[3], Takumi Konno[3], Kunihisa Sugimoto[4], Shintaro Kobayashi[5], Shogo Kawaguchi[5], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo, 2. Graduate School of Engineering, Kyushu University, 3. Graduate School of Science, Osaka University, 4. Department of Chemistry, Faculty of Science and Engineering, Kindai University, 5. SPring-8/JASRI)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[F1234-4pm-04]
Correlation Between Metal-metal Distance and Assembly-induced Luminescence of One-dimensional d^8 Metal Complexes Based on Temperature and Pressure Effects

○Masaki Yoshida[1], Kai Mitani[1], Kaito Segawa[1], Daichi Eguchi[1], Naoto Tamai[1], Masako Kato[1] (1. Kwansei Gakuin Univ.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[F1234-4pm-05]
Self-assembly of N^C^N-coordinated platinum(II) complex assisted by carbon dioxide in basic aqueous solution

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○Shingo Hattori[1], Hiroyuki Mita[1], Kazuteru Shinozaki[1] (1. Yokohama City Univerisity)

English

2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[F1234-4pm-06]

Crystal-downsizing Effect on Dual-emission Behavior in an Au(I)-based Coordination Polymer

○Haruka Yoshino[1], Takumi Ehara[2], Kiyoshi Miyata[2], Ken Onda[2], Hitoshi Miyasaka[1] (1. IMR, Tohoku University, 2. Graduate School of Science, Kyushu University)

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Multimetalic co-accumulation of precious and base metals in phenylazomethine dendrimer

(*[1]Lab. Chem. Life Sci., Tokyo tech, [2]Institute of Industrial Science, University of Tokyo, [3]Clean Energy Research Center, University of Yamanashi*)
○Tadatoshi Iitsuka,[1] Tatsuya Moriai[1], Takamasa Tsukamoto[2], Akiyoshi Kuzume[3], Takane Imaoka[1], Kimihisa Yamamoto[1]

Keywords: *dendrimer; metallic accumulation*

We have developed various metal and alloy clusters using a phenylazomethine dendrimer (TPM-G4) as a template, examining their physical properties and functionalities (Figure 1) 1,2). However, synthesizing alloy clusters presents a challenge due to the requirement for multimetallic co-accumulation on the dendrimer. This process is complicated by the differing conditions necessary for each metal species combination (Figure 2). This challenge is particularly pronounced when combining precious (noble) metals with base metals, as they often necessitate distinct accumulation conditions. Moreover, the variety of metals that can be successfully integrated into multielemental clusters is currently limited.

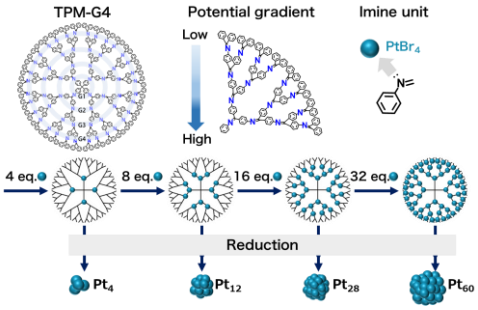

Figure 1 Accumulation on TPM-G4 and synthesis of metal clusters.

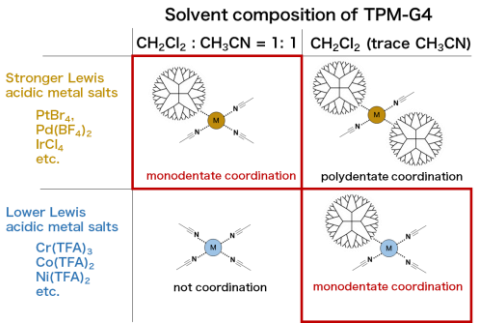

Figure 2 Difference of complexation conditions for TPM-G4 by metal salts.

In this study, our goal is to broaden the spectrum of multimetallic combinations of noble and base metals on the dendrimer. Our focus is on identifying noble metal complexes that can be co-accumulated under conditions amenable to base metals.

1) T. Imaoka *et al*., *Angew. Chem. Int. Ed*, **2015**, *54*, 9810.
2) T. Tsukamoto *et al*., *Nat. commun*, **2018**, *9*, 3873.

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Observation of vapochromic phase transition and micro motions in molecular crystals using confocal laser microscopy

([1] *IIS, The Univ. of Tokyo*, [2] *Graduate School of Science, University of Hyogo*) ○XIAO MA[1], Kyoko Enomoto[1], Kazuyuki Ishii[1], Yuki Matsuda[2], Masaaki Abe[2]

Keywords : Re complex; Micro motions; Vapochromism; Single-crystal-to-single-crystal phase transition; Soft crystals

In recent years, molecular crystals undergo structural transformations in the presence of specific stimuli, which is called "Soft Crystals".[1] In relation to "Soft Crystals", various phenomena, such as vapochromism and mechanochromism, have been extensively investigated. In these studies, single-crystal-to-single-crystal phase transitions are one of important targets, because molecular structural transformations can be investigated by X-ray structural analyses in nanoscopic scale.

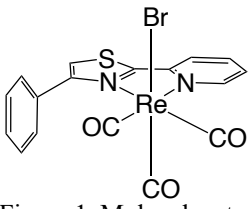

Figure 1. Molecular structure of [Re(CO)$_3$Br(ppt)]

In this study, we have investigated vapochromic single-crystal-to-single-crystal phase transition in microscopic scale by confocal laser microscopy, because our laboratory has previously demonstrated that super-resolution microscopy techniques are useful for directly observing time-dependent vapochromic behaviors.[2] Here, we employed *fac*-[Re(CO)$_3$Br(ppt)] (Figure 1), whose molecular crystal exhibits chloroform vapor-induced single-crystal-to-single-crystal phase transition.[2] By modifying the attachment, dynamic, vapochromic behaviors were successfully observed in microscopic scale after $CHCl_3$ vapor exposure (Figure 2a). Importantly, the 1 μm-sized boundaries were found between the regions before and after vapochromism, i.e., initial and final phases (Figure 2b). The phosphorescence peak of the final phase (Figure 2e) becomes intense and shifts to the blue side compared with that of the initial phase (Figure 2c), while that of the boundary region was obviously weak (Figure 2d). The details will be discussed in the presentation.

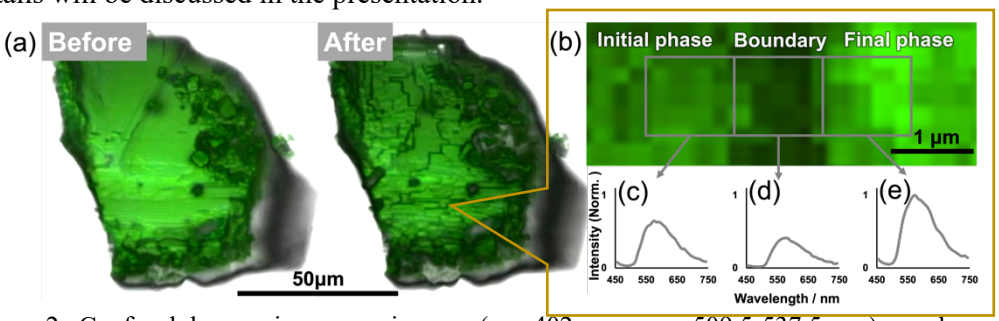

Figure 2. Confocal laser microscopy images (ex. 402 nm, em. 509.5-537.5 nm) overlapped with transmitted light microscopy images (402 nm) of a crystal of *fac*-[Re(CO)$_3$Br(ppt)] before and after $CHCl_3$ vapor exposure (a), an expanded image (b), and phosphorescence spectra of initial phase (c), boundary region (d), and final phase (e).

1) M. Kato, *Soft Crystals*, K. Ishii, Eds., Springer Nature, Singapore, **2023**.
2) K. Ishii, *et al.*, *J. Phys. Chem. C.*, **2021**, *125*, 38, 21055–21061.
3) Y. Matsuda, *et al.*, *71st Conference of Japan Society of Coordination Chemistry,* **2021**, PF2-40.

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Vapor-Induced Structural Transformation Dynamics of Photoluminescent Coordination Network Crystals

([1]*Graduate School of Science, University of Hyogo*, [2]*Graduate School of Engineering, Kyushu University*, [3]*Graduate School of Science*, *Osaka University*, [4]*Department of Chemistry*, *Faculty of Science and Engineering*, *Kindai University*, [5]*SPring-8/JASRI*) ○Yuki Matsuda,[1] Ryota Nakamura,[1] Yoshiki Ozawa,[1] Keishiro Tahara,[1] Toshikazu Ono,[2] Nobuto Yoshinari,[3] Takumi Konno,[3] Kunihisa Sugimoto,[4] Shintaro Kobayashi,[5] Shogo Kawaguchi,[5] Masaaki Abe [1]

Keywords: Photoluminescent Rhenium(I) Complex; Non-porous Crystal; Intramolecular Interactions; Gate-Open-Close Behaviors; In-situ Synchrotron Powder X-ray Diffraction

Noncovalent weak interactions among atoms and molecules, such as hydrogen bonds, halogen bonds, and CH/π interactions, are ubiquitous in natural and artificial systems from nanometer-to-micrometer scales and play vital roles especially in molecular assembly, recognition, catalysis, solid-state chemical processes, and biological events such as protein folding. As for porous crystalline solids, metal-organic frameworks (MOFs), extended 3D network solids via coordination bonds, may exhibit "gate-open-and-close" behavior upon guest-adsorption and desorption while retaining its crystallinity. Herein we report a new nonporous molecular solid to exhibit, besides MOFs, guest-induced structural transformation including reversible gate-open-and-close hysteresis or unidirectional gate-open behavior that is strictly guest-dependent under gaseous environments of volatile organic compounds (VOCs). The *in situ* and real-time probe for the transformation dynamics, unexplored in molecular crystals to date, was successfully carried out by photoluminescence (PL) spectroscopy, adsorption isotherms, and a sub-second *in situ* synchrotron PXRD method.

Complex **1**, *fac*-[Re(CO)$_3$Br(ppt)] (ppt = 2-pyridyl-4-phenylthiazole), was synthesized and characterized. Recrystallization of **1** with varied choice of solvents gave either guest-free nonporous **1** (denoted as Type O) or two types of guest (G)-inclusion crystals formulated **1**•***n*G** with n = 0.5 and 1.0 which are denoted as Types A and B, respectively. All of those crystals contain highly extended network assemblies with noncovalent multiple intermolecular interactions in the crystal lattice (Fig. 1). In Type A, the guests were trapped in a discrete void, whereas in Type B were incorporated into a 1D channel void. We found that nonporous "desolvated" **1** showed vapor-dependent gate-open-and-close hysteresis upon VOC-exposure-and-pump cycles. Unidirectional guest-substitution, from Type B to A, was detected for specific VOCs (Fig. 1, bottom). Thermodynamic stability of the crystalline solids was determined by TG analysis. Crystal size-dependence in the vapochromic response will also be presented.

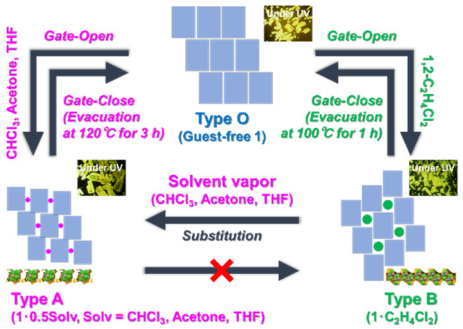

Fig. 1. Guest-induced transformation dynamics of nonporous molecular solids

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温度および圧力効果に基づく一次元 d^8 金属錯体の金属間距離と集積発光の詳細検討

（関学大生命環境 [1]・関学大理 [2]）○吉田 将己 [1]・三谷 開 [1]・瀬川 海斗 [1]・江口 大地 [2]・玉井 尚登 [2]・加藤 昌子 [1]

Correlation Between Metal-Metal distance and Assembly-induced Luminescence of One-dimensional d^8 Metal Complexes Based on Temperature and Pressure Effects

(Kwansei Gakuin University) ○Masaki Yoshida, Kai Mitani, Kaito Segawa, Daichi Eguchi, Naoto Tamai, Masako Kato

One-dimensional d^8 metal complexes such as Pt(II) and Pd(II) complexes are well known to show assembly-induced luminescence based on metal-metal interactions. However, there are still unresolved issues regarding the correlation of metal-metal distances and the delocalization of excited states via metal-metal interactions. In this study, we have investigated the excited states of a one-dimensional Pt(II) complex [Pt(dFppy)(pic)] (**1** in Fig. 1; dFppy = 2-(4,6-difluorophenyl)pyridinate, pic = α-picolinate) with a relatively long metal-metal distance (3.7053(3) Å) based on the variable-temperature and pressure measurements.

Keywords : Cyclometalated complexes, d^8 Metal complexes, Intermolecular interactions, Luminescence, Self-assembly

白金(II)錯体やパラジウム(II)錯体のような d^8 金属錯体は積層することで金属間相互作用に基づく特異な発光を示すため、光機能材料の基盤として盛んに研究がなされている。従来、この金属間相互作用を介した励起状態の形成・非局在化については慣例的に van der Waals 半径に基づいて議論されてきたが、詳細については未解明な点も多い。本研究では、結晶中で van der Waals 半径の和よりも長い金属間距離を有する一次元白金(II)錯体 **1**（図 1、上段）に対し、温度や圧力を用いて金属間距離を変化させることで、その励起状態の詳細を検討した。

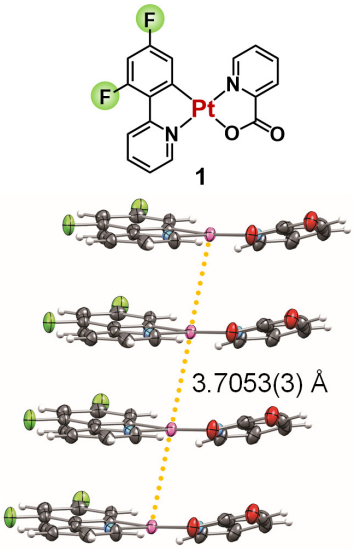

図 1. 錯体 **1** の分子構造と積層構造（水和水は省略）

錯体 **1** の 1 水和物結晶の 240 K における積層構造を図 1 に示す。この錯体は結晶中で白金の van der Waals 半径の 2 倍である 3.5 Å よりも長い 3.7053(3) Å という白金間距離を有する。それにもかかわらず、この結晶は室温において 623 nm 付近に発光極大を有する黄橙色発光を示し、種々の光物理測定からこの発光が金属間相互作用に由来することが判明した。さらに、この結晶に圧力を印加したところ、3.63 GPa 付近において発光極大波長が 721 nm 付近にまでシフトしたことから、白金間距離の収縮にともなう励起状態の多量化の促進 [1]が示唆された。当日は、温度可変測定の結果および類似の積層型パラジウム(II)錯体の発光性についても報告し、金属間距離と励起状態の非局在化について詳細に議論を行う予定である。

1) M. Nakagaki, S. Aono, M. Kato, S. Sakaki, *J. Phys. Chem. C* **2020**, *124*, 10453–10461.

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塩基性水溶液中で二酸化炭素によって誘起される N^C^N 型白金(II)錯体の自己集合

（横浜市大理[1]）○服部 伸吾[1]・三田 博之[1]・篠﨑 一英[1]

Self-Assembly of N^C^N-Coordinated Platinum(II) Complex Assisted by Carbon Dioxide in Basic Aqueous Solution ([1]*School of Science, Yokohama City University*) ○Shingo Hattori,[1] Hiroyuki Mita,[1] Kazuteru Shinozaki[1]

We report an unprecedented result of self-aggregation of Pt(II) complex triggered by CO_2 in basic aqueous solution. The color of basic aqueous solution containing Pt(II) complex changes from yellow to blue-green during the aggregation resulted from a reaction with CO_2 in air. Upon CO_2 gas bubbling, strong and broad absorption bands of aggregate assigned to the metal-metal-to-ligand charge transfer transition appeared at 701 and 1152 nm. Recrystallization of Pt(II) complex from Na_2CO_3 aqueous solution afforded polymorphic crystals of red and blue-green forms. A single X-ray crystallography revealed that the red form of crystal consists of a Pt-Pt stacked dimer bridged by CO_3^{2-} ion. An elemental analysis provided evidence that the blue-green crystal is constructed by linear array consisting of the Pt(II) complex.

Keywords : Self-assembly; Carbon dioxide; Pt(II) complex

CO_2 捕捉貯蔵技術は持続可能な社会を実現するために重要な概念である。これまで、金属錯体の CO_2 捕捉は報告されてきた一方、金属錯体の自己集合により劇的な色変化を伴って CO_2 捕捉した例はなかった。最近我々は、N^C^N 型白金(II)錯体($[Pt(L^1)Cl]^{2-}$, HL^1 = 1,3-di(5-carboxy-2-pyridyl)benzene)塩基性水溶液では CO_2 を捕捉することで白金(II)錯体が自己集合し、水溶液の色が黄色から青緑色へと変化することを見出した[1]。本発表ではその詳細について報告する。

CO_2 ガスバブリング前は、白金錯体のπ-π*/MLCT 遷移に由来する吸収帯が 400 nm 付近に観測された。一方、CO_2 ガスバブリング 10 秒後には、400 nm 付近にあった吸収帯のピークは短波長シフトし、600 nm 付近に二量体に由来する吸収帯が観測された。CO_2 ガスバブリング 30 秒後には、600 nm 付近の吸収帯は減少し、700 nm 付近と 1150 nm 付近に新たな吸収帯が観測された。観測された波長から、ブロードな吸収帯は四量体以上の会合度を持つ会合体であることが示唆された。また、Ar, N_2, O_2 ガスバブリングではこのようなスペクトル変化は起こらなかった。これより、$[Pt(L^1)Cl]^{2-}$ が CO_2 のみと反応することで会合体が形成されることが明らかとなった。

赤色結晶と青緑色結晶を作製した。赤色結晶は X 線単結晶構造解析により、CO_3^{2-} が白金に架橋配位子した二量体構造をとることが明らかとなった。青緑色結晶は X 線単結晶構造解析が困難であったが、元素分析により、$Na_3[Pt(L^2)(CO_3)]\ 6H_2O$ (HL^2 = 1,3-di(5-carboxylate-2-pyridyl)benzene)であることが示唆された。$[Pt(L^2)(CO_3)]^{3-}$の吸収スペクトルの時間変化を速度論解析と特異値分解を行うことにより、青緑色会合体が少なくとも３２量体であることが示唆された。

1) H. Mita, S. Hattori, T. Sasaki, S. Takamizawa, K. Shinozaki, *ChemSusChem*, **2023**, *16*, e202301174.

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Crystal-downsizing Effect on Dual-emission Behavior in an Au(I)-based Coordination Polymer

([1]*Institute for Materials Research, Tohoku University*, [2]*Graduate School of Science, Kyushu University*) ○Haruka Yoshino,[1] Takumi Ehara,[2] Kiyoshi Miyata,[2] Ken Onda,[2] Hitoshi Miyasaka[1]

Keywords: Coordination polymer; Metal–organic framework; Metallophilic interactions; Dual-emission behavior; Crystal size control

Coordination polymers (CPs) and metal–organic frameworks (MOFs), a new class of crystalline and functional materials, are being extensively developed in the field of materials science. In addition, it has recently become clear that the particle size of the CPs/MOFs with flexible coordination networks impacts the functional properties of the framework. However, most of the studies have focused on gas adsorption, and the influence of domain size on the physical properties incorporated in CPs/MOFs and mechanical properties using physical stimulus has not been sufficiently investigated to date.

Herein, we report a novel luminescent CP $\{Cd^{II}(pmd)[Au^{I}(CN)_2]_2\}$ (pmd = pyrimidine; **1**) that exhibits an intense dual emission behavior (**Fig. 1**). The particle size of **1** can be controlled under various conditions such as solution diffusion, stirring, and reverse micelle method, yielding single crystals (**SC**; > 100 μm), microcrystalline (**bulk**; ~ 20 μm), and powder state (**W5**; < 10 μm), respectively (**Fig. 2(a)**). Importantly, the luminescence features of the **1** were strongly influenced by the domain size; the decrease in particle size (**SC**→**bulk**→**W5**) increases the fraction of low-energy emission (λ2 in **Fig. 2(b)**), which was also directly confirmed by the fluorescence microscope images (**Fig. 2(c)**). The details of dual emission behaviors for **1** was investigated through time-resolved photoluminescence analyses, demonstrating that the particle size of the resultant CP remarkably manipulated the excited state dynamics.

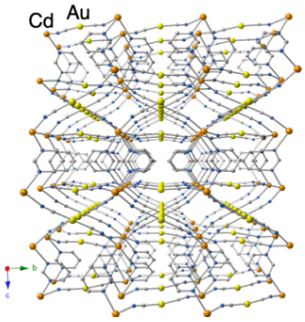

Fig. 1. Crystal structure of **1**

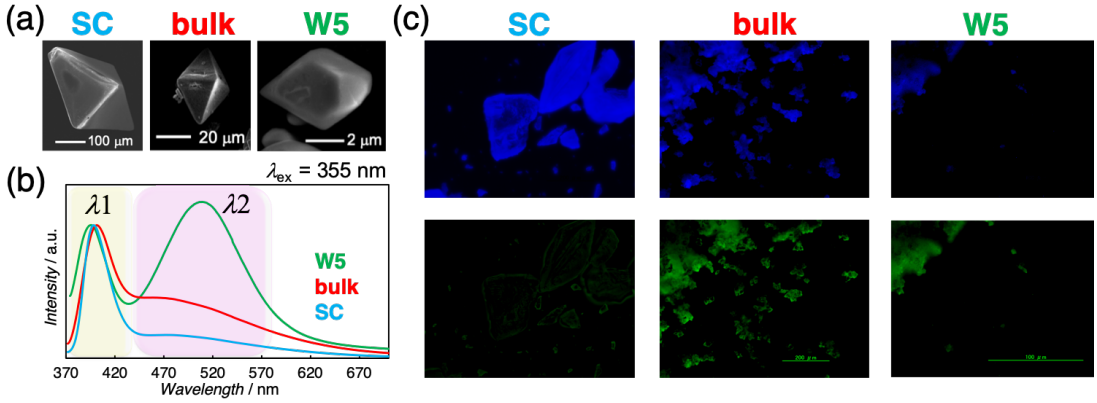

Fig. 2 (a) SEM images of **SC**, **bulk**, and **W5**. **(b)** Emission spectra of **SC**, **bulk**, and **W5**. **(c)** Fluorescence microscope images of **SC**, **bulk**, and **W5** (λ_{ex} = 365 nm).

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Academic Program [Oral A] | 10. Organic Chemistry -Organometallic Compounds-：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:00 AM UTC E1111(1111, Bldg. 11 [1F])

[E1111-4pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Masaaki Namamoto, Takashi Kurogi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1111-4pm-01]
Reductive *anti*-Dimetalation of Alkynes

○Haruka Yamaguchi[1], Fumiya Takahashi, Takashi Kurogi[1], Hideki Yorimitsu[1] (1. Kyoto University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1111-4pm-02]
Calcium-Mediated Mechanochemical Birch Reduction

○Yamato Fukuzawa[1], Keisuke Kondo[1], Yunpeng Gao[1], Kouji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1111-4pm-03]
Reduction of amide compounds to aldehydes using strontium metal

○Tatuya Watanabe[1], Masaharu Ueno[1], Norikazu Miyoshi[1] (1. Faculty of Science and Technology, Tokushima University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1111-4pm-04]
Development of a convenient and useful transesterification reaction using a catalytic amount of strontium alkoxide

○Chisato Kamada[1], Ryosuke Shimoda, Masaharu Ueno[1], Norikazu Miyoshi[1] (1. Tokushima University)

English
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1111-4pm-05]
Reactivity of Germanium Enolates Generated from Allenylesters with Ge(II) Salts

○Taishi Nojima[1], Akihito Konishi[1], Makoto Yasuda[1] (1. Graduate School of Engineering Osaka University)

1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
Break

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1111-4pm-06]
Defluoroborylation of *gem*-difluoroalkenes with borylstannane reagents via radical chain mechanism

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Yoshihiro Nishimoto[1], ○Naoya Ito[1], Makoto Yasuda[1] (1. Graduate School of Engineering, Osaka University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1111-4pm-07]

Reactivity of Germapyramidane Towards Organolithium Reagents

○Junkang Wang[1], Vladimir Ya. Lee[2], Katsuhiko Takeuchi[3], Norihisa Fukaya[3], Takahiro Sasamori[2,4] (1. Graduate School of Science and Technology, University of Tsukuba, 2. Institute of Pure and Applied Sciences, University of Tsukuba, 3. National Institute of Advanced Industrial Science and Technology, 4. TREMS, University of Tsukuba)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1111-4pm-08]

Studies for Silylene Generation Using Silylboranes with Leaving Group

○Rikuro Takahashi[1], Hajime Ito[2,3] (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University, 3. WPI-ICReDD, Hokkaido University)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1111-4pm-09]

Synthesis of *gem*-difluoro allyl compounds from trifluoromethyl alkenes via the defluorination process

○Harue Kinoshita[1], Itaru Suzuki[2], Ikuya Shibata[2] (1. Graduate School of Engineering Osaka University, 2. Research Center for Environmental Preservatior, Osaka University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[E1111-4pm-10]

Synthesis of 2-Iodoarylstannanes by Iodostannylation of Arynes

○Taiga Obayashi[1], Masaaki Nakamoto[1], Takumi Tsushima[1], Hiroto Yoshida[1] (1. Hiroshima University)

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アルキンの還元的 *anti*-ジメタル化反応

（京大院理）○山口華佳・高橋郁也・黒木尭・依光英樹
Reductive *anti*-Dimetalation of Alkynes (*Graduate School of Science, Kyoto University*)
○Haruka Yamaguchi, Fumiya Takahashi, Takashi Kurogi, Hideki Yorimitsu

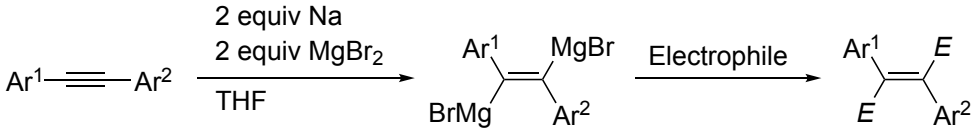
1,2-Dimetalloalkenes are useful precursors to afford various multi-substituted alkenes. Recently, we have reported the reductive *anti*-1,2-dimagnesiation of alkynes by means of sodium metal and a Grignard reagent.[1] The resulting 1,2-dimagnesium species could be converted to various tetrasubstituted alkenes by reacting with electrophiles. However, the use of excess electrophile was required for further transformation due to the reaction of the organometallic moieties derived from the Grignard reagent with the electrophile. Herein, we achieved reductive dimetalation of alkynes using simple metal halides as metalating reagents.

Reduction of diarylacetylenes **1** with sodium metal in the presence of $MgBr_2$ resulted in the reductive 1,2-*anti*-dimagnesiation to afford *trans*-1,2-dimagnesioalkenes **2**. Treatment of **2** with a smaller amount of electrophiles afforded tetrasubstituted alkenes **3** efficiently.

Keywords : metalation; sodium metal; reduction; alkyne

1,2-ジメタロアルケンは多置換アルケンの有用な合成前駆体である。最近我々は金属ナトリウムと Grignard 反応剤によるアルキンの還元的 *anti*-1,2-ジマグネシウム化を報告した[1)]。生じた 1,2-ジマグネシウム種は、求電子剤と反応させることで様々な四置換アルケンへと変換可能であった。しかし求電子剤との反応の際に、Grignard 反応剤由来のカルボアニオン部位も求電子剤と反応するため、求電子剤を大過剰量用いる必要があった。このような背景のもと我々は、単純な金属ハロゲン化物を用いるアルキンの還元的ジメタル化に取り組んだ。

臭化マグネシウム共存下、ジアリールアセチレン **1** に対し金属ナトリウムを作用させたところ、アルキン部位の還元的 *anti*-ジマグネシウム化が進行した。また、生じた 1,2-ジマグネシウム種 **2** に対し求電子剤を作用させる際、小過剰の求電子剤でも良好な収率で四置換アルケン **3** が得られた。



1 **2** **3**

1) F. Takahashi, T. Kurogi, H. Yorimitsu, *Nat. Synth.* **2023**, *2*, 162.

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メカノケミストリーを用いたカルシウム金属によるバーチ還元

（北大院工[1]・北大 WPI-ICReDD[2]）○福澤 大和[1]・近藤 恵祐[1]・Yunpeng Gao[1]・久保田 浩司[1,2]・伊藤 肇[1,2]

Calcium-Mediated Mechanochemical Birch Reduction

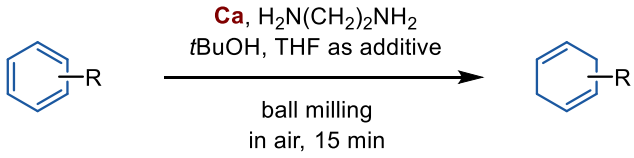
([1]*Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*)
○Yamato Fukuzawa,[1] Keisuke Kondo,[1] Yunpeng Gao,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

In the Birch reduction, highly reactive reducing agents such as lithium are commonly used. However, such alkali metals are potentially hazardous. Therefore, the development of safer alternatives using less reactive calcium metals have attracted attentions. Nonetheless, existing solution-based methodologies necessitate complicated experimental operations under inert gas atmospheres and long reaction time. Here, we discovered that a ball-milling technique allows using commercial, unactivated calcium metal for Birch reduction. In this approach, mechanical activation of calcium metal by ball milling facilitates highly efficient Birch reduction of various aromatic compounds. Furthermore, this method is characterized by the simplicity of operation, short reaction time, and solvent-minimized conditions.

Keywords : Mechanochemistry; Ball mill; Birch reduction; Calcium

バーチ還元では、リチウムなどの強力な還元剤が主に用いられているが、発火性や爆発性の懸念がある。このような背景のもと、それらアルカリ金属に比べて反応性の低いカルシウム金属を使用した方法が、より安全な代替法として期待されている[1]。しかし、既存の溶液条件の方法では、不活性ガス雰囲気下や禁水環境での煩雑な実験操作が必要である上、比較的長い反応時間が必要であった[2]。

本研究では、メカノケミカル法を活用したカルシウム金属によるバーチ還元法を開発した。この方法では、ボールミルの強い機械的な作用によりカルシウム金属が活性化され[3,4]、高い反応性を実現している。また、操作の簡便性や短い反応時間、溶媒量の削減の観点からも有用である。



easy-to-handle, cheap and abundant metal reductant
yields comparable with alkali metal reductants

1) Hwu, J. R.; Wein, Y. S.; Leu, Y-J. *J. Org. Chem.* **1996**. *61*, 1493–1499.
2) Benkeser, R. A.; Laugal, J. A.; Rappa, A. *Tetrahedron Lett*. **1984**, *25*, 2089–2092.
3) Gao, P.; Jiang, J.; Maeda, S.; Kubota, K.; Ito, H. *Angew. Chem. Int. Ed.* **2022**, *61*, e202207118.
4) Gao, Y.; Kubota, K.; Ito, H. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217723.

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金属ストロンチウムを用いたアミド化合物のアルデヒドへの還元反応

（徳島大学院理工）○渡邊　達哉・上野　雅晴・三好　徳和

Reduction of amide compounds to aldehydes using strontium metal

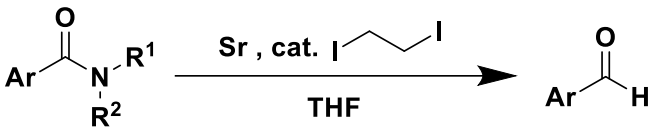
(*Graduate School of Science and Technology, Tokushima University*) ○ Tatsuya Watanabe, Masaharu Ueno, Norikazu Miyoshi

We have reported the Birch-type reduction of polycyclic aromatics with ammonium salts in the presence of strontium metal. In this study, we found that the reduction of aromatic amides with strontium metal and a catalytic amount of activator proceeded smoothly to afford the corresponding aldehydes in high yields. This reaction is different from the aforementioned reactions in that it does not involve the addition of a hydrogen source for the reduction. This time, we will wish to report on the details and some novel reactions found during the research.

Keywords : strontium; reduction; amide

Grignard 試薬に代表されるアルカリ土類元素を用いた有機金属試薬に関する研究は数多くあるが、有機ストロンチウム化合物の調製と反応性に関する研究は、我々の研究以外ではほとんど報告されていない。一方我々は、ストロンチウム化合物を用いた有機合成反応を研究し、ストロンチウム金属の独特で有用な性質による新規かつ新奇有機合成反応を見出してきた[1-4]。

当研究室では、金属ストロンチウム存在下、アンモニウム塩を用いる多環芳香族の Birch 型還元反応を見出し報告している[3]。今回我々は芳香族アミドと金属ストロンチウム、触媒量の活性化剤存在下、還元された芳香族アルデヒドが高収率で得られることを見出した。また本反応は、還元に必要な水素源も添加しておらず、前述の反応とは異なるものである。今回その詳細と検討途中で明らかとなった新奇な反応について報告する。



1) N. Miyoshi, A. Miyoshi, Y. Miyazaki, S. Kubo, M. Ueno, *Chem. Commun*., **2022**, *58*, 6312-6315.
2) N. Miyoshi, S. Kimura, S. Kubo, S. D. Ohmura, M. Ueno, *Asian J. Org. Chem*., **2020**, 9, 1660-1664.
3) S. D. Ohmura, M. Ueno, N. Miyoshi, *Tetrahedron Lett*., **2018**, *59*, 2268-2271.
4) S. D. Ohmura, Y. Miyazaki, D. Kanehiro, Y. Yamaguchi, S. Kitakata, S. Tateda, T. Nishizawa, R. Shimoda, G. Nagaoka, M. Ueno, N. Miyoshi, *Asian J. Org. Chem.,* **2017**, *6*, 821-824.

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ストロンチウムアルコキシド触媒を用いる簡便かつ有用なエステル交換反応の開発

（徳島大学理工学部）○鎌田 知里・下田 亮介・上野 雅晴・三好 徳和

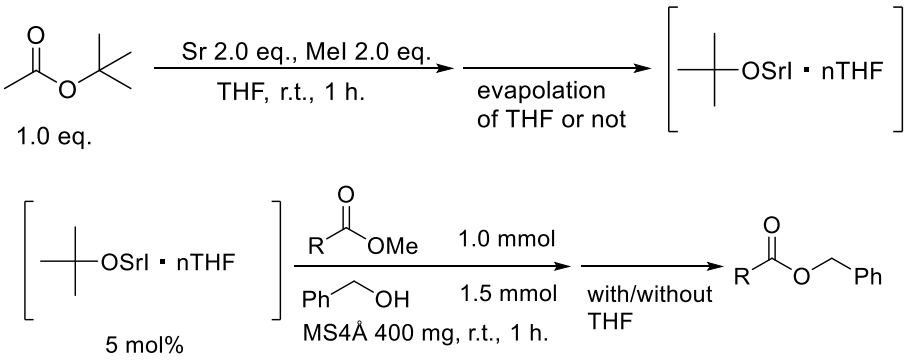
Development of a convenient and useful transesterification reaction using a catalytic amount of strontium alkoxide (*Faculty of Science and Technology, Tokushima University*) ○Chisato Kamada, Ryosuke Shimoda, Masaharu Ueno, Norikazu Miyoshi

We have found a new synthetic method of strontium *tert*-butoxide as a storable solid reagent. Strontium *tert*-butoxide undergoes alkoxide exchange reactions with various alcohols, and the alkoxides are found to have high nucleophilicity. As the above results, we have found that when various methyl esters reacted with various alcohols in the presence of a catalytic amount of strontium *tert*-butoxide and molecular sieves without a solvent, the reaction proceeded smoothly to afford the transesterificated compounds with excellent yields.

Keywords : Transesterification; Strontium; Neat

金属ストロンチウムは、比較的安価で入手が容易にも関わらず、これを有機合成反応に用いた報告例は非常に少ない。そこで、ストロンチウムを用いた有機合成反応を開発することができれば、有機合成化学的観点から有用であると考えた。今回、ストロンチウムアルコキシドに着目し、新たなエステル交換反応の開発を試みた。

我々は、保存可能な固体試薬として、ストロンチウム *tert*-ブトキシドを調製する方法を見出した。このストロンチウム *tert*-ブトキシドは様々なアルコールと円滑に反応し、新たなストロンチウムアルコキシドを生成した。このアルコキシドはメチルエステルを用いるとエステル交換反応を円滑に進行させることがわかった。エステル交換反応は、可逆反応であることが推測され、メチルエステルから生成するメタノールを除去できれば、ストロンチウム *tert*-ブトキシドは、触媒量でも反応は進行するはずである。そこで、THF 溶媒下、メタノールを吸着する MS4Å を用い反応を試みた結果、対応するエステルが良好な収率で得られた。さらに驚くべきことに、基質のエステル 1 mmol 及びアルコール 1.5 等量を、MS4Å 400 mg と固体のストロンチウムアルコキシドをわずか 5 mol%用い無溶媒条件下で攪拌するだけで、短時間でエステル交換反応が定量的に進行することも見出した。これらの反応の詳細について発表する。



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Reactivity of Germanium Enolates Generated from Allenylesters with Ge(II) Salts

(*Graduate School of Engineering Osaka University*) ○Taishi Nojima, Akihito Konishi, Makoto Yasuda

Keywords: Germylene, Allene, Cheletropic Reaction, Aldol Reaction, Diastereoselectivity

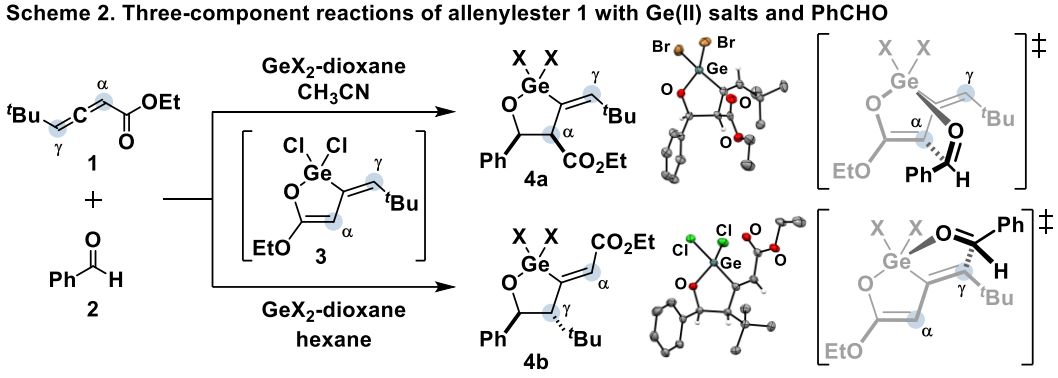
Divalent group 14 species, tetrylenes, are heavier carbene analogues that have high reactivity due to vacant p orbital and high reducing ability. Germylene exhibits moderate stability compared with silylene and stannylene, and its high reactivity has shown promise in the development of organic synthetic reactions. Cheletropic reaction of germylenes with conjugated double bonds has long been known as a method of trapping germylenes,[1] but the synthetic applications of generated germacycles remain undeveloped (**Scheme 1**).[2] Herein, we focus on the cheletropic reaction of allenylesters with germylene.

Scheme 1. Cheletropic reaction of conjugated double bond with Ge(II)



A three-component reaction of allenylester **1** with GeX_2-dioxane (X = Cl or Br) and benzaldehyde **2** was examined, and in situ generated germyl enolate **3** reacted with aldehyde to give five-membered germacycle **4** (**Scheme 2**). The rigid structure of cyclic enolate **3** facilitates the highly diastereoselective reactions. The regioselectivity of the products was switched by the solvent polarity. The optimized conditions were applicable to the reaction with various aromatic aldehydes. The reaction mechanisms will be discussed in the meeting.

Scheme 2. Three-component reactions of allenylester 1 with Ge(II) salts and PhCHO



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2) a) Minami, Y.; Konishi, A.; Yasuda, M. *Org. Lett*. **2018**, *20*, 4148. b) Minami, Y.; Konishi, A.; Yasuda, M. *Org. Lett*. **2019**, *21*, 9818.

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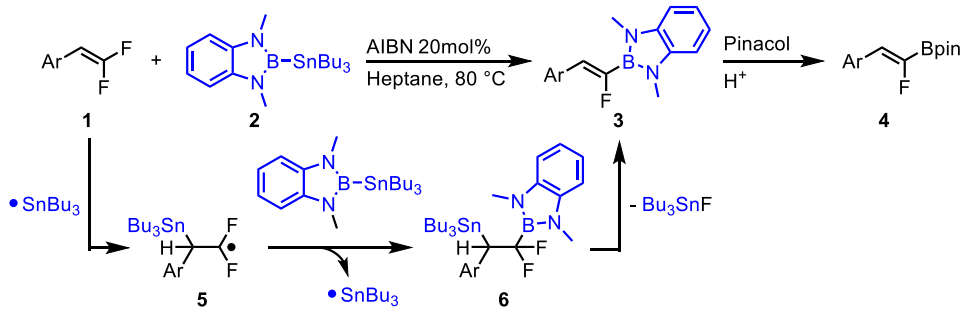
ボリルスズ試薬を用いたラジカル連鎖機構を経由するジフルオロアルケンの脱フッ素ホウ素化

（阪大院工）西本 能弘・○伊藤 直也・安田 誠
Defluoroborylation of *gem*-difluoroalkenes with borylstannane reagents via radical chain mechanism (*Graduate School of Engineering, Osaka University*) Yoshihiro Nishimoto, ○ Naoya Ito, Makoto Yasuda

Fluoroalkenes are expected to be used as pharmaceuticals because they are bioisosteres of amides. The defluoroboronation of *gem*-difluoroalkenes is a promising synthetic method for fluoroalkene derivatives, but only a few examples have been reported. In this study, we developed the defluoroborylation of *gem*-difluoroalkenes with the borylstannane reagents. This reaction proceeded stereoselectively under radical reaction conditions using a radical initiator. The reaction of *gem*-difluoroalkenes with the borylstannane reagent in the presence of 20 mol% AIBN in heptane gave the targeted defluoroboronated product in 70% yield.
Keywords : Borylstannane; Defluoroborylation; Stereoselectivity; Radical chain mechanism; Radical addition

フルオロアルケンはアミドの生物学的等価体であることから医薬品としての利用が期待されている。フルオロアルケン誘導体の合成法として *gem*-ジフルオロアルケンの脱フッ素ホウ素化があるが、その報告例は数例のみとなっており、新たな手法の開発が求められている。当研究室ではラジカル条件下のホウ素化試薬として利用可能である新規ボリルスズ試薬を開発した[1]。本研究では、このボリルスズ試薬を用いた *gem*-ジフルオロアルケンの脱フッ素ホウ素化を達成した。本反応はラジカル開始剤を用いたラジカル条件で立体選択的に進行する。

gem-ジフルオロアルケン **1** とボリルスズ試薬 **2** との反応を AIBN (20 mol%)の存在下、ヘプタン中で行うと、目的の脱フッ素ホウ素化体 **4** が 70%収率で得られた。本反応では、開始段階により発生したスズラジカルが *gem*-ジフルオロアルケンに付加し、ラジカル種 **5** が生成する。その後、**5** とボリルスズ試薬 **2** とのラジカル置換反応が進行し、続いて Bu_3SnF が脱離することで生成物 **3** が得られる。



1) K. Suzuki, Y. Nishimoto, M. Yasuda, *Chem. Eur. J.* **2021**, *27*, 3968.

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有機リチウム試薬に対するゲルマピラミダンの反応性

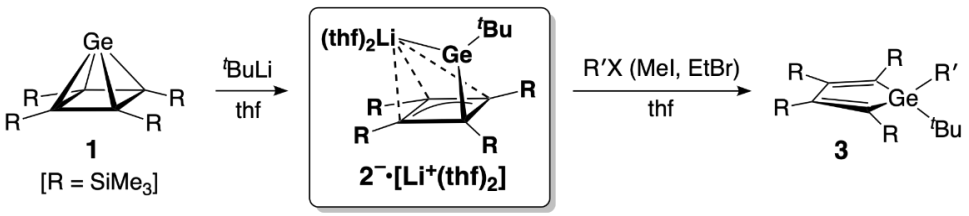
(筑波大院数理[1]・筑波大数理物質[2]・産業技術総合研究所[3]・TREMS[4]) ○王 峻康[1]・Lee Vladimir Ya.[2]・竹内 勝彦[3]・深谷 訓久[3]・笹森 貴裕[2,4]
Reactivity of Germapyramidane Towards Organolithium Reagents([1] *Graduate School of Science and Technology, University of Tsukuba,* [2]*Institute of Pure and Applied Sciences, University of Tsukuba,* [3]*National Institute of Advanced Industrial Science and Technology,* [4]*TREMS, University of Tsukuba*) ○Junkang Wang,[1] Vladimir Ya. Lee,[2] Katsuhiko Takeuchi,[3] Norihisa Fukaya,[3] Takahiro Sasamori[2,4]

Pyramidane is the non-classical organic compound with the square-pyramidal skeleton and invertedly tetrahedral apical atom. The heavier analogues of pyramidanes with the Main Group element at the top of the square-pyramid only recently became synthetically accessible. In this presentation, we report the reactivity of Ge-pyramidane towards organolithium reagents, leading to the formation of highly reactive germyllithium derivatives that can be used for preparation of novel Ge-containing cyclic compounds.

Thus, germapyramidane **1**[1] reacted with ^{t}BuLi at low temperature to form unusual germyllithium derivative **2**$^{-}$•**[Li^{+}(thf)$_2$]**, isolated by recrystallization from *n*-hexane as orange crystals in 60% yield and structurally characterized by XRD analysis (Scheme). The peculiar spectroscopic and structural features of **2**$^{-}$•**[Li^{+}(thf)$_2$]**, along with its specific reactivity towards organohalides R′X, finally forming substituted germoles **3** (Scheme), will be also discussed.
Keywords : cluster; germanium; pyramidane

ピラミダンは、正四角錐骨格と逆四面体の頂端原子を持つ非古典的な有機化合物である。最近、ゲルマピラミダン **1**[1] をはじめ、種々の正四面体の頂点に高周期典型元素を有する持つピラミダン誘導体が合成された。本発表では、有機リチウム試薬に対する Ge-ピラミダンの反応性について報告し、新規な Ge 含有環状化合物の調製に使用できる反応性の高いゲルミリチウム誘導体の形成につながった。

ゲルマピラミダン **1**[1] は低温で tBuLi と反応し、ゲルミルリチウム誘導体 **2**$^{-}$·[Li^{+}(thf)$_2$] を与えることがわかった。ヘキサンからの再結晶により、収率 60%でオレンジ色の結晶として単離され、単結晶 X 線結晶構造解析によりその構造パラメータを明らかとした(Scheme)。**2**$^{-}$·[Li^{+}(thf)$_2$]の分光学的および構造的特徴と、有機ハロゲン化物 R′X との反応により、最終的にゲルモール **3** が得られた結果についても報告する。



Scheme

1) (a) Lee, V. Ya. *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 8794–8797; (b) *Organometallics,* **2016**, *35*, 346−356.

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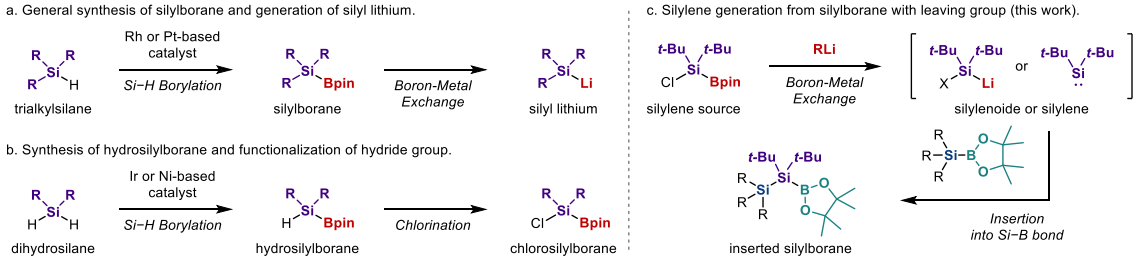
脱離基をもつシリルボランを用いたシリレンの一般的発生法の研究

（北大院総化[1]・北大院工[2]・北大 WPI-ICReDD[3]）○髙橋 陸朗[1]・伊藤 肇[2,3]
Studies for Silylene Generation Using Silylboranes with Leaving Group ([1]*Graduate School of Chemical Science and Engineering, Hokkaido University*, [2]*Graduate School of Engineering, Hokkaido University,* [3]*WPI-ICReDD, Hokkaido University*) ○Rikuro Takahashi,[1] Hajime Ito[2,3]

Silylenes, silicon analogs of carbenes, are intriguing due to their chemical properties. Typically generated by the reduction of dihalosilanes with alkali metals, their harsh synthesis conditions limit organic applications. To enhance silylene utility, milder generation conditions are imperative.[1] Recently we developed the general method to synthesize diverse silylboranes, and these reagents can be converted to silyl metals with boron-metal exchange (Figure a, b).[2] Based on these results, we assumed that various silylenes could be generated from chlorosilylbornaes by boron-metal exchange. The in situ generated silylene species insert into Si–B σ bonds, providing the inserted product in high yield (Figure c).

Keywords : Silylenes ;Silylboranes; Boron-Metal Exchange; Organosilicon Compounds; Organoboron Compounds

シリレンはカルベンのケイ素類縁体であり、その化学的特性に対する興味から多くの単離報告がなされている。一般的に、シリレンを発生させる場合、ジハロシランのアルカリ金属による還元が必要であり、その厳しい反応条件から有機合成への応用は限られていた[1]。我々は、様々なシリルボランの一般的な合成法を開発しており、これらはホウ素-金属交換によりシリル金属種に変換可能である[2] (図 a, b)。我々は、ホウ素-金属交換を利用することで、クロロシリルボランからジアルキルシリレンなどの様々なシリレンを簡便に生成できると考えた。また、生成したシリレンは Si–B σ 結合に挿入し、高収率で生成物を得ることに成功した(図 c)。



1) Selected examples: a) J. Ćiraković, T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2002**, *124*, 9370. b) T. Ohmura, K. Masuda, M. Suginome, *J. Am. Chem. Soc.* **2008**, *130*, 1526. c) P. B. Glaser, T. D. Tilley, *J. Am. Chem. Soc.* **2003**, *125*, 13640.
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脱フッ素過程を経るトリフルオロメチルアルケンからの *gem*-ジフルオロアリル化合物の合成

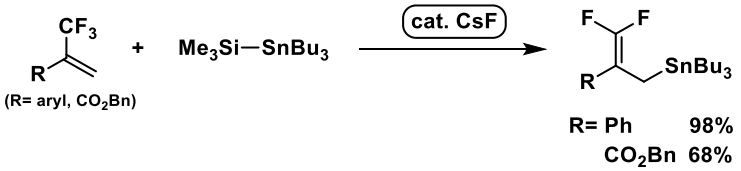
（阪大院工[1]・環境安全研究管理センター[2]）○木下 晴絵[1]・鈴木 至[2]・芝田 育也[2]
Synthesis of *gem*-difluoro allyl compounds from trifluoromethyl alkenes via the defluorination process ([1]*Graduate School of Engineering, Osaka University*, [2]*Research Center for Environmental Preservation, Osaka University*) ○Harue Kinoshita,[1] Itaru Suzuki,[2] Ikuya Shibata[2]

The *gem*-difluoromethylene group is a useful functional group with unique properties such as a role as a biological isotope of oxygen atoms. As a method for introducing this group into organic molecules, the Hosomi Sakurai type reaction using a *gem*-difluoro allylic metal species and a carbonyl compound has been used, and silicon and boron species have been used so far. On the other hand, a practical method has not been developed for allylic tin species, which requires the use of strong bases and CFC gas.

In this study, stannylation of trifluoromethyl alkenes accompanying defluorination was investigated for the synthesis of *gem*-difluoro allylstanannes. We found that *gem*-difluoro allylstanannes were obtained by a simple method using trifluoromethylalkenes and stannylsilanes with a weak base, cesium fluoride, as a catalyst. This reaction has a wide substrate application range, and various *gem*-difluoro allylstanannes were successfully synthesized. The obtained allylstanennes were able to react with various electrophiles.
Keywords : Allylstananne; Strong base Free; Stannylation; Defluorination

gem-ジフルオロメチレン基は代謝安定性や脂溶性の向上といった特異な性質に加え、酸素原子の生体内同位体としての役割をもつなど有用な官能基である。入手容易なトリフルオロメチル基と比較した場合、*gem*-ジフルオロメチレン基の導入法の開発は途上段階であり、開拓の余地を残している。これを有機分子中に導入する手法として *gem*-ジフルオロアリル金属種とカルボニル化合物を用いた細見桜井型の反応があり、これまでケイ素、ホウ素種が利用されている。一方で、アリルスズ種の合成は強塩基や使用困難なフロンガスを使用しなければならず、実用的な手法は開発されていない[1)]。

本研究では、*gem*-ジフルオロアリルスズ種の合成を目的に脱フッ素化を伴うトリフルオロメチルアルケンのスタニル化を検討した。その結果、トリフルオロアルケンとスタニルシランに対し、弱塩基であるフッ化セシウムを触媒量用いるという簡便な手法で *gem*-ジフルオロアリルスズが得られることを見出した。本反応は広い基質適応範囲を有しており、様々な *gem*-ジフルオロアリルスズの合成に成功した。また、得られたアリルスズは種々の求電子剤と反応が可能であった。



1）D. Seyferth, K.R. Wursthorn, *J. Organomet. Chem.* **1979**, *182*, 455.

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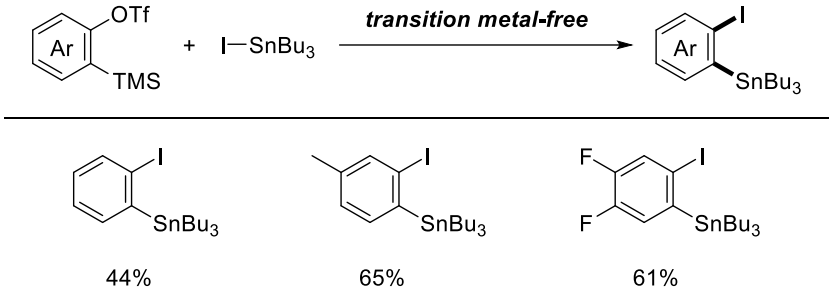
アラインのヨードスタニル化反応による２−ヨードアリールスズ合成

（広島大院先進理工）○大林 泰雅・中本 真晃・対馬 拓海・吉田 拡人
Synthesis of 2-Iodoarylstannanes by Iodostannylation of Arynes (*Hiroshima University*) ○ Taiga Obayashi, Masaaki Nakamoto, Takumi Tsushima, Hiroto Yoshida

Highly electrophilic arynes have been well established to undergo insertion reactions into nucleophilic–electrophilic σ-bonds to directly afford a variety of *ortho*-substituted arenes. In particular, the Kobayashi method with *ortho*-silylaryl triflates, which can generate arynes under almost neutral conditions, is commonly used for this purpose. In this regard, we previously reported on the aryne insertion reactions into carbon–tin and fluorine–tin bonds. Herein we disclose that arynes are smoothly inserted into an iodine–tin bond of iodostannanes under transition metal catalyst-free conditions, giving a direct and convenient method of synthesizing various 2-iodoarylstannanes, which are otherwise difficult to obtain.

Keywords : aryne; iodostannylation; 2-iodoarylstannanes

極めて高い求電子性を示すアラインは，求核部−求電子部からなる σ 結合に容易に挿入し，種々のオルト置換アレーンを一段階で与えることが知られている．中でも *ortho*-シリルアリールトリフラートとフッ化物イオンを用いた小林法はほぼ中性条件でアラインを発生させることができ，この挿入反応開発に多用される．既にわれわれは，この手法を用いて炭素−スズ結合，フッ素−スズ結合へのアライン挿入反応を達成し，種々のオルト位官能基化アリールスズの直截合成に成功している [1),2)]．今回，スズヨージドのヨウ素−スズ結合に，遷移金属触媒フリーな条件でアラインが円滑に挿入し，古典的手法では合成が困難であった一群の 2-ヨードアリールスズが一段階で合成できることを見つけた．



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2) H. Yoshida, R. Yoshida, K. Takaki, *Angew. Chem. Int. Ed*. **2013**, *52*, 8629

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Academic Program [Oral A] | 10. Organic Chemistry -Organometallic Compounds-：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:20 AM UTC E1112(1112, Bldg. 11 [1F])

[E1112-4pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Takuya Kochi, Takuya Shinbayashi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1112-4pm-01]
Rhodium(III)-Catalyzed Arylation of Itaconic Acid Derivatives
○Yuito Takatsuji[1], Yoshinosuke Usuki[1], Tetsuya Satoh[1] (1. Osaka Metropolitan University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1112-4pm-02]
Synthesis of cyclopentanes by reductive coupling of benzoylalkenes in the presence of rhodium/isocyanide catalyst and diboron
○Yuji Nakamuta[1], Ken-ichi Fujita[1], Takuya Shimbayashi[1] (1. Kyoto University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1112-4pm-03]
Rhodium-catalyzed Exchange Reaction between Peptide Trisulfide and Disulfides/Diselenides
Masana Yazaki[1], ○Wataru Sonoda[2], Mieko Arisawa[3] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Fac. Sch. Agric., Kyushu Univ., 3. Grad. Agric., Kyushu Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1112-4pm-04]
Rhodium-catalyzed Insertion Reaction of Arylarsines into Peptide Disulfides in Water
○Masana Yazaki[1], Mieko Arisawa[2] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Fac. Agric., Kyushu Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1112-4pm-05]
Rhodium-catalyzed chain-walking hydrothiolation of *N*-allylamides
○Naoki Hikida[1], Hirotsugu Suzuki[1] (1. University of Fukui)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1112-4pm-06]
Synthesis of Naphthalene Derivatives by Rhodium-Catalyzed Hydroaminative Cyclization of 1,5-Diynes
○Hibiki Goto[1], Takuya Kochi[1], Fumitoshi Kakiuchi[1] (1. Keio University)

2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
Break

Japanese

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2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[E1112-4pm-07]

Rhodium-catalyzed Synthesis of Selenoisocyanates Using Isocyanides and Selenium.

Masana Yazaki[1], ○Takahiro Goto[2], Mieko Arisawa[3] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Grad. Sch. Agric., Kyushu Univ., 3. Fac. Agric., Kyushu Univ.)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[E1112-4pm-08]

Synthesis of Triarsoles by Rhodium-catalyzed *cyclo*-$(PhAs)_6$ Addition Reaction to Alkynes

○Hiiro Otsuka[1], Mieko Arisawa[2] (1. Grad. Sch. Bioenv Sci., Kyushu Univ., 2. Fac. Agric., Kyushu Univ.)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[E1112-4pm-09]

Rhodium-catalyzed Synthesis of Carbamoylphosphine Derivatives

Kohei Fukumoto[2], ○Xiaoyi Zhang[1], Shinnya Shirakawa[2], Mieko Arisawa[3] (1. Fac. Agric. Kyushu Univ, 2. Grad. Sch. Bioenv Sci. Kyushu Univ, 3. Grad. Sch. Agric. Kyushu Univ)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[E1112-4pm-10]

Enantioselective Synthesis of Tetrahydroindole Derivatives via Rh-Catalyzed [2+2+2] Cycloaddition

○Kairi Yamashiro[1], Fujii Kohei, Koji Masutomi, Ryota Shimotsukue, Yuki Nagashima[1], Ken Tanaka[1] (1. Department of Chemical Science and Engineering, Tokyo Institute of Technology.)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[E1112-4pm-11]

Rhodium-Catalyzed Single Carbon Atom Doping into Acyl Chlorides Using Isocyanide Derivatives.

○Kazuya Imachi[1], Teruki Nishioka[2], Rio Nishimura[3], Hayato Fujimoto[1,4], Mamoru Tobisu[1,4] (1. Graduate School of Engineering, Osaka Univ., 2. School of Engineering, Osaka Univ., 3. Graduate School of Science, Osaka Univ., 4. ICS-OTRI)

Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[E1112-4pm-12]

Enantioselective Synthesis of Axially Chiral 1,8-Diarylnaphthalenes by Rh-Catalyzed [2+2+2] Cycloaddition

○Hinako Nikawa[1], Mamoru Ito[1], Takanori Shibata[1] (1. Waseda University)

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ロジウム触媒を用いるイタコン酸誘導体のアリール化反応の開発

(阪公大院理)○髙辻唯翔・臼杵 克之助・佐藤 哲也
Rhodium(Ⅲ)-Catalyzed Arylation of Itaconic Acid Derivatives (Graduate School of Science, Osaka Metropolitan University) ○Yuito Takatsuji, Yoshinosuke Usuki, Tetsuya Satoh

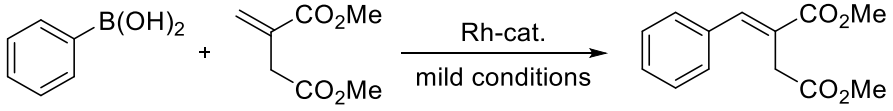
Benzylidenesuccinic acid derivatives have attracted much attention because of their various biological activities as well as of their utility as synthetic intermediates for various functional molecules and natural products. The classical Stobbe condensation and Wittig-type reactions have been used for their synthesis. However, these reactions usually require the addition of strong bases and/or high temperature conditions. In contrast, the catalytic arylation of itaconic acid esters has recently been developed as a useful method for the synthesis of benzylidenesuccinic acids. Itaconic acid is known as one of the bio-based platform chemicals and is therefore, a promising renewable building block. However, its Mizoroki-Heck arylation using aromatic halides as aryl sources still requires high temperature conditions.

We have found that the desired benzylidenesuccinic acid derivative can be synthesized under mild conditions through the rhodium-catalyzed arylation of dimethyl itaconate using phenylboronic acid as an aryl source. Results for the reactions of various arylboronic acids will also be presented.

Keywords : Rhodium catalyst; Benzylidenesuccinic acid; Itaconic acid; Bio-based platform chemicals; Arylation

ベンジリデンコハク酸誘導体は、様々な生物活性を示すことに加えて、種々の機能性分子や天然物の合成中間体として有用であることから近年注目されている化合物群である。その合成には古典的な Stobbe 縮合や Wittig 型反応等が用いられてきたが、強塩基の添加や高温条件などを必要とするため、適用範囲が制限される。これに対し最近、イタコン酸エステル類の触媒的アリール化反応が、有力なベンジリデンコハク酸合成法として注目を集めている。イタコン酸はバイオベースプラットフォーム化学品の一つとして知られ、入手のしやすさ、および有機資源由来である点から有望なビルディングブロックである。しかしそのアリール化には、主に芳香族ハロゲン化物をアリール基源とする溝呂木－Heck 反応が用いられてきたため、依然高温条件が必要とされてきた [1]。

我々はロジウム触媒存在下、フェニルボロン酸をアリール基源としてイタコン酸ジメチルと反応させたところ、温和な条件下で目的のベンジリデンコハク酸誘導体が合成できることを見出した。また多様な置換基を有するフェニルボロン酸の反応についても検討を行ったので併せて発表する。



1) L. Botella, C. Nájera, *J. Org. Chem.* **2005**, *70*, 4360-4369.

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ロジウム/イソシアニド触媒とジボロンを用いたベンゾイルアルケン類の還元的カップリングによるシクロペンタン類の合成

(1. 京都大学) ○中牟田 勇仁[1]、藤田 健一[1]、新林 卓也[1]

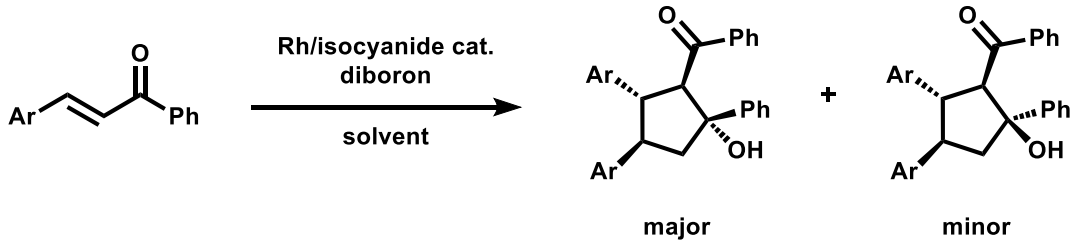
Synthesis of cyclopentanes by reductive coupling of benzoylalkenes in the presence of rhodium/isocyanide catalyst and diboron (1. Kyoto University) ○Yuji Nakamuta[1], Ken-ichi Fujita[1], Takuya Shimbayashi[1]

Reductive coupling reactions of carbonyl compounds are synthetically important carbon-carbon bond-forming transformation, which have been achieved by employing reducing agents such as diborones[1)]. Here, we report reductive dimerization reaction of chalcones, as α,β-unsaturated ketones, leading to cyclopentane derivatives in the presence of a rhodium catalyst with an isocyanide ligand. This reaction shows different stereoselectivity from the previously reported dimerization of chalcones thorough radical reactions using metallic reductants[2),3)], hence, this method is complementary to such ones.
The cyclopentane products were obtained by reductive dimerization reaction of chalcones with B_2pin_2 in toluene using $[Rh(OMe)(cod)]_2$ catalyst and *t*-BuNC ligand.

Keywords : Rhodium Catalyst, Reductive Coupling, Cyclopentanes, Diboron

カルボニル化合物の還元的カップリング反応は、炭素-炭素結合を形成する合成上重要な反応であり、ジボロンを還元剤として用いた還元的カップリング反応が開発されている[1)]。本研究では、イソシアニドを配位子としたロジウム触媒系を用いて、α,β-不飽和ケトンであるカルコンの二量化反応によりシクロペンタン骨格を持つ化合物を合成した。この反応はこれまでに報告されている、金属試薬を用いたラジカル反応によるカルコンの二量化反応[2),3)]とは異なる立体選択性を示しており、既存の合成法と相補的な合成手法である。

$[Rh(OMe)(cod)]_2$ を触媒とし、配位子として *t*-BuNC、還元剤として B_2pin_2 を加え、トルエン中でカルコンを反応させることで二量化体としてシクロペンタン誘導体が得られた。



1) Meyer C. C., Ortiz E., and Krische M. J. *Chemical Reviews* **2020,** *120*, 3721.
2) Cabrera A., Lagadec R. L., Sharma P., Arias J. L., Toscano R. A., Velasco L., Gavino R., Alvarez C., and Salmon M. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 3609.
3) Kumar A., Kumar S., and Kapoor K. K. *Australian Journal of Chemistry*, **2007** *60*, 621.

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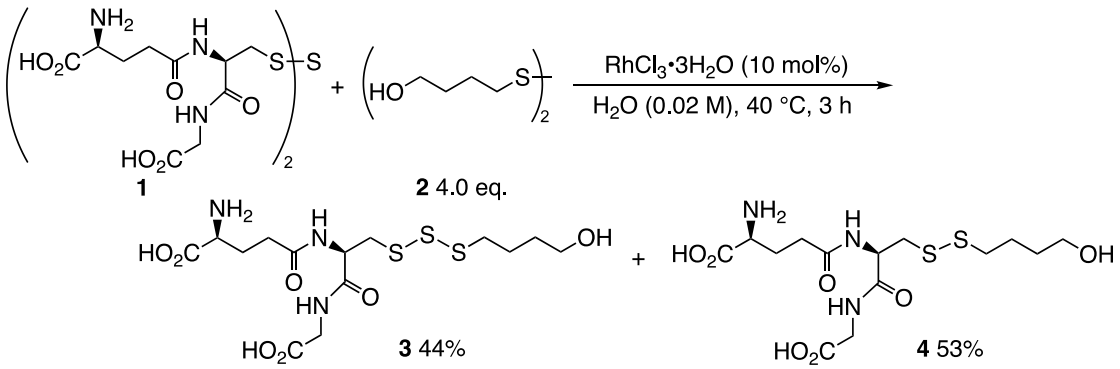
ペプチドトリスルフィドとジスルフィド/ジセレニド化合物とのロジウム触媒交換反応

（九大院生資環[1]・九大農[2]・九大院農[3]）矢崎雅菜[1]・○苑田和大留[2]・有澤美枝子[3]
Rhodium-catalyzed Exchange Reaction between Peptide Trisulfide and Disulfides /Diselenides
([1]*Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University*, [2]*Faculty of Agriculture, Kyushu University,*[3]*Graduate School of Agriculture, Kyushu Univetsity*) Masana Yazaki,[1] ○Wataru Sonoda,[2] Mieko Arisawa[3]

Peptide polysulfides have strong antioxidant activity and are expected to be used as pharmaceuticals. Previously, we reported rhodium-catalyzed synthesis of peptide polysulfides by insertion of sulfur into unprotected peptide disulfides. Rhodium-catalyzed synthesis of unsymmetric polysulfide derivatives containing –S–S–S–/–S–S–Se– bonds using exchange reaction between peptide trisulfide and disulfides/diselenides is found. This method requires the addition of a rhodium catalyst and proceeds in water and under mild conditions.
Keywords : Rhodium-catalyzed exchange; Peptide Trisulfide; Disulfide Compounds; Diselenide Compounds

ペプチドポリスルフィドは強い抗酸化作用を示し、医農薬品としての利用が期待される。当研究室ではこれまでに、無保護ペプチドジスルフィド S–S 結合間へのイオウ原子のロジウム触媒挿入反応を開発した[1]。今回、グルタチオントリスルフィドとジスルフィド/ジセレニド化合物とのロジウム触媒交換反応によって、–S–S–S–/–S–S–Se– 結合を有する非対称ペプチドトリカルコゲニド化合物を簡便に合成する反応を見出した。

$RhCl_3 \cdot 3H_2O$ 触媒 (10 mol%) 存在下、グルタチオントリスルフィド **1** と 4,4'-ジチオビスブタン-1-オール **2** (4.0 eq.) を水中 40 ℃ で 3 時間反応させると、非対称ペプチドトリスルフィド **3** と非対称ペプチドジスルフィド **4** が、それぞれ 44% と 53% の収率で得られた。**3** と **4** は逆相カラムクロマトグラフィーで容易に分離可能である。本反応はロジウム触媒の添加が必須で、温和な水中均一系条件下進行する。水溶性ジセレニドに適用可能で、多様な非対称ペプチドトリカルコゲニド誘導体合成が可能である。



1) Fukumoto, K.; Yazaki, M.; Arisawa, M. *Org. Lett*. **2022**, *24,* 8176.

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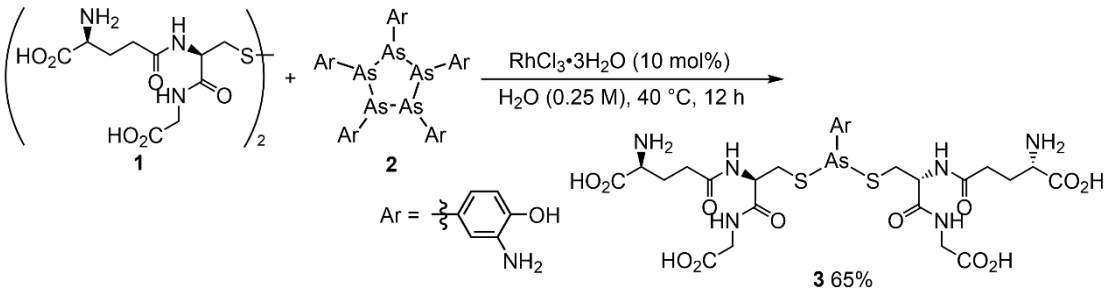
無保護ペプチドジスルフィドへの水中均一系ロジウム触媒アリールアルシン挿入反応

（九大院生資環[1]・九大院農[2]）○矢﨑雅菜[1]・有澤美枝子[2]
Rhodium-catalyzed Insertion Reaction of Arylarsines into Unprotected Peptide Disulfides in Water ([1]*Graduate School of Bioenvironmental Science, Kyushu University*, [2]*Faculty of Agriculture, Kyushu University*) ○Masana Yazaki,[1] Mieko Arisawa[2]

The high affinity of organoarsenic compounds with thiols has be exploited to label two or more cysteine thiols in proteins. Insertion of organoarsenic compounds into cystine disulfide in proteins/peptides has not been reported. Rhodium-catalyzed insertion reaction of arylarsines to unprotected peptide disulfides is developed. This method is applicable to unprotected peptide disulfides containing diverse amino acids, and proceeds under mild conditions in homogenerous water.
Keywords : Organoarsenic Compounds; Rhodium-catalyzed Insertion; Peptide Disulfide; Water; Salvarsan

シスチンジスルフィド S–S 結合間に直接官能基を挿入する化学修飾法は、三次元構造を損なうことなく機能を付与できる点で有用である。当研究室ではこれまでに、無保護ペプチドジスルフィド S–S 結合間へのイオウ原子[1)]およびパーフルオロアリール基[2)]のロジウム触媒挿入反応を報告した。ところで、有機ヒ素化合物はチオールとの親和性が高く、タンパク質中のシステインチオール S–H 結合の標識化剤として利用されている。今回、無保護ペプチドジスルフィド S–S 結合間に直接アリールアルシニル基を挿入するロジウム触媒反応を見出した。これまでに、シスチンジスルフィド S–S 結合間に直接有機ヒ素官能基を挿入した例はない。

$RhCl_3 \cdot 3H_2O$ 触媒 (10 mol%) 存在下、酸化型グルタチオン **1** と環状ポリアルシン化合物 **2** を水中 0.25 M、40 °C で 12 時間反応させると、**1** の S–S 結合間にアリールアルシニル基が挿入した生成物 **3** が収率 65% で得られた。本法は温和な条件下水中均一系で進行し、多様なアミノ酸残基を有する無保護ペプチドジスルフィド[3)]に適用可能である。



1) Fukumoto, K.; Yazaki, M.; Arisawa, M. *Org. Lett.* **2022**, *24*, 8176. 2) Fukumoto, K.; Yazaki, M.; Arisawa, M. *Asian J. Org. Chem.* **2022**, *11*, e202200340. 3) Arisawa, M.; Fukumoto, K.; Yamaguchi, M. *ACS Catal.*, **2020**, *10*, 15060.

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ロジウム触媒による *N*-アリルアミドへの Chain-walking 型ヒドロチオ化反応

（福井大工）○疋田 直樹・鈴木 弘嗣
Rhodium-catalyzed chain-walking hydrothiolation of *N*-allylamides (*School of Engineering, University of Fukui*) ○Naoki Hikida, Hirotsugu Suzuki

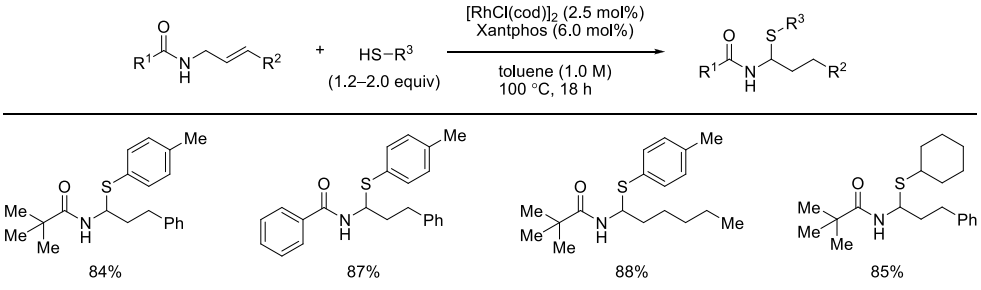
Chain-walking hydrofunctionalization has garnered attention as a versatile method introducing various functional groups into the specific position of organic molecules. Unlike transition metal-mediated C(sp^3)–H bond cleavage, the chain-walking process can introduce nucleophiles under redox-neutral conditions. However, despite recent progress, a chain-walking hydrothiolation remains elusive. Previous reports on chain-walking hydrothiolation have several drawbacks: poor reactivity toward internal alkenes and employment of a hydride source. To approach these problems, we investigated a rhodium-catalyzed chain-walking hydrothiolation.

N-allylamide was reacted with thiol in the presence of $[RhCl(cod)]_2$/xantphos in toluene at 100 °C for 18 h, furnishing the desired *N*,*S*-acetals in high yields. Various thiols and *N*-allylamides participated in this hydrothiolation, indicating good functional group tolerance.

Keywords : Rhodium-catalysts; Hydrothiolation; Thiols; N-Allylamides; Chain-walking

C(sp^3)–H 結合官能基化法として、Chain-walking 型ヒドロ官能基化が近年、注目されている。このプロセスでは、特定の C(sp^3)–H 結合に求核試薬を酸化還元中性条件下で導入でき、原子効率に優れる手法である。しかしヘテロ原子、特に硫黄原子を導入する方法は少なく、これまでに二例しか報告されていない [1]。この二例の反応では、還元剤が必要であることや内部アルケンでは反応が進行しないことなど、改善の余地が残されている。これらの問題を解決すべく、本研究では Rh 触媒による Chain-walking 型ヒドロチオ化反応を検討した。

$[RhCl(cod)]_2$ の存在下、*N*-アリルアミドとトルエンチオールをトルエン溶媒中、100 ℃で 18 時間撹拌した。その結果、目的物である *N*,*S*-アセタールを 84%の収率で得た。また、様々な構造のチオール、*N*-アリルアミドを用いた場合でも反応が進行することを見出した。



1) (a) Zhang, Y.; Xu, X.; Zhu, S. *Nat. Commun*. **2019**, *10*, 1752; (b) Kathe, P. M.; Fleischer, I. *Org. Lett.* **2019**, *21*, 2213.

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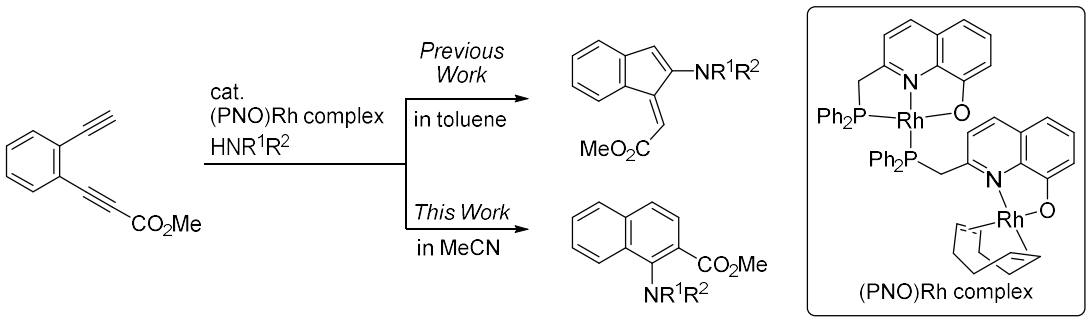
ロジウム触媒を用いた 1,5-ジイン類のヒドロアミノ化環化反応によるナフタレン誘導体の合成

（慶大理工）○後藤 響己・河内 卓彌・垣内 史敏
Synthesis of Naphthalene Derivatives by Rhodium-Catalyzed Hydroaminative Cyclization of 1,5-Diynes (*Faculty of Science and Technology, Keio University*) ○Hibiki Goto, Takuya Kochi, Fumitoshi Kakiuchi

Fischer carbene complexes have often been used in organic synthesis, but stoichiometric amounts of the complexes were required for most of these reactions. There are still only a limited number of reactions involving catalytic construction of Fischer carbene intermediates from simple organic substrates. Our group has reported a hydroaminative cyclization of enynes and 1,6-diynes with secondary amines via (amino)carbene intermediates using rhodium catalysts bearing a phosphine-quinolinolate (PNO) ligand.[1,2] Recently we also found a similar reaction of 1,5-diynes with secondary amines to offer benzofulvene derivatives.[3] Herein we report that a different type of hydroaminative cyclization of the 1,5-diynes with secondary amines using (PNO) rhodium catalysts proceeds to provide naphthalene derivatives depending on the secondary amines and solvents used in this reaction.

Keywords : Rhodium Catalysts, Phosphine-Quinolinolate Ligands, 1,5-Diynes, Secondary Amines, Naphthalene Derivatives

Fischer 型カルベン錯体はしばしば有機合成に利用されてきたが、その多くは化学量論量の対応するカルベン錯体を必要とし、単純な有機分子から Fischer 型カルベン錯体を触媒的に構築し利用した触媒反応の例は少ない。当研究室ではホスフィン–キノリノラト配位子を有するロジウム触媒を用いた、アミノカルベン中間体を経由するエンイン類および 1,6-ジイン類と第二級アミンのヒドロアミノ化環化反応を見出している[1,2]。また最近では、1,5-ジイン類と第二級アミンを用いた同様のヒドロアミノ化環化反応によりベンゾフルベン誘導体が得られることを見出している[3]。今回我々は、本反応において第二級アミンや溶媒の種類を変えることで異なるタイプのヒドロアミノ化環化反応が進行し、ナフタレン誘導体が得られることを見出した。



1) S. Takano, R. Shiomi, Y. Morimoto, T. Kochi, F. Kakiuchi, *Angew. Chem. Int. Ed*. **2020**, *59*, 11754.
2) 塩見亮介, 河内卓彌, 垣内史敏, 日本化学会第 101 春季年会, A15-4pm-08.
3) 後藤響己, 河内卓彌, 垣内史敏, 日本化学会第 103 春季年会, K404-4am-10.

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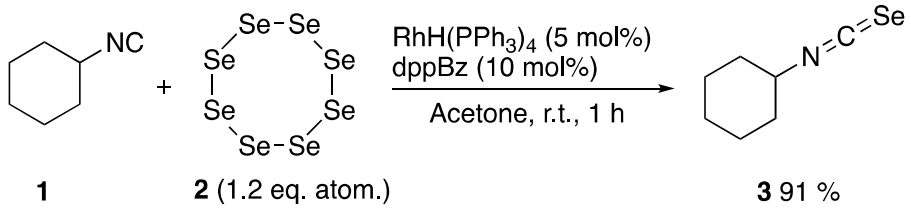
イソニトリルと単体セレンを用いるイソセレノシアネートのロジウム触媒的合成

（九大院生資環[1]・九大農[2]・九大院農[3]）矢﨑雅菜[1]・○後藤貴宏[2]・有澤美枝子[3]
Rhodium-catalyzed synthesis of selenoisocyanates using isocyanides and selenium. ([1]*Graduate School of Bioenvironmental Science, Kyushu University*, [2]*School of Agriculture, Kyushu University*, [3]*Graduate School of Ugriculture, Kyushu University*)Yazaki Masana,[1] ○Goto Takahiro,[2] Arisamwa Mieko[3]

Utilization of selenium is a challenging synthetic methodology for the preparation of organoselenium compounds. Based on this background, we investigated an efficient synthetic method in which elemental selenium Se_8 is activated using a catalytic amount of rhodium complex, and directly converted into useful organoselenium compounds. As a result, the rhodium-catalyzed reaction of selenium Se_8 and isocyanides was found to give selenoisocyanide in high yields.
Keywords : Rhodium-catalyst; isocyanide; organoselenium compounds; Elemental Selenium; selenoisocyanide

イオウと同族のセレンは、抗酸化および抗炎症作用などヒトの生体恒常性に関与する。そのため、有機セレン化合物は医薬用途が高いと考えられるが、あまり利用されていない。これは、有機セレン化合物の合成に不可欠な C–Se 結合の効率的な合成法がほとんどないためである。ところで、単体セレンの中で入手容易な金属セレンは、セレン原子が連なったポリマー構造を有し、有機溶媒に不溶である。そのため本研究では、金属セレンを加熱融解後、二硫化炭素溶媒で抽出および再結晶して得られた八員環単体セレン Se_8 に着目した。これまでに当研究室では、ロジウム触媒を用いて単体イオウ S_8 を直接活性化して有用有機イオウ化合物に変換する方法を多数開発した[1)]。このような背景から今回、ロジウム触媒存在下、単体セレン Se_8 を有機イソシアニドに付加する反応を開発した。

$RhH(PPh_3)_4$ 触媒 (5 mol%) と 1,2-ビス(ジフェニルホスフィノ)ベンゼン (dppBz, 10 mol%) 存在下、シクロヘキシルイソシアニド **1** と単体セレン Se_8 **2** (1.2 equiv. atom) をアセトン中室温で 1 時間反応させると、シクロヘキシルイソセレノシアネート **3** が収率 91% で得られた。本反応は、無塩基条件下速やかに収率よく進行し、複素環やステロイド骨格を有する様々なイソシアニドに適応可能である。



1 **2** (1.2 eq. atom) **3** 91 %

1) Arisawa, M. *et al. Molecules,* **2020**, *25,* 3595; Arisawa, M. *et al. Synlett*, **2019**, *30*, 1621.

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ヘキサフェニルシクロヘキサアルシン *cyclo*-$(PhAs)_6$ のアルキンへのロジウム触媒付加によるトリアルソールの合成

（九大生資環[1]・九大院農[2]）○大塚 陽彩[1]・有澤 美枝子[2]

Synthesis of Triarsoles by Rhodium-catalyzed *cyclo*-$(PhAs)_6$ Addition Reaction to Alkynes

([1]*Grad. Sch. Bioenv Sci., Kyushu Univ.*, [2]*Fac. Agric., Kyushu Univ.*) ○Hiiro Otsuka,[1] Mieko Arisawa[2]

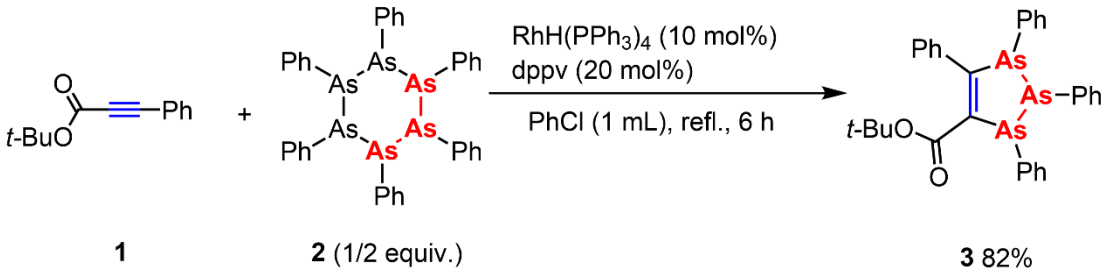
Triarsoles are a unique and novel group of heterocyclic organoarsenic compounds. Rhodium-catalyzed addition reaction of *cyclo*-$(PhAs)_6$ to alkynes gave the corresponding triarsoles in high yields. This reaction is a novel catalytic method for synthesizing diverse triarsoles from *cyclo*-$(PhAs)_6$ and alkynes containing alkyl, aryl and arylthio groups.

Keywords : Rhodium-catalyzed Addition, cyclo-$(PhAs)_6$, Alkyne, Triarsole, C-As bond

五員環複素環は、様々な医薬品や殺虫剤の基幹構造として重要である。1,3-双極子がアルキンなどの不飽和有機化合物に協奏的に付加する 1,3-双極子付加環化反応は、五員環複素環化合物を合成する有力な手法である。しかし、3 原子のヘテロ元素を導入した五員環複素環の合成例は、アジド ($-N_3$) やホスファアジド ($-PN_2R$) などの付加環化反応に限られる。今回、連続した 3 つのフェニルアルシニル PhAs 基をアルキンに付加して As–As–As 結合を有する五員環有機ヒ素化合物のロジウム触媒的合成法を開発した。

$RhH(PPh_3)_4$ 触媒 (10 mol%)と *cis*-1,2-ビス(ジフェニルホスフィノ)エチレン配位子 (dppv, 20 mol%) 存在下、アルキン **1** (1.2 equiv.) とヘキサフェニルシクロヘキサアルシン *cyclo*-$(PhAs)_6$ **2** をクロロベンゼン中加熱還流下 6 時間反応させると、**1** に 3 つの PhAs 基が付加したトリアルソール **3** を収率 82% で与えた (Scheme 1)。本反応にロジウム触媒の添加は必須である。なお、収率良く生成物が得られたことから、*cyclo*-$(PhAs)_6$**2** 中の 6 つの PhAs 基が全て効率的に反応に利用されることが分かった。本反応は多様な置換アルキンに適用可能であり、得られたトリアルソール誘導体 **3** は全て新規化合物である。

Scheme 1



1 **2** (1/2 equiv.) **3** 82%

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カルバモイルホスフィン誘導体のロジウム触媒合成

（九大農学部[1]・九大院生資環[2]・九大院農[3]）福本 昴平[2]・○張 小一[1]・白川 真也[2]・有澤 美枝子[3]

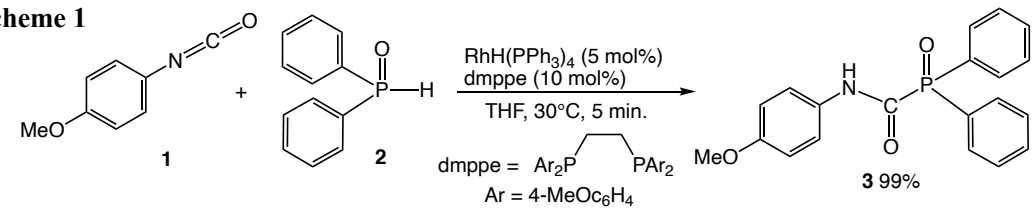
Rhodium-catalyzed synthesis of carbamoylphosphine derivatives *([1]Grad. Sch. Agric. Kyushu Univ, [2]Grad. Sch. Bioenv Sci. Kyushu Univ, [3]Fac. Agric. Kyushu Univ.)* Kohei Fukumoto,[2] ○ Xiaoyi Zhang,[1] Shinnya Shirakawa,[2] Mieko Arisawa[3]

Carbamoylphosphine derivatives in which one nitrogen atom of ureas is replaced with a phosphorus atom, are expected to exhibit biological activities different from corresponding ureas. It was found rhodium-catalyzed synthesis of carbamoylphosphine derivatives using addition of phosphine P–H bond to an isocyanate N=C bond. This method enables the facile synthesis of various alkyl, aryl and heteroaryl carbamoylphosphines under mild conditions.
Keywords : Rhodium catalyst; Carbamoylphosphines; Isocyanates; Phosphines

水素結合可能な NH 基を有する非対称ビス複素環ウレア HetAr–X–HetAr’ 化合物は、タンパク質や核酸等の生体高分子との相互作用が期待できる。当研究室では、HetAr–NHCONH–HetAr’ 化合物の新規合成法を確立し、合成化合物の一部が気孔閉鎖を誘導することを示した[1)]。今回この結果を基に、周期表で窒素と同族のリン原子に着目して、ウレア構造の一方の窒素原子をリン原子に置換したカルバモイルホスフィン誘導体の簡便な合成法を開発した。

カルバモイルホスフィン誘導体の合成にあたって、ロジウム触媒を用いて芳香族イソシアネート C=N 結合への芳香族ホスフィン P–H 結合の触媒的付加反応を検討した。$RhH(PPh_3)_4$ (5 mol%)、1,2-bis{di(4-methoxyphenyl)phosphino}ethane (10 mol%, dmppe) 存在下、*p*-tolylisocyanate **1** と diphenyl phosphine **2** (1 equiv.) をテトラヒドロフラン (0.5 mL) 中 30 度で 5 分間反応させたところ、di(phenylphosphoryl)-*N*-(4-methoxyphenyl)formamide **3** が収率 99% で得られた (Scheme 1)。本反応は、化学量論量の金属塩基の利用が不要で、ロジウム触媒の添加のみで単結合切断と付加が極めて速やかに進行することが特徴である。導入するリン官能基は、5 価脂肪族/芳香族ホスフィンオキシド $R_2P(O)$–H、5 価脂肪族/芳香族ホスファイト $(RO)_2P(O)$–H、および 3 価脂肪族/芳香族ホスフィン R_2P–H のいずれにも適用可能で、多様な脂肪族/芳香族カルバモイルホスフィン誘導体を効率的に合成できることを示した。

Scheme 1



1) Arisawa, M. *et al.*, *Org. Lett.*, **2021**, 23, 9382.

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ロジウム触媒を用いた[2+2+2]付加環化反応によるテトラヒドロインドール誘導体の不斉合成

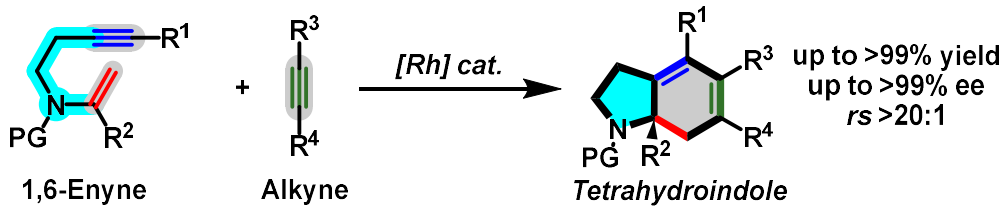
（東工大物質理工[1]）○山城 魁里[1]・藤井 航平[1]・益富 光児[1]・下机 涼太[1]・永島 佑貴[1]・田中 健[1]

Enantioselective Synthesis of Tetrahydroindole Derivatives via Rh-Catalyzed [2+2+2] Cycloaddition ([1] *Department of Chemical Science and Engineering, Tokyo Institute of Technology*)○Kairi Yamashiro,[1] Kohei Fujii,[1] Kouji Masutomi,[1] Ryota Shimotsukue,[1] Yuki Nagashima,[1] Ken Tanaka[1]

Chiral indole reductions with a chiral center on the fused ring carbon are known to possess a variety of biological activities, and numerous synthetic studies have been reported.[1] On the other hand, the transition metal-catalyzed [2+2+2] cycloaddition of 1,6-eneynes with alkynes is atomically efficient and useful for the one-step construction of 5,6-fused ring structures. The [2+2+2] cycloaddition of 5,6-enynes with alkynes is a useful reaction because it is atomically efficient and allows the construction of 5,6-fused ring structures in a single step. In this study, we investigated the development of asymmetric construction of tetrahydroindole skeleton by rhodium-catalyzed [2+2+2] cycloaddition of 3-bridged 1,6-enynes with alkynes. Initially, an efficient and general method for the synthesis of 1,6-enynes was established. The synthesis of tetrahydroindole derivatives was achieved by rhodium-catalyzed [2+2+2] cycloaddition of the obtained 1,6-eneynes with alkynes with high enantio- and regioselectivity. The reaction mechanism was elucidated by control experiments, and the conversion reactions of the products were investigated.

Keywords : Asymmetric Catalysis; Cycloaddition; 1,6-Enynes; Indoles; Rhodium

縮環炭素上に不斉中心を有するキラルインドール還元体は、多様な生物活性をもつことが知られており、多数の合成研究が報告されている[1–2]。一方で、遷移金属触媒を用いた 1,6-エンインとアルキンとの[2+2+2]付加環化反応は原子効率に優れ、5,6-縮環構造を一段階で構築できるため有用な反応である[3]。本研究では、ロジウム触媒を用いた 3 位架橋 1,6-エンインとアルキンとの[2+2+2]付加環化反応によるテトラヒドロインドール骨格の不斉構築の開発を検討した。はじめに、効率的かつ一般的な 1,6-エンインの合成法を確立した。得られた 1,6-エンインとアルキンとのロジウム触媒による[2+2+2]付加環化反応により、高いエナンチオおよび位置選択性でテトラヒドロインドール誘導体の合成を達成した。コントロール実験による反応機構の解明、生成物の変換反応の検討を行った。



1) Wang, S.-G.; Park, S. H.; Cramer, N. *Angew. Chem. Int. Ed.* **2018**, *57*, 5459-5462.
2) Zhang, S.-L.; Zhang, W.-W.; Li, B.-J. *J. Am. Chem. Soc.* **2021**, *143*, 13010.
3) Evans, P. A.; Lai, K. W.; Sawyer, J. R. *J. Am. Chem. Soc.* **2005,** *127*, 12466.

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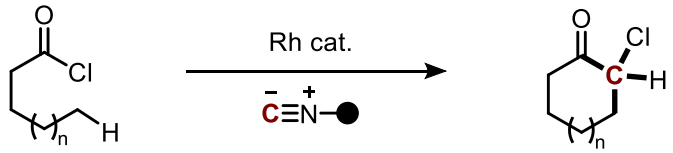
ロジウム触媒による酸塩化物への炭素原子挿入反応

（阪大院工[1]・阪大工[2]・阪大院理[3]・阪大 ICS-OTRI[4]）○井町 和哉[1]・西岡 輝騎[2]・西村 里桜[3]・藤本 隼斗[1,4]・鳶巣 守[1,4]
Rhodium-Catalyzed Single Carbon Atom Doping into Acyl Chlorides Using Isocyanide Derivatives ([1]*Graduate School of Engineering, Osaka Univ.*, [2]*School of Engineering, Osaka Univ.*, [3]*Graduate School of Science, Osaka Univ.*, [4]*ICS-OTRI, Osaka Univ.*) ○Kazuya Imachi,[1] Teruki Nishioka,[2] Rio Nishimura,[3] Hayato Fujimoto,[1,4] Mamoru Tobisu[1,4]

Although several reactions of naked atomic carbons generated by physical or chemical methods have been reported, short life time of an atomic carbon limits its use for practical synthetic purposes. We have previously reported the synthesis of γ-lactam derivatives by an atomic carbon transfer from N-heterocyclic carbenes (NHCs) to α,β-unsaturated amides. We report herein a rhodium-catalyzed single carbon atom doping reaction into acyl chlorides using isocyanide derivatives as an atomic carbon source.
Keywords : Rhodium Catalyst; Isocyanide; Acyl Chloride; Carbon Atom Insertion

これまで、一炭素増炭反応に用いる試薬が数多く開発されてきたが [1]、最も単純な C1 源である原子状炭素は、有機合成の観点からはほとんど検討されていない。物理的手法により発生した原子状炭素の反応 [2]や、不安定前駆体から原子状炭素を化学的に遊離させて反応させる例 [3]はあるものの、原子状炭素の不安定性から実用的な合成展開には限界があった。最近われわれは、N-ヘテロ環状カルベン（NHC）を原子状炭素等価体として用いる α,β-不飽和アミドから γ-ラクタム誘導体への変換反応を報告した [4]。今回、ロジウム触媒下でイソシアニド誘導体と酸塩化物とを反応させると、炭素原子挿入反応が進行し、環状生成物が得られることを見出した。



catalytic single-carbon atom doping reaction

1) Review: L. Castoldi.; S. Monticelli.; R. Senatore.; L. Ielo.; V. Pace. *Chem. Commun.* **2018**, *54*, 6692.
2) For example: B. M. Armstrong.; F. Zheng.; P. B. Shevlin. *J. Am. Chem. Soc.* **1998**, *120*, 6007.
3) For example: P. B. Shevlin. *J. Am. Chem. Soc.* **1972**, *94*, 1379.
4) (a) M. Kamitani.; B. Nakayasu.; H. Fujimoto.; K. Yasui.; T. Kodama.; M. Tobisu. *Science* **2023**, *379*, 484. (b) H. Fujimoto.; B. Nakayasu.; M. Tobisu. *J. Am. Chem. Soc.* **2023**, *145*, 19518.

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ロジウム触媒を用いた[2+2+2]付加環化反応による軸不斉 1,8-ジアリールナフタレンのエナンチオ選択的合成

（早大先進理工）○二川 日菜子・伊藤 守・柴田 高範

Enantioselective Synthesis of Axially Chiral 1,8-Diarylnaphthalenes by Rh-Catalyzed [2+2+2] Cycloaddition (*School of Advanced Science and Engineering, Waseda University*) ○Hinako Nikawa, Mamoru Ito, Takanori Shibata

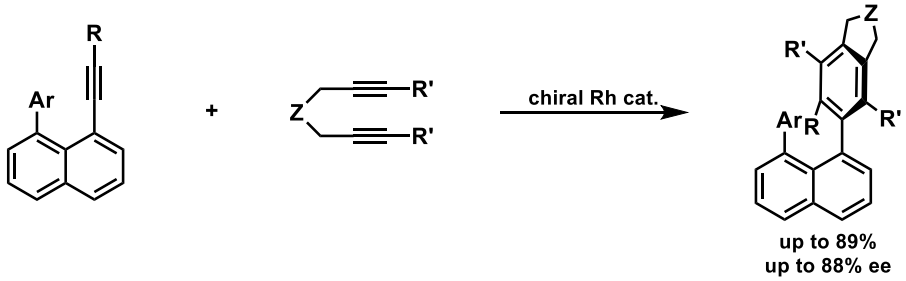
The π-π interaction occurs between the two aryl groups in 1,8-diarylnaphthalenes due to non-free rotation of them. Furthermore, introduction of unsymmetric aryl groups induces axial chirality. Thus, their use as chiral luminescent scaffolds and chiral ligands are anticipated.[1] Various synthetic methods using transition metal catalysis such as Suzuki-Miyaura and Stille couplings have been reported, and asymmetric synthesis via optical resolution was also reported.[2] Against this background, we investigated an enantioselective synthesis of axially chiral 1,8-diarylnaphthalenes by Rh-catalyzed [2+2+2] cycloaddition.

In the presence of a chiral rhodium catalyst, [2+2+2] cycloaddition of diynes and naphthalenes with aryl and alkynyl groups at their peri-positions gave axially chiral 1,8-diarylnaphthalenes in good yield and ee.

Keywords : Rhodium Catalyst; [2+2+2] Cycloaddition; Axial Chirality; 1,8-Diarylnaphthalenes

1,8-ジアリールナフタレン類は、アリール基が自由回転できないため、2 つのアリール基間にπ-π相互作用が生じ、さらに非対称なアリール基を導入すると軸不斉が誘起される。そのため、発光性キラル素子やキラル配位子などへの応用が期待されている [1]。これまで鈴木・宮浦カップリングや Stille カップリングなど遷移金属触媒を利用した合成法が多く報告されており、光学分割による不斉合成も知られている [2]。そこで我々は、ロジウム触媒を用いた[2+2+2]付加環化反応による軸不斉 1,8-ジアリールナフタレンのエナンチオ選択的合成を目指した。

本研究では、キラルなロジウム触媒存在下、ペリ位にアリール基とアルキニル基を持つナフタレンとジインを反応させると[2+2+2]付加環化反応が進行し、軸不斉 1,8-ジアリールナフタレンが良好な収率および不斉収率で得られた。



1) A. V. Gulevskaya, E. A. Ermolenko, *Eur. J. Org. Chem.* **2022**, *48*, 1-58.
2) H. Ghosh, R. Vavilala, A. M. Szpilman, *Tetrahedron: Asymmetry* **2015**, *26*, 79–84.

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Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds-：Oral B

Thu. Mar 21, 2024 9:30 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:30 AM UTC
E1111(1111, Bldg. 11 [1F])

[E1111-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Akihito Konishi, Masaharu Ueno

English
9:30 AM - 9:50 AM JST | 12:30 AM - 12:50 AM UTC
[E1111-4am-01]

Synthesis of Cage-shaped Borate with Heteroaromatics for Selective Activation of Aromatic Aldehydes

○Yuya Tsutsui[1], Akihito Konishi[1,2], Makoto Yasuda[1,2] (1. Osaka University, Graduate School of Engineering, 2. ICS-OTRI)

English
9:50 AM - 10:10 AM JST | 12:50 AM - 1:10 AM UTC
[E1111-4am-02]

In-Silico-Assisted Derivatization of Triarylboranes for the Catalytic Reductive Functionalization of Amino Acids with H_2

○Yusei Hisata[1], Takashi Washio[2], Shinobu Takizawa[3], Ogoshi Sensuke[1], Yoichi Hoshimoto[1,4] (1. Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2. Department of Reasoning for Intelligence and Artificial Intelligence Research Center, SANKEN, Osaka University, 3. Department of Synthetic Organic Chemistry and Artificial Intelligence Research Center, SANKEN, Osaka University, 4. Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University)

English
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC
[E1111-4am-03]

Anti-Selective 1,2-Diboration of Alkynes by Using Potassium Reductants

○Ziwei Zhang[1], Takashi Kurogi[1], Hideki Yorimitsu[1] (1. Kyoto university)

10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC

Break

English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[E1111-4am-04]

Stereoselective Hydroxyallylation of Cyclopropenes with Cyclopropanols via NHC Control of Enolized Zinc Homoenolate

○Kento Tsukiji[1], Kazuya Kanemoto[1], Arimasa Matsumoto[2], Yoshikai Naohiko[1] (1. Tohoku Univ, 2. Nara Women's Univ)

Japanese
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[E1111-4am-05]

Zn/F Carbenoids: Preparation, Stability, Structure, and Application to Nucleophilic Monofluoroalkylation

○Kohei Miyamoto[1], Emiko Kawaguchi[1], Kazuhiro Morisaki[1], Yoshihiro Sato[1] (1. Fac. Pharm. Sci., Hokkaido Univ.)

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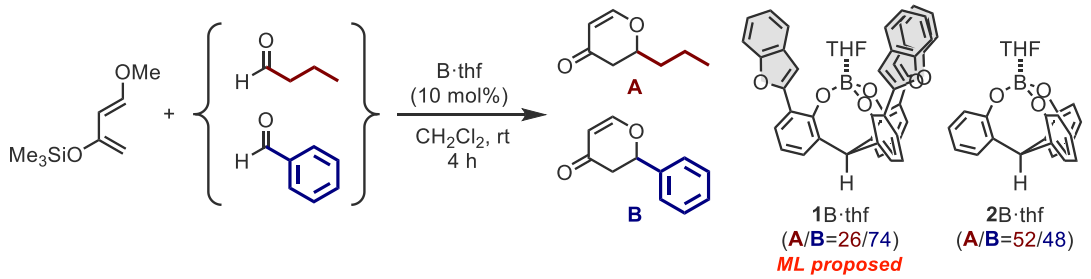
Synthesis of Cage-shaped Borate with Heteroaromatics for Selective Activation of Aromatic Aldehydes

([1]*Graduate School of Engineering, Osaka University*, [2]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI),Osaka University*)
○Yuya Tsutsui,[1] Akihito Konishi,[1,2] Makoto Yasuda[1,2]
Keywords: Lewis Acid Catalyst; Molecular Recognition; Boron Complex; Heterocyclic Ring; Machine Learning

A selective recognition of hydrocarbon moieties has been a longstanding issue for organic synthesis. We have been developing the π-pocket Lewis acid catalyst distinguishing between aliphatic and aromatic aldehydes with nearly identical electronic and steric properties.[1] Although the correlation between catalyst structure and selectivity have been confirmed by many experimental results,[2] conventional knowledge such as the steric or electrostatic environment of the π-pocket cannot explain this correlation. This may be because molecular recognition is defined by multiple cooperative non-covalent interactions within the π-pocket. Recent advances in machine learning (ML) applications to organic synthetic chemistry have significantly contributed to the predictions of yields and selectivities.[3] Since the underlying patterns and relationships in multiple chemical factors of the π-pocket catalyst should be analyzed and explored by data-driven methods, the application of ML may provide insight to design the π-pocket catalyst.

Using 7963 explanatory variables extracted from model hetero-Diels–Alder reactions, the ensemble algorithm predicted the chemoselectivity of unlearned borate catalysts. The catalyst **1**B·thf having three 2-benzofuryl groups around boron center, which is predicted to show high selectivity, exhibits the highest selective recognition of aromatic aldehydes in the inter- and intramolecular competitive hetero Diels-Alder reactions. Furthermore, a shapley additive explanations (SHAP) method clarified that the selectivity originates from the three-dimensional size weighted by the polarizability of the catalyst. These insights provide an evocative principle for the design of Lewis acid catalysts with non-covalent interactions.



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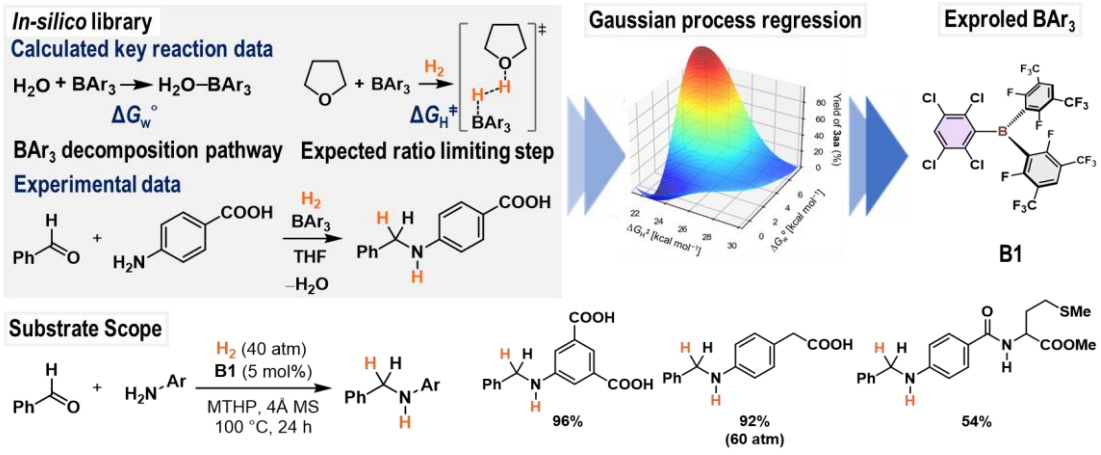
In-Silico-Assisted Derivatization of Triarylboranes for Catalytic Reductive Functionalization of Amino Acids with H_2

([1]*Department of Applied Chemistry, Faculty of Engineering, Osaka University,* [2]*Department of Reasoning for Intelligence and Artificial Intelligence Research Center, SANKEN, Osaka University,* [3]*Department of Synthetic Organic Chemistry and Artificial Intelligence Research Center, SANKEN, Osaka University,* [4]*Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University*) ○Yusei Hisata,[1] Takashi Washio,[2] Shinobu Takizawa,[3] Sensuke Ogoshi,[1] Yoichi Hoshimoto[1,4]

Keywords: Triarylboranes, Amino Acids, Gaussian process regression, Machine lerning, Reductive alkylation

Compared with the approach to the development of the Lewis base such as phosphine and *N*-heterocyclic carbenes, the application of machine learning (ML) in catalytic reactions using Lewis-acidic main-group elements has been constrained due to the absence of candidate library and effective parameters for the prediction of the activity of main-group elements. In this study, we report the development of a triarylborane (BAr_3) library and its application in an ML-assisted approach for the reductive alkylation of amine with H_2.[1] As reactions for collecting experimental data, amino acids containing carboxy groups that could potentially quench reactivity of FLP even under high-pressure H_2 and for long reaction time were applied. More than 50 kinds of BAr_3 from the library were theoretically applied for the prediction of turnover frequencies (TOF) based on the GPR analysis to demonstrate that the deformation energy can be a useful parameter.[2] The reaction system with optimal catalyst **B1** and 4-Methyltetrahydropyran (MTHP) as Lewis base and solvent showed a broad substrate scope, including aromatic amino acids with aniline moieties and peptide compounds.



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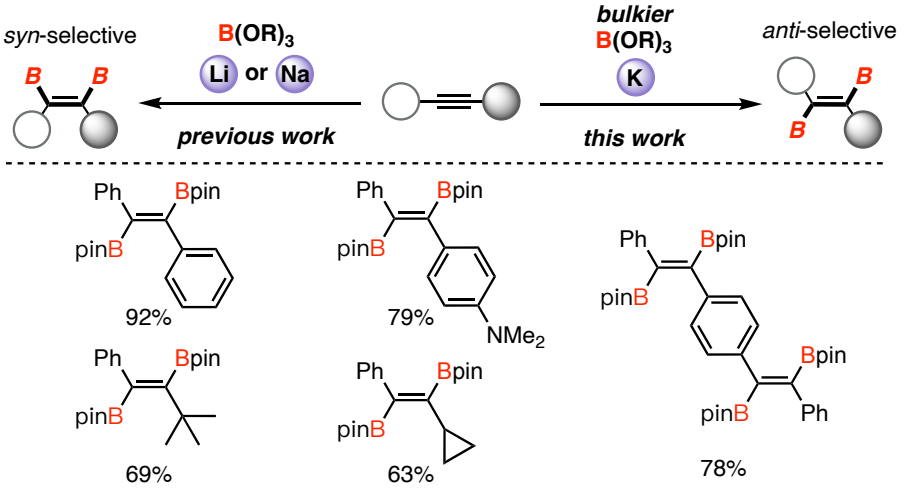
カリウム還元剤を用いたアルキンの *anti*-二重ホウ素化

（京大院理）○張 紫薇・黒木 尭・依光 英樹
Anti-Selective 1,2-Diboration of Alkynes by Using Potassium Reductants (*Graduate School of Science, Kyoto University*) ○Ziwei Zhang, Takashi Kurogi, Hideki Yorimitsu

The stereoselective synthesis of 1,2-diborylalkenes has attracted attention in organic synthesis since they can be further transformed into a diverse range of pharmaceuticals and functional materials. Therefore, the development of efficient stereoselective methods for synthesizing of 1,2-diborylalkenes is very important. Recently, we have developed a reductive *syn*-1,2-diboration of alkynes with lithium- or sodium-based reductants in the presence of trialkoxyborane as a reduction-resistant electrophile.[1] Herein, we report that the stereoselectivity is reversed by the use of potassium-based reductants instead of lithium- or sodium-based ones. Reduction of alkynes with potassium naphthalenide in the presence of bulky trialkoxyborane such as *i*PrOBpin resulted in *anti*-1,2-diboration exclusively to afford *trans*-1,2-diborylalkenes. The role of the countercation for the stereoselectivity will be discussed in this presentation.
Keywords : 1,2-diboration; stereocontrol; alkali metal arenide; single-electron reduction

1,2-ジボリルアルケンは医薬品や機能性材料中に多くみられる多置換アルケンの有用な合成前駆体であり、その立体選択的合成法の開発は重要である。近年我々は、一電子還元に耐えうるトリアルコキシボランの共存下、リチウムまたはナトリウム還元剤を用いたアルキンの還元的 *syn*-二重ホウ素化を報告した。[1] 今回我々は、カリウム還元剤を作用させると、二重ホウ素化の立体選択性が逆転することを発見した。すなわち、アルキンに対し嵩高いホウ素求電子剤である *i*PrOBpin の共存下でカリウムナフタレニドを作用させたところ、*anti*-二重ホウ素化が進行し、*trans*-ジボリルアルケンが単一の立体異性体として生成した。立体選択性に対する対カチオンの効果についても本発表中で議論する。



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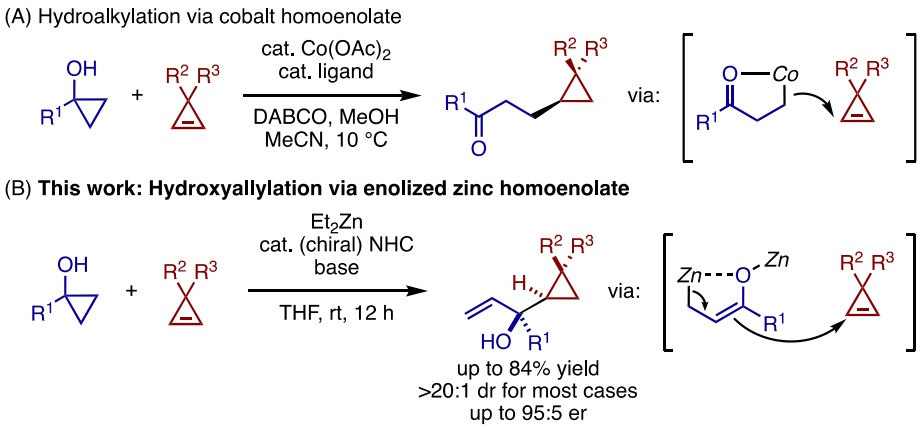
Stereoselective Hydroxyallylation of Cyclopropenes with Cyclopropanols via NHC Control of Enolized Zinc Homoenolate

([1]*Graduate School of Pharmaceutical Science, Tohoku University*, [2]*Faculty of Science, Nara Women's University*) ○Kento Tsukiji,[1] Kazuya Kanemoto,[1] Arimasa Matsumoto,[2] Naohiko Yoshikai[1]

Keywords: Cyclopropene; Cyclopropanol; Organozinc Compound; NHC

Cyclopropanes are important building blocks in medicinal chemistry and useful as versatile synthetic building blocks in organic synthesis. Besides the well-established methods for cyclopropanation, the addition to the C=C bond of cyclopropenes is an attractive approach to constructing densely functionalized cyclopropanes. While various stereoselective carbofunctionalization reactions of cyclopropenes have been developed over the last few decades, the addition reaction of cyclopropenes with prochiral nucleophiles, which generates a new stereogenic center outside the cyclopropane ring, remains rare.

Recently, Meng and co-workers reported a cobalt-catalyzed enantioselective hydroalkylation of cyclopropenes with cyclopropanols (**Scheme A**).[1] The reaction is believed to involve a cobalt homoenolate, which is generated through the ring-opening of a cobalt cyclopropoxide. Herein, we report on a zinc-mediated hydroxyallylation reaction of the same reactants that involves an "enolized zinc homoenolate,"generated in equilibrium via deprotonation of a zinc homoenolate, as a prochiral nucleophile (**Scheme B**). The reaction is enabled by *N*-heterocyclic carbene (NHC)-accelerated catalysis and affords densely functionalized cyclopropanes with excellent diastereocontrol over three contiguous stereocenters, including one outside the cyclopropane ring. Furthermore, an enantioselective variant of this hydroxyallylation has been achieved using a chiral NHC. In the presentation, we will discuss the details of the reaction optimization, the full substrate scope, the enantioselective variant, the plausible mechanism, and the synthetic utility.



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亜鉛/フッ素カルベノイド： 調製、安定性、構造および求核的モノフルオロアルキル化反応への応用

（北大院薬 [1]）○宮本 公平 [1]・川口 瑛美子 [1]・森崎 一宏 [1]・佐藤 美洋 [1]
Zn/F Carbenoids: Preparation, Stability, Structure, and Application to Nucleophilic Monofluoroalkylation ([1]*Fac. Pharm. Sci., Hokkaido Univ.*) ○Kohei Miyamoto,[1] Emiko Kawaguchi,[1] Kazuhiro Morisaki,[1] Yoshihiro Sato[1]

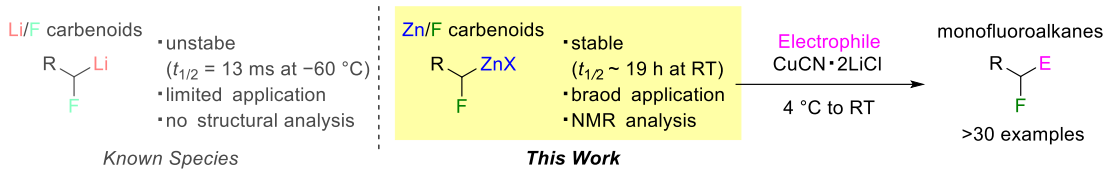
Whereas carbenoids have been recognized as important reactive intermediates, studies on metal/fluorine carbenoids have been quite limited due to their instability. For example, lithium/fluorine carbenoids[1] have lifetime of 13 ms at −60 ℃, limiting their synthetic utilities as well as investigation of their chemical properties.

In this study, we have revealed that zinc/fluorine carbenoids can be prepared without cryogenic conditions. Their half-life times are around ten hours at ambient temperature, representing a more than 10^6-fold increase compared to that of lithium/fluorine carbenoids. Zinc/fluorine carbenoids can be applied to various coupling reactions with the assistance of copper reagents, offering a concise access to various monofluoroalkanes with functional groups at the α-position of the fluorine. We also succeeded in detailed NMR structural and kinetic analysis of zinc/fluorine carbenoids.
Keywords : Carbenoid; Fluorine; Zinc; Monofluoroalkylation

金属/フッ素カルベノイドは不安定であるため、その物性や応用に関する研究が限られていた。例えば、リチウム/フッ素カルベノイド[1]の寿命は−60 ℃でわずか 13 ms であり非常に安定性に乏しい。そのため反応に応用するためには、極低温で調製後速やかに他の求電子剤と反応させる必要がある。

そこで今回我々は、比較的電気陰性度の大きく、フッ素との結合エネルギーが小さい亜鉛に着目し、対応する金属/フッ素カルベノイドである「亜鉛/フッ素カルベノイド」に関する検討を行った。

検討の結果、亜鉛/フッ素カルベノイドは容易に調製可能であり、室温で数時間の半減期を有することが分かった。これは従来のリチウム/フッ素カルベノイドよりも 100 万倍以上の半減期である。また、本試薬はシアン化銅の存在下、様々なカップリング反応にも適応可能であった。これにより、フッ素の α 位に官能基を有する様々なモノフルオロアルカンの収束的合成が可能となった。さらに我々は、本カルベノイドの NMR 解析にも成功したので併せて報告する。



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Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- : Oral B

Thu. Mar 21, 2024 9:30 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:30 AM UTC
E1112(1112, Bldg. 11 [1F])

[E1112-4am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Ken-Ichi Fujita, Shogo Kuriyama

Japanese
9:30 AM - 9:50 AM JST | 12:30 AM - 12:50 AM UTC
[E1112-4am-01]

Catalytic Borylation of C(sp^3)-H Bonds of Ethers by Iron Complexes with Anionic PCP-type Pincer Ligands

○Shogo Kuriyama[1], Ken Sakata[2], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo, 2. Faculty of Pharmaceutical Sciences, Toho University)

English
9:50 AM - 10:10 AM JST | 12:50 AM - 1:10 AM UTC
[E1112-4am-02]

Decarboxylative Functionalization of Carboxylic Acids with Easily Oxidizable Functional Groups Catalyzed by Iron Complexes under Photo-irradiation

○Sota Tamaki[1], Tetsuro Kusamoto[1], Hayato Tsurugi[1] (1. Graduate School of Engineering Science, Osaka Univ.)

English
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC
[E1112-4am-03]

Iron-Catalyzed C–H Functionalization of Aromatic Ketones via Enyne Cyclization

○Yoichi Kitazawa[1], Takuya Kochi[1], Fumitoshi Kakiuchi[1] (1. Keio University)

10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC

Break

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[E1112-4am-04]

Effects of chalcogen elements in the ligand on the olefin metathesis activity of Hoveyda-Grubbs-type catalysis

○Tsubasa Kinugawa[1], Shun Hirota[1], Takashi Matsuo[1] (1. Div. Mat. Sci., NAIST)

English
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[E1112-4am-05]

Ruthenabicyclic Borohydride Complexes (RUCY®-BH) for Asymmetric Hydrogenation of Ketones and Asymmetric Formal Hydroamination of Allylic Alcohols under Base-Free Conditions

○Tomohiro Ishizaka[1], Yuji Nakayama[1], Taichiro Touge[1], Yamato Yuki[1], Kazuhiko Matsumura[1], Taiga Yurino[2,3], Takeshi Ohkuma[2,3] (1. Takasago International Corporation, 2. Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center, Hokkaido University)

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アニオン性 PCP 型ピンサー配位子を有する鉄錯体を触媒としたエーテル類の C(sp^3)–H 結合ホウ素化反応

（東大院工[1]・東邦大薬[2]）○栗山 翔吾[1]・坂田 健[2]・西林 仁昭[1]

Catalytic Borylation of C(sp^3)-H Bonds of Ethers by Iron Complexes with Anionic PCP-type Pincer Ligands

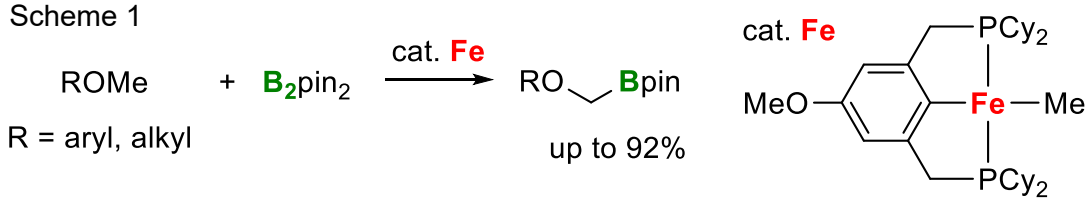
([1]*School of Engineering, The University of Tokyo,* [2]*Faculty of Pharmaceutical Sciences, Toho University*) ○Shogo Kuriyama,[1] Ken Sakata,[2] Yoshiaki Nishibayashi[1]

Recently, C–H borylation by earth-abundant metals such as iron has received much attention. We previously found that iron complexes with anionic PCP-type pincer ligands worked as effective catalysts toward C–H borylation of arenes. As an extensive study, we have found that novel iron complexes bearing anionic PCP-type pincer ligands with electron-donating groups worked as more efficient catalysts for C–H borylation, where various aryl and alkyl ethers underwent borylation at C(sp^3)–H bonds. The results of stoichiometric reactions of these iron complexes will be presented.

Keywords : Iron Complex; C–H Activation; C–H Borylation; Pincer Ligand

有機合成において有用な合成中間体である有機ホウ素化合物を直截的に得る手段として、遷移金属触媒を用いた C–H 結合ホウ素化反応が活発に研究されている。近年では、イリジウム等の貴金属触媒に代わり安価で豊富な鉄を触媒に用いた C–H ホウ素化反応が注目されている。最近、当研究室ではアニオン性 PNP 型ピンサー配位子を有する鉄メチル錯体が芳香環の C(sp^2)–H 及びアニソール類のメトキシ基 C(sp^3)–H ホウ素化に対して有効な触媒として働くことを報告した[1]。また以前に我々はアニオン性 PCP 型ピンサー配位子を有する鉄錯体の合成と C–H 結合ホウ素化反応への反応性を報告した[2]。今回、ピンサー配位子に電子供与性基を導入した鉄錯体がより高活性な C–H ホウ素化反応の触媒として働き、様々なアリールおよびアルキルエーテル類の C(sp^3)–H 結合のホウ素化反応が進行することを見出した (Scheme 1)。鉄錯体の化学量論反応によって反応中間体についての知見も得られたので、合わせて発表予定である。

Scheme 1



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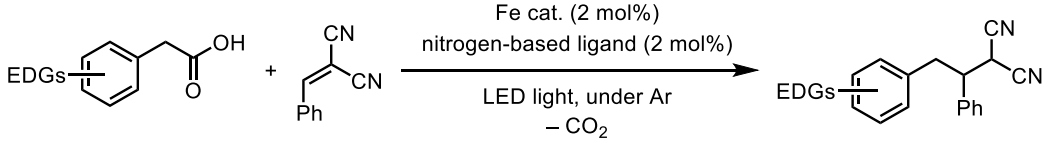
Decarboxylative Functionalization of Carboxylic Acids with Easily Oxidizable Functional Groups Catalyzed by Iron Complexes under Photo-irradiation

(*Graduate School of Engineering Science, Osaka University*) ○ Sota Tamaki, Tetsuro Kusamoto, Hayato Tsurugi

Keywords: Photocatalyst; Iron Complex; Carboxylic Acid; Phenol; Amino Acid

Decarboxylation of aliphatic carboxylic acids for generating alkyl radicals has attracted attention in radical-mediated organic synthesis due to the abundance and versatility of the carboxylic acids.[1] Single-electron oxidation of carboxylate anions by anodic oxidation or photocatalysis has been developed for generating carboxylate radicals as the key intermediates prior to the decarboxylation; however, oxidation of the carboxylate anions leads to degradation of easily oxidizable functional groups such as phenol and indole groups bound to the carboxylic acids, resulting in a limitation of substrate applicability.[2] In this regard, photo-induced homolysis of metal–carboxylate covalent bonds is a suitable method to avoid the undesired oxidation of the easily oxidizable functional groups during the carboxylate radical generation.[3] Herein, we report that decarboxylative C–C bond formation of carboxylic acids having phenol and indole functionalities is achieved by a catalytic amount of iron(III) salt and nitrogen-based ligand under visible light irradiation. Treatment of 4-hydroxyphenylacetic acid with benzylidenemalononitrile (1.5 equiv.) in the presence of iron salt (2 mol%) and nitrogen-based ligand (2 mol%) under argon atmosphere with 427 nm blue LED irradiation (45 W) resulted in the formation of 2-(2-(4-hydroxyphenyl)-1-phenylethyl)malononitrile in 95% yield. Other arylacetic acids with electron-donating substituents on the aromatic ring were applicable under the similar reaction conditions by changing the wavelength of the light source. In addition, various *N*-protected amino acids served as functionalized alkyl radical sources. Optimization of the reaction conditions, scope of the substrates, and details on the catalytically active species are disclosed in this presentation.



EDGs = electron-donating groups

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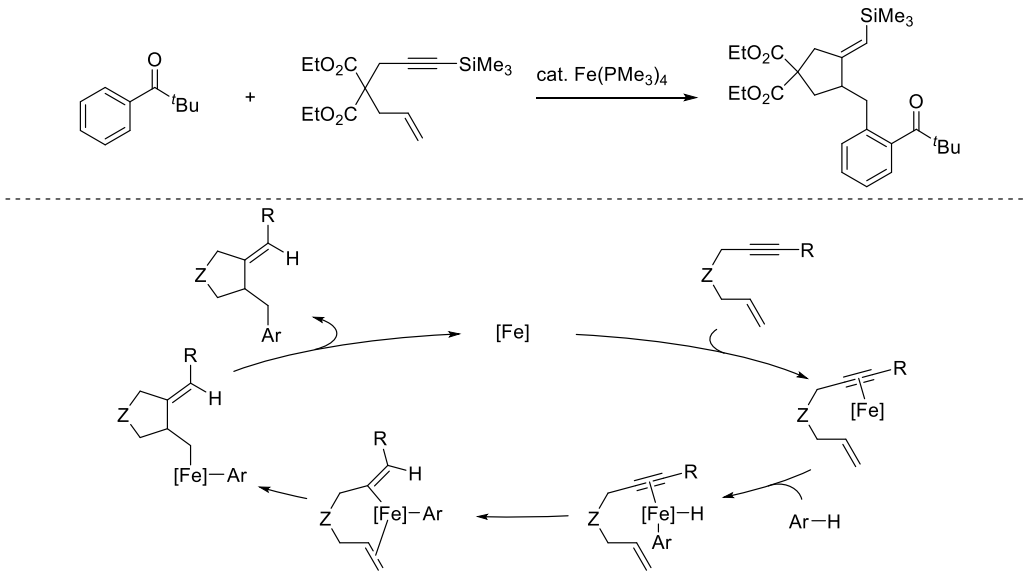
Iron-Catalyzed C–H Functionalization of Aromatic Ketones via Enyne Cyclization

(*Faculty of Science and Technology, Keio University*) ○Yoichi Kitazawa, Takuya Kochi, Fumitoshi Kakiuchi

Keywords: *Iron Catalyst; C–H Bond Cleavage; Aromatic Ketones; Enynes; Cyclization*

C–H functionalizations using iron catalysts have been widely studied, but expansion of its scope is still desired.[1] Our group has found that an iron phosphine complex, $Fe(PMe_3)_4$, catalyzes ortho-selective C–H/olefin and C–H/alkyne couplings of aromatic ketones.[2] Here we report that the iron complex also catalyzes a C–H functionalization of aromatic ketones via enyne cyclization.

When the reaction of pivalophenone with 1,6-enyne containing an internal alkyne and a terminal alkene moiety was carried out using a catalytic amount of $Fe(PMe_3)_4$, hydroarylative enyne cyclization proceeded to give a methylenecyclopentane derivative by regioselectively introducing hydro and phenyl groups onto the alkyne and the alkene moieties, respectively. This reaction is considered to proceed via coordination of the alkyne moiety of the enyne to the Fe center, oxidative addition of the ortho C–H bond of the ketone, regioselective insertion of the alkyne moiety into the Fe–H bond, cyclization by subsequent insertion of the alkene moiety, and reductive elimination.



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Hoveyda-Grubbs 型触媒のオレフィンメタセシス活性に対するベンジリデン配位子上のカルコゲン元素の効果

（奈良先端大・物質創成 [1]）○衣川 翼 [1]・廣田 俊 [1]・松尾 貴史 [1]

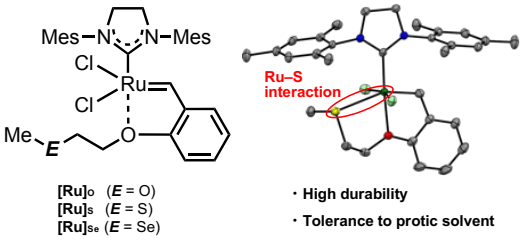
Effect of a Sulfur Atom in the Benzylidene Ligand of Hoveyda-Grubbs-type Complexes on Their Catalytic Activities ([1]*Dvision of Material Science of Science and Technology , Nara Institute of Science and Technology*) ○Tsubasa Kinugawa,[1] Shun Hirota,[1] Takashi Matsuo.[1]

Hoveyda-Grubbs second generation complex (HG-II) is a catalyst for olefin metathesis reactions. Various derivatives of HG-II have been developed to regulate the complex reactivities. We previously reported that an HG-type complex with an ethyleneamide group in the benzylidene ligand controls its reactivities through second-coordination sphere effect with a hydrogen bond between the amide moiety and a chlorido ligand.[1)] In this study, we have investigated the chalcogen atom effects in the phenoxy terminal of benzylidene ligand on the complex structures and reactivities. The complex with a sulfur atom at the phenoxy moiety was found to suppress the catalyst decomposition with the Ru–S interaction, resulting in the tolerance in polar solvents.[2)] Moreover, we extended the study to the HG-type complex with selenium atom (**[Ru]$_{Se}$**) and investigated its reactivities.

Keywords : Hoveyda-Grubbs 2nd generation catalyst; *Olefin Metathesis*; *Chalcogen Elements*; *Ruthenium–Chalcogen Element Interaction*

Hoveyda-Grubbs 第 2 世代錯体(HG-II)は、*N*-ヘテロカルベン配位子とベンジリデン配位子を有するオレフィンメタセシス触媒であり、熱的安定性の高さに起因する利便性から、さまざまな構造修飾様式による反応性の制御が試みられている。以前、我々は、ベンジリデン配位子のフェノキシ部位末端にアミド部位を導入することで、第 2 配位圏効果によって錯体の安定性および反応性制御が可能であることを報告した [1)]。そこで本研究では、16 族元素(O, S)を導入したベンジリデン配位子を有する錯体 **[Ru]$_O$**, **[Ru]$_S$** を合成し、それらの構造と触媒活性について検証した [2)]。

硫黄原子を有するベンジリデン配位子と HG-II 錯体を 1:1 の化学量論比で配位子交換反応を行ったところ、錯体**[Ru]$_S$**の収率が 50%を超えたことから、**[Ru]$_S$** は HG-II 錯体よりも安定であることが分かった。また錯体の結晶構造から、配位子末端の S 原子と中心金属の相互作用が錯体の安定化に寄与し、極性溶媒存在下における触媒反応では、触媒の分解が抑制され、HG-II 触媒よりも高い反応活性を示した [2)]。さらに我々は、セレン (Se)元素を導入したホベイダ配位子と錯体 **[Ru]$_{Se}$** を合成し、その反応活性についても調査した。



1) T. Matsuo *et al*, *Dalton Trans*., **2020**, *49*, 11618. 2) T. Matsuo *et al*, *Dalton Trans*., **2023**, *52*, 9499.

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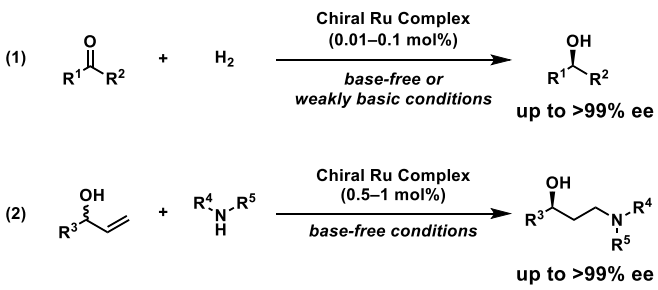
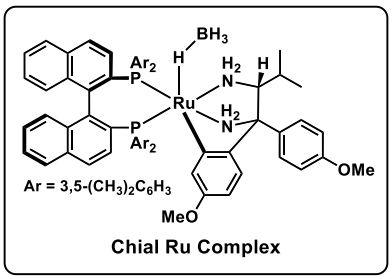
Ruthenabicyclic Borohydride Complexes (RUCY®-BH) for Asymmetric Hydrogenation of Ketones and Asymmetric Formal Hydroamination of Allylic Alcohols under Base-Free Conditions

([1]*Takasago International Corporation*, [2]*Division of Applied Chemistry, Faculty of Engineering, Hokkaido University,* [3]*Frontier Chemistry Center, Hokkaido University*)
○ Tomohiro Ishizaka,[1] Yuji Nakayama,[1] Taichiro Touge,[1] Yamato Yuki,[1] Kazuhiko Matsumura,[1] Taiga Yurino,[2,3] Takeshi Ohkuma[2,3]
Keywords: Ruthenium; Borohydride Ligand; Base-Free Condition; Asymmetric Hydrogenation; Asymmetric Hydroamination

Catalytic asymmetric hydrogenation of ketones is a well-known method to obtain chiral secondary alcohols. We have previously reported an extremely rapid and enantioselective hydrogenation of ketones using the ruthenabicyclic complex RuCl(daipena)(xylbinap)/base catalyst system.[1] However, the need for a base puts restrictions on the asymmetric hydrogenation of base-labile ketones. In this study, novel ruthenabicyclic complexes bearing a η^1-BH_4 ligand, Ru(η^1-BH_4)(daipena)(diphosphine)[2] were developed to achieve asymmetric hydrogenation even under base-free conditions, based on the previous observation that RuH(η^1-BH_4)(diphosphine)(diamine)[3] catalyzed the reaction without addition of a base.

The hydrogenation of acetophenone using the borohydride complexes proceeded in high catalytic activity with >99% ee of the product under base-free conditions or weakly basic conditions. Under base-free conditions, base-labile ketones, such as α-chloroketone and trimethylsilyl-protected alkynyl ketone, were reduced to the corresponding alcohols in high yield and enantioselectivity. The borohydride complexes also catalyzed the asymmetric formal hydroamination of racemic allylic alcohols in the absence of an inorganic base. This reaction proceeds via a borrowing hydrogenation mechanism, which includes: (1) dehydrogenative oxidation of allylic alcohol, (2) aza-Michael addition, (3) asymmetric reduction of the β-amino ketone intermediate. This protocol provides a short-step process to give a variety of chiral γ-amino alcohols in high enantioselectivity (up to >99 % ee).





1) K. Matsumura, N. Arai, K. Hori, T. Saito, N. Sayo, T. Ohkuma, *J. Am. Chem. Soc.* **2011**, *133*, 10696. 2) T. Ishizaka, Y. Nakayama, T. Touge, Y. Yuki, K. Matsumura, T. Yurino, T. Ohkuma, *Tetrahedron* **2023**, *149*, 133705. 3) T. Ohkuma, M. Koizumi, K. Muñiz, G. Hilt, C. Kabuto, R. Noyori, *J. Am. Chem. Soc.* **2002**, *124*, 6508.

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1113(1113, Bldg. 11 [1F])

[E1113-4am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Fumitaka Ishiwari, Yoshihiro Miyake

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1113-4am-01]
Synthesis and properties of anthracene-fused aromatic compounds with multiple helical sites
○Takehiro Kihara[1], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1113-4am-02]
Synthesis and Properties of Acene Derivatives by Domino Cross-Scholl Reaction
○Shuri Yamaoka[1], Haruka Nakanishi[1], Haruki Nishimura[1], Masahiro Muraoka[1], Michihisa Murata[1] (1. Osaka Institute of Technology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1113-4am-03]
Synthesis and Properties of π-Extended Cyclobisbiphenylenecarbonyls
○Junichiro Hirano[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2] (1. Nagoya University, 2. JST PRESTO)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1113-4am-04]
Enantio- and Diastereoselective Synthesis and Spiral-Stair-Like Chiral Single Helix Assembly of Figure-Eight Cyclophenylenes
○Kohei Adachi[1], Juntaro Nogami[1], Daisuke Hashizume[2], Masashi Hasegawa[3], Yuki Nagashima[1], Ken Tanaka[1] (1. Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2. RIKEN Center for Emergent Matter Science (CEMS), 3. Graduate School of Science, Kitasato University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1113-4am-05]
Synthesis and Physical Properties of Molecular Penrose Stairs via Catalyst-Free Double Friedel-Crafts Reaction
○Zhiyan Jiang[1], Yoichiro Kuninobu[1] (1. Kyushu Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1113-4am-06]
Synthesis and Property of Dihetero[8]circulenes
○Chihiro Maeda[1], Koki Akiyama[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Tech., Okayama Univ.)

Japanese

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10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

[E1113-4am-07]

Effect of N-Substituents on the Azahelicene Synthesis

Chihiro Maeda[1], ○Sayaka Michishita[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Technol., Okayama Univ.)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1113-4am-08]

Synthesis of Mono-Arylated Figure-Eight Cyclobisbiphenylenecarbonyl Derivative and Its Isomerization to Non-twisted Molecule

○Hiyori Idei[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2] (1. Nagoya University, 2. JST PRESTO)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1113-4am-09]

Synthesis and chiroptical properties of highly elongated fused anthracene-type expanded helicenes

○Hiroki Fukuda[1], Eiji Tsurumaki[1], Masashi Hasegawa[2], Shinji Toyota[1] (1. Tokyo Tech, 2. Kitasato Univ.)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1113-4am-10]

Asymmetric synthesis of three-dimensionally π-extended carbohelicenesand and their circularly polarized luminescence properties

○Futo Morita[1], Yu Sato[1], Yuki Nagashima[1], Naoyuki Toriumi[2], Masanobu Uchiyama[2], Gaku Fukuhara[1], Hidehiro Uekusa[1], Ken Tanaka[2,1] (1. Tokyo Institute of Technology, 2. The University of Tokyo)

English

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1113-4am-11]

Synthesis and optical properties of stimuli-responsive helicene-fused xanthene dyes

○Sorachi Miwa[1], Daichi Mizutani[2], Masaki Kawamoto[2], Yuuya Nagata[3], Kiyosei Takasu[1], Hiroshi Takikawa[1] (1. Graduate School of Pharmaceutical Sciences, Kyoto University, 2. Faculty of Pharmaceutical Sciences, Kyoto University, 3. Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1113-4am-12]

Stereoselective synthesis of multiple carbohelicenes via asymmetric [2+2+2] cycloaddition and Scholl reaction

○Ryota shimizu[1], Futo Morita[1], Yuko Kishida[2], Yu Sato[1], Yuki Nagashima[1], Hidehiro Uekusa[2], Ken Tanaka[1] (1. Materials and Chemical Technology Tokyo Institute of Technology, 2. Science Tokyo Institute of Technology)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

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[E1113-4am-13]

Catalytic Synthesis of Antiaromatic Norcorroles

○Satoshi Kato[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, Nagoya University, 2. Institute for Advanced Research, Nagoya University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1113-4am-14]

Functionalization of 5,15-dioxaporphyrin for elucidation of conductive properties of antiaromatic molecules

○Yukako Kawashige[1], Soji Shimizu[1] (1. Graduate School of Engineering, Kyushu University)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1113-4am-15]

Synthesis of free-base norcorroles from borylated dipyrrins

○Shotaro Hirayama[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, 2. Institute for Advanced Research, Nagoya University)

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複数のらせん部位をもつアントラセン縮合型芳香族化合物の合成と性質

（東工大理）○木原 丈裕・鶴巻 英治・豊田 真司

Synthesis and properties of anthracene-fused aromatic compounds with multiple helical sites

(*School of science, Tokyo Institute of Technology*) ○Takehiro Kihara, Eiji Tsurumaki, Shinji Toyota

We reported the synthesis of a series of π-expanded helicenes **[n]HA**, in which multiple anthracenes were fused in a helical manner (Figure 1)[1]. Herein, we synthesized new aromatic compounds with double helical sites and investigated their structures and properties. **[3]DHA** and **[5]DHA** with three and five anthracene units, respectively, were synthesized by Pt-catalyzed cycloisomerization of ethynyl substituted dianthrylbenzene derivatives and characterized by NMR and mass spectra. X-ray structure analysis revealed that **[3]DHA** has a non-planar structure with C_i symmetry, in which the anthracene rings at the both ends were twisted in the opposite directions relative to the central anthracene ring. We will discuss the effects of the type of fusion of aromatic rings on the structure and properties from spectroscopic data and DFT calculations.

Keywords: Anthracene, Aromatic compound, Helical structure, Cycloisomerization

我々はこれまでに，らせん形に複数のアントラセンを縮合した一連のπ拡張ヘリセン**[n]HA** の合成を報告した(Figure 1)[1]．本研究では，縮合の向きがを異なる分子内に 2 つのらせん部位をもつ類縁体を合成し，その構造と性質について調査した．3 つおよび 5 つのアントラセンが縮合した**[3]DHA** と**[5]DHA** は，エチニル置換ジアントリルベンゼン誘導体に対して Pt 触媒を用いた環化異性化反応を行うことで合成した．これらの化合物の構造は，NMR および質量分析によって同定した．X 線構造解析から，**[3]DHA** は C_i 対称の非平面構造をもち，中央のアントラセン環に対して，両端のアントラセン環が反対側にねじれていることが明らかになった．分光データおよび DFT 計算の結果から，芳香環の縮合様式が構造や性質に及ぼす効果を考察する．

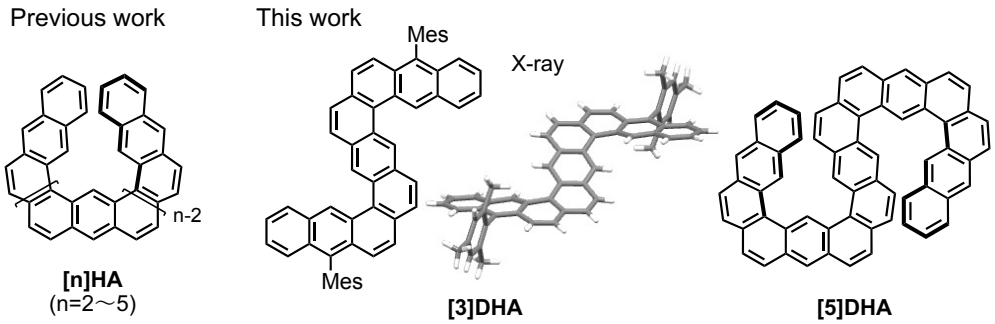

Figure 1. Structures of **[n]HA**, **[3]DHA**, and **[5]DHA** (Mes = mesityl).

1) a) K. Fujise, E. Tsurumaki, G. Fukuhara, N. Hara, Y. Imai, S. Toyota, *Chem. Asian J.* **2020**, *15*, 2456.
b) K. Fujise, E. Tsurumaki, K. Wakamatsu, S. Toyota, *Chem. Eur J.* **2021**, *27*, 4548.

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分子間ドミノ Scholl 反応を用いたアセン誘導体の合成と性質

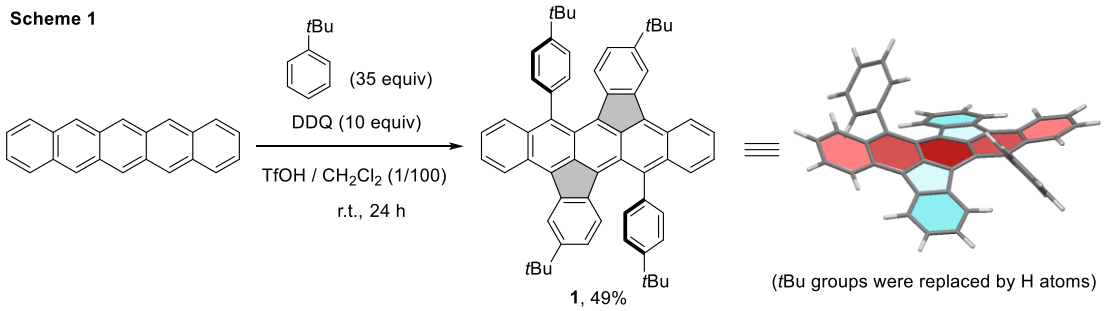
（阪工大院工）○山岡 珠理・中西 晴香・西村 元希・村岡 雅弘・村田 理尚
Synthesis and Properties of Acene Derivatives by Domino Cross-Scholl Reaction
(*Graduate School of Engineering, Osaka Institute of Technology*) ○Shuri Yamaoka, Haruka Nakanishi, Haruki Nishimura, Masahiro Muraoka, Michihisa Murata

We have recently reported a domino-type multiple C–H functionalization of tetracene with benzene. Under the typical conditions of the Scholl reaction, a domino reaction occurs between tetracene and six molecules of benzene in one pot to furnish an aromatic compound with a curved π-system. In this work, we examined the direct functionalization of pentacene via the domino-type functionalization. The reaction proceeded at room temperature to furnish a bisindeno-annulated pentacene derivative. The DFT calculations indicate that the resulting molecule possesses a saddle-type curved π-surface. One pot functionalization of anthracene will also be reported.

Keywords : Polycyclic Aromatic Hydrocarbon; Scholl Reaction; Dehydrogenative Coupling; Direct Functionalization; Curved π-System

ペンタセンおよびその誘導体は，高い電荷移動度や一重項励起子分裂などの興味深い物性を示すことが知られているが，溶解性や安定性の低さから，直接的な誘導体化に関して十分に研究されていない。当研究室では先に，テトラセンにベンゼンが連続して反応する分子間クロスドミノ Scholl 反応を見出している [1]。本研究では，この反応をペンタセンに適用することにより，一段階での直接的構造変換を検討した (Scheme 1)。DDQ/TfOH を酸化剤に用いる Scholl 反応の条件下で *t*-ブチルベンゼンと反応させたところ，ペンタセンに対して 4 個の *t*-ブチルベンゼンが結合したビスインデノペンタセン [2] 誘導体 **1** (49%) が良好な収率で単離された。化合物 **1** は光照射に対して高い安定性を示し，DFT 計算の結果からサドル型に曲がったπ共役面をもつことが示唆された。アントラセンの構造変換についても発表する。

Scheme 1



1) 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.
2) A. N. Lakshminarayana, J. Chang, J. Luo, B. Zheng, K.-W. Huang, C. Chi, *Chem. Commun.* **2015**, *51*, 3604.

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π拡張されたシクロビスビフェニレンカルボニルの合成と物性

（名大院工[1]・JST さきがけ[2]）○平野 純一朗[1]、忍久保 洋[1]、福井 識人[1,2]

Synthesis and Properties of π-Extended Cyclobisbiphenylenecarbonyls

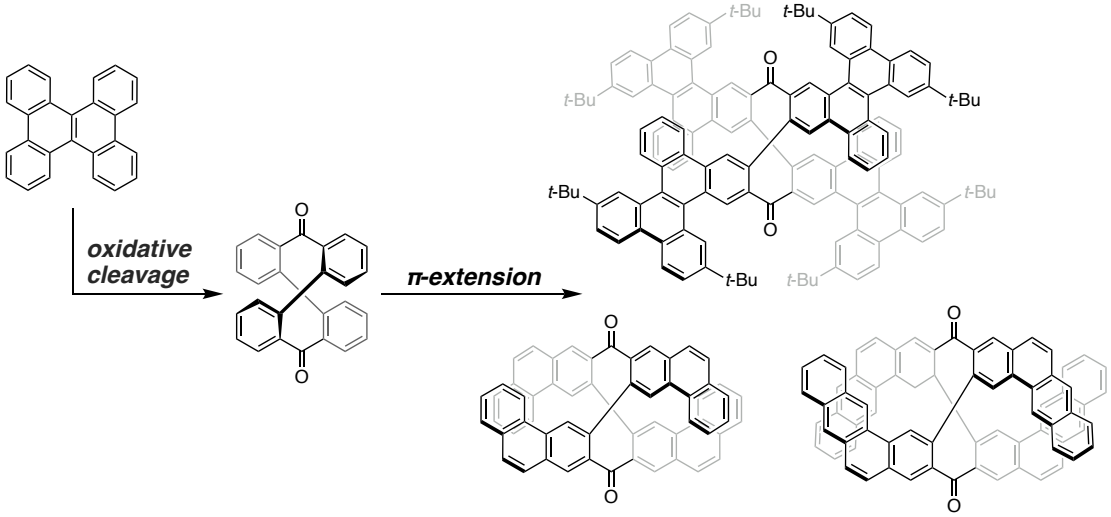
([1]*Graduate School of Engineering, Nagoya University*, [2]*JST PRESTO*)○Junichiro Hirano[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2]

A figure-eight π-conjugated molecule adopts a chiral three-dimensional structure with D_2 symmetry. Various figure-eight molecules have been synthesized via bottom-up approaches. Recently, we have demonstrated that one-step oxidative cleavage of an internal C–C double bond of dibenzo[*g,p*]chrysene affords cyclobisbiphenylenecarbonyl (CBBC), a figure-eight π-system, via a top-down approach.[1] In this study, we have synthesized three new π-extended cyclobisbiphenylenecarbonyl derivatives and investigated the effect of π-extension.

Keywords: π-conjugated molecules, figure-eight molecule, chirality

８の字型π共役分子はD_2対称性のキラルな３次元構造をもつ。これまでにさまざまな８の字型分子がボトムアップ的手法によって合成されてきた。最近我々はジベンゾ[*g,p*]クリセンの骨格内部の二重結合を酸化的に開裂することで、８の字型π共役分子であるシクロビスビフェニレンカルボニル(CBBC)をトップダウン的に１ステップで合成できることを明らかにした[1]。

今回我々はCBBCのπ拡張により３種類の新規８の字型π共役分子を創出した。得られた分子の同定はNMR測定および質量分析によって行った。また、一部の分子については単結晶 X 線構造解析に成功している。また、それぞれの化合物を光学分割するとともに、各種分光分析によってπ拡張の効果を調査した。



1) N. Fukui, *et al., ChemRxiv* **2023**. DOI: 10.26434/chemrxiv-2023-f1djk.

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8 の字型シクロフェニレンの不斉合成とキラルな単らせん状集積

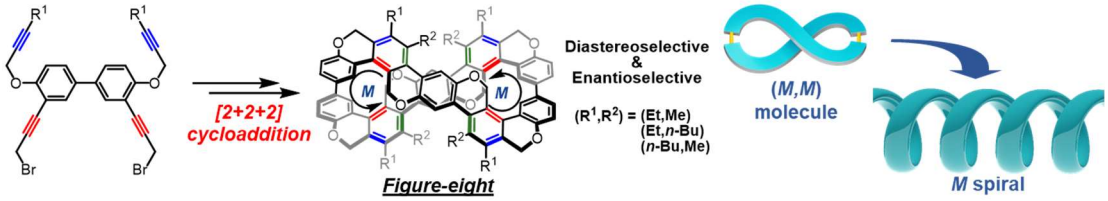
（東工大物質理工[1]・理研 CEMS[2]・北里大院理[3]）○安達 考平[1]・野上 純太郎[1]・橋爪 大輔[2]・長谷川 真士[3]・永島 佑貴[1]・田中 健[1]

Enantio- and Diastereoselective Synthesis and Spiral-Stair-Like Chiral Single Helix Assembly of Figure-Eight Cyclophenylenes ([1]*Department of Chemical Science and Engineering, Tokyo Institute of Technology*, [2]*Center for Emergent Matter Science (CEMS),* [3]*Graduate School of Science, Kitasato University*) ○ Kohei Adachi,[1] Juntaro Nogami,[1] Daisuke Hashizume,[2] Masashi Hasegawa,[3] Yuki Nagashima,[1] Ken Tanaka[1]

Figure-eight π-conjugated molecules have attracted much attention from the viewpoint of optical properties because of their unique structure and helical chirality due to the highly twisted π-skeleton. However, their synthesis has been limited due to the difficulty of constructing the torsion, and only one reported case of asymmetric synthesis to date. Furthermore, the diastereomer was formed to the same extent in this case. Here we report the first enantioselective and diastereoselective synthesis of figure-eight cyclophenylene by π-extension of a portion of the substrate to a flexible biphenyl skeleton. The *(M,M)* form of the target compound was successfully obtained in up to 87% yield and 78% ee. Recrystallization from a solution of the optically pure *(M,M)* form resulted in the preparation of a counterclockwise chiral helical crystal with six molecules forming one winding.

Keywords : Cyclophenylene, [2+2+2] Cycloaddition, Enantioselective Synthesis, Rhodium, Helical Assembly

8 の字型π共役系分子は、高度にねじれたπ骨格に起因する特異な構造やらせん不斉から、光学物性の観点で大きく注目されている分子である。しかし、その合成はねじれの構築の難しさゆえに手法が限られており、不斉合成については当研究室が最近報告した、ロジウム触媒を用いた[2+2+2]付加環化反応による 8 の字型シクロフェニレンの合成の 1 例に限られている[1)]。また、この 1 例についても、目的物のほかにジアステレオマーが同程度生成するという課題が残されている。そこで本研究では、基質の一部をフレキシブルなビフェニル骨格へとπ拡張することで、8 の字型シクロフェニレンのエナンチオ選択的かつジアステレオ選択的合成を初めて達成した。実際に、目的化合物の(*M,M*)体を最大 87%収率、78%ee で得ることに成功した。また、光学純度の高い(*M,M*)体の溶液から再結晶を行った結果、6 分子で 1 巻きとなる反時計回りのキラルらせん結晶を作成することに成功した。



1) Nogami, J. Hashizume, D. Nagashima, Y. Miyamoto, K. Uchiyama, M. Tanaka, K. *Nat. Synth*. **2023**, *2*, 888.

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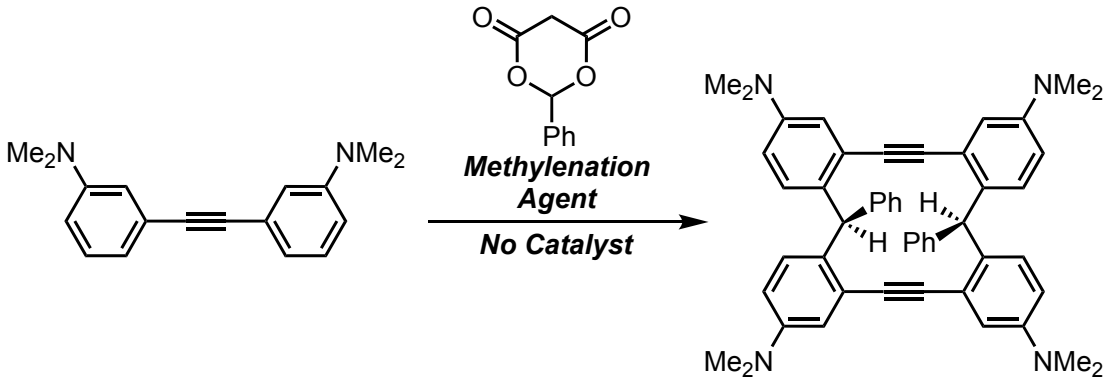
二重 Friedel-Crafts 反応によるペンローズ階段型環状分子の合成と物性解析

（九大先導研[1]・九大院総理工[2]）○姜 志彦[2]・國信 洋一郎[1,2]
Synthesis and Physical Properties of Molecular Penrose Stairs via Catalyst-Free Double Friedel-Crafts Reaction ([1]*Institute for Materials Chemistry and Engineering, Kyushu University,* [2]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*)
○Zhiyan Jiang,[2] Yoichiro Kuninobu[1,2]

We have recently developed a new methylenation agent, the Meldrum's acid derivative, which was found to be able to promote carbon-carbon bond formation at the two electron-rich reaction sites of biphenyl derivatives via double Friedel-Crafts reaction.[1] In this study, we succeeded in synthesizing cyclic π-conjugated molecules from electron-rich biarylalkynes using the reaction. Single crystal X-ray structure analysis revealed that the cyclic molecule has a twisted structure like Penrose stairs. The physical properties of molecular Penrose stairs were investigated by DFT calculations, UV-vis and fluorescence spectra.
Keywords : Molecular Penrose Stairs; Friedel-Crafts Reaction; Methylenation; C-C Bond Formation; Twisted Structure

我々は最近、新しいメチレン化剤であるメルドラム酸誘導体を開発し、このメチレン化剤を利用することで、電子豊富なビフェニル誘導体の二重 Friedel-Crafts 反応により、炭素-炭素結合形成反応が進行し、フルオレン誘導体を合成できることを見出した[1]。本研究では、この反応を利用し、電子豊富なビアリールアルキンとメルドラム酸誘導体から環状π共役系分子の合成に成功した。単結晶 X 線構造解析の結果、合成した環状分子はペンローズ階段のようにねじれた構造を有していることがわかった。また、DFT 計算、UV-vis や蛍光スペクトルの測定により、ペンローズ階段型分子の性質を明らかにした。



1) Jiang, Z.; Sekine, K.; Kuninobu, Y. *Chem. Commun.* **2022**, *58*, 843-846.

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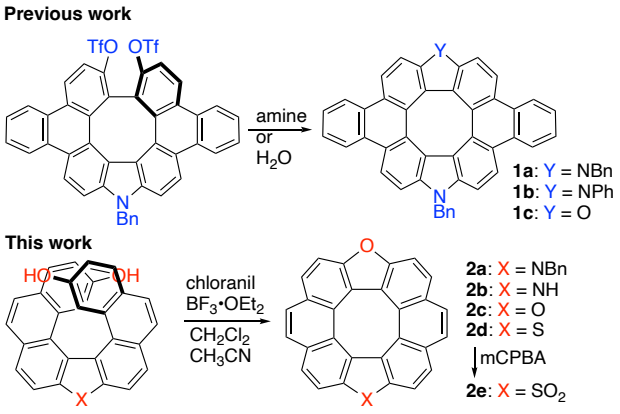
ジヘテロ[8]サーキュレンの合成と性質

（岡山大院自然）○前田千尋・秋山幸希・高石和人・依馬 正
Synthesis and Property of Dihetero[8]circulenes (*Graduate School of Natural Science and Technology, Okayama University*) ○Chihiro Maeda, Koki Akiyama, Kazuto Takaishi, Tadashi Ema

Oxidation of dihydroxyhetero[7]helicenes gave dihetero[8]circulenes via the concomitant C–C coupling and dehydrative furan formation. The pristine dihetero[8]circulenes were synthesized in four steps and characterized for the first time. X-ray crystal structures and DFT-optimized structures revealed the distorted saddle-like structures, and the degree of the distortion was found to be correlated with the photophysical properties.
Keywords *: Circulene; Helicene; Carbazole; Scholl Reaction*

サーキュレンとはベンゼン環あるいはヘテロ環がオルト位で縮環し環状化したπ共役系化合物であり、その芳香環の数 n によって[n]サーキュレンと呼ばれる。ベンゼン環 8 個からなる[8]サーキュレンが歪んだ非平面構造をとるのに対して、ヘテロ環を含むヘテロ[8]サーキュレンの多くは平面構造をとる。特に、ヘテロ環を合計 8 個または 4 個含む骨格はこれまで数多く報告されてきた。しかし、ヘテロ環を 2 個含む化合物は金属表面で合成された 1 例しか報告されておらず、結晶構造や光学特性も調査されていなかった。[1] 最近我々はダブルアミノ化反応により π 拡張型ジヘテロ[8]サーキュレン **1a–c** を合成し、その結晶構造と光学特性について明らかにした。[2] これらの蛍光量子収率は 1–2%と低く、ベンゾ拡張部位により振動緩和が促進された原因が考えられた。そこで本研究では π 拡張していないジヘテロ[8]サーキュレンを合成することで骨格本来の性質を明らかにすることとした。



今回我々は、ジヒドロキシヘテロ[7]ヘリセンの酸化反応を行ったところジヘテロ[8]サーキュレン **2a–d** が得られることを発見した。置換基やベンゾ縮環を含まないジヘテロ[8]サーキュレンを 4 段階で初めて合成し構造決定した。X 線結晶構造及び計算構造はサドル型の構造を示し、そのねじれの程度と光物性の相関について考察した。[3]

1) K. Nakamura, Q.-Q. Li, O. Krejčí, A. S. Foster, K. Sun, S. Kawai, S. Ito, *J. Am. Chem. Soc.* **2020**, *142*, 11363.
2) C. Maeda, S. Nomoto, K. Akiyama, T. Tanaka, T. Ema, *Chem.–Eur. J.* **2021**, *56*, 15699.
3) C. Maeda, K. Akiyama, T. Ema, *Org. Lett.* **2023**, *25*, 3932.

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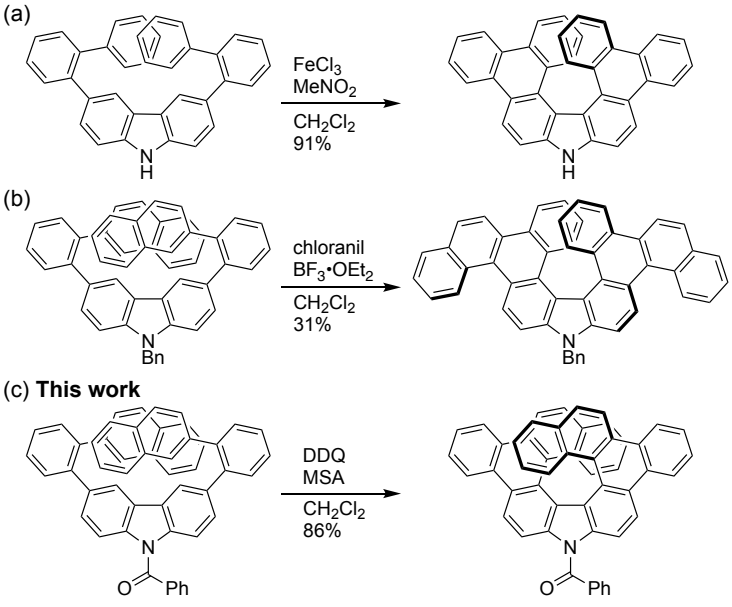
アザヘリセン合成に及ぼす窒素上の置換基効果

（岡山大院自然）前田千尋・○道下 紗也加・高石和人・依馬 正
Effect of N-Substituents on the Azahelicene Synthesis (*Graduate School of Natural Science and Technology, Okayama University*) Chihiro Maeda, ○ Sayaka Michishita, Kazuto Takaishi, Tadashi Ema

Helicenes, ortho-fused chiral aromatic compounds, have received much attention because of the intense circular dichroism and circularly polarized luminescence. We have successfully synthesized various azahelicenes by the Scholl reaction of 3,6-bis(biphenyl-2-yl)carbazole and its analogues. Interestingly, a rearrangement product was obtained from the substrate with 2-naphthylphenyl groups instead of the aza[9]helicene. In the previous study, the reactive 3,6-positions of the carbazole likely accelerated the rearrangement. In this study, we tried to synthesize aza[9]helicenes by introducing electron-withdrawing groups on the nitrogen atom to suppress the rearrangement. We successfully obtained the aza[9]helicene with a benzoyl group which was confirmed by the X-ray diffraction analysis. The reaction mechanism was investigated by DFT calculations, which also supported that the pathway to the aza[9]helicene was more favorable than that to the rearrangement product.
Keywords : Carbazole; Helicene; Rearrangement; Scholl Reaction

ヘリセンは複数の芳香環がオルト位で縮環したキラル化合物であり，強い円二色性や円偏光発光を示すことから注目されている。当研究室では 3,6 位にビフェニル基を導入したカルバゾール及びその類縁体の Scholl 反応により様々なアザヘリセンの合成に成功している(Scheme 1a)[1]。興味深いことに 2-ナフチルフェニル基を有する基質からは転位生成物が得られた(Scheme 1b)[2]。本研究では窒素上に電子求引性基を導入し、カルバゾール 3,6 位の反応性を下げることで転位を抑制しアザ[9]ヘリセンの選択的合成を試みた(Scheme 1c)。実際にベンゾイル基を導入した基質からアザ[9]ヘリセンが 86%収率で得られ、X 線結晶構造解析にも成功した。DFT 計算によって反応機構を調査したところ、ベンゾイル基を導入した基質からは転位よりもアザ[9]ヘリセンを与える経路が優勢であることが示された。



Scheme 1

1) Maeda, C.; Nagahata, K.; Shirakawa, T.; Ema, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 7813.
2) Maeda, C.; Nomoto, S.; Akiyama, K.; Tanaka, T.; Ema, T. *Chem. Eur. J.* **2021**, *27*, 15699.

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8の字型分子シクロビスビフェニレンカルボニルのモノアリール化体の合成と非ねじれ分子への異性化

(名大院工[1]・JST さきがけ[2])・○出井 ひより[1]・忍久保 洋[1]・福井 識人[1,2]

Synthesis of Mono-Arylated Figure-Eight Cyclobisbiphenylenecarbonyl Derivative and Its Isomerization to Non-twisted Molecule ([1]*Graduate School of Engineering, Nagoya University*, [2]*JST PRESTO*) ○Hiyori Idei,[1] Hiroshi Shinokubo,[1] Norihito Fukui[1,2]

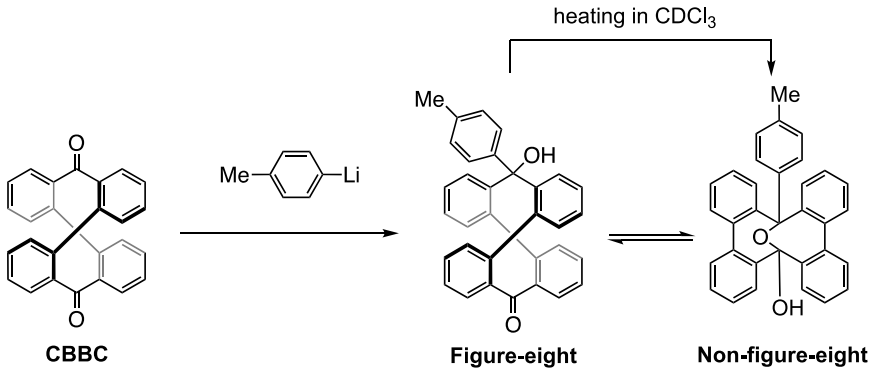
Figure-eight π-systems adopt D_2-symmetric chiral structures, exhibiting efficient circularly polarized luminescence. The development of a rational strategy to induce a figure-eight structure is demanding. There have been several pioneering reports on the induction of figure-eight structures via metal-complexation into macrocyclic ligands[1].

Cyclobisbiphenylenecarbonyl (CBBC) represents a figure-eight π-system[2]. Herein, we demonstrate that the treatment of CBBC with an organolithium reagent results in highly selective mono-arylation at one of the two carbonyl groups. The product underwent reversible intramolecular hemiacetal formation to provide a non-twisted hemiacetal structure.

Keywords : nonplaanar π -system; figure-eight molecule; cyclobisbiphenylenecarbonyl; selective mono-arylation; isomerization

８の字型π共役分子は D_2 対称なキラルな構造を有するとともに、優れた円偏光発光といった興味深い性質を示す。そのため、８の字型構造を外部刺激によって誘起させる手法の開発は魅力的な課題である。これまで、大環状配位子に対する金属錯化によって８の字型構造を誘起した例が報告されている[1]。

シクロビスビフェニレンカルボニル(CBBC)は８の字型構造を有するπ共役分子である[2]。今回我々はCBBCのカルボニル基の変換を狙い、CBBCに有機リチウム試薬を作用させたところ、２つのカルボニル基の片方のみが高選択的に求核付加を受けることを見いだした。生成物は、カルボニル基とヒドロキシ基との間で分子内ヘミアセタール化を起こし、ねじれを持たない非８の字型構造へと可逆的に変化した。



1) Nabeshima, T., *et al.*, *Chem. Commun.* **2016**, *52*, 10727; Furuta, H., *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 14252.

2) N. Fukui, *et al., ChemRxiv* **2023**. DOI: 10.26434/chemrxiv-2023-f1djk.

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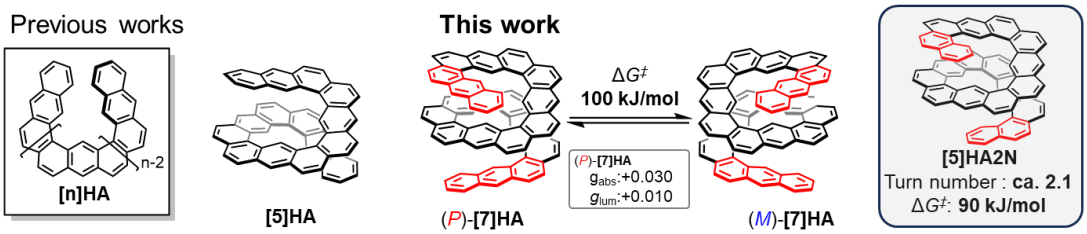
高度に伸長したアントラセン縮合型拡張ヘリセンの合成とキラル光学特性

（東工大理[1]・北里大院理[2]）○福田 大輝[1]・鶴巻 英治[1]・長谷川 真士[2]・豊田 真司[1]
Synthesis and chiroptical properties of highly elongated fused anthracene-type expanded helicenes ([1]*School of Science, Tokyo Institute of Technology*, [2]*Graduate School of Science, Kitasato University*) ○Hiroki Fukuda,[1] Eiji Tsurumaki,[1] Masashi Hasegawa,[2] Shinji Toyota[1]

We reported the synthesis and structures of expanded helicenes **[n]HA** (n = 2–5) with triangularly fused anthracenes.[1] Although the longest analog **[5]HA** had a helical turn number of ca.1.6, the resolution of its enantiomers was unsuccessful. We here synthesized two expanded helicenes **[5]HA2N** and **[7]HA**, with additional fused naphthalenes or anthracenes at both ends of **[5]HA**, respectively. Even though enantiomers of these compounds having turn numbers exceeding 2 were successfully resolved by chiral HPLC, racemization via helical inversion took place at room temperature. The CD and CPL spectra of enantiopure **[7]HA** revealed its very high chiroptical properties with g_{abs} = 0.030 and g_{lum} = 0.010, respectively. The structures, spectroscopic properties, and DFT calculations of these elongated extended helicenes will be presented.
Keywords : Expanded Helicene; Anthracene; Chiroptical properties; DFT calculation

我々は以前，アントラセンを三角形状に縮合した拡張ヘリセン**[n]HA** (n = 2–5) の合成と性質を報告した[1]．最長の**[5]HA** は約 1.6 の巻数をもち，分子内の芳香環の重なりに由来する特徴的な発光を示した．しかし，この化合物のエナンチオマーは分割できず，キラル光学特性は未解明である．そこで本研究では，らせん構造をより伸長した誘導体として，**[5]HA** の末端にナフタレンおよびアントラセンをそれぞれ縮合した拡張ヘリセン**[5]HA2N** および**[7]HA** を合成した．いずれの化合物もキラル HPLC を用いてエナンチオマーが分割でき，キラル光学特性を評価した．興味深いことに，これらの化合物は巻数 2 を超えるらせん構造を持つにも関わらず，溶液中，室温で，徐々にらせん反転にともなうラセミ化が進行した．**[7]HA** のエナンチオマーの CD, CPL スペクトルを測定したところ，非常に高いキラル光学特性（g_{abs}=0.030, g_{lum}=0.010）を示すことが分かった．拡張ヘリセンの分子構造，分光学的計算および DFT 計算の結果を報告する．



[1] K. Fujise, E. Tsurumaki, G. Fukuhara, N. Hara, Y. Imai, S. Toyota, *Chem. Asian J.* **2020**, *15*, 2456; K. Fujise, E. Tsurumaki, K. Wakamatsu, S. Toyota, *Chem. Eur. J.* **2021**, *27*, 4548.

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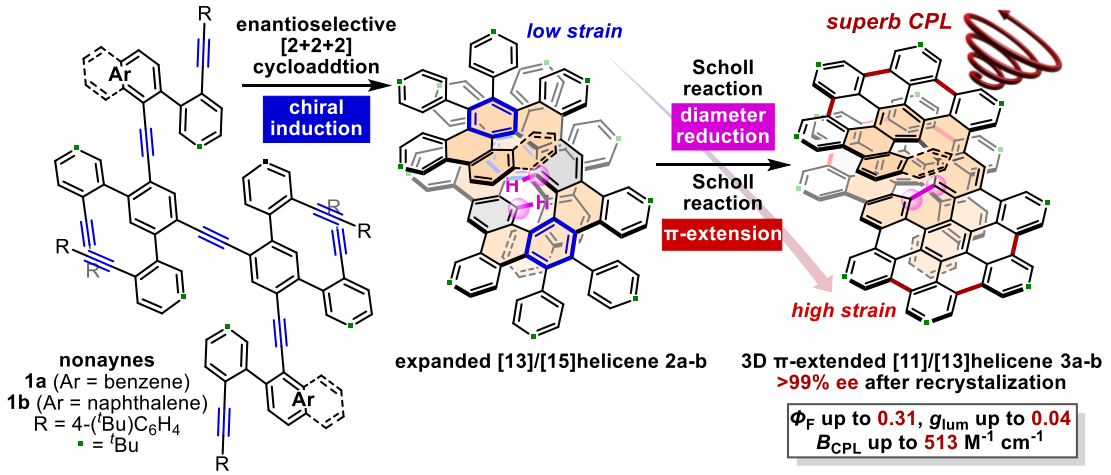
三次元状にπ拡張されたカルボヘリセンの不斉合成と円偏光発光特性評価

（東工大物質理工[1]・東大院薬[2]・東工大理[3]）○森田 楓人[1]・佐藤 悠[1]・永島 佑貴[1]・鳥海 尚之[2]・内山 真伸[2]・福原 学[3]・植草 秀裕[3]・田中 健[1]
Asymmetric synthesis of three-dimensionally π-extended carbohelicenesand and their circularly polarized luminescence properties ([1]*Department of Chemical Science and Engineering, Tokyo Institute of Technology*, [2]*Graduate School of Pharmaceutical Sciences, The University of Tokyo*, [3]*Department of Chemistry, Tokyo Institute of Technology*,) ○Futo Morita,[1] Yu Sato,[1] Yuki Nagashima,[1] Naoyuki Toriumi,[2] Masanobu Uchiyama,[2] Gaku Fukuhara,[3] Hidehiro Uekusa,[3] Ken Tanaka[1]

Helicenes with extended π-conjugated systems in the helical and lateral directions are a useful group of compounds with high luminescence brightness and circular polarization. In this research, we have achieved in the asymmetric synthesis of π-extended [11] and [13] carbohelicenes via a two-step cyclization reaction, the [2+2+2] cycloaddition reaction followed by the Scholl reaction. We also found that the obtained helicene molecule exhibited the highest CPL brightness among helicene derivatives.
Keywords : Carbohelicene; Nanographene; [2+2+2] Cycloaddition; Scholl Reaction; Circularly Polarized Luminescence

らせん方向及び側面方向へπ共役系を拡張されたヘリセンは、高い発光輝度およびキ円偏光度が期待できる有用な化合物群である[1]。本研究では、[2+2+2]付加環化反応と Scholl 反応の２段階の環化反応によりπ拡張[11]/[13]カルボヘリセンの不斉合成に成功した。また、得られたヘリセン分子がヘリセンの中で最高の CPL 輝度を示すことを見出した。



1) Y.-J. Shen, N.-T. Yao, L.-N. Diao, Y. Yang, X.-L. Chen, H.-Y. Gong, *Angew. Chem. Int. Ed.* **2023**, *62*, e202300840.

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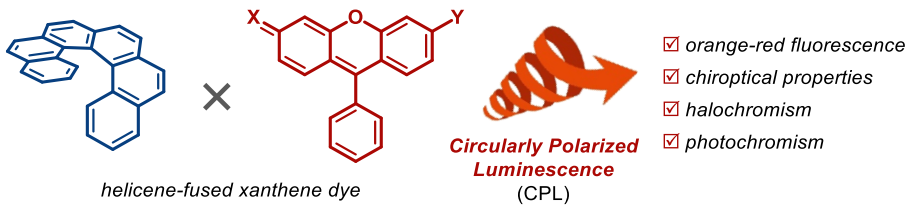
外部刺激に応答する含ヘリセンキサンテン色素の合成と光学特性

（京大院薬[1]・京大薬[2]・北大 ICReDD[3]）○三和　空知[1]・水谷　大地[2]・河本　真輝[2]・長田　裕也[3]・高須　清誠[1]・瀧川　紘[1]
Synthesis and optical properties of stimuli-responsive helicene-fused xanthene dyes ([1]*Graduate School of Pharmaceutical Sciences, Kyoto University*, [2]*Faculty of Pharmaceutical Sciences, Kyoto University*, [3]*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University*) ○Sorachi Miwa,[1] Daichi Mizutani,[2] Masaki Kawamoto,[2] Yuuya Nagata,[3] Kiyosei Takasu,[1] Hiroshi Takikawa[1]

Luminophores that change their optical properties in response to external stimuli have potential applications in chemical probes, light-emitting displays, and memory devices. Organic materials exhibiting variable chiroptical properties, including circular dichroism (CD) and circularly polarized luminescence (CPL), have garnered substantial interest.[1] In this study, we have developed new chiral luminophores by fusing xanthenes with [6]helicenes. This fusion leads to two key features: (1) a bathochromic shift in xanthene fluorescence by π-extension with a helicene scaffold, and (2) the ability to modulate CPL characteristics through external stimuli, i.e., pH changes (halochromism) and UV light exposure (photochromism). In this presentation, we will show the preparation methods and molecular structures of helicene-fused xanthenes, and their halochromic and chiroptical properties.
Keywords: Circularly Polarized Luminescence, Xanthene Dye, Helicene

外部刺激に応答して光学特性が変化する発光材料は、化学プローブや発光ディスプレイ、記憶デバイスなどへの応用が期待されている。特に近年では、円二色性（CD）や円偏光発光（CPL）などのキラル光学特性が外部刺激に応じて変化する有機材料に関する研究が盛んに行われている。[1]

今回、我々はフルオレセインやローダミン類などのキサンテン色素と[6]ヘリセンとを融合させた新しいキラル発光色素を開発した。この分子の特徴は、（１）ヘリセン構造の導入に基づいたπ共役系の拡張により蛍光発光波長が長波長シフトすること、および（２）pH 変化や紫外光照射といった外部刺激によって CPL の波長及び符号が切り替わること、の２点である。本講演では、これら新奇な発光分子の合成、構造、ハロクロミズム特性、そして CD や CPL を含むキラル光学特性について報告する。



Reference
1) Ma, J.-L.; Peng, Q.; Zhao, C.-H. *Chem. Eur. J.* **2019**, *25*, 15441–15454.

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不斉[2+2+2]付加環化反応と Scholl 反応を経由したマルチカルボヘリセンの立体選択的合成

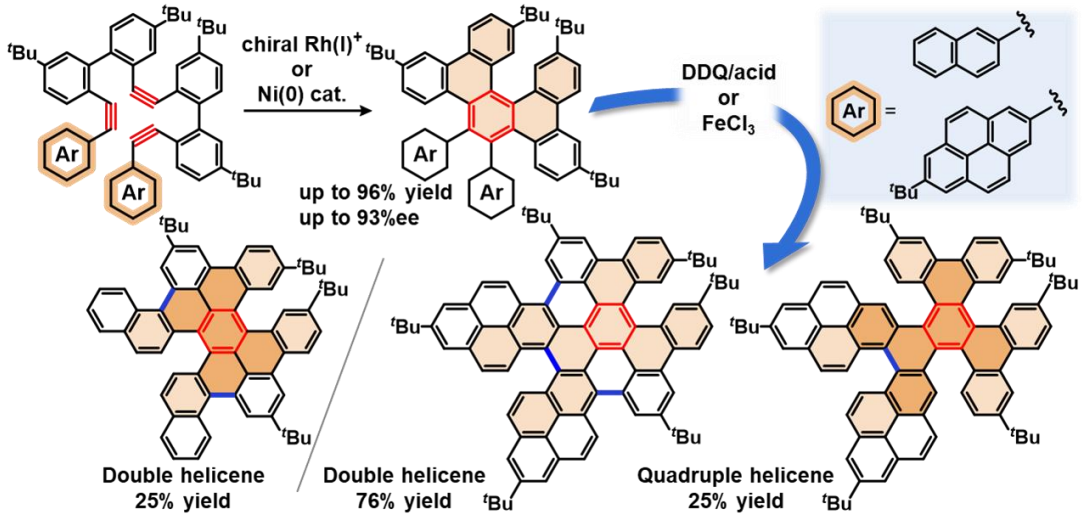
（東工大物質理工 [1]・東工大理 [2]）○清水　亮太 [1]・森田　楓人 [1]・岸田　裕子 [2]・佐藤　悠 [1]・永島　佑貴 [1]・植草　秀裕 [2]・田中　健 [1]

Stereoselective synthesis of multiple carbohelicenes via asymmetric [2+2+2] cycloaddition and Scholl reaction ([1]*Materials and Chemical Technology, Tokyo Institute of Technology*, [2] *Science, Tokyo Institute of Technology*) ○Ryota shimizu,[1] Futo Morita,[1] Yuko Kishida,[2] Yu Sato,[1] Yuki Nagashima,[1] Hidehiro Uekusa,[2] Yuko Kishida [1]

Multiple helicenes, which have multiple-helical structures, have attracted much interest due to their characteristic electronic, physical, and chiroptical properties. [2+2+2] Cycloaddition reactions have been used for their asymmetric synthesis. Herein, we report the stereoselective synthesis of double and quadruple carbohelicenes from triynes with readily modifiable aryl groups by the asymmetric [2+2+2] cycloaddition followed by the Scholl reaction.

Keywords : Multiple carbohelicenes; Polycyclic aromatic hydrocarbons; Asymmetric catalysis; [2+2+2] *cycloaddition; Scholl reaction*

分子内に複数のらせん構造をもつマルチヘリセンは、特異な電子的/物理的性質やキラル特性に関心が集まっている。これらの不斉合成には[2+2+2]付加環化反応が用いられ、これまでに 2 重/3 重のマルチヘリセンの不斉合成が報告されている [1,2]。しかし、さらなる高次らせん構造を有するマルチヘリセンの立体選択的合成は達成されていなかった。本研究では、容易に Ar 基を導入できるトリインに対し [2+2+2]付加環化反応を行うことで[5]ヘリセンを不斉合成し、Scholl 反応を行うことで 2 重/4 重のマルチカルボヘリセンが立体選択的に得られることを見出した。



1) A. Yubuta, K. Kamikawa *et al. J. Am. Chem. Soc*. **2020**, *142*, 10025.
2) S. Kinoshita, K. Tanaka *et al. Angew. Chem. Int. Ed*. **2020**, *59*, 11020.

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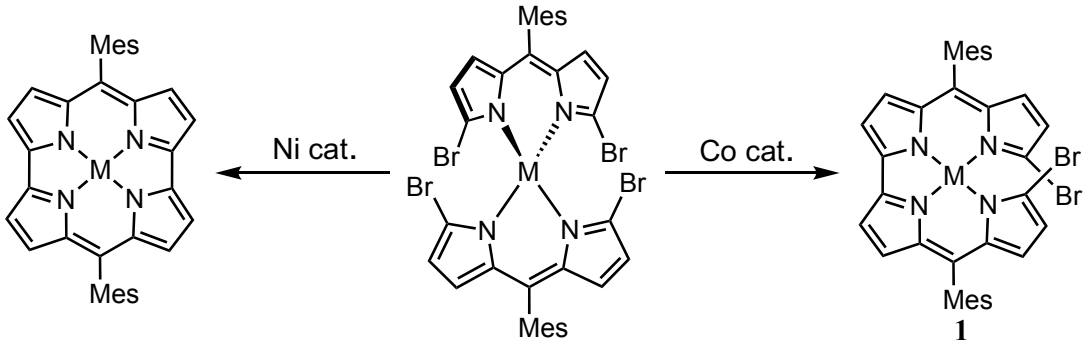
反芳香族ノルコロールの触媒的合成法

（名大院工[1]・名大高等研究院[2]）○加藤 賢[1]・髙野 秀明[1,2]・忍久保 洋[1]
Catalytic Synthesis of Antiaromatic Norcorroles (*Graduate School of Engineering, Nagoya University, [2]Institute for Advanced Research, Nagoya University*)○Satoshi Kato[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1]

Norcorrole is an antiaromatic porphyrinoid with a 16π conjugated system, which lacks two carbons at *meso* positions from regular porphyrins. Although considerable attention has been directed toward its antiaromatic properties and reactivity, the synthesis of norcorroles requires an excess amount of low-valent nickel reagents. We herein report the catalytic synthesis of norcorroles through an intramolecular reductive coupling reaction. In this presentation, we disclose the optimization of the reaction conditions and the substrate scope. During the optimization, we found a selective reductive coupling reaction to synthesize dibromobis(dipyrin) nickel complex **1** by the proper choice of the metal catalyst.
Keywords : Norcorrole; Reductive Coupling; Nickel Catalyst; Antiaromatic Compound

ノルコロールはポルフィリンの *meso* 位の炭素を 2 つ取り除いた骨格を持ち、16π 電子系に由来する反芳香族性を示すことから、その性質や反応性に注目が集まっている。しかし、従来のノルコロール合成法では反応剤として当量以上の低原子価ニッケル錯体を必要とし[1)]、改善の余地があった。今回我々は、分子内還元的カップリング反応を利用したノルコロールの触媒的合成法を開発した。本発表では、触媒、溶媒、配位子、基質濃度などの条件検討について言及し、本反応の基質適用範囲に関しても報告する。さらに、触媒を適切に選択することでジブロモビスジピリンニッケル錯体 **1** の選択的な合成にも成功した。



1) Kobayashi, N.; Shinokubo, H., *et al. Angew. Chem. Int. Ed.* **2012**, *51*, 8542–8545.

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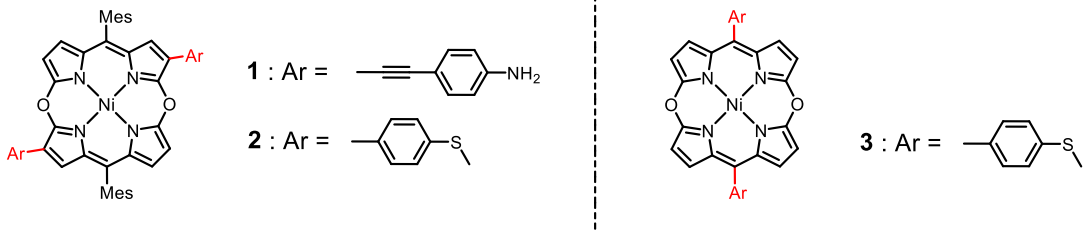
反芳香族分子の伝導特性解明を指向した 5,15-ジオキサポルフィリンの官能基化

（九大院工）○川重 友香子・清水 宗治
Functionalization of 5,15-dioxaporphyrin for elucidation of conductive properties of antiaromatic molecules (*Graduate School of Engineering, Kyushu University*) ○Yukako Kawashige, Soji Shimizu

Because of the narrow band gap, antiaromatic molecules are expected to exhibit prominent conductive properties. However, the inherent instability has prevented the elucidation of the molecular conductivity of the antiaromatic molecules. Recently, we have reported 5,15-dioxaporphyrin (DOP) as a stable antiaromatic molecule and its conversion to aromatic dication species upon oxidation. In this study, to estimate the single molecular conductivities arising from aromatic and antiaromatic states using the STM break-junction method, peripheral functionalization to introduce linker units to the STM tip and surface was examined.
Keywords : Antiaromatic molecule

反芳香族分子は芳香族分子と比べて、狭小なバンドギャップを持つことから、優れた伝導性を示すことが予想されるが、一般的に不安定であり実証例はほとんど無い [1]。当研究室では安定な 5,15-ジオキサポルフィリン（DOP）を報告している [2]。DOP は 1 電子 2 過程の酸化により、芳香族ジカチオンへと変換することが可能であることから [3]、STM-ブレイクジャンクション（BJ）法を用いて、捕捉した DOP を電解しながら単分子伝導度を測定することで、反芳香族性及び芳香族性に起因する伝導特性を解明できると期待している。

本研究では、STM の金電極と架橋構造を形成しやすい官能基として、アミノ基及びスルフィド基の導入を試みた。本発表では合成と STM-BJ 法を用いた物性評価について報告する。



1) S. Fujii, S. Marqués-González, J. Shin, H. Shinokubo, T. Masuda, T. Nishino, N. P. Arasu, H. Vázquez, M. Kiguchi, *Nat. Commun.* **2017**, *8*, 15984.
2) A. Nishiyama, M. Fukuda, S. Mori, K. Furukawa, H. Fliegl, H. Furuta, S. Shimizu, *Angew. Chem. Int. Ed.* **2018**, *57*, 9728.
3) J. Hao, A. Nishiyama, S. Mori, K. Furukawa, S. Shimizu, *Angew. Chem. Int. Ed.* **2023**, *62*, e202307862.

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ホウ素化ジピリンを用いたフリーベースノルコロールの合成

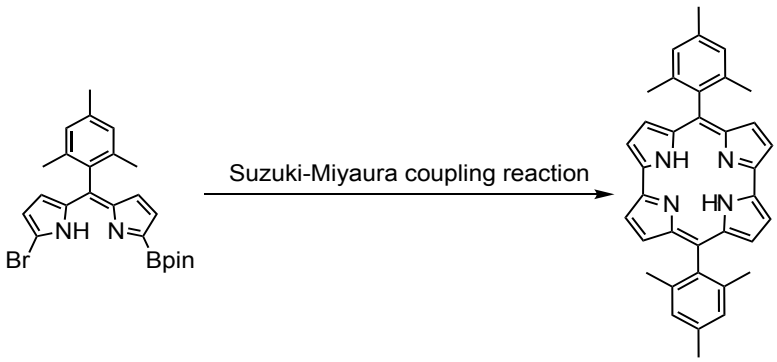
（名大院工[1]・名大高等研究院[2]）○平山 翔太郎[1]・髙野 秀明[1,2]・忍久保 洋[1]
Synthesis of freebase norcorroles from borylated dipyrrins ([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute for Advanced Research, Nagoya University*) ○ Shotaro Hirayama,[1] Hideaki Takano,[1,2] Hiroshi Shinokubo[1]

Norcorrole nickel complexes are stable antiaromatic porphyrinoids.[1)] We have developed a synthetic route of norcorrole nickel complexes using nickel as a template to synthesize various norcorroles and investigate their physical properties. On the other hand, norcorrole palladium and platinum complexes with bowl-shaped structures display different stacking arrangements from norcorrole nickel complexes.[2,3)] To synthesize other metal norcorroles, the use of free-base norcorroles is desirable. However, the current synthetic route of free-base norcorroles has several problems.[3)] Here, we report the improved synthesis of free-base norcorroles from borylated dipyrrins without the use of the metal template.

Keywords：antiaromatic; porphyrinoid; norcorrole; borylated compound; Pd-catalyst

ノルコロールニッケル錯体は、安定な反芳香族ポルフィリノイドである[1)]。これまで我々は、ニッケルをテンプレートとして用いるノルコロールニッケル錯体の合成法を開発し、その物性を調べてきた。一方、ニッケルをパラジウムやプラチナで置き換えたノルコロール錯体は、分子の立体構造や結晶中での積層状態が変化することが知られている[2,3)]。それらを効率的に合成するためには、中心金属をもたないフリーベースノルコロールの利用が望ましい。しかし、従来のフリーベースノルコロールの合成経路は収率が低いことや、不安定な中間体を経由する必要があるといった問題があった[3)]。

そこで我々は、ホウ素化ジピリンを用いるより簡便なフリーベースノルコロールの合成法を開発したので報告する。分子内にボリル基および臭素をもつジピリンに対して鈴木−宮浦カップリング反応を適用することによりフリーベースノルコロールを得ることに成功した。発表では異なる置換基をもつフリーベースノルコロールの合成についても述べる。



1) Kobayashi, N.; Shinokubo, H. *et al*., *Angew. Chem. Int. Ed.* **2012**, *51*, 8542.
2) Phung, Q. M.; Shinokubo, H. *et al*., *Cell Rep. Phys. Sci.* **2022**, *3*, 101045.
3) Shinokubo, H. *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 11822.

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1121(1121, Bldg. 11 [2F])

[E1121-4am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Ryo Inoue, Yusuke Inagaki

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1121-4am-01]

Chemical Modification Using Coupling Reaction for Boron Complex Containing Imidazodiazaborole Ring and Their Emission Properties

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

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1121-4am-02]

Impact of Intramolecular Boron–Sulfur Interaction on Photophysical Properties of Stimuli-Responsive Donor–Acceptor-Type Organoboron Fluorophores

○Ryoma Yamazaki[1], Tatsuya Mori[2], Mika Sakai[1], Shigehiro Yamaguchi[3,2,1] (1. Department of Chemistry, Graduate School of Science, Nagoya University, 2. Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, 3. Institute of Transformative Bio-Molecules (ITbM), Nagoya University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1121-4am-03]

Effects of Monodentate Ligands on the Intermolecular Interactions and Photophysical Properties of 9-Hydroxyphenalenone Boron Complexes

○Yuga Tarumi[1], Yuto Aoyama[1], Shunichiro Ito[1], Kazuo Tanaka[1] (1. Grad. Sch. of Eng. Kyoto Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1121-4am-04]

Boron-Bridged Benzobisthiazole Derivatives and Their Photophysical Properties

○Ryota Uchida[1], Masashi Mamada[1], Takuji Hatakeyama[1] (1. Kyoto University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1121-4am-05]

Incorporation of reactive site to tetra-BF_2 complex with bipyrrole skeleton and creation of photofunctional materials

○Ayano Tani[1], Yu Hoshino[2,3], Toshikazu Ono[2,3] (1. Faculty of Engineering, Kyushu University, 2. Graduate School of Engineering, Kyushu University, 3. Center for Molecular Systems (CMS), Kyushu University)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1121-4am-06]

Multi-Bladed Donor-Acceptor π-Electronic Systems Exhibiting Unique Emission Properties

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○Yunyi Song[1], Yoshiaki Shoji[1], Fukushima Takanori[1] (1. CLS, Tokyo Tech.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1121-4am-07]

Diverse Photofunctions of tetra-BF_2 Complexes with Bipyridine Skeleton

○Ryoji Furuta[1], Luxia Cui[1], Yu Hoshino[1,2], Toshikazu Ono[1,2] (1. Graduate School of Engineering, Kyushu University, 2. Center for Molecular Systems (CMS), Kyushu University)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1121-4am-08]

Synthesis and Photophysical Properties of Boron-Containing Polycyclic Aromatic Hydrocarbons with Intramolecularly-Coordinating Phorphorus Groups

○Yoshiharu sano[1], Tatsuya Mori[4], Shigehiro Yamaguchi[3,4,2] (1. Nagoya University, Department of Chemistry, School of Science, 2. Nagoya University, Department of Chemistry, Graduate School of Science, 3. Nagoya University, Institute of Transformative Bio-Molecules (ITbM), 4. Nagoya University, Integrated Research Consortium on Chemical Sciences (IRCCS))

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1121-4am-09]

Synthesis of *B*-*O*-fused-pyrrolopyrrole aza-BODIPY toward creating its cyclic oligomers with prominent chiroptical properties

○Shuhei Fukami[1], Soji Shimizu[1] (1. The Graduate School of Engineering, Kyushu University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1121-4am-10]

Au(I)-Catalyzed Cycloisomerization for the Synthesis of Fused BODIPYs

○Fumika Ohashi[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, Nagoya University, 2. Institute for Advanced Research, Nagoya University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1121-4am-11]

Iterative synthesis of donor-acceptor-type oligosilanes

○Natsumi Hammyo[1], Mingoo Jin[2], Hajime Ito[2,3] (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. Graduate School of Engineering, Hokkaido University)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1121-4am-12]

Substituent Effects on the Photophysical Properties of Disilane-Bridged Trimer Thiophenophane

○Yuya Kaneko[1], Yoshinori Yamanoi[1], Teppei Yamada[1] (1. The Univ. of Tokyo)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

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[E1121-4am-13]

Synthesis and Optical Evaluation of π-Conjugated Systems Based on Hypervalent Silicon Compounds

○Ippei Kanetani[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Graduated School of Engineering, Kyoto University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1121-4am-14]

Synthesis and Properties of Aromatic-Fused Phospholes via β-Substituted Phospholes

○Riku Minobe[1], Tomohiro Higashino[1], Hiroshi Imahori[1,2,3] (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-iCeMS, Kyoto Univ., 3. ILAS, Kyoto Univ.)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1121-4am-15]

Synthesis and Properties of Antimony Dipyrrin Complexes

○Shunsuke Kuroiwa[1], Hiroki Fukumoto[1], Tomohiro Agou[2], Tatsuya Nabeshima[3] (1. Ibaraki University, 2. University of Hyogo, 3. University of Tsukuba)

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イミダゾジアザボロール環を主骨格とするホウ素錯体に対するカップリング反応を用いた化学修飾とその発光特性

（慶大理工）○毛利 匡佑・三浦 洋平・吉岡 直樹

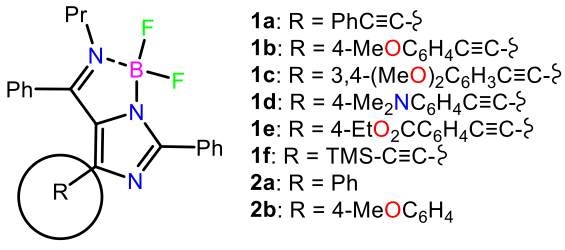
Chemical Modification Using Coupling Reaction for Boron Complex Containing Imidazodiazaborole Ring and Their Emission Properties (*Faculty of Science and Technology, Keio University*) ○Kohsuke Mohri, Youhei Miura, Naoki Yoshioka

We have studied the boron complexes containing a rigid imidazo[1,5-*c*][1,3,2]diazaborole ring because they have versatile luminescence properties. In this study, we investigated the chemical modification of the boron complex with an iodo group by Sonogashira or Suzuki-Miyaura coupling reactions and their fluorescence properties. All of obtained products **1, 2** exhibited fluorescence properties in both solution and solid states, and the substituent effect that compounds with electron donating groups have long wavelength fluorescence. Furthermore, several derivatives exhibit mechanofluorochromism in which the fluorescence properties in the solid state are changed by grinding. Their synthetic methods and substituent effects on the fluorescence properties will be discussed.

Keywords : Mechanofluorochromism, Organoboron Complex, Imidazole, Organic Fluorescent Molecule, Organic Crystal

我々は、剛直なイミダゾ[1,5-*c*][1,3,2]ジアザボロール環を主骨格としたホウ素錯体が良好な発光特性を示すことに着目し、発光特性に関する研究を行っている。本研究では、ヨード基を持つホウ素錯体に対する薗頭カップリングまたは鈴木-宮浦カップリングを用いて **1, 2** (**Scheme 1**)を合成し、それらの蛍光特性を検討した。

カップリング反応により得た **1, 2** は溶液・固体の双方で蛍光特性を示し、置換基の電子供与性が高いほど蛍光波長は長波長側にシフトした(**Fig. 1**)。また、一部の結晶ではすり潰すことによって蛍光特性が変化するメカノフルオロクロミズムを確認した。当日は、**1, 2** の合成および蛍光特性の置換基効果の詳細について報告する。



1a: R = PhC≡C-ʢ
1b: R = 4-MeOC$_6$H$_4$C≡C-ʢ
1c: R = 3,4-(MeO)$_2$C$_6$H$_3$C≡C-ʢ
1d: R = 4-Me$_2$NC$_6$H$_4$C≡C-ʢ
1e: R = 4-EtO$_2$CC$_6$H$_4$C≡C-ʢ
1f: R = TMS-C≡C-ʢ
2a: R = Ph
2b: R = 4-MeOC$_6$H$_4$

Scheme 1. Molecular structures of **1**, **2**.

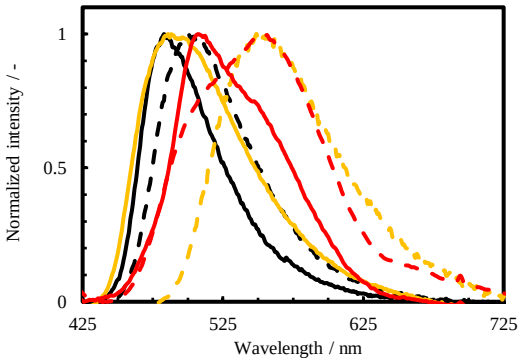


Fig. 1. The fluorescence spectra of **1a**(Black), **1c**(yellow), and **2b**(red) in solid state (solid line) and ground sample (dashed line).

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刺激応答性 D–A 型ホウ素π電子系の光物性に及ぼす分子内ホウ素–硫黄相互作用の効果

（名大院理[1]・名大 IRCCS[2]・名大 ITbM[3]）○山﨑 伶真[1]・森 達哉[2]・坂井 美佳[1]・山口 茂弘[1,2,3]

Impact of Intramolecular Boron–Sulfur Interaction on the Photophysical Properties of Stimuli-Responsive Donor–Acceptor-Type Organoboron Fluorophores

([1]*Graduate School of Science, Nagoya University*, [2]*Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University,* [3]*Institute of Transformative Bio-Molecules (ITbM), Nagoya University*) ○Ryoma Yamazaki,[1] Tatsuya Mori,[2] Mika Sakai,[1] Shigehiro Yamaguchi[1,2,3]

Boron-containing π-electron systems exhibit reversible complex formation with weak Lewis bases, which can be exploited for developing stimuli-responsive materials. In this study, we synthesized a series of donor–acceptor-type fluorophores consisting of a diarylboryl group in which two aryl groups were connected with a sulfur-containing alkyl linker. In te ground state, the boron atom adopted a tetracoordinate structure with an intramolecular coordination by the sulfur atom. In the excited state, dissociation of the B–S coordination bond proceeded, resulting in an emission from a donor–acceptor tricoordinate boron species. The structural optimization by the DFT calculation in the excited state showed that the boron and sulfur atoms retained their proximity with a B---S distance shorter than the sum of their Van der Waals radii, indicating that through-space orbital interaction was still present even in the dissociated state.
Keywords : Boron; Donor–Acceptor; Fluorescence; Excited State; Stimuli Response

ホウ素を含むπ電子系は，弱いルイス塩基との可逆な錯体形成により刺激応答性を付与できる．本研究では，新たな刺激応答性蛍光体の創製を目的に，弱ルイス塩基性の硫黄を含むアルキル鎖で連結したジアリールボリル基をアクセプターとするドナー–アクセプター型ホウ素π電子系を合成した．

この分子は，基底状態では，ホウ素と硫黄が分子内配位した 4 配位構造をとるのに対し，励起状態では，配位結合の解離が進行し，3 配位ホウ素に由来する蛍光を示した．励起状態での構造最適化を DFT 計算により行ったところ，解離は進行するものの，アルキル鎖での構造固定により，ホウ素と硫黄原子が近接した構造を維持していることがわかった（Figure 1）．その距離はファンデルワールス半径の和以下であり，遊離した硫黄とホウ素の間にスルースペース軌道相互作用が存在することが示唆された．さらに，ドナー置換基の電子供与性を強めることで，励起状態において，結合が解離した三配位構造がより安定化されることがわかった．

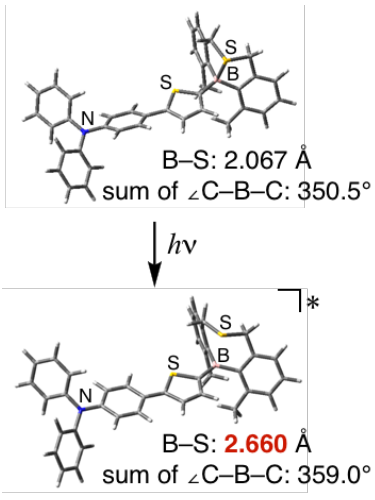

Figure 1. Optimized structures in the ground and excited states.

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9-ヒドロキシフェナレノンホウ素錯体における単座配位子の光物性と分子間相互作用への影響

（京大院工）○樽見 勇我・青山 侑冬・伊藤 峻一郎・田中 一生
Effects of Monodentate Ligands on the Intermolecular Interactions and Photophysical Properties of 9-Hydroxyphenalenone Boron Complexes (*Graduate School of Engineering, Kyoto University*) ○Yuga Tarumi, Yuto Aoyama, Shunichiro Ito, Kazuo Tanaka

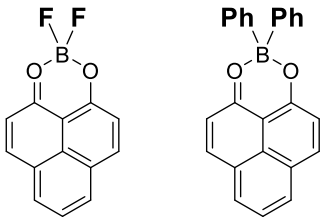
π-Conjugated molecules have been recently applied to organic photovoltaic cells and organic light-emitting diodes due to their high processability and tunability of photophysical properties. It has been reported that various four-coordinated boron complexes bearing π-conjugated ligands show excellent optical and electronic properties, such as highly efficient luminescence, stimuli-responsive emission, and high electron mobility. However, there are still limited studies on the synthesis and structure–property relationships of boron complexes with extended π-conjugation systems, although these complexes should potentially possess useful functions derived from their large π-system, like stimuli-responsiveness, stable redox property, and high charge mobility.[1,2] Herein, we synthesized the 9-hydroxyphenalenone (HP) boron complexes with different monodentate ligands (Figure 1) and evaluated their photophysical properties in dilute solution and solid states. It was revealed that the photoluminescence intensity and color depend strongly on the monodentate ligand (Figure 2). In this presentation, we will discuss their synthesis and origins of the differences in their optical and electronic properties.

Keywords : Group 13 Complex; Emission; Boron; Intermolecular Interactions; π-Conjugated Molecules

π 共役系分子は高い成型加工性を有するとともに、物性を自在に制御できることから、有機太陽電池や有機 EL などに応用されている。なかでも、π 共役系配位子をもつ四配位ホウ素錯体は刺激応答性発光や電子輸送特性などの優れた性質を示すものの、拡張 π 平面をもつものの例は限られていた。そこで本研究では、新たな π 拡張型配位子として 9-ヒドロキシフェナレノン(HP)に着目した。この HP 錯体は剛直な π 平面に由来する光·電子機能が期待されるがその報告例は僅少である[1,2]。

単座配位子の異なる新規の HP ホウ素錯体 **1** と **2** を合成し（Figure 1）、その希薄溶液及び固体状態での光物性を評価した。その結果、希薄溶液における発光強度や発光色が単座配位子の種類に強く依存することを見出した（Figure 2）。発表では、錯体の合成と物性変化の機構について詳述する。

1) Haddon, R. C. *et al. J. Am. Chem. Soc.* **2006**, *128*, 1982.
2) Bensch, L. *et al. Chem. Eur. J.* **2017**, *23*, 10551.



1 2

Figure 1. Chemical structures of HP complexes **1** and **2**.

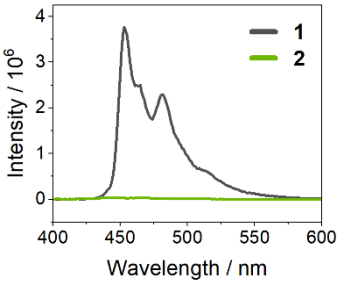


Figure 2. Photoluminescence spectra of **1** and **2** in $CHCl_3$ solutions (1.0×10^{-5} M).

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ベンゾビスチアゾール誘導体のホウ素架橋と光学特性

（京大院理）○内田 峻太・儘田 正史・畠山 琢次

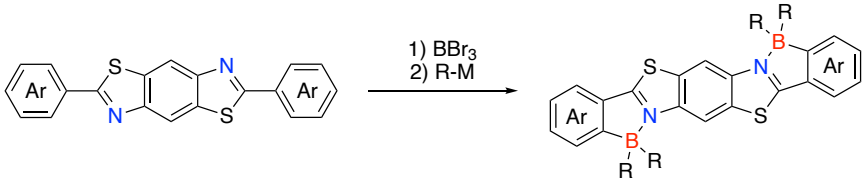
Boron-Bridged Benzobisthiazole Derivatives and Their Photophysical Properties

(*Graduate School of Science, Kyoto University*) ○Ryota Uchida, Masashi Mamada, Takuji Hatakeyama

Four-coordinate organoboron compounds with π-conjugated structures have been used as the functional materials in a variety of organic electronic devices because of their promising photophysical and electrochemical properties.[1)] They can be efficiently synthesized by the coordination of a nitrogen atom in heterocycles to BBr_3, followed by an intramolecular electrophilic aromatic borylation reaction.[2)] Herein, we applied the same method to diaryl benzobisthiazole derivatives and synthesized a new π-conjugated system with four-coordinate organoboron. The spectroscopic measurements revealed that the boron-bridging strategy increased the photoluminescence quantum yield and radiative rate constant. Moreover, amplified spontaneous emission (ASE) was observed for the boron-bridged benzobisthiazole derivatives. In this presentation, we will discuss the details of the photophysical properties of the compounds.

Keywords : Intramolecular B-N Coordinates; Thiazole-Borane Complex; Luminescent Material; Amplified Spontaneous Emission

π 共役骨格を有する 4 配位ホウ素化合物は，その優れた光物理特性や電気化学特性により，様々な有機エレクトロニクスデバイス応用に向けた有用な材料として注目されている [1)]。その有力な合成法の一つとして，含窒素ヘテロ環の三臭化ホウ素への配位と引き続く分子内求電子的芳香族ホウ素化反応が利用されている [2)]。今回我々は，ベンゾビスチアゾール誘導体に対して同手法を適用し，新たな π 共役 4 配位ホウ素化合物を合成した。分光測定の結果，ホウ素架橋によって蛍光量子収率や放射速度定数が向上することがわかった。さらに，ホウ素架橋体において自然放射増幅光（ASE）を観測することにも成功した。本講演では，これらの化合物の光学特性の詳細について報告する予定である。



1) a) Mamada, M.; Tian, G.; Nakanotani, H.; Su, J.; Adachi, C. *Angew. Chem. Int. Ed.* **2018**, *57*, 1238; b) Hayakawa, M.; Kameda, M.; Kawasumi, R.; Nakatsuka, S.; Yasuda, N.; Hatakeyama, T. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217512.
2) a) Ishida, N.; Moriya, T.; Goya, T.; Murakami, M. *J. Org. Chem.* **2010**, *75*, 8709; b) Kondrashov, M.; Provost, D.; Wendt, O. *Dalton Trans.* **2016**, *45*, 525.

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ビピロール骨格を有する四核ホウ素錯体への反応部位の導入と光機能材料の創製

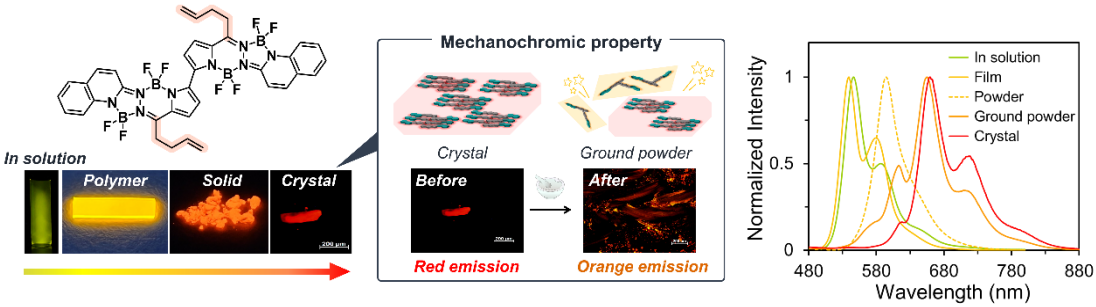
（九大工[1]・九大院工[2]・九大 CMS[3]）○谷 綾乃[1]・星野 友[2,3]・小野 利和[2,3]

Incorporation of reactive site to tetra-BF_2 complex with bipyrrole skeleton and creation of photofunctional materials ([1]*Faculty of Engineering, Kyushu University*, [2]*Graduate School of Engineering, Kyushu University,* [3]*Center for Molecular Systems (CMS), Kyushu University*)
○Ayano Tani,[1] Yu Hoshino,[2,3] Toshikazu Ono[2,3]

Luminescent boron complexes are typically known as functional dyes, which shows excellent optical properties and structural diversity, and are expected to apply bioimaging and sensor materials. Recently, our group have reported a series of tetra-BF_2 complex with bipyrrole skeleton that showed strong photoluminescence properties with large Stokes shift by adjusting the bending angle and conjugated system of these complexes. In this study, we extended this system and synthesized tetra-BF_2 complexes bearing reactive site. We created photofunctional materials through chemical modification of the reactive sites of these complexes and hybrid materials with polymers by hydrosilylation reaction. The emission color changed by c.a. 110 nm depending on the various environments such as in solution, polymer film, solid state, and single crystals, achieving multicolor from yellowish green to red with a single molecule. Furthermore, the single crystal was found to have mechanochromic property by grinding.
Keywords : Boron complexes; Bipyrrole; Schiff base; Fluorescence

発光性ホウ素錯体は優れた光学特性や構造多様性を有する機能性色素であり、バイオイメージングやセンサ材料への応用が期待されている。近年我々は、ビピロール骨格を有する旗蝶番型四核ホウ素錯体を合成し、その屈曲角度や共役系の調整により、強発光かつ大きなストークスシフトを示す光機能材料の創製を報告した[1)]。本研究ではこの系を拡張し、反応部位を有する四核ホウ素錯体を合成した。ヒドロシリル化反応によって、反応部位への化学修飾や高分子材料とのハイブリッド材料を作製した。

溶液中、高分子フィルム中、固体状態、単結晶など環境に応じて発光色が約 110 nm 変化し、単一分子で黄緑色から赤色までのマルチカラーを達成した。また、単結晶はすりつぶしによるメカノクロミック特性を有することが明らかとなった。



1) L. Cui, T. Ono *et al., Angew. Chem. Int. Ed.,* **2022**, *61*, e202204358.
This study is supported by MEXT Program: Data Creation and Utilization-Type Material Research and Development Project Grant Number JPMXP1122714694.

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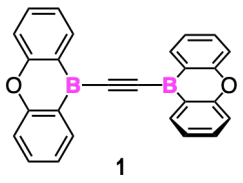
Multi-Bladed Donor-Acceptor π-Electronic Systems Exhibiting Unique Emission Properties

([1]*Lab. Chem. Life Sci., Tokyo Tech.*) ○Yunyi Song[1,2], Yoshiaki Shoji[1,2], Takanori Fukushima[1,2]
Keywords: *Diborylbenzene*; *Diborylacetylene*; *D-π-A system*; *Excimer*; *Long-lifetime emission*

We recently reported a chemically stable diborylacetylene (**1**) composed of 9-oxaboraanthracene, which exhibits reactivities typical of alkyne species and thus is useful as a synthetic building block to construct boron-rich molecules.[1)] For instance, upon heating with tetraarylcyclopentadienones, Diels-Alder reaction followed by elimination of carbon monooxide take place, giving the corresponding multi-bladed benzene derivatives with the boraanthracene units at the 1,2-positions.[1)] Interestingly, we found that carbazole-appended derivatives (**2**) show excimer emission in solution even at very low concentration conditions.[2)] We also prepared a new derivative (**3**) having phenoxazines in place of the carbazole units, which was found to display long-lifetime emission in solution at room temperature. Here we report details of the synthesis and photophysical properties of these multi-bladed aromatic systems.



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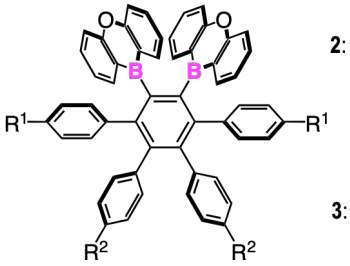
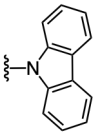
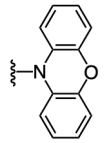


2: R^1 = carbazole, R^2 = H
R^1 = H, R^2 = carbazole
R^1 = R^2 = carbazole



3: R^1 = phenoxazine, R^2 = H



1) T. Tsukada, Y. Shoji, K. Takenouchi, H. Taka, T. Fukushima, *Chem. Commun*. **2022**, *58*, 4973.
2) Y. Song, Y. Shoji, T. Fukushima, 第 33 回基礎有機化学討論会, 1P028.

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ビピリジン骨格を有する四核ホウ素錯体の多様な光機能

（九大院工[1]・九大 CMS[2]）○古田 龍嗣[1]・崔 潞霞[1]・星野 友[1,2]・小野 利和[1,2]
Diverse Photofunctions of tetra-BF_2 Complexes with Bipyridine Skeleton ([1]*Graduate School of Engineering, Kyushu University*, [2]*Center for Molecular Systems (CMS), Kyushu University*)
○Ryoji Furuta,[1] Luxia Cui,[1] Yu Hoshino,[1,2] Toshikazu Ono,[1,2]

The luminescent boron complex BODIPY [1], have been applied to large variety of functional materials based on their excellent optical properties and its structural diversity. Recently, we have focused on BODIPY analogues such as BOPPY and BOPAHY, and reported various opto-functional materials such as white solid emission, strong multicolor emission, and circularly polarized luminescence by using dimerization strategy [2, 3]. In this study, we have tried to synthesize novel tetra-BF_2 complex with bipyridine skeleton by dimerization of BOAPH [4], one of the latest luminescent boron complexes. As a result, two types of tetra-BF_2 complexes, compound **1** and compound **2** were simultaneously generated (**Fig 1.**). In this presentation, the synthesis and photofunctional properties of these complexes will be presented.

Keywords : Boron Complex; B–O–B Bridged Complex; Circularly Polarized Luminescence Materials; Fluorescent Materials; Schiff Base Skeleton

発光性ホウ素錯体である BODIPY [1]は、優れた光学特性と構造多様性から、機能性色素として多様な用途に応用されている。近年我々は、BODIPY 類縁体である BOPPY や BOPAHY に着目し、二量化戦略を利用することで、固体白色発光材料の開発や、強発光性の多色発光、軸不斉に基づく円偏光発光材料への応用を達成した [2, 3]。本研究では、BOAPH[4]と呼ばれる二核ホウ素錯体の直結二量体として、ビピリジン骨格を有する四核ホウ素錯体の合成を検討した。その結果、目的とした化合物 **1** に加え、ホウ素が酸素架橋した化合物 **2** の、2 種類の四核ホウ素錯体が同時に生成することを新たに見出した(**Fig 1.**)。本発表ではこれら一連のホウ素錯体の合成と光機能特性について報告する。

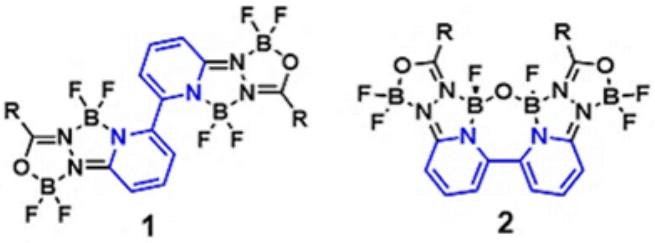

Fig 1. 2 種類の四核ホウ素錯体

1) A. Treibs, F.-H. Kreuzer, et al., *Justus Liebigs Ann. Chem*, **1968**, *718*, 208.
2) M. Ihara, T. Ono, et al., *Chem. Lett.*, **2022**, *51*, 300.
3) L. Cui, T. Ono, et al., *Angew. Chem. Int Ed.,* **2022**, *61*, e202204358.
4) C. Yu, E. Hao, et al., *J. Org. Chem.,* **2021**, *86, 17*, 11492.

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分子内配位リン置換基を有する含ホウ素多環芳香族炭化水素の合成と光物性

（名大理化[1]・名大 IRCCS[2]・名大院理[3]・名大 ITbM[4]）○佐野 嘉治[1]・森 達哉[2]・山口 茂弘[2,3,4]

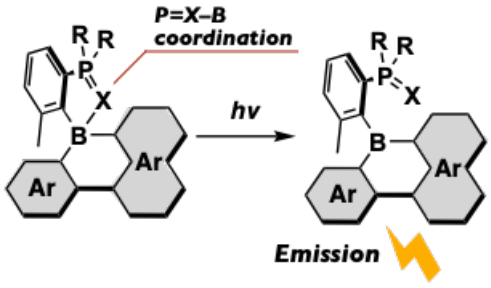
Synthesis and Photophysical Properties of Boron-Containing Polycyclic Aromatic Hydrocarbons with Intramolecularly-Coordinating Phorphorus Groups

([1]*School of Science*, *Nagoya University*, [2]*Integrated Research Consortium on Chemical Sciences*, *Nagoya University*, [3]*Graduate School of Science*, *Nagoya University*, [4]*Institute of Transformative Bio-Molecules*, *Nagoya University*) ○ Yoshiharu Sano,[1] Tatsuya Mori,[2] Shigehiro Yamaguchi[2,3,4]

Boron-containing polycyclic aromatic hydrocarbons (PAHs) exhibit attractive photophysical and electronic properties due to their electron-accepting character and Lewis acidity derived from the boron atoms. Herein, we synthesized a series of boron-containing PAHs with P=X-substituted phenyl groups (X = heteroatoms) on the boron atom, which enables the intramolecular coordination and the steric protection at the same time. In the ground state, the boron atom adopts a tetracoordinate structure owing to the intramolecular coordination of the P=X moiety. In contrast, the P=X–B coordination bond undergoes dissociation upon photoexcitation, giving rise to fluorescence from a tricoordinate boron species. The extent of bond dissociation and resulting emission behavior were modulated by not only the size of PAH skeleton and substituents on phosphorus atom but also surrounding environment such as solvent polarity and temperature.

Keywords : Boron; Polycyclic Aromatic Hydrocarbons; Fluorescence; Excited State; Stimuli-response

ホウ素を含む多環芳香族炭化水素（PAH）は、ホウ素の電子受容性やルイス酸性に由来した魅力的な光電子物性を示すことから、発光ダイオードなど多様な応用展開がなされている。本研究では、それらへの刺激応答性の付与を目的に、ホウ素保護基上に分子内配位能を有するリン置換基を導入した含ホウ素 PAH を合成した。得られた化合物は、基底状態では、ホウ素がリン置換基からの分子内配位を受け 4 配位構造をとり、ホウ素上にメシチル基をもつ 3 配位類縁体と比較して短波長に吸収スペクトルを示した。一方で、励起状態では、配位結合の解離が進行し、3 配位状態からの蛍光が得られた[1,2]。励起状態での解離挙動は含ホウ素 PAH の π 骨格の大きさに依存し、また、溶媒極性などの周囲環境の変化によっても、発光特性が変化することもわかった。



1) K. Matsuo, S. Saito, S. Yamaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 12580.
2) M. Kawashiro, T. Mori, M. Ito, N. Ando, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2023**, e202303725.

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キラル光学特性に優れた環状分子の創出を指向した *BO* 縮環ピロロピロールアザ BODIPY の合成

（九大院工）○深水 柊兵・清水 宗治

Synthesis of *B*-*O*-fused-pyrrolopyrrole aza-BODIPY toward creating cyclic oligomers with prominent chiroptical properties. (*Graduate School of Engineering, Kyushu University*)

○Shuhei Fukami, Soji Shimizu

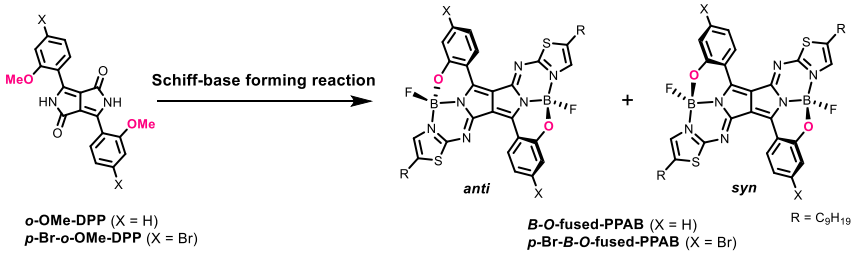
Pyrrolopyrrole aza-BODIPY (PPAB)[1] exhibits intense absorption and fluorescence in the visible and near-infrared regions. PPABs are synthesized from diketopyrropyrrole (DPP) by a facile one-pot Schiff base formation reaction with azaarylamine in the presence of triethylamine and titanium tetrachloride followed by a boron complexation reaction. This research attempted to synthesize cyclic oligomers of PPAB derivatives called *B*-*O*-fused-PPABs bearing fused structures around boron atoms to develop prominent chiral optical properties. There are two types of diastereomers (***anti*** and ***syn***) of *B*-*O*-fused-PPABs depending on the orientation of the axial ligand on the boron. Among them, ***syn*** isomer is chiral and exhibits chiroptical properties.

In this presentation, the synthesis of DPP precursor having *p*-bromo-*o*-methoxyphenyl groups (**p-Br-*o*-OMe-DPP**) and the corresponding *B*-*O*-fused-PPAB (**p-bromo-*B*-*O*-fused-PPAB**) will be reported.

Keywords : diketopyrrolopyrrole; aza-BODIPY; cyclic oligomer

BODIPY 類縁体であるピロロピロールアザ BODIPY（PPAB）は可視近赤外領域に強い吸収および蛍光を示す。PPAB はジケトピロロピロール（DPP）とヘテロ芳香族アミンから、トリエチルアミンと四塩化チタンを用いた Schiff 塩基形成反応と、続く BF_2 錯化により、簡便に合成することができる [1]。本研究では、優れたキラル光学特性の発現を指向して、ホウ素周りで縮環した構造を有する PPAB（***B*-*O*-fused-PPAB**（**Scheme 1**））からなる環状オリゴマーの創出を目的としている。***B*-*O*-fused-PPAB** の合成ではホウ素上の軸配位子の向きの違いにより、***anti*** と ***syn*** の 2 種類のジアステレオマーが得られ、***syn*** はキラル化合物であるためキラル光学特性を示す。

本発表では、環状オリゴマーの前駆体となる *p*-ブロモ *o*-メトキシフェニル基を有する DPP（**p-Br-*o*-OMe-DPP**）および ***p*-Br-*B*-*O*-fused PPAB** の合成を行ったので報告する。



Scheme 1. Synthesis of ***B*-*O*-fused-PPABs**.

1) S. Shimizu, *Chem. Commun.* **2019**, *55*, 8722.

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金(I)触媒を用いた環化異性化反応による縮環型 BODIPY の合成

（名大院工[1], 名大高等研究院[2]）○大橋 史夏[1]・髙野 秀明[1,2]・忍久保 洋[1]

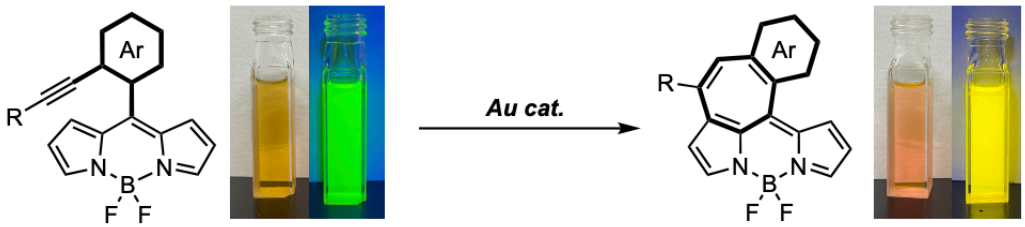
Au(I)-Catalyzed Cycloisomerization for the Synthesis of Fused BODIPYs (*Graduate School of Engineering, Nagoya University*[1], *Institute for Advanced Research, Nagoya University*[2]) ○ Fumika Ohashi[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1]

BODIPYs have excellent optical properties and are used in various applications. Among them, π-extended BODIPYs display characteristic photophysical properties derived from their expanded π-conjugation and rigid structures.[1)] Au(I)-catalyzed cycloisomerization of an alkyne with a benzene ring is recognized as a promising method for the construction of extended π-systems.[2)] Here, we report the synthesis of π-extended BODIPYs via Au(I)-catalyzed cycloisomerization. We have developed the transformation of a BODIPY with an alkynylphenyl group at the *meso* position to a 7-membered-ring-fused BODIPY in the presence of an Au(I) catalyst. The structure was determined by NMR, MS, and single crystal X-ray diffraction analyses. The obtained π-expanded BODIPY shows different optical properties from the non-fused BODIPY.

Keywords : BODIPY, Gold(I) catalyst, Cycloisomerization, π-extension

BODIPY は優れた光学特性を示し幅広い応用分野で利用されている。なかでもπ拡張した BODIPY は、共役系の伸長や骨格の剛直性に由来する特徴的な光学特性を示す[1)]。一方、金触媒を用いたアルキンとベンゼンの環化異性化反応は、縮環したπ共役系を効率的に構築することが可能であるため、π共役分子の合成法として有用である[2)]。

今回我々は、金(I)触媒による環化異性化反応を用いた新たなπ拡張 BODIPY の合成に成功した。*meso* 位にアルキニルフェニル基をもつ BODIPY を基質として金触媒存在下反応を行うことにより、７員環が縮環した BODIPY 誘導体を得た。その構造は、NMR、MS、および単結晶 X 線構造解析によって決定した。また、π拡張により原料とは顕著に異なる光学特性を示すことを見いだした。



1) Shinokubo, H. *et al*., *Org. Lett.* **2012**, *14*, 866–869.
2) Martínez-Díaz, M. V.; Torres, T. *et al*., *Chem. Sci.* **2020**, *11*, 10778–10785.

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ドナーアクセプター型オリゴシランの段階的合成

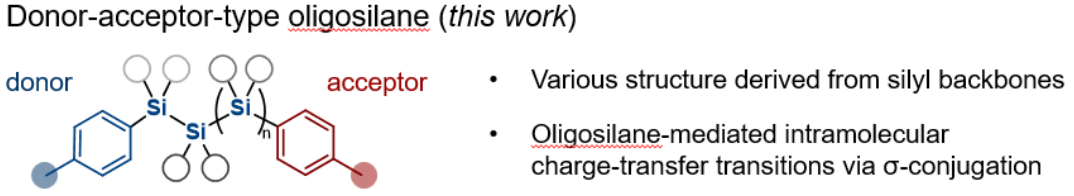
（北大院総化[1]・北大 WPI-ICReDD[2]・北大院工[3]）○半妙 夏海[1]・陳 旻究[2]・伊藤 肇[2,3]

Iterative synthesis of donor-acceptor-type oligosilanes ([1]*Graduate School of Chemical Science and Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*, [3]*Graduate School of Engineering, Hokkaido University*) ○Natsumi Hammyo,[1] Mingoo Jin,[2] Hajime Ito[2,3]

Disilane-bridged donor-acceptor molecules show unique absorption and emission properties based on intramolecular charge-transfer transitions via σ-conjugation in disilyl unit.[1,2] However, their structural diversity still remains limited due to the difficulty of their synthesis. Recently, we have developed a general synthetic method for sophisticated oligosilanes by iterative synthesis using silylboranes as the building blocks, which enables the synthesis of various oligosilanes that have been difficult to be obtained.[3] In this study, we have developed oligosilane-bridged donor-acceptor molecules by utilizing the iterative synthesis. It is expected to create various molecular structures derived from silyl backbones as well as unique optical properties based on oligosilane-mediated intramolecular charge-transfer. The synthesized molecules and the photophysical properties will be discussed in the presentation.

Keywords: Organosilicon compounds; Oligosilane; Silylborane; Donor-acceptor; σ-conjugation

ジシランで架橋したドナーアクセプター型分子は、σ 共役を介した分子内電荷移動遷移に基づく光吸収、発光を示すことが知られている[1,2]。しかし、複雑な骨格のオリゴシランは合成が困難であるため、ドナーアクセプター型オリゴシランの構造の多様性は限られていた。最近我々は、シリルボランをビルディングブロックとしたオリゴシランの段階的合成法を確立しており、この手法を用いることで多種多様なオリゴシランの合成が可能となった[3]。本研究では、オリゴシランで架橋した様々なドナーアクセプター型分子の段階的合成およびそれらの新規機能開拓を目的としている。ケイ素のバックボーンの違いに由来する構造の多様性に加え、オリゴシリル部位の σ 共役を介したドナーからアクセプターへの分子内電荷移動に基づく光吸収が期待される。



1. Z. Zhou, L. Gai, L. Xu, Z. Guo, H. Lu, *Chem. Sci.* **2023**, *14*, 10385.
2. M, Shimada, Y. Yamanoi, T. Matsushita, T. Kondo, E. Nishibori, A. Hatakeyama, K. Sugimoto, H. Nishihara, *J. Am. Chem. Soc.* **2015**, *137*, 1024.
3. T. Takeuchi, A. Roy, H. Ito, *J. Am. Chem. Soc.* **2023**, *145*, 16249.

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Substituent Effects on the Photophysical Properties of Disilane-Bridged Trimer Thiophenophane

○Yuya Kaneko[1], Yoshinori Yamanoi[1], Teppei Yamada[1] (1. The Univ. of Tokyo)

Keywords : luminescent molecules, disilane-bridged architectures

Compounds with electron-donating and electron-accepting groups connected by π-conjugated linkers have garnered attention as luminescent molecules [1]. These donor–acceptor (D/A) molecules display absorption and emission in the near UV and/or visible regions driven by intramolecular charge transfer (ICT) between the donor and the acceptor groups. Conventional solid-state D/A molecules often show emission quenching due to intermolecular π···π stacking, resulted in the limited use as intense fluorescence materials.

To overcome the drawback, we have designed organic silicon luminophores with a σ–π conjugated system, utilizing Si–Si σ and C=C π bonds, whose bulky nature suppresses intermolecular π···π stacking and enhances efficient solid-state emission by suppressing non-radiative decay. In the previous study, some disilane-bridged D-A-D linear triads behaved as fluorescent organic materials [2].

In this study, disilane-bridged trimeric thiophenophanes were synthesized using a coupling reaction between hydrosilane and aryl iodide (Fig. 1). Their optical properties were investigated both in solution and in solid. D-A-D molecule (c-Th_2Thpz) showed higher luminescence quantum yields in solid-state (ϕ_F: 0.24) than that in solution (ϕ_F: 0.09). This molecule has higher ϕ_F than linear structure in solution (ϕ_F: 0.02 < 0.09) and longer fluorescence life (τ: 0.58 ns < 2.92 ns). The thermal vibrational relaxation was effectively suppressed by ring formation. We also compared c-Th_2Thpz with c-Th_3 (D-D-D structure) to clarify the effect of the acceptor. Fluorescence wavelength of c-Th_2Thpz indicated a red shift in comparison with that of c-Th_3 (399 nm → 491 nm; Fig. 2).

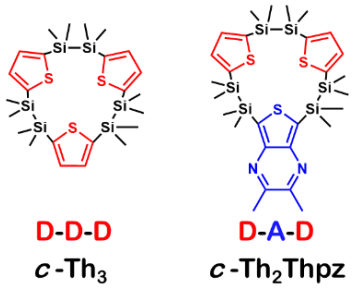

Fig. 1 Synthesized molecules

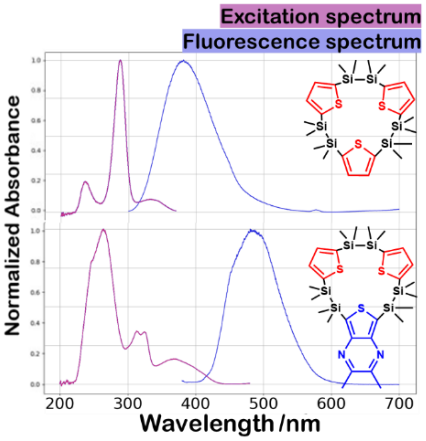

Fig. 2 Fluorescence spectrum in DCM

In the presentation, other synthesized molecules will be reported and their photophysical properties will be evaluated from DFT calculations.

[1] Guo, Z.-H.*et al*, *Chem. Commun*., 50, 6088-6090(2014).
[2] Usuki, T., et al, *Molecules* 24(3), 521(2019).

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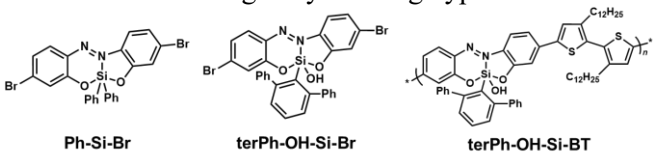
Synthesis and Optical Evaluation of π-Conjugated Systems Based on Hypervalent Silicon Compounds

([1]*Graduate School of Engineering, Kyoto University*)
○Ippei Kanetani[1], Masayuki Gon[1], Kazuo Tanaka[1]

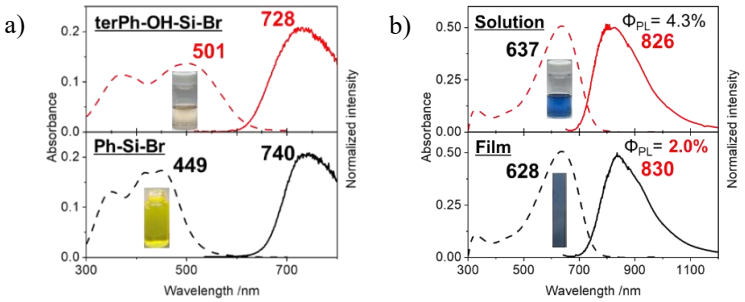
Keywords: Silicon; Luminescence; Near Infrared; Hypervalent; π-Conjugated Polymer

Near-infrared (NIR, 700 nm~) light-emitting materials are expected to be applied in the field of bioimaging and the optical communication. Recently, donor–acceptor (D–A) type π-conjugated polymers have been reported as a molecular design to achieve long wavelength absorption and luminescence. In this molecular design, longer wavelength absorption and luminescence can be accomplished by introducing acceptor units with lower LUMO energy level. Our group have synthesized acceptor units by making coordination between azobenzene and heteroatoms such as boron and tin.[1] In addition, D–A type π-conjugated polymers including these compounds showed luminescence in the NIR region. In this study, we focused on silicon atoms, which are available to coordinate to nitrogen by forming hypervalent states.

We aimed to tune acceptor properties and functionalities by modifying the substitution groups on silicon. We newly synthesized **terPh-OH-Si-Br**, which has a bulky terphenyl (terPh) group and a hydroxy group (OH) on silicon (Scheme 1). Compared to **Ph-Si-Br**, the absorption spectrum of **terPh-OH-Si-Br** was observed in the longer wavelength region (Figure 1a). According to DFT calculation, the energy gap of **terPh-OH-Si-Br** became narrower than that of **Ph-Si-Br**. It is assumed that the LUMO energy level of **terPh-OH-Si-Br** are reduced compared with that of **Ph-Si-Br** because the Si–N interaction of **terPh-OH-Si-Br** is strengthened by the bulky substitution groups. Finally, an alternating D–A copolymer (**terPh-OH-Si-BT**, Scheme 1) showed the emission in the NIR region in solution state. Moreover, the luminescent intensity was maintained even in film (Φ_{PL}= 4.3% in solution and 2.0% in film) because of a bulky substituent (Figure 1b).



Scheme1. Chemical structure of synthesized compounds.



←**Figure 1.** UV–vis–NIR absorption (dashed line) and photoluminescence (dotted line) spectrum of (a) **terPh-OH-Si-Br** in $CHCl_3$ (1.0×10^{-5} M) and **Ph-Si-Br** in toluene (1.0×10^{-5} M) and (b) **terPh-OH-Si-BT** in $CHCl_3$ (1.0×10^{-5} M) and film.

1) a) Gon, M.; Tanaka, K.; Chujo, Y. *Angew. Chem. Int. Ed.* **2018**, *57*, 6546–6551.
b) Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, *27*, 7561–7571.

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ベータ位置換ホスホールを用いた縮環ホスホール誘導体の合成と物性

（京大院工[1]・京大 WPI-iCeMS[2]・京大 ILAS[3]）○美濃部　陸[1]・東野　智洋[1]・今堀　博[1,2,3]

Synthesis and Properties of Aromatic-Fused Phospholes via β-Substituted Phospholes

([1]*Graduate School of Engineering, Kyoto University*, [2]*WPI–iCeMS, Kyoto University,* [3]*ILAS, Kyoto University*) ○Riku Minobe,[1] Tomohiro Higashino,[1] Hiroshi Imahori[1,2,3]

Phosphole, due to its unique optical and electrochemical properties, has garnered significant interest. Aromatic-fused phospholes, in particular, have been the subject of extensive research due to their fascinating photophysical and electronic properties. Specifically, methylene-bridged aromatic-fused phospholes are known for their high fluorescence quantum efficiency and superior photostability. However, the synthesis of methylene-bridged aromatic-fused phospholes presents considerable challenges, limiting their widespread use. In this study, we successfully synthesized a methylene-bridged fused phosphole and a dihydrophosphapentalene using β-substituted phospholes and have evaluated their properties.

Keywords : Phosphole; Phosphorus; Luminescence

ホスホールは、リン原子の構造的、電子的性質に由来した特異な物性を示すことから注目を集めている。リン原子を含むπ共役分子であるホスホールに芳香環を縮環させることにより、優れた発光特性や高い電子輸送能の実現が可能である。特に、メチレン架橋縮環ホスホールは、高い発光量子収率と光安定性を実現している[1)]。しかし、メチレン架橋縮環ホスホール化合物の合成法は限られており、分子設計上の制約が存在していた。そこで本研究では、ベータ位置換ホスホールの合成法を確立するとともに、β-ヒドロキシメチルホスホールを用いた分子内環化反応の検討を行った。その結果、2,5-ジナフチルホスホール誘導体を用いた場合には期待通りメチレン架橋縮環ホスホール誘導体を得ることに成功した。一方で興味深いことに、2,5-ジフェニルホスホール誘導体を用いた場合にはメチレン架橋縮環ホスホール誘導体は得られず、ジヒドロホスファペンタレン誘導体が得られることを見出した。当日は、ベータ位置換ホスホール誘導体の合成法、分子内環化反応の詳細および一連の化合物の物性について発表する。

1) Fukazawa, A. et al. *Angew. Chem. Int. Ed.* **2015**, *54,* 15213.

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アンチモンジピリン錯体の合成と性質

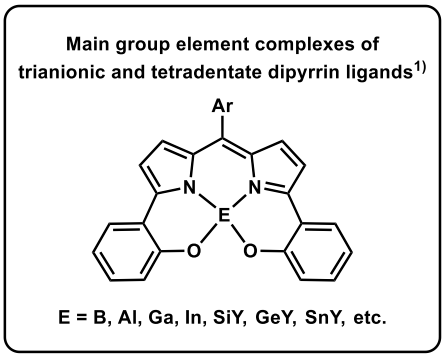
（茨城大院理工[1]・兵庫県大院理[2]・筑波大数理物質[3]）○黒岩 駿介[1]・福元 博基[1]・吾郷 友宏[2]・鍋島 達弥[3]

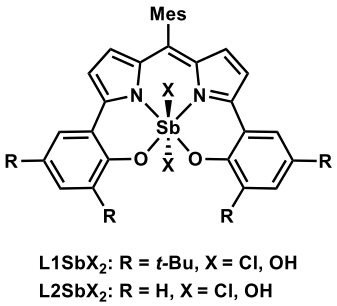
Synthesis and Properties of Antimony Dipyrrin Complexes ([1]*Graduate School of Science and Engineering, Ibaraki University*, [2]*Graduate School of Science, University of Hyogo,* [3]*Faculty of Pure and Applied Sciences, University of Tsukuba*) ○ Shunsuke Kuroiwa,[1] Hiroki Fukumoto,[1] Tomohiro Agou,[2] and Tatsuya Nabeshima[3]

Trianionic and tetradentate dipyrrin ligands are known to form stable complexes with various main group and transition metal elements, and these complexes exhibit intriguing properties such as long-wavelength absorption and emissions[1] and catalytic activity[2]. In this study, we investigated the developments of antimony dipyrrin complexes, **L1SbX$_2$** and **L2SbX$_2$** with the expectation of unique characteristics originating from the electronic interactions between the antimony atoms and the dipyrrin π-systems. Herein, synthesis, structures, and optical properties of these antimony dipyrrin complexes will be reported.

Keywords : Dipyrrin; Antimony; Optical properties

トリアニオン性の四座ジピリン配位子は様々な典型元素や遷移金属元素と安定な錯体を形成し、得られた錯体は赤～近赤外領域の吸収・蛍光発光性 [1]や触媒活性 [2]などの興味深い性質を示すことが知られている。今回我々は、アンチモン原子とジピリンπ共役系との電子的相互作用に起因したユニークな性質の発現を期待して、アンチモンジピリン錯体 **L1SbX$_2$** および **L2SbX$_2$** の合成を検討した。発表では、これらのアンチモンジピリン錯体の合成、構造、および光学的性質について報告する。





1) T. Nabeshima *et al. Chem Commun.* **2009**, 2544; *J. Am. Chem. Soc*. **2011**, *133*, 4726; *Inorg Chem.* **2014,** *53*, 1355; *Dalton Trans*. **2019**, *48*, 13169; *Synlett* **2020**, *31*, 1663.

2) K. Nozaki *et al*. *J. Am. Chem. Soc*. **2011**, *133*, 10720.

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

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC E1113(1113, Bldg. 11 [1F])

[E1113-4pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Masatoshi Ishida, Masayoshi Takase

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1113-4pm-01]

Synthesis of Dianionic Species of Cross-Conjugated γ-Thiolactone and Evaluation of its Aromaticity

○Takumi Shiokawa[1], Aiko Fukazawa[2] (1. Graduate School of Engineering, Kyoto University, 2. WPI-iCeMS, Kyoto University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1113-4pm-02]

Synthesis and properties of metal complexes of 20π antiaromatic diazaporphyrins

○Koubei Ohtake[1], Takahiro Sakurai[1], Hideaki Takano[1,2], Hiroshi Shinokubo[1] (1. Graduate School of Engineering, Nagoya University, 2. Institute for Advanced Research, Nagoya University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1113-4pm-03]

Synthesis and Properties of Diphenyldiaza-*m*-benziporphyrin Derivatives

○Emi Suzuki[1], Yoshihiro Matano[2] (1. Graduate School of Science and Technology, Niigata Univ., 2. Faculty of Science, Niigata Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1113-4pm-04]

Synthesis and physical properties of metal complexes of 5,10,20-triaryl-5,15-diazaporphyrin

○Yui Murata[1], Yoshihiro Matano[1] (1. Faculty of Science, Niigata Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1113-4pm-05]

Synthesis of Tin Complexes of 5,10,15,20-Tetraaryl-5,15-diazaporphyrin

○Hiroya Suzuki[1], Yoshihiro Matano[2] (1. Graduate School of Science and Technology, Niigata Univ., 2. Faculty of Science, Niigata Univ.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1113-4pm-06]

Creation of supramolecular architectures using TTF-annulated subphthalocyanine

○Riku Kitahara[1], Soji Shimizu[1] (1. Kyushu University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1113-4pm-07]

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Phthalocyanine Near-Infrared Photocatalyst for Direct Modification on Aromatic Rings

○Tasuku Iba[1], Taniyuki Furuyama[1] (1. Kanazawa Univ.)

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

Break

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[E1113-4pm-08]

Synthesis of dodeca-substituted tetrabenzoporphyrin via a coupling reaction

○Osuke Fukuda[1], Kenta Horikoshi, Makoto Roppongi[1], Satoshi Ito[1] (1. Faculty of Engineering, Utsunomiya University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[E1113-4pm-09]

Synthesis of stacked metal complexes with porphyrin dimer ligands

○Yusei Ohnishi[1], Shigeki Mori[2], Kan Miyamoto, Masayoshi Takase[1], Tetsuo Okujima[1], Uno Hidemitsu[1] (1. Graduate School of Science and Engineering, Ehime Univercity, 2. Advanced Research Support Center(ADRES),Ehime University ADRES)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[E1113-4pm-10]

Synthesis of calix[4]phyrins bearing spiro-fluorene subunits

○Masaaki Suzuki[1], Eisuke Tsurumi[2] (1. Graduate School of Natural Science and Technology, Shimane University, 2. Interdisciplinary Faculty of Science and Engineering, Shimane University)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[E1113-4pm-11]

Ion-Pairing Assembly of Electron-Deficient π-Electronic Cations

○Kantaro Omine[1], Yuya Hashimoto[1], Yohei Haketa[1], Hiromitsu Maeda[1] (1. Ritsumeikan University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[E1113-4pm-12]

Synthesis and physicochemical properties of new π-conjugated *meso*-substituted porphycene

○Chihiro Sonoda[1], Takashi Hayashi[1] (1. Osaka university)

Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[E1113-4pm-13]

Synthesis and charge transfer properties of tetrabenzo-10-heterocorrole

○Kento Teranishi[1], Kyohei Matsuo[1], Yoshiyuki Mizuhata[1], Yamada Hiroko[1] (1. Institute for Chemical Research, Kyoto University)

Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[E1113-4pm-14]

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Synthesis of ABCD-ABCD Cofacial Porphyrin Dimers

○Ryo Inoue[1], Mayu Kobayashi[1], Yasuhiro Morisaki[1] (1. Kwansei Gakuin University)

Japanese

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

[E1113-4pm-15]

Ion-Pairing Assembly of *meso*-Oxoporphyrin Au^{III} Complexes

○Shota Seki[1], Yohei Haketa[1], Hiromitsu Maeda[1] (1. Ritsumeikan University)

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ペンタフルバレンと等電子構造をもつ交差共役型γ-チオラクトンの還元種の合成と芳香族性の評価

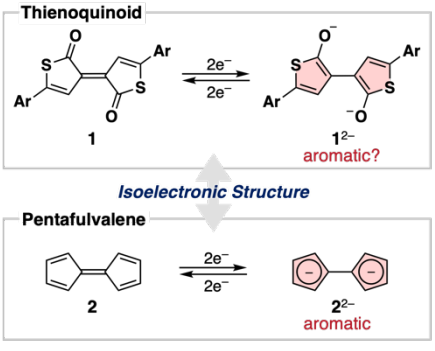
（京大院工[1]・京大 iCeMS[2]）○塩川 拓実[1]・深澤 愛子[2]

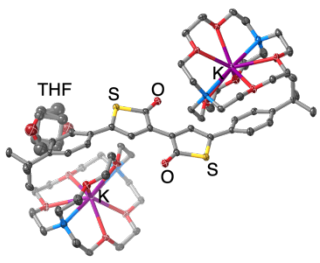
Synthesis of Dianionic Species of Cross-Conjugated γ-Thiolactone and Evaluation of its Aromaticity ([1]*Graduate School of Engineering, Kyoto University*, [2]*WPI-iCeMS, Kyoto University*) ○Takumi Shiokawa,[1] Aiko Fukazawa[2]

Thienoquinoids are an important class of compounds in organic electronics materials as electron-acceptor units. Although their high electron-accepting character has long been explained based on the aromatic character in the reduced state, quantitative evaluation has not yet been addressed. We herein report the synthesis of the dianionic species of a cross-conjugated γ-thiolactone **1**, which is one of the thienoquinoids previously reported by our group,[1] and quantitative insights into its aromaticity and electronic structure based on both experiments and theory. Comparison of the aromaticity and electron density distribution of $\mathbf{1}^{2-}$, with those of pentafulvalene dianion $\mathbf{2}^{2-}$ on the basis of their isoelectronic character revealed the smaller aromatic character and characteristic charge delocalization of $\mathbf{1}^{2-}$.
Keywords : aromaticity; π conjugation; electron-accepting character; quinoid; thiolactone

チエノキノイド類は高い電子受容性をもつため，有機エレクトロニクス材料における電子受容性ユニットとして近年活発に研究されている．チエノキノイド類の高い電子受容性は，還元状態での芳香族性の獲得に起因すると古くから説明されてきたが，定量的な知見は未だ報告されていない．そこで我々は，チエノキノイドの一種である交差共役型γ-チオラクトン（S-ペックマン色素）**1**[1] を対象とし，ジアニオン種 $\mathbf{1}^{2-}$ の芳香族性や電子構造を実験と理論の両面から定量的に評価した．チオエステルの電子効果を明らかにする上で，**1** がペンタフルバレン **2** と等電子構造をもつことに着目し，$\mathbf{1}^{2-}$ の芳香族性や電子密度分布をペンタフルバレンジアニオン $\mathbf{2}^{2-}$ と比較した．

標的化合物である $\mathbf{1}^{2-}$ は，KC_8 を用いた化学還元により合成した．X 線単結晶構造解析および量子化学計算の結果，$\mathbf{1}^{2-}$ の γ-チオラクトン骨格は芳香族性をもつものの，その度合いは $\mathbf{2}^{2-}$ と比べて顕著に小さいことがわかった．これは，チオフェン環の芳香族性の低さを反映した結果であると考えられる．本発表では，チオエステルが電荷の非局在化に及ぼす影響についても述べる．





X-ray crystal structure of $[\{K^+([2.2.2]cryptand)\}_2(\mathbf{1}^{2-})]\cdot THF$ (Ar = 4-*t*Bu-C_6H_4)

[1] (a) A. Fukazawa *et al. Chem. Commun.* **2013**, *49*, 7117. (b) A. Fukazawa, I. Osaka *et al. Chem. Mater.* **2021**, *33*, 8183.

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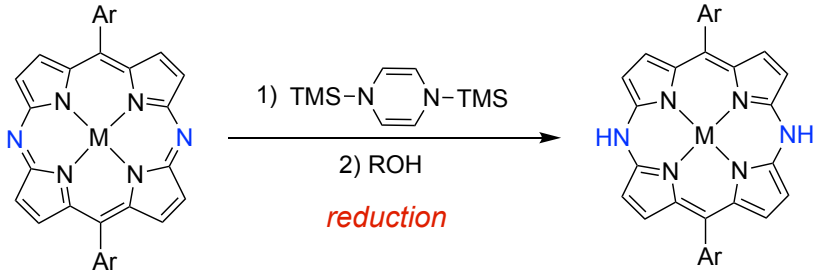
20π 反芳香族ジアザポルフィリン金属錯体の合成と物性

(名大院工[1],名大高等研究院[2])○大竹 耕平[1]・櫻井 貴浩[1]・髙野 秀明[1,2]・忍久保 洋[1]
Synthesis and properties of metal complexes of 20π antiaromatic diazaporphyrins (*[1]Graduate School of Engineering, Nagoya University, [2]Institute for Advanced Research, Nagoya University*) ○Kohei Ohtake[1], Takahiro Sakurai[1], Hideaki Takano[1,2], and Hiroshi Shinokubo[1].

Diazaporphyrin is an 18π aromatic porphyrinoid, in which two *meso* positions of porphyrin are substituted with nitrogen atoms. A diazaporphyrin can be converted to a 20π antiaromatic diazaporphyrin because of its excellent electron-accepting property[1,2]. On the other hand, 16π antiaromatic Ni(II) norcorroles with pentafluorophenyl or phenyl groups at *meso* positions exhibit stacked-ring aromaticity by close π-stacking.[3,4] In the present research, we have synthesized metal complexes of 20π antiaromatic diazaporphyrins with pentafluorophenyl or phenyl groups at *meso* positions to induce stacked-ring aromaticity. We will report structures and properties of these complexes in the solution and solid states.
Keywords : diazaporphyrin, antiaromaticity, stacked-ring aromaticity, aromaticity, π-conjugation

ポルフィリンの２つの *meso* 位を窒素で置換したジアザポルフィリンは 18π 芳香族ポルフィリノイドである。ジアザポルフィリンは優れた電子受容性をもつため、二電子還元により 20π 反芳香族ジアザポルフィリンへと変換可能である[1,2]。一方、16π 反芳香族化合物であるノルコロールニッケル錯体の *meso* 位にペンタフルオロフェニル基やフェニル基を導入すると、近接積層化による積層芳香族性が発現することが報告されている[3,4]。本研究では、積層芳香族性の発現を目指し 20π 反芳香族ジアザポルフィリン金属錯体の合成を行った。*meso* 位にペンタフルオロフェニル基やフェニル基を導入した 18π 芳香族ジアザポルフィリン金属錯体を合成し、これをジシリルジヒドロピラジンにより還元することで目的とする反芳香族ジアザポルフィリン金属錯体を合成した。発表では中心金属やアリール置換基によるその構造や物性の変化と溶液中や固体中での積層の可能性について報告する。



1) Y. Matano *et al*., *Angew. Chem. Int. Ed.* **2016**, *55*, 2235.
2) H. Shinokubo *et al., Chem. Eur. J.* **2016**, *22*, 3956.
3) H. Shinokubo *et al., Nat. Commun.* **2016**, *7*, 13620.
4) H. Shinokubo *et al., ChemRxiv* **2023**. DOI: 10.26434/chemrxiv-2023-2brcz.

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ジフェニルジアザ-*m*-ベンジポルフィリン誘導体の合成と物性

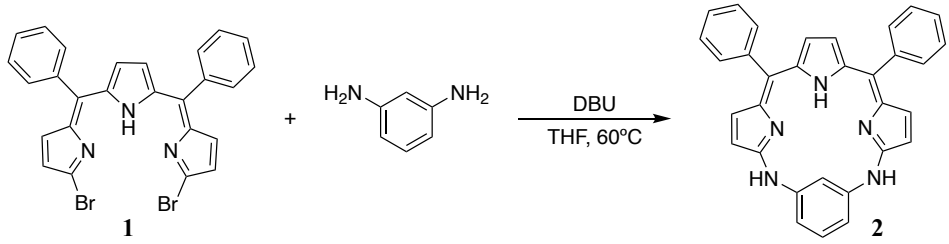
（新潟大院自然[1]・新潟大理[2]）○鈴木咲美[1]・俣野善博[2]
Synthesis and Properties of Diphenyldiaza-*m*-benziporphyrin Derivatives ([1]*Graduate School of Science and Technology, Niigata Univ.*, [2]*Faculty of Science, Niigata Univ.*) ○Emi Suzuki,[1] Yoshihiro Matano[2]

Porphyrins are 18π-electron macrocyclic compounds that exhibit characteristic aromatic, photophysical, and electrochemical properties. Nitrogen substitution at the *meso* position of the porphyrin ring is known as a method for modulating these properties, and we have designed and synthesized various 5,10-diazaporphyrins and their derivatives. However, little attention has been paid to the chemistry of 5,10-diazaporphyrins.

We report herein diphenyldiaza-*m*-benziporphyrins, the first example of core-modified diazaporphyrin derivatives. Diphenyldiaza-*m*-benziporphyrins were prepared by the nucleophilic substitution reaction of dibromodiphenyltripyrins with 1,3-phenylenediamine, and their aromaticity was evaluated by NMR spectroscopy. The optical and electrochemical properties and coordination behavior of the diaza-*m*-benziporphyrins will also be reported.
Keywords: *azaporphyrin, core-modification, optical property, electrochemical property*

ポルフィリンは 18π 電子系の大環状化合物であり、特徴的な芳香族性、光物性、電気化学特性を示す。ポルフィリンの物性を調節する手段の一つとして *meso* 位の窒素による置換が知られており、当研究室ではこれまでに 5,15-ジアザポルフィリンおよびその誘導体を設計・合成してきた。しかしながら、隣り合う *meso* 位が窒素で置換された 5,10-ジアザポルフィリンの化学はほとんど注目されていなかった[1]。本研究では、核置換 5,10-ジアザポルフィリンを研究対象とし、その合成と物性の解明に取り組んだ。

Scheme 1 に示す通り、DBU 存在下、ジブロモトリピリン **1** と 1,3-フェニレンジアミンを THF 中で加熱すると求核置換反応が進行し、核置換ジアザポルフィリンの最初の例となるジフェニルジアザ-*m*-ベンジポルフィリン **2** が 63%の収率で得られた。^{1}H NMR スペクトルを測定した結果、**1** と **2** のピロール β 水素は、それぞれ 6.76–6.31 ppm と 6.46–5.67 ppm に観測されたことなどから、核置換ジアザポルフィリン **2** が弱いながらもグローバル常磁性環電流効果を示すことが示唆された。また、ジアザ-*m*-ベンジポルフィリンの光学特性および電気化学特性を明らかにしたほか、錯形成反応についても検討したので、それらの結果についても併せて報告する。



Scheme 1

Ref. (1) Umetani, M.; Kim, G.; Tanaka, T.; Kim, D.; Osuka, A. *J. Org. Chem.* **2020**, *85*, 3849.

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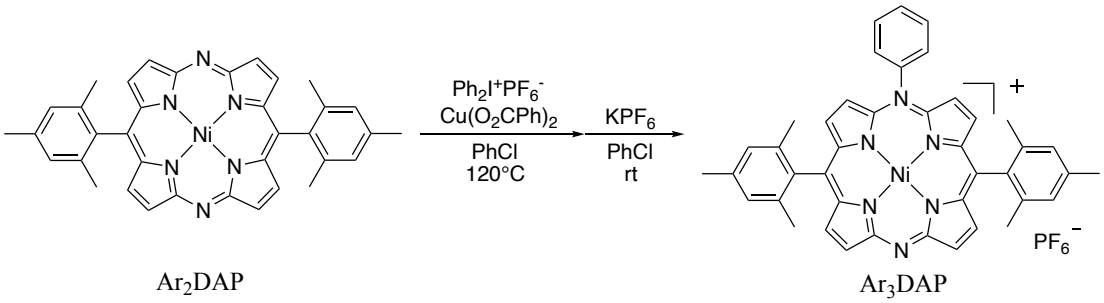
5,10,20-トリアリール-5,15-ジアザポルフィリン金属錯体の合成と物性

（新潟大理）○村田 優衣・俣野 善博
Synthesis and Physical Properties of Metal Complexes of 5,10,20-Triaryl-5,15-diazaporphyrin
(*Faculty of Science, Niigata University*)○Yui Murata, Yoshihiro Matano

5,10,20-Triaryl-5,15-diazaporphyrins (Ar_3DAP) exist as cations in the 18π-electron state. Accordingly, redox potentials of Ar_3DAP are largely shifted to the positive side compared to the corresponding values of 10,20-diaryl-5,15-diazaporphyrins (Ar_2DAP), and Ar_3DAP exhibit high electron-accepting ability and considerably red-shifted Q bands. However, there were limitations in the previous synthetic method for Ar_3DAP. To develop Ar_3DAP-based sensitizers, we have established a new method for the synthesis of Ar_3DAP. Heating a chlorobenzene solution containing a nickel(II) complex of Ar_2DAP, an excess amount of diphenyliodonium hexafluorophosphate, and a catalytic amount of copper(II) benzoate afforded a nickel(II) complex of Ar_3DAP cation in good yield (Scheme 1). Furthermore, we investigated the scope and limitation of this new protocol. The optical, electrochemical, and aromatic properties of TriADAP were also clarified using various spectroscopic methods.
Keywords : diazaporphyrin; optical property; electrochemical property; aromaticity

5,10,20-トリアリール-5,15-ジアザポルフィリン（Ar_3DAP）は、窒素上に置換基を一つ持つため、等電子構造を持つ 10,20-ジアリール-5,15-ジアザポルフィリン（Ar_2DAP）とは異なり 18π 電子状態がカチオンとなる。したがって、Ar_3DAP の酸化還元電位は Ar_2DAP の該当値に比べて大きく正側にシフトし、高い電子受容性と長波長化した Q 帯を示すことが知られている [1]。しかしながら、既知の Ar_3DAP の合成法には制約があった。本研究では、Ar_3DAP の特徴を活かした増感剤の開発を念頭に置き、より簡便な Ar_3DAP 合成法の開発を最初の目的とした。下記スキームに示す通り、クロロベンゼン中 Ar_2DAP ニッケル錯体と過剰量のジフェニルヨードニウム塩を触媒量の安息香酸銅存在下で加熱することにより、目的とする Ar_3DAP ニッケル錯体が良好な収率で得られた。本法は、Ar_2DAP の *meso* 位窒素上を直接フェニル化している点で従来の合成法よりも効率的である。さらに、種々の Ar_2DAP 誘導体を基質として本法の適用範囲を調べた。また、各種分光法を用いて、得られた Ar_3DAP の光学特性、電気化学特性、および芳香族性を明らかにしたので併せて報告する。



Ar_2DAP Ar_3DAP

1) K. Sudoh, Y. Matano, et al. *J. Porphyr. Phthalocyanines* **2018**, *22*, 542.

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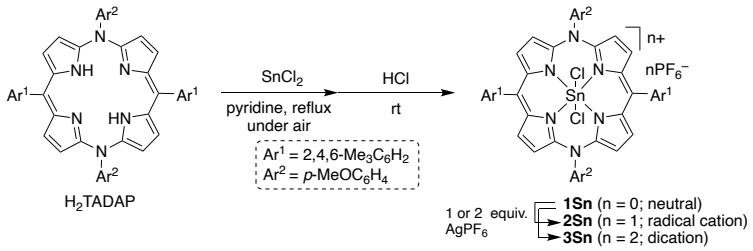
5,10,15,20-テトラアリール-5,15-ジアザポルフィリンのスズ錯体の合成

（新潟大院自然[1]・新潟大理[2]）○鈴木 裕也[1]・俣野 善博[2]
Synthesis of Tin Complexes of 5,10,15,20-Tetraaryl-5,15-diazaporphyrin ([1]*Graduate School of Science and Technology, Niigata University,* [2]*Faculty of Science, Niigata University*) ○Hiroya Suzuki,[1] Yoshihiro Matano[2]

5,10,15,20-Tetraaryl-5,15-diazaporphyrins (TADAPs) show the characteristic optical and electrochemical properties that differ considerably from those of the corresponding 5,10,15,20-tetraarylporphyrins.[1] In this study, we synthesized dichlorotin(IV) complexes of TADAP ($SnCl_2$TADAP) from the corresponding freebases (H_2TADAP). Treatment of H_2TADAP with $SnCl_2$ in pyridine at reflux under atmospheric condition afforded an inseparable mixture of tin(IV) complexes of TADAP with different axial ligands. To isolate a single tin(IV) complex, the resulting mixture was reacted with HClaq. to convert all axial ligands to chloride ions. Oxidation of 20π-electron **1Sn** with appropriate amounts of $AgPF_6$ produced 19π-electron radical cation **2Sn** and 18π-electron dication **3Sn**. The optical and electrochemical properties and aromaticity were elucidated by spectroscopic methods. The results of several attempts to exchange the axial ligands of **1Sn** will also be reported.
Keywords : Porphyrin; Diazaporphyrin; Tin complexes; Optical property; Electrochemical property

5,10,15,20-テトラアリール-5,15-ジアザポルフィリン（TADAP）は、メソ窒素の電子効果により、対応するポルフィリンとは大きく異なる光物性と電気化学特性を示す[1]。本研究ではフリーベース（H_2TADAP）から対応する塩化スズ(IV)錯体（$SnCl_2$TADAP）を合成した。H_2TADAP と $SnCl_2$ を大気下ピリジン中で還流することにより、異なる軸配位子を持つスズ錯体の混合物が得られるが、この混合物を塩酸で処理することにより、塩化物イオンを軸配位子とする $SnCl_2$TADAP **1Sn** として単離した。20π電子系を有する **1Sn** は、適切な量の酸化剤と反応させることにより、19π型ラジカルカチオン **2Sn**、18π型ジカチオン **3Sn** に変換することができる。得られたスズ錯体の光物性、電気化学特性、芳香族性を評価した。また、**1Sn** の軸配位子を交換する反応を検討したので、その結果についても併せて報告する。



1) (a) T. Satoh, M. Minoura, H. Nakano, Y. Matano, *Angew. Chem. Int. Ed.* **2016**, *55*, 2235. (b) K. Sudoh, T. Satoh, Y. Matano, et al. *Chem. Eur. J.* **2017**, *23*, 16364. (c) Y. Satoh, Y. Kudoh, K. Furukawa, Y. Matano, *Org. Lett.* **2022**, *24*, 3839.

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TTF 縮環サブフタロシアニンを用いた超分子集積体の構築

（九大院工）○北原 陸・清水 宗治
Creation of supramolecular architectures using TTF-annulated subphthalocyanine (*Graduate School of Engineering, Kyushu University*) ○Riku Kitahara, Soji Shimizu

Axially-fluoro-substituted subphthalocyanine (SubPc) is known to form an H-type stacking due to the bowl-shaped structure. In our previous study, we developed tetrathiafulvalene-annulated SubPc (TTF-SubPc) and successfully controlled this stacking behavior using redox-responsive intermolecular interactions of TTF moieties. Due to the strong π-π stacking interaction, TTF-SubPc also formed columnar stacking in apolar solvents or by lowering temperatures.

In this study, to enhance the intermolecular interactions at the neutral state, long alkyl chains were introduced, and the supramolecular polymer formation of TTF-SubPc was investigated by UV-Vis absorption spectroscopy and atomic force microscopy (AFM). In this presentation, the synthesis of a series of TTF-SubPcs bearing long alkyl chains and their supramolecular polymer formation will be discussed.

Keywords : Subphthalocyanine; Tetrathiafulvalene; Supramolecular chemistry;

軸配位子にフッ素を有するサブフタロシアニン（SubPc）は、そのお椀型構造により H 型会合体を形成しやすいことが知られている。我々はテトラチアフルバレン（TTF）縮環 SubPc（TTF-SubPc）を合成し、TTF 部位の酸化還元反応による分子間相互作用の変化を利用することで、積層挙動の制御に成功した。また、TTF-SubPc は強いπ-π相互作用により、無極性溶媒中や低温下においても会合体を形成することを見出している。

本研究では、中性状態において、より強い分子間相互作用を実現するために、長鎖アルキル基を導入した。得られた TTF-SubPc について、超分子ポリマーの形成を紫外可視吸収分光法と原子間力顕微鏡（AFM）を用いて明らかにした。本発表では、長鎖アルキル基を有する一連の TTF-SubPc の合成とその超分子ポリマー形成について議論する。

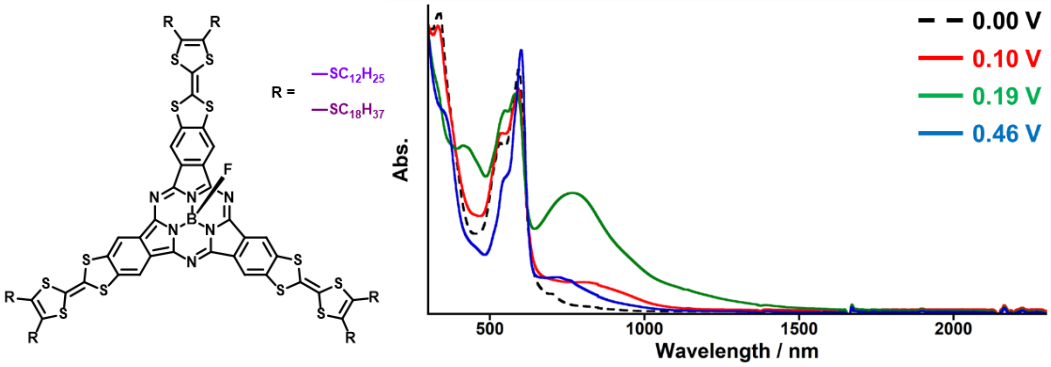

図. TTF-SubPc の分子構造と電解吸収スペクトル（溶媒：MCH）

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フタロシアニン近赤外光触媒を用いた芳香環上直接修飾反応の開発

（金沢大院自然科学[1]、金沢大ナノマテリアル研[2]）○射場 佑[1]・古山 渓行[2]

Phthalocyanine Near-Infrared Photocatalyst for Direct Modification Reactions on Aromatic Rings

([1]*Graduate School of Natural Science and Technology, Nanomaterials Research Institute, Kanazawa University*)
○Tasuku Iba[1], Taniyuki Furuyama[2]

Near-infrared (NIR) light attracts attention because of its high transparency and low toxicity. We have developed NIR photocatalyst zinc phthalocyanine (**PcZn, Fig. 1a**), which can generate singlet oxygen ($^1O_2$) through strong interaction with NIR light[i]. This presentation focused on aryl radical generation by the reaction of $^1O_2$ and phenylhydrazine[ii]. We hypothesized that **PcZn** can generate aryl radicals using NIR light as an energy source. After screening reaction conditions, various substituents could be introduced on aromatic rings with NIR light using various electrophiles (**Fig. 1b**).

Keywords : Near infrared light; Phthalocyanine; Photocatalyst; Singlet oxygen; Phenyl hydrazine

光駆動による有機分子変換は有用であり注目される一方、従来の紫外・可視光反応は環境や基質に制限がある。そこで、当研究室ではより長波長の近赤外 (NIR) 光の利用に着目した結果、NIR 光と強く相互作用し、一重項酸素 ($^1O_2$) 発生が可能な亜鉛フタロシアニン (**PcZn, Fig. 1a**) を触媒とする分子変換反応の開発に成功した[i]。本触媒系の更なる展開として $^1O_2$ とフェニルヒドラジンの反応によるアリールラジカルの発生[ii]に注目した。本研究では **PcZn** を NIR 光触媒とし、フェニルヒドラジンからのアリールラジカルの発生について各種条件検討を行い発生できたアリールラジカルに対し、様々な求電子剤を反応させた。結果、種々の官能基が導入でき、NIR 光をエネルギー源とした、芳香環上修飾反応が可能であることを明らかとした (**Fig. 1b**)。

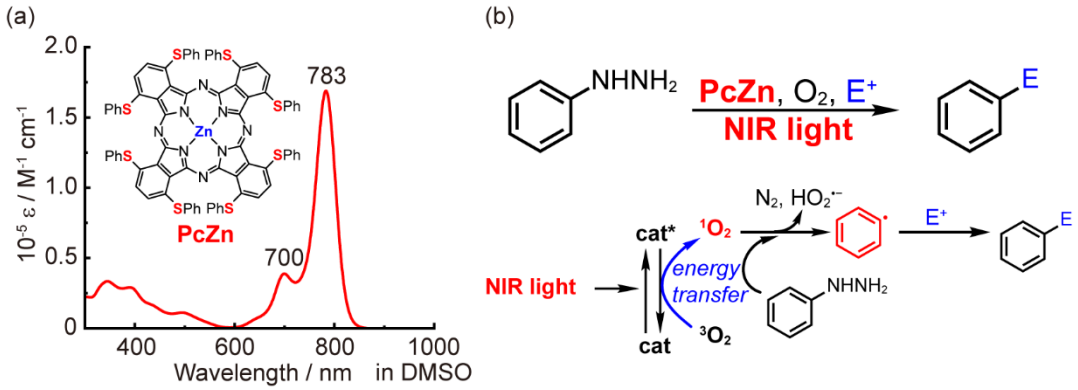

Fig. 1 (a) **PcZn** の光特性 (b) 近赤外光照射によるアリールラジカル発生

[i]Furuyama, T. *et. al. Chem. Eur. J.* **2022**, *28*, e202103223.
[ii]Koohgard, M. *et al. Org. Biomol. Chem.* **2021**, *19*, 5905.

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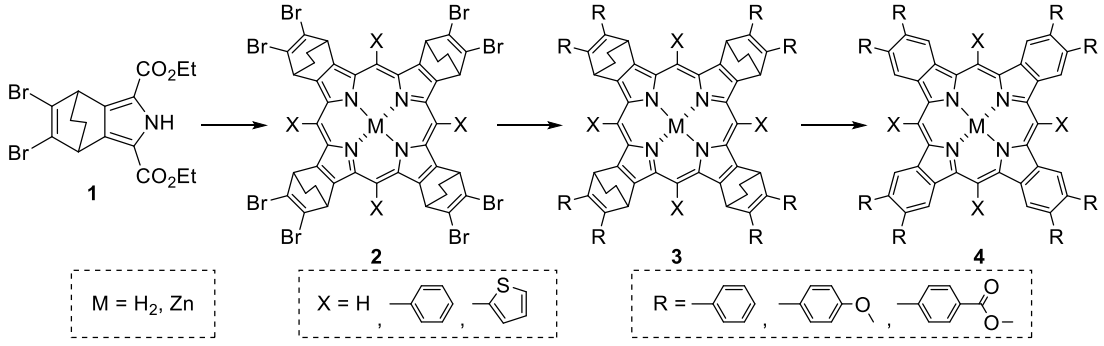
カップリング反応を経由する 12 置換 tetrabenzoporphyrin 類の合成

（宇都宮大工）○ 福田 旺佑・堀越 健太・六本木 誠・伊藤 智志
Synthesis of dodeca-substituted tetrabenzoporphyrins via a coupling reaction (*Faculity of Engineering, Utsunomiya University*) ○ Osuke Fukuda, Kenta Horikoshi, Makoto Roppongi, Satoshi Ito

Tetrabenzoporphyrin (BP), which is benzene fused to the β-position of porphyrin has been difficult to modify. This is because of the instability of isoindole, and the insolubility of BP in organic solvents. Therefore, we attempted to synthesize dodeca-substituted BPs **4** through suzuki coupling reaction involving *meso*-tetraaryloctabromobicycloporphyrins (*meso*-tetraaryloctabromoCPs: **2**). Diethyl 5,6-dibromo-4,7-dihydro-4,7-ethano-*2H*-isoindole-1,3-dicarboxylate **1**[1] was converted to *meso*-tetraaryloctabromoCP **2** by decarboxylation, tetramerization and oxidation. Dodeca-substituted BP **4** was synthesized via a coupling reaction with *meso*-tetraaryloctabromoCP **2**, followed by *retro* Diels-Alder reaction.
Keywords : Organic chemistry, Tetrabenzoporphyrin, Coupling reaction

テトラベンゾポルフィリン (BP) に対する化学修飾は、前駆体であるイソインドールの不安定性、BP の難溶性により困難であった。多置換 BP の合成は、置換基を持つビシクロピロールを用いれば可能だが、対応するピロールを用意する必要がある。我々の研究室では 5,6-ジブロモビシクロピロール **1**[1]の合成に成功している。そこで、本研究では、オクタブロモビシクロポルフィリン (オクタブロモ CP: **2**) に対するカップリング反応を行うことで、12 置換 BP **4** の合成を試みた。まず、5,6-ジブロモビシクロピロール **1** に対する脱炭酸反応、アルデヒドとの四量環化、DDQ による酸化を経ることでオクタブロモ CP **2** を合成した。次いでアリールボロン酸とのカップリング反応、加熱による *retro* Diels-Alder 反応により、縮環部位に 8 つの置換基を持つ BP 類 **4** の合成に成功した。本合成法によりメソ無置換 BP の合成が可能となった。得られた CP 類 **3** および BP 類 **4** について、各種物性の測定を行った。



Scheme. Synthesis of tetrabenzoporphyrins **4**

1) S. Ito, M. Tobata, M. Asakura, Y. Shinozaki, Y. Iwabe, L. Sakamoto, S-p. Ito, M. Roppongi, T. Oba, *Tetrahedron Lett*.,**58**, 4141-4144 (**2017**)

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ポルフィリン二量体を配位子とした新規積層型金属錯体の合成

(愛媛大院理工[1]・愛媛大 ADRES[2]) 大西 悠生[1]・森 重樹[2]・宮本 侃[1]・高瀬 雅祥[1]・奥島 鉄雄[1]・宇野 英満[1]

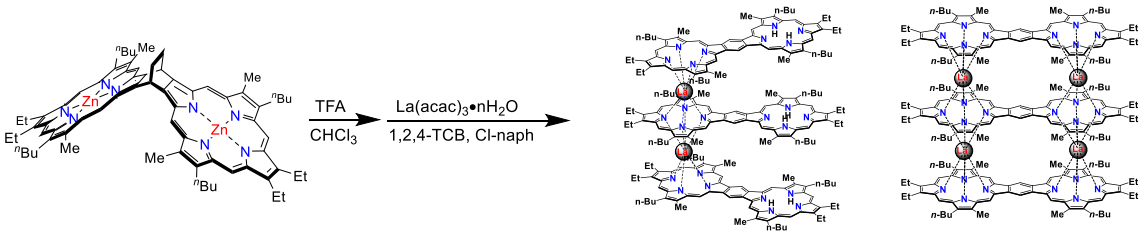
Synthesis of stacked metal complexes with porphyrin dimer ligands ([1]*Graduate School of Science and Engineering, Ehime University* [2]*Advanced Research Support Center (ADRES) , Ehime University)* ○Yusei Ohnishi[1], Shigeki Mori[2], Kan Miyamoto[1], Masayoshi Takase[1], Tetsuo Okujima[1], Hidemitsu Uno[1]

Porphyrins and phthalocyanines, known as functional dyes, are π-conjugated compounds that have been studied in various fields due to their unique absorption and redox properties, high aromaticity, metal coordination behavior. These molecules form 1:1 complexes with metal ions of small ionic radii, but are known to give double and triple decker-type complexes on metalation with lanthanide ions. However, in most cases, the ligands are used as monomers in such stacked metal complexes, and complexes with oligomers are extremely limited due to difficulty of synthesis and poor solubility. We have previously reported the efficient synthesis of benzo-bridged porphyrin dimer via a precursor method incorporating bicyclo[2.2.2]octadiene (BCOD) moiety. In this study, we synthesized stacked metal complexes with the porphyrin dimer as a ligand. The desired stacked complexes were synthesized and isolated by gel permeation chromatography. Two complexes were characterized by MALDI-TOF-MS and spectroscopic measurement.

Keywords：Porphyrin; stacked metal complexes

機能性色素として知られているポルフィリンやフタロシアニンは、特有の吸収や酸化還元特性、高い芳香族性、金属錯体形成などの性質により様々な分野へ応用されているπ共役系化合物である。これらの分子は、イオン半径の小さな金属イオンに対しては環内部に取り込んだ 1:1 錯体を形成するのに対し、ランタノイドイオンの場合、環内部に収まらずに配位子が上下に配位した積層型の金属錯体を構築することが知られている。しかし、このような積層型金属錯体において、配位子を単量体として用いる場合がほとんどであり、多量体を用いた錯体は、合成の複雑化や溶解性の乏しさから極めて限定的である。

当研究室で、ビシクロ[2.2.2]オクタジエン(BCOD)を導入した前駆体法により、効率的にベンゾ架橋ポルフィリン二量体を合成する方法を過去報告している。本研究では、この二量体を用いて積層型金属錯体の合成を達成した。分離・精製後、MALDI-TOF-MS、NMR、吸収スペクトルで物性評価をした。



BCOD-Zn2 **BBB-La2** **BBB-La4**

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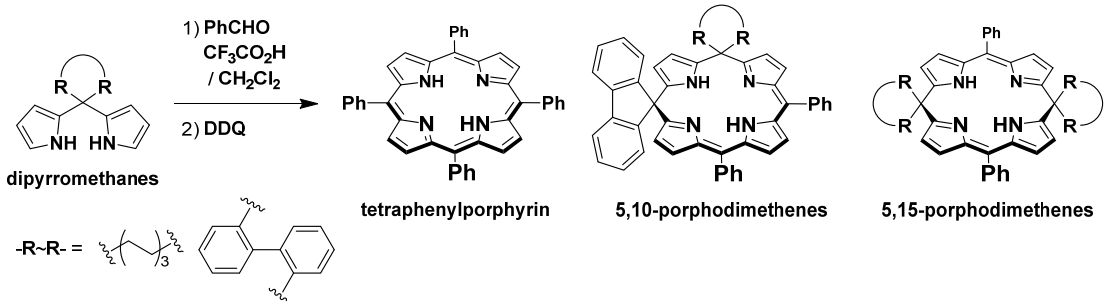
スピロフルオレン構造を有するカリックス[4]フィリン類の合成

（島根大院自然[1]・島根大総理[2]）○鈴木 優章[1]・鶴見 英亮[2]

Synthesis of calix[4]phyrins bearing spiro-fluorene subunits ([1]*Graduate School of Natural Science and Technology, Shimane University*, [2]*Interdisciplinary Faculty of Science and Engineering, Shimane University*), ○Masaaki Suzuki,[1] Eisuke Tsurumi[2]

Among calix[4]phyrins, porphodimethene possesses two sp^3 hybridized carbons at their *meso*-positions. When dipyrromethanes bearing fluorene or cycloheptane moieties in a spiro manner were condensed with benzaldehyde under acidic conditions and were oxidized subsequently, not only the presumable 5,15-porphodimethenes but also 5,10-porphodimethenes and tetraphenylporphyrin, which were thought to be derived from the scrambling of dipyrromethanes, were also obtained. Since some of these products could not be separated via a silica gel column, they were characterized using ^{1}H NMR spectrum of the mixture and X-ray crystal structure analysis by sorting out of each single crystal. This kind of reactions formally can be regarded as a synthesis of tripyrrin due to the partial structure of 5,10-derivatives.
Keywords : Porphyrinoid; Calix[4]phyrin; Porphodimethene; Spiro Compound

カリックス[4]フィリンは、環状テトラピロール骨格のメゾ位炭素の一部が sp^3 となっているもののことで、うち二箇所がそうであるものはポルホジメテンと呼ばれる。当研究室では、シクロアルキルジピロメタンを経由したメゾ位にシクロアルキル基がスピロ結合した 5,15-ポルホジメテン類の合成・分離・同定を達成した。[1] 今回、フルオレンあるいはシクロヘプタンがスピロ結合したジピロメタンをベンズアルデヒドとともに酸性条件下で縮合し酸化したところ、想定される 5,15-ポルホジメテンだけでなく、ジピロメタンのスクランブリングが原因と考えられる 5,10-ポルホジメテンやテトラフェニルポルフィリンも得られた。これらの一部はシリカゲルカラムでは分離できなかったので、混合物の ^{1}H-NMR スペクトルと単結晶の選別による X 線結晶構造解析を用いて同定した。5,10-ポルホジメテンはトリピリン部分構造をそのマクロ環内に有するため、本反応は、合成とその後の分離が煩雑であるトリピリン骨格を容易に得られる手法としても有用である。[2]



1) M. Suzuki, Y. Suzuki, Y. Uetake, *J. Porphyr. Phthalocyanines* **2023**, *27*, 1097–1102.
2) (a) M. Imafuku, S. Oki, M. Suzuki, *ChemistrySelect* **2020**, *5*, 7217–7221. (b) M. Suzuki, M. Imafuku, *Chem. Lett.* **2023**, *52*, 22–24.

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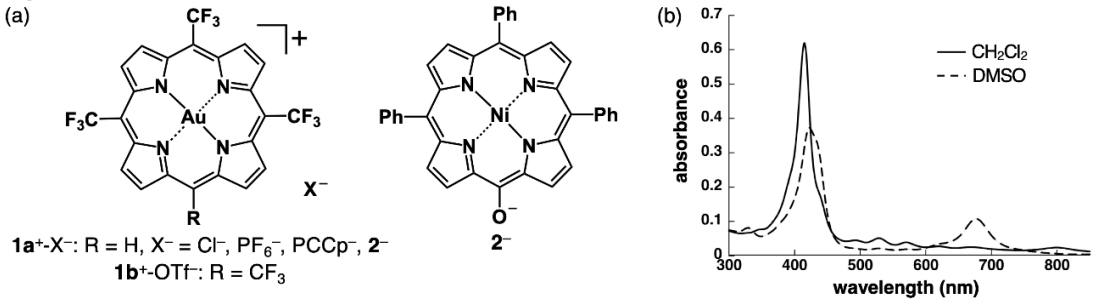
電子不足な π 電子系カチオンのイオンペア集合化

（立命館大生命科学）○大峯 貫太郎・橋本 祐也・羽毛田 洋平・前田 大光
Ion-Pairing Assembly of Electron-Deficient π-Electronic Cations (*College of Life Sciences, Ritsumeikan University*) ○Kantaro Omine, Yuya Hashimoto, Yohei Haketa, Hiromitsu Maeda

Porphyrin Au^{III} complexes as monovalent π-electronic cations form ion pairs in combination with various counteranions. In particular, activated π-electronic ion pairs exhibit intra-ion-pair electron transfer and resulting radical pair formation. In this study, CF_3 as a highly electron-withdrawing group was introduced to the *meso*-positions of the porphyrin Au^{III} complex to modulate the electronic states. Various ion pairs were obtained from the tri-CF_3-substituted cation in combination with counteranions. Furthermore, the stabilization of the non-charged porphyrin Au^{II} complex was achieved by the introduction of four CF_3 units.
Keywords : charged π-electronic systems; porphyrin Au^{III} complexes; ion pairs

平面状–2 価 4 座配位子であるポルフィリンの Au^{III} 錯体は対アニオンによる軸配位子が不要であるため、+1 価のπ電子系カチオンを形成する。[1] ポルフィリン Au^{III} 錯体は、適切な周辺置換基の導入による電子状態の調節によってイオンペア内電子移動を発現することを明らかにしている。[2] 本研究ではポルフィリン Au^{III} 錯体のメゾ位に電子求引性 CF_3 基を導入し、その置換数に応じた電子状態の制御を検討した（Figure 1a）。CF_3 3 置換ポルフィリンを AgOTf 共存下 $HAuCl_4{\cdot}4H_2O$ で処理することで Au^{III} 錯体を合成し、つづくイオン交換樹脂による処理で **1a**$^+$-Cl^-を得た。さらに、イオンペアメタセシスによって種々のアニオンの導入を行った。「活性化」ポルフィリンアニオンを導入した **1a**$^+$-**2**$^-$の UV/vis 吸収スペクトル（3.0 μM）から、DMSO 中ではイオンペアとして存在するのに対し、相対的に極性の低い CH_2Cl_2 中ではラジカルペア **1a**$^{\bullet}$-**2**$^{\bullet}$ を形成することが示唆された（Figure 1b）。C_6F_5 3 置換ポルフィリン Au^{III} 錯体は CH_2Cl_2 中でも **2**$^-$とイオンペアとして存在したことから、[2] CF_3 基導入による電子不足性の向上によってラジカルペアの形成傾向が上昇した。さらに、CF_3 4 置換ポルフィリンの Au^{III} 錯化にも成功し、1 電子還元された非荷電型 Au^{II} 錯体 **1b**$^{\bullet}$の安定化が示唆された。

Figure 1



1) Review: Haketa, Y.; Yamasumi, K.; Maeda, H. *Chem. Soc. Rev.* **2023**, *52*, 7170.
2) Tanaka, H.; Kobayashi, Y.; Furukawa, K.; Okayasu, Y.; Akine, S.; Yasuda, N.; Maeda, H. *J. Am. Chem. Soc.* **2022**, *144*, 21710.

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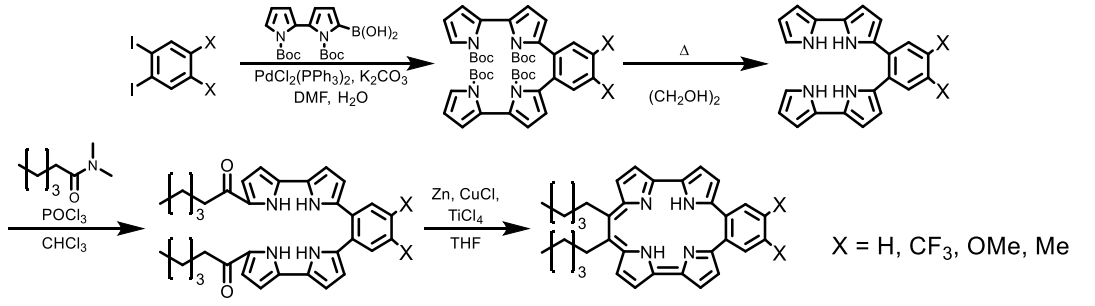
新規π共役拡張メソ置換ポルフィセンの合成と性質

（阪大院工）○苑田 千央・林 高史
Synthesis and Physicochemical Properties of New π-Conjugated *meso*-Substituted Porphycene
(*Graduate School of Engineering, Osaka University*) ○Chihiro Sonoda, Takashi Hayashi

Porphycene, which is a constitutional isomer of porphyrin, has remarkable photo- and redox features. Recently, porphycene analogues are expected to be applied as photosensitizers due to their excellent photochemical properties. The modification of the ethylene crosslinking sites (*meso*-positions) of porphycenes provides a particularly large π-conjugation extension effect[1]. Moreover, the alkylation at the *meso*-position is known to strengthen the NH–N hydrogen bonds within the ring[2]. In this study, we report on the synthesis and physicochemical properties of new π-conjugated extended monobenzoporphycenes, focusing on the substituents at the *meso*-fused benzene ring of porphycene. To confirm the effect of the substituents in these compounds on the physicochemical properties, monobenzoporphycenes in which two EDGs or two EWGs were introduced onto the benzene ring were prepared using Suzuki-Miyaura cross coupling and intramolecular McMurry coupling. ^{1}H NMR spectra of monobenzoporphycene analogues show that the inter NH peaks are found to be significantly affected by the electronic effects of the substituents attached to the benzene ring.

Keywords : Porphycene, Extension of π-Conjugation, Porphyrinoid, meso-Position

近年、ポルフィセン類縁体はその優れた可視光吸収能から色素増感剤への応用が期待される。ポルフィセンのエチレン架橋部位 (*meso*-位)への共役修飾は π 共役拡張効果が大きい[1]。また、*meso*-位へアルキル基修飾は分子内水素結合をより強固にすることが知られている[2]。本研究では、新規π共役拡張ポルフィセンとして *meso*-位にベンゼン環とアルキル基を修飾したポルフィセンの合成と物性について報告する。ベンゼン環上に電子供与基もしくは電子求引基を導入した類縁体も同時に合成し、この化合物の電子密度分布が物性に与える影響を確認した。合成戦略において、鈴木-宮浦カップリング反応、Boc 脱保護、*n*-オクタノン修飾はともに良好な収率で反応が進行し、その後に McMurry 反応を用いて計 4 ステップで合成を達成した (Scheme 1)。ポルフィセン類縁体の環内の NH はベンゼン環に結合した置換基 X による電子状態の変化に起因して ^{1}H NMR の NH ピークのシフトが観測された。



Scheme 1. Synthesis of monobenzoporphycenes.

1) T. Hayashi *et al., Angew. Chem. Int. Ed.* **2015**, *54*, 6227.
2) E. Vogel *et al.*, *Isr. J. Chem*. **1989**, *29*, 257.

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テトラベンゾ-10-ヘテロコロールの合成と電荷輸送特性

（京大化研[1]）○寺西 建登[1]・松尾 恭平[1]・水畑 吉行[1]・山田 容子[1]
Synthesis and Charge Transfer Properties of Tetrabenzo-10-heterocorrole ([1]*Institute for Chemical Research, Kyoto University*)○Kento Teranishi,[1] Kyohei Matsuo,[1] Yoshiyuki Mizuhata,[1] Hiroko Yamada [1]

Recently, bent-shaped ladder-type π-conjugated molecules have attracted much attention as organic field effect transistor (OFET) materials due to their improved solubility and thermal stability of the crystalline phase compared to linear π-conjugated molecules[1]. While most of the bent-shaped OFET materials utilized heteroles as a bending point, we focused on 10-heterocorroles, which is a class of ring-contracted porphyrinoids. 10-Heterocorroles are expected to be used as a conjugated core for bent-shaped OFET materials because of their two-dimensionally extended π-conjugated system in addition to the in-plane dipole moment (Figure 1a). We have designed a tetrabenzothiacorrole nickel complex, **Ni-TBTC**, in which sulfur is introduced to *meso*-position. **Ni-TBTC** was successfully synthesized from the thiacorrole derivative **Ni-CTC** by a thermal precursor method (Figure 1b). In this presentation, we will report on the synthesis and charge transport properties of **Ni-TBTC**.

Keywords : Heteroporphyrinoid; Precursor Approach, Crystal Structure Analysis; Organic Field-effect Transistors

近年、屈曲した縮環様式を有する拡張π共役分子は、直線状に共役を拡張した分子と比較して、溶解性や結晶相の熱安定性などが向上することから有機電解効果トランジスタ(OFET)材料として注目を集めている[1]。従来の屈曲型 OFET 材料のほとんどはヘテロールを屈曲点として利用しているのに対して、我々は環縮小ポルフィリノイドの一種である 10-ヘテロコロールに着目した。10-ヘテロコロールは屈曲構造に由来する双極子モーメントに加え、二次元的に広がったπ共役系を有するため、屈曲型 OFET 材料の主骨格として有望であると考えた(Figure 1a)。今回、我々はヘテロ原子として硫黄を導入したテトラベンゾチアコロールニッケル錯体 **Ni-TBTC** を設計した。**Ni-TBTC** はチアコロール誘導体 **Ni-CTC** から熱前駆体法によって合成することができた(Figure 1b)。本発表では得られた化合物の合成および OFET 特性について報告する。

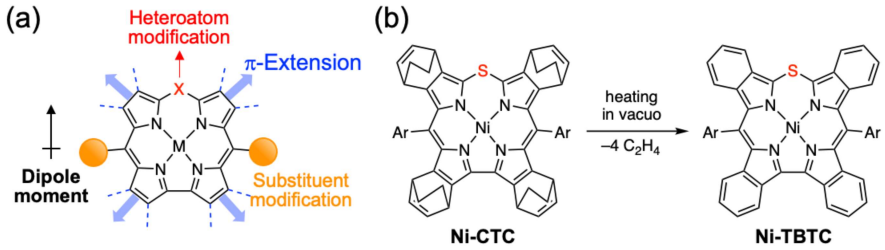

Figure 1. (a) 10-ヘテロコロールの分子構造と(b) **Ni-TBTC** の合成スキーム

1) T. Okamoto *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 9083.

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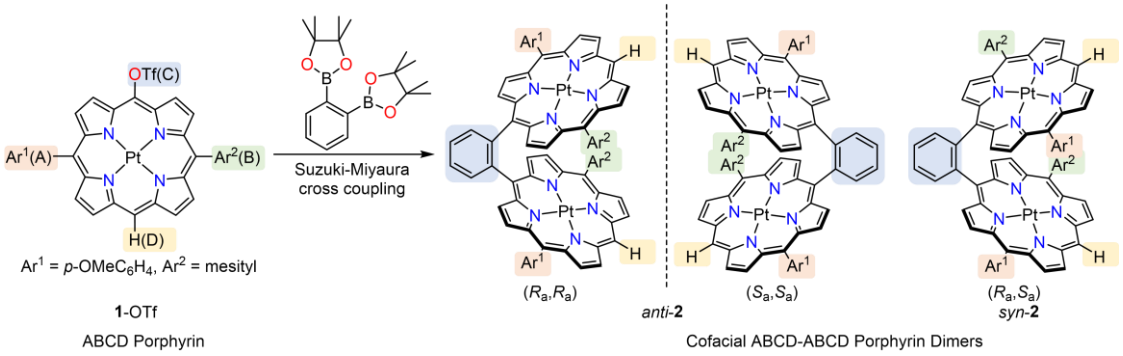
光学活性な ABCD-ABCD ポルフィリンダイマーの合成と物性

（関西学院大院理工）○井上 僚・小林 真由・森崎 泰弘
Synthesis of Cofacial ABCD-ABCD Porphyrin Dimers (*Graduate School of Science and Technology, Kwansei Gakuin University*) ○Ryo Inoue, Mayu Kobayashi, Yasuhiro Morisaki

The ABCD-porphyrins bearing four different substituents at the meso-position have been attracted much attention to develop the chemical sciences. We previously developed direct synthesis of ABCD-hydroxyporphyrin using a platinum template. In this work, we successfully synthesized meso and chiral ABCD-ABCD porphyrin dimers via sulfonylation and Suzuki-Miyaura cross coupling reaction of ABCD-hydroxyporphyrin. The chiroptical properties of the obtained compound will be also reported.
Keywords : Porphyrin; Template Synthesis; Chiral; Platinum Complex

ポルフィリンの機能の精密制御を目的とし、メソ位に異なる置換基を持つ ABCD-ポルフィリンの合成が注目されている。我々は最近、白金を鋳型とすることで進行する、“錯形成・環化・脱水芳香族化”を含むカスケード反応を用いた ABCD-ヒドロキシポルフィリンの合成法を開発した[1]。

本研究では、ヒドロキシ基のスルホニル化により得られる **1**-OTf を用い、対応するホウ素化合物と鈴木-宮浦カップリング反応を行うことで、ABCD-ABCD ポルフィリンダイマー *anti*-**2**/*syn*-**2** の合成・単離に成功した。得られた化合物 *anti*-**2** は、ABCD 環境に由来した軸不斉を有する光学活性化合物であり、キラル HPLC による光学分割が可能であった。当日は得られた化合物のキロプティカル特性についても併せて報告する。



1) R. Inoue, M. Yokoyama, I. Maruyama, Y. Morisaki, *Chem. Eur. J.* **2023**, *29*, e202301717.

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メゾオキソポルフィリン Au^{III} 錯体のイオンペア集合化

（立命館大生命科学）○関 翔太・羽毛田 洋平・前田 大光
Ion-Pairing Assembly of *meso*-Oxoporphyrin Au^{III} Complexes (*College of Life Sciences, Ritsumeikan University*) ○Shota Seki, Yohei Haketa, Hiromitsu Maeda

Porphyrin Au^{III} complexes as monocationic π-electronic systems show various ion-pairing assemblies depending on the counteranions. In this study, *meso*-oxoporphyrin Au^{III} complexes were synthesized as new electron-deficient π-electronic cations. Single-crystal X-ray analysis of *meso*-oxoporphyrin Au^{III} complex as a $B(C_6F_5)_4^-$ ion pair revealed the formation of the assembly with slip-stacked cation dimers due to the dipole–dipole interaction at the carbonyl groups.
Keywords : π-electronic cations; ion pairs; meso-oxoporphyrins; Au^{III} complexes

荷電π電子系は静電力と分散力をおもな寄与とする ${}^{i}\pi-{}^{i}\pi$ 相互作用により多様な集合体を形成する。[1] 積層形態の極限構造として、異種電荷種が交互に積層した電荷積層型集合体および同種電荷種が積層した電荷種分離配置型集合体があり、構成π電子系の構造・電子状態、また対イオンの組み合わせを調節することで積層形態を制御することができる。ポルフィリン Au^{III} 錯体は+1 価の荷電π電子系であり、適切な周辺置換基により電子状態を制御することでイオンペア内の電子移動が可能である。[2] 本研究では電子不足なカチオンとしてメゾオキソポルフィリン Au^{III}錯体の合成とイオンペア集合化を検討した（Figure 1a）。メゾオキソポルフィリン **1** を $KAuCl_4$ で処理することで非荷電型 Au^{II} 錯体 **1Au˙**の生成を確認した。さらに、**1Au˙** に $AgClO_4$ を作用させ、$LiB(C_6F_5)_4$ とのイオンペアメタセシスによって Au^{III}錯体イオンペア **1Au**$^+$-$B(C_6F_5)_4^-$を合成した。**1Au**$^+$-$B(C_6F_5)_4^-$の単結晶 X 線構造解析から、**1Au**$^+$が双極子–双極子相互作用の寄与によって部分積層した 2 量体を形成することを明らかにした（Figure 1b）。

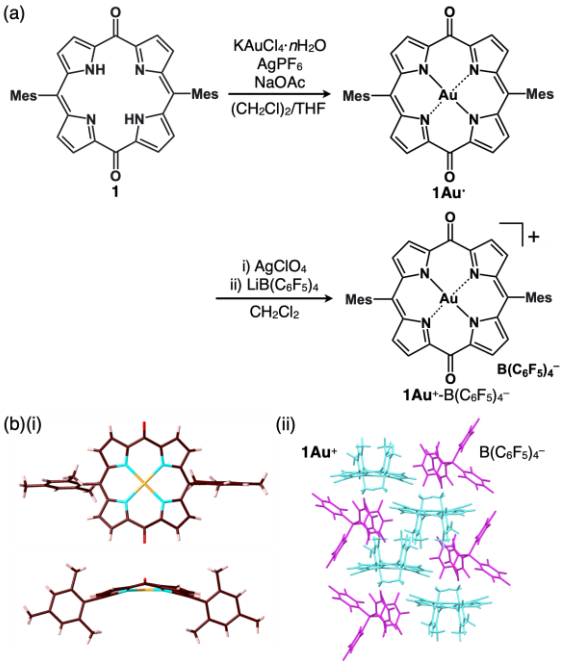

Figure 1 (a) Synthesis of **1Au**$^+$-$B(C_6F_5)_4^-$ and (b) single-crystal X-ray structure of **1Au**$^+$-$B(C_6F_5)_4^-$: (i) top and side views of **1Au**$^+$ and (ii) packing structure (cyan and magenta refer to cation and anion, respectively).

1) Review: Haketa, Y.; Yamasumi, K.; Maeda, H. *Chem. Soc. Rev.* **2023**, *52,* 7170.
2) Recent study: Tanaka, H.; Kobayashi, Y.; Furukawa, K.; Okayasu, Y.; Akine, S.: Yasuda, N.; Maeda, H. *J. Am. Chem. Soc.* **2022**, *144*, 21710.

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Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
E1122(1122, Bldg. 11 [2F])

[E1122-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Shunsuke Ohtani, Tomoya Fukui

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1122-4am-01]
Mechanofluorochromic properties of 1,4-diphenylanthracene derivatives exhibiting a hypsochromic shift

○Fumihiro KANNEN[1], Tadatoshi ADACHI[1], Manato Nishimura[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1122-4am-02]
Structure and inclusion ability of γ-cyclodextrin dimer linked by 1,4- and 2,3-dimethylnaphthalene

○Toru Kataoka[1], Yoshihiro Ishimaru[1] (1. Saitama University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1122-4am-03]
Inner chemical modification of an $M_{60}L_{60}$ peptide cage

○Shiori Hino[1], Michito Yoshizawa[1], Tomohisa Sawada[1,2] (1. Lab. for Chem. & Life Sci., Tokyo Tech, 2. JST-PRESTO)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1122-4am-04]
Upward vibrational frequency shift due to electron–phonon polar-coupling interaction in $C_{12}H_{17}ClN_4OS{\cdot}HCl{\cdot}H_2O$ crystals

○Masae Takahashi[1], Hiroshi Matsui[1], Eunsang Kwon[1], Yuka Ikemoto[2] (1. Tohoku Univ., 2. JASRI)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1122-4am-05]
Solid-state self-complementary assembly of anthracene-based molecular tweezers: selective construction of discrete assemblies and dynamic structural transformation

○Koki Okabe[1], Masahiro Yamashina[1], Eiji Tsurumaki[1], Shinji Toyota[1] (1. Tokyo Tech)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1122-4am-06]
Formation of an optically active micelle bearing terpene frameworks and its cavity chirality

○Yoshihisa Hashimoto[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

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10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

Break

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[E1122-4am-07]

Chiral Optical Properties of Axially Chiral Molecules within Aromatic Micelles

○Tomohiro Yasuda[1], Yoshihisa Hashimoto[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech.)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1122-4am-08]

Metal-mediated confinement of dye molecules within an acetylene-containing aromatic micelle

○Shinnosuke Hirata[1], Yuya Tanaka[1], Michito Yoshizawa[1] (1. Tokyo Institute of Technology)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1122-4am-09]

Synthesis of azaylide-based gemini-amphiphiles and their unique aggregation behavior caused by alkyl linker length

○Akiyama Yoshimori[1], Yamashina Masahiro[1], Toyota Shinji[1] (1. Tokyo Tech)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1122-4am-10]

Construction of Silver Nanoclusters Driven by Cooperative Acetylene Coordination

○Tasuki Tsurumi[1], Takahiro Nakagawa[2], Yuya Domoto[1], Kiyohiro Adachi[3], Takuma Kaneko[4], Tomoya Uruga[4,5], Daisuke Hashidume[3], Yosuke Nakamura[1], Makoto Fujita[2,6] (1. Gunma Univ., 2. The Univ. of Tokyo, 3. RIKEN, 4. JASRI, 5. The Univ. of Electro-Communications, 6. IMS)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1122-4am-11]

Detection of phosphonic acids and nucleotides using aggregation-induced emission of tetraamidine

○Yusuke Yamamoto[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1122-4am-12]

Cooperative Molecular Recognition of Macrocyclic Tetrakisporphyrin

○Kouta Tanabe[1,2], Naoyuki Hisano[1], Haino Takeharu[1,2] (1. Grad. Sc. Adv. Sci. Eng., Hiroshima Univ., 2. International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM²))

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1122-4am-13]

Supramolecular Complexes Formed by Molecular Recognition of Multi-Layered Zinc Porphyrin

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○Tomoki Kodama[1,2], Naoyuki Hisano[1], Takeharu Haino[1,2] (1. Grad. Sc. Adv. Sci. Eng., Hiroshima Univ., 2. WPI-SKCM², Hiroshima Univ.)

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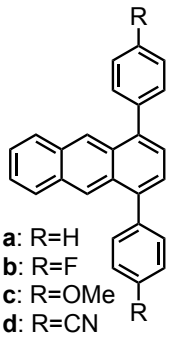
浅色シフトを示す 1,4-ジフェニルアントラセン誘導体のメカノクロミズム特性

（京工繊大院・工芸科学）○閑念 郁尋・足立 忠駿・西村 愛翔・楠川 隆博
Mechanofluorochromic properties of 1,4-diphenylanthracene derivatives exhibiting a hypsochromic shift (Kyoto Institute of Technology) ○Fumihiro Kannen, Tadatoshi Adachi, Manato Nishimura, Takahiro Kusukawa

Recently, mechanofluorochromism, a phenomenon in which fluorescence color changes due to mechanical stimulation, has attracted much attention. In this study, we investigated the mechanofluorochromic properties of 1,4-diphenylanthracene derivatives. For the derivatives **1a** (R = H) and **1b** (R = F), the obtained pristine samples showed blue emission during 365 nm UV irradiation and no mechanofluorochromism were observed. On the other hand, for the derivatives **1c** (R = OMe) and **1d** (R = CN), showed yellow-green emission for the pristine state and exhibit blue shift of the emission color (yellow-green to green) was observed after grinding (Figure 1). These phenomena may be attributed to the decrease in π–π stacked excimer emission after grinding.
Keywords: diphenylanthracene; fluorescence; mechanochromism



1

近年、力学的刺激によって光学的な変化を引き起こすメカノクロミズムが注目を集めている。当研究室では、構造が単純な 1,8-ジフェニルアントラセンをすりつぶすことで、発光色が青色から緑色に変化し、発光波長が長波長シフトすることを明らかにしている [1]。本研究では、フェニル基の置換位置が異なる 1,4-ジフェニルアントラセン誘導体のメカノクロミズム特性を調査したところ、誘導体 **1a** (R = H) , **1b** (R = F)では青色の発光を示し、メカノクロミズムを示さなかった。一方、**1c** (R = OMe), **1d** (R = CN)では黄緑色の発光を示し、すりつぶし後に発光波長が短波長にシフトするメカノクロミズムを示すことを見出した(Figure 1a)。さらに、**1d** のすりつぶし後には、蛍光寿命が短くなり、蛍光量子収率が向上した(Figure 1a)。さらに、単結晶 X 線構造解析から **1d** のすりつぶし前の黄緑色発光はエキシマー形成に由来していることが示唆された (Figure 1b)。これらのことから、**1d** のすりつぶしによる発光色の変化は、アントラセン環同士のπ–πスタッキングが弱まることで、エキシマー発光の寄与が減少することに由来すると考えられる。

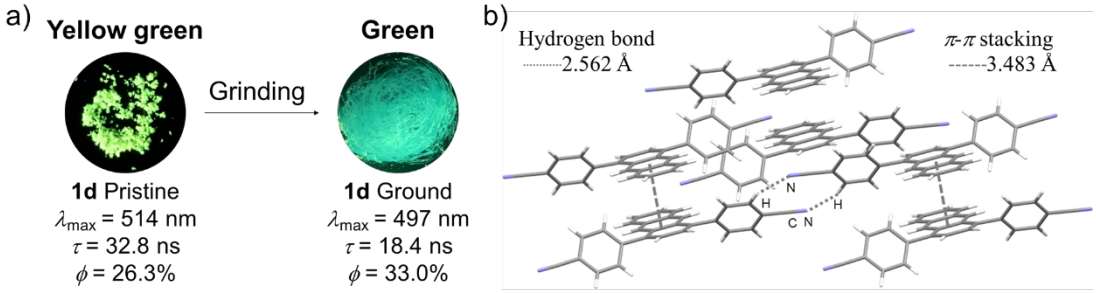


Figure 1. Fluorescence photograph of **1d** (a) and crystal structure of **1d** (b).

1) T. Kusukawa *et al*., *Chem. Lett.* **2019**, *48*, 1213.

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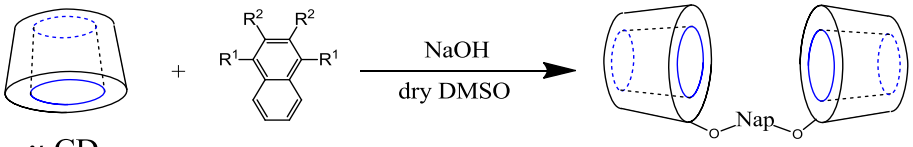
1，4ー及び2，3ージメチルナフタレンを架橋基として持つγ−シクロデキストリン二量体の構造と包接能

（埼玉院理工）○片岡 徹・石丸 雄大
Structure and inclusion ability of γ-cyclodextrin dimers linked by 1,4- and 2,3-dimethylnaphthalene (*Science and Engineering, Saitama University*) ○ Toru Kataoka, Yoshihiro Ishimaru

γ-Cyclodextrin (γ-CD) is renowned for its ability to encapsulate organic matter in water, owing to the internal cavities of its ring structure. Previous studies have explored synthesizing dimers by linking cyclodextrins (CDs) with various cross-linking groups. This study focuses on elucidating the impact of these cross-linking groups on the internal cavities of CD dimers. We synthesized γ-CD dimers using xylene and naphthalene as cross-linking groups and assessed their functionalities. Specifically, we present the synthesis of a γ-CD dimer linked by a naphthalene ring and examine its structural integrity and inclusion capabilities with benzene sulfonate (BNS). Table 1 outlines the thermodynamic parameters for the inclusion of 2,2-type CD dimers with 1,4-dimethylnaphthalene (1,4-Nap) and 2,3-dimethylnaphthalene (2,3-Nap) as cross-linking agents and BNS. The CD dimer with 1,4-Nap exhibited a 1:2 inclusion ratio, whereas the CD dimer with 2,3-Nap as the cross-linker demonstrated a 1:1 inclusion ratio. This presentation will detail the inclusion properties of CD dimers with each cross-linked group.
Keywords : cyclodextrin; dimer; inclusion ability

γ-シクロデキストリン(γ-CD)は水中で有機物を環内部の空孔に包接することが知られている。一方、CD 同士を架橋基で結合し、より大きな空孔を持つ CD 二量体を合成する研究も行われている。当研究室では架橋基が、キシレン及びナフタレンを架橋基とした γ-CD 二量体の合成及び機能評価を行ってきた。本研究では、1,4-及び 2,3-ジメチルナフタレンを架橋基として持つ γ-CD 二量体の合成を行い、構造及び sodium 6-(4-*tert*-butylanilino)- naphthalene-2-sulfonate (BNS)との包接能評価を行った。



γ-CD

Scheme 1 γ-CD dimers の合成

1; $R^1 = CH_2Br$, $R^2 = H$
2; $R^1 = H$, $R^2 = CH_2Br$

合成は 1,4-及び 2,3-ビス(ブロモメチル)ナフタレンをリンカーとして NaOH 存在下、γ-CD と反応を行い、γ-CD の 2 位二級水酸基同士が架橋した 2,2-Nap$^{(1,4)}$-及び 2,2-Nap$^{(2,3)}$-CD 二量体を得た。得られた二量体は BNS をゲスト分子として等温滴定カロリメトリー(ITC)により測定を行った。その結果、2,2-Nap$^{(1,4)}$-γ-CD 二量体は BNS と 1:2 の包接状態をとることが分かり、2,2-Nap$^{(2,3)}$-γ-CD 二量体は 1:1 の包接状態をとることが分かった。このことから架橋基であるナフタレンが γ-CD 二量体がつくる空孔内に異なる状態で存在していると考えており、発表ではこの詳細について報告する。

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$M_{60}L_{60}$ ペプチドケージの内面化学修飾

（東工大化生研[1]・JST さきがけ[2]）○日野栞[1]・吉沢道人[1]・澤田知久[1,2]

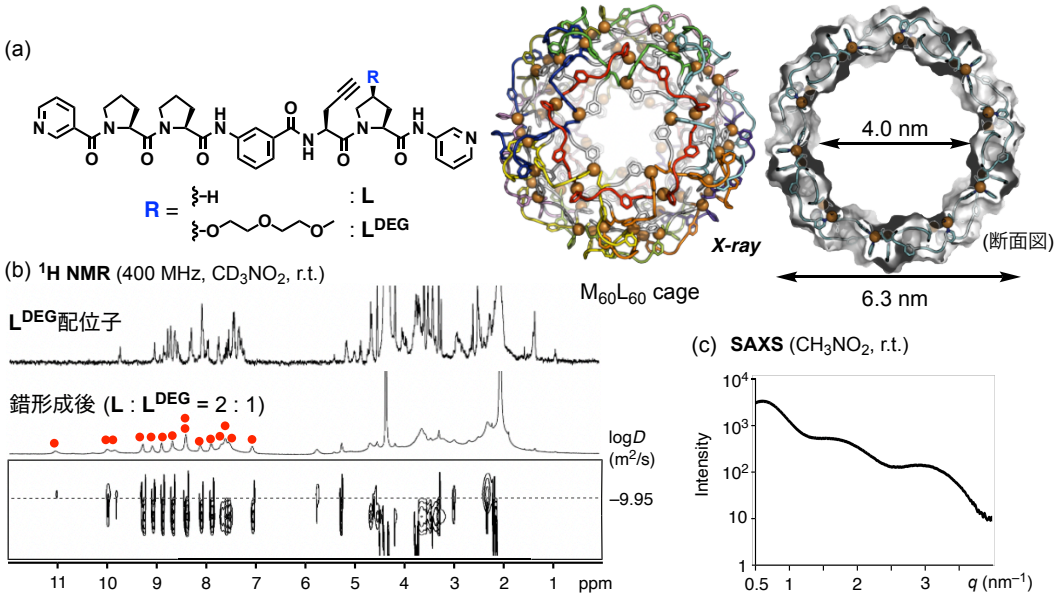
Inner chemical modification of an $M_{60}L_{60}$ peptide cage

(*[1]Lab. for Chem. & Life Sci., Tokyo Tech*, *[2]JST PRESTO*) ○Shiori Hino,[1] Michito Yoshizawa,[1] Tomohisa Sawada[1,2]

Folding and assembly of a pentapeptide ligand (L) and Cu^+ ions (M) afford an $M_{60}L_{60}$ cage (Fig. a, The 102nd CSJ Annual Meeting H201-1am-10). Here, to utilize the huge 4-nm-sized inner cavity, we examined inner chemical modification of the cage. Peptide ligand $\mathbf{L}^{\mathbf{DEG}}$ with a diethylene glycol (DEG) group was synthesized. Complexation of Cu^+ ions and $\mathbf{L}^{\mathbf{DEG}}$ resulted in severe signal broadening in the ^{1}H NMR spectrum, which suggested no convergence to the cage. Complexation of mixed ligands of unmodified one and $\mathbf{L}^{\mathbf{DEG}}$ in 2:1 ratio with Cu^+ ions was then examined. ^{1}H NMR showed broadened signals with the same pattern to those of the unmodified cage, which was confirmed as *ca.* 6 nm-sized structure by DOSY (Fig. b). SAXS data also supported formation of a *ca.* 6 nm-sized spherical particle (Fig. c), indicating successful formation of the DEG-modified $M_{60}L_{60}$ cage.

Keywords: self-assembly, folding, peptide, coordination cage, chemical modification

無修飾ペンタペプチド配位子 L と Cu^+イオン(M)のフォールディング集合により、$M_{60}L_{60}$ 組成のケージが組み上がる(図 a、CSJ 第 102 春季年会 H201-1am-10)。今回、その 4 nm 径の巨大内部空間の活用を目指し、内面官能基化を検討した。まず、ジエチレングリコール(DEG)基を導入した新規配位子 $\mathbf{L}^{\mathbf{DEG}}$ を合成した。$\mathbf{L}^{\mathbf{DEG}}$ と Cu^+イオンの錯形成では、^{1}H NMR シグナルの著しいブロード化が見られ、ケージ形成が確認できなかった。そこで、配位子 L と $\mathbf{L}^{\mathbf{DEG}}$ の 2 : 1 の混合による錯形成を検討した。^{1}H NMR において芳香族・アミド領域に、無置換のケージと同一パターンの 15 本のシグナルがブロード化して観測され、DOSY NMR より、これらは約 6 nm 径の構造であると確認された（図 b)。さらに、SAXS 測定からも約 6 nm 径の球状粒子が観測され（図 c)、DEG 基を導入した $M_{60}L_{60}$ ケージの形成に成功した。



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Upward vibrational frequency shift due to electron–phonon polar-coupling interaction in $C_{12}H_{17}ClN_4OS{\cdot}HCl{\cdot}H_2O$ crystals

([1]*Graduate School of Science, Tohoku University*, [2]*Japan Synchrotron Radiation Research Institute*) ○Masae Takahashi,[1] Hiroshi Matsui,[1] Eunsang Kwon,[1] Yuka Ikemoto[2]

Keywords: Electron–phonon interaction; Terahertz spectroscopy; first-principles calculations

The temperature-dependent upward frequency shifts (blueshifts) of vibrational transitions are scarce in molecular crystals, although downward shifts (redshifts) often been reported. The temperature-dependent frequency shifts of sharp Lorentzian peaks in crystals can be mainly caused by electron–phonon (e–p) interactions at and below the vibrational time scales, and thermal expansion of the crystal. The e–p interactions occur through distinct elastic and inelastic mechanisms. The elastic mechanism is the polar coupling through the electric field of the lattice polarization, and the inelastic mechanism is the deformation potential coupling through the dependence of electronic energies on lattice structural properties. The polar-coupling interaction between excited-state electrons and longitudinal LO phonons shifts the frequency upward with increasing temperature, while the temperature-dependent downward frequency shift is caused by inelastic scattering with thermal excited phonons [1] (Fig. 1). The polar-coupling interaction in crystals has recently attracted a lot of attention, because it is a driving mechanism of carrier–phonon dynamics for cooling hot charge carriers in lead halide perovskites, which is the most promising next-generation photovoltaic devices. However, considerable ambiguity existed regarding the phonon modes involved in the e–p polar-coupling interactions.

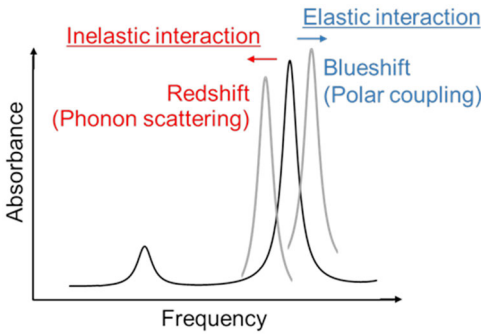

Fig. 1. Vibrational frequency shifts (Reproduced from Fig.1 of Ref. [2]).

In this study, electron–phonon polar-coupling interactions in $C_{12}H_{17}ClN_4OS{\cdot}HCl{\cdot}H_2O$ crystals exhibiting an upward frequency shift with increasing temperature are investigated using terahertz and far-infrared spectroscopies. X-ray crystallography and first-principles calculations reveal that the key structure is an open cavity near the considered vibration. Based on the temperature-dependent frequency shift proportional to the Bose−Einstein statistical factor, the interaction strength and characteristic frequency of phonons interacting with electrons are determined. From the phonon dispersion curves exhibiting LO–TO splitting, we find that the highest frequency LO phonon participates in the polar-coupling interaction. [2].

[1] M. Takahashi, M. Kowada, H. Matsui, E. Kwon, Y. Ikemoto, *Appl. Phys. Lett*. **2022**, *120*, 051104.
[2] M. Takahashi, H. Matsui, E. Kwon, Y. Ikemoto, *Chem. Phys. Impact* **2024**, in press.

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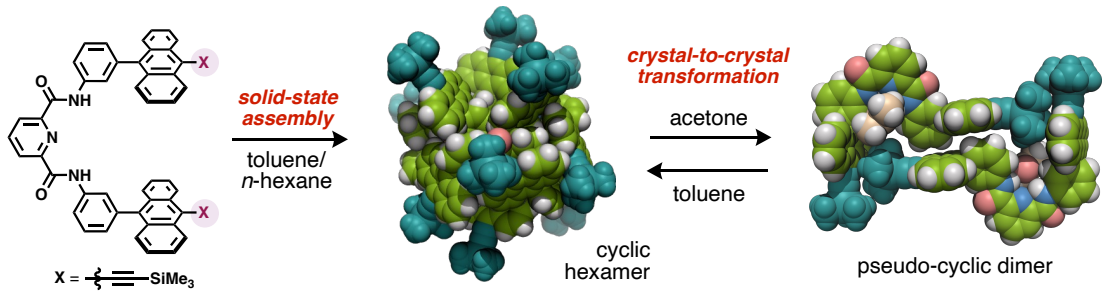
アントラセン分子ピンセットの固相における自己相補性集合：有限集合体の選択的構築と動的構造変換

（東工大理）○岡部洸輝・山科雅裕・鶴巻英治・豊田真司
Solid-state self-complementary assembly of anthracene-based molecular tweezers: selective construction of discrete assemblies and dynamic structural transformation (*School of Science, Tokyo Institute of Technology*) ○Koki Okabe, Masahiro Yamashina, Eiji Tsurumaki, Shinji Toyota

We reported that anthracene-based molecular tweezers formed cyclic hexamer via self-complementary assembly in the solid state. Herein, we synthesized various molecular tweezers with 10-substituted anthracenes and investigated their assembling behavior. In particular, the molecular tweezers with (trimethylsilyl)ethynyl groups formed cyclic hexamer in a crystal obtained from a toluene/*n*-hexane solution, while it formed pseudo-cyclic dimer in a crystal obtained from the solution in the presence of acetone. These two types of assemblies underwent dynamic structural interconversion in the solid state upon exposure to a solvent vapor. Other properties of these assemblies in the solid state as well as the assembling behavior of other molecular tweezers will be presented.
Keywords : Self-complementary assembly; Molecular tweezers; Anthracene; Substituent effect; Dynamic structural transformation

固相中での超分子構築は、溶液中とは異なる集合構造を与えることから、近年注目されている[1]。最近我々は、アントラセンを含む分子ピンセットが自己相補的に集合し、結晶中で環状六量体を構築することを報告した[2]。本研究では、分子ピンセットのアントラセン 10 位に様々な置換基を導入し、置換基が集合体構築に及ぼす影響を調査した。そのうちトリメチルシリルエチニル基を導入した分子ピンセットは，トルエン/ヘキサン溶液から結晶化すると環状六量体を形成した一方で、この溶液にアセトンを加えて結晶化すると擬環状二量体を形成した。興味深いことに、２種類の集合体の粉末に溶媒蒸気を暴露すると、固体中で相互に動的構造変換することが明らかとなった。本発表では、これら集合体の固体物性に加え、他の置換基をもつ分子ピンセットの集合挙動についても報告する。



[1] Y. Liu, F.-Z. Liu, K. Yan, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116980.
[2] M. Yamashina, S. Toyota, *et al*., *Nat. Commun*. **2022**, *13*, 5648.

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テルペン骨格を持つ光学活性ミセルの構築と空間キラリティ

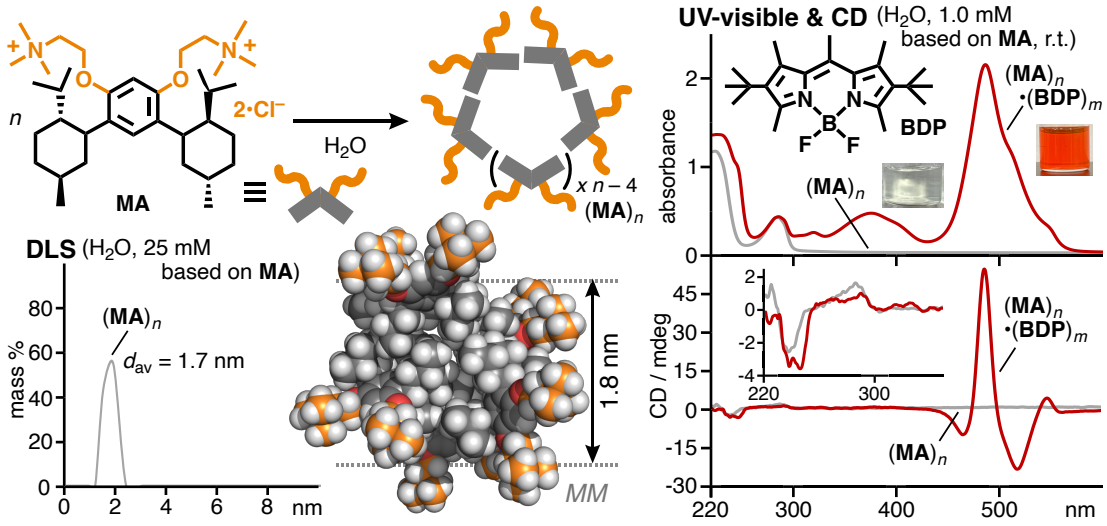
（東工大 化生研）○橋本義久・田中裕也・吉沢道人

Formation of An Optically Active Micelle Bearing Terpene Frameworks and Its Cavity Chirality (*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Yoshihisa Hashimoto, Yuya Tanaka, Michito Yoshizawa

Artificial chiral cavities formed through covalent, coordination, and hydrogen bonds are relatively rigid for guest binding. Here we report optically active micelle $(\mathbf{MA})_n$ formed in water from new bent amphiphiles **MA** with menthane frameworks. Micelle $(\mathbf{MA})_n$ encapsulated achiral guests **BDP** in a flexible cavity and the resultant host-guest complex displayed strong guest absorption and emission bands as well as the Cotton effect and CPL bands derived from host-to-guest chirality transfer.
Keywords: terpenes, bent amphiphile, micelle, optical activity, circular dichroism

キラルな空間は、生体内のタンパク質などに多く存在する。共有結合や配位結合、水素結合などを利用した人工キラル空間は比較的剛直なため、ゲスト内包能に制限がある。今回、入手容易なテルペン類のメンタン骨格を導入した新規Ｖ型両親媒性分子 **MA** を合成した。また、その光学活性ミセルの形成と分子内包能を明らかにした。

MA は根岸カップリングを含む６段階の反応で合成し、水中で主に疎水効果を駆動力として、約 1.7 nm サイズのミセル $(\mathbf{MA})_n$が定量的に形成することを DOSY NMR, DLS 解析により明らかにした（下図左）。CD スペクトルから、このミセルは光学活性であることが示された。また、$(\mathbf{MA})_n$は水中・室温で疎水性分子を効率的に内包した。例えば、**MA** とアキラルな **BDP** をすりつぶし、水を加えて得られた透明な赤色の溶液の UV-visible スペクトルにおいて、300~560 nm に内包された **BDP** に由来する吸収帯が出現した（下図右）。内包体 $(\mathbf{MA})_n\cdot(\mathbf{BDP})_m$ の CD 測定において 480 nm 付近に強い正のコットン効果が観測されたことから、**MA** から **BDP** へのキラル転写が確認された。さらに、内包された **BDP** に由来する CPL を観測した。



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芳香環ミセル内での軸不斉分子のキラル光学特性

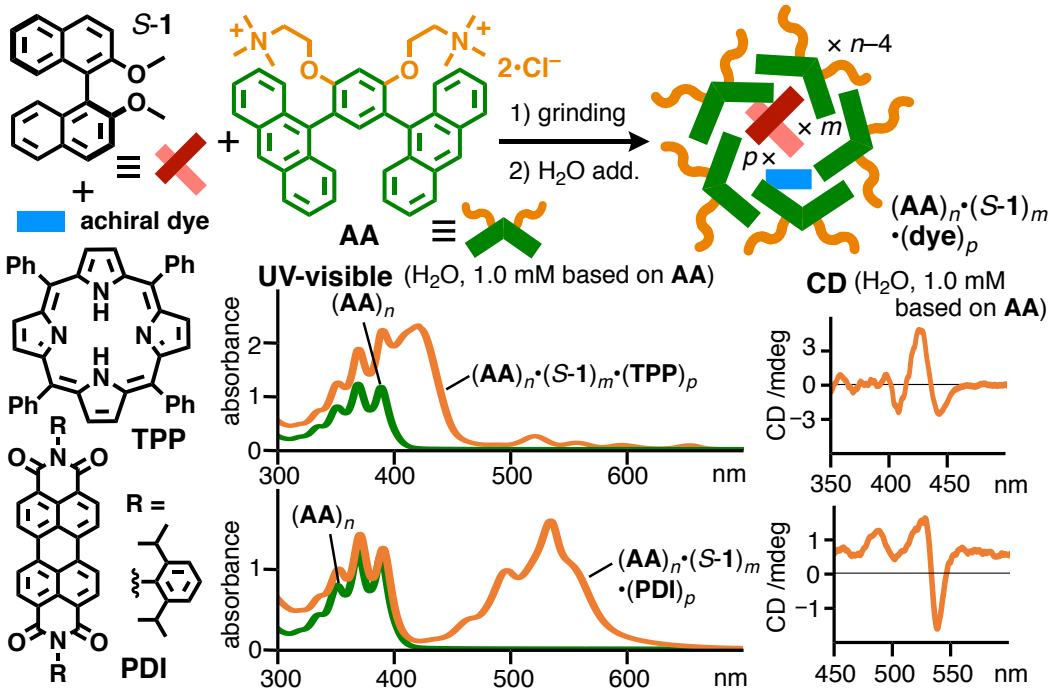
（東工大 化生研）○安田朋弘・橋本義久・田中裕也・吉沢道人

Chiral Optical Properties of Axially Chiral Molecules within Aromatic Micelles (*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Tomohiro Yasuda, Yoshihisa Hashimoto, Yuya Tanaka, Michito Yoshizawa

Efficient interactions of chiral molecules are essential for the detection and transcription of chiral information. Here we present the co-encapsulation of axially chiral binaphthol derivatives and achiral organic dyes by aromatic micelles in water. The CD spectra of the resultant host-guest composites displayed the Cotton effect derived from the binaphthols as well as the dyes, due to guest-to-guest chirality transfer within the micelles.
Keywords: chirality transfer, axially chiral molecule, bent amphiphile, aromatic micelle, water solubilization

不斉分子の効果的な相互作用はキラリティ情報の検出や転写に重要である。今回、水中で芳香環ミセルに軸不斉分子のビナフトール誘導体とアキラルな色素分子を共内包することで、分子間相互作用によりゲスト間での不斉転写に成功した。

V 型両親媒性分子 **AA** とビナフトール誘導体 *S*-**1** をすりつぶし、水を加えることで内包体(**AA**)$_n$·(*S*-**1**)$_m$の溶液を得た。同様に、**AA** と *S*-**1** とテトラフェニルポルフィリン(**TPP**)またはペリレンジイミド誘導体(**PDI**)から共内包体を得た。それらの CD スペクトルでは、*S*-**1** に加えて **TPP** と **PDI** に由来するコットン効果が観測された。すなわち、内包による色素へのキラル転写を観測した。一方、**TPP** の金属錯体や嵩高い置換を持たない **PDI** を含む共内包体では転写がほとんど観測されなかった。



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アセチレン含有芳香環ミセルの金属架橋による色素分子閉じ込め

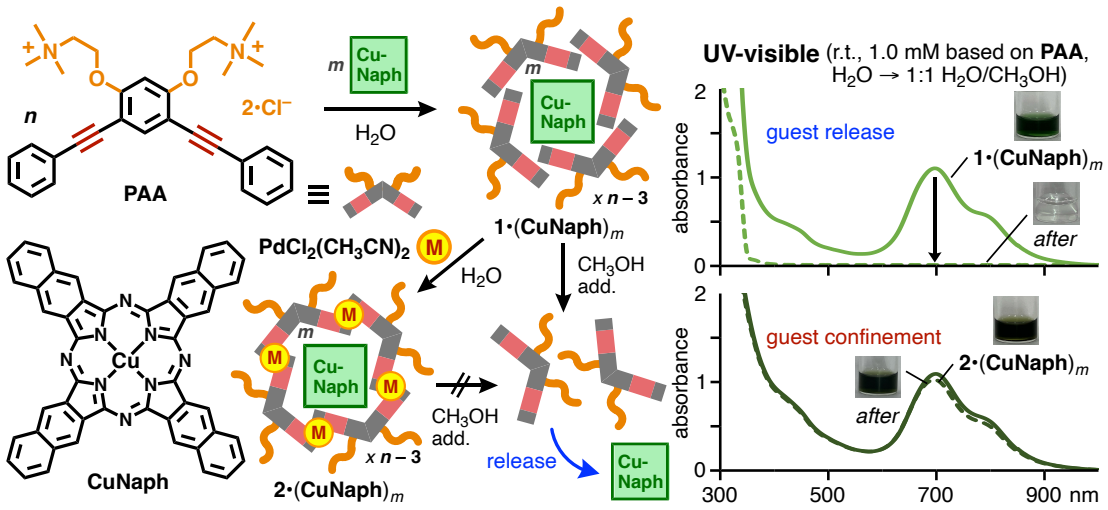
（東工大 化生研）○平田慎之介・田中裕也・吉沢道人

Metal-mediated confinement of dye molecules within an acetylene-containing aromatic micelle (*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Shinnosuke Hirata, Yuya Tanaka, Michito Yoshizawa

Bent amphiphiles with two phenylacetylene frameworks form an aromatic micelle that shows host capability in water. Here we demonstrate the confinement of large dyes within the micelle by metallo cross-linking. The micelle effectively encapsulated Cu(II)-naphthalocyanines in water through a grinding method. The resultant host-guest composite was cross-linked by the addition of Pd(II) salts, and then the metal-linked product showed high stability against the addition of organic solvents.
Keywords: acetylene, aromatic micelle, metal cross-linking, encapsulation, confinement

フェニルアセチレン骨格を持つ V 型両親媒性分子 **PAA** からなる芳香環ミセル **1** (= (**PAA**)$_n$)は水中で形成され、色素分子を内包する。また、金属塩の添加により、金属架橋ミセル **2** が得られる。今回、**1** による巨大な色素分子の内包とその金属架橋による内包体の安定化を達成したので報告する。

芳香環ミセル **1** は水中・室温で疎水性色素分子を効率的に内包した。**PAA** と銅(II)ナフタロシアニン(**CuNaph**)をすりつぶし、水を加えることで、内包体 **1**·(**CuNaph**)$_m$ の緑色溶液を得た。その UV-visible スペクトルにおいて、600~900 nm に内包された **CuNaph** に由来する吸収帯が出現した。次に、この水溶液に $PdCl_2(CH_3CN)_2$ を加え、30 分攪拌して得られた金属架橋内包体 **2**·(**CuNaph**)$_m$は、色素に由来する吸収帯を維持していた。さらに、この水溶液に同体積量のメタノールを加えた場合、色素分子の放出は大きく抑制(94%)されることが UV-visible スペクトルから確認された。一方、**1**·(**CuNaph**)$_m$は同条件で色素を完全に放出した。



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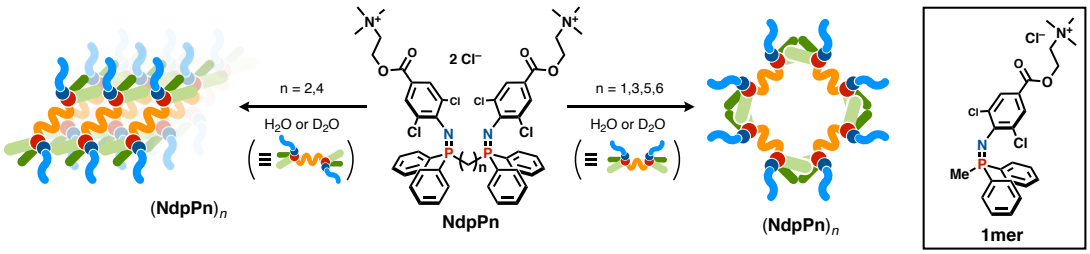
アザイリド形成によるジェミニ型両親媒性分子の合成とアルキルリンカー長による集合能変化

（東工大理）○秋山 善守・山科 雅裕・豊田 真司
Synthesis of azaylide-based gemini-amphiphiles and their unique aggregation behavior caused by alkyl linker length (School of Science, Tokyo Institute of Technology) ○Yoshimori Akiyama, Masahiro Yamashina, Shinji Toyota

Gemini-amphiphiles, in which two amphiphilic molecules are connected by a spacer, are known to have low critical micelle concentrations and various aggregation forms.[1] Here we report gemini-amphiphiles synthesized from various bidentate phosphines with different methylene carbons and a hydrophilic azide using azaylide (N=P) formation by the Staudinger reaction.[2] The hydrolysis of azaylide is significantly suppressed over the control compound without Cl groups. The obtained amphiphiles formed either micelles or hydrated crystals in water depending on the number of methylene carbons. Furthermore, all amphiphiles showed uptake capability toward hydrophobic aromatic compounds (e.g., perylene and C_{60}) in water.
Keywords: Gemini-amphiphile; Azaylide; Bidentate phosphine; Host–guest

２つの両親媒性分子をスペーサーで連結したジェミニ型両親媒性分子は、低い臨界ミセル濃度（CMC）や多様な集合形態を有することが知られている[1]。本研究では、シュタウディンガー反応による N=P 結合（アザイリド）形成[2]を利用し、メチレン炭素数が異なる種々の二座ホスフィンと親水性アジドから対応するジェミニ型両親媒性分子 **NdpPn**（n = 1–6）を合成した。水中における **NdpP3** の加水分解は、クロロ基を含まない対照分子と比較して顕著に抑制された。また、**NdpPn** の水中での集合挙動を NMR、動的光散乱、原子間力顕微鏡測定で評価した。その結果、**NdpPn** は、下式に示すようにメチレン炭素数に応じて水中で直径約 2 nm のミセルまたは約 1 μm の水和結晶を形成することが明らかになった。また、**NdpPn** の CMC は、対応するモノメリック型両親媒性分子 **1mer** の 1/10 以下に低下した。さらに、全ての **NdpPn** は水中で疎水性芳香族化合物（ペリレンや C_{60} など）を強く内包した。



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[1] F. M. Menger and J. S. Keiper, *Angew. Chem. Int. Ed.* **2000**, *39*, 1906.
[2] M. Yamashina, S. Toyota *et al.*, *Angew. Chem. Int. Ed.* **2021**, *60*, 17915.

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アセチレン協働配位に駆動された銀ナノクラスター群の構築

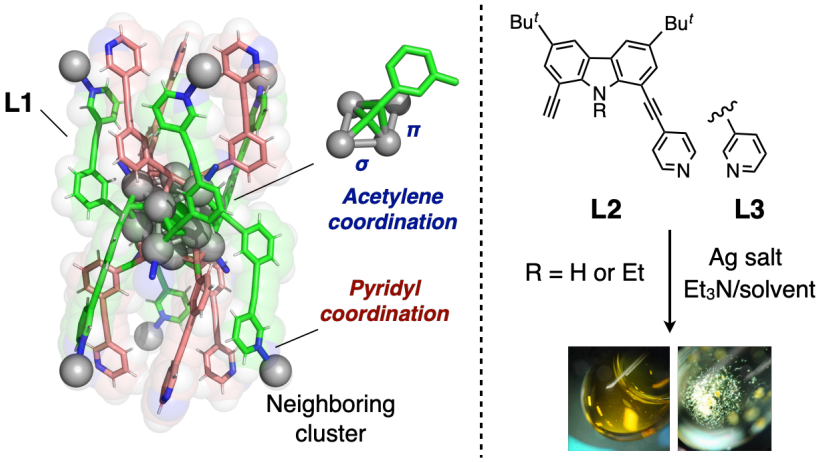
(群馬大理工[1]・東大院工[2]・群馬大院理工[3]・理研 CEMS[4]・JASRI[5]・電通大[6]・分子研[7]) ○鶴見 侑樹[1]・中川 崇弘[2]・堂本 悠也[3]・足立 精宏[4]・金子 拓真[5]・宇留賀 朋哉[5,6]・橋爪 大輔[4]・中村 洋介[3]・藤田 誠[2,7]

Construction of Silver Nanoclusters Driven by Cooperative Acetylene Coordination ([1]*Sch. of Sci. and Technol., Gunma Univ.,* [2]*Grad. Sch. of Eng., The Univ. of Tokyo,* [3]*Grad. Sch. of Sci. and Technol., Gunma Univ.,* [4]*RIKEN CEMS,* [5]*JASRI,* [6]*The Univ. of Electro-Communications,* [7]*IMS*) ○Tasuki Tsurumi,[1] Takahiro Nakagawa,[2] Yuya Domoto,[3] Kiyohiro Adachi,[4] Takuma Kaneko,[5] Tomoya Uruga,[5,6] Daisuke Hashizume,[4] Yosuke Nanakmura,[3] Makoto Fujita[2,7]

We have developed the self-assembly of polyhedral coordination complexes via cooperative acetylene coordination[1)] and applied to the synthesis of networked silver nanoclusters[2)]. Here, we present our recent results on single-crystalline XAFS and other analyses, and furthermore construction of novel structures incorporated with carbazole moieties into the alkynyl protecting ligands bearing pyridyl groups.

Keywords : Nanocluster; Self-assembly; Coordination polymer; Acetylene; Carbazole

近年、構造精密な金属ナノクラスターの合成およびその配列制御が注目を集めている。我々は最近、独自に開発したアセチレンの協働的金属配位による自己集合構築法[1)]を応用することで、末端アルキン保護された銀ナノクラスターを構築している。さらに放射光を用いた単結晶 X 線構造解析より、ナノクラスターが配位子 **L1** 末端のピリジル基を介して相互配位することによる超分子ネットワーク錯体の形成が観察された[2)]。本発表では、単結晶の X 線吸収微細構造(XAFS)解析などさらに詳細な解析について議論する。また、保護配位子の中心ベンゼン環をカルバゾールに置換した **L2** および **L3** を用いた銀(I)塩との配位自己集合においても単結晶が得られ、ナノクラスターの形成が X 線観察から示唆された。これらの溶液中および単結晶における各種分光法による解析も併せて報告する。



1) Y. Domoto, M. Fujita, *Coord. Chem. Rev.* **2022**, *466*, 214605.
2) 中川, 堂本, 藤田, 日本化学会第 103 春季年会(**2023**), K606-1am-05.

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テトラアミジンの凝集誘起発光によるホスホン酸およびヌクレオチドの検出

（京工繊大・工芸科学）○山本 祐輔・楠川 隆博
Detection of phosphonic acids and nucleotides using aggregation-induced emission of tetraamidine (Kyoto Institute of Technology) Yusuke Yamamoto, and Takahiro Kusukawa

The design and synthesis of fluorogenic chemosensors for the selective recognition of biologically important species is of current interest for the applications in the field of analytical and medical science. Recently, we reported the fluorescence detection of α,ω-dicarboxylic acids using tetraphenylethylene-based tetraamidine **1** in DMSO/MeCN mixed solvents.[1] In this study, we found that tetraamidine **1** showed blue fluorescence by the addition of various monophosphonic acids, including methylphosphonic acid, a degradation product of the chemical warfare sarin. The fluorescence detection of nucleotides such as CMP (cytidine monophosphate, **3b**) using tetraamidine **1** will also be discussed in this presentation.
Keywords: Amidine; Phosphonic acid; Nucleotide; Aggregation-induced emission

当研究室では、テトラフェニルエチレン骨格を有するテトラアミジン **1** が DMSO 溶媒中で α,ω-ジカルボン酸と 1：2 会合体および凝集体を形成し、蛍光発光を示すことを明らかにしている[1]。本研究では、テトラアミジン **1** が DMSO 中でホスホン酸 **2** およびリン酸誘導体 **4** と、会合体および凝集体を形成することで、青色の蛍光発光を示すことを見出した。一方で、ヒドロキシ基が少ないホスホン酸エステル **5** およびテトラアミジン **1** 単独では、蛍光発光は観測されなかった (**Figure 1**)。また、テトラアミジン **1** とヌクレオチド **3a-3d** を混合したところ、ヌクレオチドの構造の違いにより蛍光発光に選択性が観測されたため、併せて報告する予定である。

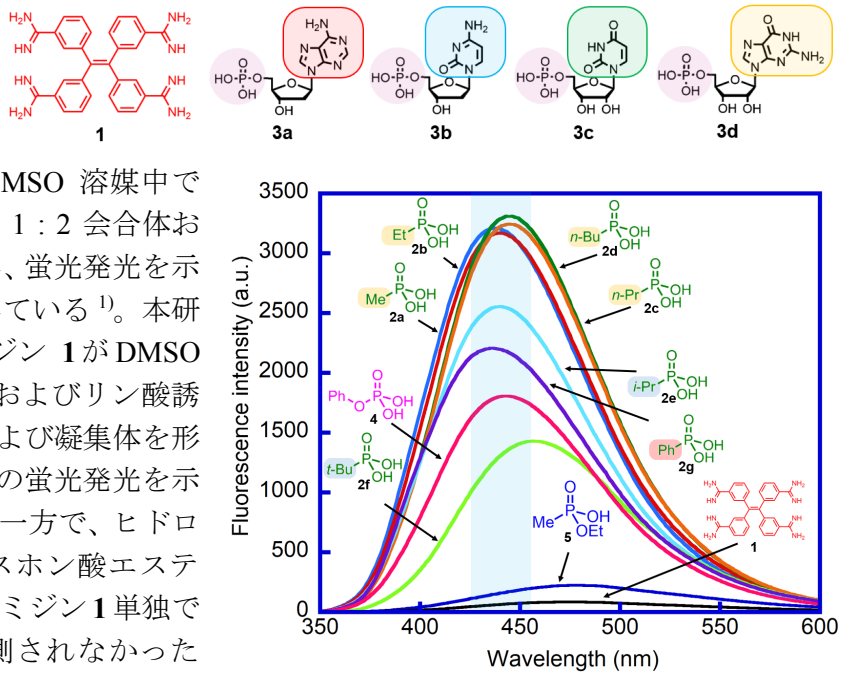

Figure 1. Fluorescence spectra of the tetraamidine **1** upon the addition of phosphoic acids ([**1**] = 200 μM, DMSO, λ_{ex} = 326 nm).

1) T. Kusukawa *et al.*, *Tetrahedron* **2021**, *92*, 132254.

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大環状テトラキスポルフィリンの協同的分子認識

(広大院先進理工[1]・広島大 持続可能性に寄与するキラルノット超物質拠点[2]) ○田辺 航太[1,2]・久野 尚之[1]・灰野 岳晴[1,2]

Cooperative Molecular Recognition of Macrocyclic Tetrakisporphyrin exhibiting ([1]*Graduate School of Advanced Science and Engineering, Hiroshima University, WPI-SKCM*[2]*, Hiroshima University*) ○Kouta Tanabe,[1,2] Naoyuki Hisano,[1] Takeharu Haino[1,2]

We have developed S-shaped tetrakisporphyrin possessing two bisporphyrin clefts connecting with a butadiyne linker. In this study, we developed a macrocyclic tetrakisporphyrin **1** and novel chiral macrocyclic tetrakisporphyrin **2** which were synthesized by connecting the carboxyl groups with xylylene glycol and (L)-tartaric acid derivative respectively. In this presentation, the guest binding behaviors and molecular recognition of macrocyclic tetrakisporphyrin **1** and **2** will be discussed.

Keywords : Molecular Recognition; Host-Guest Interaction; Porphyrin

当研究室は、二つのクレフト型ビスポルフィリン分子をブタジインで連結したS字型テトラキスポルフィリンを合成し，自己会合およびゲスト包接挙動について報告している[1]。本研究はS字型テトラキスポルフィリンの両末端をキシリレングリコールで架橋した大環状ホスト分子 **1** のゲスト分子包接挙動の調査を目的とした。**1** は互いに連動した二つの包接空孔をもち，一つ目のゲスト包接現象が二つ目のゲスト包接を促進する正の協同性を示す。

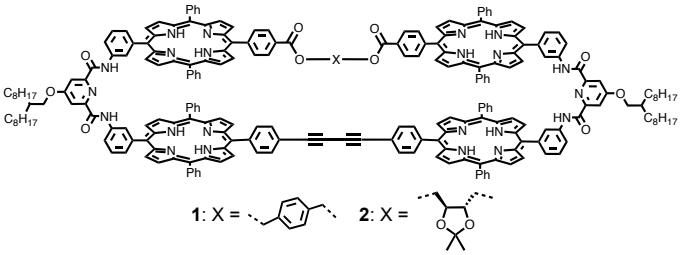

Figure 1. Molecular structures of **1** and **2**.

溶液中のゲスト包接挙動について，UV/vis スペクトルを用いて検討した。**1** の溶液に **G1** を加えたところ，**1** のポルフィリンに帰属される吸収帯が等吸収点を与えながら減少し，新たに会合体に帰属される吸収帯が現れた(Figure 2a)。Job プロットの結果より，ホストゲスト会合比は 1:2 であることがわかった(Figure 2b)。得られた滴定曲線から非線形解析を行い会合定数を算出したところ，**1** と **G1** の会合定数は K_1, K_2 ともに 10^6 L mol^{-1} 以上の値を示した。協同性を議論するために，相互作用パラメータ α を求めたところ $\alpha = 3.4$ という値が得られ，**1** のゲスト包接における強い正の協同性の発現が示唆された。

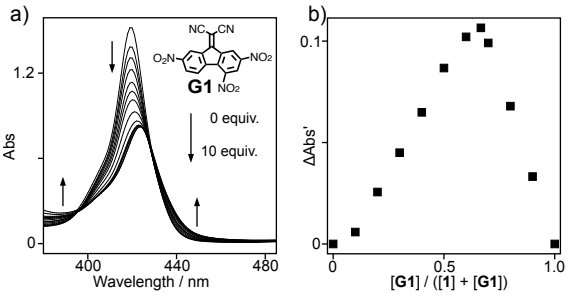

Figure 2. (a)UV/vis spectra and (b) Job plots of **1** with **G1**.

また，酒石酸由来のキラルなジオールを用いて架橋した新規大環状ホスト分子 **2** の合成にも成功している。**2** の構造に関する性質や，ゲスト包接挙動についての結果は本発表で詳細に議論する。

1) Nadamoto, K.; Maruyama, K.; Fujii, N.; Ikeda, T.; Kihara, S.; Haino, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 7028-7033

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積層型亜鉛ポルフィリンの分子認識により生じる多成分超分子錯体

(広島大院先進理工[1]・持続可能性に寄与するキラルノット超物質拠点[2]) ○児玉 知輝[1,2]・久野 尚之[1]・灰野 岳晴[1,2]

Synthesis and guest binding behavior of tris(zinc-porphyrin)

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University, WPI-SKCM*[2]*, Hiroshima University*) ○ Tomoki Kodama[1], Naoyuki Hisano[2], Takeharu Haino[2,3]

In this study, I synthesized pentakis(zinc-porphyrin) **2** and investigated its guest binding behaviors (Figure 1a). **G1** and **L1** were together encapsulated within the cleft cavities of **2** in a ratio of 2:2:1, respectively, through donor-acceptor interactions and dative bonds, respectively. The four guest molecules are located within **2** in alternating order of **G1**-**L1**-**G1**-**L1**, which is most likely directed by strong negative cooperativity.

Keywords : Molecular recognition; Host-guest interaction; Porphyrin

当研究室は二つのゲスト包接部位を有する積層型トリスポルフィリンが，電子不足な芳香族ゲスト分子の包接に負の協同性を示す事を報告している[1]。また，亜鉛を導入した **1** が負の協同性により電子不足な芳香族ゲスト分子と軸配位性ゲスト分子を一分子ずつ同時に包接することで，三元錯体を選択的に形成する事がわかっている(Figure 1a)。三元錯体は結晶中において **L1** によって架橋され，ゲスト分子を交互に配列した超分子錯体を形成していた(Figure 1b)。本研究では，四つの包接空間をもつ積層型亜鉛ポルフィリン **2** を合成し，そのゲスト包接挙動を調べた。三元錯体の結晶構造から，**2** は負の協同性によりゲスト分子 **G1** および **L1** を交互に包接することが予想される。

2 のゲスト分子包接挙動を調べるため，^{1}HNMR スペクトルを測定した。ゲスト分子が交互に包接される場合，錯体の対称性から，包接された **L1** に由来するプロトンは Ha, Hb, Hc の 3 種類存在する。**2** および **G1, L1** を 1:2:2 で混合した溶液を測定したところ，交互配列錯体に由来する **L1** のプロトン Ha, Hb, Hc が積分比 1:1:2 で観測された(Figure 1c)。以上から，**2** はゲスト分子 **G1** および **L1** を交互に包接することが示唆された。

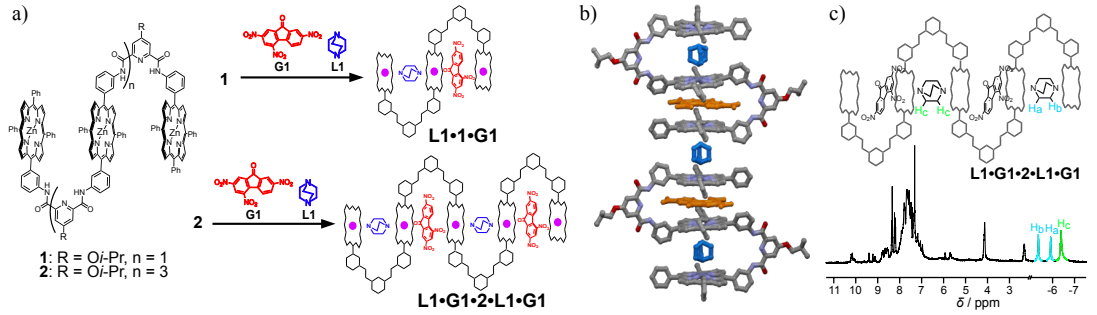

Figure 1. (a) Molecular structures and guest binding behavior of **1** and **2**. (b) Crystal structure of **1** with **G1** and **L1**. (c) Partial ^{1}H NMR spectra of 1:2:2 mixture of **2**, **L1** and **G1**.

[1] Hisano, N.; Kodama, T.; Haino, T. *Chem. Eur. J.* **2023**, e202300107.

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Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
E1123(1123, Bldg. 11 [2F])

[E1123-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Ayumi Imayoshi, Naoya Morohashi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1123-4am-01]
Development of Regioselective Catalyst Using Hydrogen Bonding between Amides
○Joto Yabe[1], Nobuhiro Kihara[1] (1. Kanagawa University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1123-4am-02]
Photoreduction control of anthraquinone derivatives using hydrogel
○Ayuna Nishiyama[1], Yoshinori Okayasu[1], Yuki Nagai[1], Yoichi Kobayashi[1,2] (1. Ritsumeikan University, 2. PRESTO JST)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1123-4am-03]
Development of stimuli-responsive photoluminescent liquid materials
Takumi Omura[1], Shogo Morisako[1], ○Kyosuke ISODA[1] (1. SCRI)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1123-4am-04]
Afterglow sensing for metal ions using room-temperature phosphorescence properties
○Margarita Claudya Maida[1], Satoshi Takegawa[1], Masato Ito[1], Yuji Kubo[1] (1. Tokyo Metropolitan University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1123-4am-05]
The functional evaluation of a supramolecular hydrogel formed from amphiphilic bis-urea
○Minami Ishii[1], Shinya Kimura[1], Masashi Yokoya[1], Masamichi Yamanaka[1] (1. Meiji Pharm. Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1123-4am-06]
Supramolecular Gel Formation by Ring Opening Reaction of Cyclic Monourea
○Noriaki Kimishima[1], Shinya Kimura[1], Masashi Yokoya[1], Masamichi Yamanaka[1] (1. Meiji Pharm. Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1123-4am-07]

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Development of a separation method for aromatic carboxylic acid regioisomers with crystals of a tetranuclear zinc(II) complex ligated by 2,2'-thiodiphenol derivative

○Reon Sato[1], Keisuke Hara[1], Ikuko Miyoshi[1], Naoya Morohashi[1], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1123-4am-08]

Selective solid-phase extraction of rare metal ions from water with bis(tetramethylammonium) salt crystals of *p-tert*-butylcalix[4]arene-1,3-diphosphonic acid

○Ryuki Takahashi[1], Mayu Osawa[1], Seiya Ikarashi[1], Naoya Morohashi[1], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1123-4am-09]

Synthesis and Physicochemical Properties of Diphenylquinoline *N*-oxyl Derivatives with Alkyl Substituents at 6-Position

○Jumpei Yazawa[1], Kento Morinaka[1], Masaomi Takii[1], Youhei Miura[1], Naoki Yoshioka[1] (1. keio university)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1123-4am-10]

Racemization of cross-chain bridging cryptands featuring different combination of oligo(ethylene glycol) linkers

○Taisei MARUYAMA[1], Syogo NIMI[1], Masaya NAITO[1], Shinobu MIYAGAWA[1], Yuji TOKUNAGA[1] (1. University of Fukui)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1123-4am-11]

Chiral Anion Recognition By Phosphoric Triamide

○Seiichi Yoshino[1], Shin-ichi Kondo[1] (1. Yamagata University)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1123-4am-12]

Thermal isomerization behavior and metal ion response of azobenzene derivatives with crown ether structure

○Yuto Hirayama[1], Runze Lin[2], Nobuyuki Tamaoki[2], Akitaka Ito[3], Rico Tabor[4], Masayuki Izumi[1], Rika Ochi[1] (1. Kochi University, 2. Hokkaido University, 3. Kochi University of Technology, 4. Monash University)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1123-4am-13]

Hydrogen-bond-directed supramolecular polymerization of a U-shaped thienoacene derivative

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○Chen Liu[1], Shogo Nakajima[1], Soichiro Ogi[2], Tatsuya Mori[2], Shigehiro Yamaguchi[1,2,3] (1. Graduate School of Science, Nagoya University, 2. Integrated Research Consortium on Chemical Sciences, Nagoya University, 3. Institute of Transformative Bio-Molecules, Nagoya University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1123-4am-14]

Aqueous nanoparticles of luminescent chromophores by using aqueous bilayer membranes and their application to photon upconversion

○Keita Kuge[1], Naoyuki Harada[1], Nobuo Kimizuka[1,2] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ.)

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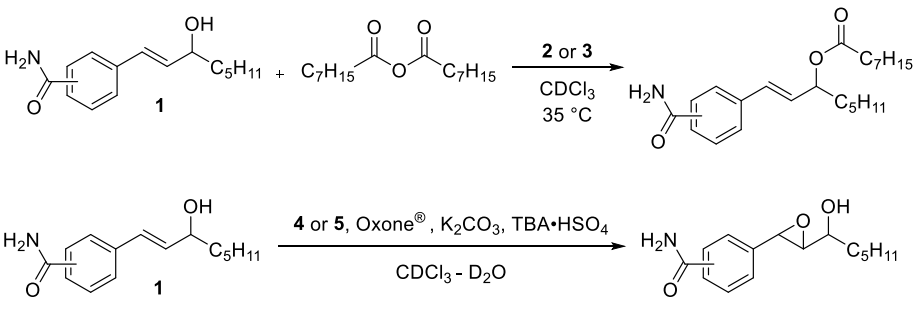
アミドの水素結合を利用した位置選択的反応場の開発

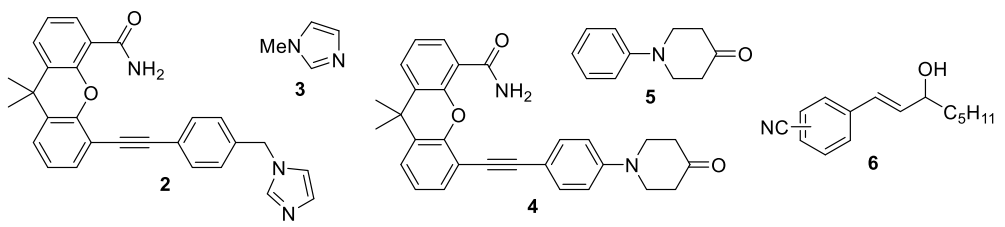
（神奈川大院理）○矢部 丈登・木原 伸浩
Development of Regioselective Catalyst Using Hydrogen Bonding between Amides（Graduate School of Science, Kanagawa University）○Joto Yabe, Nobuhiro Kihara

One of the most important features of enzymatic reaction is high regioselectivity. If an artificial catalyst has a substrate recognition site that fixes the substrate at the specific position around the catalytic functional group, high regioselectivity is expected as is observed for the enzyme. Acylation of **1** using **2** as the catalyst was carried out, although regioselectivity was not observed. Epoxidation of **1** using keto-amide **4** as the catalyst was also carried out. Slight acceleration was observed for *o*- and *p*-isomer of **1**. Epoxidation of **6** was also carried out to realize the role of the amide group in **1**.

Keywords : regioselective reaction; ketone-catalyzed epoxidation; DMAP-catalyzed acylation; amide; hydrogen-bonding

酵素は、基質認識部位によって基質を反応場内で空間的に固定し、触媒性官能基が反応場内の特定の位置にある反応性官能基のみに作用することで、高い位置選択性を実現している。人工的な触媒でも、酵素と同様に基質認識部位と触媒性官能基を併せ持つ反応場を設計して用いれば酵素のような高い位置選択性が実現できると期待される。アミド部位を持つアリルアルコール **1** のアシル化を行ったが、触媒として基質認識部位のアミド基を持つ **2** を用いたときの反応速度を基質認識部位を持たない **3** を用いた場合の反応速度と比べたところ、ベンゼン環上の置換位置によらず、加速は見られなかった。そこでケトンを触媒とする **1** のエポキシ化を検討したところ、アミドを基質認識部位として持つケトン **4** を触媒として用いると基質認識部位を持たない **5** を触媒として用いたときに比べ、*o* 体および *p* 体で加速が見られた。現在、この加速が基質認識部位に由来するのかどうかを明らかにするために **6** のエポキシ化を検討している。





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ハイドロゲルを用いたアントラキノン誘導体の光還元制御

（立命館大生命科学[1]・JST さきがけ[2]）○西山 歩那[1]・岡安 祥徳[1]・永井 邑樹[1]・小林 洋一[1,2]
Photoreduction control of anthraquinone derivatives using hydrogel ([1]*College of Life Sciences, Ritsumeikan Univ.*, [2]*PRESTO JST*) ○Ayuna Nishiyama,[1] Yoshinori Okayasu,[1] Yuki Nagai,[1] Yoichi Kobayashi[1,2]

Anthraquinone derivatives exhibit reversible redox reactions upon light or electric stimuli, making them valuable for applications in energy storage and chromic materials. However, storing the reduced forms under an air atmosphere has been challenging because of the rapid oxidation by oxygen. In this study, we addressed this issue by regulating the oxygen supply in the gas phase using hydrogels. As a result, we achieved long-term storage of the reduced forms, and the on-demand air oxidation under an air atmosphere.

Agarose was dissolved in an aqueous solution of sodium anthraquinone sulfonate (AQS) and triethanolamine by heating. The solution was left at 10 °C to give the air-saturated gel. Irradiating the gel with 365 nm-light (37.7 mW/cm^2) for 30 minutes caused photoreduction of AQS, and absorption bands of the reduced form were observed (Fig. 1, red→blue). The reduced form remained stable over several hours in the gel state, while solation upon heating triggered oxygen supply from the air to bring oxidation of the reduced form to the original form (Fig. 1, blue→green). We will also report modulation of the stimulus responsivity by changing the gelator in the presentation.

Keywords : photochromism; sol-gel transition; agarose; oxygen molecule; hydrogen peroxide

アントラキノン誘導体は、光や電気によって可逆的な還元・酸化を示すため、エネルギー貯蔵材料やクロミック材料として有用である。一方、還元体は酸素により直ちに酸化されるため、還元体の空気下での長期貯蔵は困難であった。本研究では、ハイドロゲルを用いて気相からの酸素供給を制御することにより、空気下において光生成した還元体の長期貯蔵と、ゾルーゲル転移によるオンデマンドな空気酸化に成功した。

アントラキノンスルホン酸ナトリウム (AQS) とトリエタノールアミンの水溶液にアガロースを加熱溶解させ、10 °C で静置することにより、AQS の空気飽和ゲルを調製した。このゲルに紫外光（37.7 mW/cm^2）を 30 分間照射すると、AQS の還元反応が進行し、400 nm 付近に還元体由来のピークが観測された (Fig. 1, 赤→青)。この還元体は 1 時間安定に保持されたが、加熱によってゾル化させると空気から供給された酸素により還元体が酸化され、元のスペクトルへと戻った (Fig. 1, 青→緑)。発表では、ゲル化剤の種類を変えることによる刺激応答性の制御についても報告する予定である。

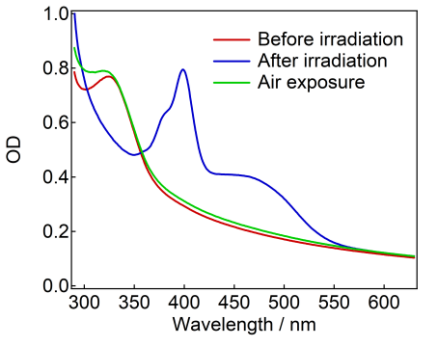

Fig. 1 Absorption spectra of an AQS agarose gel before and after 365-nm light irradiation.

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外部刺激応答型発光性液体材料の開発

(相模中研 [1]、北里大院 [2]) 大村 拓実 [1,2]、森迫 祥吾 [1]、○磯田 恭佑 [1]
Development of stimuli-responsive photoluminescent liquid materials ([1]*SCRI*, [2]*Graduate School of Science, Kitasato University*) Takumi Omura[1,2], Shogo Morisako[1], ○Kyosuke ISODA[1]

Solvent-free liquid materials have much attention as low environmental-loaded soft materials that can be used by anyone, anytime, anywhere, without using volatile organic solvents., which have the potential to achieve some of the Sustainable Development Goals (SDGs) as an alternative to solid materials. Herein, we report on development stimuli-responsive photoluminescent liquid materials. These liquid materials are based on pyromellitic diimide as solvent dissolving π-conjugated molecules as solute. Among them, some liquid materials can respond upon external stimuli as scratching and heating, leading to change photoluminescent colors. These results suggest that these liquid materials are expected to be sensing materials measuring shear stress.
Keywords : Stimuli-responsive materials; Stimuli-responsive liquid materials; Supramolecular chemistry; Charge-transfer complex; Sensing material

有機溶媒フリーの液体材料は、揮発性有機溶剤を使用せず、いつでも、どこでも、誰でも使用できる環境負荷の低いソフトマテリアルとして注目されており、固形材料に代わる持続可能な開発目標 (SDGs) の一部を達成する可能性を秘めた機能性材料である。そこで本研究では、液体材料の中でも発光特性を有するπ共役液体材料の開発とその刺激応答特性について評価を行ったので、報告する。

今回開発した液体材料は、pyromellitic diimide を母骨格とする液体材料 (溶媒) と様々なπ共役分子 (溶質) を溶解した溶液からなる。[1] pyromellitic diimide からなる液体材料はほとんど発光特性を示さない。一方、溶質を溶解した溶液は発光特性を示し、その特性は溶質の構造により制御可能である。調製した溶液は、希釈用の有機溶媒を用いずにそのままガラス基板への塗布が可能であり、また紙などに含浸することで印字なども行えるインクとして利用可能である。ガラス基板へ塗布した溶液は、スパチュラなどで掻き混ぜると発光色が橙色から水色へと変化するといった外部刺激応答特性を示した。これらの結果より、本液体材料は、応力を検出可能なセンシング材料としての応用が期待される。

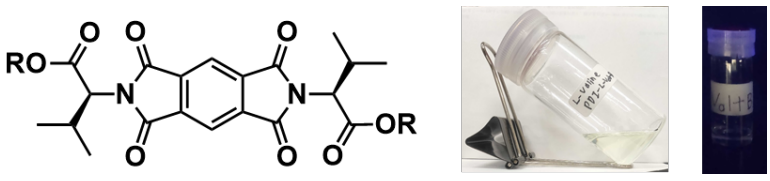

Figure 1. pyromellitic diimide を母骨格とする液体材料
(左 : 分子構造; 中 : 室内光の写真; 右 : ブラックライト下での写真)

1) in preparation

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Afterglow sensing for metal ions using room-temperature phosphorescence properties

(*Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*)
○Margarita Claudya Maida, Satoshi Takegawa, Masato Ito, Yuji Kubo
Keywords: *room temperature-phosphorescence; boronic acid; afterglow; poly(vinyl alcohol); chemosensor.*

Chemosensors that can be used for trace sensing of analytes have been progressively developed in the disciplinary research area between analytical chemistry and supramolecular chemistry. Among the detection modes, fluorometry is advantageous as an amplified signal due to a non-invasively high response. However, the optical response is often affected by short-lived autofluorescence arising from analyte solution and scattering of light caused by irradiation. Afterglow arising from phosphorescence with a significant Stokes shift is an alternative emission for the output signal of the sensing materials. In this study, our ongoing program to develop afterglow-based chemosensors allowed us to dope metal ion-detectable rhodamine dyes into room-temperature phosphorescence (RTP)-active poly(vinyl alcohol).

RTP-active PVA films were fabricated by drop-casting a DMSO solution (500 μL) of PVA (0.4 unitM) and thiophene-2,5-diboronic acid (0.5 mol%). After drying, the resultant **T-PVA** showed a blue emission as phosphorescence at 481 nm with a phosphorescent lifetime of 211 ms after ceasing excitation light of 254 nm. On the other hand, spirolactam ring-opening reaction of **1** was induced by Al^{3+}, which caused an increase in longer-wavelength absorption and fluorescence bands at 534 nm and 563 nm, respectively. Subsequently, the phosphorescence arising from **T-PVA** significantly overlapped with the absorption band of the Al^{3+}-triggered fluorescence band of **1**. It means that Al^{3+}-binding can be detected by a change in the afterglow through a *triplet-to-singlet* Förster-type resonance energy transfer (FRET) process from the thiophene-linker unit of PVA to spirolactum ring-opened **1**, which enabled us to detect the cations by afterglow stemmed from the film. The latest result will be presented.

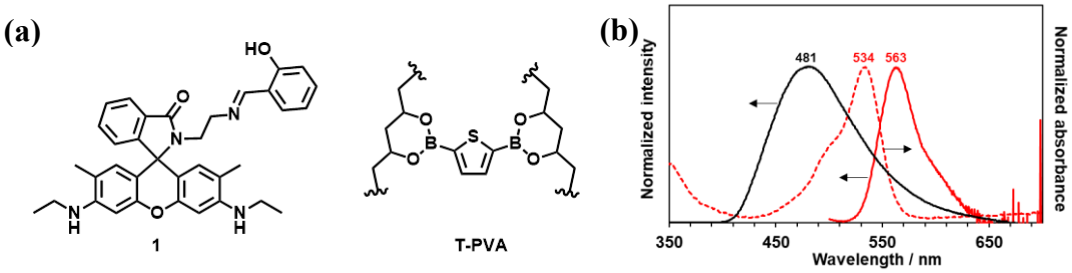

Fig. 1. (a) Chemical structures of **1** and **T-PVA**. (b) Phosphorescence spectrum of **T-PVA** (black solid line) and absorption (red dotted line) and fluorescence (red solid line) spectra of **1** plus Al^{3+} (5 eq.) in PVA. [**TDB**] = 0.5 mol%, [**1**] = 0.03 mol%, [Al^{3+}] = 5 eq., λ_{ex} = 254 nm. delay time = 50 ms for the phosphorescence measurement.

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両親媒性ビスウレアより形成する超分子ヒドロゲルの機能評価

（明治薬大）○石井 未菜美・木村 真也・横屋 正志・山中 正道

The functional evaluation of a supramolecular hydrogel formed from amphiphilic bis-urea

(*Meiji Pharm. Univ.*) ○Minami Ishii, Shinya Kimura, Masashi Yokoya, Masamichi Yamanaka

Supramolecular hydrogels are formed by self-assembly of small molecules called low-molecular-weight hydrogelators. Since their formation is based on weak noncovalent interactions, the fragility of supramolecular hydrogels often prevents their practical application. To increase the strength of supramolecular hydrogels, we designed an amphiphilic bis-urea with a hydrophilic carboxyl group as a novel low-molecular weight gelator. The amphiphilic bis-urea was synthesized in three steps from commercially available compounds. Mixture of amphiphilic bis-urea and basic aqueous solution was spontaneously transformed into a supramolecular hydrogel upon addition of an acid. The physical properties of the supramolecular hydrogels were evaluated by measuring their viscoelastic properties. A supramolecular hydrogel was also formed using PEG 2000 instead of acid.

Keywords : Supramolecular gel; Self-assembly; Amphiphilic; Urea; pH

超分子ヒドロゲルは、低分子ゲル化剤が非共有結合を駆動力に自己集合することで形成する。超分子ヒドロゲルは、弱い非共有結合により形成するため、物理的強度が低いことが実用化の課題である。高い強度を有する超分子ヒドロゲルの開発を目的として、多点での非共有結合形成による高強度化を期待して、水素結合性のウレイド基を 2 つ導入し、親水基にカルボキシ基を持つ両親媒性ビスウレアを分子設計した。両親媒性ビスウレアは 3 段階で合成した。両親媒性ビスウレアの塩基性水溶液に、室温で酸を添加すると超分子ヒドロゲルが形成した。超分子ヒドロゲルの pH を測定したところ、pH が 3 以下のときに超分子ヒドロゲルが形成していることが明らかになった。得られた超分子ヒドロゲルの動的粘弾性を測定し、その物性を評価した。両親媒性ビスウレアの塩基性水溶液に、PEG 2000 を添加することでも、超分子ヒドロゲルを形成できることを見出した。



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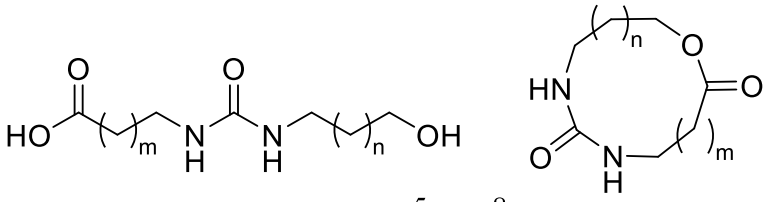
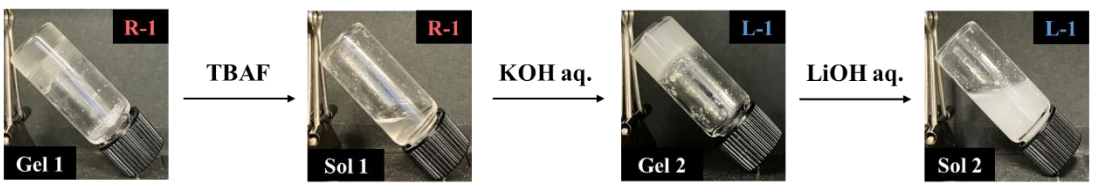
環状モノウレアの開環による超分子ゲル形成

(明治薬大) ○君島仙晃・木村真也・横屋正志・山中正道
Supramolecular Gel Formation by Ring Opening Reaction of Cyclic Monourea (*Meiji Pharmaceutical University*) ○ Noriaki Kimishima, Shinya Kimura, Masashi Yokoya, Masamichi Yamanaka

Supramolecular gels are formed by self-assembly of small molecules called low-molecular-weight gelators. We designed and synthesized a linear and cyclic monourea **L-1** and **R-1** as a novel low-molecular-weight gelators. We investigated the gelation conditions of **L-1** and **R-1**. Supramolecular gel of **L-1** was formed under basic condition whereas supramolecular gel of **R-1** was formed under neutral condition. The gelation of **L-1** depended on the kind of counter cation of the base. Additionally, the topological transformation based on the ring opening reaction of **R-1** to **L-1** induced the supramolecular gel formation. A serial gel-sol-gel-sol phase transition was achieved by using chemical stimuli responsive properties and topological transformation.
Keywords : Supramolecular gel; Self-assembly; Urea; pH; Topology

DNA やペプチドのような生体高分子、さらには合成高分子において鎖状構造と環状構造というトポロジーの違いにより異なる特性が発現することが報告されている。一方で、低分子量化合物においては、鎖状構造と環状構造というトポロジーに着目した研究例は少ない。我々は、低分子量化合物のトポロジーが、自己集合にどのような影響を及ぼすのかという点に興味を持ち、鎖状モノウレア **L-1** と環状モノウレア **R-1** のゲル化を評価した。**L-1** と **R-1** のゲル化条件を精査したところ、**L-1** は塩基性条件下、**R-1** は中性条件下で超分子ゲルを形成した。この時、**L-1** のゲル化は塩基のカウンターカチオンの種類に依存することを見出した。さらに、**R-1** の **L-1** への開環というトポロジー変換によって超分子ゲルが形成することを明らかにした。また、ゲル化における化学刺激応答性とトポロジー変換を利用することでゲルーゾルーゲルーゾル相転移という連続した相転移を実現した。





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2,2'-チオジフェノール誘導体を配位子とする四核亜鉛錯体の結晶を用いた芳香族カルボン酸位置異性体の選択的な分離法の開発

（東北大院工）○佐藤玲温・原 佳祐・三好 幾子・諸橋 直弥・服部 徹太郎

Development of a separation method for aromatic carboxylic acid regioisomers with crystals of a tetranuclear zinc(II) complex ligated by 2,2'-thiodiphenol derivative (*Graduate School of Engineering, Tohoku University*) ○ Reon Sato, Keisuke Hara, Ikuko Miyoshi, Naoya Morohashi, Tetsutaro Hattori

The development of separation materials that recognize hard to separate organic molecules with high efficiency and selectivityis highly desired in industry. We previously reported the selective inclusion method of organic molecules with crystals of *p-tert*-butylthiacalix[4]arene (**TCA**). Since the inclusion of **TCA** crystals has drawbacks of guest scope and quantitativity, we have also studied the development of metal complex type host ligated by 2,2'-thiodiphenol derivative (H_2**L**) having partial structure of **TCA**. In this study, we try the separation of aromatic carboxylic acid regioisomers using crystals of a tetranuclear zinc(II) complex **2**. In competitive inclusion experiment by suspending the crystals of **2** in a solution containing a regioisomer mixture of anisic acid or naphthoic acid (2 molar equiv. each for **2**), *o*-anisic acid and 1-naphthoic acid were selectivity included, respectively. Mechanistic consideration for guest selectivity has been also performed.

Keywords : Calixarene; Host crystal; Metal complex; Selective capture; Aromatic carboxylic acids

有機分子の分離は工業的に重要であり，難分離性有機分子を高効率・高選択性に捕捉する分離材料の開発が望まれている。我々は，*p-tert*-ブチルチアカリックス[4]アレーン(**TCA**)の結晶による有機分子の選択的捕捉に成功している[1]。しかし，ゲスト適用性や定量性などに課題があったため，**TCA** 部分構造である2,2'-チオジフェノール誘導体(H_2**L**)を配位子とした金属錯体型ホストの開発も行っている。本研究では，四核亜鉛錯体 **2** の結晶による，芳香族カルボン酸の位置異性体の分離について検討した。

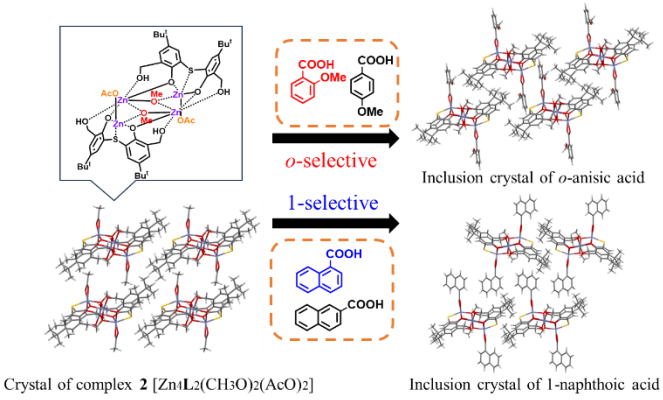

Fig. 1 Selective inclusion of a regioisomer of aromatic carboxylic acids with a crystal of **2**.

アニス酸およびナフトエ酸の各異性体を **2** に対して 2 モル当量ずつのみ含む溶液中に，**2** の結晶を懸濁させたところ，*o*-アニス酸，1-ナフトエ酸がそれぞれ高選択的に捕捉された。さらに，包接結晶の構造解析などから選択性の発現機構についても考察したので報告する。

1) N. Morohashi, T. Hattori, *J. Inclusion Phenom. Macrocyclic Chem.* **2018**, *90*, 261.

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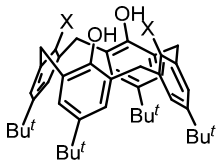
p-tert-ブチルカリックス[4]アレーン-1,3-ジホスホン酸ビス(テトラメチルアンモニウム)塩の結晶を用いた水中レアメタルの選択的固相抽出

（東北大院工）○髙橋 流輝・大澤 眞由・五十嵐 成也・諸橋 直弥・服部 徹太郎
Selective solid-phase extraction of rare metal ions from water with bis(tetramethylammonium) salt crystals of *p-tert*-butylcalix[4]arene-1,3-diphosphonic acid (*Graduate School of Engineering, Tohoku University*) ○Ryuki Takahashi, Mayu Osawa, Seiya Ikarashi, Naoya Morohashi, Tetsutaro Hattori

For the separation of rare metals, solvent extraction method is generally and widely used. If rare metals can be directly and highly selectively separated from water using solid extractants, the environmental loading will be reduced. We have succeeded in the selective collection of Yb(III) using crystals of bis(tetramethylammonium) salt **2** prepared from calix[4]arene-1,3-diphosphonic acid **1**. In this study, we investigate the selective extraction of other rare metal ions using crystals of compound **2**. After stirring crystals of **2** in an aqueous solution containing two metal ions, its extraction selectivity was evaluated by calculating Extraction % for each metal ion. As a result, it was found that crystals of **2** can selectively extract hard rare metal from aqueous solution. For example, In^{3+} and Ga^{3+} are selectively extracted in the presence of Al^{3+}, respectively (**Fig. 1**). Furthermore, In^{3+} is selectively extracted in the competitive extraction of In^{3+} and Ga^{3+}.

Keywords : Calixarene; Rare metal; Solid-phase extraction

レアメタルの分離には溶媒抽出法が広く用いられている。固体抽出剤を用いて水中から直接かつ高選択的にレアメタルが分離できれば、環境負荷低減につながる。当研究室ではカリックス[4]アレーンジホスホン酸 **1** のアンモニウム塩 **2** の結晶を用いた水中からの Yb(III)選択的捕捉に成功している[1]。本研究では、**2** の結晶を利用した他のレアメタルの選択的抽出を検討した。二種の金属イオンを含む水溶液中で、**2** の結晶を攪拌後、抽出率を算出することで捕捉選択性を評価した。その結果、**2** の結晶が水中からのハード性のレアメタルの選択的抽出に利用できることが明らかとなった。例えば、Al^{3+}共存下、In^{3+}、Ga^{3+}がそれぞれ選択的に捕捉され、In^{3+}、Ga^{3+}の競争的抽出においても、In^{3+}が選択的に捕捉されることを見出した (**Fig. 1**)。



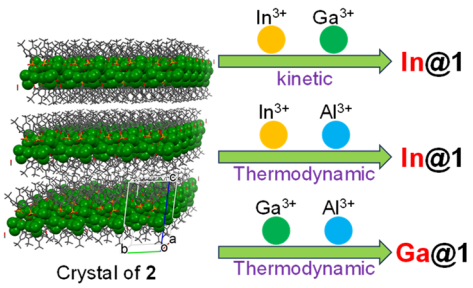


Fig. 1 Competitive extractions of In^{3+}, Ga^{3+}, and Al^{3+} with a crystal of compound **2**.

1) N. Morohashi, M. Osawa, V. Bhalla, S. Sumida, Y. Kato, R. Takahashi, N. Iki, T. Hattori, *CrystEngComm* **2023**, *25*, 5072.

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6 位にアルキル基を導入したジフェニルキノリン *N*-オキシル誘導体の合成と物理化学的性質

（慶大理工）○矢澤 純平・森中 賢人・瀧井 優臣・三浦 洋平・吉岡 直樹

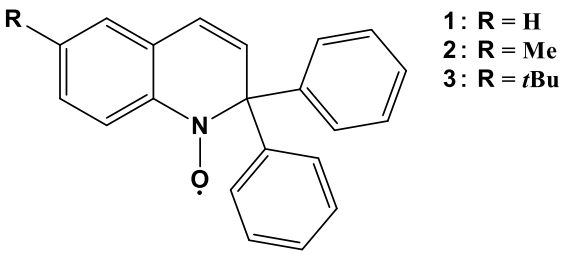
Synthesis and Physicochemical Properties of Diphenylquinoline *N*-oxyl Derivatives with Alkyl Substituents at 6-Position (*Faculty of Science and Technology*, *Keio University*)○ Jumpei Yazawa, Kento Morinaka, Masaomi Takii, Youhei Miura, Naoki Yoshioka

Aromatic nitroxyl radical derivatives such as diphenylnitroxide are known to be stabilized by methoxy group at *p*-positions with high spin density. However, we have reported that 2,2-diphenyl-1,2-dihydroquinoline *N*-oxyl (DPQN, **1**) showed a characteristic reaction at the 6-position. To suppress unexpected reaction on the aromatic nitroxyl radical derivatives, it is necessary to explore new substituents instead of the methoxy group. In this study, DPQN derivatives, **2** and **3** with methyl group and *tert*-butyl group at the 6-position, respectively, were synthesized and their chemical stability, physicochemical properties, and solid-state magnetic properties were investigated to discuss the steric effects of the substituent.

Keywords : Radical, Nitroxide, π-Conjugated System, Molecule-Based Magnetism, Organic Crystal

ジフェニルニトロキシドなど芳香族ニトロキシルラジカルでは、*p*-位などスピン密度の高い部位にメトキシ基導入により安定化することが知られている。当研究室では、2,2-ジフェニル-1,2-ジヒドロキノリン *N*-オキシル(DPQN, **1**)のキノリン環にメトキシ基を導入した誘導体では、キノリン環 6 位に特異な反応が観測されることを報告している[1]。

π 共役ニトロキシルラジカルにおける予期せぬ反応を抑制するためには、メトキシ基以外の置換基の探索が必要である。本研究では、6 位置換基の立体的な嵩高さが与える影響を比較することを目的として、メチル基と *tert*-ブチル基を 6 位に導入した DPQN 誘導体 **2**，**3** (**Scheme 1**)を合成し、化学的安定性、物理化学的性質および固体磁気特性を検討した。



Scheme 1

[1] 瀧井，三浦，吉岡，日本化学会第 103 春季年会, K605-3pm-12 (2023 年 3 月、理科大(野田))

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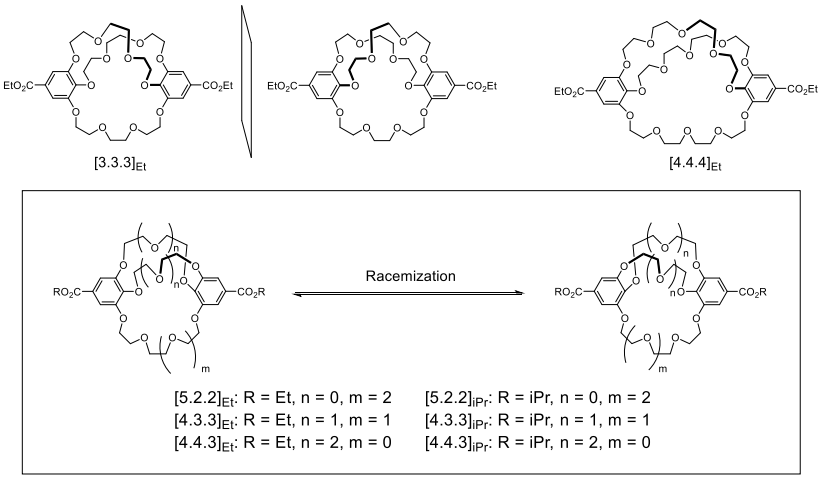
異なる組のエチレングリコール鎖を持つ交差型キラルクリプタンドのラセミ化挙動

（福井大工）○丸山 泰世・新美 翔悟・内藤 順也・宮川 しのぶ・徳永 雄次
Racemization of Cross-Chain Bridging Cryptands Featuring Different Combinations of Oligo-(ethylene glycol) Linkers (*Faculty of Engineering, University of Fukui*)○Taisei Maruyama, Shogo Niimi, Masaya Naito, Shinobu Miyagawa, Yuji Tokunaga

Previously, we have synthesized cross-chain bridging cryptands featuring tri- and tetra(ethylene glycol) linkers, respectively.[1)] The cryptand $[3.3.3]_{Et}$ possessing three tri(ethylene glycol) linkers was chiral without any chiral centers, and racemization of the other one $[4.4.4]_{Et}$ bearing three long linkers proceeded at room temperature. In this study, we synthesized three types of cryptands, $[5.2.2]_{R}$, $[4.3.3]_{R}$, and $[4.4.3]_{R}$, featuring medium-sized macrocycles, and monitored the racemization behavior of them. At first, we examined to isolate enantiomers of $[5.2.2]_{Et}$, $[4.3.3]_{Et}$, and $[4.4.3]_{Et}$ through chiral HPLC, however we were unable to separate them. Transesterification of them gave the corresponding cryptands, possessing bulky isopropyl groups. After isolation of both enantiomers of three cryptands, racemization was monitored by chiral HPLC. The fastest rate of racemization was $[5.2.2]_{iPr}$, followed in order by $[4.3.3]_{iPr}$ and $[4.4.3]_{iPr}$, even though these cryptands possess the same size of macrocycles.
Keywords : Entanglement; Cryptand; Molecular chirality; Racemization

我々は 2 個のベンゼン環に対して 3 つの同じ長さのオリゴエチレングリコールで架橋することにより、交差構造を持つクリプタンドの合成に成功している[1)]。架橋鎖に 3 ユニットのエチレングリコールを 3 本持つクリプタンド（$[3.3.3]_{Et}$）は、交差構造に由来したキラリティを持つことを明らかにし、長い架橋鎖を持つ$[4.4.4]_{Et}$では、室温で速いラセミ化が進行することを確認した。今回、これら 2 種のクリプタンドに対して中間の大きさの大環状部を持つ 3 種のクリプタンド $[5.2.2]_{Et}$、$[4.3.3]_{Et}$、および$[4.4.3]_{Et}$を合成し、それらのラセミ化挙動に関する検討を行った。その結果、いずれのクリプタンドにおいて、キラルカラムを用いた HPLC による分析では、光学分割ができなかった。HPLC タイムスケールよりもラセミ化が速いものと類推し、嵩高いイソプロピルエステルに変換したところ、キラル HPLC による光学分割に成功した。3 種のクリプタンドのエナンチオマーを単離後、ラセミ化挙動を観測すると、最も大きい環サイズが同一でありながらラセミ化速度は異なり、$[5.2.2]_{iPr}$が最も速く、続いて$[4.3.3]_{iPr}$、$[4.4.3]_{iPr}$の順であった。



1) H. Fujihara, M. Naito, T. Yashima, Y. Okada, N. Kobayashi, S. Miyagawa, H. Takaya, Y. Tokunaga, Synthesis of cross-chain bridging cryptands and induction of molecular chirality, *Org. Lett.*, 2023, **25**, 8959–8964.

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リン酸トリアミドを用いたキラルアニオン認識

（山形大理）○吉野誠一・近藤慎一
Chiral Anion Recognition by Phosphoric Triamide (*Faculty of Science, Yamagata Univ.*) ○ Seiichi Yoshino, Shin-ichi Kondo

Since chiral anions play important roles *in vivo* and in the environment, chiral anion receptors have been extensively studied in recent years. In general, chiral receptors with a chiral center on the carbon atom have been designed and synthesized for the chiral recognition. We focused on phosphoric triamides by which have recently been studied for anion recognition. This receptor is a three-dimensional extended version of the widely studied urea functionality. Thus, the phosphoric triamide with three different substituents on the nitrogen atoms should form a chiral anion receptor with a chiral center on the phosphorus atom.

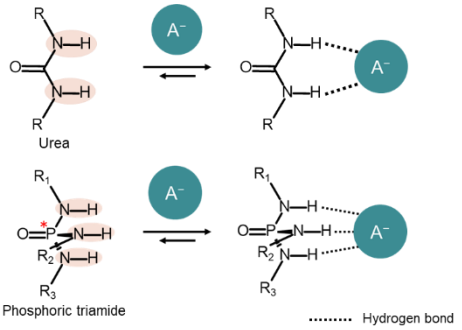

Figure1. Comparison of a urea and a phosphoric triamide.

We have prepared racemic phosphoric triamide, which has *P*-chirality and showed binding ability for L-mandelic acid as a chiral guest, however, the peaks corresponding to the diastereomeric complexes were not confirmed by ^{1}H NMR. In this study, we prepared receptor **1**, which has two chiral centers on the phosphorus atom of the phosphoric triamide and the carbon atom of the amino acid substituent. We proved the *P*-chirality by ^{1}H NMR and HPLC and examine their chiral recognition ability by fractionating the diastereomer.

Keywords : Anion Recognition, Chiral Recognition

生体内や環境中に存在するキラルアニオンは重要な役割を担っており、これらを選択的に認識可能なアニオンレセプターの開発は近年盛んに行われている。一般的にキラル認識可能なレセプターは不斉中心を炭素原子上に有する化合物が設計されてきた。そこで我々は、リン酸トリアミドに注目した。このリン酸トリアミドはウレアを 3 次元的に拡張したもので、異なる 3 つの置換基を有する場合リン原子上に不斉中心を有するアニオンレセプターとなることが期待される。

先行研究ではキラリティを有することが期待されたリン酸トリアミドのラセミ体を合成し、キラルゲストである L-マンデル酸との会合が見られたが、^{1}H NMR 上でジアステレオメリックなピークが確認できず、リン酸トリアミドの *P*-キラリティを確認できなかった。そこで本研究では、側鎖にキラリティを有するアミノ酸を導入し、ジアステレオマーへと誘導したリン酸トリアミド **1** を合成した。^{1}H NMR と HPLC により *P*-キラリティの証明を達成し、さらにこれらを分取することによってキラル認識能を検討した。

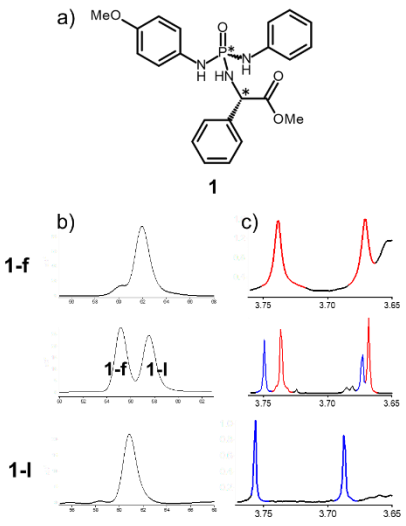

Figure2. (a) Structure of **1**. (b) HPLC analysis and (c) partial ^{1}H NMR spectra fast and later purification of **1** by preparative HPLC.

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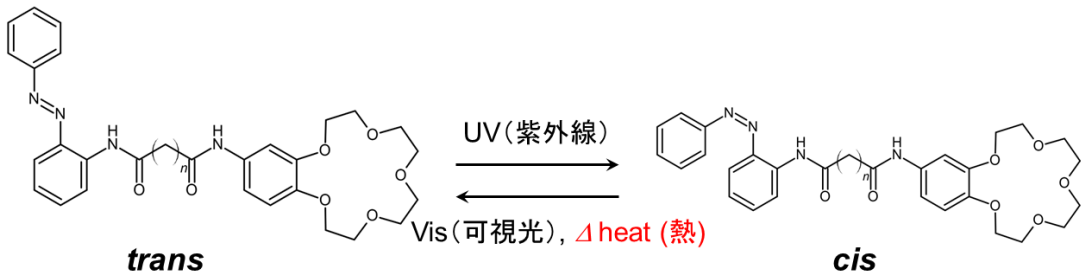
クラウンエーテル構造を有するアゾベンゼン誘導体の熱異性化挙動ならびに金属イオン応答性

(高知大院総合[1]・北大院生命[2]・高知工大院工[3]・Monash Univ.[4]) ○平山 湧人[1]・林 潤澤[2]・玉置 信之[2]・伊藤 亮孝[3]・Rico Tabor[4]・和泉 雅之[1]・越智 里香[1]

Thermal isomerization behavior and metal ion response of azobenzene derivatives with crown ether structure ([1]*Kochi University*, [2]*Hokkaido University,* [3]*Kochi University of Technology*, [4]*Monash University*) ○Yuto Hirayama,[1] Runze Lin,[2] Nobuyuki Tamaoki,[2] Akitaka Ito,[3] Rico Tabor,[4] Masayuki Izumi,[1] Rika Ochi[1]

Azobenzene derivatives are known to exhibit photoresponses which undergoes *trans*/*cis* isomerization upon light irradiation or heat. Their isomerization properties have been actively studied. For example, we have reported *cis*→*trans* thermal isomerization rate of *o*-substituted azobenzene derivatives responds to pH and the presence of metal ions.[1] Thus, the chemical environment around the azo group should be an important factor to control functionalities of an azobenzene derivative. In this study, we synthesized azobenzene derivatives **Azo-C*n*-CR15** in which a metal ion coordination moiety (benzo-15-crown-5) was introduced at the *o*-position *via* a linker with various lengths (C*n*, *n* = 2–4) as shown below. We have found that the linker length and added metal ion species influence thermal isomerization behavior of the derivatives.
Keywords : Azobenzene; Crown Ether; Thermal Isomerization; Host-guest Chemistry; Metal Ions

アゾベンゼン骨格は光照射や熱によって *trans*/*cis* 異性化する光応答性を示すことから、その異性化特性について盛んに研究がなされている。たとえば講演者らは、pHや金属イオンの存在に応答して *cis*→*trans* 熱異性化速度が変化する *o*−位置換型アゾベンゼン誘導体を報告している[1]。それゆえ、アゾ基近傍の化学的環境を通して、アゾベンゼン誘導体の機能性を制御できると考えられる。本研究では、アゾベンゼンの*o*-位に異なる鎖長のリンカー（C*n*, *n* = 2-4）を介して金属イオン包接部位（benzo-15-crown-5）を導入したアゾベンゼン誘導体群 **Azo-C*n*-CR15** を合成した（下図）。これらについて *cis*→*trans* 熱異性化挙動ならびに金属イオン応答性を評価した結果、分子中のリンカー長が長いほど熱異性化反応が抑制されることが明らかとなった。また、添加する金属イオン種（Na^+または K^+）に依存して熱異性化速度が変化することを見出した。



1) R. Ochi, N. Tamaoki, *et al.*, *Tetrahedron*, **2015**, 71, 3500.

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水素結合を用いたU字型チエノアセン誘導体の超分子重合

（名大院理[1]・名大 IRCCS[2]・名大 ITbM[3]）○劉 晨[1]・中島 尚吾[1]・大城 宗一郎[2]・森 達哉[2]・山口 茂弘[1,2,3]

Hydrogen-bond-directed supramolecular polymerization of a U-shaped thienoacene derivative ([1]*Graduate School of Science, Nagoya University*, [2]*Integrated Research Consortium on Chemical Sciences, Nagoya University*, [3]*Institute of Transformative Bio-Molecules, Nagoya University*) ○ Chen Liu,[1] Shogo Nakajima,[1] Soichiro Ogi,[2] Tatsuya Mori,[2] Shigehiro Yamaguchi[1,2,3]

In this study, we designed and synthesized a U-shaped thienoacene derivative having amide-functionalized chiral alkyl chains to investigate its assembly properties. Spectroscopic and electron microscopic studies revealed that the molecule self-assembled into a fibrous nanostructure through intermolecular hydrogen bonding interactions between the amide groups upon cooling its hot solutions in solvents of low polarity. Furthermore, a 3,3′-dibenzo[*b*]thiophene derivative without the central sulfur bridge in the U-shaped thienoacene skeleton was also synthesized to elucidate the effects of the sulfur bridge on its supramolecular polymerization.

Keywords : self-assembly; hydrogen bond; thienoacene; supramolecular polymerization; chirality

非共有結合により π 共役分子が一次元に配列した超分子ポリマーは，π 電子の相互作用により特異な光・電子物性を示すことから，有機エレクトロニクス分野の鍵材料として有望である．水素結合は π 共役分子を配列させるのに有効な非共有結合であるが，複数の超分子ポリマー間に働く相互作用を精密に制御するのは未だ困難である．そこで我々は，分子間カルコゲン-カルコゲン相互作用により超分子ポリマーを束ねた階層構造の構築を目指した．本研究では，U字型のチエノアセン骨格[1)]に着目し，超分子重合を促すアミド基とキラルなアルキル鎖を導入した分子 **1** を合成し，集合特性を評価した (Figure 1a)．低極性溶媒に加熱溶解させ室温に冷却し，スペクトル測定および電子顕微鏡観察を行った結果，アミド基同士の水素結合によりファイバー状集合体を形成することがわかった (Figure 1b)．U字型チエノアセン骨格において，中央の硫黄架橋を除いた3,3′-ジベンゾチオフェン誘導体は無秩序な集合体を形成し，硫黄架橋により超分子ポリマー化が促進されることを確認した．さらに，これらの π 骨格部位が分子配列様式に与える影響を理論計算により調べた．

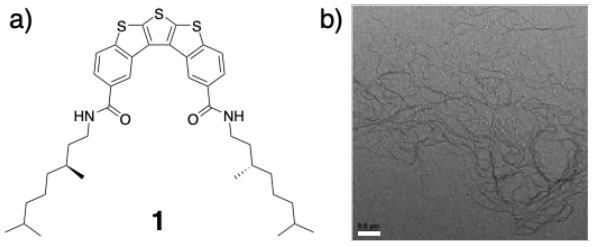

Figure 1. a) Chemical structure of **1**, and b) TEM image of **1** in the aggregate state. Scale bar: 0.5 μm.

1) T. Mori, T. Oyama, H. Komiyama, T. Yasuda, *J. Mater. Chem. C* **2017**, *5*, 5872.

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二分子膜による発光性有機ナノ粒子の水分散化とフォトンアップコンバージョンへの応用

（九大院工[1]・九大 CMS[2]）○久家恵大[1]・原田直幸[1]・金子賢治[1]・君塚信夫[1,2]
Aqueous nanoparticles of luminescent chromophores by using aqueous bilayer membranes and their application to photon upconversion (*[1]Graduate School of Engineering, [2]CMS, Kyushu University*) Keita Kuge[1], Naoyuki Harada[1], Kenji Kaneko[1], Nobuo Kimizuka[1,2]

Aqueous nanoparticles consisting of lipid bilayer **L1** and **Perylene,** or **L1** and **TIPS-Ac** showed high fluorescent quantum yields (85 and 70%, respectively). In the ternary aqueous systems consisting of L1, PdTPTBP, and Perylene or L1, PdTPTBP, and TIPS-Ac, where donor and acceptor ratio is 1:50, both systems showed UC emission with threshold intensity of 425, and 565 mW/cm^2 respectively.

Keywords : Photon upconversion; Triplet-triplet annihilation; Self-assembly

フォトンアップコンバージョン(UC)は、低エネルギーの光を高いエネルギーの光へと変換できる技術であり、その中でも三重項―三重項対消滅（TTA）を用いる手法は、低い励起光強度でも駆動可能なため注目されている。TTA-UC の高度な実用展開のためには、水系における分子組織化 TTA-UC 技術の開発が必要である。[1)] そこで本研究では、合成二分子膜を基盤として水中でも高い発光特性を示す有機ナノ粒子を調製及び、調製したナノ粒子を利用した水系での TTA-UC を試みた。

合成脂質 **L1** を用いて、**Perylene** 並びに **TIPS-Ac** のナノ粒子化を試みた。調製したナノ粒子は、水分散状態においても高い発光強度を示し、その蛍光量子収率は有機溶媒中と遜色ない値を示した(85%, 70%)。また、ドナーとして **PdTPTBP**、アクセプターとして **Perylene** もしくは **TIPS-Ac** をそれぞれ用いて、ドナー：アクセプター比が 1 : 50 となる二種類の複合ナノ粒子を調製した。Ar 雰囲気下、635nm のレーザーを照射したところ、どちらのナノ粒子分散液においても UC 発光(図 1b, c) を観測した。このときのしきい励起光強度 I_{th} はそれぞれ 425、565 mW/cm^2 であった。講演では、UC 特性と分子組織化状態との相関についても議論する予定である。

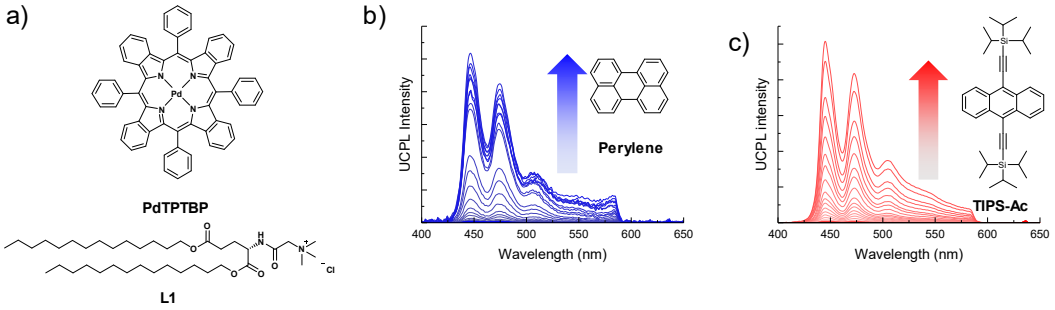

図 1. (a)本研究で用いた TTA-UC 色素と人工脂質分子の構造、並びに Ar 雰囲気下、水中での Perylen もしくは TIPS-Ac をアクセプター、PdTPTBP をドナーとして用いた際の UC 発光スペクトル

1) N. Kimizuka, M-a. Morikawa, N. Yanai, *Langmuir*, **2016**, 32, 12304 (Feature Article).

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Academic Program [Oral A] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:00 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:00 AM UTC
E1131(1131, Bldg. 11 [3F])

[E1131-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Keiichi Imato, Kazuko Nakazono

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1131-4am-01]
Photoinduced solid–liquid transitions by thermally stable molecular photoswitches
○Naoki Kaneda[1], Keiichi Imato[1], Ichiro Imae[1], Yousuke Ooyama[1] (1. Hiroshima University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1131-4am-02]
Sensing behavior of stimuli-responsive liquid materials based on pyromellitic diimide
○Takumi Omura[1], Shogo Morisako[1], Kyosuke Isoda[1] (1. Sagami Chemical Research Institute)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1131-4am-03]
Rotaxane-based Supramolecular Mechanophores Using Acenes as the Fluorophores
○Keigo Nonaka[1], Yoshimitsu Sagara[1] (1. Tokyo Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1131-4am-04]
Formation of a hetero porphyrin tetramer from a pair of carboxy and aminoquinolino porphyrins.
○Kento Otani[1], Masaki Kimura[1], Masahiro Ueda[1], Yuki Akada[1], Shinobu Miyagawa[1], Masaya Naito[1], Yuji Tokunaga[1] (1. The University of Fukui)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1131-4am-05]
Stabilization of crown/ammonium type rotaxanes through ionic interaction
○Takumi Takizawa[1], Kento OTANI[1], Masaya NAITO[1], Shinobu MIYAGAWA[1], Yuji TOKUNAGA[1] (1. University of Fukui)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1131-4am-06]
Self-assembly of Benzoxadiazole Dyad into Fluorescent Nanorings
○Hina OCHIAI[1], Natsuki SUDA[2], Hiroki HANAYAMA[1], Shiki YAGAI[3] (1. Chiba University, 2. Chiba University Graduate School of Science and engineering, 3. Institute for Advanced Academic Research)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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Break

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1131-4am-07]
Self-assembly of quinazolinedione-functionalized π-conjugated molecules

○Yuhei Yamada[1], Hiroki Hanayama[3], Shiki Yagai[2] (1. Chiba University, 2. Chiba University Institute for Advanced Academic Research, 3. Chiba University Graduate School of Engineering)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1131-4am-08]
Molecular recognition behaviors of tertiary amine-type azacyclophanes

○Takeru Okura[1], Kazuko Nakazono[1] (1. Tokyo institute of Technology)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1131-4am-09]
Preparation of planar triphenylborane nanoparticles and their application to boron neutron capture therapy

○Ikumi Koyama[1], Yuichi Kitamoto[1], Yoshitaka Koseki[2], Asuka Mizutani[2], Hitoshi Kasai[2], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1131-4am-10]
Synthesis, Structure and Fluorescent Properties of *meta*-Phenylenediamine-Based Sulfonylaniline Fluorescent Dyes

○Hiroki Sato[1], Kaito Okubo[1], Aki Sato[2], Hiroshi Katagiri[1,2] (1. Grad. Sch. of Org. Mater. Sci., Yamagata Univ., 2. Grad. Sch. of Sci. and Eng., Yamagata Univ.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1131-4am-11]
A 1D tube structure from hexa-nuclear Europium(III) complexes

○Kotaro Yakuwa[1], Junpei Yuasa[1] (1. Tokyo University of Science)

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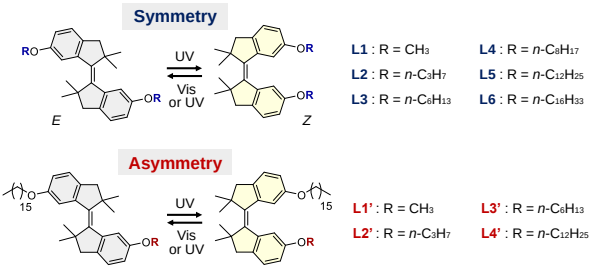
熱安定な光応答性分子スイッチによる固体–液体の光転移

（広島大院先進理工）○兼田直輝・今任景一・今榮一郎・大山陽介
Photoinduced Solid–Liquid Transitions by Thermally Stable Molecular Photoswitches (*Graduate School of Advanced Science and Engineering*, *Hiroshima University*) ○Naoki Kaneda, Keiichi Imato, Ichiro Imae, Yousuke Ooyama

Photoinduced reversible transitions between solids and liquids (phototransitions), in which melting points (T_ms) change across room temperature (RT) by photoisomerization of molecular photoswitches, have attracted considerable attention because of the large changes in physical properties, transmittance, and enthalpy. Particularly, those of azobenzene derivatives have been studied and applied to photoresponsive materials such as photoswichable adhesives. However, there are only a few reports on phototransitions other than AB, and the mechanism is not clearly explainable. Therefore, phototransitions of new photoswitches are required to be studied.

In this study, we focused on a new photoswitch, sterically hindered stiff stilbene (HSS), offering high thermal stability, high photoisomerization yields, and large structural changes,[1] synthesized HSS derivatives that were symmetrically and asymmetrically modified with different lengths of alkyl chains, and investigated changes in T_ms between the *E* and *Z* isomers and their phototransitions. The *E* isomer with two *n*-C_6H_{13} chains was liquid at RT, whereas the *Z* isomer was solid. On the other hand, the HSS derivative with *n*-C_6H_{13} and *n*-$C_{16}H_{33}$ chains showed the opposite behavior, i.e., the *E* isomer was solid and the *Z* isomer was liquid at RT.

Keywords: Molecular Switch; Photoisomerization; Photoinduced Phase Transition; Melting Point; Crystal



分子スイッチの光異性化により、融点（T_m）が室温をまたいで変化し、固体と液体の間で光可逆的に転移する現象（光転移）は、力学物性や透過率、エンタルピーなどが大きく変わるため、その応用に注目が集まっている。特にアゾベンゼン（AB）の光転移が精力的に研究され、光可逆性接着剤などへの応用が検討されてきた。しかし、AB 以外の分子スイッチで光転移を示した報告例は少なく、機構も明確には説明できていない。新しい分子スイッチによる研究が必要と考えられる。

そこで本研究では、高い熱安定性と高い光異性化率、大きな構造変化を示す新たな分子スイッチのヒンダードスティッフスチルベン（HSS）に着目し、異なる長さのアルキル鎖を対称的または非対称的に修飾した低分子 HSS を合成して、*E*/*Z* 異性体の T_m の変化および光転移を調査した。HSS の両端に *n*-C_6H_{13} を修飾した **L3** の *E* 体は室温で液体であったが、*Z* 体は固体だった。一方、*n*-C_6H_{13} と *n*-$C_{16}H_{33}$ を非対称に修飾した **L3'**は反対の物性変化（*E*：固体、*Z*：液体）を示した。

1) K. Imato, N. Kaneda, Y. Ooyama et al., ***J. Org. Chem.*** **2022**, *87*, 15762; ***JACS Au*** **2023**, *3*, 2458.

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ピロメリット酸ジイミド骨格を有する刺激応答性液体材料のセンシング特性

(相模中研 [1]、北里大院 [2]) ○大村 拓実 [1,2]、森迫 祥吾 [1]、磯田 恭佑 [1]
Sensing behavior of stimuli-responsive liquid materials based on pyromellitic diimide ([1]*SCRI*, [2]*Graduate School of Science, Kitasato University*) ○Takumi Omura[1,2], Shogo Morisako[1], Kyosuke ISODA[1]

Solvent-free functional liquid materials have attractive attention as low environmental-loaded soft materials that can be used by anyone, anytime, anywhere, without using volatile organic solvents, which have the potential to achieve some of the Sustainable Development Goals (SDGs) as an alternative to solid materials. Herein, we report on development stimuli-responsive photoluminescent liquid materials. These liquid materials are based on a pyromellitic diimide framework as solvent can dissolve more than equimolar π-conjugated molecules as solute. Luminescent properties of liquid materials can be tuned by selecting dissolved π-conjugated molecules. In particular, some liquid materials can respond upon external stimuli as scratching, leading to the change in photoluminescent colors. These results suggest that these liquid materials are expected to be sensing materials measuring shear stress.
Keywords : Supramolecular chemistry; Charge-transfer complex; Sensing material; Stimuli-responsive liquid materials; Stimuli-responsive materials

有機溶媒フリーの液体材料は、いつでも、どこでも、誰でも使用できる環境低負荷型のソフトマテリアルとして注目されており、固形材料に代わる持続可能な開発目標 (SDGs) の一部を達成する可能性を持つ機能性材料である。本研究では、ピロメリット酸ジイミドを母骨格とする室温液体材料の合成を行った。合成した液体材料 (Figure 1 左) は、様々なπ共役分子を溶解することが可能であり、分子により発光特性を制御することが可能である。調製した溶液の種類によっては、擦るなどの外部刺激により発光色の変化が確認された。紙などに調製した溶液を含浸し、スパチュラ等で擦ることで、擦った部位の発光色が大きく変化する現象が観察された。そこで、印加した外部刺激について定量性を議論するために、摩擦摩耗試験機を用いた評価を行ったので、報告する。

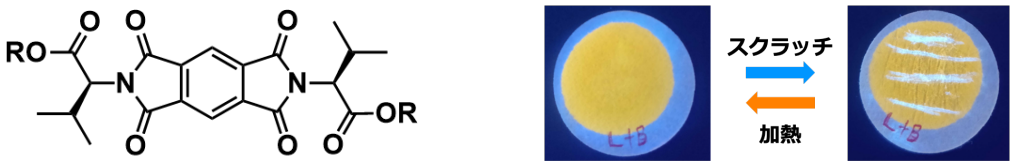

Figure 1. pyromellitic diimide を母骨格とする液体材料 (右) と外部刺激応答試験 (左)

1) in preparation

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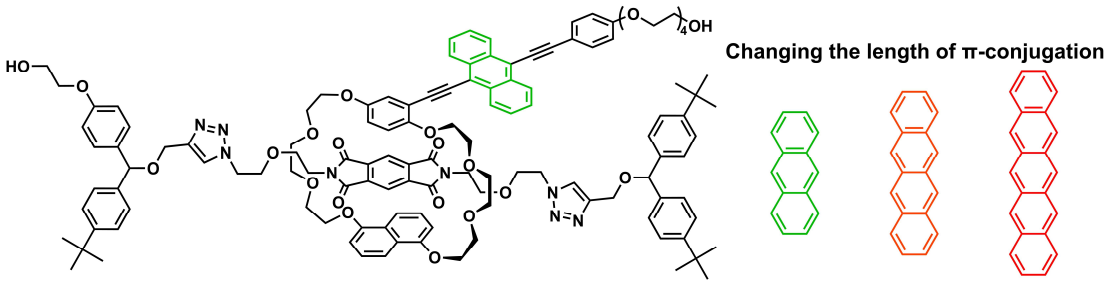
アセン類を蛍光団に用いたロタキサン型超分子メカノフォア

（東工大物質）○野中 慧悟・相良 剛光
Rotaxane-based Supramolecular Mechanophores Using Acenes as the Fluorophores (*Department of Materials Science and Engineering*, *Tokyo Institute of Technology*) ○Keigo Nonaka, Yoshimitsu Sagara

Mechanochromic mechanophores are molecular structures that change absorption and/or fluorescence properties in response to mechanical stimuli. We have developed rotaxane-based supramolecular mechanophores that exhibit rapid and reversible changes in fluorescence intensity.[1] The interaction between the fluorophore and quencher strongly affects the mechanoresponsiveness. In this study, we investigated differences in the photophysical properties of rotaxane-based supramolecular mechanophores having anthracene, [2] tetracene, and pentacene groups as fluorophores. These three mechanophores were separately introduced into polyurethane elastomers. When the three different elastomer films were deformed, distinct mechanoresponsive properties were observed because both charge transfer interaction and photoinduced electron transfer between the fluorophores and quenchers became weaker with extending π-conjugated structure.
Keywords: Mechanophore, Rotaxane, Acene, Charge Transfer Interaction

機械的刺激に応答して吸収・発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。これまで当研究室では、瞬時かつ可逆的に蛍光強度変化を示す超分子メカノフォアの一つとして、ロタキサン型超分子メカノフォアを開発してきた[1]。これまでの研究から、蛍光団と消光団との間の相互作用が、当該メカノフォアの応答特性に大きな影響を及ぼすことがわかってきた。本研究では、既報のアントラセン誘導体[2]に加え、縮環数が異なるアセンであるテトラセン、ペンタセンを蛍光団に導入したロタキサン型超分子メカノフォアを開発した。これら三種のメカノフォアを、それぞれ異なるポリウレタンエラストマーに導入して製膜し、dog-bone 型に切り抜いて延伸すると、それぞれのメカノフォアのアクティベーション挙動が異なることがわかった。これは、縮環数の増加に伴い、蛍光団と消光団との間の電荷移動相互作用と光誘起電子移動が弱くなったためである。



1) Y. Sagara, M. Karman, E. Verde-Sesto, K. Matsuo, Y. Kim, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.* **2018**, *140*, 1584.
2) R. Mori, C. Weder, Y. Sagara, *Macromolecules* **2023**, *56*, 9248.

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日本化学会 第104春季年会 (2024)

カルボキシおよびアミノキノリノポルフィリンの対からなるヘテロポルフィリン４量体の形成

（福井大院工）○大谷 謙斗・木村 元紀・上田 将宏・赤田 祐貴・宮川 しのぶ・内藤 順也・徳永 雄次

Formation of a Hetero Porphyrin Tetramer from a Pair of Carboxy and Aminoquinolinoporphyrins (*Graduate School of Engineering, University of Fukui*) ○Kento Otani, Masaki Kimura, Masahiro Ueda, Yuki Akada, Shinobu Miyagawa, Masaya Naito, Yuji Tokunaga

Self-assembling molecular capsules are attractive because they can recognize guest molecules inside, and the recognition behaviours can be controlled in response to the external environments. We have already constructed a heterodimeric capsule formed from two different porphyrin derivatives **1a** and **2** through aminoquinolinium/carboxylate interactions. In this study, we report a different type of a complex from a pair of the carboxy porphyrin **2** and an aminoquinolinoporphyrin **1b**, bearing linear alkyl chains instead of neopentyl groups (**Fig. 1**). The ^{1}H NMR spectrum of a 1:1 mixture of **1b** and **2** in $CDCl_3$ featured the corresponding heterodimer **1b**-**2** and an additional complex from **1b** and **2**, and a mass spectrum (ESI) of the complex showed a peak of a heterotetramer (**1b**-**2**)$_2$. VT NMR experiments revealed entropy-driven formation of the tetramer.

Keywords : Self-assembly; Entropy-Driven; Porphyrin; Aminoquinolinium/carboxylate interaction

複数の成分が分子間相互作用によって形成されるカプセルは、内部にゲストを認識することができ、また外部環境に応じてこの認識をコントロールできることから注目を集めている。当研究室では、アミノキノリニウム/カルボキシレート相互作用を利用し 2 種のポルフィリン誘導体 **1a** および **2** から、ヘテロ 2 量体カプセルが形成することを見出している。今回我々は、ポルフィリン誘導体 **1a** の側鎖をネオペンチル基からヘキシル基へ変更したところ、異なる集合体が形成することを見出した(**Fig. 1**)。**1b** と **2** の 1 : 1 混合物の $CDCl_3$ 溶液を ^{1}H NMR により観察したところ、2 量体に加え新たな集合体が観測され、質量分析により本集合体はヘテロ 4 量体であると推定した。また、温度可変 NMR 実験により 2 量体と 4 量体形成の熱力学的考察を実施したところ、4 量体形成はエントロピー支配で進行していることが判明した。

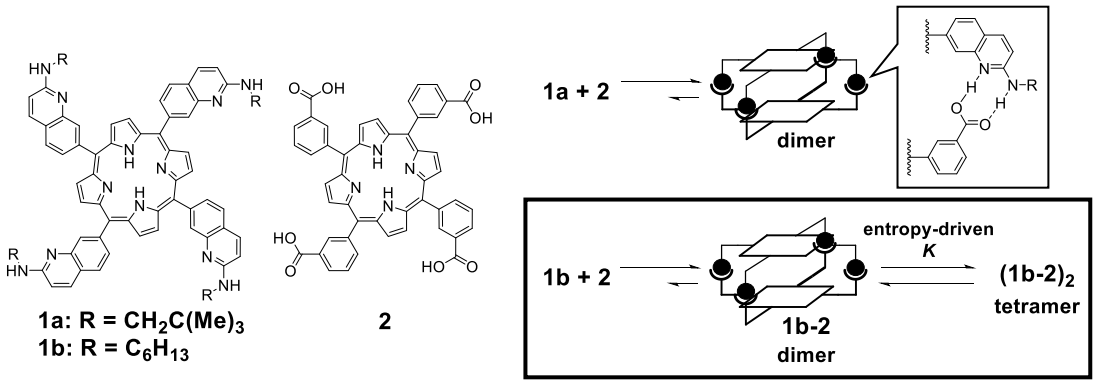

Fig. 1 Equilibrium between the heterodimer and the heterotetramer of porphyrins **1b** and **2**.

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イオン間相互作用を用いたクラウン/アンモニウム型ロタキサンの安定化

（福井大工）○瀧澤 拓巳・大谷 謙斗・内藤 順也・宮川 しのぶ・徳永 雄次
Stabilization of crown/ammonium type rotaxanes through ionic interaction (*Faculty of Engineering, University of Fukui*) ○Takumi Takizawa, Kento Otani, Masaya Naito, Shinobu Miyagawa, Yuji Tokunaga

Crown ether and secondary ammonium ion pair is typical combination in rotaxane formation, and each component has been modified to achieve high yielding synthesis of rotaxanes. Here, we report construction of crown/ammonium ion type rotaxanes futuring borate anion part in macrocycle through ion pairing as well as hydrogen bonding and by means of reversible borate formation reaction. Intramolecular borate formation reaction of biscatechol **1** possessing an oligo(ethylene) glycol linker and boric acid in the presence of dibenzylamine **2a** afforded the corresponding crown/ammonium type [2]rotaxane **3a**. The structure was confirmed by NMR and X-ray analyses. Similarly, borate formation reaction of **1** in the presence of secondary amine **2b** proceeded to form the pseudo[2]rotaxane **3b**, even though DMSO-d_6/chloroform-d_3 was used as a solvent. This observation suggests that the ion paring enhances the binding affinity between both components.
Keywords : Rotaxane; Ionic interaction; Dynamic covalent chemistry

クラウンエーテルと第二級アンモニウムイオンのペアーは、ロタキサン形成における代表的な組み合わせである。これまで、これらを用いた高い比率でのロタキサン形成が検討されてきた。我々は、ボレートイオンをクラウン環に導入し、イオンペアリングによる（擬）ロタキサンの安定化、並びに可逆的なボレート形成反応を用いた高比率でのロタキサン形成を達成した。オリゴエチレングリコールで連結したビスカテコール **1** を環前駆体として合成した。**1** とホウ酸をダンベル型化合物であるジベンジルアミン **2a** 存在下に加熱すると、ボレートおよびアンモニウムイオンの形成に伴い、分子内での環化反応が進行し、クリッピングにより[2]ロタキサン **3a** が定量的に形成した **(Figure 1)** 。NMR や結晶解析などからロタキサン構造が支持された。続いて、両成分に働く水素結合とイオンペアリングによる本ロタキサンの形成能を見る目的で、DMSO-d_6/$CDCl_3$ を溶媒に用いアミン **2b** と **1** からボレート形成反応を行ったところ、擬[2]ロタキサン **3b** の形成が観測され、通常のクラウン/アンモニウム型ロタキサンに比べイオンペアリングによる高い形成能が支持された。

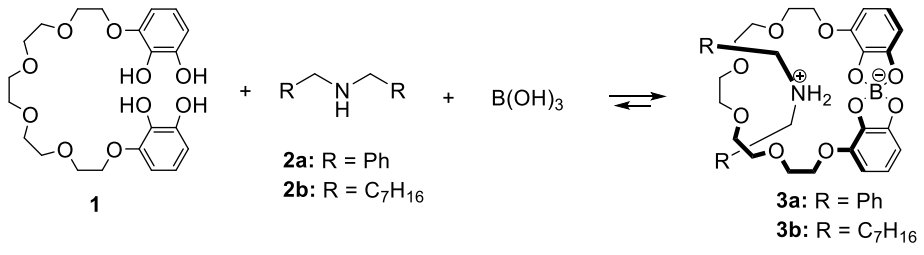

Figure 1. Synthesis of (pseudo)[2]rotaxanes through ion pairing as well as hydrogen-bonding.

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ベンゾオキサジアゾール二量体の自己集合による蛍光性ナノリングの形成

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Self-assembly of Benzoxadiazole Dyad into Fluorescent Nanorings ([1]*Faculty of Engineering, Chiba University,* [2]*Graduate School of Science and Engineering, Chiba University,* [3]*Institute for Advanced Academic Research, Chiba University*) ○Hina Ochiai[1], Natsuki Suda[2], Hiroki Hanayama[1], Shiki Yagai[2]

We have investigated the self-assembly of a series of scissor-shaped π-conjugated dyads connected via a xylylene unit (Figure 1a). Recently, we found that a diphenylbenzothiadiazole dyad **1** self-assembled into nanorings that exhibit green emission (Figure 1b). In this study, we newly synthesized diphenylbenzooxadiazole dyads **2** (Figure 1c) analogous to **1**. Upon rapidly cooling (> 20 °C/min) a hot monomeric solution of **2** in nonpolar solvent, AFM and spectroscopic measurements revealed the formation of irregularly shaped nanorings emitting yellow fluorescence (Figure 1c). We will discuss the self-assembly behavior and photophysical properties of **2** by comparing with those of **1**.

Keywords: Self-assembly; Nanoring; Benzoxadiazole; Benzothiadiazole; fluorescence

当研究室では可溶性部位を介してπ共役部位を連結したハサミ型色素二量体分子の自己集合について研究を行ってきた(Figure 1a)。[1] 最近、π共役部位としてジフェニルベンゾチアジアゾールを有する分子**1**が緑色の蛍光を示すナノリングへ自己集合することを見出した(Figure 1b)。本研究では、ベンゾチアジアゾールの類縁体であるベンゾオキサジアゾールを導入した分子**2**を新規に合成した(Figure 1c)。低極性溶媒に加熱溶解させた分子**2**の溶液を室温まで急冷(> 20 °C/min)すると、興味深いことに不均一な形の非常に大きなナノリングが形成されることがAFMにより明らかになった(Figure 1c)。また、**2**のナノリング溶液は黄色の蛍光を示した。分子**2**の自己集合挙動や光物性を分子**1**と比較しながら議論する。

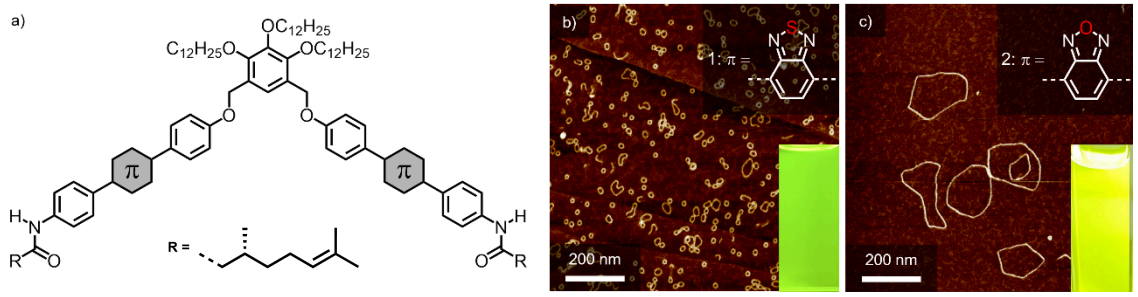

Fig. 1. a) Molecular structure of scissor-shaped dyad. b,c) AFM images of nanorings formed by (b) **1** and (c) **2**, respectively. Insets show photographs of the solution of nanorings taken under 365 nm-light illumination.

1) K. Tashiro, S. Yagai et al., *Chem. Rec*. **2022**, *22*, e202100252.

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キナゾリンジオンを有するπ共役分子の自己集合

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○山田 悠平[1]・花山 博紀[2]・矢貝 史樹[3]

Self-assembly of quinazolinedione-functionalized π-conjugated molecules ([1]*Faculty of Engineering, Chiba University,* [2]*Graduate School of Engineering, Chiba University,* [3]*Institute for Advanced Academic Research, Chiba University*) ○Yuhei Yamada,[1] Hiroki Hanayama,[2] Shiki Yagai[3]

We have reported that a series of barbituric acid-functionalized π-conjugated molecules form hydrogen-bonded cyclic hexamers (rosette) that further self-assemble into various supramolecular polymer structures depending on the π-conjugated core.[1)] However, we have not yet found alternative hydrogen-bonding units for barbituric acid. Herein, we newly designed and synthesized a π-conjugated molecule **1** bearing quinazolinedione as a hydrogen-bonding unit (Fig. 1a). Upon cooling a hot methylcyclohexane solution of **1**, it self-assembled to form linear fibers as confirmed by AFM (Fig. 1b). Concentration-dependent ^{1}H NMR spectra showed a characteristic lower-field shift of the two N-H protons similar to the rosette formation of barbituric acid[2)] (Fig. 1c). We will discuss the similarities and differences in the self-assembly behaviors between **1** and barbituric acid molecules.

Keywords: Self-assembly; Supramolecular Polymer; Hydrogen-bonding; Quinazolinedione; Barbituric Acid

我々がこれまでに報告してきたバルビツール酸で修飾されたπ共役分子は、バルビツール酸部位の水素結合により環状六量体を形成し、それらが積層することで、π共役部位の形に依存した様々な自己集合構造を与える。[1)] 一方で、バルビツール酸に代わる水素結合部位は見出されておらず、その開発は新たな機能性材料の開発に繋がりうる。本研究では同様の水素結合様式をとると期待できるキナゾリンジオンを導入した分子 **1** を新規に合成した（Fig. 1a)。重クロロホルム中で濃度可変 ^{1}H NMR を測定すると、バルビツール酸系分子と同様の N-H プロトンのピークシフト[2)]が確認され、環状六量体の形成が示唆された(Fig. 1c)。次に、分子 **1** をメチルシクロヘキサン中で加熱溶解させ冷却すると、直線状のファイバーが AFM により観察された（Fig. 1b)。分子 **1** とバルビツール酸系分子の自己集合挙動における類似点と差異を議論する。

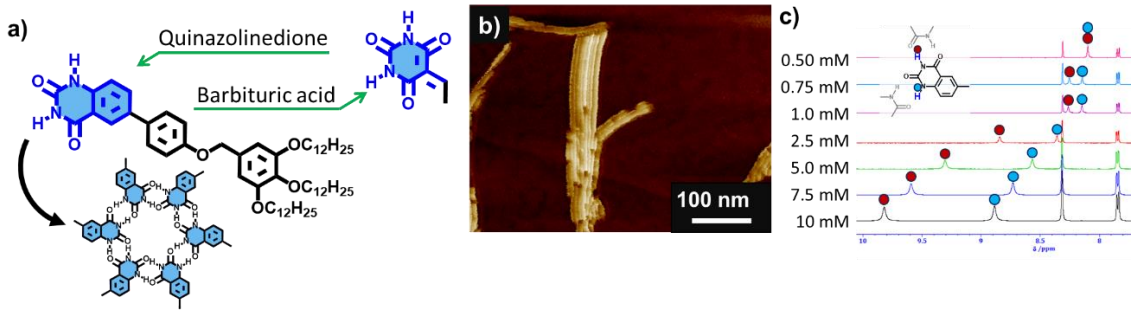

Figure 1. a) Molecular structure of **1** and its cyclic hexamer (rosette). b) AFM image of liner fibers of **1**. c) concentration-dependent ^{1}H-NMR spectra of **1**.

1) a) S. Yagai et al., *Acc. Chem. Res.* **2019**, *52*, 1325.; b) S. Yagai et al., *Acc. Mater. Res*. **2022**, *3*, 259.
2) X. Lin, S. Yagai et al., *Sci Rep* **2017**, *7*, 43098.

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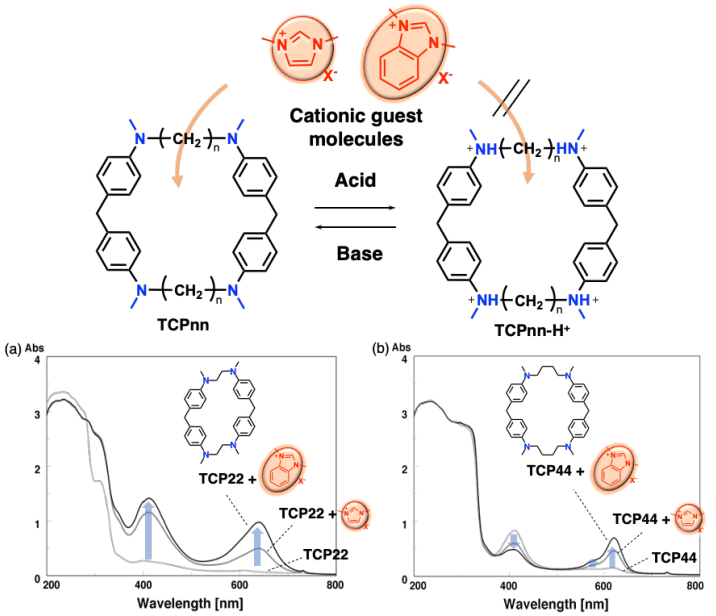
第三級アミン型アザシクロファンの分子認識

（東工大物質理工）○大倉 豪留・中薗 和子
Molecular Recognition Behaviors of tertiary Amine-type Azacyclophane (*Department of Chemical Science and Engineering, Tokyo Institute of Technology*) ○Takeru Okura, Kazuko Nakazono

To develop host molecules that can transform their cavity's molecular recognition properties in response to stimuli, novel azacyclophanes possessing *tert*-amine groups (**TCPnn**) in the cyclic skeleton were synthesized. **TCPnn** selectively recognized cationic guest molecules within the cavity framed by four electron-rich aromatic rings, affording green-colored inclusion complexes. The treatment of the inclusion complex with acids to generate *tert*-ammonium-type azacyclophane **TCPnn-H**$^+$, in which amine moieties were protonated, resulted in the dissociation of cationic guest molecules. Furthermore, the molecular recognition property of **TCPnn** was also utilized for the new rotaxane synthesis.

Keywords：Molecular recognition; pH Responsive host-guest complex; Cyclophane; Rotaxane

窒素官能基をシクロファン骨格に含むアザシクロファンは、蛍光色素等を包接する水溶性ホスト材料として研究されている[1,2]。一方、最近、我々は第三級アミンを骨格に含む新規アザシクロファンの有機溶媒中における分子認識特性を検討し、カチオン性ゲストを包接することを見出した。本研究では４つの第三級アミンを有するアザシクロファンの有機溶媒中におけるカチオン性ゲスト包接の分子認識特性を明らかにすることを目的として、二つのサイズの異なる新規アザシクロファン(**TCPnn**, n = 2, 4) を合成し、種々のゲスト分子との会合特性について NMR および紫外可視吸収スペクトルを用いて検討した。



UV-vis spectra of (a) **TCP22** with 1,3-dimethylimidazolium salt or 1,3-dimethylbenzimidazolium salt, and (b) **TCP44** with 1,3-dimethylimidazolium salt or 1,3-dimethylbenzimidazolium salt (1 : 1 mol/mol, 0.4 mM in $CHCl_3$ / CH_3CN = 7 / 3, 20 °C)

TCP22 および **TCP44** に 1,3-ジメチルイミダゾリウム塩および 1,3-ジメチルベンゾイミダゾリウム塩を加えたところ、溶液の色が変化し、吸収スペクトルにおいて新たな吸収ピークの出現が確認された。**TCP22** は緑色に、**TCP44** は青色を示したことから包接されたカチオン性ゲストと **TCPnn** の電子豊富な芳香環とのカチオン-π 相互作用による包接錯体の形成が示唆された。また酸を加えて第三級アミンをプロトン化するとゲスト分子と会合しないことが確認された。この包接特性を利用した新規ロタキサンも合成したので報告する。

1）小田嶋 和徳，薬学雑誌, 108, 91-108 (1988), 2）林田 修，有機合成化学協会誌, 64, 1041-1048 (2006).

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プラナートリフェニルボランナノ粒子の調製とホウ素中性子捕捉療法への応用

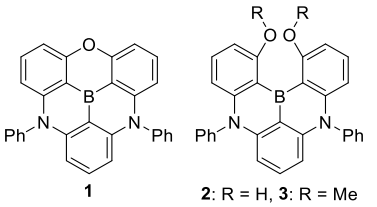
（東北大院工[1]・東北大多元研[2]）○小山 育珠[1]・北本 雄一[1]・小関 良卓[2]・水谷 明日香[2]・笠井 均[2]・服部 徹太郎[1]

Preparation of planar triphenylborane nanoparticles and their application to boron neutron capture therapy ([1]*Graduate School of Engineering, Tohoku University*, [2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○Ikumi Koyama,[1] Yuichi Kitamoto,[1] Yoshitaka Koseki,[2] Asuka Mizutani,[2] Hitoshi Kasai,[2] Tetsutaro Hattori[1]

Boron neutron capture therapy (BNCT) is a noninvasive cancer treatment method based on the nuclear reaction of ^{10}B with thermal neutrons. Although some approaches for their accumulation to cancer tissues are explored, there is an issue of low boron content in drugs. We have developed the function of heteroatom-bridged planer triphenylboranes with good hydrolysis resistance. In this research, we prepared nanoparticles from planer triphenylboranes bridged by phenylimino groups (**1**–**3**) and evaluated their *in vitro* BNCT effectiveness.

Keywords : Neutron Capture Therapy; Boron Neutron Capture Therapy; Cancer Therapy; Boron Compounds; Nanoparticles

ホウ素中性子捕捉療法（BNCT）は、^{10}B 原子への熱中性子線照射による $^{10}B(n,\alpha)^{7}Li$ 反応を利用したがん治療法である。生じる ^{4}He 核（α線）の飛距離は細胞径と同程度であることから、低侵襲な治療法として知られている。薬剤の腫瘍選択的な集積には、ナノ粒子化による EPR 効果の利用やキャリア部位の導入が有効だが、既報の多くの手法では薬剤一分子あたりのホウ素原子含有量の低下を招いてしまう。当研究室では、オキソ基などのヘテロ元素架橋基を有するプラナートリフェニルボラン類の研究を行っている[1]。これらの分子群は、ホウ素に対してアリール基が三座配位構造を取ることで高い加水分解耐性を示すことから、水共存下での応用展開が期待される。本研究では、フェニルイミノ基を架橋基に有する **1**–**3** からのナノ粒子の調製と、中性子捕捉療法への応用について検討した。



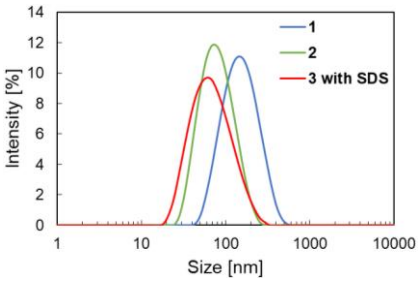


Fig. 1 DLS measurement for nanoparticle dispersions of **1**–**3** (100 μM) in H_2O/DMSO (100/1, vol/vol) monitored in an hour after the fabrication.

10 mM の **1**–**3** 各 DMSO 溶液 100 μL を貧溶媒である水 10 mL にインジェクションし、**1**–**3** を再沈殿させること（再沈法）[2]によりナノ粒子分散液を調製した（Fig. 1）。**1** と **2** はそれぞれ粒径が約 143 nm、73 nm のナノ粒子を形成した。**3** は調製直後に沈殿を生じたため、分散安定剤としてドデシル硫酸ナトリウム（SDS）を **3** に対して 100 wt%添加したところ、沈殿が抑制され約 62 nm のナノ粒子分散液が得られた。発表では、BNCT への応用についても報告する。

1) Y. Kitamoto, T. Hattori *et al.*, *J. Org. Chem.* **2023**, *88*, 5852.
2) H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada. H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mokoh, H. Nakanishi, *Jpn. J. Appl. Phys.* **1992**, *31*, L1132.

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メタフェニレンジアミン骨格を基盤とするスルホニルアニリン蛍光色素の合成と構造および蛍光特性

（山形大院有機[1]・山形大院理工[2]）○佐藤 大幹[1]・大久保 快人[1]・佐藤 亜紀[2]・片桐 洋史[1,2]

Synthesis, Structure and Fluorescent Properties of *meta*-Phenylenediamine-Based Sulfonylaniline Fluorescent dyes ([1]*Graduate School of Organic Materials Science, Yamagata University,* [2]*Graduate School of Science and Engineering, Yamagata University*) ○Hiroki Sato,[1] Kaito Okubo,[1] Aki Sato,[2] Hiroshi Katagiri[1,2]

The push–pull system has been widely employed for the tuning of optical properties in π-conjugated molecules. We have reported sulfonylaniline dyes having amino and sulfonyl groups in the benzene ring[1-4]. In particular, 2,5-BMeS-*p*-A exhibits green fluorescence with high quantum yield, solid-state fluorescence, and a large Stokes shift. In this study, we synthesized the *meta*-phenylenediamine-based sulfonylaniline dye 2,5-BMeS-*m*-A, investigated its structure and fluorescence properties, and compared it with the positional isomer 4,6-BMeS-*m*-A (Figure 1). A comparison of the optical properties in acetonitrile revealed that the absorption and fluorescence spectra of 2,5-BMeS-*m*-A were more red-shifted than those of 4,6-BMeS-*m*-A, with higher quantum yields and larger Stokes shifts (Table 1). These results suggest that longer absorption and fluorescence wavelengths and higher quantum yields are obtained when the amino and sulfonyl groups are in ortho and meta positions relative to each other.

Keywords: Fluorescent Dye; meta-Phenylenediamine; Sulfonylaniline; Push-pull System; Positional Isomer

Push–pull系はπ共役系分子の光学特性を調整するために広く用いられている. 我々はこれまでに, ベンゼン環にアミノ基とスルホニル基を持つスルホニルアニリン蛍光色素を報告している[1-4]．特に，2,5-BMeS-*p*-A は高い量子収率，固体蛍光，ならびに大きなストークスシフトを有する緑色蛍光色素である．今回我々は，メタフェニレンジアミン骨格を基盤とする 2,5-BMeS-*m*-A を合成し，その構造と蛍光特性相関を調査するとともに位置異性体 4,6-BMeS-*m*-A と比較した(Figure 1)．アセトニトリル中の光学特性を比較すると，2,5-BMeS-*m*-A の吸収および蛍光波長は 4,6-BMeS-*m*-A に比べて長波長化し，高い量子収率と大きなストークスシフトを示した(Table 1). 本結果は，アミノ基とスルホニル基が互いにオルトとメタの位置関係になる場合に吸収と蛍光波長の長波長化と高い量子収率が得られることを示唆している．

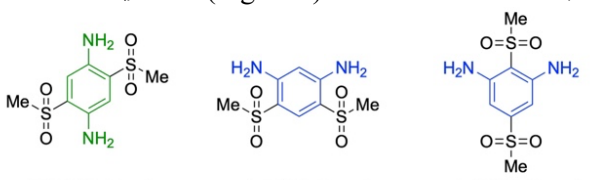

Figure 1. Sulfonylaniline fluorescent dyes.

Table 1. Optical properties of sulfonylaniline in CH_3CN.

Compounds	λ^{max}_{abs} [nm]	λ^{max}_{em} [nm]	Φ [-]	Stokes shift [nm]
2,5-BMeS-*p*-A	382	492	0.49	110
4,6-BMeS-*m*-A	300	348	0.004	48
2,5-BMeS-*m*-A	357	415	0.48	58

1) T. Beppu, *et al*., *ChemPlusChem*, **2014**, *79*, 536–545. 2) T. Beppu, *et al*., *Angew. Chem. Int. Ed.*, **2015**, *54*, 7332–7335. 3) S. Kudo, *et al., ChemPhysChem,* **2019**, *20*, 1581–1589. 4) T. Mochizuki, *et al*. *Tetrahedron Lett*. **2022**, *90*, 153625.

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6 核 Eu(III)錯体をビルディングブロックとする 1 次元性チューブ構造の構築

（東理大院理）○八鍬 光大郎・湯浅 順平
A 1D tube structure from hexa-nuclear Europium(III) complexes
(*Grad. Sch. Sci., TUS*) ○Kotaro Yakuwa, Junpei Yuasa

In this work, we synthesized the tube-like nona-coordinated Eu(III) complex. Eu(III) complex structure hexa-nuclear complex and has 1D-tube hole from single crystal X-ray diffraction. Also, crystal color of pyrrole in Eu(III) complex changed after UV irradiation.
Keywords : Lanthanide complex; β-diketonate ligand; Host-guest chemistry

チューブ構造は 1 次元性のポーラス構造であり、ナノレベルのチューブ構造は物質輸送やその輸送性を利用した触媒反応場として魅力的である。一方で、人工的に 1 次元性のナノポーラス構造を構築することは未だ困難である。その構築法として、1D metal-organic framework(1D MOF)や、中央空隙をもつ環状化合物を無限積層させることが一般的である。しかし、これらの人工的なナノチューブ構造は配位結合角の明確さ、共有結合の固定された角度性から、なめらかな同心円状の 1 次元空洞をつくることは困難である。これに対し、タバコモザイクウイルスに代表される天然のチューブ構造は、ビルディングブロックとなるタンパク質が一定の回転角度をもち、周期的に集積することでなめらかな同心円状の 1 次元空洞を形成している[1]。

本研究では、希土類イオンの配位結合の柔軟性に着目し、多核希土類錯体を周期的に配列させることで同心円状の 1 次元空洞をもつ新規ナノチューブ構造を構築した(**Figure 1**)。新規架橋配位子 L_1 を用いて Eu(III)錯体を合成し、単結晶 X 線構造解析を行ったところ、中央部に同心円状の 1 次元空洞をもつナノチューブ構造を構築していた。このナノチューブ構造は Eu(III)イオン核 3 つからなる三角形型の平面構造を繰り返し単位としてもち、これが配位結合および非共有性相互作用によって一定の回転角度をもちながら 1 次元方向に集合化した周期構造をもつことがわかった。光酸化反応を調べるために、結晶スポンジ法を用いて 6 核 Eu(III)錯体内にピロールを含侵させたあと、UV 照射を行った。その結果、UV 照射前と比べて、結晶の黄色みが増した(**Figure 2**)。ここから光照射を行うと Eu(III)イオンからピロールへの光誘起電子移動が生じ、ポリマー化が進行したと考えられる。

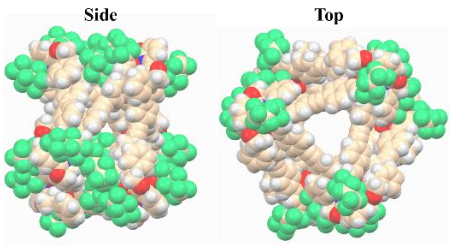

Figure 1. Crystal structure of Eu(III) complex.

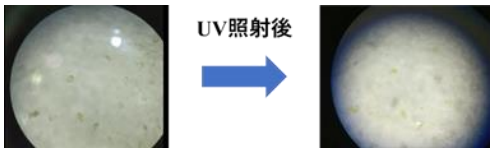

Figure 2. Crystal color of pyrrole in Eu(III) complex before(left) and after(right) UV light.

1) Klug, A. *Philosophical Transactions of the Royal Society of London B.* **1999**, *354*, 531-535.

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Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC E1122(1122, Bldg. 11 [2F])

[E1122-4pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Junpey Yuasa, Yuki Ide

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1122-4pm-01]
Design of ionic liquid crystals by integrating a mesogen core with flexible tails via a rotaxane structure

○Gosuke Washino[1], Suzushi Nishimura[2], Atsushi Shishido[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech, 2. Sch. of Mater. & Chem. Technol., Tokyo Tech)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1122-4pm-02]
Switching the Emission of Two-Dimensional COFs by Tuning Interlayer Stacking Arrangements

○SIYUAN YE[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. School of Engineering, The Univ. of Tokyo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1122-4pm-03]
Material design and condition optimization for generating higher force of photomechanical crystals by machine-learning

○Kazuki ISHIZAKI[1], Toru ASAHI[1], Takuya TANIGUCHI[1] (1. Waseda University)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[E1122-4pm-04]
Analysis of light-driven self-oscillatory crystal under polarized light irradiation from a mathematical model based on reaction velocity

○Yoshiyuki Kageyama[1], Makiko Matsuura[1] (1. Hokkaido Univ.)

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Design of Ionic Liquid Crystals by Integrating a Mesogen Core with Flexible Tails via a Rotaxane Structure

([1]*Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology,* [2]*School of Materials and Chemical Technology, Tokyo Institute of Technology*)
○Gosuke Washino,[1] Suzushi Nishimura[2], Atsushi Shishido[1]
Keywords: Rotaxane; Ionic Liquid Cyrtal; Supramolecule; Thermotropic Liquid Crystal; Crown ether

Ionic liquid crystals (iLCs) are attractive for creating unique material functions by arranging ionic molecules with higher-order structures and for the versatility of molecular design approaches in LCs. Besides introducing a mesogen core and flexible tails into a single molecule, iLCs can utilize counterions to enable LC phase expression by controlling a hydrophobic-hydrophilic balance. Rigid cations, known for crucial molecular structures in the iLC design, are also essential molecular components in the supramolecular field. For instance, in the synthesis of rotaxanes, typical mechanically interlocked structures, rigid cations like viologen derivatives serve as axle molecules to form threading structures with electron-rich ring molecules.[1] However, very few papers have reported syntheses of LC rotaxanes playing the dual roles of rigid cations in the two different fields.[2]

In this study, we present a design concept for iLCs where [2]rotaxane structure formation enables LC phase expression. We designed a [2]rotaxane (**Rtx12**) consisting of an axle molecule with only a mesogen core and a ring molecule with four flexible tails. Although neither the axle nor the ring has LC properties, **Rtx12** exhibits a smectic A phase due to integrating a mesogen core and flexible tails via a rotaxane structure. A 1:1 mixture of the axle and the ring without a rotaxane structure showed no thermotropic LCs; the rotaxane structure formation in **Rtx12** is crucial in exhibiting the LC phase. We further discuss developing this iLC design concept into a dynamic system: pseudo-rotaxane.

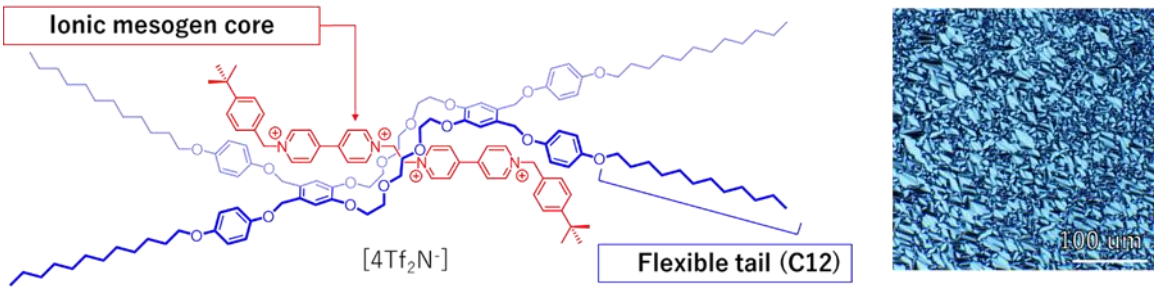

Figure 1. Chemical Structure of **Rtx12** and POM image of **Rtx12** at 140 °C upon cooling.

1) H. R. Wessels, C. Slebodnick, and H. W. Gibson, *J. Am. Chem. Soc.* **2018**, *140,* 7358. 2) N. D. Suhan, S. J. Loeb, and S. H. Eichhorn, *J. Am. Chem. Soc.* **2013**, *135,* 400.

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Switching the Emission of Two-Dimensional COFs by Tuning Interlayer Stacking Arrangements

([1]*Graduate School of Engineering, The University of Tokyo*) ○Siyuan Ye,[1] Nobuhiko Hosono,[1] Takashi Uemura[1]

Keywords: COFs; Phase transition; Two-dimensional Materials; Through-space Charge transfer

The properties of two-dimensional (2D) materials are intrinsically linked to their stacking configurations. While scientists have controlled a limited array of these materials via operation under scanning tunneling microscope (STM),[1] a comprehensive exploration of their stacking modes remains elusive. Two-dimensional porous materials, such as Metal-Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs), have garnered significant interest for their adjustable properties and crystalline structures.[2] Traditionally, altering these materials' packing patterns necessitates intricate chemical modifications.[3] However, a novel approach has emerged with the discovery of guest-modulated interlayer slip in 2D COFs,[4] allowing for simpler manipulation of stacking patterns without altering the core structure.

This study introduces a new COF consisting of pyrene and cyanostilbene moieties in the framework, designated as **1**, which we successfully manipulated in terms of interlayer stacking via electron donor-acceptor alternation. When desolvated, **1** exhibits an ordered AA stacking arrangement. This configuration shifts to a quasi-AB stacking pattern upon introducing solvents with low surface tension (Figure 1). Conversely, high surface tension solvents and carbon dioxide lead to disordered stacking. These variations in stacking profoundly influence charge transfer between layers, markedly altering its fluorescence emission characteristics. Notably, **1** demonstrates non-emissive properties in AA stacking yet displays emissive fluorescence in quasi-AB stacking. By tailoring the size distribution of **1** in solution, we can fine-tune its emission color, achieving a unique single-component white light emission.

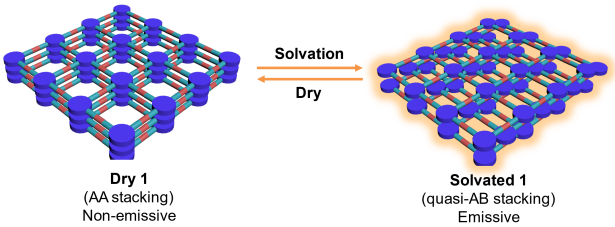

Figure 1. Schematic diagram of turning on fluorescence through changing the interlayer stacking of **1**

1) Y. Cao, V. Fatemi, and S. Fang, *Nature* 2018, **556**, 43, 2) S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem. Int. Ed.* 2004, **43**, 2334. 3) X. Wu, X. Han, Y. Liu, Y. Liu and Y. Cui, *J. Am. Chem. Soc.*, 2018, **140**, 16124. 4) C. Kang, Z. Zhang, V. Wee, A. K. Usadi, D. C. Calabro, L. S. Baugh, S. Wang, Y. Wang and D. Zhao, *J. Am. Chem. Soc.*, 2020, **142**, 12995.

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Material design and condition optimization for generating higher force of photomechanical crystals by machine-learning

([1]*Graduate School of Advanced Science and Engineering, Waseda University*, [2]*Center for Data Science, Waseda University*) ○Kazuki Ishizaki,[1] Toru Asahi,[1] Takuya Taniguchi[2]

Keywords: Generating force; Photomechanical crystal; Machine learning; Young's modulus

Photomechanical crystals show macroscopic motion under UV light irradiation. In our previous work, the generated force of the photomechanical salicylideneamine crystals was about 8.7 mN even under optimal conditions.[1] Searching a wide range of conditions is necessary to find the optimum conditions to increase generating force. In this study, photomechanical crystals with various Young's modulus were fabricated based on material design guidelines obtained by LASSO regression, and then conditions achieving larger generating force were explored by Bayesian optimization.

To design photomechanical crystals with various Young's moduli, we performed LASSO regression, one of the linear regression methods for variable reduction. LASSO regression was conducted to identify functional groups correlated with Young's modulus (Fig. 1a). Eleven types of salicylideneamine crystals were prepared based on the finding of the LASSO regression.

The conditions corresponding to a larger generating force were searched using Bayesian optimization. Bayesian optimization suggests the following experimental conditions based on the value of the acquisition function calculated by the predictions and the uncertainty of the predictions. The condition of Young's modulus, crystal size, and light intensity were suggested by Bayesian optimization. Based on the suggested conditions, the crystal was selected, and light intensity was determined. After these steps, generating force was measured (Fig. 1b). The same operation was repeated to find the experimental conditions with the highest generating force. In this research, before the actual experiments, simulations were conducted to obtain an indication of the trial number.

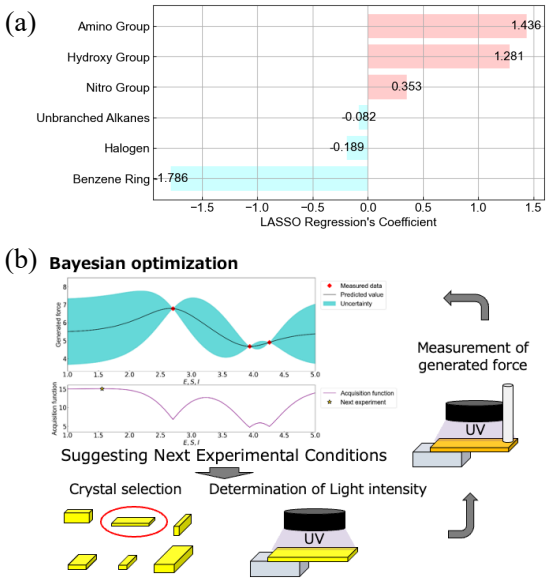

Fig. 1. (a) Molecular design by LASSO regression. (b) Condition search by Bayesian optimization.

1) K. Ishizaki, R. Sugimoto, Y. Hagiwara, H. Koshima, T. Taniguchi, T. Asahi, *CrystEngComm*, **23**, 5839-5847 (2021).

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偏光照射下における光駆動自励振動結晶の挙動の反応速度論に基づいた数理モデルからの解析

（北大院理）○景山 義之・松浦 真紀子
Analysis of light-driven self-oscillatory crystal under polarized light irradiation from a mathematical model based on reaction velocity (*Faculty of Science, Hokkaido University*) ○ Yoshiyuki Kageyama, Makiko Matsuura

We previously proposed that the light-driven self-oscillation of an azobenzene crystal is realized by the sequential behavior of the photoisomerization-triggered crystalline phase transition and its resultant alternation of the apparent photoisomerization rate constants[1]. In addition, we reported that the complexity of the self-oscillatory motion is derived when the excitation light is polarized[2]. Aiming to understand the origin of the complexity, we analyzed the observed frequency under polarization light excitation and constructed a math-model from the reaction equations. The observed behavior (**Fig. 1a**) can be explained by a kinetic model which is derived from the proposed mechanism (**Fig. 1b**). Moreover, we found that the existence of hysteresis contributes to the complexity of the behavior [3].
Keywords : Reaction Kinetics, Autonomous Motion, Far-from-equilibrium, Self-oscillatory Crystal, Hysteresis

演者らはアゾベンゼン誘導体を構成分子とした結晶の定常光照射下での継続的なフリップ運動を報告した。この現象では、光異性化が誘起する結晶構造転移が、見かけの光異性化速度定数を切り替えることで自己継続性を実現していると演者らは提案している [1]。また、照射光を偏光にした場合、偏光角度依存的な複雑な自励振動を示すことを明らかにしてきた [2]。その複雑性の起源の理解を目指し、本研究では、偏光照射下での自励振動の振動数について解析した。特徴的な振動数の偏光角度依存性(**Fig. 1a**)は、我々が提案する自励振動発現機構を基にした数理モデルの結果とよく一致した(**Fig. 1b**)。さらには、ヒステリシスの存在が挙動の複雑化に関与していることを発見した [3]。

1) T. Ikegami, Y. Kageyama, S. Takeda, *et al.*, *Angew. Chem. Int. Ed.* **55**, 8239 (2016).
2) Y. Kageyama, S. Takeda, *et al.*, *Chem. Eur. J.* **26**, 10759 (2020).
3) Y. Kageyama *et al.*, *arXiv* 2301.09873 (2023).

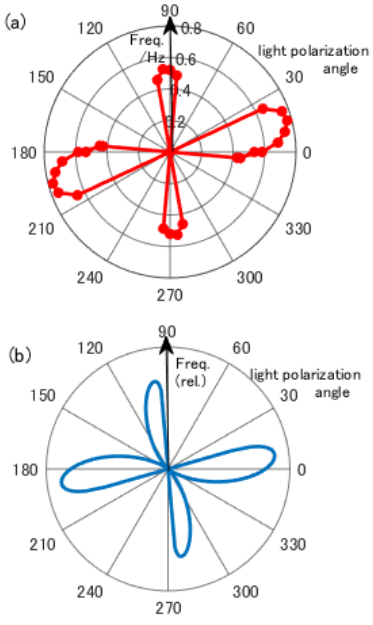

Fig. 1. Examples of the light polarization angle dependency on the frequency of the light-driven crystalline self-oscillation: (a) an experimental result and (b) a calculated result of the mathematical model.

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Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC E1123(1123, Bldg. 11 [2F])

[E1123-4pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Shinya Kimura, Yoshitaka Tsuchido

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1123-4pm-01]
Spatiotemporally-controlled photochromic reactions using supramolecular gel

○Yuki Nagai[1], Sota Fujisaki[1], Yoshinori Okayasu[1], Yoichi Kobayashi[1,2] (1. Ritsumeikan Univ., 2. PRESTO, JST)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1123-4pm-02]
Effect of atropisomer on the physical properties of alkylated diphenylanthracene liquids

Xiao Zheng[1,2], Kazuhiko Nagura[1], Yoshitaka Matsushita[1], ○Takashi Takashi[1,2] (1. National Institute for Materials Science, 2. Hokkaido University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1123-4pm-03]
Chirality-controlling supramolecular assemblies of acidic and basic pillar[5]arenes

○Dehui Tuo[1,2], Shixin Fa[3], Seigo Tanaka [2], Kenichi Kato[2], Tomoki Ogoshi[2,1] (1. WPI-NanoLSI, Kanazawa Univ., 2. Grad.Sch.Eng., Kyoto Univ., 3. Northwestern Polytechnical Univ.)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1123-4pm-04]
Construction of Homochiral Hierarchical Molecular Self-Assemblies Based on Self-Sorting of a Single Molecule with a C_{3h} Symmetric Core at the Liquid/Solid Interfaces.

○Matsuhiro Maeda[1], Steven De Feyter[2], Kazukuni Tahara[3] (1. Graduate School of Science and Technology, Meiji University, 2. Department of Chemistry, KU Leuven, 3. School of Science and Technology, Meiji University)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1123-4pm-05]
Analysis of 1:1 Host-Guest Systems with Temperature-Dependent Left- and Right-Twisted Conformational Changes

○Nozomu Suzuki[1], Daisuke Taura[2], Yusuke Furuta[2] (1. Kobe Univ., 2. Meijo Univ.)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[E1123-4pm-06]

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Vortex flow induced chiroptical response of self-assembled supramolecular objects of isoxazole-equipped platinum(II) complex

○Masaya YOSHIDA[1,2], Takehiro HIRAO[1], Takeharu HAINO[1,2] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM², Hiroshima University)

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超分子ゲルにより時空間的に制御されたフォトクロミック反応

（立命館大生命科学[1]・JST さきがけ[2]）○永井 邑樹[1]・藤崎 壮太[1]・岡安 祥徳[1]・小林 洋一[1,2]
Spatiotemporally-controlled photochromic reactions using supramolecular gel ([1]*College of Life Sciences, Ritsumeikan University*, [2]*PRESTO JST*) ○Yuki Nagai,[1] Sota Fujisaki,[1] Yoshinori Okayasu,[1] Yoichi Kobayashi[1,2]

Controlling the time evolution of photochemical reactions leads to the development of temporally-programmed multiple photofunctions. In this study, we developed photochromic reactions showing unique time evolutions based on the regulation of oxygen (O_2) supply from the air by supramolecular gel. In photoirradiation to an air-saturated gel of anthraquinone (AQ), photoreduction of its colorless original form to yellow reduced form showed an induction period until coloration because the dissolved O_2 was consumed by quenching the photoreduction. While the reduced form was retained over an hour in the gel, the decoloration was completed instantly upon the solation by heating. This is because the sol state allows quick O_2 supply from the air in contrast to the gel state. Based on the unique photochromic dynamics, spatiotemporal photopatterning (Fig. 1) and multicolor photochromic reactions were achieved.
Keywords : Anthraquinone; Photopatterning; Triplet Excited State; Radical Anion; Nonlinear Response

光化学反応の時間発展の高度制御は、複数の機能が時間的にプログラムされた光機能材料の開発に繋がる。本研究では、超分子ゲルを用いて気相からの酸素供給を制御することにより特異な時間発展を示すフォトクロミック反応を開発した。

還元剤存在下でアントラキノン (AQ) に紫外光照射を照射すると、無色の酸化体から黄色の還元体へと光還元される。この光還元を空気飽和ゲル中において行うと、溶存酸素が光還元を阻害して次第に消費されていくため、光照射開始から着色までに誘導期間を示した。また、還元体由来の着色はゲルが空気からの酸素供給を抑制するために 1 時間以上も安定に存在した一方、加熱によってゾル化させると還元体の空気酸化により直ちに消色することができた。更に着色までの誘導期間を応用し、時空間的フォトパターニング (Fig. 1) やマルチカラーフォトクロミック反応を実現した。

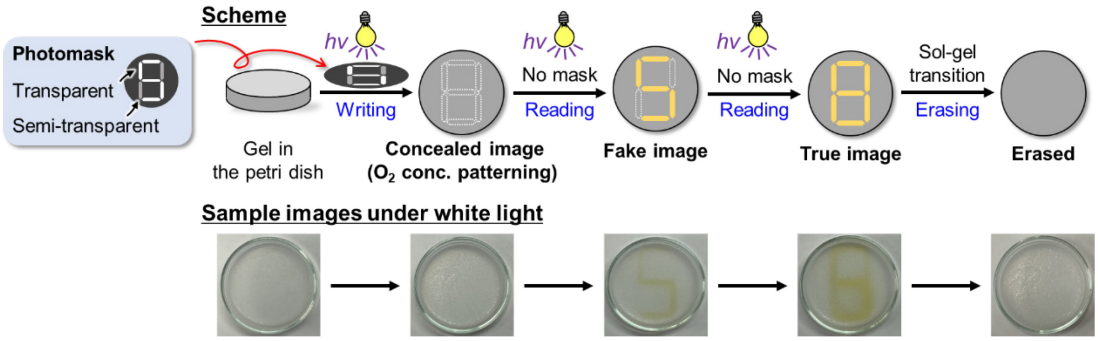

Fig. 1 (Top) The experimental scheme and (Bottom) the sample images in the spatiotemporal photopatterning.

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アルキル化ジフェニルアントラセン液体の物性に及ぼすアトロプ異性体の効果

（物質・材料研究機構 [1]・北大院先端生命 [2]）Zheng Xiao[1,2]・名倉 和彦 [1]・松下 能孝 [1]・○中西 尚志 [1,2]

Effect of atropisomer on the physical properties of alkylated diphenylanthracene liquids ([1]*National Institute for Materials Science*, [2]*Graduate School of Life Science, Hokkaido University*) Xiao Zheng,[1,2] Kazuhiko Nagura,[1] Yoshitaka Matsushita,[1] ○Takashi Nakanishi,[1,2]

By appropriate molecular design, π-conjugated molecules modified and protected with branched alkyl chains can be obtained as low-viscosity, practically stable, room-temperature liquids that do not solidify or become supercooled liquids[1-3]. For example, structural isomers with different substitution positions for the branched alkyl chain may have different viscosity of the alkyl-π molecular liquid and may even exhibit supercooling liquid properties[2,3]. In this study, we succeeded in separating and purifying *syn*- and *anti*-atropisomers of an alkylated diphenylanthracene liquid, which was unprecedented in π molecular liquids. We also investigated the structure-property relationships of each atropisomer and the effects of isomer mixtures on liquid properties by means of rheology, DSC, optical spectroscopies, and so forth.
Keywords : Functional Molecular Liquid; Atropisomer; Viscosity; Supercooled Liquid; Fragility

分岐アルキル鎖で修飾・保護されたπ共役分子は、適切な分子設計により、固化せず且つ過冷却液体とならない低粘性の常温液体として得ることができる[1-3]。例えば、分岐アルキル鎖の導入置換位置の違う構造異性体において、アルキルーπ分子液体の粘度が異なる、更には過冷却性が生じることがある[2,3]。本研究では、アルキル化ジフェニルアントラセン液体を基材に、アルキルーπ分子液体においてこれまで前例のなかったアトロプ異性体（*syn* 体、*anti* 体）を分離精製することに成功した。また、各アトロプ異性体の構造ー物性相関、さらには異性体混合物の液体物性に与える影響に関して、レオロジー、DSC、分光測定等を用いて検討したので報告する。

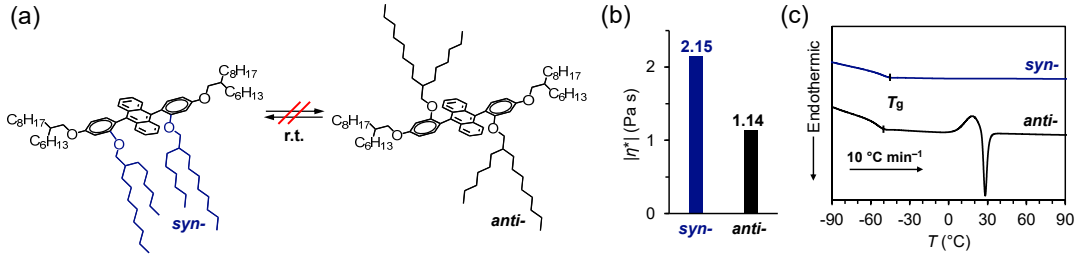

Fig. 1. (a) Chemical structure of *syn*- and *anti*-2,4-C_6C_{10}-diphenylanthracene; (b) complex viscosities ($|\eta^*|$) at 40 °C; (c) DSC thermograms under a heating scan of 10 °C min^{-1}.

1) F. Lu, T. Nakanishi et al., *Chem. Sci.* **2018**, *9*, 6774. 2) X. Zheng, K. Nagura, T. Takaya, K. Hashi, T. Nakanishi, *Chem. Eur. J.* **2023**, *29*, e202203775. 3) F. Lu, A. Shinohara, I. Kawamura, A. Saeki, T. Takaya, K. Iwata, T. Nakanishi, *Helv. Chim. Acta* **2023**, *106*, e202300050.

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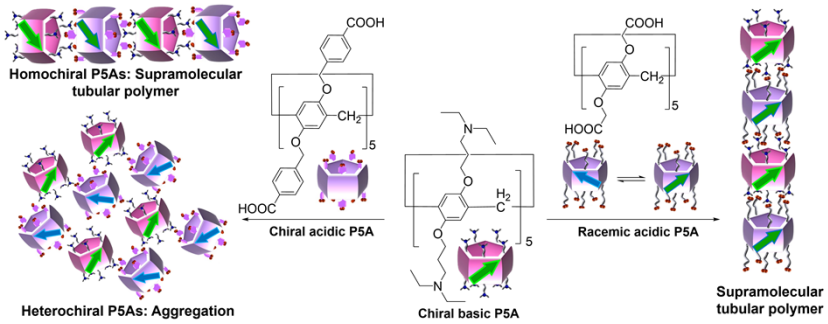
Chirality-controlling Supramolecular Assemblies of Acidic and Basic Pillar[5]arenes

([1]*WPI-NanoLSI, Kanazawa University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*School of Chemistry and Chemical Engineering, Northwestern Polytechnical University*)
○ Dehui Tuo,[1,2] Shixin Fa,[3] Seigo Tanaka,[2] Kenichi Kato,[2] Tomoki Ogoshi[1,2]
Keywords: Pillar[*n*]arenes; Chirality; Supramolecular assembly

Chirality-controlled supramolecular assembly in multicomponent systems is important for the formation of complex self-assembled structures such as living organisms, and has the potential for applications in new functional materials. Pillar[*n*]arenes (PA) exhibit unique planar chirality, and interconversion of the chiral isomers (*pR* and *pS*) by units flipping make PAs intriguing platform for exploring chirality inversion, induction and transformation.[1] We previously achieved real-time monitoring of trimeric homochiral nanotube formation through multiple ion-pairing interactions between optically resolved peramino-pillar[5]arene (P5A) and a racemic rim-differentiated P5A pentaacid.[2] To this context, we envision such kind of acidic and basic P5As would be fascinating for investigating chirality-controlled supramolecular polymerization.

When chiral basic P5A co-assembled with chiral acidic P5A, chirality-controlled self-assembly morphologies were achieved depending on chirality of P5As, in which supramolecular gels are formed in P5As with homochirality, while P5As with heterochirality form turbid aggregations. The phenomena were probably because the acid-base interactions between the P5As are well matched in the homo combination where molecular chirality is aligned. By contrast, the hetero form takes random interaction forms due to mismatches of the interactions, resulting in the difference in the supramolecular formation. When chiral basic P5A co-assembled with racemic acidic P5A, chirality transfer by matching ten ion pairs between basic and acidic P5As occurs and chiral supramolecular tubular polymers are generated.



1) K. Kato, S. Fa, T. Ogoshi, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202308316. 2) S. Fa, T.-H. Shi, S. Akama, K. Adachi, K. Wada, S. Tanaka, N. Oyama, K. Kato, S. Ohtani, Y. Nagata, S. Akine, T. Ogoshi, *Nat. Commun.*, **2022**, *13*, 7378.

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Construction of Homochiral Hierarchical Molecular Self-Assemblies Based on Self-Sorting of a Single Molecule with a C_{3h} Symmetric Core at the Liquid/Solid Interfaces

([1]*Graduate School of Science and Technology, Meiji University*, [2]*Department of Chemistry, KU Leuven*, [3]*School of Science and Technology, Meiji University*) ○Matsuhiro Maeda,[1] Steven De Feyter,[2] Kazukuni Tahara[3]

Keywords: Self-Assembled Molecular Networks; Scanning Tunneling Microscopy; Self-Sorting; Liquid/Solid Interface; Chirality Control

Self-sorting of multiple molecular components through orthogonal intermolecular recognition is a promising strategy for the construction of a hierarchical self-assembled molecular network (SAMN) on a surface. We recently reported that the dynamic self-sorting of the conformational isomers of a dehydrobenzo[12]annulene (DBA) derivative **DBA-OC14-OH** with achiral alkoxy chains and hydroxy groups in an alternating manner produces hierarchical triangular clusters of different sizes at the liquid/graphite interface (Fig. 1(a)).[1] In the self-sorting process, solvent molecules 1,2,4-trichlorobenzene and 1-hexanoic acid (HA) play significant roles. Namely, polarity modulation by changing the mixing ratio of the solvents and the co-adsorption of the HA molecules are keys for the size control of the triangular clusters.

We herein present the chirality control of these hierarchical triangular clusters using 1) a chiral molecular building block **cDBA-OC14(*S*)-OH** which has alternating chiral alkoxy chains and hydroxy groups (Fig. 1(c)),[2] and 2) a prochiral **DBA-OC14-OH** derivative in a chiral solvent 2-methyl-1-hexanoic acid (Fig. 1(b)). In both cases, the chirality information can be transferred from the single-molecule level to the hierarchical SAMN level via dynamic self-sorting (Fig. 1(c)).

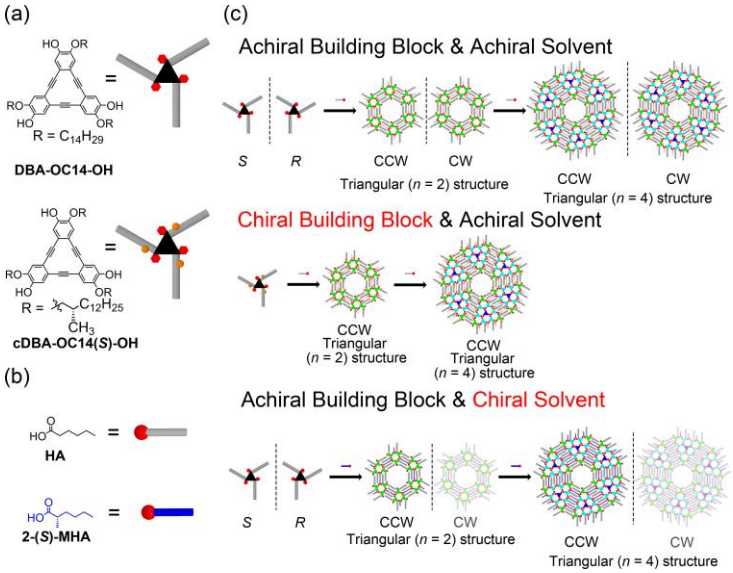

Figure 1. Chemical structures and schematic models of (a) DBA and (b) chiral solvents. (c) Formation of hierarchical triangular clusters.

1) Maeda, M.; Nakayama, R.; De Feyter, S.; Tobe, Y.; Tahara, K. *Chem. Sci*. **2020**, *11*, 9254. 2) Maeda, M.; Sato, K.; De Feyter, S.; Tobe, Y.; Tahara, K. *Nanoscale* **2023**, *15*, 19569.

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温度に依存して左右にねじれた立体配座が変換する 1:1 ホスト-ゲストシステムの解析

(神大院工[1]・名城大院理工[2]) ○鈴木 望[1]・田浦 大輔[2]・古田 裕亮[2]
Analysis of 1:1 Host-Guest Systems with Temperature-Dependent Left- and Right-Twisted Conformational Changes ([1]*Graduate School of Engineering, Kobe University*, [2]*Graduate School of Science and Technology, Meijo University*) ○Nozomu Suzuki,[1] Daisuke Taura,[2] Yusuke Furuta[2]

In host-guest systems, the design of the host molecule with a twisted structure plays an essential role in the application of chiral materials (Figure 1).[1)] To evaluate and improve the functionality of the host molecule, the circular dichroism (CD) or ^{1}H-NMR spectroscopy is often used. However, the ^{1}H-NMR is not applicable when the interconversion between the diastereomeric left- and right-twisted conformations is faster than the timescale of the ^{1}H-NMR. In this work, we have developed a novel method that enables to analyze the 1:1 host-guest systems under the equilibrium between the left- and right-twisted conformations using the temperature-dependent CD spectra.

Keywords : Host-Guest; Chiral; Molecular Recognition

左右にねじれた立体配座を有するホスト分子とゲスト分子からなる分子認識システムは、キラル材料への応用が可能である[1)]。左右にねじれた立体配座の定量化には、^{1}H-NMR を用いるが、ジアステレオメリックな左右の構造間の変化が ^{1}H-NMR のタイムスケールより速い場合には、^{1}H-NMR を利用することができない。本発表では、温度可変円二色性スペクトルを利用して、このような 1:1 ホスト-ゲストシステムを解析する新たな手法を開発したので、報告する。

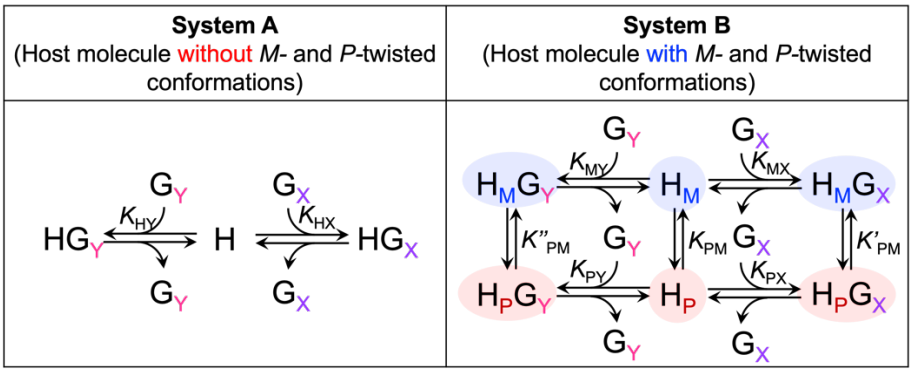

Figure 1. Host-guest systems. Guest molecules (G_X and G_Y) can be a pair of enantiomers or chiral and achiral molecules. System A: host molecule (H) *without* left- and right- (*M*- and *P*-) twisted conformations. System B: H *with* *M*- and *P*-twisted conformations (H_M and H_P).

1) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116*, 13752.

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Vortex flow induced chiroptical response of self-assembled supramolecular objects of isoxazole-equipped platinum(II) complex

([1] *Graduate School of Advanced Science and Engineering, Hiroshima University*, [2] *International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM²), Hiroshima University*) ○Masaya YOSHIDA,[1,2] Takehiro HIRAO,[1] Takeharu HAINO[1,2]

Keywords: Self-assembly; Circular dichroism; Nanostructure; Vortex flow; Orientation

Supramolecular assemblies exhibit photochemical properties unique to their assembled states. We reported that neutral platinum(II) complexes possessing isoxazole moieties were assembled to form one-dimensional fibers and micellar structures via π-π stacking, dipole-dipole, and metal-metal interactions.[1, 2] I will discuss the CD responses of the stacked assembly of platinum complex **1** (Figure 1a).

Complex **1** was self-assembled to form nanometric sheet-like structures in toluene, which did not show any CD response (Figure 1b dotted line). When the toluene solution of **1** was stirred, CD signals emerged. The intensity of the CD signals responded to the rotation frequencies of vortex flows. The rotation directions of vortices determined the signs of CD signals (Figure 1b, c). In contrast, complex **2** formed random aggregates in toluene, which did not show any CD response in vortex flows. Accordingly, the CD signals were most likely driven by the orientation of the sheet-like supramolecular objects in the solution.

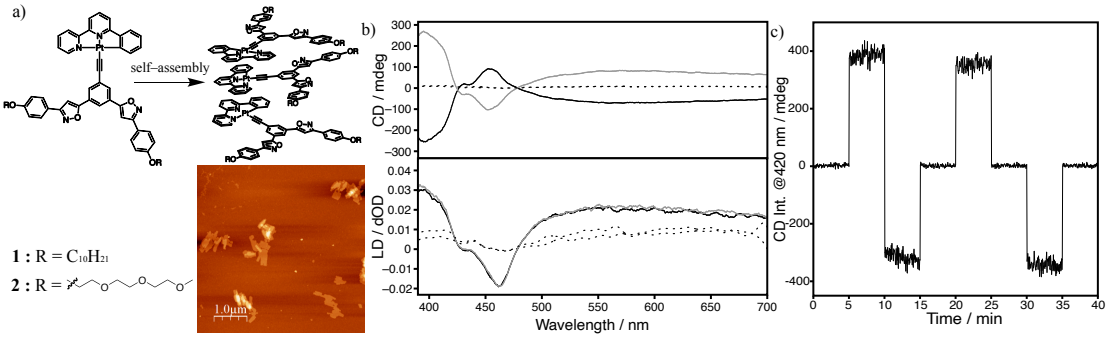

Figure 1. a) Structures of neutral Pt(II) complexes and AFM image of complex **1** on mica (5 μm × 5 μm). b) CD and LD spectra of complex **1** (0.3 mmol L^{-1}) (solid black line: clockwise 1000 rpm), (solid gray line: counterclockwise 1000 rpm), and (dotted black line: 0 rpm) at 25 °C in toluene. (C) Change in CD intensity at 420 nm in response to a stepwise variation of the stirring conditions of complex **1** (0.3 mmol L^{-1}) at 25 °C in toluene.

1) T. Ikeda, M. Takayama, J. Kumar, T. Kawai and T. Haino, *Dalton Trans.*, **2015**, *44*, 13156-13162.
2) M. Yoshida, T. Hirao, and T. Haino, *Org. Biomol. Chem.*, **2021**, *19*, 5303-5311.

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Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC E1131(1131, Bldg. 11 [3F])

[E1131-4pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Shotaro Hayashi, Yumi Yakiyama

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1131-4pm-01]
Triptycene Frameworks for Orientational Control over Electroactive Subunits in STM Break-Junction

○Colin John Martin[1], Tomoya Fukui[1], Ryosuke Takehara[1], Shintaro Fujii[2], Takanori Fukushima[1] (1. CLS, Tokyo Tech., 2. School of Science, Tokyo Tech.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1131-4pm-02]
Alkyl chain length-dependent polymorphism and phase transition behavior of N-shaped organic semiconducting molecules

○Masato Mitani[1], Craig P. Yu[2], Chizuru Sawabe[2], Chikahiko Mitsui[2], Takuya Seki[3], Yudai Shinozaki[3], Go Watanabe[3], Daisuke Hashizume[4], Shohei Kumagai[1], Jun Takeya[2], Toshihiro Okamoto[1] (1. Tokyo Institute of Technology, 2. The Univ. of Tokyo, 3. Kitasato University, 4. RIKEN)

1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
Break

English
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[E1131-4pm-03]
Solid-state magnetic properties of halogen or ethynyl substituted aromatic nitroxide with cardo structure

○Masaomi Takii[1], Youhei Miura[1], Naoki Yoshioka[1] (1. Keio University)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1131-4pm-04]
Low Dimensional Single Crystal Lasers Composed of Fumaronitrile-based π-Conjugated Molecules Exhibiting Aggregation Induced Enhanced Emission

○Takumi Matsuo[1], Shotaro Hayashi[1] (1. Kochi University of Technology)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1131-4pm-05]
Quantification of Noncovalent Arene–Fullerene Interactions Using a Molecular Torsion Balance

○Michio Yamada[1], Koki Sahara[1], Yukiyo Kurihara[1], Masaaki Koizumi[1], Kasumi Tsuji[1], Haruna Narita[1], Yutaka Maeda[1], Mitsuaki Suzuki[2] (1. Tokyo Gakugei University, 2. Josai University)

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Triptycene Frameworks for Orientational Control over Electroactive Subunits in STM Break-Junction

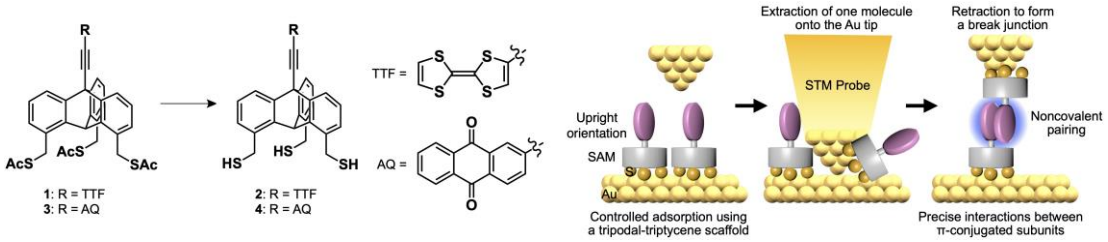
([1]*Laboratory for Chemistry and Life Science, Tokyo Tech.*, [2]*School of Science, Tokyo Tech.*)
○Colin John Martin[1], Tomoya Fukui[1], Ryosuke Takehara[1], Shintaro Fujii[2], Takanori Fukushima[1]

Keywords: STM break junction, Self-assembled monolayers, Supramolecular scaffold, Noncovalent interactions, Triptycene

In the field of molecular electronics, quantifying the properties of discrete electroactive moieties remains an important goal, with numerous developments reported in recent years. Here, our approach which allows for accurate positioning of electroactive subunits with an upright configuration on substrate surfaces will be presented.[1] We have incorporated electron-donating tetrathiafulvalene or electron-accepting anthraquinone into existing triptycene-based supramolecular scaffolds[2] containing three thiol or thioacetate surface binding points. Self-assembled monolayers of these molecules have been prepared on Au(111) and characterized by XPS and STM, with the electronic properties particular to their attached subunits retained in the monolayers.

Using previously reported STM break junction techniques[3] we have conducted studies on these SAM materials as they undergo noncovalent donor-donor, and acceptor-acceptor interactions to explore their conductive behavior at the single molecular level. The triptycene scaffolds in these systems facilitate non-covalent face-to-face interactions between homodimers adsorbed on the two electrodes. Two electrical conduction regimes are observed: one arising from single molecules sandwiched between the electrodes, and the second from intermolecularly interacting homodimers bridging between electrodes.

This presentation demonstrates the validity of the approach using tripodal triptycene scaffolds to precisely direct electroactive subunits to undergo intermolecular pairing. We believe that this work will open a new avenue for evaluating heterodimers and lead to new pathways to evaluate both hetero- and homodimer interactions at the single molecular level.



1) C. J. Martin, T. Fukui, R. Takehara, S. Fujii, T. Fukushima, *Precis. Chem.* **2023**, *1*, 6, 388–394.
2) F. Ishiwari, Y. Shoji, T. Fukushima, *Chem. Sci.* **2018**, *9*, 8, 2028–2041.
3) S. Fujii, T. Fukushima, M. Kiguchi *et al. Jpn. J. Appl. Phys.* **2019**, *58*, 035003.

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アルキル鎖長に依存した高移動度 N 字型有機半導体分子の結晶多形・相転移挙動の実測とシミュレーション

（東京工業大学[1]・東京大学[2]・北里大学[3]・理化学研究所[4]）○三谷 真人[1]・Craig P. Yu[2]・沢辺 千鶴[2]・三津井 親彦[2]・關 拓和[3]・篠崎 雄大[3]・渡辺 豪[3]・橋爪 大輔[4]・熊谷 翔平[1]・竹谷 純一[2]・岡本 敏宏[1]

Alkyl chain length-dependent polymorphism and phase transition behavior of N-shaped organic semiconducting molecules ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Graduate School of Frontier Science, The University of Tokyo,* [3]*School of Frontier Engineering, Kitasato University,* [4]*RIKEN Center for Emergent Matter Science (CEMS)*) ○Masato Mitani,[1] Craig P. Yu,[2] Chizuru Sawabe,[2] Chikahiko Mitsui,[2] Takuya Seki,[3] Yudai Shinozaki,[3] Go Watanabe,[3] Shohei Kumagai,[1] Jun Takeya,[2] Toshihiro Okamoto[1]

Control and prediction over aggregated structures of π-conjugated molecules are crucially important to effectively develop the high performance organic functional materials. During the study on the aggregated structures of alkyl-substituted N-shaped organic semiconductor (**C_n–DNBDT–NW**, Figure 1a) with high charge transporting capability, it was found that they exhibit polymorphism and unique phase transition behavior (Figure 1b). In the presentation, experimental details of crystal structure analyses and thermal analyses will be discussed, which will also compared with the results of MD simulations.

Keywords : Organic semiconducting molecules; Polymorphism; MD simulations

π 共役系からなる材料の機能は集合体構造に大きく依存しており、高キャリア移動度などの高機能化に向けては集合体構造の制御・予測が極めて重要となる。我々の研究グループで開発された N 字型 π 共役系材料（**DNBDT–NW**, Figure 1a）は、導入するアルキル鎖長に応じて二つのヘリンボーン構造（HB1・HB3）を含む結晶多形を発現するほか、劇的な集合体構造変化を伴う相転移挙動を示し（Figure 1b）、薄膜形成過程で誘起される集合体構造（HB3）では世界最高レベルの高キャリア移動度を示すことが実験的に確かめられている[1,2]。本発表では、本誘導体群の集合体構造の実測と MD シミュレーションによる予測結果について議論する。

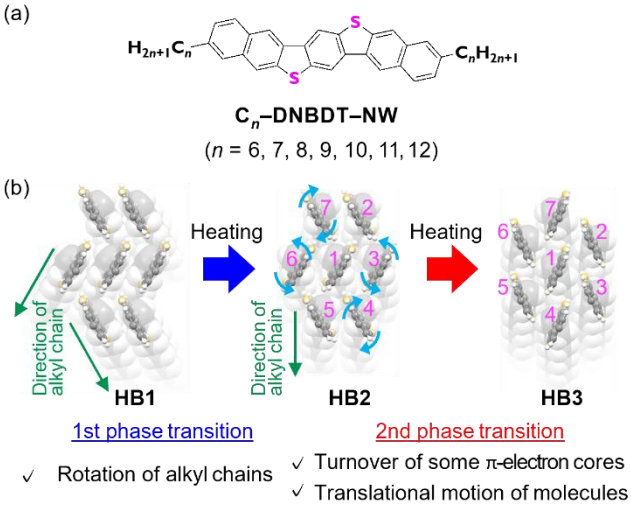

Figure 1. (a) Molecular structure of **C_n–DNBDT–NW**. (b) Phase transition behavior of **C_n–DNBDT–NW**.

1) T. Okamoto *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 9083. 2) C. Mitsui, T. Okamoto, J. Takeya *et al.*, *Adv. Mater.* **2014**, *26*, 4546.

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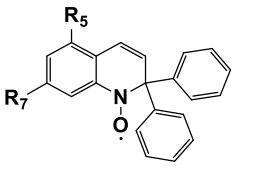
Solid-State Magnetic Properties of Halogen or Ethynyl Substituted Aromatic Nitroxide with Cardo Structure

(*Faculty of Science and Technology, Keio University*) ○Masaomi Takii, Youhei Miura, Naoki Yoshioka

Keywords: *Radical, Molecule-based Magnetism, Nitroxide, π-Conjugated System, Organic Crystal*

Aliphatic nitroxides such as TEMPO show high chemical stability, although it is difficult to be used as a spin center for molecule-based magnetic materials because of localization of SOMO and spin density around NO moiety. On the other hand, aromatic nitroxide derivatives where π-conjugated systems locate adjacent to NO moiety, often exhibit non-magnetic state through a disproportionation reaction or antiferromagnetic interaction due to close contact between NO moieties. In the case of 2,2-diphenyl-1,2-dihydroquinoline *N*-oxyl (DPQN, **1**), the steric effect of cardo structure consist of two phenyl rings at the 2-position has been found to suppress both the disproportionation reaction and the antiferromagnetic NO contact.[1] At the 6-position of the quinoline ring where SOMO distribute, the introduced substituent may undergo further reactions. However, at the 5-position the node of the SOMO, the introduced substituent tends not to undergo further reactions.[2]

In this study, DPQN derivatives substituted by halogen or ethynyl at 5- and 7-position **2**-**7** (**Scheme 1**) were synthesized to investigate the chemical modification effect on solid-state magnetic properties. According to DFT calculations, no SOMOs were observed on 5-substituents, however, 7- substituents had small SOMO distributions. A single crystal of **2** was obtained by recrystallization from ethanol/dichloromethane. Single crystal X-ray analysis reveals that **2** forms a halogen bonded chain with $d_{O\cdots I}$ = 3.154(5) Å (**Fig. 1**). SQUID measurement of **2** suggests weak antiferromagnetic interaction (**Fig. 2**).



1 : R_5 = H, R_7 = H
2 : R_5 = I, R_7 = H
3 : R_5 = −C≡C−TMS, R_7 = H
4 : R_5 = −C≡C−H, R_7 = H
5 : R_5 = H, R_7 = I
6 : R_5 = H, R_7 = −C≡C−TMS
7 : R_5 = H, R_7 = −C≡C−H

Scheme 1

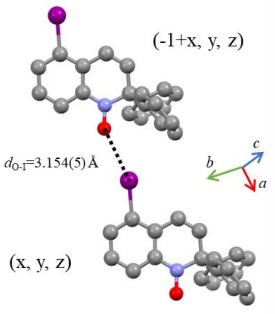


Fig. 1 Through I-O close contact of **2.**

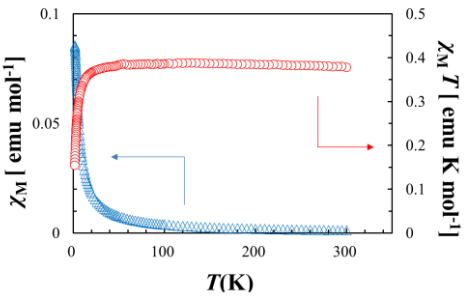


Fig. 2 Temperature dependence of $\chi_m T$ (○) and χ_m (△) for **2.**

1) M. Yao, N. Yoshioka, *et al.*, *Cryst. Growth Des.*, **2005**, *5*, 413-417.
2) M. Takii, Y. Miura, N. Yoshioka, The 103rd Annual Spring Meeting of the Chemical Society of Japan, K605-3pm-12 (March 2023, Tokyo Univ. Sci, Noda).

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凝集誘起増強発光性を示すフマロニトリル系分子から成る低次元単結晶レーザー

（高知工科大 [1]）○松尾 匠 [1]・林 正太郎 [1]
Low Dimensional Single Crystal Lasers Composed of Fumaronitrile-based π-Conjugated Molecules Exhibiting Aggregation Induced Enhanced Emission ([1]*School of Engineering Science, Kochi University of Technology*) ○Takumi Matsuo,[1] Shotaro Hayashi[1]

Fumaronitrile (FN) based π-conjugated molecules are known as aggregation induced enhanced emission (AIEE) luminogen. Although the photoluminescence quantum efficiency (Φ_{PL}) of FN solids is not so high, single crystals of bis(biphenyl)fumaronitrile (BPFN) showed higher Φ_{PL} of 0.46. Modifying the growth technique of self-assembly, BPFN was intentionally grown in various low dimensional micro-structures; crystalline 2D, 1D, and amorphous 0D. The revealed crystal structure suggested ideal conformation and molecular packing to achieve lasing; highly luminescent *E*-isomer conformation, uniaxial molecular orientations. As a result, we first achieved lasing in low dimensional structures of FN-based AIEE luminogen.
Keywords : Fumaronitrile; Aggregation Induced Enhanced Emission; Organic Solid State Lasers; Low Dimensional Structures

フマロニトリル(FN)系π共役分子は凝集誘起増強発光性(AIEE)を示す．しかし分子内電荷移動(ICT)によって固体状態の発光量子収率(Φ_{PL})はさほど高くなく，結晶材料としての光物性はほとんど知られていない.[1,2] 我々は FN 系 π 共役分子のうち，bis(biphenyl)fumaronitrile(BPFN)が FN 系分子の中で高い Φ_{PL} 値を示すことを見出した(Φ_{PL}=0.46). BPFN は溶液中での再結晶法では二次元単結晶が得られ(図 1a)，一方で BPFN 溶液を KBr 単結晶にドロップキャストすると基板上へのエピタキシャル成長に基づき一次元結晶が形成された(図 1b). ガラス基板上への溶液のドロップキャストを行うとサイズが均一なアモルファスマイクロドットが形成された(図 1c). これら低次元構造体のうち二次元薄板状結晶と一次元ニードル構造は光励起レーザー発振が観測された(図 1d). 単結晶 X 線構造解析から BPFN は結晶内で FN 部位が発光性の高い *E* 体の配座をとり，分子が結晶内で一軸配向していた．以上から BPFN 結晶は高い誘導放射効率が期待でき，故にレーザー媒質として優れることを示した．

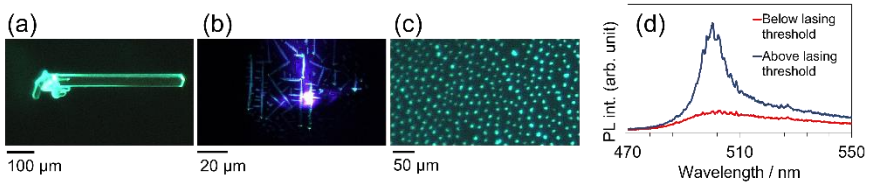

図 1 (a)-(c) 二次元薄板状結晶，一次元ニードル結晶，マイクロドットの蛍光像. (d)二次元薄板状結晶からのレーザー発振閾値前後での蛍光スペクトル.

1) In-situ photoisomerization for aggregation-induced emission of dibiphenyl fumaronitrile. H. Jeonga, K. M. Kima, S. Cho, J. K. Lee, *J. Photochem. Photobiol.* **2015**, 311, 199. 2) Fumaronitrile-Based Fluorogen: Red to Near-Infrared Fluorescence, Aggregation-Induced Emission, Solvatochromism, and Twisted Intramolecular Charge Transfer. X. Y. Shen, W. Z. Yuan, Y. Liu, Q. Zhao, P. Lu, Y. Ma, I. D. Williams, A. Qin, J. Z. Sun, B. Z. Tang, *J. Phys. Chem. C* **2012**, 116, 10541.

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ねじり天秤分子モデルを用いた芳香環–フラーレン間の非共有結合性相互作用の定量評価

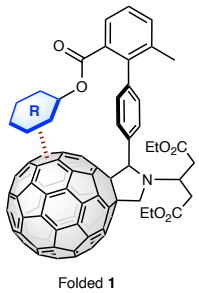
（東学芸大教[1]・城西大理[2]）○山田 道夫[1]・佐原 弘起[1]・栗原 幸代[1]・小泉 政彰[1]・辻 香澄[1]・成田 陽奈[1]・前田 優[1]・鈴木 光明[2]
Quantification of Noncovalent Arene–Fullerene Interactions Using a Molecular Torsion Balance ([1]*Department of Chemistry, Tokyo Gakugei University*, [2]*Department of Chemistsry, Josai University*) ○Michio Yamada,[1] Koki Sahara,[1] Yukiyo Kurihara,[1] Masaaki Koizumi,[1] Kasumi Tsuji,[1] Haruna Narita,[1] Yutaka Maeda,[1] Mitsuaki Suzuki[2]

The unique structure of fullerenes is of great interest in numerous fields, including materials chemistry and medicinal chemistry, owing to their peculiar hydrophobic structure and excellent electron-accepting properties. The intermolecular interactions on fullerene surfaces are intricately linked with the macroscopic properties of fullerene-based materials; hence, a quantitative understanding of these interactions is required. In this study, we designed and synthesized fullerene-based torsion balances and quantitatively evaluated the non-covalent interactions between the fullerene surface and substituted arenes by analyzing their conformational isomerism based on restricted rotation around the biphenyl C–C bond. We disclosed that the experimentally observed arene–fullerene interaction can be explained mainly by the contribution of the dispersion and electrostatic terms. Although the dispersion term is effective throughout the interaction, especially for electron-rich arenes, the electrostatic term also has a significant impact.[1–4)]

Keywords : π–π interactions; anion–π interactions; dispersion interaction; electrostatic interaction; Hammett analysis

フラーレンは，優れた電子受容能や疎水性構造を有することから，材料科学や医薬品化学などの分野で興味が持たれている。そのマクロな物性には分子間相互作用が大きく関与することから，フラーレンの応用を目指す上で，フラーレン表面に働く相互作用に対する定量的な理解が求められる。しかし，このような分子間相互作用は弱いため，その計測は容易ではない。

本研究では、フラーレンを用いたねじり天秤型のモデル分子 **1** を設計・合成し，そのビフェニル構造部の C–C 結合における束縛回転に起因する配座異性を解析することによって，種々の置換アレーン(**R**)とフラーレン表面との間に働く分子間相互作用の定量評価を行った。その結果，アレーン–フラーレン間に働く相互作用は主として分散相互作用の項と静電相互作用の項によることを明らかにした。また，全体を通じて分散相互作用の項が支配的であるものの，特に電子豊富なアレーンの場合には静電相互作用の項も充分に大きいことを見出した [1–4)]。



Folded **1**

1) M. Yamada, et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 16133–16140. 2) M. Yamada et al., *Angew. Chem. Int. Ed.* **2022**, *61*, e202212279. 3) M. Yamada, et al., *Chem. Eur. J.* **2023**, *29*, e202300877. 4) M. Yamada, *ChemPlusChem* **2023**, *88,* e202300062.

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

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC
E1132(1132, Bldg. 11 [3F])

[E1132-4am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Kei Ohkubo, Koichi Mitsudo

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1132-4am-01]
Boryl radical-mediated decyanation of malononitriles using photoredox catalyst

○Yuto Yoshida[1], Daniele Leonori[2], Naoki Yasukawa[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology, 2. RWTH Aachen University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1132-4am-02]
Study on radical reactions of a phosphatetraphene by muon spectroscopy

○Shigekazu Ito[1], Kohei Yasuda[1], Keisuke Ishihara[1], Kenji M. Kojima[2], Iain McKenzie[2] (1. Tokyo Institute of Technology, 2. TRIUMF)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1132-4am-03]
Study on Electronic Configuration of Carbenes Embedded in Cycloparaphenylene Unit

○Ku Kajikawa[1], Ryo Murata[1], Eiichi Kayahara[2], Shigeru Yamago[2], Manabu Abe[1] (1. Hiroshima University, 2. Kyoto University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1132-4am-04]
Synthesis of Highly Dispersed Hydroxylated Carbon Nanotubes by Chlorine Dioxide

○Yuki Itabashi[1], Ai Sunami[1], Kei Ohkubo[1,2] (1. Osaka Univ., OTRI, 2. Osaka Univ., IACS)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1132-4am-05]
Development of New Radical Initiators Which Decompose by Red-Light Irradiation

○Rintaro Tanikawa[1], An Shinohara[1], Kenichi Takao[1], Akihiro Ogura[1] (1. Faculty of Science and Technology, Keio University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1132-4am-06]
Effects of Solvent and Acid Catalysis on the Photosolvolysis of 3-Methoxy-2-benzyloxy-Naphthalene

○Satoshi Usui[1], Shunsuke Koyanagi[1], Chihiro Kinugawa[1] (1. Niigata University)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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Break

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1132-4am-07]
Arylcarboxylation of Alkenes with Formate Salts under Photoredox/HAT Catalysis

○Yamato Ueno[1], Wataru Kanna[1], Saeesh Rajendra Mangaonkar[2,3], Yu Harabuchi[2,3], Hiroki Hayashi[2,3], Tsuyoshi Mita[2,3], Satoshi Maeda[1,2,3] (1. Fac. of Sci., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. JST-ERATO)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1132-4am-08]
Synthesis of [3.3.1]Propellanes by Cyclopropanation of Furofurans and Thienothiophenes and Their Properties

○Toki Hirano[1], Koichi Mitsudo[1], Seiji Suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1132-4am-09]
Evaluation of decarboxylation of α-substituted diarylacetic acid derivatives generated by polymeric mechanochemical reactions

○Yuto Uchida[1], Takumi Yamamoto[1], Hajime Sugita[1], Akira Takahashi[1], Hideyuki Otsuka[1] (1. Dept. of Chem. Sci. and Eng., Tokyo Tech.)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1132-4am-10]
Effect of Polycyclic Aromatic Substituents on Positive Charge Delocalization and Antiaromaticity of Fluorenyl and Benzofluorenyl Cations

○Takao Okazaki[1], Taichi Kawakami[1], Reiji Kawai[1], Toshikazu Kitagawa[1] (1. Mie University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1132-4am-11]
Development of Eco-Friendly Synthesis of Cyclic Sulfide Using Thioamide Derivatives

○Urara Masamoto[1], Yusuke Yoshinaga[1], Daisuke Kaneno[1] (1. Kochi Univ.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1132-4am-12]
Photocatalytic Carboxylation of terminal alkynes using CO_2

○Shuhei Uno[1], Tatsushi Imahori[1] (1. Tokyo University of Science)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1132-4am-13]
Photoinduced Synthesis of α-Thiooximes by Three-Component Coupling Reaction

○Toshiki Tamura[1], Ken Yamazaki[2], Shuta Akimoto[2], Tomoya Miura[2] (1. School of Engineering, Okayama University, 2. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

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ホウ素ラジカルを用いたマロノニトリル類の光レドックス触媒的脱シアノ化反応

（名工大院工[1]・アーヘン工科大[2]）○吉田 悠人[1]・Daniele Leonori[2]・安川 直樹[1]・中村 修一[1]

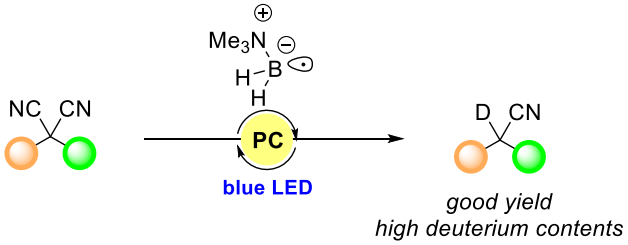
Boryl radical-mediated decyanation of malononitriles using photoredox catalyst

([1]*Graduate School of Engineering, Nagoya Institute of Technology*, [2]*RWTH Aachen University*)
○Yuto Yoshida[1], Daniele Leonori[2], Naoki Yasukawa[1], Shuichi Nakamura[1]

Cyano group is one of the most useful functional groups in various research fields such as medicinal and synthetic chemistry. Therefore, the development of a systematic synthetic method of highly functionalized cyano compounds is desired. These compounds are synthesized by α-functionalization of malononitriles and the subsequent elimination of cyano group, however, the use of strong single-electron reductants is required in the latter step. Although open shell radical-mediated decyanation reactions have been reported as an alternative approach, the use of explosive and toxic radical initiators under the harsh conditions is problematic from the viewpoint of safety and green chemistry. Herein we developed the amine-ligated boryl radical-mediated decyanative reaction of malononitriles using photoredox catalyst. In addition, deuterated products were obtained in high yield and deuterium content by the addition of deuterium oxide.

Keywords : Boryl Radical; Decyanative Reaction; Photoredox Catalyst; Deuteration

シアノ基は、創薬化学や合成化学など幅広い分野で重宝される官能基であり、高度に官能基化された含ニトリル化合物の系統的な合成法の開発は重要である。それらの合成法の一つとして、マロノニトリルα炭素上の官能基化に次ぐ、シアノ基の脱離反応が挙げられる。しかし、強固な炭素−炭素(シアノ)結合の開裂には、一般的に強力な一電子還元剤を用いる必要がある。この代替法として、開殻ラジカル種を用いる手法が報告されたが、高温で爆発性や毒性を示すラジカル開始剤を使用する必要があり、安全性や環境面で課題が残る[1)]。そこで我々は、光レドックス触媒を用いたホウ素ラジカル発生法[2)]を組み合わせることで、穏和な条件下でのマロノニトリル類の脱シアノ化が達成できると考えた。その結果、アミン−ホウ素ラジカルを用いた場合に、シアノ基の開裂反応が効率良く進行することを見出した。さらに、重水を添加することで、重水素原子が導入された生成物を高収率、高重水素化率で得ることに成功した。



1) T. Kawamoto, S. J. Geib, D. P. Curran, *J. Am. Chem. Soc*. **2015**, *137*, 8617.
2) N. Yasukawa, D. Leonori et al., *manuscript in preparation*.

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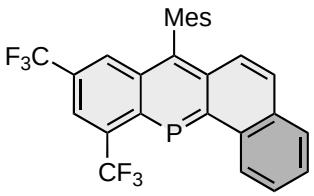
ミュオンスピン分光法によるホスファテトラフェンのラジカル反応解析

（東工大物質理工[1]・TRIUMF[2]）○伊藤 繁和[1]・安田 幸平[1]・石原 啓介[1]・小嶋 健児[2]・Iain McKenzie[2]

Study on Radical Reactions of a Phosphatetraphene by Muon Spin Spectroscopy ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*TRIUMF*) ○Shigekazu Ito,[1] Kohei Yasuda,[1] Keisuke Ishihara,[1] Kenji M. Kojima[2], Iain McKenzie[2]

In this study, we utilized muonium (Mu) composed of muon (μ^+) and electron (e^-) for investigating radical reactivity of a 12-phosphatetraphene as a π-extended 9-phosphaanthracene. We performed transverse-field muon spin rotation (TF-μSR) and muon level-crossing resonance (μLCR) measurements with a dilute THF solution of **1**. The TF-μSR spectrum showed paramagnetic signals indicating the addition of Mu to the sp^2-phosphorus atom. The μLCR spectrum of the isotropic solution sample showed the resonance of ^{31}P hyperfine coupling (hfc), confirming the regioselective muoniation. The structure of the muoniated phosphorus heterocycle of the higher energy was determined by using the DFT calculations. It was noteworthy that the 12-phosphatetraphene indicated considerably high reactivity toward muonium of a light isotope of hydrogen compared with most of the organic compounds that have been studied so far.

Keywords : Radicals; Muonium; Phosphorus Heterocycles; DFT Calculations



1

当研究室では最近、9-ホスファアントラセンのパイ拡張構造である 12-ホスファテトラフェン **1** を合成単離している[1]。**1** は 9-ホスファアントラセンと同様に素粒子ラジカル反応を示す[2]と期待されたことから、本研究では **1** のミュオンスピン回転・共鳴（μSR）分光法を用いてその可能性を検証した。まず、**1** の THF 溶液を用いて TF-μSR 測定を行ったところ、一種類のミュオニウム（Mu＝[μ^+e^-]）付加体の生成を示す常磁性シグナルが観測された。続いて、**1** の溶液試料を用いて μLCR 測定を実施し、^{31}P 核の hfc 定数を示す共鳴シグナルを観測した。μSR 測定実験で得られた hfc パラメーターをもとに DFT 計算を行ったところ、**1** の sp^2 リン原子に Mu が位置選択的に付加して対応するラジカルが生成していることがわかった。この Mu 付加体の構造はミュオンの同位体効果を反映し、若干高エネルギー状態となっていることも併せて確認した。ところで、今回の測定で用いた **1** の溶液試料はかなり低濃度であったものの、**1** の Mu 付加体が明瞭に観測された。すなわち、**1** の Mu によるラジカル反応は極めて高い効率で進行していたと考えられる。

1) K. Yasuda, S. Ito, *ChemPlusChem* **2023**, *88*, e202300277.
2) K. Koshino, K. M. Kojima, I. McKenzie, S. Ito, *Angew. Chem. Int. Ed.* **2021**, *60*, 24034.

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シクロパラフェニレン内カルベンの電子状態に関する研究

(広島大学[1]・京都大学[2])○梶川 空[1]・村田 涼[1]・茅原 栄一[2]・山子 茂[2]・安倍 学[1]

Study on Electronic Configuration of Carbenes Embedded in Cycloparaphenylene Unit

([1]*Hiroshima University*, [2]*Kyoto University*) ○Ku Kajikawa,[1] Ryo Murata,[1] Eiichi Kayahara,[2] Shigeru Yamago,[2] Manabu Abe[1]

Carbene is an electrically neutral divalent carbon species. It is known to have two electronic states, a singlet, and a triplet. Since carbene properties are significantly different depending on these different electronic states, it is important to study the control of their electronic states. CPP carbenes, carbenes embedded in cycloparaphenylene (CPP), were designed to control the electronic state using the unique molecular structure that can tune the bond angle of the carbene center. CPP is a cyclic molecule consisting of benzene rings, the smaller the ring size, the higher the HOMO energy due to benzene ring distortion. In the triplet state of CPP carbenes embedded in a small ring system, the SOHO-HOMO convention (SHC) has been found in quantum chemical calculations[1)]. SHC is a phenomenon in which the SOMO and HOMO energy levels in radicals are inverted.

In this study, we synthesized precursors and generated CPP carbenes, which are expected to have unique physical properties. The electronic properties were experimentally investigated using Electron Paramagnetic Resonance Spectroscopy (EPR Spectroscopy).

Keywords : SOMO-HOMO convention, Carbene, Cycloparaphenylene, EPR Spectroscopy

カルベンは電気的に中性な 2 価の炭素化学種であり、一重項と三重項の 2 つの電子状態をとることが知られている。カルベンはそれらの電子状態の違いによって異なる性質を示すため、その最安定スピン状態の制御に関する研究は重要である。我々は、カルベンをシクロパラフェニレン (CPP) に組み込んだ CPP カルベンを設計した。CPP はベンゼン環をパラ位で環状につなげた分子で、環の大きさによってカルベン炭素の結合角が制御でき、その最安定スピン状態を制御できるのではないかと考えた。また、CPP は環サイズが小さいほど高い HOMO エネルギーをもつという、曲がったベンゼン環の構造に由来する特異な性質を有する。我々は、環サイズが小さな CPP カルベンの三重項状態において、量子化学計算上、SOMO と HOMO のエネルギー準位が通常のエネルギー準位に比べ入れ替わる SOHO-HOMO convention (SHC)を報告している [1)]。

本研究では、スピン化学において興味深い物性が期待される CPP カルベンの前駆体の合成とその発生を行い、電子常磁性共鳴分光法(EPR Spectroscopy)を用いて、実験的に電子状態に関する物性調査を行った。

1) R, Murata.; Z, Wang.; Y, Miyazawa.; I Antol.; S Yamago.; M, Abe. *Org. Lett*. **2021**, *23*, 4955–4959.

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二酸化塩素による高分散水酸化カーボンナノチューブの合成

（阪大先導的学際研[1]・阪大高等共創研[2]）○板橋勇輝[1]・角南 愛[1]・大久保敬[1,2]

C–H Oxygenation by Simultaneous UV-Vis Light and Microwave Irradiation with Chlorine Dioxide ([1]Institute for Open and Transdisciplinary Research Initiatives, Osaka University, [2]Institute for Advanced Co-Creation Studies, Osaka University) ○Yuki Itabashi[1], Ai Sunami[1] and Kei Ohkubo[1,2]

Carbon nanotubes (CNTs) are expected to have a wide range of applications as a tough carbon material with a one-dimensional structure. However, they are prone to aggregate due to the strong interaction between CNTs. Therefore, additives such as surfactants are required to use CNTs as a material, or to chemically modify them for further functions. In this study, the oxidation of CNTs was performed using chlorine dioxide as an effective oxidant for dispersing CNTs.[1,2] An aqueous solution containing chlorine dioxide was prepared by mixing of sodium chlorite and hydrochloric acid, and then was stirred with CNTs at room temperature for 4 days to afford a black solution of highly-water-dispersed CNTs after filtration and washing with water. The xx and xx analyses indicated that hydroxyl groups were extensively introduced on CNTs. In contrast, treatments with sodium hypochlorite, CNTs was similarly oxidized and gradually dispersed in water, however it was finally completely decomposed to a clear solution. Moreover, the introduced hydroxyl groups were used as the starting point for chemical modification, and pyrene and porphyrin derivatives were successfully incorporated on the CNTs surfaces by condensation reaction with carboxyl groups, which was confirmed by spectroscopic analyses.

Keywords： Oxidation; Carbon material; Surface modification; Hydrophilization; Chlorine Dioxide

カーボンナノチューブ（CNT）は，一次元構造の強靭な炭素材料として幅広い用途で期待される物質であるが，CNT 同士の相互作用が強く，凝集しやすい性質のため，材料としての利用や CNT を化学修飾して更なる機能を付与するためには，界面活性剤などの添加剤を要する．本研究では，CNT の分散化のために二酸化塩素を酸化剤として用いて[1, 2]，CNT の酸化を行った．亜塩素酸ナトリウムと塩酸によって調整した二酸化塩素水溶液に CNT を入れて室温で 4 日間撹拌することにより，CNT の表面が水酸化され，水に対して高い分散性を有する酸化 CNT が得られることを見出した．報告されている次亜塩素酸ナトリウムによる処理では，同様に CNT が酸化されて次第に水に分散していくが，最終的に完全に分解されて透明な溶液になる．一方，本手法では最終的に黒色の分散状態のまま反応が停止する．これを濾取，洗浄を行うことで，高分散 CNT が得られた．さらに，この CNT を用いて導入した水酸基を化学修飾の起点とし，カルボキシル基との縮合反応により，CNT 表面にピレンやポルフィリンを修飾に成功し，分光分析により確認を行った．

1) K. Ohkubo, K. Hirose, *Angew. Chem., Int. Ed*. **2018**, *57*, 2126. 2) Y. Itabashi, H. Asahara, K. Ohkubo, *Chem. Commun.*, **2023**, *59*, 7506.

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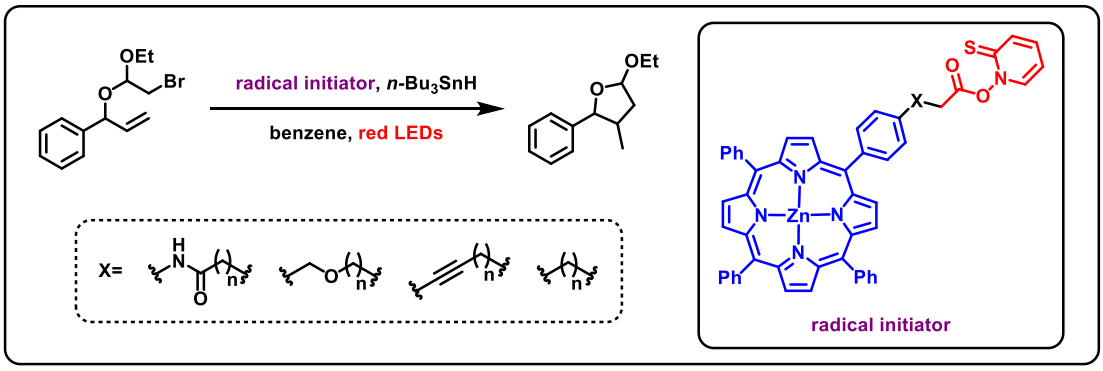
赤色光照射で駆動する新規ラジカル開始剤の開発

（慶大理工 [1]）○谷川麟太郎 [1]・篠原杏 [1]・高尾賢一 [1]・小椋章弘 [1]
Development of New Radical Initiators Which Decompose by Red-Light Irradiation ([1]*Faculty of Science and Technology, Keio University*) ○Rintaro Tanikawa,[1] Ann Shinohara,[1] Ken-ichi Takao,[1] Akihiro Ogura[1]

Azo reagents, peroxides, and triethylborane are widely used as radical initiators. However, these reagents have drawbacks such as the need for high temperatures, explosibility, and Lewis acidity. Therefore, initiators that generate radicals under mild reaction conditions and are easy to handle are desired. We have found that an energy transfer occurs when zinc(II) tetraphenylporphyrin (ZnTPP), excited by red-light irradiation, comes into contact with the ground state Barton ester, resulting in the Barton decarboxylation reaction.[1)] We conceived the development of new radical initiators by applying this reaction. We synthesized new radical initiators by connecting ZnTPP moiety and Barton ester moiety with various linkers to enhance the contact frequency. The synthesized radical initiators were evaluated by Ueno-Stork cyclization reaction as a model reaction.
Keywords : Radical Reaction; Organic Photochemistry; Photocatalyst

現在汎用されているラジカル開始剤にはアゾ試薬や過酸化物、トリエチルボランなどがある。しかし、これらには反応を高温でかける必要があることや爆発性、Lewis 酸性を有するなどの問題がある。そのため、温和な反応条件でラジカルを生成し、扱いの簡単な開始剤が求められている。当研究室では、赤色光の照射によって励起された亜鉛(II)テトラフェニルポルフィリン(ZnTPP)と基底状態の Barton エステルが接触することによってエネルギー移動が起こり、Barton 脱炭酸反応が起こることを見出した [1)]。我々は本反応を新規ラジカル開始剤に応用することを考え、接触頻度の向上を期待し ZnTPP と Barton エステルを様々なリンカーで繋いだ新規ラジカル開始剤の合成を行った。また、合成したラジカル開始剤を下記の上野-Stork 環化反応に用いることで、評価を行った。



1) Takao, K.; Ogura, A. et al. *Chem. Sci.* **2023**, *14*, 11243.

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3-メトキシ-2-ベンジルオキシ-ナフタレンのフォトソルボリシスにおける溶媒および酸触媒の効果

（新潟大理）○臼井 聡、小柳 俊介、衣川 千尋

Effects of Solvent and Acid Catalysis on the Photosolvolysis of 3-Methoxy-2-Benzyloxy-Naphthalene

(*Faculty of Science, Niigata University*) Satoshi Usui, Shunsuke Koyanagi, and Chihiro Kinugawa

Photosolvolysis of 3-MeO-2-(*p*-Me-Benzyloxy)-Naphthalene (**1**) in MeOH afforded *p*-Me-Benzyl substituted 3-MeO-2-Naphthols (**2**), which are resulted from naphthoxy - benzyl geminate pair. The photosolvolyisis of **1** in MeCN exhibited increase in the yield of 3-MeO-2-OH-naphthalene (**3**) with the formation of *p*-Me-Benzaldehyde (**5**) and Dibenzyl (**6**), suggesting that the photosolvolysis of **1** involves benzyl radical even in polar solvents. The addition of 0.1M $MeSO_3H$ to the MeCN solution accelerated the photosolvolysis rate by the factor of 4 with the suppression of **5** and **6**, affording **2** in similar yields as in the photosolvolysis in MeOH. The results indicate that the return from the geminate pair to **1** competes with the formation of **2**, which is favored by its protic solvation.

Keywords : Photosolvolysis ; 3-Methoxy-2-Benzyloxy-Naphthalene ; Solvent Effect ; Acid Catalysis

3-MeO-2-(*p*-Me-ベンジルオキシ)-ナフタレン (**1**) の MeOH 中のフォトソルボリシスでは、ベンジルエーテル結合の開裂後、ナフトキシ-ベンジル geminate 対の再結合生成物 (**2**) を高い収率で与える。**1** のフォトソルボリシスを MeCN 中で行ったところ、geminate 対の解離生成物である 3-MeO-2-OH-ナフタレン (**3**) の収率増加とともに、ベンズアルデヒド (**5**)、ジベンジル (**6**) の生成が確認された。この結果は、極性の高い MeCN 中のフォトソルボリシスにおいて、エーテル結合のホモリシスの介在を示すものである。一方、0.1 M の $MeSO_3H$ を添加した MeCN 中のフォトソルボリシスでは、反応速度が 4 倍加速されるとともに、**5** および **6** の生成は抑制され、MeOH 中のフォトソルボリシスと同様の収率で **2** を与えた。このことは、**1** のフォトソルボリシスで生成した geminate 対からの原系復帰が存在していること、geminate 対からの **2** の生成経路が protic な溶媒和により加速されていることを示している。

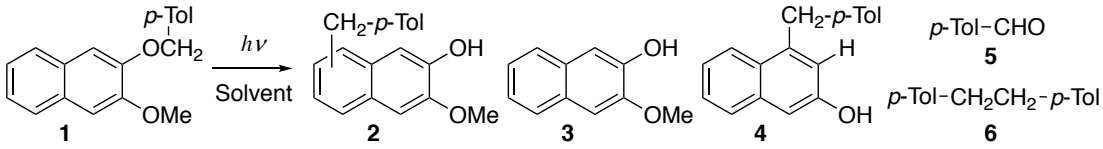

Table Photosolvolysis Products of 3-Methoxyl-2-(*p*-Me-Benzyloxy)-Naphthalene

Solvent	$MeSO_3H$	Irrad.	Conv.	**2**	**3**	**4**	**5**	**6**
CD_3OD	none	90min	38.4%	79.1%	9.5%	-	-	-
CD_3CN	none	60min	43.6%	69.0%	30.6%	0.4%	1.0%	4.0%
CD_3CN	0.1M	15min	46.0%	75.9%	24.0%	-	-	-

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光電子移動触媒/HAT 触媒を用いたギ酸塩によるアルケンのアリールカルボキシル化

（北大院理[1]・北大 WPI-ICReDD[2]・JST-ERATO[3]）○上野　和[1]・神名　航[1]・原渕　祐[2,3]・Saeesh R. Mangaonkar[2,3]・林　裕樹[2,3]・美多　剛[2,3]・前田　理[1,2,3]

Arylcarboxylation of Alkenes with Formate Salts under Photoredox/HAT Catalysis

([1] *Fac. of Sci., Hokkaido Univ.* [2] *WPI-ICReDD, Hokkaido Univ.,* [3] *JST-ERATO*) ○Ueno Yamato,[1] Kanna Wataru,[1] Yu Harabuchi,[2,3] Saeesh R. Mangaonkar,[2,3] Hiroki Hayashi,[2,3] Tsuyoshi Mita,[2,3] Satoshi Maeda[1,2,3]

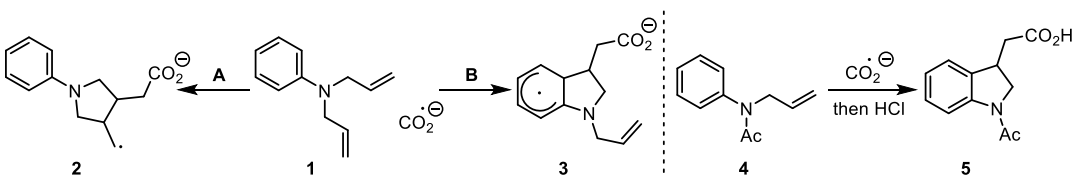
Numerous radical reactions involving the CO_2 radical anion from metal formates under photoredox/HAT catalyst conditions have been reported. Our research group identified the formation of product **2** when *N*,*N*-diarylaniline (**1**) reacts with the CO_2 radical anion. Using the artificial force induced reaction (AFIR) method, we conducted an automated reaction pathway search, revealing two pathways: pathway **A** leading to **2** and pathway **B** involving dearomative cyclization, resulting in the formation of **3**. Pathway **B** has a higher reaction barrier, and intermediate **3** cannot be obtained from substrate **1**.

The study aimed to design a substrate modification by converting one allyl group to another substituent to favor pathway **B**. Quantum chemical calculations suggested replacing an allyl group with an acetyl group, forming a cyclic structure. Synthetic experiments using *N*-acetyl-*N*-arylaniline (**4**) as the substrate successfully yielded product **5** through pathway **B**.

Keywords : CO_2 radical anions*;* Photoredox catalyst*;* AFIR method*;* Automated reaction path search*;* Arylcarboxylation

光電子移動/HAT 触媒存在下でギ酸塩から発生させた CO_2 ラジカルアニオンを利用する反応が数多く報告されている。当研究室では、*N,N*-ジアリルアニリン（**1**）が CO_2 ラジカルアニオンと反応して、生成物 **2** を与えることを見出した。この反応機構を解明するために人工力誘起反応（AFIR）法を用い、**1** および CO_2 ラジカルアニオンを初期構造として反応経路自動探索を行った結果、**2** を与える経路 **A** に加え、CO_2 ラジカルアニオンが付加した後、フェニル基と脱芳香族的に環化し **3** を与える経路 **B** が見つかったが、経路 **B** は経路 **A** に比べて反応障壁が高く、基質 **1** からは中間体 **3** は得られないことがわかった。

本研究では、一方のアリル基を適当な置換基に変換した基質を設計し、経路 **B** を実現させることを目指した。量子化学計算を用い置換基を評価したところ、2 つあるアリル基のうち一つのアリル基をアセチル基に変更することで、環化体が得られることが予想された。これに基づき、置換基をアセチル基にした *N*-アセチル-*N*-アリルアニリン（**4**）を基質として合成化学実験を実施したところ、経路 **B** を経て再芳香族化した生成物 **5** が得られることがわかった。



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フロフラン及びチエノチオフェン誘導体のシクロプロパン化による[3.3.1]プロペランの合成とその物性

(岡山大院自然[1]) ○平野 翔暉[1]・光藤 耕一[1]・菅 誠治[1]

Synthesis of [3.3.1]Propellanes by Cyclopropanation of Furofurans and Thienothiophenes and Their Properties ([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Toki Hirano,[1] Koichi Mitsudo,[1] Seiji Suga[1]

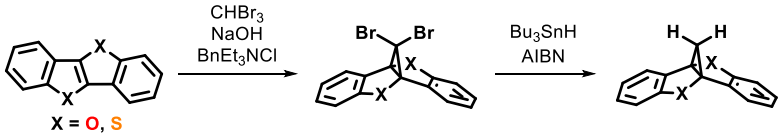
Propellanes such as PCBM, are an interesting group of molecules with unique steric and electronic properties. Heteroacenes have high stability and a dense packing structure, and they can widely be applied to organic semiconductors. However, there are no reports on the synthesis and properties of heteroacene propellanes. Therefore, the synthetic methods and elucidation of physical properties of various derivatives are highly in demand. We recently reported that [3.3.1]propellanes were obtained under the following reaction conditions.[1] In this report, we have investigated the physical properties of these propellanes. We have also developed a method for the synthesis of phenyl[3.3.1]propellane by the reaction of benzofurobenzofuran with carbene precursor and NaH in the presence of AgOTf. Physical properties of this propellane will also be presented.

Keywords : Propellane; Cyclopropanation; Carbene; Furofuran; Thienothiophene

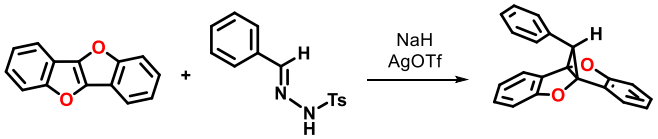
PCBM を代表とするプロペランは特異な立体構造と物性を持つ興味深い分子群である。またヘテロアセンは高い大気安定性を有し、密なパッキング構造を取ることから、有機半導体としての応用が期待され、盛んに研究されている。しかしながら、ヘテロアセンを母骨格に有するプロペランの報告例はないため、様々な誘導体の合成とその物性に興味

最近、我々はヘテロアセンにジブロモカルベンを作用させることで、[3.3.1]プロペランが得られたことを報告した (Scheme 1)[1]。本講演では、その物性を精査したので報告する。また、ベンゾフロベンゾフランに対して、AgOTf 存在下、カルベン前駆体と NaH を作用させ、フェニル[3.3.1]プロペランを合成することにも成功した (Scheme 2)。このプロペランの合成及び物性についても併せて紹介する。

Scheme 1. [3.3.1]プロペラン



Scheme 2. フェニル[3.3.1]プロペラン



(1) 平野 翔暉・桐畑 朋佳・光藤 耕一・菅 誠治, 日本化学会第 103 春季年会 [K701-1am-13]

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高分子メカノケミカル反応によって生じるα-置換ジアリール酢酸誘導体の脱炭酸反応の評価

（東工大物質理工）○内田 優斗・山本 拓実・杉田 一・高橋 明・大塚 英幸

Evaluation of decarboxylation of α-substituted diarylacetic acid derivatives generated by polymeric mechanochemical reactions (*Dept. of Chem. Sci. and Eng., Tokyo Tech.*) ○Yuto Uchida, Takumi Yamamoto, Hajime Sugita, Akira Takahashi, Hideyuki Otsuka

Chemical reactions induced by mechanical forces are known as mechanochemical reactions and have gained increasing attention. In this study, we attempted to induce a decarboxylation reaction by using a polymeric mechanoradical generated in polymer chain scission in response to mechanical stress. Density functional theory calculations have predicted a decarboxylation reaction occurs when the carboxylic hydrogen atom is abstracted by a reactive radical.[1] Our calculations also suggested that the hydrogen abstraction from the α-substituted diarylacetic acid (DAAA) derivatives by methyl radical was predicted to proceed in concert with the decarboxylation reaction (**Fig. 1**). This calculation was experimentally verified by ball-milling tests using the mixture of α-substituted DAAA derivatives and polystyrene. Electron paramagnetic resonance measurements of the ground samples showed generation of radical species, indicating that the decarboxylation reaction was induced by the polymeric mechanoradicals.

Keywords : Mechanochemistry; Molecular probe; Mechanoradical; Electron paramagnetic resonance; Decarboxylation reaction

力学的刺激を駆動力にした反応はメカノケミカル反応とよばれる。本研究では、力学的刺激による高分子鎖切断に伴い発生するメカノラジカルを用いた脱炭酸反応の誘起を試みた。カルボン酸の水素がラジカル的に引き抜かれると協奏的に脱炭酸反応が進行することが、密度汎関数理論計算から予測されている (**Fig. 1**)[1]。そこで α-置換 DAAA 誘導体を合成してポリスチレンとともにボールミルにて粉砕し、電子スピン共鳴測定を行った。その結果、ラジカル由来のシグナルが観測され、脱炭酸反応の進行が示唆された。

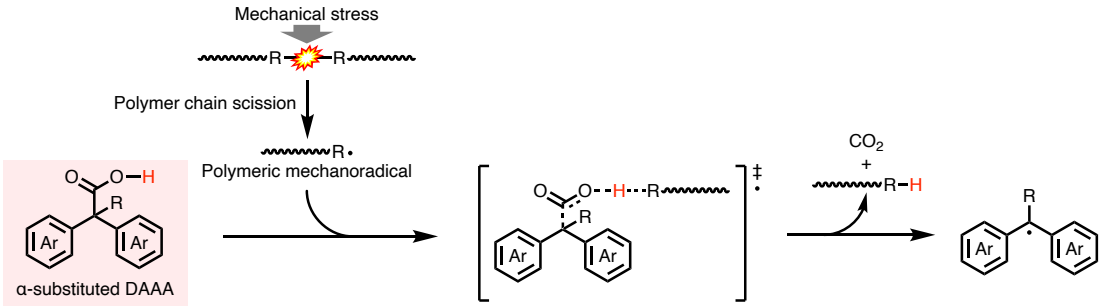

Fig. 1 Conceptual illustration of this work.

[1] E. T. Denisov, A. F. Shestakov, *Kinet. Catal.* **2013**, *54*, 22.

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フルオレニルカチオンとベンゾフルオレニルカチオンの陽電荷分布と反芳香族性に対する多環芳香族置換基の効果

(三重大院工[1]・三重大院地域イノベ[2]・三重大工[3]) ○岡崎 隆男[1,2]・河上 太一[1]・川合 玲児[3]・北川 敏一[1]

Effect of Polycyclic Aromatic Substituents on Positive Charge Delocalization and Antiaromaticity of Fluorenyl and Benzofluorenyl Cations ([1]*Graduate School of Engineering, Mie University*, [2]*Graduate School of Regional Innovation Studies, Mie University*, [3]*Faculty of Engineering, Mie University*) ○ Takao Okazaki,[1,2] Taichi Kawakami,[1] Reiji Kawai,[3] Toshikazu Kitagawa[1]

The 9-fluorenyl cation has attracted much interest due to its anti-aromaticity. Fluorenyl and benzo[*b*]fluorenyl cations with aryl substituents (**1a-1d**) were generated from the corresponding alcohols in CF_3SO_3H (Figure 1). Charge delocalization and anti-aromaticity of the cations were examined by direct NMR observation and DFT calculations.

The most deshielded ^{13}C signals were observed at 204.5 ppm (**1a**), 201.3 ppm (**1b**), 199.5 ppm (**1c**), and 195.2 ppm (**1d**). The chemical shifts of the cationic center decreased with increasing delocalization of positive charge into the π-system. Positive charges in 9-fluorenyl cations (**1a-1c**) were more delocalized into the aryl substituents in the order of phenyl < 1-naphthyl < 2-naphthyl. $NICS(1)_{zz}$ of the 5-memberd rings were calculated to be 47.7 (**1a**), 43.9/42.6 (**1b**), 43.1/42.8 (**1c**), and 35.3/34.9 (**1d**) by GIAO-B3LYP/6-311+G(2d,p), suggesting that their antiaromaticity decreased with increasing the delocalization of positive charge.

Keywords: Carbocation, Fluorenyl cation, Superacid, DFT calculations, NMR

9-フルオレニルカチオンの 5 員環は反芳香族性を持つため、興味がもたれている。本研究では、フルオレニルカチオンとベンゾ[*b*]フルオレニルカチオンにフェニル基やナフチル基を導入し、直接 NMR 観測と DFT 計算によって電子構造と反芳香族性に対する置換基効果を調べた (Figure 1)。

超強酸 CF_3SO_3H 中で、カチオン **1a-1d** を前駆体アルコールから発生させて、直接 NMR 観測した。カチオン中心の $\delta^{13}C$ は、204.5 ppm (**1a**)、201.3 ppm (**1b**)、199.5 ppm (**1c**)、195.2 ppm (**1d**)であった。π 共役系が大きくなると、非局在化のため高磁場シフトした。**1a-1c** では、フェニル基 <1-ナフチル基 <2-ナフチル基の順で、陽電荷がより多く非局在化した。GIAO-B3LYP/6-311+G(2d,p)による 5 員環の $NICS(1)_{zz}$ は、47.7 (**1a**)、43.9/42.6 (**1b**)、43.1/42.8 (**1c**)、35.3/34.9 (**1d**)であり、陽電荷がより非局在化すると、反芳香族性が低下する。

以上により、陽電荷の非局在化が大きくなると、反芳香族性が小さくなるとわかった。また、1-ナフチル基よりも 2-ナフチル基の方がより非局在化した。

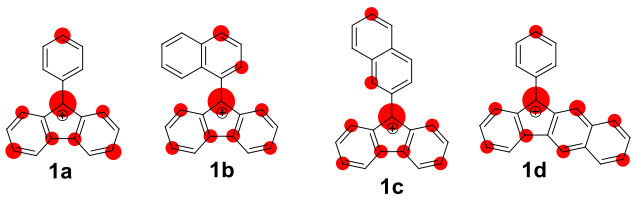

Figure 1. Positive charge delocalization of **1a-1d**. Red circles are roughly proportional to changes in ^{13}C data ($\Delta\delta^{13}C$) from those of the corresponding parent alcohols: threshold is 10 ppm.

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チオアミド誘導体を用いた環境調和型スルフィド合成法の開発

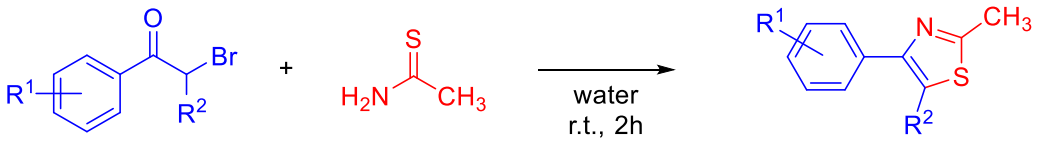
（高知大院総合）○昌本 麗・吉永 有佑・金野 大助
Development of Eco-Friendly Synthesis of Cyclic Sulfide Using Thioamide Derivatives (*Graduate School of Integrated Arts and Sciences, Kochi University*) ○Urara Masamoto, Yusuke Yoshinaga, Daisuke Kaneno

A new method of sulfide synthesis using nonvolatile and odorless thioamide derivatives instead of thiols has been developed. The Hantzsch reaction of α-halogenated ketones with thioacetamide in water proceeded under room temperature without catalyst and the corresponding thiazoles was obtained as main products. The reaction mechanism of this type reaction was also investigated by theoretical calculations.
Keywords : Eco-Friendly Synthesis; Sulfide; Thioamide

スルフィドは生理活性をもつ多くの化合物の骨格にみられることから、その合成法の研究が盛んに行われている。現在、最も一般的に用いられているスルフィド合成法はチオールを基質とした方法であるが、チオールは揮発性が高く悪臭をもつことから、近年ではより取り扱いが容易な原料を用いたスルフィド合成法の開発が研究されている。

チオール不使用のスルフィド合成法としては、チオ尿素を用いた鎖状スルフィド合成法の報告例があるが [1]、チオ尿素は一方でα-ハロケトンと容易に Hantzsch 反応を起こしてアミノチアゾールを生成することも知られている [2]。また、現代では人体や環境に対して毒性の低い試薬を用いる環境調和型の合成法が望まれる。そこで本研究ではチオアミド誘導体とα-ブロモアセトフェノンを基質とする環境にやさしい条件での環状スルフィド合成を検討した。

チオアセトアミドとα-ブロモアセトフェノンを水溶媒中室温で 2h 反応させたところ目的のフェニルチアゾールが収率 73%で得られた。本反応についてカルボニル基のα位またはフェニル基に置換基をもつ基質を用いて汎用性の検討を行った。さらにこれらの反応について分子軌道計算を用いて反応機構の解析を行った。



R^1 = H, Cl, OMe
R^2 = H, Me, Ph

1) H. Firouzababi, N. Iranpoor, M. Abbasi, *Tetrahedron,* **2009**, *65*, 5293.
2) J. R. Byers, J. B. Dickey, *Org. Synth.*, **1939**, *19*, 10.

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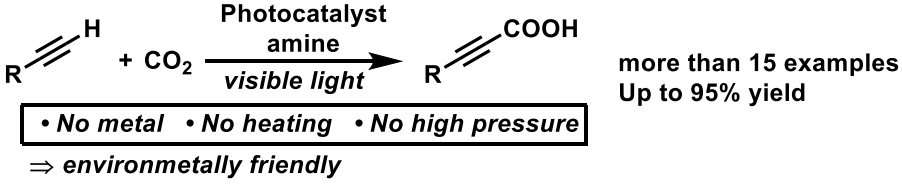
CO_2 を原料とする末端アルキンの光触媒的カルボキシル化反応

（東理大院工）○宇野 修平・今堀 龍志
Photocatalytic Carboxylation of terminal alkynes using CO_2 (*Graduate School of Engineering, Tokyo University of Science*) ○Shuhei Uno, Tatsushi Imahori

Carboxylation with CO_2 forming a C-C bond is valuable method for regeneration of chemicals from emitted CO_2 in carbon-recycle technologies. However, most of the reported reactions use metal reagent or metal catalyst at hard conditions with heating and/or high pressure, which induced waste of rare metal resource and energy. On the other hand, photoredox catalysis enables energy-efficient and low-CO_2 emission chemical transformations using sunlight. While a few reports of photoredox carboxylation with CO_2 have been reported so far,[1] more efficient photocatalytic C-H carboxylation with CO_2 is quite limited, in which applicable substrates have an appropriate C-H bond with low bond dissociation energy due to the radical mechanism. In this study, we have developed a photocatalytic C-H carboxylation of terminal alkynes with CO_2 using cyanoarene photoredox catalyst and catalytic amine system. C-H bond of terminal alkynes has extremely high bond dissociation energy. This reaction proceeds without heating, high pressure, metal catalyst, and metal reagent, and showed broad substrate scope. Mechanistic studies are currently underway.
Keywords : Photoredox catalyst; Carboxylation; Carbon dioxide; Terminal alkyne

CO_2 を原料とするカルボキシル化反応は、C—C 結合を形成し、多彩な機能性化学品を合成する手法として有効であるが、これまでに報告されている CO_2 を用いたC—C結合形成反応は、加熱や高圧条件等の高エネルギー条件が必要である点や多量の金属廃棄物を生じる点など、実用化の観点から問題がある。

光酸化還元触媒反応は太陽光エネルギーを用いた低コスト・低 CO_2 排出の化学変換であり、光酸化還元触媒を用いる CO_2 を原料とするカルボキシル化反応が数例報告されている[1]。しかしながら、より効率的な反応である C—H 結合の直接カルボキシル化反応は極めて少なく、またラジカル中間体を生成しやすい結合解離エネルギーが低い C—H 結合を有する反応基質に適用が限られる。本研究では、結合解離エネルギーの大きい末端アルキンと CO_2 の光酸化還元触媒 Csp—H カルボキシル化反応の開発を行った。シアノアレーン系光酸化還元触媒と、触媒量のアミンを用いることで、加熱・加圧を必要とせず、遷移金属を用いない基質適用性の広い CO_2 資源化を実現した。現在、反応機構解析を行なっており、更なる展開につなげる。



1) Review: J. Jung, et al., *Synthesis,* **2021**, *53*, 3263-3278

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可視光レドックス触媒を用いた三成分連結反応による α-チオオキシムの合成

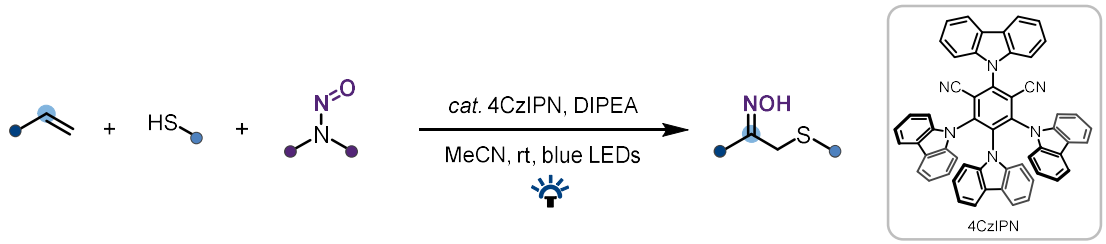
（岡山大工[1]・岡山大院環境生命自然[2]）○田村 俊樹[1]・山崎 賢[2]・秋元 秀太[2]・三浦 智也[2]

Photoinduced Synthesis of α-Thiooximes by Three-Component Coupling Reaction ([1]*School of Engineering, Okayama University*, [2]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Toshiki Tamura,[1] Ken Yamazaki,[2] Shuta Akimoto,[2] Tomoya Miura[2]

An efficient formation of C–S bonds is an important reaction because sulfur atoms are found in numerous natural products and bioactive compounds.[1] In addition, oximes are useful precursors for a wide variety of chemical transformations.[2] In this study, we have developed a three-component coupling reaction between styrenes, thiols, and *N*-nitrosamines for the efficient synthesis of α-thiooximes using 4CzIPN under blue light irradiation. This methodology exhibits an excellent functional group tolerance and substrate scope. Furthermore, α-thiooximes synthesized in this study can be further transformed into complex sulfur-containing compounds.

Keywords : α-Thiooxime; Visible-Light Photoredox Catalyst; Three-Component Coupling Reaction; N-Nitrosamine; Thiol

硫黄原子は様々な天然物や医薬品に含まれており、効率的な炭素-硫黄結合の形成は重要な反応である[1)]。また、オキシムは多様な化学変換が可能であり、有用な前駆体である[2)]。本研究では、4CzIPN 存在下で青色 LED を照射することにより、スチレン、チオール及び *N*-ニトロソアミンの三成分から α-チオオキシムが高収率で得られることを見出した。優れた官能基許容性を示しており、幅広い基質に適応可能である。さらに、得られた α-チオオキシムはさらなる変換が可能であり、複雑な含硫黄化合物の合成にも応用可能である。



1) P. Chauhan, S. Mahajan, D. Enders, *Chem. Rev.* **2014**, *114*, 8807.
2) (a) D. S. Bolotin, N. A. Bokach, M. Ya. Demakova, V. Yu. Kukushkin, *Chem. Rev.* **2017**, *117*, 13039; (b) Z. Mirjafary, M. Abdoli, H. Saeidian, S. Boroon, A. Kakanejadifard, *RSC Adv.* **2015**, *5*, 79361.

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

Thu. Mar 21, 2024 1:00 PM - 2:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:00 AM UTC E1132(1132, Bldg. 11 [3F])

[E1132-4pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Akira Takahashi, Satoshi Usui

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1132-4pm-01]

Aerobic Oxygenation of Benzene Using Fluorine-Substituted Acridinium as a Photoredox Catalyst

○Yusuke Akao[1,2], Shohei Ohno[2], Yuki Itabashi[3], Haruyasu Asahara[1], Yasuaki Koizumi[1], Kuninori Tai[1], Kazumi Kondo[1], Tsuyoshi Nagase[1], Tsuyoshi Inoue[2], Kei Ohkubo[3,4] (1. Otsuka Pharmaceutical Co., Ltd., 2. Osaka Univ., 3. Osaka Univ. OTRI, 4. Osaka Univ. IACS)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1132-4pm-02]

Mechanisms and the Role of Lewis Acids in Transition Metal Catalysts for C-O, C-F, and H-H Activation

○Panida Surawatanawong[1] (1. Mahidol University, Faculty of Science)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1132-4pm-03]

Synthesis of Phosphine Ligands through Radical Diphosphination of Strained Small Molecules

○Tsuyoshi Mita[1,2], Chandu G Krishnan[1,2], Hideaki Takano[1,2], Hitomi Katsuyama[1,2], Hiroki Hayashi[1,2], Wataru Kanna[3], Satoshi Maeda[1,2,3] (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

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フッ素置換アクリジニウムをフォトレドックス触媒としたベンゼンの空気酸化反応

(大塚製薬（株）[1]・阪大院薬[2]・阪大先導的学際研[3]・阪大高等共創研[4]) ○赤尾 祐介[1,2]・大野 祥平[2]・板橋 勇輝[3]・淺原 時泰[2]・小泉 靖明[1]・田井 国憲[1]・近藤 一見[1]・長瀬 剛[1]・井上 豪[2]・大久保 敬[3,4]
Aerobic Oxygenation of Benzene Using Fluorine-Substituted Acridinium as a Photoredox Catalyst ([1]*Otsuka Pharmaceutical Co., Ltd.,* [2]*Osaka Univ.,*[3]*Osaka Univ. OTRI,* [4]*Osaka Univ. IACS*) ○ Yusuke Akao,[1,2] Shohei Ohno,[2] Yuki Itabashi,[3] Haruyasu Asahara,[2] Yasuaki Koizumi,[1] Kuninori Tai,[1] Kazumi Kondo,[1] Tsuyoshi Nagase,[1] Tsuyoshi Inoue,[2] Kei Ohkubo,[3,4]

A series of fluorine-substituted acridinium were designed and synthesized to develop a photoredox catalyst with strong oxidation power. There is a linear relationship between the electron affinity (EA) values calculated by quantum chemical calculations and the one-electron reduction potentials at the singlet excited state determined by the electro- and photochemical measurements (Figure 1). This results indicate that computational chemistry can sufficiently predict the experimental oxidation power of acridinium derivatives without synthesis. The hydroxylation of benzene was successfully achieved under visible-light irradiation by utilizing the strong electron-transfer oxidation property of acridinium ion (AC-18), and the highest yield of phenol was observed to be 80%. The reaction mechanism was clarified by the time-resolved transient absorption spectroscopic measurements. The photochemical reaction is initiated by electron transfer from benzene to the singlet excited state of acridinium.
Keywords : Photoredox catalyst; Oxygenation; Acridinium; Benzene; Phenol

フッ素基を導入した種々のアクリジニウムイオンを設計・合成し，フォトレドックス触媒として広く用いられている 9-メシチル-10-メチルアクリジニウム（AC-01）に比べ強力な酸化力を示すアクリジニウム触媒の開発を目指した. 量子化学計算から大きな電子親和力 (EA) 値を有するアクリジニウム触媒を予測し, それらの中から合成できた化合物の一重項励起状態還元電位を実験的に求めプロットしたところ, 図 1 に示すような比例関係が認められた. この結果よりアクリジニウム化合物の酸化力の実験値を計算化学で十分に予測できることがわかった. その中でも強力な電子移動酸化特性を有する AC-18 を光触媒として用いた場合、ベンゼンの水酸化反応が可視光照射下で進行し，フェノールの最高収率は 80%に達した．レーザー過渡吸収分光解析などを用いて反応機構の詳細について明らかにした.

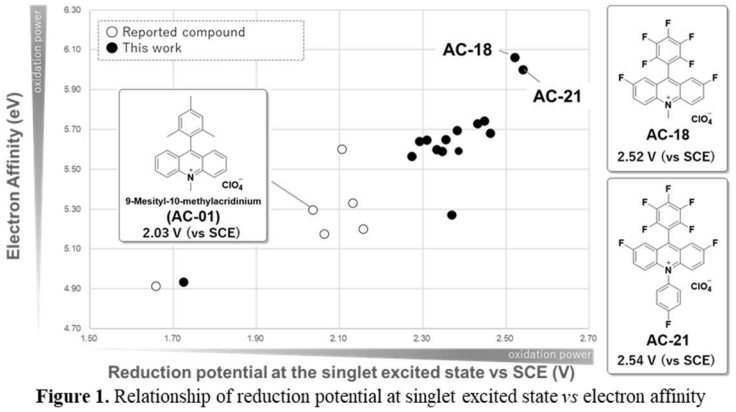

Figure 1. Relationship of reduction potential at singlet excited state *vs* electron affinity

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Mechanisms and the Role of Lewis Acids in Transition Metal Catalysts for C-O, C-F, and H-H Activation

[1]Department of Chemistry and Center of Excellence for Innovation in Chemistry,
Faculty of Science, Mahidol University, Bangkok 10400, Thailand
Panida Surawatanawaong[1], Thanapat Worakul[1], Kajjana Boonpalit[1], Chayapat Uthayopas[1]

Keywords: Transition Metal; Lewis Acid; C-O Activation; C-F Activation; Hydrogenation

Density functional calculations were performed to give insights into the mechanisms and the role of Lewis acids in transition metal catalysts for C-O, C-F, and H-H activation. In the first process, nickel complex with N-heterocyclic carbene (Ni-SIPr) has been shown to selectively catalyze C−O bond hydrogenolysis of aryl methyl ether to obtain arene and alcohol as the only products. The Lewis acid $AlMe_3$ was found to facilitate aryl C–O bond activation via the five-centered transition state by forming a Lewis acid/base adduct with 2-methoxynaphthalene (NaphOMe) with the interaction from the Me group of $AlMe_3$ to Ni. Then, we investigated the C-F activation in the hydrodefluorination of CF_3-substituted aniline derivatives, $CF_3(C_6H_4)NMe_2$, by the Ru–S complex, $[(PEt_3)Ru(DmpS)]^+$ (DmpS = 2,6-dimesitylphenyl thiolate) with $HSiMe_2Ph$ and with HAl^iBu_2. The Si-H activation on Ru-S generates Ru–H with thiosilane ligand, in which the Si-S bond must be cleaved to generate the active silylium moiety for the fluoride abstraction. In contrast, the Al-H activation of HAl^iBu_2 leads to the formation of Ru–H with the alumenium ($^+Al^iBu_2$), stabilized by the donation from both σ(Ru–H) and sulfur lone pair. For the H_2 activation, the nickel-borane complex, $Ni[(Mes)B(o\text{-}Ph_2PC_6H_4)_2]$, has been reported as an efficient catalyst for styrene hydrogenation. Following the H_2 activation, the resulting *trans*-dihydride nickel-alane complex has higher negative charges on both terminal and bridging hydrogen atoms than the corresponding nickel-borane complex. With the higher hydricity of hydrogen, nickel−alane is expected to be more reactive toward hydrogenation of styrene than nickel-borane. The role of Lewis acids in forming different types of interaction with transition metals affects their catalytic activities toward C-O, C-F, and H-H activation.

1) Worakul, T.; Surawatanawong, P. *Organometallics* **2023**, *42*, 896-907.
2) Boonpalit, K.; Uthayopas, C.; Surawatanawong, P. *Organometallics* **2022**, *41*, 259-269.
3) Uthayopas, C.; Surawatanawong, P. *Dalton Trans.* **2019,** *48*, 7817-7827.
4) Wititsuwannakul, T.; Tantirungrotechai, Y.; Surawatanawong, P. *ACS Catal.* **2016,** *6*, 1477-1486.
5) Sawatlon, B.; Wititsuwannakul, T.; Tantirungrotechai, Y.; Surawatanawong, P. *Dalton Trans* **2014,** *43*, 18123-18133.

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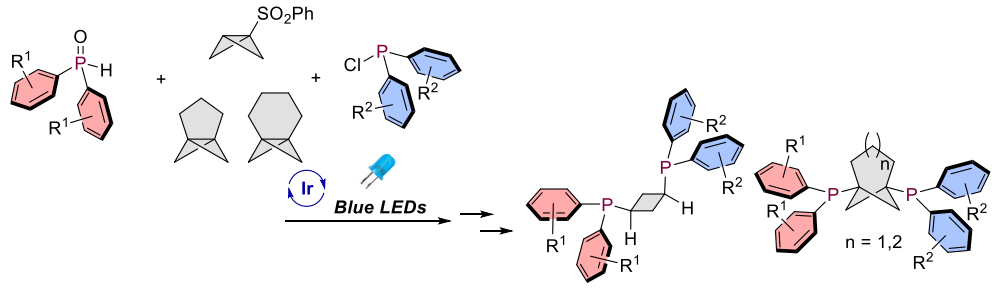
ラジカルジホスフィン化による歪んだ小分子からのリン配位子合成

（北大 WPI-ICReDD[1]・JST-ERATO[2]・北大院理[3]）○美多　剛[1,2]・Chandu G. Krishnan[1,2]・髙野　秀明[1,2]・勝山　瞳[1,2]・林　裕樹[1,2]・神名　航[3]・前田　理[1,2,3]
Synthesis of Phosphine Ligands through Radical Diphosphination of Strained Small Molecules
([1]*WPI-ICReDD, Hokkaido Univ.*, [2]*JST-ERATO*, [3]*Fac. of Sci., Hokkaido Univ.*) ○Tsuyoshi Mita,[1,2] Chandu G. Krishnan,[1,2] Hideaki Takano,[1,2] Hitomi Katsuyama,[1,2] Hiroki Hayashi,[1,2] Wataru Kanna,[3] Satoshi Maeda[1,2,3]

The chemical synthesis of diphosphinated cyclobutene, bicyclo[3.1.1]heptane, and bicyclo[4.1.1]octane-based diphosphine ligands was successfully accomplished starting from the corresponding strained molecules such as bicyclo[1.1.0]butane, [3.1.1]propellane, and [4.1.1]propellane by employing a calculation-guided ring-opening diphosphination. The feasibility of the initial radical addition can be estimated through DFT calculations using the AFIR method. This study greatly focuses the importance of integrating experimental and computational methods in the design and synthesis of new diphosphination reactions involving strain-containing small molecules.
Keywords : Radical; Cyclobutane; Propellane; Diphosphination; DFT Calculations

我々の研究グループでは以前、エチレンや[1.1.1]プロペランに対するジホスフィン化の検討を行い、非対称、および対称のリン配位子の合成に成功している[1,2]。今回、これら以外の歪んだ様々な化合物に対して $Ph_2P(O)$・がラジカル付加を進行させる活性化障壁を、AFIR 法を駆使し DFT 計算で見積もったところ、ビシクロ[1.1.0]ブタン、[3.1.1]プロペラン、および[4.1.1]プロペランの単結合もラジカル的に開環できることを見出した。その結果に基づき、新たなジホスフィン化反応を実現すべく、原料として $Ar_2P(O)H$ と $ClPAr_2$ を用いたラジカル三成分反応を実施したところ、対応するジホスフィン化合物を高収率で得ることに成功した。本反応では対称のみならず、非対称のリン化合物も効率良く合成することができた。



1) Takano, H.; Katsuyama, H.; Hayashi, H.; Kanna, W.; Harabuchi, Y.; Maeda, S.; Mita, T. *Nat. Commun.* **2022**, *13*, 7034.
2) Takano, H.; Katsuyama, H.; Hayashi, H.; Harukawa, M.; Tsurui, M.; Shoji, S.; Hasegawa, Y.; Maeda, S.; Mita, T. *Angew. Chem., Int. Ed.* **2023**, 62, e202303435.

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1133(1132, Bldg. 11 [3F])

[E1133-4am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Jumpei Taguchi, Kosuke Yasui

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1133-4am-01]
Synthesis of polyacene derivatives via dehydrative aromatization of aromatic alcohols

○Ryota Yuasa[1], Toshiyuki Hamura[1] (1. Kwansei Gakuin University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1133-4am-02]
Synthesis of [6]helicene extensions and their properties

○Masaya Miyamoto[1], Makoto Miyamoto[1] (1. Tokyo Denki University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1133-4am-03]
Desymmetrization of Naphthalene Framework Using Bromo Rearrangement and Subsequent Regioselective Transformation

○Nana Hatayama[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi University of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1133-4am-04]
Synthesis of Internal-edge-substituted Azaoxa[6]helicenes by Intramolecular C–H Amination as a Key Reaction

○Syuji Morita[1], Song Leii[1], Kazunobu Igawa[1], Katsuhiko Tomooka[2], Ryo Irie[1] (1. The Univ. of Kumamoto, 2. The Univ. of Kyushu)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1133-4am-05]
KO^{t}Bu-Catalyzed Transformation of *N*-Benzylamides to Isoindoles via 1,2-Acyl Migration

○Ryoma Shimazumi[1], Moe Morimoto[2], Mamoru Tobisu[1,3] (1. Graduate School of Engineering, Osaka Univ., 2. School of Engineering, Osaka Univ., 3. ICS-OTRI)

9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
Break

English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1133-4am-06]
One-pot Synthesis of Novel Tetraaryl-Diazachrysenes via the Povarov Reaction

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○YUANRONG SHAN[1], Takaki Kanbra[1], Junpei Kuwabara[1] (1. University of Tsukuba Graduate School of Pure and Applied Sciences)

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[E1133-4am-07]

Synthesis of dibenzofulvenes containing a trifluoromethyl group based on Friedel-Crafts type cyclization

○yusei noguchi[1], motohiro yasui[1], sigeyuki yamada[1], tsutomu konno[1] (1. kyoto institute of technology)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1133-4am-08]

Carbamoylarylation of Alkynes Using *N*-Aryl Oxamic Acids as Bifunctional Reagents

○GAOFAN YUE[2], Di Wu[2], Akira Shiozuka[2], Kohei SEKINE[1,2], Yoichiro KUNINOB[1,2] (1. IMCE, Kyushu Univ., 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu Univ.)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1133-4am-09]

Mono-Selective Mechanochemical Nucleophilic Aromatic Substitution Enabled by In-situ Crystallization

○Sota Kawamura[1], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1133-4am-10]

Stereoselective Synthesis of Trisubstituted Alkenes Enabled by the Reactivity of Sulfoximine

○Kosuke Yasui[1], Yuichiro Tomishima[2], Koji Hirano[1] (1. Graduate School of Engineering, Osaka University, 2. School of Engineering, Osaka University)

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

Break

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1133-4am-11]

Synthesis of di(1-benzothiopheno)pyrrole *via* Cadogan reaction

○Yuma Tanioka[1], Shigeki Mori[2], Masayoshi Takase[1], Hidemitsu Uno[1] (1. Graduate school of science and engineering, Ehime University, 2. Advanced Research Support Center , Ehime University)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1133-4am-12]

Formation of 2,3-benzodiazepin from *o*-vinylbenzyldiazoacetate

○Kazuki Naoi[1], Tomoya Kuroki[1], Shinji Nagumo[1] (1. Kogakuin University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1133-4am-13]

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Synthesis of Novel Heterobiaryls via Siteselective Halogenation and Crosscoupling Reactions of Naphthobenzofuranol Derivatives

○Song Lei[1], Suzuna Nakashima[1], Shuji Morita[1], Kazunobu Igawa[1], Katsuhiko Tomooka[2], Ryo Irie[1] (1. Kumamoto Univercity, 2. Kyushu University)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[E1133-4am-14]

Syntheses and properties of diazaperopyrenes with electron- donating groups

Hotsuma Inada[1], Yasufumi Masani[2], Yoshimitsu Tachi[1,2], ○Masatoshi Kozaki[1,2] (1. Osaka Metropolitan University, 2. Osaka City University)

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芳香族アルコールの脱水・芳香族化によるポリアセン誘導体の合成

（関西学院大院理工）○湯浅 遼太・羽村 季之
Synthesis of polyacene derivatives via dehydrative aromatization of aromatic alcohols (*Graduate School of Science and Technology, Kwansei Gakuin University*) ○Ryota Yuasa, Toshiyuki Hamura

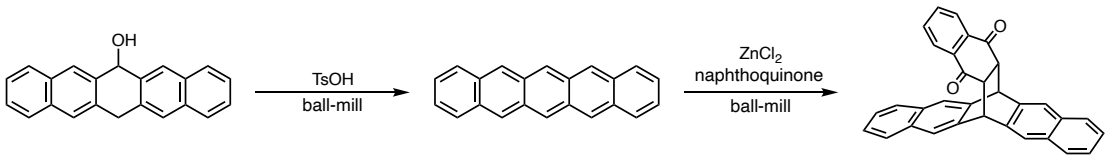
Polyacenes exhibit unique physical properties due to their characteristic pi-conjugated structures, and therefore creation of novel functional materials has been actively studied. The synthesis of high-ordered polyacenes, however, remains difficult owing to the susceptibility to photooxidation and poor solubility. Moreover, regioselective functionalization method for the polyacene skeleton is limited, which hampers the selective synthesis of functionalized derivatives. We report herein an efficient synthesis of polycyclic aromatic compounds, including high-ordered polyacenes, using dehydrative aromatization of aromatic alcohols. Also described is functionalization of these compounds.

An example is shown below. Thus, upon grinding of pentacene-mono-ol **1**, prepared by reduction of pentacenequinone, with *p*-TsOH in the ball mill, dehydrative aromatization occurred to give pentacene **2**. Subsequent solid-state cycloaddition of **2** with naphthoquinone in the presence of $ZnCl_2$ gave cycloadduct **3** in good yield.

Keyword：polyacene; pi-conjugated structure; functional material; polycyclic aromatic compounds.

ポリアセンは、その特徴的なπ共役構造に起因する独特な物性を示し、これを利用した機能性材料の創製が盛んに研究されている。しかし、ベンゼン環が高度に縮環した分子は光酸化を受けやすい上に難溶性のため、その合成は容易ではない。また、ポリアセン骨格への位置選択的な官能基導入法が欠如しているため、置換誘導体の合成も乏しいのが現状である。今回我々は、芳香族アルコールの脱水・芳香族化を利用してポリアセンを含む多環式芳香族化合物の簡便な合成法を開発した。また、得られる化合物の官能基化も検討したので、報告する。

下に、その一例を示した。すなわち、ペンタセンキノンを還元して得られるペンタセンモノオール **1** と *p*-TsOH をボールミルを用いて粉砕・混合すると、脱水・芳香族化により、ペンタセン **2** を得ることができた。さらに、これとナフトキノンとの環化付加反応をボールミルを用いて行うと、対応する環化付加体 **3** を収率良く与えた。



1 **2** **3**

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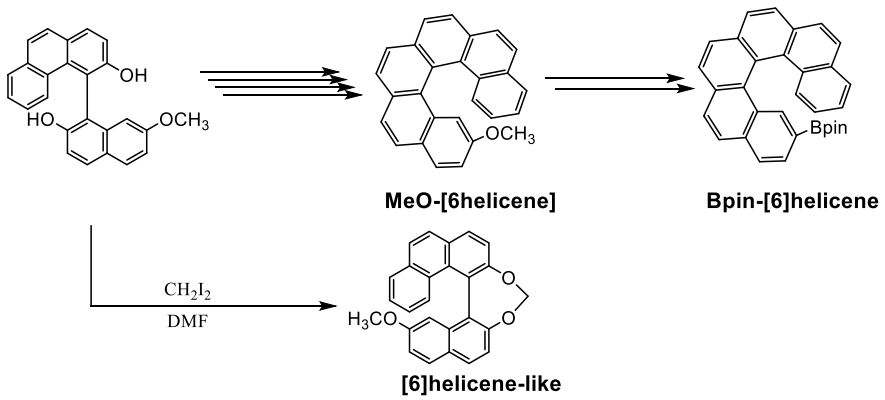
2 位に置換基を有する[6]ヘリセンの拡張体と疑[6]ヘリセンの合成およびその特性

(東電大院工)　○宮本　誠也・宮坂　誠
Synthesis and proprties of [6]helicenes, extensions of [6]helicenes with substituents at the 2-position and suspected [6]helicenes (*[1]Graduate School of Engineering, Tokyo Denki University)*○Masaya Miyamoto, Makoto Miyasaka

[*n*]Helicenes are inherent chiral molecules and exhibit unique chiroptical properties. Due to its chirality based on the helical structure, it has been attracting attention in the field of chiral materials in recent years. Specific features include high optical properties such as high optical rotation, circularly polarized luminescence (CPL), and circular dichroism (CD). On the other hand, [*n*]helicenes have the disadvantage of low fluorescence quantum yields and poor luminescence. In this study, we synthesize and characterize [6]helicene-like derivatives based on [6]helicene having a substituent at position 2 and their extensions.

Keywords : [6]Helicene , polycyclic aromatic hydrocarbon

ヘリセンとはベンゼン環がオルト位で縮環したらせん状の多環芳香族化合物である[1]。らせん構造に基づくキラリティーにより近年、キラル材料の分野で注目されている。具体的な特徴としては高い旋光性、円偏光発光(CPL)、円偏光二色性(CD)などの優れた光学特性が挙げられる[2]。一方でヘリセンは蛍光量子収率が低く発光性に乏しいという欠点が挙げられる[3]。本研究では、2 位に置換基を有する[6]ヘリセンを基盤としその拡張体の合成および対応する[6]ヘリセンライク誘導体の合成とその特性評価を行う。



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ブロモ基の転位を利用したナフタレンの非対称化とその位置選択的変換反応

（高知工大理工）○畑山 奈々・岩井 健人・西脇 永敏

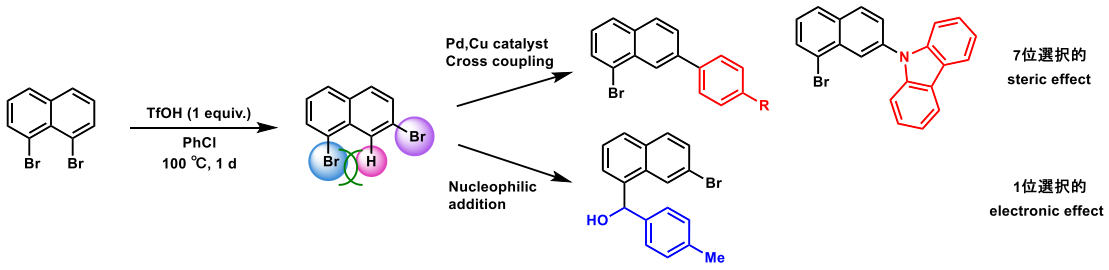
Desymmetrization of Naphthalene Framework *via* Bromo Rearrangement and the Regioselective Chemical Transformation (*School of Engineering Science, Kochi University of Technology*) ○Nana Hatayama, Kento Iwai, Nagatoshi Nishiwaki

Polyhaloarenes are useful building blocks for functional materials; especially, non-symmetric polyhaloarenes are desired to achieve the versatile molecular design. In this perspective, desymmetrization of 1,8-dibromonaphthalene and further chemical transformation were studied using steric-distortion-promoted halo-Jacobsen reaction.[1)] A reaction of 1,8-dibromonaphthalene with TfOH induced 1,2-rearrangement of a bromo group to afford 1,7-dibromonaphthalene. Two independent bromo groups of the product prompted us to study on regioselective chemical conversions. When the obtained 1,7-dibromonaphthalene was subjected to transition-metal-catalyzed cross-coupling reaction, reactions occurred regioselectively at 7-position. On the other hand, nucleophilic addition reactions to aldehydes *via* Br–Li exchange proceeded regioselectively at the 1-position. These differences might be caused by the different steric and electronic effects at each position.

Keywords : Desymmetrization of naphthalene; Bromo rearrangement; Cross coupling; Regioselective transformation

ポリハロアレーンは機能性材料の合成ユニットとして有用であり、その中でも非対称なポリハロアレーンは多彩な分子デザインを可能にする魅力的なユニットである。今回我々はジブロモナフタレンに着目し、最近開発した骨格歪みを利用した Halo-Jacobsen 反応[1)]を用いることで非対称ナフタレンの合成とその変換反応を試みた。

1,8-ジブロモナフタレンに TfOH を作用させたところ、ブロモ基の 1,2-転位が進行し、1,7-ジブロモナフタレンを与えることを見出した。1,7-ジブロモナフタレンは環境の異なる二つのブロモ基を有していることから位置選択的な変換反応が期待される。種々の変換反応の検討を行なったところ、遷移金属触媒を用いたクロスカップリングでは、7 位選択的に反応が進行し、臭素–リチウム交換を経由したアルデヒドへの求核付加反応では、1 位選択的に付加体が得られることを明らかにした。これらの反応性の違いは、各反応部位での立体的および電子的な効果が影響していると考えられる。



(1) *J. Org. Chem.* **2023**, *88*, 9409.

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分子内 C–H アミノ化を鍵反応とする螺旋環内縁部に置換基を有するアザオキサ[6]ヘリセンの合成

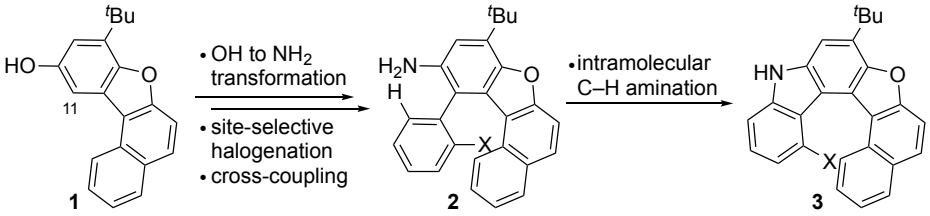
（熊大院自然[1]・熊大院先端[2]・九大先導研[3]）○守田 修士[1]・雷 松[1]・井川 和宣[2]・友岡 克彦[3]・入江 亮[2]

Synthesis of Internal-edge-substituted Azaoxa[6]helicenes by Intramolecular C–H Amination as a Key Reaction ([1]*GSST, Kumamoto University*, [2]*FAST, Kumamoto University*, [3]*IMCE, Kyushu University*) ○Syuji Morita,[1] Song Lei,[1] Kazunobu Igawa,[2] Katsuhiko Tomooka,[3] Ryo Irie[2]

Internal-edge-functionalized helicenes are fascinating chiral molecules because of their potential applications as chiral ligands and organocatalysts. However, their synthesis requires the introduction of a functional group into the sterically hindered internal-edge of helical ring flameworks and thus, has remained a challenge. In order to address this problem, we examined the synthesis of internal-edge-substituted heterohelicenes starting from the naphthobenzofuranol **1**.[1] After various attempts, **1** was successfully converted to the naphthobenzofuranamines **2** with an *o*-substituted phenyl group at the C11 position via the OH to NH_2 transformation, siteselective aromatic halogenation, and crosscoupling reactions. Furthermore, the intramolecular C–H amination of **2** was accomplished to afford the novel azaoxa[6]helicenes **3** with an internal substituent (X). In this presentation, details of the synthesis of **3** will be reported.

Keywords : Heterohelicene; Helical chirality; Stereochemical behavior; C–H amination; Intramolecular heterocyclization

螺旋環の内縁部が官能基化されたヘリセンは，不斉配位子や有機触媒としての応用が期待される興味深いキラル分子である．しかしながら，その合成は立体障害の大きな螺旋環内縁部への官能基の導入が求められるため，これまで困難とされていた．これに対して今回，ナフトベンゾフラノール **1**[1)]を出発原料として内縁置換ヘテロヘリセンの合成を種々検討した．その結果，ヒドロキシ基のアミノ基への変換，位置選択的芳香族ハロゲン化およびクロスカップリングを用いて，**1** を 11 位にオルト置換フェニル基が導入されたナフトベンゾフランアミン **2** に変換することに成功した．さらに，その分子内 C–H アミノ化によって内縁部に置換基（X）を有する新規アザオキサ[6]ヘリセン **3** の合成を達成した．本発表では，ヘテロヘリセン **3** の合成の詳細について報告する．



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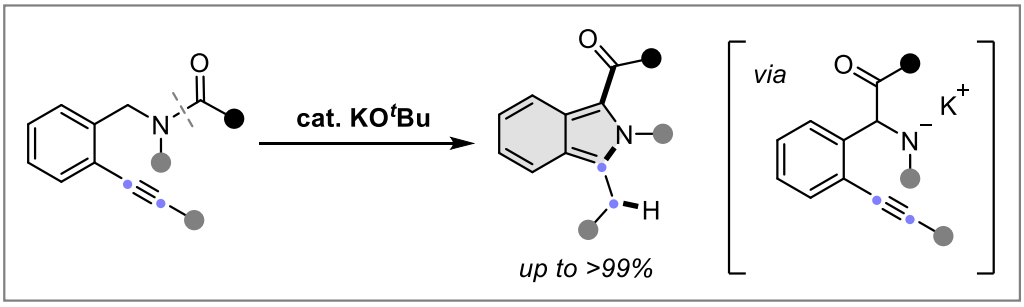
KO^{t}Bu-Catalyzed Transformation of *N*-Benzylamides to Isoindoles via 1,2-Acyl Shift

([1]*Graduate School of Engineering, Osaka Univ.*, [2]*School of Engineering, Osaka Univ.*, [3]*ICS-OTRI, Osaka Univ.*)
○Ryoma Shimazumi,[1] Moe Morimoto,[2] Mamoru Tobisu[1,3]
Keywords: Isoindole; 1,2-Acyl Shift; Amide

Isoindoles, which are aromatic heterocycles containing a benzo-fused pyrrole ring system with 10π electrons,[1] are common motifs found in a range of organic fluorescent materials and biologically active compounds.[2] However, the inherent instability of isoindole derivatives makes their preparation challenging, and simpler and more straightforward methods needs to be developed.[3]

We report herein a KO^{t}Bu-catalyzed method for the synthesis of isoindole derivatives from *N*-benzylamides bearing an ortho alkynyl group, which features an atom economy of 100%.



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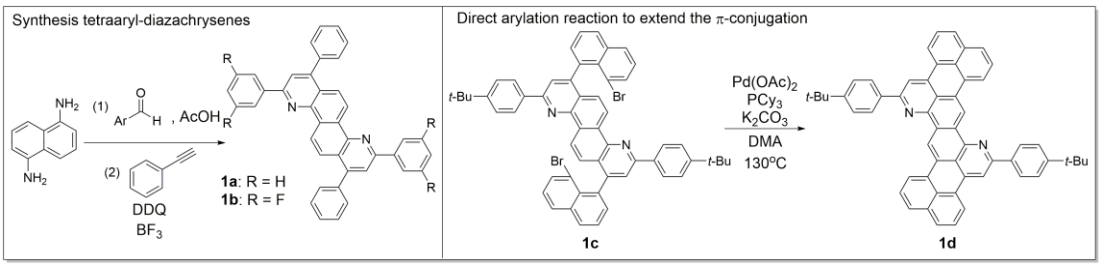
One-pot Synthesis of Novel Tetraaryl-Diazachrysenes via the Povarov Reaction

([1]*Graduate School of Pure and Applied Sciences, University of Tsukuba*) ○Yuanrong Shan,[1] Takaki Kanbara,[1] Junpei Kuwabara[1]

Keywords: aza-PAHs; Povarov reaction; Multicomponent reaction; Diazachrysene

The Povarov reaction is renowned in synthetic chemistry for its efficiency in constructing complex and diverse aza-polycyclic aromatic hydrocarbons (aza-PAHs). These structures are pivotal in various optoelectronic applications, including organic light emitting diodes (OLEDs) and organic field-effect transistors (OFETs). In previous work, the synthesis of 1,7-phenanthroline derivatives via this method has streamlined the production of intricate phenanthroline isomers, serving as optoelectronic materials[1]. This study investigates the Povarov reaction to develop novel tetraaryl-diazachrysenes, expected to exhibit more efficient charge transporting properties.



This research successfully designed and synthesized a series of 4,10-diazachrysene derivatives. After formation of the diimines from the amine and aldehyde, the alkyne, BF_3 and DDQ were added to conduct the Povarov reaction. Compounds **1a**-**1c** were obtained by this method and characterized by ^{1}H NMR and Mass spectroscopies. In addition, single crystal X-ray structure analysis revealed the crystal structure of **1a**. Intramolecular direct arylation[2] of the Br-substituted derivative (**1c**) was investigated to extend the π-conjugation.[3] Optimizing reaction conditions and purification method enable to afford compound **1d**. The structure of **1d** was determined by ^{1}H NMR and MALDI-TOF Mass spectroscopies.

On their optoelectronic properties, compound **1a** was found to serve as a hole-blocking and electron-transporting material for OLEDs. However, compound **1b** was unsuitable for device application due to inadequate film-forming. The optical properties of compound **1d** are currently being investigated to evaluate the effect of extension of π-conjugation.

The Povarov reactions of amine, aldehyde and alkyne have enabled to give tetraaryl-diazachrysenes with desired substituents (F and Br). This method is a facile method for preparation of new aza-PAHs and intermediates for synthesizing complex compounds.

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Friedel-Crafts 型環化反応を駆使した CF_3 基含有ジベンゾフルベン誘導体の合成

（京工繊大工芸）野口 悠星・安井 基博・山田 重之・今野 勉

Synthesis of dibenzofulvene derivatives containing a trifluoromethyl group *via* Friedel-Crafts type cyclization reaction (*Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology*) ○Yusei Noguchi, Motohiro Yasui, Shigeyuki Yamada, Tsutomu Konno

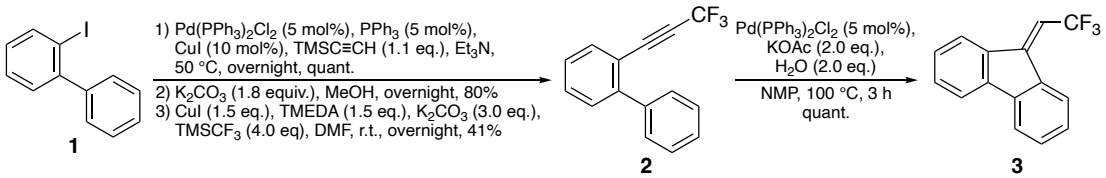
Catalytic cyclization using *o*-alkynyl biaryls is one of the most powerful synthetic tools to construct polycyclic aromatic compounds in a single step, and has been attracted enormous attention from many synthetic chemists. Despite such utilities, there has been no report on the reaction using *o*-perfluoroalkynyl biaryls so far. In this study, we examined a synthetic method for the preparation of various fluorine-containing biaryls and their catalytic cyclization.

o-Alkynyl biaryl, 2-(3,3,3-trifluoro-1-propyn-1-yl)-1,1'-biphenyl could be prepared *via* Sonogashira coupling using *o*-iodobiphenyl and TMSC≡CH, followed by the removal of TMS group and the subsequent trifluoromethylation. Then, treatment of the obtained *o*-alkynyl biaryl with a catalytic amount of $Pd(PPh_3)_2Cl_2$, 2.0 eq. each of KOAc and H_2O in NMP at 100 °C for 3 h gave the desired CF_3-containing dibenzofulvene quantitatively.

Keywords : Fluorine; o-Alkynyl biphenyl; Friedel-Crafts type reaction; 5-exo-dig Cyclization; Dibenzofulvene

o−アルキニルビアリールを用いた触媒的環化反応は，多環芳香族化合物を一挙に構築できる極めて強力な合成法の 1 つであることから，これまでに多くの合成化学者による詳細な研究例が報告されている。同様に，オルト位にペルフルオロアルキニル基を有するビアリールを用いた触媒的環化反応を行えば，これまでにない新規な含フッ素多環芳香族化合物を合成できることから，大きな期待が寄せられるが，未だ報告例は皆無である。これは，基質となる含フッ素ビアリールの調製が困難であることに由来する。そこで本研究では，各種含フッ素ビアール化合物の調製法を確立し，この基質を用いた触媒的環化反応を詳細に検討することにした。

まず，容易に入手可能な *o*−ヨードビフェニル **1** に対し[1]，トリメチルシリルアセチレンを用いた薗頭カップリング反応を行い，続いてトリメチルシリル基を除去した後，Qing らの手法に従い[2]，末端アルキンのトリフルオロメチル化を実行することで，所望の含フッ素ビフェニル **2** が調製できた。こうして得られた基質 **2** に対し，各種環化反応条件を精査したところ，NMP 溶媒中，5 mol%の $Pd(PPh_3)_2Cl_2$ 存在下，基質に対して 2.0 当量の KOAc ならびに水を作用させ，100 ℃ で 3 時間撹拌すると，環化反応が極めてスムーズに進行し，目的の CF_3 基含有ジベンゾフルベン **3** を定量的に与えることがわかった[3]。



1 **2** **3**

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*N*ーアリールオキサミン酸を二官能基化剤とするアルキンのカルバモイルアリール化反応

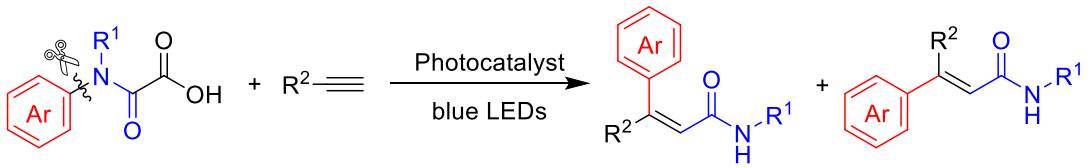
(九大先導研[1]・九大院総理工[2]) ○岳 高帆[2]・呉 迪[2]・塩塚 朗[2]・関根 康平[1,2]・國信 洋一郎[1,2]

Carbamoylarylation of Alkynes Using *N*-Aryl Oxamic Acids as Bifunctional Reagents ([1]*IMCE, Kyushu University*, [2]*IGSES, Kyushu University*) ○Gaofan Yue,[1] Di Wu,[1] Akira Shiozuka,[1] Kohei Sekine,[1,2] Yoichiro Kuninobu[1,2]

Direct bifunctionalization of alkynes is one of the most efficient approaches toward the synthesis of multi-substituted alkenes. Our group has recently developed visible-light induced carbamoylarylation of alkenes via the C(aryl)–N bond cleavage of *N*-aryl oxamic acids. In this reaction, the addition of a carbamoyl radical to an alkene, resulting in 1,4-aryl rearrangement via the cleavage of C(aryl)–N bond to afford arylpropanamides. In this study, we found that the above-mentioned carbamoylarylation was also applicable for alkynes to give the corresponding acrylamide derivatives in high yields.

Keywords : C–N Bond Cleavage; Carbamoylarylation; Aryl Migration; Alkyne; Organic Photochemical Reaction

アルキンの直接的な二官能基化は、多置換アルケンの効率的な合成法として有用である。我々は、これまでに、*N*ーアリールオキサミン酸の芳香族炭素ー窒素結合切断を伴うアルケンの可視光駆動型カルバモイルアリール化反応を開発した。この反応では、カルバモイルラジカルのアルケンへの付加、それに続く芳香族炭素ー窒素結合の切断を伴う 1, 4-アリール転位が進行し、アリールプロパンアミドが得られたものと想定している。今回、アルキンに対しても、上述の *N*ーアリールオキサミン酸を用いるカルバモイルアリール化反応が適用でき、対応するアクリルアミド誘導体が高収率で得られたので報告する。



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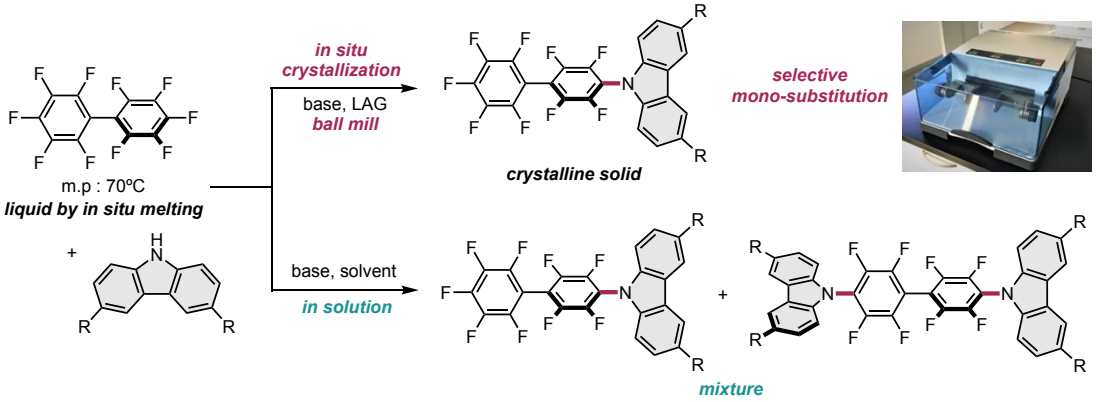
系中結晶化を利用したモノ選択的な芳香族求核置換反応

(北大院工[1]・WPI-ICReDD[2]) ○川村 聡太[1]・久保田 浩司[1,2]・伊藤 肇[1,2]
Mono-Selective Mechanochemical Nucleophilic Aromatic Substitution Enabled by In-situ Crystallization. ([1]*Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*) ○Sota Kawamura,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Nucleophilic aromatic substitution reactions are widely used for the preparation of organic materials and pharmaceuticals. However, it is difficult to synthesize a mono-substituted product with high selectivity for substrates bearing several potentially reactive sites, often leading to mixtures of multi-substituted products. Recently, our group reported a mechanochemical mono-selective arylation of dibromoarene by *in situ* crystallization.[1] In this approach, the selectivity is controlled by the reactivity difference in which liquid starting materials are more reactive than solid mono-arylated products under solvent-less mechanochemical conditions. In this study, we found that the mono-selective nucleophilic aromatic substitution of polyfluoroarenes with carbazole-based nucleophiles proceeded by utilizing analogous *in situ* crystallization strategy.
Keywords: Mechanochemistry, Ball mill, Carbazole, In-situ crystallization, Mono-selective

芳香族求核置換は、機能性材料や医薬品の合成などに幅広く用いられており、非常に重要な反応である。しかし、反応点を複数有する基質においては、一置換体を選択的に得ることは困難であり、多くの場合、多置換体との混合物として得られる。当研究室は以前、系中結晶化を利用したジブロモアレーンのモノ選択的アリール化反応を報告している[1]。無溶媒メカノケミカル反応条件においては、モノアリール化で生じる固体のモノアリール化体が、液体の出発原料に比べて反応性が低い。この反応性の違いによってモノ選択性が実現している。本研究では、この系中結晶化を利用した合成ストラテジーにより、カルバゾール類を求核剤として用いたポリフッ素芳香族化合物のモノ選択的芳香族求核置換反応の開発に成功した。



1) T. Seo, K. Kubota, H. Ito, *J. Am. Chem. Soc.* **2020**, *142*, 9884.

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スルホキシイミンの反応性に基づく 3 置換アルケンの立体選択的合成

（阪大院工[1]・阪大工学部[2]）○安井 孝介[1]・富島 佑一郎[2]・平野 康次[1]

Stereoselective Synthesis of Trisubstituted Alkenes Enabled by the Reactivity of Sulfoximine

([1]*Graduate School of Engineering, Osaka University,* [2]*School of Engineering, Osaka University*) ○Kosuke Yasui,[1] Yuichiro Tomishima,[2] Koji Hirano[1]

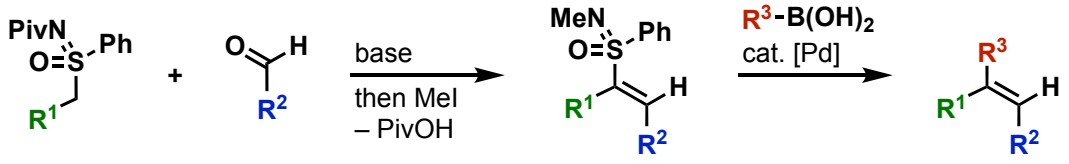
Although multi-substituted alkenes are pervasive structures in natural products and functional materials, their stereoselective construction is still challenging. Transition-metal-catalyzed cross-coupling reaction is one of the most reliable methods for the formation of this structure. However, preparation of the substrate, alkene with a leaving group, is also challenging, decreasing the synthetic utility of cross-coupling reactions.

Based on the hypothesis that condensation reaction, providing multi-substituted alkenes with a leaving group, should enhance the utility, we focused on the use of sulfoximine. As a result, we developed the condensation of alkyl sulfonimines with aldehydes, forming vinyl sulfoximines in a stereoselective manner. Furthermore, we developed a Pd-catalyzed cross-coupling reaction between the resulting vinyl sulfoximines and boronic acid, providing trisubstituted alkenes via the cleavage of the C–S bond. Since the corresponding vinyl sulfone did not undergo these reactions at all, a series of transformations is peculiar to sulfoximine.

Keywords : sulfoximine; condensation; cross-coupling; trisubstituted alkenes

多置換アルケンは天然物や機能性分子に広く見られる一方，その立体選択的な合成は依然として難しい．多置換アルケンを得る手法として，遷移金属触媒によるクロスカップリング反応が有効である．しかし，原料である脱離基をもつ多置換アルケンも同様に入手しがたいことがボトルネックであり，その有用性を最大限に活かす上で喫緊の課題となっている．

本研究では，脱離基をもつ多置換アルケンを縮合で合成できれば，その有用性を十分に活かせると考え，スルホキシイミンに着目した．その結果，アルキルスルホキシイミンとアルデヒドとの縮合によるビニルスルホキシイミンの立体選択的な合成法を見出した．ビニルスルホキシイミンの C–S 結合は Ni 触媒と有機亜鉛試薬により変換可能である．[1]より入手容易で安定な有機ホウ素試薬で代用できれば好ましいと考え，反応条件を精査した．その結果，適切な配位子をもつ Pd 触媒により有機ホウ素試薬を用いて 3 置換アルケンを立体選択的に合成できることを見出した．一連の変換は対応するスルホンでは実現できない，スルホキシイミンに特有のものである．



Piv = CO*t*Bu

1) Erdelmeier, I.; Gais, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 1125.

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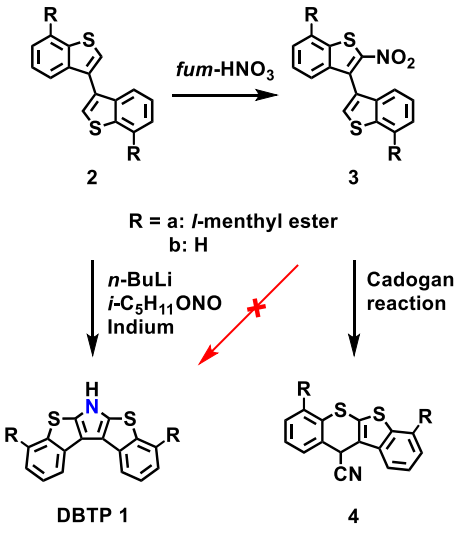
Cadogan 反応を利用したジベンゾチオフェノピロールの合成

（愛媛大院理工[1]・愛媛大 ADRES[2]）○谷岡雄真[1]・森 重樹[2]・髙瀬雅祥[1]・宇野英満[1]
Synthesis of di(1-benzothiopheno)pyrrole *via* Cadogan reaction (*[1]Graduate School of Science and Engineering and [2]Advanced Research Support Center (ADRES), Ehime University*)
○Yuma Tanioka,[1] Shigeki Mori,[2] Masayoshi Takase,[1] and Hidemitsu Uno[1]

The development of new synthetic methods to construct carbazole analogues and elucidation of their physical properties are desired due to their distinctive optical and electronic properties.[1] The Cadogan cyclization is one of the most useful method to synthesize carbazoles. In 2008, Qi *et al.* reported the synthesis of di(1-benzothiopheno)[2,3-*b*:3′,2′-*d*]pyrrole (**DBTP**) *via* the Cadogan reaction.[2] However, the synthesis of **DBTP** from **3** was unsuccessful by our hands. Therefore, we examined the products and developed a method to construct **DBTP** skeleton. The Cadogan cyclization with ester substituents at the 7- and 7'-positions of **3a** afforded the desired **DBTP 1a** in low yield. A similar reaction with pristine **3b** afforded thiophene-ring-opening products **4b** and further reacted compounds. The structure of the ring-opening products were characterized by single-crystal structure analysis and the generation mechanism of the products was deduced. Unsubstituted **DBTP 1b** was obtained from **2b** in a one-pot three-step reaction.
Keywords : Cadogan cyclization, di(1-benzothiopheno)pyrrole

カルバゾール類は興味深い光学・電子的特性を示すことから、新たな類縁体の構築と物性解明が望まれている[1]。カルバゾール骨格を構築する最も有用な合成法の一つに Cadogan 反応が知られている。2008 年、Qi らによって Cadogan 反応を用いたジ（1-ベンゾチオフェノ）[2,3-*b*:3′,2′-*d*]ピロール (**DBTP**) の合成が報告された[2]。しかし既報に従って化合物 **3** から **DBTP** の合成を試みたところ、**DBTP** とは異なる複数の生成物が得られた。そこで、生成物について調査を行うとともに、Cadogan 反応を用いた新たな **DBTP** 骨格の構築手法の開発を行った。



7 位および 7'位にエステルを有する **3a** を用いて Cadogan 反応を試みたところ、低収率で **DBTP 1a** が得られた。一方、エステル基を持たない無置換体 **3b** では、**4b** を主生成物とするチオフェン環が開環した複数の化合物が得られた。それら化合物の構造は単結晶構造解析により明らかにし、生成機構を推定した。無置換 **DBTP 1b** は、**2b** から３段階の反応をワンポットで行うことで得られた。

[1] L. A. T. Allen *et al., Org. Biomol. Chem.,* **2023**, *21*, 8956.
[2] T. Qi *et al*., *Chem. Commun*., **2008**, *46*, 6227.

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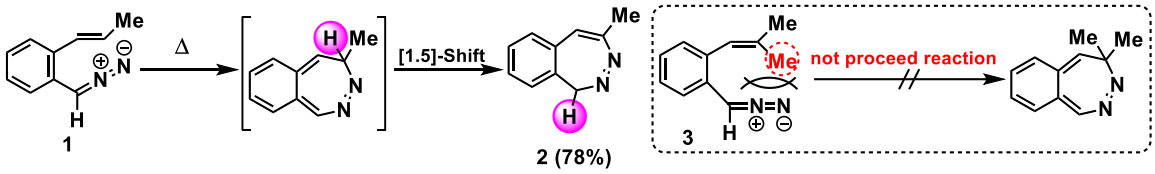
o-ビニルベンジルジアゾエステルからの 2,3-ベンゾジアゼピン形成反応

（工学院大学 先進工[1]）○直井　一樹[1]・黒木智也[1]・南雲　紳史[1]
Formation of 2,3-benzodiazepin from o-vinylbenzyldiazoester ([1]*School of Advanced Engineering, Kogakuin University*) ○Kazuki Naoi[1], Tomoya Kuroki[1], Shinji Nagumo[1]

We found that the treatment of aryl glycine hydrazonoester having dibromoethylene at the *o*-position of aryl group with MnO_2 in MeOH occurred in the sequence of oxidation, electrocyclization and 1,2-bromide Shift to give 2,3-benzodiazepins in a good yield.

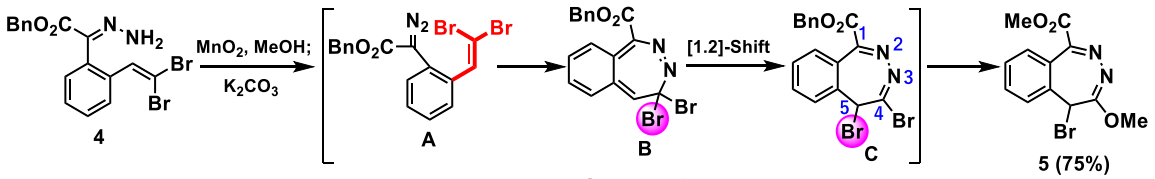
Keywards : 2,3-benzodiazepin, 1,2-bromide Shift

Sharp らは、ジアゾ化合物 **1** の電子環状反応と続く[1,5]-水素原子移動による 2,3-ベンゾジアゼピン形成反応を報告している(Scheme 1)[1]。この環化反応は立体的な影響を強く受け、**3** のような三置換アルケンや *cis*-二置換アルケンでは進行しない。



Scheme 1

これに対して我々は、ジブロモエチレンを有するヒドラゾン **4** に対しメタノール中、二酸化マンガンおよび炭酸カリウムを作用させると 2,3-ベンゾジアゼピン **5** が得られることを見出した(Scheme 2)。ヒドラゾン **4** の酸化により生じたジアゾ体 **A** は三置換アルケンを持つにもかかわらず、環化反応が円滑に進行し **B** となる。続いて、臭素原子の[1.2]転位により **C** が生じる。**C** は単離すると徐々に分解することが分かったので、反応系中に炭酸カリウムを加えた。その結果、エステル交換とともに 4 位の臭素原子がメタノールに置換し、75%の収率で **5** が生成した。



Scheme 2

1） John T. Sharp.; David P. Munro., *Tetrahedron. Lett.*, 1980. **21**. 4109-4110.

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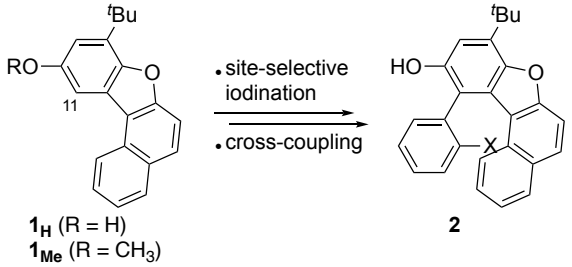
ナフトベンゾフラノール誘導体の位置選択的ハロゲン化とクロスカップリングによる新規ヘテロビアリール類の合成

(熊大院自然[1]・熊大院先端[2]・九大先導研[3]) ○雷 松[1]・中島 涼菜[1]・守田 修士[1]・井川 和宣[2]・友岡 克彦[3]・入江 亮[2]

Synthesis of Novel Heterobiaryls via Siteselective Halogenation and Crosscoupling Reactions of Naphthobenzofuranol Derivatives ([1]*GSST, Kumamoto University*, [2]*FAST, Kumamoto University*, [3]*IMCE, Kyushu University*) ○Song Lei,[1] Suzuna Nakashima,[1] Shuji Morita,[1] Kazunobu Igawa,[2] Katsuhiko Tomooka,[3] Ryo Irie[2]

Heterobiaryls with axial chirality are useful as structural units of various chiral ligands and organocatalysts, and therefore, it is an important issue to design and construct novel heterobiaryl skeletons. In this context, we have previously reported on the synthesis of a chiral C_2-symmetric heterobiarenol derivative via oxidative homocoupling of the naphthobenzofuranol $\mathbf{1_H}$ (R = H).[1] In this study, we designed novel chiral unsymmetrical heterobiaryl molecules **2** with an *o*-substituted phenyl group at the C11 position of $\mathbf{1_H}$ and addressed their synthesis. After various attempts, we were able to develop an efficient synthetic method of the heterobiaryls **2** via siteselective iodination at the C11 position of methyl ether $\mathbf{1_{Me}}$ (R = Me) and crosscoupling of the resulting iodinated naphthobenzofuran as the key reactions. Details of the synthesis of **2** and their stereochemical stability will be reported in this presentation.
Keywords : Heterobiaryl; Benzofuran; Siteselective halogenation; Crosscoupling

軸不斉を有するヘテロビアリールは, 様々なキラル配位子や有機分子触媒の構成要素として有用であり，その新規骨格の創出は重要な課題である．先に我々は，ナフトベンゾフラノール $\mathbf{1_H}$（R＝H）の酸化的ホモカップリング反応によるキラルな C_2 対称ヘテロビアレノール誘導体の合成について報告している[1)]．これに対して今回，$\mathbf{1_H}$ のC11位にオルト位置換フェニル基を有するキラルな非対称ヘテロビアリール分子 **2** を新たに設計し, その合成を目指した. 種々検討した結果, メチルエーテル $\mathbf{1_{Me}}$ (R＝CH_3) の C11 位選択的なヨード化とそれにより得られるヨード体のクロスカップリングを鍵反応とする **2** の効率的な合成法の開発に成功した．本発表では，**2** の合成の詳細と立体化学的安定性について報告する．



1) 中島涼菜, 荒江祥永, 井川和宣, 友岡克彦, 入江亮, 日本化学会第 103 春季年会, K703-3pm-12 (2023).

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電子供与性基を導入したジアザペロピレンの合成と性質

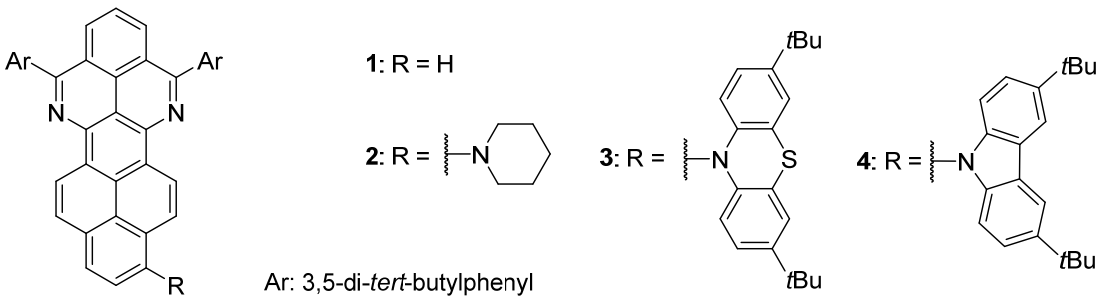
（阪公大院理[1]・阪市大院理[2]）稲田 秀真[1]・政二 康文[2]・舘 祥光[1,2]・○小嵜 正敏[1,2]
Syntheses and Properties of Diazaperopyrenes with Electron-donating Groups ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*Graduate School of Science, Osaka City University*) Hotsuma Inada,[1] Yasufumi Masani,[2] Yoshimitsu Tachi,[1,2] ○Masatoshi Kozaki[1,2]

Previously, we reported the synthesis and properties of 4,14-ditolyl-5,13-diazaperopyrene **1**. In this work, we synthesized 5,13-diazaperopyrenes with electron-donating substituents, such as piperidine **2**, phenothiazine **3**, and carbazole unit **4** at the 8-position. We prepared pyrene derivatives with electron-donating units at the 3-position and constructed the peropyrene skeletons using our previously reported method. The UV-Vis spectra of **1** and **3** in toluene exhibited low energy absorption bands at maximum wavelengths of 487 and 483 nm, respectively. Low energy bands of **2** and **4** were observed at maximum wavelengths of 519 nm and 497 nm, respectively. Upon excitation of the toluene solution of **2** at 350 nm, strong fluorescence was observed at a maximum wavelength of 573 nm (Φ_f = 0.91). The synthesis and properties will be discussed in detail.

Keywords : Peropyrene; Donor; Acceptor; Absorption; Emission

最近ペロピレン類の効率的な合成法が開発され、良好な半導体特性や光物理特性を有する誘導体が活発に探索されている。我々は先に 5, 13-ジアザペロピレン **1** の簡便な合成法を報告しており[1]、本研究ではこの方法を応用してドナーーアクセプター型のペロピレン誘導体 **2-4** を合成しその性質を解明した。

ピペリジン、3,6-ジ-*tert*-ブチルフェノチアジン、3,6-ジ-*tert*-ブチルカルバゾールをそれぞれ 2-ブロモピレンと Buchwald-Hartwig アミノ化反応させることで対応する 3-置換ピレンを得た。先に報告した合成法を応用して、これらの化合物からジアザペロピレン **2-4** を合成した。合成した化合物はいずれも有機溶媒に良好な溶解度をもっていた。トルエン溶液の紫外可視吸収スペクトルを測定すると **3** の低エネルギー吸収の極大波長（λ_{max} = 483 nm）は **1**（λ_{max} = 487 nm）とほぼ同じ値であったが、**2**（λ_{max} = 519 nm）と **4**（λ_{max} = 497 nm）ではより長波長に低エネルギー吸収が観測された。また、**2** のトルエン溶液を励起（λ^{ex} = 350 nm）すると 573 nm に極大波長をもつ蛍光（Φ_f = 0.91）が観測された。講演では化合物の構造と性質を詳細に述べる。



1) 日本化学会第 103 回春季年会、P3-2vn-22、稲田秀真、舘祥光、小嵜正敏

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-4am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kazuya Kanemoto, Yohei Ogiwara

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1141-4am-01]
Synthesis of Thiaphenanthridinones

○Keisuke Nakamura[1], Minori Suzuki, Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1141-4am-02]
Substituent Effects in the Synthesis of Dihydrobenzene Deriratives from Thiophene Dioxides and Styrenes

○Kayoko Ohira[1], Koyo Numata[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1141-4am-03]
C4 Arylation of Benzothiazoles via Pummerer Activation

○Ryota Wakabayashi[1], Shuo Wang[1], Takashi Kurogi[1], Hideki Yorimitsu[1] (1. Kyoto University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1141-4am-04]
Synthesis and Properties of Benzodithiophene Derivatives by π-Extension Reaction

○Yuki Takenaka[1], Hideji Osuga[1,2], Hidefumi Sakamoto[1,2] (1. Graduate School, Wakayama University, 2. Wakayama University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1141-4am-05]
Preparation of unsymmetrical aminodisulfides from *N*-dithiophthalimides with amines

○Hayato Asanuma[1], Kazuya Kanemoto[1] (1. Tohoku university)

9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
Break

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1141-4am-06]
Development of novel sulfurizing reagents with an adamantane-like structure

○Mizuki Oyanagi[1], Tomoya Sugai[1,2], Noriki Kutsumura[1,2] (1. College of Chem., Sch. Sci. Eng., Univ. of Tsukuba, 2. WPI-IIIS, Univ. of Tsukuba)

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Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1141-4am-07]
Development of dehydrogenative synthesis of alkenyl isothiocyanates
○Bumpei Maeda[1], Kei Murakami[1] (1. Kwansei University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1141-4am-08]
Development of Asymmetric Synthesis of Sulfinamidines
○Kana Shigenai[1], Saori Tsuzuki[2], Taichi Kano[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2. Graduate School of Science, Kyoto University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1141-4am-09]
Fe-catalyzed synthesis of thiophenes from alkyne and elemental sulfur and its application to selenophene synthesis
○Shurika Innami[1], Kento Ishida[1], Yohei Ogiwara[1], Norio Sakai[1] (1. Tokyo University of Science)

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
Break

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1141-4am-10]
Synthesis of dibenzyl selenides from benzyl esters by using elemental selenium and a hydrosilane
○Yasushi Kino[1], Kento Ishida[1], Norio Sakai [1] (1. Tokyo University of Science)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1141-4am-11]
Synthesis of Selenophene Derivatives via Selenium Cation-Mediated Sequential C-Se Bond Formation
○Iwamoto Hiroki[1], Kojima Yuki[1], Yasui Kosuke[1], Hirano Koji[1] (1. The Univ. of Osaka)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1141-4am-12]
Development of nitrogen-terminated cascade cyclization reactions using a recyclable selenenyl iodide
○Jun Kikushima[1], Takaaki Nakada[1], Satoru Kuwano[1], Kei Goto[1] (1. Tokyo Institute of Technology)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1141-4am-13]
Preparation and Electrochemical Properties of Subphthalocyanine with a Diselenet Ring
○Takeshi Kimura[1] (1. Iwate University)

Japanese

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11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1141-4am-14]

Model study of reactive intermediates involved in selenoprotein biosynthesis using molecular cavities.

○Arashi Kudo[1], Satoru Kuwano[1], Kei Goto[1] (1. Tokyo Institue of Technology)

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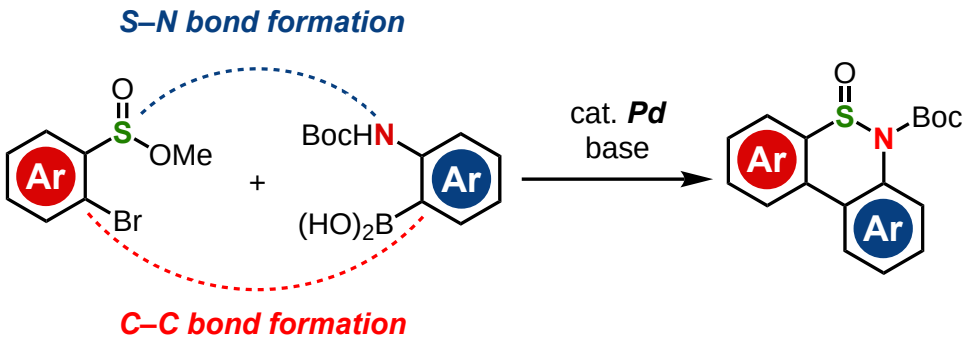
チアフェナントリジノン類の新規合成法の開発

（東理大先進工）○中村 圭佑・鈴木 美之里・吉田 優
Synthesis of Thiaphenanthridinones (*Tokyo University of Science*) ○Keisuke Nakamura, Minori Suzuki, Suguru Yoshida

We found a novel method to synthesize thiaphenanthridinones, sulfur analogues of bioactive phenanthridinones. Due to the difficulty in the formation of cyclic sulfinamides, it is not easy to synthesize thiaphenanthridinones. Indeed, sulfinate esters having 2-bromoaryl groups reacted with 2-aminophenylboronic acid derivatives catalyzed by palladium to provide thiaphenanthridinones by bromo selective C–C bond formation followed by the cyclizaton. This method enabled us to synthesize cyclic sulfinamides bearing various functional groups.
Keywords : Phenanthridinone; Analog; Bioactive compound; Suzuki-Miyaura cross coupling; Organosulfur compounds

カルボニル基と窒素原子を有する複素環式化合物であるフェナントリジノンは、生物活性化合物として注目されている[1]。生物活性化合物の構造の一部分を別の原子で置換したアナログ体は、近年の創薬のための化合物ライブラリーの構築に重要な役割を果たしている。フェナントリジノンのカルボニル炭素を硫黄原子に置き換えた硫黄アナログであるチアフェナントリジノンにも生物活性が期待されるが、環状スルフィンアミド部位の形成が困難であり、合成法はほとんど研究されてこなかった。今回、オルト位にブロモ基を持つスルフィン酸エステルと、オルト位にアミノ基を有するボロン酸からチアフェナントリジノンの合成に成功した。具体的には、鈴木・宮浦カップリングによってブロモ基選択的な C–C 結合形成を試みたところ、続く S–N 結合形成も一挙に進行し、チアフェナントリジノンを合成できた。



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日本化学会 第104春季年会 (2024)

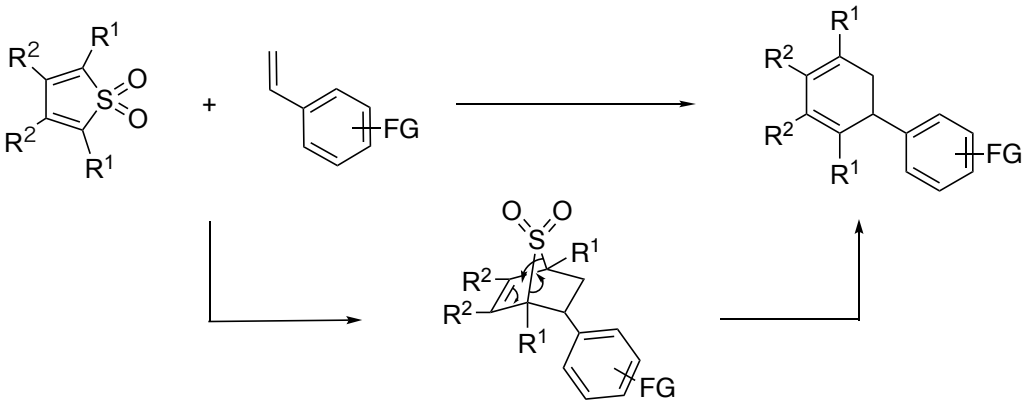
チオフェンジオキシドとスチレンを用いたジヒドロベンゼン類の合成における置換基効果

（東理大先進工）大平佳代子・沼田向陽・吉田優
Substituent Effects in the Synthesis of Dihydrobenzene Deriratives from Thiophene Dioxides and Styrenes (*Tokyo University of Science*) ○Kayoko Ohira, Koyo Numata, Suguru Yoshida

Inverse electron demand Diels－Alder (IEDDA) reactions are of great importance in click chemistry. Herein, we clarified substituent effects in the synthesis of dihydrobenzenes via IEDDA reactions from various thiophene dioxides and styrenes by using kinetic studies and DFT calculations.

Keywords : Thiophene dioxide; Inverse electron demand Diels–Alder reaction; Substituent effects; Kinetic studies; DFT calculations

逆電子要請型 Diels－Alder 反応はクリックケミストリーなどにおける重要な手法である。今回我々は、チオフェンジオキシドとスチレンとの逆電子要請型 Diels–Alder 反応を経るジヒドロベンゼン合成に着目し、反応速度の測定や DFT 計算による反応性の評価を行うことで、置換基の電子状態が反応性に与える影響を明らかにした。具体的には、様々な電子状態の置換基をそれぞれ持つスチレンとチオフェンジオキシドとを反応させることで、置換基が反応速度に与える影響を明らかにできた。本研究によって得られる知見をもとに、多彩なチオフェンジオキシドとアルケン類との反応において、反応性の高精度な予測が可能になると期待される。



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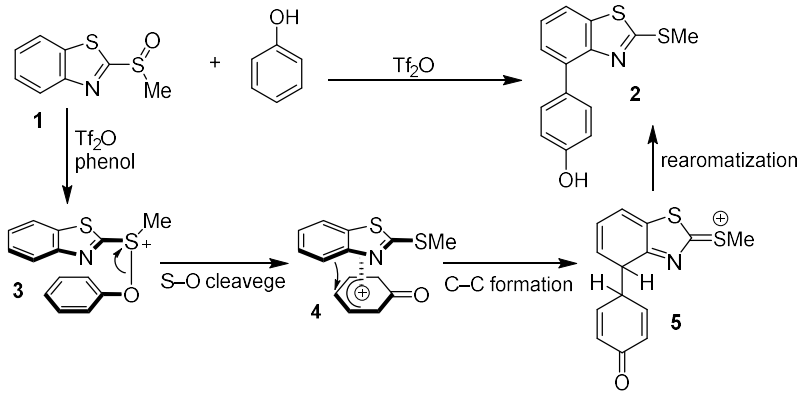
プメラー型活性化によるベンゾチアゾールの 4 位アリール化

（京大院理）○若林 亮汰・王 爍・黒木 尭・依光 英樹
C4 Arylation of Benzothiazoles via Pummerer Activation (*Graduate School of Science, Kyoto University*) ○Ryota Wakabayashi, Shuo Wang, Takashi Kurogi, Hideki Yorimitsu

2-Sulfinylbenzothiazole **1** reacted with phenol in the presence of trifluoromethanesulfonic anhydride to afford C4 arylated product **2**. The mechanistic study by DFT calculations showed that the C4 arylation reaction proceeds via the formation of π-complex **4** as an intermediate: Activated sulfoxide is attacked by phenol to form sulfonium intermediate **3**. The C–C bond formation proceeds via nucleophilic attack of the benzothiazole moiety to the phenoxonium cation in π-complex **4**. Rearomatization of **5** gives the C4 arylated product **2**.
Keywords : Benzothiazoles; Sulfoxide; Pummerer reaction; Phenol; Sigmatropic rearrangement

ベンゾチアゾール骨格は生物活性物質によく見られ、その官能基化法の開発は医農薬合成への展開が期待できる。しかし、チアゾール環部分の 2 位炭素での官能基化はよく知られているが、ベンゼン環部分での官能基化は容易ではない。今回我々は、以前報告したスルフィニルアレーンとフェノールからの脱水型ビアリール合成[1]を利用し、ベンゾチアゾールのベンゼン環部分でのアリール化を達成した。

トリフルオロメタンスルホン酸無水物存在下、2-スルフィニルベンゾチアゾール **1** とフェノールを反応させたところ、ベンゾチアゾールの 4 位に *p*-ヒドロキシフェニル基が導入されたビアリール **2** が得られた。計算化学による反応機構解析を行い、本反応がπ錯体 **4** を中間体として、転位が段階的に進行することが分かった。つまり、活性化されたスルホキシドに対するフェノールの求核攻撃により、中間体 **3** が生成する。その後 S–O 結合の不均等開裂によってπ錯体 **4** が生じる。ベンゾチアゾールによるフェノキソニウムカチオンへの求核攻撃、続く中間体 **5** の再芳香族化によって 4 位アリール化生成物 **2** が得られる。



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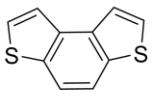
π拡張反応を利用したベンゾジチオフェン誘導体の合成と物性

（和歌山大院システム工）○竹中　裕貴・大須賀　秀次・坂本　英文
Synthesis and Properties of Benzodithiophene Derivatives by π-Extension Reaction (*Graduate School of Systems Engineering, Wakayama University*) ○Yuki Takenaka, Hideji Osuga, Hidefumi Sakamoto

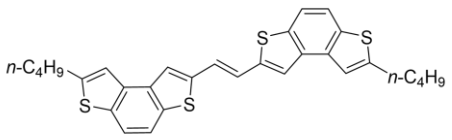
We have already reported the synthesis of benzodithiophene (BDT) derivatives and their use in the organic semiconductor layers of organic field-effect transistors (OFETs). The highest hole mobility has been exhibited by OFETs made from the alkylated BDT derivatives ($2C_4$-BDT-dimer) used in organic semiconductor layers. Mobilities can be improved by fusing BDT with more aromatic rings, such as thiophene, in order to extend the π-conjugate plane. Recently, a synthetic method for obtaining fused thiophene derivatives by heating alkynes and sulfur in organic solvents has been reported. We will report the synthesis of thiophene-fused BDT derivatives by using this synthetic method. The properties of these compounds will also be reported.

Keywords : π-Extension Reaction; Fused Polycyclic Aromatic Compounds; Benzodithiophene; Fused Thiophene; Sonogashira Coupling Reaction.

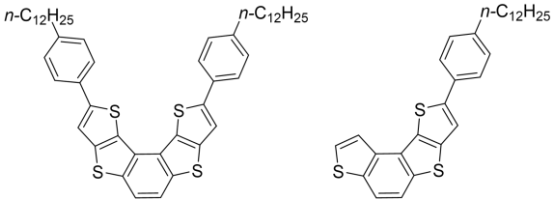
我々はこれまでに、ベンゾジチオフェン（BDT）の高い熱安定性及び平面性を利用して、アルキル化したBDT-dimer誘導体を有機半導体層に用いたところ、$2C_4$-BDT-dimerから作製した有機電界効果トランジスタ（OFET）が最大の正孔移動度（1.8 $cm^2 V^{-1} s^{-1}$）を示すことを明らかとしてきた。BDTにチオフェン環などの芳香環を縮環してπ共役平面を拡張することにより、移動度のさらなる向上が期待できる。最近、アルキンと硫黄を有機溶媒中で加熱攪拌することで、縮環チオフェン誘導体を得る合成方法が報告されている。そこで本研究では、まずヨード基を導入したBDTとアルキル化したフェニルアセチレン誘導体との間で薗頭カップリング反応を行い、さらに硫黄を用いたπ拡張反応によってBDTにチオフェン環が縮環した誘導体の合成検討を行った。合成の詳細とその物性について報告する予定である。



BDT



$2C_4$-BDT-dimer



BDTにチオフェンが縮環した誘導体

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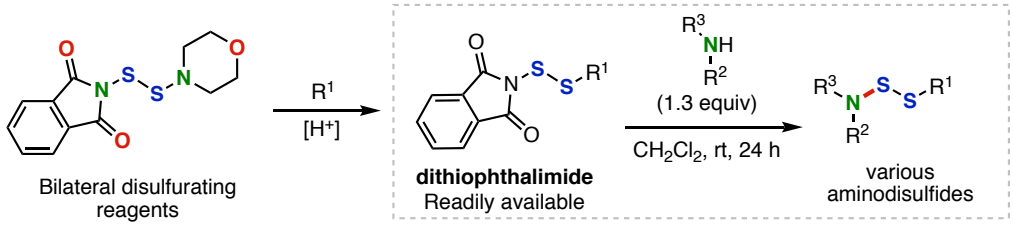
N-ジチオフタルイミドとアミンを用いる非対称アミノジスルフィドの合成

（東北大院薬 [1]）○浅沼 隼人 [1]・金本 和也 [1]
Preparation of unsymmetrical aminodisulfides from *N*-dithiophthalimides with amines ([1]*Graduate School of Pharmaceutical Sciences, Tohoku University*) ○Hayato Asanuma,[1] Kazuya Kanemoto[1]

Synthetic methods for unsymmetrical aminodisulfides are greatly needed due to their applications in drug discovery and linker chemistry. In this work, we developed an amination reaction of *N*-dithiophthalimides for the divergent synthesis of unsymmetrical aminodisulfides. The reaction proceeds under mild conditions and provides the aminodisulfides in excellent yields without cleaving the disulfide bond. The *N*-dithiophthalimides are readily available from several bilateral disulfurating reagents such as *N*-(morpholine-4-dithio)phthalimide and *N,N'*-thiobisphthalimide, and the broad substrate scope of this reaction allows for the modular synthesis of a variety of unsymmetrical aminodisulfides in two-step operations.
Keywords : Disulfide; Amine; Amination; S–N bond formation; Modular synthesis

アミノジスルフィドは，創薬化学やリンカー化学などの分野での利用が期待される化合物群である．一方で，非対称な誘導体の合成には課題が残されており，幅広く利用できる新たな合成手法の開発が求められている．

このような背景のもとで，今回我々は，*N*-ジチオフタルイミドのアミノ化を利用した非対称アミノジスルフィド誘導体の多様性合成法の開発に取り組んだ.[1] 検討の結果，*N*-ジチオフタルイミドとアミンをジクロロメタン中，室温で撹拌するのみで，非対称アミノジスルフィドを効率よく合成できることが明らかとなった．本手法は，環状および直鎖状のアミンやアミノ酸誘導体に適用できるほか，LiBr を触媒量添加することで求核性の低いアニリン誘導体を利用することも可能であった．また，多彩な置換基を有する *N*-ジチオフタルイミドにも適用できた．このような優れた基質適用範囲に加えて，*N*-ジチオフタルイミドは，二度の置換基導入が可能なジスルフィド化試薬から容易に合成できるため,[2] 幅広い置換基の組み合わせのアミノジスルフィドを二段階で多様性合成することが可能となった．



1) Asanuma, H.; Kanemoto, K. *Org. Lett.* **2023**, DOI: 10.1021/acs.orglett.3c03419.
2) Asanuma, H.; Kanemoto, K.; Watanabe, T.; Fukuzawa, S.-i. *Angew. Chem. Int. Ed.* **2023**, *62*, e202219156.

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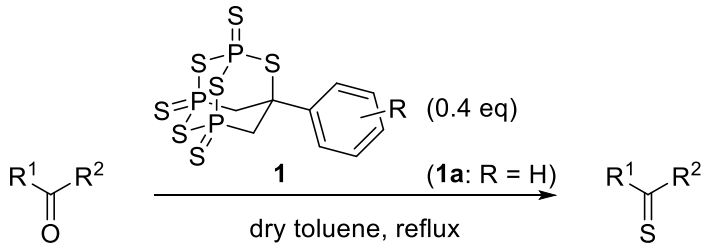
新規アダマンタン型硫化剤の開発

（筑波大理工）○小柳 瑞貴・須貝 智也・沓村 憲樹
Development of novel sulfurizing reagents with an adamantane-like structure (*School of Science and Engineering, University of Tsukuba*) ○Mizuki Oyanagi, Tomoya Sugai, Noriki Kutsumura

The thiocarbonyl group, widely found in a variety of pharmaceuticals and agrochemicals, is generally obtained by sulfurizing the carbonyl group using Lawesson's reagent (LR) or phosphorus pentasulfide (P_4S_{10}). However, both reagents emit a foul odor. On the other hand, our group discovered an odorless adamantane-like compound, **1a** (R = H), which can convert a ketone or an amide into a thioketone or a thioamide, respectively, although it was successful in only one instance for each conversion. To demonstrate the efficacy of **1** as a sulfurizing reagent, this study investigates the substrate scope and functional group tolerance, focusing on sulfurization reactions with various carbonyl compounds, including amides. Initially, we reacted **1a** with various amides, and it exhibited broad substrate generality. Subsequently, we explored the sulfurization of a range of carbonyl compounds using **1a**. In this presentation, details of the study and the potential of our adamantane-like compounds **1** as innovative sulfurizing reagents will be reported.
Keywords : Sulfurizing reagent; Sulfurization; Adamantane-like structure; Odorless

チオカルボニル基は様々な医薬品や農薬の構造中に広く見られる。チオカルボニル基は一般的に、カルボニル基を Lawesson’s 試薬(LR)や五硫化リン(P_4S_{10})と反応させることによって得られるが、これらは共に不快な臭いを発する。一方、当研究室で見出した新しい無臭のアダマンタン型化合物 **1a** (R = H)は、それぞれ 1 例だけではあるが、ケトンやアミドを対応するチオケトンやチオアミドへ変換することができた[1]。**1** の硫化試薬としての有用性を証明するため、本研究では本試薬の基質適用範囲や官能基許容性の調査を目的とし、アミドを始めとした様々なカルボニル化合物に対して硫化反応の検討を実施することとした。我々はまず、**1a** と様々なアミド化合物を反応させた。その結果、硫化剤 **1a** はアミドに対しては広範な基質一般性を示した。次に、**1a** を用いて様々なカルボニル化合物の硫化反応を検討した。本発表では本研究の詳細と我々のアダマンタン型化合物の新規硫化剤としての可能性について報告する。



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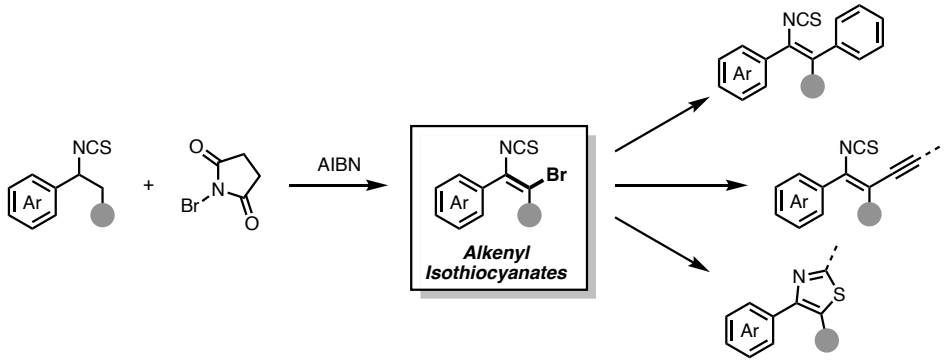
アルケニルイソチオシアネートの脱水素型合成法の開発

（関西学院大理工）○前田 文平・村上 慧
Development of dehydrogenative synthesis of alkenyl isothiocyanates (*Department of Chemistry, Graduate School of Science and Engineering, Kwansei Gakuin University*) ○ Bumpei Maeda, Kei Murakami

Isothiocyanates (ITCs) exhibit various bioactivities such as anticancer and antifungal properties thus, they are expected to be used as pharmaceuticals and agrochemicals. Additionally, numerous transformations of ITCs are developed, therefore, they are used as a valuable platform for introducing nitrogen-containing functional groups and heterocycles in synthetic chemistry. Despite these advantages, synthetic methods of alkenyl ITCs are remarkably limited compared to aryl and alkyl ITCs. Herein, we developed a novel dehydrogenative olefination with *β*-bromination of alkyl ITCs. The reaction proceeded with two equivalents of *N*-bromosuccinimide. The olefination tolerated various functional groups in good stereoselectivity. Furthermore, we developed various transformations of alkenyl ITC and demonstrated its utility as a building block.
Keywords : Isothiocyanate; Olefin; Bromination; Building block; Enamide

イソチオシアネート(ITC)化合物は様々な生物活性を示し、医農薬分野での利用が期待されている[1]。加えてその変換反応も多彩であるため、窒素官能基やヘテロ環を導入する際の合成中間体としての価値も高い重要な化合物群である。そのため、多様な ITC 化合物が合成されてきた。しかし、アルケニル ITC の合成例はアリール ITC やアルキル ITC に比べて非常に限られている[2]。今回我々はアルキル ITC 化合物に対して 2 当量の *N*-ブロモスクシンイミド(NBS)を作用させることで、β 位のブロモ化を伴う脱水素型のオレフィン化が進行することを明らかにした。本手法は様々な置換基を有するアルケニル ITC の合成に適用可能である。加えてアルケニル ITC の変換反応についても調査したので併せて報告する。



1) A. Guerrero-Alonso, M. Antunez-Mojica, J. L. Medina-Franco, *Mol. Inf.* **2021**, *40*, 2100172.
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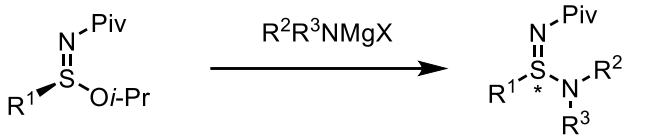
スルフィンアミジンの不斉合成法の開発

（東農工大院工[1]・京大院理[2]）○茂内　佳奈[1]・都築　咲保里[2]・加納　太一[1]
Development of Asymmetric Synthesis of Sulfinamides (1. *Graduate School of Engineering*, *Tokyo University of Agriculture and Technology*, 2. *Graduate School of Science*, *Kyoto University*) ○Kana Shigenai[1], Saori Tsuzuki[2], Taichi Kano[1]

Since some tetravalent and hexavalent organosulfur compounds such as sulfinamides and sulfonamides have unique biological activities, a number of studies have been conducted on their synthesis and application. Sulfinamidine, a nitrogen analog of sulfinamide, is a tetrahedral compound with a sulfur atom as a chiral center, and is expected to have unique biological activity. However, the synthesis of sulfinamidines has been limited to a few examples of racemic synthesis. In this study, we have developed a synthetic method for chiral sulfinamidines using optically active sulfinimidate esters. The sulfinimidate esters can be easily prepared by the oxygen-selective alkylation of sulfinamides[1)]. The desired sulfinamidines were obtained with high optical purity by the reaction of the sulfinimidate esters with metal amides as nucleophiles.

Keywords：*Organic Sulfur Compound*; *Asymmetric Synthesis*; *Sulfinamide*; *Sulfinamidine*

スルフィンアミドやスルホンアミドなどの４価や６価の有機硫黄化合物は特異な生物活性を持つものもあり、その合成法や利用法に関する多くの研究がなされている。スルフィンアミドの窒素類縁体となるスルフィンアミジンは硫黄原子を不斉中心とした四面体型化合物であり、ほかの有機硫黄化合物と同様に特異な生物活性を持つことが期待される。その一方で、スルフィンアミジンの合成例はラセミ体の合成も含め数例に限られており、その関連研究もいまだ発展途上にある。そこで本研究では、光学活性なスルフィンイミデートエステルを用いたスルフィンアミジンの不斉合成手法の開発を目指した。本手法で原料として用いるスルフィンイミデートエステルは、当研究室で最近開発したスルフィンアミドの酸素選択的なアルキル化反応によって簡便に調製できる[1)]。この硫黄原子上にアルコキシ基を脱離基として持つスルフィンイミデートエステルに、窒素求核剤を反応させたところ、目的のスルフィンアミジンが高い光学純度で得られた。



Sulfinimidate ester **Sulfinamidine**

1) S. Tsuzuki, T. Kano, *Angew. Chem. Int. Ed*. **2023**, *62*, e202300637.

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アルキンと単体硫黄を用いた鉄触媒による 3 分子間チオフェン合成法およびセレノフェン合成への応用

（東理大創域理工）○印南 朱里蘭・石田 健人・荻原 陽平・坂井 教郎

Fe-catalyzed synthesis of thiophenes from alkyne and elemental sulfur and its application to selenophene synthesis (*Faculty of Science and Technology, Tokyo University of Science*) ○ Shurika Innami, Kento Ishida, Yohei Ogiwara, Norio Sakai

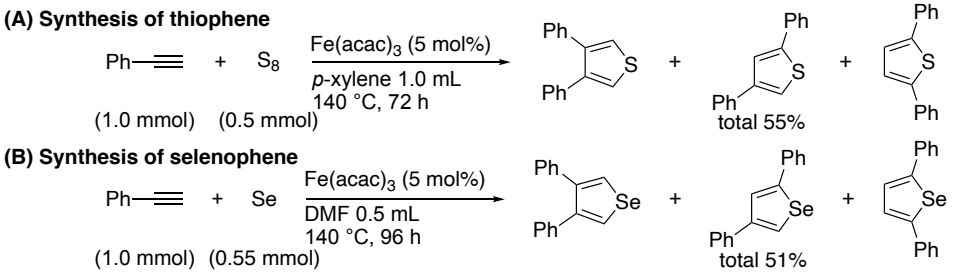
Thiophene has been constituted as the basic skeleton of useful material substances. Therefore, the development of more efficient synthesis methods is highly demanded. In this study, we demonstrated that polysubstituted thiophenes can be obtained through the reaction between elemental sulfur and alkynes with iron(III) acetylacetonate and examined that the same conditions can be applied to the synthesis of selenophene derivatives.

As a model reaction, we found that heating a *p*-xylene solution of phenylacetylene and elemental sulfur in the presence of catalytic amounts of iron(Ⅲ) acetylacetonate produced thiophenes in 55% yield. We also found that heating a DMF solution of phenylacetylene and elemental selenium in the presence of catalytic amounts of iron(Ⅲ) acetylacetonate produced selenophenes in 51% yield.

Keywords : Thiophene; Fe; [2+2+1] cycloaddition reaction; S_8; Selenophene

チオフェンは、様々な有用物質の基本骨格として用いられ、効率的な合成法の開発が求められている。特に、アルキンと硫黄源を用いた[2+2+1]型環化付加反応による例は、その優れた反応効率から、近年注目を集めているが、金属触媒によって高収率で達成する例は、数件に限られている [1]。本研究では、単体硫黄とアルキンを用いた、鉄触媒による、チオフェン合成と、セレノフェンの合成への応用について検討した。

フェニルアセチレン(1 mmol)をモデルとして反応条件を検討しところ、単体硫黄(0.5 mmol)、鉄(Ⅲ)アセチルアセトナート(5 mol%)存在下、*p*-キシレン 1.0 mL 中、120℃、72 時間反応を行なったところ、3 種類のチオフェン誘導体が、合計で 55%得られた(**A**)。同様に単体セレン(0.55 mmol)、DMF 0.5 mL 中で反応を行うと、セレノフェン誘導体が合計で 51%得られた(**B**)。



1) (a)Matsui, K.; Shibuya, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2016**, *55*, 15397–15400. (b) Wang, Y.; Yuan, Y.; Wang Z.; Gu, Y.; Fu, S.; Kong, L.; Li, Y. *Org. Lett.* **2021**, *23*, 5911–5916.

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日本化学会 第104春季年会 (2024)

単体セレンとヒドロシランを用いるベンジルエステルからのジベンジルセレニドの合成

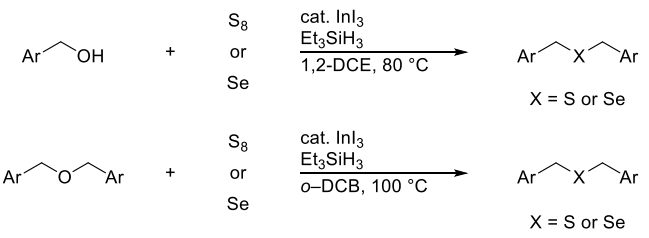
（東理大創域理工）○木野　泰・石田　健人・坂井　教郎

Synthesis of dibenzyl selenides from benzyl esters by using elemental selenium and a hydrosilane (Faculty of Science and Technology, *Tokyo University of Science*) ○ Yasushi Kino, Kento Ishida, Norio Sakai

Selenides are important compounds in organic chemistry. Elemental selenium is a useful Se-source because of its stability and availability. Previously, we reported that the reaction of benzyl alcohols or dibenzyl ethers with hydrosilanes and elemental sulfur/selenium in the presence of an indium catalyst affords dibenzyl sulfides/selenides. In this work, the synthesis of dibenzyl selenides from benzyl esters using elemental selenium and a hydrosilane was investigated. As a result, we found that the reaction of benzyl esters with elemental selenium in the presence of indium acetate and phenylsilane afforded desired dibenzyl selenides.

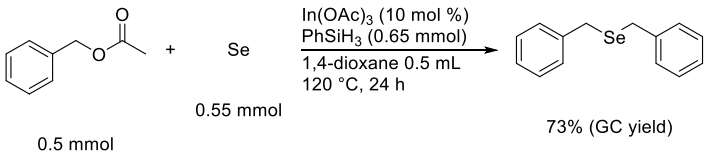
Keywords : selenide, selenium, indium catalyst, hydrosilane

セレニドは有機化学において重要な化合物である。単体セレンは安定性が高く取り扱いが容易であることから、これを Se 源とするセレニド合成は有用性があると言える。さて、当研究室では、インジウム触媒、ヒドロシラン、単体硫黄/セレンを用いて、ベンジルアルコールまたはジベンジルエーテルからジベンジルスルフィド/セレニドを合成できることを報告している[1,2] (Scheme 1) 。本研究では、単体セレンとヒドロシランを用い、ベンジルエステルからのセレニド合成について検討した。



Scheme 1. Synthesis of dibenzyl sulfides or selenides from benzyl alcohols or dibenzyl esters

検討の結果、触媒量の酢酸インジウム(Ⅲ)存在下、酢酸ベンジル、単体セレン、フェニルシランを反応させると、ジベンジルセレニドが GC 収率 73%で生成することを見出した(Scheme 2)。講演では本反応の基質一般性についての検討結果および推定反応機構について発表する。



Scheme 2. Synthesis of dibenzyl selenides from benzyl esters

1) Miyazaki, T.; Katayama, M.; Yoshimoto, S.; Ogiwara, Y.; Sakai, N. *Tetrahedron Lett*. **2016**, *57*, 676-679.
2) Sakai, N.; Takada, K.; Katayama, M.; Ogiwara, Y. *Chem. Lett.* **2018**, *47*, 791-793.

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セレンカチオン種を利用した連続的炭素－セレン結合形成反応によるセレノフェン誘導体の合成

（阪大院工）○岩本 洋樹・小島 有貴・安井 孝介・平野 康次
Synthesis of Selenophene Derivatives via Selenium Cation-Mediated Sequential C-Se Bond Formation (*Graduate School of Engineering, Osaka University*) ○Hiroki Iwamoto, Yuki Kojima, Kosuke Yasui, Koji Hirano

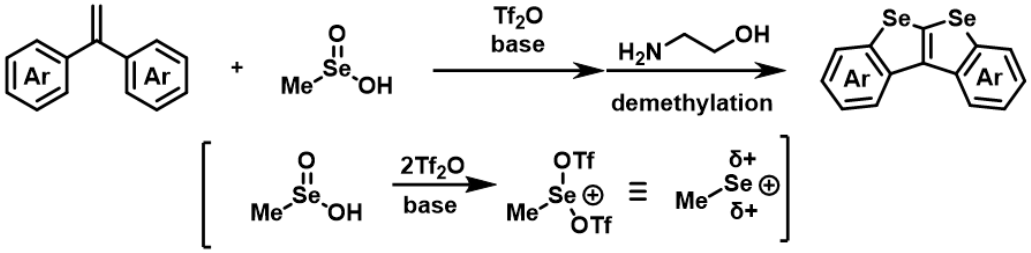
Selenium-containing heterocyclic compounds such as selenophen can be applied to various organic functional materials such as organic light-emitting diodes. However, conventional methods require multiple steps in the synthesis of selenophenes.

In the present study, we have developed the sequential C-Se bond forming reactions using methaneselenic acid, Tf_2O, and base via in-situ generated selenium cation equivalents. Upon workup with ethanolamine, the corresponding benzoselenophene derivatives were obtained directly from 1,1-diarylethenes. The same procedure was applied to the reaction with biaryls as well as sulfinic acids, giving the corresponding thiophene derivatives.

Keywords：Selenophenes; Thiophenes; C-Se bond formation; C-S bond formation; Cations

セレノフェンに代表されるセレン含有複素環化合物は、有機発光ダイオードをはじめ様々な有機機能性材料への応用が期待されている。[1]しかし、従来のセレノフェン合成法では、出発原料の調製に多段階を必要とするなど、課題が残されている。[2]

今回、我々は 1,1-ジアリールエチレンに対し、メタンセレニン酸と Tf_2O を作用させると、系中で発生する求電子的なセレニウムカチオン等価体[3]を介した連続的炭素－セレン結合形成反応が進行することを見出した。続くエタノールアミンを用いた処理により、対応するベンゾセレノフェン誘導体が得られる。本反応はビアリールにも適用できるほか、対応するスルフィン酸を用いれば、チオフェン環の構築にも展開できる。



1) Yamaguchi, S.; Xu, C.; Okamoto, T. *Pure Appl. Chem.* **2006**, *78*, 721–730.
2) Paola, H.; Thiago, P.; Filipe, P.; Luana, B.; Gelson, P.; Eder, L. *Molecules* **2020**, *25*, 5907.
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再生利用可能なヨウ化セレネニルを活用した窒素求核型カスケード環化反応の開発

（東工大理）○菊島 潤、仲田 孝明、鍬野 哲、後藤 敬

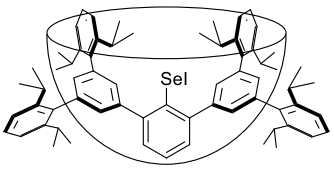
Development of Nitrogen-Terminated Cascade Cyclization Reactions Using a Recyclable Selenenyl Iodide (*School of Science, Tokyo Institute of Technology*) ○Jun Kikushima, Takaaki Nakada, Satoru Kuwano, Kei Goto

Selenenyl iodides (RSeI) are highly reactive species that usually undergo facile disproportionation. We previously reported the synthesis and isolation of a selenenyl iodide by using a cavity-type steric protection group, a Bpq group. We have developed a novel method for introducing external nucleophiles to olefins by harnessing the specific affinity of selenenyl iodide toward olefins. Herein, we report the development of *N*-terminated cascade cyclization reaction using the isolable BpqSeI. The selenenic acid generated through oxidative *β*-selenoxide elimination of the cyclized products was isolated as a stable compound, which was successfully converted back into the starting selenenyl iodide.

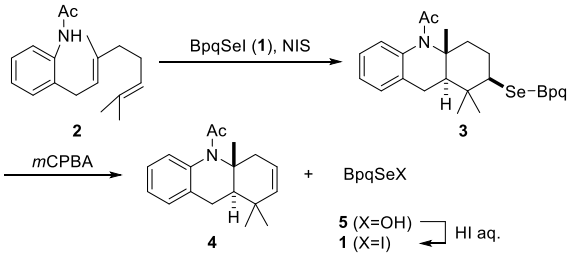
Keywords : Selenenyl iodides, Cascade cyclization reaction, Highly reactive species, β-selenoxide elimination, Selenenic acids

セレンーヨウ素結合を有するヨウ化セレネニル（RSeI）は、通常速やかに不均化する高反応性化学種である。我々は以前に、キャビティ型立体保護基である Bpq 基を活用し、安定なヨウ化セレネニル **1** の合成・単離に成功している [1)]。これまでに、ヨウ化セレネニルのオレフィンに対する特異的な親和性を活用し、オレフィンに対してアルコキシ基やアミノ基を導入する外部求核剤導入反応を開発してきた [2)]。本研究では、安定に単離したヨウ化セレネニルを用い、窒素求核部位を有するゲラニル誘導体 **2** を用いた窒素求核型カスケード環化反応の開発を検討した。

基質 **2** に対し、*N*-ヨードスクシンイミド(NIS)存在下で **1** を作用させたところ、目的の連続環化体 **3** が中程度の収率で得られた。最適条件下、様々な窒素上の保護基やベンゼン環上の置換基を有する基質についても、同様の反応が進行することを確認した。また、得られた環化体 **3** は、*β*-セレノキシド脱離によってオレフィン体 **4** へと変換され、同時に生成する高反応性化学種のセレネン酸 **5** も安定に単離された。得られたセレネン酸 **5** は、高収率でヨウ化セレネニル **1** へと再度変換することができた。



BpqSeI (**1**)



1) Goto, K.; Sonoda, D.; Shimada, K.; Sase, S.; Kawashima, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 545.

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b) Kuwano, S.; Takahashi, E.; Kikushima, J.; Sase, S.; Goto, K. *New J. Chem.* **2023**, *47*, 9569.

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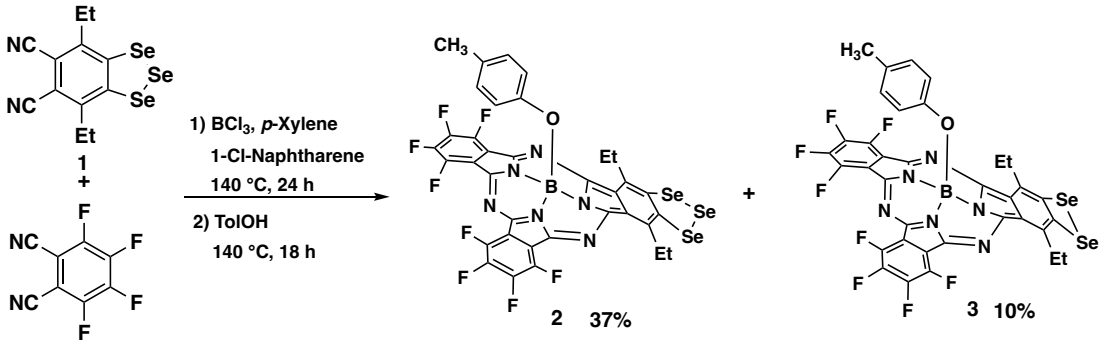
ジセレネットを縮環したサブフタロシアニンの合成と電気化学的性質

（岩手大研産セ）○木村　毅
Preparation and Electrochemical Properties of Subphthalocyanines with Triselenole and Diselenet Rings (*Center for Instrumental Analysis, Iwate University*) ○Takeshi Kimura

Unsymmetric subphthalocyanines with a triselenole ring or a diselenete ring and eight fluoro groups were prepared by the reaction of 5,6-dicyano-4,7-diethylbenzo[1,2,3]tritselenole and tetrafluorophthalonitrile with trichloroborane in *p*-xylene and the subsequent substitution reaction of the chloro group with *p*-cresol. While the reaction of **2** with triphenylphosphine gave **3**, the reaction of **3** with Woollions' reagent produced **2**. The structures of the products were determined by NMR spectra and HR-FAB-MS. Optical and electrochemical properties of the products are also reported.
Keywords : Aziridine; Subphthalocyanine; Diselenete; Triselenole

サブフタロシアニンは３つのイソインドリン骨格から構成されるフタロシアニン関連化合物であり，14π電子系を有していることから，その構造や光学的性質，電気化学的性質に興味が持たれている．本研究では 5,6-ジシアノ-4,7-ジエチルベンゾ[1,2,3]トリセレノール(1)を前駆体とし，トリセレノール環を縮環したサブフタロシアニン(2)の合成を試みた．化合物(1)は 1,4-ジエチルベンゼンを出発物質とし５段階の反応を経て合成した．次に化合物(1)とテトラフルオロフタロニトリルを混合しキシレン中三塩化ホウ素を加え，140 °C で反応させた後，*p*-クレゾールを加え，さらに同じ温度で撹拌した．その結果低収率ながらトリセレノール環を縮環した非対称サブフタロシアニン(2)が得られた．この反応では，化合物(2)と一緒にセレンが一つ脱離し，ジセレネット環に変化したサブフタロシアニン(3)も得られた．一方，化合物 2 をトリフェニルホスフィンで処理すると化合物 3 が得られることが分かった．また，化合物 3 と Woollin's 試薬を反応させると化合物 2 が得られた．これらの化合物の反応，光学的性質，電気化学的な性質についても併せて報告する．



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分子キャビティを活用したセレノプロテイン生合成に関わる活性中間体のモデル研究

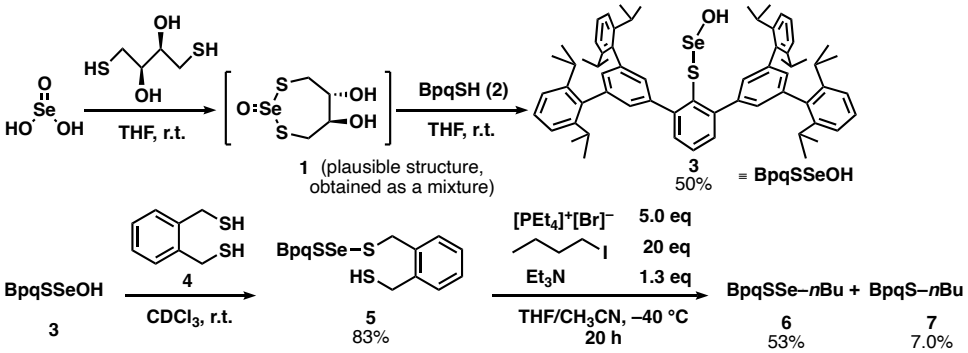
（東工大理）○工藤 嵐・鍬野 哲・後藤 敬
Model Study of Reactive Intermediates Involved in Selenoprotein Biosynthesis Utilizing a Molecular Cavity (*School of Science, Tokyo Institute of Technology*) ○Arashi Kudo, Satoru Kuwano, Kei Goto

Selenide (HSe^-), generated through the reductive metabolism of selenous acid (H_2SeO_3), serves as a selenium source in selenoprotein biosynthesis. However, the mechanism responsible for the reduction of selenous acid to selenide remains poorly understood. Here, we report the model study on the reduction of selenous acid to selenide, mediated by a cysteine residue within selenium binding proteins. A sulfan-*SeO*-selenoperoxol (R-SSeOH), a presumed crucial intermediate, was successfully synthesized and characterized by X-ray crystallography. Furthermore, our findings provide supportive evidence for the stepwise reduction process from R-SSeOH to selenide, suggesting the involvement of R-SSeOH species in the metabolic reduction of selenous acid.

Keywords : Modeling of biological reactions; Reactive intermediates; Selenium compounds; Molecular cavities

セレノプロテイン生合成では、亜セレン酸(H_2SeO_3)の還元的代謝により生成するセレニド(HSe^-)がセレン源として用いられる。細菌中での亜セレン酸の還元的代謝にはチオレドキシン 1 (TrxA)が関与しているが、具体的な反応過程については未解明である。近年、亜セレン酸と TrxA との反応生成物として亜セレン酸ジチオエステル(TrxA-SeO)の生成が確認され[1]、システイン残基を有するセレン結合タンパク質の作用により TrxA-SeO がセレニドへ還元される機構が提唱されている。本研究では、TrxA-SeO とセレン結合タンパク質のシステイン残基との反応について、分子キャビティを活用したモデル研究を行った。反応中間体として想定される R-SSeOH の合成および構造解析に成功するとともに、続く $RSSe^-$への還元反応について検証したので報告する。

亜セレン酸とジチオトレイトールの反応生成物に対しキャビティ型置換基 (Bpq 基) をもつチオール **2** を作用させ、BpqSSeOH(**3**)を単離収率 50%で合成した。**3** に対し、ジチオール **4** を作用させ、セレノトリスルフィド **5** を合成した。得られた **5** は、低温条件下、20 当量の 1-ヨードブタン存在下において塩基を加えることで、$R\text{-}SSe^-$の発生を示唆する捕捉体へと変換された。$R\text{-}SSe^-$はセレニドに変換可能であることが知られており、想定される還元過程を逐次的に検証することができた。



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

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC E1133(1132, Bldg. 11 [3F])

[E1133-4pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Koh Sugamata, Masaru Kondo

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1133-4pm-01]
Synthesis of pentaphene derivatives and their cyclotrimerization

○Hyeonju Jeong[1], Makoto Miyasaka[1] (1. Tokyo Denki University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1133-4pm-02]
Synthesis of acenophanes via cyclodimerization of isoacenofurans

○Yukino Kitamura[1], Hiroaki Yamana, Toshiyuki Hamura[1] (1. Kwansei Gakuin University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1133-4pm-03]
Construction of polysubstituted tropolone scaffold from dioxinone derivative

○Sangeun Yeom[1], Ken Ohmori[1] (1. Tokyo Inst. of Tech.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1133-4pm-04]
Synthesis and Properties of 2,3,6,7-Naphthalenetetracarboxylic Diimide Derivatives with Amino and Cyano Substituents

○Daito Nakada[1], Hideji Osuga[1,2], Hidefumi Sakamoto[1,2] (1. Graduate School, Wakayama University, 2. Wakayama University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1133-4pm-05]
Synthesis and Stereochemical Study of Naphthylisoquinoline *N*-oxide Derivatives with Axial Chirality

○Shota Kawakami[1], Damjan Trpkovski[1], Kazunobu Igawa[1], Katsuhiko Tomooka[2], Ryo Irie[1] (1. Kumamoto University, 2. Kyushu University)

1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
Break

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1133-4pm-06]
Synthesis of complexes with azaazulene derivatives as a ligand.

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○Shotaro Mori[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Faculty, Tokyo University of Science)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1133-4pm-07]

Synthesis and Characterization of 4-Pyridyl-Extended Dithieno[3,2-*b*:2',3'-*d*]arsole

○Yui Hatanaka[1], Kazuma Kikuchi[2], Hiroaki Imoto[1,2], Kensuke Naka[1,2] (1. Kyoto Institute of Technology, 2. Grad. Sch. of Sci. and Tec., Kyoto Inst. of Tech.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1133-4pm-08]

Synthesis and Gas Adsorption Properties of Metal-organic Frameworks Using Triptycene Ligands with Sulfur Functional Group at the Bridgehead Position

○Shoko Yamada[1], Koh Sugamata[1], Natsuki Amanokura[1,2], Mao Minoura[1] (1. Rikkyo University, 2. Nippon Soda Co., Ltd.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1133-4pm-09]

Synthesis and Gas Adsorption Properties of Metal-organic Frameworks with Phenothiazine Ligands

○Riko Furukawa[1], Koh Sugamata[1], Natsuki Amanokura[1,2], Mao Minoura[1] (1. Rikkyo University, 2. Nippon Soda Co., Ltd.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1133-4pm-10]

Synthesis and Property of Dibenzobarrelene-hexatriene-based O,S-Mixed Crownether

○Nanaka Umehara[1], Norio Nakata[1], Akihiko Ishii[1] (1. Graduate School of Science and Engineering, Saitama University)

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

Break

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1133-4pm-11]

Synthesis and physical properties of 3^1-thienylated chlorophyll derivatives

Hitoshi Tamiaki[1], ○Takeru Nishikawa[1] (1. Ritsumeikan University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1133-4pm-12]

Purification of Hydrophilic Ionic Liquids for Material Application and Their Biocompatibility

○Yukino Isshiki[1], Tatsuya Kaya[2], Satoshi Kitaoka[3], Kaoru Nobuoka[4] (1. Oita University Graduated School of Engineering, 2. Kindai University Graduated School of Engineering, 3. Kindai University Faculty of Engineering, 4. Oita University Faculty of Science and Technology)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[E1133-4pm-13]

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Development of donor-acceptor fluorophores with 2*H*-indazole skeleton

○Tomohiro Komuro[1], Yu Miyazaki[1], Agou Tomohiro[2], Hiroki Fukumoto[1], Masaru Kondo[3] (1. Ibaraki Univ., 2. Univ. of Hyogo, 3. Univ. of Shizuoka)

Japanese

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

[E1133-4pm-14]

The metal complex reaction of [36]trithianonaphyrin

○Taiki Nagatsu[1], Takashi FUJIHARA[2], Yoshihiro ISHIMARU[1] (1. Saitama University, 2. Saitama University, Comprehensive Analysis Center for Science)

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ペンタフェン誘導体の合成とその環化三量化

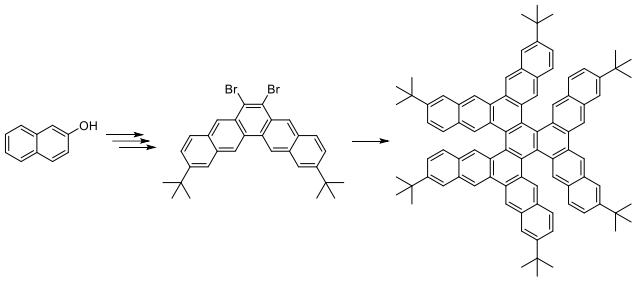
（東電大院工）○鄭　賢柱・宮坂　誠

Synthesis of pentaphene derivatives and their cyclotrimerization (*Graduate School of Engineering, Tokyo Denki University*) ○Hyeonju Jeong, Makoto Miyasaka

Polycyclic aromatic hydrocarbons (PAHs) with multiple fused benzene rings include non-planar PAHs such as helicenes, which have a torsionally conjugated backbone resulting from intramolecular steric repulsion. Chiral nonplanar PAHs have been of interest because they exhibit unique structure-derived chiroptical properties. However, due to destabilization of the π-conjugated system by distortion, the fluorescence quantum yield remains low. Therefore, it is expected to improve the luminescence properties by expanding the π-conjugated system and promoting delocalization of the π-electrons by condensing them. Recently, multi-helicenes having two or more helicene subunits in one molecule have been created, and their structural beauty and interesting properties have been reported. Among them, the [5]helicene trimer has slightly improved the low fluorescence quantum yield while possessing unique chiroptical properties. Our laboratory has also focused on the excellent optical properties of pentaphene, a V-shaped PAH derivative, and the present study is aimed at the synthesis of V-shaped PAH derivatives and the creation of self-condensing cyclized trimers containing pentaphene's in their backbone.

Keywords : pentaphene, polycyclic aromatic hydrocarbon, cyclotrimerization

複数のベンゼン環が縮環した多環芳香族炭化水素(PAHs)には、分子内の立体反発により生じるねじれ共役骨格を持つヘリセン類のような非平面 PAHs がある。キラル非平面型 PAHs は、ユニークな構造由来のキロプティカル特性を示すため、関心が注がれてきた。しかし、歪みによるπ共役系の不安定化により、蛍光量子収率は低く留まる[1]。そこで、これらを縮環させπ共役系を拡張し、π電子の非局在化を促すことで、発光特性の改善が期待される[2]。近年、１分子中に２つ以上のヘリセンサブユニットをもつ、マルチヘリセンの創製がされ、その構造美と興味深い性質が報告されている。その中でも、[5]ヘリセン三量体は、特有のキロプティカル特性を持ちつつ、低い蛍光量子収率をわずかに改善した[3]。また、当研究室では、V 字型 PAH 誘導体であるペンタフェンの優れた光学特性について注目しており、本研究では、V 字型 PAH 誘導体の合成とペンタフェン誘導体を骨格に含む自己縮合環化三量体の創製を目的としている。



1)M. Gingras, *Chem. Soc. Rev.*, **2013**, *42,* 968.
2)R. Mokrai *et.at., New J. Chem.*, **2021**, *45*, 8118.
3)M. Gingras *et.at.*, *J. Am. Chem Soc.,* **2017**, 139, *51*, 18508.

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イソアセノフランの環化二量化を用いたアセノファンの合成

（関西学院大院理工）○北村　薫乃・山名　弘祥・羽村 季之

Synthesis of acenophanes via cyclodimerization of isoacenofurans

(*Graduate School of Science and Technology, Kwansei Gakuin University*) ○ Yukino Kitamura, Hiroaki Yamana, Toshiyuki Hamura

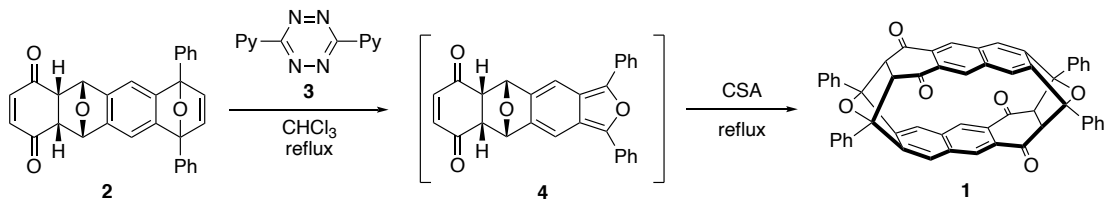
Acenophanes, which consist of two acenes connected by ansa chains, exhibit unique physical properties due to their characteristic pi-conjugated structure. We previously developed an efficient synthetic access to belt-shaped molecules by cyclodimerization of donor-acceptor type of isoacenofurans. We report herein an improved synthesis of the belt-shaped molecule and its conversion to acenophanes by functionalization and aromatization.

First, the reaction was monitored by NMR in order to find the optimum conditions for the construction of the belt structure. As a result, we found that when quinone **2** and tetrazine **3** was refluxed in $CDCl_3$ for 4 h, the starting material **2** was completely consumed. After that, addition of CSA to the reaction mixture led to the formation of isonaphthofuran by dehydrative aromatization, and subsequent cyclodimerization gave the belt-shaped molecule **1** in good yield.

Keywords : belt-shaped molecule; acenophane; isoacenofuran; cyclodimerization; pi-conjugated structure

２つのアセンをアンサ鎖で連結したアセノファンはユニークな π 共役構造に起因する独特な物性・機能の発現が期待できる。先に我々は、ドナー・アクセプター型構造を有するイソアセノフランの環化二量化を利用したベルト状分子の簡便合成法を開発している。今回、この合成法の合成ルートを再検討するとともに、ベルト状分子の官能基化・芳香族化によるアセノファンへの変換を検討したので、報告する。

まず、ベルト構造構築の最適条件を探るため、NMR による反応の追跡を行った。その結果、キノン **2** とテトラジン **3** の重クロロホルム溶液を 4 時間加熱還流したところ、原料は完全に消失し、イソベンゾフラン **4** へときれいに変換できることがわかった。そこで、これに CSA を作用させると、脱水・芳香族化によるイソナフトフランの発生と環化二量化が連続的に進行し、ベルト状分子 **1** を収率良く得ることができた。



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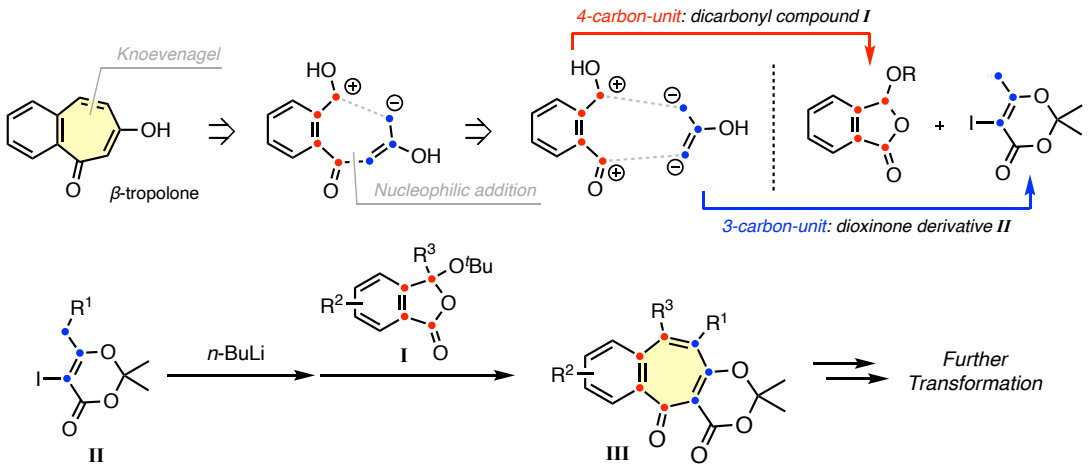
ジオキシノン合成単位を利用したトロポロン骨格の新規構築法と化学変換

（東工大理[1]）○Yeom Sangeun[1]・大森　建[1]
Construction of polysubstituted tropolone scaffold from dioxinone derivative ([1]*Department of Chemistry, Tokyo Institute of Technology*) ○Sangeun Yeom[1], Ken Ohmori[1]

Tropolones constitutes a class of seven-membered aromatic compounds and show various diverse and distinctive reactivities. However, synthesis of multi-functionalized derivatives remains challenging, and a general synthesis method has not yet been established. Herein, we will report a facile synthesis method for obtaining tropolone derivatives via the annulation reaction of a dioxinone derivative with a lactone derivative. We postulated that the formation of a 7-membered ring skeleton would occur through the reaction of an electrophile 4-carbon-unit and a nucleophile 3-carbon-unit. To realize this strategy, a lactone **I** and a dioxinone **II** were employed. We successfully obtained benzotropolone derivatives in a one-pot manner. Moreover, this reaction proved applicable to various substrates. Details will be discussed in this presentation.
Keywords : Tropolones; Annulation; Non-benzoic aromatic compounds; Reaction development

トロポロンは７員環の非ベンゼン型芳香族であり、ベンゼン系化合物には無いユニークな反応性を示す。しかし、その合成法は限られており、様々な置換様式をもつ化合物の一般的合成法はほとんどない。今回我々は多置換トロポロンの新たな構築法を見出したので報告する。本研究では、７員環骨格を求電子的な４炭素単位と求核的な３炭素単位から形成することを想定し、４炭素単位としてラクトン **I** を、また３炭素単位としてはβ-ケトエステルの等価体であるジオキシノン **II** を用いた。先に我々は昨年度の春季年会において、リチオ化した **II** と **I** を反応させ、トロポロン誘導体 **III** が一挙に得られたことを報告した。今回、反応条件の最適化と基質適用性を検討し、収率に関わる重要な条件を見出した。さらに、トロポロン誘導体 **III** を化学変換し、多様な化合物の合成への応用可能性を検討した。



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アミノ基およびシアノ基を有する 2,3,6,7-ナフタレンテトラカルボン酸ジイミド誘導体の合成と物性

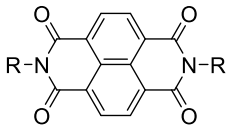
（和歌山大院システム工）○中田 大翔・大須賀 秀次・坂本 英文

Synthesis and Properties of 2,3,6,7-Naphthalenetetracarboxylic Diimide Derivatives with Amino and Cyano Substituents (*Graduate School of Systems Engineering, Wakayama University*) ○Daito Nakada, Hideji Osuga, Hidefumi Sakamoto

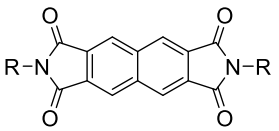
1,4,5,8-Naphthalenetetracarboxylic diimides have been extensively studied as *n*-type organic semiconductor materials due to their thermal and oxidative stabilities, as well as high mobility. In contrast, the isomeric 2,3,6,7-naphthalenetetracarboxylic diimide has been scarcely reported since the precursor is not commercially available. In this work, 1-bromo-2,3,6,7-naphthalenetetracarboxylic diimide and 1,5-dibromo-2,3,6,7-naphthalenetetracarboxylic diimide were prepared from 2,3,6,7-naphthalenetetracarboxylic anhydride in two steps, and the derivatives with amino and cyano substituents were obtained from these compounds. We will report the details of the synthesis and properties of these diimide derivatives.

Keywords : 2,3,6,7-Naphthalenetetracarboxylic Diimide; Amino Group; Cyano Group; Intramolecular Charge Transfer; Organic Semiconductors

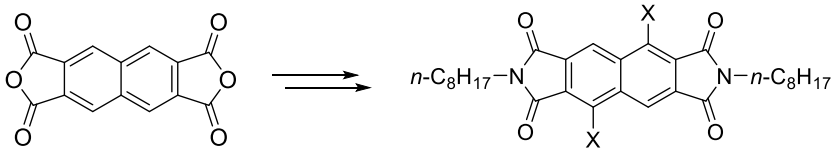
1,4,5,8-ナフタレンテトラカルボン酸ジイミドは、良好なキャリア移動度、優れた熱および酸化安定性を有することから *n* 型有機半導体材料として盛んに研究が行われている。一方、異性体である 2,3,6,7-ナフタレンテトラカルボン酸ジイミドは、前駆体の酸二無水物が一般には市販されていないため、報告例がほとんどない。そこで本研究では、2,3,6,7-ナフタレンテトラカルボン酸二無水物から 1-ブロモ-2,3,6,7-ナフタレンテトラカルボン酸ジイミドおよび 1,5-ジブロモ-2,3,6,7-ナフタレンテトラカルボン酸ジイミドを 2 段階で調製し、アミノ基およびシアノ基を置換基とする誘導体を合成した。これらのジイミド誘導体の合成の詳細と物性について報告する。



1,4,5,8-naphthalenetetracarboxylic diimide



2,3,6,7-naphthalenetetracarboxylic diimide



X = H, NH-*n*-C_8H_{17}, NH—⬡, N⬡, CN

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軸不斉を有するナフチルイソキノリン *N*-オキシド誘導体の合成と立体化学的安定性に関する研究

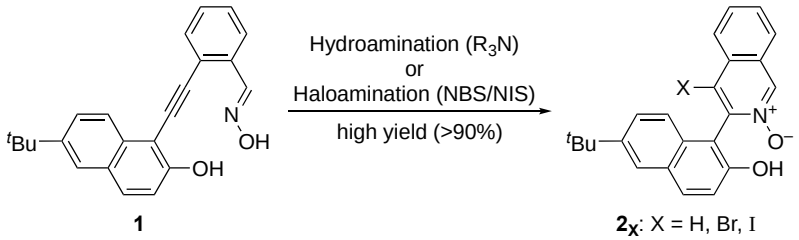
(熊大院自然科学[1]・熊大院先端科学[2]・九大先導研[3]) Damjan Trpkovski[1]・○河上 翔太[1]・井川 和宣[2]・友岡 克彦[3]・入江 亮[2]

Synthesis and Stereochemical Study of Naphthylisoquinoline *N*-Oxide Derivatives with Axial Chirality ([1]*GSST, Kumamoto University,* [2]*FAST, Kumamoto University*, [3]*IMCE, Kyushu University*) Damjan Trpkovski,[1] ○Shota Kawakami,[1] Kazunobu Igawa,[2] Katsuhiko Tomooka,[3] Ryo Irie[2]

Heterobiaryl derivatives with axial chirality are expected to find applications as chiral ligands and organocatalysts, and therefore, the design and synthesis of novel heterobiaryl skeletons is an important issue. We have previously developed the catalytic intramolecular cyclization of alkyne–benzoheteroles and succeeded in producing various chiral heterocyclic compounds.[1] In this study, we newly designed the alkyne–oxime **1** and examined its cyclization under various conditions. Consequently, the intramolecular hydroamination or haloamination of alkynes smoothly proceeded with tertiary amine or *N*-halosuccinimide to provide the novel axially chiral naphthylisoquinoline *N*-oxides **2X** (X = H, Br, I) all in high yields. In this presentation, details of the cyclization of **1** and the stereochemical study on **2X** will be reported.

Keywords: Isoquinoline N-oxide; Axial chirality; Stereochemical behavior; Hydroamination of alkynes; Haloamination of alkynes

軸不斉を有するヘテロビアリール誘導体はキラル配位子や有機触媒としての応用が期待されることから，その新規骨格の創出は重要な課題である．我々は先に，アルキン–ベンゾヘテロール系の触媒的分子内環化反応を開発し，各種のキラルなヘテロ環化合物の合成に成功している [1)]．これに対して今回，反応基質としてアルキン–オキシム系分子 **1** を新たに設計し，その環化反応を種々検討した．その結果，**1** に対して第三級アミンや *N*–ハロスクシンイミド作用させると，アルキンの分子内ヒドロアミノ化やハロアミノ化が円滑に進行し，ナフトールとイソキノリン *N*–オキシドが連結した新規軸不斉ヘテロビアリール誘導体 **2X**（X = H, Br, I）がいずれも収率良く得られることを見出した．本発表では，**1** の環化反応の詳細とともに，得られたナフチルイソキノリン *N*–オキシド **2X** の立体化学的安定性について報告する．



1 **2X**: X = H, Br, I

1) (a) S. Beppu, S. Arae, M. Furusawa, K. Arita, H. Fujimoto, M. Sumimoto, T. Imahori, K. Igawa, K.Tomooka, R. Irie, *Eur. J. Org. Chem.* **2017**, 6914. (b) S. Arae, S. Beppu, T. Kawatsu, K. Igawa, K. Tomooka, R. Irie, *Org. Lett*. **2018**, *20*, 4796.

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アザアズレン誘導体を配位子とする錯体の合成

（東理大理工 [1]）○森 翔太郎 [1]・山本 一樹 [1]・郡司 天博 [1]

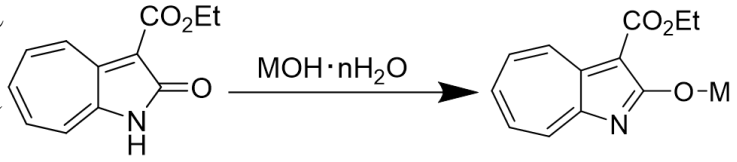
Synthesis of complexes with azaazulene derivatives as a ligand ([1] *Faculty of Science and Technology, Tokyo University of Science*) ○Shotaro Mori,[1] Kazuki Yamamoto,[1] Takahiro Gunji[1]

Azaazulene has a large polarization structure as indicated by its dipole moment and is colored. Taking advantage of these properties, the lone electron pair of the nitrogen atom and the optical and electronic properties similar to those of azulene, the synthesis of 1-azazazulene derivatives has been investigated. Among them, 3-ethoxycarbonyl-1-azaazulen-2-one (**1**) has a simple synthetic step and several structures are expected when a complex is formed. Alkali metal complexes of azaazulene derivatives can be useful precursors for the introduction of azaazulene skeletons. Therefore, in the present study, lithium, sodium, and potassium complexes were synthesized in 57%, 56%, and 55% yields, respectively, by the reaction of **1** with alkali metal hydroxides. They were identified by ^{1}H NMR and ^{13}C NMR. In this work, the synthesis and characterization of these complexes will be reported.

Keywords : Azaazulene; Complex; Alkali metal

アザアズレンは 3.05 D という双極子モーメントに示される大きな分極構造をとり、また、有色である [1,2]。このような性質と窒素原子が孤立電子対を持つこと、アズレンと似たような光学的・電子的な性質をもつことを活かして、1-アザアズレンの誘導体の研究が進められている [3]。その中で 3-エトキシカルボニル-1-アザアズレン-2-オン(**1**)は合成ステップが簡便であり、錯体を形成した際に複数の構造が予想される。また、このアザアズレン誘導体のアルカリ金属錯体はアザアズレン骨格導入のための有用な前駆体となり得る。そこで、本研究では **1** とアルカリ金属の水酸化物の反応によりアザアズレン誘導体を配位子とする錯体の合成を検討した。

1 とアルカリ金属の水酸化物の反応によりリチウム、ナトリウム、カリウム錯体をそれぞれ収率 57%、56%、55%で合成し、^{1}H NMR、^{13}C NMR により同定した。また、これらの IR スペクトルでは、**1** のエステル結合の C=O 伸縮振動による吸収帯が 1698 cm^{-1} であるのに対し、リチウム、ナトリウム、カリウム錯体のエステル結合の C=O 伸縮振動による吸収帯はそれぞれ 1655 cm^{-1}、1663 cm^{-1}、1643 cm^{-1} に低波数シフトした。



1 M = Li, Na, K

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4-ピリジル拡張型ジチエノ[3,2-*b*:2′,3′-*d*]アルソールの合成と特性評価

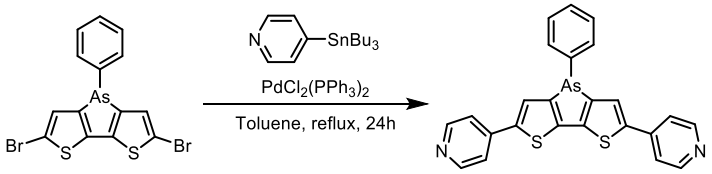
（京工繊大[1]・京工繊大院工芸[2]）○幡中 結衣[1]・菊池 一楨[2]・井本 裕顕[1,2]・中 建介[1,2]

Synthesis and Characterization of 4-Pyridyl-Extended Dithieno[3,2-*b*:2′,3′-*d*]arsole

([1]*Kyoto Institute of Technology*, [2]*Grad. Sch. of Sci. and Tec., Kyoto Inst. of Tech.*)
○Yui Hatanaka,[1] Kazuma Kikuchi,[2] Hiroaki Imoto,[1,2] Kensuke Naka[1,2]

Dithieno[3,2-*b*:2′,3′-*d*]arsoles (DTA) are arsenic-containing π-conjugated units that exhibit efficient luminescence in both solution and solid states. The electronic state of DTA can be controlled through modifications of the π-conjugated system, oxidation of the arsenic atom, and metal coordination. Various substituents have been introduced at the α-position of the thiophene skeleton in DTA. The introduction of the pyridyl group is expected to bring changes in redox behavior and complexation abilities, thereby enhancing the compound's functionalities. In this study, we successfully synthesized **DTA-py**, a DTA incorporating a 4-pyridyl group, through Stille coupling (**Scheme 1**). **DTA-py** exhibits a unique packing structure in the crystalline state and strong blue emission in solution state (λ_{em} = 473 nm, Φ = 58 %). In this presentation, the synthesis, optical properties, and advanced applications, *e.g.*, the construction of a CuI-based one-dimensional coordination polymer, of **DTA-py** will be discussed.

ジチエノアルソール（DTA）は、溶液および固体状態において強発光性を示すヒ素含有共役ユニットである。DTA の電子状態は、π 共役系の構造修飾やヒ素原子の酸化、金属配位により制御が可能であり、チオフェン骨格の α 位に種々の置換基が導入されてきた[1)]。類似構造にあたるジチエノホスホールでは、ピリジル基を π 共役系に組込んだ例がこれまでに報告されているが[2)]、DTA では未達成である。ピリジル基の導入により、酸化還元挙動の変化や新たな錯形成能の付与をはじめとする化合物の機能性の拡充が期待される。本研究では 4-ピリジル基をもつ DTA 類縁体である **DTA-py** を設計し、Stille カップリングにより合成に成功した（**Scheme 1**）。**DTA-py** は結晶中で特異なパッキング構造をとったほか、とくに溶液状態で強い青色発光 (λ_{em} = 473 nm, Φ = 58 %) を示した。本発表では、**DTA-py** の合成と発光特性、さらに左右２つのピリジル基を活用した１次元配位高分子の構築などの応用例について議論する。



Scheme 1. Synthesis of 4-Pyridyl-Extended Dithieno[3,2-*b*:2′,3′-*d*]arsole (**DTA-py**)

1) a) T. Kato, H. Imoto, S. Tanaka, M. Ishidoshiro, K. Naka, *Dalton Trans*. **2016**, *45*, 11338-11345.
b) H. Imoto, I. Kawashima, C. Yamazawa, S. Tanaka, K. Naka, *J. Mater. Chem. C* **2017**, *5*, 6697-6703.
2) P. Demay-Drouhard, T. Baumgartner, *J. Org. Chem.* **2020**, *85*, 14627-14633.

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橋頭位に硫黄官能基を有するトリプチセン配位子を用いた金属有機構造体の合成とガス吸着特性

（立教大理[1]・日本曹達(株)[2]）○山田翔子[1]・菅又 功[1]・天野倉夏樹[1,2]・箕浦真生[1]

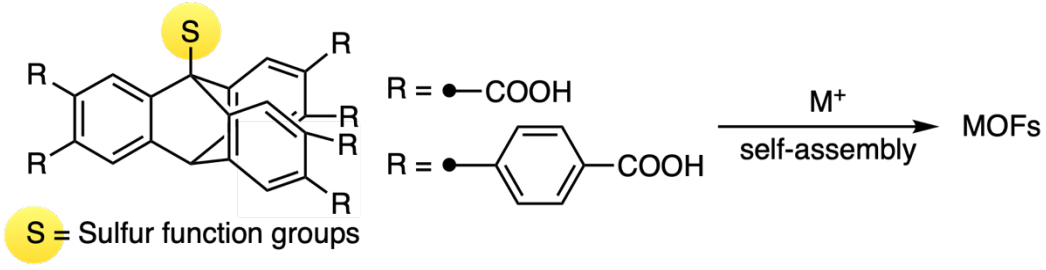
Synthesis and Gas Adsorption Properties of Metal-organic Frameworks Using Triptycene Ligands with Sulfur Functional Groups at the Bridgehead Position

([1]*College of Science, Rikkyo University,* [2]*Nippon Soda Co., Ltd.*) ○Shoko Yamada,[1] Koh Sugamata,[1] Natsuki Amanokura,[1,2] and Mao Minoura[1]

Metal-organic frameworks (MOFs) are expected to be applied to gas adsorption and separation technologies due to their high gas adsorption capability. The gas adsorption capacity can be improved by ligand functionalization through the incorporation of nitrogen and sulfur atoms. We have recently reported the MOFs with functionalized triptycene ligands showed their high porosity, high gas adsorption capacity, and high chemical stability. In this presentation, we report the synthesis of the novel sulfur-functionalized triptycene ligands and their utilization for MOFs. The structures and gas sorption properties of the MOFs will also be discussed.

Keywords : Metal-organic Framework; Triptycene; Sulfur; Porous-coordination Polymers

金属有機構造体（Metal-Organic Frameworks, MOF）は、有機配位子と金属イオンの自己集合からなる多孔質材料で、均一な細孔を有することからガス吸着や分離技術などへの応用が期待されている。MOF に用いる有機配位子への官能基導入によりガス吸着選択性を制御できることから、様々な官能基導入が試みられている[1)]。これまでに我々は、トリプチセン配位子の橋頭位にハロゲン原子やアルキル基を導入し、それらを用いた MOF が高いガス吸着特性を有することを明らかとしている[2)]。そこで、トリプチセン MOF のさらなるガス吸着量向上を期待して、吸着サイトとして知られる硫黄原子の導入を行った。また合成した硫黄官能基導入トリプチセン配位子を用いて MOF への応用を検討した。本発表では、配位子合成および得られた MOF の性質について報告する。



1) H. Wang, J. Peng, J. Li, *Chem. Rec.* **2016**, *16*, 1298-1310.
2) K. Sugamata, S. Yamada, D. Yanagisawa, N. Amanokura, A. Shirai, M. Minoura, *Chem. Eur. J.* **2023**. *29,* e202303416.

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フェノチアジン配位子を有する新規金属有機構造体の合成とガス吸着特性

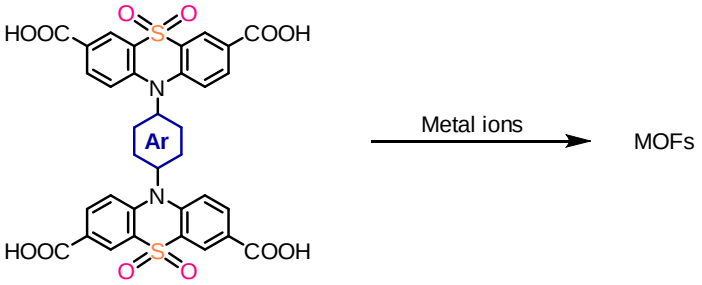
（立教大学[1]・日本曹達（株）[2]）◯古川 璃子[1]・菅又 功[1]・天野倉 夏樹[1,2]・箕浦 真生[1]

Synthesis and Gas Adsorption Properties of Metal-organic Frameworks with Phenothiazine Ligands ([1]*Rikkyo University*, [2] *Nippon Soda Co., Ltd.*) ◯Riko Furukawa,[1] Koh Sugamata,[1] Natsuki Amanokura,[1,2] Mao Minoura[1]

Metal-organic frameworks (MOFs) are expected in gas storage and separation materials because of their uniform pore and wide surface area. MOFs with diarylamine-based ligands have demonstrated high gas adsorption capacity. Moreover, the incorporation of main group elements, such as nitrogen and sulfur, into organic ligands has been found to effectively enhance the gas adsorption capacity of MOFs.[1] Herein, we report the development of novel MOFs with phenothiazine-based ligands which have sulfur moieties as adsorption sites. The ligand synthesis, structures and gas adsorption properties of the MOFs will be discussed.

Keywords : Metal-organic Frameworks; Gas Adsorption; Phenothiazine; X-ray Structural Analysis

有機配位子と金属イオンからなる金属有機構造体(MOFs)は、ガス吸着・分離材料としての応用が期待されている。中でもジアリールアミン配位子を用いた MOFs は、良好なガス吸着性を示すことが報告されている。また、配位子への硫黄などの典型元素導入が吸着サイトとして働くことで、MOFs のガス吸着量向上に効果があると報告されている[1]。我々はより高いガス吸着性能を有する新規 MOFs の開発を目的とし、ジアリールアミン部位を硫黄原子で架橋したフェノチアジン配位子類を合成した。本発表では、それらフェノチアジン配位子を用いた MOFs を合成し、構造およびガス吸着特性を調査したので報告する。



フェノチアジン配位子

1) H. Wang, J. Peng, J. Li, *Chem. Rec.* **2016**, *16* (3), 1298–1310.

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ジベンゾバレレン-ヘキサトリエン骨格を有する O,S 混合クラウンエーテルの合成と性質

（埼玉大院理工[1]）○梅原 菜々花[1]・中田憲男[1]・石井昭彦[1]

Synthesis and Property of Dibenzobarrelene-hexatriene-based O,S-Mixed Crown Ether

([1]*Graduate School of Science and Engineering, Saitama University*) ○Umehara Nanaka,[1] Norio Nakata,[1] Akihiko Ishii[1]

We have succeeded in the synthesis of tetrathiohexatriene derivative **1** fused with a dibenzobarrelene skeleton.[1)] Compound **1** does not show fluorescence but does upon cleaving the disulfide bond. In this study, we synthesized O,S-mixed crown ether **2** from **1** and investigated its photophysical properties.

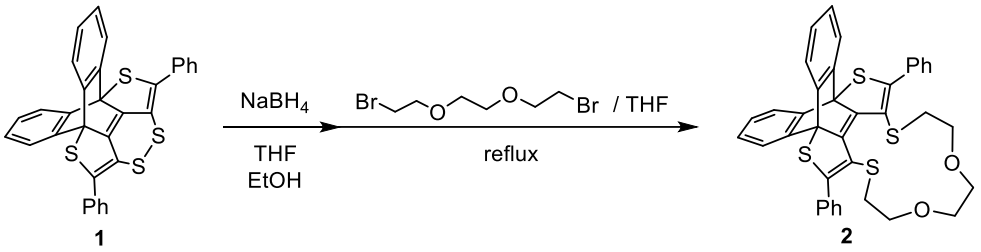
The disulfide bond in **1** was reduced with sodium borohydride, followed by treatment with 1,8-dibromo-3,6-dioxaoctane to yield the desired product **2**.

Keywords : sulfur; crown ether; dibenzobarrelene; hexatriene; fluorescence

クラウンエーテルはアルカリ・アルカリ土類金属のイオンを取り込んで錯体を作るためこれまで盛んに研究・活用されている。酸素原子の一部、または全部を異なるヘテロ原子に置き換えたクラウンエーテルも環の構造や大きさの変化がおこることから分子認識の分野においても盛んに研究されている。クラウンエーテルの酸素原子が硫黄に置き換わったチオクラウンエーテルでは、硫黄がソフトな原子であるため、ソフトな重金属イオンを取り込みやすいことが知られている。

当研究室ではジベンゾバレレン骨格を有するヘキサトリエン誘導体の合成と光物性について研究しており、その中で、硫黄誘導体 **1** の合成に成功している[1)]。化合物 **1** は蛍光を示さないが、ジスルフィド結合の切断により蛍光を示すことが分かっている。本研究ではジスルフィド切断部にエーテル鎖を組み込むことにより 0, S 混合クラウンエーテル **2** を合成した。**2** は蛍光を発するため、その光物性についても報告する。

化合物 **1** のジスルフィド結合を水素化ホウ素ナトリウムで還元し、そこに 1, 8–ジブロモ–3, 6–ジオキサオクタンを加えて加熱還流することにより目的物である **2** が得られた.



1 **2**

1) S. Kumada, M. Shoji, N. Nakata, A. Ishii, The 48th Symposium on Main Group Element Chemistry (2021), OB–26.

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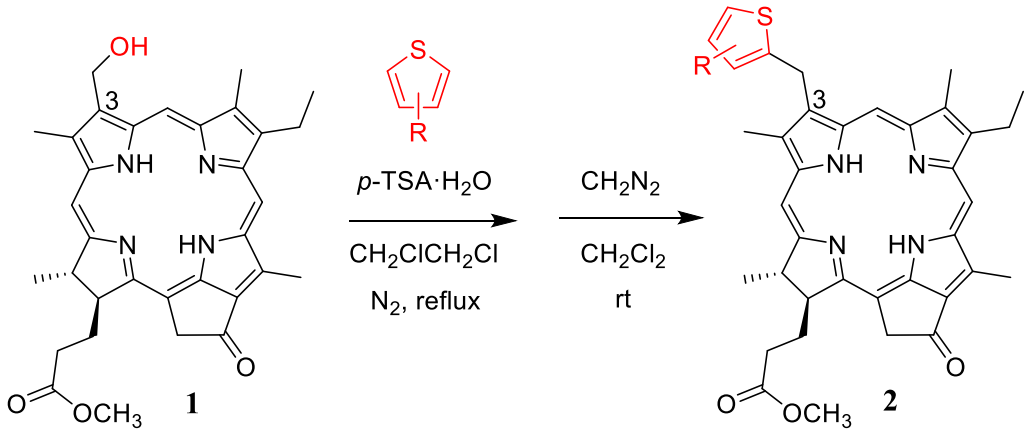
3[1]位にチエニル基を有するクロロフィル誘導体の合成と物性

（立命館大生命科学）民秋 均・○西川 尊
Synthesis and physical properties of 3[1]-thienylated chlorophyll derivatives (*Faculty of Life Sciences, Ritsumeikan University*) Hitoshi Tamiaki, ○Takeru Nishikawa

It was previously reported that Friedel–Crafts alkylation reactions of 3-(hydroxymethyl)-chlorin with electron-rich arenes in the presence of *p*-toluenesulfonic acid in refluxing 1,2-dichloroethane afforded the corresponding 3-(arylmethyl)chlorins. In this study, 3-(thienylmethyl)chlorophyll-*a* derivatives were prepared by a similar acidic intermolecular dehydration reaction using various thiophenes instead of arenes. Their physical properties in a solution will be discussed.
Keywords : Chlorophyll; Thiophene; Friedel–Crafts reaction; Dehydration; Ultraviolet–visible absorption spectroscopy

周辺部に様々な官能基を置換したクロロフィル(Chl)類は、光エネルギーの吸収・移動・変換、光線学的医療、バイオイメージング、分子認識(センシング)、触媒反応などの多くのプロセスにおいて有用である[1)]。これまで3位にアリールメチル基を導入したChl誘導体の簡便な合成法を報告してきたが[2)]、今回新たにチエニルメチル基の導入に成功したので、その合成と物性について報告する。

天然産のChl-*a*を改変した3-ヒドロキシメチルクロリン**1**とチオフェンを、*p*-トルエンスルホン酸(*p*-TSA)存在下に 1,2-ジクロロエタン中で還流すると、Friedel-Crafts アルキル化反応により、3-(2-チエニル)メチルクロリン**2a** (R = H)が主として得られた。同様の反応で、3-[(3,4-ジメチル-2-チエニル)メチル]クロリン**2b** (R = 3,4-$(OCH_3)_2$)や3-[(3,4-ジヘキシル-2-チエニル)メチル]クロリン**2c** (R = 3,4-$[(CH_2)_6H]_2$)も合成した。これらの溶液中での物性についても報告する。



1) H. Tamiaki, Chlorophylls, in *Fundamentals of Porphyrin Chemistry: A 21st Century Approach*, Chapter 17, 743–776 (2022). Doi: 10.1002/9781119129301.ch17
2) K. Sakaguchi, H. Tamiaki, *Tetrahedron,* **2022**, *123*, 132981.

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材料応用を志向した親水性イオン液体の精製法および生体親和性

（大分大院工[1]・近畿大院工[2]・近畿大工[3]・大分大理工[4]）○一色由貴乃[1]・賀屋辰哉[2]・北岡 賢[3]・信岡 かおる[4]
Puritication of Hydrophilic Ionic Liquids for Materials Application and Biocompatibility ([1]*Oita University Graduated School of Engineering,* [2]*Kindai University Graduated School of Engineering,* [3]*Kindai University Faculty of Engineering,* [4]*Oita University Faculty of Science and Technorogy*)○Yukino Isshiki[1]・Tatsuya Kaya[2]・Satoshi Kitaoka[3]・Kaoru Nobuoka[4]

The purity is a significant issues in their application. We focused on the hydrophilic ionic liquids, which are difficult to purify, and investigated their synthesis and purification. The ionic liquids examined in this study were two types: imidazolium ionic liquids with low melting point and low viscosity for optical materials applications and ammonium ionic liquids for biomaterials applications. Purity was confirmed by optical and NMR spectra, and purified ionic liquids were evaluated for their biocompatibility using HeLa cells.
Keywords : Ionic liquids

イオン液体の純度向上は，光学材料や生体材料への応用において重要な課題である．我々は，精製が困難な親水性イオン液体に着目し，低融点・低粘度の光学材料への応用を視野にイミダゾリウムイオン液体（図 1a）を，生体応用を視野にアンモニウムイオン液体（図 1b）を対象にその合成及び精製について検討した．合成は加熱攪拌，ソニーケーションを用いた．精製は，活性炭処理, および溶出溶媒にクロロホルムとクロロホルムーメタノールの混合溶媒を用いた中性フラッシュシリカゲル･酸性フラッシュシリカゲル･アルミナを使用したカラムクロマトグラフィーで検討した. 精製度は光学スペクトルや ^{1}H NMR スペクトルなどの各種スペクトルで確認した．図 2 に $[C_4C_1im][N(CN)_2]$の精製前後の蛍光スペクトルを示す．未精製（黒）では，350～450 nm 付近にかけて不純物由来と思われる幅広いピークが見られるが, 中性シリカゲルカラムクロマトグラフィー(溶離液:クロロホルム)による精製後（青）では，このピークが消失し，精製されたことが分かる．発表では $[N_{1123}][N(CN)_2]$の精製，さらに，これらのイオン液体の生体親和性を細胞実験で評価したので合わせて報告する．

(a) $[C_4C_1im][N(CN)_2]$　(b) $[N_{1123}][N(CN)_2]$

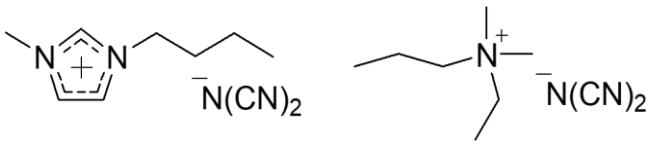

図 1. 本研究で用いたイオン液体

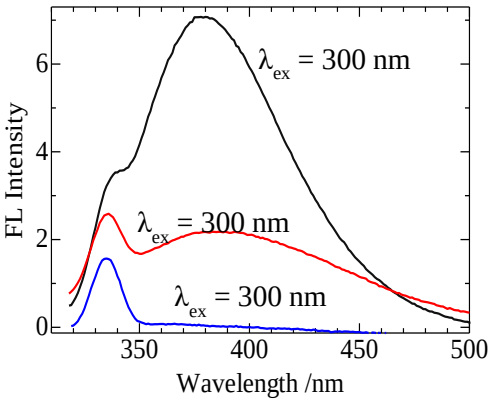

図 2. $[C_4C_1im][N(CN)_2]$ 未精製（黒），活性炭精製（赤），中性フラッシュシリカゲルカラムクロマトグラフィー（クロロホルム）精製（青）の蛍光スペクトル
(1 mM in water, 25 °C, 光路長 1 cm)

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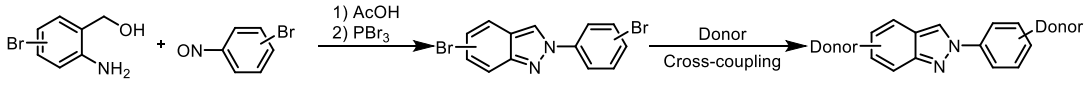
2*H*-インダゾール骨格を有するドナー・アクセプター型発光体の開発

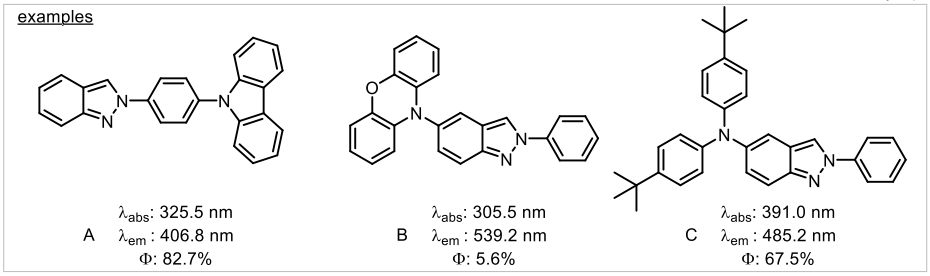
（茨大工[1]・茨大院理工[2]・兵庫県大院理[3]・静岡県大薬[4]）○小室 知広[1]・宮崎 優[2]・吾郷 友宏[3]・福元 博基[2]・近藤 健[4]
Development of donor-acceptor fluorophores with 2*H*-indazole skeleton ([1]*College of Engineering, Ibaraki University,* [2]*Graduate School of Science and Engineering, Ibaraki University,* [3]*Graduate School of Science, University of Hyogo,* [4]*School of Pharmaceutical Science, University of Shizuoka*) ○Tomohiro Komuro[1], Yu Miyazaki[2], Tomohiro Agou[3], Hiroki Fukumoto[2], Masaru Kondo[4].

2*H*-indazoles are unique quinonoid compounds with the fused ring of benzene and pyrazole. They are crucial structural motifs of various biologically active compounds. In contrast, organic fluorophores bearing the 2*H*-indazole motif have rarely been investigated. Here, we developed donor-acceptor fluorophores bearing 2*H*-indazole as an acceptor unit. In addition, the photochemical properties of these compounds are evaluated. We synthesized various donor-acceptor-type 2*H*-indazole fluorophores from 2-aminobenzyl alcohols and nitrosobenzenes. Evaluation of the luminescent properties of these compounds disclosed that compound A showed the high fluorescence quantum yield.
Keywords: Organic Fluorophore; Carbazole; N-Heterocycles

2*H*-インダゾールは、ベンゼン環とピラゾール環が縮環したキノノイド化合物であり、様々な生物活性物質の母核に含まれる。一方、その特異的な構造に着目した有機発光体への応用研究は未開拓である。本研究では、2*H*-インダゾールのアクセプター性に着目し、適切な位置にドナーを導入することで、ドナー・アクセプター型発光体を合成し、それらの光学特性を評価した。

2-アミノベンジルアルコール類とニトロソベンゼン類からブロモ基を有する 2*H*-インダゾールを合成し[1]、カルバゾールなどのドナーユニットとカップリングさせることで、様々なドナー・アクセプター型発光体を合成した。合成した発光体の発光特性を評価したところ、分子 A が高い蛍光量子収率を示した。





1) M. Kondo, S. Takizawa, Y. Jiang, H. Sasai. *Chem. Eur. J.* **2019**, *25*, 9866.

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大環状[36]トリチアノナフィリンの錯形成反応

(埼大院理工[1]・埼玉大科学分析支援センター[2]) ○長津 太己[1]・藤原 隆司[2]・石丸 雄大[1]
Metal complex reaction of [36]trithianonaphyrin (*[1]Graduate School of Science and Engineering, Saitama University*, *[2]Research and Development Bureau, Comprehensive Analysis Center for Science, Saitama University*) ○ Taiki Nagatsu[1], Takashi Fujihara[2], Yoshihiro Ishimaru[1]

Expanded porphyrins, renowned for their large, flexible π-conjugated systems and metal coordination capabilities, have garnered significant interest due to their distinctive structural and physical properties. Research in our laboratory has demonstrated that bispyrrolylthiophenes, incorporating thiophene skeletons, can react with aldehydes to yield [2+2], [3+3], and [4+4] cycloadducts. Given that the antiaromatic compound [36]trithianonaphyrin comprises three dipyrromethene skeletons, we have been investigating the coordination properties of these skeletons. The incorporation of zinc into the compound was executed using zinc chloride, with the reaction proceeding overnight at room temperature. This process was facilitated by the presence of K_2CO_3 in a $CHCl_3$/MeOH mixed solvent. The successful introduction of zinc was inferred from the disappearance of the intra-ring NH signal on the low-field side in the actual ^{1}H NMR spectrum. In this presentation, we will discuss the physical properties and structural characteristics of the resultant compounds.
Keywords : porphyrinoid; Antiaromaticity; steric hindrance

環拡張ポルフィリンは、大きく柔軟なπ共役系を持ち、金属配位能を有し、その構造や物性の変化に興味が持たれている。我々の研究室では、チオフェン骨格を組み込んだビスピロリルチオフェンとアルデヒドとの反応を行い、[2+2]、[3+3]、[4+4]環化付加体を与えることを明らかにしてきた。反芳香族化合物である[3+3]環化付加体([36]トリチアノナフィリン)は、ジピロメテン骨格を 3 つ持つことから、ジピロメテン骨格への二フッ化ホウ素部位の導入を試み、段階的に異なる配位構造ができることを明らかにした。本研究では、更なる配位部位の構築を行った。

フリーのジピロメテン骨格が 1 つ存在する化合物 **4** は、対応する[3+3]環化付加体を BF_3 と反応させ、分離することで得た。次に亜鉛の導入は、塩化亜鉛を用いて、K_2CO_3 存在下、$CHCl_3$/MeOH 中で一晩室温で反応することにより行った。実際の ^{1}H NMR から低磁場側の環内 NH シグナルの消失により、亜鉛が導入されたと考えた。講演では、得られた化合物の物性と構造についてその詳細を報告する。

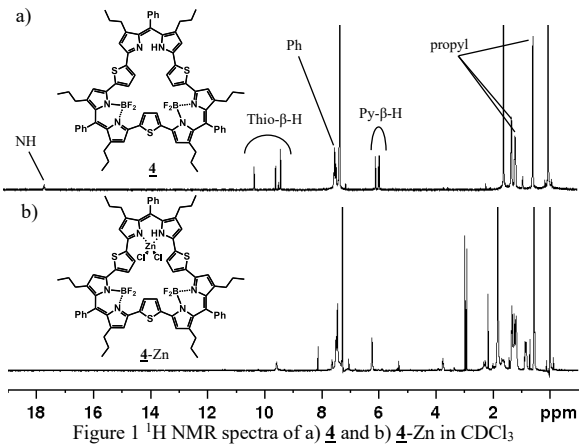

Figure 1 ^{1}H NMR spectra of a) **4** and b) **4**-Zn in $CDCl_3$

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

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC E1141(1141, Bldg. 11 [4F])

[E1141-4pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Toshifumi Dohi, Yuto Sumida

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1141-4pm-01]
Synthesis of optically active delta-lactones using enzymatic reaction and evaluation of their odors

○Masashi Kawasaki[1], Takuya Okada[2], Yasuo Tanaka[3], Naoki Toyooka[2] (1. Toyama Prefectural University, 2. University of Toyama, 3. Taiyo Corporation)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1141-4pm-02]
Asymmetric Synthesis of α-Heteroatom-substituted Aminonitriles by Hydrogen-Bonding-Donor Catalysis

○Yusuke Oyamada[1], Miku Fujii[1], Shuichi Nakamura[1] (1. Nagoya Institute of Technology)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1141-4pm-03]
Engineering the C4N4 Fluorophore to Develop Turn-On Fluorescent Probes for Heavy Metal Detection.

○Miki Kohei[1,2], Harald Gröger[2], Naoya Kumagai[1,3] (1. Graduate School of Pharmacy, Keio University, 2. Fuculty of Chemistry, Bielefeld University, 3. Institute of Microbial Chemistry)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[E1141-4pm-04]
Design and Synthesis of Self-Assembling Cyclic Trimer $[HyAl\text{-}Py]_3$ and its Strategic Applications

○Kotaro Tsuruoka[1], Naoya Kumagai[1,2] (1. Graduate School of Phramaceutical Science, Keio University, 2. Institude of Microbial Chemistry)

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酵素反応を利用した光学活性なデルタラクトン類の合成と香気評価

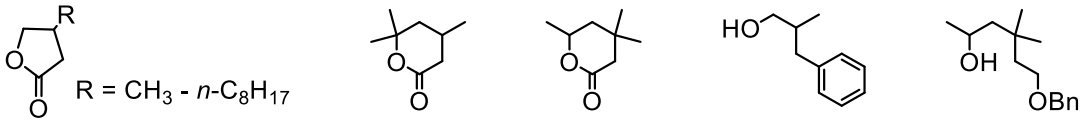
（富山県大工 [1]・富山大院理工 [2]・大洋香料 [3]）○川崎 正志 [1]・岡田 卓哉 [2]・田中 康雄 [3]・豊岡 尚樹 [2]
Synthesis of optically active delta-lactones using enzymatic reaction and evaluation of their odors ([1]*Faculty of Engineering*, *Toyama Prefectural University*, [2]*Graduate School of Science and Engineering*, *University of Toyama*, [3]*Taiyo Corporation*)○Masashi Kawasaki,[1] Takuya Okada,[2] Yasuo Tanaka,[3] Naoki Toyooka[2]

Numerous lactones have been discovered in nature and synthesized. Among them, *γ*-lactones and *δ*-lactones are considered essential compounds in the preparation of flavors and fragrances.[1] Inspired by this, we synthesized the enantiomers of eight *β*-substituted *γ*-lactones and reported on the relationship between the structures and the odors, as well as the olfactory differences between the enantiomers within the same lactone.[2] In this study, we synthesized the enantiomers of *δ*-lactones **1**, **2**[3] and evaluated the odors.

In the synthesis of the enantiomers of **1**, racemic primary alcohol (±)-**4** was optically resolved, and the resulting optically active alcohols, (*R*)- and (*S*)-**4**, were utilized as synthetic intermediates. Lipase, a kind of hydrolase, was employed for the enantioselective acetylation of (±)-**4** during the optical resolution. Similarly, utilizing racemic secondary alcohol (±)-**9**, the enantiomers of **2** were synthesized. The details of the results of odors evaluations for the enantiomers of **1** and **2** will be presented in the session.
Keywords: Lactone; Lipase; Odor

多くのラクトン類が天然から見出され、合成されている。その中の *γ*-ラクトン類、*δ*-ラクトン類はフレーバー、フレグランスの調香において必要不可欠な香料とされている [1]。そのようなことに触発され、我々は以前、8 種の *β*-置換 *γ*-ラクトンそれぞれの両鏡像異性体を合成し、構造と香気の関係および同一ラクトンにおける鏡像異性体間での香気の差異について調査、報告をした [2]。今回はラセミ体での香気が報告されている *δ*-ラクトン **1**, **2**[3]それぞれの両鏡像異性体を合成し、香気評価を行った。

δ-ラクトン **1** の両鏡像異性体の合成では、ラセミ体の 1 級アルコール(±)-**4** を光学分割し、得られた光学活性アルコール(*R*)-**4**, (*S*)-**4** を合成中間体として利用した。光学分割の際には加水分解酵素であるリパーゼを不斉触媒としたエナンチオ選択的なアセチル化反応を利用した。また、ラセミ体の 2 級アルコール(±)-**9** を利用し同様の手法で、*δ*-ラクトン **2** の両鏡像異性体を合成した。香気評価の結果は講演にて報告する。



1) 伊藤信彦、香りの技術動向と研究開発、中島基貴編、pp. 117-143、フレグランスジャーナル社、(2004). 2) M. Kawasaki *et al*., *Tetrahedron*, **2020**, *76*, 130984. 3) U. -A. Schaper *et al*., European Patent Organization, EP 0 004 978 A1 (1979).

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Asymmetric Synthesis of α-Heteroatom-substituted Aminonitriles by Hydrogen-Bonding-Donor Catalysis

(*Graduate School of Engineering, Nagoya Institute of Technology*) ○Yusuke Oyamada, Miku Fujii, Shuichi Nakamura

Keywords: nitriles; thiol; organocatalyst; enantioselective; ketals

Chiral α-aminonitriles are essential precursors to α-amino acids. In the field of aminonitrile synthesis, Strecker reaction has emerged as the most straightforward and powerful method.[1] However, several limitations remain for this type of reaction. One of the primary limitations is that this reaction is unsuitable for synthesizing α-heteroatom-substituted chiral α-amino nitriles due to the lack of electrophilicity of the electrophilic reactant (ester, amide, thioamide, etc.). Furthermore, this reaction sometimes requires the use of toxic cyanide precursors such as KCN, NaCN, $Zn(CN)_2$, etc. It should be noted that α-sulfur-substituted chiral α-amino nitriles and their derivatives are important structures because they are present in penicillin and other biologically active molecules.[2] These facts led us to become interested in the asymmetric synthesis of α-sulfur-substituted α-aminonitriles. We hypothesized that α-sulfur-substituted chiral aminonitriles could be obtained by using α-iminonitrile as a novel precursor to synthesize amino acid derivatives. Herein, we describe the first asymmetric synthesis of α-sulfur-substituted α-amino acid derivatives bearing a tetrasubstituted stereocenter (**Figure 1**).

When we used iminonitrile as an electrophile, benzyl thiol as a model nuclephile and 10 mol% of thiourea catalyst in CH_2Cl_2 for 30 minutes, we obtained the α-thio-substituted aminonitrile in 95% yield, 99% ee and only 1 mol% of the catalyst loading is still quite good for this reaction. We are delighted to find that this method enable for the construction of not only various *N*,*S*-ketal aminonitriles maintaining extremely high stereoselectivities in most cases but also *N*,*Se*-ketals. Some control experiments described the presence of nitrile plays an important role for both controlling enantioselectivity and enhancing electrophilic reactivity. This work can provide a powerful strategy for overcoming the limitation of synthesizable α-aminonitriles.

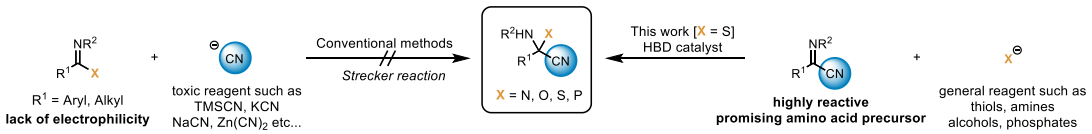

Figure 1

1) Wang, J.; Liu, X.; Feng, X. *Chem. Rev.* **2011**, *111*, 6947–6983. 2) Kohn, H.; Sawhney, K. N.; LeGall, P.; Robertson, D. W.; Leander, J. D. *J. Med. Chem.* **1991**, *34*, 2444–2452.

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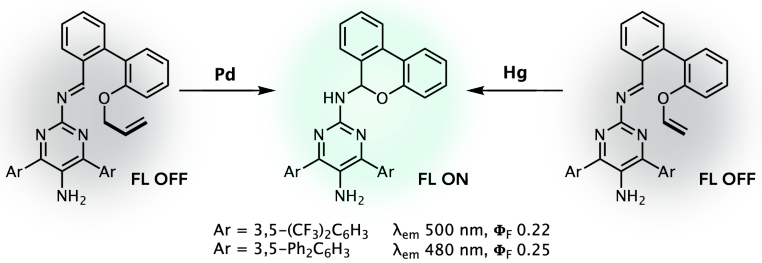
Engineering the C4N4 Fluorophore to Develop Turn-On Fluorescent Probes for Heavy Metal Detection

([1]*Graduate School of Pharmaceutical Sciences, Keio University,* [2]*Fuculty of Chemistry, Bielefeld University,* [3]*Institute of Microbial Chemistry*) ○ Miki Kohei,[1,2] Harald Gröger,[2] Naoya Kumagai[1,3]

Keywords: C4N4; Fluorescence; Probe; Palladium; Heavy Metal

Since heavy metals significantly expand the scope of chemical transformations, their use as catalysts and reagents is indispensable in the chemical industry. On the other hand, heavy metal residues are potentially harmful and subject to strict control, especially in the production of active pharmaceutical ingredients. Therefore, the development of a simple, fast, and efficient fluorometric analytical method for reliable detection of minute amounts of heavy metals is in high demand. C4N4, having free amino groups at the 2- and 5-positions of the pyrimidine core, is a new class of fluorescent materials that exhibits high quantum yield and large Stokes shift. We revealed that C4N4 can be rendered non-fluorescent by forming an imine with the 2-amino group, which can be exploited to design turn-on fluorescent probes in response to specific conditions of interest. Forming an "R^1-NH-CH(R^2)-OR^3"-subunit proved effective to regain intense fluorescence, thereby we synthesized the new derivative suitable to detect minute amounts of palladium. As a result, we confirmed that this new probe was capable to detect palladium by 30 minutes of stirring in the presence of $NaBH_4$ as a reductant in MeOH at room temperature. To note, this derivative displayed a decent selectivity form palladium among various metal cations. Furthermore, we found that the present turn-on mechanism was valid for other stimuli e.g. enzymes or other metal cations by employing appropriate substituents on the phenolic OH group, expanding the scope of probe applications. For example, mercury can be detected by switching the substituent from an allyl group to a vinyl group. The opportunity of probe application can be significantly leveraged by the orthogonal nature of absorption/emission properties, which can be independently manipulated by aromatic attachment at 4 and 6 positions. They also would be suitable in aqueous media making use of natural cofactors, opening up a perspective for being used in biological systems.



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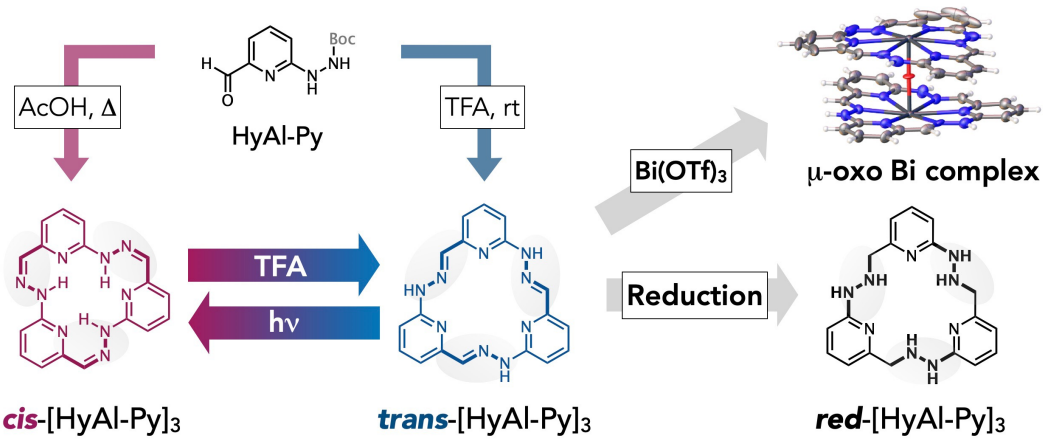
Design and Synthesis of Self-Assembling Cyclic Trimer [HyAl-Py]$_3$ and its Strategic Applications

([1]*Graduate School of Pharmaceutical Sciences, Keio University*, [2]*Institute of Microbial Chemistry*) ○ Kotaro Tsuruoka[1],Masato Nozaki[1], Naoya Kumagai[1,2]

Keywords: Pyridine; Hydrazone; Macrocyclic molecule; Metal complex; Photoisomerization

Hydrazone is used in various fields of chemistry due to its ease of synthesis, high stability, and unique structural properties. The facile hydrolytic cleavage of hydrazone also allows for its use as a key functional group in dynamic combinatorial chemistry (DCC). We have designed and synthesized a bifunctional pyridine monomer, HyAl-Py, bearing a hydrazine and a formyl group at the 2- and 6-positions for use in DCC. Exposure of HyAl-Py to TFA acidic conditions gave rise to cyclic trimer *trans*-[HyAl-Py]$_3$ in quantitative yield by triple head-to-tail *trans*-hydrazone formation. *trans*-[HyAl-Py]$_3$ has six inwardly oriented sp^2 nitrogen atoms capable to capture metal cations and formed complexes with rare earth and bismuth cations. In contrast, exposure of HyAl-Py to AcOH acidic conditions selectively gave *cis*-[HyAl-Py]$_3$ in which *cis*-configured hydrazono protons formed intramolecular hydrogen bonds to acquire a contracted planar structure. Upon irradiation with blue LED, photoexcited *trans*-[HyAl-Py]$_3$ isomerized to *cis*-[HyAl-Py]$_3$. The *cis*-[HyAl-Py]$_3$ reverted to the *trans* isomer by acidic treatment with TFA. *trans*-[HyAl-Py]$_3$ and *cis*-[HyAl-Py]$_3$ have contrasting physical properties such as solubility and fluorescence properties.

Reduction of the *trans*-[HyAl-Py]$_3$ hydrazone structure afforded a new cyclic hydrazine compound with six amino groups. Hydrazone formation was barely compromised by the presence of substituents at the 4-position of the pyridine moiety, furnishing various *trans*-[HyAl-Py]$_3$ derivatives. Each derivative is capable of reversible *trans*/*cis* isomerization, as well as metal complexation and fluorescence property.



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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1142(1142, Bldg. 11 [4F])

[E1142-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Katsuhiko Moriyama, Yoshihiro Nishimoto

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1142-4am-01]

meta-Selective Acylation of Electron-rich Arenes Using Aliphatic Carboxylic Acid Derivatives

○Yamato Goto[1], Sho Murakami[2], Yuto Sumida[3], Hirohisa Ohmiya[2] (1. Grad. Sch. Med. Sci., Kanazawa Univ., 2. ICR, Kyoto Univ., 3. IBB, Tokyo Med. & Dent. Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1142-4am-02]

A Dual Photoredox/Cobalt Catalysis Enabling Branch-Selective Hydroaminoalkylation of Alkenes

○Yunosuke Takekawa[1], Kazunori Nagao[2], Hirohisa Ohmiya[2] (1. Grad. Sch. Med. Sci., Kanazawa Univ., 2. ICR, Kyoto Univ.)

English
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1142-4am-03]

Defluoroarylation of Trifluoromethylarenes with Heteroarenes by PhotoredoxCatalysis and Tin Iodide

Naoki Sugihara[1], ○Masayuki Abe[1], Yoshihiro Nishimoto[1], Makoto Yasuda[1] (1. Graduate School of Engineering, Osaka University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1142-4am-04]

Development of Cycloaddition Reactions Using Triarylmethyl Cations as Photocatalysts

○Kazumichi Maeda[1], Tomoya Hisada[1], Yasuhiro Yamashita[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1142-4am-05]

Development of Metal Thiophenoxide Catalysts for Photoalkylation of Active Methylene Compounds

○Tomoya Hisada[1], Yuki Sato[1], Yasuhiro Yamashita[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1142-4am-06]

Photoinduced Alkylation of Stabilized Carbanions with Nonactivated Alkenes

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○Yuki Sato[1], Tomoya Hisada[1], Yasuhiro Yamashita[1], Shu Kobayashi[1] (1. The Univ. of Tokyo)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1142-4am-07]

Development of Photocatalytic alpha-Alkylation Reactions of Active Methine Compounds with Nonactivated Alkenes in the Presence of Lewis Acids

Yasuhiro Yamashita[1], ○Rentaro Enokijima[1], Tomoya Hisada[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1142-4am-08]

Development of Efficient Continuous-flow Synthetic Methods for 3-Aminochromon Scaffold Using *N*-Heterocyclic Carbene Catalysts

○Shunsuke Mouri[1], Haruro Ishitani[2], Shū Kobayashi[2] (1. NIPPON SODA CO., LTD., 2. The University of Tokyo)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

Break

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1142-4am-09]

Developments and Applications of Chiral Halonium Salts with Thiourea Moieties

○Shinano Kobayashi[1], Yasushi Yoshida[1], Takashi Mino[1] (1. Chiba University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1142-4am-10]

Development of Chiral Halonium Salts with Sulfonamide Moiety and Their Catalytic Applications

○Koki Obata[1], Yasushi Yoshida[1], Takashi Mino[1], Masami Sakamoto[1] (1. CHIBA University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1142-4am-11]

Remote Iodo-Esterification of 2-Substituted indole derivatives with Iodine Reagents

○Hiroko Wasaki[1], Katsuhiko Moriyama[1] (1. The Univ. of Chiba)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1142-4am-12]

Enantioselective Oxidative Aryl Rearrangement of α-Styryl Esters with Lewis Acid Combined Hypervalent Iodine Compound

○Honoka Kasahara[1], Yuna Nishiguchi[1], Katsuhiko Moriyama[1] (1. The Univ. of Chiba)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1142-4am-13]

Photoresponsive Cross Dehydrogenative Coupling Reaction of Tetrahydroisoquinolines with Iodide Catalyst

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○Hikari Kurihara[1], Katsuhiko Moriyama[1] (1. Chiba Univesity)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[E1142-4am-14]

Development of σ-Hole Catalyzed Iodocyanation Reactions

○Ikumi Furusawa[1], Yan Yu[1], Takayoshi Arai[1] (1. Graduate School of Science, Chiba University)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[E1142-4am-15]

Synthetic Study of 1′-Epi-7′-hydroxy-2-methyltanzawaic Acid B Amide

Takatsugu Murata[1], Hisazumi Tsutsui[1], Daiki Usukura[1], Fumiya Watabe[1], ○Hiroki Okano[1], Ryo Hirata[1], Ryunosuke Shiogama[1], Yamato Kanai[1], Yuki Asahara[1], Sayaka Chogi[1], Mai Amemiya[1], Airi Shiihashi[1], Motoyuki Shimonaka[1], Isamu Shiina[1] (1. Tokyo Univ. of Science)

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脂肪族カルボン酸誘導体を用いた電子豊富アレーンのメタ位選択的アシル化反応

（金沢大院医薬保 [1]・京大化研 [2]・医科歯科大生材研 [3]）○後藤 大和 [1]・村上 翔 [2]・隅田 有人 [3]・大宮 寛久 [2]

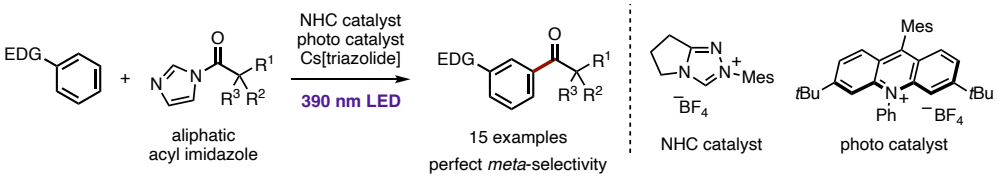
meta-Selective Acylation of Electron-rich Arenes Using Aliphatic Carboxylic Acid Derivatives

([1]*Graduate School of Pharmaceutical Sciences, Kanazawa University*, [2]*Institute for Chemical Research, Kyoto University,* [3]*Institute of Biomaterials and Bioengineering, Tokyo Medical & Dental University*) ○Yamato Goto,[1] Sho Murakami,[2] Yuto Sumida,[3] Hirohisa Ohmiya[2]

Ketones are one of the most fundamental structures found in pharmaceuticals and natural products. They are also important synthetic intermediates that are applicable to various transformations. Friedel-Crafts acylation which occurs at the *ortho*- or *para*-positions to the electron-donating group of aromatic rings is a powerful tool to construct ketones. Recently, we reported *meta*-selective acylation of electron-rich arenes enabled by N-heterocyclic carbene and photoredox cooperative catalysis[1)]. However, the reaction efficiency was poor in the case of using aliphatic carboxylic acid derivatives. In this study, we examined *meta*-selective acylation of electron-rich arenes using aliphatic acyl imidazoles. Reaction optimization revealed that 390 nm light source significantly improved the reaction efficiency. This reaction was applicable to the one-pot *meta*-selective acylation of electron rich arenes using acetic acid.
Keywords : N-Heterocyclic Carbene; Radical; Photoredox Catalyst; meta-Selective Acylation

ケトンは医薬品や天然物に普遍的にみられる重要な骨格である。また、Wittig 反応や Grignard 反応などの原料として利用できるため、有用な合成中間体である。それらケトンの合成法のうち、Friedel–Crafts 反応は強力な手法として知られている。Friedel–Crafts 反応は、芳香環上の電子供与性基に対して、オルト位またはパラ位選択的にアシル基が導入される。言い換えれば、芳香環上の電子供与性基のメタ位にアシル基を導入することは困難である。

このような背景のもと、我々は、N-ヘテロ環カルベン/光酸化還元協働触媒系と芳香族・脂肪族カルボン酸誘導体（アシルイミダゾール）を用いた、電子豊富アレーンのメタ位選択的アシル化反応を最近報告した[1)]。本反応は、芳香環上の電子供与性基のメタ位にアシル基が完璧な選択性で導入される新しいケトンの合成法である。一方で、脂肪族アシルイミダゾールの反応は、芳香族アシルイミダゾールの反応と比較して、効率が悪く、改善の余地があった。本研究では、脂肪族アシルイミダゾールを用いた電子豊富アレーンのメタ位選択的アシル化反応の収率向上を目指し、検討を行った。条件最適化の結果、390 nm の光源を用いることで反応効率が大幅に向上することを見出した。本触媒系は、酢酸を原料とした、ワンポット型の芳香環メタ位選択的アセチル化にも適用可能であった。



1) Goto, Y.; Sano, M.; Sumida, Y.; Ohmiya, H. *Nat. Synth.* **2023**, *2*, 1037.

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光酸化還元/コバルト協働触媒によるアルケンの分岐選択的ヒドロアミノアルキル化反応

（金沢大院医薬保[1]・京大化研[2]） ○武川 勇之助[1]、長尾 一哲[2]、大宮 寛久[2]

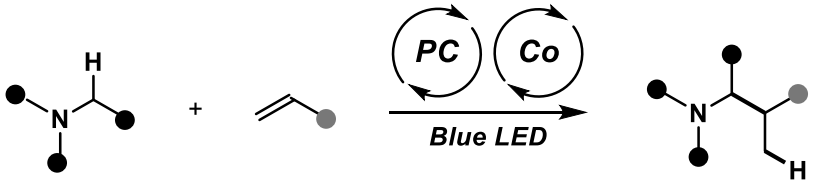
A Dual Photoredox/Cobalt Catalysis Enabling Branch-Selective Hydroaminoalkylation of Alkenes ([1]*Grad. Sch. Med. Sci., Kanazawa Univ.,* [2]*ICR, Kyoto Univ.*) ○Yunosuke Takekawa[1], Kazunori Nagao[2], Hirohisa Ohmiya[2]

We found that a dual photoredox/cobalt catalytic system promotes branch-selective hydroaminoalkylation of alkenes with various amine compounds. The reaction involves a cross radical–radical coupling between α-amino radicals from amine substrates through photochemical oxidation and alkyl radicals from alkenes through cobalt-mediated metal hydride hydrogen atom transfer.

Keywords :Photoredox Catalyst, Cobalt catalyst, Single electron transfer, Alkene, Hydroamino-alkylation

アミンの窒素隣接位炭素－水素結合がアルケンに付加するヒドロアミノアルキル化反応は、入手容易かつ安価な原料から複雑なアルキルアミン化合物を高い原子効率で与えることができる。これまでに報告されたアルケンのヒドロアミノアルキル化反応は、金属触媒を用いたものがほとんどである。しかし、これらの手法は、不安定な金属触媒の利用や反応位置の制御に問題がある。近年、光酸化還元触媒を用いた手法が報告されているが、直鎖状生成物を優先的に与えるものに限られており、分岐生成物を与える手法は未だ報告されていない。

今回我々は、光酸化還元/コバルト協働触媒[1]を用いた、アルケンの分岐選択的ヒドロアミノアルキル化反応を見出した。本手法は、幅広いアミン化合物とアルケンを基質として用いることができる。また、非天然のα-アミノ酸誘導体の合成に適用することができた。本反応では、アミンが光酸化還元触媒によって一電子酸化された後、窒素隣接位炭素－水素結合が脱プロトン化されてα-アミノラジカルが生成する。一方で、コバルト(II)触媒はアミンから取り出された一電子とプロトンを受け取ることで、コバルト(III)ヒドリド種に変換される。続いて、コバルト(III)ヒドリド種が、アルケンに対して分岐選択的な金属ヒドリド水素原子移動を引き起こすことでアルキルラジカルを与える。以上の過程により、形成されたα-アミノラジカルとアルキルラジカルが、ラジカルーラジカルカップリングすることで、所望のヒドロアミノアルキル化体が得られる。



1) Takekawa, Y.; Nakagawa, M.; Nagao, K.; Ohmiya, H. *Chem. Eur. J.* **2023**, e202301484.

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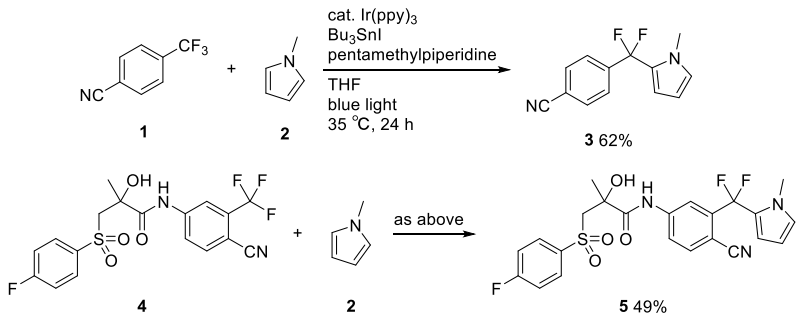
Defluoroarylation of Trifluoromethylarenes with Heteroarenes by Photoredox Catalysis and Tin Iodide

(*Graduate School of Engineering, Osaka University*) Naoki Sugihara, ○Masayuki Abe, Yoshihiro Nishimoto, Makoto Yasuda

Keywords: *photo reaction, photo catalyst, trifluoromethylarene, C-F transformation, tin compounds*

Fluorinated compounds are valuable in many fields, for example pharmaceutical chemistry and agrochemistry. Diaryldifluoromethane structures are important because of their functions as bioisosteres of diaryl ether and diaryl ketone structures.[1] A CF_2 unit would change the physical and biological properties of CF_2-containing molecules,[2] so effective methods to introduce a CF_2 unit are needed. Readily available trifluoromethylarenes ($ArCF_3$) would be efficient precursors for diaryldifluoromethanes ($ArCF_2Ar'$). However, the direct C–F bond transformation of trifluoromethylarenes is limited due to the robust C–F bond. Herein, we report that the heteroarylation of trifluoromethylarenes with pyrrole, furan, thiophen, and indole derivatives in the presence of $Ir(ppy)_3$ and Bu_3SnI under blue LED irradiation proceeded to give diaryldifluoromethanes.

The reaction of 4-(trifluoromethyl)benzonitrile **1** with *N*-methylpyrrole **2** proceeded in the presence of $Ir(ppy)_3$ (1 mol%) as a photocatalyst, 1,2,2,6,6-pentamethylpiperidine (PMP) as a base and Bu_3SnI as fluoride ion scavenger under blue LED irradiation to give the desired product **3** in 62% yield. Mechanistic studies revealed two significant functions of Bu_3SnI. Bu_3SnI functions as a fluoride ion scavenger to suppress a retro-reaction and as a single electron source to generate an Ir(II) species reducing $ArCF_3$. We also demonstrated a highly chemoselectivity in the heteroarylation of bicalutamide **4**, which is used to treat prostate cancer and has many functionalities; a C–F bond of the CF_3 group was selectively transformed to a pyrrolyl group.



1 **2** **3** 62%

4 **2** **5** 49%

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2) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev*. **2014**, *114*, 2432.

3) N. Sugihara, M. Abe, Y. Nishimoto, M. Yasuda, *Synthesis in press* DOI: 10.1055/a-2235-1380

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トリアリールメチルカチオンを光触媒として用いる付加環化反応の開発

(東大院理) ○前田一統・久田智也・山下恭弘・小林　修

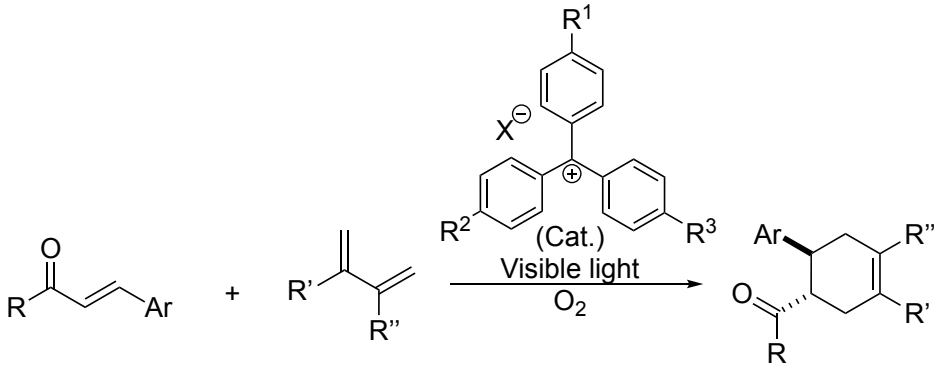
Development of Cycloaddition Reactions Using Triarylmethyl Cations as Photocatalysts

(School of Science, The Univ. of Tokyo) ○ Kazumichi Maeda, Tomoya Hisada, Yasuhiro YAMASHITA, Shū KOBAYASHI

Triarylmethyl cations are highly stable cations widely used as Lewis acid catalysts in synthetic organic chemistry. They hold promise as a new class of photocatalysts, because modification of aryl groups allows for the incorporation of diverse functionalities, expanding their potential applications. We explored their viability as photoredox catalysts in [4+2] and [2+2] cycloaddition reactions. By optimizing substituents, reaction time, and catalyst amount, we achieved high yields and regioselectivity for various substrates under green light irradiation in the presence of molecular oxygen. We also investigated immobilizing triarylmethyl cations on organic supports for continuous-flow applications. This presentation will report the details of these investigations and showcase the potential of triarylmethyl cations as versatile photocatalysts in organic synthesis.

Keywords: Homogeneous catalyst; Heterogeneous catalyst; Organocatalyst; Cycloaddition; photooxidation-reduction catalyst

トリアリールメチルカチオンは、安定なカルボカチオンであり、有機合成化学においてルイス酸触媒として広く用いられているが、光触媒としての活用はほとんどなされていなかった。一方で、トリアリールメチルカチオンは、各アリール基の構造を変換することで、様々な機能を付与することが可能であるため、大きな発展性を持つ光触媒であるといえる。そこで、本研究では、トリアリールメチルカチオンを光酸化還元触媒として用いる有機合成反応を試みた。アリール基上の置換基や反応時間、触媒量などといった反応条件の検討の結果、最適条件下で緑色光を照射した際に、様々な基質に対して[4+2]環化反応及び[2+2]環化反応が分子状酸素存在下、高収率、高位置選択的に進行することを見出した。また、連続フロー反応への応用を志向し、トリアリールメチルカチオンの有機担体への固定化も試みた。本講演では、これらの検討の詳細について報告する。



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活性メチレン化合物の光アルキル化反応における金属チオフェノキシド触媒の開発

(東大院理) ○久田智也・佐藤佑樹・山下恭弘・小林　修

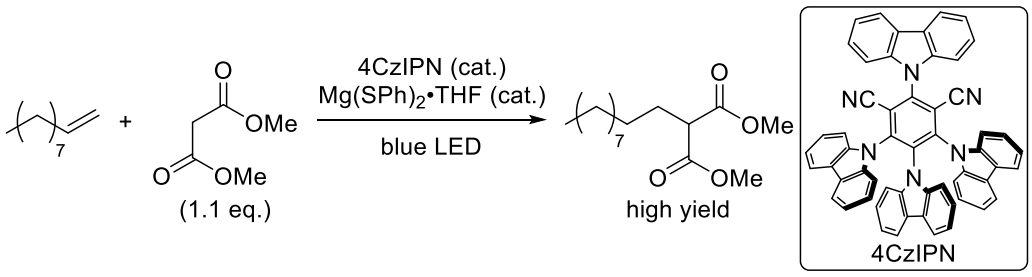
Development of Metal Thiophenoxide Catalysts for Photoalkylation of Active Methylene Compounds

(School of Science, The Univ. of Tokyo) ○ Tomoya HISADA, Yuki SATO, Yasuhiro YAMASHITA, Shū KOBAYASHI

Recently, photoredox catalysis using visible light has emerged as a powerful tool for activating and functionalizing inert substrates. As an example, our laboratory reported photo-induced α-alkylation reactions of active methylene compounds with nonactivated alkenes, demonstrating a synthetically valuable, atom-economical, and practical approach.[1] In this reaction, lithium thiophenoxide (LiSPh) is proposed to act as a multifunctional Lewis acid, Brønsted base, and Hydrogen Atom Transfer (HAT) catalyst. However, other metal thiophenoxides remains unexplored. Therefore, we synthesized a series of metal thiophenoxides and evaluated their catalytic activities in the α-alkylation reaction. Notably, magnesium thiophenoxide exhibited significantly higher activity than LiSPh, enabling a substantial reduction in catalyst loading.

Keywords: Photoreaction; Photoalkylation; Metal thiophenoxide; Active methylene compounds; Simple alkene

可視光レドックス触媒を用いた有機光反応は、従来困難とされてきた不活性な基質を反応させる手法として、近年注目されている。例えば、最近当研究室から報告された、可視光レドックス触媒を用いた、不活性アルケンによる活性メチレンの α-アルキル化反応は、合成的有用性が高いのみならず、簡便かつ原子効率の高い実用的手法でもある [1]。この反応において触媒として用いられるリチウムチオフェノキシド(LiSPh)は、ルイス酸・ブレンステッド塩基・水素原子移動(HAT)複合型触媒として機能すると考えられているが、他種の金属チオフェノキシドは十分に検討されていなかった。そこで、今回、種々の金属チオフェノキシドを合成し、その触媒活性を評価した。その結果、リチウムチオフェノキシドと比較して、マグネシウムチオフェノキシドの触媒活性は非常に高く、触媒量を大幅に低減することができた。



1) Yamashita, Y.; Kobayashi, S. *et al. J. Am. Chem. Soc.* **2023**, *145*, 23160.

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不活性アルケンを用いる安定カルボアニオンの光アルキル化反応

(東大院理)○佐藤佑樹・久田智也・山下恭弘・小林修

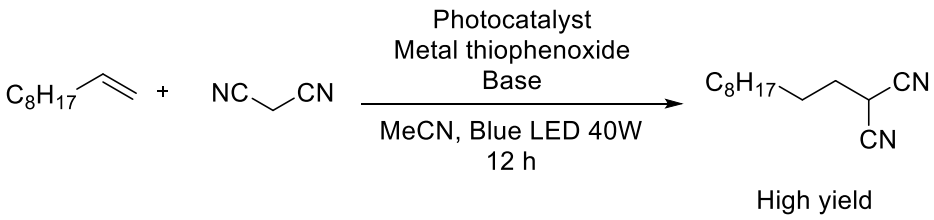
Photoalkylation of stable carbanion with nonactivated alkenes

(School of science, The Univ. of Tokyo) ○Yuki SATO, Tomoya HISADA, Yasuhiro Yamashita, Shū KOBAYASHI

Catalytic alkylation reactions using alkenes as electrophiles are highly efficient carbon–carbon bond forming reactions. We have recently reported photoinduced alkylation reactions of 1,3-dicarbonyl compounds such as malonates and β-ketoesters using nonactivated alkenes without electron-withdrawing groups.[1)] Although this reaction with catalytic amounts of organophotocatalyst and lithium thiophenoxide was applicable for various nonactivated alkenes and 1,3-dicarbonyl compounds in high yields, some stable carbanions such as malononitrile were found to be less reactive. We found that optimization of metal thiophenoxides improved the yield when malononitrile was used as a starting material. Furthermore, the additional use of a base facilitated the reaction further. Here, we report the details of this study.

Keywords: Organophotocatalyst, Metal thiophenolate, Photo reaction, Photoalkylation, Stable carbanion

アルケンを求電子剤として用いる触媒的アルキル化反応は、原子効率に優れた有用な分子骨格構築反応である。当研究室では、これまでに電子求引性基を有しない不活性アルケンを用いるマロン酸エステルや β-ケトエステル等の 1,3-ジカルボニル化合物の光アルキル化反応を報告してきた[1)]。触媒量の有機光触媒とリチウムチオフェノキシドを用いた本反応は、様々な不活性アルケンや 1,3-ジカルボニル化合物に対して低触媒量で高収率を示したが、マロノニトリル等の安定カルバニオンを用いた際には低収率でしか反応が進行しなかった。今回演者らは、鍵となる金属チオフェノキシドを最適化することで、マロノニトリルを用いる反応の収率が向上することを明らかにした。また、反応系に塩基を添加することで、目的の反応がさらに促進されることを見いだした。本講演ではこの検討の詳細について報告する。



1) Y. Yamashita.; S. Kobayashi *et al. J. Am. Chem. Soc*. **2023**, *145,* 23160.

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ルイス酸触媒を用いる活性メチン化合物の不活性アルケンによる光アルキル化反応の開発

（東大院理）山下恭弘・◯榎島蓮太朗・久田智也・小林修

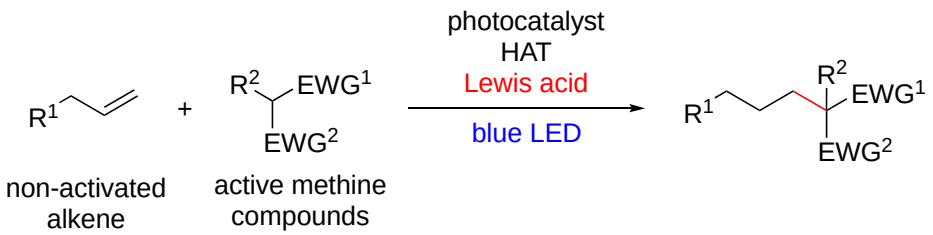
Development of Photocatalytic α-Alkylation Reactions of Active Methine Compounds with Nonactivated Alkenes in the Presence of Lewis Acids

(School of Science, The Univ. of Tokyo) Yasuhiro YAMASHITA, ◯Rentaro ENOKIJIMA, Tomoya HISADA, Shū KOBAYASHI

Alkylation using alkenes offers a highly efficient method for carbon–carbon bond formation due to its excellent atom economy. Our recent research demonstrated the remarkable impact of LiSPh in achieving high yields for photocatalytic alkylation of active methylene compounds under blue light irradiation, even when nonactivated alkenes like 1-decene was used.[1] Nonetheless, active methine compounds were found to be less reactive in such reaction system. Consequently, we focused on the influence of Lewis acids on the reaction process. This approach led to the successful development of a novel catalyst system employing a rare-earth metal triflate and a HAT catalyst under visible light irradiation. This new system boasts improved reaction rates and high efficiency, while promoting high atom economy.

Keywords: Lewis acid catalyst; Photocatalyst; Alkylation; Active methine; Nonactivated alkene

アルケンをアルキル源とするアルキル化反応は、その高い原子効率から炭素−炭素結合を生成する理想的な手法である。当研究室では、光触媒存在下 LiSPh を用いることにより、1−デセン等の不活性アルケンを用いる活性メチレン化合物のアルキル化反応が青色光照射下高収率で進行することを報告した [1]。しかし、この触媒系は活性メチン化合物に対しては反応性が低く、改善の余地が残されていた。演者らは、この反応系におけるルイス酸触媒の効果に着目し、新たな触媒系の検討を行った。その結果、希土類金属トリフラートと HAT 触媒を用いることで、目的の反応が円滑に進行することを見出した。本反応は、少ない触媒量でも短時間で高効率的に進行し、４級炭素を含む生成物を高収率で得ることができた。本講演では、本研究の詳細な結果について報告する。



1) Yamashita, Y.; Kobayashi, S. *et al. J. Am. Chem. Soc.* **2023**, *145*, 23160.

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N-ヘテロ環状カルベン触媒を用いた 3-アミノクロモン骨格の効率的連続フロー構築法の開発

(*日本曹達(株)*[1]・*アクティブファーマ(株)*[2]・*東大院 GSC 社会連携講座*[3]・*東大院理*[4])
○毛利春輔[1]・淺川俊也[2]・谷村昌俊[2]・石谷暖郎[3]・小林修[3,4]
Development of Efficient Continuous-flow Synthetic Methods for 3-Aminochromone Scaffold Using *N*-Heterocyclic Carbene Catalysts (NIPPON SODA CO., LTD.[1], ACTIVE PHARMA CO., LTD.[2], GSC Social Cooperation Lab.[3], School of Science[4], The Univ. of Tokyo) ○ Shunsuke MOURI,[1] Toshiya ASAKAWA,[2] Masatoshi TANIMURA,[2] Haruro ISHITANI,[3] Shū KOBAYASHI[3,4]

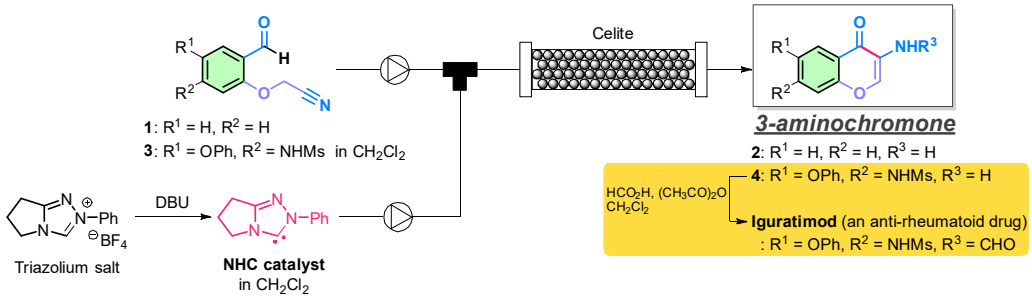
3-Aminochromone is one of the most common heterocyclic backbones found in many active pharmaceutical ingredients, and facile synthesis methods for functionalized 3-aminochromone derivatives are a key research topic in the pharmaceutical industry. In this context, we investigated synthesis of 3-aminochromone scaffold by using a *N*-heterocyclic carbene (NHC)-catalyzed intramolecular reductive carbon–carbon bond forming reaction between an aldehyde and a nitrile[1] and applied it to synthesis of iguratimod, an anti-rheumatoid drug, categorized as one of functionalized 3-aminochromone derivatives.

The desired 3-aminochromone **2** was obtained in good yield by mixing substrate **1** with 15 mol% of NHC catalyst derived from triazolium salt and DBU. When substrate **3** was used, further treatment of the product **4** under *N*-formylation conditions allows conversion to iguratimod.[2] We then applied this reaction in a continuous-flow manner. The flow reaction involved mixing the substrate and catalyst solutions in a mixer and feeding them into a suitable reactor.

Keywords: *NHC Catalyst; 3-Aminochromone; Intramolecular Cyclization; Flow Reaction*

3-アミノクロモンは、医薬品原体にしばしば含まれる骨格であり、その効率的構築法の開発は医薬品製造において重要である。今回、*N*-ヘテロ環状カルベン（NHC）触媒を用いた分子内アルデヒドーニトリル間の C−C 結合形成による効率的 3-アミノクロモン骨格構築[1]を検討し、連続フロー条件への適用を検討した。また、本法を抗リウマチ薬のイグラチモドの合成に適用したので併せて報告する。

基質 **1** に対し、トリアゾリウム塩と DBU から発生させた NHC 触媒 15 mol%をジクロロメタン中で混合することで、3-アミノクロモン **2** を得た。また、基質 **3** から導いた環化体 **4** に対して、*N*-ホルミル化を施すことでイグラチモドへの変換を確認した[2]。さらに、下図に示すように、基質と NHC 触媒のジクロロメタン溶液をミキサーで混合し、適切なリアクターに送液して反応を実施する連続フロー条件へ展開した。



1) Vedachalam, S.; Zeng, J.; Gorityala, B. K.; Antonio, M.; Liu, X. W. *Org. Lett.* **2010**, *12*, 352-355.
2) Murugesh, N.; Karvembu, R.; Vedachalam, S. *ChemistrySelect* **2020**, *5*, 13916-13918.

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チオ尿素部位を有するキラルハロニウム塩触媒の開発と応用

(千葉大工)○小林志奈野・吉田泰志・三野孝

Developments and Applications of Chiral Halonium Salts with Thiourea Moieties

(*Graduate School of Engineering, Chiba University*) ○Shinano Kobayashi, Yasushi Yoshida, Takashi Mino

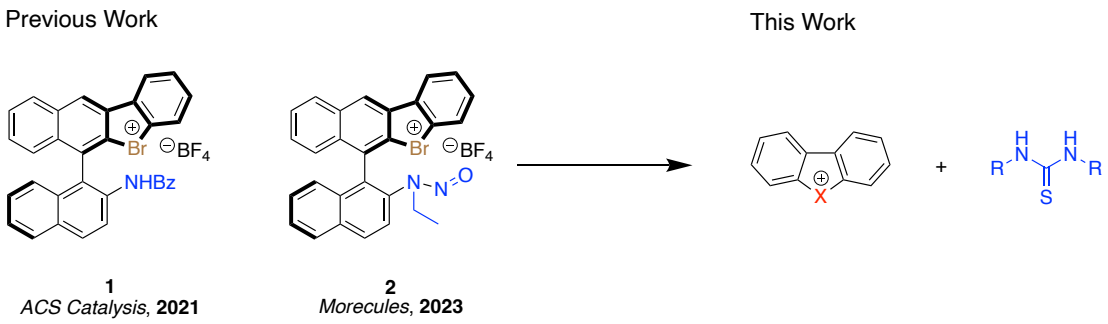
Halogen bonding is a promising interaction between halogen atoms and Lewis basic parts due to its characteristic Lewis acidity. Previously, we have developed and applied chiral halonium salts with an amide moiety **1** and with a *N*-nitrosamine moiety **2**, and found that they work as excellent asymmetric catalysts.[1)] In this study, we developed chiral halonium salts with thiourea moiety and applied them as asymmetric catalysts.

Chiral halonium salts with binaphthyl backbone were prepared from commercial (*R*)-BINAM in several steps. The synthesized molecules were tried to evaluate the abilities as asymmetric catalysts. In this presentation, we would also like to discuss about the detailed activation mechanism of our catalyst.

Keywords: Halogen Bond; Asymmetric Catalysis; Chiral Halonium Salts; Thiourea

ハロゲン結合は、その特徴的な Lewis 酸性から不斉触媒における分子認識力や活性化力として近年期待されている。当研究室では近年、アミド部位や *N*-ニトロソアミン部位を導入したキラルハロニウム塩を開発し応用することで、それらが優れた不斉触媒として機能することを明らかにしている[1)]。本研究では、キラルハロニウム塩とチオ尿素を組み合わせた分子を開発し、それらを不斉触媒として応用した。

ビナフチル骨格を有するキラルハロニウム塩は、市販されている(*R*)-BINAM を出発原料とする数段階の変換の後に合成した。得られた分子の不斉触媒としての機能を、既知の反応へ適用することで評価した。本発表では本触媒のチオ尿素部位が基質を活性化する詳細な機構に関しても報告する予定である。



1
ACS Catalysis, **2021**

2
Morecules, **2023**

1) (a) Y. Yoshida *et al*. *Chem. Commun.*, **2021**, *57*, 2519; (b) Y. Yoshida *et al*. *ACS Catal.*, **2021**, *11*, 13028; (c) Y. Yoshida *et al*. *Molecules*, **2023**, *28*, 384.

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スルホンアミド部位を有する新規キラルハロニウム塩触媒の開発とその応用

（千葉大院工）○小幡 晃己・吉田 泰志・三野 孝・坂本 昌巳

Development of Chiral Halonium Salts with Sulfonamide Moiety and Their Catalytic Applications

(*Graduate School of Engineering, Chiba University*) ○Koki Obata, Yasushi Yoshida, Takashi Mino, Masami Sakamoto

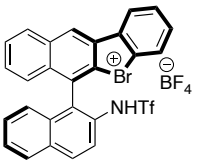
Halogen-bonding (XB) has been focused as a counterpart of hydrogen-bonding (HB), which has been widely utilized in organic chemistry for the activation and the recognition of the molecules. Although, their applications in the Lewis acidic chiral halogen-bonding catalyst have been still rare, we have previously developed chiral halonium salt with amide functionalities and applied them to several reactions as a catalyst.[1)] In this study, the more active chiral halogen-bonding catalyst with sulfonamide moiety is developed.

Chiral bromonium salts **1a** and **1b** were prepared from commercial BINAM, and were applied to various reactions. They were found to have higher catalytic activities than our previous catalysts, and were applied to the reaction with unactivated reactants to form products in good yields. These salts were also applied to Mannich reaction of ketimines with malonic esters, and the adducts were obtained in high yields with enantioselective fashion.

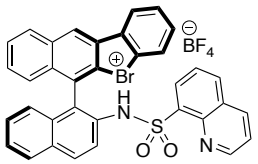
Keywords: Halogen Bond; Asymmetric Catalysis; Halonium Salts; Sulfonamide

ハロゲン結合は、現在広く利用されている水素結合に置き換わる可能性を秘めており、新たな相互作用として近年注目されているものの、その不斉 Lewis 酸触媒分野への応用例は限られている。当研究室では近年、アミド部位を有するキラルハロニウム塩を開発し、その不斉ハロゲン結合触媒としての応用を行なってきた[1)]。今回、我々はスルホンアミド部位を有するキラルハロニウム塩触媒 **1a** および **1b** を開発し、高い活性を有する触媒としての応用を試みた。

1aおよび**1b**を市販品であるBINAMから合成し、種々の反応へ適用したところ、我々の開発した従来の触媒を用いた場合では進行しなかった反応が収率良く進行するなど、高い活性化力を有していることが明らかとなった。また、マロン酸エステルのケチミンへのMannich反応に触媒として用いたところ、高収率かつ立体選択的に反応が進行した。



1a
High activity



1b
High activity
Good stereochemical control ability

1) (a) Y. Yoshida *et al*. *Chem. Commun.*, **2021**, *57*, 2519; (b) Y. Yoshida *et al*. *ACS Catal.*, **2021**, *11*, 13028.

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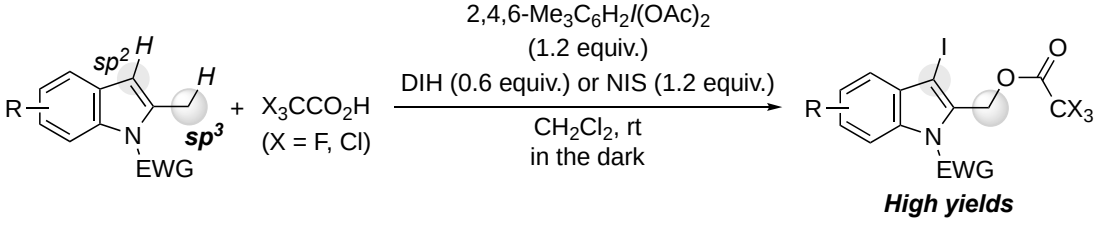
ヨウ素試薬を用いた２−置換インドール誘導体の遠隔位ヨードエステル化反応

（千葉大院理）○和崎宏子・森山克彦
Remote Iodo-esterification of 2-Substituted Indoles with Iodine Reagents (*Graduate School of Science, Chiba University*) ○Hiroko Wasaki, Katsuhiko Moriyama

The direct functionalization of organic compounds has attracted considerable attention recently as an exciting alternative for the installation of various heteroatoms into these compounds. In particular, the installation of functional groups into sp^3 carbon at the 2-position of 2-substituted indoles is achieved by transition metal catalyzed reaction and radical reaction. However, these practical methods are characterized by a simple functionalization as well as limited substrate scope and utility of the functionalized products. We developed 1,3-iodo-esterification of 2-substituted indole derivatives as regioselective remote Csp^2-Csp^3 dual functionalization, which simultaneously introduces two different functional groups into indole framework by a three-component reaction, using hypervalent iodine (III), trihalo-acetic acid, and iodine reagent to furnish the corresponding 2-(trihaloacetylmethyl)-3-iodo-indole derivatives in high yield.
Keywords : Hypervalent iodine, Iodine reagents, Dual functionalization, Iodo-esterification, 2-Substituted indole

不活性炭素一水素結合活性化を伴う直截的官能基導入反応は、挑戦的課題であり、特に、複素環化合物の直截的官能基導入反応は、機能性有機材料の効率的な合成手法として注目されている。従来の 2-置換インドール誘導体の 2 位 sp^3 炭素への直截的官能基化反応では、遷移金属触媒反応やラジカル反応を利用した sp^3 炭素へのヘテロ原子導入反応が達成されている。しかし、これらの反応は、いずれの場合もシンプルな官能基化反応に限られており、直截的官能基導入反応の汎用性は低いままである。本研究では、遠隔位 Csp^2–Csp^3 二重官能基化反応として、超原子価ヨウ素(III)、カルボン酸及びヨウ素化試薬を用いた 2-置換インドール誘導体の 1,3-ヨードエステル化反応を達成した。

実際に、2-メチルインドール誘導体にトリクロロ酢酸、ジアセトキシヨードメシチレン、及びヨウ素化試薬を、ジクロロメタン中で反応させたところ、目的の 2-トリクロロアセトキシメチル-3-ヨードインドール誘導体を高収率で得た。さらに、トリクロロ酢酸の代わりに、トリフルオロ酢酸を用いた時、1,3-ヨードエステル化及び加水分解のワンポット反応による 2-ヒドロキシメチル-3-ヨードインドール誘導体の合成に展開することができた。



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Lewis 酸複合型超原子価ヨウ素化合物を用いたα-スチリルエステルのエナンチオ選択的酸化的アリール転位反応

（千葉大院理）○笠原　ほのか・西口　由菜・森山　克彦

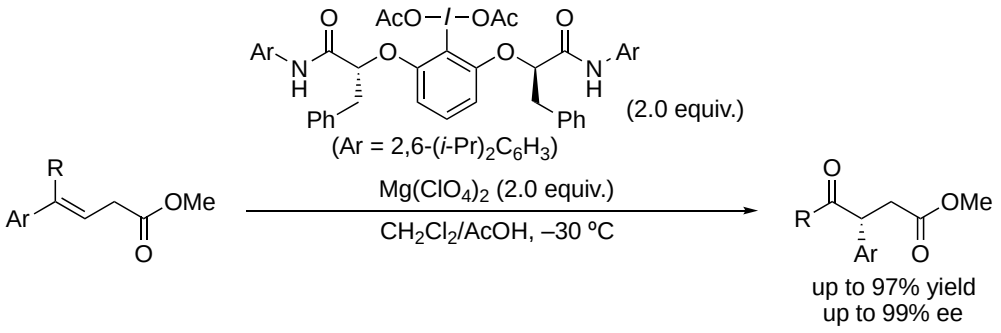
Enantioselective Oxidative Aryl Rearrangement Reaction of α-Styryl Esters Using Lewis Acid–Hypervalent Iodine (*Graduate School of Science, Chiba University*)○Honoka Kasahara, Yuna Nishiguchi, Katsuhiko Moriyama

Hypervalent iodine (III) compounds have been utilized as environmentally friendly reagents in lieu of heavy metal reagents to achieve various unique transformations. In particular, oxidative transformation using Lewis acid-combined hypervalent iodine (III), which indicates strong electrophilicity of iodine center activated by Lewis acid, has been attracting considerable attention as one of elegant and powerful methods for fine organic synthesis. On the other hand, asymmetric 1,4-dicarbonyl compounds are important molecules, including various natural products and bioactive compounds. We developed the enantioselective oxidative aryl rearrangement of α-styryl esters using $Mg(ClO_4)_2$ and chiral hypervalent iodine (III) compounds to furnish the corresponding asymmetric 1,4-dicarbonyl compounds in high yield with high enantioselectivity.

Keywords :Hypervalent Iodine; Lewis Acid; Aryl Rearrangement; 1,4-Dicarbonyl Compounds; Enantioselectivity

超原子価ヨウ素化合物は、遷移金属試薬の代用型試薬として幅広く利用されており、最近では、超原子価ヨウ素化合物と Lewis 酸を組み合わせることにより形成する Lewis 酸複合型超原子価ヨウ素複合体を利用した分子変換反応が注目されている。一方、複雑な非対称 1,4-ジカルボニル化合物は、様々な生理活性を有する化合物に含まれる重要な鍵骨格であるにもかかわらず、これら化合物の構築法は、適切なシントンがないために、挑戦的な課題である。本研究では、Lewis 酸複合型超原子価ヨウ素を利用したα-スチリルエステルのエナンチオ選択的酸化的アリール転位反応による非対称 1,4-ジカルボニル化合物の合成を検討した。

実際に、α-スチリルエステルに光学活性超原子価ヨウ素(III)化合物及び過塩素酸マグネシウム存在下、ジクロロメタン及び酢酸の混合溶液中で反応させたところ、反応が円滑に進行し、目的の 1,4-ジカルボニル化合物が高収率及び高エナンチオ選択性で得られた。



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日本化学会 第104春季年会 (2024)

ヨウ化物イオン触媒を用いたテトラヒドロイソキノリン誘導体の光応答型脱水素型クロスカップリング反応

（千葉大院理）○栗原　ひかり・森山　克彦

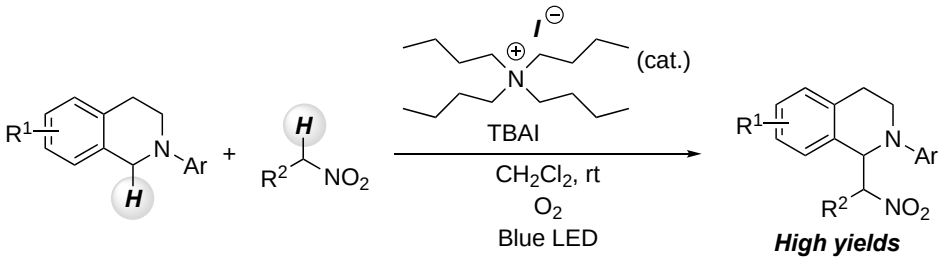
Photoresponsive Cross-Dehydrogenative Coupling Reaction of Tetrahydroisoquinolines with Iodide Catalyst (*Graduate School of Science, Chiba University*) ○Hikari Kurihara, Katuhiko Moriyama

Direct functionalization of organic molecules by inert C-H bond activation has been attracting considerable attention as one of elegant and powerful methods for organic synthesis. In particular, cross-dehydrogenative coupling reaction of heterocycles with coupling partners via oxidative direct C–C bond formation is important for constructing complex structures on natural product and bioactive compounds. We developed cross dehydrogenative coupling reaction of tetrahydroisoquinolines with nitroalkanes using TBAI as iodide catalyst and molecular oxygen as oxidant under blue LED irradiation conditions to furnish the corresponding coupling products in high yields.

Keywords : Iodide catalyst; Aerobic oxidation; Cross-dehydrogenative coupling reaction; Photo reaction; Tetrahydroisoquinolines

有機分子の不活性炭素ー水素結合の活性化による直截的官能基化反応は、効率的な分子変換反応として注目されている。特に、異なる 2 つの炭素ー水素結合を活性化することにより炭素ー炭素結合形成反応を促進させる脱水素型クロスカップリング反応は、酸化過程が重要であることが知られている。従来の方法では、遷移金属触媒を用いたヘテロ環化合物のα位選択的脱水素型クロスカップリング反応が達成されている。最近では、遷移金属触媒の代用型反応剤として酸化型ヨウ素化合物を用いたメタルフリーな反応が開発されている。しかし、従来の方法では、反応活性の高い酸化型ヨウ素化合物または酸化剤を用いる必要があった。今回、我々は究極のヨウ化物イオンの酸化による触媒的分子変換反応を追求するために、酸化剤を単体酸素に焦点をあて、光照射によるテトラヒドロイソキノリン誘導体及びニトロアルカンの脱水素型クロスカップリング反応を検討した。

実際には、テトラヒドロイソキノリン誘導体及びニトロアルカンに、触媒量のヨウ化テトラブチルアンモニウム(TBAI)を用いて、ジクロロメタン中、酸素雰囲気下及び青色 LED 照射下で反応させると、反応は円滑に進行し、目的のカップリング体が高収率で得られた。



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σ-ホール触媒を用いるヨードシアノ化反応の開発

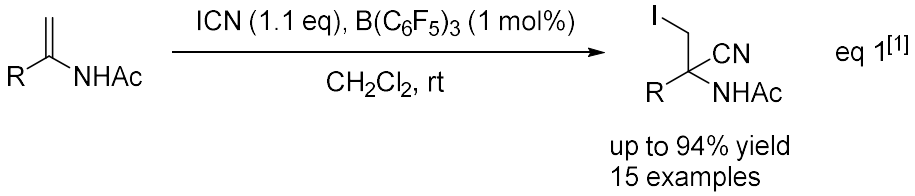
（千葉大院理）○古澤 郁実・于 言・荒井 孝義
Development of σ-Hole Catalyzed Iodocyanation Reactions (*Graduate School of Science, Chiba University*) ○Ikumi Furusawa, Yan Yu, Takayoshi Arai

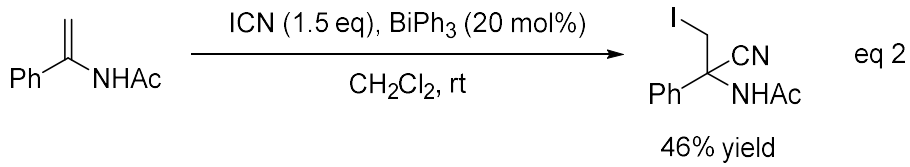
Halocyanation of alkenes is important reaction for introducing CN functionality with making a carbon-halogen bond in a single operation. A trispentafluorophenylborane ($B(C_6F_5)_3$) is realized as an efficient Lewis acid catalyst for promoting iodination/cyanation reaction of enamides (eq 1).[1]σ-hole observed on the surface of groups IV–VII elements has also received much attention as an alternative Lewis acid catalyst. Here, the Lewis acidic activity of triphenylbismuth ($BiPh_3$) was realized in the iodination/cyanation reaction of enamides with ICN to give the product in 46% yield (eq 2).

Keywords：*Halocyanation*; *σ-Hole*; *Bismuth*; *Enamide*; *Lewis acid*

アルケンのハロシアノ化は、炭素ーハロゲン結合の形成とともに、シアノ基を分子に導入できる魅力的な反応である。これまでに、トリスペンタフルオロフェニルボラン($B(C_6F_5)_3$)をルイス酸触媒に用いるエナミド基質のヨードシアノ化反応を報告している(eq 1)[1]。

一方、σ-ホールを形成する元素を含む化合物は、その正電荷によりルイス酸として利用する触媒化学の開発が注目されている。今回、トリフェニルビスマス($BiPh_3$)を触媒に用いた場合、46%収率で目的物が得られることを見出した(eq 2)。本反応はトリフェニルホウ素(BPh_3)では進行しないことから、ビスマス上の σ-ホールの活性の高さを見ることができる。





[1] Furusawa, I.; Suzuki, T.; Yu, Y.; Arai, T. *Adv. Synth. Catal.* **2023**, 365, 3247-3252.

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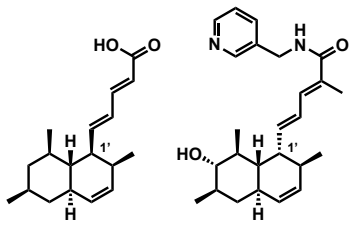
1’-エピ-7’-ヒドロキシ-2-メチルタンザワ酸Bアミドの合成研究

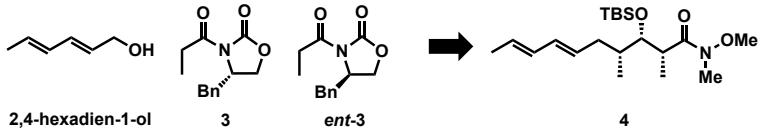
（東理大理）村田 貴嗣・筒井 久澄・臼倉 大輝・渡部 史也・○岡野 宙輝・平田 諒・塩釜 龍之介・金井 大和・浅原 侑季・長木 彩夏・雨宮 玉依・椎橋 愛莉・下仲 基之・椎名 勇
Synthetic Study of 1’-*Epi*-7’-hydroxy-2-methyltanzawaic Acid B Amide (*Faculty of Science, Tokyo University of Science*) Takatsugu Murata, Hisazumi Tsutsui, Daiki Usukura, Fumiya Watabe, ○Hiroki Okano, Ryo Hirata, Ryunosuke Shiogama, Yamato Kanai, Yuki Asahara, Sayaka Chogi, Mai Amemiya, Airi Shiihashi, Motoyuki Shimonaka, Isamu Shiina

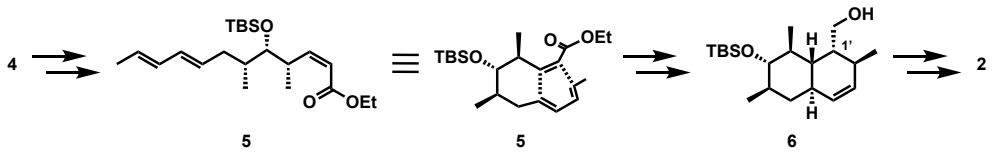
Tanzawaic acids, which are natural products, mostly have pentadienoic acid moiety and octalin skeleton. In this study, we accomplished a synthesis of 1’-*epi*-7’-hydroxy-2-methyltanzawaic acid B amide and researched the proliferation inhibitory activity against the cancer cell lines.
Keywords：Tanzawaic Acid ; Octalin; Mukaiyama Aldol Reaction; IMDA Reaction

タンザワ酸B(**1**)[1,2]は真菌ペニシリウム・シトリヌムより単離された化合物であり、ヒト白血球スーパーオキシド産生阻害剤として作用することが報告されている[3]。また、構造的特徴としてオクタリン骨格のC1’にペンタジエン酸部を有している。今回我々は、C1’の立体化学が異なる類縁化合物(**2**)の不斉合成に着手した。



2,4-hexadien-1-olを出発原料とし、**3**および*ent*-**3**を用いて炭素鎖を順次伸長することで**4**を得た[4,5]。その後、還元続く*Z*選択的な増炭反応により環化前駆体(**5**)へと導いた。加熱還流条件の熱的な分子内Diels–Alder (IMDA) 反応により二環性化合物(**6**)へと誘導し、Horner–Wadsworth–Emmons (HWE)反応を用いた側鎖部の導入、側鎖部の官能基変換を実施することで**2**の合成を達成した。





1) T. Okamura, D. Uemura *et al.*, *Chem. Lett*., **1997**, *26*, 885–886.
2) T. Murata, H. Tsutsui, I. Shiina *et al.*, *ACS Omega*, **2023**, *8*, 27703–27709.
3) Y. C. Kim, N. H. Oh *et al., Bioorg. Med. Chem. Lett*., **2014**, *24*, 5787–5791.
4) I. Shiina, Y. Umezaki, T. Yamori *et al*., *J. Med. Chem*., **2013**, *56*, 150–159.
5) I. Shiina, Y. Umezaki, T. Murata, K. Suzuki, T. Tonoi, *Synthesis*, **2018**, *50*, 1301–1306.

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

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
E1143(1143, Bldg. 11 [4F])

[E1143-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Ryosuke Masuda, Yota Sakakibara

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1143-4am-01]
Synthesis of four-membered ketones via intramolecular electrophilic addition reactions.

○Hayato Taguchi[1] (1. Hokkaido Univercity)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1143-4am-02]
Chiral amplification of aminonitriles and cyanohydrins by the sublimations

○Takumi Inoue[1], Tsuneomi Kawasaki[1] (1. Tokyo University of Science)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1143-4am-03]
Chirally and Chemically Reversible Strecker Reaction in Solid-state and Following Asymmetric Amplification (2)

○Yuya Masuda[1], Kawasaki Tsuneomi[1] (1. Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1143-4am-04]
Chiral amidine catalyzed enantioselective Strecker reaction

○Kohei Igota[1], Machida Yutaro, Kawasaki Tsuneomi[1] (1. Tokyo University of Science)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1143-4am-05]
Enantioselective addition of diisopropylzinc to the chiral organic crystal of achiral pyrimidine-5-carbaldehyde followed by asymmetric autocatalysis

○Tomohiro Ogawa[1], Daisuke Tateishi[1], Kenso Soai[1], Tsuneomi Kawasaki[1] (1. Tokyo University of Science)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1143-4am-06]
Synthetic studies of microbial hormone aveolide using biocatalytic reactions

○Keigo Sugimoto[1], Keiko Hishida[1], Takashi Monna[1], Atsushi Sakurai[1], Keigo Kakumaru[1], Ken-ichi Fuhshuku[1] (1. Meisei University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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[E1143-4am-07]

Development of Asymmetric Fluorocyclization of Difluoroalkenes with Concomitant Formation of a Trifluoromethy Group

○Chino Igarashi[1], Tomoya Mayumi[1], Hiromiti Egami[1], Yoshitaka Hamashima[1] (1. Grad. Sch. Pharm. Sci., Univ. of Shizuoka)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[E1143-4am-08]

Acceptorless Dehydrogenative Cross Coupling between Two C(sp^3)–H Bonds Enabled by Reversible Hydrogen-Atom Transfer

○Hiroki Fujita[1,2], Kosuke Ohmatsu[1,2], Takashi Ooi[1,2] (1. Grad. Sch. of Eng., Nagoya Univ., 2. WPI-ITbM, Nagoya Univ.)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[E1143-4am-09]

Development of Chiral Iron(II) Catalysts for Enantioselective Intramolecular Fluorine Transfer of *N*-Fluoroamides

○Yanghao Zhang[1], Shuhei Ohmura[1], Kazuaki Ishihara[1] (1. Nagoya University)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[E1143-4am-10]

γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [1]

○Takumi Kinoshita[1], Yota Sakakibara[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[E1143-4am-11]

Aminomethylation of unactivated alkenes enabled by α-ammonio radical

○Shumpei Nakatsuka[1], Kosuke Terada[1], Takumi Kinoshita[1], Yota Sakakibara[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[E1143-4am-12]

γ-Selective fluorination of tertiary amines enabled by α-ammonio radical

○Haruka Ono[1], Kazuki Hirate[1], Shoma Chiba[1], Yota Sakakibara[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[E1143-4am-13]

Mechanochemical C–H fluorination using generic polymers as radical initiators

○Yuri Kamakura[1], Tsubura Endo[1], Daiyo Miura[1], Satoshi Maeda[2,3], Julong Jiang[3], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. Faculty of Science, Hokkaido University)

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Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1143-4am-14]
Synthesis of Stable Tetrazene Radical Cation Salts and Their Application to Oxidation Catalysts
○Yusuke Sasano[1], Ayari Oshiro[1], Shohei Yoshinaga[2], Eunsang Kwon[1], Shinji Kajimoto[1], Yasuyuki Araki[1], Masaya Takahashi[1], Katsuhiko Sato[3], Naoki Shida[2], Mahito Atobe[2], Yoshiharu Iwabuchi[1] (1. Tohoku Univ., 2. Yokohama National Univ., 3. Tohoku Medical and Pharmaceutical Univ.)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[E1143-4am-15]
Photoinduced Coupling Reaction of Acylsilanes with Electrophilic Selenium Compounds
○Yuki Anami[1], Taisei Kuroki[1], Ryosuke Masuda[1], Hiroyuki Kusama[1] (1. Gakushuin University)

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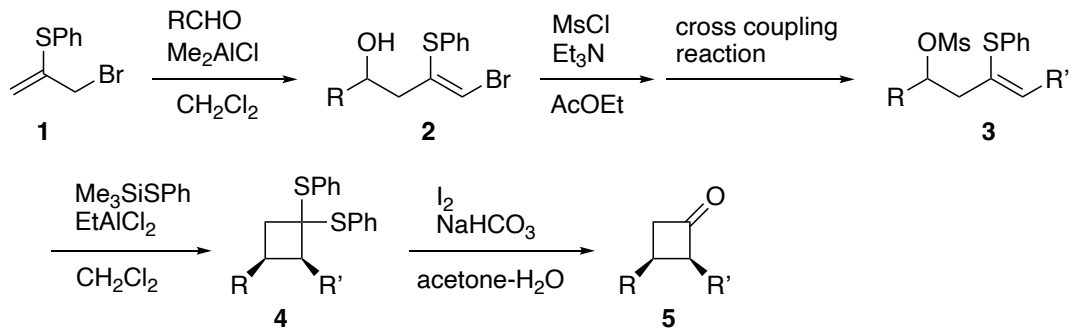
分子内求電子付加反応による 4 員環ケトン合成法の開発

（北大理 [1]・北大院総化 [2]・北大院理 [3]）○田口 颯人 [1]・竹内 貴志 [2]・佐藤 和都 [2]・石澤 公平 [2]・谷野 圭持 [3]
Synthesis of Four-membered Ketones via Intramolecular Electrophilic Addition Reactions
([1,3]*Faculty of Science, Hokkaido University,* [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*) ○Hayato Taguchi,[1] Takashi Takeuchi,[2] Kazuto Sato,[2] Kohei Ishizawa,[2] Keiji Tanino[3]

The [2+2] cycloaddition reactions of ketenes and alkenes are widely used for the synthesis of four-membered ketones. However, intermolecular versions of the cycloaddition reactions suffer from drawbacks such as limitation of substrates and lack of regio- and diastereoselectivity. In the present work, we developed an efficient method for the diastereoselective synthesis of four-membered ketones. The substrate **3** was prepared from alkene **1** and an aldehyde through a carbonyl ene reaction, mesylation, and a cross coupling reaction. Treatment of **3** with $EtAlCl_2$ and Me_3SiSPh resulted in a diastereoselective cyclization reaction to afford dithioacetal **4** which was readily converted to the corresponding ketone **5**.
Keywords : Four-membered ketone, Intramolecular addition reaction, vinyl sulfide, Lewis acid

ケテンとアルケンの[2+2]付加環化反応は、4 員環ケトンの代表的な合成法であるが分子間反応における位置および立体選択性の制御が困難であり、かつ反応基質の制約が大きい点が問題となっている。これに対して我々は、適当な脱離基を有するビニルスルフィドをルイス酸により活性化することで、4 員環ケトン等価体をジアステレオ選択的に合成する新たな手法を開発した。

まず、フェニルチオ基を有するアルケン **1** と種々のアルデヒドのエン反応を行い、*Z* 体の不飽和アルコール **2** を立体選択的に合成した。**2** をメタンスルホン酸エステルとした後、クロスカップリング反応に付して環化前駆体 **3** とした。**3** に Me_3SiSPh の共存下で $EtAlCl_2$ を作用させると、環化反応により生じたカチオン中間体がフェニルチオ基で捕捉され、ジチオアセタール **4** が得られた。本反応では、置換基 R と R’ がシスの関係にあるジアステレオマーが立体選択的に生じ、**4** は対応する 4 員環ケトン **5** に容易に変換された。講演では、本反応の基質適用範囲および、立体選択性発現のメカニズムについて述べる。



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アミノニトリルおよびシアノヒドリンの昇華による不斉増幅

（東理大理）○井上 拓実・川﨑 常臣
Chiral amplification of aminonitriles and cyanohydrins by the sublimations (*Department of Applied Chemistry, Tokyo University of Science*) ○Takumi Inoue, Tsuneomi Kawasaki

Aminonitriles and cyanohydrins are chiral intermediates for abiotic synthesis of amino acids and hydroxy acids. We have reported spontaneous absolute asymmetric synthesis of aminonitriles, forming conglomerate, through a three-components Strecker reaction.[1)]

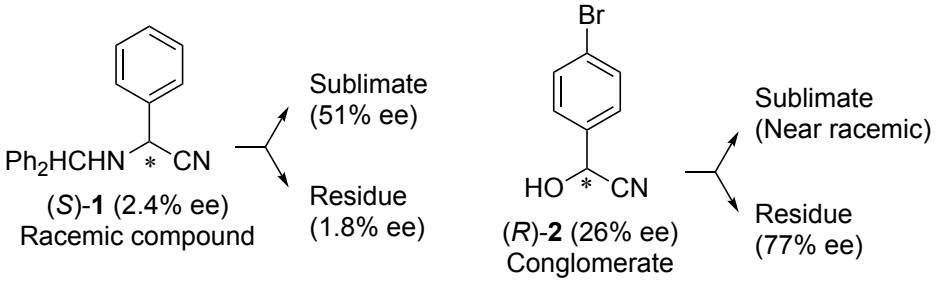
On the other hand, self-disproportionation of enantiomer (SDE) is a fundamental phenomenon that enhances the enantioenrichment of chiral compounds.[2)] Here we report on asymmetric amplification through the sublimation of the title compounds.

Aminonitrile **1** prepared from achiral benzaldehyde, benzhydrylamine and HCN underwent sublimation under reduced pressure. (*S*)-Aminonitrile **1**, initially with a 2.4% ee, resulted in a significantly enhanced 51% ee in the (*S*)-**1**, while the ee of remaining residue decreased to 1.8% ee. Furthermore, cyanohydrin **2**, forming conglomerate, was examined, in which residual **2** with amplified 77% ee (*R*) could be obtained as a result of sublimation of (*R*)-**2** with initial 26% ee.

Keywords : Self-Disproportionation of Enantiomer; Sublimation; Aminonitrile; Cyanohydrin

アミノニトリルとシアノヒドリンは、アミノ酸およびヒドロキシ酸のキラルな合成中間体である。当研究室では先に、コングロメレート形成するアミノニトリルの動的優先晶出に基づく不斉発生と増幅を報告した[1)]。一方、エナンチオマーの自己不均化（SDE）は、キラル化合物の鏡像体過剰率に変化をもたらす現象の本質である。本研究では、アミノニトリル、およびシアノヒドリンの昇華による不斉増幅を見出したので報告する。

ラセミ化合物を形成するアミノニトリル **1** の *S* 体（2.4% ee）を減圧下で加熱しながら昇華すると、不斉増幅した昇華物（51% ee）を得ることに成功した。残存固体の鏡像体過剰率は、1.8% ee に低減した。一方、コングロメレート形成するシアノヒドリン **2** の *R* 体（26% ee）を昇華したところ、残渣の鏡像体過剰率が増幅され 77% ee の(*R*)-**2** を得た。昇華物は、ほぼラセミ体であった。



1) Aiba, S.; Takamatsu, N.; Sasai, T.; Tokunaga, Y.; Kawasaki, T. *Chem. Commun*. **2016**, *52*, 10834.
2) Han, J.; Kitagawa, O.; Wzorek, A.; Klika, K. D.; Soloshonok, V. A. *Chem. Sci*. **2018**, *9*, 1718.

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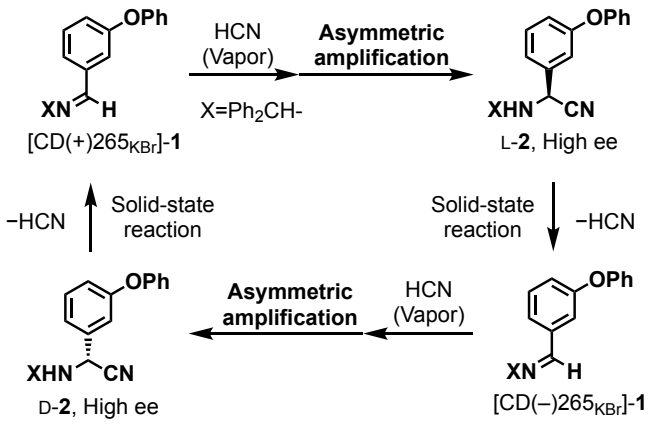
キラリティ反転を伴う可逆的ストレッカー反応と引き続く不斉増幅（２）

（東理大理）○増田 雄也・川﨑 常臣
Chirally and Chemically Reversible Strecker Reaction in Solid-state and Following Asymmetric Amplification (2) (*Department of Applied Chemistry, Tokyo University of Science*)
○Yuya Masuda, Tsuneomi Kawasaki

We have reported asymmetric HCN addition to enantiomorphic crystals of achiral imines to produce enantioenriched aminonitriles, moreover, dehydrocyanation of enantioenriched aminonitriles gave chiral crystals of achiral imines stereoselectively.[1] We found a stereoinversion of the chiral crystal of imine and enantioenriched aminonitrile in the sequence of reactions including HCN addition and elimination by using the substrates with 1-naphthyl substituent. In this research, we will discuss the reversible Strecker reaction of the compounds **1** and **2** with 3-phenoxyphenly substituent under the view point of the inversion of crystalline and molecular chirality.

Keywords : *Asymmetric Synthesis*; *Chiral Crystallization*; *Strecker Reaction*; *Asymmetric Amplification*; *Stereoinversion*

3-フェノキシベンズアルデヒドとベンズヒドリルアミンから合成されるアキラルイミン **1** が、キラル結晶化することを見出した。KBr 法による固体 CD スペクトルにより不斉認識が可能であり、265 nm 付近に正、または負のコットン効果を示す。[CD(+)265_{KBr}]-**1** をシアン化水素蒸気に晒す不斉シアン化水素付加反応を行い、従来法による不斉増幅 [2]と組み合わせることにより、L-**2** を高鏡像体過剰率で得ることに成功した。さらに、得られた L-**2** を炭酸カリウムと混合し、50 ºC で減圧するシアン化水素脱離反応を行った。反応は、立体選択的に進行しキラリティが反転した [CD(–)265_{KBr}]-**1** を与えた。なお、**1** および **2** の鏡像異性体を用いても同様の立体反転を確認した。従来の 1-ナフチル基を有する基質に加えて、本研究では、3-フェノキシフェニル基を有するアミノ酸合成中間体イミン **1**、およびアミノニトリル **2** が、可逆的ストレッカー反応によって、キラリティの反転を伴ってそれぞれ生成することを明らかにした。



1) Machida, Y.; Tanaka, Y.; Masuda, Y.; Kimura, A.; Kawasaki, T. *Chem Sci*, **2023**, 14, 4480.
2) Aiba, S.; Takamatsu, N.; Sasai, T.; Tokunaga, Y.; Kawasaki, T. *Chem Commun*. **2016**, 52, 10834.

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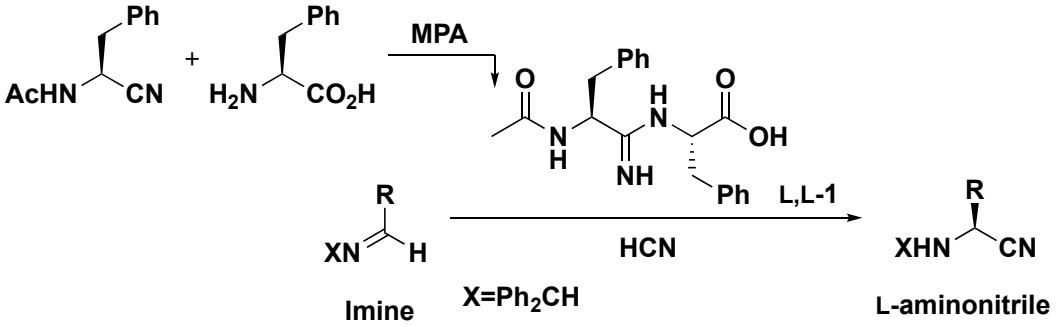
キラルアミジンを不斉触媒とするエナンチオ選択的ストレッカー反応

（東理大理）○伊吾田 光平・町田 雄太郎・川﨑 常臣
Chiral Amidine Catalyzed Enantioselective Strecker Reaction (*Department of Applied Chemistry, Tokyo University of Science*)
○Kohei Igota, Yutaro Machida, Tsuneomi Kawasaki

Strecker reaction has been considered as one of the credible methods of abiotic amino acid synthesis. Therefore, development of an asymmetric Strecker reaction is very interesting as a study to elucidate the origin of homochirality of amino acid. On the other hand, Powner et al. reported that thiol catalyzed the condensation of amino acids and amidonitriles to give corresponding amidines.[1] In this report, we focused on the Strecker reaction using amidine as an asymmetric catalyst. As a result, we found that chiral amidine **1** which synthesized from L-phenylalanine and L-*N*-acetylphenylalaninenitrile acts as an asymmetric catalyst for HCN addition reaction to aromatic aldimines. The concept of the self-replication of amino acid would be discussed via the Strecker reaction catalyzed by chiral amidine.
Keywords : Asymmetric Strecker reaction; Amidine; Asymmetric catalysis

チオールが触媒するアミドニトリルとアミノ酸とのカップリング反応が報告された[1]。本発表では、このような反応によって得られるキラルアミジンに着目し、不斉ストレッカー反応の触媒としての有効性を検証した。

まず、フェニルアラニンと *N*-アセチルフェニルアラニンニトリルのカップリング反応によって対応するアミジン **1** を合成した。これを不斉触媒として、種々の芳香族アルデヒドとベンズヒドリルアミンから得られるイミンに対して不斉シアン化水素付加反応をおこなった。その結果、*p*-トルアルデヒドとベンズヒドリルアミンから合成されるイミンに対して、(L,L)-**1** を不斉触媒として用いた際に、対応するアミノニトリルが最高で 77% ee の鏡像体過剰率で得られた。発表ではアミジン **1** のジアステレオマーや、他の基質を用いた際のエナンチオ選択性について議論する。



1) Foden, C. S.; Islam, S.; Fernandez-Garcia, C.; Maugeri, L.; Sheppard, T. D.; Powner, M. W. *Science* **2020**, *370*, 865–869.

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アキラルなピリミジン-5-カルバルデヒドが形成するキラル有機結晶を基質とする気相不斉イソプロピル化反応と引き続く不斉自己触媒反応

（東理大理）○小川 智央・立石 大佑・硤合 憲三・川﨑 常臣

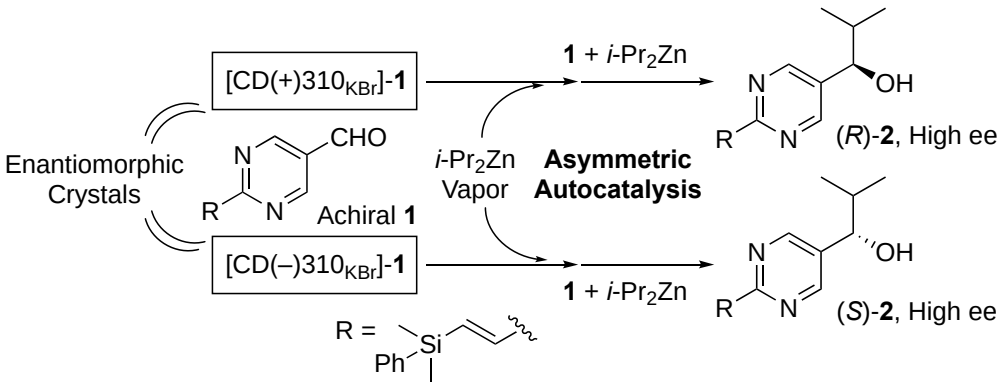
Enantioselective addition of diisopropylzinc to the chiral organic crystal of achiral pyrimidine-5-carbaldehyde followed by asymmetric autocatalysis (*Department of Applied Chemistry, Tokyo University of Science*) ○Tomohiro Ogawa, Daisuke Tateishi, Kenso Soai, Tsuneomi Kawasaki

Chiral crystallization of achiral compounds has been considered as a possible candidate for the origin of chirality. Asymmetric autocatalysis with amplification of ee, that is the Soai reaction, links the proposed origin of chirality and the biological homochirality.[1,2] We here report on the stereoselective vapor-phase reaction of diisopropylzinc (*i*-Pr_2Zn) to the chiral crystals of achiral pyrimidine-5-carbaldehyde **1**. After the amplification of ee by asymmetric autocatalysis, highly enantioenriched 5-pyrimidyl alkanol **2** could be synthesized with the corresponding absolute configuration to that of the crystal **1**.

Keywords：*Asymmetric Autocatalysis*; *Chiral Organic Crystal*; *Enantioselective Reaction*; *Vapor-phase Reaction; Amplification of ee*

ピリミジン-5-カルバルデヒド**1**は、アキラル化合物であるがキラル結晶化し、KBr法による固体CDスペクトルで310 nm付近に正、または負のコットン効果を示す。それぞれの結晶をジイソプロピル亜鉛の蒸気にさらし、不斉イソプロピル化反応をおこなった。その結果、結晶**1**の不斉に相関した絶対配置をもつピリミジルアルカノール**2**が得られた。この**2**を用いて、アルデヒド**1**と*i*-Pr_2Znを反応させる不斉自己触媒反応をおこなうことにより、対応する絶対配置の**2**を高鏡像体過剰率で合成した。

本結果は、アキラルな有機化合物のキラル結晶化を不斉の起源とし、不斉自己触媒反応によって高鏡像体過剰率の有機化合物へと至るモデルプロセスを具現化したものである。ホモキラリティの起源を検証する研究として興味深い。



1) Soai, K.; Kawasaki, T.; Matsumoto, A. *Acc. Chem. Res*. **2014**, *47*, 3643.
2) Matsumoto, A.; Tateishi, D.; Nakajima, T.; Kurosaki, S.; Ogawa, T.; Kawasaki, T.; Soai, K. *Chirality* **2023**, doi: 10.1002/chir.23617.

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生体触媒反応を利用する微生物ホルモンエバノライドの合成研究

（明星大理工）○杉本 圭伍・菱田 佳子・門奈 嵩士・櫻井 篤・角丸 啓悟・冨宿 賢一

Synthetic Studies of Microbial Hormone Avenolide Using Biocatalytic Reactions (*Department of Interdisciplinary Science and Engineering, Meisei University*) ○Keigo Sugimoto, Keiko Hishida, Takashi Monna, Atsushi Sakurai, Keigo Kakumaru, Ken-ichi Fuhshuku

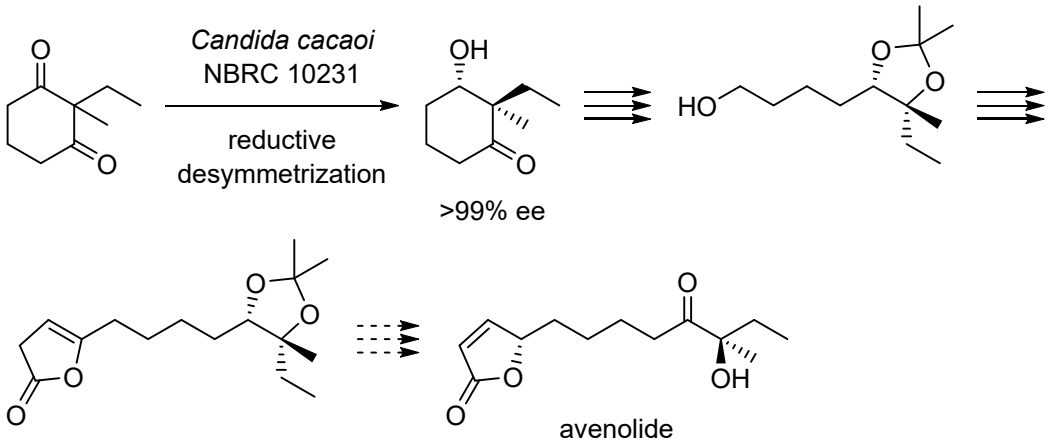
Avenolide is a signaling molecule called a microbial hormone produced by *Streptomyces avermitilis* as a secondary metabolite. It is essential for eliciting the production of the antibiotic avermectin, the important intermediate to produce ivermectin, an antiparasitic agent, at low concentrations.

The stereochemically pure hydroxyketone prepared by the microbial reduction using the yeast *Candida cacaoi* NBRC 10231 was converted to the alcohol corresponding to the side chain of avenolide via several steps of transformation. It was then coupled with furan and converted to β,γ-unsaturated butenolide structure by oxidation. The conversion to the α,β-unsaturated butenolide structure will be utilized the biocatalytic asymmetric isomerization reaction using the yeast *Ogataea polymorpha* NBRC 1476 under development in our laboratory.

Keywords : Asymmetric Synthesis; Biocatalyst; Butenolide; Desymmetrization; Isomerization

エバノライド(avenolide)は、放線菌 *Streptomyces avermitilis* が二次代謝産物として生産する微生物ホルモンとよばれるシグナル伝達物質である。その作用として、熱帯病オンコセルカ症に対する特効薬イベルメクチンの生産に重要な抗生物質エバーメクチンの産生を低濃度で誘導することが挙げられる。

酵母 *Candida cacaoi* NBRC 10231 が触媒する微生物還元により合成できる光学活性なヒドロキシケトンから数段階の変換を経て、エバノライドの側鎖に相当するアルコールへと変換した[1]。次いで、フランとカップリングし、TMS 化後の酸化によりβ,γ-不飽和ブテノライドに変換した。現在、β,γ-不飽和ブテノライドから(*S*)-α,β-不飽和ブテノライドへの生体触媒不斉異性化反応を検討している。



1) Monna, T.; Fuhshuku, K. *Mol. Catal.* **2020**, *497*, 111217.

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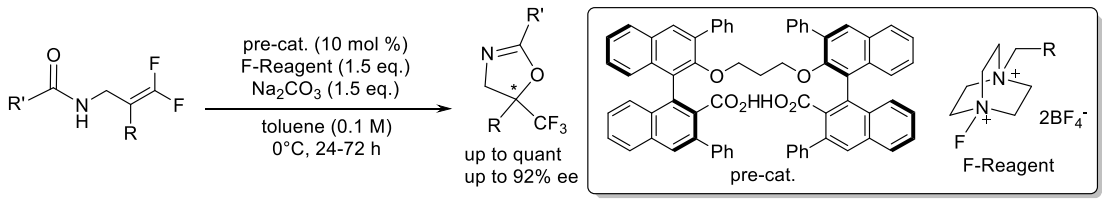
トリフルオロメチル基形成を伴うジフルオロアルケン類の不斉フルオロ環化反応の開発

（静岡県大院薬[1]） ○五十嵐 千乃[1]・眞弓 友耶[1]・江上 寛通[1]・濱島 義隆[1]
Development of Asymmetric Fluorocyclization of Difluoroalkenes with Concomitant Formation of a Trifluoromethy Group ([1]*Graduate School of Pharmaceutical Sciences, University of Shizuoka*) ○ Chino Igarashi[1], Tomoya Mayumi[1], Hiromichi Egami[1], Yoshitaka Hamashima[1]

Although stereoselective trifluoromethylation has been well-studied for the synthesis of chiral trifluoromethylated compounds, transformarions that give the corresponding products with high enantioselectivity are still limited. Thus, new approaches for the synthesis of chiral trifluoromethylated compounds are highly desirable. In this report, we achieved asymmetric fluorocyclization of difluoroalkenes with our dicarboxylate phase-transfer catalyst and a dicationic fluorinating reagent to afford chiral trifluoromethylated heterocycles in an enantioselective manner. To our knowledge, this is the first example of the asymmetric fluorocyclization of difluoroalkenes. The details will be discussed in the presentation.
Keywords: Phase-transfer catalyst; Fluorination; Trifluoromethyl groups; Difluoroalkene; Asymmetric reaction

含フッ素医農薬品のケミカルスペース拡大のために、sp^3 炭素にトリフルオロメチル(CF_3)基を置換させる試みが、近年注目を集めている。キラル CF_3 化合物を合成する端的な方法は、立体制御しながら CF_3 基を直接分子に導入する手法であるが、高エナンチオ選択的に目的物を与える基質は限られている[1)]。今回我々は、独自のジカルボキシラート型相間移動触媒[2)]を用いてジフルオロアルケン類にフッ素化を施すことで、CF_3 基の構築を行いつつ、隣接炭素にキラリティーを誘起する手法を着想した。

アミドを求核部位としたジフルオロアルケンを基質として設定し、種々条件検討したところ、目的のキラル CF_3 基含有オキサゾリン化合物を良好な収率と選択性で得ることができた。本反応はジフルオロアルケンの不斉フルオロ環化反応の初の成功例である。詳細は本発表にて議論する。



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C(sp^3)–H 結合間のアクセプターレス脱水素型クロスカップリング反応の開発

（名大院工 [1]・名大 ITbM[2]）○藤田 博貴 [1,2]・大松 亨介 [1,2]・大井 貴史 [1,2]

Acceptorless Dehydrogenative Cross Coupling between Two C(sp^3)–H Bonds Enabled by Reversible Hydrogen-Atom Transfer

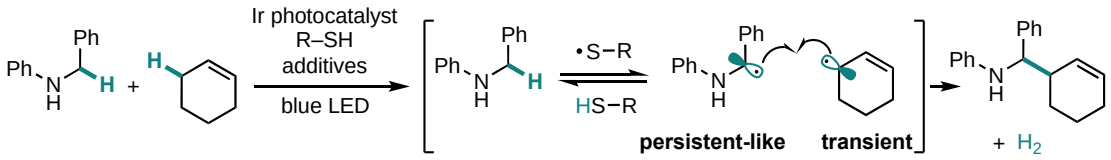
([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute of Transformative Bio-Molecules, Nagoya University*) ○Hiroki Fujita,[1,2] Kohsuke Ohmatsu,[1,2] Takashi Ooi[1,2]

Acceptorless dehydrogenative cross coupling (ADC) between two C–H bonds has garnered increasing attention in synthetic chemistry. Compared to conventional cross coupling between electrophilic organic halides and nucleophilic organometallic reagents, this mode of coupling can be implemented with less functionalized substrates, facilitating the step-economical synthesis of target molecules. In this presentation, we will disclose a strategy for realizing unprecedented ADC reaction between two different C(sp^3)–H bonds based on the photoinduced reversible hydrogen-atom transfer.

Keywords : Hydrogen-Atom Transfer; Photoredox Catalyst; Acceptorless Dehydrogenative Transformation

異なる二分子の C–H 結合を切断し、水素ガスを副生成物として放出しながら C–C 結合を生成する反応はアクセプターレス脱水素型クロスカップリング（ADC）と呼ばれ、高効率で環境負荷の少ない化学合成の実現に資する優れた手法として注目を集めている。ADC 反応は一般に、C–H 結合の切断・炭素活性種同士のカップリング・プロトン還元（水素放出）の 3 つの素反応で構成されるが、特に C–H 結合の切断はカップリングの適用範囲を決定づける重要な過程である。この観点から、広範な C(sp^3)–H 結合の切断が可能な水素原子移動（HAT）を活用する反応開発が有望となる。

HAT を起点とする ADC 反応は、我々の報告を含めていくつかの研究例が知られているが、そのほとんどは HAT で生成した炭素ラジカルの不飽和結合への付加を結合形成段階とする反応であり、必然的に C(sp^3)–H と C(sp^2)–H 結合間のカップリングに限定される [1]。2 種の異なる結合の HAT を起点とする ADC 反応も報告されているが、ベンジル位の C(sp^3)–H とホルミル C(sp^2)–H 間のカップリングに限られている [2]。今回我々は、前例のない非プロトン性 C(sp^3)–H 結合間の ADC 反応の開発に成功したので報告する。



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N-フルオロアミドのエナンチオ選択的分子内フッ素移動反応に有効なキラル鉄(II)触媒の開発

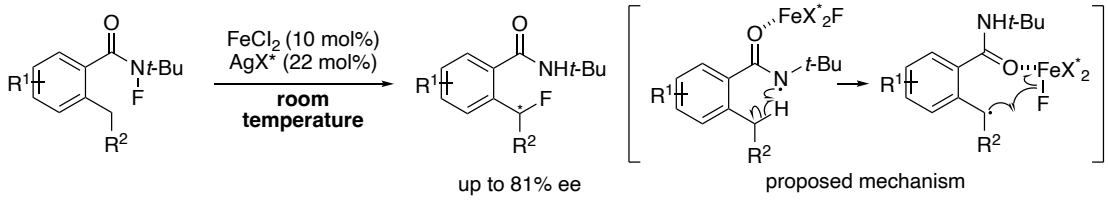
(名大院工)○張 養浩・大村 修平・石原 一彰

Development of Chiral Iron(II) Catalysts for Enantioselective Intramolecular Fluorine Transfer of *N*-Fluoroamides (*Graduate School of Engineering, Nagoya University*) ○Yanghao Zhang, Shuhei Ohmura, Kazuaki Ishihara

The replacement of C–H bonds for C–F bonds is known as an effective strategy to improve the metabolic stability and lipophilicity of pharmaceuticals, and therefore C–H fluorinations have received great attention in recent years. However, there are few reports of enantioselective methods because harsh reaction conditions are generally required to cleave robust C–H bonds.[1] Here, we found that enantioselective intramolecular fluorine transfers of *N*-fluoroamides proceeded in the presence of 10 mol% of $FeCl_2$ with 22 mol% of chiral silver salts. The cleavage of the C–H bonds under mild conditions was enabled by 1,5-hydrogen atom transfer (HAT),[2] and the subsequent asymmetric radical fluorination by chiral iron(III) fluorinating species (FeX^*_2F), which is assumed to be generated in the reaction system, afforded the corresponding C–H fluorinated compounds with good enantioselectivity.

Keywords: C–H Functionalization, Fluorination, Chiral Iron(II) Catalyst, N-Fluoroamide, Hydrogen Atom Transfer

医薬品の代謝安定性や脂溶性を向上させる手段として、分子内の水素をフッ素に置き換える手法が注目されている。こうした背景のもと、C–H フッ素化反応が近年盛んに開発されている。しかし、強固な C–H 結合を切断するために通常は加熱等の過激な反応条件を必要とするため、エナンチオ選択的手法の報告例はほとんどない[1]。今回、10 mol%の $FeCl_2$ と 22 mol%のキラル銀塩を組み合わせて用いることで、フルオロアミドの分子内フッ素移動反応がエナンチオ選択的に進行することを見出した。1,5-水素原子移動(HAT)を利用することで室温条件下での C–H 結合の切断が可能となり[2]、反応系中で生成すると想定されるキラル鉄(III)フッ素化剤(FeX^*_2F)を用いることで、目的生成物を良好なエナンチオ選択性で得た。



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第三級脂肪族アミンのγ位選択的な官能基化[1]

（関西学院理工）〇木之下 拓海・榊原 陽太・村上 慧

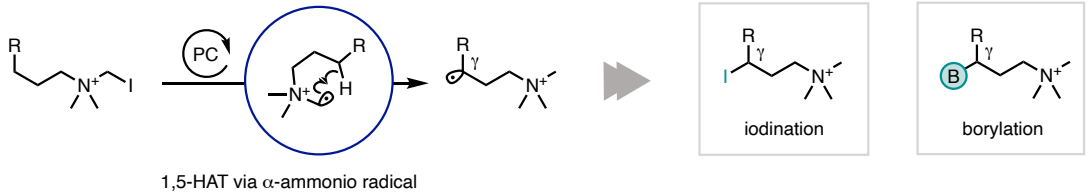
γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [1]

([1]*Graduate Department of Chemistry, School of Science and Engineering, Kwansei Gakuin University*) 〇Takumi Kinoshita, Yota Sakakibara, Kei Murakami

Tertiary alkylamines are ubiquitously found in various biologically active molecules such as pharmaceuticals, agrochemicals, and natural products. Therefore, the development of new methods that enable direct derivatization of these compounds has garnered significant attention from synthetic chemists for over half a century.[1)] However, the selective functionalization of tertiary alkylamines at remote sites from the nitrogen moiety remains a challenging research topic.[2)] Herein, we report a novel methodology for C–H functionalization at the γ-position of tertiary alkylamines. The starting tertiary alkylamines are smoothly converted to the corresponding iodomethyl ammonium salts, which can be transformed into α-ammonio radicals. Then, the resulting α-ammonio radicals abstract a hydrogen atom to form γ-ammonio radicals, which abstract an iodine atom to accomplish γ-iodination. Furthermore, the γ-ammonio radicals are trapped with diborane to achieve the formal γ-borylation of tertiary alkylamines.

Keywords : Quaternary ammonium salts; Photoredox catalysts; Radical; C–H functionalization; Halogenation

第三級アミンは医薬品や天然物などの生物活性分子に頻繁に見られる重要な化合物群である。そのため、これらの化合物の誘導体の迅速合成を可能とする直接官能基化法の開発は半世紀以上にわたり大きな関心を集めている。しかし、第三級脂肪族アミンの窒素原子から離れた位置の選択的な官能基化はいまだ難しく、新たな手法の開発が求められている。今回我々は第三級アミンの遠隔位置の官能基化を達成するために、第四級アンモニウム構造の特性を利用したラジカル反応に着目した。すなわち、第三級アミンから容易に調製可能なヨードメチルアンモニウム塩から、光触媒によって発生させたα-アンモニオラジカルが起こす分子内 1,5-水素原子移動(1,5-HAT)を利用することで窒素原子から離れた位置の官能基化を目指した。検討の結果、光触媒と還元剤を用いた条件で反応が進行し、窒素原子γ位にヨウ素原子が移動した生成物を良好な収率で得ることができた。また、ジボランを窒素原子のγ位に生じたラジカルの補足剤に用いることで遠隔位置のボリル化も可能であることを見いだした。



1,5-HAT via α-ammonio radical

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α-アンモニオラジカルが可能とする不活性アルケンのアミノメチル化反応

(関西学院大理工[1]) ○中塚 春平[1]・寺田 昂祐[1]・木之下 拓海[1]・榊原 陽太[1]・村上 慧[1]

Aminomethylation of unactivated alkenes enabled by α-ammonio radical ([1]*School of Science and Technology, Kwansei Gakuin University*) ○ Shumpei Nakatsuka,[1] Kosuke Terada,[1] Takumi Kinoshita,[1] Yota Sakakibara,[1] Kei Murakami[1]

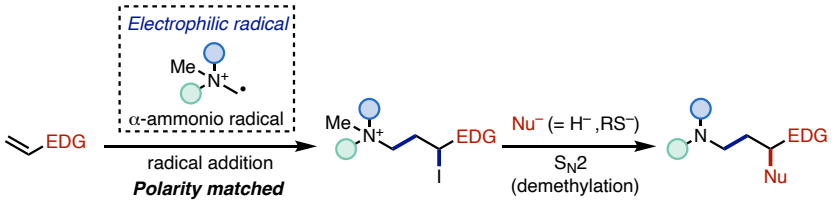
Tertiary aliphatic amines are ubiquitous scaffolds included in various bioactive molecules. Thus, the development of new synthetic methods for these compounds from abundant chemical feedstock is an important task. In terms of this, aminomethylation of alkenes, which are widely available feedstock, is an ideal reaction. However, despite its usefulness, the aminomethylation reaction of inert olefins remains underdeveloped[1)]. In this work, we have achieved the aminomethylation reaction of electron-rich unactivated alkenes by utilizing highly electrophilic α-ammonio radicals, which are easily generated under photocatalytic conditions.

Our reaction uses iodomethyl ammonium salts as radical precursors, which can be synthesized from corresponding amines. The radical precursor is converted into an α-ammonio radical by photoredox catalysis, and this radical species can react with inert alkenes. Finally, one-pot demethylation from the corresponding ammonium product by a nucleophile leads to the aminomethylation of unactivated alkenes.

Keywords : Photoredox catalyst; radical; ammonium salts; olefin; amine

第三級アミンは様々な医農薬品に含まれる重要な骨格であり、これらの化合物を入手容易なアルケンから合成する手法の開発はアミン合成に新たな選択肢を与える。しかし、その有用性にもかかわらず、不活性なアルケンを用いたアミノメチル化反応はほとんど報告されていない[1)]。このような背景から、本研究では高い求電子性と反応性を有するα-アンモニオラジカルを利用することで、電子豊富な不活性アルケンのアミノメチル化反応を達成した。

本反応では対応する第三級アミンから容易に調製可能なヨードメチルアンモニウム塩をラジカル前駆体として用いる。このラジカル前駆体に対し、光レドックス触媒を作用させることによりα-アンモニオラジカルを発生させ、このラジカル種が不活性アルケンにラジカル付加することで、アルケンのアンモニオメチル化が進行する。最後に、求核剤によって得られたアンモニウム化合物の脱メチル化をすることにより、ワンポットでの不活性アルケンのアミノメチル化に成功した。



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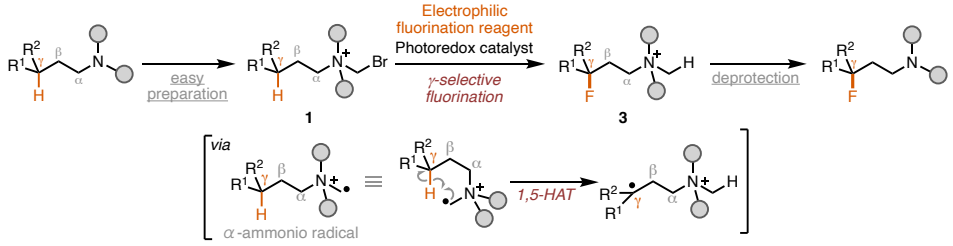
α–アンモニオラジカルを利用した第三級アミンのγ位選択的フッ素化

（関西学院大理工）○小野遥・平手和希・千葉将真・榊原陽太・村上慧
γ-Selective fluorination of tertiary amines enabled by α-ammonio radical (*Graduate School of Science and Engineering, Kwansei Gakuin University*)
○Haruka Ono, Kazuki Hirate, Shoma Chiba, Yota Sakakibara, Kei Murakami

The introduction of fluorine atoms into pharmaceuticals is one of the most effective methods for improving pharmacological activity. Thus, the development of C–H fluorination of tertiary aliphatic amines, which according to 26% of all pharmaceuticals, leads to the discovery of new bioactive molecules. Herein, we report the γ-selective functionalization of tertiary amines by utilizing α-ammonio radical. Our reaction used bromomethyl ammonium salts as radical precursors, which can be synthesized from the corresponding amines. The key to this reaction is intramolecular hydrogen atom transfer enabled by α-ammonio radical. The reaction allows the selective introduction of the fluorine atom into γ position of the nitrogen atom.

Keywords : Photoredox catalyst; Radical; Quaternary ammonium salts; C–H functionalization; Fluorination

医薬品化合物に対するフッ素原子の導入は、脂溶性や代謝安定性の向上が期待できることから医薬品の薬理活性を高める有効な手段の一つである[1]。そのため、医薬品全体の約 26%に含まれている第三級アミン構造[2]に対する位置選択的な C–H フッ素化反応を開発することができれば、新たな医薬品の創出に繋がる。しかし、C–H フッ素化反応に用いられる求電子的フッ素化剤と第三級アミンの相性の悪さから、いまだ汎用的な第三級アミンの C–H フッ素化反応は報告されていない。そこで我々は、α-アンモニオラジカルを鍵とする形式的な第三級アミンのγ位選択的なフッ素化反応を開発した。本反応では、第三級アミンから容易に調製可能なブロモメチルアンモニウム塩 **1** をラジカル前駆体として用いる。この前駆体に対して光触媒を作用させる事でα-アンモニオラジカルが発生し、このラジカル種が分子内水素移動(1,5-HAT)を起こす事で窒素原子のγ位にラジカルが移動する。最後に求電子的フッ素化剤からフッ素原子を引き抜くことで、γ-フルオロアンモニウム塩の合成を達成した。



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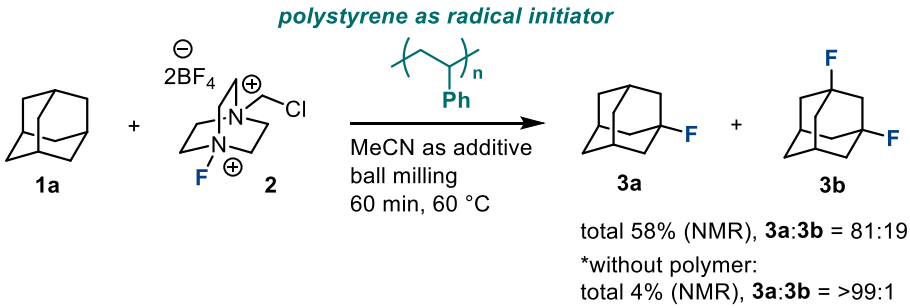
汎用ポリマーをラジカル開始剤として用いたメカノケミカル C–H フッ素化反応の開発

（北大院工[1]・北大 WPI-ICReDD[2]・北大院理[3]）○鎌倉 有里[1]・遠藤 円[1]・三浦 大洋[1]・Julong Jiang[3]・前田 理[2,3]・久保田 浩司[1,2]・伊藤 肇[1,2]
Mechanochemical C–H fluorination using generic polymers as radical initiators
([1]*Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*, [3]*Faculty of Science, Hokkaido University*) ○Yuri Kamakura[1]・Tsubura Endo[1]・Daiyo Miura[1]・Julong Jiang[3]・Satoshi Maeda[2,3]・Koji Kubota[1,2]・Hajime Ito[1,2]

Free radical reactions using radical initiators are one of important reactions in organic synthesis. However, commonly used radical initiators such as azo compounds, peroxides and organometallic reagents are highly reactive and potentially explosive, often requiring special precautions. In this study, we developed a radical C–H fluorination reaction using safe and cheap commodity plastics as a radical initiator under mechanochemical conditions.[1] In this approach, a polymeric mechanoradical, which are generated by homolytic cleavage of the polymer chains by the ball-milling process, reacts with a fluorination reagent to initiate the radical chain C–H fluorination.
Keywords : Mechanochemistry; Ball mill; Radical; Fluorination; Polymer

ラジカル開始剤を用いたフリーラジカル反応は、有機合成において重要な反応のひとつである。しかし、一般的に用いられるアゾ化合物、過酸化物や有機金属試薬などのラジカル開始剤は反応性が高く、爆発性の懸念があり、安全性の観点で課題がある[1]。本研究では、安全で安価な汎用ポリマーをラジカル開始剤として用いたメカノケミカル C–H フッ素化の開発に成功した[2]。このアプローチでは、ボールミルの機械的な作用によりポリマー主鎖が開裂し、発生した高分子メカノラジカルがフッ素化試薬を活性化することで、ラジカルチェイン型の C–H フッ素化反応が進行する。



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安定テトラゼンラジカルカチオン塩の合成と酸化触媒活性の開拓

（東北大院薬 [1]・横浜国大院理工 [2]・東北大院理 [3]・東北大多元研 [4]・東北医薬大薬 [5]）
○笹野 裕介 [1]・大城 彩里 [1]・吉永 昌平 [2]・權 垠相 [3]・梶本 真司 [1]・荒木 保幸 [4]・高橋 昌也 [1]・佐藤 勝彦 [5]・信田 尚毅 [2]・跡部 真人 [2]・岩渕 好治 [1]

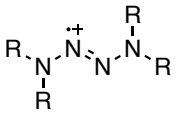
Synthesis of Stable Tetrazene Radical Cation Salts and Their Application to Oxidation Catalysts ([1]*Graduate School of Pharmaceutical Sciences, Tohoku University*, [2]*Graduate School of Science and Engineering, Yokohama National University,* [3]*Graduate School of Science, Tohoku University*, [4]*Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University,* [5]*Faculty of Pharmaceutical Science, Tohoku Medical and Pharmaceutical University*) ○Yusuke Sasano,[1] Ayari Oshiro,[1] Shohei Yoshinaga,[2] Eunsang Kwon,[3] Shinji Kajimoto,[1] Yasuyuki Araki,[4] Masaya Takahashi,[1] Katsuhiko Sato,[5] Naoki Shida,[2] Mahito Atobe,[2] Yoshiharu Iwabuchi[1]

Herein we report the first synthesis of stable tetrazene radical cation salts and their unique properties, including their catalytic activity for oxidation. A radical cation obtained by one-electron oxidation of DAD, a tetrazene with adamantane skeleton, was isolated as a salt that can exist stably under air at room temperature and pressure for a long time, and its structure and properties were elucidated by various analyses. DAD underwent a reversible two-electron redox reaction and showed high activity as a catalyst for alcohol oxidation.

Keywords : Stable Radical; Redox; Molecular Catalysis; 2-Tetrazene

2-テトラゼンは、窒素原子が直列に 4 つ繋がった構造単位を持つ化合物である。一部の 2-テトラゼンは可逆的な二電子の酸化還元活性をもつことと、これが一電子酸化を受けて生成するラジカルカチオンが ESR によって観測されることが報告されている [1)]。しかし、これらのラジカルカチオンは不安定であり、テトラゼンラジカルカチオン塩が単離および構造決定された例はない。

本発表では、初の安定テトラゼンラジカルカチオン塩の合成と、その酸化触媒活性を含むユニークな性質を報告する。アダマンタン骨格をもつテトラゼン化合物 DAD を一電子酸化して生じるラジカルカチオンを、常温常圧空気下に長時間安定に存在可能な塩として単離することに成功し、種々の分析によってその構造と性質を明らかにした。DAD は可逆的な二電子の酸化還元を起こし、アルコールの酸化触媒として高い活性を示した [2)]。



2-tetrazene radical cation

1) (a) W. M. Tolles, *et al. J. Am. Chem. Soc.* **1966**, *88*, 3476–3479; (b) S. F. Nelsen, *et al. J. Am. Chem. Soc.* **1980**, *102*, 702–711.
2) 笹野裕介、岩渕好治、大城彩里、權 垠相　特願 2023-185949

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アシルシランと求電子的セレン化剤の光カップリング反応

（学習院大理 [1]）○穴見 優樹 [1]・黒木 大生 [1]・増田 涼介 [1]・草間 博之 [1]

Photoinduced Coupling Reaction of Acylsilanes with Electrophilic Selenium Compounds

([1]*Faculty of Science, Gakushuin University*) ○ Yuki Anami,[1] Taisei Kuroki,[1] Ryosuke Masuda,[1] Hiroyuki Kusama[1]

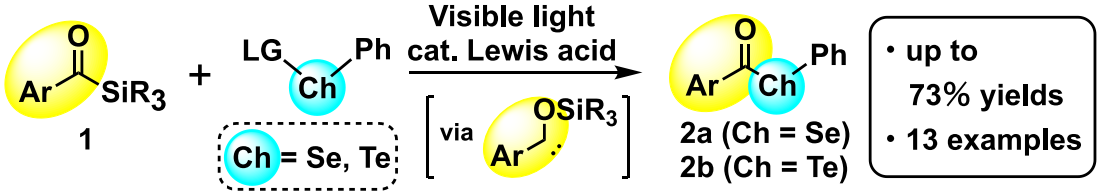
Acylselenides are crucial synthetic components on organic chemistry because they are easily converted to the corresponding acyl radicals under radical initiation conditions. However, the traditional synthesis of acyl selenides, the reactions using selenolates, often have problems of scope due to the high nucleophilicity of selenolates. We have recently reported the synthetic reactions by harnessing siloxycarbenes, which are generated by photoisomerization of acylsilanes. Here, we report a novel synthetic method for acyl selenides via the photoinduced coupling of acylsilanes with the appropriate electrophilic selenium reagents.

Treatment of aroylsilane **1** with selenium reagent in the presence of Lewis acid catalyst under photo-irradiation afforded the corresponding acylselenide **2a**. This type of reaction was applicable to various aroylsilanes. Acyltelluride **2b** was also obtained, when tellurium reagents were used instead of selenium reagents.

Keywords : Acylselenides; Acylsilanes; Siloxycarbenes; Organoselenium Compounds; Photoinduced Coupling

アシルセレニドは適切な条件下でアシルラジカルへ変換されるため、有機合成において有用な合成素子である [1]。その合成には、通常カルボン酸誘導体と求核力の高いセレノラートとの反応を経由する必要があり、官能基許容性の低さがしばしば問題となる。我々は以前から、アシルシランの光異性化によって発生するシロキシカルベンを利用した合成反応を報告してきた [2]。今回、アシルシランと適切な求電子的セレン化剤との光カップリングによる新規アシルセレニド合成法を見出したので報告する。

種々条件検討を行った結果、アロイルシラン **1** に対し、脱離基 (LG)を有する求電子的セレン化剤および触媒量のルイス酸存在下、可視光照射を行うことで対応するアシルセレニド **2a** が得られることを見出した。本反応は幅広い **1** に適用可能であった。セレン化剤の代わりにテルル化剤を用いると、同様にアシルテルリド **2b** が得られた。



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2) a) K. Ito, H. Tamashima, N. Iwasawa, H. Kusama, *J. Am. Chem. Soc.* **2011**, *133*, 3716. b) K. Ishida, F. Tobita, H. Kusama, *Chem. Eur. J.* **2018**, *24*, 543.

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

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC E1142(1142, Bldg. 11 [4F])

[E1142-4pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Yuki Saito, Keisuke Asano

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1142-4pm-01]
Sequential- and continuous-flow synthesis of tetraconazole by integrating heterogeneous catalytic processes and organometallic reactions

○Masahiro Sasaya[1], Haruro Ishitani[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1142-4pm-02]
Bead Mill-Driven Acceleration of Catalytic Depolymerization Reactions of Poly(ethylene terephthalate) under Mild Reaction Conditions

○Tomoya Kawase[1], Haruro Ishitani[1], Shū Kobayashi[1] (1. The Univ. of Tokyo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1142-4pm-03]
Multi-electron Reduction of Esters by Diazabenzoacenaphthene-based Photoredox Catalysts

○Shusuke Hattori[1,2], Shintaro Okumura[1,2], Yasuhiro Uozumi[1,2] (1. Institute for Molecular Science, 2. SOKENDAI)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1142-4pm-04]
trans-Cyclooctenes as Scavengers of Bromine Involved in Catalytic Bromination

○Ryuichi Murata[1], Kenta Shitamichi[1], Masatsugu Hiramatsu[1], Seijiro MATSUBARA[1], Daisuke URAGUCHI[2], Keisuke ASANO[2] (1. Hokkaido Univ., 2. Kyoto Univ.)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1142-4pm-05]
A Dual Cobalt and Photoredox Catalysis for Hydrohalogenation of Alkenes

○Shotaro Shibutani[1], Kazunori Nagao[1], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ.)

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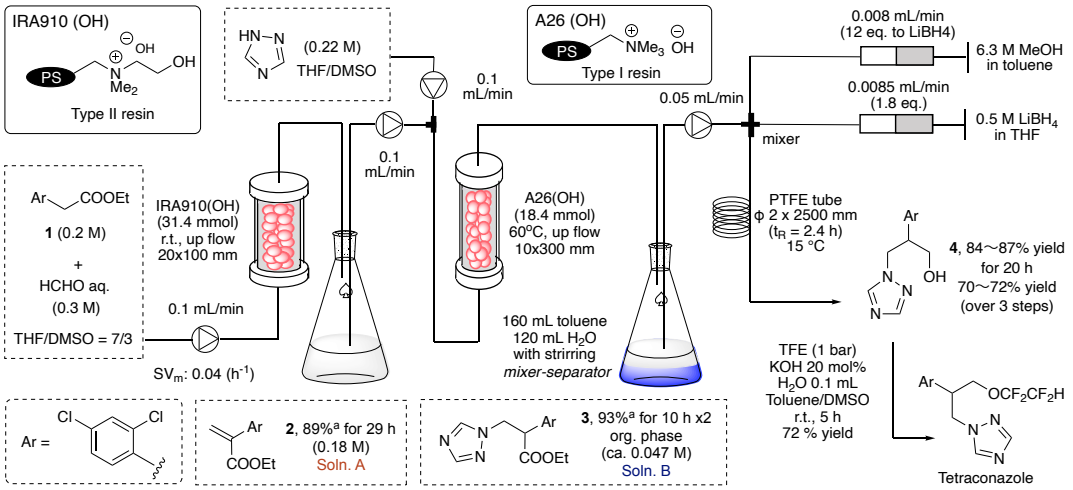
Sequential- and continuous-flow synthesis of tetraconazole by integrating heterogeneous catalytic processes and organometallic reactions

(*School of Science*[1] *and GSC Social Cooperation Laboratory,*[2] *The Univ. of Tokyo*)
○ Masahiro SASAYA,[1] Haruro ISHITANI,[2] Shū KOBAYASHI[1, 2]

Keywords: Sequential-flow reaction; Heterogeneous catalyst; α-Methylenation; Aza-Michael addition; Ester reduction

Tetraconazole, a demethylation inhibitor fungicide in high global demand, is typically synthesized through a base-promoted construction of its molecular framework through α-methylenation reaction and aza-Michael addition of 1,2,4-triazole, followed by a functional group conversion from ester to fluoroalkyl ether. In our pursuit of a sequential and continuous-flow synthesis of this valuable compound, we initially focused on exploring heterogeneous catalyses for the molecular scaffold construction. Contrary to our experience with solid base-catalyzed flow reactions,[1] a commercially available ethanol amine-type ammonium hydroxide resin exhibited the best results in terms of both selectivity and durability for the α-methylenation of ester **1** using formalin. Interestingly, the choice of solvent and ester moiety also notably influenced product selectivity. Following optimization of the two-step transformation including aza-Michael addition, we faced a challenge of reconciling the water-based reactions used for the initial scaffold construction with the ester reduction employing metal hydride reagents, which require hydrophobic conditions. Screening of reductants and fine-tuning to minimize undesirable side reactions led to the development of optimized sequential-flow system depicted below. Under these optimized conditions, alcohol **4**, a key precursor to tetraconazole, was obtained in 72% yield over 20 hours without any offline manipulation. Subsequently, tetrafluoroalkyl etherification with tetrafluoroethylene under batch conditions successfully completed the synthesis, yielding the target tetraconazole molecule.



1) Laroche, B.; Saito, Y.; Ishitani, H.; Kobayashi, S. *Org. Process Res. Dev.* **2019**, *23*, 961.

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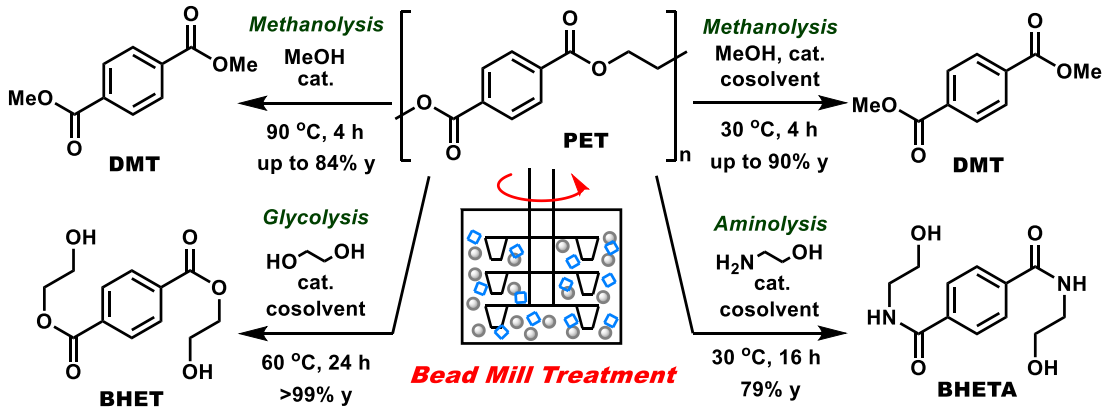
Bead Mill-Driven Acceleration of Catalytic Depolymerization Reactions of Poly(ethylene terephthalate) under Mild Reaction Conditions

(*School of Science* [1] *and GSC Social Cooperation Laboratory* [2]*, The Univ. of Tokyo*)
○Tomoya KAWASE[1], Haruro ISHITANI[2], Shū KOBAYASHI[1,2]

Keywords: Bead Milling; Poly(ethylene terephthalate); Depolymerization; Chemical Recycling; Carbon Neutral

Chemical recycling of post-consumer plastics offers a promising approach to convert waste into renewable chemical raw materials, thereby contributing to a sustainable society. However, the requirement of high temperature often renders the process economically unviable. Mass transfer limitations due to the insolubility of plastics in solvents present a significant bottleneck. We propose that pulverization technology, especially bead milling, can address this challenge. By utilizing this technology, we envisioned plastics to be physically and/or mechanochemically broken down into fine particles, which can increase the surface area and accelerate the reactions even at low temperatures. To validate this concept, we investigated depolymerization reactions of PET under mild reaction conditions. When bead milling was applied as a pretreatment, catalytic methanolysis of PET under 90 °C were remarkably accelerated to give high yields of its monomer DMT,[1] despite conventional reactions requiring temperatures exceeding 180 °C.[2] We revealed that solvent and bead material under bead mill conditions had an impact on acceleration of the subsequent methanolysis reaction: using toluene as a solvent with ZrO_2 beads was the most effective. Particle size distribution and GPC analyses disclosed that both particle size and molecular weight reduction progressed under the specified bead mill conditions. It is assumed that these changes contribute to the reaction acceleration. The optimized method employing bead milling and the identified catalyst proved successful not only for methanolysis but also for glycolysis and aminolysis reactions, all under remarkably mild conditions, showcasing the versatility of our approach. This work provides valuable insights for tackling the low-temperature recycling of other plastics.



1) T. Kawase, H. Ishitani, S. Kobayashi, *Chem. Lett*. **2023**, *52*, 745.
2) J. Chen, *et al. ACS Catal*. **2022**, *12*, 4659.

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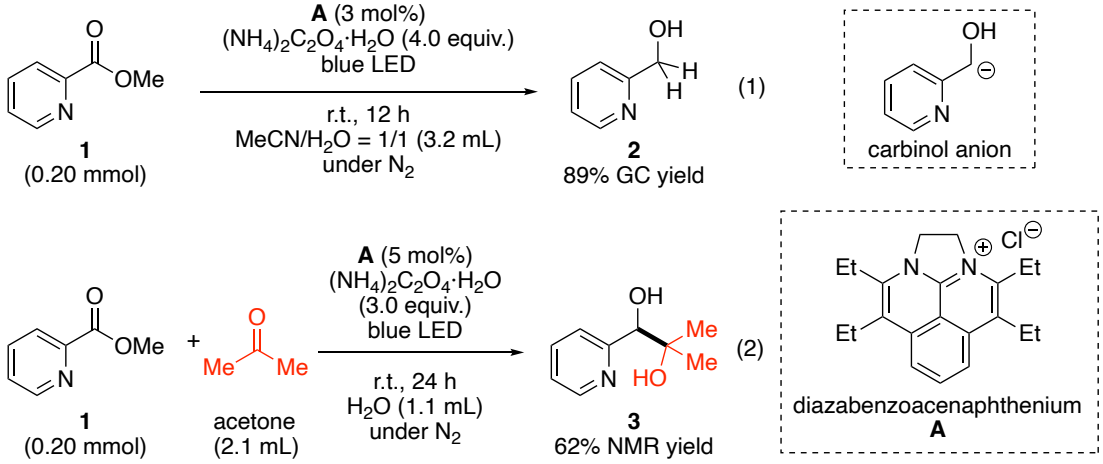
Multi-electron Reduction of Esters by Diazabenzoacenaphthene-based Photoredox Catalysts

([1]*Institute for Molecular Science,* [2]*SOKENDAI*) ○Shusuke Hattori,[1,2] Shintaro Okumura,[1,2] Yasuhiro Uozumi[1,2]

Keywords: Photoredox Catalysis; Multi-electron Reduction; Diazabenzoacenaphthenes; Esters

During the last decade, photocatalysis has been becoming a rapidly growing field in chemistry. However, photocatalytic reduction of esters remains a formidable challenge due to the poor electrophilicity of their carbonyl carbons. Photocatalytic reduction of esters into alcohols should be achieved via the carbinol anion intermediates where almost simultaneous four-electron transfer to esters is required. We have developed a novel diazabenzoacenaphthene-based photocatalyst which realized the four-electron reduction of esters, and the resulting carbinol anion intermediates underwent protonation as well as 1,2-addition with the second carbonyl compounds to give the corresponding alcohols and *vic*-diols, respectively.

Diazabenzoacenaphthenium photocatalyst **A** bearing high photoredox ability was designed in silico and prepared. Diazabenzoacenaphthenium **A** catalyzed the four-electron reduction of methyl picolinate **1** in the presence of ammonium oxalate monohydrate in acetonitrile/water under blue light irradiation for 12 hours to afford 2-pyridinemethanol **2** in 89% GC yield (eq. 1). When the reduction was conducted in acetone under similar conditions, ester **1** reacted with acetone to afford *vic*-diol **3** in 62% NMR yield (eq. 2).



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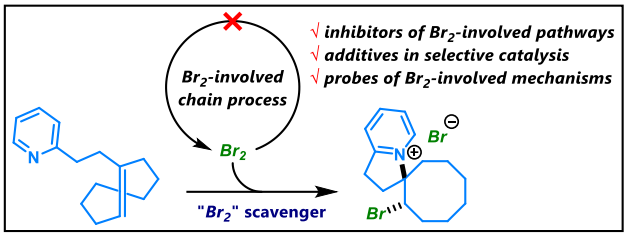
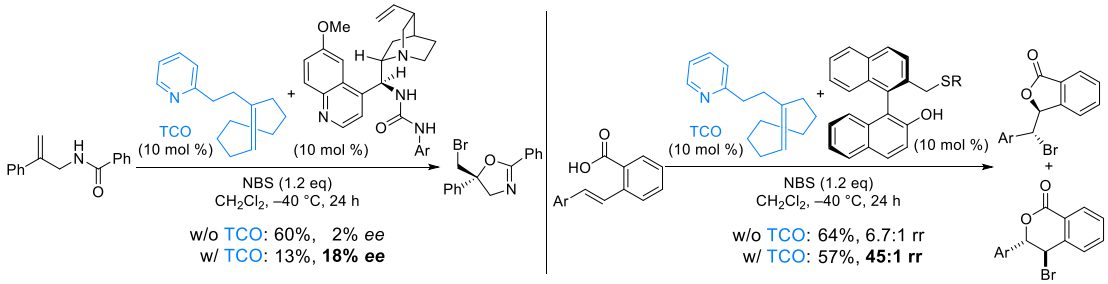
trans-Cyclooctenes as Scavengers of Bromine Involved in Catalytic Bromination

([1]*Graduate School of Engineering, Kyoto University*, [2]*Institute for Catalysis, Hokkaido University*, [3]*List Sustainable Digital Transformation Catalyst Collaboration Research Platform, Institute for Chemical Reaction Design and Discovery (ICReDD List-PF), Hokkaido University*) ○ Ryuichi Murata,[1] Kenta Shitamichi,[1] Masatsugu Hiramatsu,[1] Seijiro Matsubara,[1] Daisuke Uraguchi,[2,3] Keisuke Asano[2]

Keywords: *trans*-Cyclooctene; Scavenger; Bromine; Bromination



Scavengers that capture reactive chemical substances are used to prevent the decomposition of materials. However, in the field of catalysis, the development of scavengers that inhibit background pathways has attracted little attention, although the concept will open up an otherwise inaccessible reaction space. In catalytic bromination, fast non-catalyzed background reactions disturb the catalytic control of the selectivity, even when using *N*-bromoamide reagents, which have a milder reactivity than bromine (Br_2). Here, we developed a *trans*-cyclooctene (TCO) bearing a 2-pyridylethyl group to efficiently retard background reactions by capturing Br_2 in bromocyclization using *N*-bromosuccinimide.[1] The use of less than a stoichiometric amount of the TCO was sufficient to inhibit non-catalyzed reactions, and mechanistic studies using the TCO revealed that in situ-generated Br_2 provides non-catalyzed reaction pathways based on a chain mechanism. The TCO was useful as an additive for improving enantioselectivity and regioselectivity in catalytic reactions. Cooperative systems using the TCO with selective catalysts offer an alternative strategy for optimizing catalyst-controlled selectivity during bromination. Moreover, it also served as an indicator of Br_2 involved in catalytic reaction pathways; thus, the TCO was useful as a probe for mechanistic investigations into the involvement of Br_2 in bromination reactions of interest.



1) R. Murata, K. Shitamichi, M. Hiramatsu, S. Matsubara, D. Uraguchi, K. Asano, *Chem.—Eur. J.* Early View, e202303399.

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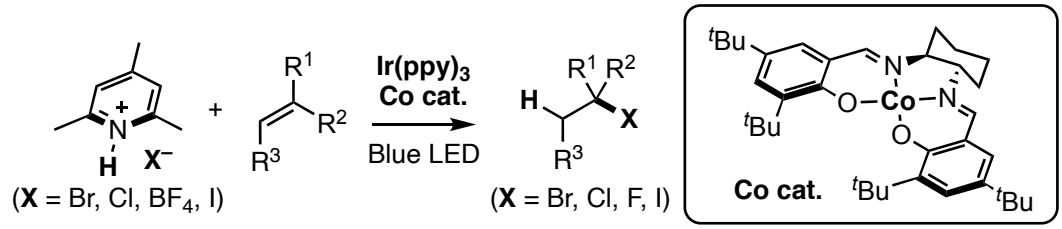
A Dual Cobalt and Photoredox Catalysis for Hydrohalogenation of Alkenes

(*ICR, Kyoto Univ.*) ○Shotaro Shibutani, Kazunori Nagao, Hirohisa Ohmiya

Keywords: Photoredox catalyst; Cobalt catalyst; Single-electron transfer; Alkene; Hydrohalogenation

Alkyl halides have been classified to one of most fundamental and important organic compounds due to the high reactivity as coupling reagents and ubiquitous structures in natural products and pharmaceutical drugs. Therefore, synthetic methods for preparation of alkyl halides have been intensively studied. Hydrohalogenation of alkenes using hydrogen halide (HX) is a simple, atom-economical and cost-effective approach for preparation of alkyl halides. However, such conventional methods suffered from strong acidic and harsh reaction conditions, resulting in low functional group compatibility. To overcome this problem, Carreira and others demonstrated a radical approach to hydrohalogenation of alkenes using a cobalt catalyst, hydrosilanes and electrophilic halogen sources.[1] Therein, the catalysis allows to deliver the hydrogen and halogen atoms from hydrosilanes and halogen sources through metal hydride hydrogen atom transfer and S_H2 reactions, respectively. Since these protocols enable to avoid the use of strong acidic HX, high functional group compatibility is ensured. However, low atom economy remained as an unresolved problem.

We demonstrate an alternative radical-based approach for hydrohalogenation of alkenes ensuring high atom economy and chemoselectivity. A dual photoredox/cobalt catalysis[2] enables to convert a proton and a halide anion from collidine·HX salt to a nucleophilic hydrogen radical equivalent and an electrophilic halogen radical equivalent through single electron reduction and oxidation and deliver them to an alkene moiety. This protocol allows for introduction of fluorine, chlorine, bromine, or iodine atom to alkene, producing highly functionalized alkyl halides by changing the halide anion source. The method was able to tolerate functional groups that are unstable under acidic conditions, such as methoxymethyl, esters, silyl ethers, and amides. This was also applicable to hydrohalogenation of alkenes derived from pharmaceuticals and natural products.



1) Gaspar, B.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 5758.

2) Nakagawa, M.; Matsuki, Y.; Nagao, K.; Ohmiya, H. *J. Am. Chem. Soc.* **2022**, *144*, 7953

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

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC E1143(1143, Bldg. 11 [4F])

[E1143-4pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Manabu Hatano, Takatsugu Murata

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1143-4pm-01]

Development of Diboronic Acid Anhydride-Catalyzed Dehydrative Amidations Using Aqueous Amine Solutions

○Hinata Iwasawa[1], Naoya Takahashi[2], Naoyuki Shimada[1] (1. The Univ. of Nihon, 2. The Univ. of Kitasato)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1143-4pm-02]

Highly Chemoselective Triflation Using *N*-Trifluoromethanesulfonylimidazole

○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
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1143-4pm-03]

Experimentally Mechanistic Study of Horner–Wadsworth–Emmons(HWE) Reaction with Weinreb Amide-type HWE Reagent

Takatsugu Murata[1], ○Hisazumi Tsutsui[1], Isamu Shiina[1] (1. Tokyo University of Science)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[E1143-4pm-04]

γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [2]

○Yota Sakakibara[1], Kosuke Hamawaki[1], Kazuki Hirate[1], Shoma Chiba[1], Kosuke Terada[1], Takumi Kinoshita[1], Kei Murakami[1] (1. Kwansei Gakuin University)

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ジボロン酸無水物触媒によるアミン水溶液を用いた脱水縮合アミド化反応の開発

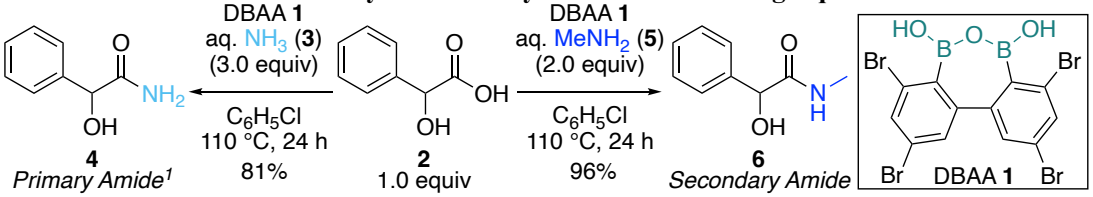
（日本大文理[1]・北里大薬[2]）○岩澤 太陽[1]・高橋 那央也[2]・嶋田 修之[1]
Development of Diboronic Acid Anhydride-Catalyzed Dehydrative Amidations Using Aqueous Amine Solutions ([1]*Department of Chemistry, Nihon University*, [2]*Department of Pharmaceutical Sciences, Kitasato University*) ○ Hinata Iwasawa,[1] Naoya Takahashi,[2] Naoyuki Shimada,[1]

Catalytic amidation of carboxylic acids with amines is an ideal synthetic method for constructing amide bonds, which is universally found in pharmaceuticals and agrochemicals. However, this synthetic method requires strict dehydrative conditions, making it difficult to use commercially available and easy to handle aqueous amine solutions as amine substrates. In this study, we have succeeded a development of an unprecedented catalytic dehydrative amidations using aqueous amine solutions catalyzed by diboronic acid anhydride, which was originally developed in our laboratory. We found the amidation reaction of mandelic acid (**2**) with aqueous ammonia solution (**3**) in the presence of DBAA **1** in chlorobenzene at 110 °C gave the corresponding amide **4** in high yield. In addition, aqueous methylamine solution (**5**) was also applicable to give secondary amide **6** in excellent yield.
Keywords : Dehydrative condensation; Organoboron Catalysis; Amide

アミドは医農薬品や天然物骨格に普遍的に含まれる重要な化学結合様式であることから，効率的な合成手法の開発が強く望まれている。これまでに，有機ホウ素触媒によるカルボン酸とアミンからの直截的なアミド化反応の開発研究が精力的に行われてきた。しかしながら，本手法は厳密な脱水操作を必須としていることから，市販で取扱容易なアミン水溶液をアミン基質として用いることは困難であった。今回我々は，当研究室で独自に開発したジボロン酸無水物触媒 DBAA **1** による前例のない，アミン水溶液を用いた触媒的脱水縮合アミド化反応の開発に成功した。

検討の結果， DBAA **1** 存在下，マンデル酸 (**2**)とアンモニア水溶液 (**3**)とのアミド化反応を行ったところ，クロロベンゼン加熱条件下，目的とする第一級アミド **4** が高収率で得られることを見出した(Scheme 1)[1)]。さらにメチルアミン水溶液 (**5**)をアミン基質とした場合にも第二級 *N*-メチルアミド **6** が得られることを明らかにした。

Scheme 1. Diboronic Acid Anhydride–Catalyzed Amidation Using Aqueous Amine Solutions



1) Takahashi, N.; Iwasawa, H.; Kinashi, T.; Makino, K.; Shimada, N. *Chem. Commun.* **2023**, *59*, 7391–7394.

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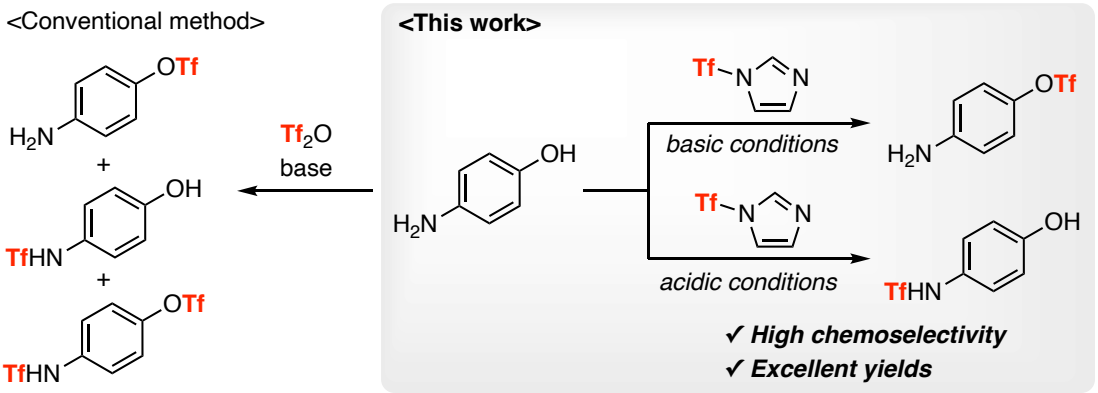
N-トリフルオロメタンスルホニルイミダゾールを用いる高化学選択的トリフリル化反応

（神戸薬大薬[1]・セントラル硝子株式会社[2]）○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 Using *N*-Trifluoromethanesulfonylimidazole ([1]*Faculty of Pharmaceutical Sciences, Kobe Pharmaceutical University*, [2]*New-STEP Research Center, Central Glass Co. Ltd.*) ○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 using *N*-trifluoromethanesulfonylimidazole. Under basic conditions, the reactions proceeded selectively at the hydroxy groups of phenols. On the other hand, under acidic conditions, the reactions proceeded selectively at the amino groups of anilines. We will propose the reaction mechanism of these chemoselective triflations of phenols and anilines.
Keywords: *Triflation; Chemoselectivity; Phenol; Aniline; Sulfonylation*

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）を用いるトリフリル化反応では、目的以外の競合する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。本研究では、*N*-トリフルオロメタンスルホニルイミダゾールを用いて、塩基性条件下におけるフェノール類の高化学選択的 *O*-Tf 化、および酸性条件下におけるアニリン類の高化学選択的 *N*-Tf 化に成功した。発表では高化学選択性の発現機構についても考察する。



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Weinreb アミド型 Horner–Wadsworth–Emmons（HWE）試薬を用いた HWE 反応の実験的機構解析研究

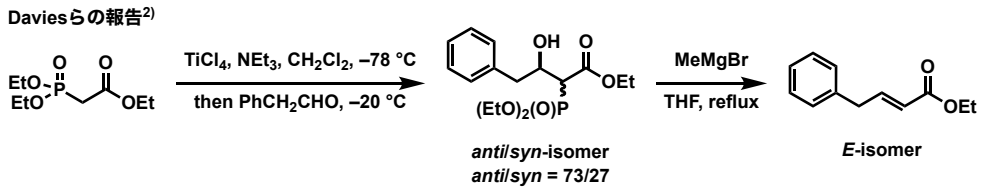
(東理大理) 村田 貴嗣・○筒井 久澄・椎名 勇

Experimentally Mechanistic Study of Horner–Wadsworth–Emmons (HWE) Reaction with Weinreb Amide-type HWE Reagent (*Faculty of Science, Tokyo University of Science*) Takatsugu Murata, ○Hisazumi Tsutsui, Isamu Shiina

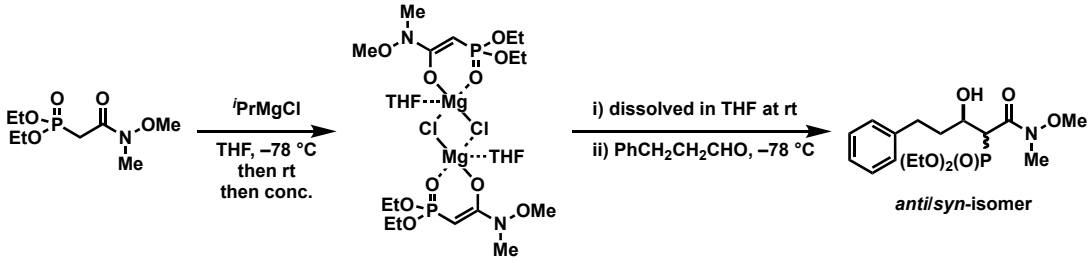
Horner–Wadsworth–Emmons reaction has been employed in a number of syntheses. In many syntheses of them, the products are subjected to the conditions of functional transformations. In the other hand, the reaction mechanism and the selectivity of HWE reaction have not been elucidated. In this study, we experimentally researched the mechanism of HWE reaction.

Keywords : Horner–Wadsworth–Emmons Reaction; Elongation Reaction; Weinreb Amide

Horner–Wadsworth–Emmons 試薬の開発や利用に関する報告例は数多く存在するが、その詳細な反応機構については解明されていない。2006 年に田辺らは、ルイス酸を用いたアルドール反応条件下にて HWE 反応中間体が単離できたことを報告している [1]。また、S. G. Davies らは田辺らが単離した中間体から HWE 反応成績体への変換が可能であることを報告している [2]。



我々は、Weinreb アミド構造を有する HWE 試薬 [3]を用いた反応の中間体であるホスホノエノラートの初の単離について報告している [4]。今回、HWE 反応の条件を制御することによって HWE 反応中間体の単離に成功した。さらに、その中間体を用いた実験化学的な反応機構の調査を行った。本講演ではこれらの詳細を報告する。



1) M. Katayama, R. Nagase, K. Mitarai, T. Misaki, Y. Tanabe, *Synlett*, **2006**, *1*, 129–132.
2) S. G. Davies *et al*., *Org. Lett.*, **2008**, *10*, *23*, 5437–5440.
3) J.-M. Nuzillard, A. Boumendjel, G. Massiot, *Tetrahedron Lett*., **1989**, *30*, 3779–3780.
4) 村田貴嗣、筒井久澄、平石真太郎、臼倉大輝、岡野宙輝、椎名勇、日本化学会第 103 春季年会、K705-2vn-04 (2023).

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第三級脂肪族アミンのγ位選択的な官能基化[2]

（関西学院理工）○榊原 陽太・濱脇 康佑・平手 和希・千葉 将真・寺田 昂祐・木之下 拓海・村上 慧

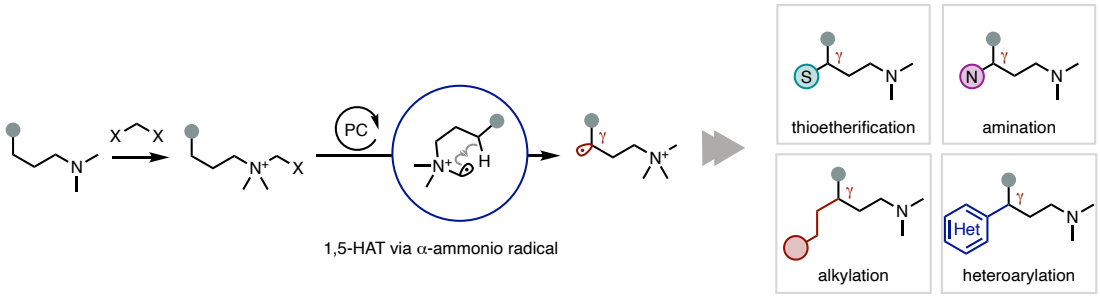
γ-Selective functionalization of tertiary alkyl amines enabled by α-ammonio radical [2]

([1]*Graduate Department of Chemistry, School of Science and Engineering, Kwansei Gakuin University*) ○Yota Sakakibara, Kosuke Hamawaki, Kazuki Hirate, Shoma Chiba, Kosuke Terada, Takumi Kinoshita, Kei Murakami

Regioselective C–H functionalization reactions of tertiary aliphatic amines, which are frequently used in pharmaceuticals and agrochemicals, are powerful tools to simplify the synthesis of complex amines. For this reason, numerous reactions using photocatalysis or transition metal catalysis have been developed. However, there are still limitations on the positions that can be functionalized, and in particular, there is no reliable method which can selectively functionalize the γ-position of the nitrogen atom. Herein, we have developed a new method to selectively functionalize the γ-position of the nitrogen atom of tertiary aliphatic amines.

Keywords : Photoredox catalysts; Radical; Ammonium salts ;C–H functionalization; Hydrogen atom transfer

第三級脂肪族アミンの位置選択的なC–H官能基化反応は複雑なアミンの合成を簡便にする強力なツールである[1]。そのため、これまでに数多くの反応が開発されている。しかし、いまだに官能基化できる位置には制限があり、特に窒素原子のγ位の官能基化は困難である。このような背景の中、今回我々は第四級アンモニウム構造を利用することで窒素原子のγ位を選択的に官能基化する手法を開発した。具体的には、α-ハロゲノアンモニウム塩から発生させたラジカル種[2]が引き起こす分子内水素原子移動(1,5-HAT)により、窒素原子のγ位に選択的にラジカル種を発生させることに成功した。なお、α-ハロゲノアンモニウム塩は、第三級脂肪族アミンから容易に調製可能である。 この活性種を用いることで多様な官能基を導入可能であることを見いだし、さらには第三級アミンへと誘導するための適切な脱メチル化条件も発見した。



[1] Dutta, S.; Li, B.; Richertsen, D. R. L.; Valles, D.; Seidel, D. *SynOpen* **2021**, *5*, 173.
[2] Rios, L. A.; Dolbier, Jr. W. R.; Paredes, R.; Lusztyk, J.; Ingold, K. U.; Jonsson, M. *J. Am. Chem. Soc.* **1996**, *188*, 11313.

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:20 AM UTC H933(933, Bldg. 9 [3F])

[H933-4am] 16. Natural Products Chemistry, Chemical Biology

Chair: Akihiro Ogura, Keisuke Murata

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H933-4am-01]
Synthetic Studies of Sterhirsutins A and B

○Yukiko Minami[1], Ryota Nomura[1], Akihiro Ogura[1], Ken-ichi Takao[1] (1. Faculty of Science and Technology, Keio University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H933-4am-02]
Synthetic Studies of Guttiferone A

○Misato Takimoto[1], Satoshi Nanataki[1], Akihiro Ogura[1], Ken-ichi Takao[1] (1. Faculty of Science and Technology, Keio University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H933-4am-03]
[2+2] Photocyclization and the Four-membered Ring Cleavage to Construct the Skeleton of Aconitine

○Kenji Ashidate[1], Masayoshi Abe[1], Tomoaki Watanuki[1], Hazuki Kobayashi[1], Masaya Nakata[1], Yoko Saikawa[1] (1. Keio University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H933-4am-04]
Asymmetric synthetic studies of Bisleuconothine A

○Hajime Yokoyama[1], Ryosuke Imai[1], Masahiro Miyazawa[1] (1. University of Toyama)

9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
Break

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H933-4am-05]
Synthetic Study of Taberyunine E

○Daiki Kaneko[1], Yasukazu Sugiyama[1], Yuichirou Shirakata[1], Yuya Kusagawa[1], Noritaka Chida[1], Okamura Toshitaka[1], Sato Takaaki[1] (1. Keio Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H933-4am-06]
Total Synthesis of Carbazomycins E and F

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○Yunosuke Shima[1], Yuxuan Feng[1], Kentaro Okano[1], Atsunori Mori[1,2] (1. Graduate School of Engineering, Kobe University, 2. Center for Membrane and Film Technology, Kobe University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H933-4am-07]

Tandem Reaction-Based Stereoselective Synthesis of Cyclic Ethers

○Tsubasa Kasai[1], Keisuke Murata[1], Haruhiko Fuwa[1] (1. The university of Chuo)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[H933-4am-08]

Synthesis, Conformational Analysis, and Biological Evaluation of Exiguolide Stereoisomers

○Reika Murakami[1], Tomo Mori[1], Keisuke Murata[1], Haruhiko Fuwa[1] (1. The Univ. of Chuo)

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

Break

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H933-4am-09]

Synthetic Studies on iriomoteolide-1a: Configuration of Side-Chain Stereogenic Centers

○Tomohiro Obana[1], Miyuu Nakajima[1], Kazuki Nakazato[1], Hayato Nakagawa[1], Keisuke Murata[1], Masashi Tsuda[2], Haruhiko Fuwa[1] (1. Chuo University, 2. Kochi University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H933-4am-10]

Synthetic Studies on the Northern Hemisphere of Amphidinolide N

○Takumi Imamura[1], Hiroaki Imamura[1], Haruhiko Fuwa[1] (1. Chuo University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H933-4am-11]

Synthetic Study on γ-Rubromycin: Late Stage Oxidation of the Naphthalene Unit

○Shuichiro Morishita[1], Yoshio Ando[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H933-4am-12]

Studies on stereoselective synthesis of the antibiotics quatromycins

○Koichi Deyama[1], Kohei Kamatani[1], Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

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日本化学会 第104春季年会 (2024)

ステルヒルスチン A および B の全合成研究

（慶大理工）○南 友紀子・野村 亮太・小椋 章弘・高尾 賢一

Synthetic Studies of Sterhirsutins A and B (*Faculty of Science and Technology, Keio University*)○Yukiko Minami, Ryota Nomura, Akihiro Ogura, Ken-ichi Takao

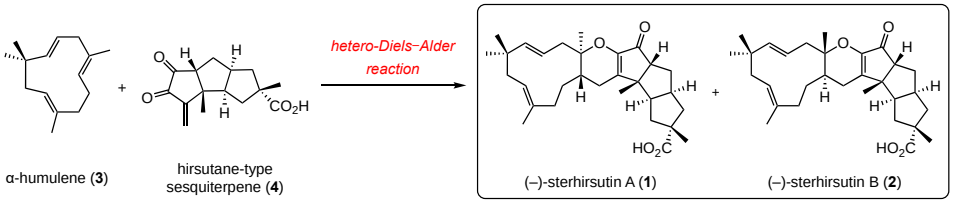
Sterhirsutins A (**1**) and B (**2**) were isolated from the culture of Chinese fungus *Stereum hirsutum* by Liu and co-workers in 2014.[1] These compounds share a unique 11/6/5/5/5-pentacyclic skeleton including a linear triquinane moiety. These are proposed to be formed by a hetero-Diels–Alder reaction between α-humulene (**3**) and a hirsutane-type sesquiterpene (**4**) in the biosynthesis hypothesis. Based on the biosynthesis hypothesis, we focused on the synthesis of **4** in this study.

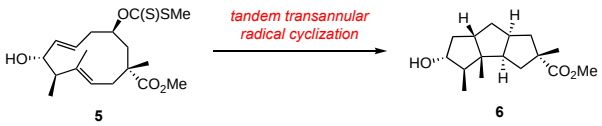
We planned to use a tandem transannular radical cyclization for constructing the linear triquinane moiety. To this end, an 11-membered ring compound **5** was synthesized by using an intramolecular Nozaki–Hiyama–Takai–Kishi reaction. The tandem transannular radical cyclization successfully constructed the 5/5/5-tricyclic skeleton to give the desired **6**.

Keywords : linear triquinane, transannular radical cyclization, Nozaki–Hiyama–Takai–Kishi reaction

ステルヒルスチン A (**1**) および B (**2**) は, 2014 年に Liu らによってキウロコタケの培養液より単離された天然有機化合物である [1]. 構造上の特徴として, 直線状トリキナンを含む特異な 11/6/5/5/5 五環性骨格を有することが挙げられる. この骨格は生合成仮説において, α-フムレン (**3**) とヒルスタン型セスキテルペン (**4**) とのヘテロ Diels–Alder 反応により形成されると提唱されている. 私たちはこの生合成仮説に基づき, **4** の合成を目指すこととした.

直線状トリキナン骨格を構築する新規な方法として, 私たちは連続的渡環ラジカル環化反応を用いることを計画した. その基質として, 分子内野崎–檜山–高井–岸反応を経て炭素 11 員環化合物 **5** を合成した. これに対して連続的渡環ラジカル環化反応を行うことにより, 5/5/5 三環性骨格を一挙に構築して望みの化合物 **6** を得ることに成功した.





1) Liu, H.-W. et al. *Org. Lett.* **2014**, *16*, 5092.

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グッチフェロン A の全合成研究

（慶大理工）○滝本 実里・七瀧 智俊・小椋 章弘・高尾 賢一
Synthetic Studies of Guttiferone A (*Faculty of Science and Technology, Keio University*)
○Misato Takimoto, Satoshi Nanataki, Akihiro Ogura, Ken-ichi Takao

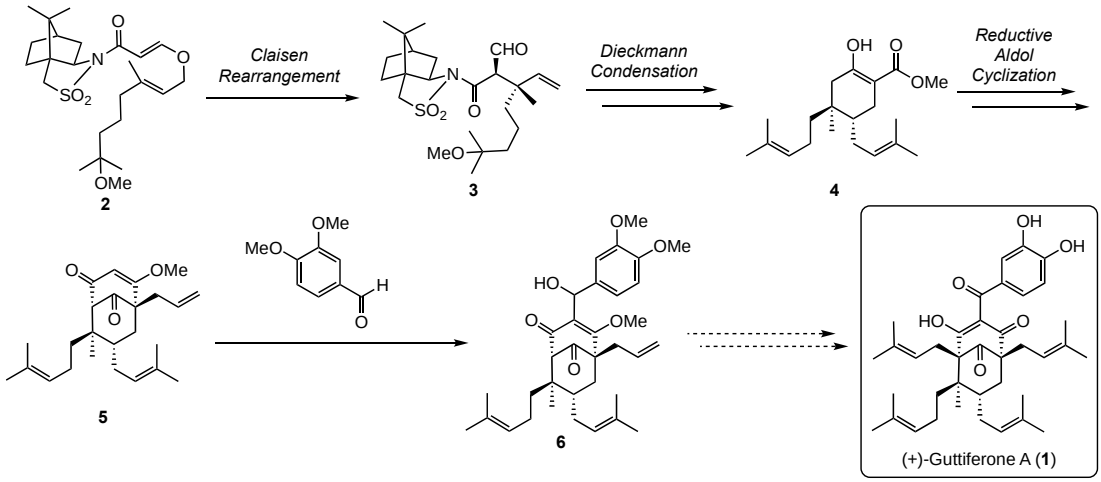
Guttiferone A (**1**) was isolated from a Clusiaceae plant by Boyd and co-workers in 1992.[1] The structural feature is an oxidated bridged bicyclic skeleton containing three all-carbon quaternary stereocenters. We have planned to construct an asymmetric quaternary carbon using the asymmetric Claisen rearrangement reaction developed in our laboratory, aiming at the asymmetric total synthesis of **1**, which has not yet been achieved.

Compound **3** was synthesized by a stereoselective Claisen rearrangement of **2** equipped with Oppolzer's auxiliary. Dieckmann condensation afforded cyclohexenol **4**, which was converted to a bridged bicyclic compound **5** via stereoselective allylation and reductive aldol cyclization. We have successfully synthesized compound **6** by coupling **5** with an aromatic unit.

Keywords : asymmetric Claisen rearrangement reaction, reductive aldol cyclization reaction, bridged bicyclic skeleton

グッチフェロン A (**1**)は, 1992 年に Boyd らによってオトギリソウ科の植物より単離された天然有機化合物である [1]. 構造上の特徴として, 3 つの第四級不斉炭素を含む酸素官能基化された架橋二環性骨格を有していることが挙げられる. 私たちは, 当研究室にて開発された不斉 Claisen 転位反応を用いて第四級不斉炭素を構築し, 未だ達成されていない **1** の不斉全合成を目指すこととした.

Oppolzer の不斉補助基を装着した **2** に対し, 立体選択的な Claisen 転位反応によって **3** を合成した. Dieckmann 縮合によってシクロヘキセノール **4** へと誘導した後, 立体選択的なアリル化, 還元的アルドール環化反応を経て架橋二環性化合物 **5** を合成した. これに対して, 芳香族ユニットとのカップリングを行うことにより化合物 **6** の合成に成功した.



1) Boyd, M. R. et al. *Tetrahedron* **1992**, *48*, 10093.

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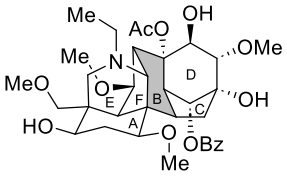
アコニチンの骨格構築を指向した[2+2]光環化反応および四員環開裂反応

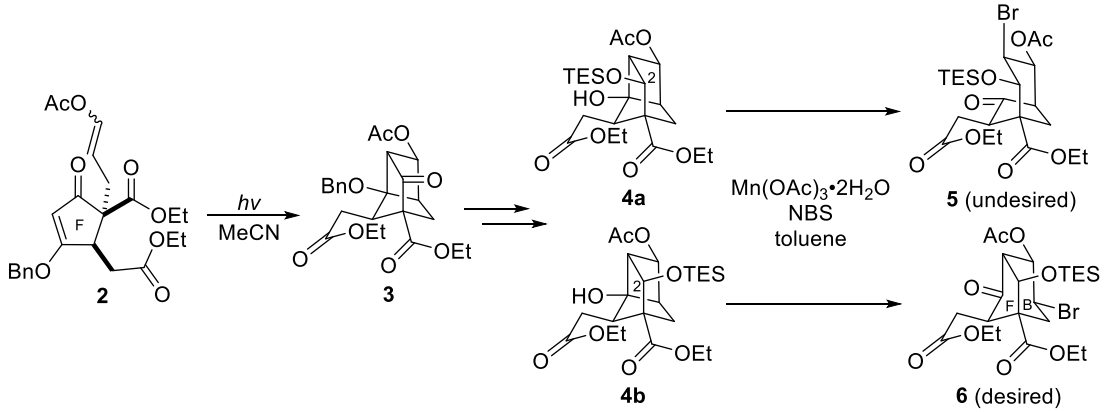
（慶大理工）○芦立 賢治・阿部 雅義・綿貫 友亮・小林 映月・中田 雅也・犀川 陽子
[2+2] Photocyclization and the Four-membered Ring Cleavage to Construct the Skeleton of Aconitine (*Faculty of Science and Technology, Keio University*) ○Kenji Ashidate, Masayoshi Abe, Tomoaki Watanuki, Hazuki Kobayashi, Masaya Nakata, Yoko Saikawa

As key reactions to construct the B-ring of aconitine (**1**), [2+2] photocyclization and four-membered ring cleavage reaction using model compounds were investigated. The F-ring segments with various substituents were subjected to [2+2] photocyclization. As a result, the segment having ethoxycarbonylmethyl group turned out to be suitable for the reaction to give the desired cyclobutane **3**. Then the homolytic cleavage of the resulting cyclobutanol **4a** and **4b** using manganese (III) triacetate with trapping the radical by NBS afforded the secondary alkyl bromides **5** and **6**, respectively. It was found that stereochemistry of the siloxy group at C2 plays as a directing group to control the cleavage site of the four-membered ring.
Keywords: *Aconitine; [2+2] Photocyclization; Four-membered Ring Cleavage; Manganese Triacetate*



aconitine (1)

当研究室では、アコニチン (**1**) の全合成に向けて、[2+2]光環化反応および四員環開裂反応により B 環を構築する合成経路を進めている。今回、モデル化合物を用いた検討により、これら 2 つの反応に成功したので報告する。A 環の足掛かりを有するモデル F 環セグメントの[2+2]光環化反応を検討し、A 環の足掛かりとしてエトキシカルボニルメチル基を有するシクロペンテノン **2** を用いた際に望みのシクロブタン **3** を得た。得られた **3** から誘導したシクロブタノール **4a**, **4b** に対して、酢酸マンガン(Ⅲ) を用いた四員環開裂反応により B 環構築に成功し、NBS によってラジカルを捕捉することで第 2 級臭化アルキル **5**, **6** をそれぞれ得た。この際、C2 位のシロキシ基の立体化学によって開裂の選択性が発現することを見出した。



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日本化学会 第104春季年会 (2024)

Bisleuconothine A の不斉合成研究

（富山大院理工）○横山 初・今井 陵輔・宮澤 眞宏

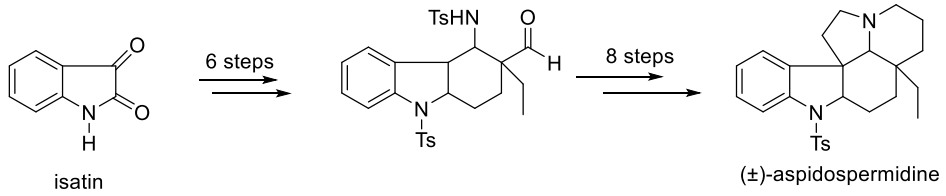
Asymmetric synthetic studies of Bisleuconothine A (*Faculty of Science, University of Toyama*)

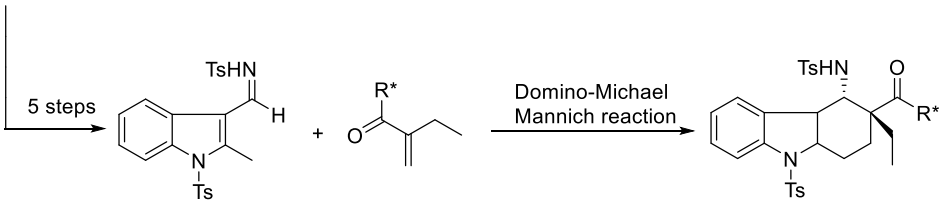
○Hajime Yokoyama, Ryosuke Imai, Masahiro Miyazawa

Bisleuconothine A is a bisindole alkaloid compound, isolated from the bark of *Leuconotis griffithii*, a member of the Apocyaneae family and has been reported to exhibit cell proliferation inhibitory activity against human cancer cells. This compound consists of an upper (+)-eburnamonine skeleton and a lower (+)-aspidospermidine skeleton. In our laboratory, we have achieved racemic synthesis of (+)-aspidospermidine in the lower skeleton for the total synthesis of bisleuconothine A. Therefore, in this study, we are considering to synthesize (+)-aspidospermidine by using domino Michael Mannich reaction with chiral group. Currently, the synthesis of imine has been achieved and the domino Michael-Mannich reaction is undergoing.

Keywords : bisleuconothine A; bisindole alkaloid; aspidospermidine; Michael-Mannich reaction

Bisleuconothine A はキョウチクトウ科の一種である *Leuconotis griffithii* の樹皮より単離されたビスインドールアルカロイド化合物であり、ヒト癌細胞に対して細胞増殖阻害活性を示すことが報告されている。構造上の特徴として上部の(+)-Eburnamonine と下部の(+)-Aspidospermidine が直結されている。しかし、未だ全合成の例は報告されていない。そこで、当研究室では Bisleuconothine A の全合成に向けて上部骨格の(+)-Eburnamonine と下部骨格の(+)-Aspidospermidine の不斉合成を検討してきた。今回は下部骨格の(+)-Aspidospermidine の不斉合成を行っている。まず Isatin から 5 段階でイミン体を合成した。その後、鍵反応である Domino Michael-Mannich 反応を、不斉補助基を導入したアミドを用いて検討した。





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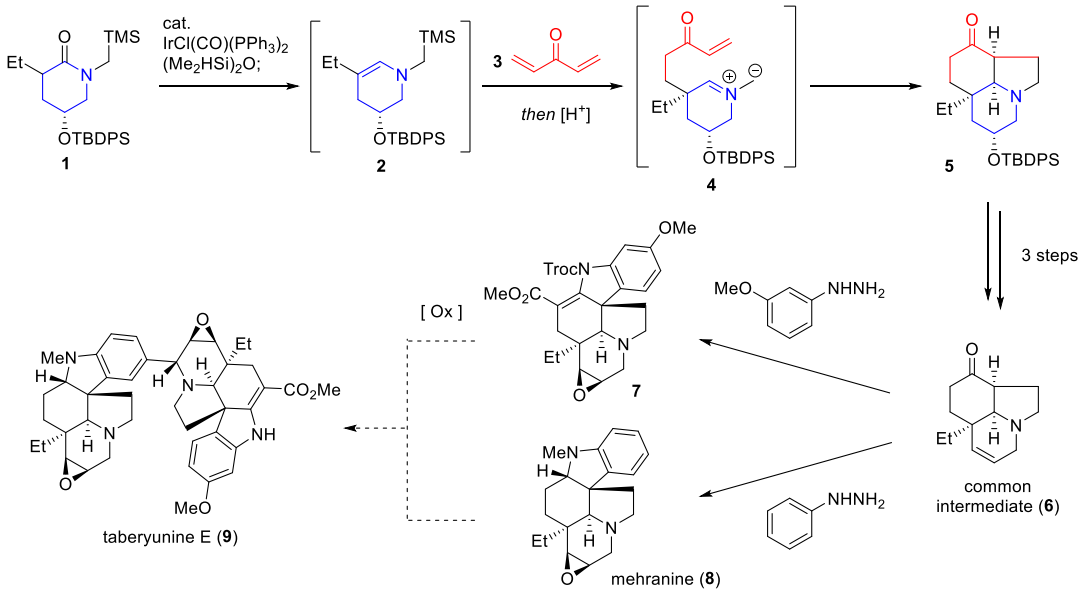
Taberyunine E の合成研究

（慶大理工）○金子大輝、杉山靖和、白方友一朗、草川裕哉、千田憲孝、岡村俊孝、佐藤隆章
Synthetic Study of Taberyunine E（*Keio Univ.*）○Daiki Kaneko, Yasukazu Sugiyama, Yuichirou Shirakata, Yuya Kusagawa, Noritaka Chida, Toshitaka Okamura, Takaaki Sato

Dimeric *Aspidosperma*-type alkaloids have been known to show better biological profile than monomeric natural products. However, medicinal research has been overlooked due to the limited supply of these complex natural products. In this study, we report our synthetic approach to taberyunine E (**9**) based on an iridium-catalyzed hydrosilylation/[3+2] cycloaddition cascade via azomethine ylide **4**. Monomeric indole alkaloids **7** and mehranine (**8**) were successfully synthesized from **6** through Fischer indole synthesis.
Keywords : Amide; 1,3-Dipole; Indole Alkaloid; Iridium; Total Synthesis

二量体アスピドスペルマ型アルカロイドは、単量体天然物に比べ強力な生物活性を示すことが知られており、医薬品のリード化合物として期待されている。しかし、複雑な構造のため、合成例は非常に限られている。本研究では、ラクタムの還元的[3+2]環化付加反応を鍵反応とした二量体天然物 taberyunine E (**9**)の合成研究に取り組んだ。

光学活性なラクタム **1** を触媒量の $IrCl(CO)(PPh_3)_2$ と$(Me_2HSi)_2O$ で処理して環状エナミン **2** とした[1]。ワンポット反応にてジエノン **3** と酸を加えると、Michael 付加反応および脱 TMS 反応が進行してアゾメチンイリド **4** を生じ[2]、分子内[3+2]環化付加反応によって三環性化合物 **5** が得られた。続いて、**5** より合成した共通中間体 **6** から、Fisher インドール合成を含む数工程の変換により、2 つの単量体中間体 **7** および mehranine (**8**)を合成した。



1) H. Nagashima *et al., Chem. Commun*. **2009**, 1574. 2) Sato, T.; Chida, N. *et al*., *Org. Lett*. **2021**, *23*, 3058.

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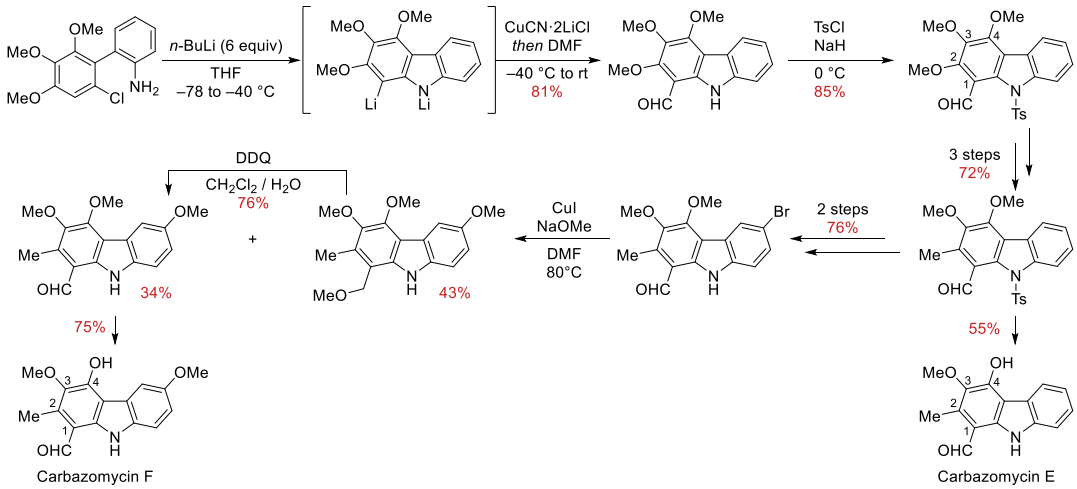
Total Synthesis of Carbazomycins E and F

([1]*Department of Chemical Science and Engineering, Kobe University,* [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Yunosuke Shima,[1] Yuxuan Feng,[1] Kentaro Okano,[1] Atsunori Mori[1,2]

Keywords: Total Synthesis; Benzyne; Carbazole

Carbazomycins E and F were isolated from KCC U-0166 of *Streptoverticillum* sp. by Marumo and co-workers in 1986.[1] Both compounds have a fully substituted benzene bearing a formyl group at the 1 position. Recently, we have synthesized carbazomycins A−D on gram scales using our original method to form carbazole via an aryne intermediate.[2] Herein we report the total synthesis of carbazomycins E and F.

The synthesis began with preparation of 1-formylcarbazole. Treatment of the aminobiphenyl with six equivalents of *n*-BuLi generated the carbazole dianion. This intermediate was then formylated to give the desired 1-formylcarbazole. Protection of the carbazole nitrogen atom was necessary for the transformation of the methoxy group at the 2 position into the methyl group. Carbazomycin E was synthesized through the regioselective demethylation of the methoxy group at the 4 position. The synthesis of carbazomycin F required to install another methoxy group. After bromination, a combination of CuI and NaOMe provided the desired carbazole; however, the other carbazole with the PMB substructure was obtained as a major product. This compound was converted into the desired carbazole by oxidation with DDQ. Finally, the first total synthesis of carbazomycin F was achieved through the regioselective demethylation at the 4 position.



1) a) Kondo, S.; Katayama, M.; Marumo, S. *J. Antibiot.* **1986**, *39*, 727. b) Knölker, H. J.; Bauermeister, M. *Heterocycles* **1991**, *32*, 2443. 2) a) Feng, Y.; Yukioka, T.; Matsuyama, M.; Mori, A.; Okano, K. *Org. Lett.* **2023**, *25*, 3013. b) 馮　宇軒, 岡野健太郎, 森　敦紀, 日本化学会 第 104 春季年会.

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タンデム反応を起点とする環状エーテルの立体選択的合成

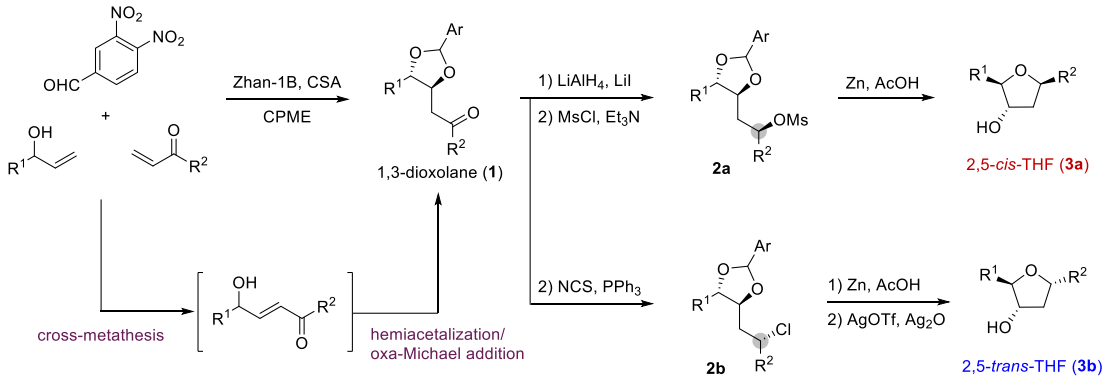
（中大理工）○笠井 翼・村田佳亮・不破春彦
Tandem Reaction-Based Stereoselective Synthesis of Cyclic Ethers (*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○Tsubasa Kasai, Keisuke Murata, Haruhiko Fuwa

There are many natural products having a tetrahydrofuran and/or tetrahydropyran ring(s), and it is therefore important to develop new methods for the efficient and stereoselective construction of these skeletons.

Previously, we reported a tandem reaction using three components, allylic/homoallylic alcohols, vinyl ketones, and aldehydes, for the synthesis of *syn*-1,2 and *syn*-1,3-diol derivatives. In this work, we examined a stereodivergent synthesis of various tetrahydrofuran and tetrahydropyran derivatives starting from our tandem reaction products, i.e., 1,3-dioxolanes or 1,3-dioxanes. Stereoselective reduction of ketone **1** and subsequent mesylation or chlorination gave mesylate **2a** or chloride **2b**, which were transformed into 2,5-*cis*- or 2,5-*trans*-tetrahydrofuran **3a** or **3b**, respectively, by means of an intramolecular etherification.

Keywords: tandem reaction; tetrahydrofuran; tetrahydropyran

生物活性天然物には、テトラヒドロフラン環やテトラヒドロピラン環を有する化合物が多く存在し、それらの骨格の効率的かつ立体選択的な構築方法の開発は重要である。我々はこれまでに、（ホモ）アリルアルコール、ビニルケトンとアルデヒドを用いた 3 成分連結型タンデム反応により種々の *syn*-1,2-および *syn*-1,3-ジオール誘導体の合成を報告した[1]。本研究ではタンデム反応の生成物である 1,3-ジオキソランまたは 1,3-ジオキサン誘導体を起点として種々のテトラヒドロフランおよびテトラヒドロピラン誘導体の立体多様合成が簡便にできることを見出した。ケトン **1** の立体選択的還元とメシル化またはクロロ化によりメシラート **2a** またはクロリド **2b** とし、ニトロ基の還元とアセタールの除去、続く分子内環化反応によりテトラヒドロフラン誘導体 2,5-*cis* 置換テトラヒドロフラン **3a** および 2,5-*trans* 置換テトラヒドロフラン **3b** を合成できた。



1) K. Murata, H. Takeshita, K. Sakamoto, H. Fuwa, *Chem. Asian. J.* **2020**, *15*, 807.

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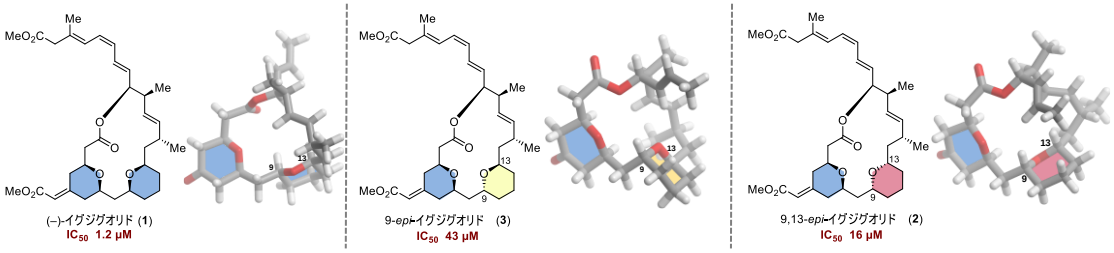
イグジグオリドの立体異性体の合成、立体配座解析と活性評価

（中央大理工）○村上怜花・森 冬萌・村田佳亮・不破春彦
Synthesis, Conformational Analysis, and Biological Evaluation of Exiguolide Stereoisomers (*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○ Reika Murakami, Tomo Mori, Keisuke Murata, Haruhiko Fuwa

(−)-Exiguolide is a marine macrolide natural product isolated from the sponge *Geodia exigua*, which inhabits the coast of Amami-Oshima. The gross structure was established by the combination of extensive 2D NMR studies and conformational analysis. The absolute configuration was determined by Lee and co-workers through the first total synthesis of the unnatural enantiomer, (+)-**1**. Our group succeeded in the first total synthesis of this natural product, demonstrated its potent growth inhibitory activity against human cancer cells, and elucidated the structure–activity relationship of the peripheral substituents and the side chain. In this presentation, we report the total synthesis of 9,13-*epi*-exiguolide and the stereostructure–activity relationship of the macrocyclic skeleton on the basis of conformational analysis and cytotoxicity evaluation.
Keywords: marine macrolide; stereostructure–activity relationship; conformation; cytotoxicity

イグジグオリド (**1**)は、奄美大島の沿岸に生息する海綿 *Geodia exigua* から単離された海洋マクロリド天然物である[1] (Figure 1)。本天然物の平面構造および相対配置は、詳細な二次元 NMR 解析によって帰属され、絶対配置は Lee らの非天然型光学異性体の全合成により決定された[2]。我々のグループは、天然型光学異性体の初の全合成に成功し、本天然物がヒト非小細胞肺がん細胞に対して強力な増殖阻害活性を示すことを明らかとしたほか[3]、側鎖やマクロ環辺縁の置換基の構造活性相関を解明してきた[4]。本研究では、マクロ環の立体配座が活性発現にどのように影響を与えるのか調査するため、当研究室が最近報告した第二世代合成戦略[5]を踏襲して、右側のテトラヒドロピラン環に含まれる 9 位と 13 位の不斉中心の立体配置を改変した 9,13-*epi* 体 (**2**)を合成し、天然物と昨年度報告した 9-*epi* 体 (**3**)とともに立体配座解析および細胞毒性評価を行ったので報告する。



1）Ohta, S. *et al*. *Tetrahedron Lett*. **2006**, *47*, 1957. 2) Lee, E. *et al*. *Angew. Chem. Int. Ed.* **2008**, *47*, 1733. 3) a) Fuwa, H. *et al*. *Org. Lett.* **2010**, *12*, 584; b) Fuwa, H. *et al*. *Chem. Eur. J.* **2011**, *17*, 2678. 4) Fuwa, H. *et al*. *Org. Biomol. Chem*. **2013**, *11*, 3442. 5) Fuwa, H. *et al. Angew. Chem. Int. Ed.* **2022**, *61*, e202202549.

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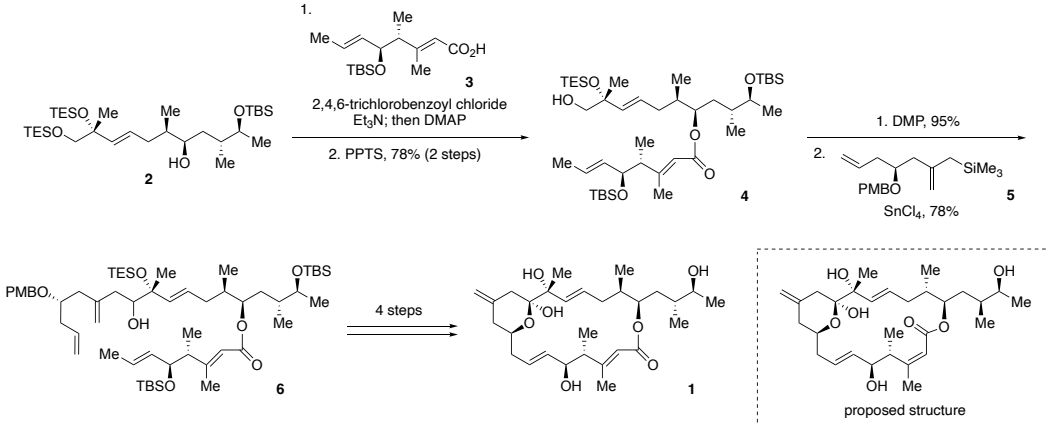
イリオモテオリド-1a の全合成研究

（中大理工[1]・高知大農林海洋科学[2]）○尾花 知紘[1]・中島 美結[1]・中里 一貴[1]・中川 颯人[1]・村田 佳亮[1]・津田 正史[2]・不破 春彦[1]
Synthetic studies on iriomoteolide-1a ([1] *Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*, [2] *Center for Advanced Marine Core Research and Department of Agriculture and Marine Science, Kochi University*) ○Tomohiro Obana,[1] Miyu Nakajima,[1] Kazuki Nakazato,[1] Hayato Nakagawa,[1] Keisuke Murata,[1] Masashi Tsuda,[2] Haruhiko Fuwa[1]

Iriomoteolide-1a is a structurally complex marine macrolide that was isolated from the dinoflagellate *Amphidinium* sp. (strain HYA024). This natural product shows significant cytotoxic activity against human B lymphocyte DG-75 cells (IC_{50}: 2 ng/mL). However, its relative and absolute configurations are yet to be determined. In this presentation, we will report on our synthetic studies on iriomoteolide-1a, aiming at the assignment of the relative configuration of the side chain. Diastereomer **1** was targeted on the basis of a DP4+ analysis. Our synthetic strategy involved a convergent assembly of three partial structures **2**, **3**, and **5** followed by a ring-closing metathesis to access **1**.
Keywords: Macrolide; Marine natural products; Configuration; Biological activity

イリオモテオリド-1aは西表島近海の海底砂泥から採集された海洋渦鞭毛藻 *Amphidinium* 属 HYA024 株から津田らによって単離されたマクロリド天然物である[1]。本天然物は DG-75 ヒト B リンパ細胞に対して IC_{50} 2 ng/mL と非常に強力な毒性を示すが、その立体配置は未だ不明である。本研究では、イリオモテオリド-1a の側鎖の立体配置の帰属を目的とした全合成研究を行ったので、その詳細を報告する。

我々はこれまでに、天然標品の NMR データの再解析、分子力場計算およびモデル合成によりマクロ環の立体配置を修正した。今回、側鎖の立体配置は DP4+解析により修正し、ジアステレオマー**1**を合成することにした。アルコール **2** とα,β-不飽和カルボン酸 **3** を山口法により縮合後、シリル基除去してエステル **4** を得た。化合物 **4** を酸化し、アリルシラン **5** との細見–櫻井アリル化を行い、ホモアリルアルコール **6** へと誘導した。その後、化合物 **6** から閉環メタセシスを含む 4 工程の変換を行い、化合物 **1** を合成した。化合物 **1** の NMR データの詳細についても報告する。



1) M. Tsuda *et al*. *J. Org. Chem.* **2007**, *72*, 4469.

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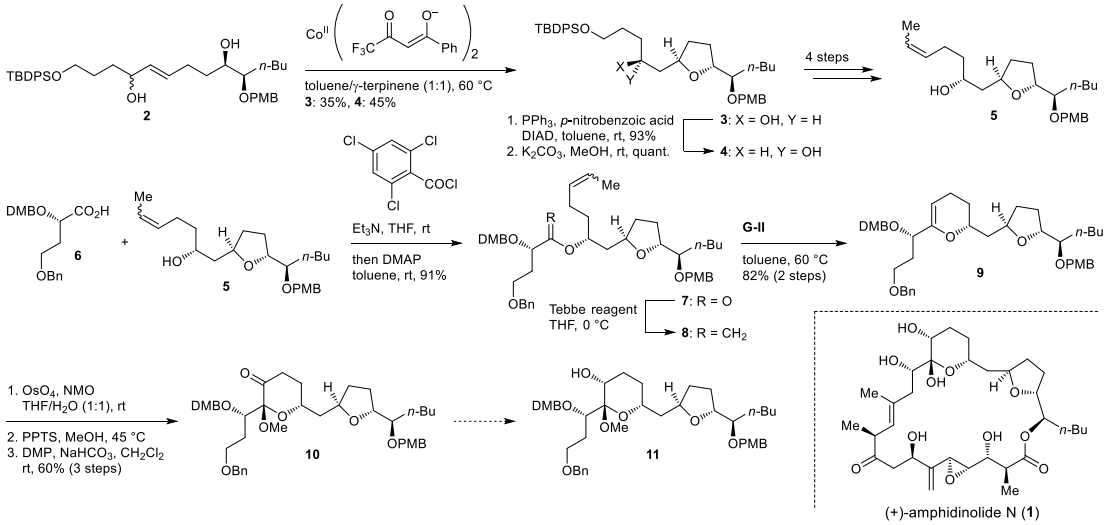
アンフィジノリドNの北半球部分の合成研究

（中大理工）○今村 巧・今村 公耀・不破 春彦
Synthetic Studies on the Northern Hemisphere of Amphidinolide N (*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○Takumi Imamura, Hiroaki Imamura, Haruhiko Fuwa

Amphidinolide N (**1**) is a 26-membered macrolide isolated from the marine dinoflagellate *Amphidinium* sp. strain Y-5 collected in Okinawa by Kobayashi et al., and shows very potent cell growth inhibitory activity against human epidermoid carcinoma KB cells and human cervical carcinoma HeLa cells. In this presentation, we will report on our synthetic studies on the northern hemisphere of **1**. Alcohol **5** and carboxylic acid **6** were condensed under Yamaguchi conditions to give ester **7**. Methylenation with Tebbe reagent followed by ring-closing metathesis using **G-II** catalyst gave enol ether **9**. A three-step sequence of dihydroxylation, methyl acetalization, and oxidation converted **9** to ketone **10**. Stereoselective reduction of **10** is currently under investigation.
Keywords: Marine macrolide; Cell growth inhibitory activity; Ring-closing metathesis

アンフィジノリドN (**1**) は小林らにより海洋渦鞭毛藻 *Amphidinium* 属 Y-5 株から単離された 26 員環マクロリド[1]であり、ヒト表皮がん KB 細胞やヒト子宮頸がん HeLa 細胞に対して非常に強力な細胞毒性を示す。今回我々は、本天然物の北半球フラグメントの合成研究を行ったので、その詳細を報告する。

アリルアルコール **2** から Co 触媒を用いた環化反応[2]を含む数工程の変換によりアルコール **5** を得たのち、カルボン酸 **6** と山口法により縮合し、エステル **7** を得た。化合物 **7** を Tebbe 試薬でメチレン化したのち、**G-II** 触媒を用いた閉環メタセシス反応を行ってエノールエーテル **9** とした。化合物 **9** をオスミウム酸化したのち、メタノール中 PPTS 処理し、最後に Dess–Martin 酸化によりケトン **10** を単一の立体異性体として得た。現在、**10** のアルコール **11** への立体選択的な還元を検討中である。



1) J. Kobayashi *et al. J. Chem. Soc., Chem. Commun.* **1994**, 1455 2) H. Fuwa *et al. J. Org. Chem.* **2021**, *86*, 5584.

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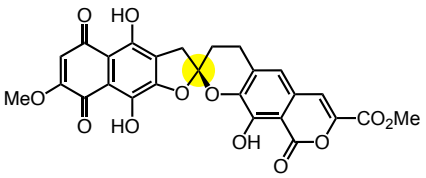
γ-ルブロマイシンの合成研究：ナフタレン部の酸化様式の調整検討

（東工大理）○森下 周一郎・安藤 吉勇・大森 建
Synthetic Study on γ-Rubromycin: Late Stage Oxidation of the Naphthalene Unit *(Department of Chemistry, Tokyo Institute of Technology)*
○Shuichiro Morishita, Yoshio Ando, Ken Ohmori

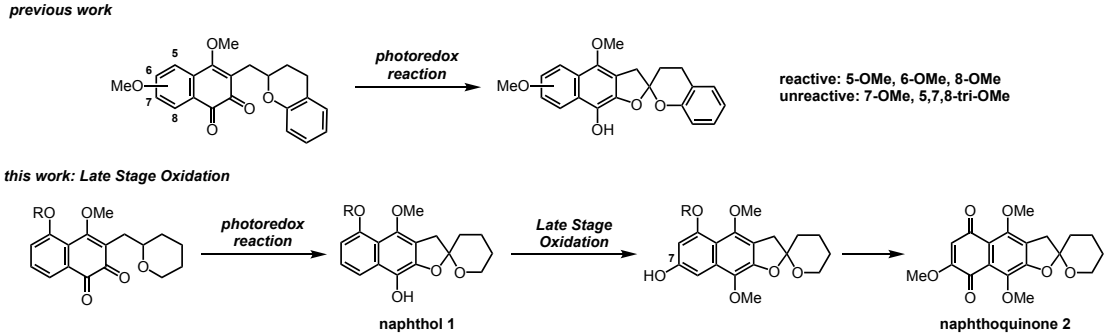
γ-Rubromycin, a polyketide-derived natural product, shows antimicrobial and telomerase inhibitory activities. The structure features a naphthazarin and an isocoumarin, which are linked through the 5,6-spiroacetal moiety having a single stereogenic center. Due to the challenges in the stereo control, asymmetric total synthesis has not been reported. We previously demonstrated the stereospecific photochemical conversion of a naphthoquinone derivative to a chiral, non-racemic spiroacetal. However, the application to the natural product failed because naphthoquinone with methoxy group at C7 is unreactive in the photoreaction. To address this issue, we planned the late stage oxidation of the naphthalene unit. We will describe herein a model study of synthesis of naphthoquinone **2** from naphthol **1**.

Keywords : γ-rubromycin; photochemical reaction; naphthoquinone; spiroacetal; natural product synthesis



γ-ルブロマイシンは放線菌から単離された天然物であり、抗菌活性やテロメラーゼ阻害活性を示す。その構造的特徴は、唯一の不斉点であるスピロアセタール炭素を介して、ナフタザリンとイソクマリンが結合している点にある。これまで多くの合成研究が報告されているが、スピロアセタール中心炭素の立体制御に成功した例はない。

この問題に対して、我々はナフトキノンの光化学反応による立体特異的なスピロアセタール合成法を開発した[1)]。しかし、ナフトキノンの７位に置換基があると、この反応は進行しない[2)]。そこで、新たな合成経路として光反応後の合成終盤に、７位の官能基化とナフトキノンへの酸化を行うことを計画した。今回、モデル化合物としてナフトキノン **2** を設定し、ナフトール **1** からの変換を検討したので報告する。



1) F. Wakita, Y. Ando, K. Ohmori, K. Suzuki, *Org. Lett*. **2018**, *20*, 3928.
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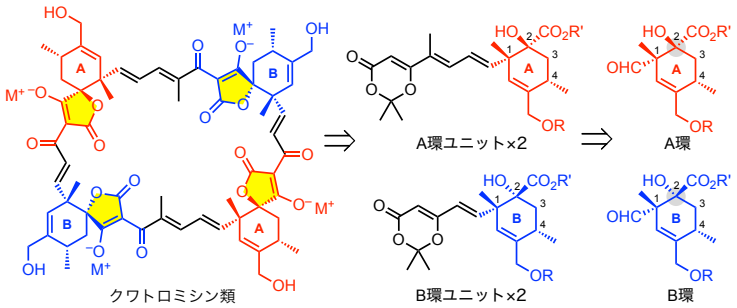
抗生物質クワトロミシン類の立体選択的合成に関する研究

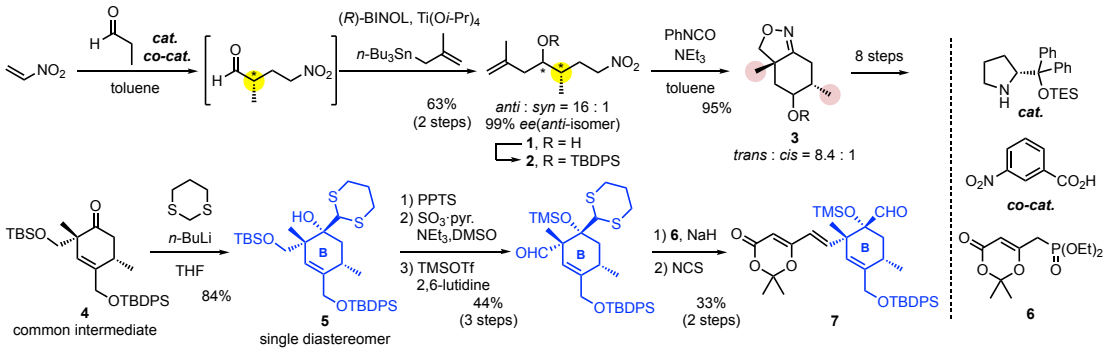
（東工大理[1]）○出山光一[1]・鎌谷耕平[1]・鈴木啓介[1]・大森 建[1]
Studies on stereoselective synthesis of the antibiotics quatromycins ([1]*Department of Chemistry, Tokyo Institute of Technology*) ○Koichi Deyama[1], Kohei Kamatani[1], Keisuke Suzuki[1], Ken Ohmori[1]

The antibiotic quartromicins share a C_2-symmetric macrocyclic carbon skeleton, consisting of two multi-substituted cyclohexene cores. Herein, we will report an efficient synthetic route to those cyclohexene cores via the common intermediate which was synthesized from the key intermediate, isoxazoline. Also, we will report the asymmetric construction of the key intermediate.
Keywords: Synthesis of Natural Products; Antibiotics; Organocatalysis; Asymmetric Synthesis; Nitrile oxide

クワトロミシン類は放線菌より単離されたポリケチド系抗生物質である。本化合物は大環状炭素骨格および分子内 C_2 対称性を有し、2 種の多置換シクロヘキセン（A 環および B 環単位）を基本構造単位として構成される。



当研究室ではこれまでに、B 環単位の合成に成功していたが、その鍵となる合成中間体 **3** の立体選択的な合成に課題を残していた。そこで本研究では、この問題を解決するための検討を行った。まず、合成序盤の不斉マイケル付加反応およびアリル化反応を検討した結果、鍵反応前駆体 **1** を高い選択性にて得ることができた。また、続くニトリルオキシドとオレフィンの分子内[3+2]付加環化反応の立体選択性向上にも成功した。さらに、8 工程の変換を経て共通中間体 **4** を合成した後、ジオキシノン部の導入を含む 6 工程の変換により **7** を得た。一方、A 環単位の合成についても検討し、いくつか有用な知見を得た。



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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC H935(935, Bldg. 9 [3F])

[H935-4am] 16. Natural Products Chemistry, Chemical Biology

Chair: Hiroshi Tanaka, Tomonari Tanaka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H935-4am-01]
Synthesis of 6-sulfo sialyl Lewis X through a protecting group strategy preventing substrate aggregation

○Takuya Yoshimoto[1], Kumpei YANO[1], Yoshiyuki MANABE[1,2], Koichi FUKASE[1,2] (1. Osaka University Department of Chemistry, Graduate, 2. Forefront Research Center)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H935-4am-02]
Precisely Controlled Glycosylation Using Cage-Shaped Borate Catalyst

○Yosuke Tanaka[1], Yoshiyuki Manabe[1], Yuka Yokoyama[1], Yuka Ikinaga[1], Tatsuya Nishitani[1], Akihhito Konishi[1], Makoto Yasuda[1], Koichi Fukase[1] (1. Osaka University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H935-4am-03]
Stereoselective furanosylation using glycosyl donors possessing a 1,2-diacetal protecting group.

○Reita Watanabe[1], Hiroshi Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H935-4am-04]
Stereoselective syntheses of sialoglycan via the use of 4,5:7,9- dicarbonyl-protected *N*-glycolyl sialyl donor and application for glycan probe

○Yutaka Takeuchi[1], Hiroshi Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H935-4am-05]
Development of a Reductive Deprotection Method for 1,2-Diacetal Protecting Groups with Trichloroethyl Groups and Application to Glycosylation

○Reki Fukushima[1], Kazuya Murakami[1], Hiroshi Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H935-4am-06]
Synthesis and functional analysis of NICOL with *O*-linked glycosylation

○Kenta Nagahama[1], Toshifumi Takao[1], Daiji Kiyozumi[2], Shun Ito[1], Hironobu Hojo[1] (1. Osaka University, 2. Nagoya University)

Japanese

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10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

[H935-4am-07]

Synthesis of glycoalbumin libraries to realize personalized medicine

○Akito Nunome[1], Kenshiro Yamada[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)

English

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[H935-4am-08]

Chemical Modification and Functionalization of Trehalose (VI): Development to Amide Condensation Reaction

○YANG YU[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Graduate School of Science and Engineering, Saitama University, 2. Strategic Research Center, Saitama University, 3. Advanced Institute of Innovative Technology, Saitama University)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

Break

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[H935-4am-09]

Investigation of glycosyl acceptors in glycosylation catalyzed by GH84 N-acetylglucosaminidase

○Shunsuke Nakada[1], Rika Okuno[1], Kisuke Tonomura[2], Takayuki Ohnuma[2], Tamonari Tanaka[1] (1. Kyoto Inst. Tech., 2. Kindai Univ.)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[H935-4am-10]

Cleavage of amide bond by Cysteine fluoro acetylation

○Yuya Matsumoto[1], Naoki Zenmyo[1], Akihiro Yasuda[1], Shohei Uchinomiya[1], Naoya Shindo[1], Kaori Tabata[1], Akio Ojida[1] (1. Pharmaceutical Science, Kyushu University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[H935-4am-11]

Synthetic Study on Lydiamycins, Cyclic Depsipeptides Containing Piperazic Acid

○Keisuke Nabata[1], Masahito Yoshida[1], Hideo Kigoshi[1] (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[H935-4am-12]

Synthetic Study of Alotamide A, a Cyclodepsipeptide

○Taishi Okamoto[1], Masahito Yoshida[1], Hideo Kigoshi[1] (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[H935-4am-13]

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Total synthesis of jamaicamide B

○Ryosuke Shigeta[1], Takahiro Suzuki[1], Kazuki Kaneko[1], Hiroaki Tanaka[1], Ibuki Haishima[1], Kanata Norio[1], Ayano Yanuma[1], Toyonobu Usuki[1] (1. Sophia University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[H935-4am-14]

Synthesis of the side-chain unit towards total synthesis of Dentigerumycin A

○Kakeru Miyamoto[1], Taiki Morita[1,2], Hiroyuki Nakamura[1,2] (1. School of Life Science and Technology, Tokyo institute of Technology, 2. Laboratory for Chemistry and Life Science, Tokyo institute of Technology)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[H935-4am-15]

Development of target protein labeling system using gold-nanoparticle probes

○Shione Kamoshita[1], Kaori Sakurai[1] (1. Tokyo University of Agriculture and Technology)

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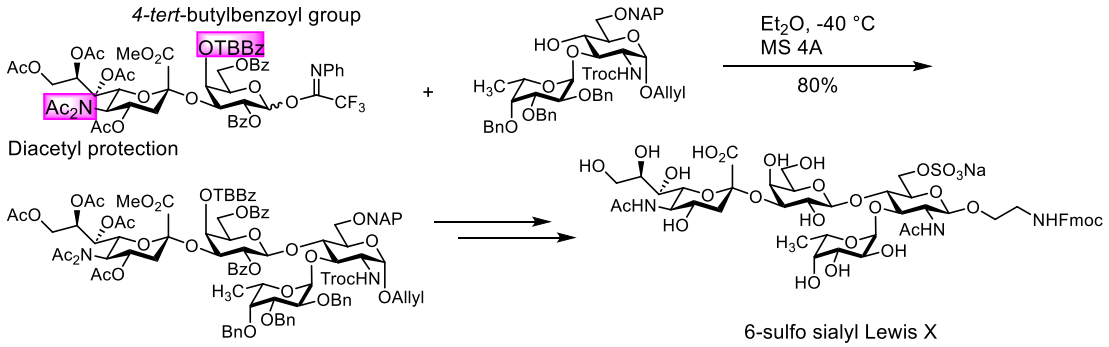
基質の凝集性に着目した保護基戦略を用いた 6-sulfo sialyl Lewis X の合成

(阪大院理[1]・阪大院理 FRC[2]) ○吉本 拓矢[1]・矢野 君晟[1]・真鍋 良幸[1,2]・深瀬 浩一[1,2]

Synthesis of 6-sulfo sialyl Lewis X through a protecting group strategy preventing substrate aggregation ([1]*Graduate School of Science, Osaka University,* [2]*Forefront Research Center, Osaka University*) ○Takuya Yoshimoto[1], Kumpei Yano[1], Yoshiyuki Manabe[1,2], Koichi Fukase[1,2]

6-sulfo sialyl Lewis X regulates cell adhesion by interacting with selectins. In this study, we achieved chemical synthesis of 6-sulfo sialyl Lewis X. Regarding the aggregative sialyl fragment, the acetamide group was protected with a diacetyl imide to prevent the intermolecular hydrogen-bond formation, and 4-*tert*-butylbenzoyl group was also employed to protect the hydroxy group to prevent its aggregation. The [2+2] key glycosylation smoothly preceded to afford the desired tetrasaccharide in 80% after optimizing reaction conditions. The following deprotection produced desired 6-sulfo sialyl Lewis X.
Keywords : Glycan, Glycosylation, Protecting group, Selectin, Sialic acid

6-sulfo sialyl Lewis X はセレクチンを介して細胞接着に関与し、がんの転移や免疫応答を制御する。本糖鎖は非還元末端にシアル酸を持つが、一般にシアル酸含有糖鎖の化学合成において、保護シアル酸含有フラグメントは有機溶媒中で自己会合による凝集性を示し、反応性が低い。そこで、シアル酸含有フラグメントに関して、アセトアミド基をジアセチルイミドとして保護して分子間水素結合の形成を防ぐとともに、ヒドロキシ基の保護基としてかさ高い 4-*tert*-butylbenzoyl 基を採用することで、その凝集性の緩和を狙った。結果として、鍵である[2+2]グリコシル化は速やかに進行し、80%で目的物を得た。さらに、得られた 4 糖の保護基を除去することで、目的の 6-sulfo sialyl Lewis X の合成を達成した。



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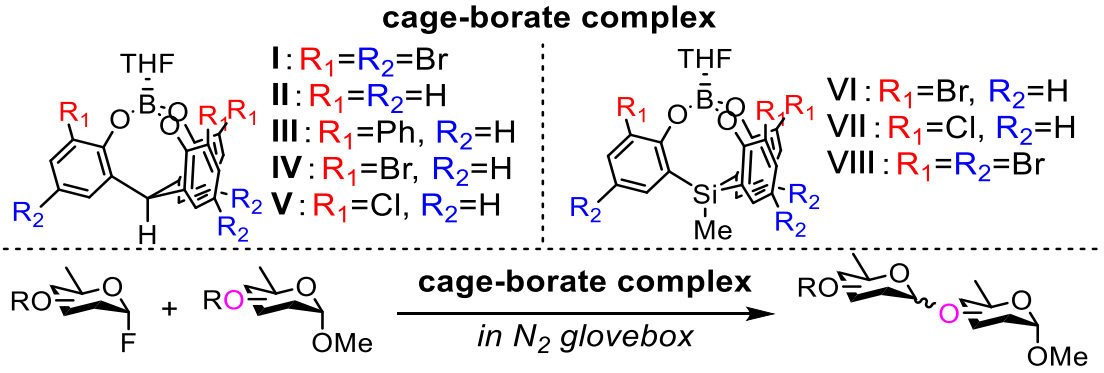
日本化学会 第104春季年会 (2024)

かご型ホウ素錯体を用いた精密グリコシル化

（阪大院理[1]・阪大院工[2]）○田中 洋輔[1]・真鍋 良幸[1]・横山 夕華[1]・生長 優香[1]・西谷 達也[2]・小西 彬仁[2]・安田 誠[2]・深瀬 浩一[1]
Precisely Controlled Glycosylation Using Cage-Shaped Borate Catalyst ([1]*Graduate School of Science, Osaka University*, [2]*Graduate School of Engineering, Osaka University*) Yoshiyuki Manabe, Yosuke Tanaka, Yuka Yokoyama, Yuka Ikinaga, Tatsuya Nishitani, Akihito Konishi, Makoto Yasuda, Koichi Fukase

Glycans are involved in a wide range of biological phenomena. The reactivity of the glycosyl donors varies significantly depending on the sugar types and the protecting groups employed. Additionally, the structure of sugar acceptors also influences reactivity in glycosylation. To overcome this issue, we investigated the glycosylation reaction using cage-shaped boron complexes as activators for glycosyl fluorides. These complexes, by changing ligands, enable precise modulation of Lewis acidity and fluorophilicity. Here, by selecting appropriate cage-shaped boron complexes that match the substrate's reactivity, we achieved various glycosylation reactions in high yields.
Keywords : Lewis acid; Glycan; Glycosylation; Complex; Catalysts

糖鎖は様々な生命現象に関与するが，合成法は十分に確立されておらず，その機能解明・制御が立ち遅れている．糖同士を結合するグリコシル化反応は，基質ごとに反応性が大きく異なり，汎用的に利用できる手法は確立されていない．我々はこの問題に対し，かご型ホウ素錯体に着目した．かご型ホウ素錯体は，フッ化糖の活性化が可能であり，ホウ素のリガンド上の置換基を変えることで，ルイス酸性や反応点周りの立体を精密にチューニングできる．これを利用して，基質の反応性に合わせて，グリコシル化反応を精密に制御できると考えた．狙い通り，かご型ホウ素錯体は基質ごとに異なる反応性を示し，錯体をスクリーニングすることで，様々なフッ化糖を触媒的に活性化し，高収率でグリコシル化成績体を得ることに成功した．



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1,2-ジアセタールで保護された糖供与体を用いる立体選択的フラノシル化反応の開発

（東工大物質理[1]）○渡邉 怜汰[1]・田中 浩士[1]

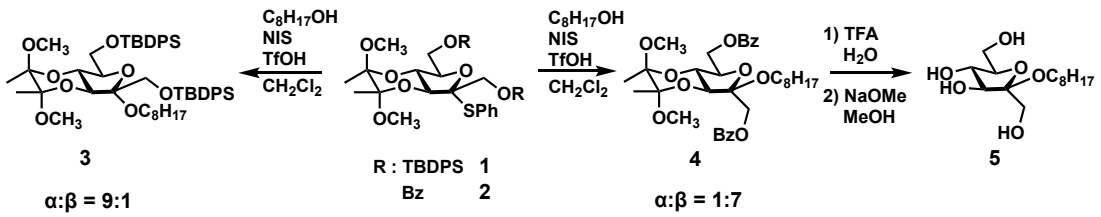
Stereoselective furanosylation using glycosyl donors possessing a 1,2-diacetal protecting group.

([1] *Departmet of Chemical Science and Engineering, Tokyo Institute of Technology*) ○Reita Watanabe,[1] Hiroshi Tanaka,[1]

The stereoselective synthesis of furanosides, particularly the synthesis of 1,2-*cis*-franosides, is one of the more challenging glycosidic linkages to form. This study explores stereoselective synthesis of furanosides by using conformationally restricted glycosyl donor with a 1,2-diacetal protecting group. Last year, we have reported that glycosylation proceeds with α-selectivity when using fructofuranosyl donors **1** with the hydroxyl group at the 1,6-position protected by silyl ether. In this study, we examined glycosyl donors **2** possessing ester protecting groups at the 1,6-position. We found that when using octanol as the glycosyl acceptor, β-selective glycosylation occurs. The glycosides **4** obtained were then deprotected without breaking the glycosidic bond by hydrolyzing the 1,2-diacetal under acidic conditions, followed by the hydrolysis of the esters under basic conditions, successfully synthesizing β-fructofuranosides **5**.

Keywords : Ketose; Inulin; Levan; Fused ring system; Furanose

フラノシドの立体選択的なグリコシル化は、特に、1,2-*cis*-フラノシド結合は、合成が困難な結合の一つである。当研究室では、1,2-ジアセタールを用いて立体配座を規定されたフラノシル糖供与体を用いる立体選択的グリコシル化を検討している。昨年は、1,6 位の水酸基をシリルエーテルで保護した 1,2-ジアセタールを有するフルクトフラノシル糖供与体 **1** では、α 選択的(α:β = 9:1)なグリコシル化が進行することを明らかにした。本研究では、1,6 位にエステル系保護基を有する糖供与体 **2** について検討した。その結果、オクタノールを糖受容体として用いた場合に、β 選択的(α:β = 1:7)なグリコシル化が進行することを明らかにした。得られたグリコシド **4** の 1,2-ジアセタールを酸性条件下、加水分解することによって、グリコシドを壊すことなく脱保護し、続いて塩基条件下エステルを加水分解することによって、β フククトフラノシド **5** を合成することに成功した。



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二つのカルボニル保護基を持つ *N*-グリコリルノイラミン酸糖供与体を用いた立体選択的シアル酸糖鎖の合成と糖鎖プローブへの応用

（東工大物質理工 [1]）○竹内 悠貴 [1]・田中 浩士 [1]

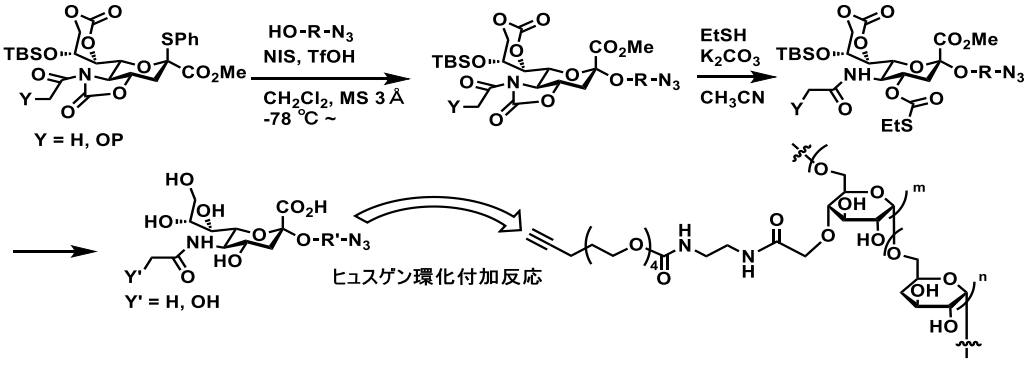
Stereoselective syntheses of sialoglycans using *N*-glycolylneuraminic acid donors with two carbonyl protecting groups and their application to the synthesis of glycan probes

([1]*Department of Chemical Science and Engineering, Tokyo Institute of Technology*)
○ Yutaka Takeuchi,[1] Hiroshi Tanaka,[1]

N-glycolylneuraminic acid (NeuGc) is specifically found in human cancer cells. Therefore, sialoglycans containing NeuGc could contribute to developing cancer therapy and diagnostic techniques. In our laboratory, we have reported the synthesis of NeuAc α(2,8)octasialic acid by *N*-acetyl-5-*N*,4-*O*:7-*O*,9-*O* dicarbonyl protected sialyl donor (1). Herein, we planned the synthesis of NeuGc-containing glycosides by using the N-glycoyl dicarbonyl protected sialyl donors. The *N*-glycoyl sialyl donor underwent glycosidation in an α-selective manner. The *N*-glycolyl 5-*N*, 4-*O*-protecting group were more sensitive to nucleophiles than the corresponding *N*-acetyl derivative and still selectively underwent opening of the carbamate. Finally, we examined the preparation of glycan probes using the NeuGc-containing glycosides bearing an azido group via Huisgen [3+2] cycloaddition.

Keywords : sialic acid, glycosylation, N-glycoly neuraminic acid, stereoselectivity, multivalency effect

N-グリコリルノイラミン酸（NeuGc）は、人間のがん細胞に特異的に検出される糖質である。そこで、NeuGc を含む糖鎖は、がん治療や診断技術の開発への利用が期待されている。当研究室では、*N*-アセチル 5-*N*,4-*O*:7-*O*,9-*O* ジカルボニル保護基を有するシアル酸の糖供与体を用いた NeuAc α(2,8)オクタシアル酸の合成を報告した（1）。ここでは、*N*-グリコリルジカルボニル保護されたシアル供与体を使用して、NeuGc を含むグリコシドの合成を検討した。*N*-グリコイルシアル供与体は、α-選択的なグリコシル化が進行した。*N*-グリコリル 5-*N*,4-*O*-カルボニル保護基は、対応する *N*-アセチル誘導体よりも、求核剤に対して鋭敏であるが、選択的な開環は可能であった。最後に、Huisgen[3+2]環化付加反応を介してアジド基を持つ NeuGc 含有グリコシドを用いたグリカンプローブの調製を検討しました



(1) R. Koinuma, K. Tohda, T. Aoyagi, H. Tanaka, *Chem. Commun.*, **2020**, *56*, 12981.

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日本化学会 第104春季年会 (2024)

トリクロロエチル基を有する 1,2-ジアセタール保護基の還元的脱保護法の開発とその糖鎖合成への応用

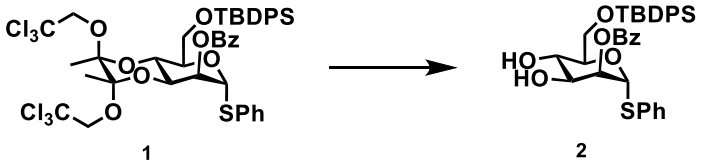
（東工大物質理工[1]）○福嶋 玲希[1]・村上 和哉[1]・田中 浩士[1]

Development of a Reductive Deprotection Method for 1,2-Diacetal Protecting Groups with Trichloroethyl Groups and Application to Glycosylation ([1] Department of Chemical Science and Engineering,Tokyo Institute of Technology) Reki Fukushima,[1] Kazuya Murakami,[1] Hiroshi Tanaka[1]

In glycosylation, protecting groups of hydroxyl groups play an important role in controlling regioselectivity and stereoselectivity of glycosylation. Butanediacetal (BDA) protecting group is one of the 1,2-diacetal protecting groups that selectively protects 1,2-trans-diols. We have developed a bisTCE-BDA protecting group that is stable under glycosylation conditions by introducing an electron-withdrawing trichloroethyl group to the BDA protecting group.While this protecting group is expected to be useful for stereoselective glycosylation by suppressing stereoinversion of the glycosyl backbone, its reactivity to deprotection with TFA, the standard deprotection reaction of diacetal protecting groups, is reduced. In this study, we planned a reductive deprotection reaction that does not involve a destabilized oxonium cation intermediate. In fact, thiomannosides with the 3,4-position hydroxyl group protected with this protecting group gave the deprotected diols in 56% yield when reacted with zinc powder and ammonium chloride in acetonitrile.

Keywords : Mannose; Glycosylation; Protection Group; Zinc

糖鎖合成において、水酸基の保護基はグリコシル化の位置選択制や立体選択性の制御において重要な役割を果たす。ブタンジアセタール（BDA）保護基は、1,2-トランスジオールを選択的に保護する 1,2-ジアセタール保護基の一つである。当研究室では BDA 保護基に電子求引性のトリクロロエチル基を導入することで、グリコシル化条件に安定な bisTCE-BDA 保護基を開発した。当保護基は糖骨格の立体反転を抑制することで立体選択的な糖鎖合成への利用が期待できる一方で、ジアセタール保護基の標準的な脱保護反応である TFA による脱保護に対する反応性の低下がみられる。そこで本研究では、不安定化されたオキソニウムカチオン中間体を経由しない還元的脱保護反応を計画した。実際に、当保護基で 3,4 位水酸基を保護したチオマンノシドに対し、アセトニトリル中亜鉛粉末と塩化アンモニウムを反応させたところ、脱保護体であるジオールが収率 56%で得られた。



1 2

entry	condition	1(%)	2(%)
1	TFA/H2O, THF, 0℃, 30min	88	0
2	Zn, NH4Cl, MeCN, r.t., 3h	0	56

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O-結合型糖鎖を有するタンパク質 NICOL の化学合成とその機能解明

(阪大蛋白研[1]・名大環研[2]) ○長濱 健太[1]・高尾 敏文[1]・淨住大慈[2]・伊藤駿[1]・北條裕信[1]

Synthesis and functional analysis of NICOL with *O*-linked glycosylation ([1]*Institute for Protein Research, Osaka University*, [2]*Research Institute of Environmental Medicine, Nagoya University*) ○Kenta Nagahama,[1] Toshifumi Takao,[1] Daiji Kiyozumi,[2] Shun Ito,[1] Hironobu Hojo[1]

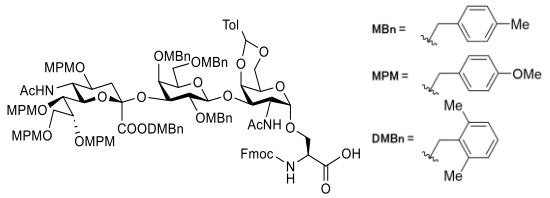
NICOL (NELL2-interacting cofactor for lumicrine signaling), a protein secreted by the testis, forms a complex with NELL2, a protein also secreted by the testis, and regulates the sperm maturation process[1]. We found that the recombinant protein of NICOL has a disialyl-T glycosylation. However, the site of glycosylation, the glycan function, and the cross-linking mode of disulfide bonds have not been clarified.

In this study, before synthesizing NICOL with disialyl-T glycans, we chemically synthesized NICOL with sialyl-T glycans at the two potential glycosylation sites. We first synthesized sialyl-T serine using the substituted-benzyl protection strategy developed in our laboratory[2), 3)], which was used for the solid-phase synthesis of NICOL. The deprotection of both glycan and peptide chain was simultaneously performed by TFA. The results of the synthesis, the characterization of the secondary structure, and the biological activity will be reported.

Keywords : glycoprotein; NICOL; sialyl-T; substituted benzyl protecting groups; glycosylation

精巣で分泌されるタンパク質の NICOL (NELL2-interacting cofactor for lumicrine signaling) は、同じく精巣から分泌されるタンパク質 NELL2 と複合体を形成し、精子の成熟過程を制御している[1)]。我々は NICOL の組換えタンパク質が disialyl-T 修飾されていることを見出した。しかし、その糖鎖付加部位、糖鎖機能、および SS 結合の架橋様式は不明である。

本研究では、disialyl-T 型糖鎖をもつ NICOL を合成する前に、2 つの潜在的糖鎖付加部位に sialyl-T 型糖鎖をもつ NICOL を化学合成した。まず、当研究室にて開発された置換型ベンジル基を用いた保護体系により sialyl-T をもつ Fmoc-セリンを合成し、ペプチド固相合成に使用することで NICOL を合成した[2), 3)]。合成結果、二次構造評価と生物活性について報告する予定である。



Sequence of NICOL

EPATGSAVPA QSRPCVDCHA FEFMQRALQD LRKTAYSLDA RTETLLLQAE RRALCACWPA GR

= potential glycosylation sites

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個別化医療を可能とする糖鎖アルブミンライブラリーの合成

（東工大物質理工 [1]・理研 開拓研究本部 田中生体研 [2]）○布目 朗人 [1]・山田 健士郎 [1]・Ambara R. Pradipta[1]・張 宗哲 [1]・田中 克典 [1,2]

Synthesis of glycoalbumin library to realize personalized medicine ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Biofunctional Synthetic Chemistry Laboratory, Cluster for Pioneering Research, RIKEN),*○Akito Nunome[1], Kenshiro Yamada[1], Ambara R. Pradipta[1], Tsung-Che Chang[1], Katsunori Tanaka[1,2]

We have so far developed a novel approach of using the glycoalbumins, which achieved the selective cancer-cell recognition depending on the glycan patterns.[1] By utilizing several glycan patterns, we have discovered a specific glycan pattern that exhibited strong interaction with particular cancer cells both in vitro and in vivo. We here in prepare a glycoalbumin library consisting of over 100 types of glycan patterns, thereby enabling the selective targeting of specific gene mutations. We will report the detailed data.

Keywords: Glycan pattern recognition, personalized medicine, cancer targeting, glycan modification

がんは多様な遺伝子変異によって引き起こされるが、患者の体内で進行するがんでは遺伝子変異の複雑性が治療の効果を低減させる。この問題に対処するため、がんに最適化した個別化医療が望まれている。これまでに我々はアルブミンに「糖鎖パターン」を付与した糖鎖アルブミン分子が、糖鎖パターンに応じて異なるがん細胞への高選択的な認識を示すことを見出した [1)]。短時間で特定のがんに対して強く相互作用する糖鎖パターンを見出すとともに、*in vivo* でのターゲティングに応用可能であることを示した。今回、がんの遺伝子変異に対応した糖鎖ターゲティングの実現に向けて、100 種類以上の糖鎖アルブミンライブラリーを構築した。さらに、遺伝子変異を持つ悪性のがん細胞に対して、強いターゲティング効果を示す糖鎖パターンを網羅的に調査した。本発表では、これらの経緯について報告する。

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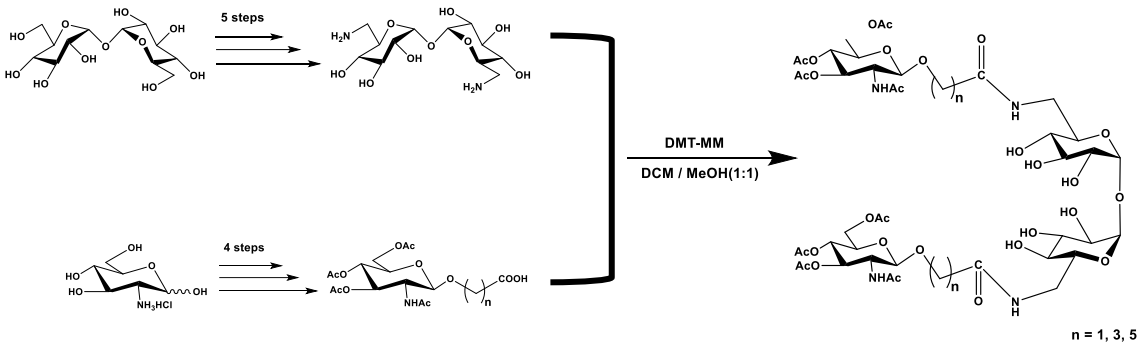
Chemical Modification and Functionalization of Trehalose (VI): Development to Amide Condensation Reaction

([1]*Graduate School of Science and Engineering, Saitama University*, [2]*Strategic Research Center, Saitama University*, [3]*Advanced Institute of Innovative Technology, Saitama University*) ○ YANG YU,[1] Takahiko Matsushita,[1,2,3] Tetsuo Koyama,[1] Ken Hatano,[1,2,3] Koji Matsuoka[1,2,3]

Keywords: Trehalose; Functionalization; Amide Condensation Reaction; Glucosamine

Trehalose is a non-reducing disaccharide consisting of two molecules of glucose bound together *via* α,α-(1→1) linkage and is widely present in plants, animals, and microorganisms. Trehalose has a highly reactive primary hydroxyl groups at its sixth positions. Because of its low sweetness, hygroscopicity, and excellent physiological functions such as insulin hyposecretion and glucose tolerance improvement, which were discovered recently, it is now used in various fields such as food, pharmaceuticals, and cosmetics. However, trehalose has not yet been developed as a scaffold molecule to introduce functional molecules. In this study, we report the functionalization of trehalose and evaluation of its ability for chemical reactions with various sugars having alkyl or carboxy groups using trehalose as a scaffold, using various means of chemical modification such as iodination, azidation, and amidation of trehalose.

The tetrasaccharidic derivatives were synthesized by amide condensation of carboxylic acid generated from glucosamine hydrochloride and trehalose with amino groups in a mixed solvent of dichloromethane and methanol with DMT-MM as a catalyst[1]. The reaction proceeded smoothly to afford the desired tetrasaccharidic derivatives, and the structures of the target compounds were confirmed by Mass spectra and NMR spectra.



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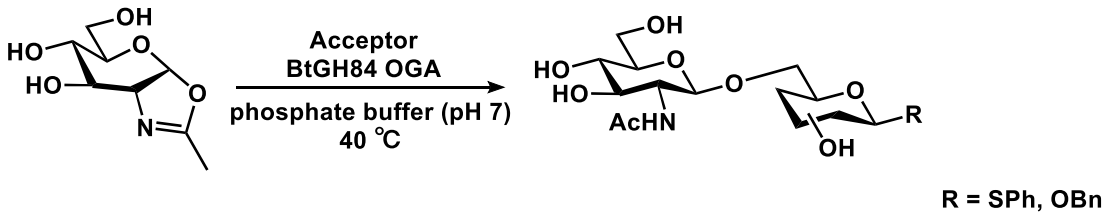
GH84 *N*-アセチルグルコサミン加水分解酵素によるグリコシル化での糖受容体の検討

（京工繊大院工芸[1]・近大院農[2]・近大アグリ技研[3]）○中田 竣介[1]・奥野 梨花[1]・殿村 規介[2]・大沼 貴之[2,3]・田中 知成[1]

Investigation of glycosyl acceptors in glycosylation catalyzed by GH84 *N*-acetylglucosaminidase ([1]*Graduate School of Science and Technology, Kyoto Institute of Technology*, [2] *Graduate School of Agriculture, Kindai University*, [3]*Agricultural Technology and Innovation Research Institute, Kindai University*) ○Shunsuke Nakada,[1] Rika Okuno,[1] Kisuke Tonomura,[2] Takayuki Ohnuma,[2,3] Tomonari Tanaka,[1]

N-Acetyl-β-D-glucosaminidase (OGA), which is classified into glycoside hydrolase family 84 (GH84), hydrolyzes β-*O*-glycosylated *N*-acetyl-D-glucosamine. OGA is found in human pathogens and its symbiotic organisms, and its hydrolysis mechanism is retaining type. In this study, enzymatic transglycosylation catalyzed by GH84 OGA from *Bacteroides thetaiotaomicron* (BtGH84 OGA) was performed using an oxazoline derivative of *N*-acetylglucosamine (GlcNAc) as a glycosyl donor. Based on the good yields of glycosylation reactions catalyzed by BtGH84 OGA using *p*-nitrophenyl glycopyranosides as glycosyl acceptors, the enzymatic transglycosylation using benzyl and thiophenyl glycopyranosides as glycosyl acceptors was investigated in order to expand the application range of glycosyl acceptors. The reaction mixtures were analyzed and purified by HPLC. The resulting transglycosylation products were β1-6 linked disaccharide derivatives.
Keywords : Glycosidase; Transglycosylation; N-acetylglucosamine;

糖質加水分解酵素ファミリー84(GH84)に分類される *N*-acetyl-β-D-glucosaminidase (OGA)は、β-*O*-グリコシル化された *N*-アセチルグルコサミン(GlcNAc)を加水分解する酵素であり、ヒトやヒト共生生物に見出されている立体保持型の加水分解機構を示す糖加水分解酵素である。本研究では、GlcNAc のオキサゾリン誘導体を糖供与体として、GH84 に分類される *Bacteroides thetaiotaomicron* 由来 OGA (BtGH84 OGA)による糖転移反応を行った。これまでの当グループでの *p*-ニトロフェニル化糖を糖受容体とした BtGH84 OGA による糖転移反応における良好な収率を基に、糖受容体の適用範囲を拡大することを目的として、ベンジル化糖やチオフェニル化糖を糖受容体とした糖転移反応を検討した。酵素反応溶液を HPLC で分取精製し構造解析行ったところ、糖転移生成物は β1-6 結合を有する二糖誘導体であることを確認した。



Scheme 1. Enzymatic glycosylation catalyzed by BtGH84 OGA.

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日本化学会 第104春季年会 (2024)

システインフルオロアセチル化によるアミド結合切断法の開発

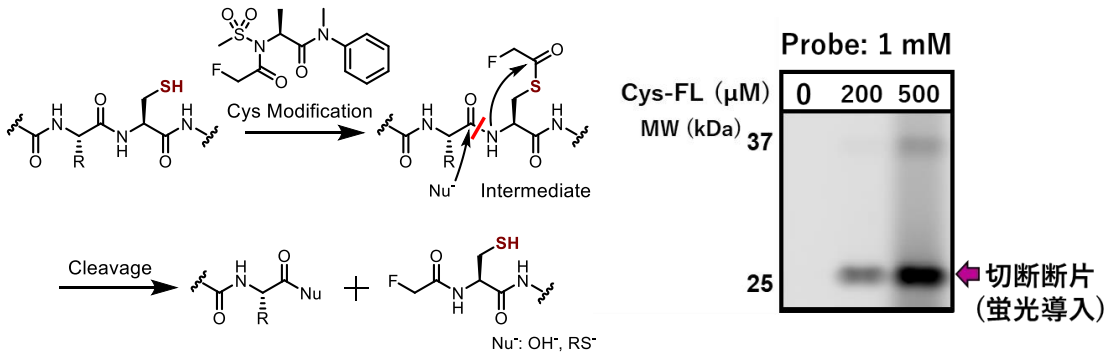
（九大院薬[1]）○松本　侑也[1]・善明 直輝[1]・安田　斉弘[1]・内之宮　祥平[1]・進藤　直哉[1]・田畑　香織[1]・王子田　彰夫[1]

Cleavage of amide bond by cysteine fluoroacetylation ([1]*Graduate School of Phamaceutical Science, Kyushu University*) [1] ○Yuya Matsumoto,[1] Naoki Zenmyo,[1] Akihiro Yasuda,[1] Shohei Uchinomiya,[1] Naoya Shindo,[1] Kaori Tabata,[1] Akio Ojida[1]

While chemical modification of proteins is widely known, there are only a few reports of chemical degradation methods. We have discovered S-formylation as a method for amide bond cleavage of protein sequences, which is achieved by modifying Cys residues. This method enables rapid amide bond cleavage. In this study, we developed a new amide bond cleavage method by cysteine haloacetylation. We found that fluoroacetylation significantly improves the stability of the Cys adduct of intermediates, and enables efficient amide bond cleavage of the peptide. We also found that thiol species as an additive can greatly accelerate the cleavage. Furthermore, we achieved introduction of fluorescent molecule to cleavage fragment by addition of nucleophiles containing fluorescent molecule.

Keywords : Protein Cleavage; Cleavage of peptide; Chemical modification; Cysteine modification; Cysteine fluoro acetylation

タンパク質を化学的に修飾する手法は広く知られている一方で、化学的・人為的に切断する手法の報告例は少ない。当研究室では Cys 側鎖を S-ホルミル化修飾することで電子求引効果によりタンパク質配列主鎖のアミド結合を効率的に切断する手法を見出している。本研究では S-ホルミル基よりも水中安定性を改善した Cys 修飾法として、S-フルオロアセチル化によるアミド結合切断法を開発した。ハロゲン置換によりアシル基カルボニル中心炭素の求電子性を高めることで、反応中間体の高い安定性を達成しながらペプチドレベルでの経時的かつ高効率でのアミド結合切断を可能とした。さらに、反応中間体に求核剤としてチオール種を反応させることで切断の大幅な促進が可能であることを明らかにした。この切断加速に伴うタンパク質切断断片への機能性分子の導入を達成したため併せて報告する。



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ピペラジン酸含有環状デプシペプチド Lydiamycin 類の合成研究

（筑波大院数理物質）○奈幡　圭亮・吉田　将人・木越　英夫
Synthetic Study on Lydiamycins, Cyclic Depsipeptides Containing Piperazic Acid (*Degree Programs in Pure and Applied Sciences, University of Tsukuba*)　○Keisuke Nabata, Masahito Yoshida, Hideo Kigoshi

Lydiamycins, isolated from actinomycetes, are cyclic depsipeptides containing non-proteogenic piperazic acids. These compounds exhibit cancer cell metastasis-inhibitory and antibacterial activities. To date, total synthesis has not been achieved, and the absolute configuration at the C29 position in lydiamycin D (**1**) is not determined. The retrosynthesis of **1** is shown below. **1** was divided into three segments **2**, **3**, and **4**. These segments would be obtained by asymmetric synthesis, which would be followed by condensation of each other to construct the desired structure. Acid **4** could be constructed using stereoselective alkylation and Ru-catalyzed asymmetric hydrogen transfer reaction as key reactions. In this presentation, we will report the results of our synthetic study of lydiamycin D (**1**).
Keywords : Natural Product; Cyclic Depsipeptide; Piperazic Acid

放線菌から単離・構造決定された、非タンパク質性アミノ酸であるピペラジン酸を含む環状デプシペプチド Lydiamycin 類は、抗菌活性やがん細胞の転移阻害活性を示す[1)2)]。現在までに全合成は達成されておらず、類縁体の Lydiamycin D については C29 位の立体配置が決定されていない。そこで、生物有機化学研究を指向した Lydiamycin 類の全合成に着手した。Lydiamycin D (**1**)の逆合成を図 1 に示す。**1** を **2**、**3**、および **4** の部分構造に分け、それぞれを不斉合成により得た後、縮合により所望の構造を構築することとした。また、脂肪酸 **4** は、立体選択的アルキル化と Ru 触媒を用いた不斉水素移動反応を鍵反応に用いることで、所望の立体配置を構築可能と考えた。本発表では、この逆合成に基づいて **1** の合成を検討した結果について報告する。

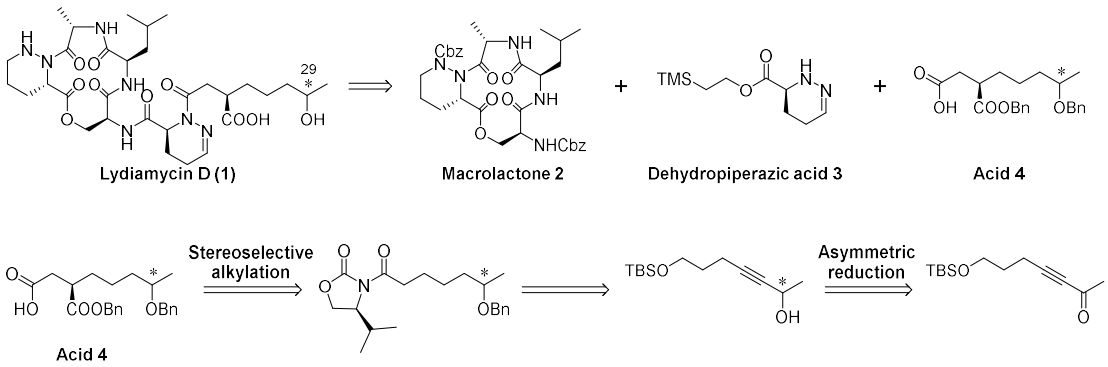

図 1　Lydiamycin D (**1**)の逆合成

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日本化学会 第104春季年会 (2024)

環状デプシペプチド Alotamide A の合成研究

（筑波大院数理物質）○岡本 大志・吉田 将人・木越 英夫
Synthetic Study of Alotamide A, a Cyclodepsipeptide (*Degree Programs in Pure and Applied Sciences, University of Tsukuba*) ○Taishi Okamoto, Masahito Yoshida, Hideo Kigoshi

Alotamide A (**1**) is a cyclodepsipeptide isolated from marine cyanobacteria. The compound **1** contains a tripeptide having a thiazoline ring and an unsaturated polyketide moiety, whose absolute configuration has not been determined. This natural product exhibits Ca^{2+} influx activity in mouse cerebral cortical neurons. To determine the absolute configuration toward further bioorganic study, we planned the total synthesis of alotamide A (**1**).

The natural product could be obtained by coupling three segments (a tripeptide, segments 1 and 2). We have synthesized a tripeptide segment containing thiazoline ring and two polyketide segments 1 and 2. We are currently investigating the coupling of three segments and macrocyclization. In this presentation, details of the synthetic study of alotamide A will be reported.

Keywords : Marine natural product, Cyclodepsipeptides

Alotamide A (**1**) は、海洋シアノバクテリアから単離・構造決定された環状デプシペプチドである [1]。**1** は、チアゾリンを含むトリペプチドと不飽和ポリケチドによって構成されており、不飽和ポリケチドについては絶対立体配置が決定されていない。この化合物について、マウスの大脳皮質神経細胞へのカルシウム流入活性を示すことが報告されている。我々は Alotamide A の生物有機化学研究を指向して、絶対立体配置の決定を目的とした全合成を計画した。

天然物は 3 つの部分構造（ペプチド、セグメント 1 および 2）のカップリングによって合成できると考えた（図 1）。これまでに、チアゾリン含有トリペプチドとセグメント 1,2 の合成を達成しており、現在、各セグメントのカップリングと大員環形成について検討を行っている。本発表では、この詳細について報告する。

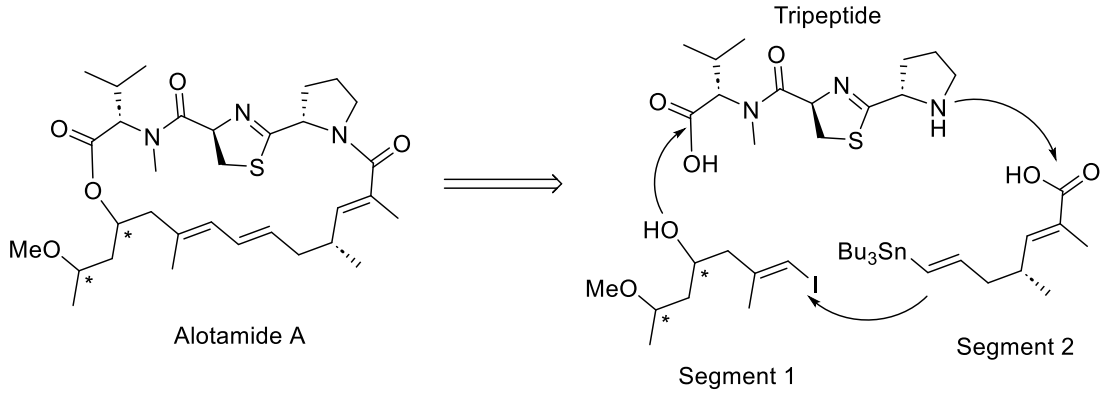

図 1　Alotamide A の逆合成

Reference

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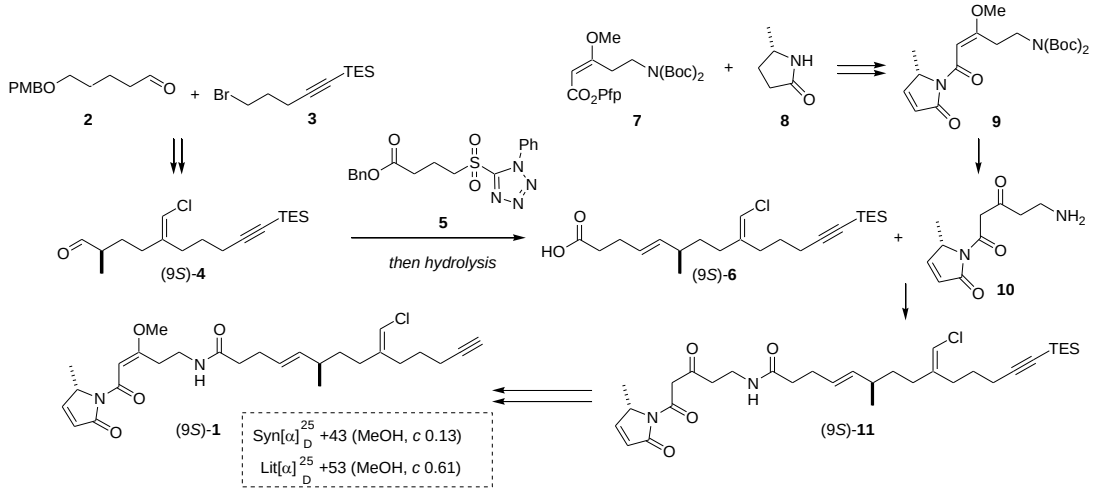
Jamaicamide B の全合成

（上智大理工）○茂田 亮介・鈴木 貴裕・金子 和樹・田中 宏明・葩島 息吹
則尾 かなた・矢沼 綾乃・臼杵 豊展
Total synthesis of jamaicamide B (*Faculty of Science and Tecnology, Sophia University*)
○Ryosuke Shigeta, Takahiro Suzuki, Kazuki Kaneko, Hiroaki Tanaka, Ibuki Haishima
Kanata Norio, Ayano Yanuma, Toyonobu Usuki

Jamaicamides B was isolated from *Moorea producens* in Jamaica by Gerwick and co-workers. These compounds have unique mixed peptide-polyketide structure, containing *E*-chloroolefin, *E*-olefin, β-methoxy enone and pyrrolinone ring. Meanwhile, stereochemistry of C9 has not been elucidated yet. In this work, first total synthesis of **1** was achieved.
Keywords : Peptide; Polyketide; Natural Marine Product

Jamaicamide B(**1**)は、ジャマイカ近海に生息するアオコの一種 *Moorea producens* から単離されたペプチドーポリケチド系海洋天然物である [1]。本研究では、未解明の C9 位立体化学解明のため、jamaicamide B の全合成を展開した。まずポリケチド部位の合成に着手した [2]。1,5-Pentanediol と 4-pentyn-1-ol から合成されたアルデヒド **2** とアルキン **3** との Grignard 反応、続く Wittig 反応と不斉メチル化により、アルデヒド(9*S*)-**4** を得た。続いて、Julia-Kocienski オレフィン化によって *E* オレフィンを構築した。次に、ペプチド部位の合成を行った [3]。Boc-β-alanine から得られた活性化エステル **7** とピロリドン **8** から **9** を得た。得られた **9** の Boc 基の除去を試みたが、β メトキシエノン部位を保持できなかった。そこで、(9*S*)-**6** と **10** とのアミド化後再度メチル化を行い、最後に TES 基の除去を行うことで(9*S*)-jamaicamide B の最初の全合成を達成した。比旋光度の比較から、C9 位の立体化学は、*S* 体であることが分かった。



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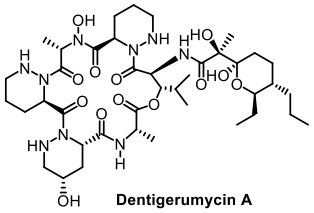
Dentigerumycin A の全合成のためのアシル側鎖ユニットの合成検討

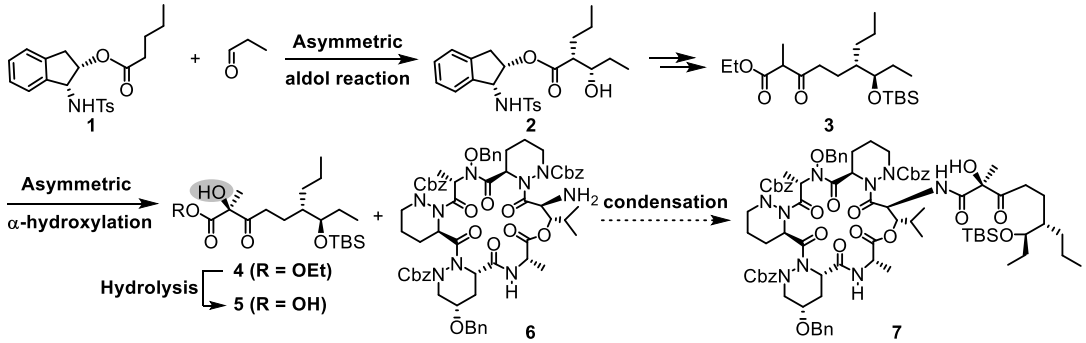
（東工大生命理工[1]・東工大化生研[2]）○宮本　駆[1]・盛田　大輝[1,2]・中村　浩之[1,2]
Synthesis of the side-chain unit towards total synthesis of Dentigerumycin A ([1]*School of Life Science and Technology, Tokyo institute of Technology*, [2]*Laboratory for Chemistry and Life Science, Tokyo institute of Technology*) ○Kakeru Miyamoto[1], Taiki Morita[1,2], Hiroyuki Nakamura[1,2]

Dentigerumycin A[1] is a peptide natural product abundant in unusual amino acids such as piperazic acid and *N*-hydroxy amino acid. Although it shows interesting antibacterial activity, there have been no synthetic reports on this natural product or its derivatives. In the last CSJ annual meeting, we reported an efficient synthesis of the cyclic depsipeptide constituting Dentigerumycin A. In this study, we have established a synthetic route for the acyl side-chain unit. Key steps include asymmetric aldol reaction[2] and asymmetric α-hydroxylation of β-keto esters.[3]

Keywords : Acyl side chain, Asymmetric aldol reaction, Dentigerumycin A, Asymmetric α-hydroxylation



Dentigerumycin A[1]は、ピペラジン酸や*N*－ヒドロキシアミノ酸といった異常アミノ酸に富むペプチド系天然物であり、興味深い抗菌活性を示すが、誘導体を含めてその合成例は無い。昨年の年会において我々は、本天然物が有する環状デプシペプチドの効率的合成法を報告した。今回は、以下に示すアシル側鎖ユニットの合成を検討した。まず、エステル **1** を用いた不斉アルドール反応[2]により *syn*-**2** を得た。数工程を経てβ－ケトエステル **3** へと導いたのち、不斉α－ヒドロキシ化反応[3]により第 3 級アルコール **4** とした。最後に加水分解を行い、アシル側鎖ユニット **5** を合成することができた。本発表では、**5** と環状デプシペプチド **6** との連結について検討した結果も併せて報告する。



1) Oh, D.-C.; Poulsen, M.; Currie, C. R.; Clardy, J. *Nat. Chem. Biol.* **2009**, *5*, 391.
2) Ghosh, K. A.; Onishi, M. *J. Am. Chem. Soc.* **1996**, *118*, 2527.
3) Cai, M., Xu, K., Jia, H., Zhang, L., Mi, X.; Luo., S. *ACS Catal*. **2023**, *13*, 7538.

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金ナノ粒子プローブを用いた標的タンパク質ラベリングシステムの開発

（農工大院工 [1]）○鴨下 潮音 [1]・櫻井 香里 [1]

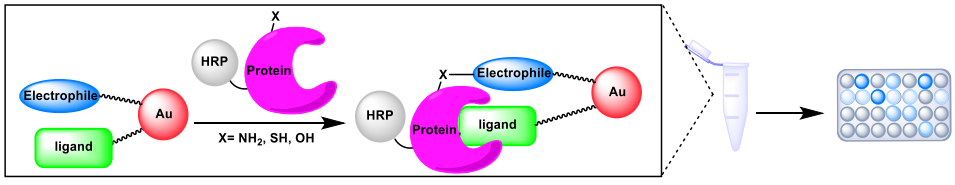
Development of target protein labeling system using gold-nanoparticle probes ([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*)

○Shione Kamoshita,[1] Kaori Sakurai[1]

Designing optimal probes for affinity labeling is critical yet is a significant challenge for exploring unknown target proteins. We have developed gold-nanoparticle probes co-functionalized with ligands and electrophilic groups, which led to the identification of aryl sulfonylfluoride group as a promising protein labeling group.[1, 2] In this study, we aimed to establish a rapid method for quantification of the probe-labeled proteins in order to analyze a wider range of electrophilic groups. Based on our previous studies,[1,2] we synthesized gold-nanoparticle probes bearing lactose as a model ligand, and each of nine different electrophilic groups. Model binding proteins labeled with horse radish peroxidase (HRP) were used for the proof of principle studies. Affinity labeling was performed using a probe and then the probe-labeled proteins were separated by centrifugation. The resulting probe containing fractions were transferred to 96-well plates and the labeled proteins were quantified by an HRP assay. This method was used to evaluate the reaction efficiency of the affinity labeling with 9 different probes under different reaction conditions. *Keywords : carbohydrate ligands; target identification; gold nanoparticle; affinity labeling; electrophilic groups*

【背景・目的】アフィニティーラベリングによる未知標的タンパク質探索において、ラベル化効率の最適化に向けたプローブの設計が課題である。当研究室ではこれまでに、リガンドと求電子基を多数・高密度に修飾した金ナノ粒子プローブを開発し、aryl sulfonylfluoride 基を有望なラベル基として見出した [1,2]。本研究は、さらに広範な種類の求電子基を探索すべく、ラベル化タンパク質の簡便な定量方法の確立を目的とした。

【方法・結果】先行研究に基づいて [1,2]、モデル系リガンドである lactose と、9 種類の異なる求電子基を共修飾した金ナノ粒子プローブを合成した。まず原理証明を行うため、モデル系結合タンパク質として horse radish peroxidase(HRP)標識タンパク質を用いた。各プローブによるアフィニティーラベリングを行い、プローブでラベル化されたタンパク質を遠心分離した。得られたプローブ画分を 96 ウェルプレートへ移し、HRP アッセイによりラベル化タンパク質を定量した。本方法により、9 種類のプローブにおける種々の反応条件下でのアフィニティーラベリングの反応効率を評価した。



1) N. Suto, S. Kamoshita, S. Hosoya, K. Sakurai, *Angew. Chem. Int. Ed*. **2021**, *133*, 2-10.
2) S. Kamoshita, S. Matsui, N. Suto, K. Sakurai, *ChemBioChem*. **2021**, e202100388.

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC H933(933, Bldg. 9 [3F])

[H933-4pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Minami Odagi, Yoshio Ando

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H933-4pm-01]
Synthetic study of Zetekitoxin AB

○Kako Maeno[1], Ayato Nureki[1], Hayate Ishizuka[1], Kanna Adachi[1], Minami Odagi[1], Kazuo Nagasawa[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H933-4pm-02]
Synthetic studies of neosaxitoxin focusing on cyclic hydroxy guanidine.

○Shuya Shinkawa[1], Toma Osawa[1], Kako Maeno[1], Minami Odagi[1], Kazuo Nagasawa[1] (1. Graduate School of Engineering, Tokyo University of Agriculture and Technology)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H933-4pm-03]
Synthetic studies on the C ring spiroguanidine of the trisguanidine alkaloid KB343

○Toma Osawa[1], Daiki Watanabe[2], Minami Odagi[1], Kazuo Nagasawa[1] (1. Tokyo university of Agriculture and Technology, 2. Tokyo university of Science)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H933-4pm-04]
Synthetic studies of Serratezomine A based on oxidative dearomatization

○Rintaro Hayakawa[1], Kengo Takibuchi[1], Taisei Matoba[1], Minami Odagi[1], Kazuo Nagasawa[1] (1. Tokyo University Agriculture and Technology)

English
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H933-4pm-05]
Design, Synthesis, and Chiroptical Properties of Mid-sized Molecules Utilizing C_2 Symmetric Alkaloidal Scaffolds

○Fumi Oki[1], Tasuku Honda[1], Hiroki Oguri[1] (1. The Univ. of Tokyo)

1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
Break

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[H933-4pm-06]
Synthetic Study on Glenthamine A: Construction of the Bicyclic Skeleton

○Sota Ajima[1], Yoshio Ando[1], Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H933-4pm-07]
Efficient synthesis of abiesanol A, C_2-symmetric flavan dimer

○Nayuta Sonoda[1], Yusuke Kawada, Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[H933-4pm-08]
Continuous flow synthesis of flavan trimers

○Naoki Narita[1], Keisuke Suzuki[1], Ken Ohmori[1] (1. Tokyo Institute of Technology)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H933-4pm-09]
Au-Catalyzed Intramolecular Hydroamination of Alkynic Benzamides for the Synthesis of Pyrrolidine Derivatives

○Hayato Nakagawa[1], Akane Yamaji[1], Haruhiko Fuwa[1] (1. Chuo University)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H933-4pm-10]
Concise Total Synthesis of Fasicularin

○Yuki Takatori[1], Haruhiko Fuwa[1] (1. Chuo University)

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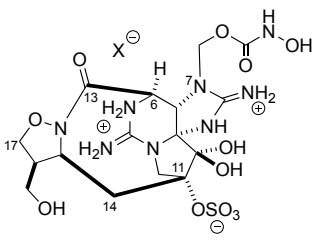
Zetekitoxin AB の合成研究

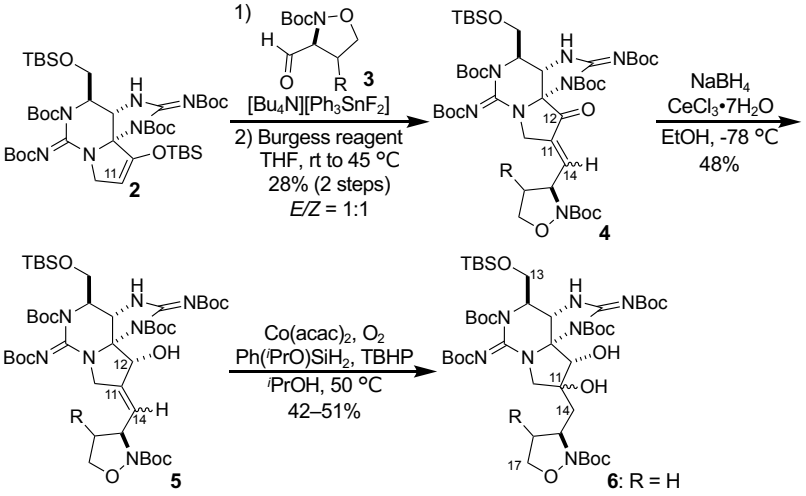
（東農工大院工）・○前野華子・濡木絢斗・石塚 颯・安達栞菜・小田木 陽・長澤和夫
Synthetic study of Zetekitoxin AB (*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Kako Maeno, Ayato Nureki, Hayate Ishizuka, Kanna Adachi, Minami Odagi, Kazuo Nagasawa

ZetekitoxinAB (ZTX; **1**) is a guanidine alkaloid isolated from a dart-poison frog, shows extremely potent voltage-gated sodium channels (Na_V) inhibitory activity. ZTX has a characteristic structure of macrolactam involving an isoxazolidine moiety at C6 to C11 and the tertiary hydroxyl group at C11. In this study, the construction of C11 moiety of ZTX was examined by Mukaiyama-type aldol reaction of silylenol ether **2** with aldehyde **3** in the presence of $[Bu_4N][Ph_3SnF_2]$. After the reduction of the ketone in **4**, the resulting allyl alcohol **5** was subjected under the Mukaiyama hydroxylation conditions to give tertiary alcohol **6**.
Keywords : zetekitoxin AB ; saxitoxin ; guanidine alkaloid ; voltage-gated sodium channel

【目的】 Zetekitoxin AB (ZTX; **1**) はパナマ産ヤドクガエルより単離されたグアニジンアルカロイドであり、強力な電位依存性ナトリウムチャネル (Na_V) 阻害活性を有する。ZTX (**1**) は C6 位から C11 位にかけてイソキサゾリジン環を含む特徴的な大環状ラクタム構造と、C11 位に第三級アルコール構造を有しており、これらの立体選択的な構築が合成上の課題である。本研究では向山型アルドール反応とつづく位置選択的な水和反応を用いた C11 位の第三級アルコール構造の合成を検討した。


Structure of ZTX (**1**)

【実験・結果】シリルエノールエーテル **2** に対し、$[Bu_4N][Ph_3SnF_2]$存在下、アルデヒド **3** を用いて向山型アルドール反応[1]を行ったのち、Burgess 試薬を 45 °C にて作用させたところ脱水反応が進行し、エノン **4** が得られた (*E*/*Z*=1:1)。**4** の C12 位カルボニル基を Luche 還元によりアリルアルコール **5** としたのち、酸素雰囲気下で Co 触媒および Ph(^{i}PrO)SiH_2[2]を作用させたところ、C11 位に位置選択的にヒドロキシル基を導入することができ、**6** をジアステレオマー混合物（1:1）として得た。



【参考文献】1) Wang C. *et al., Angew. Chem. Int. Ed.* **2016**, *55*, 11600-11603; 2) Ryan A. Shenvi, *et al., J. Am. Chem. Soc*. **2016**, *138*, 4962-4971

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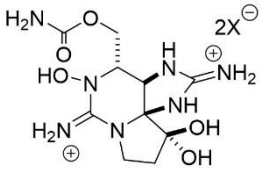
neoSTX の合成を志向した環状ヒドロキシグアニジン構造の合成研究

（東農工大院工）○新川 集也・大澤 瞳生・前野 華子・小田木 陽・長澤 和夫

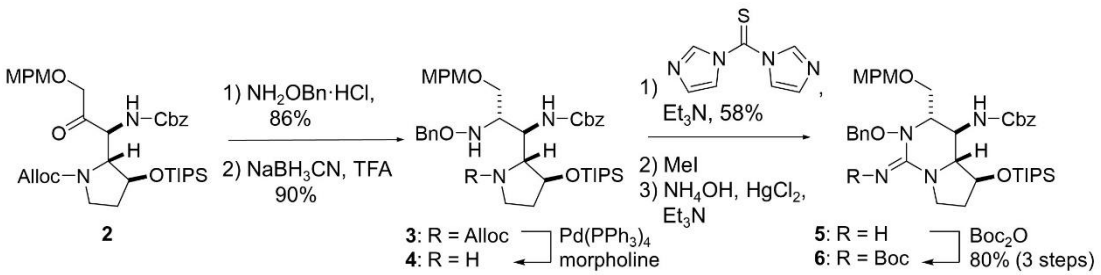
Synthetic studies of neosaxitoxin focusing on cyclic hydroxy guanidine (*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Shuya Shinkawa, Toma Osawa, Kako Maeno, Minami Odagi, Kazuo Nagasawa

Neosaxitoxin (neoSTX; **1**) is a natural analog of the shellfish toxin of saxitoxin (STX), which shows potent voltage-gated sodium channels (Na_V) inhibitory activity. NeoSTX has a characteristic structure of *N*-hydroxy cyclic guanidine. In this study, we investigated the synthesis of this unique structure in neoSTX. A ketone **2** derived from L-malic acid was subjected to reductive amination with *O*-benzylhydroxy amine to give hydroxylamine **3** as a single diastereomer in 90% yield. After removal of the Alloc group, cyclization with TCDI and subsequent guanylation was carried out to give *N*-hydroxy cyclic guanidine **6** in 80% yield.
Keywords : neosaxitosin; saxitoxin; guanidine alkaloid; voltage-gated sodium channels

【目的】ネオサキシトキシン（neoSTX; **1**）は、電位依存性ナトリャウムチャネル（Na_VCh）を阻害する貝毒サキシトキシン（STX）の類縁体である[1]。**1** は、STX の N1 位が水酸基化された環状ヒドロキシグアニジン構造を有している。本研究では当該構造の合成法の開発を目的に以下検討した。


Structure of neoSTX (**1**)

【実験・結果】L-リンゴ酸より合成したケトン **2**[2]に対し、ベンジルヒドロキシアミンを用いた立体選択的な還元的アミノ化反応を行うことでヒドロキシアミン **3** を収率 90 %で得た。次に **3** より環状ヒドロキシグアニジン構造の合成を検討した。**3** に対し Alloc 基を除去後、1, 1' -チオカルボニルジイミダゾール（TCDI）を作用させることで、環状チオウレアを収率 58%で得、ついでチオウレア基を Me 化し、NH_4OH, $HgCl_2$ を作用させることで、目的とする環状ヒドロキシグアニジンを有する **6** を収率 80% (3 工程) で得ることができた。現在、**6** より neoSTX (**1**)の合成を検討している。



【参考文献】

1) Y. Oshima, *et al., Comp. Biochem. Physiol*. **1977**, *57C*, 31-34; 2) K. Nagasawa, *et al., Asian. J.* **2009**, *4*, 277-285.

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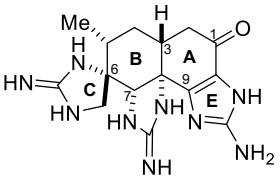
トリスグアニジンアルカロイド KB343 の C 環部スピログアニジンの合成研究

（東農工大院工[1]・東理大理[2]）○大澤 瞳生[1]・渡邉 大輝[2]・小田木 陽[1]・長澤 和夫[1]
Synthetic studies on the C ring spiroguanidine of the trisguanidine alkaloid KB343
([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Faculty of Science*, *Tokyo University of Science*) ○Toma Osawa,[1] Daiki Watanabe,[2] Minami Odagi,[1] Kazuo Nagasawa[1]

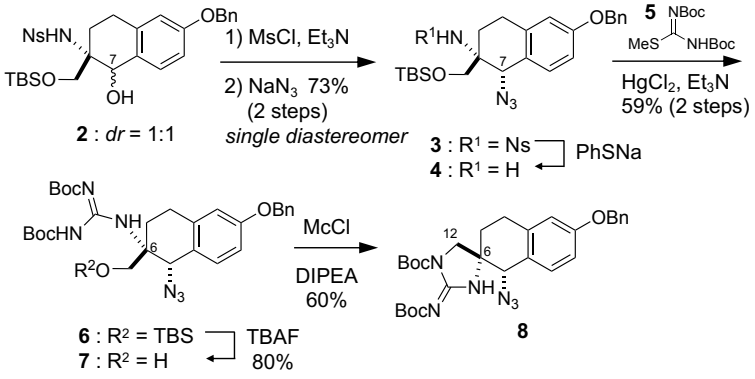
A trisguanidine alkaloid of KB343 (**1**) was isolated from a *Palauan zoantharian* by Sakai and co-workers in 2018. In this study, we examined the construction of the spiroguanidine corresponding to the C-ring of **1**. Stereoselective introductions of an azide group at C7 and a guanidine group at C6 were carried out to give **6**. Subsequently, spiroguanidine **8** was synthesized by intramolecular cyclization of **6** with McCl and DIPEA.
Keywords : KB343; guanidine alkaloid; spiroguanidine; oxidative azidation

【目的】KB343 (**1**) は、2018 年に酒井らによりパラオ産スナギンチャクより単離されたトリスグアニジンアルカロイドである[1]。**1** は *trans*-デカリン骨格上 (AB 環) に異なる三種のグアニジン環 (CDE 環) を有する。本研究では **1** の C 環部に相当するスピログアニジン環の合成について検討を行った。



KB343 (**1**)

【実験・結果】6-ヒドロキシ-1-テトラロンから数工程を経て、C7 位に水酸基を有する **2** を C7 位のジアステレオマー混合物として得た。**2** の水酸基のメシル化を経て、アジド化を行ったところ **1** と同一の立体配置を有するアジド **3** が単一のジアステレオマーで得られた。ついで **3** より C 環部スピログアニジンの構築について検討した。**3** の Ns 基を除去し、生じたアミン **4** に対し $HgCl_2$ 存在下、**5** を用いグアニジノ化を行い、収率 59%でグアニジン **6** を得た (2 工程) 。ついで、TBS 基を除去後、McCl、DIPEA を用いた分子内環化反応[2]を行ったところ、目的とするスピログアニジン **8** が収率 60%で得られた。



2 : *dr* = 1:1
3 : R^1 = Ns
4 : R^1 = H
6 : R^2 = TBS
7 : R^2 = H
8

【参考文献】 1) R. Sakai, *et al., Org. Lett.* **2018**, *20*, 3039; 2) K. Nagasawa, *et al*., *Chem. Asian J*. **2009**, *4*, 277.

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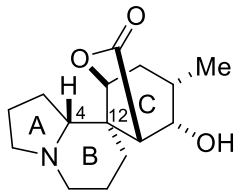
酸化的脱芳香族化反応を基盤とした Serratezomine A の合成研究

（東農工大院工） ○早川 凜太朗・滝渕 健吾・的羽 泰世・小田木 陽・長澤 和夫
Synthetic studies of serratezomine A based on oxidative dearomatization (Tokyo University of Agriculture and Technology) ○Rintaro Hayakawa, Kengo Takibuchi, Taisei Matoba, Minami Odagi, Kazuo Nagasawa

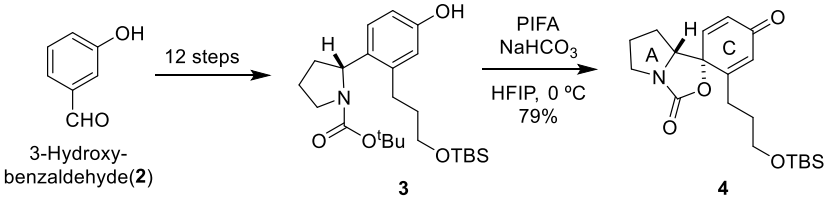
Serratezomine A (**1**) is a lycopodium alkaloid isolated from *Lycopodium serratum* var. *serratum* by Kobayashi *et al*. in 2000. **1** has a highly fused ring structure consisting of an azabicyclo[4.3.0]nonane (AB ring) and a aza-spiro ring (BC ring) including six chiral carbons. Construction of the vicinal stereogenic centers at C4 and C12 embedded in the fused core structure is a challenging issue for the synthesis of **1**. In this study, we investigated the diastereoselective construction of the highly functionalized C ring of **1** by oxidative dearomatization reactions of phenol **3** which derived from 3-hydroxybenzaldehyde (**2**). After several investigations, we found that the desired dienone **4** was diastereoselectively obtained from **3** in 79% yield by treatment with [bis(trifluoroacetoxy)iodo]benzene (PIFA) and sodium bicarbonate ($NaHCO_3$) in hexafluoro-2-propanol (HFIP) through a simultaneous oxidative dearomatization reaction with the elimination of the *tert*-Bu group.
Keywords : serratezomine A; lycopodium alkaloid; hypervalent iodine; oxidative dearomatization reactions



Serratezomine A (**1**)

【目的】Serratezomine A (**1**)は、2000 年に小林らによって *Lycopodium serratum* var. *serratum* より単離されたリコポジウムアルカロイドの一種である。**1** は、6 つの不斉炭素を含むアザビシクロ[4.3.0]ノナン (AB 環)とアザ-スピロ環 (BC 環)で構成された高度に縮環した構造を有する。**1** の合成では、上述の特徴的な環構造に含まれる C4 位および C12 位の二連続不斉炭素の効率的な構築が課題となる。本研究では、**1** の高度に官能基化された C 環部についてフェノール誘導体に対する酸化的脱芳香族化反応によるジアステレオ選択的な構築について検討した。

【実験・結果】3-Hydroxybenzaldehyde (**2**)より 12 工程で合成したフェノール誘導体 **3** に対し、ヘキサフルオロ-2-プロパノール (HFIP)中、ビストリフルオロアセトキシヨードベンゼン (PIFA)および炭酸水素ナトリウムを反応させたところ、*tert*-Bu 基の脱保護と同時に、酸化的脱芳香族化反応が進行し、ジエノン **4** がジアステレオ選択的に得られた。



3-Hydroxy-benzaldehyde(**2**)　**3**　**4**

【参考文献】Kobayashi, J. *et al*. *J. Org. Chem*. **2000**, 65, 6241-6245.

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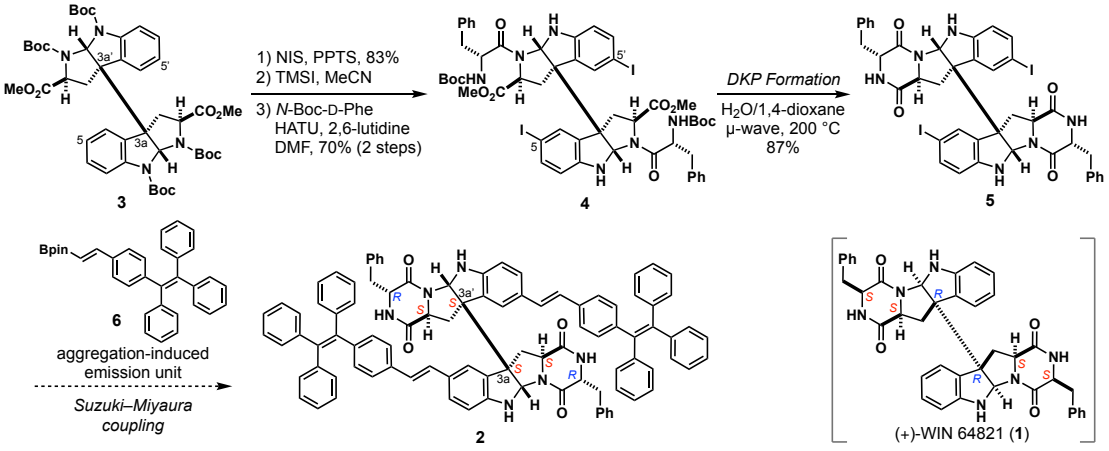
Design, Synthesis, and Chiroptical Properties of Mid-sized Molecules Utilizing C_2-Symmetric Alkaloidal Scaffolds

([1]*School of Science, The University of Tokyo*, [2]*Graduate School of Science, The University of Tokyo*) ○Fumi Oki,[1] Tasuku Honda,[2] Hiroki Oguri[2]

Keywords: Indole Alkaloids; Bispyrrolidinoindoline; Diketopiperazine; Circularly Polarized Luminescence; C_2 symmetric molecules

Bispyrrolidinoindoline diketopiperazine (BPI-DKP) alkaloids, represented by (+)-WIN64821 (**1**), have chiral C_2-symmetric dimeric structures with a rotatable 3a/3a' bond. Our group utilized the BPI unit as a preorganized chiral scaffold to efficiently assemble figure-eight-shaped macrocycles that exhibit strong circularly polarized luminescence (CPL).[1] These previous explorations indicated that strategic alterations in stereochemistry and structural modifications of the BPI scaffold could control the conformational dynamics and chiroptical properties.[1,2] In this study, we designed a series of stereochemically diverse chiral C_2-symmetric BPI-DKP alkaloidal scaffolds such as **2** bearing aggregation-induced emission (AIE) units. This study aims to develop the aggregation-induced CPL molecules through stereochemical control of both the three dimensional and conformational properties of the BPI-DKP scaffold.

The C_2-symmetric BPI scaffold **3** was synthesized in 5 steps from L-Trp.[1,2] Site-selective iodination at the 5/5' positions, followed by removal of Boc groups and condensation with *N*-Boc-D-Phe afforded **4**. Microwave-assisted cyclization in H_2O/1,4-dioxane gave the BPI-DKP scaffold **5** in 87% yield. Suzuki–Miyaura coupling of **5** with AIE unit **6** would produce the targeted chiral C_2-symmetric compound **2**. The conformational properties, chiroptical properties, and supramolecular assembly of **2** and its diastereomers will be presented.



1) Honda, T.; Ogata, D.; Tsurui, M.; Yoshida, S.; Sato, S.; Muraoka, T.; Kitagawa, Y.; Hasegawa, Y.; Yuasa, J.; Oguri, H. *Angew. Chem. Int. Ed.* **2024**, e202318548.
2) Taniguchi, T.; Tsubouchi, A.; Imai, Y.; Yuasa, J.; Oguri, H. *J. Org. Chem.* **2018**, *83*, 15284.

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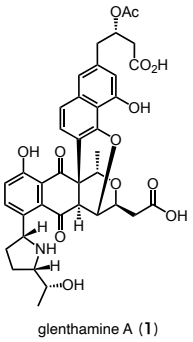
グレンタミンAの合成研究：ビシクロ骨格構築法の開発

（東工大理）○安島蒼太・安藤吉勇・鈴木啓介・大森 建
Synthetic Study on Glenthamine A: Construction of the Bicyclic Skeleton (*Tokyo Institute of Technology*) ○Sota Ajima, Yoshio Ando, Keisuke Suzuki, Ken Ohmori

Glenthamine A (**1**), isolated from the actinomycete, is a pyranonaphthoquinone-class natural product, sharing a unique bicyclic skeleton bridged by naphthol unit and a *C*-linked pyrrolidine unit. Toward the total synthesis of **1**, we studied construction of the bicyclic skeleton.

First, we developed the synthetic route to nanaomycin A (**2**), which is a core unit of **1**. The tricyclic skeleton was constructed by Hauser annulation with phthalide **3** and lactone **4**, and the methyl group was introduced on the pyran ring in high diastereoselective manner to afford **6**. Further manipulation of **6** led to **2**. Next, oxidative lactonization of **2** gave nanaomycin D (**8**). Furthermore, treatment of **8** with naphthol **9** successfully provided bicyclic compound **10**.

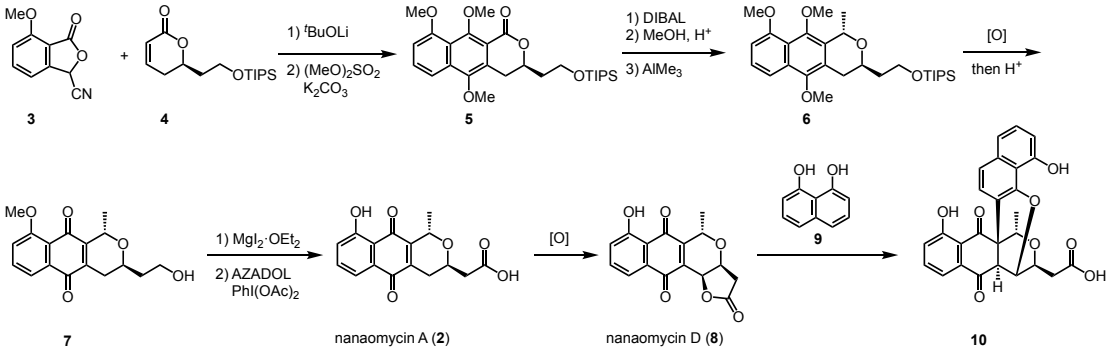
Keywords : natural product synthesis; glenthamine A; pyranonaphthoquinone; bicyclic skeleton



glenthamine A (**1**)

グレンタミン A (**1**) は、放線菌より単離・構造決定されたピラノナフトキノン系天然物であり、抗腫瘍性を示す。本化合物は、ピラノナフトキノンにナフトール単位が架橋したビシクロ骨格に加えてピロリジン単位が連結したユニークな構造を有しており、合成化学上非常に興味深い。我々は、**1** の全合成を目指し、ビシクロ骨格構築法の開発研究を行った。

本反応の開発に先立ち、まず基本単位となるナナオマイシン A (**2**) の合成経路を確立した。すなわち、フタリド **3** とラクトン **4** から三環性構造を合成した後、数工程の変換によりメチル基を立体選択的に導入し、**6** を得た。続くナフタレン環の酸化、脱メチルおよび側鎖アルコールの酸化を順次行うことにより **2** を得た。続いて、鍵となるビシクロ骨格の形成を検討した。**2** を酸化的ラクトン化によりナナオマイシン D (**8**) へと変換した後、ナフトール **9** とのモデル反応を検討した結果、収率よくビシクロ体 **10** を得る反応条件を見出した。



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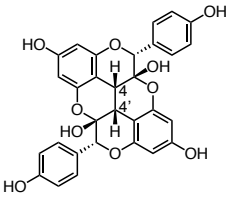
C_2 対称型フラバン二量体アビイサノール A の効率的合成

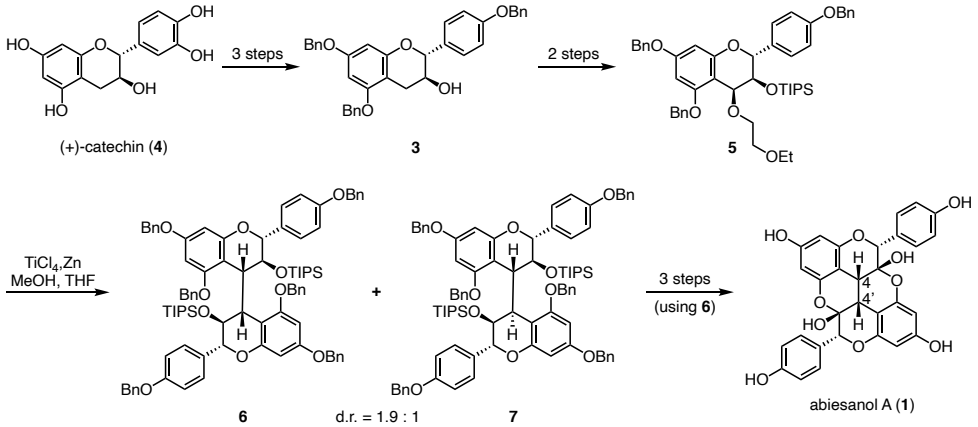
（東工大理）○園田 名佑太・川田裕介・鈴木啓介・大森 建
Efficient synthesis of abiesanol A, C_2-symmetric flavan dimer (*Department of Chemistry, Tokyo Institute of Technology*) ○Nayuta Sonoda, Yusuke Kawada, Keisuke Suzuki, Ken Ohmori

Abiesanol A, isolated from *Abies george*, is a dimeric flavan, sharing two afzelechin units in a unique C_2-symmetric hexacyclic core. The key for the total synthesis is the development of an efficient dimerization reaction, constructing the unique C4-C4' bond. In this study, we suceeded the concise synthesis of an afzelechin derivative and improved the diastereo-selectivity of dimerization reaction. Details will be discussed in this paper.
Keywords : afzelechin; flavan; C_2-symmetry; dimerization

アビイサノール A (**1**)はマツの木の一種 *Abies george* から単離構造決定されたポリフェノールの一種で、特徴的な C_2 対称型の六環式骨格を有する。本化合物は、フラバンの一種である(+)-アフゼレキン(**2**)がそれぞれの C4 位で結合した二量体である。全合成においては、この結合の効率的な形成が鍵となる。当研究室では、これまでに低原子価チタン種（$TiCl_4$ / Zn）による還元的な二量化反応を用い **1** の合成に成功しているが、二量化における立体選択性について課題を残していた。



今回我々は、アフゼレキン誘導体 **3** の簡便な合成法の開発、および二量化の際の立体選択性の改善を行ったので報告する。まず入手容易な(+)-カテキン (**4**)から選択的なトリフリル基の導入と Pd 触媒による還元を経て 3 段階で **3** の合成をすることに成功した。ついで 4 位にオキシ基を導入し、3 位の水酸基をトリイソプロピルシリル基で保護し、二量化前駆体 **5** を合成した。これに対し、低原子価チタン種（$TiCl_4$ / Zn）を作用させると、1.9 : 1 のジアステレオマー比で目的の二量化体 **6** が優先して得られた。



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自己縮合反応を経由したフラバン三量体の連続フロー合成

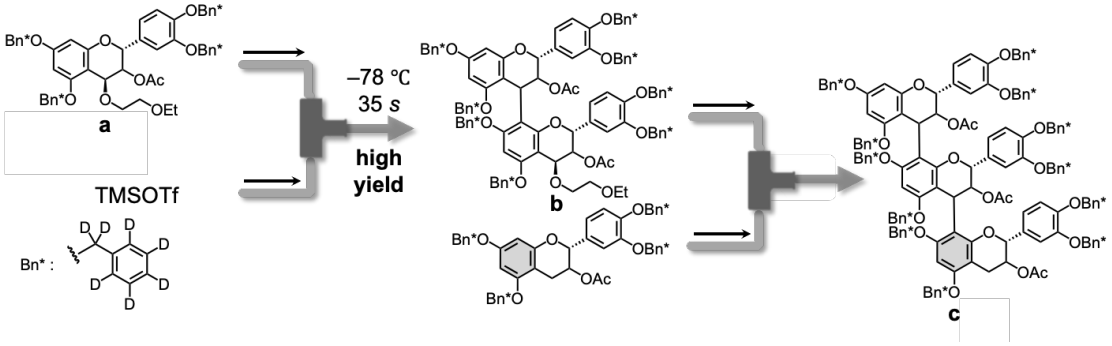
（東工大理）○成田直生・鈴木啓介・大森　建
Continuous flow synthesis of flavan trimers (*Department of Science, Tokyo Institute of Technology*) ○Naoki Narita, Keisuke Suzuki, Ken Ohmori

Flavan oligomers are widely comprised in plant kingdom and possess various biological properties. To assemble flavan oligomers, excess amount of nucleophilic flavan units are generally needed due to suppression of the undesirable over reactions between electrophilic units and products. Self-condensation reaction of electrophilic flavan units is also one of the useful method to assemble flavan oligomers. However, this reaction remains challenging in terms of the yield and controlling oligomerization.

To hance the generality and efficiency of the self-condensation reaction, the reaction conditions were investigated using microflow reactor, which was employed for the efficient mixing between electrophilic flavan unit and lewis acid and rapid quenching. After several optimization, the yield of self-condensed dimer **b** was successfully improved. Additionally, the direct formation of flavan trimer **c** was attempted by the continuous flow method with combining nucleophilic flavan monomer to the self-condensed product.
Keywords : Polyphenol; Flavonoid; Oligomer; Continuous Flow Synthesis

フラバンオリゴマーは植物中に多く含まれ、抗菌活性や増殖阻害活性、抗発癌作用など、多様な生理活性を有している。このようなオリゴマーの合成においては、モノマー同士の過剰反応を抑えるために、通常求電子成分に対して大過剰の求核成分を用いる必要がある。一方フラバンモノマーの自己縮合反応では、求核成分を用いずにオリゴマー合成が可能であるが、高次のオリゴマーが副生し、収率が中程度に留まるところに課題がある。

今回我々は、先に報告したフローマイクロリアクターを用いる求電子フラバン単位 **a** の自己縮合反応の合成効率向上を試みた。その結果、目的とする二量体 **b** を高い収率で得ることに成功した。さらに、自己縮合反応に続いて求核フラバン単位を連続的に反応させることにより、対応するフラバン三量体 **c** を一挙に得ることができた。発表では、その詳細について報告する。



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金錯体を用いたアルキンベンズアミドの分子内ヒドロアミノ化によるピロリジン合成

（中央大理工 [1]）○中川 颯人 [1]・山路 茜音 [1]・不破 春彦 [1]
Au-Catalyzed Intramolecular Hydroamination of Alkynic Benzamides for the Synthesis of Pyrrolidine Derivatives ([1]*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○Hayato Nakagawa,[1] Akana Yamaji,[1] Haruhiko Fuwa[1]

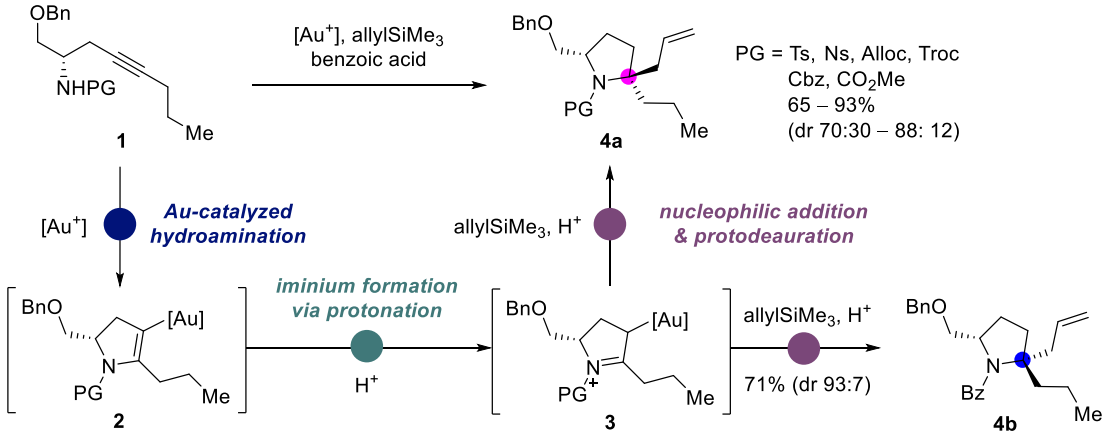
Previously, we showed that a Au-catalyzed intramolecular hydroamination of alkynes **1** and subsequent in situ iminium ion formation/allylation enabled the synthesis of 2,2,5-trisubstituted pyrrolidine derivative **4a** in an efficient and diastereoselective fashion.[1] Actually, the reaction tolerated a variety of substituents and nitrogen protecting groups and provided pyrrolidine derivatives **4a** in good to excellent yields.

In this work, we found that the diastereoselectivity of the allylation can be switched by choosing an appropriate protecting group for the amine nitrogen.[2] Thus, 2,2,5-*trans*-trisubstituted pyrrolidines **4a** were obtained from amino alkyne **1** with a sulfonamide or carbamate group, whereas 2,2,5-*cis*-trisubstituted pyrrolidines **4b** were derived from **1** with a benzoyl group.

Keywords: pyrrolidine derivatives; tandem reaction; Au catalysis; allylation; alkaloids

我々はこれまでに Au(I)錯体を用いたアルキン **1** の分子内ヒドロアミノ化とエナミド **2** のプロトン移動によるイミニウムイオン形成、続くイミニウムイオン **3** のアリル化によるタンデム反応を効率的かつ立体選択的なピロリジン骨格構築法として報告した [1]。本反応は様々な保護基や置換基を許容し、目的物を高収率で与えた。

本研究では、アミノ基の保護基によって、本反応のジアステレオ選択性が逆転する現象を見出した [2]。すなわち、スルホンアミドあるいはカルバメート系保護基を有する環化前駆体 **1** からは 2,2,5-*trans*-ピロリジン誘導体 **4a** が得られ、ベンズアミドを前駆体に用いると 2,2,5-*cis*-ピロリジン誘導体 **4b** が得られた。本発表では、**4b** について基質適用範囲も含めて検討を行ったため、その詳細について報告する。



1) A. Yoshimura, R. Hanzawa, H. Fuwa, *Org. Lett.* **2022**, *24*, 6237.
2) H. Nakagawa, H. Fuwa, *Chem. Commun.* **2023**, *59*, 10121.

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ファシクラリンの短工程全合成

（中大理工）○高取祐希・不破春彦
Concise Total Synthesis of Fasicularin (*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○Yuki Takatori, Haruhiko Fuwa

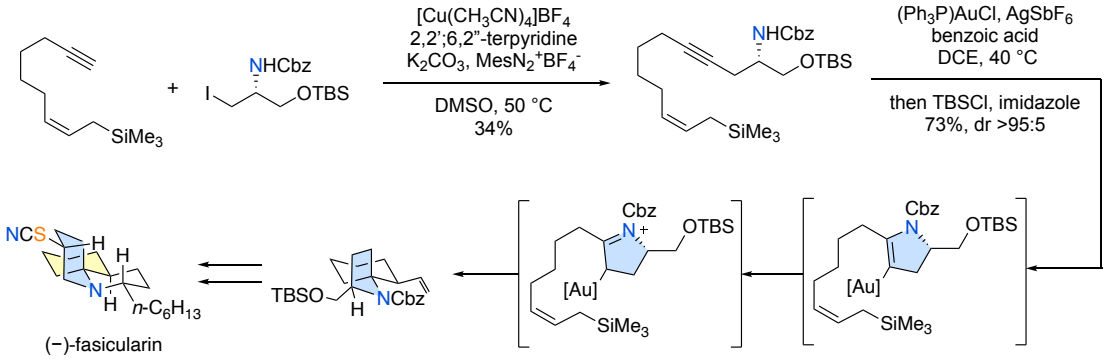
Marine tricyclic alkaloids, lepadiformines, cylindricines, and fasicularin, have been a source of inspiration for chemists to develop new synthetic methods and strategies owing to their unique structure including an azaspirocyclic framework. Fasicularin was isolated by Patil *et al*. from the Micronesian ascidian *Neptheis fasicularis* in 1997.[1] This natural product exhibits cytotoxic activity against Vero cells and induces DNA damage.[2]

In this work, we achieved a concise total synthesis of (−)-fasicularin by means of a Cu-catalyzed aryl radical-mediated coupling[3] of an alkyl iodide and a terminal alkyne and subsequent Au-catalyzed tandem azaspirocyclization of the derived amino alkyne.[4]

Keywords : tricyclic marine alkaloids; tandem reaction; radical reaction; azaspirocycles

レパジホルミン類やシリンドリシン類、ファシクラリンといった海洋三環性アルカロイドはユニークなアザスピロ骨格を有し、多くの化学者はこれら天然物をターゲットとして新しい合成法や合成戦略を開発してきた。ファシクラリンは 1997 年に Patil らによってミクロネシア沖で採取されたホヤ *Neptheis fasicularis* から単離された天然物で、Vero 細胞への細胞毒性や DNA 損傷活性を示すことが報告されている。

我々は銅錯体とアリールジアゾニウム塩を用いた末端アルキンとヨウ化アルキルのラジカルカップリングによりアミノアルキンを得たのち、カチオン性金錯体を用いたタンデム反応によりスピロ環状ピロリジン骨格を高立体選択的に構築することに成功した。本タンデム反応を用いて(−)-ファシクラリンの短工程全合成を達成したので詳細を報告する。



1) A. D. Patil *et al*. *Tetrahedron Lett*. **1997**, *38*, 363.
2) C. Kibayashi *et al. J. Am. Chem. Soc.* **2005**, *127*, 15004.
3) W. Liu *et al*. *ACS Catal*. **2023**, *13*, 2761.
4) A. Yoshimura, R. Hanzawa, H. Fuwa, *Org. Lett.* **2022**, *24*, 6237.

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Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC H935(935, Bldg. 9 [3F])

[H935-4pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Daisuke Takahashi, Kaname Sasaki

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H935-4pm-01]
N-terminal modification of polypeptides via metal-mediated aldol reaction

○Kengo Hanaya[1], Yuki Wada[2], Masaki Kawano[2], Kazuaki Taguchi[1], Kazuaki Matsumoto[1], Shuhei Higashibayashi[1], Takeshi Sugai[1] (1. Keio University, 2. Tokyo Institute of Technology)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H935-4pm-02]
In Vitro Selection of Macrocyclic Peptides Containing α-Hydrazino Acid for Exploration of Drug Candidates

○Satomi Matsumoto[1], Takayuki Katoh[1], Hiroaki Suga[1] (1. The University of Tokyo)

1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
Break

English
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[H935-4pm-03]
Intramolecular Hydrogen-Bonding-Accelerated 2,5-Diketopiperazine Formation for Facile Synthesis of Tag-Attached Peptide Thioester

○Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H935-4pm-04]
Mechanism of phase separation of UGGAA repeat RNA induced by photoswitchable RNA binding ligands

○Yusuke Fujiwara[1,2], Tomonori Shibata[1,2], Chikara Dohno[1,2], Kazuhiko Nakatani[1,2] (1. SANKEN, Osaka University, 2. CREST, JST)

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
Break

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[H935-4pm-05]
Preparation and Immunological Evaluation of Lipid Nanoparticle-based Self-adjuvanting Cancer Vaccine

○Keita Ito[1], Yoshiyuki Manabe[1,2], Shino Oshima[3], Yoshie Kametani[3], Masatoshi Maeki[4], Manabu Tokeshi[4], Koichi Fukase[1,2] (1. Osaka Univ., 2. Forefront Research Center, 3. Tokai Univ.,

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4. Hokkaido Univ.)

English
3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC
[H935-4pm-06]

Chemical synthesis and functional evaluation of acetic acid bacterial lipopolysaccharide partial structures

○Haruki Yamaura[1], Atsushi Shimoyama[1], Koichi Fukase[1] (1. Osaka university)

English
3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC
[H935-4pm-07]

Chemical synthesis of tetraantennary sialyl *N*-glycans

○Kumpei Yano[1], Yoshiyuki Manabe[1,2], Koichi Fukase[1,2] (1. Graduate School of Science, Osaka University, 2. Project Research Center for Fundamental Sciences, Osaka University)

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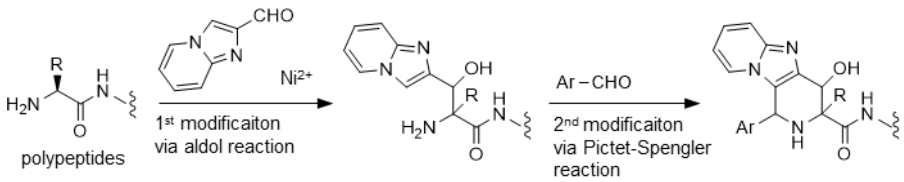
アルドール反応を用いたN末端アミノ酸の化学修飾

(慶大薬[1]・東工大理[2]) ○花屋 賢悟[1]・和田 雄貴[2]・河野 正規[2]・田口 和明[1]・松元 一明[1]・東林 修平[1]・須貝 威[1]
N-terminal modification of polypeptides via metal-mediated aldol reaction ([1]*Faculty of Pharmacy, Keio University*, [2]*Department of Chemistry, Tokyo Institute of Technology*) ○ Kengo Hanaya,[1] Yuki Wada,[2] Masaki Kawano,[2] Kazuaki Taguchi,[1] Kazuaki Matsumoto,[1] Shuhei Higashibayashi,[1] Takeshi Sugai[1]

Bioconjugation reactions have been continuously developed to fulfill the growing demand for applications in both industrial applications and fundamental chemical biology research. Since the most polypeptides possess the N-terminus as a unique reactive site, N-terminal selective modifications can provide modified polypeptides with uniform properties and structures. We present here the N-terminal selective dual modification via nickel(II)-mediated aldol reaction with imidazo[1,2-*a*]pyridine-2-carboxaldehyde at neutral pH and the following Pictet-Spengler reaction with heteroaromatic aldehydes at weakly acidic pH. The methodology allows to attach two artificial molecules such as drugs, fluorophores, and PEG in various combination to a therapeutic antibody consisting of more than 1300 residues as well as short peptides.
Keywords : Polypeptide; Chemical modification; N-terminus; Nickel; Aldol reaction

創薬やケミカルバイオロジーにおいて、ポリペプチドの特定のアミノ酸残基上に薬物や蛍光分子などの人工分子を導入する手法（化学修飾法）の開発が求められている。N末端アミノ酸は一本のポリペプチド鎖につき1箇所存在する。そのため、N末端アミノ酸の化学修飾法は、さまざまなポリペプチドに適用可能であると考えられる。本研究では、含窒素芳香族アルデヒドと金属イオンを組み合わせたアルドール反応を活用することにより、中性緩衝液中で N 末端アミノ酸を選択的に化学修飾する手法を開発した。

8残基のペプチドに対し、pH 7.5の緩衝液中、イミダゾ[1,2-a]ピリジン-2-カルボキシアルデヒド（IMPC）誘導体とニッケルイオンを組み合わせて用いると、それぞれアルドール反応した生成物が得られた。約1300残基からなるIgGに対してもアルドール反応はN末端アミノ酸上で進行した。アルドール反応の生成物に弱酸性条件下、別途アルデヒドを作用させるとPicgtet-Spengler反応が進行し、2種類の人工分子を導入することができた。



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In Vitro Selection of Macrocyclic Peptides Containing α-Hydrazino Acid for Exploration of Drug Candidates

([1]*Graduate School of Science, The University of Tokyo*) ○Satomi Matsumoto,[1] Takayuki Katoh,[1] Hiroaki Suga[1]

Keywords: α-Hydrazino acid; Nonstandard peptide drug

α-Hydrazino acid (α-Hza, **Fig. a**) is a β-amino acid analog with its β-carbon replaced by nitrogen. Introduced into a peptide chain, α-Hza is able to induce a turn structure by forming an intramolecular bifurcated hydrogen bond (**Fig. b**), allowing the peptide to fold into a reinforced hairpin structure[1] (**Fig. c**). Such α-Hza-containing peptide ligands are expected to exhibit excellent properties as drug candidates: improved binding affinity to target proteins, proteolytic resistance, and membrane permeability.

Non-proteinogenic amino acids (npAAs) like α-Hza face challenges in ribosomal peptide synthesis primarily due to the following two reasons: 1) slow accommodation of npAA-tRNA onto the ribosomal A site and 2) slow peptidyl transfer of npAA. However, our group recently achieved successful incorporation of α-Hza into model peptides by taking advantage of an engineered tRNA, $tRNA^{Pro1E2}$, in an *Escherichia coli* reconstituted translation system called the Flexible *In Vitro* Translation (FIT) system[2]. $tRNA^{Pro1E2}$ has optimized T-stem and D-arm motifs for efficient binding to elongation factors EF-Tu and EF-P[3], respectively, to enhance the incorporation of npAAs by accelerating accommodation and peptidyl transfer, respectively[4].

In this research, α-Hza-containing macrocyclic peptide libraries with more than 10^{13} diversities were constructed by optimizing conditions of FIT system. These libraries were then applied to *in vitro* selection by means of RaPID system for exploration of novel peptide drug candidates with rigid structures. Here, human factor XIIa (FXIIa) and Janus kinase 2 (JAK2) were selected as model extra- and intracellular target proteins, respectively. Consequently, α-Hza-containing binder peptides with low-nanomolar K_D values were obtained and showed high inhibitory activity against these targets. In addition, membrane permeability of the JAK2 binder peptides was also confirmed.

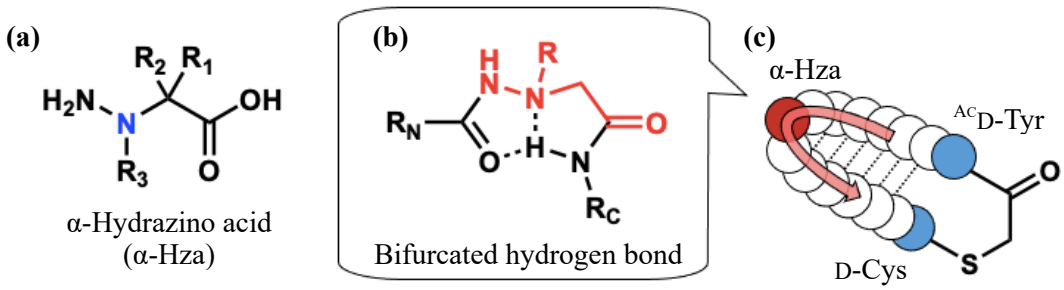

Fig. Construction of α-Hza-containing peptide library with rigid structure.
(a) Structure of α-Hza. α-Nitrogen is shown in blue.
(b, c) α-Hza in peptide chain forms intramolecular bifurcated hydrogen bond **(b)** and folds the peptide into a rigid hairpin structure **(c)**.

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[3] Katoh, T.; Iwane, Y.; Suga, H. *Nucleic Acids Res.* **2017,** *45,* 12601-12610.
[4] Katoh, T.; Suga, H. *J. Am. Chem. Soc.* **2018,** *140,* 12159-12167.

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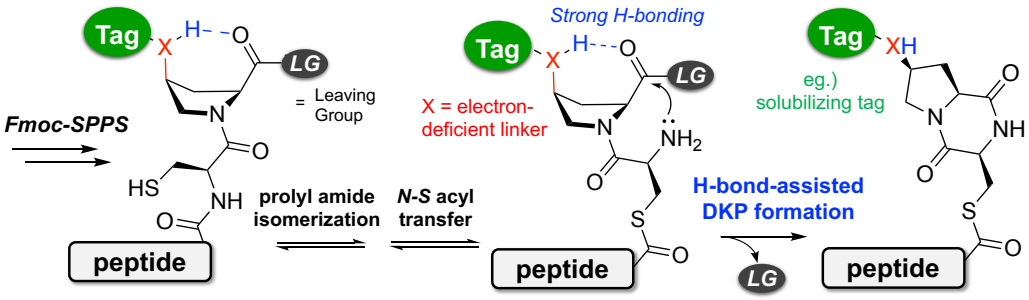
Intramolecular Hydrogen-Bonding-Accelerated 2,5-Diketopiperazine Formation for Facile Synthesis of Tag-Attached Peptide Thioester

(1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.) ○Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2]

Keywords: Proline derivatives; Thioester, Diketopiperazine; Peptide Ligation; Fmoc Solid-Phase Peptide Synthesis

Native chemical ligation (NCL) is a promising strategy to ligate side-chain unprotected peptides between an N-terminal cysteine peptide and a C-terminal peptide thioester in neutral aqueous conditions.[1] To introduce a thioester moiety through Fmoc solid-phase peptide synthesis (SPPS), various thioester surrogates have been designed and reported by peptide chemists. The moiety of cysteinyl-prolyl-leaving group (Cys-Pro-*LG*) is readily introduced to a peptide in Fmoc SPPS and converts into thioester through diketopiperazine (DKP) formation. The effect of leaving group to reaction rate in DKP formation has been explored intensively.[2–4] Proline substitutions at γ-position greatly affect the cis-trans conversion of prolyl amide and puckering of the pyrrolidine ring of proline.[5] We hypothesized that Cγ-modified proline is an effective tool to investigate the nature of DKP formation.

Herein, we demonstrate the use of prolyl 4*S* modifications for Cys-Pro-*LG* to achieve facile synthesis of tag-attached peptide thioester through Fmoc-SPPS. By conducting comparative analyses of 4*S*-NHR and 4*S*-OR substitutions, we have found that modifications bearing a hydrogen donor improve the rate of DKP-thioester formation. In addition, we performed density functional theory (DFT) calculations and indicated that intramolecular hydrogen bonding between 4*S*-substitutions and prolyl carbonyl stabilizes the transition states of DKP formation. Finally, we report chemical protein synthesis using peptide DKP-thioester with a solubilizing tag connected via an optimized linker at the prolyl γ-position.



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光応答性 RNA 結合低分子を用いた UGGAA リピート RNA の相分離体形成の光誘導とメカニズム解析

（阪大産研[1]・JST, CREST[2]）○藤原 侑亮[1,2]・柴田 知範[1,2]・堂野 主税[1,2]・中谷 和彦[1,2]

Mechanism of phase separation of UGGAA repeat RNA induced by photoswitchable RNA binding ligands ([1]*SANKEN, Osaka University*, [2]*CREST, JST*) ○Yusuke Fujiwara,[1,2] Tomonori Shibata,[1,2] Chikara Dohno,[1,2] Kazuhiko Nakatani[1,2]

RNAs containing r(UGGAA) repeat sequences form structures called RNA foci. Although RNA foci have been shown to change their components and localization depending on the surrounding environment, their individual functions are yet to be identified. Therefore, spatiotemporal control of RNA foci formation is needed for understanding their dynamics. We have reported that NCD (Naphthyridine Carbamate Dimer) binds to r(UGGAA) repeats and inhibits RNA foci formation[1)]. In this research, we introduced NCTA, a photoswitchable RNA ligand that binds to r(UGGAA) repeats. UV irradiation enhances NCTA's binding to UGGAA/UGGAA mismatches, while visible light irradiation reduces the affinity. In model cells, NCTA increased the size of r(UGGAA) RNA foci within 1 hour after UV irradiation, which is reversed by subsequent visible light irradiation within the same timeframe. These results indicated that NCTA functions as a "photoswitch" facilitating reversible changes in foci. We will also discuss the mechanisms by which NCTA promotes RNA foci formation.

Keywords : Photoswitch; Nucleic Acid; RNA foci; Phase separation; Repeat RNA

r(UGGAA)反復配列をもつ RNA は、細胞内で RNA foci と呼ばれる相分離体を形成し、転写や翻訳に影響を及ぼす。RNA foci は環境や時間変化に応じてその構成や局在を変化させるが、それらの機能の解明のためには RNA foci の時空間的な形成制御技術が必要である。当研究室ではこれまでに、r(UGGAA)反復配列に結合するリガンド NCD を開発し、NCD が細胞内で RNA foci を阻害することを報告した[1)]。そこで本研究では、2 分子の NCD をアゾベンゼンで繋げた光応答性リガンド NCTA[2)]を用いることで、光刺激による RNA foci の時間選択的な形成制御を目指した。

NCTA は 365 nm (UV) 光および 460 nm (可視) 光照射により、UGGAA/UGGAA 二本鎖に対する結合親和性がそれぞれ活性化、および抑制された。r(UGGAA)反復配列を発現するモデル細胞に NCTA を処理したところ、 UV 照射によって RNA foci の形成が促進され､続く可視光照射によって RNA foci は UV 照射前の状態まで回復した。これらの過程はそれぞれ 1 時間で完了し、NCTA が細胞内 RNA foci 形成の"光スイッチ"として働くことを示している。発表では、NCTA が細胞内 RNA foci 形成を促進するメカニズムについても議論したい。

1) Shibata T. *et al. Nat. Commun.* **2021**, *12*, 236.
2) Dohno C. *et al. Nucl. Acid. Res,* **2023**, *51*, 9533.

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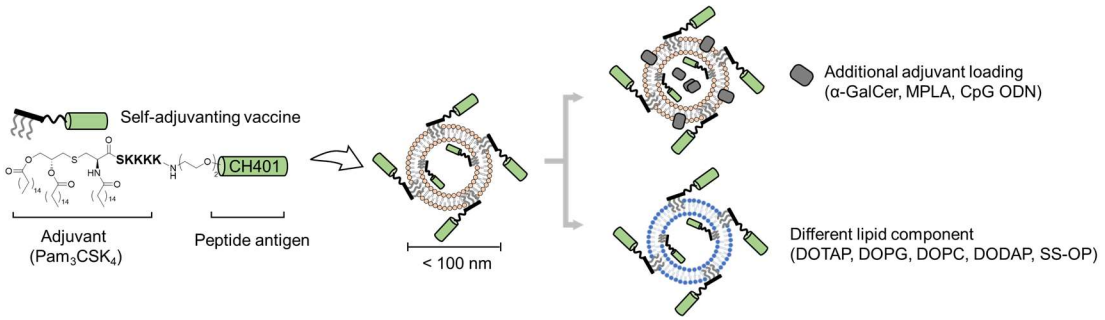
Preparation and Immunological Evaluation of Lipid Nanoparticle-based Self-adjuvanting Cancer Vaccine

([1]*Graduate School of Science, Osaka University*, [2]*Forefront Research Center, Osaka University,* [3]*School of Medicine, Tokai University,* [4]*Faculty of Engineering, Hokkaido University*) ○Keita Ito,[1] Yoshiyuki Manabe,[1,2] Shino Oshima,[3] Yoshie Kametani,[3] Masatoshi Maeki,[4] Manabu Tokeshi,[4] Koichi Fukase[1,2]

Keywords: Peptide vaccine; Adjuvant; Lipid nanoparticle

Cancer vaccine therapy garners a great attention because they expect to prevent recurrence. Especially, peptide vaccines are useful due to the easy preparation as homogeneous materials. However, the practical application of cancer peptide vaccines has been impeded by the low antigenicity of the peptide antigen. To induce robust immune responses, vaccine materials should be smoothly taken up by immune cells. Furthermore, antigen-specific immune responses should be induced to realize high potency without adverse effects. In this study, we developed antigen/adjuvant (immune stimulant)-loaded lipid nanoparticle (LNP) as a novel vaccine material. Formulation of vaccine materials to 100 nm spherical particle is expected to enable their efficient delivery to lymph nodes, and co-loading of antigen and adjuvant is expected to realize antigen-specific immune response.

We prepared the LNP that is loaded the conjugate of CH401 peptide (tumor-associated antigen of breast cancer) with an adjuvant. This LNP-based vaccine was prepared using the iLiNP microfluidic device, which allows precise size control below 100 nm.[1] In addition, to achieve the fine-tuning of immune responses, additional adjuvants were co-loaded to this vaccine material. We further investigated the lipid components of LNPs to enhance the vaccine efficacy. The *in vivo* experiments of these vaccine materials provided a guideline of efficient peptide vaccine development.



1) Kimura, N., Maeki, M., Sato, Y., Note, Y., Ishida, A., Tani, H., Harashima, H., Tokeshi, M., *ACS Omega* **2018**, *3*, 5044.

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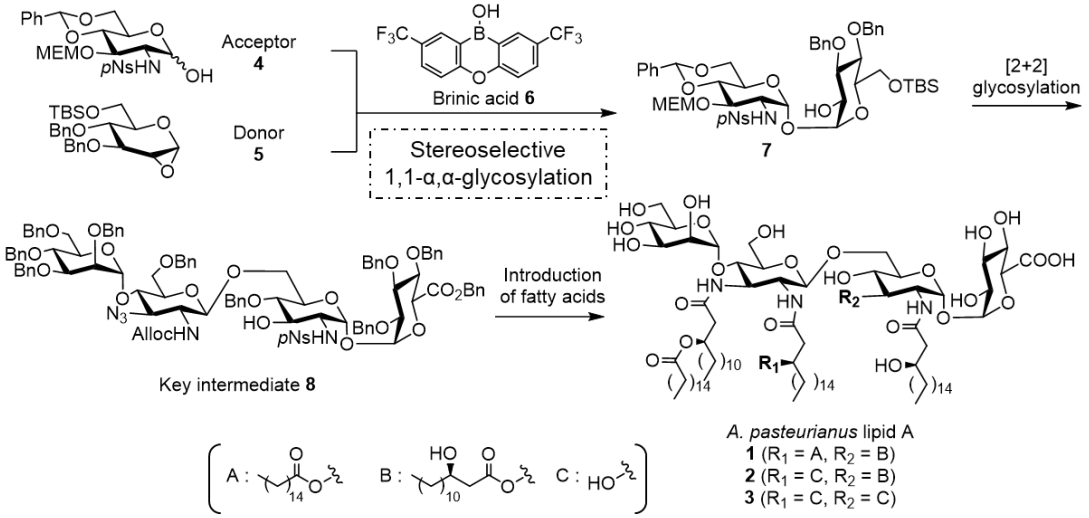
Chemical synthesis and functional evaluation of acetic acid bacterial lipopolysaccharide partial structures

(*Graduate School of Science, Osaka University*) ○Haruki Yamaura, Atsushi Shimoyama, Koichi Fukase

Keywords: innate immunity; lipid A; *Acetobacter pasteurianus*; acetic acid bacteria; kurozu

Lipopolysaccharide (LPS), one of the cell surface components of Gram-negative bacteria, activates innate immunity. *Acetobacter pasteurianus* is a Gram-negative bacterium used for the fermentation process of traditional Japanese black rice vinegar (kurozu). *Acetobacter pasteurianus* LPS, which is a candidate of immunostimulatory component of kurozu, contains lipid A with a distinctive structure[1]. Here, we achieved the first synthesis of three kinds of *A. pasteurianus* lipid A **1**-**3** to identify active principle of *A. pasteurianus* LPS. We investigated the efficient construction of 2-trehalosamin skeleton of **7** and found that 1,2-*cis*-glycosylation using borinic acid **6**[2] between **4** and **5** afforded **7** in high yield and stereoselectivity. We next performed [2+2] glycosylation to synthesize the key intermediate **8** with an orthogonal protecting group pattern. We introduced various fatty acids into appropriate positions of **8**, and removed all protecting groups by catalytic hydrogenolysis to achieve the first chemical synthesis of **1**-**3**. We further identified that the active principles of the immunostimulating activity of *A. pasteurianus* LPS is the lipid As **1-3**, confirming that LPS is an immunostimulatory component of kurozu. Structure-activity relationship studies revealed that the glucuronic acid residue, a characteristic structure of *A. pasteurianus* lipid A, is important for immune function and acid resistance ability.



[1] M. Hashimoto, K. Fukase, Y. Fujimoto, et al., *J. Bio. Chem.*, **2016**, *291*, 21184–21194. [2] Y. Takemoto, et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 14054–14059.

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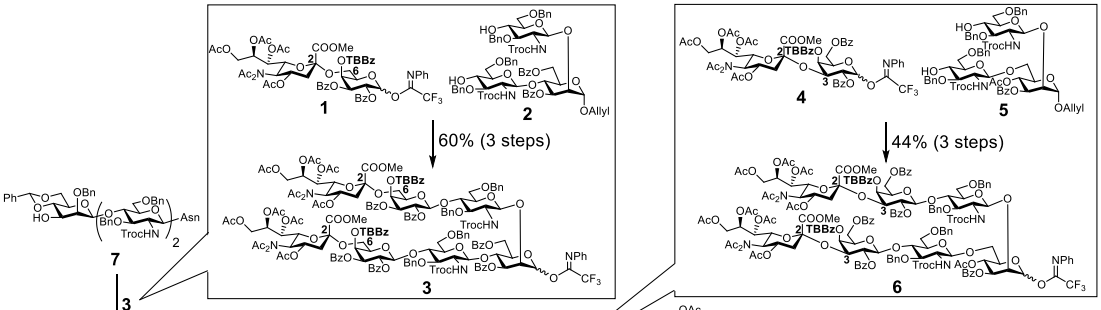
Chemical synthesis of tetraantennary sialyl *N*-glycans

([1]*Graduate School of Science, Osaka University,* [2]*Project Research Center for Fundamental Sciences, Osaka University*) ○Kumpei Yano,[1] Yoshiyuki Manabe,[1,2] Koichi Fukase[1,2]

Keywords: Sialyl *N*-glycan; glycosylation; glovebox; protecting group

Asparagine-linked glycans (*N*-glycans) play important roles in various biological events. For example, sialyl *N*-glycans interact with sialic acid-binding immunoglobulin-like lectins (Siglec) and are involved in regulation of the immune responses.

In this study, we investigated the synthesis of the fully sialylated tetraantennary *N*-glycans. Sialic acid containing fragments tend to form supramolecular aggregates, leading to reduced reactivity in glycosylations. Herein, to access this issue, we employed diacetyl protection of acetamide as well as *p-tert*-butyl benzoyl (TBBz) protection of hydroxy group to enhance the solubility of sialyl fragments.[1] First, heptasaccharides **3** and **6** were synthesized by the glycosylation using TBBz-protected siaα(2,6)gal **1** and siaα(2,3)gal **4**, respectively. The [7+3] glycosylation between **3** and **7** smoothly proceeded at low temperature to give **8** in good yield. After cleavage of benzylidene group, we found that glycosylation between **6** and **9** proceeded using mixed solvent of CH_2Cl_2 and Et_2O to obtain **10** probably due to the stabilization effect of the oxocarbenium ion intermediate by Et_2O.[2] Notably, the glycosylation without MS 4A in glovebox enabled catalytic glycosylation to afford **10** in good yield. We also investigated the synthesis of symmetric tetraantennary *N*-glycans via [7+7+3] glycosylations.



Entry	Catalysis	Temp.	Solvent	Glovebox	Yield
1	TBDPSOTf (0.9 eq)	0 °C	CH_2Cl_2/Et_2O = 1:1	out (with MS 4A)	15%
2	TBDPSOTf (0.1 eq)	rt	CH_2Cl_2/Et_2O = 1:1	in (without MS 4A)	65%

1) Sachi Asano, Hide-Nori Tanaka, Akihiro Imamura, Hideharu Ishida, Hiromune Ando. *Org. Lett.* **2019**, *21*, 4197. 2) Masahiro Nagasaki, Yoshiyuki Manabe, Naoya Minamoto, Katsunori Tanaka, Alba Silipo, Antonio Molinaro, Koichi Fukase. *J. Org. Chem.* **2016**, *81,* 10600.

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

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC H934(934, Bldg. 9 [3F])

[H934-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Kei Nishida, Yuichiro Aiba

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H934-4am-01]
Radical ring-opening reaction of cyclic ketoxime catalyzed by aldoxime dehydratase

○Haruka Nishiwaki[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Graduate School of Engineering, Osaka University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H934-4am-02]
Photo Radical Coupling Reactions between Pyruvate and N-acyloxyphthalimide Catalyzed by FAD/ThDP-Dependent Enzymes

○Yuto Adachi[1], Shuto Fujisawa[1], Kato Shunsuke[1], Hayashi Takashi[1] (1. Osaka university)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H934-4am-03]
Photoinduced Imine Reductions Catalyzed by an Artificial Photoredox Enzyme Constructed by Incorporating an Organic Photosensitizer into a Protein Matrix

○Ryusei Kano[1], Yuki Uchida[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H934-4am-04]
Photoinduced methane oxidation using particulate methane monooxygenase and photosystem II reconstituted in liposome

○Yuta Noto[1], Hidehiro Ito[1], Toshiaki Kamachi[1] (1. Tokyo Institute of Technology)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H934-4am-05]
Structural basis for the substrate inhibition mechanism of the ciliate arginine kinase

○Chihaya Baba[1], Daichi Yano[1], Yumeto Otsuka[1], Yoshino Kojima[1], Koji Uda[1], Tomohiko Suzuki[1], Shigeru Sugiyama[1] (1. kochi university)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H934-4am-06]
Creation of artificial RNA-binding proteins

○Yasuharu Yamabe[1], Kouhei Ukida[1], Kenta Yoshioka[1], Keisuke Nagao[1], Hayata Mouri[1], Tomoaki Mori[1], Koichi Mori[1], Takashi Sera[1] (1. Okayama University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

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[H934-4am-07]

Orthogonal DNA modification of proteins utilizing multiple replication initiator proteins

○Chika Komatsuzaki[1], Kei Nishida[1], Eiry Kobatake[1], Masayasu Mie[1] (1. Tokyo Institute of Technology)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

Break

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[H934-4am-08]

Lipidation of antibodies by microbial transglutaminase

○Mari Takahara[1], Noriho Kamiya[2] (1. National Institute of Technology, Kitakyushu College, 2. Graduate School of Engineering, Kyushu University)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[H934-4am-09]

Development of Decoy Molecules Introduced Dicarboxylic Acids
That Induce Oxidation of Small Molecules by Cytochrome P450BM3

○Megumi Ishigami[1], Shinya Ariyasu[1], Chie Kasai[1], Yuichiro Aiba[1], Hiroshi Sugimoto[2], Osami Shoji[1] (1. Nagoya Univ., 2. SPring-8, RIKEN)

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[H934-4am-10]

CO_2 Fixation Reaction With *Thermoplasma acidophilum* Malic Enzyme

○Yuri Oku[1], Tomoko Matsuda[1] (1. Tokyo Institute of Techonology)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[H934-4am-11]

Development of enzymatic lactate synthesis system using acetaldehyde and CO_2 as raw materials

○Kazuma Suehiro[1], Yutaka Amao[1] (1. Osaka Metropolitan University)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[H934-4am-12]

Construction and characterization of a NAD-dependent dehydrogenase which was site-specifically modified with electron acceptor

○Kurea IKEGAI[1], Junko Okuda[1,2], Truc Thanh Tran[2], Mika Hatada[2], Ryutaro Asano[1], Kazunori Ikebukuro[1], Koji Sode[2], Wakako Tsugawa[1] (1. Tokyo university of agriculture and technology, 2. University of North Carolina at Chapel Hill)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[H934-4am-13]

Protein-protein interaction-based function regulation for flexible proteins: Applicability of monobodies

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○Ibuki Nakamura[1], Hiroshi Amesaka[2], Mizuho Hara[2], Keisuke Okamoto[2], Kento Yonezawa[1], Hironari Kamikubo[1], Shun-ichi Tanaka[2], Shun Hirota[1], Takashi Matsuo[1] (1. Div. Mat. Sci., NAIST, 2. Department of Biomolecular Chemistry, Kyoto Prefectural University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[H934-4am-14]

Discrimination of proteases with similar substrate selectivity by substrates incorporating unnatural amino acids

○Shun Honjo[1], Yuuki Yamawaki[1], Tamaki Kato[1] (1. Kyushu Institute of Technology)

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日本化学会 第104春季年会 (2024)

アルドキシムデヒドラターゼを利用する環状ケトキシムのラジカル的開環反応の検討

（阪大院工）○西脇 春香・加藤 俊介・林 高史

Radical Ring-opening Reaction of Cyclic Ketoxime Catalyzed by Aldoxime Dehydratase

(*Graduate School of Engineering, Osaka University*) ○Haruka Nishiwaki, Shunsuke Kato, Takashi Hayashi

Biocatalyses using enzymes and/or microorganisms are attracting attention as an environmentally friendly processes which do not depend on depletable resources. In this study, we have investigated a biocatalytic radical ring-opening reaction of cyclobutanone oximes to expand the catalytic reaction repertoire of natural enzymes (Figure 1). In nature, aldoxime dehydratases are known to catalyze N–O bond cleavage of aldoximes to form nitriles, which proceeds via concerted interaction with heme and surrounding amino acid residues. Here, we set out to utilize this unique enzyme mechanism for a “new-to-nature” radical ring-opening reaction of cyclobutanone oximes. Aldoxime dehydratases were found to afford 3-cyanopropane-1-sulfinic acid derivatives as a main product in the presence of dithionite.

Keywords : Biocatalyst, Aldoxime Dehydratase, Hemoprotein, Sulfinilation, Radical Reaction

枯渇性資源に依存しない触媒反応技術として、酵素や微生物などの「生体触媒」を利用したバイオプロセスが注目されている。本研究では生体触媒の反応適用範囲を非天然の化学反応へと拡張することをめざし、アルドキシムデヒドラターゼを用いた環状ケトキシムのラジカル的開環反応を実施した（Figure 1）。アルドキシムデヒドラターゼは、ヘムと周辺のアミノ酸残基の協奏的な働きによりアルドキシムの N–O 結合開裂を促進し、ニトリルを合成する酵素として知られている。このユニークな酵素の反応機構に着目し、アルドキシムデヒドラターゼを含む溶液に、シクロブタノンオキシムを添加したところ、N–O 結合の開裂を駆動力とするシクロブタン骨格の開環反応が進行した。また、ジチオナイト存在下で本反応を行うことで、3-シアノプロパン-1-スルフィン酸誘導体が生成物として得られた。

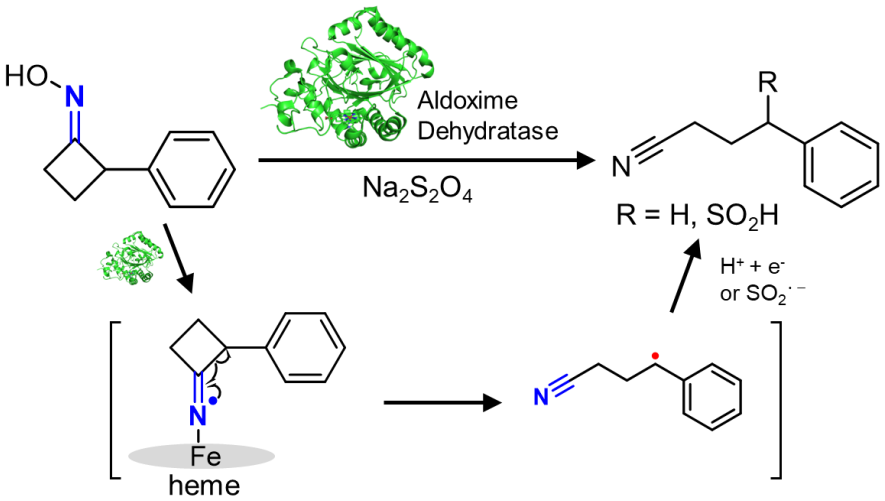

Figure 1. Radical ring-opening reaction of cyclic ketoxime catalyzed by aldoxime dehydratase.

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FAD/ThDP 依存性酵素によるピルビン酸と *N*-アシロキシフタルイミドの光ラジカルカップリング反応の検討

（阪大院工）○足立 柚斗・藤沢 修斗・加藤 俊介・林 高史

Photoradical Coupling Reactions between Pyruvate and *N*-acyloxyphthalimide Catalyzed by FAD/ThDP-Dependent Enzymes (*Graduate school of Engineering, Osaka University*) ○Yuto Adachi, Shuto Fujisawa, Shunsuke Kato, Takashi Hayashi

To expand the repertoire of catalytic reactions of natural enzymes, we have recently focused on the biocatalytic photoradical reactions between pyruvate and *N*-acyloxyphthalimides. In nature, acetolactate synthase with thiamine diphosphate (ThDP) and flavin adenine dinucleotide (FAD) as cofactors originally promotes a typical two-electron reaction as seen in NHC organocatalysts. However, we here demonstrate that acetolactate synthase from *T. bispora* (TbALS) can catalyze a radical coupling reaction between pyruvate and *N*-acyloxyphthalimides upon irradiation of blue light (**Figure 1**). Photoexcitation of the FAD cofactor was suggested to bring a new radical reactivity to the ThDP organocatalyst. Furthermore, genetic engineering of TbALS was found to improve its catalytic activity and broaden the substrate scopes.

Keywords : Biocatalysis; FAD/ThDP-dependent Enzymes; Acetolactate Synthase; Photoradical Reaction

持続可能な社会の実現に向け、近年、酵素や微生物等の生体触媒を用いた物質変換に注目が集まっている。本研究では、これら生体触媒の反応適用範囲を非天然の化学反応にまで拡張するべく、非生物学的な光駆動型ラジカル反応を触媒する FAD/ThDP 依存性酵素の開発に着手した。アセト乳酸合成酵素をはじめとする FAD/ThDP 依存性酵素は、通常、NHC 有機触媒に見られる一般的なカルボニル化合物の官能基変換を伴う二電子反応を触媒する。一方で、本研究において我々は、*T. bispora* 由来のアセト乳酸合成酵素（TbALS）が、青色光照射下でピルビン酸と *N*-アシロキシフタルイミドの非生物学的な光ラジカルカップリング反応に対して有望な触媒活性を示すことを明らかとした（**Figure 1**）。活性中心近傍に位置する FAD からの光励起電子移動を誘起することで、補因子である ThDP に新たなラジカル的な反応性が付与されたことが示唆された。また、TbALS の遺伝子工学的な改変を実施した結果、触媒活性と基質適用範囲が向上することが判明した。

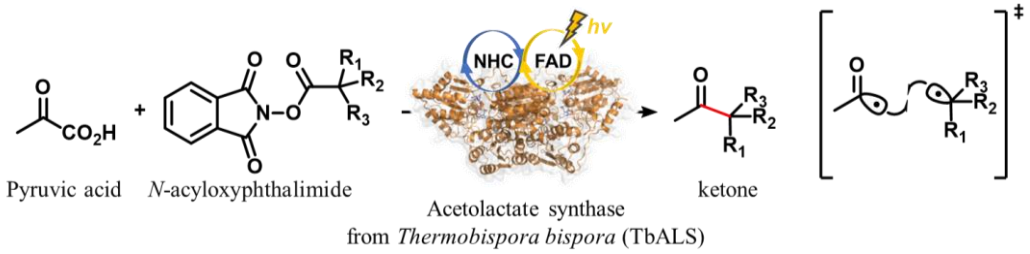

Figure 1. Photo radical coupling reaction between pyruvate and *N*-acyloxyphthalimide.

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有機光増感色素をタンパク質マトリクスに挿入した人工フォトレドックス酵素による光誘起イミン還元反応

（阪大院工）○加納 龍成・内田 裕貴・大洞 光司・林 高史

Photoinduced Imine Reductions Catalyzed by an Artificial Photoredox Enzyme Constructed by Incorporating an Organic Photosensitizer into a Protein Matrix (*Graduate School of Engineering, Osaka University*) ○Ryusei Kano, Yuki Uchida, Koji Oohora, Takashi Hayashi

Recently, photoredox catalysts and biocatalysts have been developed toward on-demand material conversion reactions. However, a simple enantioselective reaction by a photoredox catalyst incorporated into a protein matrix has been limited. In this study, we attempt to construct an artificial photoredox enzyme by incorporating fluorescein as an organic photosensitizer into lipocalin as a protein matrix. First, computational protein sequence optimization resulted in a variant with a 7-fold improvement in yield. Next, several mutants were prepared to obtain a catalyst with high catalytic activity for photoinduced imine reduction. As a result, fluoresceine incorporated into one of the mutants had a turnover number 3-fold higher than the wild-type protein.

Keywords : Photoreduction Reaction; Artificial Enzyme; Photoredox Catalyst; Lipocalin; Fluorescein

近年、自在な物質変換の実現に向け、フォトレドックス触媒や生体触媒が注目されている。しかし、タンパク質の洗練された反応場と光増感剤を組み合わせ、立体選択性を直接制御した報告例は少なく、報告されているものはフォトレドックス反応と酵素反応を多段階に組み合わせた複雑な系である[1]。そこで我々は、不斉環境を与えるタンパク質の反応場に光増感剤を配置した人工フォトレドックス酵素の開発をめざしている。本研究では、有機光増感色素 Fluorescein (Flu)に特異的に結合するタンパク質 Lipocalin (Lip)およびその変異体を採用し[2]、Flu と Lip からなる複合体の光誘起イミン還元反応に対する触媒活性を評価した(**Fig. 1**)。まず、Lip の収量向上をめざしコンピューテーショナルデザインによるアミノ酸配列の最適化を行い、収量が 7 倍に向上した三重変異体(OptLip)を得た。次に、OptLip の反応場近傍のいくつかのアミノ酸残基に変異導入した結果、特に H86D 変異体に結合した Flu が野生型に比べ 3 倍以上の触媒回転数を示した。今後、高活性・高選択的な触媒の開発をめざし、反応場近傍のアミノ酸残基のさらなる最適化を行う予定である。

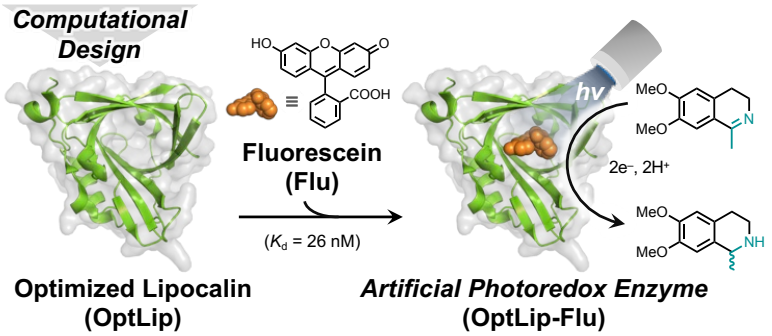

Fig. 1. Photoinduced imine reduction by an artificial photoredox enzyme.

1) O. S. Wenger *et al.*, *Chem. Sci.* **2018**, *9*, 5052, 2) A. Skerra *et al.*, *Proteins*, **2003**, *53*, 121.

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日本化学会 第104春季年会 (2024)

膜結合型メタンモノオキシゲナーゼと光化学系 II 再構成リポソームを用いた光駆動メタン酸化反応

（東京工業大学[1]）○能戸 湧太[1]・伊藤 栄紘[1]・蒲池 利章[1]
Photoinduced methane oxidation using particulate methane monooxygenase and photosystem II reconstituted in liposome ([1]*Tokyo Institute of Technology*) ○Yuta Noto[1], Hidehiro Ito[1], Toshiaki Kamachi[1]

Methanotrophs have a particulate methane monooxygenase (pMMO) which can catalyze the direct methane/methanol conversion. In our previous study, a photoinduced methane oxidation system (PSII-pMMO membrane system) was constructed by reconstitution of purified photosystem II (PSII) from thermophilic cyanobacteria into the membrane fraction containing pMMO. Light irradiation on this PSII reconstituted membrane, the electrons obtained from water catalyzed by PSII are transferred to pMMO by way of quinone pool, and photoinduced methane oxidation was achieved. However, to improve the system, membrane fraction from bacteria does not appropriate because it contains various lipids and proteins etc, which may decrease the efficiency of the photoinduced methane oxidation catalyzed by pMMO.

In this study, a new reaction system was constructed by reconstitution of solubilized pMMO, purified PSII, and decylplastoquinone into an artificial lipid bilayer liposome (PSII-pMMO liposome system). When 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) liposome was used, efficiency of the methanol production was improved.

Keywords: methane monooxygenase, photosystem II, methane oxidation, light, liposome

メタン資化細菌が持つ膜結合型メタンモノオキシゲナーゼ (pMMO)はメタンをメタノールに酸化する反応を触媒する。先行研究において、pMMO を含む菌体膜画分にシアノバクテリア由来の光化学系 II (PSII)を再構成した光駆動メタン酸化反応系(PSII-pMMO 膜画分系)を構築した (Figure 1)[1]。この反応系に光照射すると、PSII の触媒作用で、水を分解して得た電子がキノンを介して pMMO へと伝達され、メタン酸化反応が進行する。しかし、PSII-pMMO 膜画分系では、菌体膜画分を反応場として利用しているため、夾雑タンパク質への電子伝達によって、pMMO によるメタン酸化効率が低下する課題がある。

本研究では、界面活性剤で可溶化した pMMO、PSII、電子伝達体のキノンを人工脂質二分子膜リポソームに再構成した反応系(PSII-pMMO リポソーム系)を構築した。脂質分子に 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) を使用した PSII-pMMO リポソーム系では、光駆動メタン酸化反応におけるメタノール生成量が増加した。

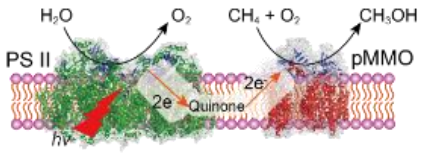

Figure 1 Schematic representation of photoinduced methane oxidation in PSII-reconstituted pMMO containing membrane.

1) H. Ito; R. Kondo; K. Yoshimori; T. Kamachi, *ChemBioChem* **2018**, *19* (20), 2152–2155.

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繊毛虫アルギニンキナーゼによる基質阻害機構の構造基盤研究

（高知大院理工）○馬場 千颯・矢野 大地・大塚 夢斗・児島 よしの・宇田 幸司・鈴木 知彦・杉山 成
Structural basis for the substrate inhibition mechanism of the ciliate arginine kinase (*Kochi University Graduate School of Natural Sciences*) ○Chihaya Baba, Daichi Yano, Yumeto Otsuka, Yoshino Kojima, Koji Uda, Tomohiko Suzuki, Shigeru Sugiyama

Substrate inhibition means that the substrate of the enzyme causes inhibition of catalytic activity. Although substrate inhibition is predicted to occur in about 20% of enzymes[1)], the detailed mechanism has not been elucidated. Probably because it was interpreted as a non-physiological phenomenon until recently. In this study, we focused on arginine kinase (AK), to elucidate the detailed substrate inhibition mechanism. AK has four subtypes (AK1-4). Only AK3 produces substrate inhibition (Figure 1), even though those subtypes have high amino acid sequence homology (70-91%). We will elucidate the mechanism of substrate inhibition by analyzing AK mutants, measuring enzyme activity, and performing crystal structure analysis. Crystal structures of the apo form of AK3 and its complexes with the substrates Arg or ADP have already been obtained. Based on these results, we are now identifying the amino acid residues involved in Arg binding and are proceeding with mutant analysis and enzyme activity measurements. Preliminary experimental results confirm that substrate inhibition completely disappears in one mutant.
Keywords : Structural Biology; enzyme; substrate inhibition; Arginine kinase

酵素の基質によって触媒活性が阻害をうけること基質阻害という。基質阻害は、酵素の約20%で生じる[1)]とされながら、その詳細な機構解明は進んでいない。おそらく、近年まで非生理的な現象と解釈されていたためと思われる。本研究は、詳細な基質阻害機構の解明を目的として、ヨツヒメゾウリムシ由来アルギニンキナーゼ（*Pt*AK）に着目した。*Pt*AK は、4 つのサブタイプ（*Pt*AK1～4）をもっている。それらは高いアミノ酸配列相同性（70～91%）にも関わらず、*Pt*AK3 のみ基質阻害を生じる(Figure 1)。本研究では、*Pt*AK の変異体解析および酵素活性測定、複合体結晶構造解析をおこなうことで基質阻害機構を解明する。既に、*Pt*AK3 の apo 体、基質 Arg または ADP との複合体の結晶構造が得られている。現在、これらの結果を基に Arg 結合に関与しているアミノ酸残基を特定し、変異体解析と酵素活性測定を進めている。予備的な実験結果から、ある変異体において基質阻害が完全に消失することを確認した。

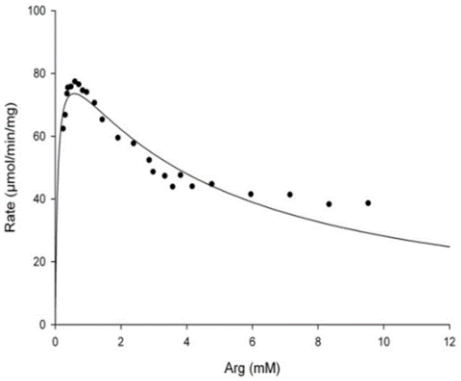

Figure 1. Michaelis-Menten plot of AK3

1) M. C. Reed, A. Lieb, H. F. Nijhout. *BioEssays.* **2010**, *32*, 422-429.

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人工 RNA 結合タンパク質の創出

（岡大院ヘルス）○山部 靖治・浮田 康平・吉岡 健太・長尾 桂輔・毛利 隼大・森 友明・森 光一・世良 貴史
Creation of artificial RNA-binding proteins (*Graduate School of Interdisciplinary Science and Engineering in Health Systems, Okayama University*) ○Yasuharu Yamabe, Kohei Ukida, Kenta Yoshioka, Keisuke Nagao, Hayata Mouri, Tomoaki Mori, Koichi Mori, Takashi Sera

RNA is involved in the regulation of various life phenomena such as transcription, translation, splicing, and RNA virus replication. Therefore, if we can create RNA-binding proteins that can bind specifically to arbitrary RNA sequences, we will be able to control various RNA-related life phenomena as we wish, independently of the target organisms. Therefore, we are focusing on natural RNA-binding proteins that regulate mRNA stabilization and translation, and are working to modify the selectivity of their recognition sequences. As one of the methods, we have constructed a selection system to select target mutants that bind strongly to target RNAs from a library of various mutants in which amino acid residues involved in base recognition have been replaced with all 20 types of amino acid residues. We are now in the process of selecting proteins with the desired binding ability from the generated library. In this report, we describe the current status of the selection process.
Keywords : RNA functional control; Artificial RNA-binding protein, Pumilio protein

RNA は転写、翻訳、スプライシング、RNA ウイルスの複製などの様々な生命現象の制御に関与している。そのため、任意の RNA 配列へ特異的に結合できる RNA 結合タンパク質を創出することができれば、それらを用いることにより、RNA が関わる様々な生命現象を対象生物とは独立して、我々が望むように制御することが可能となる。そこで、我々は、mRNA の安定化や翻訳の制御を行う、天然の RNA 結合タンパク質に着目し、その認識塩基配列の選択性を改変することを目指した研究を行っている。その一つの方法として、我々は塩基認識に関わるアミノ酸残基を 20 種類すべてのアミノ酸残基に置換した、多種多様な変異体ライブラリーを作製し、その中から標的 RNA に対して強く結合する目的の変異体の選抜を行うセレクション系を構築し、現在作製したライブラリーから目的の結合能を有するタンパク質の選抜を行っているところである。今回、その現状について報告する。

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Rep を利用したタンパク質の直交型 DNA 修飾

（東工大生命理工）○小松﨑千加・西田慶・小畠英理・三重正和
Orthogonal DNA modification of proteins utilizing multiple replication initiator proteins (*School of Life Science and Technology, Tokyo Institute of Technology*) ○Chika Komatsuzaki, Kei Nishida, Eiry Kobatake, Masayasu Mie

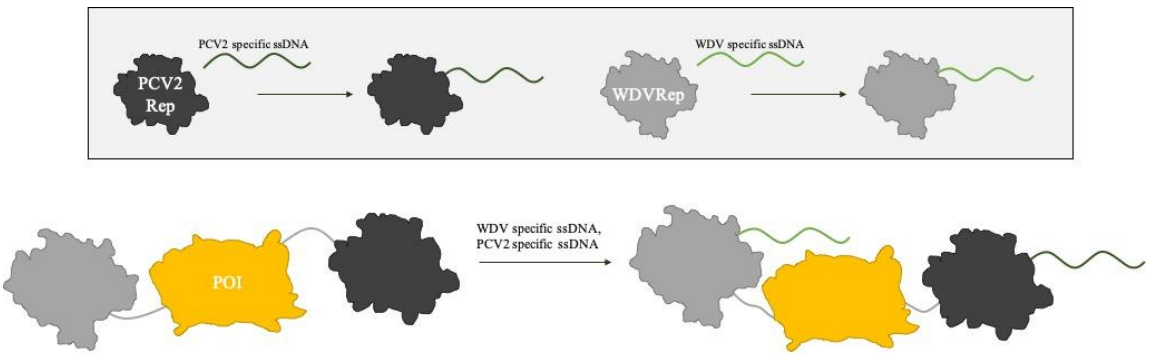
DNA-protein hybrid materials are an attractive candidate to facilitate the development of bio-functional nanodevices. Replication initiator protein (Rep), possesses the activity to recognize and bind a specific DNA sequence for initiation of DNA replication. Our group have demonstrated that the modification of single-stranded DNA (ssDNA) to protein-of-interest (POI) could be achieved by the fusion of Rep to POI.

In this study, to orthogonally modify heterologous ssDNA to POI, we paid attention to two types of Rep: Porcine Circovirus Type 2-derived Rep (PCV2Rep) and Wheat Dwarf Virus-derived Rep (WDVRep). It was reported that PCV2Rep and WDVRep binded to specific ssDNA sequences respectively[1]. In here, we constructed the fusion proteins, POIs fused with PCV2Rep and WDVRep which form DNA-protein hybrids with heterologous ssDNA.

Keywords : Replication initiator protein; DNA modification; protein engineering

Replication initiator protein(Rep)は、DNA 複製時に複製起点となる特異的な配列を認識し、結合する DNA 結合性タンパク質の一つである。当研究室では Rep の DNA 結合活性に着目し、目的タンパク質と Rep の融合により DNA-タンパク質結合体の構築およびその材料応用を推進している。Rep の DNA 結合活性は、温和な条件下で迅速に進行し、1 対 1 の反応であるため修飾する部位や数量の制御が可能といった利点を有している。この DNA-タンパク質結合体は、DNA の二重鎖形成能を利用することにより、異なる機能を有したタンパク質複合体を形成させることが出来ると期待される。しかしながら、この複合体を構成する分子を 3 個以上に拡張するためには、1 つの目的タンパク質に異なる配列を有した DNA を直交的に結合する必要がある。

本研究では、目的タンパク質に異なる配列を有した一本鎖 DNA(ssDNA)を直交的に修飾することを目指した。ここでは 2 種類の Rep、Porcine Circovirus Type 2 由来 Rep(PCV2Rep)および Wheat Dwarf Virus 由来 Rep(WDVRep)に着目した。これまで PCV2Rep と WDVRep に、それぞれ特異的に結合する DNA 配列が報告されている[1]。本研究では、目的タンパク質に PCV2Rep および WDVRep を融合したタンパク質を構築し、異なる配列を有した ssDNA を直交的に結合可能であるかを検討した。



1) Molecular underpinnings of ssDNA specificity by Rep HUH-endonucleases and implications for HUH-tag multiplexing and engineering, Tompkins KJ *et al., Nucleic Acids Res.*, 2021, **49**, 1046-1064

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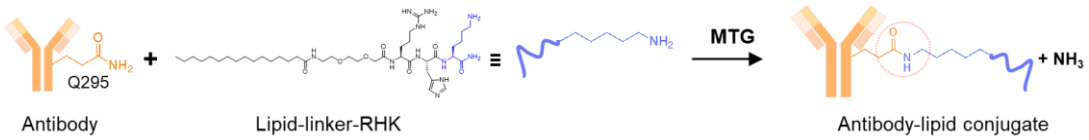
トランスグルタミナーゼによる抗体脂質修飾法の検討

（北九州高専[1]・九大院工[2]）○高原 茉莉[1]・神谷 典穂[2]
Lipidation of antibodies by microbial transglutaminase ([2]*NIT, Kitakyushu College,* [2]*Graduate School of Engineering, Kyushu University*,) ○Mari Takahara,[1] Noriho Kamiya[2]

Drug delivery technique using immunoliposomes has recently been attractive by the combination of liposomes with ability to load a sufficient amount of drugs and antibodies with targeting ability. However, conjugation between antibodies and lipids as anchoring moieties on liposomes is still of difficulty due to denaturation of hydrophilic antibodies by the hydrophobicity of lipids. Herein, we propose the lipidation of antibodies by transglutaminase and its amphiphilic lipid substrates. MTG catalyzes cross-linking reaction between specific glutamine (Q) and lysine (K) residues, and Q295 in generally available antibodies after deglycosylation can be recognized by MTG.[1)] Thus, lipid-linker-RHK peptides were designed for MTG-mediated lipidation of antibodies, and only in the case of PEG linker, lipidation of the antibody was shown.
Keywords : Antibodies, Transglutaminase, Lipids, Amphiphilic peptides

近年、薬物搭載量の高いリポソームに、標的指向部位となる抗体を係留したイムノリポソームが薬物送達手段として注目されている。しかし、リポソームへの係留部位である疎水性の高い脂質を、水溶性の抗体が変性しないように狙った部位で修飾するのは未だに困難である。そこで本研究では、微生物由来トランスグルタミナーゼ (MTG) の触媒機能と、その基質となる両親媒性脂質化ペプチドを用いた部位特異的脂質化抗体の調製を検討した。MTG は特定のグルタミン (Q) とリジン (K) 側鎖間の架橋反応を触媒する酵素で、脱糖鎖後抗体の Q295 を認識可能と報告されている[1)]。ここで、抗体に MTG を介して修飾可能な脂質化ペプチド基質として、両親媒性の lipid-linker-RHK (linker: PEG or G_3S) を設計し、リンカー配列の最適化を行ったところ、PEG リンカーの場合のみ、抗体の脂質修飾の達成が示唆された。



1) P. Dennler, A. Chiotellis, E. Fischer, D. Brégeon, C. Belmant, L. Gauthier, F. Lhospice, F. Romagne, R. Schibli, *Bioconjug. Chem*. **2014**, *25*, 569-578.

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シトクロム P450BM3 による小分子の酸化反応を誘起するジカルボン酸導入デコイ分子の開発

(名大院理[1]・理研 SPring-8[2]) ○石上 恵[1]・有安 真也[1]・笠井 千枝[1]・愛場 雄一郎[1]・杉本 宏[2]・荘司 長三[1]

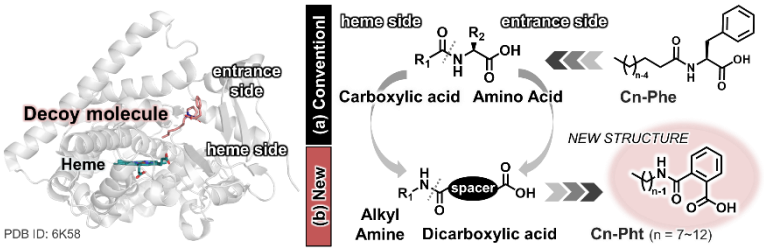
Development of Decoy Molecules Introduced Dicarboxylic Acids That Induce Oxidation of Small Molecules by Cytochrome P450BM3 ([1]*Graduate School of Science, Nagoya University*, [2]*SPring-8, RIKEN*) ○Megumi Ishigami,[1] Shinya Ariyasu,[1] Chie Kasai,[1] Yuichiro Aiba,[1] Hiroshi Sugimoto,[2] Osami Shoji[1]

Cytochrome P450BM3 which catalyzes hydroxylation of long-chain fatty acids can hydroxylate small molecules such as toluene by adding a "substrate mimic" (decoy molecule). However, the previously developed decoy molecules have limited structures based on amino acids. To improve the applicability of this system such as substrate scope, the expansion of the diversity of decoy molecules is needed. In this study, we aimed to develop new decoy molecules that consist of dicarboxylic acids instead of amino acids.

The molecules directly connecting alkyl amines and dicarboxylic acids, especially phthalic acid (Cn-Pht) accelerated toluene hydroxylation and styrene epoxidation by P450BM3. Compared with the typical decoy molecules connecting alkyl carboxylic acids and phenylalanine (Cn-Phe), it was revealed that Cn-Pht is better for styrene while Cn-Phe is suited for toluene. The new molecules are successfully developed which have different preferences of substrates.

Keywords : Cytochrome P450BM3; Decoy Molecule; Oxidation

長鎖脂肪酸水酸化酵素であるシトクロム P450BM3 に基質を模擬した偽の基質（デコイ分子）を添加すると，トルエンなど小分子の酸化反応が可能になる[1]．しかし，これまでに開発されたデコイ分子の構造はどれもアミノ酸を主体とする骨格に限られており，基質の適用範囲など本システムの利用可能性向上には構造多様性拡大が求められる．本研究では，アミノ酸に代わる部分構造としてジカルボン酸を導入した新規骨格デコイ分子の開発に取り組んだ．結果，アルキルアミンとフタル酸を縮合した分子（Cn-Pht）を P450BM3 によるトルエン水酸化とスチレンエポキシ化に用いたところ，反応が有意に加速された．アルキルカルボン酸とフェニルアラニンを縮合した従来デコイ分子（Cn-Phe）での結果と比較すると Cn-Pht はスチレンエポキシ化で，Cn-Phe はトルエン水酸化でより高い活性を示すことが明らかになり．基質に対する新たな応答性を有するデコイ分子を見出すことに成功した．



図（左）デコイ分子結合型 P450BM3 の結晶構造（右）分子構造

Ref. [1] N. Kawakami, O. Shoji *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 5315–5318.

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Thermoplasma acidophilum 由来リンゴ酸酵素を用いた CO_2 固定化反応の開発

（東工大生命理工）○奥 悠莉・松田 知子
CO_2 Fixation Reaction with *Thermoplasma acidophilum* Malic Enzyme (*Graduate School of Life Science and Technology, Tokyo Institute of Technology*) ○Yuri Oku and Tomoko Matsuda

CO_2 fixation technology has gained attention as a way to effectively utilize the CO_2 abundant in the atmosphere by converting CO_2 into useful chemicals. However, since CO_2 is a highly stable molecule, many of the currently developed methods for chemical CO_2 fixation require high temperatures, high pressures, and unstable reagents, and there are some challenges in terms of energy efficiency and sustainability. In this study, we developed a carboxylation reaction under mild conditions using a biocatalyst, *Thermoplasma acidophilum* NADP-malic enzyme (*Ta*ME).

*Ta*ME catalyzes reversible reductive carboxylation and oxidative decarboxylation (Fig. 1). Firstly, the substrate specificity for decarboxylation reactions were investigated. It was found that the relative activity towards isocitric acid was 190% of that of malic acid, a natural substrate. Next, the optimal conditions for the carboxylation reaction were investigated, resulting in an initial pH 7.5~8.5 and the presence of Mg^{2+} and K^+ ions. Under these conditions, malic acid could be synthesized from pyruvic acid and CO_2 in 65 % yield under mild conditions of 37 °C and 1 MPa CO_2.
Keywords : Malic enzyme; Enzymatic carboxylation; CO_2 fixation; CCU

CO_2 を有効利用する方法として、CO_2 を反応物として固定化する技術が注目されている。しかし CO_2 は安定であるが故に反応性に乏しく、化学的に付加させることは容易ではない。現在開発されている化学的な CO_2 固定化反応の多くは、高温高圧や不安定な試薬を必要とし、エネルギー効率と持続可能性の観点で課題がある。そこで本研究では、生体触媒である *Thermoplasma acidophilum* 由来 NADP-リンゴ酸酵素 (*Ta*ME) を用いた、温和な条件下で進行するカルボキシル化反応を開発した。

*Ta*ME は、可逆的な還元的カルボキシル化および酸化的脱炭酸反応を触媒する (Fig. 1)。まず、*Ta*ME の諸性質を明らかにするため、脱炭酸反応における至適条件および基質特異性を検討した。脱炭酸反応における基質特異性は、天然の基質であるリンゴ酸を 100%とした相対活性において、イソクエン酸が 190%の活性を示した。次に、カルボキシル化反応における至適条件を検討した。その結果、至適条件は、初期 pH7.5~8.5、Mg^{2+}および K^+イオン存在下であった。この条件下で、37 ℃、1 MPa CO_2 という穏やかな環境で、ピルビン酸と CO_2 から、65 %収率でリンゴ酸を合成できた。

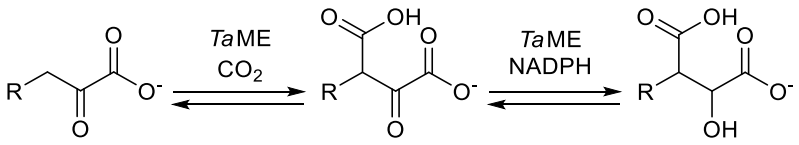

Fig. 1. *Ta*ME による還元的カルボキシル化および酸化的脱炭酸反応

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日本化学会 第104春季年会 (2024)

アセトアルデヒドおよび二酸化炭素を原料とした生体触媒利用による乳酸合成系の構築

（大阪公大院理 [1]）○末廣 和真 [1]・天尾 豊 [1]

Development of enzymatic lactate synthesis system using acetaldehyde and CO_2 as raw materials ([1]*Graduate School of Science, Osaka Metropolitan University*)

○Kazuma Suehiro,[1] Yutaka Amao[1]

Recently, various environmental problems such as global warming and plastic pollution have become more serious. CO_2 utilization technology and biodegradable polymer usage are significant for solving these problems. In this study, a synthesis system of lactate, one of the biodegradable polymer precursors, from acetaldehyde and CO_2 using two enzymes has been devised. In this system, pyruvate decarboxylase (PDC) catalyzes carboxylation from acetaldehyde to pyruvate with CO_2[1], and lactate dehydrogenase (LDH) is also used as a catalyst for reduction from the pyruvate to lactate. By using this system, 35 μM of lactate was produced after 5 h of incubation. On the other hand, no lactate production occurred in the absence of either PDC or LDH. These results suggest that acetaldehyde and CO_2 were successfully converted into lactate by both enzymes. In addition, the reaction efficiency was up to 1.9 times higher in the presence of Mg^{2+} than in the absence of Mg^{2+}. It suggests that Mg^{2+} acts as the cofactor of the CO_2 fixation by PDC.

Keywords : CO_2 fixation; Enzymatic reaction; Biodegradable polymer precursor

地球温暖化やプラスチック汚染といった環境問題の解決策として，二酸化炭素の再資源化技術および生分解性高分子の利用が注目されている。そこで本研究では，図 1 に示すアセトアルデヒドと二酸化炭素を原料とした生分解性高分子原料である乳酸合成系の構築を試みた。この系ではアセトアルデヒドへ二酸化炭素を固定化しピルビン酸を合成する触媒としてピルビン酸デカルボキシラーゼ (PDC) を [1]，ピルビン酸を還元し乳酸を合成する触媒として乳酸脱水素酵素 (LDH) を用いた。

図 1 に示す乳酸合成系により，5 時間の反応で 35 μM の乳酸が生成した。一方，PDC または LDH 非存在下では乳酸が生成しなかったことから，両生体触媒の作用によりアセトアルデヒドと二酸化炭素から乳酸が生成していることが示唆された。また，Mg^{2+}非添加時に比べ Mg^{2+}添加時では反応効率が最大 1.9 倍に向上した。これは，Mg^{2+} が PDC による二酸化炭素固定化反応において補因子として機能することを示唆している。

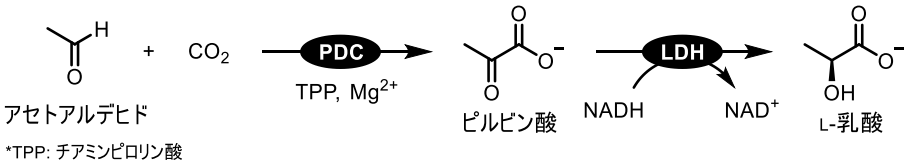

図 1. 生体触媒を用いたアセトアルデヒドおよび二酸化炭素を原料とする乳酸合成系

1) V. Kazimírová, M. Rebroš, *Int. J. Mol. Sci.*, **2021**, *22*, 4949.

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日本化学会 第104春季年会 (2024)

部位特異的に電子受容体を修飾した NAD 依存型脱水素酵素の構築と特性検討

（東農工大工[1]・ノースカロライナ大学チャペルヒル校/ノースカロライナ州立大学/生命医工[2]）○池貝 紅亜[1]・奥田順子[1]・Truc Thanh Tran[2]・畑田実香[2]・浅野竜太郎[1]・池袋一典[1]・早出広司[2]・津川若子[1]

Construction and characterization of a NAD-dependent dehydrogenase which was site-specifically modified with electron acceptor ([1]*Faculty of Engineering, Tokyo University of Agriculture and Technology,* [2]*Joint Department of Biomedical Engineering, University of North Carolina at Chapel Hill, North Carolina State University*) ○Kurea Ikegai[1], Junko Okuda[1], Truc Thanh Tran[2], Mika Hatada[2], Ryutaro Asano[1], Kazunori Ikebukuro[1], Koji Sode[2], Wakako Tsugawa[1]

NAD$^+$-dependent dehydrogenases are widely utilized in analytical kits and instruments, including the test strips of the electrochemical enzyme sensors. Besides, direct electron transfer (DET) type-enzymes are recognized as ideal biosensing molecules for the sensors of continuous monitoring systems. However, a limited number of DET-type enzymes are available. In this study, we introduce a versatile method to convert NAD$^+$-dependent dehydrogenases into quasi-DET-type dehydrogenases, by employing β-hydroxybutyrate (BHB) dehydrogenase (BHBDh) as a representative example of NAD$^+$-dependent dehydrogenase. We predict and design the positions of cysteine residues in BHBDh to modify with a thiol-reactive phenazine ethosulfate (trPES). The PES modified cys-residues-introduced mutant-BHBDhs showed characteristic dye-mediated dehydrogenase activities which were only observable as the results of using PES as the primary electron acceptor from NADH. The electrochemical sensor using trPES modified BHBDh mutants showed BHB-dependent response currents in the presence of NAD$^+$.

Keywords: NAD-dependent dehydrogenase, quasi-direct electron transfer, electrochemical enzyme sensor, phenazine

NAD 依存型脱水素酵素は計測用酵素として汎用され、遊離の電子メディエータを用いた電気化学的酵素センサが実用化されている。一方、近年注目されている連続計測センサには、遊離の電子メディエータが不要な直接電子移動 (Direct Electron Transfer: DET) 型酵素が理想的である。本研究では NAD 依存型酵素の代表例として β-ヒドロキシ酪酸脱水素酵素 (BHBDh) を選択し、擬 DET 型酵素の構築方法を提案する。すなわち、本酵素の構造情報をもとに、NADH から効率的な電子移動を行う距離にシステイン残基を導入し、チオール反応性 phenazine ethosulfate (trPES) で部位特異的に修飾した。その結果、PES を介した特徴的な脱水素酵素活性が確認された。さらに、同酵素を用いた酵素センサにおいて、NAD$^+$存在下で BHB 濃度依存的に応答電流値が上昇し、擬 DET が確認された。

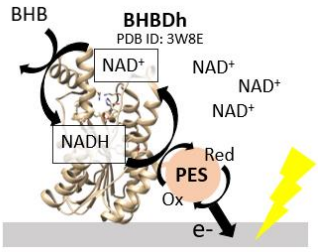

Fig.1 Scheme of enzyme sensor

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タンパク質–タンパク質間相互作用による構造柔軟性が高いタンパク質の機能制御：モノボディの適用可能性の検証

(奈良先端大 物質創成[1]・京都府立大院 生命環境[2])
○中村 伊武輝[1]、雨坂 心人[2]、原 瑞穂[2]、岡本 恵祐[2]、米澤 健人[1]、上久保 裕生[1]、田中 俊一[2]、廣田 俊[1]、松尾 貴史[1]

Protein-protein interaction-based function regulation for flexible proteins: Applicability of monobodies ([1]*Div. Mat. Sci, NAIST*, [2]*Department of Biomolecular Chemistry, Kyoto Prefectural University*) ○ Ibuki Nakamura[1], Hiroshi Amesaka[2], Mizuho Hara[2], Keisuke Okamoto[2], Kento Yonezawa[1], Hironari Kamikubo[1], Shun-ichi Tanaka[2], Shun Hirota[1], Takashi Matsuo[1]

Synthetic binding proteins, termed monobodies (mb), have emerged as modulators of protein functions through protein-protein interactions (PPIs). This study demonstrates the applicability of mb in regulating the functions of proteins that undergo tens-of-angstroms-scale conformational changes, using an example of the adenylate kinase triple mutant (Adk_{tm}; an enzyme with a conformational change between OPEN/CLOSED forms). An OPEN-form specific monobody (OP-mb) clearly inhibited the activity of Adk_{tm}. SEC-SAXS analysis indicated that OP-mb binds to the outside of the substrate-binding site of Adk_{tm}, retaining the whole OPEN-form structure of Adk_{tm}. Furthermore, X-ray crystallography of the Adk(wild-type)/OP-mb complex suggested that OP-mb binds to the outside of Adk. The titration of Ap_5A, a transition-state analog for Adk_{tm}, showed that OP-mb suppresses the conformational shift to the CLOSED-form although Adk_{tm} retained the OPEN-form. These experimental results indicate that monobodies are useful tools for regulating the functions of flexible proteins that show tens-of-angstroms-scale conformational changes.

Keywords : Synthetic binding protein, Monobodies, Conformational change, Protein-protein interactions(PPIs), Adenylate kinase

タンパク質間相互作用（PPIs）を通してタンパク質機能を制御する戦略として、人工結合タンパク質を用いる方法が知られている。これまでにモノボディ（mb）によって標的タンパク質の機能をアロステリックに制御する試みがなされているが、数十 Å の大きな構造変化を示すタンパク質の機能制御に適用可能かは明らかでない。本研究では基質の有無で OPEN⇔CLOSED の大きな構造変化を示すアデニル酸キナーゼ三変異体（Adk_{tm}）をモデルに、それぞれの構造を選択的に認識するモノボディを創出し、機能制御を試みた。OPEN 型を認識するモノボディ（OP-mb）は、Adk_{tm} の酵素活性を明確に阻害したが、CLOSED 構造を認識するモノボディは酵素活性に影響を及ぼさなかった。OP-mb の結合箇所を特定するために Adk_{tm}/OP-mb 複合体の SEC-SAXS 解析を行った結果、OP-mb は Adk_{tm} の基質結合経路上ではなく、Adk_{tm} の活性部位の外側に結合することが証明された。また、Adk 野生型（AdkWT）/OP-mb 複合体の結晶構造解析の結果からも OP-mb が Adk の外側に結合していることが示唆された。さらに、遷移状態アナログ Ap_5A による滴定実験によって、基質結合経路が空いているにもかかわらず、CLOSED 型への構造変化が阻害されていることがわかった。これらの結果は、数十 Å の大きな構造変化を示す柔軟性の高いタンパク質の人為的制御のツールとして、モノボディが有用であることを示している。

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非天然アミノ酸を組み込んだ基質による類似した基質選択性を持つプロテアーゼ判別の試み

（九工大院生命体工）○本祥　駿・山脇　裕貴・加藤　珠樹

Discrimination of Proteases with Similar Substrate Selectivity by Substrates Incorporating Unnatural Amino Acids. (*Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology*) ○Shun Honjo, Yuuki Yamawaki, Tamaki Kato

Among proteases with similar functions, substrates that only selectively react with specific enzymes have the potential to be the seeds for in vitro diagnostics and inhibitors of diseases and are currently being investigated in various ways. Although most studies of the substrate specificity of protease use 20 natural amino acids, the use of non-natural amino acids may enable the design and synthesis of substrates that react more specifically with the enzyme. Our group has therefore developed substrates including cyclohexylalanine or 2-amino-4- ethylhexanoic acid (AEH)[1].

In the present study, we investigated the effect of substrate peptides containing non-natural amino acids with small side chains on proteases. Substrates expressed as H-Ala-Ala-Pro-R-MCA were synthesized and their activities were compared using two enzymes, chymotrypsin and subtilisin, to determine their performance. The results of the synthesis and measurements showed that the substrate with norleucine had a lower enzyme activity performance and no significant differences in reactivity in each enzyme.

Keywords: Peptides; Unnatural amino acids; Protease; AMC

類似の働きを持つプロテアーゼのうち、特定の酵素とのみ選択的に反応し切断される基質は疾病の体外診断薬や阻害剤の種となる可能性を秘めており、現在さまざまな研究が進められている。多くの場合プロテアーゼの基質特異性の研究は 20 種類の天然アミノ酸が用いられるが、非天然アミノ酸を用いることでより酵素と特異的に反応する基質の合成が可能になると考えられている。そのため我々のグループではシクロヘキシルアラニンや 2-amino-4-ethylhexanoic acid (AEH)を用いた比較研究を報告している [1]。

本研究では側鎖の小さい非天然アミノ酸を含む基質ペプチドがプロテアーゼに及ぼす影響を調査した。H-Ala-Ala-Pro-R-MCA で表される基質を合成し性能を測定するためキモトリプシンとサブチリシンの 2 つの酵素を用いて活性を比較した。合成及び測定の結果、ノルロイシンを導入した基質は酵素活性性能が低く、各酵素における大きな反応性の違いも見られなかった。

1) Substrates incorporating unnatural amino acids are separately detectable for chymotrypsin and subtilisin with similar specificity. Y. Yamawaki, T. Kato, Results in Chemistry. 2023, 6, 101217.

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

Thu. Mar 21, 2024 9:30 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:40 AM UTC H932(932, Bldg. 9 [3F])

[H932-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Kazumitsu Onizuka, Takanori Oyoshi

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H932-4am-01]

Synthesis of G4-PROTAC ligand for degradation of G-quadruplex binding proteins

○Yuma Tanaya[1], Rena Nohara[1], Ma Yue[2], Kazuo Nagasawa[1], Masayuki Tera[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H932-4am-02]

Degradation of intracellular G-quadruplex binding proteins by G4-PROTAC ligands

○Rena Nohara[1], Yuuma Tanaya[1], Yue Ma[2], Kazuo Nagasawa[1], Masayuki Tera[1] (1. Department of Biotechnology and Life Science, Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H932-4am-03]

Selective photo-crosslinking of G-quadruplexes by a dual-recognition ligand

○Sayuri Shimada[1], Ryo Ishikawa[1], Kazuki Yanagida[1], Yue Ma[2], Shogo Sasaki[1], Kazuo Nagasawa[1], Masayuki Tera[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H932-4am-04]

Evaluation of chemical reactions in droplets with macrocyclic hexaoxazole-type G-quadruplex ligands

○Akari Oyama[1], Shogo Sasaki[1], Masayuki Tera[1], Kazuo Nagasawa[1] (1. Tokyo University of Agriculture and Technology)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H932-4am-05]

Synthetic studies of the selective G4 ligands using click chemistry

○Yuri Shimasawa[1], Shogo Sasaki[1], Yue Ma[2], Masayuki Tera[1], Kazuo Nagasawa[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Tokyo Medical and Dental University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[H932-4am-06]

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Synthesis of light-up type fluorescent ligands for topology selective and dynamic detection of G-quadruplexes

○Haruki Fujita[1], Naruyuki Watatani[1], Syogo Sasaki[1], Yue Ma[2], Masayuki Tera[1], Kazuo Nagasawa[1] (1. Tokyo University of Agriculture and Technology, 2. Research Core, Institute of Research, Tokyo Medical and Dental University)

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

Break

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[H932-4am-07]

Novel macrocyclic pyridone pentamers as G-quadruplex (G4) ligands

○Emina Isobe[1], Takayoshi Arai[1], Keisuke Iida[1] (1. Chiba University)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[H932-4am-08]

Photo-decomposition Mechanism of Quadruplex DNA Using Anionic Phthalocyanines

○Atsuya Momotake[1], Yusuke Odahara[1], Yasuhiko Yamamoto[1] (1. Univ. of Tsukuba)

English

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[H932-4am-09]

Investigation of pull-down unit position for large-scale analysis of RNA alkylation

○Ping-Yun Lan[1,2], Kazumitsu Onizuka[1,2], Yutong Chen[1,2], Emi Miyashita[3], Kaoru R. Komatsu[3], Hirohide Saito[3], Fumi Nagatsugi[1,2] (1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Department of Chemistry, Graduate School of Science, Tohoku University, 3. CiRA, Kyoto University)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[H932-4am-10]

Synthesis and evaluation of a turn-on fluorescent probe targeting UGGAA repeats

○Shoei Harada[1], Tomonori Shibata[1], Kazuhiko Nakatani[1] (1. Osaka Univ., SANKEN)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[H932-4am-11]

Analysis of G-quadruplex Binding Protein if EWS for Transcriptional Regulation of TERRA

○Wakana Matsudaira[1], Luthfi Lulul Ulum[2], Akinori Ishihara[1], Takanori Oyoshi[1,2,3] (1. Graduate School of integrated Science and Technology, Shizuoka University., 2. Graduate School of Science and Technology, Shizuoka University., 3. Research Institute of Green Science and Technology, Shizuoka University.)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[H932-4am-12]

Development of the functional G4 DNA binding protein regulating transcription

○Natsuki Shibata[1], Maiko Yamanashi[2], Luthfi Lulul Ulum[3], Akinori Ishihara[2], Takanori Oyoshi[2,3,4] (1. Faculty of Science Shizuoka University, 2. Graduate School of Integrated Science

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and Technology, Shizuoka University, 3. Graduate School of Science and Technology, Shizuoka University, 4. Research Institute of Green Science and Technology, Shizuoka University)

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グアニン四重鎖結合タンパク質の分解を指向した G4-PROTAC リガンドの合成

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Synthesis of G4-PROTAC ligand for degradation of G-quadruplex binding proteins ([1] *Department of Biotechnology and Life Science, Tokyo University of Agriculture and Technology*, [2] *Research Core, Institute of Research, Tokyo Medical and Dental University*) ○ Yuma Tanaya[1], Rena Nohara[1], Yue Ma[2], Kazuo Nagasawa[1], and Masayuki Tera[1]

G-quadruplexes (G4s), formed in guanine-rich nucleic acid sequences, are involved in transcription, translation, replication, and so forth. G4s are thought to show its functions together with G4 binding proteins (G4BPs). In this study, we investigated the synthesis of G4-PROTAC ligands that selectively degrade only the G4BP bound with G4 through proteosome degradation, to elucidate the biological functions of G4-G4BP interactions.

Keywords : G-quadruplexes; G4 binding protein; PROTAC; chemical biology

【目的】グアニン豊富な核酸領域では、グアニン四重鎖（G4）と呼ばれる核酸高次構造が形成される。G4 は転写、翻訳、複製などに関与しており [1)]、G4 結合タンパク質（G4BP）との相互作用を介してその機能を発揮すると考えられている [2)]。本研究では、G4-G4BP 相互作用の生物学的な意義を解明するために、G4 に結合した G4BP を選択的に分解する G4-PROTAC リガンドの合成とその機能評価を行った。
【結果】ユビキチンリガーゼであるセレブロン（CRBN）のリガンドであるポマリドミド (Pm) 及びそのネガティブコントロールとなる *N*-メチル Pm と、G4 リガンドである PhenDC3 を異なるリンカーで連結した G4-PROTAC リガンド **1–4** 合成した (Figure 1a)。**1–4** が G4 に結合するか検証するために、UV スペクトルによるテロメア G4 融解温度測定を行った。その結果、**1–4** はテロメア G4 を安定化することが分かった。次に **1–4** による CRBN と G4 の三者複合体解析を FRET (蛍光共鳴エネルギー移動) により行った。**1–4** に対して、Eu^{3+}蛍光修飾した CRBN と d2 蛍光修飾したテロメア G4 を加えたところ、**3** の存在下でのみ両者での FRET シグナルが観察された (Figure 1b)。以上から、**3** を介し G4 と CRBN が複合体を形成することがわかった。

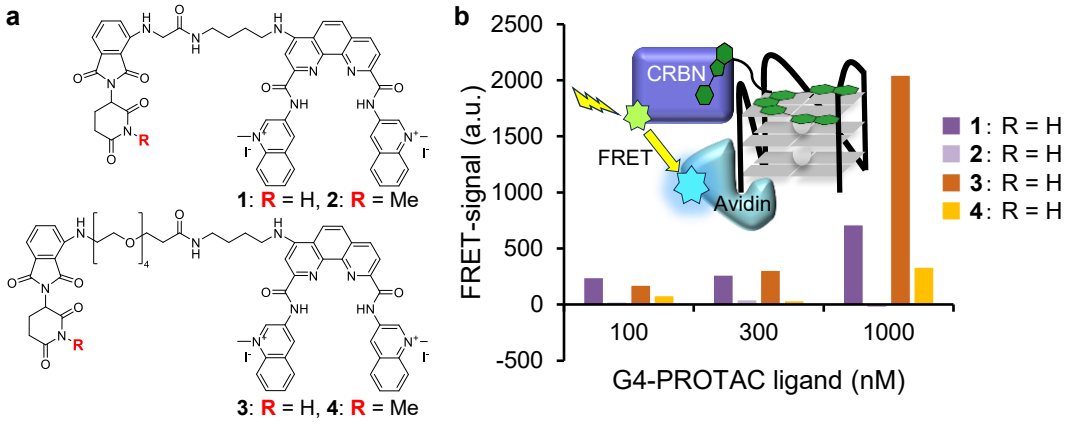

Figure 1 (a) Structure of G4-PROTAC ligands. (b) FRET-signal.

【参考文献】1) S. Balasubramanian *et al., Nat. Chem. Biol.*, **2007**, *3*, 218; 2) K. Nayun *et al., Nucleic Acids Res.*, **2023**, *51*, 9643

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G4-PROTAC リガンドによる細胞内グアニン四重鎖結合タンパク質の分解

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Degradation of intracellular G-quadruplex binding proteins by G4-PROTAC ligands

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○Rena Nohara,[1] Yuuma Tanaya,[1] Yue Ma,[2] Kazuo Nagasawa,[1] Masayuki Tera[1]

Guanine-rich sequences often form G-quadruplexes (G4s), known as thermodynamically stable secondary nucleic acids' structures. G4s and their binding proteins (G4BPs) are thought to be involved in various biological phenomena in cells. However, the biological functions of G4BP binding to G4 remain unclear. In this study, we developed a G4-PROTAC ligand, which consists of a G4 ligand linked to an E3 ligand. By treating HeLa cells with the G4-PROTAC ligand confirmed the degradation a G4BP of DHX36.

Keywords : Chemical biology, G-quadruplex, DNA, RNA, PROTAC

【目的】グアニン豊富な核酸領域で形成されるグアニン四重鎖（G4）は G4 結合タンパク質 (G4BP) と相互作用することで複製、転写、翻訳など重要な生命現象に関与すると考えられている[1)]。しかし、G4BP が G4 に結合することで生じる生物学的機能は不明な点が多い。最近、Phan らは E3（ユビキチンリガーゼ）リガンドで修飾した G4 形成オリゴヌクレオチドを Hela 細胞に導入することで G4BP がプロテアソーム分解されることを報告した[2)]。本手法では外部から加えた G4 が G4BP をリクルートするため、細胞内で自然に形成された G4 に結合する G4BP の機能解析が困難である。そこで本研究では、細胞内での G4-G4BP 相互作用解析を指向し、細胞内 G4 に結合する G4 リガンドに、E3 リガンドを連結した G4-PROTAC リガンドを開発した。

【結果】E3 ユビキチンリガーゼであるセレブロン (CRBN) のリガンドであるポマリドミドと G4 リガンド (L2H2-6OTD) を連結した G4-PROTAC リガンド **1a** を合成した。CRBN 結合のネガティブコントロールとなるメチル化ポマリドミドを導入した G4-PROTAC リガンド類 **1b** も合成した (Figure 1a)。次に、合成した G4-PROTAC リガンド類を Hela 細胞に添加し、G4BP の一つである DHX36 に着目しそのタンパク質量を定量した。その結果、**1a** を添加した場合に細胞内の DHX36 が顕著に減少することがわかった (Figure 1b)。このことから、細胞内 G4 に結合した DHX36 の G4-PROTAC リガンドによる分解が示唆された。

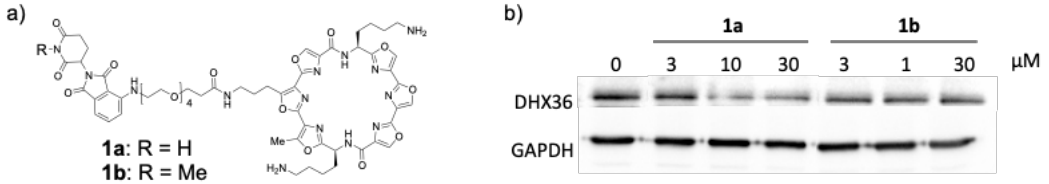

Figure 1. a) Chemical structures of **1a** and **1b**. b) Western-blotting analysis of DHX36 in Hela cells treated with **1a** or **1b** for 24 hours.

【参考文献】1) S. Balasubramanian *et al, Nat. Chem.*, **2021**, 13, 626; 2) A. T. Phan *et al, Chem. Commun.,* **2021**, 57, 12816.

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光架橋基を有する二点認識型トポロジー選択的 G4 リガンドの開発

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Selective photo-crosslinking of G-quadruplexes by a dual-recognition ligand ([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology,* [2]*Research Core, Tokyo Medical and Dental University*) ○Sayuri Shimada,[1] Ryo Ishikawa,[1] Kazuki Yanagida,[1] Yue Ma,[2] Shogo Sasaki,[1] Kazuo Nagasawa,[1] Masayuki Tera[1]

G-quadruplexes (G4s) are higher order nucleic acid structures associated with diverse biological functions. Their topology, offering characteristic grooves on the G4 structure, is involved with diverse biological effects. We have synthesized L2H2-6OTD-Bp (**1**), a ligand combining a G-quartet binder with an alkylamine groove binder and a benzophenone (Bp) photo-crosslinking group. This design allows dual recognition, targeting the G-quartet and groove for topology selective photo-crosslinking. Thiazole orange assays confirmed non-covalent binding of **1** to hybrid and parallel G4s. Photo-crosslinking studies showed that **1** selectively crosslinked with hybrid-type G4s.
Keywords : G-quadruplexes, G-quartet, groove, topology selective

【目的】G-quadruplex(G4)は核酸の一本鎖領域で形成される特殊な高次構造であり、様々な生物学的機能に関与することが示唆されている [1]。G4 は共通構造である G-quartet とそれを繋ぐループによって構成されており、その側面に位置する groove の形は、個々の G4 構造(トポロジー)を特徴付けている。G4 は配列によって生命現象に与える影響が異なるため [2]、トポロジー選択的に G4 と結合するリガンドの創製が求められている。そこで、G4 の G-quartet と groove の二点で認識するトポロジー選択的な光架橋を目的とし、G-quartet binder である L2H2-6OTD に DNA groove binder であるアルキルアミンを導入し、その先に光架橋基であるベンゾフェノン(Bp)を導入した L2H2-6OTD-Bp (**1**)を合成した(Fig. 1a)。

【結果・考察】**1** の G-quartet に対する相互作用能を評価するために、チアゾールオレンジの追い出し実験を行った。その結果、**1** は、ハイブリッド型およびパラレル型のどちらのトポロジーに対しても G-quartet に結合することがわかった。次に、光照射による G4 と **1** との架橋効率を評価するために、変性ゲル電気泳動を行った。その結果、**1** はハイブリッド型 G4 と選択的に光架橋することがわかった。以上から、**1** はトポロジー非特異的に結合するが、ハイブリッド型 G4 とのみ光架橋することがわかった(Fig. 1b)。**1** が G4 と架橋した位置を特定する為に、複合体のエキソヌクレアーゼによる分解実験を行ったところ、**1** はハイブリッド型 G4 の広い groove に位置する塩基と選択的に光架橋することがわかった。

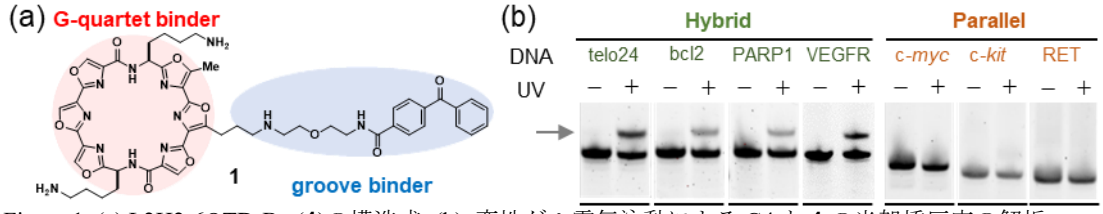

Figure 1. (a) L2H2-6OTD-Bp (**1**)の構造式. (b) 変性ゲル電気泳動による G4 と **1** の光架橋反応の解析.

【Reference】1) J. Robinson, F. Raguseo, S. P. Nuccio, D. Liano, M. Di Antonio, *Nucleic Acids Res.* **2021**, *49*, 8419–8431. 2) S. Takahashi, A. Kotar, H. Tateishi-Karimata, S. Bhowmik, Z. F. Wang, T. C. Chang, S. Sato, S. Takenaka, J. Plavec, N. Sugimoto, *J. Am. Chem. Soc.* **2021**, *143*, 16458–16469.

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大環状ヘキサオキサゾール型 G4 リガンド類による液滴内での化学反応評価

（東農工大院工[1]・甲南大 FIRST[2]）○大山 彩[1]・佐々木 捷悟[1]・三好 大輔[2]・寺 正行[1]・長澤 和夫[1]

Evaluation of chemical reactions in droplets with macrocyclic hexaoxazole-type G-quadruplex ligands ([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology,* [2]*Graduate School of Faculty of Frontiers of Innovative Research in Science and Technology, Konan University*) ○Akari Oyama,[1] Shogo Sasaki,[1] Daisuke Miyoshi,[2] Masayuki Tera,[1] Kazuo Nagasawa[1]

The droplet of LLPS would act as a spatiotemporally controlled chemical reaction space. However, the effect of reaction acceleration inside the droplet at the molecular level is not clear. In this study, we investigated the acetylation of RGG peptides in droplets using F2-6OTD-TE (**1**) in LLPS formed by $[G_4C_2]_4$ and RGG peptides. First, by adding F2-6OTD-FL (**2**) to the droplet, we confirmed that **2** was incorporated into the droplet without breaking the droplet. Then the acetylation reaction of RGG peptide by **1** was examined. By monitoring the reaction with MALDI-TOF MS analysis, we confirmed that the acetyl group transfer reaction proceeded only under the LLPS formation conditions.

Keywords : liquid-liquid phase separation; G-quadruplex; macrocyclic hexaoxazoles; RGG peptide; G4 ligand

【目的】細胞内では、タンパク質や核酸が局所的に集合することで液-液相分離 (LLPS) が進行し、液滴を形成する。例えば、ゲノム中に存在するグアニン四重鎖 (G4) とヒストン H1 は液滴を形成することで、核内のクロマチン凝集を調節し、転写制御に関わることが示唆されている[1]。このように液滴内では、局所高濃度化により、希薄条件よりも高い反応速度で生体分子の化学反応が進行し得ると考えられているが、分子レベルでの液滴内部での反応加速効果は明らかになっていない。そこで本研究では、G4 形成配列である$[G_4C_2]_4$と、G4 と相互作用する RGG ペプチドにより形成される LLPS[2] において、低分子化合物を用い化学反応の加速効果を実験化学的に検証することを目的とした。具体的には、G4 リガンドである大環状ヘキサオキサゾール (6OTD)[3]にアセチル基供与体を導入した F2-6OTD-TE (**1**) を用い、液滴内に存在する RGG ペプチドのアセチル化反応について検討した。

【実験・結果】液滴内での化学反応の加速効果を確かめるには、LLPS を壊すことなく液滴内に取り込まれる低分子化合物が必要である。そこで、当研究室で開発した G4 リガンドである F2-6OTD に着目し、これに蛍光基を導入した F2-6OTD-FL (**2**; Figure 1) を液滴に添加した。その結果、液滴内に **2** 由来の蛍光が蓄積する様子が観察され、F2-6OTD が液滴を壊さずに液滴内に取り込まれることが分かった。そこで F2-6OTD にアセチル基供与体を導入した F2-6OTD-TE (**1**) を合成した (Figure 1)。ついで、LLPS 条件下および非 LLPS 条件下における **1** から RGG ペプチドへのアセチル基転移反応について、MALDI-TOF MS により追跡した。その結果、LLPS 条件下でアセチル基の転移反応の進行が確認された。この際アセチル化反応は、RGG ペプチド鎖の 1 箇所で進行した。一方、非 LLPS 条件下では、アセチル基の転移反応は確認されなかった。

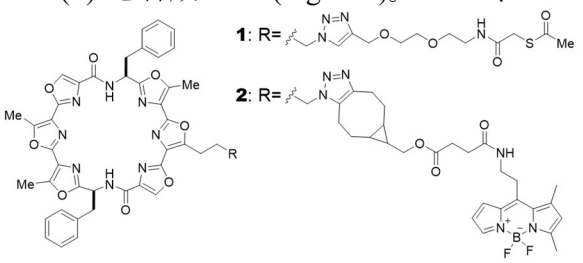

Figure 1. F2-6OTD-TE (**1**) およびF2-6OTD-FL (**2**) の構造

【References】1) R. Kurita *et al.*, *J. Am. Chem. Soc*., **2021**, *143*, 9849-9857; 2) D. Miyoshi *et al*., C*hem. Commun*., **2022**, *58*, 12931-12934; 3) K. Nagasawa *et al.*, *Angew. Chem. Int. Ed*., **2008**, *47*, 5557.

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クリックケミストリーを用いたトポロジー選択的な G4 リガンドの合成研究

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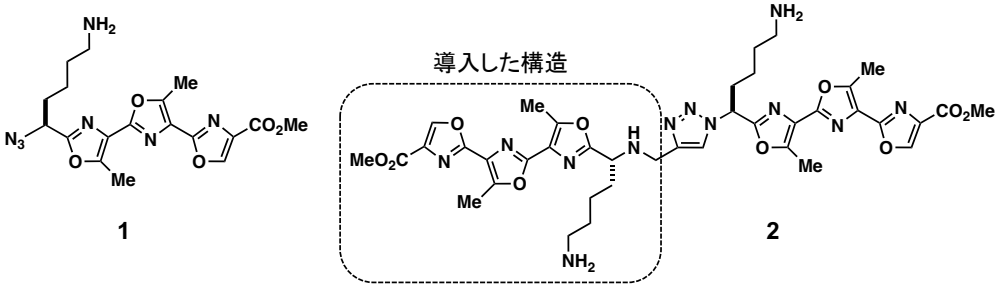
Synthetic studies of topology selective G4 ligands using click chemistry ([1]*Graduate school of Engineering, Tokyo University of Agriculture and Technology*, [2]*Research Core, Tokyo Medical and Dental University*) ○Yuri Shimasawa,[1] Shogo Sasaki,[1] Yue Ma,[2] Masayuki Tera,[1] Kazuo Nagasawa[1]

G-quadruplexes (G4s) are higher-order structures that exist genome-wide *in vivo* and are associated with various biological phenomena. In this study, we investigated the synthesis of topology-selective G4 ligands based on the trioxazole structure previously reported to recognize the G-quartet plain by our group. By the Huisgen cycloaddition reaction of azides **1** with various alkynes, which were supposed to interact with groove moiety in G4, a series of linear type compounds with trioxazoles were synthesized. Among them, the linear hexaoxazole **2** was realized to selectively stabilize the *c-kit* G4 by FRET melting analysis.

Keywords： G-quadruplex; Huisgen cycloaddition reaction; trioxazoles; c-kit G4

【目的】グアニン四重鎖 (G4) は、生体内でゲノムワイドに存在する核酸の高次構造であり、その形成配列に応じて多様な生命現象に関与している。また G4 は、塩基配列や周囲の環境に応じて固有のトポロジーを形成する [1)]。そのため、生体内における G4 の生物学的機能を理解するためには、G4 の各トポロジーを選択的に区別する手法が必要である。最近当研究室では、鎖状型ヘキサオキサゾール化合物が、G4 の G-quartet 平面と G4 固有の groove の二点を認識し、テロメア配列で形成する G4 をアンチパラレル型に制御することを見出している [2)]。そこで本研究では、トリオキサゾール構造に groove との相互作用が期待できる種々の構造を導入することで、トポロジー選択的なリガンドの創製を目的とし、以下の検討を行った。

【実験・結果】G-quartet 平面と相互作用することを確認しているトリオキサゾール構造にアジド基を導入した **1** に対し、G4 の groove との相互作用が期待される種々の構造を有するアルキン類を、それぞれ Huisgen 環化反応により結合させ、新規鎖状化合物群を合成した。合成した化合物類の種々 G4 に対する安定化能を FRET 融解実験により評価したところ、**1** のアジド基にトリオキサゾールを導入した鎖状化合物 **2** がパラレル型 G4 を形成する *c-kit* 配列を選択的に安定化することを見出した。



1 **2**

【References】1) D. Rhodes *et al.*, *Nucleic Acids Res.*, **2015**, *43*, 8627; 2) K. Nagasawa *et al.*, *RSC Adv.,* **2020,** *10*, 43319.

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グアニン四重鎖のトポロジー選択的かつ動的な検出を目的としたライトアップ型蛍光リガンドの創製

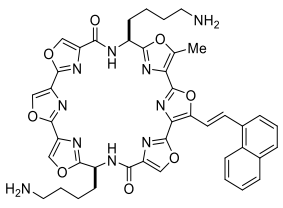
（東農工大院工[1]・医科歯科大 RCC[2]）○藤田 春希[1]・綿谷 成恭[1]・佐々木 捷悟[1]・馬 悦[2]・寺 正行[1]・長澤 和夫[1]
Synthesis of light-up type fluorescent ligands for topology selective and dynamic detection of G-quadruplexes ([1]*Gladuate school of Engineering, Tokyo University of Agriculture and Technology,* [2]*Research Core, Tokyo Medical and Dental University)* ○ Haruki Fujita,[1] Naruyuki Watatani,[1] Shogo Sasaki,[1] Yue Ma,[2] Masayuki Tera,[1] Kazuo Nagasawa[1]

G-quadruplexes (G4) form in the guanine-rich single-strand regions of nucleic acids. G4s are known to form three different topologies and to be in a dynamic equilibrium state between formation and unwinding. In this study, we synthesized trioxazole compounds **2a**-**2g** as light-up type G4 ligands. Among them, **2f** was suggested to be suitable to follow the dynamic formation of G4, especially for the parallel-type topology.
Keywords : G-quadruplex, light-up type ligands, polyoxazole compounds, telomeric G4

【目的】核酸の一本鎖領域では、グアニン四重鎖 (G4) と呼ばれる特殊な高次構造が形成される。生体内において G4 は、動的な形成・崩壊によって生命現象を制御している[1]。そのため、G4 由来の生命現象を理解するためには、G4 を選択的かつ動的に観察する手法が必要である。当研究室では大環状型ヘキサオキサゾール (6OTD) 類を基盤とし、G4 と相互作用することで蛍光を発するライトアップ型 G4 リガンド 6OTD-VN (**1**) を報告している (Figure 1a)[2]。しかし **1** は G4 との相互作用が極めて強力なため、G4 の動的挙動を観察することが困難である。そこで本研究では、動的な G4 形成を観察可能なリガンドの創製を目的とし、新規トリオキサゾール型 G4 リガンドの開発を行った。

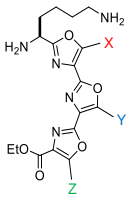
【結果】トリオキサゾール骨格 **2** に対して、ビニルナフチル基を系統的に導入した **2a**-**2g** を合成し、テロメア G4 との相互作用解析を行った (Figure 1b)。その結果、いずれのリガンドも G4 の添加により蛍光強度の増大が確認され、**1** と同様ライトアップ型の G4 リガンドであることが示唆された。その中で **2f** は、高い蛍光強度に加えて G4 配列間での選択性が見られた。そこで、**2f** に対して種々G4 配列を添加したところ、**2f** は三つのトポロジーのうち parallel 型 G4 に対して最も強い蛍光を示すことが分かった。さらに、本条件において相補鎖を添加し、G4 の動的構造変化に応じた **2f** の蛍光特性の挙動を観測したところ、G4 の巻き戻しに応じて **2f** の蛍光の速やかな減少が観測された。

(a)



1

(b)



2

	X	Y	Z
2a	VN	H	H
2b	H	VN	H
2c	H	H	VN
2d	VN	VN	H
2e	VN	H	VN
2f	H	VN	VN
2g	VN	VN	VN

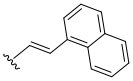
VN: 

Figure 1. (a) 6OTD-VN (**1**) の構造, (b) トリオキサゾール骨格 **2** および **2a-2g** の構造

【Reference】1) R. B. Macgregor, *et al.*, *Biophys. Chem.*, **2020**, 267, 106473.; 2) K. Nagasawa, *et al.*, *Org. Biomol. Chem.,* **2021**, *19,* 8035.

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グアニン四重鎖（G4 リガンド）としての新規大環状ピリドンペンタマーの開発

（千葉大院理）○磯部 えみな・荒井 孝義・飯田 圭介
Novel macrocyclic pyridone pentamers as G-quadruplex (G4) ligands (*Graduate School of Science, Chiba University*) ○Emina Isobe, Takayoshi Arai, Keisuke Iida

G-quadruplex (G4) is one of the higher order structures of nucleic acids formed in guanine-rich sequences. More than 700,000 G4-forming sequences have been identified throughout the human genome, and their sequences are concentrated in gene promoters.[1] Therefore, G4s are believed to play some significant roles in biological processes including gene expression. G4 binding compounds, called G4 ligands, can stabilize G4s and regulate cellular function. In this study, we synthesized novel macrocyclic pyridone pentamers as G4 ligands and evaluated G4 binding ability. Macrocyclic pyridone pentamers have been reported to have high planarity and high affinity for metal ions.[2] Ligand **1** is a macrocyclic pyridone pentamer with hydroxy ethyl side chains and an amino side chain bearing azide functionality. FRET melting assay revealed that **1** has high G4-selective stabilizing ability. Moreover, CD spectroscopy showed that **1** specifically stabilizes G4 in the presence of K^+ and Cs^+.
Keywords : G-quadruplex; G4; G4 ligand; Macrocyclic Pentamer; Pyridone

グアニン四重鎖 (G4) は、グアニン豊富な配列において形成される特殊な核酸の高次構造である。G4 を形成する配列はゲノム上において 70 万配列以上同定されており、さらに遺伝子のプロモーターに濃縮されていることが知られている [1]。そのため G4 は、遺伝子発現をはじめとした様々な生命現象に関与すると考えられている。また、ある種の化合物 (G4 リガンド) が、G4 の構造を安定化することで核酸とタンパク質の相互作用を阻害し生体機能の発現を調節することも明らかとなっている。本研究では、高い平面性を有し、金属イオンに対し高い親和性を示すことが報告されている大環状ピリドンペンタマーを種々合成し [2]、G4 との相互作用を評価した。FRET 融解実験により、アルコール側鎖と、末端がアジド基のアミン側鎖を含む Ligand **1** は、G4 選択的な高い安定化能を有することが確認できた。また CD スペクトル測定により、**1** は K^+と Cs^+存在下で特異的に G4 を安定化していることが明らかになった。

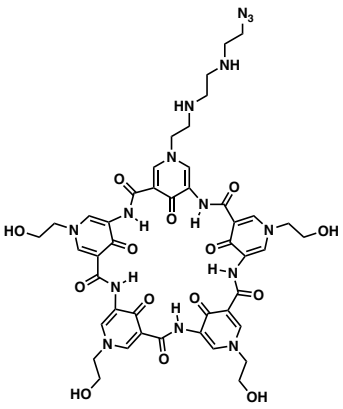

Fig 1. Structure of G4 ligand **1**

1) D. Varshney, J. Spiegel, K. Zyner, D. Tannahill, S. Balasubramanian, *Nat. Rev. Mol. Cell Biol.* **2020**, *21*, 459-474.
2) Z. Du, C. Ren, R. Ye, J. Shen, V. Maurizot, Y. Lu, J. Wang, H. Zeng, *Chem. Commun.* **2011**, *47*, 12488-12490.

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日本化学会 第104春季年会 (2024)

アニオン性フタロシアニンによる四重鎖 DNA の光分解機構

（筑波大院化[1]・筑波大化[2]）○百武 篤也[1]・小田原 佑典[2]・山本 泰彦[1]

Photo-decomposition Mechanism of Quadruplex DNA Using an Anionic Phthalocyanine

([1]*Department of Chemistry, University of Tsukuba,* [2]*Graduate School of Science and Technology, University of Tsukuba*)
○Atsuya Momotake,[1] Yusuke Odahara,[2] Yasuhiko Yamamoto[1]

The photo-decomposition of quadruplex DNA by a zinc(II) phthalocyanine with four carboxylic acid groups as side chains (ZnTCPc) has been investigated. We found that red-light irradiation to a mixture of ZnPc and a quadruplex DNA leads to the photodegradation of the DNA. We also found that generation of singlet oxygen ($^1O_2$) and hydroxyl radical (•OH) from photoexcited ZnPc is dramatically enhanced upon binding to a quadruplex DNA. Since DNA incapable of binding to ZnPc to form a 1:1 complex is not photodecomposed by photoexcited ZnPc, the formation of the complex is likely to play a crucial role in the DNA photodegradation.
Keywords : G-quadruplex DNA; Anionic phthalocyanine; Molecular recognition; Photosensitizer

グアニン豊富な DNA 塩基配列は、カリウムイオンなどのカチオンの存在下で、4 つのグアニン塩基が同一平面内に Hoogsteen 型水素結合を介して環状に連結し、G-カルテット（Fig. 1A）を形成することにより、四重鎖 DNA となることがある（D. Sen and W. Gilbert, Nature, *334*, 364-366 (1988)）。本研究では、光増感剤として期待されるアニオン性亜鉛フタロシアニン誘導体（ZnTCPc, Fig. 1B）と四重鎖 DNA の相互作用及び、ZnTCPc 存在下における光照射(680 nm)による四重鎖 DNA の光分解反応を解析した。光増感剤 ZnTCPc と DNA の相互作用とそれに続く DNA の光分解反応の解明は、光線力学的療法（PDT）の初期過程を分子レベルで理解するために有用であると考えられる。

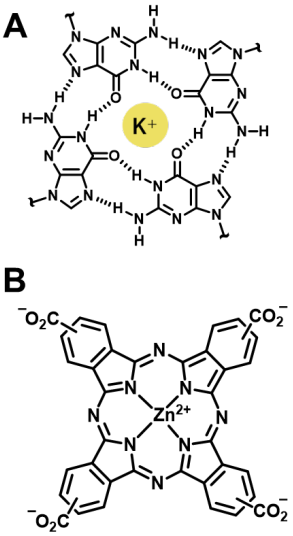

Fig. 1 Molecular structures of G-quartet (A) and ZnTCPc (B).

塩基配列 d(TTAGGG) が形成する四重鎖 DNA $[d(TTAGGG)]_4$ と ZnTCPc の混合水溶液に対して光照射したところ、四重鎖 DNA の分解が起こることが明らかになった。ZnTCPc は、単独では水溶液中で凝集するため、自己消光により失活するが、四重鎖 DNA に結合して複合体を形成すると、光照射下での一重項酸素やヒドロキシラジカルの発生量が顕著に増加した。一方、ZnTCPc と複合体を形成しない DNA の場合は、光分解は認められなかった。これらの結果は、ZnTCPc と DNA の複合体の形成が、ZnTCPc への光照射による DNA の分解に重要であることを示している。

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Investigation of pull-down unit position for large-scale analysis of RNA alkylation

(1. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2. Department of Chemistry, Graduate School of Science, Tohoku University, 3. CiRA, Kyoto University) ○Ping-Yun Lan[1,2], Kazumitsu Onizuka[1,2], Yutong Chen[1,2], Emi Miyashita[3], Kaoru R. Komatsu[3], Hirohide Saito[3], Fumi Nagatsugi[1,2]

Keywords: RNA, Alkylation, Pull-down, Large scale analysis

RNA alkylation by small molecules, which can covalently modify RNA targets, are effective to interfere the RNA biological functions. Previously, our group developed an RNA alkylator vinyl-quinazolinone (VQ) derivative with dimethylamine (NMe_2) as a leaving group.[1)] The VQ-NMe_2 is in equilibrium with reactive VQ, and VQ efficiently reacts with the U base in RNA (Fig. 1A). The VQ-NMe_2 was further applied to the large-scale analysis that enable thousands of sequences to be investigated in a single experiment for finding the true selectivity and potential targets of the alkylator. This approach was achieved by N_3-modified VQ, RNA structure library[2)] contained 3000 kinds of RNA structures and microarray analysis (Figs. 1A and 1B).

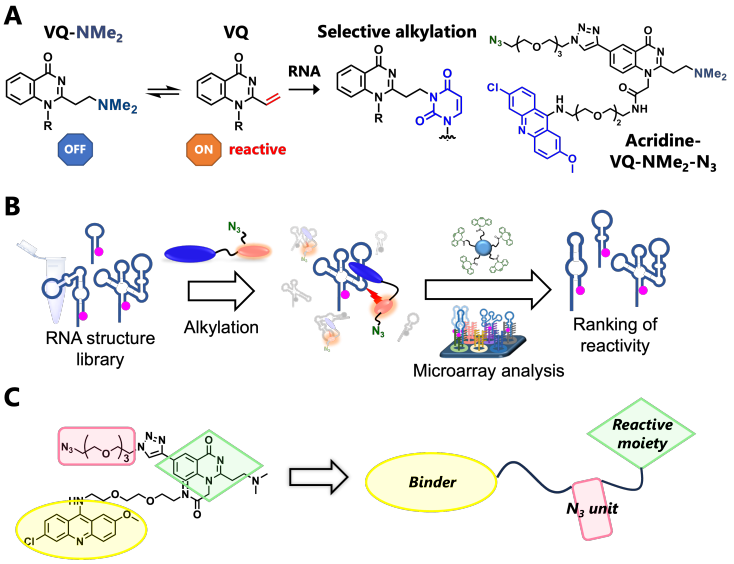

Fig. 1 (A) Alkylation by reactive VQ moiety. (B) Concept of large-scale analysis of RNA alkylation. (C) Molecular design of alkylator with new pull-down unit position.

In this study, we designed the new compounds with the N_3 pull-down unit at the linker that connects VQ and RNA binder (Fig. 1C). This new design can simplify the synthesis and is easily applicable to different reactive moieties. We synthesized VQ-acridine conjugate with the N_3 pull-down unit at the linker and investigated the alkylation and pull-down abilities. Furthermore, we performed large scale analysis of RNA alkylation and the validation. These detailed results will be reported in the presentation.

1) Y. Chen, K. Onizuka, M. E. Hazemi, F. Nagatsugi, *Bioconjugate Chem.* **2022**, 33, 2097–2102.
2) K. R. Komatsu, T. Taya, S. Matsumoto, E. Miyashita, S. Kashida, H. Saito, *Nat. Commun.* **2020**, 11, 6275.

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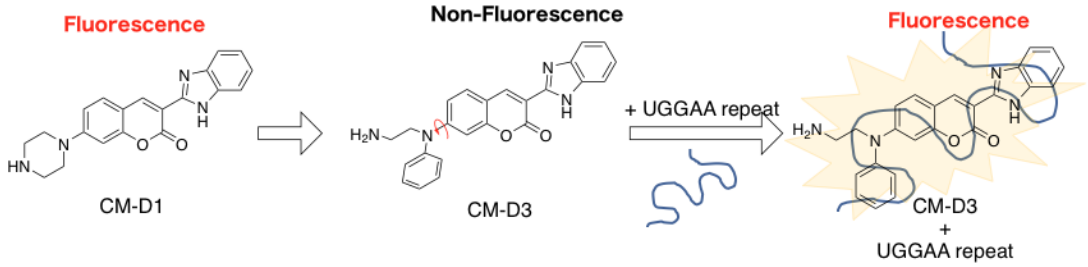
UGGAA リピートを標的とした Turn-ON 型蛍光プローブの合成と評価

（阪大産研 [1]）○原田 祥英 [1]・柴田 知範 [1]・中谷 和彦 [1]
Synthesis and evaluation of a turn-on fluorescent probe targeting UGGAA repeats ([1]*SANKEN, Osaka University*) ○Shoei Harada,[1] Tomonori Shibata,[1] Kazuhiko Nakatani[1]

Spinocerebellar ataxia type 31 is a hereditary neurodegenerative disease caused by the insertion of an abnormally expanded TGGAA repeats. UGGAA repeats, which are transcription products, capture RNA-binding proteins in cells and form RNA aggregates. In this study, we decided to synthesize and evaluate Turn-ON type fluorescent probes targeting UGGAA repeats for visualizing intracellular UGGAA repeat RNA aggregates. Based on the fluorescent CM-D1 molecule binding to the UGGAA repeat discovered in our laboratory,[1)] we designed and synthesized CM-D3 which emits fluorescence by inhibiting intramolecular twisting motion[2)] upon ligand binding to the UGGAA repeat. We report synthesis of CM-D3 and its fluorescent properties upon binding to UGGAA repeat RNA.
Keywords : Spinocerebellar ataxia type 31; repeat RNA; RNA-targeted small molecules; Fluorescence probes

脊髄小脳失調症 31 型は異常伸長した TGGAA リピートの挿入が原因で発症する遺伝性神経変性疾患である。転写産物である UGGAA リピートは、細胞内の RNA 結合タンパク質を捕捉し、RNA 凝集体を形成する。本研究では細胞内の UGGAA リピート RNA 凝集体の可視化を目的とし、UGGAA リピートを標的とした Turn-ON 型蛍光プローブの合成と評価を行うこととした。当研究室で発見した UGGAA リピートに結合する蛍光分子である CM-D1[1)]を基に、UGGAA リピートへのリガンド結合により分子内のねじれ運動を抑制することで蛍光を発する [2)]CM-D3 という分子の設計と合成を行なった。本発表では、CM-D3 の合成及び UGGAA リピート結合時における蛍光特性について報告する。



1) T. Shibata, Y. Matsumoto, A. Iihara, K. Yamada, H. Ochiai, R. Saito, S. Kusaka, T. Kume *Chem. Commun.* **2023**, *59*, 5071
2) K. Hanaoka, S. Iwaki, K. Yagi, T. Myochin, T. Ikeno, H. Ohno, E. sasaki, T. Komatsu, T. Ueno, M. Uchigashima, T. Mikuni, K. Tainaka, S. Tahara, S. Takeuchi, T.Tahara, M. Uchiyama, T. Nagano, Y Urano *J. Am. Chem. Soc.* **2022**, *144*, 19778-19790

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TERRA の転写制御における G4 結合タンパク質 EWS の解析

（静大院理[1]・静大院創造[2]・静大グリーン研[3]）○松平 和佳奈[1]・Luthfi Lulul Ulum[2]・石原 顕紀[1]・大吉 崇文[1,2,3]

Analysis of G-quadruplex Binding protein of EWS for Transcriptional Regulation of TERRA

([1]Graduate School of Integrated Science and Technology, Shizuoka University, [2]Graduate School of Science and Technology, Shizuoka University, [3]Research Institute of Green Science and Technology, Shizuoka University) ○Wakana Matsudaira[1], Luthfi Lulul Ulum[2], Akinori Ishihara[1], Takanori Oyoshi[1,2,3]

The telomere region is composed of G-quadruplex (G4DNA) and G4RNA formed by Telomeric Repeat-containing RNA (TERRA)[1,2]. G4RNA in particular promotes heterochromatinization of the telomere region and suppresses cell canceration. However, the transcriptional regulatory mechanism of TERRA is still unclear. In this study, we aim to elucidate the transcriptional regulation mechanism of TERRA by Ewing Sarcoma (EWS), a G4-binding protein. We found that EWS increases the transcriptional level of TERRA. Furthermore, the RGG region of EWS was found to bind competitively to G4DNA and G4RNA. The effect of this binding on transcription was investigated, and it was found that the transcriptional regulatory mechanism of TERRA by EWS represses transcription by negative feedback via transcribed G4RNA (Figure 1).

Keywords : G-quadruplex; G-quadruplex binding protein; Telomere; Histone modification; Transcriptional regulation

テロメア領域はグアニン四重鎖 (G4DNA) と、Telomeric Repeat-containing RNA(TERRA)が形成する G4RNA から構成されており、特に TERRA がテロメア領域のヘテロクロマチン化を促進して細胞のがん化を抑制する[1,2]。しかし、TERRA の転写制御機構は不明な点が多い。本研究において、G4 結合タンパク質である Ewing Sarcoma(EWS)の TERRA の転写制御機構の解明を目的とする。EWS は TERRA の転写量を増加させることが分かった。さらに、EWS の RGG 領域は G4DNA と G4RNA に対して競合的に結合することが分かった。この結合性が転写に及ぼす影響を調べた結果、EWS による TERRA の転写制御機構は、転写された G4RNA を介した負のフィードバックによって転写を抑制することが分かった（図 1）。

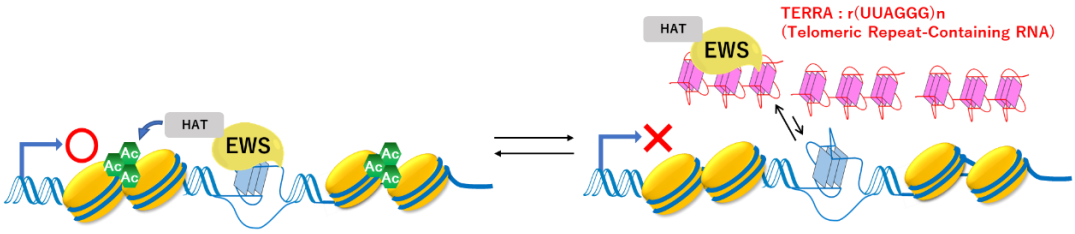

図 1：TERRA の転写制御機構における G4RNA による負のフィードバック

1)*J. Am. Chem. Soc. 2009, 131, 4301-4309.* 2)*FEBS J. 2011, 278, 988-998.*

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転写を制御する機能性 G4DNA 結合タンパク質の開発

(静大理[1]・静大院理[2]・静大院創造[3]・静大グリーン研[4]) ○柴田 奈津希[1]・山梨 舞子[2]・Luthfi Lulul Ulum[3]・石原 顕紀[2]・大吉 崇文[1,2,3,4]
Development of the functional G4 DNA binding protein regulating transcription ([1]*Faculty of Science Shizuoka University*, [2]*Graduate School of Integrated Science and Technology, Shizuoka University*, [3]*Graduate School of Science and Technology, Shizuoka University*, [4]*Research Institute of Green Science and Technology, Shizuoka University*) ○ Natsuki Shibata,[1] Maiko Yamanashi,[2] Luthfi Lulul Ulum,[3] Akinori Ishihara,[2] Takanori Oyoshi[1,2,3,4]

G-quadruplex (G4) DNA and RNA, formed by guanine-rich sequences, are abundant in the telomere region and are involved in the oncogenesis of cells[1]. However, it is unclear how the transcription of TERRA, which is formed as G4RNA, from G4DNA is regulated. To elucidate this mechanism, it is necessary to develop functional proteins that can bind to G4DNA and regulate its transcription. In this study, we developed HAT-RGGF by fusing RGGF[2], a G4DNA binding protein developed in our laboratory, with a part of CBP that has HAT activity[3]. TERRA transcription from the telomere region was promoted by HAT-RGGF (Fig. 1). It indicates that the G4DNA-binding protein with histone-modifying ability can alter histone modifications in a G4DNA-dependent manner and regulate transcription of TEERA in the telomere region.
Keywords : G-quadruplex; G-quadruplex binding protein; Telomere; Histone modification; Transcriptional regulation

グアニン豊富な塩基配列が形成するグアニン四重鎖（G4）DNA や RNA はテロメア領域に多く存在し、細胞のがん化に関与している。しかし、G4DNA から G4RNA である TERRA の転写がどのように制御されているかは不明である[1]。この機構を解明するために、G4DNA に結合し、転写を制御できる機能性タンパク質の開発が必要であると考えられる。そこで本研究では、当研究室で開発した G4DNA 結合タンパク質である RGGF[2]に、ヒストンアセチル基転移酵素（HAT）活性を有する CBP の一部[3]を融合した HAT-RGGF を作成した。HAT-RGGF 存在下における細胞中の TERRA の転写量を調べたところ、非存在下と比較して、テロメア領域からの TERRA の転写は活性化された（図 1）。このことから、テロメア領域では G4DNA 結合性とヒストン修飾能を有するタンパク質が G4DNA 依存的にヒストン修飾を変化させ、TEERA の転写を制御することが分かった。

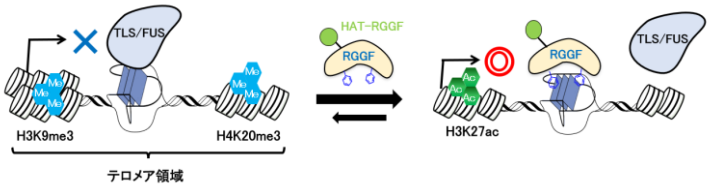

図 1. 機能性 G4 結合タンパク質による転写制御モデル

1) *Nucleic Acids Res*. **2007**, 35, 406-413　2) *Acs. Chem. Biol.* **2015**, 10, 2564-2569
3) *Nature*. **1996**, 384, 641–643

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

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC H934(934, Bldg. 9 [3F])

[H934-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Shun Hirota, Teruyuki Komatsu

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H934-4pm-01]
Preparation of an amyloid fibril with norbornene-type monomers and ring-opening metathesis polymerization on the fibril

○Hiroki Uchida[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H934-4pm-02]
Genetic Engineering of Acetolactate Synthase for Radical Coupling Reaction between α-Keto acid and α-Bromo ester

○Shuto Fujisawa[1], Shunsuke Kato[1], Takashi Hayashi[1] (1. Graduate School of Engineering, Osaka University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H934-4pm-03]
Modification of Cytochrome P450 Containing Co Porphyrin with a Photosensitizer toward an Artificial Metalloenzyme Catalyzing Photoinduced Carbon Dioxide Reduction

○Taishu Kojima[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H934-4pm-04]
Genetic and chemical modifications of a hexameric hemoprotein toward an artificial light harvesting system

○Shohei Katsumoto[1], Koji Oohora[1], Takashi Hayashi[1] (1. Osaka University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H934-4pm-05]
Construction of porous crystals with supramolecular structures using heme protein cyclic trimers

○Mizuho Kinuyama[1], Kodai Fujiwara[1], Tsuyoshi Mashima[1], Naoya Kobayashi[1], Hideaki Ogata[2], Shun Hirota[1] (1. NAIST, 2. University of Hyogo)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H934-4pm-06]
Construction of human cytochrome *c* dimer by hinge loop mutation and its intracellular effect

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○Kotori Ohta[1], Kodai Fuijwara[1], Tsuyoshi Mashima[1], Naoya Kobayashi[1], Kenichi Kanai[1], Takaaki Matsui[1], Yasumasa Bessho[1], Shun Hirota[1] (1. NAIST)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[H934-4pm-07]

Effects of ions on the formation and stability of cytochrome *c* dimers

○Kodai Fujiwara[1], Michiko Ryuuzaki[1], Masaru Yamanaka[1], Tsuyoshi Mashima[1], Naoya Kobayashi[1], Shun Hirota[1] (1. NAIST)

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

Break

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[H934-4pm-08]

Synthesis of Poly(2-alkyl-2-oxazoline)-Conjugated Serum Albumins

○Ryota Hattori[1], Junya Fujisawa[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H934-4pm-09]

Synthesis of Poly(2-alkyl-2-oxazoline)-Conjugated Hemoglobins as an Artificial O_2 Carrier

○Ryuhei Wakabayashi[1], Kota Ishii[1], Teruyuki Komatsu[1] (1. Chuo university)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H934-4pm-10]

Synthesis and Photosterilization Ability of Zinc-Phthalocyanine-Substituted Myoglobin-Albumin Fusion Protein

○Aoi Egawa[1], Mizuki Funamoto[1], Taiga Yamada[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[H934-4pm-11]

Synthesis of Polyoxazoline-Covered Hemoglobin Nanoparticle as an Artificial O_2 Carrier

○Tomoka Araki[1], Natsumi Kohyama[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[H934-4pm-12]

Nanopore formation and molecular transport of β-barrel porin

○Toshiyuki Tosaka[1], Koki Kamiya[1] (1. Grad. Sch. Sci. & Tech. Gunma Univ.)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[H934-4pm-13]

In silico panning of peptide ligands using docking simulation and molecular dynamics simulation

○Haruka Kawai[1], Daimei Miura[1], Sheng Tong[1], Ryutaro Asano[1], Tsugawa Wakako[1], Fujita Shoko[1], Ryuji Kawano[1], Takatsugu Hirokawa[2], Kaori Tsukakoshi[1], Kazunori Ikebukuro[1] (1. Tokyo

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University of Agriculture and Technology, 2. University of Tsukuba)

Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[H934-4pm-14]

Development of an oxidative protein folding promoter using host-guest interactions

○Koki Suzuki[1], Ryoya Nojiri[1], Tomohide Saio[2], Takahiro Muraoka[1,3] (1. Tokyo University of Agriculture and Technology, 2. Tokushima University, 3. KISTEC)

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ノルボルネン類縁体モノマーを提示したアミロイド線維と線維上における開環メタセシス重合

（阪大院工）○内田 浩基・大洞 光司・林 高史
Preparation of an amyloid fibril with norbornene-type monomers and ring-opening metathesis polymerization on the fibril (*Graduate School of Engineering, Osaka University*) ○Hiroki Uchida, Koji Oohora, Takashi Hayashi

In biological systems, molecular motors utilize chemical reactions and play important roles in molecular transport and other processes. Especially, a molecular motor moving on a linear track is called as a linear molecular motor. Artificial linear molecular motors driven by pH-changes or redox reaction have been investigated.[1] However, these molecular motors cannot control their back-and-forth movement. In this work, we designed a unidirectionally moving linear motor system by ring-opening metathesis polymerization (ROMP) of norbornene derivatives displayed onto an amyloid fibril as a linear track for a motor catalyst, because its driving force is a living polymerization reaction. After ROMP, mass spectrometry supports the formation of polymer on the fibril. Direct observation of the unidirectional movement of the catalyst is in progress.
Keywords : Molecular Motor; Ring-opening Metathesis Polymerization; Grubbs Catalyst; Amyloid Fibril; Peptide

分子モーターは化学反応を利用し、生体内物質輸送等の重要な役割を担っている。特に直線状に移動する分子モーターはリニア分子モーターと呼ばれており、pH 変化や酸化還元反応等を用いた人工リニア分子モーターの構築が試みられている [1)]。しかし、これらの系では平衡反応が利用されているため、モーター分子は単一方向に進行しない。本研究では Ru 触媒による開環メタセシス重合反応 (ROMP) を駆動力として直線的に Ru 触媒が移動する人工分子モーター系を設計した。この系ではリビング重合反応を駆動力とするため、一定方向に進行すると期待される（Fig.1）。

リニアモーター分子の土台部分として、ROMP の基質であるノルボルネン誘導体を修飾したアミロイド線維を調製した。さらに Ru 触媒を加え ROMP を行ったところ、重合体の形成が質量分析により示唆された。単一方向の Ru 触媒の移動の直接観察について、現在検討中である。

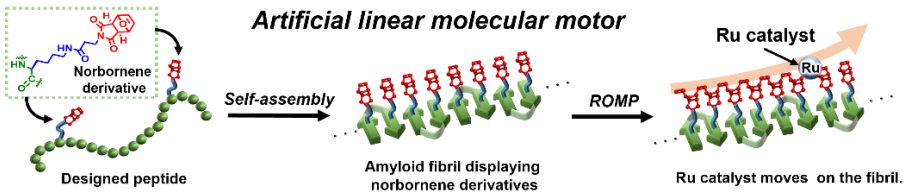

Fig. 1. Schematic representation of a linear molecular motor system based on ROMP.

1) J. F. Stoddart *et al.*, *J. Am. Chem. Soc.* **2013**, *135,* 18609–18620.

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α-ケト酸とα-ブロモエステルのラジカルカップリング反応を指向したアセト乳酸合成酵素の遺伝子工学的改変

（阪大院工）○藤沢 修斗・加藤 俊介・林 高史
Genetic Engineering of Acetolactate Synthase for Radical Coupling Reaction between α-Keto acid and α-Bromo ester (*Graduate School of Engineering, Osaka University*) ○ Shuto Fujisawa, Shunsuke Kato, Takashi Hayashi

Biocatalysis is emerging as a new method alternative to conventional chemo-catalysis for the production of sustainable chemical feedstocks. To expand the catalytic repertoire of enzymes, we here investigated a biocatalytic radical coupling reaction between α-keto acid and α-bromo ester using FAD/ThDP-dependent enzymes (Figure 1). It is supposed that the enzyme undergoes one-electron oxidation/reduction of Breslow intermediate and α-bromo ester, thereby realizing a challenging coupling reaction between these two radical species. Based on this hypothesis, various types of FAD/ThDP-dependent enzymes have been screened from genome database. As a result, an acetolactate synthase (ALS) from thermophilic actinomyces was found to catalyze the target coupling reaction between α-keto acid and α-bromo ester. Furthermore, genetic engineering based on docking simulation has afforded enzyme variants with increased catalytic activity.
Keywords : Biocatalysis; Acetolactate synthase; N-heterocyclic carbene; Radical reaction;

持続可能社会の実現にむけた新たな物質生産プロセスとして、近年、酵素や微生物等の生体触媒を用いた化学反応に注目が集まっている[1]。本研究では、これら生体触媒の反応適用範囲を非天然の化学反応へと拡張するために、FAD/ThDP 依存性酵素を用いたα-ケト酸とα-ブロモエステルのラジカルカップリング反応を実施した（Figure 1）。酵素内で ThDP とα-ケト酸から生成する Breslow 中間体とα-ブロモエステルを、FAD により選択的に一電子酸化・還元することで、二種のラジカル種のカップリング反応が進行することが期待される。この仮説に基づき種々の FAD/ThDP 依存性酵素をスクリーニングした結果、好熱性放線菌由来のアセト乳酸合成酵素（ALS）が、本反応において有望な触媒活性を示すことを見出した。さらに、基質と酵素に対するドッキングシミュレーションに基づく遺伝子工学的改変を実施することで、その触媒活性が向上することを明らかにした。

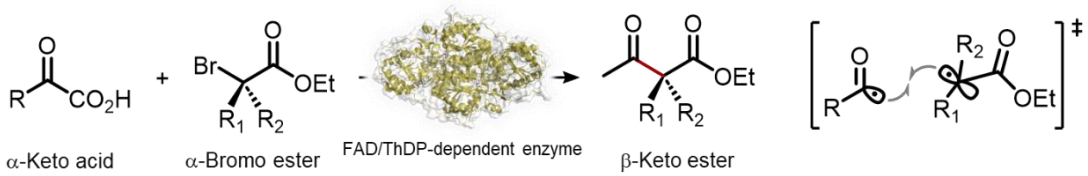

Figure 1. ピルビン酸とα-ブロモエステルのラジカルカップリング反応

1) K. Chen, F. Arnold, *Nat. Catal.* **2020,** *3,* 203-213.

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二酸化炭素の光還元触媒を指向した Co ポルフィリンを有する再構成シトクロム P450 への光増感色素への化学修飾

（阪大院工）○小島　大周・大洞　光司・林　高史

Modification of Cytochrome P450 Containing Co Porphyrin with a Photosensitizer toward an Artificial Metalloenzyme Catalyzing Photoinduced Carbon Dioxide Reduction. (*Graduate School of Engineering, Osaka University*) ○Taishu Kojima, Koji Oohora, Takashi Hayashi

Photoinduced reduction of carbon dioxide is an important research topic to realize sustainable society. In this study, we attempt to construct an artificial metalloenzyme for carbon dioxide reduction by a photosensitizer-tethering cytochrome P450BM3 reconstituted with Co porphyrin. The photoinduced electron transfer from the photosensitizer to Co porphyrin through the electron transfer pathway of cytochrome P450 is expected to generate a low-valent active species. In addition, the inherent electron and proton transfer pathways in the protein are hypothesized to enhance the efficiency of carbon dioxide reduction. We will present preparation and characterization of the artificial metalloenzyme as well as evaluation of the catalytic activity.

Keywords : Photoreduction Reaction; Artificial Enzyme; Hemoprotein; Ru Complex

二酸化炭素の光還元は、持続可能な社会の実現に向けた重要な課題である。本研究では、光により二酸化炭素を還元する人工金属酵素の構築を指向した。一原子酸素添加酵素であるシトクロム P450 は補酵素であるヘムにプロトンおよび電子を伝達する経路を有している。Cheruzel らの先行研究では、シトクロム P450BM3 への光増感剤の化学修飾により、可視光照射による光増感剤からヘムへの電子移動と、続く酸素添加反応を達成している [1)]。本研究では、二酸化炭素の光還元に向けて、光増感剤を修飾したシトクロム P450BM3 のヘムをコバルトプロトポルフィリン（CoPP）に置換した再構成体を設計した(Fig. 1)。この系では、光を使用した CoPP の還元による低原子価種の生成とタンパク質構造に起因した活性中心への電子・プロトン伝達により、効率的な二酸化炭素の還元反応が期待できる。本発表では人工金属酵素の調製・同定および二酸化炭素還元反応への活性評価について報告する。

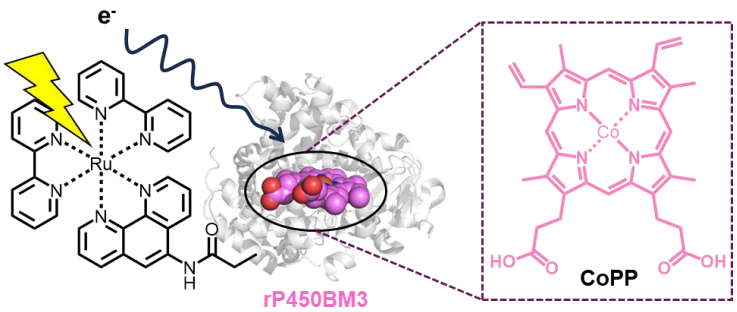

Fig. 1. Schematic representation of Ru photosensitizer-attached cytochrome P450BM3 reconstituted with CoPP

1) L. E. Cheruzel *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 14484.

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日本化学会 第104春季年会 (2024)

人工光捕集系を指向した六量体ヘムタンパク質の遺伝子工学的改変および化学修飾

（阪大院工）○勝本 照平・大洞 光司・林 高史

Genetic and Chemical Modifications of a Hexameric Hemoprotein toward an Artificial Light Harvesting System (*Graduate School of Engineering, Osaka University*) ○Shohei Katsumoto, Koji Oohora, Takashi Hayashi

Construction of artificial photosynthesis systems has a great potential to solve global energy problems, and various approaches using a wide range of materials are being considered to generate such systems. Our group has previously demonstrated an artificial light harvesting system using a hexameric hemoprotein, HTHP, as a building unit toward artificial photosynthesis.[1] In this work, we attempt to construct a large-scale artificial light harvesting system tethering a charge separation moiety. A maleimide-tethering water-soluble Sn porphyrin derivative was designed to generate a long-lifetime triplet excited state for efficient charge separation. The Sn porphyrin derivative with a maleimide group was synthesized and introduced to an HTHP mutant. The modified protein was identified by mass spectrometry. Toward a large assembly of HTHP, a self-assembling peptide was genetically attached onto each subunit of HTHP. The formation of the assembly was preliminarily confirmed by dynamic light scattering.

Keywords : Porphyrin; Artificial Photosynthesis; Energy Migration; Hemoprotein; Protein Assembly

人工光合成はエネルギー問題を解決するクリーンな手法として注目されている。我々はヘムタンパク質六量体（HTHP）のヘムを光増感剤に置換した再構成 HTHP が人工光捕集系として機能することを報告している [1)]。本研究では、人工光合成系への展開に向けて、三重項励起状態を効率よく生成する水溶性スズポルフィリンを修飾した HTHP 集合体の構築をめざしている。マレイミド基を有する水溶性スズポルフィリンを設計、合成し、HTHP 変異体への修飾を実施した（Fig. 1）。得られた修飾タンパク質は質量分析により同定した。また、巨大人工光捕集系の構築をめざし、遺伝子工学的に自己組織化ペプチドを連結した HTHP を設計、調製した。集合体の形成を、動的光散乱法を用いて予備的に確認した。今後さらなる構造評価について原子間力顕微鏡を用いて実施する予定である。

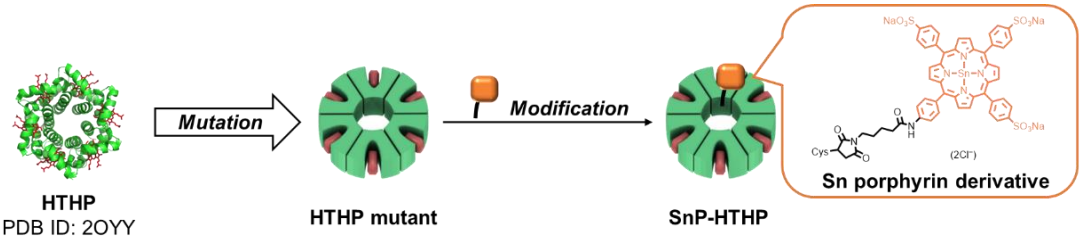

Fig. 1. Modification of an HTHP mutant with an Sn porphyrin derivative.

1) S. Hirayama, K. Oohora, T. Uchihashi, T. Hayashi, *J. Am. Chem. Soc.* **2020**, *142,* 1822–1831.

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ヘムタンパク質の環状 3 量体を利用した超分子構造の多孔質結晶の構築

（奈良先端大先端科技[1]・兵庫県大院理[2]）○絹山 瑞歩[1]・藤原 綱大[1]・真島 剛史[1]・小林 直也[1]・緒方 英明[2]・廣田 俊[1]

Construction of porous crystals with supramolecular structures using heme protein cyclic trimers ([1]*Grad. Sch. Sci. Tech., NAIST,* [2]*Grad. Sch. Sci., Uni. Hyogo*) ○Mizuho Kinuyama[1], Kodai Fujiwara[1], Tsuyoshi Mashima[1], Naoya Kobayshi[1], Hideaki Ogata[2], Shun Hirota[1]

Highly-ordered protein structures are gaining attention as new biomaterials. A circular permutated cytochrome c_{555} (CPC), which has been designed by circular permutation and helix linker insertion based on the domain-swapped structure of hyperthermophile cytochrome c_{555}, forms a cyclic trimer that can construct a tetrahedral cage structure in the crystal[1]. In this study, surface CPC variants were investigated to construct different supramolecular structures in crystals. Trimer formation of CPC variants through ethanol treatment was confirmed by size exclusion chromatography. In addition, X-ray crystallography revealed cylindrical cavities in a crystal of a CPC variant trimer.
Keywords：3D domain swapping; heme protein; protein assembly; protein design; X-ray crystallography

タンパク質集合体は新たなバイオマテリアルとして注目を集めている。超好熱菌由来シトクロムc_{555}のドメインスワッピング構造を基に循環置換とαヘリックスリンカー挿入を施した人工タンパク質 CPC は環状 3 量体を形成し、結晶中で 4 面体ケージ構造を構築することができる[1]。本研究では、CPC 表面のアミノ酸残基に変異導入を行うことで、4 面体構造とは異なるタンパク質超分子構造体の構築を試みた(図 1)。大腸菌を用いて培養・精製した CPC 変異体をエタノール処理したところ、3 量体を形成することがサイズ排除クロマトグラフィーにより確認された。X 線結晶構造解析の結果、得られた 3 量体の結晶内に筒状の空洞が存在することが分かった。

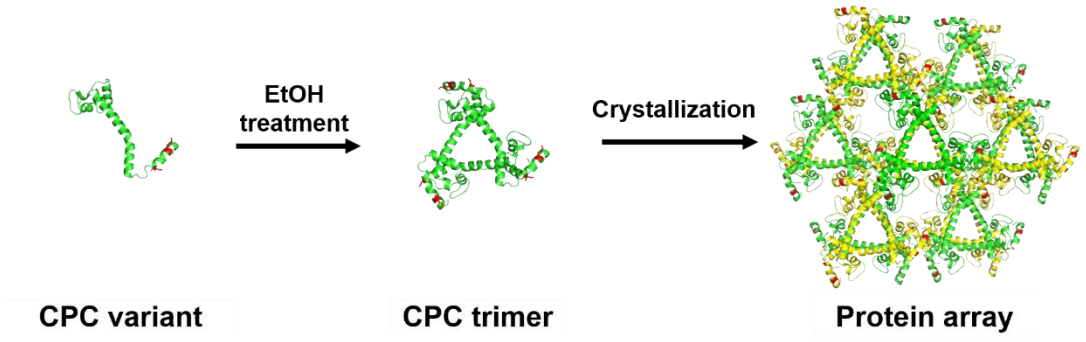

Figure 1. Schematic representation of a CPC variant and its crystal structure.

1) A. Oda, *et al.*, *Chem. Asian J.* **2018**, *13*, 964-967.

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ヒンジループの改変によるヒトシトクロム *c* 2 量体の構築とその細胞内における影響

（奈良先端大先端科技）〇太田 ことり・藤原 綱大・真島 剛史・小林 直也・金井 賢一・松井 貴輝・別所 康全・廣田 俊
Construction of human cytochrome *c* dimer by hinge loop mutation and its intracellular effect (*Grad. Sch. Sci. Tech., NAIST*) 〇Kotori Ohta, Kodai Fujiwara, Tsuyoshi Mashima, Naoya Kobayashi, Kenichi Kanai, Takaaki Matsui, Yasumasa Bessho, Shun Hirota

Cytochrome *c* (cyt *c*) is a hemoprotein that transfers electrons in the inner mitochondrial membrane. Cyt *c* also plays an important role in inducing apoptosis. We have shown that cyt *c* dimerizes through 3D domain swapping by ethanol treatment. Here, we prepared human cyt *c* variants (del8384, del82-84, del82-85, del81-85) in which 2 to 5 amino acid residues near the hinge loop were deleted to promote dimerization by 3D domain swapping. The cyt *c* variants formed more dimers than wild-type cyt *c* after incubation at 37°C. We will also present the results on the expression of cyt *c* variants and their effects in human cells.
Keywords : 3D domain swapping; cytochrome c; heme protein; protein dimerization; protein engineering

シトクロム *c*（cyt *c*）は、ミトコンドリア内膜で電子伝達を行うとともに、アポトーシス誘導において重要な役割を担うヘムタンパク質である。Cyt *c* はエタノール添加、凍結乾燥、再溶解の操作を行うことで 3D ドメインスワッピングにより 2 量化する [1]。本研究では、ヒト cyt *c* のヒンジループの長さが 3D ドメインスワッピングによる 2 量化に与える影響を調べるため、ヒンジループ近傍のアミノ酸残基を 2〜5 個欠損させた変異体（del8384、del82-84、del82-85、del81-85）を作製した（Fig. 1）。各変異体の Soret 帯は 406 nm に観測され、Met80 のヘム鉄からの解離が示唆された。各変異体は、37°Cでインキュベートすると 2 量体を形成し、その形成量はアミノ酸残基欠損数に応じて増加した（Fig. 2）。加えて、ヒト細胞内での cyt *c* 変異体の発現とその影響についても報告する。

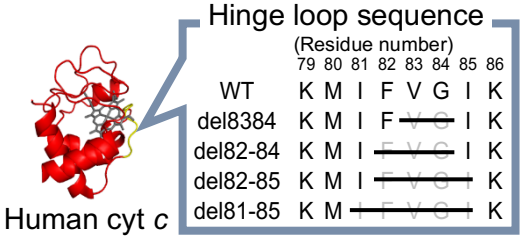

Figure 1. 本研究で用いた cyt *c* 変異体のヒンジループのアミノ酸配列。

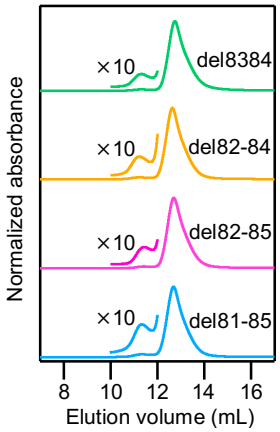

Figure 2. ヒト cyt *c* 変異体を 37℃、26 時間インキュベートした後のサイズ排除クロマトグラフィー溶出曲線。

1) S. Hirota *et al.*, *Proc. Natl. Acad. Sci. USA*, **107**, 12854–12859 (2010).

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シトクロム *c* 2 量体の形成と安定性に対するイオンの影響

（奈良先端大・先端科技）〇藤原綱大・龍﨑美智子・山中優・真島剛史・小林直也・廣田俊
Effects of ions on the formation and stability of cytochrome *c* dimers (*Grad. Sch. Sci. Tech., NAIST*) 〇Kodai Fujiwara, Ryuuzaki, Michiko, Masaru Yamanaka, Tsuyoshi Mashima, Naoya Kobayashi, Shun Hirota

The structure and stability of proteins are affected by ions. We have previously reported that cytochrome *c* (cyt *c*) forms a 3D domain-swapped dimer by ethanol treatment. The thermal stability of the domain-swapped cyt *c* dimer increased for kosmotropic ions according to the Hofmeister series. Additionally, dimers were formed by incubating cyt *c* at 50 °C in the presence of citrate ions, in which the dimerization amount increased by increasing the concentrations of cyt *c* and citrate ion.
Keywords : 3D domain swapping; cytochrome c; heme protein; Hofmeister series; protein oligomerization,

生体内では、タンパク質の機能は精密に制御されており、タンパク質の構造と安定性はイオンの影響を受ける。電子伝達タンパク質であるシトクロム *c*（cyt *c*）はエタノール処理によりドメインスワッピング 2 量体を形成する（Fig. 1a）。ドメインスワッピングした cyt *c* 2 量体の熱安定性を様々なアニオン存在下で調査したところ、ホフマイスター系列に従い、コスモトロピックなイオン共存下で増した（Fig. 1b）。また、cyt *c* をクエン酸共存下 50 °C で静置すると 2 量体が形成され、その形成量は cyt *c* 濃度およびクエン酸イオン濃度が高いほど増加した（Fig. 1c）。

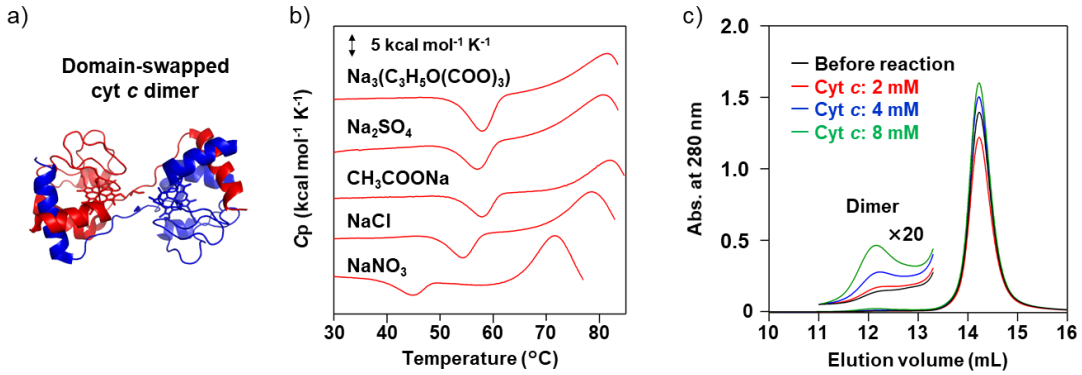

Figure 1. (a) Crystal structure of domain-swapped cyt *c* dimer. (b) DSC thermograms of domain-swapped cyt *c* dimer in the presence of various ions. (c) SEC chromatograms of cyt *c* after incubation in the presence of 1 M citrate ion.

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ポリ(2-アルキル-2-オキサゾリン)結合血清アルブミンの合成

(中央大理工)○服部 亮太・藤澤 隼矢・小松 晃之
Synthesis of Poly(2-alkyl-2-oxazoline)-Conjugated Serum Albumins
(*Faculty of Sci. and Eng., Chuo University*) ○Ryota Hattori, Junya Fujisawa, Teruyuki Komatsu

Hydroxyethyl starch (HES) solution is used as an artificial plasma expander in veterinary medicine. However, it has a short circulation half-life and side effects, such as blood clotting disorders and renal dysfunction. In this paper, we report the synthesis, structures and characteristics of poly(2-ethyl-2-oxazoline) (PEtOx, Mw: 5, 10 kDa) conjugated porcine serum albumins (PEtOx-PSAs) as plasma expander for animals. PEtOx is water-soluble polymer having biocompatibility and immunological stealth property. The average number of PEtOx on the PSA can be modulated in the range of 6 to 14 by the amount of crosslinking agent, *N*-succinimidyl 3-maleimidopropionate (SMP). Colloid osmotic pressure of PEtOx-PSA increased depending on the number of PEtOx. PEtOx-PSA solution did not exhibit cytotoxicity against HUVEC cells. The results of blood compatibility and circulation persistence using rats are also reported."
"*Keywords : Plasma Expander; Polyoxazoline; Serum Albumin; Biocompatibility; Colloid Osmotic Pressure*

動物医療では血漿増量剤としてヒドロキシエチルスターチ(HES)水溶液を使用する場合がある。しかし、HES は血中滞留時間が短く、血液凝固障害や腎機能障害などの副作用も懸念される。本研究は、ブタ血清アルブミン(PSA)にポリ(2-エチル-2-オキサゾリン)(PEtOx, Mw: 5, 10 kDa)を共有結合した一連の PEtOx 結合 PSA(PEtOx-PSA)を合成し、その構造と動物用血漿増量剤としての特性を明らかにすることを目的とした。PEtOx は生体適合性と免疫学的ステルス性に優れた水溶性高分子である [1]。架橋剤として用いた *N*-succinimidyl 3-maleimido propionate(SMP)の添加量により、PSA 一分子当りの PEtOx 平均結合数は 6~14 の範囲で制御できた。PEtOx-PSA 溶液の膠質浸透圧は PEtOx 結合数の増加に伴い上昇した。HUVEC 細胞を用いた安全性試験により、PEtOx-PSA 溶液は細胞毒性を示さないことがわかった。また、ラットを用いた血液適合性評価や血中滞留性評価の結果についても併せて報告する。

1) T. X. Viegas *et al., Bioconjugate Chem.* **2011**, *22*, 976.

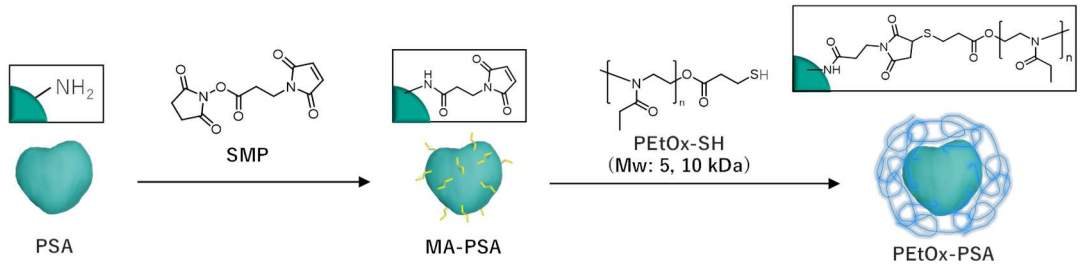

Fig. 1 Synthetic scheme of PEtOx-PSA (Mw: 5, 10 kDa).

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人工酸素運搬体としてのポリ(2-アルキル-2-オキサゾリン)結合ヘモグロビンの合成

(中央大理工)○若林 竜平・石井 幸太・小松 晃之
Synthesis of Poly(2-alkyl-2-oxazoline)-Conjugated Hemoglobins as an Artificial O_2 Carrier (*Faculty of Sci. and Eng., Chuo University*) ○Ryuhei Wakabayashi, Kota Ishii, Teruyuki Komatsu

Poly(2-ethyl-2-oxazoline) (PEtOx), water-soluble polymer having biocompatibility and immunological stealth property, attracts attention as an alternative to polyethylene glycol (PEG). We developed polyoxazoline-conjugated hemoglobin having an average PEtOx binding number of six and evaluated its safety and efficacy by animal experiments.[1] We report the synthesis, structures, and functions of PEtOx conjugated porcine hemoglobins ($PEtOx_n$-Hb) as an artificial O_2 carrier (red blood cell substitute). The average number of PEtOx (n) on the protein can be controlled in the range of 6-16 by the amount of crosslinker. Colloid osmotic pressure (COP) of PEtOx-Hb solution ([Hb] = 5 g dL^{-1}) increased depending on the number of PEtOx. Furthermore, all PEtOx-Hb showed high O_2 affinity (8-9 Torr), which was constant regardless of the number of PEtOx bonds. Comprison with PEG conjugated Hb (PEG_n-Hb) is also reported.
Keywords : Hemoglobin; Artificial O_2 carrier; Biocompatible polymer; Polyoxazoline; Red blood cell substitute

ポリ(2-エチル-2-オキサゾリン)(PEtOx)は生体適合性と免疫学的ステルス性に優れた水溶性高分子であり、ポリエチレングリコール(PEG)の代替物として注目を集めている。我々はブタヘモグロビン(Hb)に PEtOx を平均 6 本結合したポリオキサゾリン結合 Hb を合成し、動物実験から安全性と有効性を評価している [1]。本研究は、Hb に PEtOx を共有結合した一連の PEtOx 結合 Hb($PEtOx_n$-Hb)を合成し、その構造と人工酸素運搬体(赤血球代替物)としての機能を明らかにすることを目的とした。Hb 1 分子当たりの PEtOx 平均結合数(n)は添加する架橋剤の量により 6～16 本の範囲で調節可能であった。また、Hb 濃度 5%溶液の膠質浸透圧は PEtOx 結合数の増加に伴い上昇した。いずれの $PEtOx_n$-Hb も高い酸素親和性を示し(P_{50}=8-9 Torr)、PEtOx 結合数にかかわらず一定であった。PEG 結合 Hb(PEG_n-Hb)との比較についても併せて報告する。

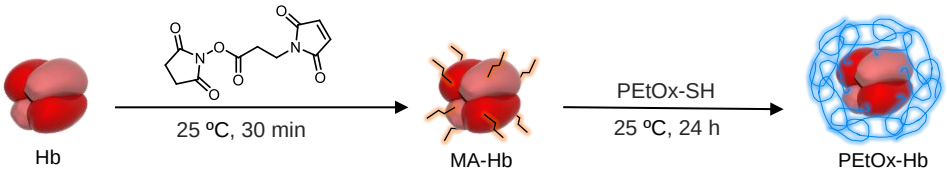

Fig. 1 Synthesis of PEtOx-Hb.

1) T. Komatsu, *et al., ACS Appl. Bio Mater.*, **2023**, *6*, 3330.

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亜鉛フタロシアニン置換ミオグロビン-アルブミン融合タンパク質の合成と光殺菌能

（中央大理工）○江川 碧・舩本 瑞稀・山田 大雅・小松 晃之
Synthesis and Photosterilization Ability of Zinc-Phthalocyanine-Substituted Myoglobin-Albumin Fusion Protein (*Faculty of Sci. and Eng., Chuo University*) ○Aoi Egawa, Mizuki Funamoto, Taiga Yamada, Teruyuki Komatsu

Bacterial infections are commonly treated with antibiotics, but they acquire drug resistance in a short period of time. On the other hand, photodynamic therapy (PDT) is a treatment to use reactive oxygen species (ROS) to kill cancer cells. Bacteria have never acquired ROS resistance, and application of PDT to antimicrobial therapy has attracted much attention recently. We synthesized zinc-protoporphyrin IX substitute of myoglobin-albumin fusion protein (Mb-HSA) in which human serum albumin (HSA) is genetically connected to the N-terminus of myoglobin (Mb), and demonstrated its PDT activity to cancer cells.[1] The aim of this research is to synthesize zinc-phthalocyanine (ZnPc) substitute of Mb-HSA (ZnPcMb-HSA, **Fig. 1**), which can be excited by biopermeable light at 600-700 nm, and to reveal its photosterilization ability. ZnPcMb-HSA was prepared by adding ZnPc to apoMb-HSA, which was obtained by removing heme from Mb-HSA by acid-butanone method. Photoirradiation (10 mW, 10 min) of Bacillus subtilis with ZnPcMb-HSA (only 1 μM) reduced the number of viable bacteria to $1/10^6$ of that before irradiation. We revealed that ZnPcMb-HSA functions as a protein photosensitizer for photosterilization.

Keywords : Photosterilization; Zinc-Phthalocyanine; Myoglobin; Albumin; Photosensitizer

細菌感染症は抗生物質による治療が一般的であるが、短期間で薬剤耐性を獲得してしまう。一方、光線力学療法（PDT）は活性酸素（ROS）を利用してがん細胞を死滅させる治療法である。細菌が ROS 耐性を獲得した例はなく、近年、抗菌治療における PDT の応用に注目が集まっている。我々は、ミオグロビン（Mb）の N 末端にヒト血清アルブミン（HSA）を遺伝子工学的に連結したミオグロビン-アルブミン融合タンパク質（Mb-HSA）の亜鉛プロトポルフィリンIX置換体を合成し、そのがん細胞に対する PDT 活性を明らかにしている [1]。本研究は、より生体透過性の高い 600～700 nm の光で励起可能な亜鉛フタロシアニン（ZnPc）で再構成した ZnPcMb-HSA（**Fig. 1**）を合成し、その光殺菌能を明らかにすることを目的とした。Mb-HSA から酸-ブタノン法によりヘムを除去して得た apoMb-HSA に ZnPc を添加することで、ZnPcMb-HSA を調製した。枯草菌に ZnPcMb-HSA を添加して光照射（10 mW, 10 min）すると、わずか 1 μM で生菌数が $1/10^6$ に減少した。ZnPcMb-HSA が光殺菌能を有するタンパク質光増感剤として機能することが明らかとなった。

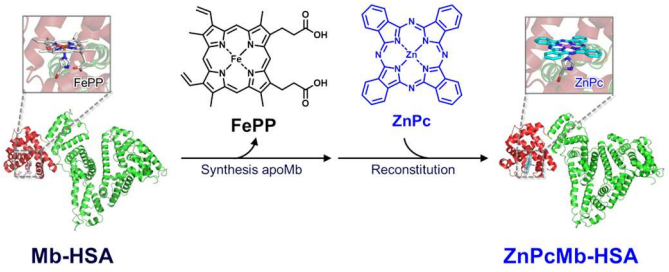

Fig. 1 Synthetic scheme of ZnPcMb-HSA.

1） T. Komatsu *et al.*, *Chem. Eur. J.* **2023**, *29,* e202203952

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人工酸素運搬体としてのポリオキサゾリン被覆ヘモグロビンナノ粒子の合成

（中央大理工）○荒木 巴佳・高山 夏実・小松 晃之
Synthesis of Polyoxazoline-Covered Hemoglobin Nanoparticle as an Artificial O_2 Carrier (*Faculty of Sci. and Eng., Chuo University*) ○Tomoka Araki, Natsumi Kohyama, Teruyuki Komatsu.

We have synthesized and developed human serum albumin-covered stroma-free hemoglobin nanoparticle (HSA-HbNP), in which HSA was conjugated to the surface of polymerized Hb sphere as an artificial O_2 carrier. Polyoxazoline (POx) is a water-soluble polymer with excellent biocompatibility. If the surface of HbNP was covered with POx, it would be possible to prepare formulation with low viscosity and high Hb concentration. The aim of this study is to synthesize HbNP covered with POx (POx-HbNP) and to evaluate its structure, O_2 binding ability, enzymetic activity, and blood compatibility. Hb was polymerized using *N*-succinimidyl 3-maleimidopropionate and dithiothreitol, yielding HbNP. Subsequent coupling of maleimide groups on the particle with a sulfhydryl-terminated POx derivative gave POx-HbNP. The particle diameter was determined to be 30 nm by dynamic light scattering. The O_2 affinity was higher than that of Hb. The Hb oxidation rate of POx-HbNP in H_2O_2 solution (20 μM) after 2 hr was only 4%. POx-HbNP is an artificial O_2 carrier with high antioxidant ability.
Keywords: Hemoglobin; Polyoxazoline; Artificial O_2 Carrier; Nanoparticle; Viscosity

我々はストロマフリーヘモグロビン（Hb）を重合して得た微粒子の表面にヒト血清アルブミン（HSA）を結合した HSA 被覆 Hb ナノ粒子（HSA-HbNP）を合成し、人工酸素運搬体としての応用を進めている[1]。一方、ポリオキサゾリン（POx）は生体適合性に優れた水溶性高分子である。Hb 微粒子の表面を POx で被覆することができれば、低粘度かつ高濃度 Hb 製剤の調製も可能になると予想される。本研究は、POx 被覆 Hb ナノ粒子（POx-HbNP、**Fig. 1**）を合成し、その構造、酸素結合能、酵素活性、血液適合性を明らかにすることを目的とした。Hb 溶液に *N*-succinimidyl 3-maleimidopropionate を加え、タンパク質表面にマレイミド基を導入した後、架橋剤 dithiothreitol を用いて重合し、Hb の微粒子を得た。続いて、表面に残ったマレイミド基とスルフヒドリル基を有する POx 誘導体を結合することにより POx-HbNP を合成した。動的光散乱測定で求めた平均粒径は 30 nm であり、酸素親和性は Hb に比べ増大した。H_2O_2 水溶液（20 μM）中における 2 時間後の Hb 酸化率はわずか 4%に留まり、POx-HbNP が高い抗酸化能を有する人工酸素運搬体であることがわかった。

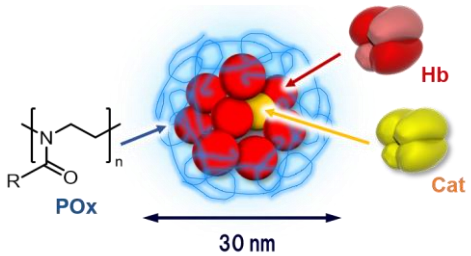

Fig. 1 Structure of POx-HbNP.

1) T. Komatsu *et al., ACS Appl. Bio Mater*. **2022**, *5*, 5853.

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β バレルポリンのナノポア化と物質透過性の検討

（群馬大院理工 [1]）○登坂俊行 [1]・神谷 厚輝 [1]
Nanopore formation and molecular transport of β-barrel porin ([1]*Graduate Science and Technology, Gunma University*,) ○Toshiyuki Tosaka,[1] Koki Kamiya,[1]

Protein nanopores have been applied as a biological sensor, such as a sequence of DNA or peptide, into bilayer lipid membrane (BLM) or liposomes[1)]. To detect a biological molecule using the protein nanopore, it is necessary to construct the protein nanopore that is capable of chemical modification and has a constant nanopore size. Outer membrane protein (Omp) from an outer membrane of gram-negative bacteria forms thermally stable β-barrel. Modified Omp has been applied as sensing for small molecule and peptide[2,3)]. In this study, to construct a novel Omp nanopore, we created BtuB nanopore by deleting amino acid residues from the inner β-barrel region of BtuB (Figure 1). Then, the molecular permeability of the BtuB nanopore was investigated using BLM systems and cell-sized liposome.
Keywords : protein nanopore; outer membrane protein; liposome

ナノポア形成タンパク質は平面脂質や人工細胞膜リポソームに再構成することで、DNA シーケンサーに代表されるバイオロジカルセンサに応用されている [1)]。様々な生体分子の検出のためには、化学修飾可能かつ、一定のナノポアを形成するナノポア形成タンパク質の構築が必要である。グラム陰性菌の外膜に存在する Outer membrane protein (Omp)は熱安定的な β バレルを形成し、変異や化学修飾を加えることで、小分子やペプチドなどのセンシングに活用されている [2,3)]。本研究では、Omp 由来の新たなナノポアを構築するため、Omp の一種である BtuB の β バレル内のアミノ酸残基を欠損させ、ナノポアの形成を試みた(図 1)。平面膜パッチクランプ法により変異 BtuB のイオン透過性を検討した。また、変異 BtuB のリポソーム膜への再構成法を検討し、球体膜上でのイオンや小分子の物質輸送を観察した。

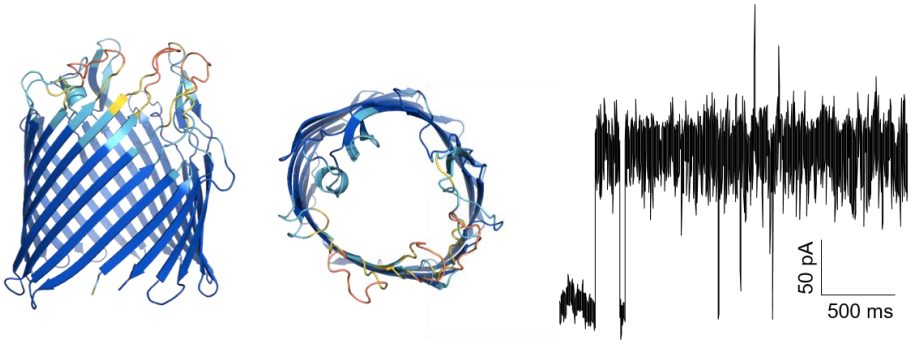

図 1. 変異 BtuB の予測構造と BtuB のイオン電流シグナル

1) Nehra, A. Ahlawat, Sing, S. K. P. *Sensors Actuators, B Chem*. 2019, 284, 595-622.
2) Minij Kim, et al., *ACS Sens*. 2023. 8, 7, 2673-2680.
3) Toshiyuki Tosaka, Koki Kamiya., *ACS Appl. Nano Mater*., 2022, 5, 5, 6149-6158

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Docking simulation および Molecular dynamics simulation を用いたペプチドリガンドの *in silico* panning

（東農工大工[1]・筑波大医[2]）○川井 春香[1]・三浦 大明[1]・桐 升[1]・浅野 竜太郎[1]・津川 若子[1]・藤田 祥子[1]・川野 竜司[1]・広川 貴次[2]・塚越 かおり[1]・池袋 一典[1]
In silico panning of peptide ligands using docking simulation and molecular dynamics simulation ([1]*Faculty of Engineering, Tokyo University of Agriculture and Technology*, [2]*Faculty of Medicine, University of Tsukuba*) ○Haruka Kawai,[1] Daimei Miura,[1] Sheng Tong,[1] Ryutaro Asano,[1] Wakako Tsugawa,[1] Shoko Fujita,[1] Ryuji Kawano,[1] Takatsugu Hirokawa,[2] Kaori Tsukakoshi,[1] Kazunori Ikebukuro[1]

Peptide ligands have numerous functions by interacting with proteins. As there are enormous peptide sequence patterns, it is inefficient to evaluate the candidate peptides *in vitro* for screening. Recently, *in silico* evaluation tools have advanced significantly. AlphaFold2, an artificial intelligence tool, can predict protein structures from amino acid sequences based on known protein structures and sequence data. We are trying to develop an efficient screening method for functional peptides through *in silico* evaluation using docking simulation and molecular dynamics simulation after structure prediction of various peptides. This method is being applied to three models: first, the development of a small single-chain antibody with protein A affinity; second, the modification of a peptide/protein pair to enable protein conjugation; third, the design of peptide ligands to improve the reaction specificity of an enzyme. The results will be presented in this presentation.
Keywords : In silico panning; Peptide; Screening; Docking simulation; Molecular dynamics simulation

ペプチドリガンドは、タンパク質と相互作用し、多くの機能を持つ可能性がある。しかし、ペプチド配列の候補は多く、多数の候補ペプチドを *in vitro* でスクリーニングすることは非効率的である。近年、*in silico* 評価ツールが著しく発達している。人工知能ツールである AlphaFold2[1)]は、学習させた既知のタンパク質構造と配列情報をもとに、アミノ酸配列からタンパク質構造を予測することが可能である。そこで、当研究室では、様々なペプチドを設計し、構造予測後、ドッキングシミュレーションおよび分子動力学シミュレーションを用いて *in silico* で評価することによる、効率的な機能的ペプチドのスクリーニング法の開発を試みている。現在、プロテイン A 精製を可能にすることを目指し、プロテイン A 親和性を付与した低分子一本鎖抗体の開発、タンパク質の連結を可能にするペプチド/タンパク質ペアの改変、スペルミジン脱水素酵素の反応特異性向上を目指したペプチドリガンドの開発の 3 つを試みている。本報告ではこれらの結果について紹介する。

1) Highly accurate protein structure prediction with AlphaFold. Jumper J, Evans R, Pritzel A, et al. *Nature.* **2021**, *596*, 583-589.

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寛容なタンパク質認識特性を持つ酸化的フォールディング促進剤の開発

（農工大院工[1]・徳島大先端酵素学研究所[2]・KISTEC[3]）○鈴木 洸希[1]・野尻 涼矢[1]・齋尾 智英[2]・村岡 貴博[1,3]
Development of an oxidative protein folding promoter using host-guest interactions ([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Institute of Advanced Medical Sciences, Tokushima University,* [3]*Kanagawa Institute of Industrial Science and Technology*) ○Koki Suzuki,[1] Ryoya Nojiri,[1] Tomohide Saio,[2] Takahiro Muraoka[1,3]

Proteins are significant biological macromolecules for pharmaceutical purposes. To express their biological functions, it is essential for them to fold into their native structure. In vivo, protein disulfide isomerase (PDI) assists oxidative protein folding. The CGHC domains of PDI promote disulfide bond formation and exchange reactions. PDI also has a hydrophobic pocket inside its U-shaped structure that captures a folding intermediate. This proximity effect between the folding intermediate and the active sites results in efficient native structure formation. Inspired by these features, we have developed a cyclodextrin-based oxidative protein folding promoter that can interact with proteins. We evaluated the effect of the developed molecule. As a result, the developed molecule showed a higher effect than glutathione, a typical folding promoter, under higher concentration conditions than in the past.
Keywords : Cyclodextrin; Protein; Folding; Thiol

バイオ医薬品の有効成分であるタンパク質は、その生物学的機能を発揮するため、天然構造へと折り畳まれる必要がある。特に、配列中にシステイン残基を含むタンパク質は、フォールディング過程においてジスルフィド結合の導入や組み換えが不可欠である。生体内では protein disulfide isomerase (PDI)が、高い酸化還元活性を示す CGHC 配列を持っており、その役割を果たしている。また、PDI は U 字型構造内部に疎水性ポケットを持っており、フォールディング中間体を取り込む性質を持つ。一般的な酵素が持つ基質認識特性と異なり、この疎水性ポケットには特異性低く基質タンパク質が取り込まれる。この性質により、PDI はタンパク質間の凝集を抑制しつつ、フォールディング中間体と活性部位を近接させる効果によって、効率的な天然構造形成を実現している。PDI が持つこれらの特徴から着想を得て、我々はタンパク質と相互作用可能なシクロデキストリンに、酸化還元活性を持つチオール基を結合させた化合物を開発した。

還元変性状態の BPTI を用いて、開発分子の酸化的フォールディング促進効果を評価した。その結果、従来よりも高濃度条件下において、代表的なフォールディング促進剤であるグルタチオンと比べ、開発分子が高いフォールディング促進効果を示した。

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

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC H931(931, Bldg. 9 [3F])

[H931-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Akihiro Iahiwata, Hidenori Okamura

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[H931-4am-01]

Synthesis of new compounds composed of organic acids and amines with hair treatment effects

○Kohtaro Katayama[1], Hiroyuki Miyamoto[1], Yuji Mochizuki[2], Natsumi Shin[2], Shoko Yamazaki[3], Hiroki Hotta[1,4], Yoshio Tsujino[4] (1. Graduate School of Maritime Sciences, Kobe University, 2. ROHTO Pharmaceutical Co., Ltd. , 3. Nara University of Education , 4. Graduate School of Science, Technology and innovation, Kobe University)

Japanese
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[H931-4am-02]

The thieno[2,3-*b*]pyridine derivative that is a neural differentiation inducer and a fluorescent molecule

○Kento Sonoda[1], Kazuya Asao[1,2], Shin-ichi Kawaguchi[1,2], Yoshinori Kawazoe[1,2] (1. Faculty of Agriculture, Saga University, 2. Graduate School of Advanced Health Sciences, Saga University)

Japanese
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[H931-4am-03]

Supramolecular hydrogelation triggered by gold catalysis

○Tomoya Yamamoto[1,2], Akiko Nakamura[2], Akari Mukaimine[2], Katsunori Tanaka[2,3] (1. Osaka University, Department of Engineering, 2. RIKEN, Cluster for Pioneering Research, Biofunctional Synthetic Chemistry Laboratory, 3. Tokyo Institute of Technology, School of Materials and Chemical Technology)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[H931-4am-04]

NIR Fluorescence analysis of the trypsin enzyme using unsymmetrical squaraine dye- peptide conjugate.

○PRIYANKA Priyanka[1,2], Shekhar Gupta[1], Tamaki Kato[1] (1. Kyushu Institute of Technology,Japan, 2. Kyushu Institute of Technology, Japan)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

Break

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[H931-4am-05]

Near Infrared Fluorescent Detection of Protease Activity using Peptide-Bound Squaraine Dye

○Shekhar Gupta[1], Priyanka Balyan [1], Sai Kiran Mavileti[1], Shyam Sudhir Pandey[1], Tamaki Kato[1] (1. Kyushu Institute of Technology)

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English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[H931-4am-06]
Internal radioisotope therapy utilizing [3+2] cycloaddition reaction with cancer metabolites

○Yudai Ode[1], Akihiro Ishiwata[2], Ambara Rachmat Pradipta[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)

English
11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC
[H931-4am-07]
Development of a new screening system to discover RNA-binding small molecules for RNA-targeting therapeutics

○Ryosuke Nagasawa[1,2], Kazumitsu Onizuka[1,2], Ryohei Iwata[1,2], Komatsu Richard Kaoru[3,4], Emi Miyashita[3,4], Sayaka Dantsuji[4], Hirotaka Murase[1,2], Mamiko Ozawa[1], Hirohide Saito[3], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku Univ., 2. Graduate School of Science, Tohoku Univ., 3. CiRA, Kyoto Univ., 4. xFOREST Therapeutics)

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日本化学会 第104春季年会 (2024)

毛髪トリートメント効果を有する有機酸とアミンの新規化合物合成

(神戸大学大学院海事科学研究科 [1]・ロート製薬株式会社 [2]・奈良教育大学 [3]・神戸大学大学院科学技術イノベーション研究科 [4]) ○片山 耕太郎 [1]・宮本 紘幸 [1]・望月 佑次 [2,4]・新 菜摘 [2]・山崎 祥子 [3]・堀田 弘樹 [1,4]・辻野 義雄 [4]

Synthesis of new compounds composed of organic acids and amines with hair treatment effects

(*[1]Graduate School of Maritime Sciences, Kobe University, [2]ROHTO Pharmaceutical Co., Ltd., [3]Nara University of Education, [4]Graduate School of Science, Technology and Innovation, Kobe University*) ○Kohtaro Katayama[1], Hiroyuki Miyamoto[1], Yuji Mochizuki[2,4], Natsumi Shin[2], Shoko Yamazaki[3], Hiroki Hotta[1,4], Yoshio Tsujino[4]

Many people are concerned about the age-related hair "waviness" and loss of shine, and techniques for treating hair to improve this are available. We have discovered that a new compound obtained from muconic acid and 2-aminoethanethiol (cysteamine) has a high ability in improving the habit and swell of the hair, Muconic acid is naturally occurring and used as a precursor for plastics and fibers[1)]. Cysteamine, on the other hand, is already a substance used as cosmetics and perm solution.

Two types of the new compounds obtained were identified, mono-adducts and bis-adducts[2)], and it was discovered that it was possible to change the proportion of the compounds produced by adjusting the equivalent amount of cysteamine in the raw material and the heating time. It was also confirmed that the bis-adducts has higher effects on hair, such as hair straightening. These compounds are expected to be applied in hair cosmetics.

Keywords : Muconic Acid, Cysteamine, Michael Addition, Hair Straightening, Hair Treatment Agent

加齢に伴う髪の毛の「うねり」とツヤの低下に悩みを抱える人は多く、これを改善する毛髪処理技術が美容院等で提供されている。我々は、天然に存在し、プラスチックや繊維などの前駆体として利用されるムコン酸 1)と、化粧品やパーマ液として使用される 2-アミノエタンチオール（システアミン）を混合・加熱することによって得られた新規化合物に、毛髪の癖やうねりを改善させる高い機能があることを発見した。

得られた新規化合物はモノ付加体とビス付加体の 2 種類が確認され、原料のシステアミンの当量および加熱時間を調整することにより生成される化合物の割合を変えることが可能であることが発見された。また、縮毛矯正をはじめとする毛髪に対する効果はビス付加体の方がより高いことも確認された。

これらの化合物は頭髪化粧品への応用が期待される。

1）Curr. Opin. Biotechnol. 2017, 45:136–143
2）特許第 7232484 号

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神経分化の誘導および蛍光特性を有するチエノピリジン誘導体

(1. 佐大農、2. 佐大院先進) ○園田 健登[1]・浅尾 和弥[1,2]・川口 真一[1,2]・川添 嘉徳[1,2]

The thieno[2,3-*b*]pyridine derivative that is a neural differentiation inducer and a fluorescent molecule

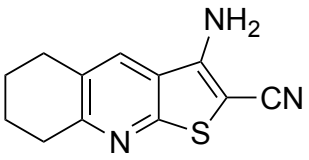
([1]*Faculty of Agriculture, Saga University,* [2]*Graduate School of Advanced Health Sciences, Saga University)* ○Kento Sonoda[1], Kazuya Asao[1,2], Shin-ichi Kawaguchi[1,2], Yoshinori Kawazoe[1,2]

Neurotrophins are proteins that have been implicated in the pathogenesis of various neurodegenerative diseases. However, due to several problems with protein reagents, alternative small molecule inducers of neural differentiation are needed. We found that small molecules of thieno[2,3-*b*]pyridine derivatives induced neural differentiation. Particularly, two derivatives exhibited significant neuritogenic activity in rat pheochromocytoma (PC12) cells. Moreover, one of the two derivatives displayed fluorescence and a discernible Stokes shift. Furthermore, several experiments indicated that this derivative induced neural differentiation in a manner independent of NGF. Therefore, this derivative has the potential as a novel neurotrophic factor and as a fluorescent reagent including bioimaging.

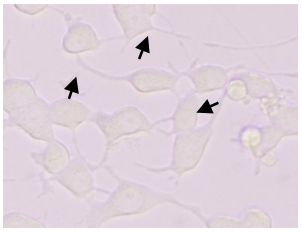
Keywords : Thienopyridine; Neural differentiation; Fluorescent reagent; PC12 cell; Bioimaging

神経成長因子（NGF）や脳由来神経栄養因子（BDNF）は神経細胞の成長や再生に関与するタンパク質であり、様々な神経変性疾患への関与が指摘されている。しかし、タンパク質試薬には価格や安定性などの問題点があるため、低分子化合物による神経分化誘導剤が必要とされている。我々は、チエノ[2,3-*b*]ピリジン誘導体が神経分化を誘導することを見出した。これを元に 13 種類の誘導体を合成し、ラット褐色細胞腫（PC12）細胞を用いて神経分化能を評価したところ、2 種類の誘導体が有意に神経分化を誘導することを示した。さらに、2 種類の誘導体のうち 3-Amino-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-2-carbonitrile（下図）は Stokes shift の大きい蛍光を示すことを確認した。

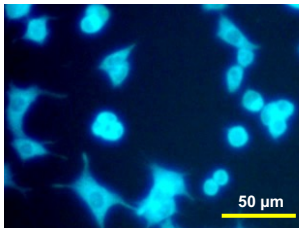
作用機序については NGF の受容体である TrkA の発現が少ない細胞でも神経分化を誘導すること、誘導体を添加した際の蛍光観察において、この誘導体は細胞膜内へ透過することが確認できたことなどから、この誘導体が NGF とは異なる作用機序で神経細胞の分化を誘導することが示唆された。したがって、この誘導体は新規の神経栄養因子としてだけでなく、化合物の蛍光特性による神経分化のバイオイメージング試薬への応用も期待される。



3-Amino-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-2-carbonitrile



Neural Differentiation



Fluorescence Imaging

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金触媒反応を引き金とする超分子ハイドロゲル形成

（阪大院工[1]・理研開拓研究本部　田中生体研[2]・東工大物質理工[3]）◯山本智也[1,2]・中村亜希子[2]・向峯あかり[2]・田中克典[2,3]
Supramolecular hydrogelation triggered by gold catalysis ([1]*Graduate School of Engineering, Osaka University*, [2]*Biofunctional Synthetic Chemistry Laboratory, Cluster for Pioneering Research, RIKEN,* [3]*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ◯ Tomoya Yamamoto,[1] Akiko Nakamura,[2] Akari Mukaimine,[2] Katsunori Tanaka[2,3]

Low-molecular-weight gelators construct gels with supramolecular fibril formation. While enzyme-triggered supramolecular hydrogelation has been extensively developed to selectively construct gels in targeted organs and cells *in vivo*, there are few enzymes that localize in targeted sites. Therefore, novel triggers for supramolecular gelation are important to expand its applicability.

In this study, we developed the low-molecular-weight gelator whose gelation is triggered by gold catalysis, aiming at the *in vivo* construction of biomaterials with biocompatible transition-metal catalysts. Gold catalysis transforms the structure of the hydrophobic core of our gelator, which induces the transformation of the fibril morphology to construct a supramolecular gel. This fibril transformation alters the cytotoxicity against cancer cells, demonstrating its potential use in cancer therapy.

Keywords : Supramolecular gel, Gold catalysis, in vivo synthesis, Cancer therapy, Self-assembly

低分子ゲル化剤は、分子間での水素結合や疎水性相互作用によって超分子繊維構造を構築し、溶媒分子を包摂することでゲルを形成する。近年は酵素反応を引き金として、疾患部位でゲルを形成するゲル化剤が広く研究されているが、疾患部位で選択的に進行する酵素反応は限定される。我々はこれまでに、生体適合性の高い遷移金属触媒を生体内に導入し、プロドラッグの活性化に応用する研究を行ってきた。このような生体内に導入された遷移金属触媒による反応は、低分子ゲル化剤のゲル化の引き金としても応用可能であると考えられる。

本研究では、生体内での遷移金属触媒反応によってバイオマテリアルを構築する手法の確立を目指して、金触媒反応を引き金としてハイドロゲルを構築する低分子ゲル化剤を開発した[1)]。金触媒反応によって構造変換される保護基を疎水性部分として導入した低分子ゲル化剤を合成し、金触媒反応を引き金としてゲル化する条件を見出した。このゲル化剤は近触媒反応によって超分子繊維構造が変化し、この構造変化がゲル化の機構に重要であることが電子顕微鏡観察により示された。形成されたゲルはこの繊維構造変化によってがん細胞に対する毒性が顕著に変化し、がん治療への応用可能性が示された。

1) T. Yamamoto, A. Nakamura, A. Mukaimine, K. Tanaka, *Tetrahedron Chem.* in press, DOI:10.1016/j.tchem.2023.100058.

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NIR fluorescence analysis of the trypsin enzyme with Unsymmetrical Squaraine Dye-Peptide Conjugate

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Keywords: Squaraine dye, Dye-peptide conjugate, aggregation, bio-imaging

For imaging applications, fluorescent probes are immensely appreciated owing to their deep tissue penetration as well as autofluorescence of biomolecules is highly diminished. Dye probes having absorption and emission in the NIR region have great potential for biosensing and bio-imaging applications. A simple and effective solid-phase peptide synthesis method was used to design a near-infrared (NIR) sensitive fluorescent probe based on the dye-peptide conjugate (USQ 1 PC) for the detection of trypsin activity. Photophysical characterization was done using absorption and emission spectroscopies in different solvents. In phosphate buffer dye's absorption intensity decreased drastically due to the formation of dye aggregation and also fluorescence intensity was effectively quenched in PBS because of a strong dye-dye interaction. Added 2U/ml of trypsin enzyme in 10uM of dye-peptide conjugate USQ-1-PC showed more than a 2-fold increase in the fluorescence intensity. Hence, the trypsin enzyme hydrolyzed the peptide-dye combination, causing an efficient and quick recovery of the quenched fluorescence of USQ 1 PC. By efficiently and quickly detecting their activities, the currently developed NIR-sensitive substrate offers potential application for the diagnosis of protease-related disorders.

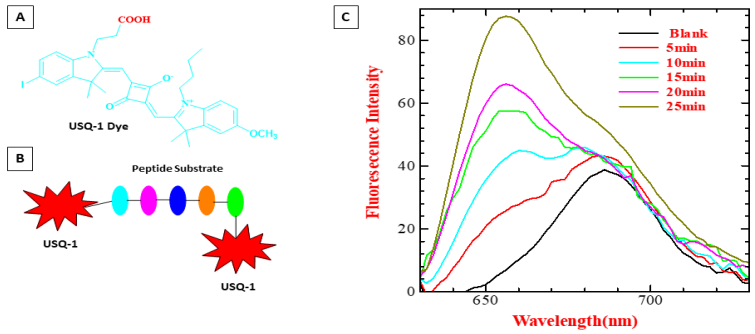

Figure 1 A) Structure of USQ-1dye B) Dye-Peptide conjugate C) Fluorescence emission spectra USQ-1 PC (10 µM) in PBS(0.1M) at pH 7.4 as a function of time after the addition of 2U/ml of trypsin enzyme.

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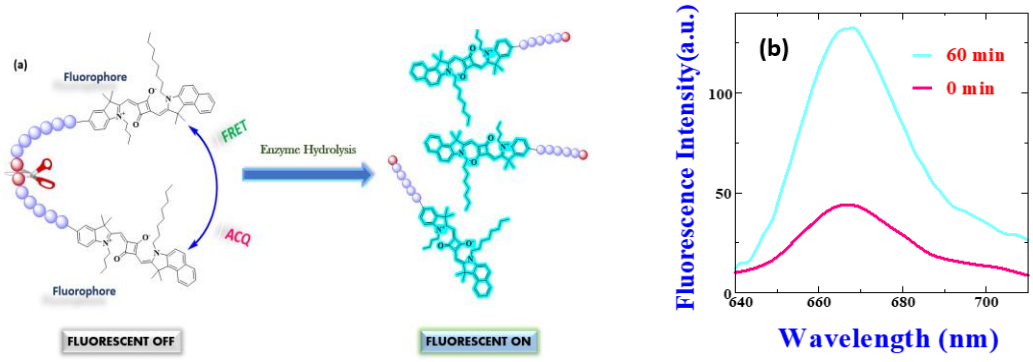
Near Infrared Fluorescent Probes for Detection of Protease Activity using Peptide-Bound Squaraine Dye

([1]*Graduate School of Life Science and System Engineering, Kyushu Institute of Technology,2-4 Hibikino, Wakamatsu-Ku, Kitakyushu-Shi, Fukuoka,808-0196, Japan*) ○ Shekhar Gupta,[1] Priyanka,[1] Sai Kiran Mavletti,[1] Shyam S. Pandey,[1] Tamaki Kato[1]

Keywords: Squaraine Dye; Dye Peptide Conjugate; NIR; Aggregation; FRET

The majority of biomarkers for diseases are enzymes, and the regulation of these enzymes is both fundamental and crucial. Abnormal enzymatic activity can lead to disorders and diseases within biological systems. Recognizing the significance of enzymes in biology, researchers have developed numerous tools to map the activity of specific enzymes, aiming to understand their function and distribution. Near-infrared (NIR) fluorescence probe studies on enzymes offer a valuable approach to gaining insights into their roles within living systems, leveraging the natural advantages of NIR probes. There is high need of designing NIR fluorescent probes, aiming to create sensors capable of visualizing enzyme activity in the NIR region.

Squaraine dyes have excellent potostability with intensive absorption and strong fluorescence in the NIR region. In this work, dye peptide conjugate, SQ122-Lys-βAla-Ala-Phe-Ala-βAla-Lys-SQ122 has been developed as an NIR-fluorescent probe that can detect chymotrypsin activity. The probe showed complete quenching in PBS buffer but after the addition of enzyme re-aapearance of fluorescence emission was observed. Addition of 40 nM of enzyme in 5μM solution of dye peptide conjugate shows >3 fold increase in fluorescence intensity within 60 minutes. This increase in fluorescence emission can be attributed to both the FRET mechanism and the quenching behavior induced by aggregation in the dye-peptide conjugate.



(a)Schematic representation for the fluorescence turn-off/turn-on mechanism. (b)Fluorescen -ce spectra upon addition of 40 nM of enzyme in 5μM dye peptide conjugate solution.

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がん代謝物との[3+2]付加環化反応を利用した RI 内用療法

（東工大物質理工[1]・理研 開拓研究本部 田中生体研[2]）○大出 雄大[1]・石渡 明弘[2]・プラディプタ アンバラ[1]・田中 克典[1,2]
Internal radioisotope therapy utilizing [3+2] cycloaddition reaction with cancer metabolites ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Biofunctional Synthetic Chemistry Laboratory*, *Cluster for Pioneering Research, RIKEN*) ○Yudai Ode,[1] Akihiro Ishiwata,[2] Ambara R. Pradipta,[1] Katsunori Tanaka[1,2]

Adverse drug reactions are a major risk factor associated with cancer chemotherapy. However, the development of internal radioisotope (RI) therapy in recent years has been impressive in overcoming this problem. Our previous research has shown that acrolein is produced in large amounts in cancer cells but is negligible in healthy cells. Furthermore, we have discovered that aryl azides can react selectively with the acrolein of cancer cells to produce diazo compounds, which can then react with the nearby organelle to form a covalent bond within the cancer cells. In this study, we have designed an internal RI therapy using the azide-acrolein reaction and have utilized various RIs. We have investigated their antitumor effects, and the details of our findings will be discussed in the symposium.

Keywords: Internal radiotherapy; Cancer; Acrolein; [3+2] Cycloaddition; Aryl azide

がん治療分子の開発において、副作用の問題を避けるため、標的がん細胞のみを攻撃する分子標的治療（ミサイル療法）の研究が盛んである[1)]。この一つとして、放射性治療分子を投与して、がん組織近傍から放射線治療を行う RI 内用療法が挙げられる。今回我々は、この RI 内用療法の新候補として、がん細胞内での有機合成化学反応と様々な RI(放射性同位体)を融合させた方法を考案した。

これまでに我々の研究室では、がん細胞内でアクロレインが大量に発生していることを発見した[2)]。さらにアジド分子ががんから産生されるアクロレインと選択的に反応することにより、アジド由来分子ががん細胞内に効果的に留まる現象を見出している。これはがん患者のサンプルでも効果的に起こり、ヒトにも一般的な現象である。そこで、アジド分子に対して様々な RI で標識した新規分子をデザインし、がん細胞内での生体内合成反応による集積効果と RI を用いた分子によるがん殺傷効果を期待した。本研究では、放射性前駆体分子の合成、RI による標識効率の検討、さらに動物実験による腫瘍増加の抑制評価と生体内分布の評価を行なったので、これらの経緯について報告する[3)]。

1) K. Fujiki, Y. Kanayama, S. Yano, N. Sato, T. Yokokita, P. Ahmadi, Y. Watanabe, H. Haba, K. Tanaka, *Chem. Sci.* **2019**, *10*, 1936.
2) T. Tanei, A. R. Pradipta, K. Morimoto, M. Fujii, M. Arata, A. Ito, M. Yoshida, E. Saigitbatalova, A. Kurbangalieva, J.-I. Ikeda, E. Morii, S. Noguchi, K. Tanaka, *Adv. Sci*. **2019**, *6*, 1801479.
3) Y. Ode, A. R. Pradipta, P. Ahmadi, A. Ishiwata, A. Nakamura, Y. Egawa, Y. Kusakari, K. Muguruma, Y. Wang, X. Yin, N. Sato, H. Haba, K. Tanaka, *Chem. Sci.*, **2023**,*14*, 8054-8060.

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Development of a new screening system to discover RNA-binding small molecules for RNA-targeting therapeutics

(*[1]IMRAM, Tohoku University, [2]Graduate School of Science, Tohoku University, [3]CiRA, Kyoto University, [4]xFOREST Therapeutics*)○Ryosuke Nagasawa[1,2], Kazumitsu Onizuka[1,2], Ryohei Iwata[1,2], Kaoru R. Komatsu[3,4], Emi Miyashita[3,4], Sayaka Dantsuji[4], Hirotaka Murase[1], Mamiko Ozawa[1], Hirohide Saito[3], Fumi Nagatsugi[1,2]

Keywords: RNA-binding small molecule, Large scale analysis, Screening, Chemical probe, FID assay

RNA-binding molecules are attractive targets as therapeutic drugs for treatments of gene-related diseases and infections. Fluorescent indicator displacement (FID) assay is a method to identify novel RNA-binding molecules (**Fig. A**). To perform FID assays for various RNAs, the identification of the targetable RNAs that indicators bind to is required due to the lack of information on RNA binding of indicators. Therefore, a method to obtain binding profiles of indicators to different RNAs can provide useful information to identify a large number of targetable RNAs and make screening more efficient.

In this study, we utilized microarray technology[1] to obtain the binding profiles of fluorescent indicators, thiazole orange (TO) type probes[2] known as a light-up probe. Based on the obtained profiles, we selected targetable disease-related RNAs and identified several RNA-binding small molecules by FID assays. Interestingly, we found that different indicators provided different hit compounds, which encouraged us to develop new indicators to obtain novel hit compounds without missing them.

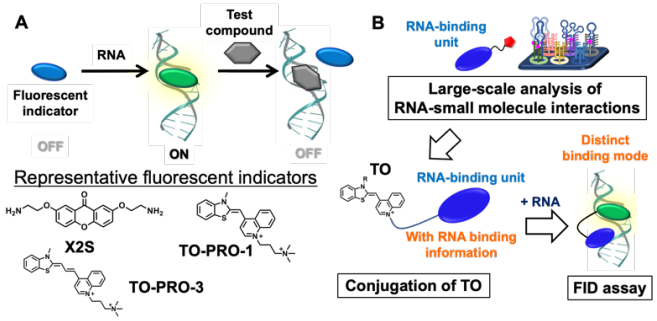

Fig. (**A**) FID assay, (**B**) novel fluorescent indicators.

We next aimed to develop new fluorescent indicators that have distinct binding modes from known indicators and discover novel RNA-binding small molecules by FID assays with the new indicators (**Fig B**). We synthesized TO-conjugated RNA-binding molecules with the large-scale data of RNA binding selectivity obtained by microarray technology, and their binding selectivity were generally retained even after conjugation with TO moiety. Furthermore, we conducted FID assays using disease-related RNAs and developed the indicators and successfully identified new hit compounds that were not detected with known TO-based indicator. In this presentation, we will report the detailed data on the novel indicators and the results of the FID assays.

1) H. Saito, et al., *Nat. Commun.* **2020**, *11*, 6275. 2) S. Nishizawa, et al., *Chem. Commun.* **2019**, *55*, 3183.

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

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC H936(936, Bldg. 9 [3F])

[H936-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Nobuhiko Hosono, Norifumi Kawakami

English
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[H936-4am-01]
Characterization of protein nanocage TIP60 with pyrene-modified interior surface
○Maika Yamashita[1], Kenji Miyamoto[1], Norifumi Kawakami[1] (1. Keio University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[H936-4am-02]
Construction of histidine clusters in a ferritin cage for the oxidase-mimetic catalysis
○Jiaxin Tian Tian[1], Basudev Maity[1], Tiezheng Pan[1], Satoshi Abe[1], Takafumi Ueno[1] (1. Tokyo Institute of Technology)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[H936-4am-03]
Removing Denatured Proteins by Selective Adsorption in Nanopores
○Hirotaka Taketomi[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[H936-4am-04]
Optical manipulation of microtubule structures by Tau-derived peptide-fused light-responsive tetrameric protein
○Soei Watari[1], Hiroshi Inaba[1], Takashi Iwasaki[2], Akira Kakugo[3], Kazunori Matsuura[1] (1. Grad. Sch. of Eng., Tottori Univ., 2. Grad. Sch. of Agric. Sci., Tottori Univ., 3. Grad. Sch. of Sci., Kyoto Univ.)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
Break

Japanese
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[H936-4am-05]
In-cell self-assembly of fluorescent protein-modified artificial viral capsid
○Kentarou Sakamoto[1], Yuka Yamamoto[1], Hiroshi Inaba[1], Kazunori Matsuura[1] (1. Grad. Sch. of Eng., Tottori Univ.)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[H936-4am-06]
Construction of enveloped viral replica equipped with spike protein derived from SARS-CoV-2

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○Hiroto Furukawa[1], Keisuke Nakamura[2], Hiroshi Inaba[1], Yoshihiro Sasaki[2], Kazunari Akiyoshi[2], Kazunori Matsuura[1] (1. Grad. Sch. of Eng., Tottori Univ., 2. Grad. Sch. of Sci., Osaka Univ.)

English

11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[H936-4am-07]

Accurate Prediction of Protein pK_a by Geometric Deep Learning

○Shijie Xu[1], Akira Onoda[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

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Characterization of protein nanocage TIP60 with pyrene-modified interior surface

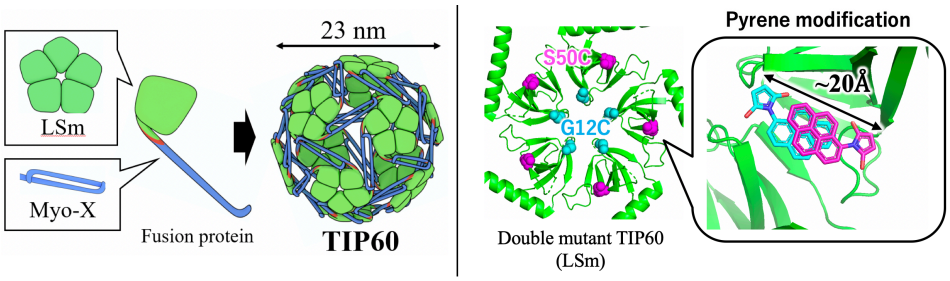
([1] *Keio University*) ([2] *Shinshu University*) ○Maika Yamashita,[1] Norifumi kawakami,[1] Ryoichi Arai,[2] Kenji Miyamoto[1]

Keywords: *Protein Nanoparticles; TIP60; Pyrene; molecular encapsulation; Thermostability*

Synthetic fluorescent molecules are widely used in various fields, from pure biology to medicine. For example, they are employed in detecting macromolecules of interest and serving as photosensitizers in photodynamic therapy. However, the poor water solubility limits their application range. The varieties of molecular materials to dissolve the hydrophobic fluorescent molecules in aqueous phase have thus developed thus far. Protein-based nanocages are one of the most promising materials for this purpose. Although natural proteins have hydrophilic surfaces, effort to hydrophobize the interior surface of nanocages provide confined hydrophobic compartments for encapsulating hydrophobic fluorescent molecules[1,2].

We recently produced a nanocage having hydrophobic interior surface based on an artificially designed 60-mer protein nanocage, TIP60[3,4](figure, left panel). The interior surface is modified by pyrenes. The singly modified TIP60, containing 60 pyrenes on the interior surface, allows for the accommodation of aromatic fluorescent molecule (Nile Red) through π-stacking[5]. However, the low encapsulation efficiency (2-3 mol./cage) is needed to improve.

In this study, to improve the efficiency, we aimed to increase the hydrophobicity of the interior surface of TIP60 by augmenting the number of modified pyrene molecules. Specifically, we designed a double mutant G12C and S50C as modification sites (figure, right panel). The modified TIP60 could encapsulate 20-30 mol./cage of Nile Red. We found that the doubly modified TIP60 exhibited higher thermostability than both unmodified and singly modified TIP60. This improvement is attributed to the π-stacking of pyrene molecules on the interior surface of TIP60. As shown in the figure, two pyrenes are positioned where they can interact with each other. Indeed, we found the excimer formation of pyrene molecules. Accordingly, the developed doubly modified TIP60 could be used as the potential nanocarrier for hydrophobic fluorescent molecules and as a component of a light harvesting system.



1.) T.G.W. Edwardson *et al., Natt. Commun.* **2020** 2.) D. Ren *et al., Adv. Function. Mater.*. **2012** 3.) N. Kawakami *et al., Angew. Chem. Int. Ed.* **2018** 4.) J. Obata *et al., Chem. Commun.*, **2021** 5.) M. Yamashita *et al., ChemPlusChem,* **2023**

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Construction of histidine clusters within a ferritin cage for oxidase-mimetic catalysis

([1]*Grad. School of Life Sci. and Technol., Tokyo Institute of Technology)*
○Jiaxin Tian[1], Basudev Maity[1], Tiezheng Pan[1], Satoshi Abe[1] and Takafumi Ueno[1]
Keywords: Ferritin cage; Histidine cluster; X-ray crystal structure; Peroxidase activity.

Developing materials that mimic the enzyme, Horseradish peroxidase (HRP) [1] has a huge practical importance as oxidative catalysis to break down harmful substances in the environment, especially the organic pollutants. Most peroxidase mimetic materials rely on metal complexes or nanoparticles, with only a few being metal-free [2]. This is due to the lack of systematic investigations to create peroxidase mimics, like how to position the side chains and other elements. With this background, we aimed to develop a simple metal-free artificial peroxidase mimic by rational design of catalytic sites on a robust protein surface.

To achieve the goal, we employed the 24-mer ferritin cage as a suitable template due to the high stability and unique structural features, especially the confined environment, which is known to be beneficial for catalytic performance. Since histidine is known to activate H_2O_2, we systematically introduced a series of histidine residues near the 2-fold symmetric interface, which is the most stable part of the ferritin cage and characterized the mutants by X-ray crystallography. Peroxidase activities were evaluated in presence of H_2O_2 and re-designed the mutants to find the key requirements for catalysis.

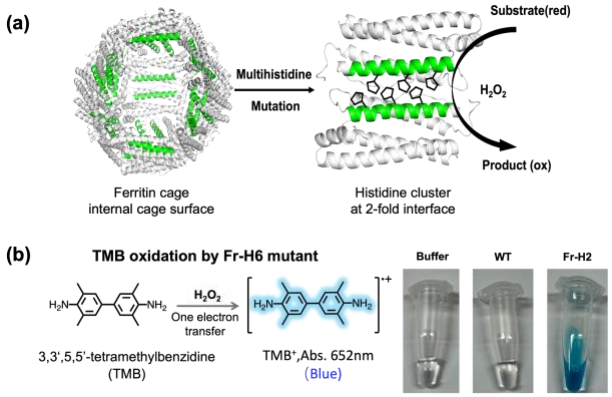

Figure1. Overview of the work. (a) Schematic representation showing the construction of a catalytic histidine-rich site near 2-fold symmetric interface (b) Oxidation of TMB substrate by a histidine-rich ferritin mutant in the presence of H_2O_2.

This presentation will describe the systematic design of metal-free peroxidase mimetic by suitable positioning of Histidine in B-helix near the 2-fold symmetric interface of the ferritin cage (Fig.1a). We evaluated the catalytic oxidation of 3,3,5,5-Tetramethylbenzidine (TMB) as a model substrate by Ferritin mutants in the presence of H_2O_2 (Fig. 1b). The detailed X-ray crystal structure analysis with comparison of catalytic activities by various ferritin mutants will be discussed.

Reference. 1) E. Derat et al., *J. Phys. Chem. B,* 2006. 2) Y. Z. Li *et al*., *ACS Appl. Matter. Interfac*es, 2017. 3) J. Fan, *et al.*, *Biomaterials*, 2012. 4)Taher, M, et al., *Angew. Chem. Int. Ed*., 2022

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Removing Denatured Proteins by Selective Adsorption in Nanopores

([1]*Graduate School of Engineering, University of Tokyo*) ○Hirotaka Taketomi,[1] Nobuhiko Hosono,[1] Takashi Uemura[1]

Keywords: Metal–organic frameworks; Nanopore; Denatured protein; Adsorption; Purification

Denatured proteins tend to form aggregates and inhibit the function of other proteins, causing serious diseases. Purification of proteins to eliminate such denatured fraction is an important technique in protein engineering and research on protein drug discovery. Although size exclusion chromatography (SEC) is commonly employed to remove denatured proteins, its limited scalability poses challenges for industrial applications.[1] In this study, we present a highly efficient and scalable technique for selectively removing denatured proteins from a mixture of native and denatured proteins using metal–organic frameworks (MOFs) (**Figure 1a**).

We chose a MOF (Cr-MIL-101) as the porous adsorbent due to its appropriate window/pore size for selectively sieving polypeptide chains. Lysozyme was chosen as the model protein, and we measured the adsorption isotherms for the lysozymes in both its native and denatured states in the solution. Interestingly, denatured lysozyme exhibited a significantly higher adsorption amount compared to its native form. We fitted the isotherms to the Langmuir model and determined the maximum loading capacity for native and denatured lysozymes to be 0.04 g/g and 0.42 g/g, respectively. Given the MOF's pore window size of approximately 1.5 nm, the denatured and fully unfolded (reduced) lysozyme, with a thickness of ~1 nm, was selectively inserted and captured in the pore, while the native folded form, with a diameter of 2-4 nm, was rejected. We performed selective adsorption experiments using a mixture of native and denatured lysozyme (at a ratio of 2:8, w/w). By adding the MOF to the protein mixture, we successfully removed only the denatured protein from the solution, achieving a purity level of >99% based on activity (**Figure 1b**).

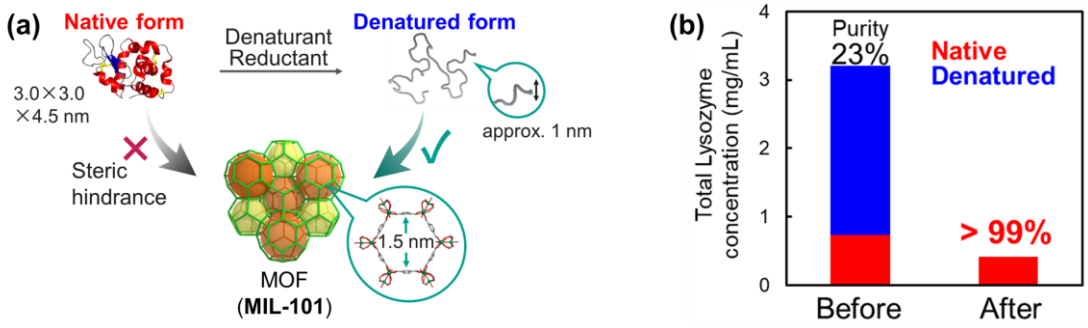

Figure 1. (a) Schematic illustration of the selective protein adsorption in the MOF. (b) Fraction of native (red) and denatured (blue) lysozyme in the solution before and after adding the MOF.

1) A. P. J. Middelerg, *Trends Biotechnol.* **2002**, *20*, 437–443.

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Optical manipulation of microtubule structures by Tau-derived peptide-fused light-responsive tetrameric protein

([1]*Graduate School of Engineering*, *Tottori University*, [2]*Graduate School of Agricultural Science*, *Tottori University*, [3]*Graduate School of Science*, *Kyoto University*) ○Soei Watari,[1] Hiroshi Inaba,[1] Takashi Iwasaki,[2] Akira Kakugo,[3] Kazunori Matsuura[1]

Keywords: Microtubule; Tubulin; Tau-derived peptide; Light-responsive protein; Optical manipulation

Microtubules are tubular cytoskeletons with a 15 nm inner diameter, which are formed by polymerization of tubulin proteins. Microtubule involves crucial cell functions such as cell division, cell deformation, and cell migration. We have previously developed a Tau-derived peptide (TP) which bound to the inner surface of microtubules.[1)] We also have succeeded in generation of various microtubule superstructures such as doublet and branched microtubules by multivalent binding of TP-fused tetrameric protein (Azami Green).[2)] Herein, we focused on other tetrameric protein Dronpa, which converts reversibly monomer and tetramer by irradiation of light with different wavelengths (Fig. 1a). In this study, we constructed TP-fused Dronpa (TP-Dronpa) to manipulate microtubule accumulation and dispersion states by light irradiation (Fig. 1b).

Firstly, we assessed binding site of TP-Dronpa to microtubules. It is indicated that TP-Dronpa can bind to microtubule outer surface by incubation with formed microtubules. Strikingly, we could observe bundled microtubules when TP-Dronpa (tetramer) bound to microtubules, while the TP-Dronpa (monomer) showed no effect to form bundled microtubules (Fig. 1b). Furthermore, we have succeeded in manipulating microtubule accumulation and dispersion states by light irradiation through changing the assembly number (tetramer and monomer) of microtubule-bound TP-Dronpa.

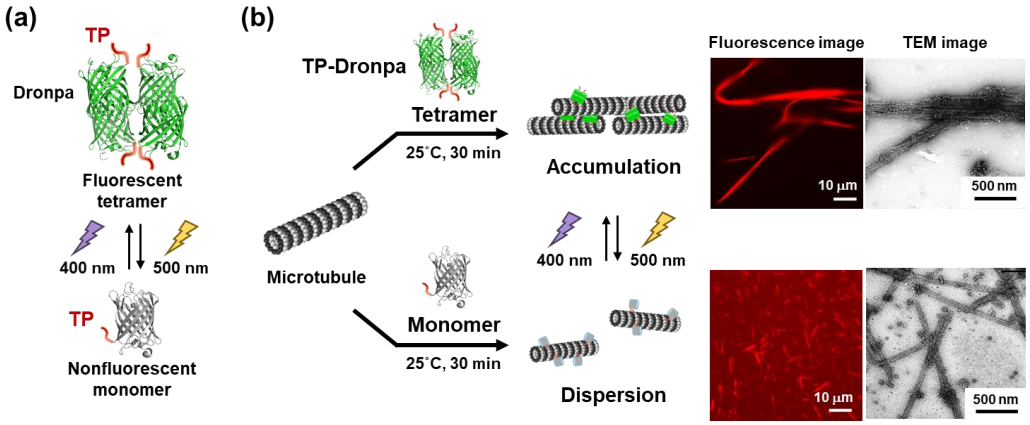

Fig. 1. (a) Photo-conversion of TP-Dronpa. (b) Optical manipulation of microtubule structures by TP-Dronpa.

1) H. Inaba, T. Yamamoto, A. M. R. Kabir, A. Kakugo, K. Sada, K. Matsuura, *Chem. Eur. J.*, **24**, 14958 (2018).
2) H. Inaba, Y. Sueki, M. Ichikawa, A. M. R. Kabir, T. Iwasaki, H. Shigematsu, A. Kakugo, K. Sada, T. Tsukazaki, K. Matsuura, *Sci. Adv.*, **8**, eabq3817 (2022).

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蛍光タンパク質修飾人工ウイルス殻の細胞内自己集合

（鳥大院工 [1]）○坂本 健太郎 [1]・山本 優香 [1]・稲葉 央 [1]・松浦 和則 [1]
In-cell self-assembly of fluorescent protein-modified artificial viral capsid ([1]*Graduate School of Engineering, Tottori University*) ○Kentarou Sakamoto[1], Yuka Yamamoto[1], Hiroshi Inaba[1], Kazunori Matsuura[1]

Peptide/protein-based self-assembling nanocages are expected to be utilized in many fields, however, they are mainly used extracellularly, and there are few papers reporting in-cell self-assembly. We have developed “artificial viral capsid” self-assembled from β-Annulus peptide derived from capsid protein of tomato bushy stunt virus.[1)] While we have been reporting intracellular delivery of artificial viral capsid self-assembled at outside of cells, it is still unknown whether the delivered capsid retain its spherical structure, and there is no report showing in-cell self-assembly of artificial viral capsid. In this presentation, we report in-cell self-assembly of the capsid and evaluation method of the assembly (Fig. 1). β-Annulus conjugated with fluorescent protein (FP) (β-Annulus-FP) is expected to form artificial viral capsid decorated with FPs. β-Annulus-FP expressed in cells were isolated and purified. The in vitro self-assembly was assessed by dynamic light scattering, transmission electron microscopy, and fluorescence polarization measurements. Fluorescence polarization measurement of cells expressing β-Annulus-FP suggested the in-cell self-assembly of the capsid. FRET measurement, TEM observation of the cells and super-resolution microscopy also implied the in-cell self-assembly.
Keywords : In-Cell Self-Assembly, Artificial Viral Capsid, Fluorescence Polarization

ペプチド／タンパク質からなる自己集合性ナノケージは多方面への応用が期待される超分子集合体であるが、これらはあくまで「細胞外」での利用が主であり、「細胞内」で自己集合するナノケージの報告例は数少ない。我々は、トマトブッシースタントウイルス由来の 24 残基β-Annulus ペプチドが水中で自己集合し「人工ウイルス殻」を形成することを見出している [1)]。人工ウイルス殻を用いた「細胞外」から「細胞内」への送達の例は複数存在する一方で、送達された人工ウイルス殻が細胞内でその形状を保持しているかどうかは不明である。本発表では人工ウイルス殻の細胞内自己集合の実現及びその評価系の構築について報告する(Fig. 1)。蛍光タンパク質 (FP) とβ-Annulus を結合したβ-Annulus-FP を培養細胞内で発現させ、単離精製した後、動的光散乱・電子顕微鏡観察・蛍光異方性測定により人工ウイルス殻の形成が確認された。β-Annulus-FP 発現細胞の蛍光異方性測定により細胞内自己集合による人工ウイルス殻の形成が示唆され、また細胞内自己集合は FRET 測定、発現細胞の電子顕微鏡観察および超解像顕微鏡観察からも示唆することができた。

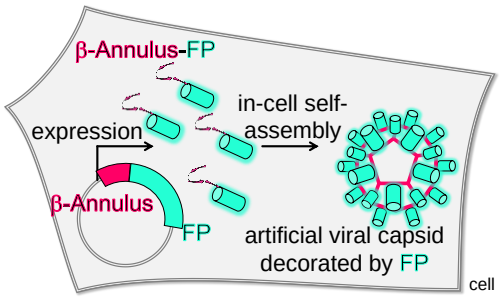

Figure 1. Schematic illustration of in-cell self-assembly of artificial viral capsid.

1) K. Matsuura, *Chem. Commun*., **2018**, *54*, 8944–8959.

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SARS-CoV-2 由来スパイクタンパク質を搭載したエンベロープウイルスレプリカの構築

（鳥取大院工[1]・京大院工[2]）○古川 寛人[1]・中村 圭祐[2]・稲葉 央[1]・佐々木 善浩[2]・秋吉 一成[2]・松浦 和則[1]

Construction of enveloped viral replica equipped with spike protein derived from SARS-CoV-2.

([1]*Graduate School of Engineering, Tottori University*, [2]*Graduate School of Engineering, Kyoto University*) ○Hiroto Furukawa,[1] Keisuke Nakamura,[2] Hiroshi Inaba,[1] Yoshihiro Sasaki,[2] Kazunari Akiyoshi,[2] Kazunori Matsuura[1]

Previously, we have demonstrated that *β*-annulus peptide derived from TBSV self-assembled into artificial viral capsids in water, which can encapsulate some guest macromolecules and can be modified with some functional materials at the surface. Recently, we have succeeded in constructing the artificial enveloped capsid via electrostatic interaction of cationic lipid bilayer and anionic capsid. In this study, we constructed enveloped viral replica equipped with spike protein derived from SARS-CoV-2 and evaluated its interaction with ACE2 receptor by imaging flow cytometry and quartz crystal microbalance. In addition, we evaluated interaction between S protein-equipped viral replica and ACE2 receptor expressed on cell membrane.

Keywords：β-Annulus peptide; Artificial Viral Capsid; Envelope; Self-assembly; SARS-CoV-2

SARS-CoV-2 は、膜上のスパイクタンパク質(S protein)が宿主細胞表面の ACE2 受容体と結合し、細胞内に侵入する[1]。最近、Ferritin や *de novo* タンパク質集合体表面へ S protein 又はその Receptor binding domain (RBD)を直接修飾した研究が報告されているが、エンベロープ型集合体表面への S protein の搭載は未だ達成されていない。我々はこれまで、TBSV 由来*β*-Annulus ペプチドの自己集合により構築される人工ウイルスキャプシドにカチオン性脂質二分子膜を複合化したエンベロープウイルスレプリカの構築に成功した[2]。本研究では、無細胞タンパク質発現系により SARS-CoV-2 由来 S protein を搭載したエンベロープ型ウイルスレプリカを構築し(Fig. 1)、ACE2 受容体との結合評価をイメージングフローサイトメトリー及び水晶振動子マイクロバランス (QCM) 法により詳細に解析した。さらに、膜局在 mlACE2-EGFP を強制発現させた HeLa 細胞への蛍光標識 S protein 搭載エンベロープウイルスレプリカの結合を CLSM 観察により評価した。その結果、ウイルスレプリカ上に搭載した S protein のおいても遊離・固定化 ACE2 受容体に nM オーダーの解離定数で強く結合し、HeLa 細胞膜上の ACE2 受容体に対しても結合することが確認された。以上の結果より、ACE2 受容体結合能を有する S protein 搭載エンベロープウイルスレプリカの構築が示唆された。

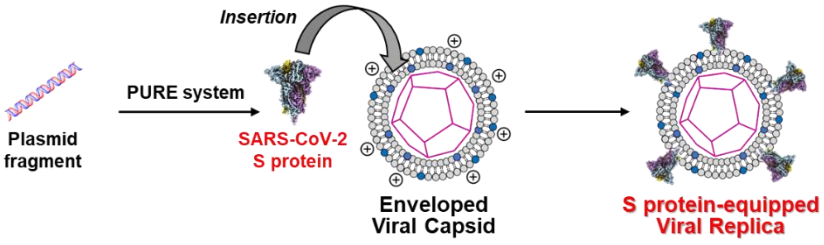

Figure 1. Schematic illustration of construction of SARS-CoV-2 S protein-equipped viral replica.

1) L. Duan et al., *Front. Immunol.*, **11**, 576622 (2020).
2) H. Furukawa et al., *Chem. Commun.*, **56**, 7092 (2020).

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Accurate Protein pK_a Prediction by Geometric Deep Learning

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Shijie Xu,[1] Akira Onoda [1,2]

Keywords: Protein pK_a prediction; Geometric deep learning

Protein pK_a plays a crucial role in many biological processes, such as protein folding, protein-ligand binding, and enzyme catalysis, by regulating the protonation states of ionizable residues. Unlike the residues in the solvent, the deeply buried residues in the protein interior are probably largely affected by the electrostatic interactions with the surrounding residues, and thus their pK_a values are often shifted from the standard values in the solvent. However, modeling such interactions is intractable due to the complexity of the protein structure and remains a challenging problem.

In the past decades, many computational methods have been developed to predict protein pK_a values and achieved great success. Among them, the most popular approach includes the continuum electrostatics methods [1], which are based on the Poisson-Boltzmann equation (PBE), and the empirical methods [2]. However, PBE methods are computationally expensive while the empirical methods are not accurate enough. Recently, machine learning methods [3] have been proposed to predict protein pK_a values, which show a great superiority in the trade-off between prediction accuracy and computational cost. Besides, most of these methods are based on black-box machine learning models, which are not capable of providing physical insights into protein pK_a values. Therefore, a new method that is both accurate, fast, and explainable is needed.

In this work, we propose a novel approach to predict protein pK_a based on geometric deep learning, termed EquipKa, which not only exhibits high prediction accuracy at a fast speed but also explains how the protein structure determines the protein pK_a shift through the learned geometric features. We demonstrate the effectiveness of our approach on a benchmark dataset and show that our approach outperforms the state-of-the-art methods, including the PBE, empirical, and machine learning methods, as shown in Fig. 1a. Besides, the pK_a shift contributions from different neighboring atoms are also visualized as cylinders in Fig. 1b where the thickness represents the strength and colors represent the direction of contributions.

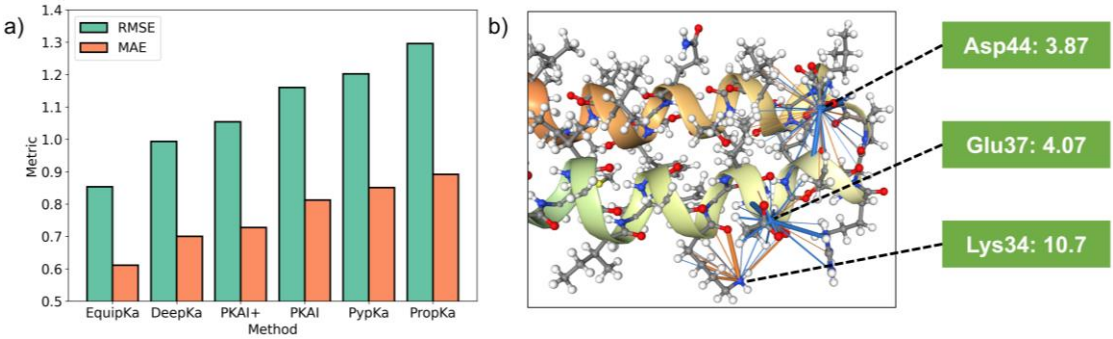

Figure 1. a) The performance of state-of-the-art pK_a predictors. Our EquipKa achieved the best score on the RMSE (root-mean-square error) and MAE (mean absolute error). b) The predicted pK_a values of Lys34, Glu37, and Asp44 in protein (1a91) by EquipKa. Blue represents higher than model pK_a while orange is lower. pK_a shift contributions from neighboring atoms are also plotted as lines with blue color (positive shift) or orange color (negative shift).

1) Reis P. B.P.S. *et al*. *J. Chem. Inf. Model.* 2020, *60*, 4442-4448. 2) Søndergaard, C. R. *et al. J. Chem. Theory Comput.* 2011, *7*, 525-537. 3) Cai, Z., *et al. ACS omega* 2021, *63*, 34823-34831.

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

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC H931(931, Bldg. 9 [3F])

[H931-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Kunihiko Morihiro, Yukiko Kamiya

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H931-4pm-01]
Developing the intracellular FRET imaging approach to elucidate the mechanism of anti-miRNA oligonucleotides

○Hongyu Zhu[1], Yukiko Kamiya[1,2], Hiroyuki Asanuma[1] (1. Nagoya University , 2. Kobe Pharmaceutical University)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H931-4pm-02]
Development of Anti-miR-21 Oligonucleotide by Acyclic Nucleic Acids

○Yukiko Kamiya[1,2], Fuminori Sato[2], Hiroyuki Asanuma[2] (1. Kobe Pharmaceutical University, 2. Nagoya University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H931-4pm-03]
Reversible optical control of receptor activity by azobenzene base-containing DNA aptamer.

○Masahiro Wakano[1], Keiji Murayama[2], Ryosuke Ueki, Hiroyuki Asanuma[2], Shinsuke Sando[1] (1. Graduate School of Engineering, The University of Tokyo, 2. Graduate School of Engineering, Nagoya University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H931-4pm-04]
The influence of methylated DNA on DNA polymerase with strand displacement ability

○Mizuki Tomizawa[1], Kiwako Watanabe[1], Kaori Tsukakoshi[1], Kazunori Ikebukuro[1] (1. Tokyo University of Agriculture and Technology)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H931-4pm-05]
Vinyl-quinazolione derivatives-based RNA alkylation and the single-nucleotide resolution analysis by next generation sequencing

○Yutong Chen[1,2], Kazumitsu Onizuka[1,2], Kaoru Richard Komatsu[3], Emi Miyashita[3,4], Kaho Maeta[3], Hirohide Saito[4], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku University, 2. Department of Chemistry, Graduate school of Science, Tohoku University, 3. xFOREST Therapeutics, 4. CiRA, Kyoto University)

English

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2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[H931-4pm-06]

Development of cancer-selective DNA aptamer using weakly acidic microenvironment-responsive artificial nucleobase

○Yuyuan Chen[1], Kunihiko Morihiro[1], Yui Nemoto[1], Akito Ichimura[1], Ryosuke Ueki[1], Shinsuke Sando[1], Akimitsu Okamoto[1] (1. The University of Tokyo)

Japanese

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[H931-4pm-07]

The Impact of Linker Structure and the Number of Fluorine-containing Functional Groups of Nucleic Acids on Cellular Uptake and siRNA Knockdown Efficacy

○Masako Takatsu[1], Kunihiko Morihiro[1], Yu Ota[1,2], Kosuke Aikawa[1], Takashi Okazoe[1,2], Akimitsu Okamoto[1] (1. The Univ. of Tokyo, 2. AGC Inc.)

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Developing the intracellular FRET imaging approach to elucidate the mechanism of anti-miRNA oligonucleotides

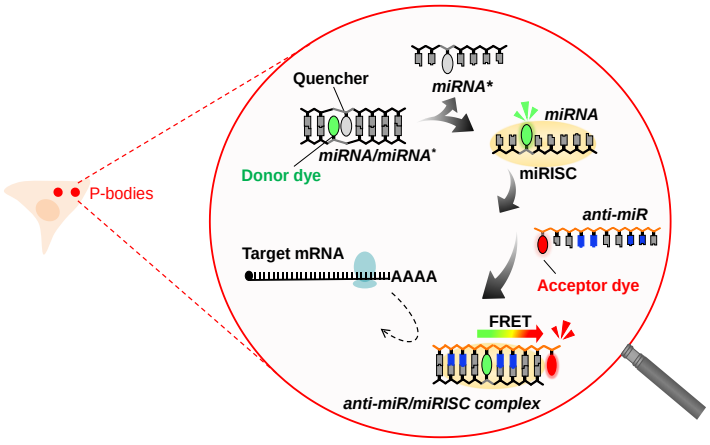
([1]*Graduate School of Engineering, Nagoya University*, [2] *Laboratory of Bioanalytical Chemistry, Kobe Pharmaceutical University*) ○Hongyu Zhu,[1] Yukiko Kamiya,[1,2] Hiroyuki Asanuma

Keywords: Anti-miRNA Oligonucleotide; Imaging analysis; FRET

The aberrant expression of microRNA (miRNA) such as miR-21 has been implicated in many human diseases, especially cancer. Therefore, miRNA inhibition has emerged as an attractive therapeutic strategy. For instance, anti-miRNA oligonucleotides (anti-miRs) are chemically modified synthetic oligonucleotides that complement and inhibit aberrant miRNA function. To enhance anti-miR efficacy, our lab has developed enzyme-resistant and effective SNA-anti-miRs with our original acyclic nucleic acid, serinol nucleic acid (SNA), backbone, and the artificial nucleobase 2,6 - diaminopurines (D) for increasing miRNA affinity.[1]

While anti-miRs exhibit efficacy in suppressing miRNA function, the molecular details of anti-miR-mediated miRNA inhibition in cells remain unclear. Key questions remain regarding the interaction between the anti-miRNA and target miRNA and the subcellular localization of the complex. To address this, we developed a Förster resonance energy transfer (FRET) system to monitor the anti-miR and miRNA interactions in cells.[2]

In this system, we designed and optimized the miRNA/miRNA* probe with the donor dye (BO) on miRNA and quencher (methyl red; MR) on miRNA*. Additionally, we paired miRNA on miRISC with Cy3 labeled SNA-anti-miR acceptor to enable FRET upon anti-miRNA and miRNA on miRISC binding.



This system provides a novel application for exploring the mechanisms underlying anti-miR action and the intracellular interactions of therapeutic agents, including anti-miRs and siRNAs in cells. More details of the FRET system properties will be presented at the conference.

1) Y. Kamiya *et al.*, *ChemBioChem*., **2017**, 18, 1917–1922.
2) Z. Hongyu *et al.*, *ACS Chem Biol,* **2023**, 18, 10, 2281–2289.

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非環状型人工核酸からなる抗 miR-21 核酸の開発

(神薬大[1]、名大工[2]) ○神谷 由紀子[1,2]、佐藤 史経[2]、浅沼 浩之[2]

Development of Anti-miR-21 Oligonucleotide by Acyclic Nucleic Acids ([1]*Faculty of Pharmaceutical Sciences, Kobe Pharmaceutical University*, [2]*Graduate School of Engineering, Nagoya University*) ○Yukiko Kamiya,[1,2] Fuminori Sato,[2] Hiroyuki Asanuma[2]

Artificial nucleic acids that have high nuclease resistance and affinity to natural oligonucleotides are promising as nucleic acid drugs. We have been attempted to develop anti-miRNA oligonucleotide (AMO) by using Serinol nucleic acid (SNA).[1] To develop SNA-based AMO against miR-21 (AMO21) which has complementary region, SNA-SNA hybridization should be avoided. For this, we prepared AMO having 2,6-diaminopurine (D) and 2-thiouracil (sU) known as the pseudo-complementary base pairs.[3, 4] As a result, self-association of the SNA-based AMO was inhibited and anti-miR21 activity was enhanced. Then, we evaluated the properties of the SNA-AMO21 in vivo using model mice. Tumor growth in the xenograft model mice was suppressed upon injection of SNA-based AMO. No significant hepatotoxicity was observed.

Keywords : Antisense; artificial nucleic acid; miR-21; miRNA

酵素耐性能や RNA 親和性を向上させる人工核酸は核酸医薬への応用が期待されている。非環状型人工核酸 Serinol nucleic acid (SNA)は、非常に高い酵素耐性を示すことから、核酸医薬品のプラットフォームとして有望である。そこで、癌や線維症などの疾患組織において過剰発現する miR-21 を標的とした SNA からなる Anti-miRNA oligonucleotide(SNA-AMO21)の開発に取り組んでいる[1]。しかし、SNA は自己親和性が高いために、自己相補配列を有する miR-21 を標的とした場合、自己相補領域を介した SNA 自身の相互作用によって、anti-miRNA 活性が低下してしまう問題があった。そこで本研究では、自己相互作用を抑制する手法を開発し、高い miR-21 阻害活性をもつ SNA-AMO21 の開発を目指した。

本研究の目的のために、まずは Pseudo-complementary 塩基対である 2,6-ジアミノプリン（D）と 2-チオウラシル（sU）の SNA アミダイトモノマーの新規合成法を確立した[2,3] 。開発した手法を用いて D, sU を導入した SNA-AMO21 を調製し、自己相互作用ならびに anti-miRNA 活性を評価した。その結果、D と sU を導入することにより、期待通りに SNA-AMO21 の二次構造形成の阻害、さらに miR-21 阻害活性の劇的な向上を達成した。そこで、D, sU を導入した SNA-AMO21 の in vivo 評価を実施した。Xenograft モデルマウスに対し、SNA-AMO21 を投与した結果、SNA-AMO21 投与群にて有意に腫瘍増殖が抑制された。また、特段の肝毒性や腎毒性は観察されなかった。以上、我々は高活性で安全性の高い SNA-AMO21 の開発に成功した。

[1] Y. Kamiya, *et al.*, *ChemBioChem*, **2017**, *18*, 1917-1922.

[2] Y. Kamiya, *et al.*, *Chem. Asian J.*, **2020**, *15*, 1266-1271.

[3] F. Sato, *et al.*, *J. Org. Chem.*, **2023**, *88*, 796-804.

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アゾベンゼン塩基含有 DNA アプタマーによる受容体活性の可逆的光制御

(東京大学大学院工学系研究科 [1]、名古屋大学大学院工学研究科 [2]) ○若野 将大 [1]・村山 恵司 [2]・植木 亮介・浅沼 浩之 [2]・山東 信介 [1]

Reversible optical control of receptor activity by azobenzene base-containing DNA aptamer.

([1] *Graduate School of Engineering, The University of Tokyo*, [2] *Graduate School of Engineering, Nagoya University*) ○Masahiro Wakano,[1] Keiji Murayama,[2] Ryosuke Ueki, Hiroyuki Asanuma,[2] Shinsuke Sando[1]

Certain cellular functions are regulated by dimerization and activation of receptor tyrosine kinases, followed by the cell signaling circuits.[1] DNA aptamers have the ability to bind to target receptors specifically, and are attracting attention as a new molecular technology for the regulation of receptor dimerization due to their ease of synthesis and potential application of DNA nano technology. However, conventional DNA aptamers generally activate the target receptors only once. To address this issue, we developed a Met-aptamer whose agonistic activity can be optically controlled by introducing azobenzene bases.[2] The azobenzene base undergoes *cis-trans* isomerization upon photoirradiation, switching between the active dimeric and inactive monomeric structures of the aptamer, allowing its activity and activation time to be reversibly regulated in response to light. We have confirmed that Met phosphorylation and downstream cell signaling in Hela cells can be regulated by the aptamer and light irradiation pattern.

Keywords: DNA aptamer, azobenzene, artificial DNA, receptor, optical control

ある種の細胞機能は、受容体チロシンキナーゼの二量体化と活性化、それに続く細胞シグナル伝達回路によって制御されている [1]。この動態を解明するため、受容体の二量化を人工的に制御する手法が求められている。DNA アプタマーは、標的受容体と特異的に結合する機能を持ち、合成の容易さや DNA ナノ工学の応用可能性から、受容体を制御する新しい分子技術として注目されている。しかし、従来の DNA アプタマーは基本的に一度しか受容体を活性化できない。この問題に対し、我々は、アゾベンゼン塩基 [2] を DNA アプタマーに導入し、光によってアゴニスト活性を可逆的に制御できる Met 受容体アプタマーを開発した。本アプタマーは、光照射によりアゾベンゼン塩基が *cis-trans* 異性化し、アプタマーの活性な二量体構造と非活性な単量体構造とが切り替わることで、その活性や活性化時間を光に応じて可逆的に調整できる。このアプタマーを用い、Hela 細胞の Met のリン酸化や下流細胞シグナルをアプタマーおよび光照射パターンによって制御できることを確かめた。

1) M. A. Lemmon and J. Schlessinger, *Cell.* **2010**, *141*, 1117–1134.
2) H. Asanuma et al., *Angew. Chem.* **2001**, *40*, 14, 2671–2673.

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The influence of methylated DNA on DNA polymerase with strand displacement ability

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*)
○Mizuki Tomizawa,[1] Kiwako Watanabe,[1] Kaori Tsukakoshi,[1] Kazunori Ikebukuro[1]

Keywords: DNA methylation, DNA polymerase with strand displacement ability

DNA methylation is an important epigenetic event which alters gene expression without a change in nucleotide sequence. The methylated cytosine bearing methyl group to the carbon 5 position of the cytosine ring is common in eukaryotes. Cytosine methylation usually occurs in CpG islands in promoter regions which CpG oligodeoxynucleotides densely present. The aberrant CpG methylation relates to inborn disorder, cancer, mental disorder and so on. Therefore, it is required to develop a method to detect CpG methylation in target genomic regions rapidly for the clinical diagnosis.

We reported that DNA structure, G-quadruplexes (G4)[1] and i-motif [2] changed by CpG methylation, and the initial elongation efficiency of PCR[3] of the template DNA bearing those structures also changed by CpG methylation. G4 and i-motif are the non-canonical steric structures formed by guanine-rich or cytosine-rich nucleic acids. Based on these findings, we developed methylated DNA detection methods by detecting DNA structure differences. In addition, it was reported that double-stranded DNA (dsDNA) cause stabilization[4] or destabilization[5] by CpG methylation recently.

Therefore, we assumed that amplification efficiency of DNA polymerase with strand displacement ability changes by CpG methylation. This DNA polymerase can displace the DNA encountered during elongation. We used loop-mediated isothermal amplification (LAMP) for use of DNA polymerase with strand displacement ability, one of the methods that amplifies DNA under isothermal conditions with strand displacement DNA synthesis[6] and have been used widely in infection test. LAMP reaction was performed to synthetic DNA bearing the sequence of upstream region of dopamine receptor D2 (DRD2) which associated with schizophrenia, and the androgen receptor (AR) promotor region which associated with hormone-independent prostate cancer of the human genomic DNA. LAMP products were measured by turbidity, fluorescence intensity and electrophoresis analysis. We observed that significant differences of amplification time from unmethylated DNA and methylated DNA. It is possible that detection of CpG methylation becomes easy and rapid by our findings.

1) H. Hasegawa, *Int. J. Mol. Sci.*, **2021**, *22*, 13159. 2) D. Oshikawa, *Int. J. Mol. Sci.*, **2022**, *23*, 6467. 3) W. Yoshida, *Anal. Chem*. **2016**, *88*, 7101-7107. 4) J. Yoo, *Nat. Commun*., **2016**, *7*, 11045. 5) A. Furukawa, *Nucleic Acids Res.*, **2021**, *49*, 2. 6) T. Notomi, *Nucleic Acids Res.*, **2000**, *28*, 12.

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Vinyl-quinazolinone derivatives-based RNA alkylation and the single-nucleotide resolution analysis by next generation sequencing

([1]*IMRAM, Tohoku University*, [2]*Department of Chemistry, Graduate School of Science, Tohoku University,* [3]*xFOREST Therapeutics,* [4]*CiRA, Kyoto University*) ○Yutong Chen,[1,2] Kazumitsu Onizuka,[1,2] Kaoru R. Komatsu,[3] Emi Miyashita,[3,4] Kaho Maeta,[3] Hirohide Saito,[4] Fumi Nagatsugi[1,2]

Keywords: Vinyl-quinazolinone (VQ); RNA alkylation; Next generation sequencing.

RNA transcripts largely participated various processes in cellular biology and disease onset, providing unlimited potential for RNA-targeted therapeutics. Small molecules with good cell-permeability and structural adaptation have been extensively studied for RNA biology investigation and regulation. Chemically reactive compounds which can form covalent bond with RNAs were exploited for probing and labeling to target RNA.

Previously, we reported that vinyl-quinazolinone (VQ) derivatives converted to a reactive-ON state and selectively reacted with higher-ordered RNA by the elimination of leaving groups (Figure 1).[1] In this study, we would report the optimization of VQ's reactivity and investigated the protonation-accelerated reaction mechanism.[2] Furthermore, we synthesized azide-functionalized VQ with two different RNA binder and analyzed the alkylation reactivity towards RNA library. In this approach, the reverse transcription to record mutations induced by probe adduct into cDNA and amplification followed by next generation sequencing analysis, enabled detection of alkylation frequency along the sequence and alkylation location at single-nucleotide resolution. We will report these results in detail.

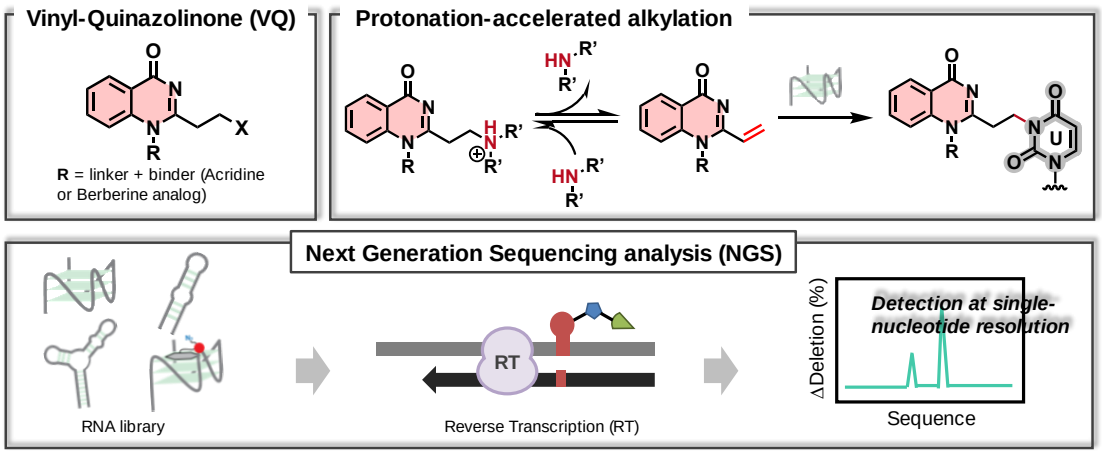

Figure 1. VQ-based RNA alkylation and large-scale analysis by next generation sequencing

1) K. Onizuka, M. E. Hazemi, F. Nagatsugi, *et al.*, *Nucleic Acids Res*. **2019**, *47*, 6578–6589.

2) Y. Chen, K. Onizuka, M. E. Hazemi, F. Nagatsugi, *Bioconjugate Chem*. **2022**, *33*, 2097–2102.

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Development of cancer-selective DNA aptamer using weakly acidic microenvironment-responsive artificial nucleobase

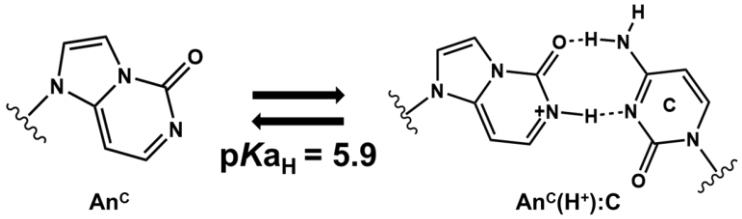
([1]*Graduate School of Engineering, The University of Tokyo*) ○Yuyuan Chen,[1] Kunihiko Morihiro,[1] Yui Nemoto,[1] Akito Ichimura,[1] Ryosuke Ueki,[1] Shinsuke Sando,[1] Akimitsu Okamoto[1]

Keywords: DNA Aptamer; pH-responsive; Artificial Nucleobase

Since the pH around cancer cells is biased to be weakly acidic (approximately 6.2-6.9) compared to that around normal cells, where the pH is maintained at approximately 7.4[1], the use of pH-responsive nucleic acid molecules in cancer drugs is expected to enhance cancer selectivity and reduce adverse effects on patients. **An^{C}**, an artificial nucleobase previously developed in this laboratory, was found to have a pKa_H of 5.9, and it is thought to be capable of reversibly forming a base pair with cytosine by protonation at pH around cancer cells[2].Therefore, we thought that it would be possible to develop highly cancer-selective nucleic acid drugs by using this artificial nucleobase **An^{C}** to the formation of versatile duplexes.

In our research, **An^{C}** nucleotides are introduced into DNA aptamer CSL1 to equip them with weakly acidic microenvironment responsiveness and cancer cell selectivity. The sequence of CSL1 was designed on the basis of SL1, which has been reported as an antagonist of C-Met.[3] We synthesized three types of DNA aptamers **CSL1s**, **CSL1-I**, **CSL1-II**, and **CSL1-III** which containing 1, 2, and 3 **An^{C}** nucleotides, respectively.

To evaluate the stabilization of **CSL1** under acidic environment, the melting temperature (T_m) of each **CSL1** was measured in PBS (pH 7.4 or pH 6.4). **CSL1-I** showed higher T_m in pH 6.4 than in pH 7.4, indicating stabilization in acidic condition by **An^{C}** introduction. We also evaluated the pH-responsive inhibitory effects of **CSL1s** by quantifying phosphorylated C-Met with ELISA in A549 cells in buffer (pH 7.4 or pH 6.4) mimicking microenvironment of normal and tumor tissue. The wound healing assay also be used to evaluate the inhibitory effect of **CSL1s** on cancer cell migration.



1) Anderson N M, Simon M C. *Current Biology*, **2020**, *30*, 921.

2) Morihiro, K, Moriyama, Y, Nemoto, Y, Osumi, H. Okamoto, A, *Journal of the American Chemical Society*, **2021**, *143*, 14207.

3) Ueki R, Sando S. *Chemical Communications*, **2014**, *50*, 13131.

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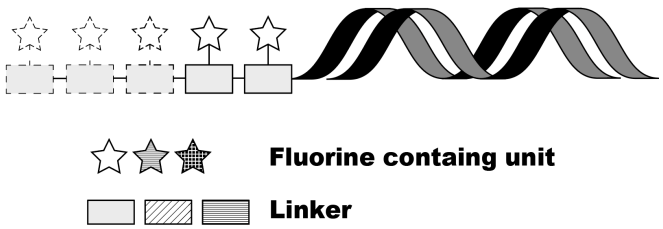
フッ素官能基修飾核酸における修飾基の数とリンカー構造が細胞取り込みおよびsiRNAノックダウン機能に与える影響

（東大院工[1]・AGC株式会社[2]）○高津 正子[1]・森廣 邦彦[1]・太田 有羽[1,2]・相川 光介[1]・岡添 隆[1,2]・岡本 晃充[1]

The Impact of Linker Structure and the Number of Fluorine-containing Functional Groups of Nucleic Acids on Cellular Uptake and siRNA Knockdown Efficacy ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*AGC Inc.*) ○Masako Takatsu[1], Kunihiko Morihiro[1], Yu Ota[1,2], Kosuke Aikawa[1], Takashi Okazoe[1,2], Akimitsu Okamoto[1]

The cellular uptake and knockdown efficacy of chemically modified siRNA are critical factors in the development of effective nucleic acid-based therapeutics. We investigated the cellular uptake of perfluoroalkyl-modified DNA and observed variations in the mode of cellular entry based on the number of conjugated perfluoroalkyl units [1)]. In this study, we designed a series of siRNAs modified with fluorine-containing functional groups, incorporating varying linker structures and numbers of modified groups. Cellular uptake was assessed through flow cytometry analysis, and knockdown efficacy was evaluated by measuring target gene expression levels. This insight will contribute to the rational design of nucleic acid therapeutics.
Keywords : Nucleic acid therapeutics; Conjugated-DNA/RNA; Drug delivery; Fluorine; Cellular uptake

核酸医薬開発において、目的に応じた細胞内送達機能を付与する化学修飾設計のためには、化学構造による細胞取り込みの違いや機能への影響を測定評価することが重要である。私たちは最近、ペルフルオロアルキル基（PFC基）を化学修飾したDNAの細胞膜透過性を評価し、PFC基の数により細胞内導入効率や導入形態が異なることを見出した[1)]。本研究では、siRNAのセンス鎖に環境負荷の少ないフッ素官能基を修飾し、そのリンカー構造や修飾ユニット数を変えた場合に細胞取り込み効率とノックダウン効果がどのように影響を受けるかを、フローサイトメトリーおよび標的mRNAの定量により評価した。



1) Cellular Penetration and Intracellular Dynamics of Perfluorocarbon-Conjugated DNA/RNA as a Potential Means of Conditional Nucleic Acid Delivery. Takatsu. M, Morihiro. K, Watanabe. H, Yuki. M, Hattori. T, Noi. K, Aikawa. K, Noguchi. K, Yohda. M, Okazoe. T, Okamoto. A, *ACS Chem. Biol*. **2023**, 18(12), 2590–2598.

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

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC H932(932, Bldg. 9 [3F])

[H932-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Eiji Nakata, Tomohiro Doura

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H932-4pm-01]
Development and structural analysis of subtype-selective photoresponsive ligands for adenosine A_{2A} receptor

○Harufumi Suzuki[1], Tomohiro Doura[1], Tsuyoshi Araya[2], Hidetsugu Asada[2], So Iwata[2], Shigeki Kiyonaka[1] (1. Nagoya University, 2. Kyoto University)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H932-4pm-02]
A novel imaging probe to quantify AMPA receptors trafficking during synaptic plasticity

○Kyohei Soga[1], Akihiro Shibata[1], Hansel Adriel[2], Takaaki Fujiwara[2], Eriko Nango[2,3], Shigeki Kiyonaka[1] (1. Grad. School. Eng. Nagoya University, 2. IMRAM, Tohoku University, 3. RIKEN SPring-8)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H932-4pm-03]
Visualization of lipid droplets in cells and tissues by using red and deep-red fluorescent molecules based on BODIPYs

○Toshitada Yoshihara[1], Risa Uda[1], Suzuna Iijima[1], Mayuko Shimanuki[1], Shuichi Shiozaki[1] (1. Gunma Univ.)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[H932-4pm-04]
Small allosteric disulfide/diselenide reagents may regulate cellular redox homeostasis

○Rumi Mikaimi[1], Shingo Kanemura[2], Masaki Okumura[3], Kenta Arai[1] (1. Tokai Univ., 2. Kwansei Gakuin Univ., 3. Tohoku Univ.)

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
Break

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H932-4pm-05]
Monitoring of RNA motility in living cells using fluorescence/bioluminescence and "mPUM technology"

○Hideaki Yoshimura[1], Masatoshi Eguchi[1], Yoshibumi Ueda[1], Takeaki Ozawa[1] (1. The University of Tokyo)

Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

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[H932-4pm-06]

Distribution analysis of thiol metabolites in the frozen tissue by using fluorescent labeling reagent coated TLC plate

○Tatsuya Nishihara[1], Gaku Suzuki[1], Koki Nishida[1], Rika Tsukame[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

Japanese

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[H932-4pm-07]

Development of new compounds using for detecting mismatch DNA

○Fumie Takei[1], Naoki Yamada[1], Sumiyo Hiruma[1] (1. National Defence Medical Colledge)

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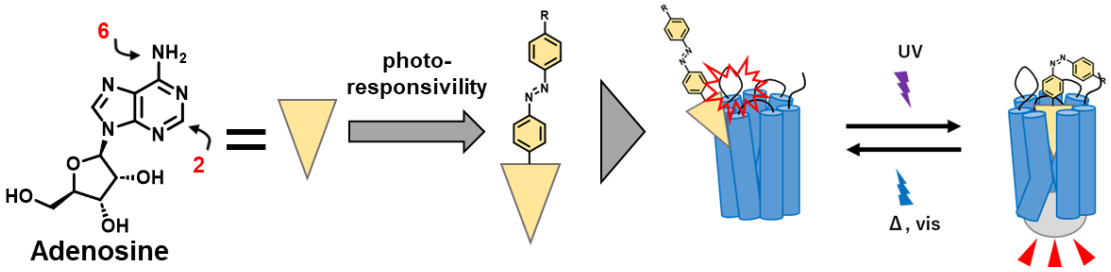
アデノシン A_{2A} 受容体サブタイプ選択的な光応答性リガンドの開発およびその構造基盤

（名大院工[1]・京大院医[2]）○鈴木 啓文[1]・松葉 佑弥[1]・堂浦 智裕[1]・荒谷 剛史[2]・浅田 秀基[2]・岩田 想[2]・清中 茂樹[1]
Development and structural analysis of subtype-selective photoresponsive ligands for adenosine A_{2A} receptor ([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Medicine, Kyoto University*) ○Harufumi Suzuki,[1] Yuya Matsuba,[1] Tomohiro Doura,[1] Tsuyoshi Araya,[2] Hidetsugu Asada,[2] So Iwata,[2] Shigeki Kiyonaka[1]

Adenosine A_{2A} receptor ($A_{2A}R$), a member of the class A G protein-coupled receptor (GPCR) family, is widely expressed *in vivo*. Elucidation of the physiological function of $A_{2A}R$ is highly desirable, because $A_{2A}R$ is involved in various diseases such as insomnia and Parkinson's disease. Here, we focused on photopharmacology, which enables the control of the activity of target molecules with high spatiotemporal resolution by light irradiation. We designed and synthesized adenosine derivatives with a photoresponsive azobenzene moiety at the 2- or 6-position of the purine group. Cell-based screening of these compounds identified $A_{2A}R$-selective photoresponsive ligands. Of note, the crystal structure of $A_{2A}R$ with the $A_{2A}R$-selective photoresponsive ligand revealed the photoresponsive mechanism and the subtype-selectivity of the ligand.
Keywords : Adenosine receptors; Photopharmacology; Azobenzene; optical control; GPCR

アデノシン A_{2A} 受容体（$A_{2A}R$）は G タンパク質共役型受容体（GPCR）の class A に属し、アデノシンを共通の内在アゴニストとする 4 つのサブタイプ（A_1、A_{2A}、A_{2B}、A_3）の 1 種である。$A_{2A}R$ は生体内で広範に発現し、不眠症やパーキンソン病をはじめとする様々な疾患に関与するため、$A_{2A}R$ が持つ生理機能のより詳細な解明が望まれる。サブタイプ選択的なリガンドは $A_{2A}R$ の生理機能の解明に有用であるが、生体内に発現する $A_{2A}R$ に広く作用するため、特定細胞における $A_{2A}R$ の生理機能の解明には適していない。そのため、$A_{2A}R$ の活性を部位特異的に制御する手法が求められる。私達は光照射により高い時空間分解能で標的分子の活性制御が可能な光薬理学に着目し、アデノシンの 2 位または 6 位に光応答性部位となるアゾベンゼン部位を持つ光応答性リガンドを設計および合成した。細胞応答に基づくスクリーニングより $A_{2A}R$ 選択的な光応答性リガンドを見出し、光応答性リガンドと $A_{2A}R$ の複合体の共結晶構造解析より光応答性リガンドの光作動性と $A_{2A}R$ に対するサブタイプ選択性の構造基盤を解明した。



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新規イメージングプローブによるシナプス可塑性時の AMPA 受容体の精密動態解析

（名大院工[1]・東北大 多元研[2]・理研 SPring-8[3]）○曽我 恭平[1]・柴田 晃大[1]・Hansel Adriel[2]・藤原 孝彰[2]・南後 恵理子[2,3]、清中 茂樹[1]

A novel imaging probe to quantify AMPA receptors trafficking during synaptic plasticity

([1]*Graduate School of Engineering, Nagoya University*, [2]*IMRAM, Tohoku University,* [3]*RIKEN SPring-8*) ○Kyohei Soga[1], Akihiro Shibata[1], Hansel Adriel[2], Takaaki Fujiwara[2], Eriko Nango[2,3], Shigeki Kiyonaka[1]

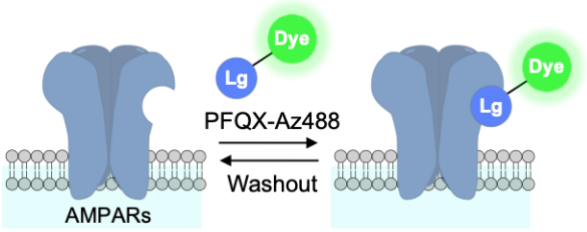
Synaptic activities are regulated by various stimuli in our brain. In the case of memory formation, the strength of synaptic transmission is changed, which is called synaptic plasticity. In this research, we developed a novel imaging probe, PFQX-Az488, to easily and reversibly visualize AMPA receptors which play a pivotal role in synaptic plasticity.

The labeling of endogenous AMPA receptors in neuronal cells with PFQZ-Az488 is accomplished within a brief 30-second. Of note, the effect of labeling to neuronal cells is minimal because PFQX-Az488 can be easily washed out after observation. In cultured hippocampal neurons, this probe allowed to quantify the change of expression levels of AMPA receptors during synaptic plasticity. Furthermore, we achieved a detailed quantification of AMPA receptors trafficking by combining PFQX-Az488 labeling method with a conventional method which we have reported previously.

Keywords : Fluorescent imaging probe; AMPA receptor; Synaptic plasticity

我々の脳内では神経細胞は様々な刺激に応じて、その活動が制御されている。特に記憶形成時にはシナプス可塑性と呼ばれる神経活動の変化が生じる。今回、我々はシナプス可塑性に密接に関与することが知られる、AMPA 型グルタミン酸受容体（AMPA 受容体）を簡便かつ可逆的に可視化可能な蛍光イメージングプローブ PFQX-Az488 を開発した。AMPA 受容体結合部位を用いた X 線結晶構造解析により、PFQX-Az488 結合の分子基盤も明らかにした。

PFQX-Az488 は神経細胞に添加するだけで AMPA 受容体を標識可能であり、その結合飽和時間は 30 秒以内と非常に高速である。また、簡便に washout を行うことができるため、AMPA 受容体のスナップショットイメージングに適している。実際に、PFQX-Az488 を用いて、海馬培養神経細胞でシナプス可塑性時における AMPA 受容体の発現量変化を解析することに成功した。また、以前に我々が報告した AMPA 受容体ケミカルラベル化法[1)]と組み合わせることで、シナプス可塑性時の AMPA 受容体の動態解析にも成功したので、本講演ではその詳細も報告する。



1) Ojima *et al*. *Nat. Commun.* 2021.

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BODIPY 類を骨格とする赤色および深赤色蛍光性分子による細胞および組織内脂質滴の可視化

（群馬大院理工）○吉原 利忠・宇田 梨紗・飯島 鈴七・嶋貫 真由子・塩崎 秀一
Visualization of lipid droplets in cells and tissues by using red and deep-red fluorescent molecules based on BODIPY (*Graduate School of Science and Technology, Gunma University*)
○Toshitada Yoshihara, Risa Uda, Suzuna Iijima, Mayuko Shimanuki, Shuichi Shiozaki

We have designed and synthesized red and deep-red fluorescent molecules based on BODIPY to visualize lipid droplets in living cells and tissues using fluorescence microscopy. The developed molecules exhibited high fluorescence quantum yields in solution. We demonstrated that these molecules selectively accumulated into lipid droplets in living cells and could be visualized lipid droplets in the liver of healthy and fatty liver model mice.
Keywords : Lipid Droplet; Fluorescence; Cell; Tissue; NAFLD

近年、アルコールを摂取しない成人において、過剰な脂質が肝臓に蓄積して発症する非アルコール性脂肪肝疾患(NAFLD)が世界中で急増している。NAFLD の初期過程では肝臓への過剰な脂質蓄積によって、肝細胞内に多数の脂質滴(LD)の発現が見られる。このため脂質滴をイメージングする方法の開発が進められている。特に脂質滴に選択性を示す小分子蛍光性色素と蛍光顕微鏡を用いた方法は、細胞内の脂質滴を高感度に検出・イメージングすることが可能である。我々は、クマリン類を用いて培養細胞だけでなく生きたマウス肝臓内の脂質滴をイメージングできる青色および緑色蛍光色素を開発した[1, 2]。本研究では、BODIPY 骨格を有する化合物 1(Fig. 1)の 2, 8 位に芳香族置換基を導入することで、赤色および深赤色領域に蛍光を示す分子(2～5、Fig. 1)を開発し、それらを用いた培養細胞およびマウス肝臓内の脂質滴イメージングについて報告する。

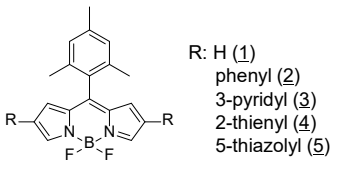

Fig. 1 Chemical structures of LD probe

ジブチルエーテル中において化合物 1 は 515 nm に蛍光極大波長(λ_{flu})を示した。一方、化合物 2～5 のλ_{flu} は 623、605、674、658 nm であり、化合物 2 および 3 では赤色蛍光、化合物 4 および 5 では深赤色蛍光を示した。よって、化合物 1 の 2、8 位に芳香族置換基を導入することでπ共役系が拡張し、蛍光極大波長が大きく長波長シフトすることが明らかとなった。化合物 2～5 を HeLa 細胞の培地に添加し 30 分培養後、共焦点蛍光顕微鏡で観察したところ、多数の顆粒状のオルガネラがイメージングされた。市販の脂質滴蛍光色素との共染色から化合物 2～5 は、脂質滴に選択的に分布することが示された。化合物 2～5 を麻酔下にある脂肪肝モデルマウスに尾静脈投与し、共焦点蛍光顕微鏡で肝臓表面を観察したところ、化合物 3、5 では投与 30 分後において、肝臓内の脂質滴をイメージングできることが示された。

1) K. Purevsuren et al., *J. Photochem. Photobiol A: Chem.* **2023**, *438*, 114562.
2) T. Yoshihara et al., *Anal. Chem.* **2020**, *92*, 4996.

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細胞内酸化還元ホメオスタシスを制御し得る低分子アロステリックジスルフィド/ジセレニド試薬

（東海大理化[1]・東海大先進生命研[2]・東北大際研[3]・関学大理化[4]）○三神 瑠美[1,2]・金村 進吾[3,4]・奥村 正樹[3]・荒井 堅太[1,2]

Small allosteric disulfinde/diselenide reagents may regulate cellular redox homeostasis ([1]*School of Science, Tokail University*, [2]*Institute of Advanced Biosciences, Tokai University,* [3]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University,* [4]*School of Science and Technology, Kwansei Gakuin University*)○Rumi Mikami,[1, 2] Shingo Kanemura,[3, 4] Masaki Okumura,[3] Kenta Arai[1, 2]

Enzymes adroitly regulate their own enzymatic activities by altering peptidyl conformations around the active sites through association of a cofactor or partial chemical modification. Mimicking such the allosteric regulation mechanism of the actual enzymes would be useful in controlling the activity of artificial catalysts to accordingly exert the catalytic functions in cells. Therefore, this study aims to develop biocompatible artificial catalysts, which mimic an allosteric enzyme and modulate their catalytic activities by changing their molecular structure with Ca^{2+} as an allosteric effector. First, diselenide (SeSe)- and disulfide (SS)-containing compounds fused with a Ca^{2+}-chelator was prepared. Coordination of Ca^{2+} into the molecules altered their own structures, decreasing the thermodynamic stability of the SeSe and SS bonds and hence readily converting into corresponding catalytically active selenol and thiol states. The compounds effectively catalyzed oxidative folding and reduction of reactive oxygen species in the presence of Ca^{2+}, and similar regulation of the activities was observed in cells.
Keywords : Pritein folding; Antioxidant; Diselenide; Disulfide; Allosteric catalyst

酵素は、補因子の会合や化学修飾を受けることで、活性部位周辺のタンパク質立体構造を変化させ、酵素活性を巧みに制御している。このような実際の酵素のアロステリック制御機構を模倣することは、低分子触媒の活性を制御し、細胞内で適切に機能を発揮させるうえで有効であると考えられる。そこで、本研究では、生体内のアロステリック酵素を模倣し、アロステリック因子とするCa^{2+}によって分子構造を変化させることで、触媒活性を変調する生体適合型の人工触媒の開発を目指した。初めに、Ca^{2+}キレーターを融合させた含ジセレニド（SeSe）およびジスルフィド（SS）化合物を合成した。合成化合物は、Ca^{2+}がその分子内に配位することで分子構造が変化し、SeSeおよびSS結合部位の熱力学的安定性が低下し、触媒活性なセレノールおよびチオール体へと変換された。合成化合物は、Ca^{2+}存在下で酸化的フォールディングならびに活性酸素種の還元を良好に促進するとともに、細胞内においても同様の触媒活性の制御が観測された。

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Monitoring of RNA motility in living cells using fluorescence/bioluminescence and "mPUM technology"

(*School of Science, The University of Tokyo*) ○ Hideaki Yoshimura, Masatoshi Eguchi, Yoshibumi Ueda, Takeaki Ozawa
Keywords: Live-cell Imaging; RNA; Fluorescence; Bioluminescence

The importance of intracellular location and motion of RNA in cell physiological phenomena has been widely recognized. For a detailed understanding of the mechanisms in these phenomena, RNA monitoring techniques are required to analyze the time course of RNA localization and distribution in living cells. Moreover, RNAs are a direct target molecule in various technologies for gene expression analysis. Technological advances in various comprehensive gene expression analyses have promoted the discovery of genes associated with a variety of physiological events by identifying and quantifying the corresponding RNAs. However, these methods are not applicable to obtain spatiotemporal information on RNAs in living cells because of their destructive properties. This emphasizes the need for non-destructive live-cell imaging techniques for spatiotemporal analysis of RNAs.

In this presentation, we introduce an RNA labeling technique named “mPUM technology” that is applicable to live cell imaging of RNA. The mPUM technology is a selective and universal RNA labeling method using RNA-binding protein PUM-HD mutants. PUM-HD can be modified in a custom-made manner to recognize and capture an 8-base RNA sequence of interest. The combination of the mPUM technology with microscopy techniques allows monitoring of localization and motility of target RNAs in living cells.

To monitor target molecules in living cells, the use of fluorescence is a major approach. The mPUM technology was applied to labeling RNAs in living cells for fluorescence microscope imaging by making a fusion protein of mPUM and fluorescent protein [1]. In this approach, a split fluorescent protein reconstitution method was often used for reducing of fluorescence background from excess probes not attached to the target RNA. The split fluorescent protein reconstitution reaction is, however, an irreversible process, and the accumulation of reconstituted fluorescent proteins prevents precise observation. To overcome the drawback in the fluorescence protein reconstitution method, we also adopted bioluminescent protein reconstitution, which is based on a reversible reaction in recovering the full-length bioluminescent protein. In this presentation, two examples of mPUM-based RNA monitoring studies will be introduced and discussed, which use fluorescence and bioluminescence to visualize endogenous target RNAs in living cells.

1) T. Yamada, H. Yoshimura, R. Shimada, M. Hattori, M. Eguchi, T. K. Fujiwara, A. Kusumi, T. Ozawa, *Sci. Rep.* **2016**, 6, 38910. 2) M. Eguchi, H. Yoshimura, Y. Ueda, T. Ozawa., *ACS Sens.* **2023**, 8, 4055.

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組織内チオール代謝物イメージング及び組成解析を実現する TLC 蛍光ラベル化剤の開発

（青山学院大理工）○西原 達哉・鈴木 我空・西田 光輝・塚目 莉加・田邉 一仁

Distribution Analysis of Thiol Metabolites in the Frozen Tissue by Using Fluorescent Labelling Reagent Coated TLC Plate (*College of Science and Engineering, Aoyama Gakuin University*)

○Tatsuya Nishihara, Gaku Suzuki, Koki Nishida, Rika Tsukame, Kazuhito Tanabe

Distribution of thiol metabolites in the tissues gives very important information for the disease assessment. However, the mass spectrometry imaging (MSI) has the drawbacks such as time-consuming steps and expensive equipment. To solve these limitations, in this study, we attempted to develop a new methodology, which imaged the distribution of thiol metabolites rapidly and easily. Toward the imaging and analysis of thiol metabolites, we developed the fluorescent labelling reagent coated TLC plate, which shows the fluorescent signal after the reaction with the thiol metabolites in the tissue slice on the TLC plate. In fact, we successfully detected the fluorescent signals derived from the adducts of thiol metabolites in the frozen liver tissue.

Keywords : Metabolite, Thin Layer Chromatography, Labelling Regent

近年、組織内の代謝物分布解析にあたり、質量分析イメージング (MSI) が有力な方法論として用いられている。しかしながら、MSI はピクセルごとの質量分析を前提としているため、測定、及び解析に膨大な時間を要する。また、反応性の高い分子種の解析に困難を伴う点も課題として挙げられる。そのため、簡便かつ、迅速な代謝物分布解析を実現可能にする新たな方法論の構築が現在求められている。

本研究では、生体内の酸化還元を担う重要な生体分子であるチオール代謝物に着目した。これまでに我々は、組織内のチオール代謝物を薄層クロマトグラフィー (TLC) へトレースし、その場で蛍光標識することで、チオール代謝物の分布イメージング可能であることを報告してきた。本研究では、新たに、リシンを母核構造とし、蛍光色素としてピレン酪酸、光切断部位としてニトロベンジル、反応部位としてマレイミドを備えたラベル化剤を設計した。本ラベル化剤をコートした TLC に対して、生体組織内物質をトレースすることで、チオール代謝物の付加体がその場で生成する。本ラベル化剤は、チオール代謝物とのマイケル付加反応、及び UV 照射によるニトロベンジルの解離の 2 条件で蛍光回復する特性を新たに付与している。そのため、TLC 全体を光照射することで、組織内に含まれるチオール代謝物の分布イメージングが未反応のラベル化剤を除去することなく実現する。さらに、解析対象領域に対して局所的に UV 照射を行った後に、展開操作を行うことにより、照射領域内に含まれるチオール代謝物の組成解析も可能となる。実際に、本ラベル化剤を塗布した機能化 TLC を用いることで、食肉用豚肝臓内に含まれるチオール代謝物の検出に成功した。本発表では、ラベル化剤の特性評価、及び組織内チオール代謝物解析についての詳細について報告する。

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新規ミスマッチ認識分子の創生とその特性

（防衛医大）○武井 史恵、山田 直生、比留間 寿美代
Synthesis and Characterization of Novel DNA Mismatch-Binding Molecule. (Faculty of Medicine, National Defense Medical College) ○Fumie Takei, Naoki Yamada, Sumiyo Hiruma

Molecules that bind specifically to special structures of DNA and emit fluorescence are of interest as molecular probes used to reveal biochemical processes. A variety of fluorescent molecules have already been developed which bind to specific structures of DNA. In particular, a fluorescent molecule with a diamino-naphthyridine derivative (DANP), which we have previously developed, binds specifically to the cytosine bulge structure of DNA and exhibits characteristic fluorescence. In this study, we synthesized a novel DNA binding ligand, DANP derivatives with the organometallic compound ferrocene as a substituent, and found to be fluorescent molecules that bind to DNA mismatch structures.

The novel molecule ferrocene DANP (FeDANP) was synthesized from DANP and ferrocene carboxylic acid. The melting temperature (T_m) of DNA containing bulge structures were little changed with or without FeDANP. On the other hand, the ΔT_m of the cytosine-cytosine mismatch structure (C-C mismatch structure) was larger than that of other mismatch DNA. Furthermore, the addition of FeDANP to the C-C mismatch DNA structure increased the fluorescence intensity. In particular, the fluorescence change in the C-C mismatch structure was greater than in the other mismatch structures, suggesting that FeDANP specifically recognises the C-C mismatch DNA structure.
Keywords : DNA Mismatch Binding ligand; Fluorescent molecule

DNA の特殊構造に特異的に結合し蛍光を発する分子は、生化学的プロセスを明らかにする際に使われる分子プローブとして注目され、すでに様々な DNA の特殊構造に結合する蛍光分子が開発されている。特に我々が以前開発したジアミノナフチリジン骨格を有する蛍光分子（DANP）は DNA のシトシンバルジ構造に特異的に結合して、特徴的な蛍光を示す。本研究ではこの DANP に有機金属化合物であるフェロセンが結合した分子を合成し、その特徴について調べた。

DANP とフェロセンカルボン酸から合成したフェロセン DANP (FeDANP)とバルジ構造を含む DNA との結合を DNA の融解温度(T_m)を用いて調べたところ、いずれのバルジ構造においても、FeDANP の有無による T_m の変化はほとんど観測されなかった。一方、シトシンと各種塩基のミスマッチ構造 DNA の組み合わせでは シトシン－シトシンミスマッチ構造(C-C ミスマッチ構造)の T_m 変化が他のミスマッチ構造に比べ大きく、FeDANP が C-C ミスマッチ構造特異的に結合していることが示唆された。蛍光についても、C-C ミスマッチ構造に FeDANP を加えると、蛍光強度は増大したことから、今までの蛍光分子では不可能であった C-C ミスマッチ構造の蛍光検出が可能となった。

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

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC H936(936, Bldg. 9 [3F])

[H936-4pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Hiroshi Nonaka, Tomonori Tamura

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[H936-4pm-01]
Solid-Phase Synthesis of Diketopiperazine Thioester Peptide for High-throughput Chemical Protein Synthesis

○Yuya Nakajima[1], Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Graduate School of Engineering, Nagoya University, 2. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[H936-4pm-02]
Elucidation of the association character and 3D domain-swapped structure of a tetramerizing antibody light chain

○Takahiro Sakai[1], Shohei Yamaguchi[1], Tsuyoshi Mashima[1], Naoya Kobayash[1], Lian Duan[2], Ryo Fujiki[2], Hengphasatporn Kowit[2], Yasuteru Shigeta[2], Hideaki Ogata[3], Emi Hifumi[4], Taizo Uda[5], Shun Hirota[1] (1. Grad. Sch. Sci. Tech., NAIST, 2. Cent. Comp. Sci., Univ. Tsukuba, 3. Grad. Sch. Sci., Univ. Hyogo, 4. Inst. Res. Mgmt., Oita Univ, 5. Nano-tech Lab., ISIT)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[H936-4pm-03]
Development of micelles bearing thiol groups to promote oxidative protein folding under crowded environment

○Mai Kitamura[1], Takahiro Muraoka[1,2] (1. Tokyo University of Agriculture and Technology, 2. KISTEC)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[H936-4pm-04]
Chemogenetic Control of the AMPA Receptor Activity Using the Moleculer Stopper Approach

○Yuta Deen Miura[1], Kento Ojima[1,2], Osamu Miyashita[3], Naotaka Tsutsumi[4], Itaru Hamachi[2], Atsuko Yamashita[4], Shigeki Kiyonaka[1] (1. Nagoya Univ., 2. Kyoto Univ., 3. RIKEN, 4. Okayama Univ.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[H936-4pm-05]
Development of N-acyl-N-aryl sulfonamide warheads for covalent protein modification and inhibition

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○Masaharu Kawano[1], Shunsuke Murakawa[1], Dai Sugihara[2], Tomonori Tamura[1], Itaru Hamachi[1,3] (1. Graduate School of Engineering, Kyoto University, 2. Kyoto University, 3. ERATO JST)

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Solid-Phase Synthesis of Diketopiperazine Thioester Peptide for High-throughput Chemical Protein Synthesis

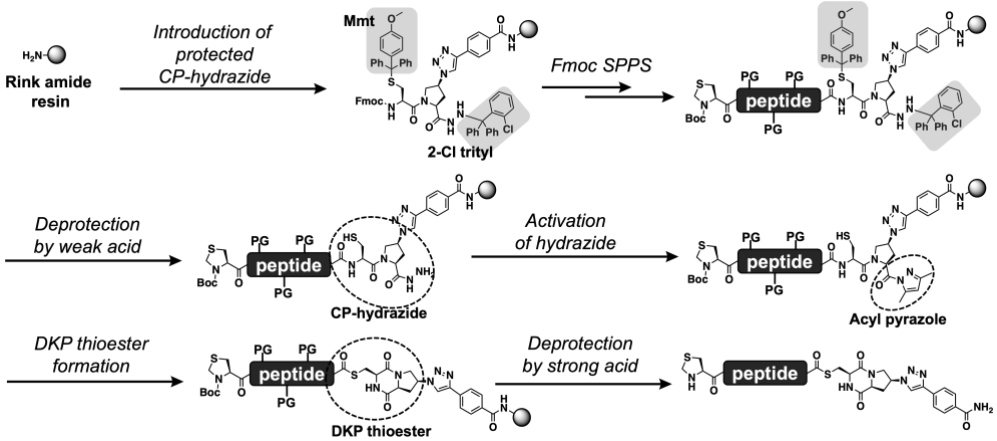
([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University*) ○Yuya Nakajima,[1] Koki Nakatsu,[1] Gosuke Hayashi,[1] Hiroshi Murakami[1,2]

Keywords: Chemical Protein Synthesis; Fmoc Solid-Phase Peptide Synthesis; Thioester Peptide; Native Chemical Ligation; Combinatorial Synthesis

C-terminal thioester peptides are frequently used for peptide ligation in chemical protein synthesis. Facile preparation of multiple thioester peptides is key for the efficient synthesis of various target proteins. However, conventional Fmoc solid-phase peptide synthesis (SPPS) cannot be applied to the direct synthesis of *C*-terminal thioester peptides due to the lability of thioester moiety in Fmoc SPPS, especially in the Fmoc deprotection procedure.

We have studied diketopiperazine (DKP) thioester peptide, which is converted from *C*-terminal cysteinylprolyl ester[1] or cysteinyl prolyl imide[2,3] by *N*-*S* acyl rearrangement of the cysteine residue followed by intramolecular cyclization. Although the DKP formation-mediated thioester synthesis proceeds almost quantitatively regardless of *C*-terminal amino acid residues, this thioesterification reaction has been exclusively performed in the liquid-phase so far.

Here, we developed a solid-phase strategy for synthesizing DKP thioester peptides, which are immobilized to resin by anchoring the γ -position of proline via CuAAC reaction. The activation of the *C*-terminal hydrazide to acylpyrazole[4] and the subsequent conversion to DKP thioester with an optimized condition gave a reliable Fmoc SPPS method for direct preparation of thioester peptides, which enables parallel synthesis of protein fragment peptides.



1) T. Kawakami, S. Aimoto, *Chem. Lett.*, **2006**, *36*, 76-77. 2) M. Yanase, K. Nakatsu, C. J. Cardos, Y. Konda, G. Hayashi, A. Okamoto, *Chem. Sci.*, **2019**, *10*, 5967-5975. 3) K. Nakatsu, M. Yanase, G. Hayashi, A. Okamoto, *Org. Lett.*, **2020**, *22*, 4670-4674. 4) D. T. Flood, J. C. J. Hintzen, M. J. Bird, P. A. Cistrone, J. S. Chen, P. E. Dawson, (2018) *Angew. Chem. Int. Ed. Engl*. **2018**, *57*, 11634-11639.

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機能超分子化学研究室

ドメインスワッピングにより 4 量化する抗体軽鎖の会合挙動と X 線結晶構造

酒井 隆裕

【序論】

近年、抗体医薬品は、がんやアルツハイマー病などあらゆる疾患に対して成功を収めています。しかし、抗体は不安定であり、互いに会合することで凝集体を形成しやすく、**凝集形成により抗原認識能が低下する場合があります。**また、生体内での抗体の凝集は疾患の原因となる場合もあり、過剰に発現された抗体の軽鎖が凝集すると、臓器に障害を及ぼします。このように、抗体の凝集機構を解明することは大変重要ですが、**凝集体の原子レベルでの情報はほとんどありません。**

一方、タンパク質会合機構の一つに 3D-ドメインスワッピング (3D-DS) という現象があります。3D-DS は、同じ分子間で、同じ構造領域を交換して会合する機構です。3D-DS による多量化は凝集を促進する報告もあります。抗体の凝集に関して広く研究されているにも関わらず、3D-DS に関する情報は非常に少なく、**抗体軽鎖が 3D-DS で多量化する報告は未だありません。**

本研究では、多量化するヒト抗体軽鎖#4 に着目し、その**会合メカニズムの解明を目指します。**まず、抗体軽鎖#4 の変異体#4C214A を調整し、溶液中での会合挙動を調べました。さらに、#4 の可変領域#4V_L の X 線結晶構造解析により、**抗体軽鎖の 3D-DS 構造を初めて明らかにしました。**

【結果・考察】

抗体軽鎖#4C214A は、大腸菌を用いて培養・発現し、各種クロマトグラフィーにより精製しました。精製した#4C214A のサイズ排除クロマトグラフィー (SEC) 分析により、#4C214A は溶液中で 4 量体を形成し、**単量体と 4 量体の平衡であることが明らかになりました（図 1a）。**

詳細に多量化挙動を調査するため、抗体軽鎖#4C214A の熱力学的解析を行いました。解離定数の温度依存性から、熱力学的パラメーターを算出すると、温度上昇に伴い、4 量体から単量体へ解離する際の標準エンタルピー変化量が増大しました。一般的に、温度が上昇すると水素結合や静電相互作用は弱くなり、標準エンタルピー変化量は減少します。しかし、増大したことから、#4C214A は**疎水性相互作用により 4 量体を形成することが示唆されました。**

4 量化メカニズムを原子レベルで解明するため、抗体軽鎖#4C214A の 4 量体の X 線結晶構造解析を行ったが、十分な分解能を得ることができなかった。そこで、定常領域を切除した抗体軽鎖可変領域#4V_L を調整しました。#4V_L は#4C214A と同様に溶液中で 4 量体を形成し、その結晶構造では、**3D-DS した 2 量体がさらに 2 量化することで、4 量体を形成していました（図 1b）。**2 量体同士の相互作用界面には多くの疎水性残基が存在し**（図 1c）**、4 量化に疎水性相互作用が大きく寄与することが結晶構造からも確認されました。本研究成果は、抗体の安定性向上と新規抗体医薬品の開発に役立つ研究として期待されます。本成果は筆頭著者として Nature Communications 誌に出版し (https://www.nature.com/articles/s41467-023-43443-4)、プレスリリースも発行されています (https://www.jst.go.jp/pr/announce/20231208/pdf/20231208.pdf)。

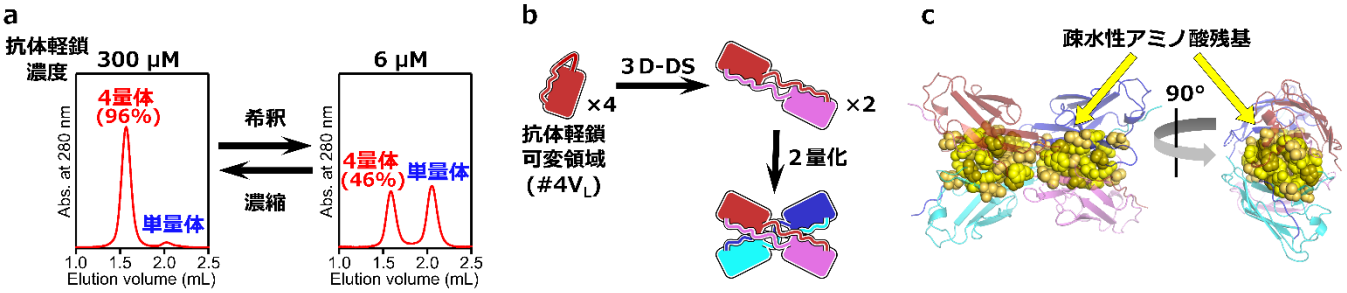

図1. これまでの研究結果。**a** 抗体軽鎖#4C214AのSEC溶出曲線。**b** 抗体軽鎖可変領域#4V_Lの4量化メカニズム。**c** #4V_Lの4量体結晶構造。2量体間に存在する疎水性アミノ酸残基を黄色で示す。

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Development of micelle bearing thiol groups to promote oxidative protein folding under crowded environment

([1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*, [2]*Kanagawa Institute of Industrial Science and Technology*) ○Mai Kitamura,[1] Takahiro Muraoka [1, 2]

Keywords: Crowded condition; Oxidative protein folding; Disulfide bonds; Micelles

Protein folding is a posttranslational modification process to gain their biological functions by forming native structures. During the folding process, proteins can be aggregated through intermolecular hydrophobic interactions and disulfide bond (SS-bond) formation, which is particularly facilitated in the crowded condition, such as the interior of cells. In cells, chaperones and oxidoreductases play important roles in inhibiting protein aggregation and promoting oxidative folding, respectively, as quality control systems of protein expression. Mimicking the mechanisms and functions of those quality-controlling proteins can be, thus, a promising approach to developing practically useful synthetic materials for preventing protein misfolding diseases, such as Parkinson's disease.

In this study, we developed a novel synthetic material to promote oxidative folding even under crowded condition. We focused on protein disulfide isomerase (PDI), which is one of the representative oxidoreductases involving in the oxidative folding. The major roles of PDI contain 1) introduction and exchange of SS-bonds for folding promotion of the client proteins and 2) aggregation inhibition of client proteins with its hydrophobic pocket. Inspired by these functions of PDI, here we developed a supramolecular PDI-mimic, CTAB-SS_{out} micelle, based on a micelle-forming lipid bearing a redox-active functionality. In the interior of CTAB-SS_{out} micelle, there is the hydrophobic space (Fig. 1).

To investigate the reactivities of the thiol groups of CTAB-SS_{out} in the oxidative folding, the chemical properties were evaluated following the previous study.[1] As a result, CTAB-SS_{out} showed better performance than cysteine-containing dipeptides conjugated with amino acids possessing amino groups.[2] Based on the evaluation of thiol groups of CTAB-SS_{out}, folding assay was conducted in a crowded condition using bovine pancreatic trypsin inhibitor (BPTI), which is a protein with three SS-bonds. In this assay, both protein aggregation inhibition effect and SS-bond introduction and exchange effect were observed with CTAB-SS_{out}. Neither CTAB micelle nor a mixture of a redox-active thiol and CTAB micelle showed such a high activity of the folding promotion. CTAB-SS_{out} micelle successfully demonstrated oxidative protein folding promotion in highly concentrated conditions.

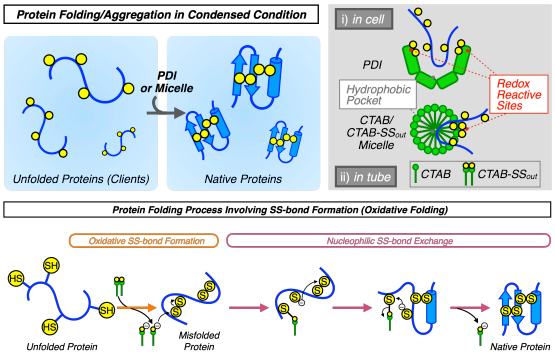

Fig. 1 Schematic illustration of the oxidative protein folding in a condensed condition.

1) S. Okada *et al.*, *Chem. Sci.*, **2023**, *14*, 7630–7636. 2) H. Nishino,† M. Kitamura† *et al.*, *RSC Adv.*, **2022**, *12*, 26658–26664 (†: equal contribution).

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構造変化を干渉する分子ストッパーによる AMPA 受容体のケモジェネティック制御

（名大院工 [1]・京大院工 [2]・理研 [3]・岡大院薬 [4]）○三浦 裕太 [1]・小島 憲人 [1,2]・宮下 治 [3]・堤 尚孝 [4]・浜地 格 [2]・山下 敦子 [4]・清中 茂樹 [1]

Chemogenetic Control of the AMPA Receptor Activity Using the Molecular Stopper Approach

([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*RIKEN Center for Computational Science,* [4]*Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Okayama University*) ○Yuta Miura,[1] Kento Ojima,[1,2] Osamu Miyashita,[3] Naotaka Tsutsumi,[4] Itaru Hamach,[2] Atsuko Yamashita,[4] Shigeki Kiyonaka[1]

AMPA receptors (AMPARs) mediate fast excitatory neurotransmission in the central nervous system and play vital roles such as synaptic plasticity. Four subunits, GluA1-4, assemble into tetramers to make up the core functional cation channel, with different combinations conferring unique trafficking behaviors and biophysical characteristics. Subunit-specific regulation is difficult due to high homology. Activation of AMPARs is triggered by structural changes in the ligand binding domain from open to closed-form. Previously, we reported novel activation methods for AMPARs termed A-CBC (allosteric activation via coordination-based chemogenetics), in which artificial coordination sites were introduced near the ligand-binding site for artificial activation by Pd(II) complex.

Here, we developed a new method for chemogenetic inhibition of AMPARs. We utilized coordination of Pd(II) complex with two of mutated His residues in the vicinity of the ligand-binding site for interfering with the structural change upon activation.

Keywords :Chemogenetics; Glutamate Receptor; Palladium; Coordination Chemistry; AMPAR

AMPA 受容体(AMPAR)は、中枢神経系での速い興奮性神経伝達を担う 4 量体カチオンチャネルであり、その発現様式が記憶や学習に大きく関連している。AMPAR には GluA1-4 と呼ばれる 4 種サブユニットが存在し、それぞれ異なる機能を有するとされるが、構造的相同性の高さからサブユニット選択的活性制御が難しい。これまでに我々は、遺伝子工学と配位化学を融合させた配位ケモジェネティクスを開発した。AMPAR は、活性化の際にリガンド結合部位が開から閉構造へと変化する事が知られている。我々は、リガンド結合部位近傍に配位性アミノ酸である His の変異導入を行い、Pd 錯体との配位結合によって人為的に閉構造へと変化させて受容体の選択的活性化に成功した [1]。

本研究では、活性化の先行研究とは異なり、錯体の嵩高さに着目した受容体選択的な阻害を行った。具体的には、2 つの His 残基をリガンド結合部位近傍に変異導入し、そこへ立体障害となる嵩高い Pd 錯体を配位させる事で、閉構造への変化を妨げて受容体の活性を阻害する新たな「ケモジェネティック活性阻害」を開発した。

1) S. Kiyonaka *et al. Nat. Chem.* (2016)

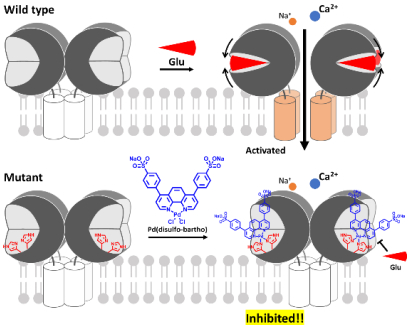

Fig. 1 Chemogenetic inhibition of AMPARs.

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N-acyl-*N*-aryl sulfonamide(ArNASA)反応基：タンパク質の化学修飾と不可逆阻害

（京大院工[1]・JST ERATO[2]）○河野 正晴[1]・村川 駿介[1]・杉原 大[1]・田村 朋則[1]，浜地 格[1,2]

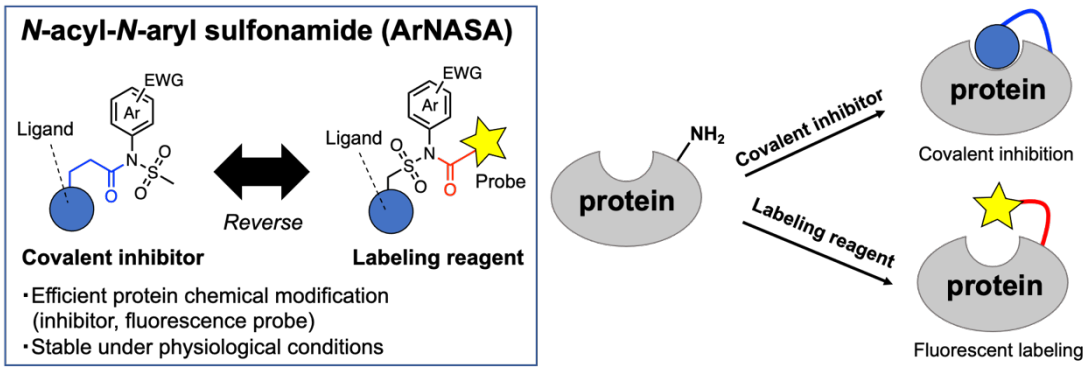
Development of *N*-acyl-*N*-aryl sulfonamide warheads for covalent protein modification and inhibition ([1]*Graduate School of Engineering, Kyoto University*, [2]*ERATO JST*) ○Masaharu Kawano,[1] Shunsuke Murakawa,[1] Dai Sugihara[1], Tomonori Tamura,[1] Itaru Hamachi[1,2]

Recently, we discovered that lysine-reactive *N*-acyl-*N*-aryl sulfonamide (ArNASA) warheads are promising for covalent inhibition strategy.[1] ArNASA warheads exhibited superior stability and biocompatibility in water compared to conventional lysine-reactive warheads. ArNASA groups can be easily introduced into ligands for target proteins by one-step coupling reaction. Contrary to this molecular design, when the ligand moiety is linked to the leaving group side (*N*-aryl sulfonamide) of ArNASA and the functional probe is introduced to the *N*-acyl group side, this molecule is expected to function as a ligand-directed labeling reagent – an affinity labeling agent that does not inhibit the protein activity. In this study, we designed and synthesized ArNASA-based labeling reagents for selective labeling of endogenous membrane proteins overexpressed in cancer cells.

Keywords : Covalent inhibitors, N-acyl-N-aryl sulfonamide, Lysine-reactive, Warhead

ごく最近、我々はリジン残基標的型不可逆阻害剤の新しい反応基として *N*-acyl-*N*-aryl sulfonamide (ArNASA)を開発した。[1)] ArNASA は既存のリジン標的型反応基と比較して優れた水中安定性・生体適合性を示し、標的タンパク質に対するリガンドのカルボン酸誘導体とワンステップで連結することで、容易に不可逆阻害剤を合成可能である。こうした分子設計とは逆に、リガンド部分を ArNASA の脱離基側(*N*-aryl sulfonamide)に連結し、機能性プローブを *N*-acyl 基側に導入すれば、その分子はリガンド指向性ラベル化剤（タンパク質活性を阻害しないアフィニティラベル化剤）として機能すると予想される。そこで本研究では、ArNASA を基盤とするリガンド指向性ラベル化剤を設計・合成し、がん細胞に過剰発現する内在性膜タンパク質の選択ラベリングを試みた。本講演ではこれらの詳細について発表する。

1) M. Kawano *et al*. *JACS*, 2023, 145, 26202-26212.



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Academic Program [Oral A] | 18. Polymer：Oral A

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC D341(341, Bldg. 3 [4F])

[D341-4am] 18. Polymer

Chair: Masayasu Totani, Yutaka Ohsedo

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[D341-4am-01]
Identification and Classification of Water-soluble Polymers Using Fluorophore-modified Proteins

○Souki Wakabayashi[1], Shion Hasegawa[1], Toshiki Sawada[1], Takeshi Serizawa[1] (1. Sch. Mat. & Chem. Tech., Tokyo Tech)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[D341-4am-02]
Control of the Capability for the Synthesis of Silver Nanoparticles of Genetically Engineered Filamentous Viruses

○Yuta Mibe[1], Takeshi Serizawa[1], Toshiki Sawada[1] (1. Sch. Mat. & Chem. Tech., Tokyo Tech)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[D341-4am-03]
Controlled Crystal Growth of Hydroxyapatite on Oriented Collagen-Peptide Composite Films for Bone Repair Materials and Its Structural Analysis

○Aika Hashizume[1], Shogo Matsubara[1], Masahiro Higuchi[1] (1. Grad. Sch. of Eng. Nagoya Inst. of Tech.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[D341-4am-04]
Synthesis of Lysine- and Isoleucine-derived Vinyl Copolymers and their cell adhesion property

○Shoma Tsukiyama[1], Shin-nosuke Nishimura[1], Tomoyuki Koga[1] (1. doshisha University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[D341-4am-05]
Synthesis of self-assembling peptide-grafted polyester

○Miki Hasegawa[1], Shin-nosuke Nishimura[1], Tomoyuki Koga[1] (1. Doshisha University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[D341-4am-06]
Construction of Chimeric Artificial Nucleic Acids (CANA) toward Pancreatic Cancer Treatments by Inhibition of Transcription Factor BACH1 III: Construction of CANA design strategy based on *in vitro* analysis

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Yuto Horiuchi[1], Yuki Igarashi[1], Masahito Inagaki[4], Kazuyo Matsumoto[1], Mika OMURA[3], Yasuyuki Araki[1], Yu Mikame[2], Masaki Nishijima[1], Asako Yamayoshi[2], Ikuhiko Nakase[3], ○Takehiko Wada[1] (1. Tohoku University, 2. Nagasaki University, 3. Osaka Metropolitan University, 4. Nagoya University)

Japanese

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC

[D341-4am-07]

Synthesis and antibacterial properties of cationic cellulose (I) −Effect of degree of substitution−

○Kohei Obuchi[1], Saito Miki[1], Saito Tamao[1], Takeoka Yuko[1], Rikukawa Masahiro[1], Fujita Masahiro[1] (1. Sophia University)

Japanese

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[D341-4am-08]

Hydrophobization of chitin nanofibers by enzymatic grafting of partially 2-deoxygenated amyloses

○Naoki Yamamoto[1], Masayasu Totani[1], Jun-ichi Kadokawa[1] (1. Kagoshima university)

Japanese

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

[D341-4am-09]

Synthesis of Glucosamino-2-Deoxyglucan by Enzymatic Copolymerization

○Yuta Miyahara[1], Masayasu Totani[1], Jun-ichi Kadokawa[1] (1. Kagoshima University)

Japanese

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

[D341-4am-10]

Development of cellulose materials with high strength by photopolymerization (I)- Effect of amount of ionic liquid monomer and cellulose on strength-

○Keito Matsumoto[1], Arata Matsui[1], Yuko Takeoka[1], Masahiro Rikukawa[1], Masahiro Fujita[1] (1. Sophia Univ.)

English

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[D341-4am-11]

Synthetic Studies of Zwitterionic Modified Cyclodextrins (VI)
Linker introduction for fluorescent group modification

○Kanta Koizumi[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Grad. Sci.&Engin. Saitama University, 2. Adv. Inst. Innov. Tech. Saitama University, 3. Strategic Res. Ctr. Saitama University)

English

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[D341-4am-12]

Synthesis of novel amylase substrates using FRET effect (VI): Synthesis of glycopolymers as amylase substrate

○Yuki Yamamoto[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Grad. Sch. Sci. & Engin., Saitama University, 2. Adv. Inst. Innov. Tech., Saitama University, 3. Strategic Res. Ctr., Saitama University)

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Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[D341-4am-13]

Construction and Evaluation of Cancer Cell Selective Drug Delivery System III: Development pancreatic cancer of a selective drug delivery system to suppress the malignant progression

○Hirari Kato[1], Ryota Azuma, Yasuyuki Araki[2], Masaki Nishijima[2], Mitsuyo Matsumoto[3], Ikuhiko Nakase[4], Mika Oomura[4], Asako Yamayoshi[1], Kazuhiko Igarashi[1] (1. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University , 2. Grduate School of Medicine, Tohoku University, 3. Graduate School of Medicine, Dentistry and Pharmacy, Nagasaki University , 4. Graduate School of Science)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[D341-4am-14]

Dehydration Condensation of Chitin Oligosaccharides by Activated Carbon Catalysts

○Tatsuki Yasuda[1], Takuya Sagawa[1], Mineo Hashizume[1] (1. Tokyo University of Science)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[D341-4am-15]

Synthesis of polyaniline/polyelectrolyte gel composites composed and its electronic conductive properties

○Ami KANEIZUMI[1], Yutaka OHSEDO[2] (1. Grad. Sch. HCE., NWU, 2. Fac., NWU)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[D341-4am-16]

Enumerations of the structural isomers of organic commodity polymers

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蛍光修飾タンパク質を利用した水溶性高分子の識別と分類

（東工大物質理工）○若林壮樹・長谷川史穏・澤田敏樹・芹澤 武

Identification and Classification of Water-Soluble Polymers Using Fluorescence-Modified Proteins

(*School of Chemical Science and Engineering, Tokyo Institute of Technology*)
○Souki Wakabayashi, Shion Hasegawa, Toshiki Sawada, Takeshi Serizawa

Water-soluble synthetic polymers play an important role in human daily life and industry fields, whereas their potential risks to the environment have gained attention recently. Therefore, facile methods to detect and identify the released water-soluble polymers in the water environment will be required. In this study, we demonstrated a strategy for the identification and classification of the polymers using fluorescently modified proteins. Multivalent discriminative fluorescence signals were generated for various analytes based on interactions of several different proteins, allowing the identification and classification of water-soluble polymers using multivariate analysis.

Keywords :Protein, Water-Soluble Polymer, Environmentally Responsive Fluorescent Molecule, Linear Discriminant Analysis

マイクロプラスチックによる海洋汚染が近年大きな問題となっており、最近ではさらに水溶性高分子による汚染も懸念されはじめている。そのため、環境中の水溶性高分子を簡便に検出・同定する手法が求められている。我々はこれまでに、高分子に結合するペプチドに環境応答性蛍光分子を導入したセンサーが、水溶性高分子の識別に有用なことを明らかにしてきた[1)]。より多様な高分子を精緻に識別するためにはペプチドの最適化が必須となるが、高分子の識別を可能とするペプチドを自在に設計することは困難である。本研究では、水溶性高分子と多点で相互作用可能なタンパク質に着目し、高分子との相互作用を同様に蛍光シグナルとして取得し、水溶性高分子識別のため素子としてタンパク質の有用性を明らかにすることを目的とした（Figure 1）。

環境応答性蛍光分子を導入した複数のタンパク質と高分子を相互作用させ、得られる蛍光シグナルに線形判別分析（LDA）を適用した結果、各高分子を適切に識別できることがわかった。これは、タンパク質それぞれと用いた高分子とが異なる相互作用を示すためと考えられ、蛍光修飾タンパク質を用いた水溶性高分子の識別が可能であることを見出した。

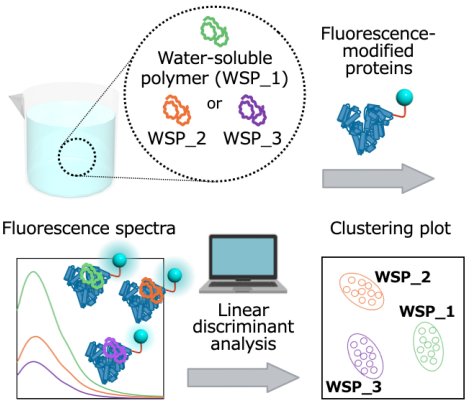

Figure 1. Schematic diagram of identification and classification of water-soluble polymers by fluorescent signals.

1) S. Suzuki, T. Sawada, T. Serizawa, *ACS Appl. Mater. Interfaces* **2021**, *13*, 55978; S. Hasegawa, T. Sawada, T. Serizawa, *ACS Appl. Bio Mater.* **2023**, *6*, 4598.

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遺伝子改変した繊維状ウイルスの銀ナノ粒子生成能の制御

（東工大物質理工）○三部優太・芹澤　武・澤田敏樹

Control of the Capability for the Synthesis of Silver Nanoparticles of Genetically Engineered Filamentous Viruses (*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Yuta Mibe, Takeshi Serizawa, Toshiki Sawada

M13 phage, one of the filamentous viruses, has attractive characteristics as material components due to the liquid crystalline properties and the designable functionalization by genetic engineering. The construction of a new strategy to control the properties of the phage expands the potential use of phage as functional soft material components. In this study, we focused on silver nanoparticles, which have high antimicrobial activity, and explored the synthetic capability of silver nanoparticles by genetically engineered phages displaying dipeptide on their surfaces. The production capabilities of silver nanoparticles by the phages were characterized by the production amounts of silver nanoparticles quantified based on optical density values after certain incubation. The results suggest that the size and shape of the silver nanoparticles can be controlled by the dipeptide sequence on the surface of the phage.

Keywords : Phage, Filamentous Viruses, Biomineralization, Silver Nanoparticle

繊維状ウイルスの一種である M13 バクテリオファージ（ファージ）は、遺伝子改変により機能化でき、さらに液晶性を示すことが知られている。近年では、それらの特性を利用することでファージ自身をマテリアル素材として利用する研究が展開されている。最近、我々はファージの遺伝子改変を適切に利用することで、ファージ集合体が示す機能物性を合目的的に制御できる可能性を見出している。本研究では、高い抗菌活性をもつ銀ナノ粒子に着目し、遺伝子工学によりファージ表層のタンパク質のアミノ酸の改変が、ファージが元来示す銀ナノ粒子生成能に与える効果を明らかにし、ファージと銀ナノ粒子からなる抗菌材料を構築することを目的とした。ファージの主要外殻タンパク質の表層に、ジペプチドを提示するよう遺伝子改変し、それらファージと硝酸銀をそれぞれ混合し、ミネラリゼーションにより生成される銀ナノ粒子の生成能を評価した（Figure 1）。その結果、ジペプチドの提示により、銀ナノ粒子のサイズや形態の制御が可能であることが示された。

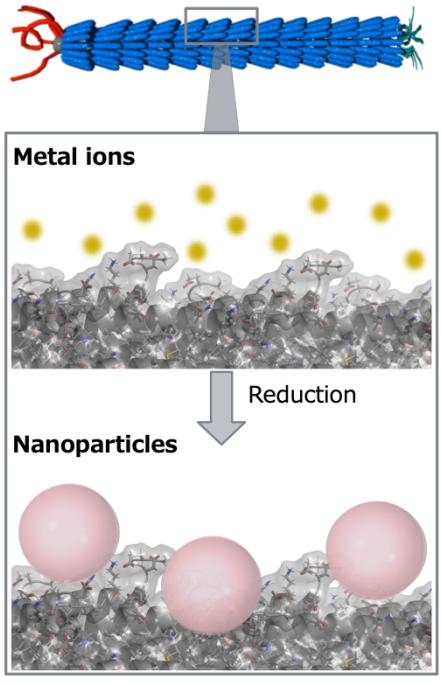

Figure 1. Schematic illustration of biomineralization at the phage surface

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骨補修材を指向したペプチド/コラーゲン配向化複合膜上でのヒドロキシアパタイトの結晶成長制御とその構造解析

（名工大院工）○橋詰 愛香・松原 翔吾・樋口 真弘

Controlled Crystal Growth of Hydroxyapatite on Oriented Collagen-Peptide Composite Films for Bone Repair Materials and Its Structural Analysis (*Graduate School of Engineering, Nagoya Institute of Technology*) ○Aika Hashizume, Shogo Matsubara, Masahiro Higuchi

Hydroxyapatite (HAp), one crystal phase of calcium phosphate, is the major inorganic component of bone. HAp has high biocompatibility, and bone repair materials are being developed using HAp. We have reported that HAp can be mineralized on *β*-turn peptides containing glutamic acid residues as templates. In addition, bone strength depends on the orientation of HAp on the template. Therefore, we suggest that creation of templates that can control the direction of HAp crystal growth could promote bone repair by mineralization.

In this study, we synthesized *β*-turn peptides having HAp mineralization ability as templates, and the peptides were grafted on collagen. The *β*-turn peptides grafted collagen fibrils were immobilized on the substrates by the vertical dipping method to form the HAP mineralization templates having aligned collagen fibril orientation. The obtained HAp orientated crystals formed on the substrate were analyzed in detail using SEM, TEM, and XRD. Furthermore, we prepared complexes with different grafting ratios of peptides to collagen. By comparing the graft rations, we determined the optimal formation conditions for bone repair materials.

Keywords : Hydroxyapatite; Mineralization; β-turn peptide; Collagen; Bone repair material

リン酸カルシウムの一結晶相であるヒドロキシアパタイト（HAp）は、骨を構成する主な無機成分であり、その生体内親和性の高さから、HAp を用いた骨の補修材の研究が進められている。我々はグルタミン酸を含む*β*-ターンペプチドをテンプレートとして HAp ミネラリゼーションが選択的に生じることを報告した。また、骨の強度は HAp の配向性に依存する。したがって、HAp の結晶成長方向を制御できるテンプレートを作製することで、ミネラリゼーションによる骨の修復を促すことが可能となる。本研究では、HAp 形成のテンプレートとして、この*β*-ターンペプチドをグラフトしたコラーゲン合成し、垂直浸漬法によりコラーゲン繊維の配向が揃ったテンプレートを基板上に形成した。作製したテンプレート上での HAp の形成と配向を SEM、TEM、XRD により確認した(Fig. 1)。また、コラーゲンに対するペプチドのグラフト率の異なる複合体を作製し、これらを比較することにより骨補修材形成に最適な条件の検討を行った。

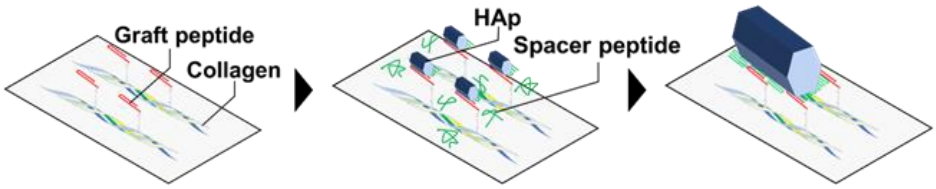

Fig. 1. Schematic picture of HAp mineralization on orientated *β*-turn peptides grafted collagen fibrils.

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日本化学会 第104春季年会 (2024)

リシンおよびイソロイシン由来ビニル共重合体の合成と細胞接着性評価

（同志社大理工[1]）○月山 聖麻[1]・西村 慎之介[1]・古賀 智之[1]

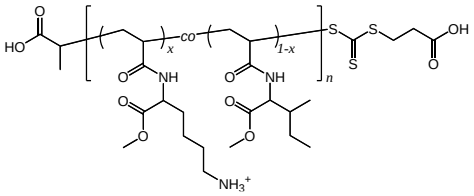
Synthesis of Lysine- and Isoleucine-derived vinyl copolymers and their cell adhesion property

([1]*Depart. of Molec. Chem. & Biochem., Doshisha University*) ○Shoma Tsukiyama,[1] Shinnosuke Nishimura,[1] Tomoyuki Koga[1]

Adsorption of growth factors on artificial scaffold materials promotes cell growth and differentiation. It has been reported that cationic/hydrophobic balance of the scaffolds is important for the adsorption of growth factors[1)]. In this study, we designed amino acid-derived amphiphilic copolymers composed of lysine- and isoleucine-derived vinyl monomers (NAKMe, NAIMe) for functional artificial scaffolds. The cationic/hydrophobic properties of these polymers can be easily adjusted by changing the copolymer composition. Five polymers (P(x)) with controlled chain length and lysine content (x) were synthesized by reversible addition-fragmentation chain transfer polymerization (Fig. 1). The polymers were immobilized on glass surfaces via photo-triggered radical reaction by using silane coupling agent containing benzophenone. Cell adhesion behaviors on the surfaces were evaluated with respect to the effect of copolymer composition.

Keywords : Amino Acid; RAFT Polymerization; Cell Adhesion; Artificial Scaffold; Amphiphilic

人工足場材料のカチオン性/疎水性バランスを適切に設計することで成長因子の吸着量を変えることができ、細胞の増殖や分化挙動の制御が可能となる[1)]。本研究では成長因子の吸着能を有する人工足場材料の開発を目指し、リシンおよびイソロイシン由来ビニルモノマー (NAKMe, NAIMe) からなるポリマーを設計した。これらは共重合組成によりカチオン性/疎水性を容易に調整することができる。具体的に、可逆的付加開裂連鎖移動重合により重合度 (*n*)、多分散度 (*Đ*) が制御されたリシン含有量 (x) の異なる 5 種類のポリマー (P(x)) を合成した (Fig. 1)。ベンゾフェノンを有するシランカップリング剤を用いることでガラス基板表面に各種ポリマーを固定化し、細胞接着性評価を行った。



Polymer	*n*	*Đ*	NAKMe : NAIMe
P(0.2)	69	1.33	0.21 : 0.79
P(0.4)	63	1.34	0.41 : 0.59
P(0.6)	56	1.32	0.60 : 0.40
P(0.8)	52	1.33	0.83 : 0.17
P(1)	52	1.33	1.00 : 0.00

Fig. 1 Molecular structure of amino acid-derived amphiphilic copolymers, P(x) (x = 0.2, 0.4, 0.6, 0.8, 1).

1) Statistic Copolymers Working as Growth Factor-Binding Mimics of Fibronectin. W. Zhang *et al.*, *Adv. Sci.*, **2022**, *9(21)*, 2200775.

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自己組織化ペプチドをグラフト鎖に有するポリエステルの合成

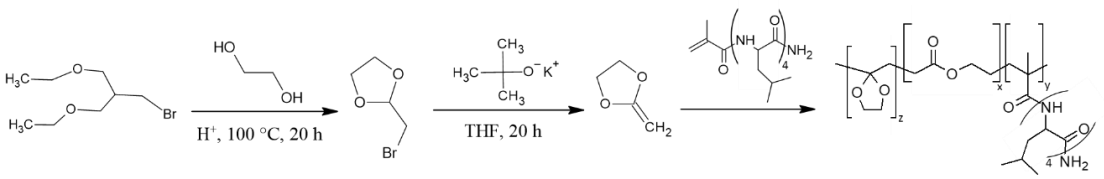
（同志社大理工 [1]）○長谷川海希 [1]・西村慎之介 [1]・古賀智之 [1]
Synthesis of self-assembling peptide-grafted polyester ([1]*Department of Molecular Chemistry and Biochemistry, Doshisha University*) ○ Miki Hasegawa,[1] Shin-nosuke Nishimura,[1] Tomoyuki Koga[1]

Peptides are known to self-assemble into various supramolecular structures through hydrogen bonding, offering nanomaterials with a wide range of properties. In particular, the presence of β-sheet structure in materials enhances their mechanical strength [1)]. Therefore, this research aims to synthesize a polyester grafted with peptides that self-assemble into β-sheets, such as leucine-based peptides. Here we report the preparation of a peptide-grafted polyester via radical copolymerization of 2-methylene-1,3-dioxolane, a cyclic ketene acetal (CKA), and tetraleucine macromonomer. Tetraleucine with methacryloyl group at *N*-terminus was produced using Solid Phase Peptide Synthesis. The CKA was obtained in a two-step synthesis with a 20% yield after purification. The CKA was then polymerized under N_2 at 120°C for 20 hours utilizing VAm-110 as an initiator, resulting in a polyester with 80% ring-opening. Similar parameters are employed to investigate the copolymerization of the peptide and CKA monomers.

Keywords: Self-assembling peptide, Polyester, Cyclic ketene acetal, Radical ring-opening polymerization

ペプチドの水素結合による自己組織化を利用して、様々な特性を持つ材料の設計が可能である。特に β-シート性ペプチドは、材料に優れた機械的特性をもたらす [1)]。本研究では、β-シート構造に自己組織化するオリゴペプチドをグラフト化したポリエステルの新規合成を目標としている。

実際にテトラロイシンペプチドマクロモノマーと 2-メチレン-1,3-ジオキソラン(CKA)のラジカル開環重合によりポリエステルの合成を行った。*N* 末端に重合性の官能基を有するテトラロイシンは固相合成法により合成した。CKA の合成は 2 段階で行い、単離・精製後回収率 20%で得られた。CKA モノマーのラジカル開環重合を、開始剤に VAm-110 を用いて、120°C で 20 時間 N_2 中で行ったところ、CKA が 80%開環したポリエステルが得られた。この重合条件でペプチドマクロモノマーと CKA モノマーの共重合について検討した。



1) Spider silk-inspired peptide multiblock hybrid copolymers for self-healable thin film materials. T. Koga, T. Morishita, Y. Harumoto, S. Nishimura, N. Higashi, *Mater. Adv.*, **2021**, *2*, 7851.

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BACH1 を標的とした高効率触媒的 RNA 切断機能付与型人工核酸 (CANA) による膵臓癌治療薬開発Ⅲ - *in vitro* 解析に基づく分子設計指針の構築 -

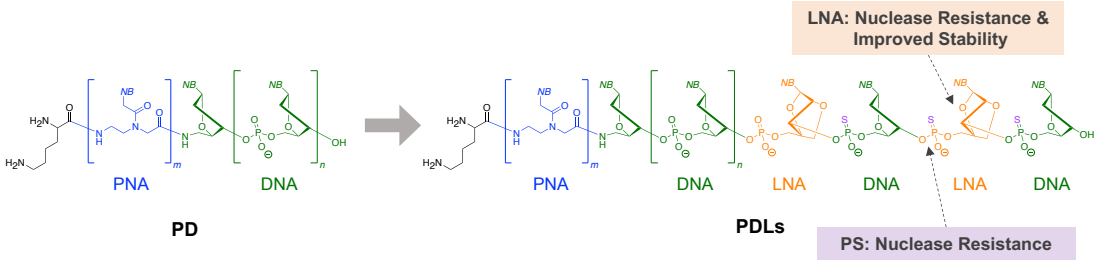
（東北大多元研 [1]・東北大院医 [2]・長崎大院医歯薬 [3]）○堀内 結翔 [1]・石渡 望 [1]・藤田 一寿 [1]・西嶋 政樹 [1]・三瓶 悠 [3]・荒木 保幸 [1]・松本 光代 [1,2]・山吉 麻子 [3]・五十嵐 和彦 [2]・和田 健彦 [1*]

Construction of Chimeric Artificial Nucleic Acids (CANA) toward Pancreatic Cancer Treatments by Inhibition of Transcription Factor BACH1 Ⅲ: Establishment of Molecular Design Strategy Based on *In Vitro* Analysis ([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Graduate School of Medicine, Tohoku University*, [3]*Graduate School of Biomedical Sciences, Nagasaki University*) ○ Yuto Horiuchi,[1] Nozomu Ishiwata,[1] Kazutoshi Fujita,[1] Masaki Nishijima,[1] Yu Mikame,[3] Yasuyuki Araki,[1] Mitsuyo Matsumoto,[1,2] Asako Yamayoshi,[3] Kazuhiko Igarashi,[2] Takehiko Wada[1*]

To apply oligonucleotide therapeutics as pharmaceuticals, we have proposed and demonstrated a novel design strategy of chimeric artificial nucleic acids (CANAs) to improve off-target effects and low therapeutic potency issues.[1)] In this study, we set the mRNA of the transcription factor BACH1, which plays an important role in the malignant transformation and metastasis of pancreatic cancer, as the target RNA and investigated the effects of DNA and PNA unit lengths and the junction position of the CANA on the hybrid stabilities *in vitro*. The enhancement of the turnover numbers of the RNase H mediated catalytic target RNA cleavage reaction was also investigated.

Keyword: Oligonucleotide Therapeutics; Chimeric Artificial Nucleic Acids; Catalytic cleavage of target RNA; RNase H; Pancreatic Cancer.

核酸医薬の実用化に向け、我々は触媒回転数の向上に基づく極少量での治療力向上が期待される高効率触媒的標的 RNA 切断機能付与型人工核酸 (CANA) の展開研究に取り組んできた[1)]。本研究では、膵臓癌悪性化に関与する転写因子 BACH1 の RNA を標的とし、DNA の 5'側に PNA を導入した従来の PD CANA を基本骨格とし、DNA 部位の 3'側を LNA および PS 結合で修飾することにより細胞内に存在するエクソヌクレアーゼ耐性を付与した 3 種類の PDLs CANA を合成した。これら CANA の *in vitro* における標的 RNA との複合体安定性や RNase H を介した触媒的 RNA 切断機能などを検討し、CANA の分子設計指針の構築に取り組んだ結果を報告する。



1) M. Inagaki, et al., *Chem. Lett.* **2019**, *48 (4)*, 341–344.

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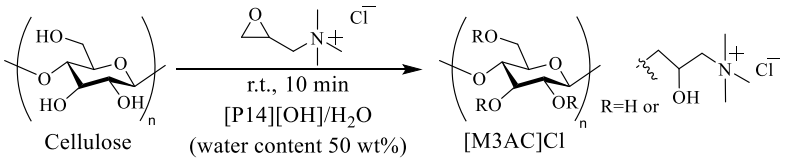
カチオン性セルロースの合成と抗菌性評価(I)-置換度による影響-

(上智大理工)○小淵康平・齋藤美希・齊藤玉緒・竹岡裕子・陸川政弘・藤田正博
Synthesis and Antibacterial Properties of Cationic Cellulose (I)- Effect of Degree of Substitution- (*Department of Materials and Life Sciences, Sophia University*) ○Kohei Obuchi, Miki Saito, Tamao Saito, Yuko Takeoka, Masahiro Rikukawa, Masahiro Yoshizawa-Fujita

Cellulose is an abundant natural material with low environmental impact. On the other hand, it is known that cationic polymers show antibacterial properties. We have synthesized cationic celluloses introduced trimethylammonium group ([M3AC]Cl) with various degree of substitution (*DS*) values. In this study, the antibacterial property of [M3AC]Cl was investigated. [M3AC]Cl with various *DS* values (0.36, 0.71, 1.4, 1.5, and 2.0) was synthesized and was used to perform disk diffusion tests for *Escherichia coli (E. coli*) and *Bacillus subtilis* (*B. subtilis*). [M3AC]Cl (*DS* value = 0.71, 1.4, 1.5, 2.0) showed the antibacterial properties for *B. subtilis*, while [M3AC]Cl showed no antibacterial property for *E. coil* regardless of the *DS* values.
Keywords : Cellulose, Pyrrolidinium hydroxide, Cationic cellulose, Antibacterial property

セルロースは、地球上に豊富に存在し、環境負荷の小さい天然材料である。一方、カチオン性ポリマーは、抗菌性を持つことが知られている。これまで、置換度(*DS* 値)の異なるカチオン性セルロースの合成を行ってきた。本研究では、それらカチオン性セルロースの抗菌性を調べた。

トリメチルアンモニウム基を有するカチオン性セルロース([M3AC]Cl)の合成を水酸化ピロリジニウム水溶液（[P14][OH]/H_2O）中で行った（式）。*DS* 値の異なる 5 種類の[M3AC]Cl (*DS* = 0.36、0.71、1.4、1.5、2.0)を用いて、ディスク拡散法により *Escherichia coli* (*E. coli*)および *Bacillus subtilis* (*B. subtilis*)に対する抗菌性を調べた。*E. coli* では、いずれの *DS* 値においても、[M3AC]Cl の周囲に阻止円は観察されなかった。一方、*B. subtilis* では、*DS* 値が 0.71 以上のとき、[M3AC]Cl の周囲に阻止円が観察された。 [M3AC]Cl は、*B. subtilis* に対して抗菌性を示すことがわかった。



Scheme. Synthesis of [M3AC]Cl in [P14][OH]/H_2O.

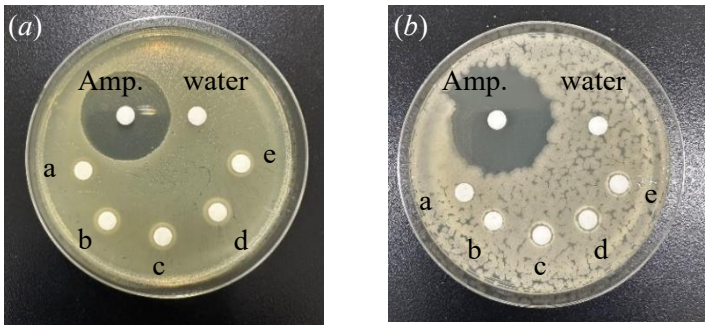


Figure. Disk diffusion test of [M3AC]Cl for *E. coli*. (*a*) and *B. subtilis* (*b*) (Amp.: ampicillin, a: *DS* value = 0.36, b: 0.71, c: 1.4, d: 1.5, e: 2.0).

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部分 2-デオキシ化アミロースの酵素的グラフト化によるキチンナノファイバーの疎水化

（鹿児島大院理工）○山本 直輝・戸谷 匡康・門川 淳一

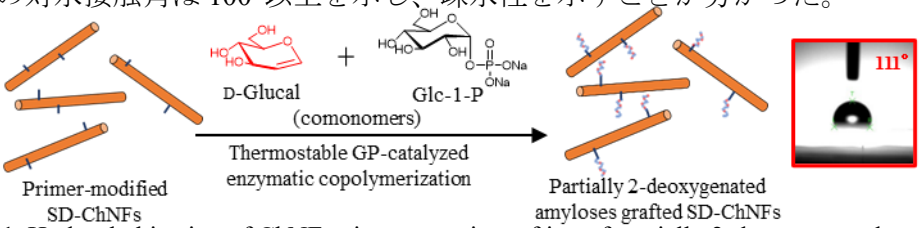
Hydrophobization of chitin nanofibers by enzymatic grafting of partially 2-deoxygenated amyloses (*Graduate School of Science and Engineering, Kagoshima University*)

○Naoki Yamamoto, Masayasu Totani, Jun-ichi Kadokawa

Chitin is one of the most abundantly distributed polysaccharides, but most of it remains as unutilized. Recently, nanofibrillation has been identified as one of the useful approaches for materialization of chitin. We previously reported the preparation of self-assembled chitin nanofibers (ChNFs) via regeneration from an ion gel with an ionic liquid using methanol[1]. Furthermore, the bundles of ChNFs were disentangled by electrostatic repulsion, giving rise to individual thin fibrillar materials, named scaled-down ChNFs (SD-ChNFs)[2]. We also found that partially 2-deoxygenated amyloses, produced by thermostable glucan phosphorylase (GP)-catalyzed enzymatic copolymerization of D-glucal and α-D-glucose 1-phosphate (Glc-1-P) as comonomers using a maltotriose primer, was hydrophobic[3,4]. In this study, we investigated the preparation of hydrophobic ChNFs via enzymatic grafting of partially 2-deoxygenated amyloses by thermostable GP-catalyzed enzymatic copolymerization from the primers modified on SD-ChNFs (**Scheme 1**). The water contact angle of partially 2-deoxygenated amylose-grafted SD-ChNF film was observed over 100°, indicating its hydrophobicity.

Keywords: Chitin nanofiber; Hydrophobization; Enzymatic polymerization; Hydrophobic polysaccharide; Partially 2-deoxygenated amylose

キチンは自然界に豊富に存在する天然多糖であるが、そのほとんどが未利用である。近年、キチンの有効な活用方法としてナノファイバー化が注目されている。我々は、イオンゲルからメタノールを用いてキチンを再生させると自己組織的にキチンナノファイバー（ChNF）が得られることを見出した[1]。また、部分的に脱アセチル化した ChNF を酢酸溶液中で超音波処理をすることで、静電反発の効果により ChNF のバンドルが解繊したスケールダウンキチンナノファイバー（SD-ChNF）が得られることも明らかにした[2]。一方、我々はマルトトリオースをプライマー、D-グルカールおよび α-D-グルコース 1-リン酸（Glc-1-P）をコモノマー、マルトトリオースをプライマーに用いた耐熱性グルカンホスホリラーゼ（GP）酵素触媒共重合で得られる部分 2-デオキシ化アミロースが疎水性を示すことを報告している[3,4]。本研究では、SD-ChNF 上にプライマーを修飾後、上記の共重合により疎水性多糖を酵素的にグラフトした（**Scheme 1**）。得られた SD-ChNF 誘導体フィルムの対水接触角は 100°以上を示し、疎水性を示すことが分かった。



Scheme 1. Hydrophobization of ChNFs via enzymatic grafting of partially 2-deoxygenated amyloses.

1) J. Kadokawa, A. Takegawa, S. Mine, K. Prasad, *Carbohydr. Polym.*, **84**, 1408(2011).
2) T. Hashiguchi, K. Yamamoto, J. Kadokawa, *Carbohydr. Polym.*, **270**, 118369(2021).
3) J. Kadokawa, S. Nakamura, K. Yamamoto, *Processes,* **8**, 1070(2020).
4) S. Abe, K. Yamamoto, J. Kadokawa, *Asian J. Org. Chem.*, **11**, e202100763(2022).

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酵素触媒共重合によるグルコサミノ 2-デオキシグルカンの合成

（鹿児島大院理工）○宮原 雄太・戸谷 匡康・門川 淳一
Synthesis of Glucosamino-2-Deoxyglucan by Enzymatic Copolymerization (*Graduate School of Science and Engineering, Kagoshima University*) ○Yuta Miyahara, Masayasu Totani, Jun-ichi Kadokawa

Natural polysaccharides express important functions depending on their chemical structures. Therefore, unnatural polysaccharides can be expected to exhibit new functions and properties. On the other hand, enzymatic polymerization is useful for the synthesis of well-defined polysaccharides because it proceeds in high control of regio- and stereoselectivities. Glucan phosphorylase (GP) is an enzyme that catalyzes the enzymatic polymerization using α-D-glucose 1-phosphate (Glc-1-P) and maltooligosaccharide as a monomer and primer, respectively, to produce amylose[1]. Moreover, GP can recognize analog substrates of Glc-1-P such as α-D-glucosamine 1-phosphate (GlcN-1-P) and D-glucal because this enzyme shows weak substrate specificity[2]. Therefore, in this study, we investigated the synthesis of glucosamino-2-deoxyglucan with highly reactive amino groups, a new unnatural polysaccharide, by GP-catalyzed enzymatic copolymerization of GlcN-1-P and D-glucal (Figure 1). We confirmed the structure of glucosamino-2-deoxyglucan by ^{1}H NMR spectrum and MALDI-TOF-MS of the isolated product.

Keywords : Enzymatic polymerization; Glucan phosphorylase; Copolymerization; Unnatural polysaccharide; Glucosamino-2-deoxyglucan

天然多糖はその化学構造に応じた重要な機能を発現している。そのため非天然型多糖からは新規な機能や様々な特性の発現が期待できる。酵素触媒重合は、位置及び立体選択的に重合が進行するため構造明確な機能性多糖の合成に有用である。グルカンホスホリラーゼ（GP）は、α-D-グルコース 1-リン酸（Glc-1-P）をモノマー、マルトオリゴ糖をプライマーとしてアミロースを得る重合を触媒する酵素である [1]。また、GP は基質特異性の緩さを有することから、Glc-1-P と構造の似た α-D-グルコサミン 1-リン酸（GlcN-1-P）および、D-グルカールを基質として認識することが見出されている [2]。本研究では、GlcN-1-P、D-グルカールをコモノマーに用いた酵素触媒共重合により高い反応性のアミノ基を有する新規な非天然型多糖であるグルコサミノ 2-デオキシグルカンの合成を検討した（Figure 1）。単離した生成物の ^{1}H NMR および MALDI-TOF-MS 測定結果から、グルコサミノ 2-デオキシグルカンの構造を確認した。

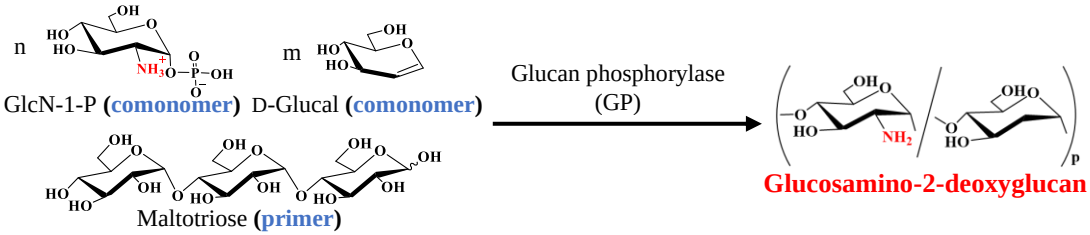

Figure 1. Enzymatic synthesis of glucosamino-2-deoxyglucan

1) S. Shoda, H. Uyama, J. Kadokawa, S. Kimura, S. Kobayashi *Chem. Rev.***2016**, 116, 2307.
2) J. Kadokawa, *Polym. J.* **2022**, 54, 413.

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光重合による高強度セルロースマテリアルの開発 (I)
–強度に及ぼすモノマー及びセルロース含量の効果–

（上智大理工）○松本恵人・松井新大・竹岡裕子・陸川政弘・藤田正博
Development of Cellulose Materials with High Strength by Photopolymerization (I) -Effect of Amounts of Monomer and Cellulose on Strength- (*Department of Materials and Life Sciences, Sophia University*) ○Keito Matsumoto, Arata Matsui, Yuko Takeoka, Masahiro Rikukawa, Masahiro Yoshizawa-Fujita.

Cellulose has attracted attention as a sustainable material due to its low cost and abundance on Earth. Although there is a need to dissolve and process cellulose under mild conditions, it is insoluble in typical solvents such as water and organic solvents. On the other hand, 3D printing, which is a processing method, is expected to be an environmentally friendly technology due to a distributed production system. In this study, the composites based on 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl), cellulose, and an ionic liquid (IL) monomer were fabricated by 3D printing and photopolymerization. To use the cellulose solution as an ink for a 3D printer, the optimum IL monomer and cellulose amounts were investigated. As a result of varying these amounts in the ink, the optimum IL monomer and cellulose amounts were 2.9 and 11 wt%, respectively, for obtaining a 3D structure.
Keywords : Cellulose; Ionic liquids; Photopolymerization; 3D printing

セルロースは、低コストで地球上に豊富に存在していることから、持続可能な材料として注目されている。温和な条件下でセルロースを溶解、加工することが求められているものの、水、有機溶媒など汎用溶媒には難溶である。一方、加工方法の 1 つに 3D プリンティングが挙げられ、生産拠点の分散化に対応できるため、環境負荷の少ない技術として期待できる。本研究では、セルロース溶解性イオン液体(IL)である 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl)、セルロース、IL モノマー[1]からなるインクを作製し、3D プリンティングと光重合により高強度 3 次元構造物を作製することを目的とした。3D プリンティング後の造形物を図 1 に示す。インク中の[C_4mim]Cl とセルロース含量をそれぞれ 3.00 と 0.30 g に固定し、IL モノマーの含量を 0.05, 0.10, 0.15, 0.20 g と変化させ、格子構造をプリントした。0.10 g の時、目的とする格子構造が得られた。IL モノマーの含量を 0.10 g に固定し、セルロースの含量を変化させた結果、0.38 g のとき、目的とする格子構造が得られた。IL モノマー0.10 g (2.9 wt%)、セルロース 0.38 g (11 wt%)のとき、最も成型忠実性が高い 3D 構造物が得られた。

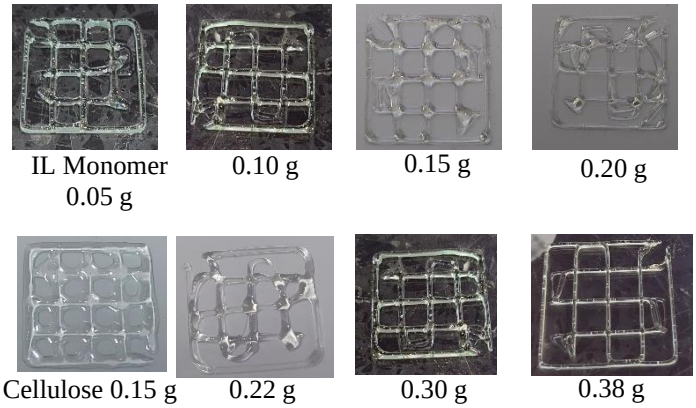

Figure 1. Grid layers after 3D printing with various amounts of IL monomer and cellulose.

1) M. Murakami, Y. Kaneko, J. Kadokawa, *Carbohydr. Polym.*, **2007**, 69, 378-381.

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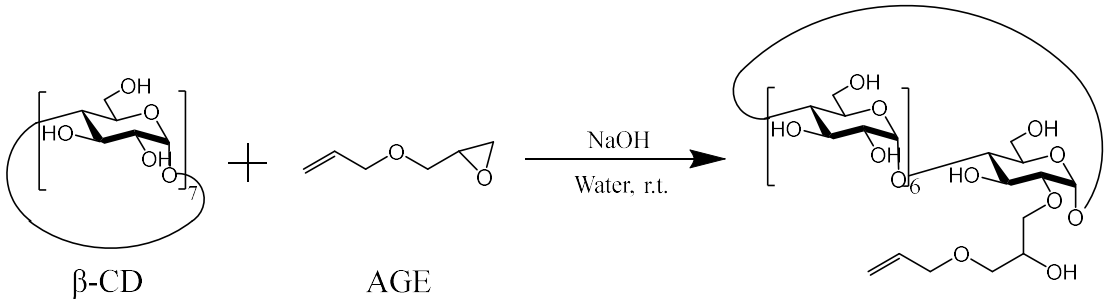
Synthetic Studies of Zwitterionic Modified Cyclodextrins (VI): Linker introduction for fluorescent group modification

(*[1]Grad. Sci.&Engin., Saitama University, [2]Adv. Inst. Innov. Tech., Saitama University, [3]Strategic Res. Ctr., Saitama University*) ○Kanta Koizumi[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3]

Keywords: Cyclodextrin, Zwitterion, Liposome

Phospholipids, the main component of biological membranes, are zwitterions with both positive and negative charges in the head group. It has been reported that spherical polymers with zwitterionic modification adhered to the cell membrane on the surface of red blood cells by electrostatic forces, causing aggregation of the red blood cells[1)]. This aggregation is thought to have occurred because the molecule is spherical and its adhesion surface to the cell membrane is not limited, and it adheres to red blood cells in all directions. We hypothesized that if a molecule that can introduce zwitterionic ions in only one direction is used, the adhesion surface to the cell membrane would be limited and cell-cell aggregation would not occur. Since cyclodextrins (CDs) have a ring structure of 6-8 glucose molecules, with a primary hydroxyl group on one side of the ring and a secondary hydroxyl group on the opposite side, the use of CDs was considered in our synthetic research. It was expected that introduction of a zwitterion on one side of the CD ring system causing adhesion to the cell membrane, and chemical modification on the other side giving possibility to provide some function on the cell membrane.

The adhesiveness of zwitterion-modified CDs to phospholipid membranes is evaluated by their affinity to liposomes, which are prepared as a cell membrane model. Introduction of fluorescent groups into zwitterion-modified CDs in advance allows to measure the fluorescence intensity of the liposomes or observe them with a fluorescence microscope. In this report, the details of the results of the introduction of a linker to modify fluorescent groups will be presented.



1) Xifei Yu, *et al.*, *Nature Materials*, **2012**, *11*, 468-476.

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Synthesis of Novel Amylase Substrates Using FRET Effect (VI): Preparation of Polymer-type Amylase Substrate

([1]Grad. Sci.&Engin. Saitama University, [2]Adv. Inst. Innov. Tech. Saitama University, [3]Strategic Res. Ctr. Saitama University) ○Yuki Yamamoto[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3]

Keywords: Glycan; Amylooligosaccharides; FRET; Polymerization; Amylase;

Human α-amylase, an enzyme involved in carbohydrate metabolism, is divided into two types: S-type amylase (HSA), secreted by the salivary glands, and P-type amylase (HPA), secreted by the pancreas. Since amylase secretion increases when there is an abnormality in each organ, the development of a rapid, sensitive, and simple method for measuring blood amylase activity and the two types of amylase isozymes will lead to the early detection of these organ diseases. Methods utilizing the FRET effect have been studied to achieve these conditions hitherto. In a previous our study[1)] , an amylase-sensitive fluorogenic polymeric substrate was reported. In the absence of amylase in the measurement system, intramolecular FRET effect occurred and acceptor-derived fluorescence was observed. However, when amylase was present in the system, hydrolysis of the donor-containing sugar chains occurred. The distance between the donor and the acceptor changed to longer, so the FRET effect went away. Therefore, when amylase was added, the acceptor-derived fluorescence decreased with time and the donor-derived fluorescence increased. In addition, synthesis of glycopolymers having sugar chains up to hexasaccharides including donor fluolophors was accpmplished, and the results suggested that the longer the sugar chain length, the greater the difference in the rate of degradation of sugar chains by HPA and HSA, and the more sensitive the amylase isozyme activity measurement became.

To improve the sensitivity of amylase isozyme activity measurement by further extending the sugar chain length was examined in this study. Thus, a glycopolymer whose sugar chain consists of eight glucose residues as a candidate of the amylase substrate was designed and the multistep synthesis was carried out.

In this presenteation, a synthetic assembly of Amylase Substrate Polymers by radical polymerization from a octasaccharidic FRET donor monomer, a FRET acceptor monomer, and acrylamide will mainly be reported.

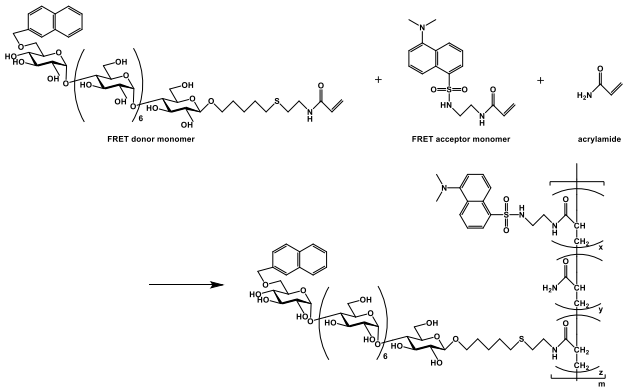

Fig. 1 Constructionsis of Amylase Substrate Polymers

1) K. Matsuoka, *et al*., *ACS Macro Lett*., **2012**, *1*, 266.

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日本化学会 第104春季年会 (2024)

癌細胞選択的薬物導入システムの構築と機能評価Ⅲ：膵臓癌悪性化抑制薬剤導入を目指して

（東北大多元研[1]・東北大院医[2]・長崎大院医歯薬[3]・阪公大院理[4]）○加藤 ひらり[1]・東 亮太[1]・荒木 保幸[1]・西嶋 政樹[1]・松本 光代[1,2]・山吉 麻子[3]・五十嵐 和彦[2]・大村 美香[4]・中瀬 生彦[4]・和田 健彦[1*]

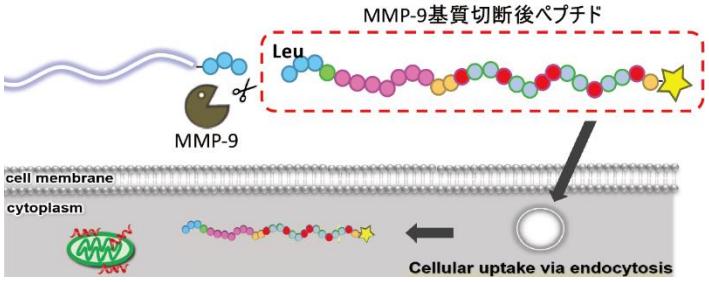
Construction and Evaluation of Cancer Cell Selective Drug Delivery System Ⅲ:Development pancreatic cancer of a selective drug delivery system to suppress the malignant progression ([1]*IMRAM, Tohoku University,* [2]*Grad. Sch. Medicine, Tohoku University,* [3]*Nagasaki University,* [4]*Osaka Metropolitan University.)* ○ [1]Hirari Kato, [1]Ryota Azuma, [1]Yasuyuki Araki, [1]Masaki Nishijima, [1,2]Mitsuyo matsumoto, [3]Asako Yamayoshi , [2]Kazuhiko Igarashi, [4]Ikuhiko Nakase, [4]Mika Omura, [1*]Takehiko Wada

Recently, a large number of anticancer drugs have been developed and used for clinical application. However, side effects and cytotoxicity, mainly due to drug delivery into normal cells, have been pointed out as serious issues to be improved. Here, we developed a cancer cell-selective intracellular delivery system consisting of three functional modules, i.e., oligoarginine peptide (R8), polyethylene glycol (PEG), and matrix metalloproteinase (MMP) substrate peptide. Oligoarginine, one of the most popular cell-penetrating peptides, has been used to enhance the cellular uptake of molecules. To provide cancer cell specificity, oligoarginine was conjugated with PEG via MMPs substrate peptide, which is expected to act as a cancer cell-responsive cleavable linker because MMPs are known to be specifically overexpressed in cancer cells. In this design, the PEG chain was used to reduce non-specific protein adsorption. We worked on its development for pancreatic cancer therapeutics and studied its effects on intracellular behavior.

Keywords: Cell penetrate peptides, Matrix metalloproteinase, Cancer cell selective delivery, Drug delivery system (DDS), Cellular membrane uptake capability, pancreatic cancer

癌は世界の主要な死因の 1 つであり、癌治療薬が数多く開発されている。しかし標的細胞のみならず正常細胞にも送達され、深刻な副作用や毒性を誘起するなど解決すべき課題が指摘されている。本課題解決法の 1 つとして、標的癌細胞のみに薬物を選択的に送達可能な DDS 開発が注目され、膨大な種類の DDS が報告されている。

我々は悪性度の高い癌細胞特異的に過剰発現される Matrix MetalloProteinases-9 (MMP-9) に注目し、標的癌細胞近傍でのみ細胞膜透過性を活性化出来得る、ポリエチレングリコール (PEG) 複合化オリゴアルギニンの設計･合成および機能評価に取組んできた。その結果、MMP-9 認識ペプチドをリンカーとした PEG 複合化オリゴアルギニンシステムが、Hep G2 など悪性度の高い癌細胞で過剰発現する内在性 MMP-9 をトリガーとし癌細胞選択的取込を実現可能であることを報告した。本研究では、膵臓癌治療薬への展開を目指し、核酸医薬との複合化と細胞取込挙動解析に取組んだ。



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日本化学会 第104春季年会 (2024)

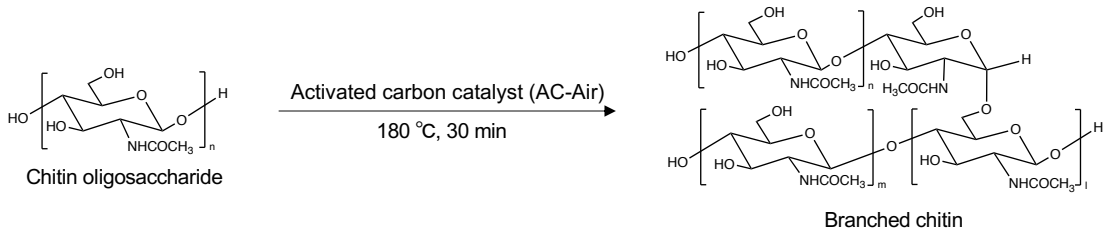
活性炭触媒によるキチンオリゴ糖の脱水縮合反応

（東理大工）○安田 辰輝・佐川 拓矢・橋詰 峰雄
Dehydration Condensation of Chitin Oligosaccharides by Activated Carbon Catalysts (*Faculty of Engineering, Tokyo University of Science*) ○Tatsuki Yasuda, Takuya Sagawa, Mineo Hashizume

Chitin is the most abundant marine biomass, and it has received attention as a feedstock of biomaterials due to its biocompatibility and antibiotics. However, its intrinsic poor solubility hinders its effective use. The purpose of this study is to synthesize branched chitin oligosaccharides, which has high solubility, from chitin oligosaccharides by mixing them with activated carbon catalyst and heating them at high temperature. Chitin oligosaccharides (containing degree of polymerization n = 1-7, average degree of polymerization: 1.18) were mixed with air-oxidized activated carbon catalyst (AC-Air) at the substrate/catalyst ratio of 1.25 (w/w) and heated and stirred at about 180 °C for 30 minutes. MALDI-TOF MS measurements and HPLC measurements using a SEC column of the obtained solid suggested that intermolecular dehydration condensation proceeded.
Keywords: Chitin; Activated Carbon Catalyst; Intermolecular Dehydration Condensation

キチンは海洋中最大の賦存量を有するバイオマスであり、その生体適合性、抗菌性からバイオマテリアルの原料として注目されているが、その難溶性が有効活用の妨げとなっている[1]。我々は直鎖状のキチンを分岐構造とすることで溶解性を向上できると着想した[2]。本研究は、キチンオリゴ糖を活性炭触媒と混合して高温加熱することにより、高い溶解性を有する枝分かれキチンを合成することを目的とする（Scheme 1）。

活性炭（AC）を空気気流下、425 °C で 4 時間加熱することで、カルボキシ基等（全酸量：2.9 mmol/g、カルボン酸量：1.3 mmol/g）を有する空気酸化活性炭（AC-Air）を調製した。キチンオリゴ糖（重合度 n = 1–7 を含む、平均重合度 1.18）を AC-Air と基質触媒比 1.25 (w/w)で混合し、約 180 °C で 30 分間加熱攪拌した。得られた固体を MALDI-TOF MS 測定や HPLC 測定（SEC カラム）を行ったところ、MALDI-TOF MS 測定では 9 量体までのキチンオリゴ糖が確認され、HPLC 測定では原料のキチンオリゴ糖と比べ、保持時間の短いピークが確認されたことから、分子間脱水縮合が進行したことが示唆された。



Scheme 1. Dehydration condensation of chitin oligosaccharides.

1) M. Yabushita, H. Kobayashi, K. Kuroki, S. Ito, A. Fukuoka, *ChemSusChem* **2015**, *8*, 3760–3763.
2) 平井宏和, 西村祐一, 三輪智弘, 高木宏基, *触媒*, **2023**, *65*, 41–47.

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ポリアニリン/高分子電解質ゲル複合体の合成と電気物性評価

（奈良女大院生活工学[1]・奈良女大院工[2]）○金泉 杏美[1]・大背戸 豊[2]

Synthesis of polyaniline/polyelectrolyte gel composites composed and its electronic conductive properties

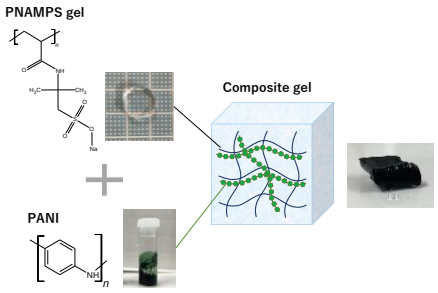
([1]*Graduate School of Human Centered Engineering, Nara Women's University*, [2]*Faculty of Engineering, Nara Women's University*) ○Ami Kaneizumi[1], Yutaka Ohsedo[2]

We synthesized conducting polymers inside polyelectrolyte gels and evaluated the electrical properties of the composite gels to create new conductive materials. The composite gels were obtained by synthesizing polyaniline through oxidative polymerization of aniline in a polyelectrolyte gel using sodium 2-acrylamido-2-methyl-1-propanesulfonic acid as the monomer. The evaluation of the electrical properties of the composite gels suggests that the internal structure of the gel affects the electronic conductivity of the composite polyaniline component.

Keywords : Polyelectrolyte gels; Composite gel materials; Gel materials; Conducting polymer

講演者らは、新規ゲル材料創製研究の一環として、高分子ゲル化剤/導電性高分子系複合材料や電解質ゲル等の導電性複合ヒドロゲル材料の新規創製を行ってきた [1−4]。本研究では新規導電性ヒドロゲル材料の創製を目的として、高分子電解質ゲルと導電性高分子との相互作用に基づく効率的な導電性網目形成が期待できる複合化法による導電性ヒドロゲル材料の合成を検討する。今回は、高分子電解質ゲル母体内での電子電導性網目形成を導電性高分子ポリアニリンについて行い、得られたゲル複合体の電気物性を評価した。

ゲル複合体の合成は、1) 高分子電解質ゲルの合成、2) ゲル内での導電性高分子の合成により行った (Scheme 1)。まず電解質ゲルとしてスルホン酸ナトリウムを含む水溶性アクリルモノマーである NAMPS を選択して種々の架橋度のヒドロゲルを合成した。次にこれら高分子電解質ゲル内でアニリン/塩酸系の過硫酸アンモニウムによる酸化重合を行うことで、高分子電解質ゲル PNAMPS と導電性高分子ポリアニリン PANI のゲル複合体を合成した。得られたゲル複合体の電気物性を評価した結果、ゲル複合体がポリアニリンに基づいた半導体レベル 10^{-4} S/cm の電子電導性を有しており、また母体である高分子電解質ゲルの網目構造がポリアニリンの電子導電性に影響していることが示唆された。



Scheme 1. Synthesis of polyaniline/polyelectrolyte hydrogel composites.

1) Y. Ohsedo, K. Saruhashi, H. Watanabe, N. Miyamoto, *New J. Chem.*, **2017**, *41*, 9602. 2) Y. Ohsedo, M. Sasaki, *Gels*, **2022**, *8*, 469. 3) Y. Ohsedo, M. Sasaki, *New J. Chem.*, **2023**, *47*, 17817. 4) Y. Ohsedo, A. Kaneizumi, *Gels*, **2023**, *9*, 819.

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プログラムを用いた汎用高分子の構造異性体全列挙

（北大院総化[1]・北大院理[2]・北大 WPI-ICReDD[3]）臼杵 義亨[1]・堤 拓朗[1,2]・長谷部 航平[1]・小林 正人[1,2,3]・松岡 慶太郎[1,2]・武次 徹也[1,2,3]・○佐田 和己[1,2]

Enumerations of the Structural Isomers of Organic Commodity Polymers ([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Faculty of Science, Hokkaido University,* [3]*WPI-ICReDD, Hokkaido University*) Gikyo Usuki[1], Takuro Tsutsumi[1,2], Kohei Hasebe[1], Masato Kobayashi[1,2,3], Keitaro Matsuoka[1,2], Tetsuya Taketsugu[1,2,3], ○Kazuki Sada[1,2]

In this study, we demonstrate the development of an enumeration program for all polymer structural isomers. The molecular formula and functional groups of the unit structure are used as inputs for the enumeration. The enumeration of nylon 6, as $C_6H_{11}NO$ and one amide group, revealed 387 polymer structural isomers. A literature survey revealed that 35 isomeric polymers had been already reported among them. Thus, the reported isomers were about 10% of the total of the isomers, indicating that many unexplored or unregistered polymers exists. We further enumerated polychloroprene and poly(vinyl phenol), and 42 and 79 structural isomers exists, respectively. These results clearly indicate that many structural isomers of commodity polymers have not been synthesized or explored yet. Therefore, at present, the variations of the polymer samples are not sufficient to elucidate the real structure-activity relationships between the unit structure of polymers and their structures or properties such as higher-order structures, mechanical properties, and thermos-responsive properties, due to their limited numbers.

Keywords : Organic Polymers, Structural Isomers, Commodity Plastics, Enumeration, Polymer Informatics

有機高分子の高次構造・物性・機能はユニット構造とユニット構造間に働く分子間相互作用によって支配されており、その分子間相互作用はユニット構造を構成する分子式と官能基に深く相関すると考えられる。そのため、ユニット構造をデザインし、機能などと相関する研究が活発に行われている。しかしながら、それらの多くは重合系が確立されたモノマーから合成される高分子に限定されており、必ずしも広い高分子空間を研究対象としたものではない。

そこで、本研究では、ユニット構造の官能基と分子式を入力とした高分子構造異性体を全列挙するプログラムの作成と、汎用高分子のユニット構造について、全列挙を行った結果について報告する。まず、ナイロン 6 の異性体全列挙したところ、387 種の高分子構造異性体が確認できた。文献検索から、報告例のあるものは 35 種類であり、全体の 1 割にも満たない。さらにポリクロロプレンやポリ（ビニルフェノール）を全列挙したところ、それぞれ 42 種類と 79 種類の高分子構造異性体が明らかになった。これらは簡単な汎用高分子であっても、その構造異性体の多くが未合成・未探索であり、研究対象となる高分子が合成法・主鎖構造に縛られたものであることを示している。このことはユニット構造と高次構造・物性・機能等との構造活性相関の解明が十分ではないことを示唆する。

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Academic Program [Oral B] | 18. Polymer：Oral B

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC D342(342, Bldg. 3 [4F])

[D342-4am] 18. Polymer

Chair: Hiroki Fukumoto, Masayoshi Higuchi

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[D342-4am-01]
Olefin Polymerization using Aluminum Complex Catalysts

○Nanako Kimura[1], Daisuke Takeuchi[1] (1. Hirosaki University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[D342-4am-02]
Substituent effects of ether-functionalized propylenes on scandium-catalyzed copolymerization with ethylene

○Mingjun Chi[1,2], Hao Wang[2], Masayoshi Nishiura[2], Lin Huang[2], Haoran Zhang[2], Zhaomin Hou[1,2] (1. Saitama University, 2. RIKEN)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[D342-4am-03]
Synthesis and Application of Polymers Containing Highly Alkaline-resistant Triarylsulfonium.

○Tomohiro Imai[1], Ryoyu Hifumi[1], Shinsuke Inagi[1], Ikuyoshi Tomita[1] (1. Tokyo Institute of Technology)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[D342-4am-04]
Synthesis of functional polyesters containing cleavable linkages and AIE luminogen via Passerini-type multicomponent polymerizations

○Chih-Feng HUANG[1], Li-Chieh CHOU[1], Yi-Shen HUANG[1] (1. National Chung Hsing University)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
Break

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[D342-4am-05]
One-pot synthesis of hydroquinone-polymers from benzene with hydrogen peroxide

○Hideki Sugimoto[1], Kenshin Miyata[1], Akiyuki Nakano[2], Hideyuki Higashimura[2], Shinobu Itoh (1. Osaka University, 2. Okayama University of Science)

English
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[D342-4am-06]
A New Synthetic Approach of Metallosupramolecular Polymer and its Electrochromic Application

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◯Satya Ranjan Jena[1], Masayoshi HIGUCHI[1], Chih-Wei Hu[1] (1. National Institute for Materials Science)

Japanese

11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[D342-4am-07]

Synthesis and Optical Properties of π-Conjugated Polymers with Fluorine-containing Benzodithiophene

◯Hidetoshi Okuzaki[1], Sera Sato[1], Tomohiro Agou[2], Toshio Kubota[1], Hiroki Fukumoto[1] (1. Graduate School of Science and Engineering, Ibaraki University, 2. Graduate School of Science, University of Hyogo)

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・有機アルミニウム触媒による不飽和炭化水素モノマーの重合・共重合

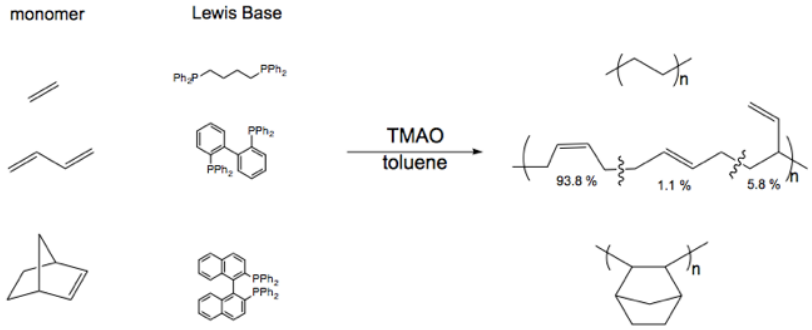
（弘前大院理工）○木村なな子・竹内大介
Polymerization and Copolymerization of Unsaturated Hydrocarbon Monomers by Organoaluminum Catalysts (*Graduate School of Science and Technology, Hirosaki University*)
○Nanako Kimura, Daisuke Takeuchi

Transition metal catalysts have been extensively used for the polymerization of olefins and conjugated dienes. Herein we report that TMAO in combination with phosphines catalyze polymerization of some unsaturated hydrocarbon monomers.

TMAO in combination with phosphines such as DPPB catalyze polymerization of ethylene. TMAO/phosphine systems are also effective for the polymerization of 1,3-butadiene. Especially, TMAO/DPPBiPh system produces polybutadiene with high cis-1,4 selectivity. TMAO/rac-BINAP system bring about norbornene polymerization efficiently. Copolymerization of these monomers was also investigated.

Keywords : Organoaluminum; Phosphine; Ethylene; Butadiene; Norbornene

エチレンやブタジエンなどの不飽和炭化水素モノマーの重合には、従来、遷移金属触媒や希土類触媒が主に用いられてきた。一方で、エチレン重合に活性を示すカチオン性有機アルミニウム触媒の例がいくつか知られている[1]。ごく最近、アルミニウム触媒によるブタジエン重合の例も報告されている[2]。最近、我々は、一般的に助触媒として用いられている TMAO（メチルアルミノキサン）と Lewis 塩基である NHC を組み合わせた触媒系が、エチレンの重合に有効であることを見出している[3]。本研究では、有機アルミニウムとホスフィンを組み合わせた触媒系による不飽和炭化水素モノマーの重合について検討を行った。



TMAO とホスフィンを組み合わせた触媒系はエチレンの重合に有効であった。特に、DPPB を用いた場合に活性が向上した。TMAO とホスフィンを組み合わせた触媒系はブタジエンの重合にも有効であった。DPPBiPh を用いた場合には、高い cis-1,4 選択性を示すポリブタジエンが得られた。ノルボルネンの重合には、TMAO と rac-BINAP を組み合わせた触媒系が有効であった。これらのモノマーの共重合についても検討を行った。

References 1) R. F. Jordan, *et al. JACS* **1997**, *119*, 8125; R. F. Jordan, *et al. JACS* **1998**, 120, 8277; V. C. Gibson, *et al. Chem. Commun.* **1998**, 2523. 2) T. Jian, *et al. Polym. Chem.* **2023**, *14*, 980. 3) N. Kimura, *et al. Des. Monomers Polym.* **2023**, *26*, 182.

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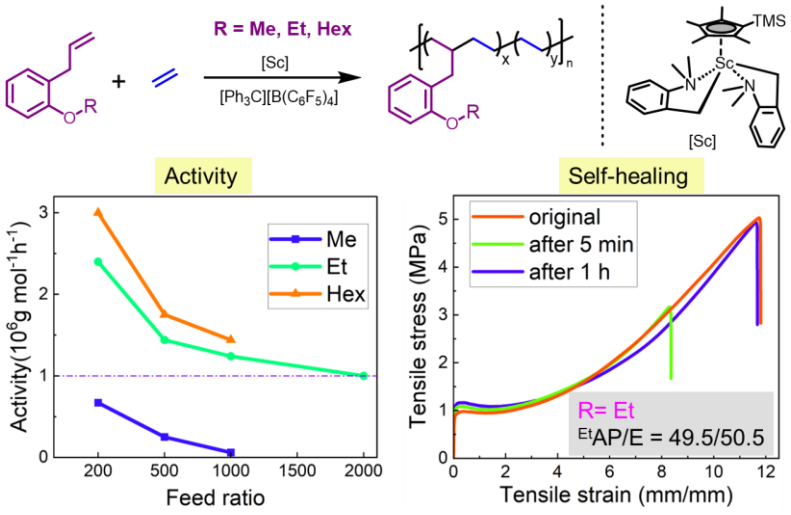
Substituent Effects of Ether-Functionalized Propylenes on Scandium-Catalyzed Copolymerization with Ethylene

([1]*Graduate School of Science and Engineering, Saitama University;* [2]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science*) ○Mingjun Chi,[1,2] Hao Wang,[2] Masayoshi Nishiura,[2] Lin Huang,[2] Haoran Zhang[2], Zhaomin Hou[1,2]

Keywords: Copolymerization; Substituent effects; Self-healing properties; Scandium catalysts

The copolymerization of nonpolar and polar olefins in a controlled fashion is of great interest and importance. We recently reported the sequence-controlled copolymerization of ethylene (**E**) and anisylpropylene (^{Me}**AP**) by a half-sandwich scandium catalyst, which afforded unique multiblock copolymers composed of relatively long **E**-*alt*-^{Me}**AP** sequences and short **E**-**E** sequences.[1,2] Such microstructure-regulated polymers exhibited excellent elasticity and self-healing properties because of the microphase separation of nanodomains of the crystalline **E**-**E** segments from a flexible **E**-*alt*-^{Me}**AP** matrix. To further investigate the influences of ether-functional groups on the copolymerization behaviors and the self-healing properties of the resulting copolymers, we then examined the analogous copolymerization by using ether-functionalized propylenes with various substituents on the oxygen atom.

Herein we report the scandium-catalyzed copolymerization of ethylene (**E**) with ether-functionalized propylenes (**AP**) having different substituents (Et (^{Et}**AP**), *n*-Hex(^{Hex}**AP**)) at the oxygen atom. The copolymerization afforded unique multi-block copolymers with relatively long alternating **E**-*alt*-$^{Et/Hex}$**AP** and **E**-**E**-$^{Et/Hex}$**AP** sequences and short **E** − **E** blocks. Significant substituent effects were observed on the copolymerization activity and self-healing properties. We found that ^{Et}**AP** and ^{Hex}**AP** showed much higher activity than that of ^{Me}**AP**. The copolymers with ethyl substituent (^{Et}**AP**) exhibited much improved elasticity and self-healing property compared with Me group (^{Me}**AP**).



1) Wang, H.; Yang, Y.; Nishiura, M.; Higaki, Y.; Takahara, A.; Hou, Z. *J. Am. Chem. Soc*. **2019**, *141*, 3249.

2) Yang, Y.; Wang, H.; Huang, L.; Nishiura, M.; Higaki, Y.; Hou, Z. *Angew. Chem. Int. Ed.* **2021**, *60*, 26192.

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Synthesis and Applications of Polymers Containing Highly Alkaline-resistant Triarylsulfonium.

([1]*School of Materials and Chemical Engineering, Tokyo Institute of Technology*)
○Tomohiro Imai[1], Ryoyu Hifumi[1], Shinsuke Inagi[1], Ikuyoshi Tomita[1]

Keywords: Polycondensation; Polymer Reaction; Triarylsulfonium Salts; Anion-exchange Membrane

To realize the low-cost hydrogen production system, the water splitting module that operates under alkaline conditions is paid much attention to, since it does not require noble metals such as Pt for electrodes. However, due to the low chemical stability of the anion-exchange membrane (AEM) which consists of polymers possessing positively charged functional groups, no module that exhibits sufficient durability has been realized yet.

To develop an AEM with high alkaline resistance, we focused on the triarylsulfonium (**TAS**) structures as ion exchange groups and they were synthesized from sulfur compounds by means of the addition reaction to arynes[1,2] or by the Friedel-Crafts arylation reaction, from which the alkaline resistant feature of the **TAS** salts proved to be strengthened dramatically by introducing sterically demanding substituents.[3] Under the conditions of 1 M KOH/CD_3OD at 80 ℃, for example, **TAS 3cH**, prepared by the Friedel-Crafts reaction, exhibits 33 times higher stability compared to benzyltrimethylammonium (BTMA), the commonly used cationic functional group (**Fig.1**). [4]

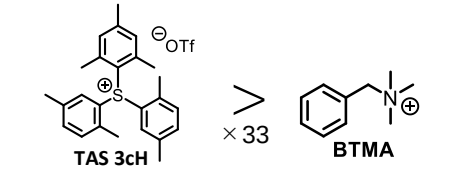
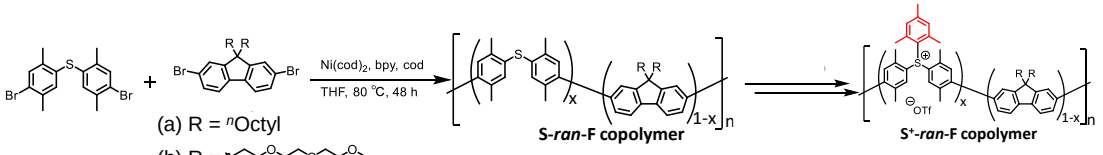


Fig. 1 Highly alkaline-resistant **TAS**

Various polymers containing highly alkaline-resistant **TAS** units in the main chain have been synthesized by the transition metal-catalyzed coupling followed by polymer reactions (**Scheme 1**). Properties of the polymers for the AEM applications will also be described.



(a) 88%, M_w/M_n =3.24, M_n = 21700, M_w = 70500
(b) 93%, M_w/M_n = 5.12, M_n = 14800, M_w = 76000

(a) 67%
(b) 52%

Scheme 1 Synthesis of polymers containing highly alkaline-resistant **TAS**

1) T. Hsu, *et al.*, *J. Am. Chem. Soc.*, **2017**, *142*, 11983-11987. 2) L. Xiajin, *et al.*, *Org. Lett.*, **2017**, *19*, 838-841. 3) T. Imai, R. Hifumi, S. Inagi, I. Tomita, *71st SPSJ Symp. Macromol.*, **2022**, 3E07. 4) T. Imai, R. Hifumi, S. Inagi, I. Tomita, *72nd SPSJ Symp. Macromol.*, **2023**, 2B18.

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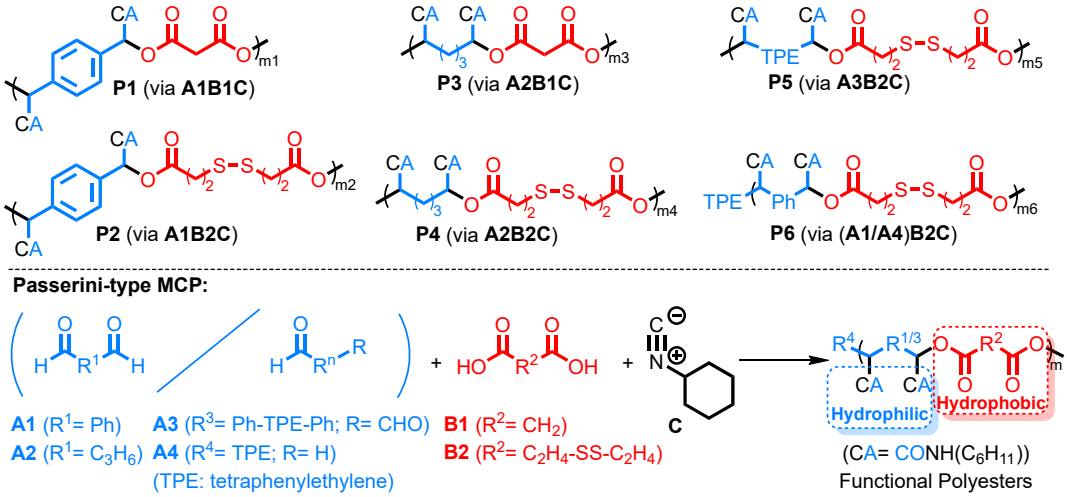
Synthesis of Functional Polyesters Containing Cleavable Linkages and an AIE Luminogen via Passerini-type Multicomponent Polymerizations

([1] *Dep. Chem. Eng., National Chung Hsing University (NCHU), Taichung 402, Taiwan*)
○Chih-Feng HUANG[1,*], Li-Chieh CHOU[1], Yi-Shen HUANG[1] (HuangCF@nchu.edu.tw)
Keywords: Passerini-type multicomponent polymerizations; Polyesters; AIE luminogen

Introduction to polymer chemistry from old reactions, new catalogs of polycondensations which are so-called "multicomponent polymerizations (MCPs)".[1] As shown in **Scheme 1**, we conducted Passerini-type multicomponent polymerizations (P-MCPs) with various monomer combinations (i.e., dialdehydes, dicarboxylic acids, and cyclohexyl isocyanide) and afforded a series of functional polyester with dual-cleavable linkages of ester and disulfide groups and an aggregation-induced emission (AIE) luminogen of tetraphenylethylene (TPE).[2] Significant AIE features were acquired in TPE-containing polyesters with increases in the H_2O contents in various DMSO/H_2O mixtures. By striking the redox and AIE features together, intriguingly, the AIE behavior of the TPE-containing polymeric micelles was "switched off" with dithiothreitol treatment. We demonstrated an efficient, diverse, and facile approach through Passerini-type MCPs to design amphiphilic-typed polyesters with dual-cleavable linkages and an AIE feature.



Scheme 1. Synthesis of P1–P6 functional polyesters via P-MCP of (di)aldehydes, diacids, and isocyanide compounds (TPE: tetraphenylethylene; CA: cyclohexyl amide).

1. a)O. Kreye, T. Tóth and M. A. R. Meier, *J. Am. Chem. Soc.*, 2011, **133**, 1790; b)J. O. Holloway, K. S. Wetzel, S. Martens, F. E. Du Prez and M. A. R. Meier, *Polym. Chem.*, 2019, **10**, 3859; c)X. X. Deng, L. Li, Z. L. Li, A. Lv, F. S. Du and Z. C. Li, *ACS Macro Lett.*, 2012, **1**, 1300; d)L. Li, A. Lv, X. X. Deng, F. S. Du and Z. C. Li, *Chem. Commun.*, 2013, **49**, 8549.
2. L.-C. Chou, M. G. Mohamed, S.-W. Kuo, Y. Nakamura and C. F. Huang, *Chem. Commun.*, 2022, **58**, 12317.

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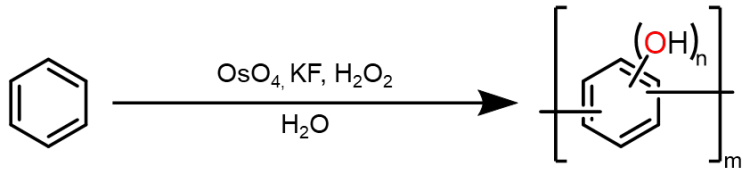
One-pot synthesis of hydroquinone-polymers from benzene with hydrogen peroxide

([1]*Graduate School of Engineering, Osaka University*, [2] *Graduate School of Science, Okayama University of Science*) ○Hideki Sugimoto[1], Kenshin Miyata[1], Akiyuki Nakano[2], Hideyuki Higashimura[2], Shinobu Itoh

Keywords: *hydroquinone-polymer*, *osmium tetroxide, hydrogen peroxide*

Hydroquinone-polymer can be a conducting polymer because it has unhybridized *p*-orbitals which lie perpendicular to its benzene ring [1)]. However, there is no method for preparing a hydroquinone-polymer in a convenient manner. We have reported an efficient phenol production from benzene using osmium tetroxide (OsO_4) as a catalyst and hydrogen peroxide (H_2O_2) as an oxidant [2)]. In this study, we find direct formation of a hydroquinone-polymer from benzene as a result of re-examination of the experimental conditions.

First, using benzene as a substrate, OsO_4 as a catalyst, potassium fluoride (KF) as a co-catalyst, and H_2O_2 as an oxidant, a reaction was conducted in water (Scheme 1). As a result, a brown solid was obtained in a 24wt% yield after isolation procedures. The polymeric structure was identified by UV-Vis and FT-IR spectra as well as GPC analysis. The analyses revealed that the obtained material was a hydroquinone-based polymer with M_n = 2400 and M_w = 6600, where benzene rings were connected through C–C bonds. The hydroxyl groups of the polymer were acetylated and the acetyl derivative was analyzed by ^{1}H-NMR spectrum, which showed that it has about 2.5 hydroxyl groups per one benzene ring. This is the first report of one-pot synthesis of a hydroquinone-polymer from benzene. Electrochemical property of the polymer in water was studied by cyclic voltammetry. At pH 9, an oxidation peak and a reduction peak based on the hydroquinone moiety were observed at 0.49 V and -0.80 V, respectively, indicating its redox-active nature as expected. As this polymer has also phenol moieties, a potentially use of this polymer as a curing agent for epoxy resin was examined. When EP4 with four epoxy groups was treated with this polymer at 250 °C and then cooled to room temperature, a black solid was obtained. On the other hand, only EP4 did not cure when treated in the same method. The results showed that this polymer has functionality as a curing agent for epoxy resins.



Scheme 1. Synthesis of phenol-polymers.

1) N. Mahato, H. Jang, A. Dhyani, S. Cho, *Polymers*, 2020, 12, 2480.
2) 植田悠太, 藤本智広, 杉本秀樹, 伊東忍, 第 54 回酸化反応討論会, 2021

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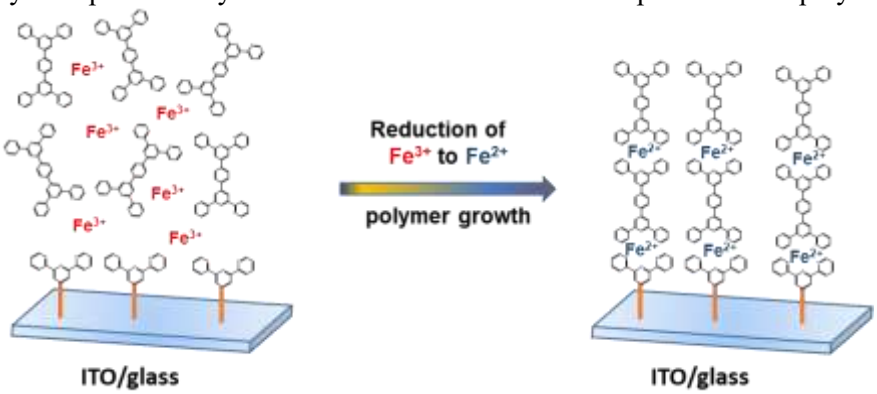
A New Synthetic Approach of Metallosupramolecular Polymer and its Electrochromic Application

([1]*Electronic Functional Macromolecules Group, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan*) ○ Satya Ranjan Jena,[1] Chih-Wei Hu,[1] Takashi Sato,[1] Jian Zhang,[1] Satoshi Moriyama,[1] Masayoshi Higuchi*[1]

Keywords: Electropolymerization, Metallosupramolecular polymers, Electrochromic, Coloration efficiency, Switching time.

The potential uses of surface functionalization make it a crucial topic in the realm of materials research. In that aspect, electropolymerization is a valuable approach to surface functionalization because it offers controlled and convenient synthetic pathways. The exploration of in-situ synthesis for metallosupramolecular polymers (MSPs), involving the utilization of coordination-driven metal ions and coordinating ligands, as well as the investigation of their potential applications through electropolymerization, has been limited. Herein, we present the formation of MSPs on a pre-terpyridine-functionalized indium tin oxide (ITO) glass substrate using Fe(III) ions and 4′,4′′′-(1,4-phenylene)-bis(2,2′:6′,2′′-terpyridine) ligand. The application of an anodic potential facilitated polymer growth, driven by the robust coordination between the reduced metal ions (Fe(II)) and the bis-terpyridine ligand. The polymer's formation was confirmed by the appearance of corresponding peaks in the cyclic voltammogram and UV-vis spectral profile. Surface morphology was characterized through atomic force microscopy (AFM). Electrochromic (EC) properties of the electro-polymerized MSP (EP-MSP) were investigated, utilizing the redox-active Fe(II)-(terpyridine)$_2$ unit. The film demonstrated an optical switching coloring time of 2.1 seconds and 5.7 seconds for bleaching, a transmittance change of 54%, and a coloration efficiency of 142.6 cm^2 C^{-1}.[1] In addition, we designed and synthesized a pyrimidylamine derivative which could be a great opportunity to explore this system in the formation of metallosupramolecular polymers.



1) C.-W. Hu, S. R. Jena, T. Sato, J. Zhang, S. Moriyama, M. Higuchi *ACS Appl. Polym. Mater.* **2023**.

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主鎖骨格に含フッ素ベンゾジチオフェンを用いたπ共役高分子の開発及び光学特性評価

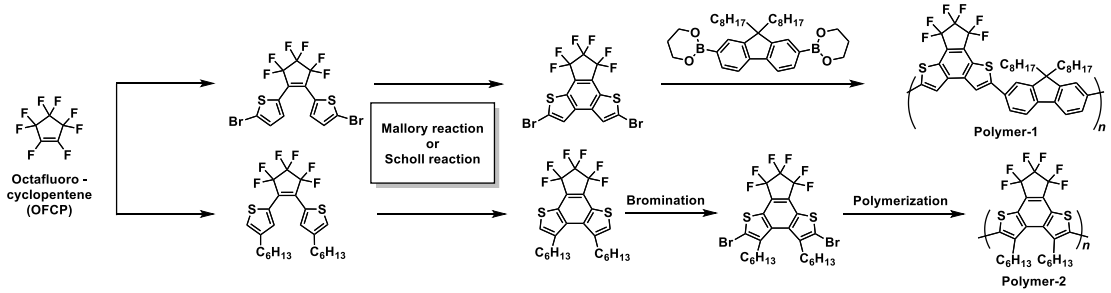
(茨大院理工[1]・兵庫県大院理[2]) ○奥崎 秀俊[1]・佐藤 世良[1]・吾郷 友宏[2]・久保田 俊夫[1]・福元 博基[1]

Synthesis and Optical Properties of π-Conjugated Polymers with Fluorine-containing Benzodithiophene ([1]*Graduate School of Science and Engineering, Ibaraki University,* [2] *Graduate School of Science, University of Hyogo*) ○ Hidetoshi Okuzaki[1], Sera Sato[1], Tomohiro Agou[2], Toshio Kubota[1], Hiroki Fukumoto[1]

Polymers including benzodithiophene (BDT) skeleton have a small band gap derived from a rigid planar π-electron system, however, they are unstable under atmospheric conditions due to their high HOMO energy levels. Recently, we found that the introduction of cyclic fluorine substituents into polycyclic aromatic hydrocarbons lowers their HOMO and LUMO energy levels and improves their antioxidant capacity[1)]. In this study, polymers containing fluorinated BDT units were synthesized and their optical properties were evaluated. Comparison of the fluorescence spectra of **Polymer-1** in solution and film revealed a red shift of the emission wavelength maximum in the film state indicating the interaction between polymer chains is considered to be stronger in the film state. On the other hand, no fluorescence was observed in **Polymer-2** in both solution and film, because of its distorted structure along the polymer main chain.

Keywords : π-Conjugated polymer; Fluorine-containing polymer; Benzodithiophene

ベンゾジチオフェン(BDT)は機能性π共役系ポリマーの母骨格として用いられている。BDT 骨格を有するポリマーの多くは高い HOMO エネルギー準位を持つため大気下で不安定である。当研究室では、多環芳香族炭化水素に環状フッ素置換基を導入すると HOMO 及び LUMO エネルギー準位が低下することを見出している。本研究では、含フッ素 BDT ユニットを含むポリマーを合成し、その光学特性を評価した。**Polymer-1** の溶液およびフィルムの蛍光スペクトルの比較から、フィルム状態における発光波長極大のレッドシフトを確認した。すなわち、フィルム状態では高分子鎖間同士の相互作用がより強く生じたと考えられる。一方、高分子主鎖がねじれた骨格である **Polymer-2** では蛍光は確認できなかった。



1) Gotsu, O.; Shiota, T.; Fukumoto, H.; Kawasaki-Takasuka, T.; Yamazaki, T.; Yajima, T.; Agou, T.; Kubota, T. *Molecules* **2018**, *23*, 3337.

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Academic Program [Oral B] | 18. Polymer：Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC D341(341, Bldg. 3 [4F])

[D341-4pm] 18. Polymer

Chair: Keitaro Matsuoka, Tatsuya Nishimura

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[D341-4pm-01]
Clarification of LCST-type thermo-responsiveness based on systematically evaluation of water soluble soft nylons

○Akari Sugano[1], Keitaro Matsuoka[1,2], Kazuki Sada[1,2] (1. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ., 2. Fac. of Sci., Hokkaido Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[D341-4pm-02]
Synthesis of ZnO nanorods grafted with liquid-crystalline polymers by controlled radical polymerization and their alignment behavior

○Kaho Nakano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[D341-4pm-03]
Mechano-responsive supramolecular hydrogel driven by stretch induced phase separation

○Sooyeon Noh[1], Akihide Sugawara[1], Yoshinori Takashima[1], Hiroshi Uyama[1] (1. Osaka Univ.)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[D341-4pm-04]
Establishment of Massive Fabrication of Water-Repellent Nanosheets as and Their Evaluation for Next-Generation Imaging Tools.

○Rai Uchida[1], Tatsuya Hiratsuka[2], Takuto Aoki[3], Yosuke Okamura[1,3,4] (1. Grad. Sch. of Eng., Tokai Univ., 2. Bachelor Sch. of Eng., Tokai Univ., 3. Grad. Sch. of Sci. & Tech., Tokai Univ., 4. Micro/Nano Tech. Center, Tokai Univ.)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[D341-4pm-05]
Stress-strain sensing using carbon composites with movable cross-links

○Ikura Ryohei[1,2], Kota kajimoto[1], Junsu Park[1,2], Yoshinori Takashima[1,2,3] (1. Grad. Sch. of Sci., Osaka Univ., 2. FRC, Osaka Univ., 3. ICS-OTRI, Osaka Univ.)

Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[D341-4pm-06]

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Triangular nanoplate formed from hybrids of Dawson-type polyoxometalates with amphiphilic diblock polypeptides and their catalytic properties.

Kai Miyamoto[1], ○Keita Kuroiwa[1] (1. Sojo University)

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水溶性ナイロンの系統的評価に基づく LCST 型温度応答性の理解

（北大院総化[1]・北大院理[2]）○菅野 明梨[1]・松岡 慶太郎[1,2]・佐田 和己[1,2]
Clarification of LCST-type thermo-responsiveness based on systematically evaluation of water soluble soft nylons ([1]*Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ.*, [2]*Fac. of Sci., Hokkaido Univ.)* ○Akari Sugano,[1] Keitaro Matsuoka,[1,2] Kazuki Sada[1,2]

Nylon is the oldest man-made fiber developed in 1935 as an alternative to silk. Research of nylon has focused on improving their physical properties in bulk to produce tough fibers. Consequently, the physical properties and functions in the solution of nylon have received little attention because of low solubility. In previous study, we developed water-soluble *N*-methylated nylon with a flexible main chain. Moreover, we determined the ideal unit formula per one tertiary amide group, $C_6H_{11}NO$, for realizing lower critical solution temperature (LCST) -type thermo-responsiveness in water. Under this criterion, we can find numerous LCST-type thermo-responsive polymer containing an amide group in the side chain for example Poly(*N*-isopropylacrylamide)[1)]. Therefore, the balance of hydrophilic tertiary amide groups and hydrophobic alkyl chain C_5H_{11} is important to LCST-type thermo-responsiveness in water. In this study, we investigate the influence of the location of alkyl chain C_5H_{11} by replacing *N*-methyl groups to other *N*-alkyl groups such as Et and Pr.
Keywords : Thermo-responsive polymer, Nylon, Polyamide, Lower Critical Solution Temperature, LCST

ナイロンは世界で初めて合成された化学繊維である。ナイロンの研究は、繊維としての高い機械的強度を求めた固体物性に集中しており、溶液物性については低い溶解性のためにほとんど研究がなされていない。当研究室では、ナイロンの第二級アミド結合を *N*-メチル化した、主鎖が柔軟な水溶性の *N*-メチル化ナイロンを開発した。さらに、アミド基１つあたりの組成式が $C_6H_{11}NO$ である *N*-メチル化ナイロン（*N*-Me-2,8/-3,7/-4,6/-5,5/-6,4）について、ある温度以上で不溶となる下限臨界共溶温度（LCST）型温度応答性を示すことを見出した。LCST 型温度応答性高分子の代表例である、ポリ（*N*-イソプロピルアクリルアミド）[1)]についても側鎖にアミド基を有しており、その組成式は $C_6H_{11}NO$ である。したがって LCST 型温度応答性の発現にはアミド基による親水性とアルキル鎖 C_5H_{11} による疎水性とのバランスが重要であることが示された。本研究では、*N*-メチル基を *N*-アルキル基（Et, Pr）とすることでアルキル基 C_5H_{11} の配置による LCST 型温度応答性への影響について検討した。

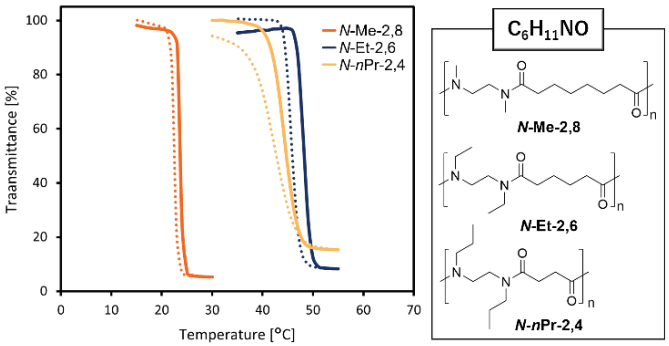

Figure. Transmittance change at 800 nm of *N*-Me-2,8, *N*-Et-2,6, *N*-*n*Pr-2,4 in H_2O (10 mg/mL) by the temperature changes (scan rate: 1.5 °C/min).

1) Aseyev, V.; Tenhu, H.; Winnik, F. M. *Adv. Polym. Sci.* **2010**, *242* (1), 29–89.

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Synthesis of ZnO Nanorods Grafted with Liquid-crystalline Polymers by Controlled Radical Polymerization and their Alignment Behavior

(*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*)
○Kaho Nakano, Shoichi Kubo, Atsushi Shishido
Keywords: Nanorod; Liquid-crystalline Polymer; Surface Modification; Alignment; Controlled Polymerization

Anisotropic inorganic nanomaterials, such as nanorods and nanotubes, have attracted great attention and have been extensively researched due to their highly anisotropic properties applicable to the development of functional devices.[1] To take advantage of the anisotropic properties, it is essential to control their alignment. Very few papers have reported achieving large-area alignment among various nanorod alignment methods. We demonstrated the unidirectional alignment of ZnO nanorods over large areas with the assistance of liquid crystals (LCs).[2,3] LC polymers were grafted from the surface of ZnO nanorods to make nanorods miscible with host LCs and to align cooperatively with surrounding host LCs over a surface-treated substrate. Increasing the fraction of nanorods could fully utilize the functions of nanorods; however, the alignment behavior of LC polymer-grafted nanorods alone remains unclear. In this study, we synthesized ZnO nanorods grafted with different LC polymers and investigated the alignment behavior of LC polymer-grafted nanorods depending on the molecular structures of the LC polymers.

ZnO nanorods were synthesized according to our previous report.[4] LC polymers with phenyl benzoate moieties in the side chains were grafted from the surface of the ZnO nanorods by controlled radical polymerization. Atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization were employed for polymers with methoxy and cyano groups at the terminal of the phenyl benzoate moiety, respectively. The LC polymer-grafted ZnO nanorods were sheared over a glass substrate under elevated temperature. The alignment behavior of mesogens in LC polymers and nanorods was evaluated by polarized optical microscopy and polarized UV-visible absorption spectroscopy.

1) S. Zhang *et al.*, *Adv. Mater.* **2018**, *30*, 1705794. 2) S. Kubo, M. Nakagawa, *et al.*, *ACS Appl. Mater. Interfaces* **2014**, *6*, 811. 3) K. Ogata, S. Kubo, A. Shishido, *et al.*, *Molecules* **2022**, *27*, 689. 4) S. Kubo, M. Nakagawa, *Chem. Lett.* **2012**, *41*, 1137.

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Mechano-responsive supramolecular hydrogel driven by stretch induced phase separation

([1]*Graduate School of Engineering, Osaka University,* [2]*Graduate School of Science, Osaka University*) ○Sooyeon Noh[1], Akihide Sugawara[1], Yoshinori Takashima[2], Hiroshi Uyama[1]

Keywords: Supramolecule, Hydrogel, Cellulose, Host–Guest Interaction, Mechano-responsiveness

Introduction: Mechano-responsive hydrogels that can induce changes in their appearance with the applied force have attracted much attention because they can visualize the mechanical stress. Supramolecular host–guest interaction is composed of hetero-molecular pairs, enabling to produce changes in the network properties in its associated and dissociated states[1]. Therefore, it can be used as a molecular switch in response to external mechanical force. In this study, mechano-responsive supramolecular hydrogels were prepared utilizing cellulose modified with adamantane (Ad) as a guest group. The hydrogels were cross-linked by host–guest complex between β-cyclodextrin (β-CD) and Ad.

Experimental: Ad-modified cellulose (Ad-cellulose) was synthesized by esterification reaction between hydroxy group of cellulose and 1-adamantanecarbonyl chloride (**Fig. 1a**). The CD-AdC*x* hydrogels were prepared by free-radical copolymerization of acrylamide (AAm) and 6-acrylamido-β-CD (β-CD-AAm) in the presence of Ad-cellulose. (*x* refers to the weight percentage of Ad-cellulose in the pre-gel solution) (**Fig. 1b**). The mechano-responsive properties of the CD-AdC*x* hydrogels upon stretching were analyzed by evaluating the opacity of the gels.

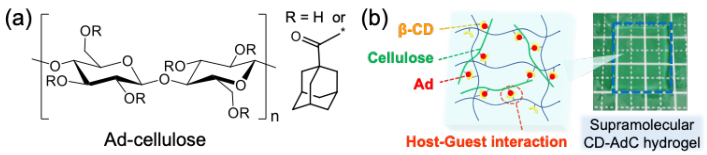

Figure 1. (a) Chemical structure of Ad-cellulose (b) Schematic illustration and photograph of the CD-AdC hydrogel.

Results and Discussion: The synthesized Ad-cellulose showed the solubility in an aqueous solution of β-CD derivatives. This result indicates that host–guest complex was formed between Ad group and host molecule, and Ad-cellulose with the complex hydrated in the aqueous media due to the enhancement of the hydrophilicity of the polymer. The appearance of the hydrogel changed from transparent to opaque upon stretching and returned to its original state upon releasing (**Fig. 2a)**. The mean gray value, which indicates the opacity, showed that the opacity of the hydrogels gradually increased upon stretching to 600% strain (**Fig. 2b)**. This property is due to the phase separation of the Ad-cellulose in the gel network induced by dissociation of the host–guest complex under mechanical force.

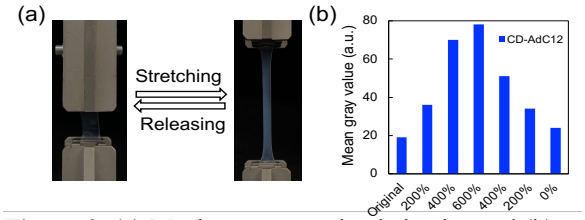

Figure 2. (a) Mechano-responsive behavior and (b) Opacity value of the CD-AdC12 gel upon stretching.

1) Sugawara, A. *et al. ACS Macro Letters* **2021**, 10 (7), 971-977.

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次世代イメージングツールへの応用を指向した撥水性ナノ薄膜の大量調製法の確立と機能評価

(東海大院工[1]・東海大工[2]・東海大院総理工[3]・東海大マイクロ・ナノ研[4]) ○内田 頼[1]・平塚 達也[2]・青木 拓斗[3]・岡村 陽介[1,3,4]

Establishment of Massive Fabrication of Water-Repellent Nanosheets and Their Evaluation for Next-Generation Imaging Tools.

([1] *Graduate School of Engineering, Tokai University*, [2] *School of Engineering, Tokai University,* [3] *Graduate School of Science & Technology, Tokai University,* [4] *Micro/Nano Technology Center, Tokai University*) ○Rai Uchida,[1] Tatsuya Hiratsuka,[2] Takuto Aoki,[3] Yosuke Okamura[1,3,4]

Polymer nanosheets with a thickness of less than 100 nm represent unique properties such as high level of adhesiveness to the various interfaces [1]. In fact, water-repellent nanosheets composed of a fluoropolymer prevented drying and blurring of biological tissues during microscopic observation, resulting in high-resolution deep tissue imaging [2,3]. In this study, we propose massive fabrication of water-repellent nanosheets by using Roll-to-Roll method and evaluate their characterizations as imaging tools. Roll-to-Roll method was used to successfully massive fabrication of water-repellent nanosheets. The nanosheet was uniquely capable of providing a coverslip-free imaging. In fact, by wrapping the tissue with a nanosheet, an extra distance of 170 μm for the movement of objective lens was obtained. We thus demonstrated that nanosheet wrapping acts as a powerful tool for high quality deep imaging of tissues.

Keywords: Water-Repellent Nanosheet, Massive Fabrication, Roll-to-Roll Method, Deep Tissue Imaging

高分子薄膜の膜厚を 100 nm 以下に加工するとナノ厚特有の高接着性が発現し、反応性官能基や接着剤を使用することなく物理吸着のみで種々の界面に対して貼付できる[1]。この特性を活用し、撥水性高分子からなるナノ薄膜を用いて生体組織をラッピングすると、観察時に生じる乾燥やブレが抑制され、高解像度のイメージングが可能になる[2,3]。現在、撥水性ナノ薄膜の調製法としてスピンコート法が提案されている。この方法は、均質なナノ薄膜が調製可能であり高い膜厚制御性を有する利点があるものの、生産性に乏しいため大量調製法の確立が急務である。本研究では、大面積かつ連続的に調製可能であるロール・ツー・ロール方式を活用した撥水性ナノ薄膜の大量調製法を確立し、次世代イメージングツールへの応用を目指す。

ロール・ツー・ロール方式は以下の工程で行った。μコーターを用いて、ポリビニルアルコール水溶液 (PVA, 4.0 wt%)をポリプロピレンフィルム (PP, 幅: 10 cm, 長さ: 100 m)に塗工 (搬送速度: 1.0 m/min) し、犠牲膜とした。次いで、フッ素系高分子溶液 (CYTOP, 1.5 wt%)を PVA-PP フィルム上に塗工 (搬送速度: 2.0 m/min)した。その後、純水に浸漬させ、CYTOP ナノ薄膜を剥離、回収した。電顕観察及び表面粗さ解析を行ったところ、ナノ薄膜には欠損が見られず、平滑性の高いことが示唆された。したがって、撥水性ナノ薄膜の大量調製に成功した。 透明化試薬によって屈折率 1.52 に統一したマウスの脳切片にナノ薄膜をラッピングした。共焦点レーザー顕微鏡を用いて、ナノ薄膜を介して神経細胞 (eYFP 発現)を撮像したところ、作動距離が劇的に向上し、従来のガラス基板を介した観察では困難である 300 μm 付近の深部まで観察可能であった。従って、ロール・ツー・ロール方式にて大量調製した撥水性ナノ薄膜を活用し、生体深部イメージングツールとして応用できる可能性を実証した。

1) Okamura Y. *et al. Adv. Mater.* **21**, 4388 (2009). 2) Zhang H. *et al. Adv. Mater.* **29**, 1703139 (2017). 3) H. Zhang *et al. PLoS ONE* **15**, e0227650 (2020).

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カーボン複合可動性架橋材料を用いた応力-ひずみセンシング

（阪大院理[1]・阪大 FRC[2]・阪大 OTRI[3]）○以倉 峻平[1,2]・梶本 晃太[1]・朴 峻秀[1,2]・高島 義徳[1,2,3]
Stress-strain sensing using carbon composites with movable cross-links ([1]*Graduate School of Science, Osaka University*, [2]*FRC, Osaka University,* [3]*OTRI, Osaka University*) ○Ikura Ryohei,[1,2] Kota Kajimoto,[1] Junsu Park,[1,2] Takashima Yoshinori[1,2,3]

We designed two kinds of composite materials with Ketjenblack (KB) and movable cross-linked elastomers to achieve high toughness, high conductivity, and strain-sensing functions. One approach is mixing a linear polymer (poly(ethyl acrylate), PEA), EA-based movable cross-linked material, and KB to obtain the stress-strain sensor showing stable responses for over 100 loading and unloading cycles. The other approach is a composite made with KB and a movable cross-network elastomer, where movable cross-links connect the CD-modified polystyrene (PSCD) and PEA. The obtained composite acts as a highly sensitive stress-strain sensor.
Keywords : Carbon composites; Movable cross-links; Toughness; Conductivity; Stress-strain sensing

本研究では、主鎖がシクロデキストリン(CD) の空孔に高分子鎖が貫通した可動性架橋[1]を有する導電性カーボンフィラー(KB)複合材料超分子材料を 2 種類開発し、強靭性･導電性･ひずみ応答性を付与した[2]。可動性架橋高分子材料(SC)と直鎖状高分子(PEA: Poly(ethyl acrylate)、KB をボールミル混合し、複合材料 SC/PEA/KB(10)を得た(**Fig. 1a**)。延伸ひずみに対して線形的に電気抵抗が増加するひずみセンサー(**Fig. 1b**)が得られ、100 回の繰り返しの延伸にも安定な応答性を示した(**Fig. 1d**)。もう一つの設計として、アセチル化 CD 修飾 Polystyrene の CD 環を PEA が貫通した材料と KB を THF 中に溶解後、乾燥して複合材料 PSCD⊃PEA/KB(10)を得た。PSCD⊃PEA/KB(10)は延伸時に被包接高分子 PEA が CD 環から脱離することで、より高いひずみ応答性を示した(**Fig. 1c**)。また、100 回の延伸により、安定的な応答に近づいた(**Fig. 1e**)。

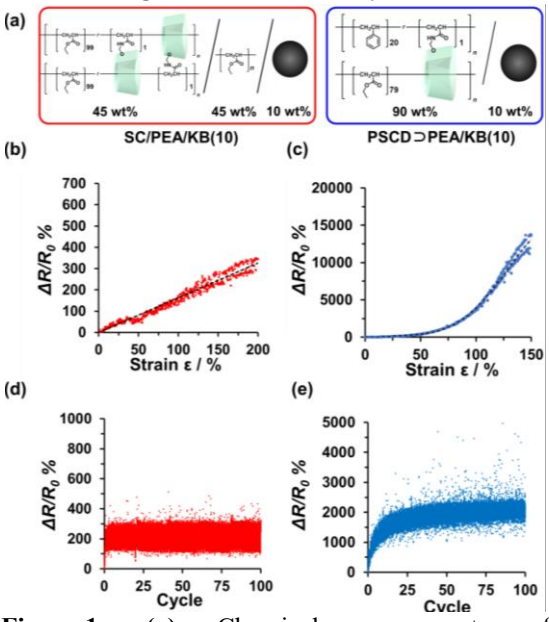

Fig. 1. (a) Chemical components of SC/PEA/KB(10) and PSCD⊃PEA/KB(10). $\Delta R/R_0$ of **(b)** SC/PEA/KB(10) and **(c)** PSCD⊃PEA/KB(10) upon tensile deformation. $\Delta R/R_0$ of **(d)** SC/PEA/KB (10) and **(e)** PSCD⊃PEA/KB (10) during 100 stretch-release cycles at 100% strain.

【参考文献】1) Fabrication and Mechanical Properties of Knitted Dissimilar Polymeric Materials with Movable Cross-Links. R. Ikura, Y. Takashima, et. al. *Mol. Syst. Des. Eng.* **2022**, *7*, 733-745. **2)** Highly stretchable stress-strain sensor from elastomer nanocomposites with movable cross-links and ketjenblack. R. Ikura, Y. Takashima, et. al. *ACS Polymers Au* **2023**, *3*, 394-405.

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両親媒性ジブロックポリペプチドと Dawson 型ポリオキソメタレートとの複合化による三角形ナノプレート構造とその触媒活性の評価

(崇城大院工 [1]))宮本 翔唯 [1]・○黒岩 敬太 [1]

Triangular nanoplate formed from hybrids of Dawson-type polyoxometalates with amphiphilic diblock polypeptides and their catalytic properties. ([1]*Graduate School of Engineering, Sojo University*) Kai Miyamoto,[1] ○Keita Kuroiwa,[1]

Diblock copolypeptide amphiphiles can form a variety of structures depending on the ratio and type of amino acids in the hydrophilic and hydrophobic regions.[1)] Polyoxometalates (POM) exhibit characteristic structures that depend on their constituents, along with multi-electron redox reactions. The goal of this study was to hybridize $[P_2W_{18}O_{62}]^{6-}$ with polypepitdes to develop functional nanomaterials with enhanced catalytic properties. The specific structures resulting from the self-assembly process and their respective catalytic effects were evaluated. Scanning Electron Microscopy (SEM) observations confirmed that the resulting hybrid material formed a distinctive triangular structure based on the triple symmetry of $[P_2W_{18}O_{62}]^{6-}$. The reaction using the hybrid material was successfully carried out in a homogeneous system under water. The hydrophilic and hydrophobic layers within the specific triangular structure are thought to be crucial elements in the reaction process.

Keywords : Diblock Copolypepitde Anphiphiles; Supramolecular Hybrid; Polyoxometalate; Nanostructure; Triangular nanoplate

両親媒性ジブロックコポリペプチドは、親水部と疎水部のアミノ酸の比率や種類、重合度に応じて、様々なナノ構造が形成される。[1)] ポリオキソメタレート（POM）は、多電子酸化還元反応とともに、その構成成分に依存した特徴的な構造と性質を示す。本研究では、$[P_2W_{18}O_{62}]^{6-}$をポリペプチドとハイブリッド化し、触媒特性を向上させた機能性ナノ材料の開発を行った。自己組織化プロセスから得られる特徴的なナノ構造を評価し、それぞれの触媒効果を評価した。走査型電子顕微鏡（SEM）観察の結果、得られたハイブリッド材料は、$[P_2W_{18}O_{62}]^{6-}$の三回対称性に基づく特徴的な三角形ナノプレート構造を形成していることが確認された。このハイブリッド材料を触媒として用いた有機合成反応では、水中の均一系で可能となった。ハイブリッド材料の特異な三角形構造内の親水層と疎水層が、反応プロセスにおける重要な要素になっていると考えられる。

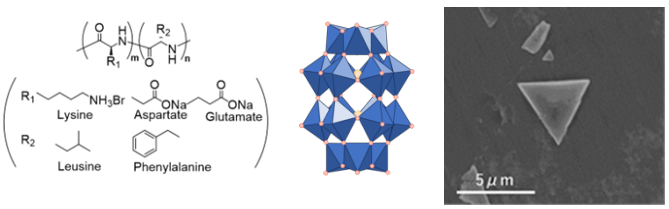

Fig.1 Chemical structure of polypeptides, schematic illustration of $[P_2W_{18}O_{62}]^{6-}$, and SEM image of hybrid $[P_2W_{18}O_{62}]^{6-}$ / Lys_{33}-*b*-Leu_1

1) Y. Tanimura, K. Miyamoto, T. Shiga, M. Nihei, K. Kuroiwa, *J. Phys. Chem. C* **2023**, *127*, 16525-16537. and references therein.

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Academic Program [Oral A] | 19. Colloid and Interface Chemistry : Oral A

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC A1443(1443, Bldg. 14 [4F])

[A1443-4pm] 19. Colloid and Interface Chemistry

Chair: Atsuhiro Fujimori, Masaki Donoshita

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1443-4pm-01]
Effect of Hyperbranched Polymers as Additive on Lubrication Properties of Base Oil

○Yutaka Takahashi[1], Yuzhong He[2], Masatoshi Tosaka[2], Masashi Mizukami[1], Shigeru Yamago[2], Kazue Kurihara[1] (1. Tohoku Univ., 2. Kyoto Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1443-4pm-02]
Hydroxyapatite Deposition on Boron-Doped Diamond Thin Films Using Simulated Body Fluids

○Nanami Takahashi[1], Takuya Sagawa[1], Takeshi Kondo[1], Mineo Hashizume[1] (1. Tokyo University of Science)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1443-4pm-03]
Structurally controlled assembly of filamentous viruses and their characterization

○Hiroki Narita[1], Takeshi Serizawa[1], Toshiki Sawada[1] (1. Sch. Mat. & Chem. Tech., Tokyo Tech)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1443-4pm-04]
Effect of Surfactant Addition to Lipid Vesicle Dispersions including Fluorescent Probes

○Chinatsu Asaoka[1], Masaki Hanzawa[2], Taku Ogura[2], Yuna Kim[1], Ken-ichi Iimura[1] (1. Utsunomiya Univ., 2. Nikko Chemicals Co., Ltd.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1443-4pm-05]
Fabrication of metal monolayer films by suppressing pinning at the droplet contact line

○Toru Shimada[1], Mohammad Kamal Hossain[2], Kohei Shibamoto[3], Yukihiro Yonemoto[4], Tomoaki Kunugi[5], Masahiro Kitajima[6,7] (1. Hirosaki Univ., 2. KFUPM, 3. TMU, 4. Kumamoto Univ., 5. Zhejiang Univ., 6. NIMS, 7. YNU)

English
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1443-4pm-06]
Synthesis of an unsymmetrically substituted π-extended tetrathiafulvalene derivative and its immobilization onto a gold electrode

○Masaki Donoshita[1], Miho Yamauchi[1,2,3,4] (1. IMCE, Kyushu Univ., 2. WPI-I2CNER, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-AIMR, Tohoku Univ.)

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2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

Japanese

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[A1443-4pm-07]

New developments in the control of phase separated morphology in mixed monolayers of non-amphiphilic fluorinated derivatives and comb copolymers

○Yoshiki Shioda[1], Itsuki Fujii[2], Atsuhiro Fujimori[1] (1. Graduate School of Science and Engineering, Saitama University, 2. Faculty of Eng., Saitama Univ.)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[A1443-4pm-08]

Characterization of 12-Hydroxystearate-Modified Nanodiamonds Using Method of Organized Molecular Films

○Yui Yamagishi[1], Shoma Sakamoto[2], Yuka Hasunuma[1], Atsuhiro Fujimori[1] (1. Graduate School of Science and Engineering, Saitama University, 2. Faculty of Engineering, Saitama University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[A1443-4pm-09]

Preparation and Evaluation of Coting Films of Thixotropic Solvent Gel Containing 12-Hydroxystearate-Modified Nanodiamonds

○Yuka Haunuma[1], Yui Yamagishi[1], Kai Xu[1], Atsuhiro Fujimori[1] (1. Saitama University)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[A1443-4pm-10]

Formation of Organized Molecular Films and Metal Scavenging Behavior of Azacalyxarene-containing Copolymers with Spherulite-Forming Ability

○Ryoma Terui[1], Yoshiki Shioda[2], Yuji Shibsaki[3], Atsuhiro Fujimori[2] (1. Faculty of Engineering, Saitama Univesity, 2. Graduate School of Science and Engineering, Saitama University, 3. Faculty of Sci. and Eng., Iwate Univ.)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[A1443-4pm-11]

Morphogenesis and Its Control of Interfacial Molecular Films Using Glycan-based Polymers

○Ryoma Nakada[1], Chisato Nara[1], Rokibul Hasan Rumon[2], Atsuhiro Fujimori[2] (1. Faculty of Engineering, Saitama Univesity, 2. Graduate School of Science and Engineering, Saitama University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[A1443-4pm-12]

Structure and properties of drawn-oriented fluorinated polymer/carbon nanotube composite film containing two types of functional organic fillers

○Pinjung Chu[1], Rokibul Hasan Rumon[1], Kai Xu[1], Atsuhiro Fujimori[1] (1. Saitama Univ.)

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日本化学会 第104春季年会 (2024)

潤滑油の特性に及ぼす超分岐高分子の添加効果

(東北大 NICHe[1]・京大化研 [2])
○高橋 裕 [1]・He Yuzhong[2]・登阪 雅聡 [2]・水上 雅史 [1]・山子 茂 [2]・栗原 和枝 [1]

Effect of Hyperbranched Polymers as Additive on Lubrication Properties of Base Oil

([1]*New Industry Creation Hatchery Center, Tohoku University*, [2]*Institute for Chemical Research, Kyoto University*) ○ Yutaka Takahashi,[1] Yuzhong He,[2] Masatoshi Tosaka,[2] Masashi Mizukami[1], Shigeru Yamago,[2] Kazue Kurihara[1]

Polymers have been used as additives of lubricants. The polymers used in these previous studies have been limited to those of linear chain structures. In this study, we studied the lubrication properties of hyperbranched polymers as additives in a base oil (PAO) by employing resonance shear measurement and macro friction measurement. These measurements revealed that lubricity of the hyperbranched polymers was superior to that of the linear polymers.

Keywords : Hyperbranched polymer; Lubricant; Polymer additive; Surface forces measurement; Resonance shear measurement

潤滑油の添加剤として高分子は用いられているが、その構造のほとんどが直鎖状のものである。一般的に、潤滑油の低粘度化は低摩擦に有効であるが、境界潤滑 (低速度・高荷重) では、摩耗や焼き付けを引き起こしてしまう。本研究ではこの課題に対し、基油 (PAO) に超分岐高分子を添加した潤滑油の特性を評価した。

5 mg/ml に調製した PAO 溶液の粘度を測定したところ、超分岐高分子 A と直鎖状高分子 B の PAO 溶液の粘度は、それぞれ 16.2 mPa·s と 17.7 mPa·s であった。これらの粘度は PAO の粘度 (13.7 mPa·s) とほぼ同じで低粘度であった。

Fig. 1 は、様々な荷重 (L) における高分子 A を添加した潤滑油の共振ずり測定の結果である。空気中で基板同士が接触している状態 (MC、摺動しない状態) を基準としたとき、ピーク強度 (U_{out}/U_{in}) は閉じ込め状態の試料の摩擦に相関する。L = 4.0 mN での MC ピークに対する強度比は、高分子 A (12%) < 高分子 B (20%) < PAO (35%) であり、高分子 A が低摩擦、より高い潤滑性を示すことが分かった。**Fig. 2** は摩擦試験の測定結果である。境界潤滑 ((速度)/(荷重) <0.05) では、高分子 A の添加によって摩擦係数が大きく減少し、優れた潤滑性を示した。これは、共振ずり測定の結果による高分子 A が閉じ込め状態において構造化しにくいという結果とよく一致した。

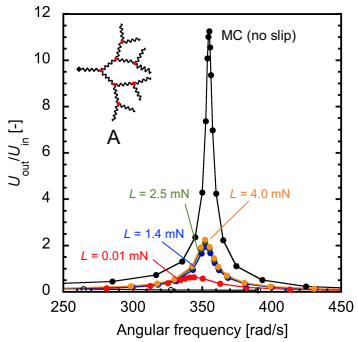

Fig. 1 Resonance curves for in PAO solutions of the hyperbranched polymer, A.

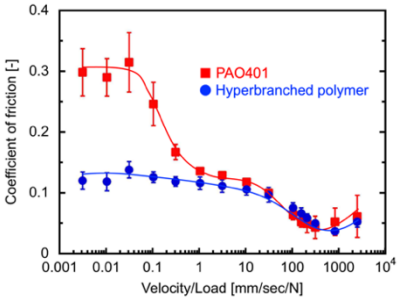

Fig. 2 Friction coefficients of lubricants as a function of velocity/load. The solid lines are included to guide the eye.

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擬似体液を用いたボロンドープダイヤモンド薄膜へのヒドロキシアパタイト複合化

（東理大工[1]・東理大創域理工[2]）○高橋 菜々海[1]・佐川 拓矢[1]・近藤 剛史[2]・橋詰 峰雄[1]

Hydroxyapatite Deposition on Boron-Doped Diamond Thin Films Using Simulated Body Fluids ([1]*Faculty of Engineering, Tokyo University of Science*, [2]*Faculty of Science and Technology, Tokyo University of Science*) ○Nanami Takahashi,[1] Takuya Sagawa,[1] Takeshi Kondo,[2] Mineo Hashizume[1]

Boron-doped diamond (BDD) is expected to be used as conductive materials because it exhibits excellent hardness, chemical stability, and electrical conductivity. In this study, the deposition of bioactive hydroxyapatite (HAp) layers on BDD thin films using biomimetic processes was performed in order to prepare artificial bone materials that can be stimulated electrically. The BDD substrates were pretreated with UV light irradiation for hydrophilization and then soaked in aqueous $CaCl_2$ and K_2PO_4 solutions alternately (alternated soaking process, ASP) to deposit calcium phosphate on the substrate. Finally, the substrates were incubated in 1.5SBF, 1.5-fold concentrated simulated body fluids (SBF). The resulting substrates were evaluated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The deposits consisting of plate-like structures, corresponding to HAp, were observed on the substrate surfaces by SEM. EDX measurements confirmed that these deposits contained Ca and P elements. The results demonstrated that the pretreated BDD substrates induced HAp deposition in SBFs.

Keywords: Hydroxyapatite; Boron-Doped Diamond; Simulated Body Fluid

ボロンドープダイヤモンド（BDD）は高い硬度、化学的安定性をもつ導電性材料としての利用が期待されている[1)]。本研究では、電気刺激を印加可能な人工骨材料の作製のため、BDD 薄膜表面にバイオミメティックな手法により生体活性なヒドロキシアパタイト（HAp）を析出させる方法について検討した（Fig. 1）。シリコン基板上に BDD 薄膜を成膜することで BDD 基板を作製した。この基板に対して UV 光照射を行って親水化したのち、塩化カルシウム溶液とリン酸カリウム溶液に交互に浸漬すること（ASP 処理）によって基板表面にリン酸カルシウムを沈着させた。これら前処理後の基板を擬似体液（SBF）の 1.5 倍濃度の溶液（1.5SBF）に 36.5 ℃で所定時間浸漬した。得られた基板の走査型電子顕微鏡（SEM）観察では、親水化および ASP 処理を施した BDD 基板は未処理のものと比較してより多くの HAp に特有の板状構造を有する析出物が確認された。またエネルギー分散型 X 線分光（EDX）による評価では析出物から Ca および P 元素が検出された。以上より、適切な前処理を施すことで擬似体液中において BDD 薄膜表面への HAp 析出を実現できることが示された。

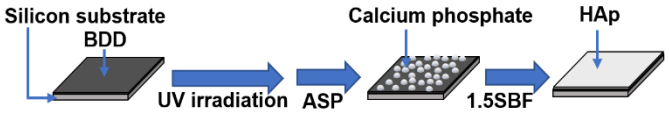

Fig.1. Schematic illustration of this study.

1) I. Yagi, H. Notsu, T. Kondo, D. A. Tryk, A. Fujishima, *J. Electroanal. Chem.* **1999**, *473*, 173–178.

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繊維状ウイルスの集合化制御とその特性評価

（東工大物質理工） ○成田裕紀・芹澤　武・澤田敏樹
Structurally controlled assembly of filamentous viruses and their characterization (*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Hiroki Narita, Takeshi Serizawa, Toshiki Sawada

M13 phage, which is one of the filamentous viruses, is known to self-assemble into regularly ordered liquid crystalline structures. We have previously reported that the hierarchical assembly of M13 phages acts as components of various functional materials. In this study, we demonstrated the preparation and characterization of M13 phage-based assemblies with a structure controlled in two-dimensional direction on a macro scale to characterize assembled structures and their physical properties. Phage assemblies (in this case, films) were prepared on substrates by dipping the substrates into phage solutions and sweeping up them vertically under various conditions. The assembled structures were characterized. Atomic force microscopy observations revealed that the assembled and oriented structures were dependent on sweeping speed, pH value of the solvent and substrate species. These results indicated that the assembled structure of M13 phage on a substrate was controlled by various factors in phage assembling processes. The results of functional characterizations of the assemblies will be reported in the presentation.

Keywords : Phage, Liquid crystal, Film, Oriented structures, Genetic engineering

M13 ファージは繊維状ウイルスの一種であり、高濃度では液晶配向するほど規則的に集合化することが知られている。我々はM13 ファージの階層的な集合体が様々な機能性マテリアルとしてはたらくことを見出している。本研究では、ファージの集合構造とそれが示す機能物性を評価することを目指し、二次元方向の集合構造がマクロスケールに制御された集合体を構築するための手法を確立することを目的とした。様々な条件下でファージ溶液に基板を浸漬させ、垂直に掃引することで基板上にファージ集合体（フィルム）を調製し、その集合構造や特性を評価した。原子間力顕微鏡観察の結果、基板の種類や、掃引速度、また溶媒の pH の変化によってファージの集合構造や配向状態が変化することがわかった。この際、ファージ分子が形成するドメインのサイズなども変化しており、ファージの集合化時の様々な因子による自在な集合構造形成が可能であることを見出した。発表では、集合構造に加えて集合体の機能物性を評価した結果についても併せて報告する。

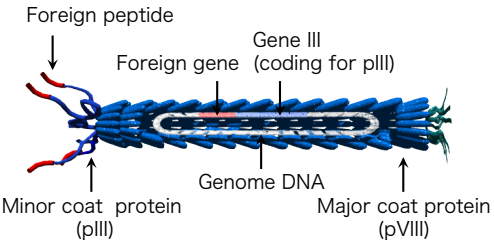

Figure 1. Schematic illustration of M13 phage

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蛍光プローブ含有脂質ベシクル分散液に対する界面活性剤の添加効果

(宇都宮大院[1]・日光ケミカルズ(株)[2]) ○浅岡 千夏[1]・半澤 将希[2]・小倉 卓[2]・キム ユナ[1]・飯村 兼一[1]

Effect of Surfactant Addition to Lipid Vesicle Dispersions Including Fluorescent Probes

([1]Utsunomiya Univ., [2]Nikko Chemicals Co., Ltd.)○Chinatsu Asaoka[1], Masaki Hanzawa[2], Taku Ogura[2], Yuna Kim[1], Ken-ichi Iimura[1]

Inactivation of viruses by surfactants has been reported. In this study, to develop a simple evaluation method for structural changes in a lipid membrane depending on molecular structure and concentration of surfactant, we added various aqueous surfactant solutions to a lecithin vesicle dispersion containing Nile Red as fluorescent probe and evaluated spectroscopic changes in fluorescence and UV-Vis spectra. An anionic sodium lauryl sulfoacetate (LSA-F) and a nonionic nonaethylene glycol monododecyl ether ($C_{12}E_9$), for example, showed different tendency of changes of maximum fluorescence peak position in fluorescence spectra and of absorbance at 300 nm in UV-vis spectra (Fig. 1).

Keywords：Envelope, Surfactant, Vesicle, Virus Inactivation, Fluorescent Probe

界面活性剤によるウイルスの不活化が報告されている。本研究では、界面活性剤の分子構造や濃度に依存した脂質二重膜の構造変化の簡便な評価法の構築を目的とし、蛍光プローブとしてナイルレッドを含むレシチンベシクル分散液に対して様々な界面活性剤の水溶液を添加し、分光学的特性の変化を検討した。

例として、アニオン性界面活性剤のラウリルスルホ酢酸ナトリウム(LSA-F)とノニオン性界面活性剤のノナエチレングリコールモノドデシルエーテル($C_{12}E_9$)を用いた場合の蛍光スペクトルにおける最大蛍光波長と吸収スペクトルにおける 300 nm での吸光度の濃度による変化を Fig. 1 に示す。LSA-F を用いた場合には、臨界ミセル濃度（cmc）以下の濃度で蛍光ピークは高波長側にシフトし、吸光度は低下した。これは LSA-F の添加により、ナイルレッドの周囲環境およびレシチンのベシクル構造が顕著に変化したことを示している。一方、$C_{12}E_9$ を用いた場合には、蛍光ピークの波長は LSA-F の場合と同程度までシフトしたものの、濃度依存性は大きく異なり、吸収スペクトルにおける吸光度の変化もわずかであるなど、LSA-F とは異なる変化の傾向が見られた。

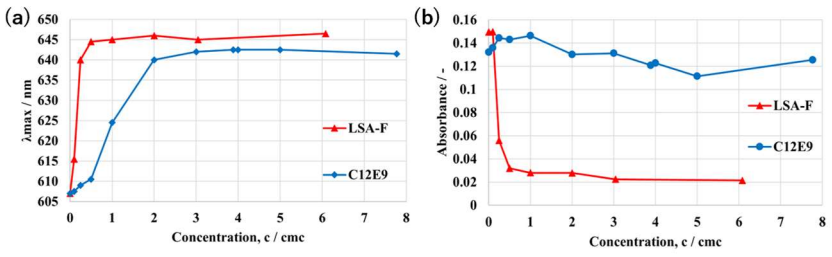

Fig. 1 (a) Wavelength of maximum fluorescence peak in fluorescence spectra and (b) absorbance at 300 nm in UV-vis spectra as a function of concentration for LSA-F and $C_{12}E_9$ aqueous solutions.

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液滴の接触線におけるピン止め抑制による金属単層膜の作製

(弘大教育[1]・キング・ファハド石油鉱物大[2]・都立大理[3]・熊大工[4]・浙江大[5]・物材機構[6]・横国大工[7]) ○島田 透[1]・モハマド カマル ホサイン[2]・芝本 幸平[3]・米本 幸弘[4]・功刀 資彰[5]・北島 正弘[6,7]

Fabrication of Metal Monolayer Films by Suppressing Pinning at the Droplet Contact Line

([1]*Faculty of Education, Hirosaki University*, [2]*King Fahad University of Petroleum and Minerals,* [3]*Department of Chemistry, Tokyo Metropolitan Public University,* [4]*Faculty of Engineering, Kumamoto University,* [5]*College of Energy Engineering, Zhejiang University,* [6]*National Institute for Materials Science,* [7]*Faculty of Engineering Science, Yokohama National University*) ○Toru Shimada[1], Mohammad Kamal Hossain[2], Kohei Shibamoto[3], Yukihiro Yonemoto[4], Tomoaki Kunugi[5], Masahiro Kitajima[6,7]

Two-dimensional nanoparticle arrays (2DNAs) have created many applications including sensors, printings, diagnostics and photonics. Therefore, the development of a simple fabrication method for 2DNA is required. However, simply dropping an aqueous metal colloidal solution onto a substrate and allowing it to dry as is does not produce a 2DNA; a ring-shaped deposit is formed on the substrate. This phenomenon is known as the coffee ring effect. However, it was found that if the droplet is sandwiched between two other substrates during drying, the pinning of the contact lines is removed and a monolayer pattern is formed[1)]. We report on the optical properties of the 2DNA fabricated by this method, as well as simulation results on the supply of nanoparticles during film formation.

Keywords: Metal Colloidal Solution; Coffee Ring Effect; Metal Nanoparticle Monolayer; Surface Enhancement; Navier-Stokes Equation

金属コロイド粒子が配列した単層膜は、センサー、印刷技術、診断、フォトニクスなど様々な分野での活用が期待されている。このため、簡便な金属コロイド単層膜の作製法の開発が求められている。金属コロイド水溶液を基板上に滴下し、そのまま乾燥させただけでは単層膜は作製されず、リング状の堆積物が基板に形成されてしまう。この現象はコーヒーリング現象として知られている。しかし、液滴を乾燥させる際に、液滴を別の基板で挟むと、接触線のピン止めが外れ、均一な単層膜のパターンを形成できることがわかった[1)]。本発表では、この方法で作製した金属単層膜の光学特性や、膜形成の際のナノ粒子の供給に関するシミュレーション結果について報告をする。

1) Formation and characterization of 2D closely packed arrays of bare gold nanoparticles without aggregation. T. Fujita, K. Shibamoto, ACS Omega **2022**, *7*, 44711.

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Synthesis of an unsymmetrically substituted π-extended tetrathiafulvalene derivative and its immobilization onto a gold electrode

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Keywords: Redox; π-extended tetrathiafulvalene

Chiral electrodes can be used for various purposes, including asymmetric electrosynthesis[1] and spin filtering.[2] Systems capable of switching chirality (handedness) offer advantages for more advanced applications. However, the reports on such chirality-switchable electrodes are limited, including DNA-based[3] and molecular-motor-based[4] systems. Notably, these systems have chiral carbon centers, and hence, they are regarded as diastereomers. We are aiming at the construction of chirality-switchable metal electrodes based on chiral/achiral conversion, focusing on π-extended tetrathiafulvalene (TTF) derivatives that exhibit changes in molecular shape along with reduction/oxidation (**Fig. 1a**).[5] In an unsymmetrically substituted derivative, neutral/dication conversion is expected to result in chiral/achiral conversion, and the introduction of any external chirality sources during the redox processes may lead to the induction of chirality that can be used for chirality switching. Here, we newly designed and synthesized an unsymmetrically substituted π-extended TTF derivative bearing thiol anchors (compound **1**; **Fig. 1b**) and further prepared gold electrodes modified with **1**.

Four-step synthesis yielded the target compound **1**. The production of **1** was confirmed via ^{1}H NMR experiments. By immersing gold electrodes in the solution of **1**, modified electrodes were obtained. The attachment of **1** was confirmed through the redox wave observed in the cyclic voltammogram obtained using a standard three-electrode system. The surface coverage on Au/mica was determined to be ~2 × 10^{-10} mol cm^{-2} from the area of the oxidation peak.

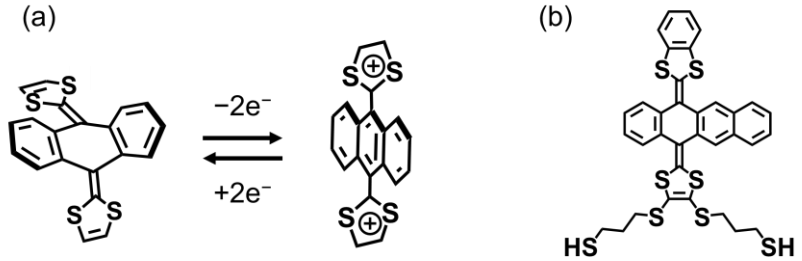

Figure 1. (a) Change in molecular shape of π-extended tetrathiafulvalene derivative on redox process. (b) Molecular structure of compound **1**.

1) Q. Lin *et al.*, *Chem. Eur. J.* **2019**, *25*, 10033. 2) R. Naaman *et al.*, *Nat. Rev. Chem.* **2019**, *3*, 250. 3) T. J. Zwang *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 15551. 4) M. Suda *et al.*, *Nat. Commun.* **2019**, *10*, 2455. 5) M. R. Bryce *et al.*, *Angew. Chem. Int. Ed.* **1990**, *29*, 1450.

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非両親媒性フッ素系誘導体とくし形共重合体の混合分子膜中に於ける相分離形態制御の新展開

（埼玉大院理工[1]・埼玉大工[2]）○塩田 祥貴[1]・藤井 一輝[2]・藤森 厚裕[1]

New Developments in the Control of Phase Separated Morphology in Mixed Monolayers of Non-amphiphilic Fluorinated Derivatives and Comb Copolymers

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Abstract: It has attempted to refine the control of phase separation in a mixed Langmuir monolayer of a non-amphiphilic fluorinated *s*-triazine derivative and a comb copolymer by utilizing a patterning technique for long chain fatty acid-based mixed monolayers.

Keywords: Mixed Monolayers, Phase Separation, Fluorinated *s*-Triazine Derivatives, Comb Copolymers, Patterning

【序論】 フッ化炭素鎖と炭化水素鎖は混和性に乏しく，これを有する化学種同士は相分離を示す．凝集した炭化水素鎖の「島」を取り囲む，フッ化炭素鎖の膨張相の「海」が形成する『海-島状』相分離形態は一般にナノメーター次元のサイズ制御が難しく，加えてフッ素系界面活性剤の人体残留性の懸念から，昨今の研究発展が停滞する傾向にある．本研究では，ジアミノ-*s*-トリアジン環含有のくし形共重合体と，親水基を持たないフッ素化トリアジン誘導体の系[1, 2]に於いて，長鎖脂肪酸活用時の挙動と比較することで，相分離形態の精密制御を目指した．

【実験】 凝縮相対応の炭化水鎖素成分として，2-vinyl-4, 6-diamino-1, 3, 5-triazine (以下，VDAT)と，octadecyl acrylate (以下，OA)との共重合体を，様々な組成比で得，実験に使用した．また，親水基を持たない tris(perfluorononyl)-*s*-triazine (3[$CF_3(CF_2)_8$]-triazine)を，膨張相対応のフッ化炭素鎖成分として使用した．炭化水素相の形成比較分子としてアラキジン酸($C_{20}A$)を用いた．VDAT : OA 共重合体と 3[$CF_3(CF_2)_8$]-triazine，および $C_{20}A$: 3[$CF_3(CF_2)_8$]-triazine の混合水面上単分子膜を調製し，表面圧-面積(π-A)等温曲線による状態変化(15 ℃)と，原子間力顕微鏡(AFM)による固体基板上転写膜の形態観察を行った．

【結果と考察】 π-A 等温曲線の測定から，VDAT : OA 共重合体と 3[$CF_3(CF_2)_8$]-triazine, 並びに $C_{20}A$: 3[$CF_3(CF_2)_8$]-triazine の混合水面上単分子膜は，いずれも相分離系であることが示された．VDAT : OA 共重合体と 3[$CF_3(CF_2)_8$]-triazine の混合膜形態は，円形ドメイン状，ドーナツ状，中央突起状ドメイン形成など，各種パラメータを振ることによって様々に変化した[1]．ここで，比較として用いた $C_{20}A$ を凝縮相として用いた場合の混合単分子膜形態は，微細な不定形ドメインの形状と被覆面積が混合比に対応して系統的に変化することが示された(Fig. 1)．不定形ドメインの成分は凝集力の高い炭化水素系の $C_{20}A$ であると予測され，$C_{20}A$ 比率の増加と共に，混合膜表面に於けるドメイン被覆率が，合理的に高くなる傾向が観察された．

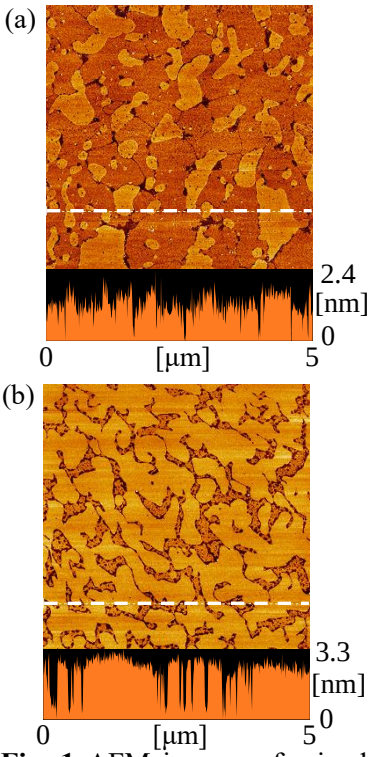

Fig. 1 AFM images of mixed monolayers of (a) $C_{20}A$: 3[$CF_3(CF_2)_8$]-triazine = 3 : 1, and (b) $C_{20}A$: 3[$CF_3(CF_2)_8$]-triazine = 5 : 1 on solids (15 ℃, 20 mN·m^{-1}).

Reference: 1) Y. Shioda, M. Maeda, A. Fujimori, *Colloids Surf. A*, **2023**, *669*, 131475.
2) M. Maeda, Y. Shioda, A. Fujimori, *Colloids Surf. A*, **2022**, *649*, 129429.

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組織分子膜の手法による 12-ヒドロキシステアリン酸修飾ナノダイヤモンドのキャラクタリゼーション

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Characterization of 12-Hydroxystearate-Modified Nanodiamonds Using Method of Organized Molecular Films

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Abstract: As a new candidate for lipophilized nanoparticles to be introduced into cosmetic formulations, 12-hydroxystearate-modified nanodiamonds were prepared and characterized using method of organized molecular films.

Keywords: 12-Hydroxystearic Acid, Nanodiamond, Surface-Modification, Single Particle Layers, Method of Organized Molecular Films

【序論】長鎖脂肪酸によって親油化されたナノ粒子は，化粧品製剤等への導入により紫外線散乱能や無機顔料としての構造色発現の期待がもたれる[1, 2]．本研究ではチキソトロピー性添加剤としての能力を有する 12-ヒドロキシステアリル鎖修飾の無機ナノ粒子を新規に調製した．ここでは先行研究に於いて扱ったステアリン鎖修飾ナノダイヤモンドと比較を行いながら，その界面単層膜挙動について検討した．

【実験】粒径 5 nm のナノダイヤモンド(以下, ND. ダイセル(株)提供)の最外層表面に，油/水界面修飾法[1, 2]を用いて，12-ヒドロキシステアリン酸，およびステアリン酸による化学修飾を行った．化学修飾の達成は赤外(IR)分光法，並びに熱重量測定(TG)による修飾鎖の昇温脱離挙動から確認した．それぞれ超純水上に単粒子膜展開を行い，表面圧-面積(π-A)等温曲線の測定を行った(15 °C)．各単粒子膜の固体基板上への転写は，Langmuir-Blodgett(LB)法により行った．

【結果と考察】表面改質反応に於いて，12-ヒドロキシステアリン酸，並びにステアリン酸を作用させた ND は，IR にアルキル鎖由来の振動バンドが出現し，TG に於いては修飾鎖脱離由来の昇温時の重量減少が確認された．これら 2 種の有機修飾 ND に於ける π-A 等温曲線では，12-ヒドロキシステアリル修飾 ND 単粒子膜に，低表面圧域での膨張相の存在が確認された(Fig. 1)．この挙動は，両試料における修飾鎖分子自体の単分子膜挙動の差異とも酷似しており，低表面圧域では一部の修飾鎖中の 12 位の水酸基が下相水側を向いた配座をとることで，膨張相が形成されると予測された．

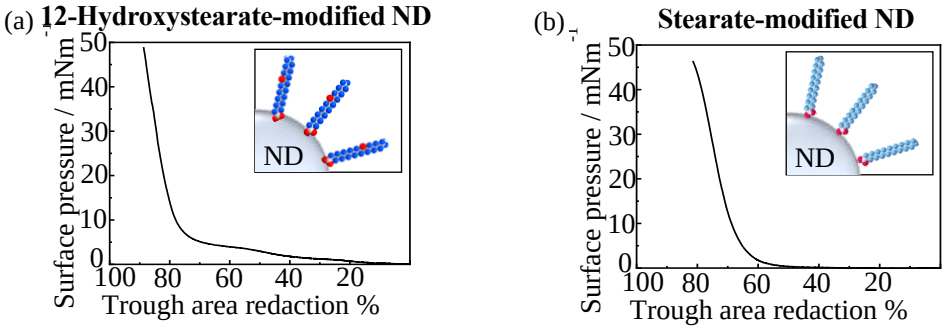

Figure 1 π-A isotherms of single-particle layers on the water surface of (a) 12-hydroxystearate-modified and (b) stearate-modified NDs (15 °C).

Reference: 1) Y. Yamagishi, N. Kikuchi, A. Fujimori, *Colloids Surf. A*, **2023**, *677*, 132309.
2) N. Kikuchi, Y. Yamagishi, A. Fujimori, *ChemistrySelect*, **2023**, *8*, e202300061.

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12-ヒドロキシステアリン酸修飾ナノダイヤモンドを含むチキソトロピー性溶媒ゲル塗膜の調製とその評価

（埼玉大院理工[1]）○蓮沼 優香[1]・山岸 由衣[1]・徐 愷[1]・藤森 厚裕[1]

Preparation and Evaluation of Coting Films of Thixotropic Solvent Gel Containing 12-Hydroxystearate-Modified Nanodiamonds

([1]Grad. Sch. Sci. Eng., Saitama Univ.)
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Abstract: It has aimed to develop thixotropic nanoparticles to be incorporated into cosmetic formulations, with a view to their use as ultraviolet scattering agents and inorganic pigments. The surface of nanodiamond (ND), which is said to exhibit antibacterial properties, was organically modified with 12-hydroxystearic acid (12-HSt), which has the ability to form a thixotropic supramolecular gel derived from hydrogen bonding. Solvent gelation and coating film formation were investigated using 12-HSt-modified ND or a mixed additive with thixotropic additive molecules of diamide derivative containing two-hydrocarbons.

Keywords: 12-Hydroxystearic Acid, Nanodiamond, Surface-Modification, Coating Films, Gelation

【序論】12-ヒドロキシステアリン酸，並びにその誘導体は特定の溶液中で超分子ゲルを形成し，同時にチキソトロピー能を示すことが知られる[1, 2]．本研究では 12-ヒドロキシステアリル鎖で表面に親油化処理を施したナノダイヤモンド(ND)微粒子を用いて，化粧膜開発に資する，塗布膜の調製(Fig. 1(左))とその状態評価を行った．

【実験】試料は，12-ヒドロキシステアリン酸(以下，12-HSt)と粒子径 5 nm の ND を用いて調製した．得られた 12-HSt 修飾 ND はトルエン:エタノール=9:1 混合溶媒中に，ゲル化補助剤として二量化された 12-HSt(ヘキサメチレンジアミンと脱水縮合した 2 鎖型ジアミド)と共に導入された．スパーテルによって塗布された薄膜の表面状態は原子間力顕微鏡(AFM)によって観察された．

【結果と考察】12-HSt 修飾 ND とゲル化補助剤である二鎖型ジアミドの導入は，トルエン:エタノール=9:1 混合溶媒を効率的にゲル化した．このゲルの塗膜に対する AFM 像には，螺旋状に成長した二鎖型ジアミドナノ繊維の表面に，粒子状の凝集物が確認された．これらが 12-HSt 修飾 ND と推察され，親和性の高い 12-ヒドロキシステアリル鎖同士の相互作用により，螺旋繊維の表面近傍に集積化された思われる(Fig. 1(右))．

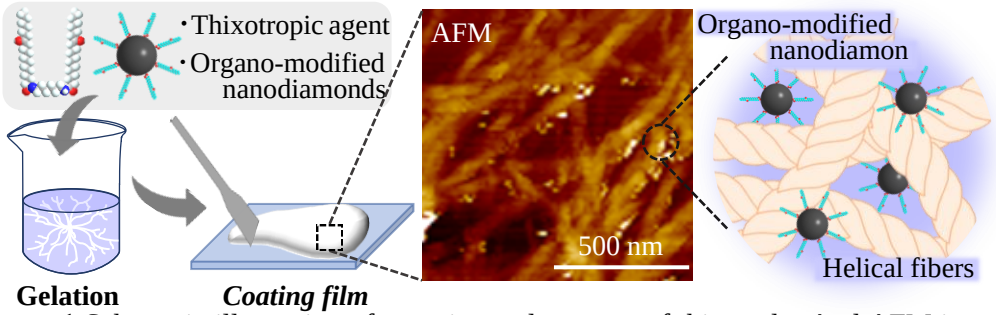

Figure 1 Schematic illustration of experimental strategy of this study. And AFM image of coating film composed by a diamide-based thixotropic additive with two-hydrocarbons and organo-modified nanodiamonds.

Reference: 1) Y. Hasunuma, A. Fujimori, et al, *ChemistrySelect*, **2023**, *8*, e202303005.
2) Y. Mashiyama, Y. Hasunuma, A. Fujimori, *ChemistrySelect*, **2022**, *7*, e202200918.

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球晶形成能を有するアザカリックスアレーン含有共重合体の組織分子膜形成と金属捕集挙動

(埼玉大工[1]・埼玉大院理工[2]・岩手大理工[3])
○照井 綾真[1]・塩田 祥貴[2]・芝崎 祐二[3]・藤森 厚裕[2]

Formation of Organized Molecular Films and Metal Scavenging Behavior of Azacalyxarene-containing Copolymers with Spherulite-Forming Ability

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Abstract: It has evaluated the behavior of organized molecular films behavior of a copolymer with a repeating unit in which a polyethylene glycol chain was attached as a linker to the azacalixarene moiety.

Keywords: Azacalixarene, Polyethylene Glycol Chain, Metal Scavenging Properties, Langmuir-Blodgett Films, Spherulite

【序論】包摂化合物やホスト-ゲスト相互作用など，分子レベルの「超空間制御」による機能発現に関わる研究は，薬物送達技術･分子認識･分子ネックレス等に代表される幅広い発展を遂げている．これまでアザカリックスアレーン環を有するポリグアナミン系誘導体の水面上単分子膜が，下相水中の金属カチオンを選択捕集･脱離回収できるという報告[1]がなされてきた．本研究では，高次構造制御により，バルク状態で球晶形成が可能となった新規誘導体[2]を合成し，その界面分子膜挙動を検討した．

【実験】試料は，トリアジン環とフェニル環を其々2つずつ，-NH-基でつないだ環状部位と，両端を-NH_2基置換したポリエチレングリコール(PEG)リンカーで構成された繰り返し単位を有する新規共重合体を合成し，実験に使用した．当該共重合体の水面上単層膜の挙動は表面圧-面積(π-A)等温線により評価し(15 °C)，金属捕集能は固体基板上転写膜に対するX線光電子分光(XPS)により確認した．

【結果と考察】アザカリックスアレーン環とPEG鎖を繰り返し単位としてもつ共重合体は，気/水界面場で分子占有面積の大きい単層膜を形成することが判明した(Fig. 1)．また，下相水をCd^{2+}イオンを含む緩衝溶液にすると等温線が膨張傾向となり，共重合体と金属イオンとの相互作用の存在を示唆した．ここで，当該の固体基板上転写膜に対し，XPSの測定を行ったところ，Cdの存在が確認された(Fig. 2)．即ち，アザカリックスアレーン環内部に，Cd^{2+}イオンが捕集されたことが示唆される．環内部方向には，多数のN原子由来の豊富な孤立電子対が配向し，印電場を形成していると予測された．

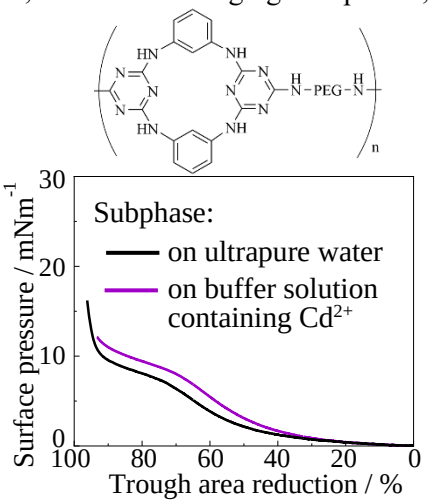

Fig. 1 π-A isotherms of monolayers of azacalixarene-containing copolymer on ultrapure water and aqueous buffer solution containing Cd^{2+}.

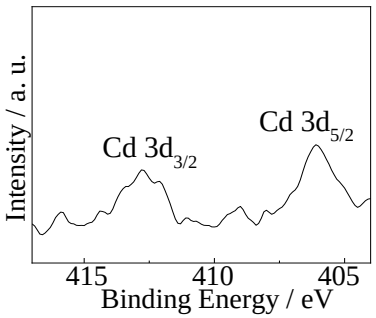

Fig. 2 X-ray photoelectron spectrum of LB multilayers of azacalixarene-containing copolymer transferred from the surface of buffer solution containing Cd^{2+}.

References: 1) J. Yamaguchi, S. Sugita, Y. Otsuki, T. Tsukamoto, Y. Shibasaki, A. Fujimori, *Colloids Surf. A*, **2023**, *656*, 130479.
2) Y. Otsuki, R. Terui, Y. Shibasaki, Y. Hoshino, T. Suzuki, A. Fujimori, *Macromol. Chem. Phys.*, **2023**, *224*, 2300117.

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糖鎖系高分子を用いた界面分子膜の形態形成とその制御

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○中田 遼真[1]・奈良 知叡[1]・Rokibul Hasan Rumon[2]・藤森 厚裕[2]

Morphogenesis and Its Control of Interfacial Molecular Films Using Glycan-based Polymers

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Abstract: A two-dimensional mixed monolayer was created using soluble starch and organo-modified montmorillonite. In this system, we also aimed to control the morphology by varying the mixed ratio. Starch, known as an insoluble natural polymer, can be spread into a Langmuir monolayer on the water surface as amylodextrin by solubilizing it. Insoluble starch formed a spherical single particle layer at the air/water interface field. It was found that organo-modified montmorillonite shows dependence on the spreading solvent and can be miniaturized by using a solvent suitable for spreading insoluble starch.

Keywords: Soluble Starch, Montmorillonite, Interfacial Molecular Films, Single Particle Layers, Phase Separation

【序論】持続可能性とプラスチック海洋汚染回避の観点から，天然高分子材料の更なる有効活用が望まれている．糖鎖高分子由来のナノセルロース研究も盛隆を迎えており，界面分子膜技術からのアプローチ[1]も生まれている．デンプンはアミロース成分が不溶性のため，組織化膜研究には不向きとされてきたが，可溶化処理によって気/水界面への展開が可能となる[2]．本研究では共に天然由来のデンプンとナノクレイの二次元ハイブリッド膜を調製し，その形態制御に取り組んだ．

【実験】試料は，可溶化処理によりアミロデキストリン転移させた可溶性デンプンを用いた．また，表面に長鎖四級アンモニウムカチオン処理を施したモンモリロナイトを，有機修飾ナノクレイとして使用した．混合膜の評価は，水面上単層膜に対する表面圧-面積(π-A)等温曲線(15)と，基板上への転写単分子膜に対する原子間力顕微鏡(AFM)観察を行った．

【結果と考察】様々な混合比で調製した可溶性デンプン:有機修飾ナノクレイ水面上混合単分子膜は，π-A 等温線の測定に於いて，比率に対して不連続な崩壊圧値の変化を示し，メゾスコピックな相分離系であることが示唆された．転写単層膜の表面形態を AFM により観察すると，可溶性デンプンは水面上で「単粒子膜」を形成することが分かった．一方でクレイ由来の板状形態は展開溶媒の選択によって，微細化していく様子が見られた．この結果，Fig. 1 のようにデンプン:ナノクレイ=1:8 の比率程度まで，明瞭なクレイの板状形態の存在が確認できなかった．発表日当日は，ナノクレイを微細化させた上述の展開方法の影響についても詳細に説明する．

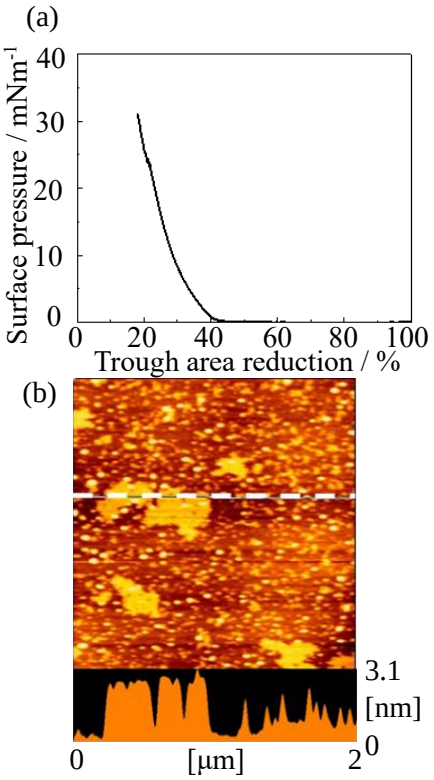

Fig. 1 (a) π-A isotherm (15 ℃) of mixed monolayer on the water surface and (b) AFM image of transferred mixed monolayer on solid (10 $mN{\cdot}m^{-1}$) of soluble starch : organo-modified nanoclay = 1 : 8.

References: 1) S. Sugita, R. Nakada, A. Fujimori, *Polym. Eng. Sci.* **2023**, *63*, 2745.
2) T. Yokoyama, A. Fujimori, et al, *Colloids Surf. A*, **2022**, *643*, 128784.

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2 種の機能性有機フィラーを含む延伸配向フッ素系ポリマー/カーボンナノチューブ複合材フィルムの構造物性

(埼玉大院理工 [1]) ○朱 品榕 [1]・Rokibul Hasan Rumon[1]・徐 愷 [1]・藤森 厚裕 [1]

Structure and properties of drawn-oriented fluorinated polymer/carbon nanotube composite film containing two types of functional organic fillers

([1]Grad. Sch. Sci. Eng., Saitama Univ.)
○Pinjung Chu[1], Rokibul Hasan Rumon[1], Kai Xu[1], Atsuhiro Fujimori[1]

Abstract: It has prepared a fluorinated polymer/surface-modified carbon nanotube composite film containing polyrotaxane and cellulose nanofibers as organic fillers and investigated its drawn-orientation properties.

Keywords: Single-walled Carbon Nanotube, Polyrotaxane, Cellulose Nanofiber, Polymer Composite, Compression Molding Film

【序論】結晶性高分子に対する延伸配向は，マクロスコピックな延伸加工によって約 10 nm 周期のラメラ配列を制御可能なメカノケミカルな特性である[1]．異方性をもつ針状のナノフィラーを含む高分子複合体では，延伸によってフィラーの配向制御すら可能になる[2]．本研究では，ポリロタキサン(p-rtx)とナノセルロース(CNF)を有機フィラーとして含む，力学物性に優れた高分子複合材[3,4]に対し，表面を有機分子鎖で修飾した単層カーボンナノチューブ(SWCNT)を更に含有させ，結果として得られた有機/無機ハイブッリドに対する一軸延伸配向特性について検討を行った．

【実験】高分子基材(マトリックス)として，フッ素系樹脂であるポリフッ化ビニリデン(PVDF)を用い，p-rtx，CNF，有機修飾 SWCNT，更には分散剤として有機修飾剤であるフッ素化フッ素化ホスホン酸(FDPA)を加えて，溶融混練によるナノ複合化を行った．得られた複合体は，ホットプレス機によって圧縮成形フィルムとされ，手動延伸機によって配向化された．延伸はマトリックスの融点近傍で行われ，延伸倍率(DR)2~7 倍までの試料が作成された．複合体中のフィラーの配向性は偏光顕微鏡(POM)で観察され，複合体の力学物性は引っ張り試験(A＆D テンシロン RTG1310)によって行われた．

【結果と考察】Fig. 1(a)に示すように，得られた複合材料は POM レベルのメゾスコピック次元で，SWCNT の凝集体が延伸方向に一軸配向している様子が確認された．また Fig. 1(b)の応力-歪み(S-S)曲線に於いては，延伸倍率の向上と共に最大応力値のみならず，横軸に沿った伸び特性の向上が確認され，これは DR=5 で最大値を示した．

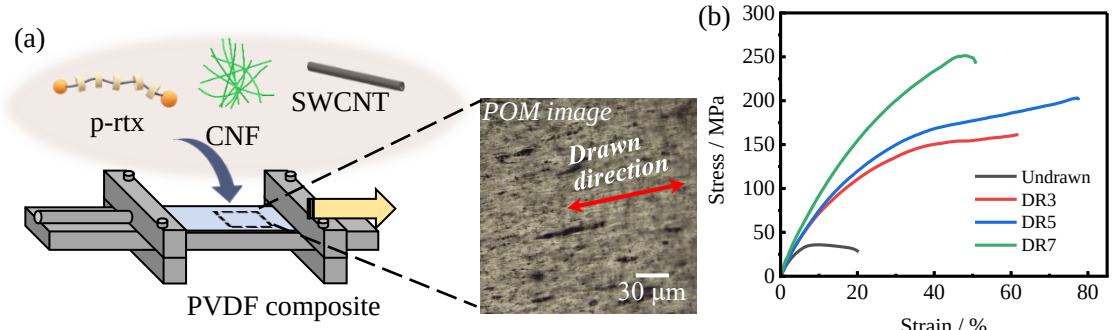

Figure 1. (a) POM image of drawn composite film containing p-rtx, CNF and SWCNT. (b) Strain-Stress curves of drawn composite films with different ratios.

References:
1) Y. Hayasaka, A. Fujimori, Macromoleucles, **2008**, *41*, 7606.
2) K. Xu, K. Harada, T. Hayasaki, AA. Almarasy A. Fujimori, *Polym. Compos.*, **2022**, *43*, 3457.
3) K. Harada, P. Chu, K. Xu, and A. Fujimori, *Polym. Compos.*, **2023**, *44*, 2977.
4) P. Chu, K. Harada, K. Xu, A. Fujimori, *Polym. Eng. Sci.*, **2024**, *64*, in press. (DOI: 10.1002/pen.26535)

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Academic Program [Oral B] | 19. Colloid and Interface Chemistry : Oral B

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC A1442(1442, Bldg. 14 [4F])

[A1442-4pm] 19. Colloid and Interface Chemistry

Chair: Tatsuya Kameyama, Tetsuya Kambe

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[A1442-4pm-01]

Exploration of highly active catalysts for hydrogen evolution reaction in multi-element alloy nanoparticles by machine learning

○Yuto Maruta[1], Kohei Kusada[1,2], Okkyun Seo[5], Osami Sakata[5], Shogo Kawaguchi[5], Yoshiki Kubota[6], Hiromasa Kaneko[7], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. HAKUBI Centre, Kyoto Univ., 3. URC, Kyushu Univ., 4. Grad. Sch. Eng., Kyushu Univ., 5. JASRI-SPring-8, 6. Grad. Sch. Sci., Osaka Metropolitan Univ., 7. Grad. Sch. Sci. and Tech., Meiji Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[A1442-4pm-02]

Machine learning guided development of size and shape controlled inorganic nanoparticles

○Quan ZOU[1], Kiyoshi Kanie[1,2] (1. International Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai, Miyagi 980- 8577, Japan, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[A1442-4pm-03]

Element–Electronic Structure–Product Selectivity Relationship in CO_2 Hydrogenation over Multi-Element Alloy Nanoparticle Catalysts

○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Shogo Kawaguchi[5], Toshiaki Ina[5], Yoshiki Kubota[6], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. HAKUBI Center, Kyoto Univ., 3. URC, Kyushu Univ., 4. Grad. Sch. Eng., Kyushu Univ., 5. JASRI/SPring-8, 6. Grad. Sch. Sci., Osaka Metro. Univ.)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[A1442-4pm-04]

Vesicle Formation via Self-Assembly of Au-Fe_3O_4 Janus Nanoparticles at a Liquid-Liquid Interface

○Takehiro Yachi[1,2], Hideyuki Mitomo[2,4], Kiyoshi Kanie[3,4], Kuniharu Ijiro[2] (1. JSPS, 2. RIES, Hokkaido Univ., 3. SRIS, Tohoku Univ., 4. IMRAM, Tohoku Univ.)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC

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[A1442-4pm-05]

Highly ordered $L1_0$-type Pt-*M*-Zn Nanoparticles for Electrocatalysts

○Wu Tian[1], Ryota Sato[2], Yoshiharu Uchimoto[3], Toshiharu Teranishi[1,2] (1. Grad. Sch. of Sci., Kyoto Univ., 2. Inst. for Chem. Res., Kyoto Univ., 3. Grad. Sch. of Human and Environ. Stud., Kyoto Univ.)

English

2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[A1442-4pm-06]

Synthesis of 3D Ag nanoparticle superlattices and their structure-specific functions

○ZHU LINGKAI[1], SARUYAMA MASAKI[2], TERANISHI TOSHIHARU[1,2] (1. Graduate School of Science, Kyoto University, 2. Institute for Chemical Research, Kyoto University)

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Exploration of highly active catalysts for hydrogen evolution reaction in multi-element alloy nanoparticles by machine learning

([1]Grad. Sch. Sci., Kyoto Univ., [2]Hakubi Center, Kyoto Univ., [3]URC, Kyushu Univ.,[4]Grad. Sch. Eng., Kyushu Univ, [5]Japan Synchrotron Radiation Research Institute [6]Grad. Sch. Sci., Osaka Pref. Univ. [7]Grad. Sch. Tech., Meiji Univ.) ○Yuto Maruta[1], Kohei Kusada[1, 2], Tomokazu Yamamoto[3], Takaaki Toriyama[3], Yasukazu Murakami[3, 4], Okkyun Seo[5], Shogo Kawaguchi[5], Osami Sakata[5], Yoshiki Kubota[6], Hiromasa Kaneko[7], Hiroshi Kitagawa[1]

Keywords: Nanoparticles, Multi-element alloys, Catalysts, Machine learning, Hydrogen evolution reaction

Multi-element solid-solution alloy nanoparticles (NPs) have attracted much attention as a new class of catalysts because they have both high activities and stabilities for many kinds of reactions. For example, equimolar platinum-group metal (PGM) quinary alloy NPs show extremely high catalytic activity for electrochemical hydrogen evolution reaction (HER)[1,2]. However, it is quite difficult to find their optimized compositions because of their compositional complexities. One possible way to overcome this difficulty is to use machine learning, and here, we explored a PGM multi-element alloy HER catalyst by machine learning.

We firstly synthesized PGM quinary alloy NPs with more than 70 different compositions directly on carbon support. Turnover frequency (TOF) which shows an activity normalized by electrochemical active surface area was used as a target variable to discuss the intrinsic activity. Cross terms and three-factor interaction terms of compositions from XRF were used as descriptors to search multi-element alloy compositions. It is found that the Gaussian-process regression (GPR) model using only experimental variables shows a very high generalization performance (Fig.1-a). The virtual experiment with 10,000 compositions was conducted using the obtained model to predict the optimal composition. A catalyst with the predicted optimal composition was synthesized and showed 6.3 times higher HER activity than Pt NPs (Fig.1-b). Moreover, this activity value is consistent with the estimated value from the GPR model, indicating that the optimal composition was successfully predicted by using a simple dataset consisting only of the experimental results. Since there are more than 10,000 compositions covering the quinary alloys in increments of 5%, our method can make compositional optimization more than 100 times more efficient. This method could be applied to other complex alloy systems.

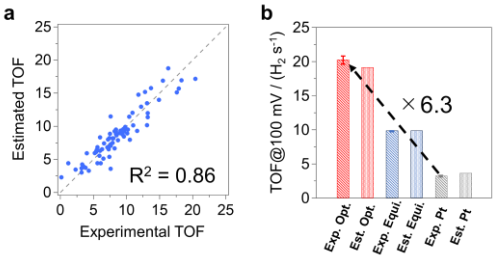

Figure 1 (a) Parity plot of TOF at 100 mV (b) Experimental and estimated TOF at 100 mV of the optimized sample (red), equimolar sample (blue) and Pt NPs (grey).

1) D. Wu et al., *Chem. Sci.*, 2020,11, 12731-12736. 2) Y. Maruta et al., *Chem Commun.*, 2022, 58, 6421-6424.

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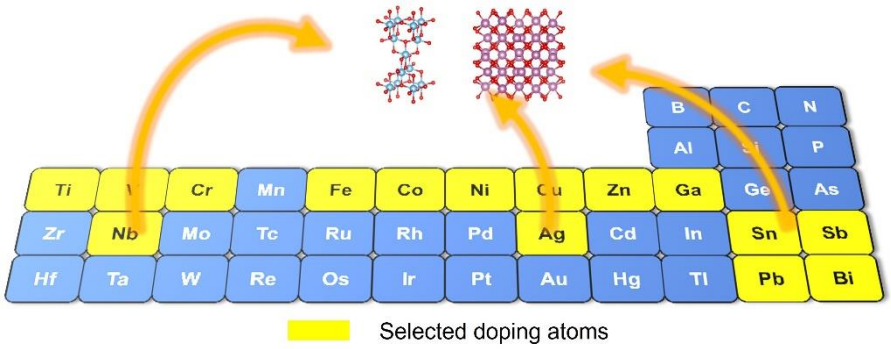
Machine learning guided development of size and shape controlled inorganic nanoparticles

(*[1] International Center for Synchrotron Radiation and Innovation Smart (SRIS), Tohoku University, Sendai, 980-8577, Japan, [2] Institute of Multidisciplinary Research for Advanced Materials Institution, Tohoku University, Sendai, 980-8577, Japan*)

○Quan Zou[1], Kiyoshi Kanie[1,2]

Key words: inorganic nanoparticles, size and shape, machine learning

Controlling the size and shape of nanoparticles (NPs) was deemed as an effective method to ameliorate their properties[1,2]. Thus, it was adopted as a controllable strategy to synthesize functional materials. However, conventional methods of controlling the size and shape of inorganic NPs involve a wide range of factors, which led to a dilemma that development of inorganic NPs was mainly focused on the trail-and-error method. Lack of theoretical guidance in controlling the size and shape of NPs was regarded as one of the most crucial bottlenecks hindering the development of NPs. On the other hand, artificial intelligence (AI), considered as a rising power to surpass human and further develop novel materials from a new perspective, attracted our interests. Machine learning (ML) was adopted to develop promising and novel NPs.



In this work, 2 metal oxides and 13 doping atoms were selected to prepare size and shape-controlled NPs. All the NPs were synthesized in a unified procedure, from which the features for database construction were extracted. XRD and TEM were used to investigate the structural and compositional information and determine the synthesis of NPs. Finally, ML was adopted to analyze the database and predict promising candidates for practical applications.

1) *J. Am. Chem. Soc.* 2011, 133, 39, 15743–15752

2) *J. Am. Chem. Soc.* 2014, 136, 396−404

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Element–Electronic Structure–Product Selectivity Relationship in CO_2 Hydrogenation over Multi-Element Alloy Nanoparticle Catalysts

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○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Takaaki Toriyama[3], Tomokazu Yamamoto[3], Yasukazu Murakami[3,4], Shogo Kawaguchi[5], Toshiaki Ina[5], Yoshiki Kubota[6], Hiroshi Kitagawa[1]
Keywords: Multi-Element Alloy Nanoparticles; CO_2 Hydrogenation; Selectivity; XANES

Multi-element alloys nanoparticles (MEA NPs) are now one of the dominant subjects of catalyst development.[1] Recent studies have demonstrated their attractive catalytic properties; extraordinary enhancement in activity,[2] realization of complicated catalysis[3] or excellent durability.[4] Nevertheless, the product selectivity control has poorly been studied in the field of MEA NPs catalysts. It would require systematic understanding about how elemental combinations in alloys affect their electronic structures and catalytic properties.

Here, we targeted a series of alloy NPs composed of elements with different electronic natures, platinum-group metals (PGMs) and base metals (*p*-block or 3*d* metals), and developed their versatile synthesis method. Then, their electronic structures and catalytic activities as CO_2 hydrogenation catalysts (**Fig.**) were investigated. As a result, we found the evident correlation between the whiteline peak heights in XANES of PGM *L* egdes and CO/CH_4 selectivities. This indicates that the elemental interaction in the alloy would affect their electronic structures, consequently leading to the change in their catalytic properties.

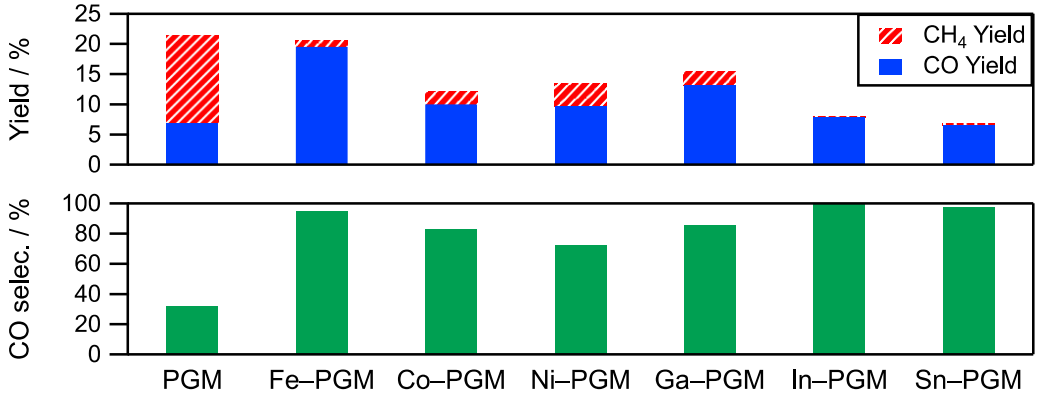

Fig. CH_4 and CO yields (top) and CO selectivity (bottom) in CO_2 hydrogenation over PGM quinary NPs and X–PGM senary NPs (X=Fe, Co, Ni, Ga, In and Sn) at 450 °C.

1) Y. Sun and S. Dai, *Sci. Adv.*, **2021**, *7*, eabg1600. 2) D. Wu *et al.*, *Chem. Sci.*, **2020**, *11*, 12731. 3) D. Wu *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 13833. 4) K. Mori *et al.*, *Nat. Commun.*, **2021**, *12*, 3884.

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Au-Fe_3O_4 ヤヌスナノ粒子の液液界面における自己組織化によるベシクル形成

（日本学術振興会 [1]・北大電子研 [2]・東北大 SRIS [3]・東北大多元研 [4]）○谷地 赳拓 [1,2]・三友 秀之 [2,4]・蟹江 澄志 [3,4]・居城 邦治 [2]

Vesicle Formation via Self-Assembly of Au-Fe_3O_4 Janus Nanoparticles at a Liquid-Liquid Interface

([1]*JSPS*, [2]*RIES, Hokkaido University,* [3]*SRIS, Tohoku University,* [4]*IMRAM, Tohoku University,*) ○ Takehiro Yachi,[1,2] Hideyuki Mitomo,[2,4] Hideyuki Mitomo,[2,4] Kiyoshi Kanie,[3,4] Kuniharu Ijiro[2]

Au-magnetic Janus nanoparticles (NPs) have great potential in bioapplication because they show unique optical and electromagnetic properties as well as high biocompatibility. In addition, the assembled state can be controlled by modifying each surface differently, allowing for further functionalization through self-assembly. In this study, we synthesized Au-Fe_3O_4 Janus NPs with hydrophilic ligands on the Au surface and hydrophobic ligands on the Fe_3O_4 surface to form self-assembled vesicle structures at the liquid-liquid interface. The results showed that vesicles of about 100 nm are stably formed at the interface of $CHCl_3$/sodium citrate aqueous. The resulting vesicles are expected to be used for applications such as drug delivery.

Keywords：Au nanoparticles, Magnetic nanoparticles, Self-assembly, Janus nanoparticle, Vesicles

金ナノ粒子と磁性ナノ粒子からなるヤヌスナノ粒子は，それぞれの光学特性や磁気特性を併せ持ち，高い生体適合性を示すことから生体応用などにおいて注目を集めている．また，それぞれの表面に対して異なる表面修飾が可能であるため，異なる表面特性を利用した自己集合化によるさらなる機能化が期待される．本研究では，Au-Fe_3O_4 ヤヌスナノ粒子の合成と表面修飾を行い，自己組織化によるベシクルの形成を行った．

【実験】まず，オレイルアミンで被覆された Au ナノ粒子の合成を行い，これを種粒子として Au-Fe_3O_4 ヤヌスナノ粒子を合成した [1,2]．次いで得られた粒子の Au 表面を親水性の 11-Mercaptoundecanol hexaethyleneglycol ether で修飾し，親水面と疎水面を併せ持つ粒子を得た．その後，$CHCl_3$ とクエン酸ナトリウム水溶液の界面にて粒子を自己組織化させることによってベシクル構造の形成を行った．

【結果・考察】**Fig. 1a** に得られた粒子の TEM 像を示す．結果として，8.8 ± 0.8 nm の Au 粒子，13.5 ± 1.7 nm Fe_3O_4 粒子からなるヤヌス粒子が得られた．また，Au 表面を親水性配位子で修飾した粒子では，$CHCl_3/H_2O$ の界面に集合する様子が見られ，親水・疎水表面の双方を有することが示唆された．**Fig. 1b** に液液界面における自己組織化によって形成されたベシクルの TEM 像を示す．結果より，100 nm 程度のベシクル構造の形成が確認され，親水面・疎水面を併せ持つ Au-Fe_3O_4 ナノ粒子の自己組織化によってベシクルの形成が可能であることが示された．本手法では，ベシクル内部への薬物内包を利用した薬物送達への応用などが期待されるほか，Fe_3O_4 粒子表面を有機分子で修飾することでさらなる機能化が期待される．

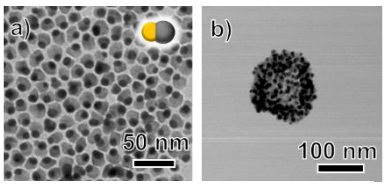

Fig. 1 a) Au-Fe_3O_4 ナノ粒像および b) 自己組織化により形成されたベシクルの TEM 像

1) H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White, S. Sun, *Nano Lett.*, 5, 379 (**2005**)
2) M. Niehues, S. Engel, B. J. Ravoo, *Langmuir*, 37, 11123 (**2021**)

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Highly Ordered $L1_0$-Type Pt–*M*–Zn Nanoparticles for Electrocatalysts

([1]*Graduate School of Science, Kyoto University*, [2]*Institute for Chemical Research, Kyoto University*, [3]*Graduate School of Human and Environmental Studies, Kyoto University*) ○Wu Tian,[1] Ryota Sato,[2] Yoshiharu Uchimoto,[3] Toshiharu Teranishi[1,2]

Keywords: Inorganic Nanoparticle; $L1_0$-Type Ordered Alloy; Low-Temperature Ordering; Strain Effect; Electrocatalyst

$L1_0$-ordered Pt*M* (*M* is typically a 3d transition metal) intermetallic compounds (IMCs) have been regarded as promising electrocatalysts for sluggish reactions like oxygen reduction reaction (ORR) for fuel cells because of their superior acid corrosion resistance and much higher activity in acid media. Although there are many reports on the synthesis of binary $L1_0$-Pt*M* or ternary $L1_0$-type Pt(M_1,M_2) nanoparticles (NPs) as electrocatalysts, they require high-temperature annealing to induce the phase transformation from disordered Pt–*M* alloy into ordered Pt–*M* IMCs.[1] However high-temperature annealing of supported NP catalysts causes severe sintering of NPs, which is unfavorable to electrocatalytic performance. Taken in consideration that $L1_0$-PtZn possesses much lower phase transformation temperature, we envisioned that the incorporation of Zn as an ordering promoter would allow the phase transformation of $L1_0$-Pt*M* NPs to be initiated at relatively low temperature without sintering.

In this study, we used organometallic zinc complexes to incorporate the hard-to-reduce Zn into Pt–*M* NPs by a facile wet-chemical way (Fig. 1). This method allowed us to precisely control the composition of the NPs. The addition of Zn reduced the ordering temperature of Pt–*M*–Zn NPs and made it possible to transform into ordered IMCs at lower temperature, which helps to suppress sintering and achieves higher ordering degree. To improve ORR activity, i.e., to optimize the strain effect on the Pt outermost layer formed by acid treatment, compositionally controlled $L1_0$-type Pt(*M*,Zn) (*M* = Co and/or Ni) NPs with high ordering degree were synthesized through low temperature annealing. This approach is expected to address simultaneous improvements in ORR activity and durability.

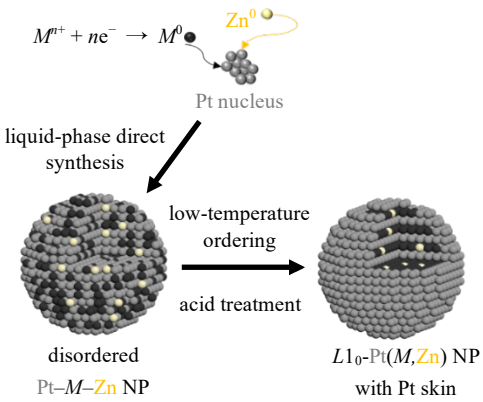

Figure 1. Schematic illustration of the synthetic route to core-shell $L1_0$-Pt(*M*,Zn) NP

This work is supported by NEDO (JPNP 20003).

1) J. Li *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 19209.

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三次元 Ag ナノ粒子超格子の合成と構造特異的機能

（京大院理[1]・京大化研[2]）○Zhu Lingkai[1]・猿山 雅亮[2]・寺西 利治[1,2]
Synthesis of 3D Ag nanoparticle superlattices and their structure-specific functions ([1]*Graduate School of Science, Kyoto University,* [2]*Institute for Chemical Research, Kyoto University*) ○ Lingkai Zhu[1], Masaki Saruyama[2], Toshiharu Teranishi[1,2]

Nanoparticle (NP) superlattices show unique concerted properties which are not exhibited by isolated NPs. Especially, the superlattices consisting of NPs with localized surface plasmon resonance properties have been expected as a new type of plasmonic materials due to their unique optical properties derived from plasmon coupling. In this study, we investigated the simple one-pot synthesis of 3D Ag NP superlattices and their structure-specific functions. Ag NP superlattices were obtained as a blue powder, which showed broad optical absorption from visible to near-infrared region due to the plasmon coupling. The film of the superlattice showed superhydrophobicity derived from the micro-meter scale surface roughness and has a potential as a substrate for highly sensitive Raman scattering measurements.
Keywords : Self-assembly, LSPR, Ag nanoparticles, Small-angle X-ray scattering

局在表面プラズモン共鳴（LSPR）特性をもつナノ粒子の超格子は、プラズモンカップリング現象によって共鳴波長の変化や局所増強電場の形成を示すことから、新しい光学応用が期待される。本研究では、Ag ナノ粒子の三次元超格子を一段階反応で合成する方法を開発するとともに、その構造特異的な機能について検証した。

$AgNO_3$ をドデシルアミン中で加熱することで青色の沈殿物が得られ、これが約 10 nm の Ag ナノ粒子が最密充填した多面体構造をもつ数 μm の三次元超格子であることを確認した（Fig. 1）。Ag ナノ粒子分散液が 400 nm にのみ LSPR 吸収を示すのに対して、この超格子はプラズモンカップリングにより可視～近赤外域にかけて幅広い光を吸収できることが分かった（Fig. 2a）。また、三次元超格子を基板上に成膜することで、自然に形成される μm オーダーの凸凹によって超撥水性が発現することを見出しており（Fig. 2b）、基質濃縮効果をもつ高感度ラマン散乱用の基板としての利用も検討したので報告する。

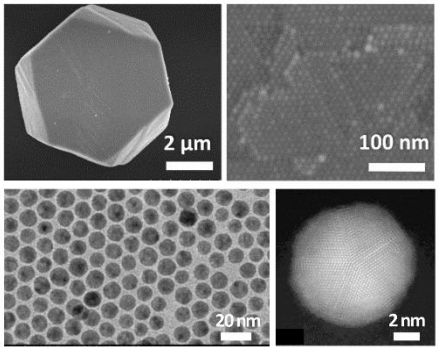

Fig. 1. (upper) SEM images of Ag NP superlattice. (lower) TEM images of Ag NPs.

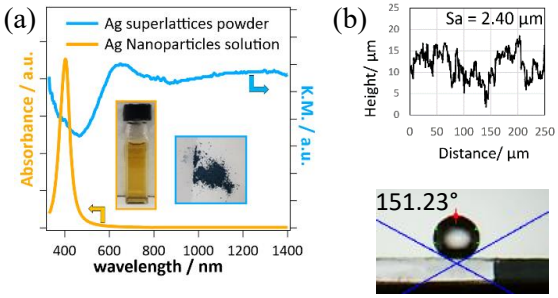

Fig. 2. (a) Absorption spectra of Ag NPs and their superlattices. (b) Surface roughness of Ag NP superlattices film and the contact angle with water droplet.

1) F. Nakagawa, M. Saruyama, T. Teranishi *et al*., *J. Am. Chem. Soc*. **2022**, 144, 5871–5877.

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

Thu. Mar 21, 2024 10:30 AM - 11:20 AM JST | Thu. Mar 21, 2024 1:30 AM - 2:20 AM UTC C442(442, Bldg. 4 [4F])

[C442-4am] 20. Materials Chemistry -Basic and Application-

Chair: Hiroki Mori, Osamu Tsutsumi

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[C442-4am-01]

Photoresponsive behavior of oligothiophene-doped liquid crystals containing an acrylate monomer by irradiation with a circularly polarized beam

○Soichiro Koyama[1], Mirai Motoyama[1], Junki Yokota[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology, 2. PREST, JST)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[C442-4am-02]

Photoinduced molecular reorientation of liquid crystals doped with dichroic dyes toward visible light dimming

○Yuya Nakata[1], Junki Yokota[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology, 2. PRESTO, JST)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[C442-4am-03]

Controlling Helical Axis Orientation by Gradient Photopolymerization of Chiral Liquid-Crystalline Monomer

○Yuki Shikata[1], Shohei Sugiyama[1], Maki Yanagihara[1], Kohsuke Matsumoto[1], Osamu Tsutsumi[1] (1. The Univ. of Ritsumeikan)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[C442-4am-04]

Development of Semiconducting Polymers Based on Vinylene-Bridged Bisdifluoroquinoxaline and Their Application to Organic Photovoltaic Cells

○Yamane Hiroki[1], Hiroki Mori[2], Yasushi Nishihara[2] (1. Grad. Sch. of Environ. Life Nat. Sci. and Tech., Okayama Univ., 2. RIIS, Okayma Univ.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[C442-4am-05]

Effect of the number of fluorine atoms on the functionalization degree and photoluminescent properties of butylated single-walled carbon nanotubes

○Yasuhiro Suzuki[1], Yui Konno[1], Nobuhiro Kikuchi, Michio Yamada[1], Yutaka Maeda[1], Pei Zhao[2], Masahiro Ehara[2], Masaya Mitsuishi[3], Anh T. N. Dao[4], Hitoshi Kasai[5] (1. Tokyo Gakugei University, 2. Institute for Molecular Science, 3. Graduate School of Engineering, Tohoku University, 4. Graduate School of Engineering, Nagasaki University, 5. Institute of Multidisciplinary Reseach for Advanced Materials, Tohoku Universityity)

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アクリレートモノマーを添加したオリゴチオフェンドープ液晶の円偏光応答挙動

（東工大化生研[1]・JST さきがけ[2]）○小山 宗一郎[1]・本山 未来[1]・横田 純輝[1]・相沢 美帆[1,2]・久野 恭平[1]・久保 祥一[1]・宍戸 厚[1]

Photoresponsive Behavior of Oligothiophene-doped Liquid Crystals Containing an Acrylate Monomer by Irradiation with a Circularly Polarized Beam ([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*, [2]*PRESTO, JST*) ○ Soichiro Koyama,[1] Mirai Motoyama,[1] Junki Yokota,[1] Miho Aizawa,[1,2] Kyohei Hisano,[1] Shoichi Kubo,[1] Atsushi Shishido[1]

Irradiation of dye-doped LCs with a linearly polarized laser beam induces molecular reorientation, leading to the formation of diffraction rings. Recently, we discovered that the irradiation of polymer-stabilized dye-doped LCs with a circularly polarized laser beam causes the unidirectional rotation of the elliptical diffraction rings. However, the mechanism remained unexplored. In this study, we prepared dye-doped LCs containing non-polymerized acrylate monomers and investigated the effect of monomers on the rotation behavior of diffraction rings.

A liquid crystal 5CB and an acrylate monomer A6CB were mixed with various ratios, and an oligothiophene dye TR5 was added. The mixtures were injected into a glass cell treated with a homeotropic alignment layer and irradiated with a circularly polarized beam at a wavelength of 488 nm. The concentration of A6CB and the incident light intensity affected the rotation speed of the induced diffraction rings. The observation with the probe beam at a wavelength of 633 nm, which is not absorbed by the dye, revealed that the rotation of the diffraction rings was derived from the molecular rotation of LCs.

Keywords: Liquid crystal; Monomer; Molecular reorientation; Dye; Circularly polarized light

色素を少量添加した液晶（色素ドープ液晶）に直線偏光を入射すると，分子配向変化に基づくリング状の回折光が発現する[1)]。最近当研究室では，高分子安定化した色素ドープ液晶に円偏光を入射すると，発現した楕円状の回折リングが一方向に回転する現象を見出した[2,3)]。しかしながら，回折リングが回転するメカニズムは未解明な点が多い。本研究ではアクリレートモノマーを添加した色素ドープ液晶に光重合を施さずに円偏光を入射し，モノマー添加が回転挙動に及ぼす影響について調べた。

低分子液晶 5CB とアクリレートモノマーA6CB を種々の物質量比で混合し，オリゴチオフェン色素 TR5 を少量添加した試料を，垂直配向処理を施したガラスセルにそれぞれ封入した。液晶セルに波長 488 nm の円偏光を入射したところ，モノマー濃度や入射光強度によって回折リングの回転速度が変化することがわかった。また，色素が吸収しない波長（633 nm）のプローブ光を同軸で入射することで，回折リングの回転は内部の分子配向の回転に起因していることを明らにした。

1）Y. Aihara, A. Shishido, *et al*., *Adv. Opt. Mater.* **2013**, *1*, 787.
2）K. Usui, A. Shishido, *et al.*, *ACS Appl. Mater. Interfaces* **2021**, *13*, 23049.
3）K. Matsumoto, A. Shishido, *et al*., *The 101st Annual Meeting of the CSJ Prepr. Jpn*. **2021**, A27-3pm-06.

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可視域調光を志向した二色性色素ドープ液晶の光誘起分子配向変化

（東工大化生研 [1]・JST さきがけ [2]）○中田 優也 [1]・横田 純輝 [1]・相沢 美帆 [1,2]・久野 恭平 [1]・久保 祥一 [1]・宍戸 厚 [1]

Photoinduced Molecular Reorientation of Liquid Crystals Doped with Dichroic Dyes toward Visible Light Dimming ([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*, [2]*PRESTO, JST*) ○Yuya Nakata,[1] Junki Yokota,[1] Miho Aizawa,[1,2] Kyohei Hisano,[1] Shoichi Kubo,[1] Atsushi Shishido[1]

When a linearly polarized light above a certain intensity is incident on dichroic oligothiophene dye-doped liquid crystals (LCs), the orientation of the photo-excited dye and LC molecules changes parallel to the polarization direction. The molecular reorientation of dyes increases the absorbance, making it applicable to light-dimming functions. We previously reduced the incident light intensity required to induce molecular reorientation through a series of studies, including polymer stabilization and substrate treatment. However, transmittance control was limited within the short-wavelength range due to the absorption of the oligothiophene dyes. The transmittance control over a broader wavelength range is highly desired. In this study, we investigated the photoinduced molecular reorientation behavior of dye-doped LCs containing a squaraine dye, which absorbs the longer wavelength region.

Small amounts of oligothiophene dye (TR5) and squaraine dye (JSq) were added to a nematic LC (5CB). The prepared sample was injected into a 100-μm-thick glass cell whose inner surfaces had been treated with a homeotropic alignment layer. The photoresponsive behavior of the prepared sample cell upon irradiation with a polarized laser beam was investigated. The results showed that the addition of JSq extended the transmittance-controllable wavelengths.

Keywords: Liquid Crystals; Dye; Transmittance; Molecular Reorientation

二色性のオリゴチオフェン色素を少量添加した色素ドープ液晶に一定強度以上の直線偏光を入射すると，光励起した色素分子と液晶分子の配向が偏光方向と平行に変化する [1–4]。色素分子の配向変化に伴い材料の吸光度が増大するため，調光材料への応用が期待できる。これまでに当研究室では，高分子の添加 [2]や基板処理 [3]などに関する一連の研究によって，本現象を誘起するために必要な光強度を低下することに成功している。しかしながら，既報の材料系ではオリゴチオフェン色素が吸収を示す短波長領域での透過率制御にとどまっている。調光材料への応用を考慮すると，幅広い波長領域における透過率制御が望ましい。そこで本研究では，より長波長領域に吸収を有するスクアライン色素を液晶に新たに添加し，光分子配向変化挙動を検討した。

室温でネマチック相を示すシアノビフェニル液晶(5CB)に，オリゴチオフェン色素（TR5）とスクアライン色素（JSq）を少量添加し，色素ドープ液晶試料とした。垂直配向処理を施した厚さ 100 μm のガラスセルにこの試料を封入し，液晶セルとした。液晶セルに直線偏光のレーザー光を入射し，光応答挙動を観察したところ，JSq の添加により透過率制御可能な波長領域を拡張できることがわかった。

1) H. Zhang, A. Shishido, *et al*., *Adv. Mater.* **2000**, *12*, 1336. 2) Y. Aihara, A. Shishido, *et al.*, *Adv. Opt. Mater.* **2013**, *1*, 787. 3) J. Wang, A. Shishido, *et al*., *Sci. Rep*. **2015**, *5*, 1. 4) K. Usui, A. Shishido, *et al.*, *ACS Appl. Mater. Interfaces* **2021**, *13*, 23049.

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キラル液晶モノマーの傾斜光重合によるらせん軸配向制御

（立命館大）○四方 優輝・杉山 翔平・柳原 真樹・松本 浩輔・堤 治
Controlling Helical Axis Orientation by Gradient Photopolymerization of Chiral Liquid-Crystalline Monomer. (*Ritsumeikan University*) ○Yuki Shikata,[1] Shohei Sugiyama,[1] Maki Yanagihara,[1] Kohsuke Matsumoto,[1] Osamu Tsutsumi,[1]

Liquid crystals have potential use in various optical materials such as diffractive gratings and reflectors. The spatial distribution of refractive index in liquid crystal materials can be manipulated by controlling their molecular orientation. However, achieving arbitrary control of the molecular orientation with periodicity below a few micrometers over large areas is still challenging. Chiral nematic liquid crystals have attracted much attention because they intrinsically possess helically twisted molecular orientation with a periodicity below about a micrometer. This means that the controlled periodic pattern of the refractive index can be obtained by controlling the helical axis orientation of chiral nematic liquid crystals. However, the arbitrary controlling method for the helical axis orientation has not yet been established. Previously, we have found that helical axis orientation was spontaneously controlled by photopolymerization with intensity-gradient patterned light. In this study, we discussed the mechanism of the formation of periodic structures.
Keywords： Chiral Nematic Liquid Crystal; Helical Axis Orientation; Photopolymerization

近年, 高機能光学フィルムの開発を目的として, 液晶フィルムが脚光を浴びている。液晶は複屈折を示すため, 液晶分子配向をパターン制御することで材料内部に屈折率分布を作ることができる。そのため，分子配向を大面積かつ精密にパターン制御した液晶フィルムは回折格子や反射素子などへ応用されている。しかしながら，ナノオーダーわたる微細な分子配向パターン制御は未だ困難である。キラルネマチック液晶はナノからマイクロオーダーの周期をもつらせん状配向を自発形成する。らせん軸に沿った屈折率の周期構造を形成するため，らせん軸配向を制御することで種々の光学機能を発現させることができる。例えば，らせん軸を材料の面内方向に配向させると，光回折特性や偏光変換特性を発現する。しかしながら，らせん軸配向を簡便かつ精密に制御する手法は未だ確立されていない。これまでに，われわれは，強度が空間的に連続的に変化する光を用いた光重合（傾斜光重合）によりキラル液晶ポリマーを合成すると，らせん軸配向が制御されることを見出した。そこで，本研究では，らせん軸配向の形成メカニズム解明を目的とした。

シランカップリング処理を施したガラスセルに光重合性液晶混合物を封入し，フォトマスクを介して紫外光（$\lambda = 365$ nm）を照射することで傾斜光重合を行った。得られた高分子フィルムを偏光顕微鏡観察すると，縞状の光学組織が観察された。縞状組織の構造周期と理論的に算出されるらせん周期が一致したことから傾斜光重合によりらせん軸の面内一軸配向が形成されたと考察した。本発表では，らせん軸配向の形成メカニズムについて議論する。

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ビニレン架橋ビスジフルオロキノキサリンを基盤とする半導体ポリマーの開発と有機薄膜太陽電池への応用

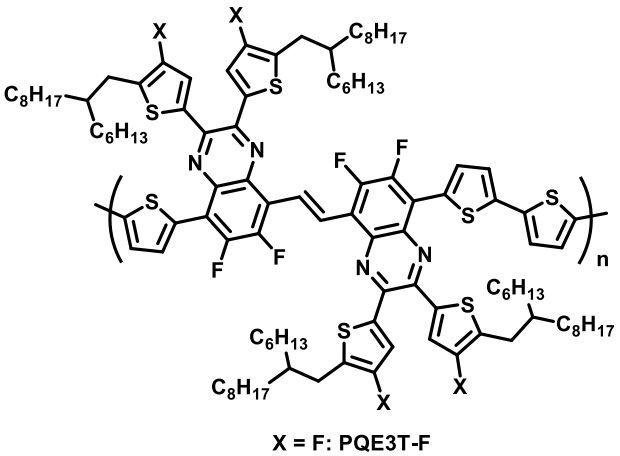
（岡山大院環境生命自然[1]・岡山大基礎研[2]）○山根浩暉[1]・森 裕樹[2]・西原康師[2]

Development of Semiconducting Polymers Based on Vinylene-Bridged Bisdifluoroquinoxaline and Their Application to Organic Photovoltaic Cells ([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*, [2]*Research Institute for Interdisciplinary Science, Okayama University*) ○Hiroki Yamane,[1] Hiroki Mori,[2] Yasushi Nishihara[2]

In order to achieve higher power conversion efficiency (PCE) in organic photovoltaics (OPVs), the development of high-performance p-type semiconducting polymers with a wide- bandgap character is highly important. In this study, we report the synthesis and characterization of two novel p-type semiconducting polymers, **PQE3T-F** and **PQE3T-HD**, based on a vinylene-bridged bisdifluoroquinoxaline (FQxE) unit as a new electron acceptor. In addition, their solar cells with typical low-bandgap n-type semiconductors were fabricated and characterized. The synthesized polymers have a relatively wide bandgap of ca. 1.7 eV, which enables complementary absorption with the low-bandgap n-type semiconductors. **PQE3T-F**-based OPV showed a poor PCE of ca. 6%, whereas the **PQE3T-HD**-based cell exhibited a high PCE of over 13%.

Keywords : Semiconducting polymers; Organic photovoltaic cells; Conjugated polymers; Quinoxaline

有機薄膜太陽電池 (OPV) のさらなる高効率化を達成するためには，広いバンドギャップを有する優れた p 型半導体ポリマーを開発することが重要である。そこでわれわれは，新規アクセプター骨格であるビニレン架橋ビスジフルオロキノキサリン (FQxE) をターチオフェンと組み合わせた 2 種の p 型半導体ポリマー **PQE3T-F** および **PQE3T-HD** を合成した。さらに，代表的な低バンドギャップ n 型半導体と組み合わせた OPV を作製し，その特性を調査した。合成した 2 種のポリマーはいずれも 1.7 eV 程度の広いバンドギャップを有しており，低バンドギャップ n 型半導体と相補的な光吸収を可能とした。また，順構造型 OPV を作製し，その特性を調査したところ，**PQE3T-F** を用いた OPV は約 6% の変換効率に留まったのに対し，**PQE3T-HD** を用いた OPV は 13% を超える高い変換効率を示した。



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ブチル化単層カーボンナノチューブ付加体の化学修飾率と発光特性に及ぼすフッ素原子置換数の効果

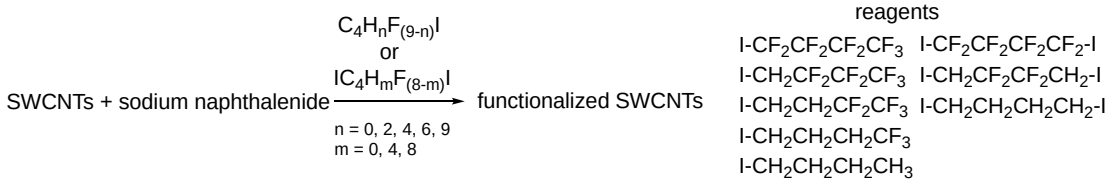
（東学芸大院[1]・分子研[2]・東北大多元研[3]・長崎大院工[4]・東北大院工[5]）○鈴木康浩[1]・紺野優以[1]・菊地展弘[1]・山田道夫[1]・前田優[1]・Pei Zhao[2]・江原正博[2]・三ツ石方也[3]・Anh T. N. Dao[4]・笠井均[5]

Effect of the number of fluorine atoms on the functionalization degree and photoluminescent properties of butylated single-walled carbon nanotubes ([1]*Graduate School of Education, Tokyo Gakugei University*, [2] *Research Center for Computational Science, Institute for Molecular Science,* [3]*Graduate School of Engineering, Tohoku University,* [4]*Graduate School of Engineering, Nagasaki University,* [5]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○ Yasuhiro Suzuki,[1] Yui Konno,[1] Nobuhiro Kikuchi,[1] Michio Yamada,[1] Yutaka Maeda,[1] Pei Zhao,[2] Masahiro Ehara,[2] Masaya Mitsuishi,[3] Anh T. N. Dao,[4] Hitoshi Kasai[5]

Semiconducting single-walled carbon nanotubes (SWCNTs) possess intrinsic band structure depending on their diameter and angle of six-membered ring relative to the axis. The functionalization of SWCNTs is a useful method to control their PL characteristics. For example, butylated (6,5) SWCNTs exhibit two new PL peaks at 1100 nm and 1230 nm with an intrinsic PL peak at 980 nm. Here, we report the effect of the influence of the number and position of fluorine atoms in butyl groups on the PL characteristics of SWCNTs adducts prepared using fluorinated 1-iodobutane and 1,4-diiodobutane derivatives.

Keywords : carbon nanotubes; functionalization; near-infrared photoluminescence

半導体型の単層カーボンナノチューブ（SWCNTs）は、六員環格子の角度や直径に応じた固有バンド構造をもつ。SWCNTsの化学修飾は発光特性制御に有効であり、例えばナフタレニドとブロモブタンを用いて合成したブチル化 (6,5) SWCNTsは、1100 nmと1230 nmに新しい発光を示す[1,2]。Wangらは、次亜硫酸ナトリウムと炭酸水素ナトリウム、ヨードヘキサンを用いて合成したヘキシル化SWCNTs について、水素原子をフッ素原子に置換する数や位置を制御することで、(6,5) SWCNTsから1096 nm－1155 nmの範囲で選択的な発光が発現すると報告している[3]。今回我々はナフタレニドとフッ素化された1-ヨードブタン及び1,4-ジヨードブタン誘導体を用いて合成したSWCNTs付加体の発光特性について評価したところ、フッ素原子の置換数の増加に伴い発光波長が長波長化し、結果として発光波長の発現範囲が、1110 nm－1320 nmに拡張できることを明らかにした[4]。



1) Y. Maeda, et al., *Chem. Commun.* **2023**, *59*, 14497. 2) Y. Maeda, et al., *Nanoscale.* **2016**, *8*, 16916. 3) Y. Wang, et al., *J. Am. Chem. Soc.* **2016**, *138*, 16916. 4) Y. Maeda, et al., *Commun. Chem.* **2023**, *6*, 159.

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Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral A

Thu. Mar 21, 2024 9:30 AM - 11:20 AM JST | Thu. Mar 21, 2024 12:30 AM - 2:20 AM UTC
A1454(1454, Bldg. 14 [5F])

[A1454-4am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Takeo Suga, Tatsuya Kameyama

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1454-4am-01]

Selective Generation of Gaseous Species in Water Electrolysis Using Redox Reaction of Iodine

○Asuna Kai[1], Mai Tomisaki[2], Kentaro Ogawa[1], Hiroshige Matsumoto[1,2] (1. Kyushu Univ., 2. I2CNER, Kyushu Univ.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1454-4am-02]

Synthesis of Ni-Pt-Ir composite nanoparticles by ionic liquid/metal sputtering and their electrocatalytic activity for urea oxidation

○kento hiraide[1], Liu Yixiong[1], Kazutaka Akiyoshi[1], Susumu Kuwabata[2], Tsukasa Torimoto[1] (1. The Univ. of Nagoya, 2. The Univ. of Osaka)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1454-4am-03]

Nitrogen and phosphorus co-doped carbon as an efficient electrocatalyst for oxygen reduction reaction

○Naoki Tachibana[1], Hiromasa Namiki[1], Shoichi Somekawa[1] (1. Tokyo Metropolitan Industrial Technology Research Institute)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1454-4am-04]

Effects of Carotenoid Coating on Chlorin-Modified Pt/TiO_2 Nanoparticles for Photocatalytic Hydrogen Evolution

○Shin-ichi Sasaki[1], Yanxiang Liu[2], Ritsuko Fujii[3], Xiao-Feng Wang[2] (1. Nagahama Inst. Bio-Sci. Tech., 2. Jilin Univ., 3. Osaka Metropolitan Univ.)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1454-4am-05]

Preparation of Near-IR-responsive Ag-Ge-S Quantum Dots and Enhanced Photoluminescence Property through Core-Shell Structure Formation

○Masayuki Soto[1], Kazutaka Akiyosi[1], Tatsuya Kameyama[1], Norikazu Fujihira[2], Tsukasa Torimoto[1] (1. The Univ. of Nagoya, 2. Murata Manufacturing Co., Ltd.)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1454-4am-06]

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Controlling the nano-structure in silver nano arrays for solid state Vis-to-UV photon upconversion.

○Yusei Sawada[1], Kodai Matsumoto[1], Yuya Watanabe[1], Yoichi Sasaki[1,2], Shigenori Fujikawa[1,2,3,4], Nobuo Kimizuka[1,2,3] (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. K-NETs, Kyushu Univ., 4. WPI-I2CNER, Kyushu Univ.)

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

Break

Japanese

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC

[A1454-4am-07]

Perovskite Solar cells Using Rhodanine Derivatives as Electron Collecting Monolayers

○Yuki Miyake[1], Tomoya Nakamura[1], Minh Anh Truong[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Kyoto university, institute for chemical research)

Japanese

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC

[A1454-4am-08]

Relationship between hysteresis and capacitance in Organic Lead Halide Perovskite Solar Cell

○Masumi Saito[1], Satoshi Uchida[1], Kazuteru Nonomura[1], Ajay Kumar Jena[1], Hiroshi Segawa[1] (1. The University of Tokyo)

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[A1454-4am-09]

Enhanced Efficiency of 4-Terminal Spectral Splitting Solar Cell Utilizing Perovskite Solar Cells

○Kei Ito[1], Kazuteru Nonomura[1], Ryota Kan[1], Keishi Tada[1], Ching Chang Lin[1], Takumi Kinoshita[1], Takeru Bessho[1], Satohsi Uchida[1], Hiroshi Segawa[1] (1. The University of Tokyo)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[A1454-4am-10]

All Inorganic Perovskite Layer Formation and Surface Passivation by Bar-coating Method Assisted by Ink Additives.

○Rio Shimizu[1], Kota Haseyama[1], Kenichi Oyaizu[1], Hiroyuki Nishide[1], Takeo Suga (1. Waseda University, School of Advanced Science and Engineering)

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ヨウ素のレドックス反応を用いた水電解による選択的な気体の発生

（九大院工[1]・九大 I²CNER[2]）○甲斐 明日奈[1]・冨﨑 真衣[1]・小川 健太朗[1]・松本 広重[1, 2]

Selective Generation of Gaseous Species in Water Electrolysis Using Redox Reaction of Iodine

([1]*Graduate School of Engineering, Kyushu University*, [2]*International Institute for Carbon-Neutral Energy Research, Kyushu University*) ○Asuna Kai,[1] Mai Tomisaki,[2] Kentaro Ogawa,[1] Hiroshige Matsumoto[1, 2]

Hydrogen production by water electrolysis has been investigated aiming to achieve hydrogen energy-based society[1]. Durable separation facility is necessary to prevent low purity and explosions caused by gas mixing due to simultaneous generation of hydrogen and oxygen in water electrolysis. In this study, the redox reaction between iodide and iodate ions is combined with water electrolysis to generate hydrogen and oxygen with time lag. The redox reactions of each reactant were studied by linear sweep voltammetry. The current-voltage characteristics during electrolysis were measured, and products were analyzed by gas chromatography and liquid chromatography to investigate the selectivity and current efficiency of each product.

Water electrolysis using iodine redoxes were conducted, and the redox reactions of iodide and iodate proceeded without the generation of gas in one compartment while gaseous species generated in the other.

Keywords : Alkaline Water Electrolysis; Redox Reactions; Iodine

水素社会の実現に向け、水電解による水素製造の開発が進んでいる[1]。通常の水電解では水素と酸素が同時に発生するため、両ガスの混合による純度低下や爆発を防ぐために耐久性のある分離機構を備える必要がある。本研究ではヨウ化物イオンとヨウ素酸イオンの間のレドックス反応を水電解と組み合わせることにより、水素と酸素を時間差で発生させることを目的とした。各反応物の酸化還元反応特性をリニアスイープボルタンメトリーにより調べた。また、電解時の電流－電圧特性を測定するとともに、生成物をガスクロマトグラフィーおよび液体クロマトグラフィーにより調べ、各生成物の選択性や電流効率について検討した。

片側の電解槽にヨウ化物イオンもしくはヨウ素酸イオンを共存させることにより、条件によって気体を発生させずにヨウ素を含む化合物の酸化還元反応のみが進行し、反対側の電極においては水素もしくは酸素が発生することが判明した。



1) D. Agrawal, N. Mahajan, S. A. Singh, I. Sreedhar, *Fuel* **2024**, *359*, 130131.

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イオン液体/金属スパッタ法による Ni-Pt-Ir 複合ナノ粒子の合成と尿素酸化電極触媒活性

(名大院工[1]・阪大院工[2]) ○平出健人[1]・劉 一雄[1]・秋吉一孝[1]・桑畑 進[2]・鳥本 司[1]
Synthesis of Ni-Pt-Ir composite nanoparticles by ionic liquid/metal sputtering and their electrocatalytic activity for urea oxidation ([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Engineering, Osaka University*) ○Kento Hiraide,[1] Yixiong Liu,[1] Kazutaka Akiyoshi,[1] Susumu Kuwabata,[2] Tsukasa Torimoto[1]

Urea is a promising hydrogen carrier due to its relatively high energy density and low toxicity. Electrocatalysts showing a high activity for urea oxidation has been actively investigated for the development of efficient fuel cells. While Ni-based alloy catalysts have shown electrocatalytic activity for urea oxidation (UOR), there has been limited research on improving the activity through alloying or combining Ni with noble metals. In this study, composite nanoparticles consisting of Ni, Pt, and Ir were synthesized by simultaneous sputter deposition of corresponding metals onto ionic liquids, and their electrocatalytic activity for UOR was evaluated. Ni-Pt-Ir nanoparticles were supported on carbon black particles (CB), referred as Ni-Pt-Ir/CB. The obtained catalysts with the Ni content of < ca.20% exhibited a higher activity for UOR compared to Ni/CB , the activity being optimal for Ni-Pt-Ir/CB with 9% Ni content.
Keywords: *Composite nanoparticle; NiPtIr; Electrocatalyst; Urea oxidation reaction; Fuel cell*

尿素は無毒で安定であることから水素キャリアとしての応用が期待されている。尿素酸化に高い活性を示す電極触媒の開発が活発に行われ、Ni 系合金触媒が高い活性を示すことが報告された [1)]。これまでに私たちは、イオン液体(IL）に金属をスパッタ蒸着することで、様々な組成をもつ単分散合金ナノ粒子の合成に成功している [2)]。本研究では、Ni, Pt, Ir をイオン液体に同時スパッタ蒸着することで Ni-Pt-Ir 複合ナノ粒子を合成し、尿素酸化に対する電極触媒活性を評価した。

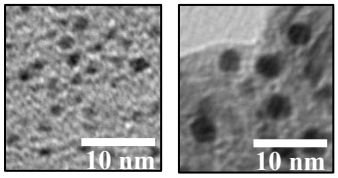

Fig. 1 TEM Images of sputter-deposited Ni-Pt-Ir NPs in IL (left) and those loaded on CB particles (right).

イオン液体に Ni-Pt-Ir 交互配列ターゲットを用いてスパッタ蒸着することで Ni-Pt-Ir ナノ粒子を合成した(Fig.1 左)。得られたナノ粒子をカーボンブラック(CB)粉末に担持することで Ni-Pt-Ir 担持 CB 触媒(Ni-Pt-Ir/CB)を得た(Fig. 1 右)。 Fig. 2 に Ni-Pt-Ir/CB と Ni/CB の尿素酸化に対する Ni ECSA あたりの比活性を示す。Ni 含有率が 30%以上の触媒粒子では、Ni/CB よりも低い活性となった。しかし Ni 含有率が約 20%以下に減少するにつれ尿素酸化活性が増大し、Ni 含有率 9 %の Ni-Pt-Ir/CB では Ni/CB 粒子に比べて 3 倍高い酸化活性を示した。

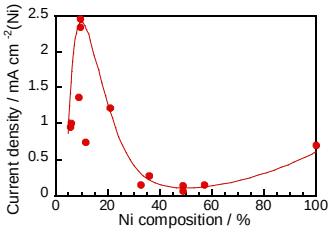

Fig. 2 Specific activity of Ni-Pt-Ir/CB for UOR as a function of the Ni fraction.

1) W. Yan, *et al*., *Electrochim. Acta*, **61**, 25 (2012). 2) M. Hirano, *et* al., *Phys. Chem. Chem. Phys.*, **15**, 7286 (2013).

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窒素及びリンドープカーボン触媒の酸素還元特性

（東京都立産業技術研究センター）○立花　直樹，並木　宏允，染川　正一
Nitrogen and phosphorus co-doped carbon as an efficient electrocatalyst for oxygen reduction reaction (*Tokyo Metropolitan Industrial Technology Research Institute*)○Naoki Tachibana, Hiromasa Namiki, Shoichi Somekawa

Metal-air batteries and fuel cells are attracting attention as next-generation power sources due to their high theoretical energy density. Recently, nitrogen- and phosphorus-doped carbons have attracted attentions as electrocatalysts for the oxygen reduction reaction at the cathodes. However, the amount of nitrogen and phosphorus doped in carbon black (CB) was limited to ~1% by a heat treatment method. In this study, CB was doped with nitrogen by a solid-gas mechanochemical reaction using a planetary ball mill, followed by a heat treatment method. The obtained nitrogen and phosphorus co-doped CB (N, P-CB) had high nitrogen and phosphorus concentrations of 1.60% and 1.91%, respectively, and large surface area of 540 $m^2 g^{-1}$. The N, P-CB showed higher oxygen reduction catalytic activity than N-doped CB and P-doped CB. The high nitrogen and phosphorus concentrations and large surface area of N, P-CB would effectively form many catalytic sites for the oxygen reduction reaction.
Keywords : Oxygen reduction; Nitrogen and phosphorus co-doped carbon; Mechanochemical method; Metal-air battery; Fuel cells

金属空気電池や燃料電池は理論エネルギー密度が極めて大きいため，次世代の電源としての応用が期待されている．近年，その正極で進行する酸素還元反応を促進する触媒として低コストな窒素やリンをドープしたカーボンが注目されているが，カーボンブラック（CB）に対して，一般的な熱処理法による窒素やリンのドープ量は 1%程に限られ，そのドープ量は満足できるものではない．本研究では CB にメカノケミカル法による窒素ドープ [1]を施した後，熱処理法によってリンをドープした (Fig. 1)．得られた窒素及びリンドープ CB（N, P-CB）の窒素，リンの濃度はそれぞれ 1.60%，1.91%と高く，微粉砕によって比表面積が約 8 倍に増加していることがわかった．この N, P-CB は窒素及びリンが高濃度かつ比表面積が大きいため，その表面に触媒サイトを多数，有効に形成することができ，窒素ドープ CB（N-CB）およびリンドープ CB（P-CB）より優れた酸素還元活性を示したと考えられる（Fig. 2）.

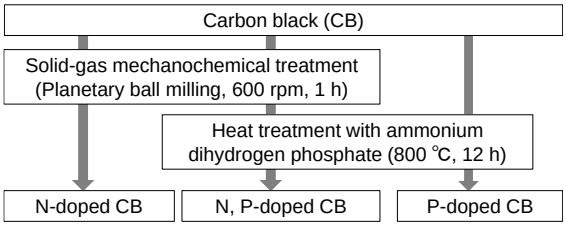

Fig. 1. Flowchart for preparation of samples.

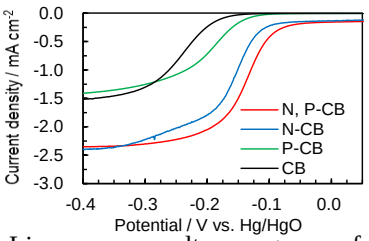

Fig. 2. Linear sweep voltammograms of samples.

1) N. Tachibana, H. Namiki, and S. Somekawa, *Electrochemistry*, **2023**, *91*, 117003.
（本研究の一部は JSPS 科研費 23K13700 の助成を受けたものです。）

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Effects of Carotenoid Coating on Chlorin-Modified Pt/TiO_2 Nanoparticles for Photocatalytic Hydrogen Evolution

([1]*Nagahama Inst. Bio-Sci. Tech.*, [2]*Jilin Univ.*, [3]*Osaka Metropolitan Univ.*) ○Shin-ichi Sasaki,[1] Yanxiang Liu,[2] Ritsuko Fujii,[3] Xiao-Feng Wang[2]

Keywords: Photocatalyst; Hydrogen Generation; Carotenoids; Chlorophylls; Titanium Oxide

Photocatalytic hydrogen production is one of the most attractive and challenging research topics in the field of artificial photosynthesis. By utilizing chlorophyll-*a* as a starting material, we have successfully developed a series of carboxylated-chlorins as organic sensitizers for inorganic Pt/TiO_2 photocatalysts [1]. Here we demonstrate a simple and effective method of coating chlorin-modified Pt/TiO_2 photocatalysts with β-carotene (**Car**) as mimicking the natural photosynthetic systems.

Chl-1~4 possessing different characteristics of C17-propionate (R in Figure 1) were adsorbed on Pt/TiO_2 nanoparticles in EtOH through C3^2-carboxy binding site. The obtained **Chls**@Pt/TiO_2 were suspended in THF solutions of **Car**, and subjected to spontaneous evaporation of the solvent to leave the **Car**@**Chls**@Pt/TiO_2 composites. The lipophilic **Car** is assumed to keep attaching to the chlorin molecules of **Chls**@Pt/TiO_2 through hydrophobic interaction in the aqueous environments and contribute to more efficient charge separation in the surface of photocatalysts. It is confirmed that the performance of **Chls**@Pt/TiO_2 can be much improved by simply adding **Car** with a facile solution evaporation method.

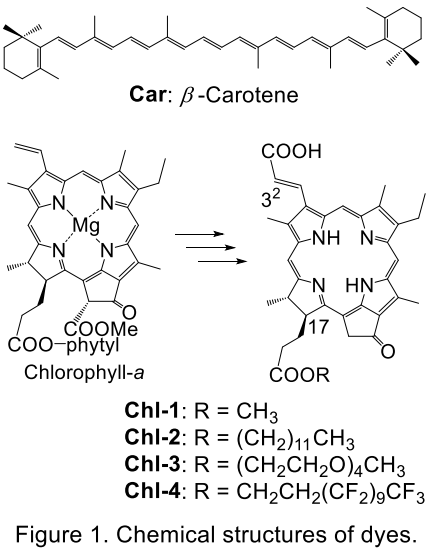

Figure 1. Chemical structures of dyes.

Table 1. Performance of (**Car**)@**Chls**@Pt/TiO_2 photocatalysts for hydrogen evolution.[a]

Chls	H_2 production (mmol h^{-1} g^{-1}) under illumination of visible light			
	$\lambda > 420$ nm		$\lambda > 600$ nm	
	without **Car**	with **Car**[b]	without **Car**	with **Car**[b]
Chl-1	17.8	31.5	3.8	10.3
Chl-2	28.1	41.7	5.3	16.9
Chl-3	10.1	20.4	1.9	9.1
Chl-4	20.5	34.7	3.9	10.8

[a]Reactions were performed in 55 mM aqueous ascorbic acid (pH = 2.8). [b]One equivalent mole of **Car** to each **Chl** was used, based on the optimization result to **Chl-2**.

1) a) Y. Sun *et al. Int. J. Hydrog. Energy* **2017**, *42*, 15731; b) Y. Sun *et al. ACS Appl. Energy Mater.* **2018**, *1*, 2813; c) Y. Liu *et al. Adv. Mater. Interfaces* **2021**, *8*, 2101303; d) T. Zheng *et al. Appl. Surf. Sci.* **2023**, *619*, 156570.

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日本化学会 第104春季年会 (2024)

近赤外応答する Ag_8GeS_6 量子ドットの液相合成とコアシェル構造形成による発光特性向上

(名大院工[1]・株式会社村田製作所[2]) ○外 昌之[1]・秋吉 一孝[1]・亀山 達矢[1]・藤平 紀一[2]・鳥本 司[1]

Preparation of Near-IR-responsive Ag-Ge-S Quantum Dots and Enhanced Photoluminescence Property through Core-Shell Structure Formation ([1]*Nagoya University*, [2]*Murata Manufacturing Co., Ltd.*) ○ Masayuki Soto,[1] Kazutaka Akiyosi,[1] Tatsuya Kameyama,[1] Norikazu Fujihira[2], Tsukasa Torimoto.[1]

Near-IR-responsive quantum dots (QDs) have been intensively investigated for developing efficient solar light conversion systems and bright luminescent probes for biological imaging. In this study, we report the solution-phase synthesis of less-toxic Ag_8GeS_6 QDs having an energy gap in the near-IR region. Ag_8GeS_6 QDs were synthesized through the thermal decomposition of silver diethyldithiocarbamate (I), germanium glycolate (IV), and thiourea in a mixture of oleylamine (OLA) and 1-dodecanethiol. The obtained QDs were spherical particles with an average diameter of 3.4 nm, the absorption onset of which was ca. 800 nm. They exhibited a broad PL peak at around 900 nm with the PL quantum yield (QY) of 2.3%. Surface coating of QDs with ZnS and InS_x shells increased the PL QYs to 6.4% and 16.7%, respectively.

Keywords *: Quantum Dot; Near-IR responsivity; Photoluminescence; Low toxicity*

量子ドット（QD）は、数 nm の半導体ナノ粒子からなる材料であり、バルクと異なる光化学特性を示す。近年、高効率な太陽光変換系の開発や新規生体イメージング材料開発のために、近赤外領域で応答を示す QD の開発が活発に行われている。本研究では、低毒性元素からなる Ag_8GeS_6 ナノ粒子に着目し、その液相化学合成と、コアシェル構造化による発光特性向上を目指した。

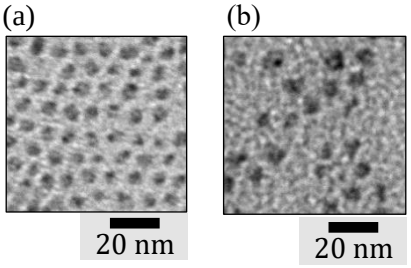

Fig. 1 TEM images of (a)Ag_8GeS_6 and (b)Ag_8GeS_6@InS_x QDs.

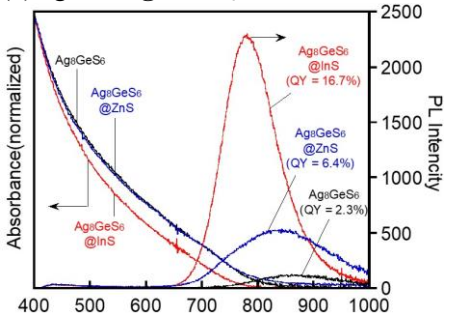

Fig. 2 Absorption and PL spectra of the QDs.

ジエチルジチオカルバミン酸銀(Ⅰ)、グリコール酸ゲルマニウム(Ⅳ)、チオ尿素を前駆体として、オレイルアミン(OLA)と 1-ドデカンチオールの混合溶媒中、窒素雰囲気下 150℃で熱分解することで Ag_8GeS_6 ナノ粒子を合成した。得られたナノ粒子は Fig. 1 のように球状粒子であり、その平均粒径は 3.4 nm であった。Ag_8GeS_6 ナノ粒子は、吸収端を近赤外領域の 800 nm にもち、そのエネルギーギャップは 1.55 eV と見積もられた。この Ag_8GeS_6 粒子は、700-900 nm にブロードな発光（PL）を示し、その発光量子収率（PLQY）は 2.3%だった。このナノ粒子表面を ZnS あるいは InS_x で被覆してコアシェル構造とすると、PLQY はそれぞれ 6.4%あるいは 16.7%へと大きく増大した。これは、表面に存在する無輻射失活サイトがシェル被覆によって除去されたためである。

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銀ナノアレイの集積構造制御と固体系可視—紫外フォトン・アップコンバージョンへの応用

（九大院工[1]・九大 CMS[2]・九大 K-NETs[3]・九大 WPI-I^{2}CNER[4]）○澤田 侑星[1]・松本 昂大[1]・渡辺 侑哉[1]・佐々木 陽一[1,2]・藤川 茂紀[1,2,3,4]・君塚 信夫[1,2,3]

Controlling the nano-structure in silver nanoarrays for solid-state Vis-to-UV photon upconversion ([1]*Graduate School of Engineering, Kyushu University*, [2]*CMS Kyushu University,* [3]*K-NETs Kyushu University,* [4]*WPI-I^{2}CNER Kyushu University*) ○ Yusei Sawada[1], Kodai Matsumoto[1], Yuya Watanabe[1], Yoichi Sasaki[1,2], Shigenori Fujikawa[1,2,3,4], Nobuo Kimizuka[1,2,3]

Triplet-triplet annihilation-based photon upconversion (TTA-UC) is a methodology that converts low-energy light into high-energy light. However, the excitation light intensity required to maximize efficiency in solid-state UC materials remains high. To solve this problem, we focused on the enhancement effect of silver nanoparticle's localized surface plasmon resonance (LSPR) by making nano-gapped arrays (NPAs). This enhancement becomes significant in densely aligned nano-gapped arrays, and up to a 10^6-fold stronger electric field has been expected. Here, we developed high-density silver NPAs with controlled gaps to realize highly efficient solid-state visible-to-ultraviolet TTA-UC under low excitation intensity.

When a triplet donor molecule $Ir(ppy)_3$ was evaporated on a quartz substrate with silver NPAs, we observed a 19-fold enhancement of the phosphorescence compared with the one without NPAs. This suggests that LSPR enhanced the excitation light intensity, and the amount of light absorbed by the donor molecule increased. In the presentation, we will discuss UC properties of the donor-acceptor-silver NPAs hybrids.

Keywords : Photon Upconversion; Triplet-Triplet Annihilation; Vis-to-UV UC; Localized Surface Plasmon Resonance; Silver Nanoparticles

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) は太陽光程度の弱い光で低エネルギー光を高エネルギー光に変換可能な方法論である。しかし、実用化に適する固体 UC 材料においては、効率を最大化するために必要な励起光強度が依然として高い[1]。そこで我々は、局所的な光強度を増強できる局在表面プラズモン共鳴 (LSPR) に着目した。これは、自由電子の集団的振動によって粒子近傍の光強度が増大する現象であり、粒子間の間隔を nm オーダーにまで狭くすることによって、最大で 10^6 倍もの光増強が期待できる[2]。本研究では、高密度な銀ナノ粒子アレイの作製ならびに、銀ナノ粒子アレイ(AgNPA)上に UC 分子を修飾した系を構築することによって 、低強度励起光条件下における固体系可視-紫外 TTA-UC の実現を目指した。

石英基板上にドナー分子である $Ir(ppy)_3$ を蒸着し、りん光を測定したところ AgNPA により発光強度が 19 倍増大した (Fig. 1)。これは LSPR による局所的な励起光強度の増強を示唆している。当日は TTA-UC 特性について報告する予定である。

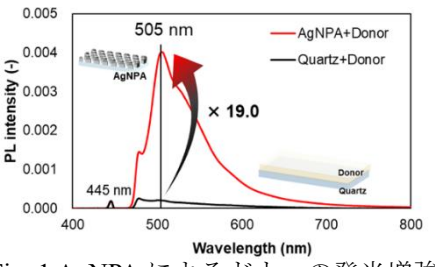

Fig. 1 AgNPA によるドナーの発光増強

1) V. Gray et al. *Coord. Chem. Rev.*, **2018**, 362, 54-71
2) B. sun et al. *Adv. Funct. Mater*., **2019**, 29, 26, 1900541

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ロダニン誘導体を単分子電子回収材料として用いたペロブスカイト太陽電池の特性評価

（京大化研）○三宅 悠季・中村 智也・Minh Anh Truong・Richard Murdey・若宮 淳志

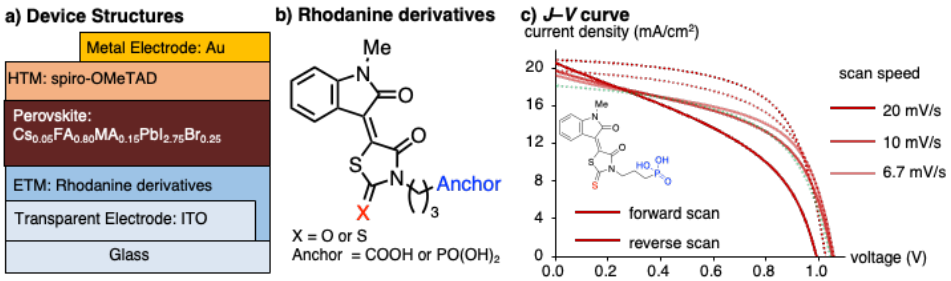
Perovskite Solar cells Using Rhodanine Derivatives as Electron Collecting Monolayers

(*Institute for Chemical Research, Kyoto University*)
○Yuki Miyake, Tomoya Nakamura, Minh Anh Truong, Richard Murdey, Atsushi Wakamiya

The development of efficient charge collecting materials are crucial for improving the performance of perovskite solar cells. Recently, charge collecting materials used as adsorbed monolayers have been reported to give high efficiency and stability of PSCs.[1] A series of rhodanine derivatives with various anchoring units for ITO substrates were synthesized as the electron collecting monolayer materials for perovskite solar cells. Perovskite solar cells with these rhodanine derivatives showed 8% PCE. We also found that by reducing the scan speed in *J-V* measurement, the open-circuit voltage and fill factor got larger, and PSCs showed 11.2% PCE with the lower hysteresis. In this presentation, the characterization of perovskite solar cells will be discussed.

Keywords : Perovskite solar cells; Monolayer; Electron collecting materials; n-Type organic semiconductor

ペロブスカイト太陽電池の高性能化には、光吸収によりペロブスカイト層で生成した電荷を効率的に取り出す電荷回収材料の開発が重要である。近年、単分子膜として用いる電荷回収材料が高い効率と安定性を示すペロブスカイト太陽電池を与え、注目されている[1)]。本研究ではペロブスカイト太陽電池の単分子電子回収材料として、ITO基板への吸着基と電子構造の異なる一連のロダニン誘導体を合成した（図b）。これらのロダニン誘導体を単分子電子回収材料として用いたペロブスカイト太陽電池では、8%程度の光電変換効率が得られた。電流−電圧測定において、掃引速度を20 mV/sから6.7 mV/sまで小さくすることで、開放電圧と曲線因子が向上し、ヒステリシスが解消されることを見出した（図c）。本発表では、ペロブスカイト太陽電池の特性評価について報告する。



1) A. Magomedov, A. A.-Ashouri, E.Kasparavičius, S. Strazdaite, G. Niaura, M. Jošt, T. Malinauska, S. Albrecht and V. Getautis, *Adv. Energy Mater.*, **2018**, *8*, 1801892.

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ペロブスカイト太陽電池におけるヒステリシスとキャパシタンスの関係

（東京大学 [1]）○齊藤 眞珠美 [1]・内田 聡 [1]・野々村 一輝 [1]・Ajay Jena[1]・瀬川 浩司 [1]
Relationship between hysteresis and capacitance in Organic Lead Halide Perovskite Solar Cell ([1]The University of Tokyo)○Masumi Saito,[1] Satoshi Uchida, [1] Kazuteru Nonomura,[1] Ajay Kumar Jena,[1] Hiroshi Segawa[1]

Perovskite solar cells, which have garnered attention in recent years, exhibit hysteresis in current-potential measurements. The primary cause of this hysteresis is believed to be the capacitance between the layers. In this study, we investigated the relationship between hysteresis and capacitance, focusing specifically on the perovskite layer.

We measured the current potential of perovskite solar cell devices with various types of perovskite layers and expressed the hysteresis as a hysteresis coefficient. The results confirmed that capacitance generally increases when hysteresis is large. During this investigation, we measured the dielectric constant of MAPI and found it to be 6.13×10^{-5}. Based on this value, we calculated the capacitance of the device, which was determined to be 20mF. This result was consistent with the device capacitance value determined by the DC method.
Keywords : Perovskites, Solar cells, Permittivity, Hysteresis

近年注目されているペロブスカイト太陽電池は、電流電位測定においてヒステリシスが発生しやすく、このヒステリシスの主要因は層間にあるキャパシタンスが原因であると考えられている。本研究では、このヒステリシスとキャパシタンスに焦点を当て、双方の関係性を考察し、またペロブスカイト層のみに注目した時の誘電率の計測を行っている。

各種類のペロブスカイト層を持つペロブスカイト太陽電池デバイスの電流電位測定を行い、そのヒステリシスをヒステリシス係数として表すと、ヒステリシスが大きい時概ねキャパシタンスが大きくなることが確認された。また、この時 MAPI の誘電率を測定した所、6.13×10^{-5} となり、これをもとに計算でデバイスのキャパシタンスを求めた所、20mF となった。この値は DC 法で求めたデバイスのキャパシタンスの値と殆ど変わらないことが確認された。

1) L. Cojocaru, S. Uchida, V. V. J. Piyankarage, S. Kaneko, J. Nakazaki, T. Kubo and H. Segawa, Chemistry Letters **2015**, 44(12), 1750-1752.
2) L. Cojocaru, S. Uchida, P.V.V. Jayaweera, S. Kaneko, J. Nakazaki, T. Kubo and H. Segawa, Scientific Reports **2017**, 7, 11790.
3) L. Cojocaru, S. Uchida, P.V.V. Jayaweera, S. Kaneko, Y. Toyoshima, J. Nakazaki, T. Kubo and H. Segawa, Applied Physics Express **2017**, 10(2), 025701.
4) T.W. Kim, M. Kim, L. Cojocaru, S. Uchida and H. Segawa, ACS Energy Letters **2018**, 3, 2743–2749.

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ペロブスカイト太陽電池を用いた 4 端子分光タンデム太陽電池の高効率化

（東大院工[1]・東大院総合文化[2]・東大先端研[3]）○伊藤 蛍[1]・野々村 一輝[2]・菅 亮太[2]・多田 圭志[2]・林 京璋[2]・木下 卓巳[2]・別所 毅隆[3]・内田 聡[3]・瀬川 浩司[1,2,3]

Enhanced Efficiency of 4-Terminal Spectral Splitting Solar Cell Utilizing Perovskite Solar Cells ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Arts and Sciences, The University of Tokyo,* [3]*Resrach Center for Advanced Science and Technology, The University of Tokyo*) ○Kei Ito,[1] Kazuteru Nonomura,[2] Ryota Kan,[2] Keishi Tada,[2] Ching Chang Lin,[2] Takumi Kinoshita[2], Takeru Bessho[3], Satoshi Uchida[3], Hiroshi Segawa[1,2,3]

The research investigates the bandgap-tunable perovskite solar cell (PSC) and its potential application in a multi-junction solar cell comprising several cells with varying bandgaps, aiming to surpass the S-Q limit. The study primarily focuses on manipulating the composition of organometal halide perovskite to develop two distinct PSCs, each with a different spectral response wavelength range. Finally, the research assembles a spectroscopic double junction solar cell using these two PSC types: one is a mesoscopic wide-bandgap PSC, and the other is an inverted narrow-bandgap PSC. This design effectively divides incident light into long and short wavelength sides using a dichroic mirror, with the goal of enhancing power conversion efficiency.

Keywords : Perovskite Solar Cell; Tandem; Spectral Split

有機金属ハライドペロブスカイト太陽電池（PSC）は、組成によってバンドギャップの幅広い調整が可能である。ここ数年、これらの PSC は、単接合太陽電池のエネルギー変換効率の理論限界（S-Q リミット）を超えるために、異なるバンドギャップを有するセルを積層した「多接合太陽電池」に応用されてきた。特に 2 接合太陽電池では、ワイドギャップを有するペロブスカイト（PVK）がトップセルに用いられ、一方、ボトムセルにはナローギャップを有する PVK が使用される。しかし、前者は Pb-PVK を用いた「順構造型」の、後者は Sn-Pb 混合 PVK を用いた「逆構造型」の性能が高く、製造工程上これらを組み合わせることが困難であった。本研究では、トップセルとボトムセルの構造に依存しない、疑似太陽光を長波長側と短波長側に波長分割する手法を採用し、順構造型 Pb-PSC と逆構造型 Sn-Pb PSC を組み合わせた 4 端子分光タンデム太陽電池の作製に取り組んだ。入射光は 775 nm と 801 nm で分光され、801 nm の分光により、トップセルでは 20.6%、ボトムセルで 4.71%の光電変換効率（PCE）が得られ、4 端子太陽電池としては 25.3%の PCE が得られた。これは、先行研究で逆構造型 PSC を使用した 4 端子分光タンデム太陽電池の PCE である 23.26%[2)]よりも高く、今後 2 接合 2 端子ペロブスカイト太陽電池においても、順構造型 PSC と逆構造型 PSC を組み合わせる重要性が示唆された。

1) K. Ito., et al., ACS Omega, **2023**, https://pubs.acs.org/doi/10.1021/acsomega.3c09654.
2) Y. Yao., et al., Sol. RRL, **2020**, 4, 1900396.

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日本化学会 第104春季年会 (2024)

バーコート塗布による全無機ペロブスカイト層の形成とインク添加剤による表面改質効果

（早大理工）〇志水 利緒・長谷山 航大・小柳津 研一・西出 宏之・須賀 健雄

All Inorganic Perovskite Layer Formation and Surface Passivation by Bar-coating Method Assisted by Ink Additives. (*Dept. of Applied Chem., Waseda University*) 〇Shimizu Rio, Kota Haseyama, Kenichi Oyaizu, Hiroyuki Nishide, Takeo Suga

Recent research focus has been paid to develop fabrication processes suitable for large-area perovskite solar cells for practical applications. Here we investigate ammonium salts with different alkyl chain lengths as a surfactant additive to improve perovskite crystal formation. The alignment characteristics were improved by applying the additive to the precursor solution. Bar-coating process enabled the formation of thick perovskite layer (~700 nm), which also enhanced the cell performance.

Keywords : Perovskite Solar Cell; Wide Band-gap; Surface Passivation; Bar-coating

ペロブスカイト太陽電池の実用化に向け、大面積化に適した作製プロセスの確立が求められるが、バーコート法によるペロブスカイト層の形成では大面積化に伴う平滑性の低下に課題が残る。有機無機ハイブリッドペロブスカイト層では界面活性剤の添加による層表面の平滑性向上と、質高いペロブスカイト層の析出形成が報告されている [1]。本研究では、バーコート法を適用した全無機(セシウム鉛ハライド)ペロブスカイトを対象に、アルキル側鎖の異なるアンモニウム塩の界面活性効果を期待し、ペロブスカイト前駆体溶液へ添加、界面活性効果および表面改質効果による光電変換特性の向上を目的とした。また、添加したアルキルアンモニウム塩と同じ側鎖長を持つポリ(3-アルキルチオフェン)をホール輸送層として素子を作製した。

多孔質酸化チタン層上にバーコート法によりアルキル鎖長の異なる各アルキルアンモニウム塩を添加したペロブスカイト前駆体溶液を塗布・製膜、2 段階加熱法により膜厚 700 nm のペロブスカイト層を質高く形成できた(Figure 1)。界面活性剤の添加によりペロブスカイト層のモルフォロジーが向上した。変換効率は約 12%で歩留まりよく平均値が上昇し、ペロブスカイト層/正孔輸送層界面の正孔抽出能も向上した。

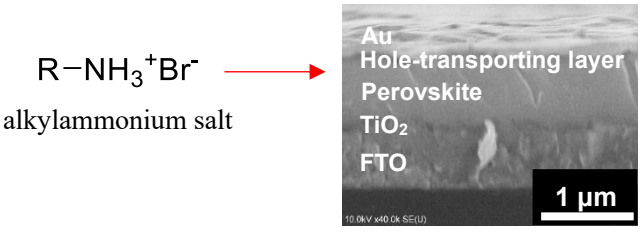

Figure 1 Cross-sectional SEM image of the perovskite solar cell.

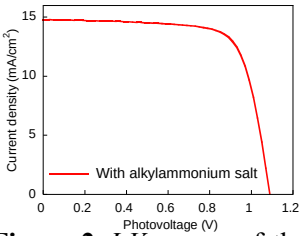

Figure 2 *J-V* curves of the perovskite solar cell.

1) J. Huang *et al.*, *Nature Energy*, **2018**, 560-566.

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Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral A

Thu. Mar 21, 2024 1:00 PM - 3:10 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:10 AM UTC A1455(1455, Bldg. 14 [5F])

[A1455-4pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Atsushi Sakuda, Yuko Takeoka

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1455-4pm-01]
Preparation of crosslinked bis(benzoquinones) and their evaluation as active cathode materials of lithium ion batteries

Tsumugi Inaba[1], Kobayashi Aoi[1], Takato Yokoji[1], Yao Masaru[2], ○Hiroshi Matsubara[1] (1. Osaka Metropolitan University, 2. AIST)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1455-4pm-02]
Synthesis of naphthoquinone dimers and their application to lithium-ion batteries

○Tsumugi Inaba[1], Hiroshi Matsubara[1], Masaru Yao[2] (1. Osaka Metropolitan University, 2. AIST)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1455-4pm-03]
Aqueous solution synthesis of Li_4SnS_4 electrolytes and its application to NMC composite positive electrode

○Takashi Hashii[1], Hayata Tanigaki[1], Takuya Kimura[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1455-4pm-04]
Synthesis of Na_5FeS_4 positive electrode active material via sodium polysulfides

○Yuta Doi[1], Tomoya Otono[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1455-4pm-05]
Preparation of amorphous MoS_4 through thermal decomposition for positive electrode active materials in all-solid-state batteries

○Keitaro Imai[1], Tatsuki Shigedomi[1], Tomohiro Furukawa[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1455-4pm-06]
Mechanochemical synthesis of solid electrolytes in the system Li_2S–P_2S_5–AlF_3.

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○Sotaro Sato[1], Taichi Asakura[1], Hiroe Kowada[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

Japanese

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[A1455-4pm-07]

Mechanochemical synthesis of solid electrolytes in the system $NaTaCl_6$-NaCl

○Kenta Koga[1], Eiji Kurioka[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[A1455-4pm-08]

Ionic conduction properties of $La_{0.9}Ba_{0.1}F_{2.9}B_2O_3$ composite

○Shinsuke Toyoda[1], Yuki Hayashi[1], Kota Motohashi[1], Atsushi Sakuda[1], Akitoshi Hayashi[1] (1. Osaka Metropolitan University)

Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[A1455-4pm-09]

Development of Lithium-ion Conductors Using Ionic Plastic Crystals (I) -Effect of Li-salt Concentration on Ionic Conductivity-

○Hiroki Obuchi[1], Takuto Ootahara[1], Shuho Akakabe[1], Yuko Takeoka[1], Masahiro Rikukawa[1], Masahiro Fujita[1] (1. Sophia Univ.)

Japanese

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[A1455-4pm-10]

Development of Na-ion Conductors Using Ionic Plastic Crystals (I) -Evaluation of Pyrrolidinium-salt/Na-salt composites

○Yoshifumi Hirotsu[1], Ootahara Takuto[1], Akakabe Shuho[1], Fujita Masahiro[1], Rikukawa Masahiro[1], Takeoka Yuko[1] (1. Sophia University)

Japanese

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[A1455-4pm-11]

Preparation and evaluation of Na-ion conductors using zwitterionic polymers (I) -Preparation of ion gels-

○Rei Doai[1], Masaya Sato[1], Mina Yamaguchi[1], Masahiro Rikukawa[1], Masahiro Fujita[1], Yuko Takeoka[1] (1. Sophia University)

Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[A1455-4pm-12]

Electrochemical characteristics of supercapacitors using anion-conducting polymer electrolyte membranes

○Yusuke Inawashiro[1], Takahumi Uchino[1], Junji Inukai[1], Kenji Miyatake[1], Shinji Nohara[1] (1. Univ. of Yamanashi)

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架橋ビスベンゾキノン類の合成と正極活物質としての評価

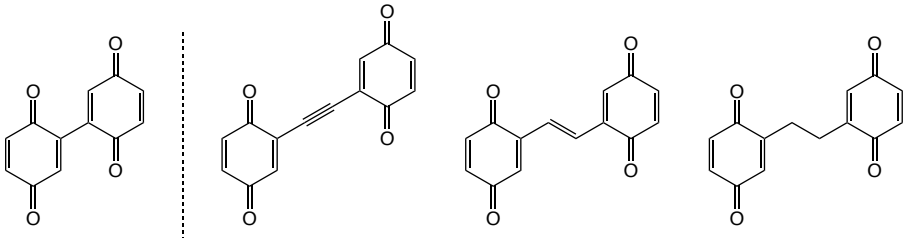
（阪公大院理[1]・産総研[2]）稲葉 紬[1]・小林 蒼[1]・横地 崇人[1]・八尾 勝[2]・○松原 浩[1]
Preparation of crosslinked bis(benzoquinones) and their evaluation as cathode active materials of lithium ion batteries ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*National Institute of Advanced Industrial Science and Technology, AIST*) Tsumugi Inaba,[1] Aoi Kobayashi,[1] Takato Yokoji,[1] Masaru Yao,[2] ○Hiroshi Matsubara[1]

As portable information devices and electrical vehicles continue to evolve, rechargeable lithium-ion batteries (LIBs) with high performance are required. Inorganic cathode active materials (CAMs) composed of heavy metals such as $LiCoO_2$ are currently used in LIBs. On the other hand, organic materials consisting of lighter elements have been considers to be attractive as CAM alternatives, because of their high mass energy density, low cost, environmental compatibility, and safety advantages. We have prepared and evaluated benzoquinone derivatives (BQs) as CAMs for use in LIBs, and showed that BQ dimers (BBQs)[1] are particularly interesting CAM candidates.

In this presentation, we report on the preparation of several benzoquinone dimers with various crosslinkers, and evaluation of these compounds as CAMs for use in LIBs. Some of the prepared compounds are shown in the following figure.

Keywords : Lithium Ion Battery; Benzoquinone; Cathode Active Material

携帯端末や EV の急速な発展に伴い、高性能のリチウムイオン二次電池（LIB）が求められている。現在普及している LIB はコバルト酸リチウムなど重金属を正極活物質に用いているが、軽元素から構成される有機化合物が正極活物質の代替候補として注目される。我々は 2 電子授受が可能であるベンゾキノン（BQ）に注目し、その誘導体について LIB 正極活物質として評価を行ってきた。その中で、p-BQ 二量体（BBQ）が正極活物質として優れていることを見出した[1]。今回、エチレンやアセチレンなど種々の架橋鎖で p-BQ を連結した化合物を合成し、正極活物質としての性能を評価した。合成した活物質例を以下に示す。



[1] Y. Yokoji, Y. Kameyama, N. Maruyama, H. Matsubara, "High-capacity organic cathode active materials of 2,2'-bis-p-benzoquinone derivatives for rechargeable batteries", *J. Mater. Chem. A* **2016**, *4*, 5457–5466.

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ナフトキノンダイマー類の合成とリチウムイオン二次電池への応用

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Synthesis of naphthoquinone dimers and their application to lithium-ion batteries ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*National Institute of Advanced Industrial Science and Technology, AIST*) ○Tsumugi Inaba,[1] Masaru Yao,[2] Hiroshi Matsubara[1]

Lithium-ion batteries have been widely used in smartphones and laptops. To achieve a higher battery capacity, the use of redox-active organic compounds as cathode active materials (CAMs) is garnering attention because of their advantages in terms of abundant raw materials, high theoretical capacities, and flexible molecular designability. As benzoquinone (BQ) has a high theoretical capacity of 496 mAh/g, BQ is suitable for CAMs. However, because of its high solubility in organic electrolyte solutions, the capacity retention of BQ during cycling is low. Therefore, developing benzoquinone derivatives with low solubility is required.

In this study, we prepared three types of naphthoquinone dimers (Figure 1) and evaluated their battery performance. Among three compounds, orthoquinones exhibited higher discharge voltages than paraquinones. In addition, quinones with more rings exhibited better cycle stabilities.

Keywords : lithium ion battery, naphthoquinone, cathode active material

リチウムイオン二次電池はスマートフォンやノートパソコンなどに利用されており、その需要はますます高まっている。さらなる高容量化に向けて、豊富な原材料、高い理論容量、柔軟な構造設計性などの利点から正極材料として酸化還元活性な有機化合物の利用が注目されている。例えばベンゾキノン（BQ）の理論容量は 496 mAh/g と高容量であるため有用性が期待される一方、電解液への溶出により容量維持率については問題がある。そのため、溶解性が低い BQ 誘導体を合成する必要がある。

我々は BQ より分子量の大きいナフトキノンを二量化した骨格を有する３つの有機化合物を合成し（Figure 1）、これらの活物質を用いてコイン型リチウムイオン電池を作製して性能評価を行った。その結果、オルトキノン類はパラキノンよりも高い出力電位を示した。一方、サイクル特性については、より多環構造であるキノンの方が優れた結果を示した。

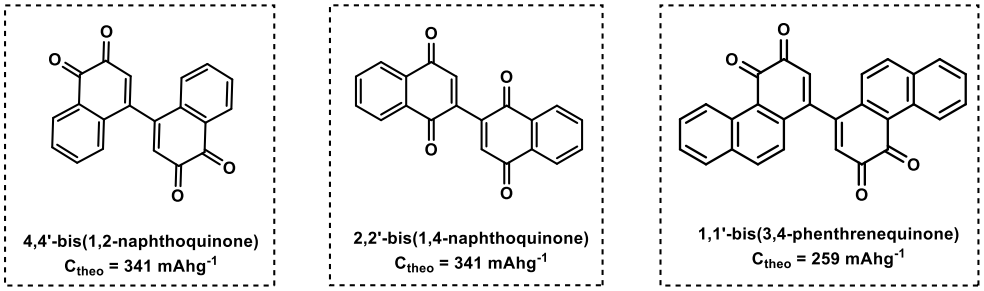

Figure 1

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Li_4SnS_4 電解質の水溶液合成と NMC 正極複合体への適用

（大阪公立大学）○橋井 貴士・谷垣 隼大・木村 拓哉・本橋 宏大・作田 敦・林 晃敏

Aqueous solution synthesis of Li_4SnS_4 electrolyte and its application to NMC composite positive electrode

(*Osaka Metropolitan University*) ○Takashi Hashii, Hayata Tanigaki, Takuya Kimura, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

All-solid-state batteries with solid electrolytes are expected to be the next-generation batteries for their high safety and high-energy densities. Hexagonal Li_4SnS_4 electrolytes exhibit a conductivity of 1.1×10^{-4} S cm^{-1} at room temperature[1] and form hydrates when exposed to humid atmosphere.[2] Liquid-phase syntheses have attracted attention for large-scale production of solid electrolytes. In this study, the Li_4SnS_4 solid electrolyte was synthesized by liquid-phase reaction using water as a reaction media, and then it was applied to $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) composite positive electrode. Li_2S, Sn, and S were mixed in de-ionized water and stirred at 80°C for 24 hours. The aqueous solution was dried at 150°C for 3 hours to obtain the powder sample. The composite positive electrode was prepared by mixing the Li_4SnS_4 and $LiNbO_3$-coated NMC powders using a mortar. The all-solid-state cells using the prepared composite electrode exhibited an initial discharge capacity of 134 mAh g^{-1} and operated as a secondary battery.

Keywords : All-solid-state battery; Lithium-ion battery; Solid electrolyte

固体電解質を用いた全固体電池は、高い安全性・エネルギー密度から次世代電池として期待されている。固体電解質として、硫化物系材料は優れたイオン伝導性と成形性を示すことが知られている。中でも、Li_4SnS_4 電解質は、室温で 1.1×10^{-4} S cm^{-1} の導電率を示し[1]、水分を含む大気に曝した際にも水和物を形成して安定化することが報告されている[2]。固体電解質の合成プロセスとしては、量産化に適した液相法が注目されている。

本研究では、水を反応媒に使用した Li_4SnS_4 電解質の液相合成を行い、得られた電解質を $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) 正極複合体へ適用した。

出発原料である Li_2S と Sn、S を所定の組成比となるように秤量した後、イオン交換水を加え 80℃で 24 時間攪拌した。その後、水溶液を 150℃で 3 時間真空熱乾燥することで粉末試料を作製した。得られた試料と NMC を乳鉢混合することで、正極複合体を作製した。Fig. 1 に、作製した正極複合体を用いた全固体セル (Li-In / Li_3PS_4 / NMC-Li_4SnS_4) の充放電曲線を示す。このセルは 134 mAh g^{-1} の初期放電容量を示し、繰り返し充放電が可能であった。

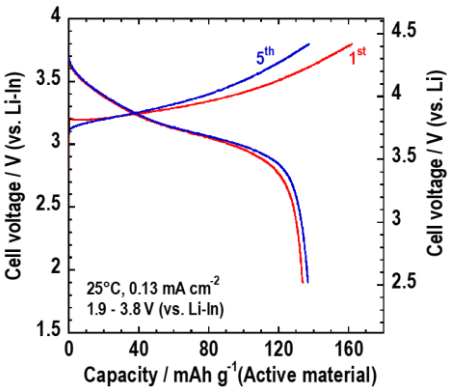

Fig. 1 Charge-discharge curves of an all-solid-state cell using the composite positive electrode composed of the prepared Li_4SnS_4 and NMC.

1) K. Kanazawa *et al.*, *Inorg. Chem.*, **57** (2018) 9925.
2) T. Kimura *et al.*, *J. Phys. Chem. C*, **127** (2023) 1303.

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多硫化ナトリウムを介した Na_5FeS_4 正極活物質の合成

（大阪公立大学）○土居 勇太・音野 智哉・本橋 宏大・作田 敦・林 晃敏

Synthesis of Na_5FeS_4 positive electrode active material via sodium polysulfides (*Graduate School of Engineering, Osaka Metropolitan University*) ○Yuta Doi, Tomoya Otono, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

All-solid-state sodium secondary batteries are promising next-generation batteries because of the high safety and low cost. Sodium iron sulfides, which are inexpensive and have low toxicity, are attracting attention as positive electrode active materials. We have reported that all-solid-state sodium batteries using Na_2FeS_2 as positive electrode active materials stably operated for long cycles. We have found that a variety of sulfide materials can be synthesized by an ambient pressure heat treatment via sodium polysulfides, which have a relatively high boiling point.

In this study, a positive electrode active material of Na_5FeS_4 was prepared by heat treatment of Na_2S, Fe, and S, and subsequent quenching. XRD measurement revealed that Na_5FeS_4 was obtained. All-solid-state cells using Na_5FeS_4 exhibited a high reversible capacity of 480 mAh g^{-1}.

Keywords : All-solid-state sodium battery; Positive electrode active material; Transition metal sulfide

全固体ナトリウム二次電池は、高い安全性と低コスト化が可能な次世代電池として期待されている。その正極材料として安価で毒性の低いナトリウム鉄硫化物が注目されている。我々は、Na_2FeS_2 正極活物質を用いた全固体ナトリウム二次電池が長期間安定に作動することを報告した。[1] また、硫化物の合成において、比較的沸点の高い多硫化ナトリウムを介することで、高温での硫黄の揮発を抑制でき、非密閉系での熱処理により様々なナトリウム含有硫化物材料を合成できることを見出した。[2] 本研究では、充放電容量の増加を期待し、ナトリウムリッチな組成である Na_5FeS_4 に着目し、多硫化ナトリウムを介した手法により合成した。

Na_2S、Fe、S の混合物を、カーボンるつぼを用いて常圧の Ar 雰囲気中で 700 ºC、10 h 溶融し、アイロンプレス急冷することで Na_5FeS_4 正極活物質を作製した。X 線回折測定において、Na_5FeS_4 の回折パターンを確認した。直流分極法により測定した Na_5FeS_4 の電子伝導度及びイオン伝導度はそれぞれ、6.6×10^{-7} S cm^{-1}、1.3×10^{-6} S cm^{-1} であった。Fig. 1 に Na_5FeS_4 正極活物質を用いて作製した全固体電池 (Na-Sn / Na_3PS_4 / Na_5FeS_4) の充放電曲線を示す。作製した電池は、室温において約 480 mAh g^{-1} の高い容量で、繰り返し充放電が可能であった。

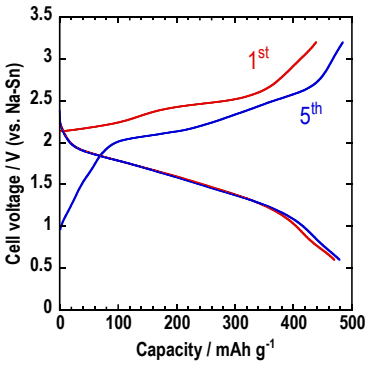

Fig. 1 Charge-discharge curves of all-solid-state cell (Na-Sn / Na_3PS_4 / Na_5FeS_4) at 25 ºC under the current density of 0.13 mA cm^{-2}.

1) A. Nasu *et al.*, *Small*, **18** (2022) 2203383.
2) 音野 智哉ら, 第 63 回電池討論会, 1C03 (2022).

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熱分解法を用いた非晶質 MoS_4 の作製と全固体電池用正極への応用

(大阪公立大学) ○今井 奎太朗・重冨 竜輝・古川 奉寛・本橋 宏大・作田 敦・林 晃敏

Preparation of amorphous MoS_4 through thermal decomposition for positive electrode active materials in all-solid-state batteries

(*Osaka Metropolitan University*) ○Keitaro Imai, Tatsuki Shigedomi, Tomohiro Furukawa, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

All-solid-state lithium batteries have attracted attention in terms of safety and reliability. High-capacity positive electrodes are required to realize all-solid-state lithium batteries with high-energy densities. Amorphous transition metal polysulfides such as TiS_3[1] and NbS_x[2] are considered as promising positive electrode materials due to their high electronic conductivity and capacity. Among them, amorphous molybdenum trisulfide (a-MoS_3) electrodes exhibited a high specific capacity[3].

In this study, a-MoS_4 samples were prepared by thermal decomposition of $(NH_4)_2[Mo_3S(S_2)_6]\cdot H_2O$ at 340 ºC. Broad XRD peaks with low intensities were observed for a-MoS_4. The electronic conductivities of a-MoS_4 measured by DC polarization were 5.0×10^{-4} S cm^{-1} at room temperature. All-solid-state lithium cells using a-MoS_4 exhibited high reversible capacities of 460 mAh g^{-1} for 150 cycles, and the capacity retention of 99.6%.

Keywords : All-solid-state battery; Lithium battery; Positive electrode active material; Transition metal sulfide; Thermal decomposition

全固体リチウム電池は安全性・信頼性の観点から注目されているが、高エネルギー密度化に向けて、高容量の正極活物質の開発が求められている。TiS_3[1]や NbS_x[2]などの非晶質遷移金属多硫化物は比較的高い導電性に加え、高い硫黄含量のため、高容量かつ高導電性の正極活物質として期待されている。中でも、非晶質 MoS_3 (a-MoS_3) を正極に適用した全固体電池は高容量を示す[3]。

本研究では、より硫黄含有量の多い a-MoS_4 を全固体リチウム電池の正極活物質として評価した。a-MoS_4 は $(NH_4)_2[Mo_3S(S_2)_6]\cdot H_2O$ を 340 ºC で 14 時間、Ar 雰囲気で熱処理することにより作製した。XRD 測定の結果、ハローパターンが観測され、a-MoS_4 は非晶質であることが示された。直流分極法により算出した電子伝導度は 5.0×10^{-4} S cm^{-1} であった。Fig. 1 に a-MoS_4 を正極活物質として用いた全固体リチウム電池 (Li-In / Li_3PS_4 glass / a-MoS_4) のサイクル特性を示す。この電池は、室温で 150 サイクルの間安定に作動し、460 mAh g^{-1} の高い可逆容量と 99.6%の容量維持率を示した。

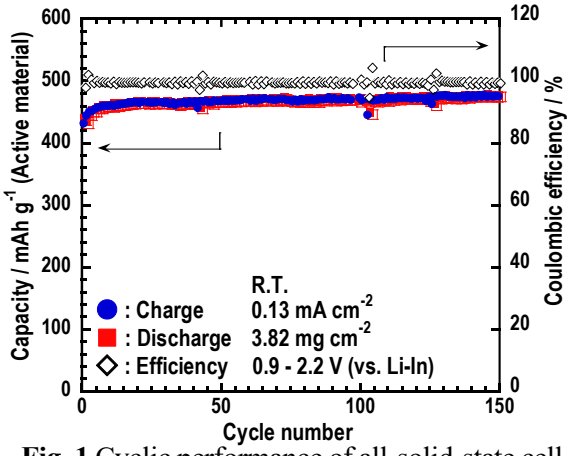

Fig. 1 Cyclic performance of all-solid-state cell (Li-In / Li_3PS_4 glass / a-MoS_4).

1) A. Hayashi *et al.*, *Chem. Lett.*, **41** (2012) 886.

2) A. Sakuda *et al.*, *ECS Electrochem. Lett.*, **3** (2014) A79.

3) T. Matsuyama *et al.*, *J. Mater. Chem. A*, **3** (2015) 14142.

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メカノケミカル法を用いた $Li_2S–P_2S_5–AlF_3$ 系固体電解質の作製

（大阪公立大）○佐藤 宗太朗・朝倉 大智・小和田 弘枝・本橋　宏大・作田 敦・林 晃敏

Mechanochemical synthesis of solid electrolytes in the system $Li_2S–P_2S_5–AlF_3$.

(*Osaka Metropolitan University*) ○Sotaro Sato, Taichi Asakura, Hiroe Kowada, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

All-solid-state batteries are expected to be the next-generation batteries with high safety because of the use of non-flammable inorganic solid electrolytes. Sulfide glass electrolytes in the system $Li_2S–P_2S_5$ have attracted attention due to their high conductivities and excellent formabilities. However, their reduced compounds generated by reacting with Li negative electrode are a problem because it leads to short-circuiting. In this study, we focused on fluorine-doping to sulfide electrolytes. Fluorine-doping has a possibility to improve the reduction tolerance of sulfide electrolytes. The glass electrolytes in the ternary system $Li_2S–P_2S_5–AlF_3$ were prepared and their structures and ionic conductivities were evaluated. The electrolytes were prepared by ball milling at 510 rpm for 20 h using the mixture of Li_2S, P_2S_5, and AlF_3. Halo patterns were observed for the prepared samples. The ionic conductivity of $75Li_2S·25P_2S_5·5AlF_3$ was 2.6×10^{-4} S cm^{-1} at 25 ºC. The Li stripping/plating performance at 100 ºC for the cells (Li / $Li_2S–P_2S_5–AlF_3$ / Li) was evaluated.

Keywords: All-solid-state batteries; Solid electrolyte; Sulfide glass; Fluoride; Lithium-ion conductor

全固体電池は、難燃性の無機固体電解質を用いることから高い安全性を有する次世代電池として期待されている。固体電解質として $Li_2S–P_2S_5$ 系に代表される硫化物ガラス電解質は高い導電率と優れた成形性から注目されている。しかし、Li 金属負極を用いた際に、還元分解されて生じる反応層によって電池が短絡するという課題がある。本研究では、硫化物へのフッ素添加に着目し、耐還元性の向上を目指した。メカノケミカル法を用いて $Li_2S–P_2S_5–AlF_3$ 系電解質を作製し、電解質の構造や導電率を評価した。また、得られた電解質を用いて Li 対称セルを構築し、Li 溶解析出特性を評価した。

出発原料として Li_2S, P_2S_5, AlF_3 を用いて、メカノケミカル法により $75Li_2S·25P_2S_5·5AlF_3$(mol%)を作製した。Fig. 1 に示すように、得られた電解質の XRD パターンは AlF_3 の添加の有無に関わらず、主にハローパターンを示した。また、$75Li_2S·25P_2S_5·5AlF_3$ の 25 ℃での導電率は 2.6×10^{-4} S cm^{-1} であった。Li 溶解析出試験の結果に関しては当日報告する。

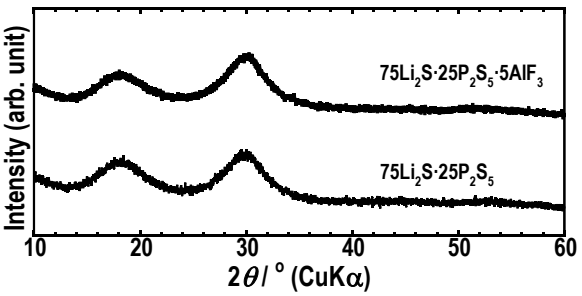

Fig. 1 XRD patterns of $75Li_2S·25P_2S_5·5AlF_3$ and $75Li_2S·25P_2S_5$ electrolytes.

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メカノケミカル法を用いた $NaTaCl_6$–NaCl 系固体電解質の作製

（大阪公立大学）○古賀 健太· 栗岡 英司· 本橋 宏大· 作田 敦· 林 晃敏

Mechanochemical synthesis of solid electrolytes in the system $NaTaCl_6$–NaCl

(*Osaka Metropolitan University*) ○Kenta Koga, Eiji Kurioka, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

Solid electrolytes with high Na-ion conductivity and oxidation tolerance are essential for all-solid-state sodium batteries. Chloride electrolytes have attracted attention due to their high ionic conductivity and oxidation tolerance. We have reported that the chloride electrolytes $Na_{3-x}In_{1-x}Zr_xCl_6$ showed a high Na-ion conductivity[1]. In this study, chloride electrolytes in the system $NaTaCl_6$－NaCl were prepared by the mechanochemical method. The enhancement of ionic conductivity was observed with an increase in the molar ratio of NaCl to $NaTaCl_6$. The maximum ionic conductivity (4.3×10^{-4} S cm^{-1}) was observed in the sample at the composition $NaTaCl_6$·3NaCl. It showed the XRD patterns attributable to crystalline $NaTaCl_6$ and NaCl.

Keywords: All-solid-state battery; Solid electrolyte; Sodium ion conductor; Chloride; Mechanochemical synthesis

全固体ナトリウム電池の実用化に向けて、高いナトリウムイオン伝導度と耐酸化性を有する固体電解質の探索が不可欠である。塩化物電解質は優れたイオン伝導性と耐酸化性を持つことが知られており、例えば当研究グループではこれまでに、$Na_{3-x}In_{1-x}Zr_xCl_6$ 電解質が高いナトリウムイオン伝導度を示すことを報告している[1]。本研究では $NaTaCl_6$[2]及び、$NaTaCl_6$ へ過剰の NaCl を添加した $NaTaCl_6$–NaCl 系塩化物電解質を、遊星型ボールミル装置を用いたメカノケミカル法によって作製し、イオン伝導度を測定した。

$NaTaCl_6$ に対する NaCl の添加量を増加させるとイオン伝導度が増加する傾向がみられ、モル比で 3 倍の NaCl を添加した $NaTaCl_6$·3NaCl は最大の室温イオン伝導度(4.3×10^{-4} S cm^{-1})を示した。$NaTaCl_6$·3NaCl の XRD パターンからは $NaTaCl_6$ と NaCl のパターンのみが観測された（Fig. 1)。

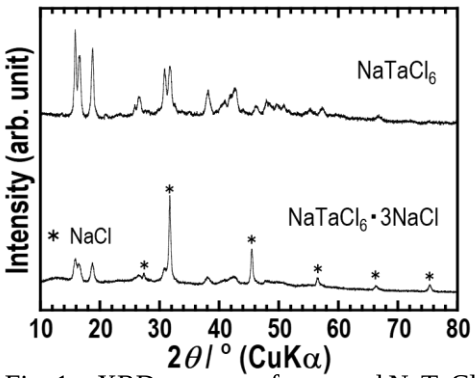

Fig. 1 XRD patterns of prepared $NaTaCl_6$ and $NaTaCl_6$·3NaCl electrolytes.

1) Y. Okada *et al., Electrochemistry* **2023**, 91, 077009.
2) K. Motohashi *et al*., submitted.

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$La_{0.9}Ba_{0.1}F_{2.9}$ – B_2O_3 系複合体のイオン伝導特性

（大阪公立大学）○豊田 真輔・林 侑希・本橋 宏大・作田 敦・林 晃敏
Ionic conduction properties of $La_{0.9}Ba_{0.1}F_{2.9}$ – B_2O_3 composite
(*Osaka Metropolitan University*) ○Shinsuke Toyoda, Yuki Hayashi, Kota Motohashi, Atsushi Sakuda, Akitoshi Hayashi

All-solid-state fluoride-ion batteries are attracted as one of the next-generation batteries because of its high volumetric energy density. For their practical application, solid electrolytes with a high ionic conductivity are required. The single crystalline $La_{0.9}Ba_{0.1}F_{2.9}$ (LBF) has a high ionic conductivity of 10^{-4} S cm^{-1} at room temperature[1]. However, the conductivity of the polycrystalline LBF is lower than that of single crystalline LBF due to its poor formability and large grain boundary resistance[2], and then, it needs to be sintered at high temperature. To increase the ionic conductivity of the polycrystalline LBF, the composites of LBF and B_2O_3 were prepared. The XRD patterns of the heated samples were attributed to the reported $La_{0.93}Ba_{0.07}F_{2.93}$ pattern. The sintered pellet of the 95LBF·5B_2O_3 sample showed the highest ionic conductivity of 1.3×10^{-5} S cm^{-1} at 25 ºC in the prepared samples.
Keywords : All-solid-state battery; Solid electrolyte; Fluoride-ion conductor

全固体電池は有機電解液の代わりに難燃性の無機固体電解質を用いることから、高い安全性が期待される。その中で、全固体フッ化物イオン電池は高い体積エネルギー密度を有することから、次世代電池として注目されている。その実用化には、イオン伝導性の高い固体電解質が必要である。$La_{0.9}Ba_{0.1}F_{2.9}$ (LBF) 固体電解質は、単結晶では 10^{-4} S cm^{-1} 程度のフッ化物イオン伝導体の中では高い室温導電率を有する [1]。一方で、成形性が低く、粒界抵抗が高いため、多結晶体では導電率が低下するという課題があり [2]、高温焼結が必要である。本研究では、多結晶体 LBF の導電率の増加を目指し、LBF と低融性酸化物 B_2O_3 の複合体の作製と評価を行った。

出発原料である LaF_3、BaF_2、B_2O_3 を遊星型ボールミル装置によりメカノケミカル処理することで (100－x)LBF·$x$$B_2O_3$ (x = 0, 5, 10, 15 mol%) 試料を得た。これらを 800 ºC で熱処理して得られた試料の X 線回折パターンは、$La_{0.93}Ba_{0.07}F_{2.93}$ に帰属できた。交流インピーダンス法により得られた焼結体の室温導電率は 95LBF·5B_2O_3 で最大の 1.3×10^{-5} S cm^{-1} であった。当日は、LBF – B_2O_3 系複合体のイオン伝導特性と形態の相関について報告する。

1) A. Roos and J. Schoonman *Solid State Ionics*, **13** (1984) 205.
2) C. Rongeat *et al., ACS Appl. Mater. Interfaces*, **6** (2014) 2103.

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柔粘性イオン結晶を用いたリチウムイオン伝導体の開発(I)
–イオン伝導度に及ぼす Li 塩濃度の影響–

（上智大理工）○小渕 弘貴・大田原拓人・赤壁 秀歩・竹岡 裕子・陸川 政弘・藤田 正博
Development of Lithium-ion Conductors Using Ionic Plastic Crystals (I) -Effect of Li-salt Concentration on Ionic Conductivity- (*Department of Materials and Life Sciences, Sophia University*,) ○Hiroki Obuchi, Takuto Ootahara, Shuho Akakabe, Yuko Takeoka, Masahiro Rikukawa, Masahiro Yoshizawa-Fujita.

Lithium-ion batteries, which are currently widely used in cell phones and other devices, have high energy density and excellent charge-discharge properties, but pose the risk of ignition due to liquid leakage. We have been developing ionic plastic crystals (IPCs) as a new solid electrolyte to solve the problem. In this study, two IPCs with the same molecular weight were used to prepare Li-salt composites, and the effects of pyrrolidinium cation and Li-salt concentration on the thermal and electrochemical properties were investigated. The 5% weight loss temperature ($T_{d\text{-}5\%}$) was determined by Thermogravimetry. The $T_{d\text{-}5\%}$ values of [P1i3][FSA] and [P22][FSA] were 310 and 300 ºC, respectively. [P1i3][FSA] exhibited the solid-solid transition temperatures ($T_{s\text{-}s}$) at –30 and 15 ºC, and the melting point (T_m) at 187 ºC . On the other hand, [P22][FSA] exhibited $T_{s\text{-}s}$ at –35 ºC and T_m at 131 ºC .
Keywords : Ionic plastic crystals, Lithium-ion batteries, Solid electrolytes

現行のリチウムイオン二次電池は、可燃性電解液を使用しているため、引火や爆発の危険がある。この問題を解決するために、難燃性・難揮発性の特徴を有する柔粘性イオン結晶(IPC)に着目した。本研究では、分子量が同じである 2 種類のピロリジニウム塩([P1i3][FSA]及び[P22][FSA])に所定量の Li 塩を添加することで複合体を作製し、熱的・電気化学的特性に及ぼすピロリジニウムカチオン及び Li 塩濃度の影響を調査した。図 1 に[P1i3][FSA]、[P22][FSA]及び LiFSA の化学構造を示す。熱重量測定により、5%重量減少温度（$T_{d\text{-}5\%}$）を求めた。[P1i3][FSA]と[P22][FSA]の $T_{d\text{-}5\%}$は、それぞれ 310 と 300 ºC であり、[P1i3][FSA]の方が 10 ºC 高いことがわかった。図 2 に[P1i3][FSA]と[P22][FSA]の DSC 曲線を示す。[P1i3][FSA]は固相間転移温度($T_{s\text{-}s}$)を–30 と 15ºC に示し、融点(T_m)を 187ºC に示した。一方、[P22][FSA]は $T_{s\text{-}s}$ を-35 ºC に示し、T_m を 131ºC に示した。

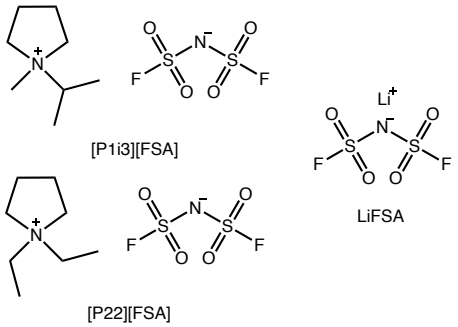

Figure 1. Chemical structures of [P1i3][FSA], [P22][FSA] and LiFSA.

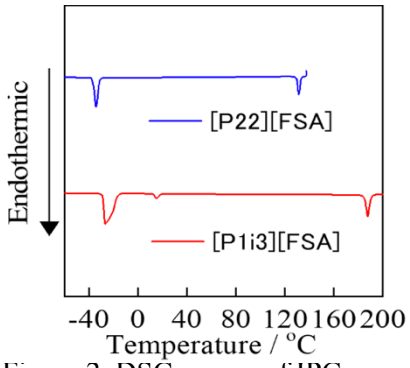

Figure 2. DSC curves of IPCs.

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柔粘性イオン結晶を用いた Na イオン伝導体の開発(I)
−ピロリジニウム塩/Na 塩複合体の特性評価−

（上智大理工）○廣津義史・大田原拓人・赤壁 秀歩・竹岡 裕子・陸川 政弘・藤田 正博

Development of Na-ion Conductors Using Ionic Plastic Crystals (I) -Evaluation of Pyrrolidinium-salt/Na-salt Composites (*Department of Materials and Life Sciences, Sophia University*,) ○Yoshifumi Hirotsu, Takuto Ootahara, Shuho Akakabe, Yuko Takeoka, Masahiro Rikukawa, Masahiro Yoshizawa-Fujita

Since Li-ion batteries (LIBs) are concerned about resource depletion, Na-ion batteries (NIBs), which have abundant resources, are attracting attention. This research aims to develop electrolytes for NIBs using ionic plastic crystals (IPCs) as a new solid electrolyte. In this study, we investigated the effects of Na-salt addition on the thermal and electrochemical properties of IPC/Na-salt composites. The composites were prepared by adding 10 to 50 mol% of NaFSA to *N*,*N*-diethylpyrrolidinium bis(fluorosulfonyl)amide ([P22][FSA]) and *N*-ethyl-*N*-isopropylpyrrolidinium bis(fluorosulfonyl)amide ([P2i3][FSA]). [P22][FSA]/NaFSA composite showed the highest ionic conductivity of 2.7×10^{-3} S cm^{-1} at 25ºC, when the NaFSA concentration was 20 mol%. [P2i3][FSA]/NaFSA composite showed the highest ionic conductivity of 2.2×10^{-3} S cm^{-1} at 25ºC, when the NaFSA concentration was 10 mol%.

Keywords : Ionic conductivity; Ionic plastic crystals; Sodium-ion batteries

Li イオン電池は資源枯渇が懸念される電池であることから、資源量が豊富な Na イオン電池(NIB)が注目されている。一方、安全性の観点から、電解液を固体電解質に置き換えた全固体電池の開発が活発化している。本研究では、新規固体電解質として柔粘性イオン結晶（IPC）を用いた NIB 用電解質の開発を目的とした。今回は、IPC に Na 塩を添加することで、Na 塩が IPC の諸特性に及ぼす影響を調査した。本研究で用いた IPC、Na 塩の化学構造を図 1 に示す。DSC 測定の結果、[P22][FSA]、[P2i3][FSA]は IPC であることが示唆された。それぞれの IPC に NaFSA を 10～50 mol%加えて複合体を作製した。[P22][FSA]に NaFSA を 10 mol%添加した複合体のみが室温で固体であり、その他の複合体では液体となった。図 2 に NaFSA 添加量と 25℃でのイオン伝導度の関係を示す。[P22][FSA]系では、NaFSA 添加量が 20 mol%のときイオン伝導度が最も高く、2.7×10^{-3} S cm^{-1} であった。[P2i3][FSA]系では、NaFSA 添加量が 10 mol%のときにイオン伝導度が 2.2×10^{-3} S cm^{-1} であった。その後、NaFSA 濃度の増加とともに、イオン伝導性は低下した。

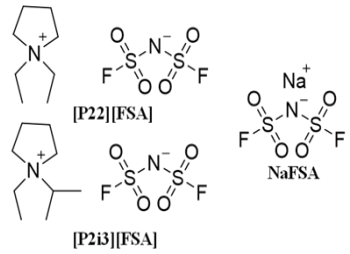

Figure 1. Chemical structure of IPCs and Na salt.

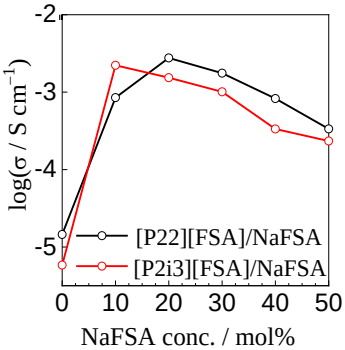

Figure 2. Relationship between ionic conductivities at 25ºC and NaFSA concentration.

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双性イオン型ポリマーを用いた Na イオン伝導体の作製と評価（I）-イオンゲルの作製-

（上智大理工）○土合　麗・山口 美那・佐藤 雅也・竹岡 裕子・陸川 政弘・藤田 正博

Preparation and Evaluation of Na-ion Conductors Using Zwitterionic Polymers (I) -Preparation of Ion Gels-

(*Department of Materials and Life Sciences, Sophia University*) ○Rei Doai, Mina Yamaguchi, Masaya Sato, Yuko Takeoka, Masahiro Rikukawa, Masahiro Yoshizawa-Fujita

Na-ion batteries are attracting attention as an alternative to Li-ion batteries, which are concerned about resource depletion. We have developed electrolyte materials using ionic liquids (ILs) that are nonflammable and nonvolatile, and zwitterions (Zw) that have high polarity. In this study, we developed gel electrolytes by photopolymerization after adding Zw monomers to IL/Na-salt composites. IL and NaFSA were mixed at the molar ratio of 6.8 : 1.0, and three samples with various zwitterionic polymer contents of 5, 7, and 10 mol% were prepared. All the gels showed almost the same ionic conductivities in the temperature range above their melting points. The ionic conductivity of the ion gels was 1.7×10^{-3} Scm^{-1} at 25°C.

Keywords : Sodium-ion secondary batteries; Ionic liquids; Zwitterions

資源の枯渇が懸念される Li イオン電池の代替として、資源的に豊富な Na イオン電池が注目されている。これまで、難燃性・難揮発性液体であるイオン液体(IL)と高極性である双性イオン(Zw)を用いて電解質の開発を行ってきた。本研究では、IL/Na 塩複合体に Zw モノマーを添加し、光重合によりイオンゲルを作製することで新規ゲル電解質を開発した。IL([P13][FSA])、Na 塩(NaFSA)、Zw モノマーの化学構造を図 1 に示す。[P13][FSA]と NaFSA の物質量比が 6.8 : 1.0 となるように混合した後、Zw モノマーをそれら複合体に 5, 7, 10 mol%となるように添加することで、3 種類の 3 成分系複合体を作製した。イオン伝導度のアレニウスプロットを図 2 に示す。IL/ Na 塩複合体およびイオンゲルのイオン伝導度の温度依存性は上に凸の曲線となり、VFT 型であった。IL/Na 塩複合体のイオン伝導度は、25 ℃において 6.1×10^{-3} S cm^{-1} であった。いずれのゲルも融点以上の温度域でのイオン伝導度は、25 ℃において約 1.7×10^{-3} S cm^{-1} であり、Zw の添加量によらず同等であった。

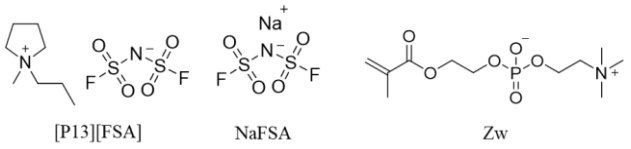

Figure 1. Chemical structure of IL, Na-salt, and Zw.

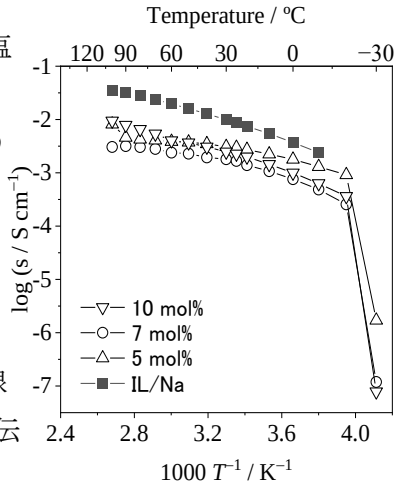

Figure 2. Arrhenius plots of ionic conductivities for IL/Na and ion gels.

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アニオン導電性高分子電解質膜を用いたスーパーキャパシタの電気化学特性

(山梨大院医工農総教[1]・山梨大クリエネ研セ[2]・山梨大工基礎教セ[3]) ○猪苗代優介[1]・内野貴文[1]・犬飼潤治[2]・宮武健治[2]・野原愼士[3]
Electrochemical Characteristics of Supercapacitors Using Anion-Conducting Polymer Electrolyte Membranes ([1]*Integrated Graduate School of Medicine, Engineering, and Agricultural Sciences*, [2]*Clean Energy Research Center,* [3]*Faculty of Engineering, Basic Education Center, University of Yamanashi*) ○Yusuke Inawashiro,[1] Takafumi Uchino,[1] Junji Inukai,[2] Kenji Miyatake,[2] Shinji Nohara[3]

In this study, novel supercapacitors were constructed using anion-conducting polymer electrolyte membranes developed for use in fuel cells, and their electrochemical characteristics were evaluated. As a result, the supercapacitors showed performances superior to those using aqueous solution by optimization of the membrane thickness and/or cell configuration. This clearly indicates good applicability of the polymer electrolyte membrane to supercapacitors.
Keywords : Electric Double Layer Capacitor; Asymmetric Supercapacitor; Anion-Conducting Polymer Electrolyte Membrane; Activated Carbon Electrode; Manganese Oxide

近年、スーパーキャパシタの分野において二次電池と同様に全固体化に関する研究開発が盛んに行われている。本研究では、燃料電池用に開発したアニオン導電性高分子電解質膜（QPAF-4）膜[1)]に電解液を含侵させ、新規な電気二重層キャパシタ（EDLC）および酸化マンガン系非対称キャパシタを構築した。セルの電気化学特性（25℃）について、従来型セパレータ（120 μm）に電解液を含侵したものと比較検討した。

まず、両極に活性炭（AC）を用いた EDLC では、膜厚が 10 および 20 μm の QPAF-4 を用いたセルは従来型（1 M KOH aq.）よりも優れたレート特性を示した（Fig. 1）。優れたイオン伝導性と機械的強度を併せ持つ燃料電池用 QPAF-4 膜は薄膜化により従来型 EDLC の特性を超えるセルを構築できる可能性を強く示唆している。さらに、$Mn_{0.75}Ni_{0.25}O$/C 電極および AC 電極を用いた 2.5 V 級非対称キャパシタ[2)]にも QPAF-4 膜を応用した結果、含侵する LiCl 水溶液濃度とセル構成の最適化により、従来の水溶液型セルより優れた特性を示すことが明らかとなった。

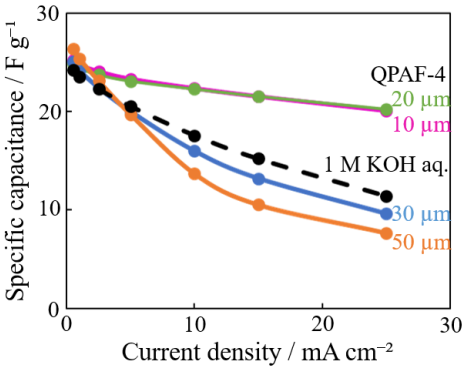

Fig. 1 Rate capability for EDLCs with QPAF-4 membranes and 1 M KOH aqueous solution (separator).

謝辞 本研究は JSPS 科研費（19K05596、22K05189）、文部科学省科学技術試験研究委託事業（JPMXP1122712807）の助成を受けたものである。
1) H. Ono, T. Kimura, A. Takano, K. Asazawa, J. Miyake, J. Inukai, K. Miyatake, *J. Mater. Chem. A* **2017**, *5*, 24804.
2) Y. Niwa, J. Inukai, S. Nohara, *Electrochemistry* **2021**, *89*, 211.

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Academic Program [Oral B] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral B

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
A1455(1455, Bldg. 14 [5F])

[A1455-4am] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Kazuhiko Maeda, Tsukasa Torimoto

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC
[A1455-4am-01]
Efficient separation of HTO from H_2O by membrane distillation using gas-liquid exchange

○Hirokazu Miyoshi[1], Masahiro Fujiwara[2] (1. Tokushima University, 2. Osaka University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC
[A1455-4am-02]
Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

○Susmita Roy[1], Masayoshi Higuchi Higuchi[1], Sanjoy Mandal[1] (1. National Institute for Materials Science (NIMS), 1 -1 Namiki)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[A1455-4am-03]
Spontaneous-Symmetry-Breaking Charge Separation in Organic Photovoltaic Material

○Takeaki Zaima[1,2], Wataru Ota[1,2], Naoki Haruta[1,2], Motoyuki Uejima[3], Hideo Ohkita[2], Tohru Sato[1,2] (1. FIFC, Kyoto Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. MOLFEX, Inc)

English
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[A1455-4am-04]
Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

○Wentao Zhang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
Break

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC
[A1455-4am-05]
Electrochemical water oxidation by layered-perovskite oxyfluoride $Pb_3Fe_2O_5F_2$

○Ryusuke Mizuochi[1], Yuuki Sugawara[1], Takeo Yamaguchi[1], Kazuhiko Maeda[1] (1. Tokyo Institute of Technology)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC
[A1455-4am-06]

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Improvements in long-term durability of electrochemical reactors producing formate from CO_2 and water

○Naohiko Kato[1], Yasuaki Kawai[1], Natsumi Nojiri[1], Masahito Shiozawa[1], Yoshihiro Kikuzawa[1], Nobuaki Suzuki[1], Satoru Kosaka[1], Tsuyoshi Hamaguchi[1], Yasuhiko Takeda[1] (1. TOYOTA CENTRAL R&D LABS., INC.)

Japanese

11:10 AM - 11:30 AM JST | 2:10 AM - 2:30 AM UTC

[A1455-4am-07]

Photocatalytic membrane electrode assemblies with proton conductive coordination polymers

○Yuji Namiki[1,2], Hiroyasu Tabe[1], Satoshi Horike[1] (1. Kyoto Univ., 2. POLA Chemical Industries, Inc.)

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膜蒸留と気液交換を融合した HTO の H_2O からの効率的分離

（徳島大放セ [1]・阪大環境安全セ [2]）○三好 弘一 [1]・藤原 正浩 [2]
Efficient separation of HTO from H_2O by membrane distillation using gas-liquid exchange ([1] *Adv. Rad. Res., Edu., Mgmt. Ctr., Tokushima University*, [2]*Res. Ctr. Environ. Preserv., Osaka University*) ○Hirokazu Miyoshi,[1] Masahiro Fujiwara[2]

H_2O containing HTO loaded on a hydrophobic membrane with a photothermal black dye was exposed to an artificial sunlight for 1.5 h. The heat generated from the sunlight vaporized the water to penetrate the vapor through the membrane. The water vapor thus permeated was mixed in H_2O impregnated in hydrophilic filters under the membrane. Gas-liquid exchange occurred in these filters to decrease the content of HTO in the recovered water under all filters. The increases both of the filter number and the water content of the hydrophilic filters further enhanced the separation effect of HTO. When four hydrophobic membranes and four water-containing hydrophilic filters were set alternately, the ratio of HTO recovered under these filters was reduced to 12%.

Keywords：Tritiated water; Membrane distillation; Light irradiation; Gas-liquid exchange; rectification

光熱変換性の色素ソルベントブラック 5(SB-5)を塗布した疎水性膜(PTFE 製 PF100)上に HTO 含有水(HTO 濃度: 3026 Bq/mL)を導入し、上方から人工太陽光(994 Wm^{-2})を 1.5 時間照射した（図左)。光熱変換効果により HTO 含有水は蒸気となり疎水性膜を透過する。その際、膜下にセットした含水の親水性フィルター中で気液交換が起き、全てのフィルター下部に回収された水中の HTO 濃度は減少していた。親水性フィルターの枚数や含水量を増やすことで、回収水中の HTO 濃度をさらに下げることができた。親水性フィルターであるガラスフィルター(GB-140)に H_2O を約 2.5 g 含水させた場合、フィルター下部に回収された水中の HTO 濃度は約 77%まで減少した。さらに、含水ガラスフィルターと疎水性膜の組み合わせを 4 セット計 8 枚まで増やしたところ、HTO 量を約 12%までに減少させることに成功した（図右)。一方、水を含まないフィルターでは HTO 濃度はほとんど減少しなかった。

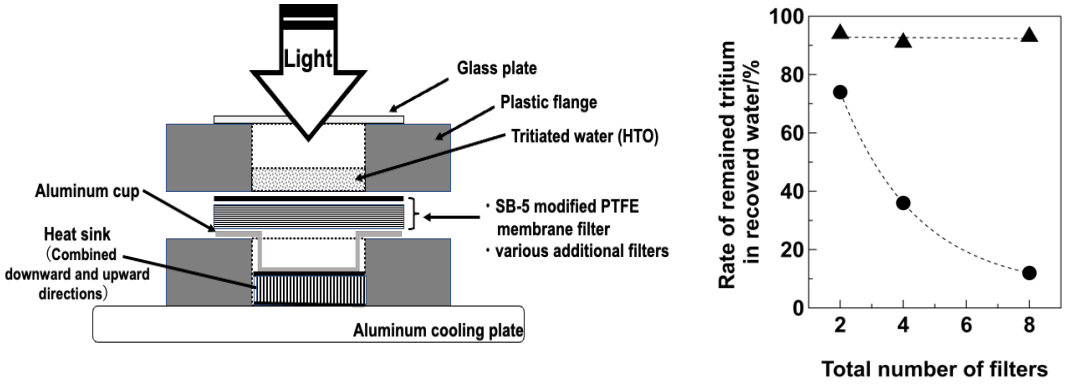

Figure (Left) Schematic diagram of experimental apparatus of tritiated water separation. (Right) Relation between the remained tritiated water rate in recovered water and the total number of PF100 and GB-140. ▲: Dry GB-140. ●: GB-140 with 1 g of water.

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Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

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Keywords: Electrochromism; Metallo-supramolecular Polymer; Electrochromic Device; Durable Electrochromic Device; Electrochromic memory

An solid-state electrochromic device (ECD) of Fe(II)-based metallo-supramolecular polymer (polyFe) with excellent durability was fabricated by incorporating Nickel hexacyanoferrate (NiHCF) as a charge-balancing layer. The solid-state ECD displayed bleaching and coloring at small potential window, with maximum optical contrast. The minimalization of the potential difference during EC changes enabled ultra-high cycle stability and improved optical memory. For the further improvement of the EC properties, it was revealed that the optimization of the film thickness of the polyFe and NiHCF is critical to maintaining the charge balance between the working and counter electrodes. At last, the cyclic stability for the repeated color changes over 100,000 cycles were achieved.[1] This finding will help engineers and scientists to fabricate a low-voltage-driven, long-lasting ECD for real-life application in smart electrochromic window technology.

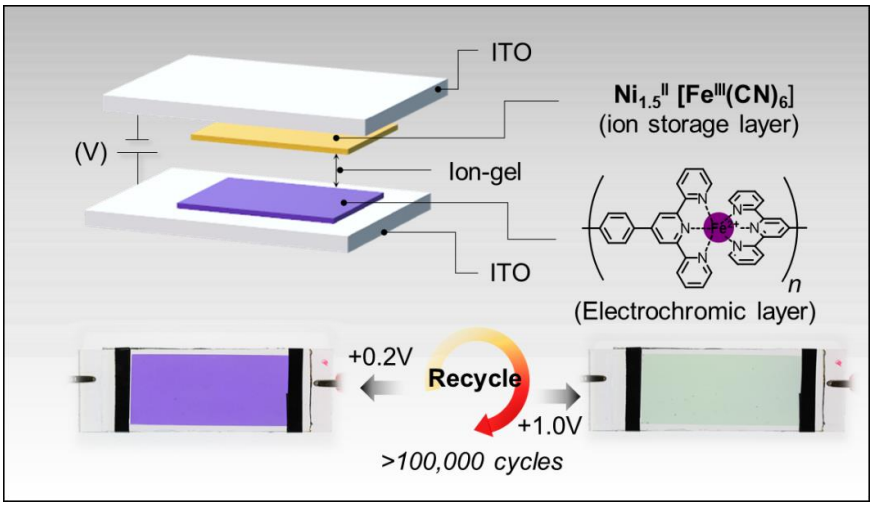

Figure 1. Highly Durable Electrochromic Device of Fe(II)-Based Metallo-Supramolecular Polymer

1) S. Mondal, S. Roy, Y. Fujii, M. Higuchi *ACS Appl. Electron. Mater.* **2023**, *5*, 6677–6685.

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Spontaneous-Symmetry-Breaking Charge Separation in Organic Photovoltaic Material

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Keywords: Photovoltaic conversion; ITIC; Density functional theory; Pseudo-Jahn–Teller effect; Vibronic coupling

In organic photovoltaics (OPV), the driving force of the charge separation has been considered to be an energy offset, i.e., the LUMO (or HOMO) energy difference between donor and acceptor materials.[1] However, highly efficient OPV materials with small energy offsets were recently reported.[2,3] In such OPV materials, the driving force of the charge separation remains unclear. Symmetry-breaking charge separation (SB-CS) that causes the intra- or intermolecular charge separation between identical fragments could be an initial charge separation step in small offset systems.[4] This study aims to theoretically identify the driving force of charge separation in the small offset system using ITIC[3], a non-fullerene acceptor material for OPV devices.[5]

In the previous study, ITIC has been considered packed through the terminal π-π stacking.[6] Hence, we constructed the edge-stacking dimer model of ITIC. According to our density functional theory calculations, the pseudo-Jahn–Teller (PJT) distortion[4] of the S_1 excimer state induces spontaneous SB-CS (SSB-CS) between the identical ITIC molecules even without the asymmetry of the surrounding environment (Fig. 1). The strong PJT effect arises from the vibronic coupling between the pseudo-degenerate S_1 and S_2 excited states with different irreducible representations, i.e., A_u for S_1 and A_g for S_2, via the asymmetric vibrational mode of A_u. The vibrational mode responsible for the spontaneous polarization is the intramolecular C-C stretching vibration between the core IT and terminal IC units. These results suggest that the charge separation efficiency in the initial photovoltaic conversion process can be improved by controlling the PJT effect.

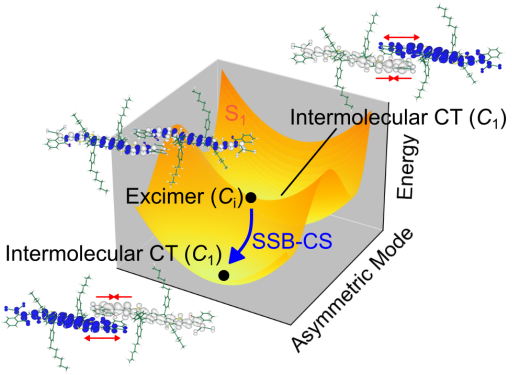

Fig. 1: Schematic illustration of the SSB-CS in ITIC dimer.

1) P. Peumans *et al.*, *J. Appl. Phys.* **2003**, *93*, 3693. 2) K. Kawashima *et al.*, *Nat. Commun.* **2015**, *6*, 1. 3) Y. Lin *et al.*, *Adv. Mater.* **2015**, *27*, 1170. 4) A. N. Bartynski *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 5397. 5) T. Zaima *et al.*, *J. Phys. Chem. Lett.* **2023**, *14*, 9706. 6) G. Han *et al.*, *J. Mater. Chem. C* **2017**, *5*, 4852. 7) I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, 1989).

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Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

(*Graduate School of Engineering, Nagoya University*) ○Wentao Zhang, Kazutaka Akiyoshi, Tatsuya Kameyama, Tsukasa Torimoto

Keywords: Semiconductor nanocrystal; Quantum size effect; $AgBiS_2$; Light energy conversion; Low toxicity

The energy structure and light absorption properties of semiconductor quantum dots (QDs) can be controlled by changing their size and composition. The QDs have been intensively investigated for the application to photovoltaic, photocatalysis, and bio-imaging. In recent years, I-V-VI semiconductors (e.g. $NaBiS_2$[1], $AgBiS_2$[2]), composed of low-toxic elements, are regarded as potential alternatives to toxic IV-VI and II-VI semiconductors (PbSe[3], CdS[4]). Notably, $AgBiS_2$ QDs are expected to be an excellent light absorber for photovoltaic application due to their remarkable light-harvesting capabilities from the visible to the near-IR regions. However, there are limited reports on controlling their particle size and composition to enhance light-electricity conversion efficiency. In this study, we report a solution-phase synthesis of Ag-Bi-S QDs and their utilization in sensitized solar cells.

Ag-Bi-S QDs were prepared by heating the precursors of Ag(OAc), $Bi(OAc)_3$ and S in a mixture solution of oleylamine and dodecane thiol at different temperatures. As the preparation temperature increased from 100 ºC to 200 ºC, the particle size increased from 2.7 to 8.1 nm, accompanied by the change in particle composition from Ag-deficient ones to the stoichiometric $AgBiS_2$. The energy gap of QDs decreased from 1.45 to 1.05 eV with an increase in the particle size from 2.7 to 8.1 nm.

Figure 1a shows the electronic energy structure of Ag-Bi-S QDs prepared at different temperatures. The level of valence band was negatively shifted with an increase in the reaction temperature, while the level of conduction band was almost constant. The level of defect sites in the energy gap was evaluated by measuring the photocurrent onset potential of QD-immobilized electrodes: The defect sites were present in the energy gap for QDs prepared at 100 and 120 ºC, but they were absent for the QDs with almost the stoichiometric composition, prepared at temperatures higher than 150 ºC. Sensitized solar cells were fabricated by immobilizing Ag-Bi-S QDs on porous TiO_2 electrodes. Figure 1b shows the *J-V* curves of resulting cells. The use of the QDs prepared at 150 ºC gave the highest performance, the power conversion efficiency reaching 0.76%.

[1] J. Vela *et al*., *Chem. Mater.* **2020**, *32*, 6085. [2] Y. Wang *et al*, *Nat. Photon.* **2022**, *16*, 235. [3] S. Liu *et al*., *ACS Nano* **2021**, *15*, 3376. [4] R. Zeng *et al*., *Anal. Chem.,* **2019**, *91*, 2447.

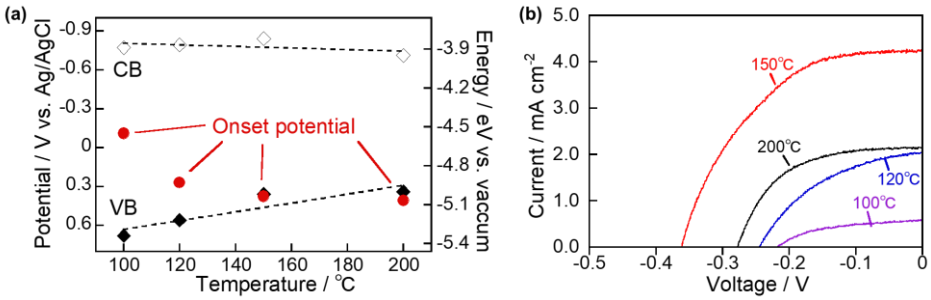

Fig. 1 (a) Energy structures of Ag-Bi-S QDs. (b) *J-V* curves of Ag-Bi-S QD-sensitized solar cells under the irradiation of AM1.5G simulated solar light.

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Electrochemical water oxidation by layered-perovskite oxyfluoride $Pb_3Fe_2O_5F_2$

([1]*School of Science, Tokyo Institute of Technology*, [2]*Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology*) ○Ryusuke Mizuochi,[1] Yuuki Sugawara,[2] Takeo Yamaguchi,[2] Kazuhiko Maeda[1]

Keywords: Electrochemical water splitting; Oxygen evolution reaction electrocatalyst; Layered material; Mixed-anion compound

Hydrogen production by water electrolysis has attracted attention as a sustainable way to achieve carbon neutrality in the future, with a strong focus on oxygen evolution reaction (OER), compared to hydrogen evolution reaction (HER). It is because the OER is more sluggish with four-electron transfer than the HER. An OER electrocatalyst without noble metal is desired from the viewpoint of industrial application for cost-effectiveness. We have focused on iron-based oxyfluorides as OER electrocatalysts and, indeed, found that a lead-iron oxyfluoride, $PbFeO_2F$, achieved the functionality.[1] Oxyfluorides are mixed anion compounds, which include oxide and fluoride anions coordinated to a metal center. They have physical and chemical properties, which do not appear in a single anion counterpart (i.e., oxides and fluorides).[2] In this study, we investigated another lead-iron oxyfluoride, $Pb_3Fe_2O_5F_2$, with layered double perovskite structure as an OER electrocatalyst. 2D-layered compounds have attracted attention not only as electrocatalysts but also in other applications due to their unique structural and electronic properties. However, there is no report utilizing a single-phase 2D-layered oxyfluoride as an OER electrocatalyst. Therefore, we focused on the 2D-layered $Pb_3Fe_2O_5F_2$ as the OER electrocatalyst and compared to the $PbFeO_2F$ with 3D-cubic perovskite structure.

Electrodes of the lead-iron oxyfluorides were fabricated by drop-casting oxyfluoride particle suspension with a conductive carbon support onto a carbon substrate. Electrochemical OER activities and properties were investigated for the as-prepared electrodes. It was found that $Pb_3Fe_2O_5F_2$ had relatively high OER activity and superior electrochemical property compared to $PbFeO_2F$ and even general iron-based perovskite oxides (such as $SrFeO_3$, $LaFeO_3$ and $BiFeO_3$). Comparison between $Pb_3Fe_2O_5F_2$ samples with different parameters in the synthesis revealed that the presence of (0*k*0) crystal facets on the $Pb_3Fe_2O_5F_2$ enhanced the OER activity. Furthermore, density functional theory calculations in the OER process indicated that the higher activity of $Pb_3Fe_2O_5F_2$ than $PbFeO_2F$ was attributed to the greater exposed area of the crystal facets with lower OER overpotential, supporting the results confirmed by the above electrochemical investigation.

1) R. Mizuochi, K. Izumi, Y. Inaguma, K. Maeda, *RSC Adv.* **2021,** *11*, 25616.

2) H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun.* **2018,** *9*, 772.

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CO_2 と水からギ酸を生成する電気化学リアクタの長期耐久性向上

（豊田中研 [1]）○加藤直彦 [1]・河合康明 [1]・野尻菜摘 [1]・塩澤真人 [1]・菊澤良弘 [1]・鈴木伸明 [1]・小坂悟 [1]・濱口豪 [1]・竹田康彦 [1]

Improvements in long-term durability of electrochemical reactors producing formate from CO_2 and water ([1] Toyota Central R&D Labs., Inc.) ○Naohiko Kato*, Yasuaki Kawai, Natsumi Nojiri, Masahito Shiozawa, Yoshihiro Kikuzawa, Nobuaki Suzuki, Satoru Kosaka, Tsuyoshi Hamaguchi and Yasuhiko Takeda.

We previously developed a 1 m^2-sized artificial photosynthetic cell consisting of an electrochemical (EC) reactor featuring a Ru-complex polymer (RuCP) cathode catalyst integrated with Si solar cells to convert CO_2 to formate, and realized a solar-to-chemical energy conversion efficiency of 10.5%[1,2]. In this study, we improved the durability of the EC reactor. A pyrrole derivative containing amino group introduced in the RuCP and carboxyl group created on the carbon supports by a UV-ozone treatment formed strong chemical bond, reducing the detachment of the RuCP catalyst. A newly developed chemically-resistant graphite adhesive prevented the carbon supports from peeling off from the conductive substrates. We constructed 75 cm^2-sized EC reactors facing the cathodes and durable IrO_x-TaO_x/Pt-Metal oxide/Ti anodes with porous separators between them. High Faradaic efficiency (*FE*) of formate production over 80% was secured under inclined installation even after 3000 h intermittent operation (Figure 1). *Keywords: Solar fuels; Long-term durability; Artificial photosynthesis; Electrochemical reactors; Solar-driven CO_2 reduction; Formate.*

我々は、これまでに、Ru 錯体ポリマー（RuCP）からなる CO_2 還元触媒を用いた電気化学(EC)リアクタと Si 太陽電池を組み合わせた 1 m^2 サイズの人工光合成セルを構築し、太陽光-化学エネルギー変換効率 10.5%を達成した [1,2]。今回、EC リアクタの耐久性を向上させた。アミノ基を含むピロール誘導体を RuCP に導入し、炭素担体への UV オゾン処理により生成するカルボキシル基と化学結合させることによって、RuCP の脱離を抑制した。更に、高化学耐性のグラファイト接着剤を開発し、炭素担体の導電基板からの剥離を防止した。対向させたカソードと高耐久性の IrO_x-TaO_x/Pt-Metal oxide/Ti アノードの間に多孔質セパレータを挿入した 75cm^2 の EC リアクタを、屋外環境を想定した傾斜設置で間欠動作させた 3000 時間後にギ酸生成ファラディー効率（*FE*）80%以上が維持された（図 1）。

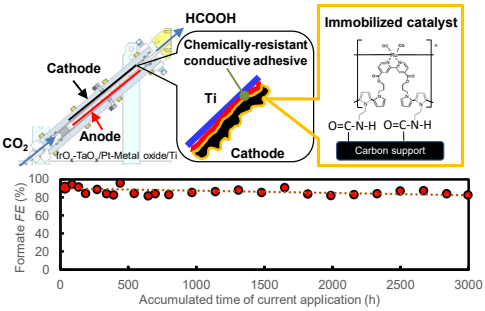

Fig.1 EC reactor designed for integration with solar cells and *FE* of formate production for 3000 h.

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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光触媒型膜-電極接合体へのプロトン伝導性配位高分子の適用

（京大院工[1]・ポーラ化成[2]・京大高等研究院[3]・京大院理[4]）○竝木 裕司[1,2]・田部 博康[3]・堀毛 悟史[4]
Photocatalytic membrane electrode assemblies with proton conductive coordination polymers
([1]*Graduate School of Engineering, Kyoto University*, [2]*POLA Chemical Industries, Inc.*,[3]*Institute for Advanced Study, Kyoto University*, [4]*Graduate School of Science, Kyoto University*,) ○Yuji Namiki[1,2], Hiroyasu Tabe[3], Satoshi Horike[4]

Photocatalytic solar cells are a promising power supply system because of their higher cell voltage than conventional solar cells.[1] The photocatalytic solar cells consist of membrane-electrode assemblies composed by electrolyte membranes, electrodes, and photocatalysts. In this study, we used proton (H^+)-conductive coordination polymers as solid electrolytes.[2,3] Electric power was generated under the solar irradiation by MEAs with coordination polymers consisting of Zn^{2+} ions, phosphate ions, and alkylamines for 72 hrs, while the current decrease was observed in the MEAs consisting of conventional electrolyte membranes such as Nafion®.

Keywords：Photocatalytic reaction, Coordination polymer, Proton conductivionl, Solar cell

従来の太陽電池と比べ高い起電力を特長とする光触媒式太陽電池に注目が集まっている[1]。光触媒式太陽電池は、電解質膜と光触媒電極によって構成される膜ー電極接合体（MEA）からなり、負極側に加湿アルゴンを、正極側に加湿酸素をフローさせ、太陽光を照射することで作動する。光触媒式太陽電池の安全面や省スペース性を向上させるには、固体電解質の利用が望ましい。本研究では機械的耐久性と耐湿性に優れ、光触媒との融合も近年報告された配位高分子（CP）を固体電解質として適用した[2]。亜鉛イオン、リン酸イオン、アルキルアミンからなるCP[3]から構築されるMEAに疑似太陽光を照射したところ72時間にわたり安定に発電できることを確認した（図1）。一方、Nafion®を適用すると、72時間後の電流出力は初期値と比較して75%低下した。

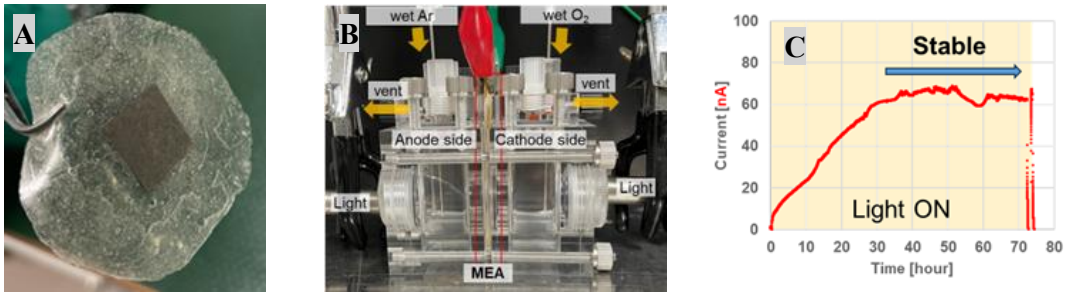

Figure 1. MEA with CP(A), H-type cell system(B), Stability test of MEA with CP(C)

1) Y. Ogura, S. Okamoto, T. Itoi, Y. Fujishima, Y. Yoshida, Y. Izumi, *Chem. Commun.*, **2014**, *50*, 3067.
2) H. Izu, H. Tabe, Y. Namiki, H. Yamada, S. Horike, *Inorg. Chem*., **2023**, *62*, 11342.
3) T. Ogawa, K. Takahashi, S. S. Nagarkar, K. Ohara, Y. Hong, Y. Nishiyama, S. Horike. *Chem. Sci.*, **2020**, *11*, 5175.

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Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
B1325(1325, Bldg. 13 [2F])

[B1325-4am] Award Presentations, Special Lectures

Chair: Aritomo Yamaguchi, Kosei Ueno, Mio Ishida, Tatsuya Nishimura

Japanese CSJ Award for Young Chemists in Technical Development
9:00 AM - 9:30 AM JST | 12:00 AM - 12:30 AM UTC
[B1325-4am-01]
Development of Printed Semiconductor Devices Using Semi-conductive Carbon Nanotubes

○Kazuki Isogai[1], Shota Kawai[1] (1. Toray Industries, Inc.)

Japanese CSJ Award for Technical Development
9:30 AM - 10:00 AM JST | 12:30 AM - 1:00 AM UTC
[B1325-4am-02]
Development of Manufacturing Technology for Sustainable Surfactant “Internal Olefin Sulfonate”

○Yudai Yamada[1], Koutaku Yuasa[1], Sara Sumioka[1], Shingo Takada[1], Masato Nomura[1] (1. Kao Corporation)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
Break

Japanese CSJ Award for Technical Development
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[B1325-4am-03]
Development of Unique a-Olefin Copolymer with High Stress Absorption Performance and Their Applications

○Masahiko Okamoto[1], Takayuki Uekusa[1] (1. Mitsui Chemicals, Inc.)

Japanese CSJ Award for Technical Development
10:40 AM - 11:10 AM JST | 1:40 AM - 2:10 AM UTC
[B1325-4am-04]
Development of dental restorative materials with structural color

Hironobu Akizumi[1], ○Hiroshi Morisaki[1], Takuma Matsuo[1] (1. Tokuyama Dental Corporation)

Japanese CSJ Award for Technical Development
11:10 AM - 11:40 AM JST | 2:10 AM - 2:40 AM UTC
[B1325-4am-05]
Development and Commercialization of Negative-type Photodefinable Polyimide Film for Electronic Components

○Kazuyuki Matsumura[1], Keigo Kato[1], Yoshiko Tatsuta[1], Daisuke Kanamori[1], Yuki Katsurada[1] (1. Toray Industries, Inc.)

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半導体カーボンナノチューブを用いた塗布型半導体デバイスの開発

（東レ[1]）○磯貝 和生[1]・河井 翔太[1]

Development of Printed Semiconductor Devices Using Semi-conductive Carbon Nanotubes

([1]*Toray Industries, Inc.*) ○Kazuki Isogai[1], Shota Kawai[1]

Printed semiconductor devices that are manufactured by using printable materials have been strongly expected to be realized because of their low cost, energy efficiency and flexibility. However, a significant improvement in the performance of printable semiconductor materials is required. In this work, we developed the semi-conductive carbon nanotube (semi-CNT) technology to improve the performance of printable semiconductor materials. By controlling the nanostructure and uniform dispersion of semi-CNTs, we achieved the highest level of mobility in the world as a printable semiconductor material (Fig.1). In addition, we realized an air-stable N-type semiconductor material by unique electronic doping of semi-CNTs (Fig.2). By combining the semi-CNT technologies and our device technologies, wireless communications of RFIDs and sensors printed on general-purpose films were achieved (Fig.3). Currently, a wide range of applications are being developed, including inventory managements and urination detections. Furthermore, we established the element technology for device production using a Roll-to-Roll process, which is a high-productivity and energy-saving continuous printing process (Fig.4).

Keywords : Printed Semiconductor; Semi-conductive Carbon Nanotube; TFT; Wireless Communication

塗布型材料を印刷して作製する塗布型半導体デバイスは、安価・省エネルギーでフレキシブル性に優れる特徴から、その実現が強く期待されている。しかしデバイスを構成する各要素回路を十分に実現できておらず、塗布型材料の大幅な性能向上が求められている。例えば、高周波電力を変換する整流回路には極めて高移動度の半導体材料が必要である。また、情報処理を行う論理演算回路の低消費電力化にはP型及びN型の半導体が必要だが、N型半導体材料は大気下で劣化しやすい課題がある。本研究では、キーとなる半導体材料の性能向上に向けて半導体カーボンナノチューブ(CNT)技術の開発に取り組み、さらに各塗布型材料及び微細加工技術を融合したデバイス技術の開発も進め、塗布型半導体デバイスを創出した。以下に要点を記載する。

【半導体CNT技術の開発】

我々は独自の半導体ポリマーを用いた分散技術により半導体 CNT の均一ネットワークを実現し、従来塗布型半導体を上回る移動度を達成してきた。今回、ネットワーク中の CNT 間の接触抵抗を低減し CNT 本来の優れた移動度をより引き出すことを狙い、半導体CNTの構造制御(長尺化、直径分布制御) に取り組み、CNT 合成方法及び半導体CNT分離工程を詳細に検討し、従来比長さを1.5倍かつ直径分布幅を1/2とすることに成功した。さらに半導体ポリマーの主鎖及び側鎖の構造改良に加えてCNTと相互作用しやすい溶媒設計を追究し、分散の難しい上記半導体CNTの均一な

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分散を実現した。これにより、塗布型半導体として世界最高レベルの移動度(182 cm^2/Vs, Fig.1)を達成し、塗布型整流回路での高周波電力(920MHz, UHF 帯)の変換に成功した。

一方、半導体 CNT は通常、大気下では P 型で機能するため、電子供与性化合物により半導体 CNT へ電子ドーピングし N 型へと変換する方法が知られるが、大気下では P 型へ戻るという課題がある。我々は脱ドーピングの要因である大気中水分の排除に加え、電子供与性化合物の電子準位及び立体構造に着目して電子ドーピングの安定化を追究し、低吸水マトリックス樹脂に独自の電子供与性化合物を組み合わせた新規 N 型半導体材料を見出した。これにより、大気下で長期安定な N 型 TFT を実現し(Fig.2)、塗布型の論理演算回路での大気下安定動作を達成した。

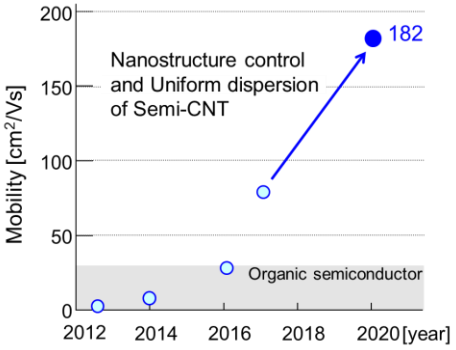

Fig.1 Mobility of TORAY CNT-TFT

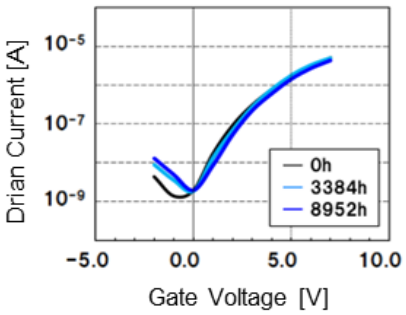

Fig.2 Transfer characteristics of n-type TFT storing at air

【塗布型半導体デバイスの創出】

上記半導体 CNT 技術をキーとして塗布型絶縁層材料・電極材料及び微細加工技術を組み合わせることで各要素回路を塗布型で実現できたため、汎用の PET フィルム上に様々な塗布型半導体デバイスを創出することが可能となった(Fig.3)。具体的には、PET フィルム上に各要素回路を組み合わせた RFID タグを塗布形成し、塗布型半導体デバイスとして世界で初めて、UHF 帯電波での無線通信に成功した。さらに水分検知や開封検知等の様々な機能を持つ塗布型半導体デバイスの開発にも成功した。現在は実用化に向け、顧客と連携し実証試験を進めつつ、物品管理や排尿検知など幅広い用途への展開を図っている。また、実用化に向けて重要なデバイス製造技術として省エネルギー・高生産性な連続塗布プロセスであるロール・トゥー・ロール(R2R)プロセスでの生産技術構築も進めている。今回開発した塗布型半導体デバイス技術により R2R パイロットラインでロールフィルム上への半導体デバイス製造が可能と確認し、デバイス生産の基本技術を確立した(Fig.4)。現在、歩留まり向上等の量産技術確立に取り組んでいる。

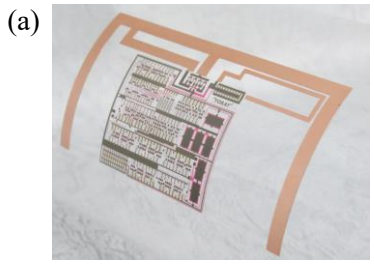

Fig.3 (a) printed RFID, (b) printed water sensor

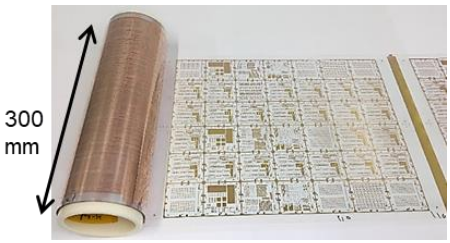

Fig.4 R2R process sample

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サステイナブル界面活性剤－内部オレフィンスルホン酸塩の製造技術開発

（花王）○山田雄大・湯浅皓卓・住岡沙羅・高田慎吾・野村真人

Development of Manufacturing Technology for Sustainable Surfactant “Internal Olefin Sulfonate” ([1]*Kao Co., Ltd.*) ○Yuudai Yamada, Koutaku Yuasa, Sara Sumioka, Shingo Takada, Masato Nomura

Internal olefin sulfonate (IOS) is sustainable surfactant that exhibits high water solubility and surfactant performance. It can be produced from oleic oils with carbon number 16 and 18 which have been difficult to use due to low water solubility. IOS is produced by converting alcohols obtained from oils to internal olefins, followed by sulfonation and neutralization reactions. However, conventional production methods have issues with color and impurities. We have established the internal olefin production technology using the developed catalyst that produces almost no byproducts which cause coloration. Furthermore, we have achieved both low color and high productivity through industrialization studies based on the use of inert gas to suppress sulfonation overreaction and numbering up. In addition, the high-speed shear technology used in emulsification technology was applied to neutralize sulfonates to suppress the impurities. This technology is expected to enable the stable supply of high-quality IOS and to solve the shortage of surfactants for detergents in the future.

Keywords : Anionic surfactant; Sustainability; Internal olefin sulfonate; Vegetable oil

内部オレフィンスルホン酸塩(IOS)は高い水溶性と界面活性能を有し、従来まで十分に利用出来なかった炭素数 16 及び 18 が主のオレイン系油脂から製造可能なサステイナブル界面活性剤である。IOS は油脂から得られるアルコールを内部オレフィンへ変換の後、スルホン化と中和反応を経て製造されるが、従来製造法では色相等の品質に課題があり洗浄剤向け界面活性剤としての用途は限られてきた。我々は独自開発した弱酸触媒を用いスルホン化の着色原因物質である副生物を殆ど生成しない内部オレフィン製造技術の確立に成功した。スルホン化工程では、独自の反応器構造を開発し、良好な色相と高い生産性を両立するに至った。続く中和工程においては乳化技術等に用いられる高速せん断技術を応用し不純物の抑制に成功した。

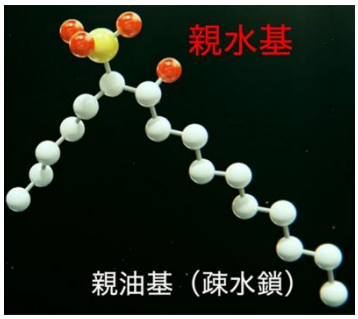

Figure 1. Molecular structure model of IOS

本技術は良好な色相と不純物の少ない高品質な IOS の大量生産を可能とし、将来で起こり得る洗浄剤原料不足の解決の一助となる事が期待される。

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高応力吸収性能を有する特異なα–オレフィン共重合体の開発とその用途展開

（三井化学）○岡本 勝彦・植草 貴行
Development of Unique α-Olefin Copolymer with High Stress Absorption Performance and Their Applications (*Mitsui Chemicals. Inc.*) ○Masahiko Okamoto, Takayuki Uekusa

In this presentation, we talk about the development of unique α-olefin copolymer that has high stress absorption performance. We found that α-olefin copolymer containing with bulky side chains as main monomer using novel metallocene catalyst is flexible and has a maximum loss tangent at room temperature. This material exhibits unique properties such as rubber elasticity in addition to excellent vibration damping and stress relaxation properties. Currently, we are promoting the development of differentiated products and applications by combining it with blending and molding processing technologies.
Keywords：α-olefin copolymer; Metallocene catalyst; elastomer; stress relaxation properties

近年、SDGs や循環型社会への変革に向けて、プラスチックに対して石油由来原料削減やリサイクル性等が強く求められている。ポリオレフィン（PO）はそのプラスチック総生産量の約半分を占め、優れた機械特性、軽量性や加工性から広く使用されており、現在も多種多様な材料が各社で開発、製品化されている。一方で、PO は炭素と水素から構成されているため相互作用は分子間力のみであり、柔軟化すると各種物性が低下してしまう等の課題があった。PO で柔軟かつ特長的な性能を設計・制御できれば、リサイクル可能で今後のサステナブルな社会に貢献することができる。そこで、振動、力や音等の応力を制御できる機能（応力吸収性能）に着目して、新規なα-オレフィン共重合体を開発した。

1. 精密ポリマー設計と重合触媒開発

従来、振動や衝撃からモノを保護するために使用されている加硫ゴムは、分子構造や配合で応力吸収性能を制御している。応力吸収性能は、物質に振動、衝撃や音等のエネルギーを印加した際、物質内で熱エネルギーに変換し、散逸する特性である。効率よくエネルギーを散逸するためには、力学的な損失正接 (=損失弾性率/貯蔵弾性率) を高くすることが必要になる。そこで、新たなポリマー設計として、分子鎖同士の摩擦熱を利用することを閃いた。摩擦熱が発生しやすいように嵩高い側鎖を有する特殊なα-オレフィンを主モノマーに選定し、さらに、コモノマーと共重合して非晶性にすることで、柔軟かつ室温で損失正接を最大化する組成を見出した。

ポリマー設計と同時に、新たな重合触媒の開発に着手した。既存のチーグラー・ナッタ触媒やシングルサイト触媒を用いて合成したα-オレフィン共重合体では、立体規則性や分子量が不足し、また低活性であった。そこで、シクロペンタジエニル-フルオレニル骨格を有するシングルサイト触媒を抽出し、改良した。具体的には配位子の

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置換基変更による活性点周辺の立体配置、電子状態を制御することにより、嵩高いα-オレフィンとの（共）重合性が良く、高活性・高分子量化が可能になった。

開発した触媒を用いて合成したα-オレフィン共重合体は、損失正接が既存の熱可塑性エラストマーに比べて 2 倍あり、世界最高レベルの性能を発現した。また、性能追及のみならず各種用途へ適応させるため、ペレット形状の製品とした。これにより長期保管が可能で、各種成形加工が容易になった。

2. 特長的な性能と用途展開

現在、開発したα-オレフィン共重合体が有する特長的な性能を活かしつつ、ブレンド技術、成形加工技術と組み合わせることで差別化製品・用途への展開を推進している。

本ポリマーは、室温で損失正接が高いため、荷重を減衰する性能（応力緩和性）に優れる。さらに非晶性のランダム共重合体にも関わらず、優れたゴム弾性を示した。架橋しなくともゴム弾性が発現する理由は、嵩高いα-オレフィン構造に起因していることが放射光を用いた解析から確認されている [1)]。ゴム弾性によるフィット感と応力緩和性による締め付け感の軽減を両立する、ゴムに変わる快適な伸縮部材として採用が進んでいる。

本ポリマーは非晶性であるため、低温加工かつ木粉やフィラー等の充填材を多量にブレンドすることが可能である。また、充填材の添加により、応力緩和性、ゴム弾性や伸びを保持しながら射出成形性が大幅に改善した。プラスチック使用量削減に貢献しつつ様々な形状への展開が可能となり、長時間着用しても疲れや痛みのないイヤフォンピース等で採用されている。

エチレン・プロピレンゴムに本ポリマーをブレンドすると、微分散して制振特性や振動減衰性を改良できる。既存の制振ゴムに対して、軽量性かつ同等の制振特性を保有する [2)]。

本ポリマーは嵩高い構造の側鎖を有しており、主鎖の凝集力が低いため、界面張力が小さい。ポリエチレンやポリプロピレンに本ポリマーを少量添加して成形したフィルムは、表面に微分散して局在化する。撥水性や粘着テープからの剥離性が改質され、産業用フィルム部材へ展開されている。

1) M. Okamoto, K. Mita, T. Uekusa, M. Takenaka, M. Shibayama, *Polymer*, 191. 122369-122378. (2020).
2) 植草貴行, *日本ゴム協会誌,* 第 95 巻 第 8 号 248-254. (2022).

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構造色による発色機構をもつ歯科用修復材料の開発

（株式会社トクヤマデンタル）秋積 宏伸・○森﨑 宏・松尾 拓馬
Development of Dental Restorative Materials with Structural Color (Tokuyama Dental Corporation) Hironobu Akizumi, ○Hiroshi Morisaki, Takuma Matsuo

Dental resin composites are among the most important materials for caries treatment. For natural-looking restorations, high color-matching ability of resin composites with natural teeth is necessary because shades of natural teeth have individual differences. We found that a resin composite containing uniform-sized spherical particles of 260 nm in diameter as an inorganic filler prepared by the sol-gel method could generate yellowish to reddish structural color and showed superior color-matching ability with a wide range of tooth shades.
Keywords: Structural Color; Dental Restorative Materials; Spherical Inorganic Particle; Composite Materials; Chemistry of Inorganic Materials

コンポジットレジン（CR）は重合性モノマー、無機フィラー、重合開始剤を主成分とするペースト状の複合材料（Fig.1. (b)上部）であり、歯科医療においてう蝕治療に欠かせない重要な材料の一つである。CR を用いた歯牙の修復は、審美的であり比較的短時間で治療が完結することから、世界中の歯科医院で日常的に行われている。天然歯の色調は一般的に「白色」と表現されるが、実際は淡い黄～赤色の領域に分布しており、かつ個人差がある。市販の CR はこのような天然歯の色の違いに対応するために、顔料で様々な色調・透明性に調整されており、その色の種類（シェード）は一つの製品あたり多いもので数十種類にも及ぶ。そのため、歯科医師は複数色の CR を在庫として管理し、患者の歯に適合する色調を都度選択して用いる必要があった。

我々は、無機フィラーが発現する構造色に着目し、ゾルゲル法で合成した 260 nm の球状シリカ系複合酸化物粒子が天然歯の色調に近い黄～赤色の構造色を呈することを見出し、この知見に基づいて非常に幅広い天然歯への色調適合性を有する CR の開発に成功した（Fig.1）。これは、発色機構として構造色を応用した独創的な歯科用修復材料である。これにより、歯科医療における CR の色調選択工程や在庫管理といった負担を軽減する効果が期待できる。

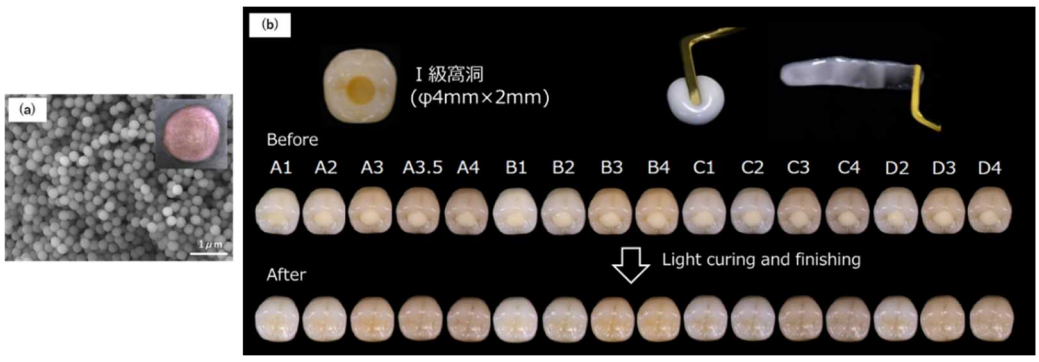

Fig. 1 (a) A 260 nm spherical filler and structural color on a black background
(b) Color-matching ability test using resin composite with structural color

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電子部品用ネガ型感光性ポリイミドシートの開発と実用化

（東レ[1]）○松村　和行[1]・加藤　圭悟[1]・龍田　佳子[1]・金森　大典[1]・桂田　悠基[1]
Development and Commercialization of Negative-type Photodefinable Polyimide Film for Electronic Components ([1]*Toray Industries, Inc.*) ○Kazuyuki Matsumura,[1] Keigo Kato,[1] Yoshiko Tatsuta,[1] Daisuke Kanamori,[1] Yuki Katsurada[1]

Photodefinable polyimide materials are expected to be widely used in advanced technologies as protective films and interlayer insulating films for semiconductors and electronic components. On the other hand, as the performance of electronic products continues to improve, the materials technology used to assemble semiconductors and electronic components must be able to handle a variety of structures that are becoming more complex. Then, we have developed the dry film type material that can form a flat surface on an uneven structure more easily than conventional varnish materials. In the process of developing the material, we found an application for forming a roof with a cavity structure that could only be achieves with a sheet form. We report on the development of a negative-type photodefiable polyimide sheet material optimized for this application.
Keywords : Photodefinable polyimide; Insulating film, Dry film; Hollow structure

感光性ポリイミド材料は、フォトリソグラフィによる微細構造の形成が可能で、ポリイミド由来の高い耐熱性と絶縁性を有する事から、半導体や電子部品の保護膜や層間絶縁膜として、先端技術の普及に寄与している。一方、エレクトロニクス製品の高性能化が進み、半導体や電子部品を実装する材料技術は、高度化及び複雑化した様々な構造に対応することが求められている。そこで、我々は、従来のワニス材料と比較して、凹凸構造に対して平坦膜を容易に形成できるシート状の材料開発に着手した。検討を進める中で、シート形状でのみ実現可能な中空構造の屋根形成用途を見出し、その用途に最適化された、新しいネガ型感光性ポリイミドシート材料を開発した。

東レがこれまで培ってきた感光性ポリイミド技術をもとにシート化に最適な材料設計を開発した。開発した材料は、ポリイミドと光硬化性樹脂のポリマーアロイで、それぞれの分子設計技術により、ｓｅｍｉ―ＩＰＮ構造を形成する。本技術により、微細なパターン加工と、熱硬化後のポリイミド由来の高い引張強伸度およびガラス転移温度を両立し、屋根構造とした際に、高温にも耐えうる十分な強度を担保する信頼性の高い永久膜を提供することが可能となった。

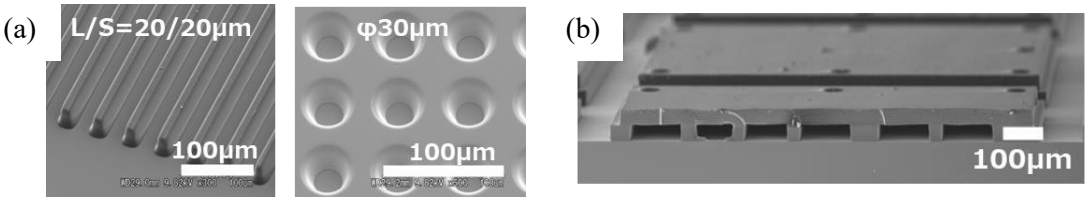

Fig. 1 SEM image of photopatterned material after curing (a) Top view of line and via pattern, (b) cross-sectional view of cavity structure.

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Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 9:00 AM - 11:10 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:10 AM UTC
B1326(1326, Bldg. 13 [2F])

[B1326-4am] Award Presentations, Special Lectures

Chair: Kosuke Suzuki, Tetsuya Taketsugu

Japanese CSJ Award for Outstanding Young Women Chemists
9:00 AM - 9:30 AM JST | 12:00 AM - 12:30 AM UTC
[B1326-4am-01]
Development of Visible/Near-Infrared Light Driven Photoreactions Using Organometallic Complexes

○Kei Murata[1] (1. IIS, The Univ. of Tokyo)

Japanese Young Scholar Lecture
9:30 AM - 10:00 AM JST | 12:30 AM - 1:00 AM UTC
[B1326-4am-02]
Synthesis and Characterization of Novel Organic Molecules Based on Spatial Arrangement of π-Conjugated Skeletons

○Kenichi Kato[1] (1. Kyoto Univ.)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
Break

Japanese Young Scholar Lecture
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[B1326-4am-03]
Development of efficient hydrogenation and dehydrogenation reactions using multifunctional solid catalysts

○Xiongjie Jin[1] (1. The University of Tokyo)

Japanese Young Scholar Lecture
10:40 AM - 11:10 AM JST | 1:40 AM - 2:10 AM UTC
[B1326-4am-04]
Topical Formulation Design using Computational Chemistry and Machine Learning Modellings

○Hiromi Baba[1] (1. Maruho Co., Ltd.)

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有機金属錯体を用いる可視・近赤外光反応の開発

（東大生研）○村田 慧
Development of Visible/Near-Infrared Light Driven Photoreactions Using Organometallic Complexes (*Institute of Industrial Science, The University of Tokyo*) ○Kei Murata

A combination of organometallic complexes possessing a flexible metal–carbon bond and light energy is attractive as it enables diverse and functional molecular transformations. In particular, visible and near-infrared light driven reactions are important from the viewpoints of utilization of renewable solar energy and application to biological systems, respectively. The presenter has worked on the development of various visible/near-infrared light driven photoreactions using organometallic complexes. In this presentation, the following reactions developed by the presenter will be introduced: (i) the catalytic immobilization reactions of carbon dioxide (CO_2) driven by visible light, and (ii) the photouncaging reactions using near-infrared light oriented toward application to photodynamic therapy.
Keywords : Organometallic Complex; Visible Light; Near-Infrared Light; Photocatalyst; Photouncaging

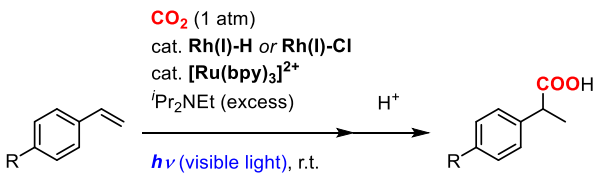
柔軟な金属－炭素結合を有する有機金属錯体と光エネルギーの融合は、多様かつ機能的な分子変換を可能にすることから魅力的である。特に、可視光反応は再生可能な太陽光エネルギー利用の観点から、近赤外光反応は生体組織への応用の観点から、それぞれ重要である。演者は、これまで有機金属錯体を用いる様々な可視・近赤外光反応の開発に取り組んできた。本講演では特に、[1] 可視光を駆動力とする二酸化炭素（CO_2）の触媒的固定化反応、および [2] 光線力学的療法への応用を志向した近赤外光を用いる光アンケージング反応について紹介する。

1. 可視光エネルギーによる遷移金属触媒カルボキシル化反応の開発

CO_2 を有機化合物中に固定化する手法の開発は、化石燃料の大量消費に伴い排出される CO_2 の再資源化の観点から重要である。CO_2 を有機分子中に固定化する一手段として、遷移金属触媒を用いるカルボキシル化反応がある。同反応では一般に、有機金属種を CO_2 に付加させたのち、カルボン酸を生成物として遊離させるとともに、触媒活性種であるヒドリド金属種や低原子価金属種を再生させる必要がある。従来法では、この変換に有機亜鉛試薬などの金属還元剤を化学量論量以上添加する必要があるが、これらは反応性が高いため、取り扱いや環境調和性に課題があった。

こうした背景から本研究では、遷移金属触媒カルボキシル化反応に可視光エネルギーを利用する方法論の開発に取り組み、光酸化還元触媒作用に基づく変換法を開発した。具体的には、ロジウム触媒と光酸化還元触媒の二元触媒系を用いると、アルケン類の可視光駆動型

式1. アルケン類の可視光駆動型ヒドロカルボキシル化反応



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ヒドロカルボキシル反応が進行することを見出した（式１）[1,2]。この触媒系では、アミンを電子源とする還元過程に基づき、触媒量のみの金属種による環境調和性に優れた反応が実現する。一連の反応機構解析により触媒サイクルの全素過程を実証し、同反応では可視光エネルギーがロジウム触媒の還元のみならず、CO_2 付加の過程にも寄与することを明らかにした。さらに、同様の還元過程をパラジウム触媒に適用すると、アリールハライドの可視光駆動型カルボキシル化反応が進行することもわかった [3]。このように、カルボキシル化触媒と光酸化還元触媒を組み合わせた二元触媒系は、様々な CO_2 固定化反応に応用できることから有用である。

2. 有機金属フタロシアニン錯体による赤色光アンケージング反応の開発

光線力学的療法は、生体内に投与した光増感剤の光化学反応により、腫瘍細胞を選択的に攻撃するがん治療法である。同療法には、治療に伴う副作用を通常の薬剤療法に比べ低減できるメリットがあるが、細胞攻撃の活性種が系中酸素から生成する「活性酸素種」に限られること、ゆえに腫瘍細胞に含まれる低酸素領域の治療効果が低いことなどに課題があった。

こうした背景から本研究では、生体組織透過性の高い赤色光により腫瘍細胞の攻撃に有用な「活性炭素種」を放出する手法の開発に取り組み、有機金属フタロシアニン錯体を用いる反応系を開発した（図１）[4]。具体的には、ロジウムフタロシアニン錯体の軸位に種々の有機配位子を導入し、同錯体が赤色光の一光子または段階的二光子励起によってアルキルラジカルを放出することを見出した。このラジカルは、ロジウム中心の作用により、酸素共存下で速やかに末端アルデヒドへと変換される。本原理を利用し、アルデヒドを活性基とするアポトーシス誘導物質の光放出に成功した。さらに、同錯体が適切な作用濃度下で、ヒト腫瘍細胞に対し光線力学的効果を発現することを示した。本研究で開発した光アンケージング系は、多様な活性種の放出に応用できること、低酸素環境下においても機能し得ることから、生体内の多様な酸素環境に対応した光治療システムとしての応用が期待される。

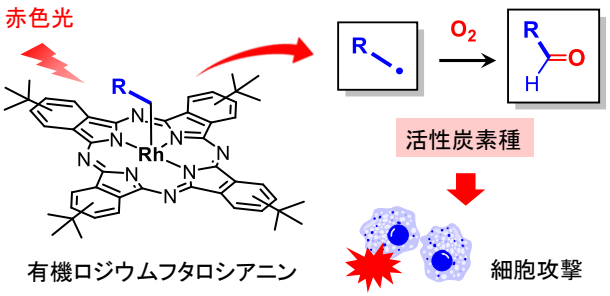

図1. 赤色光アンケージング反応の概念図

1) K. Murata, N. Numasawa, K. Shimomaki, J. Takaya, N. Iwasawa, *Chem. Commun.* **2017**, *53*, 3098.
2) K. Murata, N. Numasawa, K. Shimomaki, J. Takaya, N. Iwasawa, *Front. Chem.* **2019**, *22*, 371.
3) K. Shimomaki, K. Murata, R. Martin, N. Iwasawa, *J. Am. Chem. Soc.* **2017**, *139*, 9467.
4) K. Murata, Y. Saibe, M. Uchida, M. Aono, R. Misawa, Y. Ikeuchi, K. Ishii, *Chem. Commun.* **2022**, *58*, 11280.

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π共役骨格の立体配置に基づく新規有機分子の合成と物性評価

（京大院工）○加藤 研一

Synthesis and Characterization of Novel Organic Molecules Based on Spatial Arrangement of π-Conjugated Skeletons (*Graduate School of Engineering, Kyoto University*) ○Kenichi Kato

π-Conjugated molecules play a central role in organic functional materials because they have rigid molecular skeletons and show interesting optical, electrochemical, and magnetic response. For the elaboration and innovation of these properties, the control of solid-state assembling structures is as important as the development of novel π-conjugated planes themselves. However, most π-conjugated skeletons have been planar. They tended to form π-stacked dimers interacting weakly with outside molecules, especially in the case of π-extended ones with superior electronic properties. For these backgrounds, the speaker have designed and characterized a few series of molecules based on spatial arrangement of plural π-skeletons. Two sets of molecules are introduced in this presentation, focusing on the functionalization using late-stage reactions and properties deriving from three-dimensional structures.

Pillar[*n*]arenes are macrocyclic oligomers in which 1,4-dialkoxybenzene units are connected with each other by methylene linkages (Figure 1). Among π-conjugated macrocycles, pillar[*n*]arenes are unique because the symmetric targets are selectively obtained without difficulties in synthesis and isomeric separation.[1)] The speaker have synthesized new molecules with altered electronic properties by using direct functionalization on the π-cores. In a set of molecules arylated on one rim of the cylinder, two-sided chiroptical macrocycles were produced, and the effect of dipolar characters was studied.[2)] Pillar[5,6]arenes arylated at all the substitution positions were synthesized at the first time. The products showed high luminescence efficiency and crushed structures causing low dissymmetry factors.[3)]

The research also is extending to new derivatives of π-fused propellanes in which a single-bonded sp^3 carbon pair are fused with three aromatic rings (Figure 2). They retain π-accessible naphthalene rings, which can be located at nodes in porous frameworks. Indeed, porous polymers and molecular solids base on π-fused propellanes exhibited selective adsorption of small molecules reflecting the chemical structures, in the low pressure regions inducing monolayer adsorption.[4,5)] [4.3.3]Propellane selectively afforded di-functional derivatives[6)] and revealed a twist along the central C–C single bond. Furthermore, the latest results supported the flexibility and intrinsic chirality, making a sharp contrast to triptycene derivatives.

Keywords : π-Conjugated System; Three-dimensional Structure; Symmetry; Chiroptical Properties; Molecular-size Space

π共役分子は剛直な分子骨格を持ち，π電子に基づいた光学，酸化還元，磁気応答を示すために有機機能性材料の中核を占める．これら物性の向上と革新のために一枚のπ共役平面として新奇なものを追求する方向性と並んで，非溶液系でのπ共役骨格の集合構造制御も材料物性の鍵となる．しかし，π共役骨格は「平面的」な分子が大半を占めており，特に機能に優れるπ拡張分子は積層型の二量体を形成して外部とは外縁部で比較的弱く相互作用する集合構造をとる傾向にある．以上の背景の

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もとで講演者は，複数のπ共役骨格を「立体的な構造へと組み上げる」分子設計戦略に着目し，立体配置と物性の関係を理解しながら機能を開拓する研究に取り組んできた．本講演では 2 つの分子群について，後期修飾による新規分子合成，立体構造がもたらす物性を中心に成果を紹介する．

所属研究室で活発に研究されているピラー[*n*]アレーンは，1,4-ジアルコキシベンゼンがメチレン基を介して 2,5 位で連結した環状多量体であり（図 1a），他の環状多量体では合成単離が難しい対称性の大環状分子を選択的に得られる点に特徴がある．[1] 講演者は，研究例の少ない環本体への直接修飾反応に着目し，電子物性を改変した分子群を創出してきた．円筒の片縁にアリール置換基を導入した系では，二面性と光学活性を同時に示す分子系列における分極の影響を明らかにした（図 1b）．[2] ピラー[5,6]アレーンの円筒両縁すべての置換位置に芳香環を直接導入した初の分子では，発光効率に顕著な向上が見られ，つぶれた円筒のため非対称性因子は低下した（図 1c）．[3]

単結合を持った sp^3 炭素 2 つを中心に，3 つのπ共役平面が縮環したプロペラン類にも着目して誘導体の開発を行った（図 2）．多孔性構造体を形成した際，「節」と呼ばれる分岐部分に相互作用能力を保持したナフタレン環が位置する点に着目し，多孔性の高分子および有機固体を合成した．[4,5] これらは特に低圧下での単分子層吸着挙動において，化学構造を反映した選択性で小分子吸着特性を示した．基盤骨格を[4.3.3]型とすることで 2 官能性の誘導体が選択的に合成できることも見出された．[6] 直近では，骨格中央の炭素-炭素結合がねじれやすく，トリプチセン類に比べてπ縮環プロペランが柔軟で，内在的掌性を持ちうることを示唆する結果が得られている．

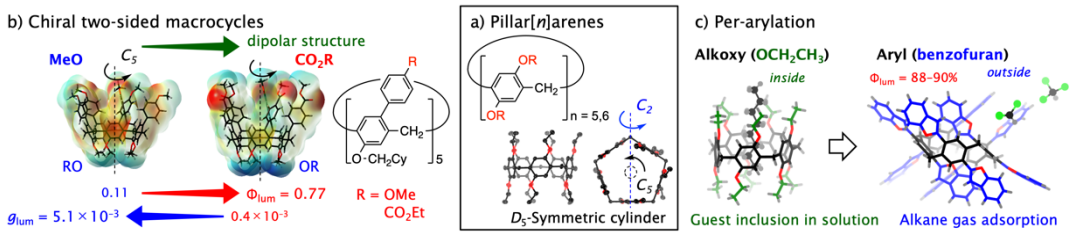

図1. a) ピラー[*n*]アレーンの化学構造，結晶構造と溶液中での対称要素．b) 二面性と光学活性を同時に示す円筒分子の化学構造と基底状態での静電ポテンシャル図．c) アルコキシ型およびアリール型ピラー[*n*]アレーンの比較．

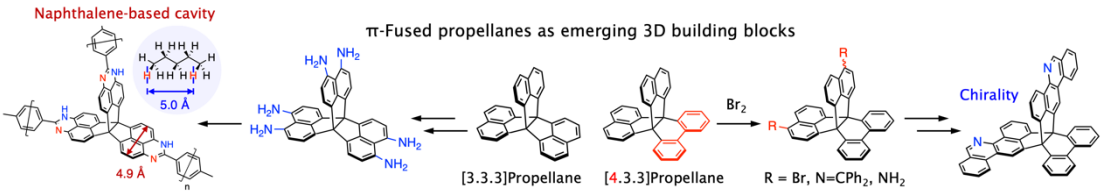

図2. π縮環プロペランの化学構造および新規誘導体への変換．

1) K. Kato, S. Fa, T. Ogoshi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202308316. (Minireview) 2) K. Kato, Y. Kurakake, S. Ohtani, S. Fa, M. Gon, K. Tanaka, T. Ogoshi, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209222. 3) K. Kato, T. Kaneda, S. Ohtani, T. Ogoshi, *J. Am. Chem. Soc.* **2023**, *145*, 6905–6913. 4) K. Kato, N. Seto, K. Chida, T. Yoshii, M. Mizuno, H. Nishihara, S. Ohtani, T. Ogoshi, *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1296–1302. 5) K. Kato, T. Hiroi, N. Seto, S. Ohtani, T. Ogoshi, *Chem. Lett.* **2022**, *51*, 975–977. 6) K. Kato, S. Tanaka, N. Seto, K. Wada, M. Gon, S. Fa, S. Ohtani, K. Tanaka, T. Ogoshi, *Chem. Commun.* **2023**, *59*, 7080–7083.

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多機能固体触媒による精密水素化・脱水素反応の開発

（東大院工）○金 雄傑
Development of Efficient Hydrogenation and Dehydrogenation Reactions Using Multifunctional Solid Catalysts (*Graduate School of Engineering, The University of Tokyo*)○ Xiongjie Jin

Catalysts have been classified into heterogeneous and homogeneous catalysts, and each of which has developed as a completely different field. Among these, heterogeneous catalysts have an advantage over homogeneous catalysts for molecular transformations because they can be easily recovered and reused. However, precise control of the active site is extremely difficult, and catalyst design still largely relies on experience. On the other hand, with homogeneous catalysts, active sites can be tuned through rational ligand design, and reaction control is much easier than with heterogeneous catalysts. Therefore, it is important to merging the design concept of homogeneous catalysts into the development of heterogeneous catalysts and to rationally design truly powerful heterogeneous catalysts that possess the advantages of both homogeneous and heterogeneous catalysts, by which synthetic chemistry can be revolutionized toward sustainable society.

Recently, we have been keen to develop the field of “fusion catalyst” chemistry, which goes beyond the conventional framework of heterogeneous and homogeneous catalysts. Specifically, by merging the catalyst design concept in homogeneous catalysis, namely “metal-ligand cooperation” to heterolytically cleave chemical bonds, to the design of heterogeneous catalysts, we have successfully developed a series of highly efficient heterogeneous supported metal catalysts for hydrogenolysis and dehydrogenation reactions by employing “metal-support cooperation” for catalyst design. The important point in our catalyst design is that the metal and the support cooperatively activate the substrate and promote the reactions benefiting from the support material. The as-described catalyst design concept for heterogeneous catalysts allowed us to develop highly selective and efficient (1) C−O bond hydrogenolysis[1,2] and (2) C−C bond dehydrogenation reactions,[3−5] which are of significant importance in sustainable chemical synthesis using renewable sources. The heterogeneous-homogeneous fusion catalyst system developed in our works combines the characteristics of a heterogeneous catalyst, which is easy to recover and reuse, and the characteristics of a homogeneous catalyst, which allows precise control of reactions.

Keywords : heterogeneous catalysts; metal-support cooperation; hydrogenation; dehydrogenation

触媒は現代の合成化学を支える要であり、これまでに不均一系触媒と均一系触媒に分類され、それぞれ異なる学問分野として発展してきた。なかでも、不均一系触媒は回収再利用が容易であることから、次世代環境調和型物質合成において均一系触媒に比べ優位性があるが、活性点構造の精密制御が極めて困難であり、触媒設計は未だ経験に頼る部分が多い。一方で、均一系触媒は合理的な配位子設計による活性点のチューニングが可能であり、反応制御が不均一系触媒に比べ遥かに容易である。したがって、均一系触媒の設計理念を不均一系触媒の開発に取り入れ、均一系触媒と不均一系

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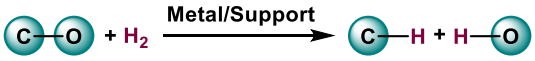
触媒の長所を併せ持つ真に力量のある不均一系触媒を合理的に設計することは物質合成の革新を成し遂げるうえで必要不可欠である。

我々はこれまでに、従来の不均一系触媒と均一系触媒の枠を超えた「融合触媒」の開発を目指し、触媒および反応開発を行ってきた。特に均一系触媒に広く応用されてきた「金属–配位子協働作用」による結合の不均等活性化を不均一系触媒の設計に融合させ、「金属–担体協働作用」を触媒設計の基本コンセプトとすることにより、多機能不均一系担持金属触媒を合理的に設計し、高難度分子変換反応を開発した。すなわち、金属と担体が協働で基質を活性化し、反応の促進を図るものである。これにより、ファインおよびバルクケミカル合成両方において重要な（1）C–O 結合の選択的水素化分解反応、および（2）C–C 結合の脱水素反応の開発を行い、数々の新触媒および新反応の創出に成功した。我々が開発した融合触媒系は、回収・再利用が容易である不均一系触媒の特徴と、反応の精密制御が可能である均一系触媒の特徴を併せ持つ。

■ This work：Metal-support cooperation in heterogeneous catalysis for efficient hydrogenolysis and hydrogenation reactions

(a) C–O bond hydrogenolysis



Nature Catal. **2021**, *4*, 312. (Cover)
J. Am. Chem. Soc. **2023**, *145*, 3454. (Cover)

(b) C–C bond dehydrogenation



Selected papers:

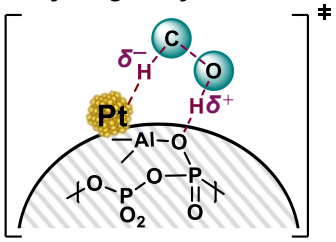
Dehydrogenative aromatization reactions

Chem. Sci. **2016**, *7*, 5371. (SYNFACTS)
Chem. Commun. **2017**, *53*, 5267. (Cover, SYNFACTS)
Chem. Commun. **2017**, *53*, 10827.
J. Am. Chem. Soc. **2017**, *139*, 13821. (Cover)
Angew. Chem. Int. Ed. **2019**, *58*, 10893. (SYNFACTS)

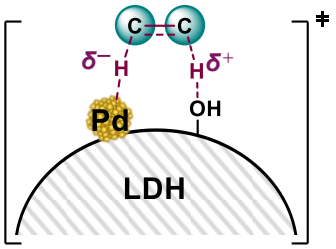
Dehydrogenative molecular transformations

Angew. Chem. Int. Ed. **2016**, *55*, 7212. (SYNFACTS)
ACS Catal. **2019**, *9*, 3011.

✓ **Hydrogenolysis**



✓ **Dehydrogenation**



1) K. Yuan, Y. Yamazaki, X. Jin, K. Nozaki, *J. Am. Chem. Soc.* **2023**, *145*, 3454.
2) X. Jin, R. Tsukimura, T. Aihara, H. Miura, T. Shishido, K. Nozaki, *Nature Catal*. **2021**, *4*, 312.
3) Y. Koizumi, X. Jin, T. Yatabe, R. Miyazaki, J. Hasegawa, K. Nozaki, N. Mizuno, K. Yamaguchi, *Angew. Chem. Int. Ed.* **2019**, *58*, 10893.
4) X. Jin, Y. Koizumi, K. Yamaguchi, K. Nozaki, N. Mizuno, *J. Am. Chem. Soc.* **2017**, *139*, 13821.
5) X. Jin, K. Taniguchi, K. Yamaguchi, K. Nozaki, N. Mizuno, *Chem. Commun*. **2017**, *53*, 5267.

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計算化学を用いた外用製剤処方設計

（マルホ株式会社トランスレーショナルリサーチ推進部）○馬場 廣海
Topical Formulation Design Using Computational Chemistry and Machine Learning Modellings (Translational Research Department, Maruho Co., Ltd.) ○Hiromi Baba

Designing formulations that can ensure the spatiotemporal delivery of active pharmaceutical ingredients (APIs) is crucial for the development of pharmaceutical products, in addition to discovering APIs. However, owing to the expansive design space resulting from the numerous combinations of formulation ingredients, optimization of formulations is an extremely challenging and expensive process. Herein, we developed a methodology to streamline a formulation optimization process by constructing prediction models for formulation properties of systems comprising diverse compounds using machine learning and molecular dynamics simulations.

Keywords : Pharmaceutical Formulation; Molecular Dynamics; Machine Learning; Solvent Effect;

有効性・品質等の同時最適化を実現する製剤開発は、主薬創出等とともに医薬品開発の基幹プロセスの 1 つである。しかしながら、製剤を構成する医薬品添加物は、使用前歴のあるものだけでも一千種以上を数え、その膨大な組み合わせ処方から、所望の特性を示す製剤を見出すことは困難な作業である。一方、近年発展の目覚ましい機械学習法や分子シミュレーション技術により、医薬品製剤を構成する各種分子間に働く相互作用や複雑な製剤特性を予測・推定できる可能性がある。

私たちは、外用製剤の pre-formulation（開発初期工程）の主要評価項目である溶解剤混合処方における主薬の安定性、溶解性および経皮吸収性について、in-house ならびに文献よりデータを取得の上、機械学習法（support vector regression や random forest）を用いて予測モデルを構築した。それらは、80～140 種程度の未知処方データに対して、いずれも予測－実測間の決定係数（R^2）は 0.85 を超えており、複雑な添加物混合の影響を高精度に予測可能であった。それらを統合的に用いることで、pre-formulation の最適化システムを構築の上、実務運用している。

一方、外用剤開発の後期工程における軟膏・ゲル・クリームなどの各種剤形の処方を最適化する機械学習モデルは、網羅的な学習用データの集積が難しく、容易には実現できない。そこで、分子動力学シミュレーションの応用を検討し、混合物内の物質挙動、混和・分離、ミセル特性などを高精度に予測し得ることを確認してきた。現在、さらなる技術開発とともに、製剤特性解析・処方設計への活用を進めている。本講演では、これらの計算化学・情報化学技術を用いた処方設計について紹介する。

1) H. Baba, et al., *Pharm. Res.* **2015**, *32*, 2360−2371. 2) H. Baba, et al., *Pharm. Res.* **2015**, *32*, 3604−3617. 3) H. Baba, et al., *Int. J. Pharm.* **2017**, *522*, 222−233. 4) H. Baba, et al., In: K. Sugibayashi (ed), *Skin Permeation and Disposition of Therapeutic and Cosmeceutical Compounds*, Springer, Tokyo, **2017**, pp. 363−376. 5) H. Baba, et al., *ACS Spring 2022,* **2022**, Paper ID: 3641993. 6) H. Baba, et al., *J. Comput. Chem.* **2022**, 43, 1892−1900.

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Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 1:00 PM - 2:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:00 AM UTC B1325(1325, Bldg. 13 [2F])

[B1325-4pm] Award Presentations, Special Lectures

Chair: Yoshihiro Nishimoto, Yuichi Negishi

Japanese Young Scholar Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[B1325-4pm-01]
Novel Transformations of Organic Molecules Based on Selectivity Control Unique to Supported Nanoparticle Catalysts

○Takafumi Yatabe[1,2] (1. The University of Tokyo, School of Engineering, 2. JST, PRESTO)

Japanese Young Scholar Lecture
1:30 PM - 2:00 PM JST | 4:30 AM - 5:00 AM UTC
[B1325-4pm-02]
Catalytic Bond Cleavage Enabled by Zirconocene and Photoredox Catalysis

○Eisuke Ota[1] (1. Waseda University)

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担持金属ナノ粒子触媒特有の選択性制御に立脚した新規有機分子変換

（東大院工[1]・JST さきがけ[2]）○谷田部 孝文[1,2]

Novel Transformations of Organic Molecules Based on Selectivity Control Unique to Supported Nanoparticle Catalysts ([1]*School of Engineering, The University of Tokyo*, [2]*JST, PRESTO*) ○Takafumi Yatabe[1,2]

While inorganic solid catalysts have attracted attention as environmentally benign catalysts that can be easily reused and applied to flow synthesis, the development of novel organic reactions utilizing their unique structures and properties, which differ significantly from those of homogeneous catalysts such as metal complex catalysts, has been hardly explored. In this study, I focused on supported metal nanoparticle catalysts, which have zero-valent metal bonds and can be functionally integrated, and I achieved various novel organic molecular transformations by controlling selectivity using catalytic properties unique to supported metal nanoparticle catalysts such as multi-site adsorption, concerted electron transfer, and bimetallic structure control. In this presentation, I will talk about three topics: a) novel tandem reactions via α-methylene regiospecific aerobic oxidation of tertiary amines catalyzed by Au nanoparticles,[1,2] b) selectivity switch of flavonoid synthesis from one-pot flavone synthesis to aurone synthesis by function integration,[3,4] and c) efficient oxidative dehydrogenation of saturated ketones via concerted C–H activation by nanooxides-on-nanoparticles.[5,6]

Keywords : Supported Metal Nanoparticle Catalysts; Selectivity Switch; C–H Functionalization; Aerobic Oxidation; Oxidative Dehydrogenation

無機固体触媒は分離再使用・フロー合成への応用が容易な環境調和型触媒として注目されている一方で、錯体触媒等とは大きく異なる構造や特性を利用した新規有機反応開発はほとんど未開拓であった。本研究では、特に 0 価の金属結合を有し機能集積が可能な担持金属ナノ粒子触媒に着目し、多点吸着や協奏的電子移動、二元金属の構造制御など、特有の触媒特性を利用した選択性制御を行うことで、数々の新規有機分子変換を達成した。本講演では、まず、単金属ナノ粒子触媒上での多点吸着や協奏的電子移動を利用した新規有機分子変換として、担持 Au ナノ粒子触媒による α-メチレン基特異的アミン酸素酸化を経るタンデム反応による選択的アミド・プロパルギルアミン・エナミノン合成について講演する (図 a)[1,2]。Au ナノ粒子触媒上において第三級アミンから酸素分子への協奏的な二電子一プロトン移動が起こりイミニウムカチオン様の遷移状態となることで特異な選択性が発現したことが示唆されている。続いて、機能集積やモルホロジー制御による選択性制御を利用した新規有機分子変換であるフラボン one-pot 合成からオーロン合成への選択性スイッチ (図 b)[3,4]、関連して、ナノ酸化物クラスター-on-ナノ粒子という特異な活性点構造を利用した協奏的 C–H 結合活性化を経る飽和ケトンの高効率酸化的脱水素 (図 c)[5,6] について講演する。固体触媒特有の触媒設計により、均一系触媒でも実現できていなかった分子変換を達成しており、新規有機反応開発に対する固体触媒の潜在可能性を実証したと考えられる。

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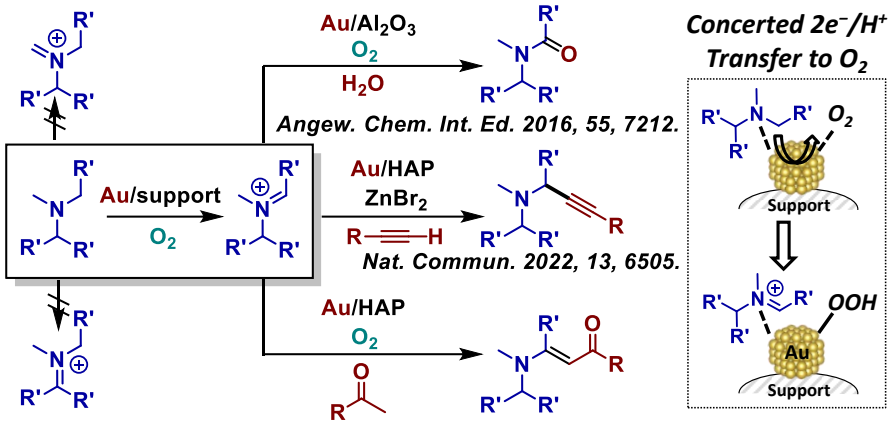
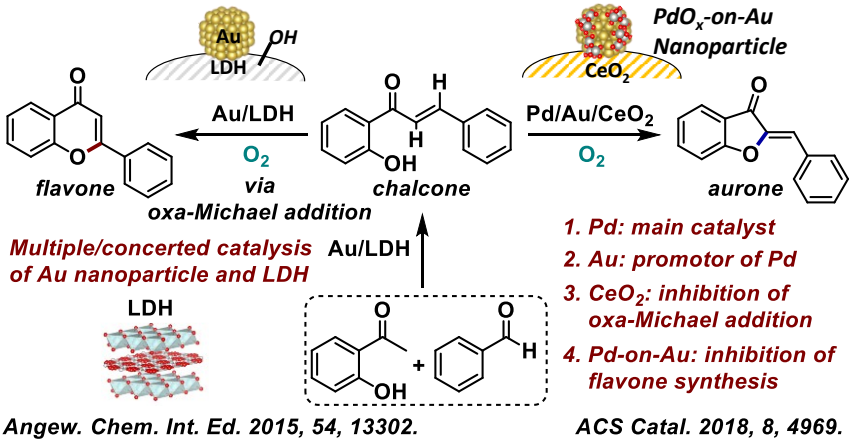
a) Auナノ粒子触媒によるα-メチレン基特異的アミン酸化を経るタンデム反応

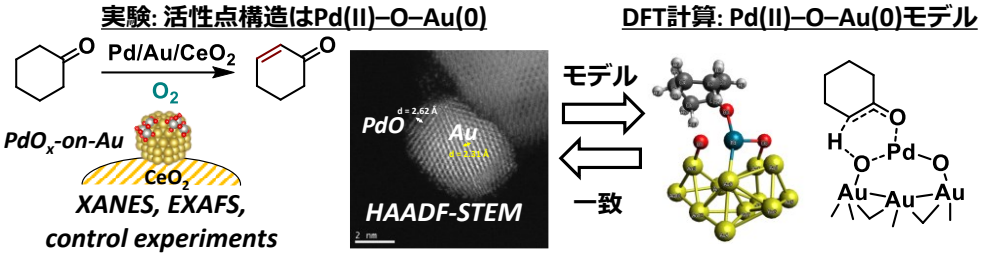


b) 機能集積型固体触媒によるフラボノイド合成の選択性スイッチ



Angew. Chem. Int. Ed. 2015, 54, 13302. *ACS Catal. 2018, 8, 4969.*

c) 特異な金属ナノ触媒活性点構造による高効率脱水素および反応機構の解明



JACS Au, 2022, 2, 394; ACS Catal. 2020, 10, 5057.

隣接するルイス酸-ブレンステッド塩基対が高効率C–H結合活性化に寄与

1) X. Jin, K. Kataoka, T. Yatabe, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2016**, *55*, 7212.
2) T. Yatabe, K. Yamaguchi, *Nat. Commun*. **2022**, *13*, 6505.
3) T. Yatabe, X. Jin, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2015**, *54*, 13302.
4) T. Yatabe, X. Jin, N. Mizuno, K. Yamaguchi, *ACS Catal*. **2018**, *8*, 4969.
5) D. Takei, T. Yatabe, X. Jin, T. Yabe, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2020**, *10*, 5057.
6) D. Takei, T. Yatabe, T. Yabe, R. Miyazaki, J. Hasegawa, K. Yamaguchi, *JACS Au* **2022**, *2*, 394.

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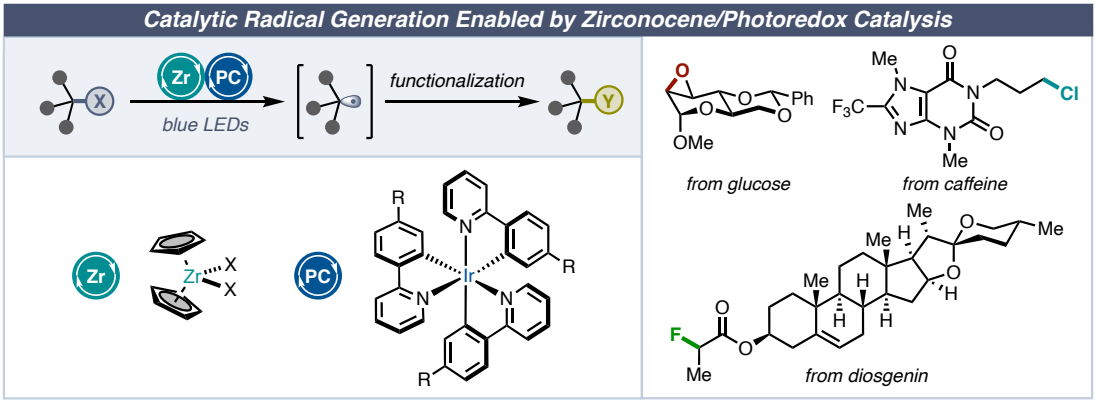
ジルコノセンと可視光レドックス触媒に着目した触媒的結合開裂反応の開発

（早大理工）○太田 英介
Catalytic Bond Cleavage Enabled by Zirconocene and Photoredox Catalysis (*School of Advanced Science and Engineering, Waseda University*) ○Eisuke Ota

Carbon-centered radicals, intrigued intermediates in organic synthesis, have been generally formed from well-designed radical precursors. The methodologies to produce carbon-centered radicals by σ-bond cleavage of the previously inaccessible bonds would significantly contribute to the expansion of synthetic strategy. Herein, we achieved the cleavage of C–O, C–Cl, and C–F bonds by zirconocene/photoredox catalysis. These protocols are proposed to be engaged with zirconocene (III) and affords carbon-centered radicals, which can undergo functionalization with different radical trapping agents. The processes proceeded under mild conditions and accommodated a wide range of substrates, including biologically active compounds.
Keywords : Photoredox Catalysis, Zirconocene, Radical, Bond Cleavage

可視光レドックス触媒反応は、近年目覚ましい発展を遂げるが、反応の起点となるラジカル生成段階に着目すると、その選択肢は未だ十分とは言えない。特に原子移動反応に関しては、主に水素原子移動もしくは臭素やヨウ素を対象とするハロゲン原子移動に限られる。これら原子移動では、反応前後の結合エネルギーの利得が反応の駆動力となる。従来は困難であった C–X 結合開裂をともなう原子移動を実現するには、X 原子と強固な結合を形成するラジカル種が必要となる。

我々は酸素や塩素、フッ素原子と強く結合を形成する Zr 原子に着目し、可視光レドックス/ジルコノセン協働触媒系を開発した [1-3]。可視光レドックス触媒による還元で生成する Zr(III)ラジカルは、強固な Zr–X 結合の形成を駆動力として C–X 結合を開裂する。本反応は室温付近で進行し、生物活性物質を含む様々な分子に適用できた。



1) Aida, K.; Hirao, M.; Funabashi, A.; Sugimura, N.; Ota, E.; Yamaguchi, J. *Chem* **2022**, *8*, 1762.
2) Aida, K.; Ota, E.; Yamaguchi, J. *Synlett* **2023**, eFirst.
3) Okita, T.; Aida, K.; Tanaka, K.; Ota, E.; Yamaguchi, J. *Precis. Chem*. **2023**, *1*, 112.

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Award Presentations, Special Lectures | Award Presentations, Special Lectures：Award Presentations, Special Lectures

Thu. Mar 21, 2024 1:00 PM - 2:20 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:20 AM UTC B1326(1326, Bldg. 13 [2F])

[B1326-4pm] Award Presentations, Special Lectures

Chair: Izumi Imai, Masato Ito

Japanese CSJ Award for Merits for Chemical Education
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[B1326-4pm-01]
Improvement of chemistry education through textbook authorization

○Kiyotaka Shigehara[1] (1. Tokyo University of Agriculture and Technology)

Japanese CSJ Award for Chemical Education
1:30 PM - 2:20 PM JST | 4:30 AM - 5:20 AM UTC
[B1326-4pm-02]
Outstanding education activity in analytical and inorganic chemistry

○Kazuo Miyamura[1] (1. Tokyo University of Science)

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教科書検定を通じて行った化学教育の改善

（農工大工・名誉教授）　重原淳孝
Improvement of Chemistry Education Through Textbook Authorization.
(*Honorary Prof., Graduate School of Engineering, Tokyo University* of Agriculture & Engineering)　Kiyotaka Shigehara

The present author has been involved in MEXT authorization workshop of basic chemistry and chemistry textbooks for about 7 years until 2021. Since the actions and roles in the workshop committee were evaluated to be worthy for “The Chemical Society of Japan Award for Merits for Chemical Education” for 2024, several examples of the improvements of textbooks are presently introduced.

As the fundamental law of education and the school education act had been proclaimed in 1947, printing and issue of evaluated textbooks has started. 67 years had passed since then, the supplements of textbooks necessary to deal with the new findings and inventions have been advanced and the corresponding revisions were made. Although the academic field continued from olden days as like chemistry is expected to generate textbooks with enough completeness, it is our regret that the present situation is not reaching there. Rather, not a few fundamental errors continued to be overlooked and described in the textbooks till the present days. If such errors were overlooked in the authorization workshop, no revisions maybe available for the successive 4 years. Descriptions on Volta cell, $Fe(OH)_3$, VSEPR, intermolecular force, allotropes, several chemical terms, etc., were typical inconsistencies corrected very recently. Still, many has been remained uncompleted, deep participation of The Chemical Society of Japan is sincerely expected.

Keywords : Education;Textbook Authorization; Basic Chemistry; Highschool Chemistry

著者は令和３年３月迄の７年弱，小中学校理科(化学領域)及び高校の化学基礎・化学の教科書の検定に携わって来た。その活動が化学教育の改善に繋がったと評価されて化学教育有功賞を授与されるに至ったので，若干説明させて頂きたい。

1947 年(昭和 22 年)に行われた教育基本法・学校教育法(School education act)の公布に伴い，検定教科書の編集・発行が始められた。以来，67 年程が経って，教科書の内容には新しい発明発見に対応した補足がその都度行われ，必要な改定も進められてきた。化学のような比較的古くから続いている学問領域であると，教科書も完成度が高くて良い筈なのだが，残念ながら実情はそこまで至っていない。むしろ、基本的な問題が見逃されて今日まで誤った記載が続けられていた例も枚挙にいとまがない。検定作業で見逃してしまうと４年間は訂正されないままになってしまうので、文科省当該事務局には多大の迷惑をかけてなるべく多くの改定を行ってきた。ボルタ電池に関する訂正、純物質として存在していない $Fe(OH)_3$（化学式 FeO(OH)で代表される酸化水酸化物に変わってしまう）の抹消、VSEPR，分子間力や同素体に関する提言、各種化学用語の変更、などである。然しながら未だ完全には程遠いので、日本化学会が主たる役割を果たして頂けるよう、切に希望する次第である。

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分析・無機化学分野における優れた教育活動

（東理大）宮村 一夫
Outstanding Educational Activity in Analytical and Inorganic Chemistry (*Tokyo University of Science*) ○Kazuo Miyamura

Since 1982, when I started my career as an assistant professor, I worked for 16 years at the University of Tokyo and, from 1998, headed a laboratory at the Tokyo University of Science for 25 years. During that time, more than 300 bachelors, 140 master course students and 12 doctor course students graduated from my laboratory. The duties of a university professor can be classified into administration, research and education. I served as a director in 4 academic associations and reported over 100 papers. In addition, I also chaired the Editorial Board of the Journal of Chemistry and Education and the Chemical Heritage Committee of JCS.

Now that I have received the Chemistry Education Award from JCS with regard to education, I would like to look back on my academic activities and introduce how I managed my laboratory, focusing on the research results of my PhD students.

Keywords : University of Tokyo, Tokyo University of Science

1982 年に東京大学工学系大学院の博士課程を 1 年で中退して助手に採用されて以来、東京大学工学部に 16 年間勤め、さらに 1998 年から東京理科大学理学部で 25 年間研究室を主事して昨春、定年退職した。その間、300 名を超える学士、140 名の修士、12 名の課程博士を世に送り出してきた。大学教員の業務は、管理、研究、教育に分類できるが、管理では 4 学協会（日本化学会、日本分析化学会、日本分光学会、日本鉄鋼協会）で理事職、学内では学部長および評議員を務めさせていただいたし、研究では分子集合系の解析をテーマに、100 編を越える論文を報告することができた。なお、日本化学会においては、理事以外に化学と教育誌編集委員会および化学遺産委員会の委員長を務めさせていただいた。

今回、教育に関して化学教育賞を受賞しましたので、教員人生を振り返り、博士課程学生の研究成果を中心に、研究室をどのように運営してきたか、紹介したい。

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Symposium | Co-Innovation Program (CIP)：Innovative catalysts for challenging carbon negativity

Thu. Mar 21, 2024 9:00 AM - 11:30 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:30 AM UTC
A1431(1431, Bldg. 14 [3F])

[A1431-4am] Innovative catalysts for challenging carbon negativity

Chair, Symposium organizer: Hideshi Sasakura, Kazuhiro Sayama, Koichi Matsushita, Yutaka Amao, Yuusuke Sunada

2020年10月に「2050年カーボンニュートラル」宣言を契機として、2030年度までの温室効果ガス削減目標を2013年度比で46%削減することとし、将来的には80%削減に向けて新たな方針も示されております。これらの目標達成のためには、人工光合成を含む再生可能エネルギーを用いた水素製造や二酸化炭素利用に加えて，二酸化炭素フリー水素製造技術、二酸化炭素の水素化や二酸化炭素の有価物への触媒的変換技術を急速に発展・成熟させ、二酸化炭素排出実質ゼロを超えるマイナスに転じるカーボンネガティブ技術が必要です。本セッションでは、これらの研究について世界をリードする研究者に紹介いただきます。カーボンニュートラルは本当に達成できるか、それを超えるカーボンネガティブ実現に向け、どんな挑戦が必要か、活発な議論の場の提供を考えております。

聴講後のアンケートへのご協力をお願いいたします。

9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC

Opening Remarks

Japanese Invited Lecture

9:10 AM - 9:40 AM JST | 12:10 AM - 12:40 AM UTC

[A1431-4am-01]

Development of innovative catalysts for organic synthetic reactions using carbon dioxide

○Tetsuaki Fujihara[1] (1. Kyoto University)

Japanese Invited Lecture

9:40 AM - 10:10 AM JST | 12:40 AM - 1:10 AM UTC

[A1431-4am-02]

Development of CCU technologies by NIPPON STEEL CORPORATION

○Ayaka Miura[1] (1. NIPPON STEEL CORPORATION)

10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC

[4A143101-03-4add]

Incubation Time

Japanese Keynote Lecture

10:20 AM - 11:20 AM JST | 1:20 AM - 2:20 AM UTC

[A1431-4am-03]

Transitions towards carbon neutrality and the future of the energy and chemical sectors

○Yasushi Sekine[1] (1. Waseda Univ.)

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[4A143101-03-6add]

Incubation Time

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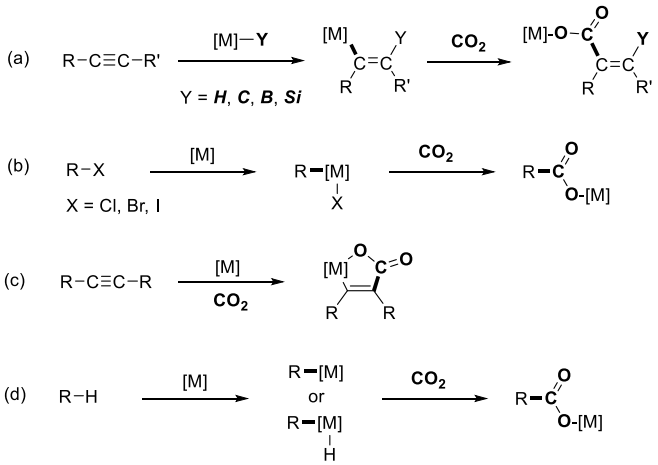
二酸化炭素を利用する有機合成反応のための革新的触媒開発

（京大院工）○藤原 哲晶
Development of innovative catalysts for organic synthetic reactions using carbon dioxide (*Graduate School of Engineering, Kyoto University*) Tetsuaki Fujihara

The chemical transformation of carbon dioxide (CO_2) into useful carbon resources is an important research issue. The development of new organic reactions using CO_2 as a C1 source is an attractive research subject from the viewpoint of effective utilization of CO_2 as well as the development of new organic reactions.[1] Herein, the author will review the recent progress and future prospects of organic reactions using CO_2 catalyzed by transition metal complexes.
Keywords : Carbon Dioxide; Transition Metal Complexes; Homogeneous Catalysts

二酸化炭素 (CO_2) を有機資源へと再生する物質変換法の開発は，CO_2 の排出削減や隔離技術の開発と並び, エネルギー問題の解決ならびに地球環境保全の観点からも重要な研究課題である．均一系の遷移金属錯体触媒を活用して CO_2 固定化を実現する反応開発は，CO_2 有効活用の観点からも新しい有機合成反応開発の観点からも注目を集めてきた [1]．均一系触媒の最大の特徴は，様々な有機基質の精密カルボキシル化反応が可能な点にある．この遷移金属 (M) を触媒とする CO_2 の利用では，M-C 結合をもつ求核的な化学種の触媒的な生成が鍵となる（Scheme 1）.



Scheme 1. Organometallic elementary steps for carboxylation reactions: (a) addition reaction, (b) oxidative addition, (c) oxidative cyclization, and (d) C-H activation

本講演では，均一系金属錯体触媒を活用する触媒的カルボキシル化反応において，これまでに達成された代表的な反応例を，我々の成果も踏まえながら紹介する.

1) (a) T. Fujihara, “Carboxylation with Carbon Dioxide as a C1 Source via Carbon-Carbon Bond Forming Reactions” *in The Chemical Transformations of C1 Compounds*, X.-F. Wu, B. Han, K. Ding, Z. Liu, Eds., Wiley-VCH, Weinheim, **2022**, p 909.

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日本製鉄が取り組む CCU 技術開発

（日本製鉄株式会社[1]）三浦　理華[1]
Development of CCU technologies by NIPPON STEEL CORPORATION ([1]*NIPPON STEEL CORPORATION*)○Ayaka Miura[1]

NIPPON STEEL CORPORATION is taking on the challenge to realize of achieving carbon neutrality by 2050 as the most important management task. While developing technologies for carbon neutral ironmaking processes, we are also developing CCUS technologies to further reduce CO_2 emissions. In this presentation, we will present an overview of our CCU technology development activities.
Keywords : Carbon dioxide, Catalyst, CCU

鉄は他素材に比べ、製造時の単位鉄重量あたりの CO_2 発生が少なく、リサイクル性にも優れ、ライフサイクルアセスメントの視点でも環境負荷が低い。一方で、鉄は他素材に比べ、用途が幅広く、大量に使用されるため、必然的に製造量が多くなることから、鉄鋼業からの CO_2 発生量が多いことが課題である。

日本製鉄では、気候変動問題への取り組みを経営の最重要課題と位置付け、当社独自の取り組みとして「日本製鉄カーボンニュートラルビジョン 2050」を掲げ、2050 年カーボンニュートラルの実現にチャレンジしている。大型電炉での高級鋼の量産製造や水素還元製鉄などの開発に鋭意取り組んでいるが、熱源の確保などを目的に引き続き石炭の使用が必要なため、CCUS 等によるカーボンオフセット対策も含めた複線的なアプローチを進めている（図 1）。当社が取り組む CCUS 取り組み全体像を図 2 に示す。CCUS 技術の開発として、当社では、①CO_2 分離回収技術、②H_2 製造技術、③CCU 技術の開発に取り組んでおり、特に CCU 技術においては、CO_2 削減の期待が大きい種々の化成品や燃料合成に国プロにて取り組んでいる。

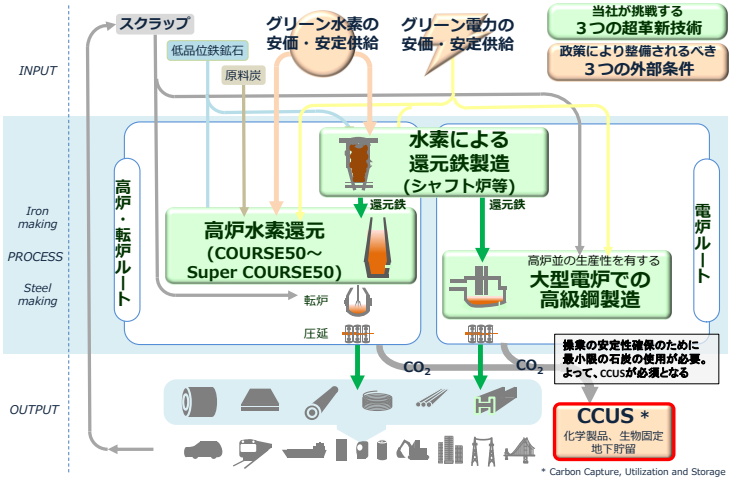

図 1 日本製鉄が目指すカーボンニュートラル生産プロセス

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当社は CCU 技術の一つとして、CO_2 からのメタノール及びパラキシレン合成プロセスの開発に取り組んでいる。メタノールは化成品の基幹物質や燃料となり、パラキシレンは PET 樹脂の原料ともなる有用化成品である。現状、天然ガスやナフサの改質から合成しているが、CO_2 から合成することができれば、大幅な CO_2 削減が期待できる。2020 年度から NEDO/カーボンリサイクル・次世代火力発電等技術開発/CO_2 排出削減・有効利用実用化技術開発/化学品への CO_2 利用技術開発事業にて「CO_2 を原料としたパラキシレン製造に関する技術開発」のテーマに参画し、富山大学、三菱商事、千代田化工建設、ハイケム、日鉄エンジニアリングとの 6 社共同開発を実行している。

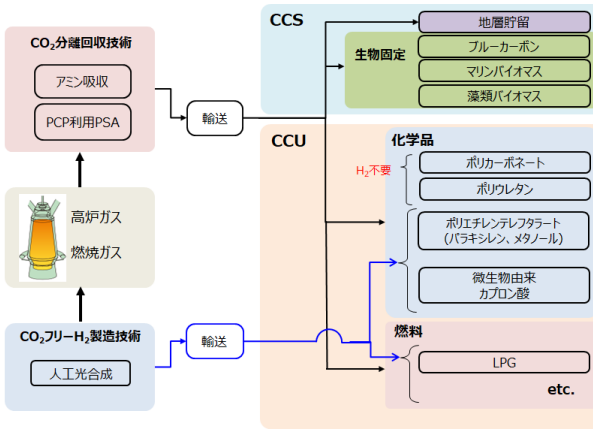

図 2 日本製鉄における CCUS 取り組み全体像

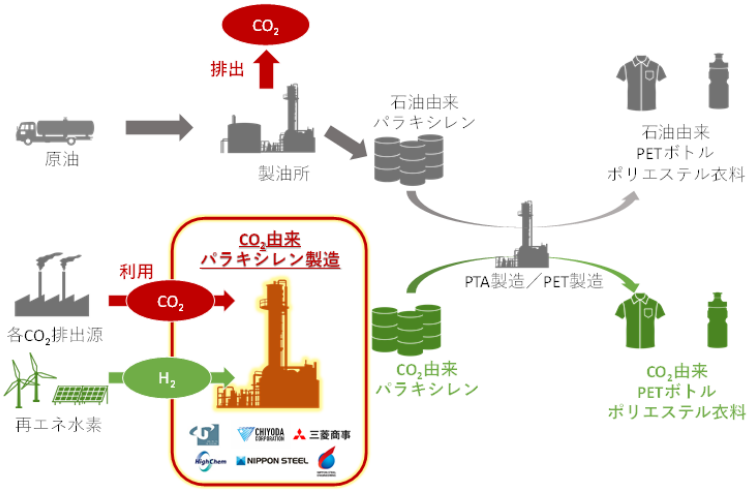

図 3 CO_2 からのパラキシレン合成における体制

本講演では、上記の他、日本製鉄におけるカーボンニュートラルに向けた全体概要、化学品原料の製造を目的とした CCU に関わる触媒研究開発の取り組みについて紹介する。

【謝辞】パラキシレン合成について、本研究は，新エネルギー・産業技術総合開発機構の委託事業「カーボンリサイクル・次世代火力発電等技術開発/CO_2 排出削減・有効利用実用化技術開発/化学品への CO_2 利用技術開発」の中で行った。関係諸氏に感謝の意を表す。

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カーボンニュートラルに向けたトランジション・GX とエネルギー・化学分野の今後

（早大理工）○関根　泰

Transition and green transformation towards carbon neutrality and future of the energy and chemical sectors

(*Waseda University*) ○Yasushi Sekine

With global carbon dioxide concentrations exceeding 420 ppm, what to do about global warming has become a pressing issue. At the G7 Climate, Energy, and Environment Ministerial Meeting held in Sapporo in 2023, the urgency of climate change countermeasures was emphasized. An international framework to become carbon neutral by 2050 was discussed, and efforts to reduce plastic pollution to zero by 2040 based on the Osaka Blue Ocean Vision were also agreed upon. Concerned about climate change, the G7 called for a 43% reduction in CO_2 emissions by 2030 and a 60% reduction by 2035, and urged cooperation in economic transformation. This would facilitate the transition from petrochemistry to catalytic chemistry in the renewable energy era. Hydrogen, ammonia, and carbon dioxide recycling were emphasized, and the elimination of inefficient fossil fuel subsidies by 2025 was also confirmed.

In Japan, a 2 trillion-yen Green Innovation Fund and a 20 trillion-yen GX policy are underway, and a shift away from petroleum-based chemical synthesis is underway. Domestic chemical manufacturers have also announced their intention to move away from upstream processes and are focusing on high-value-added products to improve ROIC. In this context, we would like to summarize the direction that chemistry should take in the Transition GX toward carbon neutrality.

Keywords : Carbon neutral; Chemical reaction; Green innovation; Green transformation

世界の二酸化炭素濃度が 420ppm を超え、温暖化をどうするかは喫緊の改題となっている。2023 年に札幌で開催された G7 気候・エネルギー・環境大臣会合では、気候変動対策の緊急性が強調された。2050 年のカーボンニュートラルへの国際的な枠組みが議論され、大阪ブルー・オーシャン・ビジョンに基づき 2040 年までにプラスチック汚染をゼロにする取り組みも合意された。気候変動への懸念から、G7 は 2030 年までに CO_2 排出を 43%、2035 年までに 60%削減するよう要請し、経済変革への協働を求めた。これは石油化学から再エネ時代の触媒化学への移行を促進するものである。議論では、水素・アンモニアや二酸化炭素の再資源化が重要視され、2025 年までの非効率な化石燃料補助金の廃止も確認された。我が国では、グリーンイノベーション 2 兆円基金と 20 兆円の GX 政策が進行中で、石油を基軸とした化学合成からの転換が進んでいる。国内の化学メーカーも川上行程からの離脱を表明し、高付加価値品に注力して ROIC を向上させている。このような中で、カーボンニュートラルに向けたトランジション・GX において、化学がこれから進むべき方向を整理したい。

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Symposium | Co-Innovation Program (CIP)：Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1432(1432, Bldg. 14 [3F])

[A1432-4am] Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Chair, Symposium organizer: Hiroaki Iino, Ryo Koga, Shunpei Hitosugi, Yasunobu Ando

現実の現象をコンピュータ上で再現し現実の世界へフィードバックするサイバー・フィジカルシステムが化学・材料の研究開発から実用化に至るあらゆるフェーズで必要とされています。本セッションでは、マテリアルズ・インフォマティクスを用いた材料開発に加え、製造プロセス開発やサプライチェーンのデジタル化を含めた化学・材料の研究開発から実用化に向けたシステムの活用事例について講演頂きます。

聴講後のアンケートへのご協力をお願いいたします。

9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
Opening Remarks

Japanese Keynote Lecture
9:10 AM - 10:00 AM JST | 12:10 AM - 1:00 AM UTC
[A1432-4am-01]
Policy Development for Industrial Data Space as International Government Initiative

○Noriaki Izumi[1] (1. Ministry of Economy, Trade and Industry)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[4A143201-03-3add]
Incubation Time

Japanese Invited Lecture
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[A1432-4am-02]
Cyber-physical exploration system using powder-film-formation Process Informatics

○Keisuke Nagato[1] (1. The University of Tokyo)

10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[4A143201-03-5add]
Incubation Time

Japanese Invited Lecture
10:50 AM - 11:20 AM JST | 1:50 AM - 2:20 AM UTC
[A1432-4am-03]
Acceleration in the development of materials with dipersed silver nanoparticles using multiscale optical response calculations and machine learning

○Ko Osawa[1], Tsuneo Kashiwagi[1], Shigeru Kojima[1] (1. KONICA MINOLTA, INC.)

11:20 AM - 11:40 AM JST | 2:20 AM - 2:40 AM UTC
[4A143201-03-7add]
Incubation Time

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日本化学会 第104春季年会 (2024)

グローバル戦略としての国内外データ連携と政策展開

（経済産業省 情報経済課）和泉憲明

経済産業省では、「2025 年の崖」問題を乗り越えるための DX 推進政策を、グローバル戦略を見据えた社会インフラ整備の政策へと展開している。今回は、Gaia-X や Manufacturing-X 等を含む国際データ連携の動向を踏まえ、ウラノス・エコシステムやデジタルライフライン全国総合整備計画による政策展開を紹介する。

なかでも、デジタル時代の政策推進における課題として、デジタルという未知技術に起因する「想定外」への対応があげられる。そこで、官民が一丸となり、スピーディーな意思決定と政策推進を目的として、政府と業界団体の合意形成に基づく新しい政策推進スキームをウラノス・エコシステムとして実装している。今回は、国内外のデータ連携に関する官民の動向を交え、産学官から専門家を結集させて政策の立案（アーキテクチャ設計）から展開（社会実装）までを一気通貫で実施する仕組みを中心に紹介する。

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粉体成膜プロセスインフォマティクスを用いたサイバー・フィジカル探索システム

（東大工）○長藤 圭介
Cyber-physical exploration system using powder-film-formation Process Informatics
(*Graduate School of Engineering, The University of Tokyo*) ○Keisuke Nagato

Film formation of functional materials for next-generation energy devices such as batteries and fuel cells is based on powder film formation. As with powdered dishes, nano- and micro-scale complex phenomena in each kneading, coating, and drying affect the macroscopic physical phenomena. The process development, which has been Japan's strength, is required to achieve high throughput in the DX era. I introduce Process Informatics as one solution to this requirement with an example in a powder-film-formation process.
Keywords : Process Informatics; powder film formation; autonomous exploration; Bayesian Optimization

畜電池・燃料電池をはじめとした次世代エネルギーデバイスの機能性材料の成膜は粉体成膜を基本としていますが，粉もの料理と同様に，混錬・塗布・乾燥それぞれのナノ・マイクロスケールの物理現象がマクロな現象に影響する複雑現象です．だからこそ日本の強みであったプロセス開発は，DX の時代でハイスループット化が求められています. その一つの解決策としてのプロセスインフォマティクスを粉体成膜プロセスの事例で紹介します.

(a) (b)

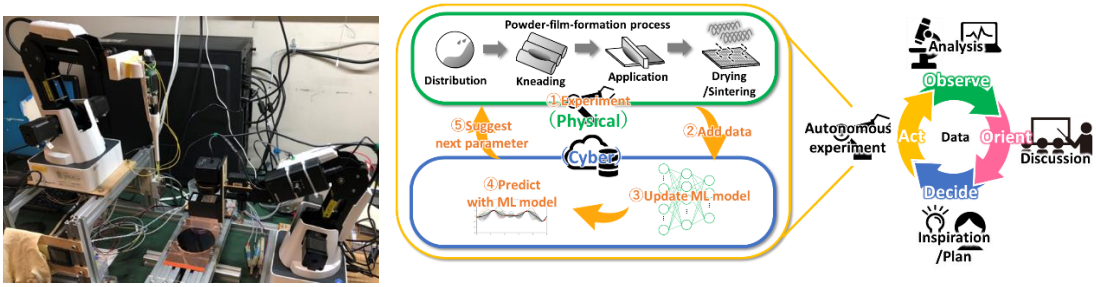

図　(a) 自律プロセス探索実験装置の概要（左が滴下ロボット，右が撮影ロボット）, (b) 粉体成膜プロセスインフォマティクスの活用方法の概要

1) 長藤圭介ほか「粉体成膜プロセス研究のハイスループット化のためのデータ駆動型粉体プロセス・インフォマティクス」機械の研究，2020 年 7 月号，511-516.
2) 未来社会創造事業「マテリアル探索空間拡張プラットフォーム(MEEP)」https://meep.nagato-u-tokyo.jp/
3) K. Nagai, T. Osa, G. Inoue, T. Tsujiguchi, T. Araki, Y. Kuroda, M. Tomizawa, K. Nagato, “Sample-efficient parameter exploration of the powder film drying process using experiment-based Bayesian optimization”, *Sci. Rep.* **2022**, *12*, 1615. https://doi.org/10.1038/s41598-022-05784-w
4) YouTube video; https://youtu.be/z1pIU1X_jW8

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マルチスケール光学応答計算と機械学習を用いた銀ナノ粒子分散材料開発の加速

（コニカミノルタ株式会社）○大澤 耕・柏木 恒雄・小島 茂
Acceleration in the development of materials with dispersed silver nanoparticles using multiscale optical response calculations and machine learning (*KONICA MINOLTA, INC.*)
○Ko Osawa, Tsuneo Kashiwagi, Shigeru Kojima

Nanoparticle-dispersed materials have potential applications in numerous fields, including energy-saving thermal barrier films, highly efficient solar cells, and color materials that can be decorated on demand with less waste. However, achieving the desired optical response necessitates a considerable development time. In this presentation, using the development of materials with dispersed silver nanoparticles as a case study, we describe how computational science, machine learning, and high-throughput synthesis can accelerate R&D process.

Our development process involved the amalgamation of computational science, high-throughput synthesis, and measurement through machine learning. Initially, automated liquid hander and UV-Vis plate reader were used for the synthesis and characterization of silver nanoparticles[1]. This system allowed for the synthesis and evaluation of 96 different conditions using various dispersants and additives within a few days, marking a significant time savings compared to manual experimentation. Subsequently, we developed a multi-scale optical calculation framework that amalgamated first-principles calculations, electromagnetic optical calculations, and theoretical geometric domain equations. The validity of these calculations was verified by employing an individual particle shape measurement technique[2] using atomic force microscopy (AFM).

We further leveraged machine learning to enhance the efficiency of calculations, processes, and measurements. By utilizing active learning in large-parameter scanning calculations, we were able to reduce the required number of computations by a factor of four. The shape of the silver nanoparticles was transformed into latent variables using a variational autoencoder (VAE)[3], and a shape search (chromaticity optimization), conducted through Bayesian optimization[4] decreased the number of necessary calculations by a factor of 3.4 compared to a random search. Moreover, high-throughput experiments combined with machine learning optimized the quantity of material added to the coating ink, reducing the number of experiments by a factor of four in comparison to a random search. Additionally, we estimated the shape of silver nanoparticles using rapidly measurable spectroscopic measurements[5] and confirmed that the estimated shape moderately corresponded with the measurements obtained from scanning electron microscopy (SEM).

Keywords : silver nanoparticle, high-throughput synthesis, optical simulation, machine learning

ナノ粒子分散材料は冷暖房の省エネルギー化を実現する遮熱フィルム、高効率太陽電池、オンデマンド加飾が可能で廃棄の少ない色材などへの応用が期待されているが、所望の光学応答実現に多くの開発期間を要する問題があった。本報告では、銀ナノ粒子分散材料の開発を事例に、計算科学・機械学習・高速試作プロセスを活用した開発

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加速について述べる。

本研究では計算科学・プロセス・計測を機械学習により融合させる三位一体の開発プロセスを用いた。まず、銀ナノ粒子合成プロセスについて、自動分注装置と紫外可視域のプレートリーダーを併用し、分散剤や添加剤の種類等を変えた 96 条件を 2 日で合成および評価できる仕組みを構築した[1]。人の手による実験数と比較して大幅な時間短縮ができる。次に、第一原理計算と電磁光学計算および幾何領域の理論式を組み合わせたマルチスケール光学計算の枠組みを整理した。また、原子間力顕微鏡(AFM)を用いた個別粒子形状計測[2]により計算の妥当性を確認した。

機械学習の活用により、計算、プロセスおよび計測の更なる効率化を実現した。大量パラメータ走査計算において、能動学習を用いることで 1/4 倍の計算量削減を行った。さらに、変分オートエンコーダ(VAE)[3]を用いて銀ナノ粒子形状の潜在変数化を行ない、ベイズ最適化[4]を用いた形状探索(色度最適化)により、計算回数をランダム探索と比較して 1/3.4 倍に短縮した。そして、ハイスループット実験と機械学習を組み合わせて、塗布用インクの材料添加量の最適化を行ない、ランダム探索と比較して 1/4 倍の実験回数短縮が行えることを示した。また、高速測定可能な分光測定から銀ナノ粒子形状を推定[5]し、推定した形状が走査型電子顕微鏡(SEM)測定と類似していることを確認した。

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(NEDO)の委託業務(JPNP16010)の結果得られたものです。プロジェクトの成果を活かして 2022 年 4 月に「データ駆動型材料設計技術利用推進コンソーシアム」が設立されており[6]、データ駆動型材料開発」の入り口・情報交流の場・業界全体の技術力向上への貢献が期待されています。

本研究を進めるにあたり国立研究開発法人産業技術総合研究所の、中村恒夫先生、松井正冬先生、陶究先生、竹林良浩先生、小野巧先生、時崎高志先生、重藤知夫先生にご指導いただきました。この場を借りて御礼申し上げます。

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Symposium | Co-Innovation Program (CIP)：Cutting-edge research in polymer science for a sustainable society

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1433(1433, Bldg. 14 [3F])

[A1433-4am] Cutting-edge research in polymer science for a sustainable society

Chair, Symposium organizer: Kenichi Kasuya, Kenji Hara, Ryotaro Tsuji, Yoshihiro Ikari

石油化学は高分子科学工業を生み出し、衣食住にわたって我々の生活を豊かにしてきた一方で、近年では温室効果ガス排出やプラスチックごみの環境拡散といった新たな課題を生み出しています。これらの課題に対して、サーキュラーエコノミーコンセプトは、高分子科学による革新的な解決策創出の後押し要因となっています。樹脂を再利用するための技術や、特定の環境下で分解するような材料、CO2やバイオマスなどから合成される新規材料等、様々な研究成果が生まれつつあり、高分子科学は大転換期を迎えようとしています。本セッションでは、持続可能社会を創出する高分子科学の研究前線を紹介すると共に、これからの高分子科学の在り方について議論します。

聴講後のアンケートへのご協力をお願いいたします。

9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
Opening Remarks

Japanese Keynote Lecture
9:10 AM - 10:10 AM JST | 12:10 AM - 1:10 AM UTC
[A1433-4am-01]
Development of high-performance marine biodegradable biomass plastics

○Tadahisa Iwata[1] (1. The University of Tokyo)

Japanese Invited Lecture
10:10 AM - 10:40 AM JST | 1:10 AM - 1:40 AM UTC
[A1433-4am-02]
Practical application of Biodegradable-biopolymer

○Shunsuke Sato[1] (1. KANEKA CORPORATION)

Japanese Invited Lecture
10:40 AM - 11:10 AM JST | 1:40 AM - 2:10 AM UTC
[A1433-4am-03]
Development of bio-based bifuran moiety capable of replacing benzene ring

○Yuya Tachibana[1] (1. Gunma University)

Japanese Invited Lecture
11:10 AM - 11:40 AM JST | 2:10 AM - 2:40 AM UTC
[A1433-4am-04]
Sustainable Cross-Linked Polymer Materials Based on Radical-type Dynamic Covalent Chemistry

○Hideyuki Otsuka[1] (1. Tokyo Tech)

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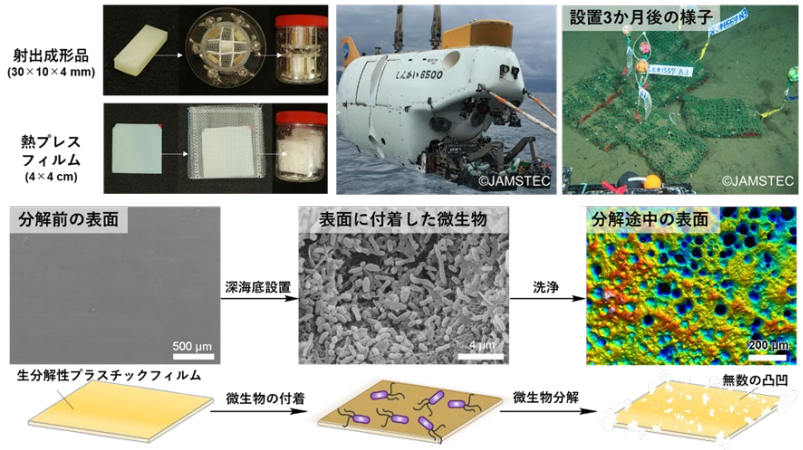
高性能な海洋生分解性バイオマスプラスチックの開発を目指して

（東大院農）岩田 忠久
Development of high-performance marine biodegradable biomass plastics
(*Graduate School of Agricultural and Life Sciences, The University of Tokyo*)
○Tadahisa Iwata

This presentation will introduce a series of our laboratory's research results on biodegradable biomass plastics, including the development of molding and processing technologies for high-performance real materials using biodegradable aliphatic polyesters and polysaccharide ester derivatives, elucidation of the correlation between structure and physical properties using synchrotron radiation, elucidation of mechanisms controlling biodegradability rate using degradation enzymes, addition of biodegradation initiation switch functions, and marine degradability evaluation.
Keywords : Biodegradable Biomass Plastics, Marine Biodegradation, Microbial Polyesters, Polysaccharide Ester Derivatives, Biodegradable Initiation Switch

生分解性脂肪族ポリエステル、高分子多糖類エステル誘導体などを用いた高性能な実部材への成形加工技術の開発[1)]、大型放射光を用いた構造と物性との相関解明、分解酵素を用いた生分解性速度の制御機構の解明、生分解開始スイッチ機能の付与[2, 3)]、海洋分解性評価[4)]など、一連の生分解性バイオマスプラスチックに関する当研究室の研究成果を紹介する。



1) Recent developments in microbial polyester fiber and polysaccharide ester derivative research. T. Iwata, H. Gan, A. Togo, Y. Fukata, *Polym. J.* **2021**, *53*, 221.
2) Enzymatic Self-Biodegradation of Poly(l-lactic acid) Films by Embedded Heat-Treated and Immobilized Proteinase K. Q.Y. Huang, T. Iwata, *et al.*, *Biomacromolecules*, **2020**, *21*, 3301.
3) A Strategy for Improving Polyester Biodegradation in Seawater: Thermal Embedding of *Humicola insolens* Cutinase. Q.Y. Huang, S. Kimura, T. Iwata, *Biomacromolecules*, **2023**, *24*, 5836.
4) Microbial decomposition of biodegradable plastics on the deep-sea floor. T. Omura, T. Iwata, *et al., Nat. Commun.*, **2024**, in press.

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生分解性バイオポリマーの社会実装

（(株) カネカ [1]）○佐藤　俊輔 [1]

Practical application of Biodegradable-biopolymer

([1]*Agri-bio&Supplement Research Laboratories, KANEKA CORPORATION*)
○Shunsuke Sato,[1]

We have been developing biodegradable-biopolymer (PHBH) to create a sustainable polymer industry. PHBH is a random copolymer of (*R*)-3-hydroxybutyrate (3HB) and (*R*)-3-hydroxyhexanoate (3HHx) (Fig.1). This polymer is produced by bacteria from renewable carbon sources such as vegetable oils and sugars. The mechanical properties of the PHBH depends on the fractions of 3HHx. Thus, it is highly important to regulate the fractions of 3HHx of the polymer. Therefore, we examined the precise control of the 3HHx fractions by fine-tuning the expressions of several genes. Following to the fermentation process, PHBH is purified in a downstream process by using “water process” without any solvent.

Keywords : Polyhydroxyalkanoate, PHBH, Biodegradable-polymer

（株）カネカでは、持続可能なポリマー産業の創造を志し、生分解性を有するバイオベースポリマー、PHBH の開発を行っている。 PHBH は植物油脂や糖質などの再生可能原料から微生物発酵により生産されるポリヒドロキシアルカン酸の一種であり、（*R*）-3-ヒドロキシ酪酸、並びに（*R*）-3-ヒドロキシヘキサン酸(3HHx)の両モノマーから構成される共重合ポリエステルである（Fig.1）。PHBH の物性はその 3HHx 分率によって変化するため、PHBH の 3HHx 分率を制御することが実用化には極めて重要となる。そこで、我々は PHBH 生産微生物を改良することで、3HHx 分率を精密に制御する技術を開発し、産業生物の育種を行った。PHBH は開発した微生物を培養し、更に後工程にて細胞から回収、精製されることで、材料となる。特に、精製プロセスは溶剤不使用とし、環境に優しいプロセスを開発した。

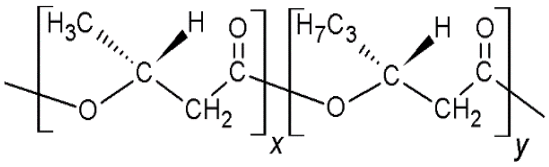

Fig.1　PHBH の構造

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ベンゼン環を代替可能なバイオベースビフラン骨格の開発

（群大院理工[1]・群大食健セ[2]）○橘 熊野[1,2]

Development of bio-based bifuran moiety capable of replacing benzene ring. ([1]Graduate School of Science and Technology, Gunma University & [2]Gunma University Center for Food Science and Wellness)○Yuya Tachibana[1,2]

Almost furan compounds are produced from furfural which is converted from hemicellulose. Recently, we have been focusing on the bifuran moiety, which is constructed through the coupling reaction at the 5,5'-position of single furan derivatives, as a novel biobased building block. The bifuran moiety adopts a rigid structure and has an expanded π-conjugation between two furan rings to enhance the properties of polymers. In this presentation, we will be discussing the synthesis and characteristic properties including recyclability of the following polymers: poly(Schiff base) from bifurfural, poly(bifurfurylene succinate) from bi(furfuryl alcohol), poly(bifurylidene bisglycerol succinate) from bifurylidene bis(glycerol acetal), polyamide from bifurfurylamine, and polycarbosilane from dihydrosilylbifuran.

Keywords : Bio-based polymer; furan; inedible biomass; recycling

バイオベース高分子：バイオマスであれば何でも良いという時代は過ぎ，非食用かつ廃棄物系のバイオマスの利用が求められている。ヘミセルロースとセルロースから製造されるフラン誘導体の中でも，フルフラールは化学工業の原料として安価かつ大量供給可能なバイオマス由来化合物であるが，現在の用途は，金属鋳造バインダーのフラン樹脂にほぼ限定されている。一方，２０世紀終盤からは，非可食バイオマス資源であるフラン誘導体をバイオ燃料や高分子に利用する研究が行われてきた[1]。

ビフラン骨格：私たちはフラン環の 5 位同士で連結したビフラン骨格に着目して研究を進めている。ビフラン骨格は 2 つのフラン環が逆並行で完全平面のコンフォメーションが再安定である。ビフラン骨格を高分子鎖に導入することで，光学特性の付与，剛直性の付与，高分子鎖間のπ-πスタッキングによる耐熱性の強化に繋がる。本発表では，ビフラン骨格を有する様々な高分子を合成すると共に，ビフラン骨格とフラン環，ベンゼン環を有する高分子との比較を通じて，**ビフラン骨格がバイオベース由来のビルディングブロック**として有望であることを示す。

ビフラン骨格含有高分子：フフルフラール（BFF）とジアミンの脱水中縮合によってポシリッフ塩基（PSB）を合成した (Figure 1a)[2]。フラン環含有ポリシッフ塩基と比較すると，ガラス転移温度（T_g）の上昇（9 °C）と UV-vis スペクトルの長波長シフト（50 nm）に加えて，引張試験のヤング率 2.3 倍，破断強度 2.3 倍という高強度化が達成された。ビフルフリルアルコール（BFAl）とジカルボン酸無水物との脱水縮合によりポリエステル（PBFD）を合成した (Figure 1b)[3]。フラン環含有のポリエステルと比較すると，T_g と融点（T_m）の上昇（28 °C と 78 °C）が観測された。また，ビスマレイミド

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を用いて PBFD の架橋反応を行ったところ, ネットワーク構造ではなくハシゴ状高分子へと変換されていた。ビフラン骨格とアセタール骨格を有するビフリデンビス(グリセリロールアセタール) (BFG) を合成し，コハク酸無水物（フルフラールから合成可能）との脱水縮合によってポリ(ビフリデンビス(グリセロールアセタール)サクシネート) (PBFGS) を合成した (Figure 1c)[4]。アセタール骨格は，亜鉛触媒とグリセロールで処理することで, BFG へと定量的に変換可能であった。また，酸触媒を添加することでアセタール骨格の加水分解が進行し，BFE の原料でもある BFF へと定量的に変換可能であった。ビフルフリルアミン（BFAm）とジカルボン酸クロライドとの重縮合によってポリアミド（PA）を合成した (Figure 1d)[5]。ベンゼン環含有ポリアミドと比較すると，α 緩和温度の上昇（16°C）と UV-vis スペクトルの長波長シフト（79 nm 以上）が観測された。フランのカップリングで得られるビフランをジヒドロシリルビフラン（DSBF）へと変換し，それと末端アルケン化合物とのヒドロシリル化重合を行うことで，ビフラン骨格含有ポリカルボシラン（PBFSi）を合成した(Figure 1e)[6]。フラン環含有ポリカルボシラン(PFSi), ベンゼン環含有ポリカルボシラン（PPhSi）と比較すると，PBFSi と PPhSi はほぼ同等の熱安定性・T_g・T_m を有してたが，PFSi はアモルファスであり耐熱性・T_g ともに大幅に低く観察された。また PBFSi のみ蛍光発光を示し，プロト脱シリル化によるケミカルリサイクル性付与が達成可能であった。

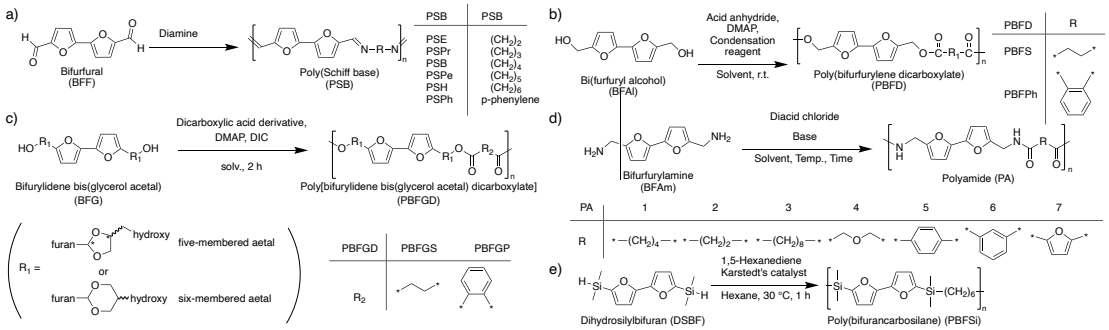

Figure 1. a) poly(Schiff base) from bifurfural, b) poly(bifurfurylene succinate) from bi(furfuryl alcohol), c) poly(bifurylidene bisglycerol succinate) from bifurylidene bis(glycerol acetal), d) polyamide from bifurfurylamine, e) polycarbosilane from dihydrosilylbifuran

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ラジカル系の動的共有結合化学が拓くサステナブルな架橋高分子材料

（東工大物質理工）○大塚 英幸
Sustainable Cross-Linked Polymer Materials Based on Radical-Type Dynamic Covalent Chemistry (*Department of Chemical Science and Engineering*, *Tokyo Institute of Technology*)
○Hideyuki Otsuka

In this presentation, the self-healing, recycling, stress relaxation, and degradation of chemically cross-linked polymers based on radical-type dynamic covalent chemistry are introduced. Specifically, sustainable cross-linked polymer materials were developed by introducing sterically hindered diaminodisulfide bonds as dynamic covalent bonding units at the cross-linking points of chemically cross-linked polymers. The reactivity, characteristics, and working mechanism of the obtained chemically cross-linked polymers are introduced.
Keywords : Dynamic Covalent Chemistry; Cross-linked Polymers; Recycling; Self-healing; Polymer Reactions

架橋高分子は三次元空間に広がった網目構造を有しており、その構造によって高強度や耐熱性が求められる構造材料から、高弾性や柔軟性が求められるゴムやゲルといったソフトマテリアルまで、特有の物性を活用して幅広く利用されている。網目構造の一部が可逆的な分子間相互作用で構成される物理架橋高分子は、外部環境に応じて比較的容易に構造を変えることが可能であり、易加工性、自己修復性、リサイクル性などの魅力的な機能を発現する。一方で、すべてが共有結合で構成される化学架橋高分子の場合、通常は不溶不融の高分子ネットワーク構造となるため、「高分子の最終形態」とも言われてきた。

近年、特定の環境下において可逆的な開裂・結合の平衡状態を与え、組み換え可能な共有結合を活用する動的共有結合化学が大きな注目を集めている。化学架橋高分子に動的共有結合を導入することで、超分子化学に基づく物理架橋高分子と同様に、さまざまな構造再編成に基づく機能発現が期待できる。本講演では、加熱条件で互いに組み換わる動的共有結合骨格を有する化学架橋高分子の合成、さらには得られる化学架橋高分子の応力緩和特性、修復性、再成形性、接着性に関して、演者のグループの研究成果を紹介する（**Figure 1**）。

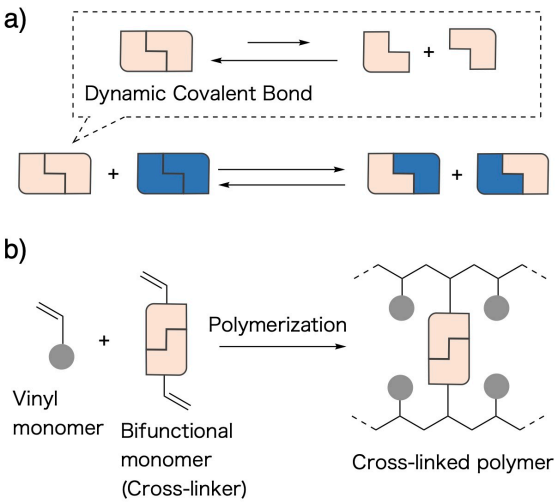

Figure 1. (a) Conceptual illustration of an exchange reaction of dynamic covalent bonds. (b) Synthesis of a cross-linked polymer by polymerization using a cross-linker with a dynamic covalent bond.

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ラジカル系の動的共有結合化学に基づく架橋高分子の修復・再成形・融合

自己修復系高分子の設計に活用できる動的共有結合骨格として、ビス（2,2,6,6-テトラメチルピペリジン-1-イル）ジスルフィド（BiTEMPS, **Figure 2a**）を開発した。複数の BiTEMPS 誘導体を用いてジスルフィド結合の熱的な均一開裂挙動、および熱的な結合交換特性などについて評価を行った結果、室温では全くラジカル種が観測されず、100 °C 程度の加熱により交換反応が進行し、酸素の影響を全く受けないことが明らかとなった [1]。また、BiTEMPS をスペーサーとする架橋剤を用いて、架橋点に BiTEMPS 骨格を有するポリ（メタクリル酸エステル）を合成し、BiTEMPS の熱的な結合組み換えに基づく自己修復性について評価した結果、24 時間後には破断強度および破断伸びも切断前のサンプルと同程度まで修復した。さらに、BiTEMPS 骨格を有する化学架橋高分子を粉砕して鋳型中で加熱すると、再成形性を示した [2]。BiTEMPS 骨格の組み換えを利用した異種架橋高分子の融合にも成功した [3]。演者のグループでは、これらの反応系以外にも、高い官能基許容性を利用して、BiTEMPS 骨格の組み換え反応に基づく様々な高分子反応系の構築にも成功している [4–12]。

ラジカル系の動的共有結合化学に基づく分子内架橋高分子の可逆架橋

BiTEMPS 骨格を架橋点に有する架橋高分子を分子内架橋された 1 本の高分子鎖 (Single-chain nanoparticles, SCNP) へと直接変換する手法を開発した（**Figure 2b**）。また、SCNP どうしの分子間架橋反応によって架橋高分子の復元を達成し、ラジカル系の動的共有結合化学に基づく網目構造の再編成によるサステナブルな架橋トポロジー変換系を構築した [13]。

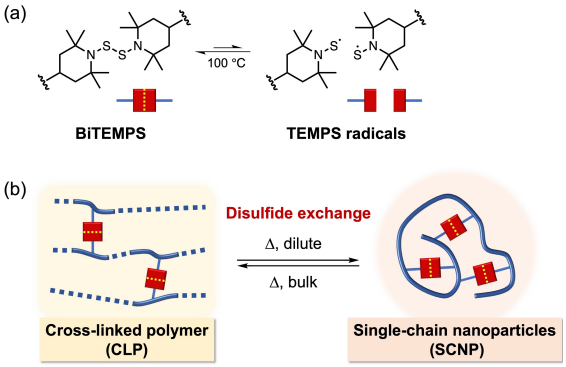

Figure 2. (a) Equilibrium between BiTEMPS and TEMPS radicals under heating conditions. (b) Interconversion between cross-linked polymer and single chain nanoparticles based on radical-based dynamic covalent chemistry of BiTEMPS.

謝辞　高橋 明先生（東京工業大学助教）、青木大輔先生（千葉大学准教授）をはじめとする共同研究者の皆様に深く感謝いたします。本研究は、JST 未来社会創造事業などの財政的支援により実施されました。

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Symposium | Co-Innovation Program (CIP)：Innovative catalysts for challenging carbon negativity

Thu. Mar 21, 2024 1:00 PM - 2:50 PM JST | Thu. Mar 21, 2024 4:00 AM - 5:50 AM UTC A1431(1431, Bldg. 14 [3F])

[A1431-4pm] Innovative catalysts for challenging carbon negativity

Chair, Symposium organizer: Hideshi Sasakura, Kazuhiro Sayama, Koichi Matsushita, Yutaka Amao, Yuusuke Sunada

2020年10月に「2050年カーボンニュートラル」宣言を契機として、2030年度までの温室効果ガス削減目標を2013年度比で46%削減することとし、将来的には80%削減に向けて新たな方針も示されております。これらの目標達成のためには、人工光合成を含む再生可能エネルギーを用いた水素製造や二酸化炭素利用に加えて，二酸化炭素フリー水素製造技術、二酸化炭素の水素化や二酸化炭素の有価物への触媒的変換技術を急速に発展・成熟させ、二酸化炭素排出実質ゼロを超えるマイナスに転じるカーボンネガティブ技術が必要です。本セッションでは、これらの研究について世界をリードする研究者に紹介いただきます。カーボンニュートラルは本当に達成できるか、それを超えるカーボンネガティブ実現に向け、どんな挑戦が必要か、活発な議論の場の提供を考えております。

聴講後のアンケートへのご協力をお願いいたします。

Japanese Invited Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[A1431-4pm-01]
Heterogeneous organic synthesis contributing to carbon neutrality
○Hiroki Miura[1] (1. Tokyo Metropolitan University)

Japanese Invited Lecture
1:30 PM - 2:00 PM JST | 4:30 AM - 5:00 AM UTC
[A1431-4pm-02]
Development of CO_2 electrolysis technology towards the realization of a carbon recycling society
○Ryota Kitagawa[1] (1. Toshiba Corporation)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[4A143104-06-3add]
Incubation Time

Japanese Invited Lecture
2:10 PM - 2:40 PM JST | 5:10 AM - 5:40 AM UTC
[A1431-4pm-03]
Development of Catalytic Systems for Small Molecule Conversions based on Molecular Assembly
○Mio Kondo[1,2] (1. Tokyo Institute of Technology, 2. JST PRESTO)

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
Closing Remarks

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炭素資源循環に資する不均一系有機合成反応

（都立大都市環境）○三浦 大樹
Heterogeneous organic synthesis contributing to carbon neutrality (*Tokyo Metropolitan Univ.*)
○Hiroki Miura

The universal transformation of abundant C(sp^3)–O bonds should be a key technology for achieving carbon neutrality since the C(sp^3)–O bond is often found not only in oxygenated chemical feedstock such as alcohols, ethers, and esters, but also in natural biomass compounds. In this study, we successfully developed various efficient transformations of C(sp^3)–O bonds mainly by utilizing cooperative catalysis of Au nanoparticles and acid-base site on supports.
Keywords : Heterogeneous catalysts; Gold nanoparticles; C–O transformation

二酸化炭素を吸収して生長するバイオマスを原料として高付加価値な化成品を製造することは高度な炭素資源循環の実現ための鍵となる。バイオマス由来化合物には多くの C–O 結合が含まれるため、効率的な C–O 結合変換手法の開発は極めて重要である。一方、サステイナブルケミストリーの観点から、触媒の再利用などを可能にする不均一系触媒を用いた有機合成プロセスが注目されている。なかでも担持金属触媒は酸化還元特性やルイス酸性を示す金属ナノ粒子に加えて、担体である金属酸化物上に酸塩基点を豊富に有する点で非常に魅力的な材料である。特に Au ナノ粒子は 1 電子酸化還元能やソフトなルイス酸性など特異な触媒機能を示すことから、担体上の他の元素との協働を利用することにより、他の触媒にはない特異な分子変換が実現できると考え、種々検討を行った。

例えば、表面に酸点を高密度に有する金属酸化物に Au ナノ粒子を担持した触媒はアリルエステルの C(sp^3)–O 結合のボリル化に対して極めて活性を示す [1]。ここではソフトルイス酸である Au ナノ粒子と，金属酸化物表面のハードルイス酸が反応基質を同時に活性化することで C(sp^3)–O 結合のヘテロリシスが効率的に進行することが鍵となる。一方、両性金属酸化物に Au ナノ粒子を担持した触媒は、エステルやエーテルに含まれる極めて安定な C(sp^3)–O 結合を C(sp^3)–Si 結合へと効率的に変換することができる [2,3]。この場合、塩基点によって活性化されたケイ素源であるジシランを Au ナノ粒子が 1 電子酸化することで反応性の高いシリルラジカルを発生させ、それが酸点によって活性化されたエステルを攻撃することで安定な C(sp^3)–O 結合のホモリシスが進行することが鍵となる。このように本講演では、Au ナノ粒子とその周辺に存在する酸塩基点との協働を活用することで、従来にない効率的な C–O 結合変換の開発に成功した成果について概説する。

1) Miura, H.; Hachiya, Y.; Nishio, Y. Fukuta, T. Toyomasu, H.; Kobayashi, K.; Masaki, Y.; Shishido, T. *ACS Catal.* **2021**, *11*, 758–766.
2) Miura, H.; Doi, M.; Yasui, Y.; Masaki, Y.; Nishio, H.; Shishido, T. *J. Am. Chem. Soc.* **2023**, *145.* 4613–4625.
3) Miura, H.; Yasui, Y.; Masaki, Y.; Doi, M.; Shishido, T. *ACS Catal.* **2023**, *13,* 6787–6794.

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炭素循環社会の実現に向けた CO_2 電解技術の開発

(東芝研究開発セ) ○北川 良太
Development of CO_2 electrolysis technology towards the realization of a carbon recycling society (*Corporate Research & Development Center, Toshiba Corporation*) ○Ryota Kitagawa

Recent efforts towards carbon neutrality have made the reduction and absorption of CO_2 essential. Toshiba is developing Power to Chemicals (P2C) technology, which converts CO_2 into raw materials for fuel and chemicals. A challenge has been increasing cell throughput. We've adopted a zero-gap CO_2 electrolysis cell and improved current density by promoting CO_2 diffusion in the cathode catalyst layer. To further increase throughput, we've developed a CO_2 electrolysis cell stack with a large electrode area and cooling mechanism to reduce efficiency loss from heat. This stack has a capacity of 60NL-CO_2/h, approximately 1t-CO_2 annually. I will present our CO_2 resource technology and the current development status of our CO_2 electrolysis cell.
Keywords : CO_2 electrolysis;CO_2 electrochemical reduction ;catalyst ;Cell stack

近年、政府や企業によるカーボンニュートラルへの取り組みが活発化しており、その実現のためには化石資源利用に依存する産業部門や運輸部門での CO_2 削減や吸収が不可欠となっている。この課題に対する一つの解決策として、当社は CO_2 を再エネ電力により電解し、高環境価値の燃料や化成品へと転換する Power to Chemicals (P2C) 技術の開発を推進している。

CO_2 電解における課題の一つはセルの高スループット化（高電流密度化、セルの大面積・積層化）である。当社はこの課題を解決するため、ゼロギャップ型 CO_2 電解セルを採用し、カソードの三相界面制御と多孔質化により、電流密度を大幅に向上することに成功した。カソード触媒層に意図的に設けた空孔の存在によって CO_2 の拡散が促進されることで触媒層全体に CO_2 が供給されて電流密度の向上に大きく寄与した[1)]。また、セルの更なる高スループット化を図るには、大面積化、セルの積層化が必要となる。当社は上記独自開発した触媒電極を用いて、電極面積 100cm^2、4 セル以上積層した CO_2 電解セルスタックを開発した。積層したセル間に冷却機構を設けることで、CO_2 電解時に生じる発熱による効率低下を抑制した。開発したセルスタックは 60NL-CO_2/h(年間最大約 1t-CO_2)の処理能力となる。本講演では、東芝の取り組む CO_2 電解技術の内容を紹介するとともに、現在進めている実機級 CO_2 電解セルの開発状況についても紹介する。

謝辞
本研究の一部は、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（多量二酸化炭素排出施設における人工光合成技術を用いた地域適合型二酸化炭素資源化モデルの構築実証）」で実施した。

1) Y. Kofuji et. al., Chem. Lett. (2021), 50, 482.

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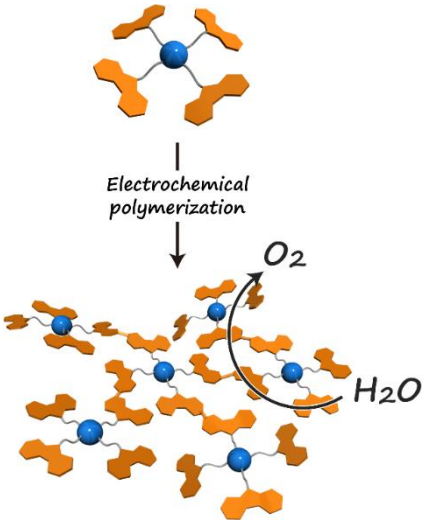
分子集積に立脚した小分子変換材料の創出

（東工大院理[1]・JST さきがけ[2]）○近藤 美欧[1,2]
Development of Catalytic Systems for Small Molecule Conversions based on Molecular Assembly ([1]*Graduate School of Science, Tokyo Institute of Technology*, [2]*JST PRESTO*) ○Mio Kondo,[1,2]

Four electron oxidation of water is a reaction which is considered a bottleneck for achieving artificial photosynthetic reactions. Therefore, the development of a highly active catalyst for the reaction is strongly demanded. We anticipated that the key to promote a water oxidation reaction is the acceleration of multielectron transfer process. In this work, novel multinuclear metal complexes bearing carbazole moieties, which can form charge-transporting biscarbazoles upon electrochemical oxidation, was synthesized and characterized. By the electrochemical oxidation of the complexes, polymer-based materials were successfully deposited on electrodes. The catalytic activity of the polymers for water oxidation was the highest among the relevant metal-complex-based catalytic systems.
Keywords : Small Molecule Conversion, Metal Complex, Water Oxidation, Electrochemical Polymerization

水の４電子酸化による酸素発生反応（$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$）は、人工光合成においてボトルネックとされる反応であり、この反応に対する良好な触媒の開発が強く望まれている。本研究では、(1) 酸素発生能を有する多核金属錯体[1]に、(2) 電荷輸送サイトを組み込む戦略を立案した（右図）。



上記の戦略に基づき、電気化学的酸化によって二量化し、電荷輸送サイトを形成するカルバゾール骨格を組み込んだ複数の新規多核金属錯体を設計・合成した。合成した各種錯体を、グラッシーカーボン電極上で電解重合することでポリマー電極を作成し、紫外-可視-近赤外吸収分光法、赤外吸収分光法 SEM、EDS を使って詳細に分析した。また、ポリマー電極の触媒能を調査したところ、得られたポリマー膜はいずれも酸素発生反応を触媒した。さらに、触媒活性(TOF)を他の関連する触媒系と比較したところ、本材料は最高クラスの触媒活性を有することを見出した[2),3)]。

1) (a)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. (b) M. Kondo, S. Masaoka, *Acc. Chem. Res.*, **2020**, *53*, 2140.
2) H. Iwami, M. Okamura, M. Kondo, S. Masaoka, *Angew. Chem. Int. Ed*. **2021**, *60*, 5965.
3) T. Matsuzaki, H. Iwami, K. Kosugi, T. Kambe, H. Kiuchi, T. Uematsu, S. Kuwabata, Y. Saga, M. Kondo, S. Masaoka, *Manuscript in preparation*

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Symposium | Co-Innovation Program (CIP)：Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Thu. Mar 21, 2024 1:00 PM - 3:30 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:30 AM UTC A1432(1432, Bldg. 14 [3F])

[A1432-4pm] Frontiers of cyber-physical system from R&D to practical application in chemistry andmaterials

Chair, Symposium organizer: Hiroaki Iino, Ryo Koga, Shunpei Hitosugi, Yasunobu Ando

現実の現象をコンピュータ上で再現し現実の世界へフィードバックするサイバー・フィジカルシステムが化学・材料の研究開発から実用化に至るあらゆるフェーズで必要とされています。本セッションでは、マテリアルズ・インフォマティクスを用いた材料開発に加え、製造プロセス開発やサプライチェーンのデジタル化を含めた化学・材料の研究開発から実用化に向けたシステムの活用事例について講演頂きます。

聴講後のアンケートへのご協力をお願いいたします。

Japanese Invited Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[A1432-4pm-01]
Materials innovation based on polymer informatics
○Masanobu Naito[1] (1. National Institute for Materials Science)

Japanese Invited Lecture
1:30 PM - 2:00 PM JST | 4:30 AM - 5:00 AM UTC
[A1432-4pm-02]
Methane oxidation catalysts design via catalysts informatics
○Keisuke Takahashi[1] (1. Hokkaido University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[4A143204-07-3add]
Incubation Time

Japanese Invited Lecture
2:10 PM - 2:40 PM JST | 5:10 AM - 5:40 AM UTC
[A1432-4pm-03]
Simulation in the development of electronic materials
○Satoshi Yotsuhashi[1] (1. Panasonic Holdings Corporation)

Japanese Invited Lecture
2:40 PM - 3:10 PM JST | 5:40 AM - 6:10 AM UTC
[A1432-4pm-04]
Organic transistor-based chemical sensors with pattern recognition techniques
○Tsuyoshi Minami[1] (1. IIS, The Univ. of Tokyo)

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC
[4A143204-07-6add]
Incubation Time

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マテリアルズインフォマティクスを活用した高分子材料開発

（NIMS[1]）○内藤昌信 [1]

Development of Polymer Materials with Materials Informatics ([1]*Research Center for Macromolecules and Biomaterials, National Institute for Materials Science*) ○Masanobu Naito[1]

Artificial intelligence (AI) creates recipes, and IoT-enabled automated experimental devices autonomously search for materials. Such a science fiction-like era is just around the corner. The core technology for this is a smart lab, a collection of automated devices that work in conjunction with AI. The introduction of smart laboratories in the pharmaceutical and other fields has been preceded by the introduction of smart laboratories in the pharmaceutical and other fields, but in the past few years, smart laboratories have rapidly spread to various material fields in response to the spread of material informatics (MI). In this presentation, we will introduce our recent efforts to develop new materials using MI tools such as SmartLab, including several examples.

Keywords：Materials Informatics; Polymer Smart Lab; Data-driven Polymer Design;

人工知能（AI）がレシピをつくり、IoT 化した自動実験装置が自律的に材料探索を行う。そんな SF のような時代がすぐそこまで来ている。そのコア技術となるのが、AI と連動したスマートラボとよばれる自動装置群である。製薬分野などへの導入が先行してきたが、マテリアルインフォマティクス（MI）の浸透に呼応するように、ここ数年で様々な材料分野に急速に広まりつつある。

材料開発では、合成のみならず、物性・材料特性までを総合評価する必要がある。また、先端材料に求められる性能・特性は刻々と変化する。そのため、ポリマースマートラボには、臨機応変に対応できるロバスト性が求められる。演者らのポリマースマートラボでは、これらの課題解決のため、技術仕様を予め固めずに、様々な AI ツールやデータサービスを組み合わせていくアジャイル的な開発手法を採っている。その AI ツールやデータベースとして、NIMS が整備を進める材料プラットフォーム「DICE」が提供する電子ラボノート、データ解析 AI、IoT 化ツール、データサーバなどの各種モジュールを利用できることも、システム開発の迅速化に大きなメリットとなっている。また、従来の材料評価は、サンプル作製や測定に多くの時間・労力・職人技などが求められ、材料開発のハイスループット化を困難にしてきた。この問題に対し、我々は MI 駆動研究に特化した装置を開発することで、合成から材料評価までの一連の工程を自動化・高速化することに取り組んできた。すでに接着材料や超撥水材料、また複数素材の特性を取り入れた傾斜材料などの新たな機能性樹脂材料の開発で威力を発揮している。課題解決の迅速化に、ポリマースマートラボが強力なツールとなることは間違いない。一方で、サーキュラーエコノミーやカーボンニュートラルなど、高分子材料を取り巻く課題は多い。本発表では、スマートラボをはじめとした MI ツールを駆使しながら、新規材料の開発について、いくつかの事例を挙げならが、最近の我々の取り組みについて紹介する。

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触媒インフォマティクスによるメタン酸化触媒開発

（北大理[1]）○髙橋　啓介[1]
Methane oxidation catalysts design via catalysts informatics ([1]*Graduate School of Sciencey*)○ Keisuke Takahashi[1]

Catalytic informatics consists of three main components. These are the "catalyst database," the "process of extracting knowledge from data," and the "platform. "1,2,3 Catalyst data sets can be created through high-throughput experiments and calculations with large-scale data acquisition and the use of literature data. The knowledge extraction process can actively utilize data mining and network methods as well as machine learning-based prediction. The construction of the platform does not require advanced programming techniques, and an environment for practicing catalytic informatics is readily available. These elements harmonize with each other and catalytic informatics is formed. This presentation will focus on the development of methane oxidation catalysts using catalyst informatics.
Keywords：Catalysts Informatics; Machine Learning; High-throughput Experiment

触媒インフォマティクスは、三つの主要な構成要素から成り立っている。これらは、「触媒データベース」、「データから知識を引き出す過程」、「プラットフォーム」である[1,2,3]。触媒データは、ハイスループット実験・計算に大規模データの取得、文献データの活用などによってデータセットが作成可能である。知識の抽出プロセスでは、機械学習による予測だけでなく、データマイニング法やネットワーク法なども積極的に活用できる。プラットフォームの構築には、高度なプログラミング技術などが不要で、触媒インフォマティクスを実践するための環境が手軽に利用できる。これらの要素が相互に調和し合い、触媒インフォマティクスが成り立っている。今回の講演では、触媒インフォマティクスを駆使したメタン酸化触媒の開発を中心に紹介する。

1) K Takahashi, el.al, *ChemCatChem* 11 (4), 1146-1152(2019)
2) K Takahashi,et.al, *Cheml Comm* 59 (16), 2222-2238 (2023)
3) T Taniike, K Takahashi, *Nature Catalysis* 6 (2), 108-111 (2023).

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エレクトロニクス材料開発におけるシミュレーション

（パナソニック ホールディングス株式会社）○四橋　聡史
Simulation in the development of electronic materials (Technology Division, Panasonic Holdings Corporation) ○Satoshi Yotsuhashi

In recent years, informatics and simulation have played an increasingly important role in materials development. We report here on some of the simulation efforts for the development in the Panasonic Group. There are two main types of simulation technologies that we promote. One is a multi-scale calculation method that combines the electronic structure calculations and molecular dynamics or CAE calculations, and the other is a new material search by the combination of material simulations and machine learning technology. As an example of multiscale calculation, we will introduce a method for deriving the pressure-enthalpy diagram and temperature glide defining as difference between the dew and boiling point using quantum chemical calculations and molecular dynamics, which is necessary for calculating theoretical efficiencies of environmentally friendly refrigerants. Another topic is a new molecular search scheme for nonlinear optical response materials using DFT and machine learning techniques.

We will also introduce our recent activities to promote the use of computational techniques in materials development and to study the use of quantum computing.
Keywords : Quantum Chemistry; Molecular Dynamics; Machine Learning

近年、材料開発におけるインフォマティクスとシミュレーションの役割はますます重要になってきている。本講演では、パナソニックグループにおける材料開発のためのシミュレーション取組みの一端を報告する。我々が進める材料開発シミュレーション技術は主に２種類ある。一つは電子状態計算からスタートして、そこから計算されるパラメータを分子動力学計算や CAE 計算などにつなぐことでマクロ物性までの算出を可能にするマルチスケール計算手法、もう一つは電子状態計算や分子動力学計算と機械学習技術を活用した新規材料探索である。マルチスケール計算の例として、環境配慮型冷媒の理論効率算出に必要な圧力-エンタルピー線図及び沸点と露点の温度差を示す温度グライドに関する量子化学計算と分子動力学を用いた導出手法の構築について、また新規材料探索の例として非線形光学応答材料の分子探索を機械学習アルゴリズムと量子化学計算を組み合わせて行った事例[1]について紹介する。

当日の講演では、材料開発現場への計算技術の普及活動や、量子コンピューティング活用検討などの最近の事例も併せて紹介する。

1) ハイスループット計算と機械学習を活用した光機能性有機材料の新規構造探索，大越 孝洋，大越 昌樹，長尾 宣明，四橋 聡史, *Panasonic Technical Journal*, **2021,** 67, 78.

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パターン認識技術を活用した有機トランジスタ型化学センサ

（東大生研）〇南 豪
Organic Transistor-based Chemical Sensors with Pattern Recognition Techniques (*Institute of Industrial Science, The University of Tokyo*) ○Tsuyoshi Minami

Chemical information derived from various essential markers plays a significant role in diagnosis, environmental assessment, and food analysis, whereas chemical sensors for facile detection and analysis have not been fully established. To this end, the author has used organic transistors functionalized with supramolecular receptors for pattern recognition-driven chemical sensing. The presentation will contain the details of sensor designs and their applicability to real-sample analysis by using pattern recognition techniques.
Keywords : Organic Transistor; Pattern Recognition; Chemical Sensor; Artificial Receptors; Real-Sample Analysis

体液や環境水、食品サンプルには、多種多様な構造を持つ標的分子・イオン種が存在しており、マーカーの種類とその濃度を含む化学情報は、病理診断や環境分析、食品管理の場面で重要な役割を担う[1)]。レセプタとトランスデューサで構成される化学センサは、目には見えない標的種を捕捉し、その認識情報を可視化するための分析手段である[2)]。社会実装が加速する物理センサに対して、化学センサの開発が萌芽段階にあるのは、水中で分子認識能を発揮するレセプタの設計・具現化とそれらをセンサデバイスへと組み込む手法が確立されていないことに起因する[1)]。本講演では、分子認識化学に基づくレセプタ設計と固液界面での化学センシングを達成するデバイス構造の両面から、多種多様な標的種に対する同時分析を実現する化学センサデバイスの設計指針に関して紹介する。

交差応答性を示す化学センサの設計には、天然の分子認識機構の一つである哺乳類の嗅覚系に着想を得たパターン認識型のレセプタ設計が求められる[3),4)]。類似構造を有する標的種に対して、比較的緩やかな結合能を有するレセプタを必要とするパターン認識において、交差応答的な認識を得意とする超分子レセプタは有利となる[5),6),7)]。他方、センサプラットフォームとして採用した有機トランジスタ (OFET) は、溶液法によって作製可能な電子デバイスであり、適切な分子認識能を賦与することで、標的種捕捉に伴う化学情報は閾値電圧または電流値の変化として読み出すことができる[1),8)]。センサの設計において、駆動部の OFET と検出部を分離した延長ゲート構造では、固液界面での化学センシングにおいても安定したデバイス駆動が達成される[1),8),9)10)]。本研究では、パターン認識駆動型の化学センシングを指向し、超分子レセプタを自己組織化単分子膜として修飾した延長ゲート型 OFET 化学センサについて紹

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介する。

標的種の構造や濃度の違いによって変化する様々なトランジスタ特性は、多成分分析において有効な指紋パターンとなり得るため、データ解析技術[3),11)]を駆使することによって、マーカー種を判別する定性分析や実サンプル中に含まれる標的種の未知濃度予測を行う定量分析へと展開できる[12),13)]。

本講演では、パターン認識駆動型 OFET 化学センサの汎用性について議論するための分析例として、ヒト体液中に含まれるオキソアニオン類[12)]と果汁に含まれるポリアミン類検出[13)]について紹介する。具体的には、超分子レセプタの設計、デバイス作製プロセス、パターン認識技術の特徴と活用法を含めた内容について触れ、分子認識化学と有機エレクトロニクスの融合技術に基づく化学センサデバイス開発のアプローチについて論じる。

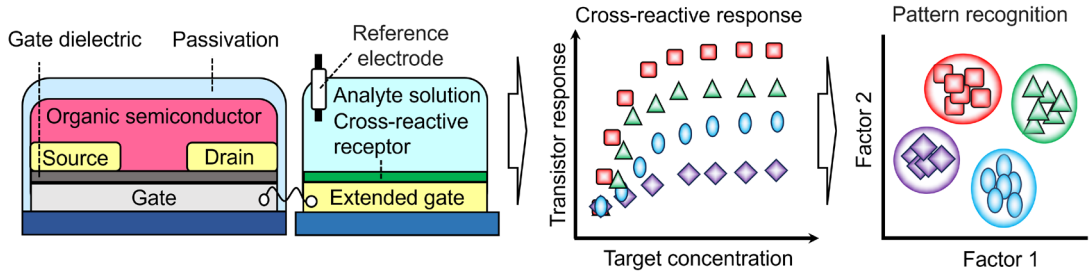

Fig. 1 (a) Schematic illustration of the extended-gate-type OFET chemical sensor functionalized with a cross-reactive receptor for pattern recognition. The OFET-based chemical sensor shows various transistor characteristics depending on analyte structures and their concentrations, which can be used as fingerprint-like profiles for pattern recognition.

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13) T. Minami et al., *J. Mater. Chem. C* **2021**, *9*, 11690 (**Cover, HOT Paper**)

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Symposium | Co-Innovation Program (CIP)：Cutting-edge research in polymer science for a sustainable society

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1433(1433, Bldg. 14 [3F])

[A1433-4pm] Cutting-edge research in polymer science for a sustainable society

Chair, Symposium organizer: Kenichi Kasuya, Kenji Hara, Ryotaro Tsuji, Yoshihiro Ikari

石油化学は高分子科学工業を生み出し、衣食住にわたって我々の生活を豊かにしてきた一方で、近年では温室効果ガス排出やプラスチックごみの環境拡散といった新たな課題を生み出しています。これらの課題に対して、サーキュラーエコノミーコンセプトは、高分子科学による革新的な解決策創出の後押し要因となっています。樹脂を再利用するための技術や、特定の環境下で分解するような材料、CO2やバイオマスなどから合成される新規材料等、様々な研究成果が生まれつつあり、高分子科学は大転換期を迎えようとしています。本セッションでは、持続可能社会を創出する高分子科学の研究前線を紹介すると共に、これからの高分子科学の在り方について議論します。

聴講後のアンケートへのご協力をお願いいたします。

Japanese Keynote Lecture
1:00 PM - 2:00 PM JST | 4:00 AM - 5:00 AM UTC
[A1433-4pm-01]
Development of catalytic resin-degradation reactions and their application to chmical recycling

○Kyoko Nozaki[1] (1. The University of Tokyo)

Japanese Invited Lecture
2:00 PM - 2:30 PM JST | 5:00 AM - 5:30 AM UTC
[A1433-4pm-02]
Depolymerization of super engineering plastics toward chemical recycling

○Yasunori Minami[1,2] (1. National Institute of Advanced Industrial Science and Technology, 2. University of Tsukuba, Cooperative Graduate School)

Japanese Invited Lecture
2:30 PM - 3:00 PM JST | 5:30 AM - 6:00 AM UTC
[A1433-4pm-03]
Advanced Plastic Resource Circulation Based on the Physical Degradation and Physical Regeneration Theory.

○Shigeru Yao[1] (1. Fukuoka University)

Japanese Invited Lecture
3:00 PM - 3:30 PM JST | 6:00 AM - 6:30 AM UTC
[A1433-4pm-04]
Direct Air Capture by free-standing nanomembranes

○Shigenori Fujikawa[1] (1. Kyushu University)

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
Opening Remarks

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樹脂分解触媒反応の開発とケミカルリサイクルへの展開

（東大院工）野崎京子
Development of catalytic resin-degradation reactions and their application to chemical recycling (*Graduate School of Engineering, The University of Tokyo*) Kyoko Nozaki

Conventionally, organic-polymer materials were synthesized from fossil resources and were intended to be discarded after use, namely, the one-way use. On the other hand, these wastes can be considered as attractive carbon resources. Accordingly, research aimed at reusing polymer materials is actively conducted globally. In this lecture, the author will present the current status of their “Resin Degradation Project” since 2021, focusing on catalyst development for the thermosetting-resin recycling[1]. Tricks to facilitate decomposition of olefin-based polymers[2] and synthesis of CO_2-based polymers[3] will be also briefly presented to initiate discussions on their potential application in society.
Keywords : Resin; Degradation; Catalyst; Chemical Recycling

従来、有機高分子材料は化石資源を原料として合成され、使用後は廃棄されるという一方向の使用が前提であった。しかし、これらの廃棄物は魅力的な炭素資源ととらえることができる。このため、高分子材料の再利用を目指した研究が国内外で活発に行われている。本講演では、演者らが 2021 年より「樹脂分解プロジェクト」で取り組んでいる、熱硬化性樹脂のリサイクルに向けた触媒開発について現状を報告する [1]。併せてオレフィン系材料分解のための工夫 [2]、二酸化炭素を原料とする高分子 [3] についても簡単に紹介し、社会実装の可能性について議論するための話題提供としたい。

1) (a) Y. Liao, K. Takahashi, K. Nozaki, *J. Am. Chem. Soc. in press*. 10.1021/jacs.3c09061. (b) T. Iwasaki, K. Tsuge, N. Naito, K. Nozaki, *Nat. Commun.* **2023**, *14*, 3279.
2) (a) G. Yonezaki, F. Seidel, K. Takahashi, K. Nozaki, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 545–549. (b) S. Tang, F. W. Seidel, K. Nozaki, *Angew. Chem. Int. Ed.* **2021**, *60*, 26506–26510.
3) (a) M. Hill, S. Tang, K. Masada, Y. Hirooka, K. Nozaki, *Macromolecules* **2022**, *55*, 3311–3316. (b) S. Tang, Y. Zhao, K. Nozaki, *J. Am. Chem. Soc.* **2021**, *143*, 17953–17957. (c) R. Nakano, S. Ito, K. Nozaki, *Nature Chem.* **2014**, *6*, 325–331.

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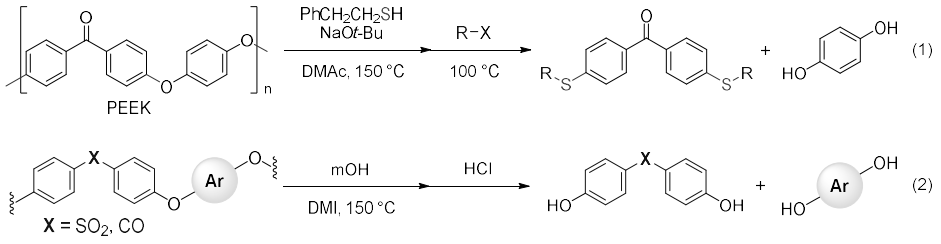
スーパーエンジニアリングプラスチックのケミカルリサイクルを拓く解重合法の開発

（産総研 IRC3）○南　安規 [1,2,3]
Depolymerization of super engineering plastics toward chemical recycling ([1]*Interdisciplinary Research Center for Catalytic Chemistry (IRC3), National Institute of Advanced Industrial Science and Technology (AIST)*, [2]*PRESTO, Japan Science and Technology Agency (JST),* [3]*U. of Tsukuba*) ○Yasunori Minami[1,2]

Super engineering plastics show high thermal stability and mechanical strength as well as chemical resistance. On the other hand, chemical recycling for these plastics has not been developed due to their stability. In this lecture, I report our recent development of the depolymerization of super engineering plastics toward the chemical recycling. One is that the depolymerization of polyetheretherketone (PEEK) with organo thiolates to form dithiofunctionalized benzophenone and hydroquinones. The products were applicable to the synthesis of various polymers. Second is the depolymerization of various super engineering plastics such as polysulfone (PSU), polyethersulfone (PESU), and PEEK by alkali hydroxides to form corresponding bisphenols.
Keywords : Chemical Recycling; Depolymerization; Phenol; Plastic; Sulfur

スーパーエンジニアリングプラスチックスは、高い熱安定性と機械的強度、耐薬品性を示す。一方、その安定性からケミカルリサイクルの研究がほとんど進んでいないのが現状である。本講演では、ケミカルリサイクルに向けたスーパーエンプラの解重合法の開発について報告する。一つは、ポリエーテルエーテルケトン（PEEK）を有機チオレートで解重合し、ジチオ官能化ベンゾフェノンやハイドロキノンを生成する方法である（式１）[1)]。この生成物は様々なポリマーの合成に応用可能であった。第二は、アルカリ水酸化物による各種スーパーエンジニアリングプラスチックの解重合で、対応するビスフェノール類を形成する（式２）[2,3)]。



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物理劣化・物理再生理論により構築される新たなプラスチック資源循環

（福岡大研究推進部）八尾　滋
Advanced Plastic Resource Circulation Based on the Physical Degradation and Physical Regeneration Theory (*Central Research Institute Fukuoka University*) Shigeru Yao

In Japan, the recycling ratio of plastics is about 85%. However, about 70% of the recycled plastics are used for energy recovery, about 5% for chemical recycling, and about 25% for mechanical recycling.

Our laboratory is engaged in the research and development of the advanced repelletizing process based on the "Physical Degradation/Physical Regeneration Theory" and its fundamental meso-region internal structure analysis method. In the pelletizing system, we have devised a new device element called a “Molten Resin Reservoir : MRR”, and are investigating a very effective mechanism for improving the physical properties of the material derived from this element. In meso-area internal structure analysis, we are proposing new analysis methods using SAXS and AFM.

Keywords : Plastic mechanical recycle, Physical degradation, Physical regeneration, Meso-scale inner structure

2022 年に施行された「プラスチック資源循環促進法」では、設計・製造段階から販売・提供段階、そして排出・回収・リサイクル段階において、事業者や自治体などが実施すべき行動指針が示されている。この中のリサイクルに関して福岡大学は高度物性再生プロセス構築に関して、Fig.1 に示す「物理劣化・物理再生理論」を基盤として、各大学・研究機関ならびに企業とともに基礎ならびに応用の研究開発を行っている。その結果、①プラスチックは過度なせん断履歴を受けることで力学特性、特に伸びや靭性が大きく低下する物理劣化が生じること、②一方で動的変形などを与えることで物性が再生できること、③各々の力学特性の変化に応じて生じている、メソ領域のラメラ積層構造の変異が種々の手法で解析できること、④力学特性の変化は、系中の絡み合いの数ならびにそれによるタイ分子数が変化したためであると考えられること、などを示す成果が得られている。さらに、実用的なマテリアルリサイクルプロセスとして、樹脂

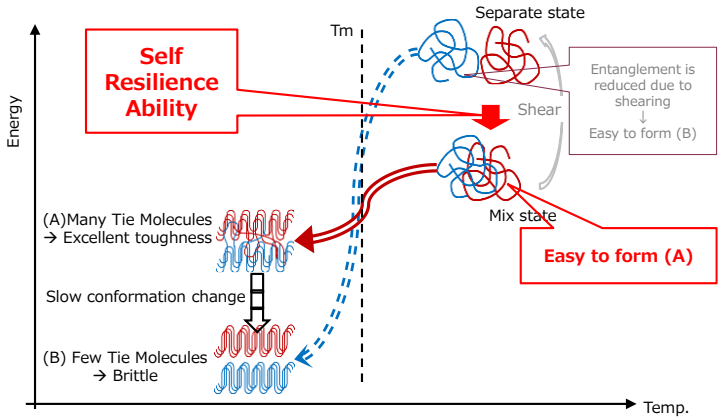

Fig.1 Diagram of Physical Degradation and Physical Regeneration Theory

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溜まり部（Molten Resin Reservoir : MRR）を設けた押出機を考案し、その性能や拡張の研究も行っている。この課題に関しては、実生産機レベルを目指したスケールアップ研究を実施し、2022 年度末に吐出量が 300kg/hour の MRR が設置された 70mm φ の実証試験機を作製し、現在性能評価・運転条件検討を行っている。

また「物理劣化・物理再生理論」は、成形品の物性がせん断履歴に大きく依存することを示している。実際にゲート付近から採取した試験片の力学物性は、ゲートから離れた部位と比較すると著しく低下している。これは、ゲート付近がもっともせん断速度が大きく、ゲートから離れるに従って小さくなるためである。即ち射出成形品の物性は部位依存性を持つ不均質なものであり、さらにゲート付近の部位のリサイクル性も大きく低下する。この課題を解決するために、三光合成では新規な成形プロセスの開発研究を行っている。Fig.2 は成果の一例である。これまでの成形で得られた試料②はバージン品①よりも物性が低下していることが分かる。さらにリサイクルした試料③は、元の 1/5 までに物性低下していることが分かる。一方金型内でのせん断履歴を均質にする新たな成形手法で作製した試料④は、物性が①とほぼ同じで維持されており、またリサイクルを行っても⑤に示すように物性低下が全くないことが分かる。この結果は、せん断履歴を均質化するという工夫を行うことで、初期物性においても力学特性が非常に均質に高くなるだけでなく、リサイクル時にも物性が維持されており、高度な再利用が効率的に可能になることが示されている。

プラスチックの資源循環を、社会負担やコスト課題なども考慮して、効率的・効果的に実施するためには、製品製作段階からの環境配慮設計を行うことが重要である。現状環境配慮設計としては一般的には、易解体やモノマテリアル化などが想定されているが、物性の高度化による薄肉化・軽量化、高耐久性付与による長寿命化、さらにリサイクル時の物性維持など、高分子物性の根本にかかわる取り組みが不可欠である。今回示したように、「物理劣化・物理再生理論」は、プラスチックの成形からリサイクルまでの成形プロセスと物性に関する関連性を網羅的に示しているものであり、この理論を展開することで、成形時の環境配慮設計から高度リサイクルまで、一貫したプラスチック資源循環を構築することが可能となる。

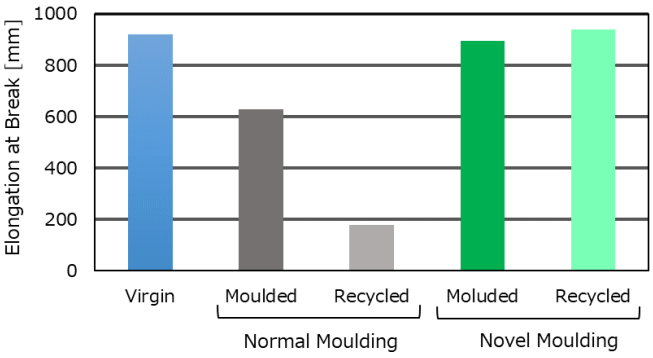

Fig.2 Molding method dependence of Elongation at break

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(JPNP20012)の結果得られたものです。

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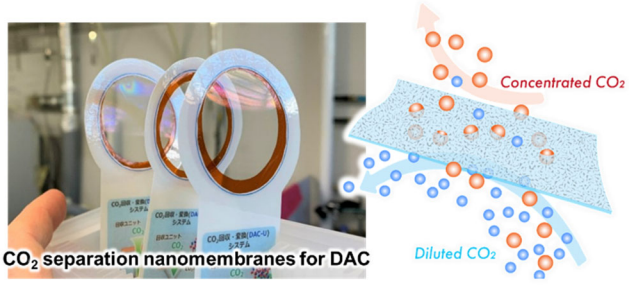
自立分離膜を用いた大気からの直接的 CO_2 回収

（九大 WPI-I2CNER[1]・九大 K-NETs[2]）藤川 茂紀[1,2]
Direct Air Capture by free-standing nanomembranes ([1]*International Institute for Carbon-Neutral Energy Research, Kyushu University*, [2]*Reseach Center for Negative Emissions Technologies, Kyushu University*) ○Shigenori Fujikawa[1,2]

CO_2 capture directly from the atmosphere, known as Direct Air Capture (DAC), is essential to achieving carbon neutrality. CO_2 capture by membranes is inherently superior to other technologies because there are no site limitations. However, conventional membranes have low permeability and their application to DAC has been considered impossible. To change this common perception, we fabricated a nanomembrane with a thickness of 34 nm and free-standing properties using a crosslinked polydimethylsiloxane material, and achieved an overwhelmingly high CO_2 permeability, several tens of times higher than the world's highest value.[1] Further membrane thinning with the thickness of the membrane to 17 nm was succeeded and its CO_2 permeability has reached about 50,000 GPU.[2] In such an ultra-thin membrane, the sorption behavior of gas molecules on the membrane surface becomes the rate-limiting step. In other words, the surface molecular design of the separation membrane is extremely important to improve the membrane performance. We have achieved high CO_2/N_2 selectivity by modifying the membrane surface in various ways.
Keywords : CO_2 capture, Direct Air Capture, DAC, free-standing nanomembrane

大気からの直接的 CO_2（Direct Air Capture, DAC)は、カーボンニュートラル実現に必須である。設置場所に制限のない膜分離での CO_2 回収は、DAC 用途として他技術に比べて優位である。しかしながら、従来の CO_2 分離膜はその透過量が極めて少ないため、DAC への適用は不可能と考えられてきた。これに対し我々は、架橋性ポリシロキサン材料を用いて、厚みが 34nm で自立性をもつナノ膜の作製し、従来の CO_2 透過度世界最高値の数十倍という、圧倒的に高い CO_2 透過度を実現した。[1)] さらなる薄膜化（膜厚:約 17nm）を進め、約 50,000GPU という極めて高い CO_2 透過度を実現した。[2)] またこのような超薄膜化された分離膜では、分離膜表面での気体分子の収着挙動が律速段階になる。すなわち分離膜の表面分子設計が分離膜性能向上に極めて重要となる。我々は様々な分離膜表面の修飾を行い、高い CO_2/N_2 選択性を実現した。



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Symposium | Asian International Symposium：Asian International Symposium - Colloid and Surface Chemistry -

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1422(1422, Bldg. 14 [2F])

[A1422-4am] Asian International Symposium - Colloid and Surface Chemistry -

Chair, Symposium organizer: Ryo Murakami, Syuji Fujii, Taku Iiyama, Taku Ogura

9:00 AM - 9:05 AM JST | 12:00 AM - 12:05 AM UTC
Opening Remarks

English Keynote Lecture
9:05 AM - 9:40 AM JST | 12:05 AM - 12:40 AM UTC
[A1422-4am-01]
Particle Adhesion on Thin Liquid Layer

○Sanghyuk Wooh[1] (1. Chung-Ang University)

English Invited Lecture
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC
[A1422-4am-02]
Solution and Foam Properties of Homogeneous Polyoxyethylene-Type Nonionic Surfactants with Multi-Branched Chains

○Shiho Yada[1] (1. Tokyo University of Science)

English Invited Lecture
10:00 AM - 10:20 AM JST | 1:00 AM - 1:20 AM UTC
[A1422-4am-03]
Lipid Based Artificial Multicellular Systems for Compartmentalized and Stimuli-Responsive Drug Delivery

○Richard James Archer[1], Tsuyoshi Inaba[1], Shin-Ichiro M. Nomura[1] (1. Tohoku University)

10:20 AM - 10:25 AM JST | 1:20 AM - 1:25 AM UTC
Break

English Invited Lecture
10:25 AM - 10:45 AM JST | 1:25 AM - 1:45 AM UTC
[A1422-4am-04]
Colloidal interaction-mediated wrapping of zeolite crystals with graphene oxide sheets

○Hayato Otsuka[1], Kei Kubo[1], Katsumi Kaneko[1] (1. Shinshu university)

English Invited Lecture
10:45 AM - 11:05 AM JST | 1:45 AM - 2:05 AM UTC
[A1422-4am-05]
The influence of electrostatic and hydrodynamic interactions on gelation of colloidal particles

○Joeri Opdam[1], Michio Tateno[1], Hajime Tanaka[1,2] (1. Research Center for Advanced Science and Technology, The University of Tokyo, 2. Department of Fundamental Engineering, Institute of Industrial Science, The University of Tokyo)

English Keynote Lecture
11:05 AM - 11:40 AM JST | 2:05 AM - 2:40 AM UTC

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[A1422-4am-06]

Clathrate hydrates: A cool way to store carbon dioxide permanently

○Praveen Linga[1] (1. National University of Singapore)

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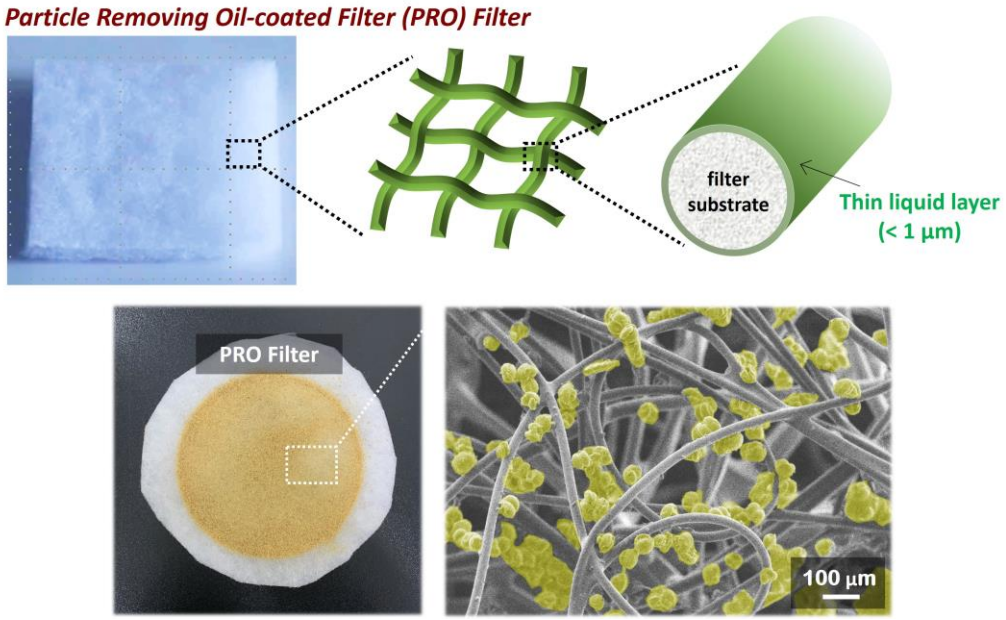
Particle Adhesion on Thin Liquid Layer

(*Department of Chemical Engineering, Chung-Ang University*) ○Sanghyuk Wooh
Keywords: Adhesion; Air Filter; Capillary Force; Surface Modification; Thin Liquid Film

Dry dust filters with small pores have been worldwide used to clean air and now are everywhere in our daily life. Dust, also called particulate matter (PM), are captured at the pore of the filters, therefore smaller pores result in higher PM capturing efficiency. However, air becomes more difficult to pass through the filter as the pores get smaller, which decreases the air permeability and increases the air pressure drop across the filter. This dilemma, caused by the low adhesion of solid PMs to the dry solid surface of the filters, has been one of the most important issue to be overcome on dry dust filter for several decades. Here, inspired by human nose filtering system with thin mucus coated nasal hairs, we create a dry dust filter having a thin non-volatile liquid layer at the surface of the pores. The strong adhesion of PM on liquid thin film improves the PM capturing efficiency without affecting the air permeability of the filter. The liquid thin film coated filter particularly exhibits outstanding dust filtering capability at fast speed filtering system with no re-dispersion of captured PMs. In addition, the suppressed PMs re-dispersion allows a new bi-directional dust filtering. The Particle Removing Oil-coated Filter (PRO) filter proposes a new paradigm of dust filtering and opens a new door for fast and efficient air cleaning.



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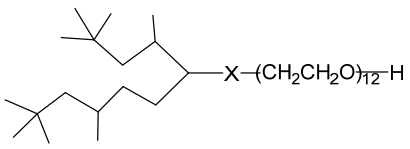
Solution and Foam Properties of Homogeneous Polyoxyethylene-Type Nonionic Surfactants with Multi-Branched Chains

(*Faculty of Engineering, Tokyo University of Science*) ○Shiho Yada

Keywords: Multi-branched chain; Polyoxyethylene-type surfactant; Aggregation; Foam; Small-angle neutron scattering

1. Introduction Double-chain surfactants, comprising two hydrophobic groups and one hydrophilic group, have been known to exhibit some interesting properties, such as low surface tension, excellent wetting ability, and formation of vesicles in dilute aqueous solutions. Surfactants containing branched alkyl chains also exhibit low Krafft temperature, low surface tension, excellent penetration, and high salt resistance. Herein, we are focusing on branched double-chains-containing surfactants, which are expected to possess properties of both the double-chain and branched chain-containing compounds. In this presentation, I would like to introduce two homogeneous polyoxyethylene (EO) alkyl ether and ester-type nonionic surfactants with multi-branched double chains: bC$_7$-bC$_9$EO$_{12}$ and bC$_7$-bC$_9$COOEO$_{12}$, where bC$_7$ and bC$_9$ represent branched chains with total carbon numbers of 7 and 9, respectively, while EO$_{12}$ represents dodecaoxyethylene (Fig. 1). Their solution and foam properties were investigated and compared to those of homogeneous EO alkyl ether and ester-type nonionic surfactants with symmetric and asymmetric linear double chains (C$_8$-C$_8$X and C$_6$-C$_8$X; C$_6$ and C$_8$ represent linear hexyl and octyl chains, respectively; X represents EO$_{12}$ in dodecaoxyethylene ether and COOEO$_{12}$ in dodecaoxyethylene ester) as well as a conventional surfactant with a linear single chain (C$_{18}$EO$_{12}$). The effects of structures of the branched and linear alkyl chains, number of alkyl chains, and structure of the ether or ester group between the alkyl and EO chains on the solution and foam properties were also investigated.



bC$_7$-bC$_9$COOEO$_{12}$(X = COO)
bC$_7$-bC$_9$EO$_{12}$(X = CH$_2$O)

Fig. 1 Structures of homogeneous EO-type nonionic surfactant.

2. Experiment Their solution properties were investigated through cloud point, surface tension, and small-angle X-ray scattering measurements installed at the BL40B2 beamline of the SPring-8 facility. These foam properties were measured by small-angle neutron scattering (SANS) using an i-MATERIA installed on the BL20 beamline at the MLF of the J-PARC in combination with other techniques.

3. Results and Discussion

3. 1. Solution properties[1)] The surface tension at the critical micelle concentration (CMC) of homogeneous EO-type nonionic surfactants decreased in the order of linear single chain (38.2 mN m^{-1}) > linear double chain (30.4–32.5 mN m^{-1}) > multi-branched double chain (27.9–28.8 mN m^{-1}) (Fig. 2). An increase in the ratio of methyl groups to the total carbon number of the hydrophobic group reduced the surface tension. The effectiveness of the adsorption and

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micellization process (CMC/C_{20}) ratio increased in the order of linear single chain < linear double chain < multi-branched double chain. In particular, the CMC/C_{20} ratio of the multi-branched double-chain-type surfactants (bC$_7$-bC$_9$EO$_{12}$ and bC$_7$-bC$_9$COOEO$_{12}$) was considerably higher than that of the linear single-chain and double-chain ones: this indicates that the former easily adsorbed at the air/water interface. These results suggest that the adsorption ability at the air/water interface for multi-branched double-chain surfactants was higher than that of the linear counterparts. In the temperature vs. concentration phase diagram (Fig. 2), the regions of lamellar liquid crystals were extensive because of the small interfacial curvature induced by the steric hindrance of the multi-branched chains.

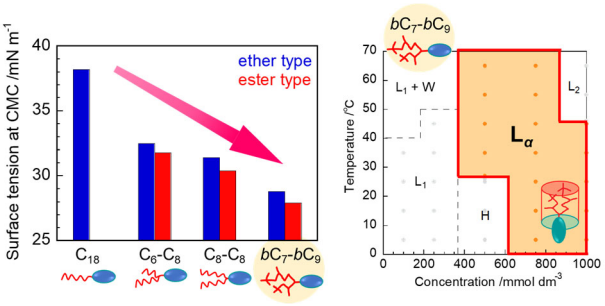

Fig. 2 Surface tension at CMC and temperature vs. concentration phase diagrams.

3. 2. Foam properties[2] SANS can provide insight into the microstructure of the surfactant-stabilized foam. We performed SANS experiments to assess the structures and stabilities of the homogeneous EO-type nonionic surfactants (bC$_7$-bC$_9$EO$_{12}$, C$_8$-C$_8$EO$_{12}$, and C$_{18}$EO$_{12}$)-stabilized foams, thereby revealing the existence of micelles in the films between bubbles containing the plateau border and determining the average radius of the bubble. The bC$_7$-bC$_9$EO$_{12}$ and C$_8$-C$_8$EO$_{12}$ surfactants with multi-branched chains and double-chains increased the foam stability compared to C$_{18}$EO$_{12}$. The films between bubbles contained micelles similar to those found in the bulk solution. For bC$_7$-bC$_9$EO$_{12}$ and C$_8$-C$_8$EO$_{12}$, the average radius of the bubbles immediately after foaming was of the order hundreds of μm, and finally, these radii became large to the order of thousands of μm. On the other hand, in the case of the C$_{18}$EO$_{12}$, the radii rapidly increased after foaming and the bubbles collapsed (Fig. 3). The bC$_7$-bC$_9$EO$_{12}$ and C$_8$-C$_8$EO$_{12}$ exhibited fast adsorption rates, high interfacial elasticity, and unlike linear C$_{18}$EO$_{12}$, formed rod-like micelles in the foam film. These anisotropic aggregates with their high interfacial activity were found to stabilize the foam considerably. Thus, this study presents a first-time account in terms of using SANS to probe the structure of foams stabilized by homogeneous EO-type nonionic surfactants. The information on the structure and stability of these foams is expected to be useful in food, cosmetics, and other industries.

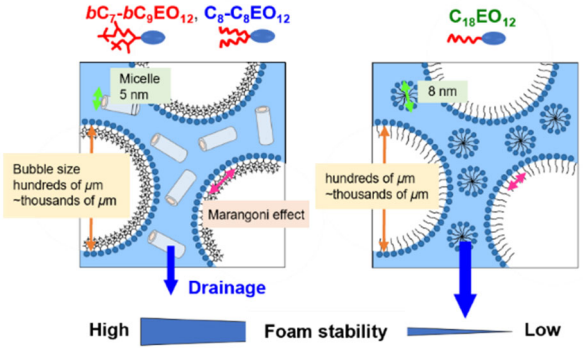

Fig. 3 Microstructure of the surfactant-stabilized foam.

References 1) S. Yada, et al., *Colloids Surf. A* **2022**, *648*, 129247. 2) S. Yada, et al., *Langmuir* **2023**, 39(43) 15355–15361.

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Multicellular lipid compartments for efficient and scalable micro-compartmentalization with stimuli-responsive release.

Richard Archer,[1] *Tsuyoshi Inaba,*[1] *Shin-Ichiro Nomura.*[1]

[1]*Graduate School of Engineering, Department of Robotics, Tohoku University*

Keywords: Self-assembly; Micro-compartmentalization; Lipids; Controlled release, HIPE.

Multicellular Lipid Compartments (MCLCs) are lipid stabilized High Internal Phase Emulsions (HIPE), which show remarkable encapsulation efficiencies, with dispersed phase concentrations far exceeding the continuous phase (Fig 1a). MCLCs have typical internal phase contents of over 88% leading to tight packed droplets delineated by lipid rich membranes, leading to their "cellular-like" morphologies (Fig 1b).[1,2] "Cellular" micro-compartment sizes are typically between 50 to 500 µm depending on formation conditions. The synthesis process easily achieves milliliter scales within minutes and is highly scalable. The MCLC can be simply pipetted into an external water phase to create a double emulsion. Due to MCLCs semi-solid-like properties, 3D printing of vast arrays of micro-compartments within external aqueous media has been demonstrated (Fig. 1c). MCLC systems are extremely stable with months-long observations showing no loss of structure or unwanted release of internal contents. A proposed application for this system is in transdermal drug delivery by creation of portable and appliable MCLC patches by gelling the external aqueous phase. Using membrane solubilization techniques to release the contents, we show the unique morphology can confer advantages in control of the release rate. We also show the controlled release of the internal contents by environmental triggers which could lead to environmentally dependent delivery of encapsulated compounds (Fig. 1d).

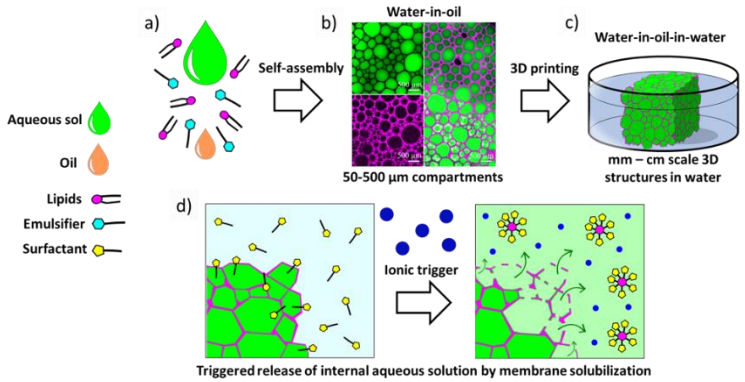

Fig.1 Schematic of MCLC system showing (a) Initial components for self-assembly (b) confocal micrograph of formed MCLC with aqueous phase (green), oil phase (pink) and combined image, (c) 3D MCLC in external aqueous phase (d) Salt triggered membrane solubilization to release internal contents.

(1) Nomura, S. M.; Shimizu, R.; Archer, R. J.; Hayase, G.; Toyota, T.; Mayne, R.; Adamatzky, A.. *ChemSystemsChem* **2022**, *4* (5), (2) Archer, R. J.; Hamada, S.; Shimizu, R.; Nomura, S.-I. M. *Langmuir* **2023**, *39* (14), 4863–4871.

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Colloidal interaction-mediated wrapping of zeolite crystals with graphene oxide sheets

([1]*Research Initiative for Supra-Materials: RISM, Shinshu University*, [2]*Faculty of Engineering, Shinshu University*) ○Hayato Otsuka,[1] Kei Kubo,[1] Daisuke Saeki,[1,2] Katsumi Kaneko[1]

Keywords: Graphene oxide; zeolite; wrapping; salting out; colloidal stability

Wrapping of inorganic and organic solids is an approach to modify the colloidal properties of the solids. Graphene oxide (GO)/graphene-wrapping imparts high dispersibility or electrical conductivity to the solids and has application potentials for batteries and supercapacitors. GO spontaneously wraps positively charged particles due to the Coulombic interaction with negatively charged GOs. Wrapping of negatively charged particles is not that easy way and salting out enables to wrap the negatively charged particles with GO. Control of the surface properties of GO also is important for better wrapping because the properties of GO changes with time in colloidal states.[1] In this study, we examined wrapping of negatively charged zeolite crystals with GO by addition of ammonium chloride (NH_4Cl) with an aid of colloid chemistry.

We prepared GO dispersions via improved Hummers' method from Madagascar graphite. MFI zeolite crystals dispersed in water were mixed with GO dispersion under the different concentrations of NH_4Cl solution. The mixture was shaken vigorously and then left under the dark to obtain GO wrapped MFI zeolite crystals (GO-MFI).

The formation of GO-MFI flocculation depends on the concentration of NH_4Cl. MFI zeolite crystals and GOs separate below 0.01 mol dm^{-3}, above which GO-MFI flocculation is formed at the bottom. The negative zeta potential of MFI zeolite and GO particles increases with increasing the concentration and GO wraps MFI zeolites, when the zeta potential is low enough. The wrapping process is divided into three stages depending on the concentration (Fig. 1). MFI zeolite and GO particles are separately disperse in the low concentration region and GO partially wraps MFI zeolites in the middle. Wrapping completes and some GO sheets bridge GO−MFI particles in the high concentration range. GO wrapping improves the colloidal stability of zeolite and the GO−MFI are stable in aqueous solution for more than two weeks.

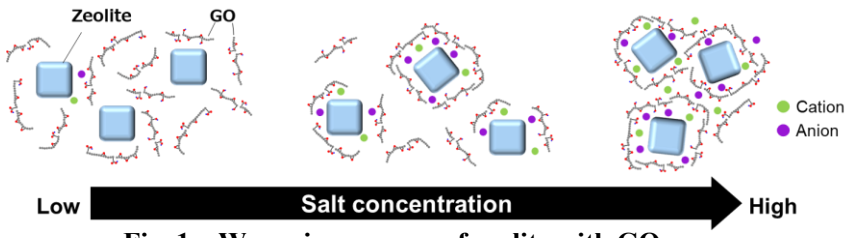

Fig. 1 Wrapping process of zeolite with GO.

1) H. Otsuka, K. Kaneko, *et. al.*, *Nat. Commun.* in third revision.

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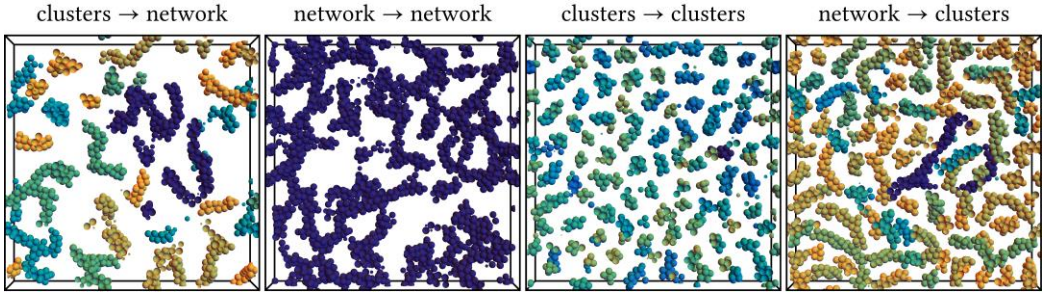
The influence of electrostatic and hydrodynamic interactions on gelation of colloidal particles

([1]*Research Center for Advanced Science and Technology, The University of Tokyo*, [2]*Department of Fundamental Engineering, Institute of Industrial Science, The University of Tokyo*) ○Joeri Opdam,[1] Michio Tateno,[1] Hajime Tanaka[1,2]

Keywords: Charged colloids; Gelation; Cluster phase; Hydrodynamic interactions; Fluid particle dynamics simulations

Colloids with short-range attractive interactions can form gels as a result of dynamically arrested phase separation. Such gels are soft solid materials consisting of a colloidal network and an intertwined solvent. Due to their interesting transport and mechanical properties, colloidal gels have many applications in products such as foods, cosmetics and drug delivery. Generally, colloids in such systems exhibit long-range repulsive electrostatic interactions in addition to the short-range attraction. The combination of these competing interactions strongly influences the gelation process[1]. For example, previous studies have shown that gelation can occur by the percolation of equilibrium clusters[2] that have a preferred cluster size due to the relatively large increase in the number of repulsive interactions upon increasing cluster size.

In this talk, the structure evolution of charged colloidal systems that do not exhibit an equilibrium cluster phase is discussed. Systematic computer simulations were performed for different concentrations and interaction potentials. At early stages the aggregation of particles either results in compact clusters or in a percolating network with thin branches. In both cases, the final structure can be either a cluster phase or a gel phase depending on the simulation parameters. The final structures, and thus the mechanical and transport properties, can be remarkably different depending on the simulation parameters and the structure evolution pathway, as seen in the figure below which shows slices of representative obtained structures. Finally, we briefly discuss the influence of hydrodynamic interactions on the structure evolution. Accounting for hydrodynamic interactions is computationally demanding and investigating their role in gelation processes is important to guide future simulation studies.



1) A. I. Campbell, V. J. Anderson, J. S. van Duijneveldt, and P. Bartlett, *Phys. Rev. Lett.* **2005**, *94*, 208301.
2) J. Ruiz-Franco and E. Zaccarelli, *Annu. Rev. Condens. Matter Phys.* **2021**, *12*, 51.

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Clathrate hydrates: A cool way to store carbon dioxide permanently.

([1]*Department of Chemical and Biomolecular Engineering, College of Design and Engineering, National University of Singapore, Singapore*) ○Praveen Linga[1]

Keywords: *Gas Hydrates*; Clathrate Hydrates; CO_2 Sequestration, CCS, Ocean Sequestration

Climate change is known to be dominantly caused by the increased concentration of greenhouse gases in the atmosphere, in particular carbon dioxide (CO_2). The clathrate hydrate process has been demonstrated over the years as promising technology for innovative applications like natural gas storage, carbon dioxide capture, seawater desalination, cold energy storage etc. CO_2 hydrate, a solid compound made of molecular CO_2 enclathrated in crystalline lattices formed by water molecules, is an attractive option to capture and for long-term CO_2 sequestration. Methane (CH_4) hydrates in oceanic sediments have been stable for millions of years. As a natural analog, is it possible to store CO_2 in the form of hydrates in oceanic sediments forever? In this presentation, the state of the art on clathrate hydrate technology pertaining to carbon capture and storage will be discussed in detail. Furthermore, future research and development opportunities and pathways for commercialization will be discussed.

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Symposium | Asian International Symposium：Asian International Symposium - Photochemistry -

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1422(1422, Bldg. 14 [2F])

[A1422-4pm] Asian International Symposium - Photochemistry -

Chair, Symposium organizer: Ayumi Imayoshi, Hajime Shigemitsu, Hiroshi Ikeda, Jiro Abe, Masashi Hasegawa, Shinnosuke Horiuchi, Tadashi Mori, Takashi Hirose, Takuya Nakashima, Yoichi Kobayashi

1:00 PM - 1:05 PM JST | 4:00 AM - 4:05 AM UTC

Opening Remarks

English Keynote Lecture

1:05 PM - 1:40 PM JST | 4:05 AM - 4:40 AM UTC

[A1422-4pm-01]

Coordination Assembly of Photofunctional Lanthanide-Organic Architectures

○Qing-Fu Sun[1] (1. Fujian Institute of Research on the Structure of Matter)

English Invited Lecture

1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC

[A1422-4pm-02]

Achieving Circularly Polarized Luminescent Materials Based on Chiral Multinuclear Complexes

○Toshikazu Ono[1] (1. Kyushu University)

English Invited Lecture

2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC

[A1422-4pm-03]

Synthesis of aza[n]helicenes (n=9-19) and systematic studies on their (chir)optical and electrochemical properties

○Takayuki Tanaka[1], Yusuke Matsuo[1], Masayuki Gon[1], Kazuo Tanaka[1], Shu Seki[1] (1. Kyoto University)

English Keynote Lecture

2:20 PM - 2:55 PM JST | 5:20 AM - 5:55 AM UTC

[A1422-4pm-04]

Helical Synthetic Nanographene with Atomic Precision

○Jiaobing Wang[1] (1. Sun Yat-Sen University)

English Invited Lecture

2:55 PM - 3:15 PM JST | 5:55 AM - 6:15 AM UTC

[A1422-4pm-05]

Vibronic analysis and design strategy for circularly polarized luminescent molecules with large dissymmetry factors

○Fumitaka Ishiwari[1,2] (1. Osaka University, 2. JST PRESTO)

English Invited Lecture

3:15 PM - 3:35 PM JST | 6:15 AM - 6:35 AM UTC

[A1422-4pm-06]

Analysis of non-radiative decay pathways using quantum chemical calculations: Application to photoredox-catalyzed radical reaction

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◯Yu Harabuchi[1,2] (1. WPI-ICReDD, 2. JST-ERATO)

3:35 PM - 3:40 PM JST | 6:35 AM - 6:40 AM UTC

Closing Remarks

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Coordination Assembly of Photofunctional Lanthanide-Organic Architectures

Metallosupramolecular architectures have a wide range of application prospects in recognition and sensing, biomimetic catalysis, and drug delivery. We have introduced rare earth metal ions, which bear excellent optoelectromagnetic and catalytic properties, into the structural design of coordination supramolecular systems. The lanthanide supramolecular edifices overcome the problem that many metals in coordination supramolecular systems are only used as connecting nodes and lack their own functionality. We have developed precise assembly and luminescence control strategies for rare earth coordination supramolecules, and further promoted their applications in optical sensing, up-conversion luminescence, extraction, and multimodal biological imaging based on the synergistic effect of inorganic and organic components.

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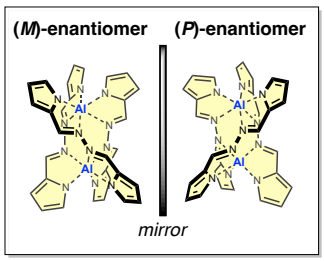
Achieving Circularly Polarized Luminescent Materials Based on Chiral Multinuclear Complexes

([1]*Graduate School of Engineering, Kyushu University*, [2]*Center for Molecular Systems (CMS), Kyushu University*) ○Toshikazu Ono,[1,2]

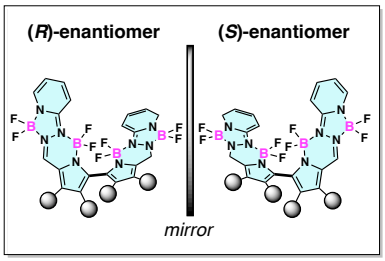
Keywords: *Boron Complexes*; *Aluminum Complexes*; *Axial Chirality*; *Helical Chirality*; *Circularly Polarized Luminescence*

Materials that exhibit strong fluorescence in both solution and solid states, particularly those showing two types of left- and right-handed circularly polarized luminescence (CPL), have recently garnered significant interest. Notably, metal complexes are at the forefront of CPL materials due to their ability to form various chiral structures based on ligand and metal ion coordination. However, the propensity to form complexes often compromises their stability, leading to potential racemization and reduced CPL activity. Therefore, metal complexes that maintain chiral stability while exhibiting strong luminescence are the subject of intense modern research.

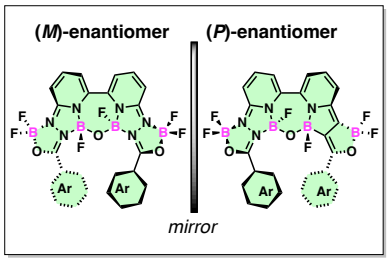
In this context, our study advances the development of functional dyes derived from multinuclear complexes of typical elements, highlighting their chiroptical properties. Specifically, we have focues on synthesizing dinuclear triple-helical complexes,[1-3] tetranuclear complexes,[4,5] and helicene-like complexes[6] featuring elements such as aluminum and boron. Our research demonstrates that these complexes' enantiomers, or mirror-image counterparts, serve as dyes that display both circular dichroism (CD) and CPL activity. This presentation will delve into the synthesis processes of these complexes and share detailed insights into their synthesis techniques and chiral luminescent properties.



T. Ono et al.,
Angew. Chem. Int. Ed. **2021**, *60*, 2614.



T. Ono et al.,
Angew. Chem. Int. Ed. **2022**, 61, e202204358.



T. Ono et al.,
in preparation

1) T. Ono and K. Ishihama et al., *Angew. Chem. Int. Ed.* **2021**, *60*, 2614. 2) K. Ueno and T. Ono et al., *submitted.* 3) Y. Konishi and T. Ono et al., *in preparation.* 3) L. Cui, H. Shinjo and T. Ono et al., *Angew. Chem. Int. Ed.* **2022**, *61*, e202204358. 4) L. Cui and T. Ono et al., *J. Mater. Chem. C.* **2023**, *11*, 2574-2581. 5) L. Cui, R. Furuta and T. Ono et al., *submitted.*

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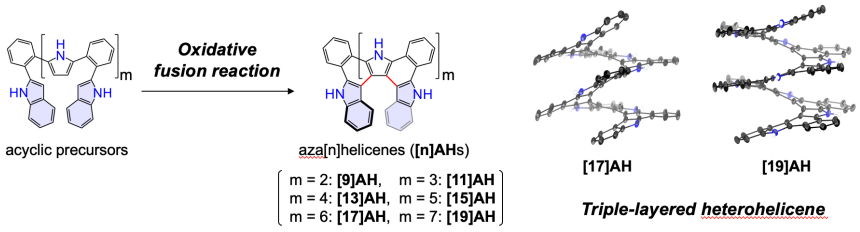
Synthesis of aza[n]helicenes (n = 9-19) and systematic studies on their (chir)optical and electrochemical properties"

([1]*Graduate School of Engineering, Kyoto University*) ○Takayuki Tanaka[1], Yusuke Matsuo[1], Masayuki Gon[1], Kazuo Tanaka[1], Shu Seki[1]

Keywords: Heterohelicene; Oxidative Fusion Reaction; Aromaticity; Hydrogen Bonding; Circularly Polarized Luminescence

Heterohelicenes, in which heteroatoms are embedded into the helicene backbones, have attracted attention because of their excellent luminescence and redox properties. Generally, heterohelicenes are more electron-rich compared with carbohelicenes, thus their HOMO energy levels are continuously destabilized with the π-extension. Therefore, it is difficult to synthesize long heterohelicenes with full conjugation, whereas several heterohelicenes with a double-layered structure have been synthesized; one example is diazatrioxa[13]helicene.[1)] Furthermore, a triple-layered structure was accomplished with oxa[n]helicene (n=17, 19) albeit with disrupted π-conjugation.[2)] To qualitatively evaluate the electronic properties of helicenes, however, it is necessary to systematically synthesize fully conjugated heterohelicenes of different lengths, and a new synthetic strategy toward longer heterohelicene would be indispensable.

We recently reported oxidative fusion reactions of *ortho*-phenylene-bridged oligopyrroles to afford various heterocirculenes and heterohelicenes.[3)] Notably, tetraaza[8]circulenes, with planar structures excluding any sterically encumbering substituents, are fairly soluble in THF and DMSO. This property arises from effective hydrogen-bonding interactions between the pyrrolic NH site and the H-bond accepting solvent molecule. Inspired by this molecular design principle, herein we report a synthetic challenge for longer azahelicenes with outer-pointing pyrrolic NH sites, and a series of benzannulated aza[n]helicenes up to n=19 were successfully obtained from the corresponding acyclic precursors.[4)] Comprehensive characterizations by NMR, UV/Vis and fluorescence spectroscopy, electrochemistry, as well as CD and CPL spectra of the enantiomers revealed the π-conjugation along the helix and between the layers.



1) S. K. Pedersen, K. Eriksen, M. Pittelkow, *Angew. Chem. Int. Ed.* **2019**, *58*, 18419. 2) J. Nejedlý, I. G. Stará, I. Starý *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 5839. 3) T. Tanaka, *Bull. Chem. Soc. Jpn.* **2022**, *95*, 602. 4) Y. Matsuo, M. Gon, K. Tanaka, S. Seki, T. Tanaka, *ChemRxiv*. DOI:10.26434/chemrxiv-2023-4z7z6.

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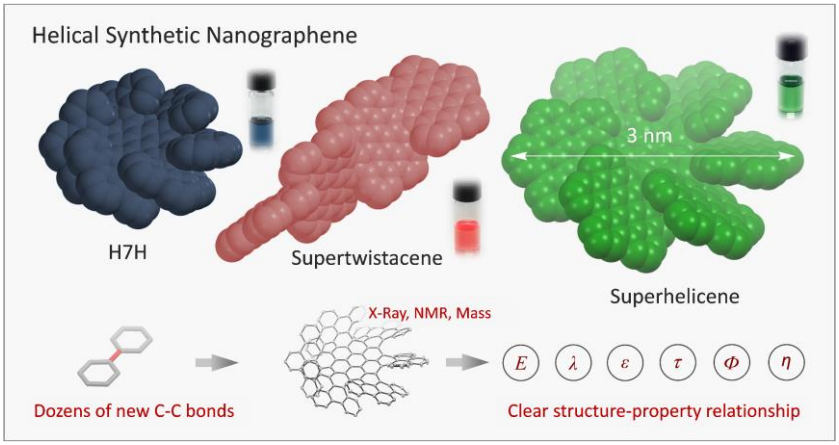
Helical Synthetic Nanographene with Atomic Precision

(*School of Chemistry, Sun Yat-Sen University*) ○Jiaobing Wang
Keywords: Nanographene; Helical; PAH; Chiroptical Properties; Conjugation

Atomically precise synthesis of novel 3D molecular nanographene (NG), comprising hundreds of conjugated carbon atoms and possessing excellent properties, is one of the most challenging research topics in modern synthetic chemistry. We create a new research line featured by a series of giant helical NGs such as superhelicene and supertwistacene,[1-6] which are prepared in a highly efficient manner via the cyclotrimerization of alkyne and the Scholl oxidation. These synthetic achievements set a series of new records, which include the biggest chiral NG ever synthesized in solution, the first helical graphene nanoribbon having a thermally stable configuration, the polycyclic aromatic hydrocarbon displaying the most prominent light absorption capability, and the chiral NG showing the strongest Cotton effect. These studies provide fundamental knowledge for understanding the structure-property relationship of synthetic NG at a new level of sophistication.



1) Y. Zhu, et al. *J. Am. Chem. Soc.* **2018**, *140*, 4222. 2) Y. Zhu, et al. *J. Am. Chem. Soc.* **2019**, *141*, 5511. 3) Y. Wang, et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 16966. 4) S. Ma, et al. *J. Am. Chem. Soc.* **2020**, *142*, 16887. 5) Y. Chen, et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 7796. 6) Y. Zhu, et al. *Acc. Chem. Res.* **2023**, *56*, 363.

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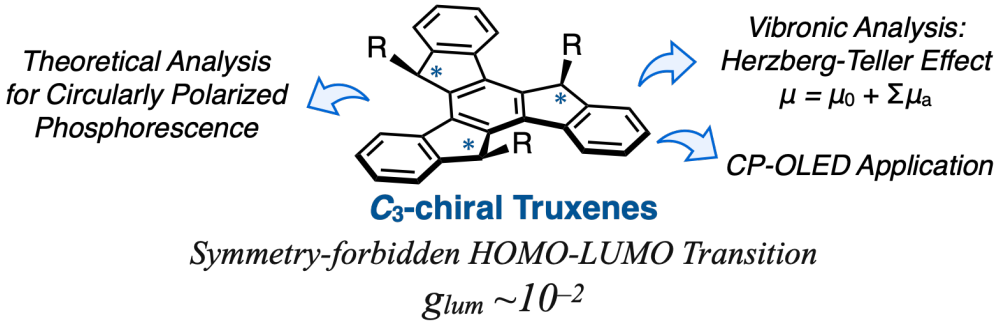
Vibronic Analysis and Design Strategy for Circularly Polarized Luminescent Molecules with Large Dissymmetry Factors

([1]*Graduate School of Engineering, Osaka University,* [2]*JST-PRESTO*)
○Fumitaka Ishiwari[1,2]

Keywords: *Circularly Polarized Luminescence, Truxene, Vibronic Analysis, Herzberg–Teller Effect*

Recently, significant effort has been devoted to creating new molecules that show circularly polarized luminescence (CPL) and can be applicable to devices from both experimental and theoretical approaches. The g_{lum} value is approximately represented by $g_{lum} \propto (|\boldsymbol{m}|/|\boldsymbol{\mu}|)\cdot\cos\theta$, where θ is the angle between electric transition dipole moment $\boldsymbol{\mu}$ and magnetic transition dipole moment $\boldsymbol{m}$. Lanthanide complexes are representative examples that exhibit large g_{lum} values due to their small $|\boldsymbol{\mu}|$ values arising from the *symmetry-forbidden* nature of *f-f* transitions. Here we show a new design strategy to achieve a large g_{lum} for based on the *symmetry-forbidden* transition of π-conjugated molecules. This approach was successfully demonstrated by the fact that trivial *syn*-5,10,15-trisubstituted truxenes[1] exhibit excellent CPL of the order of 10^{-2}. We showed that the molecular vibration dramatically lowers the CPL property through Herzberg-Teller vibronic analysis[2] and variable-temperature CPL measurement. Furthermore, at low temperatures, *syn*-5,10,15-trimethyltruxene exhibits long-lifetime and strong phosphorescent CPL, which can be analyzed by calculating transition dipole moments using molecular orbitals in the triplet excited state. Finally, a conformationally rigid double-decker-type truxene with robust CPL properties at high temperatures was applied as an emitter of electroluminescence device exhibiting circularly polarized electroluminescence with high *g* value. This study provides not only a new design strategy to achieve high *g* values, but also insights into the gap between experimental and theoretical CPL properties, as well as phosphorescent CPL property of molecules.



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量子化学計算を用いた無輻射失活過程の解析：光電子移動触媒を用いたラジカル反応への応用

（北大 WPI-ICReDD[1]・JST-ERATO[2]）○原渕 祐[1,2]

Analysis of non-radiative decay pathways using quantum chemical calculations: Application to photoredox-catalyzed radical reaction ([1]WPI-ICReDD, Hokkaido Univ., [2]JST-ERATO)

○Yu Harabuchi[1,2]

The Photoresponse of molecules is understood by four processes, i.e. internal conversion, intersystem crossing, fluorescence, and phosphorescence. In the mechanistic analysis of photoreactions based on quantum chemical calculations, it is important to obtain the conical intersection (CI) and seam of crossing (SX) regions because non-radiative decays efficiently occur via these regions. We proposed systematic search methods for CI and SX geometries and analyzed various types of photofunctional molecules. Explorations of non-radiative decay paths were effective in the mechanistic analyses of molecular fluorescence, ultrafast decay processes of molecules, and photoreactions of metal complexes where both singlet and triplet states contribute. Recently, we investigated the mechanism of Knowles's light-promoted catalytic intramolecular hydroamination using systematic reaction path exploration. The obtained reaction path network includes reaction paths via transition states and non-radiative decay paths through SXs between different electronic states. It was shown that the bond formation/cleavage competes with single electron transfer (SET) between the catalyst and substrate. The energetically favorable SET path was determined by introducing a practical computational model representing SET as non-adiabatic transitions via SXs between the substrate's potential energy surfaces for different charge states adjusted based on the catalyst's redox potential. Calculations showed that the reduction and proton shuttle process proceeded concertedly. Also, the relative importance of SET paths varies depending on the catalyst's redox potential, affecting the yield.

Keywords : Quantum chemical calculations; Reaction path network; Reaction path search; Conical intersection; Seam of crossing

光反応では、励起した分子は、内部転換過程、項間交差過程、蛍光過程、りん光過程により基底状態へと失活する。一般に内部転換及び項間交差過程はポテンシャル交差（円錐交差および交差シーム）領域を通じて効率的に起こるため、光反応の理論解析では、ポテンシャル交差構造を求めることが重要である（**図 1**）。しかし、これらの構造は基底状態の分子の安定構造とは異なる場合が多く、その推定は容易ではない。これに対して、我々は、時間依存密度汎関数理論と反応経路探索法に基づきポテンシャル交差構造を網羅的に探索する

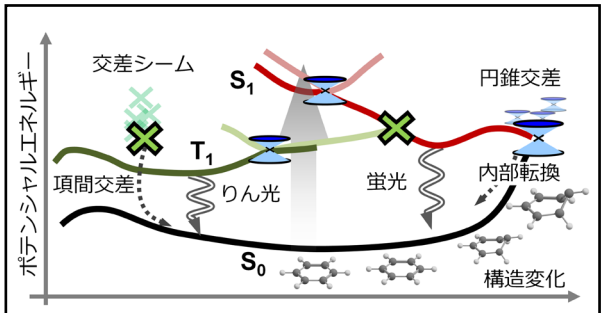

図 1. 光反応における失活経路の概念図

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手法を開発してきた[1-5]。

我々は、上述のポテンシャル交差探索に基づく無輻射失活経路の解析により、多様な分子の光応答機構を解析できることを示してきた。多環芳香族炭化水素の蛍光量子収率に関する研究では、内部転換経路の反応障壁に基づき蛍光量子収率の大小を定性的に説明できることを示した[6-8]。また、大環状芳香族分子の蛍光に関する研究を通じて、実際に分子設計が進められるような大きさの分子に対してもこの議論が適用できることを示した[5]。最近では、熱活性遅延蛍光で重要となる逆項間交差過程の速度定数が交差シーム構造計算に基づき高精度に予測できることを明らかにし、この速度定数予測が分子設計にも利用可能であることを示した[9]。さらに複数の応用計算を通じて、分子の超高速過程や金属錯体における一重項・三重項状態が複雑に関与する過程の機構解析にも同手法が応用可能であることを示した[10-12]。最近では、Knowles らによって報告されたイリジウム光電子移動触媒を用いたヒドロアミノ化反応[13]に対して、無輻射失活経路探索に基づく解析を適用した（**図 2**）。基質の一重項基底状態および二重項基底状態の電子エネルギーを触媒の酸化還元電位に基づき補正することで、触媒—基質間の電子授受と基質の反応過程を簡便に記述する方法を開発し、光電子移動触媒を用いた触媒反応サイクルの全貌を明らかにした[14]。講演では、無輻射失活経路探索の開発と応用に加え、キラルな化合物への応用に向けた取り組みについて紹介する。

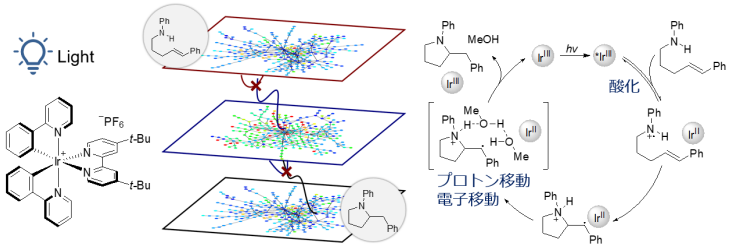

図 2. 光電子移動触媒を用いた触媒反応サイクルの機構解析

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Symposium | Special Program：Functional Systems and Utilization Using Particle and Molecular Aggregation, Dispersion, andAssembly

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1423(1423, Bldg. 14 [2F])

[A1423-4am] Functional Systems and Utilization Using Particle and Molecular Aggregation, Dispersion, andAssembly

Chair, Symposium organizer: Shinich Takeda, Tetsu Yonezawa

このシンポジウムでは、４つの講演を予定し、それぞれが異なる視点から粒子と分子の集合による革新的なシステムの開発と利用について紹介する。ナノ粒子と機能分子の集合を用いた光機能や光誘起電荷分離分子集合体を活用した光電変換素子の開発などの学術的基本研究成果について議論したのち、テーマをシフトして、分子集合が導触感がヒトそっくりの人工皮膚に与える影響について、さらに感性価値を高めるO/W 乳化の進化についての最新の研究成果を共有します。最後に、企業の観点から、化粧品にかかわる粒子分散・凝集系と機能構築を紹介する。本シンポジウムを通じて、粒子と分子の凝集・分散・集合が科学と産業の両面でどのように利用され、新たな機能性システムの可能性を広げているかについて議論したい。

9:00 AM - 9:05 AM JST | 12:00 AM - 12:05 AM UTC

Opening Remarks

Japanese
9:05 AM - 9:40 AM JST | 12:05 AM - 12:40 AM UTC
[A1423-4am-01]

Assembling and aggregation of plasmonic nanoparticles towards efficient use of photoenergy

○Tsuyoshi AKIYAMA[1] (1. The University of Shiga Prefecture)

Japanese
9:40 AM - 10:20 AM JST | 12:40 AM - 1:20 AM UTC
[A1423-4am-02]

Emulsification and dispersion in cosmetics and skin cleaning

○Yoshimune Nonomura[1] (1. Yamagata University)

Japanese
10:20 AM - 11:00 AM JST | 1:20 AM - 2:00 AM UTC
[A1423-4am-03]

Physicochemical property of emulsions stabilized with interfacial membrane generated through vesicle/disc structural transition

○Kei Watanabe[1] (1. Mukogawa Women's University)

Japanese
11:00 AM - 11:35 AM JST | 2:00 AM - 2:35 AM UTC
[A1423-4am-04]

Preparation of cosmetic emulsions and their evaluation

○Sadanori Ban

11:35 AM - 11:40 AM JST | 2:35 AM - 2:40 AM UTC

Closing Remarks

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光の高効率利用をめざしたプラズモニックナノ粒子の組織化・集合化

（滋賀県大工）○秋山 毅
Assembling and aggregation of plasmonic nanoparticles towards efficient use of photoenergy
(*School of Engineering, The University of Shiga Prefecture*) ○Tsuyoshi Akiyama

Plasmonic gold and silver nanoparticles absorb light due to their plasmon resonance. When such nanoparticles absorb light, localized enhanced electric fields are generated around the nanoparticles within nano-space. These electric fields can excite photoactive molecules and substances same as light, which can be used as nano light source. Further strong electric fields are generated between micro gap between nanoparticles, whose estimated maximum intensity achieve few tens of thousands of times comparing to irradiated light power. Hence, the control of distance and arrangement of plasmonic nanoparticles is important issue.

Our research group has developed and fabricated assemblies consisting of plasmonic gold and silver nanoparticles as dispersed particles on flat substrates, two-dimensional ultra-thin film assemblies of nanoparticles, and three-dimensional nanostructures consisting of fused nanoparticles. The preparation principal of these nanoparticle assemblies, and practical fabrication protocols will be summarized and introduced in the presentation.
Keywords : Plasmonic Nanoparticles; Gold Nanoparticles; Liquid-liquid Interfacial Precipitation; Salting Out; Electrostatic Adsorption

金や銀のナノ粒子は、そのプラズモン共鳴にもとづいて可視光を吸収する。この時、ナノ粒子の表面直近のナノ空間には、局所的に増強された電場が生じる。この電場は、光と同様に分子や物質を励起することが可能であり、実質的なナノ光源として扱うことができる。また、ナノ粒子間のギャップにはより強い電場が生じ、その強度は照射光量に対して最大数万倍に達する。従って、これらの増強電場の応用の際には、ナノ粒子間の距離や配置の制御は重要である。

我々の研究グループでは、既報に基づいてクエン酸イオンで保護された金・銀ナノ粒子を合成し、各種のプラズモニック材料の素構造として用いてきた [1, 2]。具体的には、これらのナノ粒子を微粒子の分散・凝集状態の制御の概念に基づいて、孤立分散・二次元凝集薄膜・三次元融合体の状態で基板表面に担持し、蛍光・ラマン散乱の増強や光電変換の高効率化などに適用してきた [3-5]。本発表では、これらのナノ粒子の組織化・集合化の原理と具体的な作製法について概説し、あわせて応用の事例をいくつか紹介したい。

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化粧品･皮膚洗浄における乳化と分散

（山形大院理工）○野々村 美宗
Emulsification and dispersion in cosmetics and skin cleaning (*Graduate School of Science and Engineering, Yamagata University*) ○Yoshimune Nonomura

An important science for developing cosmetics is interfacial chemistry, in addition to dermatology and hair science because cosmetics contain water, oil, and powder, that are inherently immiscible. Therefore, emulsions and dispersions have long been studied as a core technology for cosmetics and skin cleansers. As a result, not only preparation technologies for long-term stable emulsions and dispersions, but also formulations such as nanoemulsions, bi-continuous emulsions, and Pickering emulsions have been developed and applied. This presentation will review a bird's-eye view of the history of these emulsions and dispersions in the field of cosmetics and body cleansers, and will also introduce raw materials of plant origin that have recently attracted attention.
Keywords : Emulsion; Dispersion; Cosmetic; Body cleanser

一般には、「画期的な化粧品やヒット商品の基盤となるサイエンス」、と聞いてすぐに思いつくのは、細胞を対象とした実験を行って植物エキスなどから有効成分を探索したり、臨床の観点から皮膚のバリア機能を高めたりアンチエイジングの手法を提案する皮膚科学や毛髪科学なのではなかろうか。確かに、これらの研究によって、1990年代以後、さまざまな機能性化粧品のカテゴリーが生まれ、世界中のひとびとの皮膚や毛髪を健康かつ美くしくするための貢献がなされてきた。

一方で、もう一つ忘れてはならない重要な化粧品の基盤として界面化学が挙げられる。化粧品や皮膚洗浄料は目的とするスキンケア・メイクアップ・クレンジング効果を実現するとともに、塗り心地や香りが心地よいことも求められることから、水・油・粉体という本来は混じり合わない材料を配合し、実感できるレベルの効果効能が現れるような高いレベルの処方に仕上げることが求められる。そのため、水の中に液滴や固体粒子を分散したエマルションやディスパージョンはヒトの皮膚や毛髪を健康かつ美しくする化粧品や汚れを落として清潔にする皮膚洗浄料を開発するためのカギとなるコアテクノロジーとされ、長年にわたって研究がなされてきた。その結果、1970年代以後、長期間安定なエマルションやディスパパージョンの調製技術だけでなく、細かい液滴が分散したナノエマルション、水相と油相の両方が連続相を形成したバイコンティニュアスエマルション、いわゆる界面活性剤の代わりに粘土鉱物や固体粒子を利用してエマルションを安定化する粘土鉱物乳化やピッカリングエマルションなど、実に数多くの製剤が開発され、最新の化粧品や身体洗浄料に応用展開されてきたのだ。本講演では、これらの化粧品・身体洗浄料分野におけるエマルション・ディスパージョンの歴史を俯瞰的に振り返るとともに、最近注目されている植物由来の原材料などについて紹介する。

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ベシクル/ディスク構造転移により生成した界面吸着層で安定化された乳化物の物性

（武庫川女子大・薬）〇渡辺啓

Physicochemical property of emulsions stabilized with interfacial membrane generated through vesicle/disc structural transition (*School of Pharmacy and Pharmaceutical Science, Mukogawa Women's University*) 〇Kei Watanabe

Emulsions are non-equilibrium. For this reason, the products vary depending on the preparation process, and their state changes with time. Furthermore, it is known empirically that emulsification properties (preparation and stability) vary with the type of oils. In this study, emulsions with a lamellar liquid crystal phase as the adsorption layer at the emulsion interface were investigated. The properties of O/W emulsions formed with water and oil phases, which are the excess solvent phase separated from the lamellar liquid crystal phase were studied based on the phase equilibria of a ternary system.

Keywords : Emulsion, Lamellar liquid crystalline phase, Vesicle, High internal phase emulsion, Electron microscopy

乳化物は熱力学的に非平衡系であるため、時間とともに状態が変化する。また、乳化剤や油相の組成などによって生成物の物性や安定性が異なる。このように乳化研究では制御すべき変数が多いため、産業応用では経験則に負うところが大きかった。本研究ではポリエーテル変性シリコーン（PEMS）によるベシクル水分散液を油とともに強撹拌することでラメラ液晶を界面吸着層として有する乳化物が生成することを見出し、調製と安定性の観点から評価を行った[1]。まず、同一組成の乳化物を調製する際（Fig. 1）に、本法ではベシクルを経由しない場合と比較して合一に対する安定性が高いことを見出した。これはベシクルが油と衝突することで均一な界面膜を形成し安定性に有利な状態となるためと考えられた。次に、油としてジメチルシロキサン（6cs）、トリイソオクタン酸グリセリル（TIOG）および両者の混合物を用いた場合、混合物の場合に合一に不安定になり、乳化安定化が難しいとされる TIOG 単独の場合も混合物よりも安定性は良好であった。この結果は PEMS と油との相溶性に帰結できる。さらには合一に強い性質を活かし、高内相比乳化物調製を試みたところ、TIOG を用いた場合に 86vol%もの内相比を有する乳化物が調製された。当日は、電子顕微鏡観察のデータを含めた考察も紹介する。

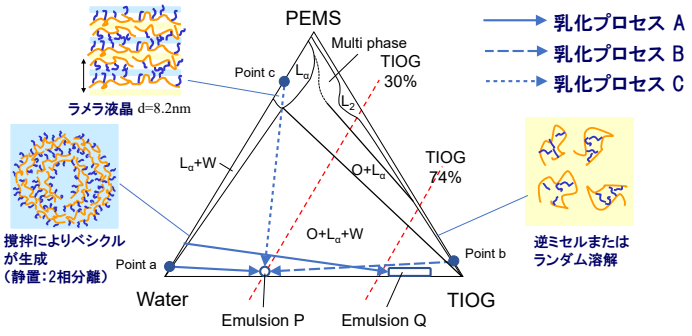

Fig. 1 PEMS 系相平衡図における乳化物調製プロセス

1) K. Watanabe et al., *J. Oleo. Sci.*. **2023**, *72*, 693-708.

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化粧品エマルションの調製とその評価

○坂 貞徳

Preparation of cosmetic emulsions and their evaluation

Sadanori Ban

Most cosmetics are dispersed colloids, which are thermodynamically unstable systems. Among cosmetics, skin care cosmetics include emulsions composed of water and oil, and the composition of water and oil changes according to the skin care application. Depending on the composition of water and oil, the viscosity, a physical property of cosmetics, can range from high to low. On the other hand, emulsions are prepared by either the dispersion method or the condensation method, and in the cosmetics field, the latter is used due to the manufacturing process. In this presentation, we will explain the preparation method of emulsions used in cosmetics and report on the evaluation method of the stability of cosmetic emulsions. In particular, the evaluation methods for each cosmetic material type from the prototype to the product level, such as particle system measurement, zeta potential measurement, thermal measurement, X-ray diffraction, and electron microscopic observation, will be explained with actual examples.

Keywords：Cosmetic, emulsion, Stability, dispersion

化粧品の多くは分散コロイドであり、熱力学的には不安定な系である。化粧品の中でもスキンケア化粧品では水と油を成分としたエマルションがあり、スキンケアの用途に合わせて水と油の組成が変わり、化粧品の物性である粘性は高いものから低いのものまで幅広く使われる。一方、エマルションの調製は分散法と凝縮法があり、化粧品分野では製造プロセスから後者の凝縮法が使われる。本公演では化粧品に使われるエマルションの調製法を解説し、化粧品エマルションの安定性の評価方法について報告する。特に、化粧品のプロトタイプから製品レベルまで、粒子系測定、ゼータ電位測定、熱測定、X線回折、電子顕微鏡観察など、それぞれの化粧品材型に対する評価法を実例をあげて解説する。

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Symposium | Special Program：Informatics and AI in Chemistry

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1423(1423, Bldg. 14 [2F])

[A1423-4pm] Informatics and AI in Chemistry

Chair, Symposium organizer: Kazue Kurihara, Kei Terayama, Mitsuru Ohno, Nobuharu Iwasawa, Norie Momiyama, Seijiro Matsubara

現在，高度に発達した情報学手法が既存のビッグデータである化合物情報を全て利用できることを可能にしつつあり，実験・理論に加えて情報学という３つの視点で駆動するこれまでにない手法が化学を変えつつある。これまでの手法では開発できなかった物質を，考えられないような短期間で，しかも自動的に得ることが現実に起きている。それらの結果と化学産業のプロセスの制御・保全にまで結び付ける試みも進められつつある。この新しい手法の革新性は，化学の研究力、化学産業の生産力に大きな変革をもたらすものと期待される。このような中で，これからの化学の担い手である若い研究者・学生に向けて，我が国の情報化学を利用する化学の現状と今後の展望をこの分野を先導する研究者から紹介していただく。

1:00 PM - 1:05 PM JST | 4:00 AM - 4:05 AM UTC

Opening Remarks

Japanese

1:05 PM - 1:30 PM JST | 4:05 AM - 4:30 AM UTC

[A1423-4pm-01]

History and prospects of data-driven chemistry

○Kimito Funatsu[1] (1. Nara Institute of Science and Technology)

Japanese

1:30 PM - 1:55 PM JST | 4:30 AM - 4:55 AM UTC

[A1423-4pm-02]

Opportunities and Challenges in Data-Driven Materials Research: Overcoming the Barrier of Limited Data

○Ryo Yoshida[1] (1. The Institute of Statistical Mathematics)

English

1:55 PM - 2:20 PM JST | 4:55 AM - 5:20 AM UTC

[A1423-4pm-03]

Materials Integration for inverse materials/process design from desired performance

○Masahiko Demura[1] (1. National Institute for Materials Science)

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

Break

Japanese

2:30 PM - 2:45 PM JST | 5:30 AM - 5:45 AM UTC

[A1423-4pm-04]

Government initiatives based on Materials Innovation Strategy

○Hiroko Takuma[1] (1. Ministry of Education, Culture, Sports, Science and Technology)

Japanese

2:45 PM - 3:05 PM JST | 5:45 AM - 6:05 AM UTC

[A1423-4pm-05]

Integration of automated robotic experiments and artificial intelligence accelerates discovery of novel materials for advanced rechargeable batteries

○Shoichi Matsuda[1] (1. National Institute for Materials Science)

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Japanese
3:05 PM - 3:20 PM JST | 6:05 AM - 6:20 AM UTC
[A1423-4pm-06]
Utilization of Batch-Type Automated Reactor and Construction of Chemical Reaction Space
○Norie MOMIYAMA[1] (1. Institute for Molecular Science · SOKENDAI)

Japanese
3:20 PM - 3:35 PM JST | 6:20 AM - 6:35 AM UTC
[A1423-4pm-07]
Function-oriented design and control of the amino acid sequence of filamentous virus through machine learning
○Toshiki Sawada[1] (1. Tokyo Institute of Technology)

3:35 PM - 3:40 PM JST | 6:35 AM - 6:40 AM UTC
Closing Remarks

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データ駆動化学の歴史と展望

（奈良先端大院・データ駆動型サイエンス創造センター）船津公人
History and Prospects of Data-Driven Chemistry (Data Science Center, Institute of Science and Technology) Kimito Funatsu

In 1965, the DENDRAL project was started at Stanford University[1]. It was the world's first challenging project in chemistry by Edward A. Feigenbaum, Bruce Buchanan, Joshua Lederberg, and Carl Djerassi, to analyse data obtained from mass spectrometry and use knowledge of organic chemistry to determine the structure of organic compounds of unknown structure. It was the first challenging project of its kind in the world for chemistry. As software, DENDRAL is considered the world's first expert system and artificial intelligence, as it automates the decision-making and problem-solving process as a chemist would do. Sixty years have passed since then and the state of the world of data-driven chemistry has changed dramatically, and there is no longer any turning back of the trend and awareness of the need for it. This lecture provides an overview of the history of data-driven chemistry at home and abroad, as well as a full overview of the current targets of data-driven chemistry initiatives, with a focus on what issues have been addressed in the history of the field. It will also touch on what data-driven chemistry aims to achieve in the future and consider what chemical researchers should consider while developing data-driven chemistry.
Keywords: Data-driven chemistry, Chemoinfomatics, Materials Informatics, Process Informatics, Research transformation cycle.

1965 年、スタンフォード大学で DENDRAL プロジェクトがスタートした [1]。質量分析装置から得られるデータを分析し，有機化学の知識も使って構造未知の有機化合物の構造を決定することを目的に、Edward A. Feigenbaum, Bruce Buchanan, Joshua Lederberg, Carl Djerassi による化学を対象とした世界初の挑戦的プロジェクトであった。ソフトウェアとしての DENDRAL は、化学者が行うような判断と問題解決の過程を自動化したものであるため、世界初のエキスパートシステム、人工知能と言われている。それから６０年が経過しデータ駆動化学の世界の在り様は大きく変貌し、もはやその流れと必要性の意識が後戻りすることはない。国内外のデータ駆動化学の歴史を概観すると同時に、その歴史の中で何が課題として取り組まれたのかにフォーカスしながら、現在のデータ駆動化学の取り組み対象の全貌を概観する。また、今後データ駆動化学が目指す事柄にも触れつつ、化学研究者はデータ駆動化学を展開しながら何を考えるべきかを考える。

1) Lindsay, Robert K., Bruce G. Buchanan, Edward A. Feigenbaum, and Joshua Lederberg, Applications of Artificial Intelligence for Organic Chemistry: The Dendral Project. McGraw-Hill Book Company, 1980.

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データ駆動型材料研究の諸問題：限られたデータの壁を乗り越える

（情報・システム研究機構 統計数理研究所）○吉田 亮[1]

Opportunities and Challenges in Data-Driven Materials Research: Overcoming the Barrier of Limited Data ([1]*The Institute of Statistical Mathematics, Research Organization of Information and Systems*) ○Ryo Yoshida[1]

Needless to say, the most crucial resource in data-driven materials research is data. In this talk, we will present machine learning methodologies and strategy for overcoming the hurdle of limited data, and our collaborative efforts between academia and industry for co-creating common foundational database of polymer properties. One strategy to overcome the barrier of limited data resources is the integrated analysis of limited amounts of experimental data and massive data obtained from computer simulations. To achieve this, we are developing the open-source software RadonPy, which automates polymer property calculations through all-atom classical molecular dynamics simulations [2]. Currently, we have formed an industry-academia collaboration consortium (involving 5 universities and 32 companies) and are developing a comprehensive polymer property database covering the chemical space of 10^5-10^7 polymers using the supercomputer "Fugaku." In this talk, we will showcase several key applications of RadonPy, such as polymer property prediction based on Sim2Real transfer learning using the RadonPy database, polymer material automated design system consisting of automated computational experiments with RadonPy, molecular design using generative AI, and a sequential experimental planning through multi-objective Bayesian optimization.

Keywords : Machine Learning; Descriptor; Explainable AI; Database; Crystal Structures

データ駆動型材料研究における最も重要な資源はデータである．本講演では，高分子材料研究において，限られたデータ資源の壁を乗り越えるための機械学習の方法論や産学連携による共通基盤データ共創の取り組み等を紹介し，マテリアルズインフォマティクスの現状と将来展望を論じる．データ資源の壁を乗り越えるための一つの方策は，実験データとシミュレーションデータの統合解析である．我々は全原子古典分子動力学シミュレーションによる高分子物性計算を全自動化するオープンソースソフトウェア RadonPy の開発を推進している[2]．産学連携コンソーシアム（現時点で 1 国研・5 大学・32 企業に属する 189 名が参画）を形成し，スーパーコンピュータ「富岳」を用いて 10^5-10^7 ポリマーが張るケミカルスペースを網羅する高分子物性データベースを開発している．本講演では，RadonPy データベースを用いた Sim2Real 転移学習に基づく高分子物性予測，RadonPy 自動計算機実験・生成 AI・多目的ベイズ最適化から構成される高分子材料自動設計システムとその実証例などを紹介する．

[1] Aoki et al., Multitask machine learning to predict polymer-solvent miscibility using Flory-Huggins interaction parameters. Macromolecules 56, 5446–5456 (2023).
[2] Hayashi et al., RadonPy: automated physical property calculation using all-atom classical molecular dynamics simulations for polymer informatics. npj Computational Materials 8, 222 (2022).

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マテリアルズインテグレーション：欲しい性能から材料・プロセスをデザインする

（NIMS[1]）○出村 雅彦[1]

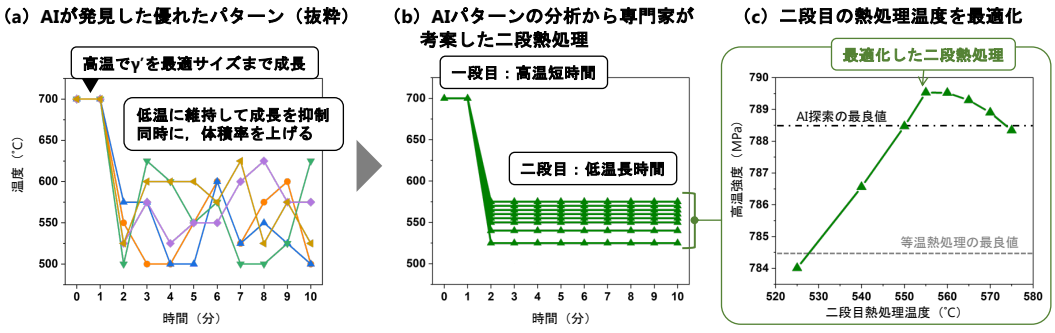
Materials Integration for inverse materials/process design from desired performance

([1]*National Institute for Materials Science*)○Masahiko Demura

Designing materials and processes from the desired performance is a typical inverse problem of materials development, which follows the reverse of the causality relation. Solving this requires a trial-and-error approach with repeated analysis of forward problems. The idea of accelerating it by utilizing computation and artificial intelligence is materials integration, and MInt is the system that implements this concept. Although the proof of concept has been demonstrated mainly for metallic structural materials, the approach and concept can be widely applied to materials in general. In this presentation, the author will introduce a case study in which a new heat treatment method was devised through collaboration between AI and experts, utilizing MInt.

Keywords : Computational Materials/Process Design; Structural Materials; Academia-Industry collaboration digital platform; Data-driven R&D

欲しい性能から材料・プロセスをデザインすることが材料開発と言えるが、これは因果律の逆を辿る典型的な逆問題である。これを解くには順問題の解析を繰り返しながら試行錯誤していくことになる。この試行錯誤を計算機と人工知能を活用して加速するという考えがマテリアルズインテグレーションであり、これを具現化したシステムが MInt である [1)]。これまで金属系構造材料を中心にコンセプト実証されてきたものの、そのアプローチや考え方は広く材料全般に展開できる。講演では MInt を活用して、AI と専門家の協業によって新しい熱処理方法を考案した事例 [2)]を紹介する。



1) マテリアルズインテグレーションの挑戦. 出村 雅彦, 鉄と鋼. **2023**, 109, 490.
2) Artificial intelligence inspired design of non-isothermal aging for γ - γ' two-phase, Ni-Al alloys. V. Nandal, S. Dieb, D.S. Bulgarevich, T. Osada, T. Koyama, S. Minamoto, M. Demura, Sci. Rep. **2023**, 13, 12660.

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日本化学会 第104春季年会 (2024)

マテリアル革新力強化戦略に基づく政府の取組について

（文科省・内閣府）宅間裕子
Government initiatives based on Materials Innovation Strategy (*Ministry of Education, Culture, Sports, Science and Technology*) Hiroko Takuma

Materials are an important fundamental technology that contributes to the realisation of Society 5.0 and the transformation to the sustainable society that balances economic development and the resolution of social issues. Innovation in this field needs to be accelerated through the use of data and AI, based on Japan's strengths.

In April 2021, the Japanese Government formulated the Materials Innovation Strategy. This presentation will introduce the Government's efforts to promote 'data-driven R&D' based on this strategy, with a focus on the Ministry of Education, Culture, Sports, Science and Technology's initiative, Materials DX Platform.

マテリアルは、Society5.0 を実現し、経済発展と社会課題解決を両立する持続可能な社会への転換に貢献する重要な基盤技術であり、我が国の強みに立脚した、データや AI の活用によるイノベーションの加速が求められています。

政府は、2021 年 4 月に「マテリアル革新力強化戦略」を策定しました。本講演では、本戦略に基づく「データ駆動型研究開発」を推進する政府の取組を文部科学省のマテリアル DX プラットフォームを中心としてご紹介する予定です。

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ロボット実験と AI の連携による蓄電池材料開発の革新

（物質・材料研究機構 [1]）○松田 翔一 [1]
Integration of automated robotic experiments and artificial intelligence accelerates discovery of novel materials for advanced rechargeable batteries ([1]*National Institute for Materials Science*) ○Shoichi Matsuda,[1]

The electrolyte material is an important factor that determines the performance of storage batteries, but there are a huge number of combinations of liquid compositions, and the search space for materials is extremely wide. Recent advances in automated experiment technology and artificial intelligence (AI) technology are establishing methodologies to efficiently discover electrolyte compositions that maximize battery performance from such a vast material space. In this lecture, we will provide an overview of the electrolyte search method using automated experiment technology and provide an overview of its future prospects.
Keywords : rechargeable batteries, electrolyte, automated experiments

電解液材料は、蓄電池の性能を決める重要な因子であるが、液組成の組み合わせは膨大であり、材料の探索空間が非常に広大である。近年の自動実験技術と人工知能（AI）技術の進展により、このような広大な材料空間から、電池性能を最大化する電解液組成を効率的に発見するための方法論が確立されつつある。本講演では、自動実験技術を活用した電解液探索手法の概要と今後の展望について紹介する。

筆者らの研究グループでは、バイオ分野で確立された液体ハンドリング技術、プレート搬送技術を積極的に採用することで、蓄電池用電解液探索用の自動実験ロボットを開発してきた(ref.1)。具体的には、96 ウェルタイプのマイクロプレートの各ウェル内部に電極・電解液を配置した微小電気化学セル（マイクロプレート型電気化学セル）を独自に開発し(図 1a)、NIMS 電気化学自動実験ロボット（NAREE）を構築した(図 1b)。非接触分注装置、ロボットアーム、電気化学測定ユニットが連動的に制御され、電解液の調合・電池特性評価を連続的に実施することができ、測定スループット 1000 sample/day での自動実験が可能となる(ref.1)。

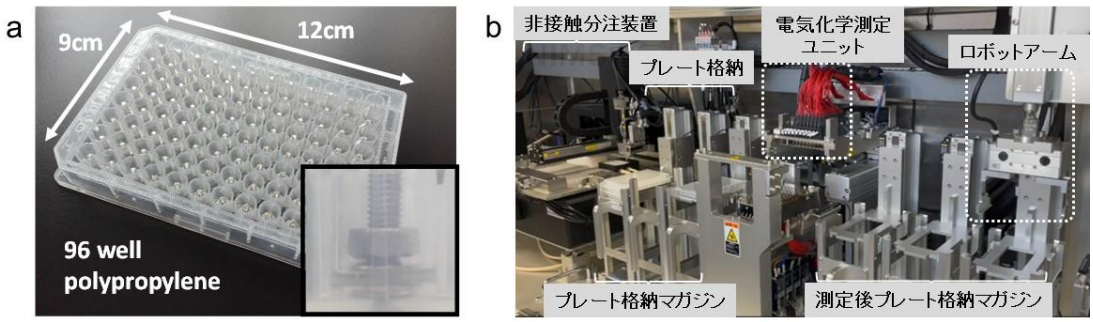

図 11：(a) マイクロプレート型電気化学セル、(b)NIMS 電気化学自動実験ロボット（NAREE）

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ロボット実験の高い能力をより有効に活用するためには、材料探索 AI とロボット実験の有機的な連携が必要となる。従来、実験データの解析から材料設計指針を抽出し、次に検討すべき材料を提案する材料探索 AI が数多く開発されてきた（ref.9-11）。一方で、このような材料探索 AI の開発は、ロボット実験装置の開発とは独立に行われてきた。そのため、実験研究者の視点からは、材料探索 AI をロボット実験装置に直接組み込むことは、技術的なハードルが高く、両者が有機的に連携した自律自動実験の実施例は非常に限られていた。上記課題認識のもと、筆者らの研究グループでは、材料探索 AI とロボット実験をシームレスに連携させる汎用的ミドルウェアとして、NIMS-OS（NIMS Orchestration System）を開発した(ref.2)。NIMS-OS では、ロボット実験装置、材料探索 AI をそれぞれモジュールとして扱うことで、様々な種類の材料探索 AI を容易にロボット実験装置に実装することが可能となっている(図 2)。特に、ベイズ最適化手法(PHYSBO)を含め、複数の材料探索 AI が標準的に搭載されており、実験研究者においても簡便に材料探索 AI を利用することができる。実際に、NIMS-OS によって制御された電気化学自動実験ロボットにおいて、材料探索 AI としてベイズ最適化を用い、電解液探索の自律自動実験を実施した。実験は、並列実験数を 32 に設定し、ランダム実験を 1 回、ベイズ最適化とロボット実験の連携を 11 サイクル実施することで、合計 384 個について電解液の調整・電池評価を実施した。その結果、ベイズ最適化の 6 サイクル目において、最も高い電池性能を示す添加剤の組合せを発見することに成功した。重要なことに、一連のロボット実験において、途中溶液を補充する操作を 1 回行った以外に、人間の介入は一切ない。本結果は、電解液材料探索の自律自動実験における NIMS-OS の有効性を示すものである。

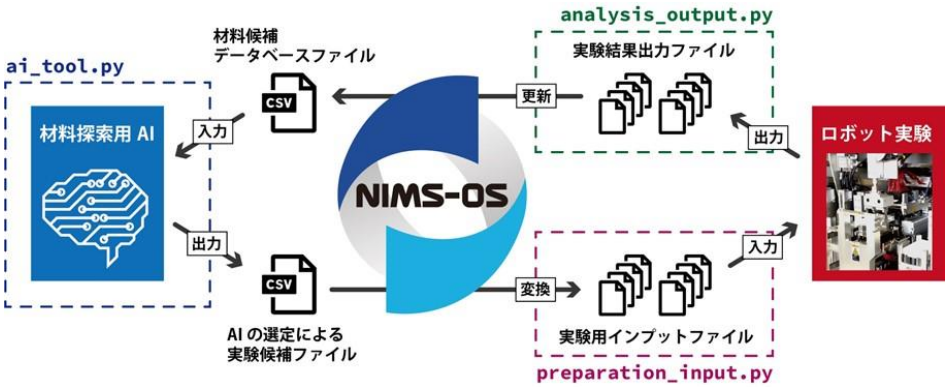

図 2：材料探索 A とロボット実験の連携を可能とする NIMS-OS（NIMS Orchestration System）

1) S. Matsuda et al. Scientific Reports, 9, 6211 (2019)
2) R. Tamura, S. Matsuda et al. STAM method, 3, 2232297 (2023)

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日本化学会 第104春季年会 (2024)

バッチ型自動反応実験装置の活用と化学反応空間の構築

（分子研・総研大[1]）○椴山 儀恵[1]

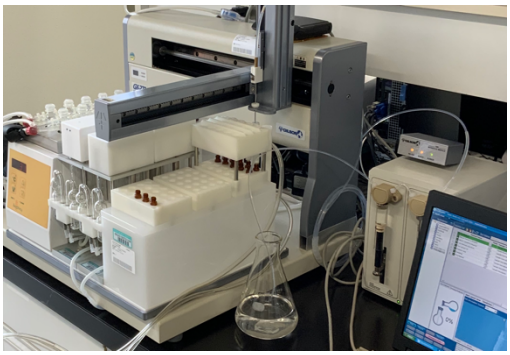
Utilization of Batch-type Automated Reactor System and Construction of Chemical Reaction Space ([1]*Institute for Molecular Science·SOKENDAI (The Graduate University for Advanced Studies)*○Norie Momiyama[1]

The development of reactions is fundamentally important to produce valuable functional molecules in the field of organic synthesis. In the course of conventional research process, exploring chemical reaction is essential, enabling a variety of molecular transformations in organic synthesis. Over the past 25 years, digital technology has been dramatically advanced, playing a crucial role in organic synthesis. However, the approach in organic synthesis has not significantly changed over the past 25 years. Since 2020, we have examined the development of chemical reactions utilizing automated reactor system and the construction of chemical reaction space by machine-learning. In this presentatiom, we introduce our recent success in synthesizing small-molecule drug analogs, providig an overview of our new approach to the development of chemical reactions.

Keywords : Automated Synthesis; AI; Machine-Learning; Organic Synthesis; Physicochemical Parameters

有機合成反応の開発は、機能性分子の精密合成を達成するうえで重要な鍵となる。文献情報と研究データをもとに分子設計の戦略が立てられ、試行錯誤しながら標的分子の合成が進められる。一連の研究プロセスにおいて、化学反応の探索は必要不可欠な研究工程であり、各組織で培われてきた技術・経験・知見に基づいて、多彩な有機化学反応が創り出されてきた。一方、この 25 年余りの間、デジタル技術が著しく進歩し、有機合成を支える存在になっている。分子に固有の物性データから化学反応の実験・計算データに至るまで、有機合成化学者が入手できる情報も増え続けている。しかし、有機合成化学者による合成反応の開発手法は、この 25 年余りの間、大きく変わっていない。有機合成の近未来に向け、有機合成化学者とデジタル技術との協調が強く望まれる。

当グループでは、2020 年頃より、有機合成反応の開発における新しい試みとして、バッチ型自動反応装置を活用した反応実験データの収集と機械学習を活用した化学反応空間の構築を推進している。本講演では、この新たなアプローチについて概説しながら、低分子医薬品の類縁体合成に関する私たちの最近の成果[1)]を紹介する。



1) Manuscript is under preparation for submission.

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機械学習による繊維状ウイルスの合目的的な配列制御に基づく機能物性創出

（東工大物質理工）○澤田敏樹
Function-Oriented Control of the Amino Acid Sequence for Filamentous Virus through Machine Learning (*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Toshiki Sawada

M13 phage, a filamentous virus, is composed of its genetic DNA and plural proteins. M13 phages are well-known to be self-assembled into regular structures in a liquid crystalline fashion and are genetically modified to introduce various functions. We have found that M13 phages are utilized as material components with various functions such as hydrogels and films. In this study, we constructed a phage library displaying dipeptides by genetic engineering and their functional properties are measured. The data was used as train data for machine learning to construct a prediction model of the genetically engineered M13 phage. As a result, we found that amino acid sequences of phage proteins to express desired material functions can be predicted by machine learning.
Keywords : Filamentous Virus; M13 bacteriophage; Genetic Engineering; Machine Learning; Thermal Diffusivity

繊維状ウイルスの一種である M13 ファージは（Figure 1）、遺伝子改変により自在に機能化でき、また液晶配向するほど規則的に集合化する。近年では、それらを利用してファージそのものを素材として様々なソフトマテリアルを構築する研究も展開されている。ファージがもつ構造（特にアミノ酸配列）を、機能や物性に対してを合目的的に改変・制御する方法論を新たに確立できれば、マテリアル素材としてのファージの利用可能性を大きく拡張できるものと期待される。本研究では、ファージの新たな機能物性創出を目指し、遺伝子工学によりファージ表層のタンパク質を改変したライブラリーを構築し、それらアミノ酸の改変がファージの機能物性与える効果を明らかにするとともに、機械学習を利用してその特性を予測し、それに基づいて向上させることを目的とした。

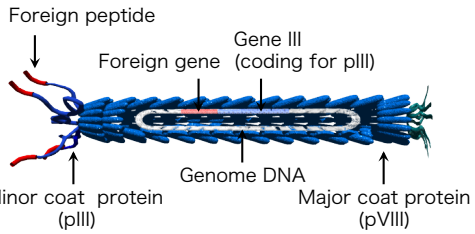

Figure 1. Schematic illustration of M13 phage

ファージの主要外殻タンパク質表層にジペプチドを提示したファージライブラリーを構築した。遺伝子改変したファージもしくはその集合体の物性や機能をそれぞれ評価した。それらの値を訓練データとし、Leave-One-Out 交差検証により適切な機械学習アルゴリズムや記述子を決定した。その結果適切なモデルを構築することができ、さらに予測の妥当性を評価した結果、遺伝子改変されたファージが示す分子機能を機械学習により予測に基づいて高機能化できることがわかり、遺伝子改変と機械学習の組み合わせにより生体高分子の機能物性を合目的的に制御できる可能性を見出した。

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Symposium | Special Program：The next generation of medical technology innovated by analytical chemistry

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1424(1424, Bldg. 14 [2F])

[A1424-4pm] The next generation of medical technology innovated by analytical chemistry

Chair, Symposium organizer: Hiroyuki Nakamura, Hiroyuki Tani, Ichiro Okura, Satoshi Ohtsuka, Yuki Okada, Yuriko Matsumura

近年、実際に医療に応用可能となる技術が多く開発され、様々な臨床現場での応用が期待されている。特に、質量分析をはじめとする機器分析は、未病における発症予測から診断に至るまで幅広く活用されており、医療分野への貢献度が高い技術である。さらにこれらの技術は、疾患の早期発見や早期診断に関する学際的研究も活発に行われており、次世代の医療技術になることが期待される。本企画では、産官学が連携した医工連携により研究を進めている講演者が集い、医療技術における機器分析の果たせる役割に焦点を当て、未病・診断で活用されている技術を紹介するとともに、最先端の研究事例について紹介する。

1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC

Opening Remarks

Japanese

1:10 PM - 1:40 PM JST | 4:10 AM - 4:40 AM UTC

[A1424-4pm-01]

Application of mass spectrometry to the elucidation of the pathogenesis of allergic diseases and their diagnosis and treatment

○Takahisa Murata[1] (1. The University of Tokyo)

Japanese

1:40 PM - 2:10 PM JST | 4:40 AM - 5:10 AM UTC

[A1424-4pm-02]

Facilitating medical research and development by global data sharing

○Makoto Suematsu[1] (1. Central Institute for Experimental Medicine and Life Science)

Japanese

2:10 PM - 2:40 PM JST | 5:10 AM - 5:40 AM UTC

[A1424-4pm-03]

Analytical measurement, automation, and AI technologies for regenerative medicine and next-generation therapeutic drug development

○Toru Ezure[1] (1. Shimadzu Corporation)

Japanese

2:40 PM - 3:10 PM JST | 5:40 AM - 6:10 AM UTC

[A1424-4pm-04]

Shimadzu Effort for Helthcare business

○Hiroki Nakajima[1] (1. Shimadzu Corporation)

Japanese

3:10 PM - 3:40 PM JST | 6:10 AM - 6:40 AM UTC

[A1424-4pm-05]

Alzheimer's disease plasma analysis by mass spectrometry

○Yoshiya Oda[1] (1. The University of Tokyo, Graduate School of Medicine)

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リピドミクスを応用したアレルギー性疾患の病態解明と診断・治療への応用

（東大院農[1]）○村田　幸久[1]

Application of mass spectrometry to the elucidation of the pathogenesis of allergic diseases and their diagnosis and treatment ([1]*Graduate School of Agriculture and Life Sciences, The University of Tokyo*) ○Takahisa Murata [1]

The number of patients suffering from allergic diseases such as food allergy, hay fever, atopic dermatitis, and asthma continues to increase every year, and one-third of the population now suffers from some form of allergic disease. However, there are still many unknowns, and no methods have yet been proposed to reduce the number of patients.

Lipid metabolites that are metabolized and produced from fatty acids extracted from cell membranes and have physiological activity are called "bioactive lipids. Although prostaglandins and leukotrienes are well-known as bioactive lipids that cause inflammatory reactions, it has become clear that there are many fatty acid metabolites in our bodies, including those whose bioactivity has not yet been clarified. By looking at the dynamics of their production in vivo, we can understand when and where biological reactions are occurring.

Our laboratory has been conducting research applying lipidomics technology to animal models and human patients to clarify (1) what allergic reactions are, (2) why changes in the living environment have increased allergic diseases, and (3) how they can be cured. We have also conducted numerous evaluations using specimens such as urine, stool, tears, and nasal discharge, which can be collected noninvasively and easily applied to actual diagnosis, and have identified various candidate disease markers.

This talk, entitled "Lipidomics Applied to the Pathophysiology of Allergic Diseases and its Application to Diagnosis and Therapy," will introduce the results obtained in the above research.

Keywords：Lipidomic, Allergy, Bioactive lipid, Mass spectrometer

食物アレルギーや花粉症、アトピー性皮膚炎、喘息などのアレルギー性疾患を患う患者さんの数は年々増加の一途をたどり、現在国民の 3 分の 1 が何らかのアレルギー性疾患にかかっているとも言われる。これらの疾患が増加した理由として生活環境の変化や、食生活の近代化からくる腸内細菌叢の乱れなどが挙げられている。しかし依然として不明な点は多く、患者数を減らす方法の提案には至っていない。

細胞膜などから切り出される脂肪酸から代謝・産生され、生理活性をもつ脂質代謝物を“生理活性脂質”と呼ぶ。生理活性脂質として、プロスタグランジンやロイコトリエンなど炎症反応を引き起こすものが有名であるが、私達の体には、生理活性が明らかにされていないものを含め、非常に多くの脂肪酸代謝物が存在することが明らかになってきた。生体内におけるこれらの産生動態を見れば、いつどこでどのような生体反応が起きているのかを把握することができる。

私達の研究室では、①アレルギー反応とはそもそも何か、②生活環境の変化がなぜアレルギー性疾患を増やしたのか、③どうしたら治すことができるのか、を明らかに

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すべく、動物モデルやヒト患者を対象としてリピドミクス技術を応用した研究を進めてきた。尿や便、涙、鼻汁などの非侵襲的に採取でき、実診断にも応用しやすい標本を用いた評価も数多く行っており、様々な疾患マーカー候補を同定している。

本講演は、「リピドミクスを応用したアレルギー性疾患の病態解明と診断・治療への応用」と題し、上記研究で得られている成果を紹介する。

1) PGD2 deficiency exacerbates food antigen-induced mast cell hyperplasia. Nakamura T, et al. Nature Communications. 6:7514 2015.
2) Production of lipid mediators across different disease stages of dextran sulfate sodium-induced colitis in mice. Hamabata T, et al. Journal of Lipid Research. 59(4):586-595.2018.
3) Urinary PGDM, a prostaglandin D2 metabolite, is a novel biomarker for objectively detecting allergic reactions of food allergy. Inagaki S,et al..J Allergy Clin Immunol. S0091-6749(18)30995-3.2018.
4) 5,6-dihydroxy-8Z,11Z,14Z,17Z-eicosatetraenoic acid accelerates the healing of colitis by inhibiting transient receptor potential vanilloid 4-mediated signaling. Kobayashi K, et al. The FASEB journal. 35(4):e21238. 2021.
5) Urinary lipid profile of atopic dermatitis in murine model and human patients. Nagata N, et al. FASEB J. 35(11):e21949. 2021.

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分析データの集積と共有による医療課題の解決：新型コロナからの教訓

Facilitating medical research and development by global data sharing

○ (公財)実中研　所長・慶大名誉教授　末松 誠
○ Central Institute for Experimental Medicine and Life Science, Professor Emeritus Makoto Suematsu

Multiple gaps among different stakeholders in medical development result in considerable delay for the achievements. One of such gaps includes never-sharing behavior of individual researches who might compete each other. To maximize benefits for patients, data sharing among many different institutions and hospitals benefits patients through accelerating medical development. Experience happening in Japan during the COVID-19 period serves as an important lesson for fighting against infection and other medical task in the near-future.

医療研究開発には異なるStakeholderの間にGapが存在し、開発速度の律速段階となる。また個々の研究者による「データの囲い込み」も大きな障害となる。医療において患者の利益を最大限に生かすためには、多数の研究者や医療機関のデータ共有が必要な場合が少なくない。新型コロナ感染症においてはウイルスゲノムの国際データベースが大いに威力を発揮したが、残念ながら日本はデータベースを介したグローバルデータシェアリングでは大きな後れを取ったと言わざるを得なかった。広域な連携・分散した統合システムにより、病原体の遺伝情報だけでなく、付随した簡単な臨床タグ情報をつけてデータベース化することによって、近未来の感染症蔓延に備えることができると考えられる。

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再生医療、次世代治療薬開発の向けた、分析計測、自動化、AI 技術の活用

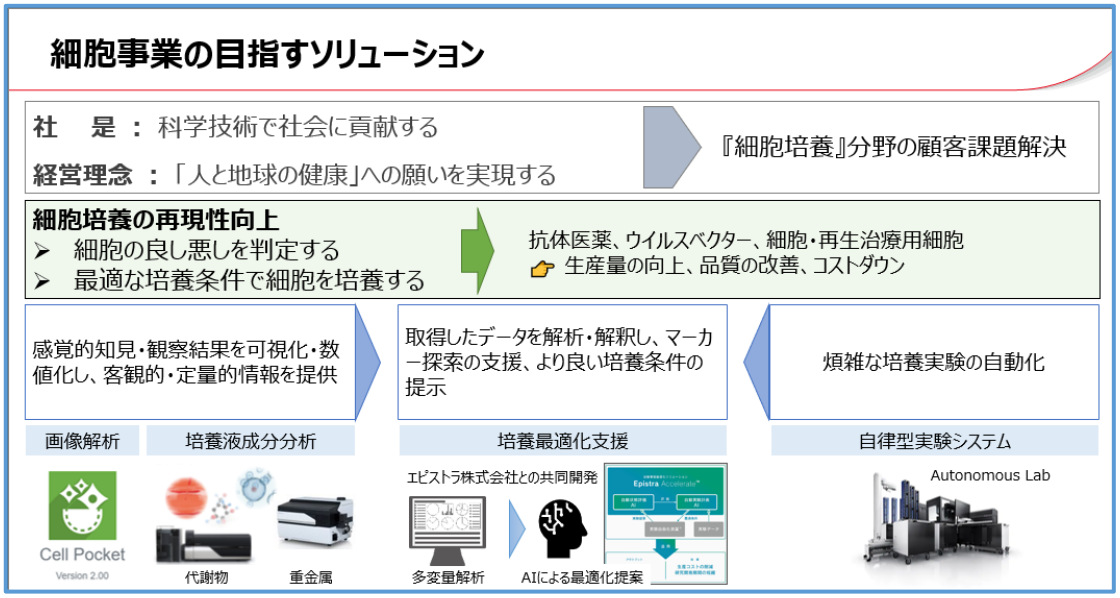
（島津製作所 分析計測事業部 ）江連　徹
Analytical measurement, automation, and AI technologies for regenerative medicine and next-generation therapeutic drug development (*Analytical & Measuring Instruments Division, Shimadzu Corporation*) ○Toru Ezure

To apply pluripotent stem cells to regenerative medicine and drug discovery applications, it is essential to establish the technology to manufacture high quality and large amount of stem cells. To realize the technology, it is important to establish a method to evaluate the quality of stem cells, and this has become a major challenge.

Therefore, we have established the methods to evaluate cell quality through cell culture media analysis and morphological observation. In this presentation, I will introduce our evaluation technology, including the latest examples of optimization and quantification of cell culture conditions using these analysis technologies and AI.
Keywords : Analytical Measurement, Automation, AI Technologies

多能性幹細胞を再生医療や創薬応用へと展開するために幹細胞を高品質かつ大量に供給する技術が必須である。この技術を実現するためには，幹細胞の品質評価方法の確立が重要であり、大きな課題にもなっている。

そこで我々は培地分析と形態観察による細胞の品質評価法の確立に取組んできた。本講演では、これら分析技術と AI を活用した培養条件の最適化や培養状態の定量化の最新事例を交え、当社の細胞品質評価技術をご紹介する。



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ヘルスケアに向けての島津製作所の取り組み

（株式会社 島津製作所）中島 宏樹
Shimadzu Effort for Healthcare Business (*Shimadzu Corporation*) Hiroki Nakajima

In the clinical business with utilizing analytical technology that we are promoting, we are focusing on three areas: clinical diagnosis, microbial testing, and cell business. Among these, in the fields of ① clinical diagnosis and ② microbial testing (clinical), we will aim to create new customer value by mainly deploying mass spectrometers as medical devices in the market.
① In clinical diagnosis, immunoassay devices are currently mainly used for clinical tests using blood and urine as a samples, but mass spectrometers have features such as simultaneous multi-component analysis and low running costs. We are leveraging group companies acquired through M&A to expand our testing reagent kits, strengthen connections between hospital networks and equipment, and promote the widespread use of mass spectrometers as a platform.
② In microbial testing (clinical), by combining our mass spectrometer with identification and susceptibility testing equipment and culture media, we can improve the speed of testing and provide one-stop solutions for the entire testing workflow.
Keywords : Healthcare; Mass Spectrometry; Clinical Laboratory Tests; Microbial Testing

当社が推進している分析技術を活用した臨床事業では、臨床診断・微生物検査・細胞事業の 3 つの領域に注力している。中でも①臨床診断及び②微生物検査（臨床）領域では、主に質量分析装置を医療機器として市場に展開し、新たな顧客提供価値の創造を目指している。

①臨床診断では、現在血液や尿を用いた臨床検査には主に免疫法装置が利用されている一方で、質量分析装置は多成分同時分析や安価なランニングコスト等の特長を有する。当社は M&A により獲得したグループ会社を活用し検査用試薬キットの拡充と院内ネットワークと装置の接続を強化し、プラットフォームとしての質量分析装置の普及を進めている。

②微生物検査（臨床）では、当社質量分析装置と菌種同定・薬剤感受性試験装置や培地を組み合わせることで、検査の迅速性向上やワンストップでのソリューション提供など、検査ワークフロー全体の価値向上を図る。



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質量分析によるアルツハイマー病血漿解析

（東大院医 [1]）○小田吉哉 [1]
Alzheimer's disease plasma analysis by mass spectrometry ([1]*Graduate School of Medicine, The University of Tokyo*) ○Yoshiya Oda,[1]

Plasma proteomics using mass spectrometry is not easy to detect low-expression proteins such as cytokines, and its quantitative accuracy is not good. Therefore, plasma proteomics using the Proximity Extension Assay, an immuno-PCR method, was performed. Mass spectrometry was used for plasma lipidomics. These two methods were performed on 282 Alzheimer's disease plasma samples. 1000 plasma proteins and approximately 700 lipids were detected. Among them, many of which are involved in vascular injury and protection, were altered. In addition, several lipid-associated proteins were significantly altered. In some cases, individual proteins altered neighboring factors, but there were also several factors that moved in the opposite direction of what would be expected. It seems that the body has a feedback mechanism to try to maintain homeostasis. For lipids, the relationship with the degree of unsaturation is of interest, and the degree of unsaturation of fatty acids has been implicated in cardiovascular risk. Some bile acids can damage the vascular endothelium. Considering the results obtained in this study together with the events already reported, slight changes in homeostatic function may be related to vascular endothelial cells, as Alzheimer's disease is a chronic disease that progresses very slowly, from the Preclinical stage to the onset.
Keywords : Alzheimer's disease; LC/MS; Proximity Extension Assay; Proteomics; Lipidomics

質量分析を使った血漿プロテオミクスはサイトカインなど発現量が少ないタンパク質を検出することは容易ではなく、定量精度も良くない。そこでイムノ PCR 法である Proximity Extension Assay による血漿プロテオミクスを実施した。血漿リピドミクスでは質量分析を用いた。この２つの方法をアルツハイマー病血漿サンプル 282 検体に対して実施した。その結果約 1000 個の血漿タンパク質と約 700 個の脂質が定量でき、有意に変化した分子の多くが血管傷害と保護に関与していた。さらに、いくつかの脂質関連タンパク質が有意に変化していた。その中の幾つかについては、個々のタンパク質が隣接する因子を変化させることもあったが、予想とは逆の方向に動く因子もいくつかあった。生体には恒常性を維持しようとするフィードバック機構があるため相反する変化が観測されたと思われる。脂質については、不飽和度との関係が興味深く、脂肪酸の不飽和度は心血管リスクに関与している。胆汁酸の中には血管内皮にダメージを与えるものもある。本研究で得られた結果とすでに報告されている事象を合わせて考えると、アルツハイマー病が前臨床段階から発症まで非常にゆっくりと進行する慢性疾患であることから、恒常性維持機能のわずかな変化が血管内皮細胞の機能低下と関係している可能性がある。

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Co-organized Symposium | Co-organized Symposium [organized by CSJ partners]：Toward Social Implementation of Mechanochemical Organic Synthesis

Thu. Mar 21, 2024 9:00 AM - 11:40 AM JST | Thu. Mar 21, 2024 12:00 AM - 2:40 AM UTC
A1421(1421, Bldg. 14 [2F])

[A1421-4am] Toward Social Implementation of Mechanochemical Organic Synthesis

メカノケミカル有機合成は、反応溶媒をほとんど使わずに、ボールミルなどの攪拌装置を用いて有機合成反応を実施する新しい技術である。メカノケミカル有機合成では、幅広い反応に対して反応溶媒が大幅に削減でき（例：１５分の一)、さらに反応時間も短縮できる（例：３００分の一）。また有機合成で扱いにくい溶解性の悪い化合物を反応させることができるなど、有機合成を大幅に進化させるポテンシャルを持っている。このメカノケミカル有機合成は、社会で活用されてこそ、その真価を発揮する。しかし、ヨーロッパを中心に事業化へ大きな興味を持たれているのに対し、日本ではまだ活用が進んでいない。本企画は、メカノケミカル有機合成の社会実装にむけた情報交換や議論を深めることを目的とする。
プログラムはこちら

9:00 AM - 11:40 AM JST | 12:00 AM - 2:40 AM UTC

[A1421-4am]

Toward Social Implementation of Mechanochemical Organic Synthesis

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Co-organized Symposium | Co-organized Symposium [organized by CSJ partners]：Science on Process of All-solid-state Lithium Ion Batteries

Thu. Mar 21, 2024 1:00 PM - 3:40 PM JST | Thu. Mar 21, 2024 4:00 AM - 6:40 AM UTC A1421(1421, Bldg. 14 [2F])

[A1421-4pm] Science on Process of All-solid-state Lithium Ion Batteries

全固体電池で実用的な性能を達成するためには、電池材料を稠密化して材料間の界面面積を拡大するとともに、この界面のイオン伝導を良好なものにする必要があります。これらの要請を両立するためには、個々の電池材料を接合するためのサイエンスの構築が不可欠です。文部科学省「材料の社会実装に向けたプロセスサイエンス構築事業(Materealize)」におけるプロジェクト「全固体電池を実現する接合プロセス技術革新」では、酸化物型全固体電池におけるプロセスサイエンスに関するシンポジウムを行います。３回目の開催となる今回のシンポジウムでは、実用材料として期待されるガーネット型電解質に関する話題を中心に、招待講演とプロジェクト成果の紹介を行います。皆様のご参加をお待ちしております。
プログラムはこちら

1:00 PM - 3:40 PM JST | 4:00 AM - 6:40 AM UTC

[A1421-4pm]

Science on Process of All-solid-state Lithium Ion Batteries

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Event | Event：The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

Thu. Mar 21, 2024 10:00 AM - 12:00 PM JST | Thu. Mar 21, 2024 1:00 AM - 3:00 AM UTC CST
MUSEUM(Technoplace 15)

[SD] The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

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[SD]

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Event | Event：The 19th Special Exhibition: Surveying is the “Physical Measurement of the National Land”

Thu. Mar 21, 2024 1:00 PM - 5:00 PM JST | Thu. Mar 21, 2024 4:00 AM - 8:00 AM UTC CST
MUSEUM(Technoplace 15)

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Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 1434(1434, Bldg. 14 [3F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

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9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

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[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

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Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 624(624, Bldg. 6 [2F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

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Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 741(741, Bldg. 7 [4F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

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Rest Area | Rest Area：Rest Area

Thu. Mar 21, 2024 9:00 AM - 3:40 PM JST | Thu. Mar 21, 2024 12:00 AM - 6:40 AM UTC 833(833, Bldg. 8 [3F])

[RA] Rest Area

9:00 AM - 3:40 PM JST | 12:00 AM - 6:40 AM UTC

[RA]

Rest Area

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Speaker Ready Room | Speaker Ready Room：Speaker Ready Room

Thu. Mar 21, 2024 8:30 AM - 1:30 PM JST | Wed. Mar 20, 2024 11:30 PM - 4:30 AM UTC 1438(1438, Bldg. 14 [3F])

[SR] Speaker Ready Room

8:30 AM - 1:30 PM JST | 11:30 PM - 4:30 AM UTC

[SR]

Speaker Ready Room

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Speaker Ready Room | Speaker Ready Room：Speaker Ready Room

Thu. Mar 21, 2024 8:30 AM - 1:30 PM JST | Wed. Mar 20, 2024 11:30 PM - 4:30 AM UTC 625(625, Bldg. 6 [2F])

[SR] Speaker Ready Room

8:30 AM - 1:30 PM JST | 11:30 PM - 4:30 AM UTC

[SR]

Speaker Ready Room

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