Wed. Mar 20, 2024

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

Wed. Mar 20, 2024 1:00 PM - 3:10 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:10 AM UTC H937(937, Bldg. 9 [3F])

[H937-3pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Masahiro Higashi, Ryohei Kishi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H937-3pm-01]

Development of an Organic Structure-Directing Agents Design Algorithm for Zeolite Utilizing Large-Scale Language Models

○Shusuke Ito[1], Koki Muraoka[1], Akira Nakayama[1] (1. The Univ. of Tokyo)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H937-3pm-02]

Theoretical study on solvatochromism in tetracyanoquinodimethane(TCNQ)

○Sumire Tobe[1], Mikako Higa[2], Hirofumi Sato[3,4], Masahiro Higashi[5] (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering and Science University of the Ryukyus, 3. Guraduate School of Engineering, Kyoto University , 4. Fukui Institute for Fundamental Chemistry, Kyoto University, 5. Guraduate School of Informatics, Nagoya University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H937-3pm-03]

Theoretical analysis of electronic structures and reaction mechanism for NH_3-SCR reaction using binuclear Cu complexes

○Ryusei Morimoto[1], Kanami Sugiyama[2], Masahiro Higashi[3], Hirofumi Sato[2,4] (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. Graduate School of Informatics, Nagoya University, 4. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H937-3pm-04]

Analysis of a Reaction Route Network of Water Gas Shift Reaction

○Akane Emura[1], Kanami Sugiyama[2], Shin-ichi Minato[3], Masahiro Higashi[4], Hirofumi Sato[2,5] (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. Graduate School of Informatics, Kyoto University, 4. Graduate School of Informatics, Nagoya University, 5. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H937-3pm-05]

Extension of Global Area Search (GLAS) method to reactions with spin-state crossing and Application to small organic molecules

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○Takechika Kikkawa[1], Syusuke Yamanaka[1], Takashi Kawakami[1], Mitsutaka Okumura[1], Mitsuo Shoji[2] (1. Osaka University, 2. University of Tsukuba)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H937-3pm-06]

Linear response analysis of electron density in polypeptides

○Ren Oike[1], Takechika Kikkawa[1], Tomohiro Maruyama[1], Takasi Kawakami[1], Shusuke Yamanaka[1], Mitsutaka Okumura[1] (1. Osaka University)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H937-3pm-07]

Development of *ab initio* divide-and-conquer method under periodic boundary condition

○Gen Ogawa[1], Masatsugu Nishida[2], Tomoko Akama[3], Masato Kobayashi[3,4], Tetsuya Taketsugu[3,4] (1. Sch. Sci., Hokkaido Univ., 2. Grad. School Chem. Sci. Eng., Hokkaido Univ., 3. WPI-ICReDD, Hokkaido Univ., 4. Fac. Sci., Hokkaido Univ.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[H937-3pm-08]

Raman intensities of conformation-dependent low-frequency modes of chalcogenoanisole: analysis by singular value decomposition

○Akira Mizushina[1], Keigo Yamaguchi[2], Yoshihiro Yamakita[2] (1. School of Informatics and Engineering, University of Electro-Communications, 2. Graduate School of Informatics and Engineering, University of Electro-Communications)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H937-3pm-09]

Theoretical study on the muonium adduct structure of N-heterocyclic carbene by path integral molecular dynamics

○Satoshi Orikono[1], Kazuaki Kuwahata[1], Tomomi Shimazaki[1], Masanori Tachikawa[1] (1. Yokohama City University)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H937-3pm-10]

Theoretical study on hydrogen-bonded structures of EGFP using first principles calculations

○Mio Takakuwa[1], Tomomi Shimazaki[1], Masanori Tachikawa[1], Yukiumi Kita[1] (1. Yokohama City University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[H937-3pm-11]

Surface hopping *ab initio* molecular dynamics simulation on nonadiabatic dissociation process of OCS^{2+} induced by photo ionization

○Ryuto Kambara[1], Takuro Tsutsumi[2], Kenji Furuya[3,4], Tetsuya Taketsugu[2,5] (1. Grad. Sch. Chem. Sci. Eng., Hokkaido Univ., 2. Fac. Sci., Hokkaido Univ., 3. Fac. Arts Sci., Kyushu Univ., 4. Dep. Mol. Mat. Sci., Kyushu Univ., 5. WPI-ICReDD, Hokkaido Univ.)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[H937-3pm-12]

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Heating Mechanism in Near-Infrared Laser-Induced Growth Reactions from Polyhydroxy Fullerenes to Carbon Nanotubes

○Mahiro Honkai[1], Manabu Kanno[2], Fuminori Misaizu[2], Hirohiko Kono[2] (1. Faculty of Science, Tohoku University, 2. Gradurate School of Science, Tohoku University)

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

Wed. Mar 20, 2024 1:00 PM - 3:00 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:00 AM UTC
A1452(1452, Bldg. 14 [5F])

[A1452-3pm] 03. Physical Chemistry -Structure-

Chair: Mitsuhiko Miyazaki, Toshiaki Ando

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1452-3pm-01]

Photoreactions of the C_2H_4-SO_2 complex in a low-temperature matrix (II): A pursuit of reaction pathways

○Fumiyuki Ito[1], Toshihiro Omokawa[2], Jun Miyazaki[2] (1. AIST, 2. TDU)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1452-3pm-02]

Observation of Ar Atom Migration in the Resorcinol-Ar_n (n = 1, 2) Clusters by MATI-IR Spectroscopy

○Yumeno HIGO[1], Mitsuhiko MIYAZAKI[1] (1. Ochanomizu University)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1452-3pm-03]

Formation and gas-phase photoelectron spectroscopy of dimers of open-shell superatom anions $[PtAu_{24}(SC_nH_{2n+1})_{18}]^-$

○Yosuke NAKASHIMA[1], Shun ITO[1], Kiichirou KOYASU[1], Tatsuya TSUKUDA[1] (1. Graduate School of Science, The University of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1452-3pm-04]

Spectral changes in the far-ultraviolet region caused by the structure of lipid bilayers

○YOSHIKI Hanjo[1], Yusuke Morisawa[1] (1. kindai university)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1452-3pm-05]

Study of electronic structure of adamantane in condensed phase by far-ultraviolet spectroscopy

○Tomoyuki Komoto[1], Yusuke Morisawa[1] (1. kinki university)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1452-3pm-06]

Relation between solution states and electronic states of water in high concentrated lithium and sodium salt aqueous electrolyte

○Yusuke Morisawa[1], Shoichi Higashi[1], Ayano Nanba[1], Ryotarou Wake[1] (1. Kindai University)

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

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[A1452-3pm-07]

Construction and evaluation of optical measurement system for excitation-emission map using Fourier transform spectroscopy

○Shintaro Yamamoto[1], Takumi Ehara[1], Shuji Kimura[1], Ami Takada[1], Tomohiro Ogawa[1], Kiyoshi Miyata[1], Ken Onda[1] (1. Kyushu University)

Japanese

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

[A1452-3pm-08]

Effect of 2′-OH Group of Sugar Moiety in Nucleotides on Intermolecular Dynamics of Their Aqueous Solutions

○Masako Shimizu[1], Hideaki Shirota[1] (1. Chiba University)

Japanese

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

[A1452-3pm-09]

Infrared spectroscopic analysis of Ca^{2+}-coordination structure of parvalbumin: Effect on Glu at the 12th position by an amino-acid replacement

○Masayuki Nara[1], Hisayuki Morii[1], Akira Sakamoto[2], Takuya Miyakawa[3], Masaru Tanokura[4] (1. Tokyo Medical and Dental University, 2. Aoyama Gakuin Univ., 3. Kyoto Univ., 4. The Univ. of Tokyo)

Japanese

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

[A1452-3pm-10]

Analysis of Conformational Change of Perfluoroalkanes by Heating Measurement

○Taisuke Araki[1], Taizo Mori[1], Takayuki Oka[1], Nobutaka Shioya[1], Takeshi Hasegawa[1] (1. Kyoto University)

Japanese

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

[A1452-3pm-11]

Free-energy analysis of the cosolvent effects on the peptide amorphous aggregation through molecular dynamics simulation

○Yudai Tagawa[1], Kento Kasahara[1], Nobuyuki Matubayasi[1] (1. Osaka University)

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

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC
A1441(1441, Bldg. 14 [4F])

[A1441-3pm] 04. Physical Chemistry -Properties-

Chair: Takashi Takeda, Tomoko Fujino

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1441-3pm-01]

Crystal Structures and Conducting Properties of Molecular Conductors Composed of an Unsymmetrical Palladium(II)-Dithiolene Complex Containing a TTF Skeleton

○Satomi Mochizuki[1], Kiyonori Takahashi[2], Takayoshi Nakamura[2], Tomohiro Agou[1], Kazuya Kubo[1] (1. Graduate School of Science, University of Hyogo, 2. Research Institute for Electronic Science, Hokkaido University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1441-3pm-02]

Theoretical studies on electronic and spin properties in trinuclear Mn complex of single molecular magnets

○Takashi Kawakami[1,2], Mizuki Otsuka[2], Koichi Miyagawa[3], Yuta Suzuki[2], Shusuke Yamanaka[2], Mitsutaka Okumura[2], Takahito Nakajima[1], Kizashi Yamaguchi[2,1] (1. RIKEN, 2. Osaka Univ., 3. Univ. Tsukuba)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1441-3pm-03]

Correlations between intermolecular interactions and FET characteristics in both carriers of d/π-conjugated ambipolar semiconductors

○Masatoshi Ito[1], Tomoko Fujino[1], Toshiki Higashino[2], Mafumi Hishida[3], Hatsumi Mori[1] (1. ISSP, the Univ. of Tokyo, 2. AIST, 3. Dept. of Chemistry, Faculty of Science, TUS)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1441-3pm-04]

Electronic and steric effects of halogen substituents on spin crossover iron(III) complexes

○Mai Hirota[1], Takahiro Sakurai[2], Hitoshi Ohta[3], Kazuyuki Takahashi[1] (1. Graduate School of Science, Kobe University, 2. Research Facility Center for Science and Technology, Kobe University, 3. Molecular Photoscience Research Center, Kobe University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1441-3pm-05]

Orbital hybridization of donor and acceptor to enhance conductivity of mixed-stack complexes

○Tomoko Fujino[1], Ryohei Kameyama[1], Kota Onozuka[1], Kazuki Matsuo[1], Shun Dekura[1], Tatsuya Miyamoto[1], Zijing Guo[1], Hiroshi Okamoto[1], Toshikazu Nakamura[2], Kazuyoshi Yoshimi[1], Shunsuke Kitou[1], Taka-hisa Arima[1,3], Hiroyasu Sato[4], Kaoru Yamamoto[5], Akira Takahashi[6], Hatsumi Mori[1] (1. The Univ. of Tokyo, 2. Institute for Molecular Science, 3. RIKEN Center for Emergent Matter Science, 4. Rigaku Corporation, 5. Okayama University of Science, 6. Nagoya Institute of Technology)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC

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[A1441-3pm-06]

Molecular Perovskite Solid Solution (H_2dabco,H_2hmta)(NH_4)(BF_4)$_3$ Synthesized by Mechanochemical Method

○Jumpei Moriguchi[1], Atsuko Masuya-Suzuki[1], Nao Tsunoji[2], Masahiro Sadakane[2], Ryo Tsunashima[1] (1. Graduate School of Science and Technology for Innovation, Yamaguchi University, 2. Graduate School of Advanced Science and Engineering, Hiroshima University)

Japanese

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[A1441-3pm-07]

Phase transition and dielectric behavior of rod-shaped camphor sulfonamide derivatives

○Chisato Sato[1], Dekura Shun[1,2], Tomoyuki Akutagawa[1,2] (1. Graduate School of Engineering, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

Japanese

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

[A1441-3pm-08]

Structure and physical properties of [Ni(dmit)$_2$] salts with supramolecular cations composed of 2-hydroxy-2-methylpropan-1-aminium/[18]crown-6 derivatives

○Kazuya Kanamaru[1], Kiyonori Takahashi[1,2], Rui-kang Huang[1,2], Chen Xue[1,2], Jiabing Wu[1,2], Takayoshi Nakamura[1,2] (1. Hokkaido University Graduate School of Environmental Science, 2. Research Institute for Electronic Science, Hokkaido University)

Japanese

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

[A1441-3pm-09]

Negative thermal expansion and dielectric behavior of 2,2'-disulfanediylbis(ethan-1-aminium)([18]crown-6)$_2$[Ni(dmit)$_2$]$_2$

○Masato Haneda[1], Kiyonori Takahashi[2,1], Ruikang Huang[2,1], Jiabing Wu[2,1], Chen Xue[2,1], Takayoshi Nakamura[2,1] (1. Grad. School of Env. Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ.)

Japanese

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

[A1441-3pm-10]

Crystal Structure and Phase Transition Behaviors of Monoprotonated 1,3,5-Triaza-7-Phosphoadamantane Salts

○Yukino Ohtsubo[1], Yuki Ohishi[2], Atsuko Masuya-Suzuki[2], Ryo Tsunashima[2] (1. Yamaguchi University, 2. Graduate School of Science and Technology for Innovation)

Japanese

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

[A1441-3pm-11]

Preparation of and dielectric property of Preyssler-type polyoxometalate-LDH composite films.

○Yuta Kawamura[1], Masaru Fujibayashi[2], Atsuko Suzuki[3], Sadafumi Nishihara[4], Ryo Tsunashima[3] (1. Yamaguchi University, 2. National Institute of Technology, Ube College, 3. Graduate School of Science and Technology for Innovation, Yamaguchi University, 4. Graduate School of Advanced Science and Engineering, Hiroshima University)

English

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

[A1441-3pm-12]

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Optical and low-temperature transport properties of an organic conductor with disordered anion structure κ''-$(ET)_2Cu[N(CN)_2]Br$

○Soichiro Yasaka[1], Yukihiro Yoshida[1], Yuto Nakamura[2], Hideo Kishida[2], Hiroshi Kitagawa[1], Mitsuhiko Maesato[1] (1. Kyoto University, 2. Nagoya University)

Japanese

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

[A1441-3pm-13]

Dielectric properties related to structural transformation of basket-shaped polyoxometalate

○Masaru Fujibayashi[1] (1. NIT, Ube College)

English

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

[A1441-3pm-14]

Physical Properties and Redox Chemistry of Copper Hexahydroxytriptycene MOFs

○Qi Chen[1], Zhongyue Zhang[2], Kunio Awaga[1] (1. Nagoya University, Graduate School of Science, 2. Kumamoto University, International Research Organization for Advanced Science and Technology)

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

Wed. Mar 20, 2024 9:00 AM - 10:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 1:30 AM UTC
A1454(1454, Bldg. 14 [5F])

[A1454-3am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Muneyuki Matsuo, Nobuhiko Suematsu

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1454-3am-01]

Belousov-Zhabotinsky reaction in nonionic surfactant emulsion system

Kotarou Oda[1], ○Akiko Kaminaga[1] (1. Kagoshima University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1454-3am-02]

Self-propelled motion switching of a thymol acetate droplet depending on concentration of aqueous surfactant solutions

○Takuya Fujino[1], Muneyuki Matsuo[1,2], Satoshi Nakata[1] (1. Graduate School of Integrated Sciences for Life, Hiroshima University, 2. Graduate School of Arts and Sciences, The Unicersity of Tokyo)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1454-3am-03]

Anion effects in the aqueous phase on motion of a camphor self-propelled object

○Mai Tateishi[1], Muneyuki Matsuo[1,2], Satoshi Nakata[1] (1. Hiroshima University, 2. The Univ. of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1454-3am-04]

Effects of flow rate and solubility product in chemical gardens

○Yujin Kubodera[1], Muneyuki Matsuo[1,2], Masashi Fujii[1], Oliver Steinbock[3], Satoshi Nakata[1] (1. Hiroshima Univ., 2. The Univ. of Tokyo, 3. Florida State Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1454-3am-05]

Real-time Mode-switching of a Self-propelled Droplet Controlled by the Photosensitive Belousov–Zhabotinsky Reaction

○Nobuhiko J. Suematsu[1,2], Satoshi Udagawa[1] (1. Meiji University, 2. Meiji Institute for Advanced Study of Mathematical Sciences (MIMS))

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1454-3am-06]

Droplet size dependence of chemical state in BZ droplets in oil phase

○Keigo Takeda[1], Satoshi Udagawa[2], Nobuhiko J Suematsu[2,3] (1. Meiji Univ., School of Interdisciplinary Mathematical Sciences, 2. Meiji Univ., Graduate School of Advanced Mathematical Sciences, 3. Meiji Institute for Advanced Study of Mathematical Sciences (MIMS))

Japanese

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

[A1454-3am-07]

Effects of Differences in Mixing Condition of Reaction System and Precipitation Behavior on the Chiral Asymmetry Amplification of Soai Reaction System

○Kazuma Furuya[1], Taisuke Banno[1], Ken-ichi Takao[1], Kouichi Asakura[1] (1. Keio University)

Japanese

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

[A1454-3am-08]

Propagation of precipitate bands produced by precipitation and redissolution reaction of aluminum hydroxide

○Yuhei Onishi[1], Nobuhiko J. Suematsu[1,2] (1. Graduate School of Advanced Mathematical Sciences, 2. Meiji Institute for Advanced Study of Mathematical Sciences)

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

Wed. Mar 20, 2024 3:55 PM - 5:05 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:05 AM UTC
A1455(1455, Bldg. 14 [5F])

[A1455-3vn] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Masashi Arakawa, Sadahiro Masuo

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[A1455-3vn-01]

Observation of carrier dynamics in a quasi-two-dimensional lead halide perovskite crystal with naphthylmethylamine

○Tatsuya Fujii[1], Yuichi Ikura[1], Tetsuro Katayama[1], Akihiro Furube[1] (1. Tokushima University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[A1455-3vn-02]

Substrate dependence of carrier dynamics in $MoSe_2$ monolayer by using femtosecond transient absorption microscopy

○Sho Yamanochi[1], Akira Yamamoto[1], Naohiko Endo[2], Kenji Watanabe[3], Takashi Taniguchi[3], Yasumitsu Miyata[2], Tetsuro Katayama[1], Akihiro Furube[1] (1. Tokushima University, 2. Tokyo Metropolitan University, 3. National Institute for Materials Science(NIMS))

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[A1455-3vn-03]

Spin coherence in a spin correlated triplet pair observed by pulsed EPR

○Yasuhiro Kobori[1,2], Masaaski Fuki[1,2], Taku Hasobe[3] (1. Kobe University, 2. CREST, JST, 3. Keio University)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[A1455-3vn-04]

Observation of hydrogen bubble evolution reactions at micro-structured electrodes

○Itsuki Abe[1], Daiki Ashizawa[2], Daiki Sato[2], Kazuma Kobashigawa[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. School of Science, Hokkaido University, 2. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 3. Faculty of Science, Hokkaido University)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[A1455-3vn-05]

In situ Observation of Adsorption of Ionomers onto Pt Electrode Surface by Electrochemical Quartz Crystal Microbalance

○Kaede Takei[1], Takatoshi Noguchi[2], Katsumi Chikama[2], Toshihiro Kondo[1] (1. Ochanomizu University, 2. Nissan Chemical)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[A1455-3vn-06]

Electric field catalyzed isomerization of di-pyridyl-tetrazine and dihydrofuran Diels -Alder adduct

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○Kentaro Adachi[1], Masaki Furusawa[2], Ken Albrecht[2] (1. Interdisciplinary Graduate School of Engineering Sciences (IGSES), Kyushu University, 2. Institute for Materials Chemistry and Engineering (IMCE), Kyushu University)

English

4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[A1455-3vn-07]

Advancement of the r-BS+G electrocatalyst with high stability for the oxygen evolution reaction

○Linghui Li[1], Satoshi Hagiwara[2], Cheng Jiang[3], Haruki Kusaka[1], Norinobu Watanabe[1], Takeshi Fujita[4], Fumiaki Kuroda[2], Akiyasu Yamamoto[5], Masashi Miyakawa[6], Takashi Taniguchi[6], Hideo Hosono[6,7], Minoru Otani[2], Takahiro Kondo[8,9] (1. Graduate School of Pure and Applied Sci., Univ. of Tsukuba, Tsukuba, 2. Center for Computational Sci., Univ. of Tsukuba, Tsukuba, 3. Inst. of Technical and Macromolecular Chemistry, RWTH Aachen Univ., Aachen, 4. School of Environmental Sci. and Engineering, Kochi Univ. of Tech., Kochi, 5. Tokyo University of Agriculture and Technology, 6. Research Center for Functional Materials, National Institute for Materials Science, 7. MDX Res. Center for Element Strategy, Tokyo Inst. of Tech., Yokohama, 8. Department of Materials Sci. and Tsukuba Res. Center for Energy Materials Science, Inst. of Pure and Applied Sci., Univ. of Tsukuba, Tsukuba, 9. Advanced Institute for Materials Research, Tohoku University, Sendai)

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Academic Program [Oral A] | 06. Analytical Chemistry：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC
A1453(1453, Bldg. 14 [5F])

[A1453-3pm] 06. Analytical Chemistry

Chair: Atsuko Masuya-Suzuki, Tsuyoshi Minami

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1453-3pm-01]

Design of chemical nuclease for searching G4 sites on the genome

○Shigeori Takenaka[1], Shinobu Sato[1], Sanada Yukina[1], Fujii Satoshi[2] (1. Dept. Appl. Chem. Kyutech, 2. Dept. Biosci. Bioinfor. Kyutech)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1453-3pm-02]

Development of biotin-modified cyclic naphthalene diimide for detection of G4 in the genome

○Shinobu Sato[1], Satoshi Fujii[1], Ryuki Hidaka[1], Shigeori Takenaka[1] (1. Kyushu Inst. Tech.)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1453-3pm-03]

Electrochemical telomerase assay using naphthalene diimide immobilized electrode

○Yudai Higashi[1], Shinobu Sato[1], Shigeori Takenaka[1] (1. Kyushu Inst. Tech.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1453-3pm-04]

Detection of anionic surfactants using microfluidic devices with optodes as detectors

○Ryu Konno[1], ryo yamada[1], mika hanayama[1], takashi masadime[1] (1. shibaura institute of technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1453-3pm-05]

Forming of TRDF using PEG-copper ion (Ⅱ) aqueous two phase system and effects of coexisting substances

○Yoshiki Hiramatsu[1], Daiki Isikawa[1], Takeshi Iharada[1], Kazuhiko Tsukagoshi[1] (1. Doshisha University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1453-3pm-06]

Investigation of analysis conditions and practical sample measurement in hydrogen peroxide analysis using reactions with hypochlorite and phenol

○Ikko Mikami[1], Takahiro Fukase[1] (1. Tokai University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[A1453-3pm-07]

High-speed fluorescence mode XAFS measurement in wide-energy range using the X-ray image detector CITIUS

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○Tomoya Uruga[1,2], Yoshiaki Honjo[2], Takuma Kaneko[1,2], Nobuhiro Yasuda[1], Oki Sekizawa[1], Yasuhiko Imai[1,2], Kyosuke Ozaki[2], Haruki Nishino[1,2], Takaki Hatsui[2] (1. JASRI, 2. RIKEN)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[A1453-3pm-08]

Retention Behavior of Oligopeptides in MOF Column Chromatography

○Yosuke Higuchi[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1453-3pm-09]

Chemoinformatics Analysis on Retention Behavior of MOF Column Chromatography

○Akihiro Torimoto[1], Yosuke Higuchi[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. Grad. Sch. Eng., The Univ. of Tokyo)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1453-3pm-10]

Fabrication of MOF@SiO2 Core-Shell Stationary Phases for High-Precision Polymer Separation

○Toshiaki Matsumura[1], Nobuhiko Hosono[1,2], Takashi Uemura[1,2] (1. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[A1453-3pm-11]

Cationic/anionic-exchange mode switching chromatography utilizing pH-responsive mixed charge polymer-modified silica beads

○Koichi Deura[1], Taisei Kaku[1], Tomoka Yoshii[1], Daniel Citterio[1], Yuki Hiruta[1] (1. Keio university)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[A1453-3pm-12]

Mutual separation of main metal elements Fe/Nd/Dy in neodymium magnets by crystallization

○Natsuki Hasegawa[1], Atsuko Suzuki[2], Ryo Tsunashima[2] (1. Faculty of Science, Yamaguchi University, 2. Graduate School of Sciences and Technology for Innovation, Yamaguchi University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[A1453-3pm-13]

Effect of chemical enhancer on peroxidase catalyzed luminol chemiluminescence in kosmotropic salt solution

○Hajime Karatani[1] (1. Kyoto luminous science lab.)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[A1453-3pm-14]

Effect of aminopropyl sulfate-ester group in zwitterionic surfactant on the thermosensitive phase-separation

○Yuto Kusunoki[1], Taichi Nakagawa[1,2], Willie L. Hinze[3], Yoshitaka Takagai[1] (1. Fukushima Univ., 2. JAEA, 3. Wake Forest Univ.)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
A1444(1444, Bldg. 14 [4F])

[A1444-3am] 07. Inorganic Chemistry

Chair: Soichi Kikkawa, Takamasa Tsukamoto

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1444-3am-01]

the properties of precisely synthesized metal cluster–metal oxide cluster complexes

○TAISHI Suzuki[1], Tomoki Matsuyama[1], Soichi Kikkawa[1], Naoki Nakatani[1], Seiji Yamazoe[1] (1. Tokyo Metroporitan University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1444-3am-02]

Synergistic hydrogen storage properties of POM-based porous ionic crystals with Pd nanoparticles

○Yuki Iwata[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
[A1444-3am-03]

Synthesis of crystalline proton conductors based on polyacids and polyvinyl alcohols.

○Yuta Yamada[1], Sayaka Uchida[1], Tukasa Iwano[1] (1. The Univ. of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1444-3am-04]

Hydrogen evolution reaction using porous ionic crystals composed of salen complexes and polyoxometalates

○Tsutsumi Yutaro[1], Yuto Shimoyama[1], ryota Imashioya[1], Yudai Suzuki[1], Naoki Ogiwara[1], Sayaka Uchida[1] (1. The Univ. of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1444-3am-05]

Selective synthesis and photophysical properties of two isomers of unsymmetric Pt and Pt_2Ag_3 complexes having two pyrazole derivatives

○Yiming Yang[1], Shinnosuke Horiuchi[2], Kenichiro Omoto[1], Eri Sakuda[1], Yasuhiro Arikawa[1], Keisuke Umakoshi[1] (1. nagasaki university, 2. The Univ. of Tokyo)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1444-3am-06]

Control of structures and electronic states of silver nanoclusters within ring-shaped polyoxometalates and their properties

○Daiki Yanai[1], Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

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

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[A1444-3am-07]

Synthesis and property of palladium nanoclusters within a ring-shaped polyoxometalate

○Rui Xi[1], Yoshihiro Koizumi[1], Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

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

[A1444-3am-08]

Synthesis of metal clusters with porous ionic crystals based on Preyssler-type polyoxometalate

○Hsinyun Lu[1], Naoya Haraguchi[1], Sayaka Uchida[1] (1. The Univ. of Tokyo)

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

[A1444-3am-09]

Reduction-induced selective adsorption of Cs^+ based on Keplerate-type polyoxometalates

○Ken Wang[1], Tsukasa Iwano[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

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

[A1444-3am-10]

Redox-Induced Proton Uptake Based on Polyoxometalate Capsules

○Tsukasa Iwano[1], Nanako Tamai[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

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

[A1444-3am-11]

Development of a synthesis method of lacunary polyoxomolybdates in organic solvents

○Atsuhiro Jimbo[1], Chifeng Li, Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

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

[A1444-3am-12]

Synthesis of Polyoxothiotungstates by Oxygen–Sulfur Substitution Reactions

○Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

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

[A1444-3am-13]

Developing a mild synthesis method and elucidating the physical properties of heavy metal subnanoparticles based on tungsten

○Hiroki Tomizaki[1], Takamasa Tsukamoto[2,3], Tatsuya Moriai[1,4], Augie Atqa[1], Tetsuya Kambe[5], Wang Jae Chun[6], Takane Imaoka[1,4], Kimihisa Yamamoto[1,4] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. IIS., The Univ. of Tokyo, 3. JST-PRESTO, 4. JST-ERATO, 5. Osaka Univ., 6. ICU)

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

[A1444-3am-14]

Precise controlled synthesis of group 15 metal element subnanoparticles with hydrolysis method and exploration of their physical properties

○Hiroaki Nabe[1], Takamasa Tsukamoto[2,3], Tatsuya Moriai[1,4], Tetsuya Kambe[5], Takane Imaoka[1,4], Kimihisa Yamamoto[1,4] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-PRESTO, 3. IIS, The Univ. of Tokyo, 4. JST-ERATO, 5. Osaka Univ.)

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
A1456(1456, Bldg. 14 [5F])

[A1456-3am] 08. Catalysts and Catalysis

Chair: Kosuke Beppu, Yugo Miseki

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1456-3am-01]

AFM imaging of photo-corrosion on $SrTiO_3$ wafers in $FeCl_3$ solution

○Kyohei Matsui[1], Hiroshi Onishi[1,2] (1. Kobe University, 2. Institute for Molecular Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1456-3am-02]

Liquid-phase chemo-selective reduction of nitrobenzenes with a photocatalytic fixed bed flow-type reactor

○Katsumi Tanimoto[1], Atsuhiro Tanaka[2], Hiroshi Kominami[2] (1. Graduate School of Science & Engineering, Kindai University, 2. Faculty of Science & Engineering, Kindai University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1456-3am-03]

Active sites for nitrate-to-ammonia photocatalytic reduction on copper-doped titanium dioxide

○Wataru Hiramatsu[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Osaka University)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1456-3am-04]

Enhanced Stability of Cu_2O Photocathode in Nitrate Solution

○Rizki Marcony Surya[1], Surya Pratap Singh[1], Takuya Okazaki[1], Kosuke Beppu[1], Fumiaki Amano[1] (1. Tokyo Metropolitan University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1456-3am-05]

Preparation of Au/AgCl catalysts by microwave-assisted reduction methodand hypochlorous acid generation

○Yoko Hiroaki[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Osaka University)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1456-3am-06]

Hydrophobic and Visible-light Responsive TiO_2 Photocatalyst for Efficient Hydrogen Peroxide Production in a Two-phase System

○Yifan Zhao[1], Yoshifumi Kondo[1], Yasutaka Kuwahara[1], Kohsuke Mori[1], Hiromi Yamashita[1] (1. Osaka University)

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

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[A1456-3am-07]

Hydrogen Peroxide Synthesis from Pure Water Using rGO/$BiVO_4$ Photocatalyst

○Nozomi Suzuki[1,2], Takumi Okada[1,2], Masanori Kodera[1], Yugo Miseki[1], Takahiro Gunji[2], Kazuhiro Sayama[1,2] (1. AIST, 2. Tokyo University of Science)

Japanese

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

[A1456-3am-08]

Simultaneous generation of hydrogen and chlorine from NaCl solution using TiO_2 photocatalyst

○Takumi Okada[1,2], Masanori Kodera[1], Yugo Miseki[1], Hitoshi Kusama[1], Takahiro Gunji[2], Kazuhiro Sayama[1,2] (1. AIST, 2. Tokyo University of Science)

Japanese

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

[A1456-3am-09]

Development of a dye-sensitized molecular photocathode incorporating Ru(II)- and Os(II)-complex photosensitizers and its application to photoelectrochemical CO_2 reduction

○Jo Onodera[1], Yusuke Tamaki[2], Osamu Ishitani[1,3] (1. Tokyo Institute of Technology , 2. National Institute of Advanced Industrial Science and Technology, 3. Hiroshima University)

Japanese

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

[A1456-3am-10]

Photocatalytic CO_2 reduction by hybrid photocatalysts composed of organic polymer semiconductor and dinuclear Ru(II)-Re(I) complex

○Shotaro Sakamoto[1], Noriaki Sakakibara[1], Ewan McQueen[2], Sebastian Sprick[2], Osamu Ishitani[1,3] (1. Tokyo Institute of Technology, 2. Univ. of Strathclyde, 3. Hiroshima Univ.)

Japanese

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

[A1456-3am-11]

Visible-light CO_2 reduction by hybrid photocatalysts consisting of soluble conjugated polymers with long alkyl chains and a Ru(II) complex

○Shunsuke Asai[1], Akinobu Nakada[2,3], Hajime Suzuki[2], Osamu Tomita[2], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese

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

[A1456-3am-12]

Effects of crystal phase mixture in Ga_2O_3 photocatalysts and roles of each phase on photocatalytic CO_2 reduction with water

○Naoto Ota[1], Yukie Takashiro[1], Muneaki Yamamoto[1], Tetsuo Tanabe[1], Tomoko Yoshida[1] (1. Osaka Metropolitan Univ.)

Japanese

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

[A1456-3am-13]

Effect of various metal dopants into $SrTiO_3$ photocatalyst on photocatalytic activity for CO_2 conversion

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○Takechi Nakamoto[1], Shoji Iguchi[1], Shimpei Naniwa[1], Tsunehiro Tanaka[1,2,3], Kentaro Teramura[1,2,3] (1. Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, 2. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 3. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese

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

[A1456-3am-14]

The effect of Zn/Ta ratio in $ZnTa_2O_6$ photocatalyst on the activity for the photocatalytic conversion of CO_2

○Kio Kawata[1,2], Masamu Nishimoto[1], Shoji Iguchi[2], Shimpei Naniwa[2], Tsunehiro Tanaka[2,3], Kentaro Teramura[2,3,4] (1. Sumitomo Metal Mining Co., Ltd., 2. Graduate School of Engineering, Kyoto University, 3. Kyoto University Elements Strategy Initiative for Catalysts and Batteries (ESCIB), 4. Kyoto University Fukui Institute for Fundamental Chemistry)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
A1458(1458, Bldg. 14 [5F])

[A1458-3am] 08. Catalysts and Catalysis

Chair: Megumi Okazaki, Shoji Iguchi

English
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1458-3am-01]

Convolutional Neural Network Prediction of the photocurrent−voltage curve directly from scanning electron microscopic image for Hematite

○shinichi fujiwara[1], Yuta Hayashi[1], Yuya Nagai[1], Zhenhua Pan[1], Kenji Katayama[1] (1. Chuo Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1458-3am-02]

Arc plasma deposition for loading effective cocatalysts on water-splitting photocatalysts

○Hajime Suzuki[1], Toshiki Abe[1], Masanobu Higashi[2], Masanobu Higashi[1], Akinori Saeki[3], Ryu Abe[1] (1. Kyoto University, 2. Osaka Metropolitan University, 3. Osaka University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1458-3am-03]

Expanding visible-light absorption by bismuth substitution of perovskite layer metal species in layered oxyhalide photocatalysts

○Wataru Sato[1], Akinobu Nakada[2,3], Hajime Suzuki[2], Osamu Tomita[2], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1458-3am-04]

Flux synthesis and surface modification of an oxyiodide photocatalyst $Ba_2Bi_3Nb_2O_{11}I$ toward efficient water splitting under visible light

○Reiya Takahashi[1], Hajime Suzuki[2], Osamu Tomita[2], Akinobu Nakada[2,3], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1458-3am-05]

Development of noble-base metal composite cocatalysts for hydrogen evolution in Z-scheme water splitting systems

○Xinru Sui[1], Hajime Suzuki[2], Osamu Tomita[2], Akinobu Nakada[2,3], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate school of Eng., Kyoto Univ., 3. PRESTO/JST)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1458-3am-06]

Z-scheme Water Splitting System Consisting of $BaTaO_2N$-Based Hydrogen Evolution Photocatalyst and Carbon-Based Electron Mediator

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○LI WENPENG[1], Gu Chen[2], Hisatomi Takashi[2,3], Takata Tsuyoshi[2], Zettsu Nobuyuki [1], Domen Kazunari [2] (1. Shinshu university, 2. Research Initiative for Supra-Materials, 3. PRESTO, JST)

English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1458-3am-07]

Photocatalyst sheets employing narrow-bandgap GaN:ZnO for oxygen evolution in Z-scheme pure water splitting

○Swarnava Nandy[1], Hiroka Sandaiji[1], Natsutogi Iwasa[1], Shuji Sekimori[1], Takashi Hisatomi[1,2], Tsuyoshi Takata[1], Kazunari Domen[1,3] (1. Shinshu University, 2. PRESTO, JST, 3. The University of Tokyo)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1458-3am-08]

Synthesis of GaN:ZnO using Mg_3N_2 as a solid nitrogen source and its photocatalytic actiity

○Kosuke Ebihara[1], Shintaro Abe[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Shinshu University, 2. Graduate School of Science and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Shinshu University, 4. PRESTO, JST)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1458-3am-09]

Enhancement of water splitting activity of GaN:ZnO solid solutions under visible light by molten salt treatments

○Natsutogi Iwasa[1], Shintaro Abe[1], Guijun Ma[3], Takashi Hisatomi[1,2], Kazunari Domen[1] (1. Shinshu University, 2. PREST JST, 3. ShanghaiTech University)

English
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1458-3am-10]

Non-oxide photocatalyst sheet based on metal-free conductors for Z-scheme water splitting

○Rhauane Almeida Galvao[1], Swarnava Nandy[1], Chen Gu[1], Tsuyoshi Takata[1], Takashi Hisatomi[1,2], Nobuyuki Zettsu[1], Kazunari Domen[1,3] (1. Shinshu University, 2. Presto, JST, 3. The Univ. of Tokyo)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1458-3am-11]

Synthesis and photocatalytic activity of $SrTaO_2N$ synthesized from $SrTa_2O_6$ as a starting material

○Shunya Kono[1], Takashi Hisatomi[2,3], Kazunari Domen[2] (1. Graduate School of Science and Technology, Shinshu University, 2. Research Initiative for Supra Materials , Shinshu University, 3. PRESTO, JST)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1458-3am-12]

Synthesis of $LaTiO_2N$ Photocatalysts via Flame Spray Pyrolysis and Their Hydrogen Evolution Activity

○Mayu Inose[1,2], Shuhei Nakakura[1], Takashi Hisatomi[3], Tsuyoshi Takata[3], Kazunari Domen[3] (1. Sumitomo Metal Mining Co., Ltd., 2. Graduate School of Medicine, Science and Technology, 3. Research Initiative for Supra-Materials, Shinshu University)

Japanese

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

[A1458-3am-13]

Study on synthesis conditions and water splitting activity of gallium nitride prepared from sulfides

○Atsuto Terui[1], Shintaro Abe[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Department of Materials Chemistry, Faculty of Engineering, Shinshu University, 2. Department of Engineering, Graduated School of Science and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4. PRESTO, JST)

Japanese

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

[A1458-3am-14]

Metal cation doping of $Y_2Ti_2O_5S_2$ photocatalytic particles intended for improvement of water splitting activity

○Riku Kumemoto[1], Yosuke Kageshima[1], Katsuya Teshima[1], Kazunari Domen[2], Hiromasa Nishikiori[1] (1. Shinshu University, 2. Tokyo University)

Japanese

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

[A1458-3am-15]

Preparation of $SrTiO_3$ particulate photoelectrodes intended for application to impedance analysis

○Yusuke Sasai[1], Yousuke Kagesima[1], Katuya Tesima[1], Kazunari Doumen[2], Hiromasa Nisikiori[1] (1. Shinshu University, 2. The University of Tokyo)

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
A1457(1457, Bldg. 14 [5F])

[A1457-3pm] 08. Catalysts and Catalysis

Chair: Shingo Hasegawa, Tomohiro Yabe

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1457-3pm-01]

Selective reduction reactions of organic molecules by powdered silicon as a reducing agent

○Takuya Shiroshita[1], Yurino Sasaki[1], Shingo Hasegawa[1], Ken Motokura[1] (1. Yokohama National University.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1457-3pm-02]

Silica-immobilized Pd-base catalyst for Suzuki-Miyaura coupling without homogeneous base

○Mariko Honda[1], Shunichi Sakai[1], Shingo Hasegawa[1], Ken Motokura[1] (1. Yokohama National University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1457-3pm-03]

Selective pyrrole synthesis through oxidative dehydrogenative aromatization using a supported Au–Pd nanoparticle catalyst

○Kenshiro Sekine[1], Takafumi Yatabe[1], Yasutaka Tomiki[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1457-3pm-04]

Hydrogenation of Aromatic Compounds by Supported Ni Nanoparticle Catalysts under Ambient Pressure

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

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1457-3pm-05]

Selective acetone hydrodeoxygenation over supported polyoxometalate catalysts

○Takaaki Suzuki[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1457-3pm-06]

Ni-catalyzed Kumada–Tamao–Corriu double cross-coupling of diaryl sulfides via desulfurization

○Ikuya Sugimoto[1], Takahumi Yatabe[1], Takehiro Matsuyama[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1457-3pm-07]

Aerobic oxidation of sulfides catalyzed by Ru-doped hexagonal perovskite oxides

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○Masashi Makizawa[1], Keiju Wachi[1], Takeshi Aihara[1], Keigo Kamata[1] (1. MLS, Tokyo Tech)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[A1457-3pm-08]

Sustainable aviation fuel formation by hydrocracking of *n*-heptadecane using Y-zeolite-Al_2O_3 composite-supported Pt catalyst

Shunma Mitsuoka[1], Kosuke Murata[1], Tadanori Hashimoto[1], Ning Chen[2], Yuki Jonoo[2], Sho Kawabe[2], Keita Nakao[2], ○ATSUSHI ISHIHARA[1] (1. Graduate School of Engineering, Mie University, 2. Tosoh Corporation)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1457-3pm-09]

Cu-containing atom-hybridized subnanoparticles for catalysis

○Ryusuke Iijima[1], Makoto Tanabe[1,2], Kimihisa Yamamoto[2] (1. Fukushima Medical University, 2. Lab. Chem. Life Sci., Tokyo Tech.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1457-3pm-10]

Development of improved photo-responsive thiourea/DMAP combined catalyst that switches catalytic activity

○Yusuke Nakamura[1], Akihiro Kawaguti, tatsushi Imahori[1] (1. The Tokyo Univ. of Science)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[A1457-3pm-11]

Ti_2Ni Alloys Catalyzed β-Alkylation of Alcohols

○Itsuki Kawasaki[1], Chihiro Yamaguchi[1], Ryo Kanishi[1], Ryota Kondo[1], Yasushi Obora[1] (1. Fac. Chem. Matl. & Bioeng., Kansai Univ.)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[A1457-3pm-12]

Ceria-catalyzed oxidative C-C bond cleavage of 1,2-diols

○Nakamura Yukino[1], Miura Hiroki[1], Shishido Tetsuya[1] (1. Tokyo Metropolitan University)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[A1457-3pm-13]

Aerobic oxidation of alcohols with supported Pt-Bi catalysts

○Kazuki Haruguchi[1], Hinata Yamamoto[1], Yasutaka Kawai[1], Eiji Yamamoto[1], Haruno Murayama[2], Akina Yoshizawa[1], Makoto Tokunaga[1] (1. Kyushu University, 2. Kanagawa Institute of Technology)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[A1457-3pm-14]

Creation of active structure derived from Al_2O_3-supported Cu-Al LDH in ammoxidation of aldehydes

○Ryota Yodose[1], Takayoshi Hara[1], Enggah Kurniawan[1], Yessi Permana[2], Nobuyuki ichikuni[1] (1. Chiba University, 2. Institut Teknologi Bandung)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1231(1231, Bldg. 12 [3F])

[F1231-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Shun Ohta, Takashi Komuro

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1231-3am-01]

Paramagnetic one-dimensional chains with reduced Pt–Fe–Pt complex bridged by pivalamidate in trans fashion

○Iori Yoshida[1], Tomonori Adachi[2], Kazuhiro Uemura[1] (1. Faculty of Engineering, Gifu Univ., 2. Graduate School of Natural Science and Technology, Gifu Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1231-3am-02]

Crystal structures and properties of one-dimensional assembles consisting of octamolybdate-typed polyoxometalates and tetranuclear platinum complex

○Takayuki Oda[1], Momoka Oshika[2], Yuma Ito[2], Kazuhiro Uemura[1] (1. Faculty of Engineering, Gifu Univ., 2. Graduate School of Natural Science and Technology, Gifu Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1231-3am-03]

Synthesis of Anionic Pt(0) and Pd(0) Complexes Bearing Trigonal Bipyramidal Geometry

○Tokoro Miyazaki[1], Daisuke Izumi, Hajime Kameo[2], Hiroyuki Matuzaka[2] (1. Osaka Prefecture University, 2. Osaka Metropolitan University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1231-3am-04]

Synthesis and propeties of platinum complexes bearing cyclometalated ligands

○Shinnosuuke Hada[1], Satoshi Inoue[1], Katsunori Yamanishi[1], Tatsuya Kawamoto[1] (1. The Univ. of Kanagawa)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1231-3am-05]

Synthesis and Reaction of Rhodium dinuclear Sandwich Complexes Bearing Bow-shaped π-Conjugated Unsaturated Hydrocarbon Ligands

○Iori Inoue[1], Yukiho Aida[1], Koji Yamamoto[2], Tsubasa Omoda[1], Tetsuro Murahashi[1] (1. Tokyo Tech., 2. National Defense Academy)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1231-3am-06]

Reactions of chlorosilylene supported by bulky iminophosphonamido ligands with Group 9 transition metal complexes

○Ayana Kawanishi[1], Shintaro Takahashi[2], Akihiko Ishii[2], Daisuke Hashizume[3], Norio Nakata[2] (1. Faculty of Science, Saitama Univ., 2. Graduate School of Science and Engineering, Saitama Univ., 3. Riken)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1231-3am-07]
Ligand-induced Reversible Assembly of Rh Atoms within a Sandwich Framework
○Yukiho Aida[1], Iori Inoue[1], Koji Yamamoto[2], Tsubasa Omoda[1], Tetsuro Murahashi[1] (1. Tokyo Tech., 2. National Defense Academy)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1231-3am-08]
Metal selectivity in the complexation using by a terpyridine-based biradical ligand
○Yota Nagumo[1], Takuya Kanetomo[1], Masaya Enomoto[1] (1. Tokyo Univ. of Sci.)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[F1231-3am-09]
Synthesis of Zinc Complexes Bearing Isoindoline-based Pincer-type Polyprotic Pyrazole Ligand
○Yuki Kajitani[1], Wei-Syuan Lin[2], Kuwata Shigeki[1] (1. Ritsumeikan University, 2. Tokyo Institute of Technology)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1231-3am-10]
Reactions of iminophosphonamido-chlorosilylene with anionic transition metal carbonyl complexes
○Haruna Sato[1], Shintaro Takahashi[1], Akihiko Ishii[1], Norio Nakata[1] (1. Graduate school of science and engineering, Saitama Univ.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1231-3am-11]
Synthesis and Structures of First-Row Transition Metal Complexes of Amide Ligands Having Aromatic Rings as Coordinating Groups
○Kazuma Tanaka[1], Shinnosuke Otsuka[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1231-3am-12]
Construction of Iron-Sulfur Clusters in a Cavity of a Cage-Type Ligand
○Koki Nagamatsu[1], Kenta Ochiai[1], Keita Yamanaka[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1231-3am-13]
Synthesis of nickel complexes with imidazole moieties
○Kakeru Shinkai[1], Satoshi Inoue[1], Katsunori Yamanishi[1], Tatsuya Kawamoto[1] (1. Kanagawa University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[F1231-3am-14]
Synthesis and Properties of Heterobimetallic Complexes Containing a Vanadocene Skeleton, and Their Application to Dinitrogen Activation

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○Asahi Suzuki[1], Hinano Kusunose[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

English

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

[F1231-3am-15]

Synthesis of a Quadruple-Pyridylated Imidazo[1,5-*b*]pyridazine-7-ylidene Ligand for Aiming the Formation of Bimetallic Complexes

○Márton Nagyházi[1], Miyu Sato[2], Kosuke Higashida[1], Masaya Sawamura[1,2] (1. Hokkaido University, WPI-ICReDD, 2. Hokkaido University, Faculty of Science)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1232(1232, Bldg. 12 [3F])

[F1232-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Takashi Matsuo, Tomoya Ishizuka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1232-3am-01]

Reactions of molybdenum nitride complexes with unsaturated compounds toward nitrogen–carbon bond formation

○Tomoyuki MIYAZAKI[1], Shun SUGINOME[1], Yoshiaki NISHIBAYASHI[1] (1. School of Engineering, The University of Tokyo)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1232-3am-02]

Molybdenum–Catalyzed Dinitrogen Borylation with Hydroboranes

○Atsushi Okochi[1], Shun Suginome[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1232-3am-03]

Capture and catalytic silylation of dinitrogen with novel molybdenum complexes bearing tripodal ligands

○Shoki Yabutani[1], Yuko Wasada[1], Tomohiko Inomata[1], Tomohiro Ozawa[1], Hideki Masuda[2] (1. Graduate School of Engineering, Nagoya Institute of Technology, 2. Aichi Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1232-3am-04]

Reaction of dioxo-ruthenium(VI) porphyrin complex with proton

○Arimi Mori[1], Yuki Honda[1], Hiroshi Fujii[1] (1. Nara Women's University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1232-3am-05]

Formation and reactivity of Ru(IV)-hydroxo complexes having N-heterocyclic carbene (NHC) ligands

○Shotaro Takeshita[1], Tomoya Ishizuka[1], Ayako Nagahara[1], Hiroto Fujisaki[1], Hiroaki Kotani[1], Takahiko Kojima[1] (1. Univ. of Tsukuba)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1232-3am-06]

Electrochemical Ammonia Oxidation Catalyzed by Ruthenium Complexes with Multidentate Ligand Containing N-Heterocyclic Carbene Moiety

○Takuma Shimada[1], Takashi Inagaki[2], Shogo Kuriyama[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo, 2. TDK Corporation)

Japanese

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

[F1232-3am-07]

Photocatalytic substrate oxidation with a heteroaromatic ligand bound to a ruthenium(II) complex as an active site using dioxygen as a terminal oxidant through an Anti-Kasha mechanism

○Taichiro NISHI[1], Tomoya ISHIZUKA[1], Nanse NAMURA, Hiroaki KOTANI[1], Mamoru FUJITSUKA[2], Takahiko KOJIMA[1] (1. University of Tsukuba, 2. Osaka University)

Japanese

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

[F1232-3am-08]

Effects of Conjugated-Anchor Molecule Side Chain on Metal Oxide Surface Modification and Photocatalytic Hydrogen Generation

○Morihiro JO[1], Qichun JIANG[1], Atsushi KOBAYASHI[2], Hiroshi MASAI[1], Shin-ya TAKIZAWA[1], Tomohiro IWAI[1], Jun TERAO[1] (1. Graduate School of Arts and Sciences, The University of Tokyo, 2. Graduate School of Sciences, Hokkaido University)

Japanese

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

[F1232-3am-09]

Carbazole-modified mononuclear metal complex photocatalysts workable for visible-light CO_2 reduction without the aid of external photosensitizers

○Yuya Tomiura[1], Akinobu Nakada[2,3], Hajime Suzuki[2], Osamu Tomita[2], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese

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

[F1232-3am-10]

Development of machine-learning models for the ruthenium complex-catalyzed hydrogenation of ketones

○Haruno Nakajima[1], Chihaya Murata[1], Naoki Noto[2], Susumu Saito[2,1] (1. The Univ. of Nagoya, 2. IRCCS)

Japanese

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

[F1232-3am-11]

Synthesis and Reactivities of Ruthenium-Porphyrin-Based Supramolecular Frameworks Constructed by Intermolecular Non-Covalent Interaction

○Akira Yoneda[1], Kento Kosugi[1], Yutaka Saga[1], Tetsuya Kanbe[1], Mio Kondo[2], Shigeyuki Masaoka[1] (1. Osaka Univ., 2. Tokyo Tech.)

Japanese

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

[F1232-3am-12]

Effects of sulfur atoms in the ligand of Hoveyda-Grubbs-type complexes on their reactivities in polar solvents

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

Japanese

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

[F1232-3am-13]

Synthesis and characterization of amide-containing N2S3-type nitrosyl Ru(II) complex

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○Yuya Terada[1], Yuko Wasada[1], Tomohiko Inomata[1], Tomohiro Ozawa[1] (1. Graduate School of Engineering, Nagoya Institute of Technology)

Japanese

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

[F1232-3am-14]

C-C Bond Formation between Two μ-Ethylidyne Ligands in a Diruthenium Bis(μ-ethylidyne) Complex Accompanied by the incorporation of an Iron Fragment

○Naoya Noguchi[1], Toshiro Takao[1] (1. Tokyo Institute of Technology)

Japanese

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

[F1232-3am-15]

Skeletal Rearrangement of a μ-η^2:η^4-Trienyl Ligand on a Diruthenium Site via a μ-Cyclohexadienyl Intermediate

○Taiki Taniguchi[1], Yohei Tsurumaki[1], Toshiro Takao[1] (1. Tokyo Institute of Technology)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1233(1233, Bldg. 12 [3F])

[F1233-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaki Yoshida, Tomohiro Ogawa

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1233-3am-01]

Proton Control of Emission Behaviors in Heteroleptic Copper(I) Dinuclear Complex and Development of Transparent Emissive Material

○Naoki Takaishi[1], Hajime Kamebuchi[1], Zhou Biao[1], Chihiro Shibuya[1] (1. Nihon Univercity)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1233-3am-02]

Synthesis of novel macrocyclic molecular gears using NHC Cu(Ⅰ) complex and the solid-state emission property

○Ryunosuke Tomita[1], Rempei Ando[1], Hajime Ito[2,3], Mingoo Jin[3] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University, 3. WPI-ICReDD, Hokkaido University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1233-3am-03]

Development of crystalline molecular rotors using asymmetric NHC metal complexes and the solid-state emissive properties

○Yusuke Fujisawa[1], Rempei Ando[1], Motohiro Mizuno[2], Hajime Ito[3,4], Mingoo Jin[4] (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. NanoMaterials Research Institute, Kanazawa University, 3. Graduate School of Engineering, Hokkaido University , 4. WPI-ICReDD, Hokkaido University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1233-3am-04]

Crystal structures and photoluminescence vapochromism of multinuclear copper(I) complexes in hydrogen-bonding network assemblies

○Rin Suhara[1], Syun Fujioka[1], Yoshiki Ozawa[1], Masaki Abe[1] (1. University of Hyogo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1233-3am-05]

Photophysical property of tetrahedral copper(I) complexes with dibenzophenanthroline ligands

○Shun Yamamura[1], Ayano Okuda, Shinichi Saito[1], Yusuke Yoshigoe[1] (1. Tokyo University of Science)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1233-3am-06]

Vapor-induced photoluminescence switching response of crystalline-state hexanuclear copper(I) and silver(I) complexes

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○Yuki Takenaka[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1233-3am-07]

Crystal structures and thermo/piezochromic photoluminescence of silver(I) coordination polymers with N-heterocyclic ligands

○Itaru Tsuchiya[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. University of Hyogo)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[F1233-3am-08]

Structural and Luminescent Changes Induced by the Exposure of acid vapor in 0-Dimensional Organic-Inorganic Hybrids Metal Halides

○Takumi Ide[1], Sotaro Kusumoto[1], Yoshihiro Koide[1] (1. Kanagawa University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[F1233-3am-09]

Exciton Transfer in Photoluminescent Dipyrrin-Zn(II) Molecular Wires in Polymer Films

○Haru Taniguchi[1], Ryojun Toyoda[1], Shinya Takaishi[1], Ryota Sakamoto[1] (1. Tohoku University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1233-3am-10]

Luminescent-Property Variations Based on Assembled Structures of Cationic Terpyridine Platinum(II) Complexes Having Alkynyl Ligands

○Rina Hiura[1], Shuichi Suzuki[1], Takeshi Naota[1] (1. Osaka University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1233-3am-11]

Synthesis and optical properties of pincer-type Pt complex linked by chiral isocyanide ligand

Kohei Yamada[1], Takaki Kanbra[1], ○Junpei Kuwabara[1] (1. University of Tsukuba)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1233-3am-12]

Polymorphism-Dependent Crystalline-State Photoluminescence of a Tetranuclear Au(I) Complex with Iminothiolato Bidentate Ligands

○Syumpei Semba[1], Kenji Nakauchi[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. University of Hyogo)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1233-3am-13]

Theoretical study on substituent effects on phosphorescent emission wavelengths of Ir(III) complexes with phenylpyridine ligands

○Naoya Nakayama[1], Yasutaka Kitagawa[1,2,3,4,5], Ryohei Kishi[1,2,3,4] (1. Osaka University, 2. QIQB, Osaka University, 3. ICS-OTRI, Osaka University, 4. RCSEC, Osaka University, 5. ICS-SRN, Osaka University)

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

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[F1233-3am-14]

Luminescence behavior of the helicate Eu complexes with two independent π-electronic systems

○Fuuto Kojima[1], Yuki Murata[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

Japanese

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

[F1233-3am-15]

Circularly polarized luminescence of chiral Eu(III) complex with aromatic ring functionalized camphor-type ligands

○Ryohei Takizawa[1], Makoto Tsurui[2], Mengfei Wang[3,4], Yuichi Kitagawa[3,4], Yasuchika Hasegawa[3,4] (1. Sch. Eng., Hokkaido Univ., 2. Grad. Chem. Sci. Eng., Hokkaido Univ., 3. Fac. Eng., Hokkaido Univ., 4. WPI-ICReDD, Hokkaido Univ.)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1234(1234, Bldg. 12 [3F])

[F1234-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaaki Sadakiyo, Yuki Wada

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1234-3am-01]

The luminescence and heat-responsive properties of NDI-based MOF with biphenyl derivatives as guest

○Shoto Yamashita[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2] (1. Graduate School of Faculty of Frontiers of Innovative Research in Science and Technology, Konan University, 2. Konan University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1234-3am-02]

Unique photodimerization behavior of Cd coordination polymer with 4-styrylpyridine ligands

○ARATA TATEISHI[1], Yun Chen[1], Yunya Zhang[1], Yuki Saito[1,2], Xin Zheng[1,2], Shin-ichiro Noro[1,2] (1. Grad. Sch. of Env. Sci.,Hokkaido Univ., 2. Fac. of Env.Earth Sci., Hokkaido Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1234-3am-03]

Quantum sensing by persistent radicals photo-generated in metal-organic frameworks

○Miku Inoue[1], Akio Yamauchi[1], Bhavesh Parmar[1], Orihashi Kana[1], Mizue Asada[2], Toshikazu Nakamura[2], Nobuhiro Yanai[1,3] (1. Kyushu University, 2. Institute for Molecular Science, 3. CREST, JST)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1234-3am-04]

Structural Analysis of Low-boiling Compounds by Soaking in the Gas Phase State Using the Crystalline Sponge Method

○Kazuhiko Sakaguchi[1], Nao Tamaki[1], Akihiro Kawaraya[1], Satoru Moriya[1], Yoshihiro Yaguchi[1] (1. Takasago international corporation)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1234-3am-05]

Structural analysis using microcrystal sponges with hierarchical clustering analysis as the key.

○Satoshi Yoshida[1], Seiki Baba[2], Yuki Nakamura[2], Sota Sato[1,3], Makoto Fujita[1,3,4] (1. School of Engineering, TheUniv. of Tokyo, 2. JASRI, 3. IMS, 4. UTIAS, The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1234-3am-06]

A series of adaptable porous frameworks constructed from different positional isomers of tris-pyridyl hexaazaphenalene for crystalline sponge method

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○Tomoki Nakagawa[1,2], Yuki wada[2], Pavel M Usov[2], Yiying Zhu[2], Makoto Tadokoro[1], Masaki Kawano[2] (1. Tokyo Institute of Technology, 2. Tokyo University of Science)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1234-3am-07]

Effects of defect and particle size on the structural transformation properties of Al-based MOFs

○Shintaro Tanaka[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2] (1. Konan graduate school , 2. Konan University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1234-3am-08]

Rational synthesis of hierarchical metal-organic framework using structual transformation reaction

○Reon Teramoto[1], Yohei Takashima[1], Takaaki Tsuruoka[1], Kensuke Akamatu[1] (1. Konan University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[F1234-3am-09]

Morphology-controlled synthesis of a metal-organic framework generated from sphere amorphous precursor

○Takumi Kakuchi[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2] (1. Konan graduate school, 2. Konan University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1234-3am-10]

Fabrication of metal-organic framework composite membranes for CO_2 separation

○Jieru CHEN[1], Xin ZHENG[2], Yuki SAITO[2], Shin-ichiro NORO[1,2] (1. Grad. Sch. of Env. Sci., Hokkaido Univ., 2. Fac. of Env. Earth Sci., Hokkaido Univ.)

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1234-3am-11]

Removal of Perchlorate Anion from Water Using Coordination Polymers

○Umme Fariha Tasnim[1], Aditya Irfan Witono[1], Xin Zheng[1], Shin-ichiro Noro[1] (1. Hokkaido University)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1234-3am-12]

Substituent introduction effect on CO_2 adsorption properties in three-dimensional SiF_6-bridged porous coordination polymers

○Zhongjie Gu[1], Jia-bing Wu[2,3], Xin Zheng[2], Yuki Saito[2], Shin-ichiro Noro[1,2] (1. Grad. Sch. of Env. Sci., Hokkaido Univ., 2. Fac. of Env. Earth Sci., Hokkaido Univ., 3. Res. Ins. for Ele. Sci., Hokkaido Univ.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1234-3am-13]

Separation of Amino Acids by a Zirconium Metal–Organic Framework Having Small-Sized Pores and High Acid Tolerance

○Kyoko Shiraishi[1], Masaaki Sadakiyo[1] (1. Tokyo Univ. of Sci.)

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Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[F1234-3am-14]

Synthesis of novel phosphoramide ligand and their application in metal-organic frameworks

○Sho KOBAYASHI[1], Koh SUGAMATA[1], Natsuki AMANOKURA[1,2], Akihiro SHIRAI[1,2], Mao MINOURA[1] (1. Rikkyo Univ., 2. Nippon Soda Co., Ltd.)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[F1234-3am-15]

Reversible structural change of a cyano-bridged coordination polymer with Zn^{2+} ion induced by water adsorption and desorption

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

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1111(1111, Bldg. 11 [1F])

[E1111-3am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kazuhiko Semba, Tetsuya Satoh

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1111-3am-01]

A Strategy for Modulating the Lewis Acidity of Triarylboranes by Remote Back Strain

○Taichi Morishita[1], Mahiro Sakuraba[1], Taiki Hashimoto[1], Sensuke Ogoshi[1], Yoichi Hoshimoto[1,2] (1. Osaka University, 2. Center for Future Innovation)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1111-3am-02]

Mechanistic Study on Hydrogenation of *N*-Heteroaromatics Using H_2/CO/CO_2 Mixed Gas

○Taiki Hashimoto[1], Yu Harabuchi[4,5], Sensuke Ogoshi[1], Satoshi Maeda[3,4,5], Yoichi Hoshimoto[1,2] (1. Faculty of Engineering, Osaka University, 2. Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University, 3. Faculty of Science, Hokkaido University, 4. WPI-ICReDD, Hokkaido University, 5. JST-ERATO)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1111-3am-03]

Introduced Position Effect of Pyrenes affecting on the Lewis Acidity and Catalytic Activity of Cage-shaped Boron Complexes

Yuya Tsutsui[1], ○Yuta Uchiyama[1], Akihito Konishi[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
[E1111-3am-04]

Synthesis of Multi-substituted Allyl Boronates from Cyclic Allylborates and Allyl Halides

○Hiroki Murata[1], Go Yamagiwa[1], Kazuhiko Semba[1], Tetsuaki Fujihara[1] (1. Kyoto University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1111-3am-05]

Boron-catalyzed Michael Reaction between Carboxylic Acid Donors and α,β-Unsaturated Carboxylic Acid Acceptors

○Yukiho Yoshida[1], Yohei Shimizu[1,2], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1111-3am-06]

Lewis acidity-controlled aryl oxazaborolidinones for iterative Heck reactions

○Takaki Nojiri[1], Takashi Nishikata[1] (1. Yamaguchi University)

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

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[E1111-3am-07]

Palladium-Catalyzed Direct Suzuki–Miyaura Cross-Coupling of Lewis Acidity-Diminished Organoboron Reagents with Weak Bases

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

Japanese

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

[E1111-3am-08]

Development of the methods for direct functionalization of anthracenes

○Haruki Katayama[1], Yoshinosuke Usuki[1], Tetsuya Satoh[1] (1. Osaka Metropolitan University)

Japanese

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

[E1111-3am-09]

Pd-catalyzed oxidative arylation of alkenes with aryltrimethylsilanes

○Tetsu Uemura[1], Miyu Takato[1], Shinya Tanaka[1], Shuichi Oi[1] (1. Tohoku University)

Japanese

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

[E1111-3am-10]

Palladium-catalyzed *anti*-Michael-type hydroalkoxylation

○Yuya Denda[1], Hirotugu Suzuki[1] (1. University of Fukui)

Japanese

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

[E1111-3am-11]

Computational Analysis of Relative Stability of Cationic 1,10-Phenanthroline Alkylpalladium Complexes

○Kazuma Muto[1], Miho Hatanaka[1], Fumitoshi Kakiuchi[1], Takuya Kochi[1] (1. Keio University)

Japanese

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

[E1111-3am-12]

L-Region Selective Annulative π-Extension of Aromatic Compounds

○Kanami Nakata[1], Kou Kawahara[1], Wataru Matsuoka[1], Hideto Ito[1], Kenichiro Itami[1] (1. Nagoya Univ.)

Japanese

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

[E1111-3am-13]

Catalytic Synthesis of Vinylic Isonitriles and Transformation into Bioactive Disubstituted Pyrroles

○Ryota Saeki[1], Asuka Hachiya[1], Taiga Yurino[2,3], Takeshi Ohkuma[2,3] (1. The Univ. of Hokkaido, 2. Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center)

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1112(1112, Bldg. 11 [1F])

[E1112-3am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Yusuke Yoshigoe, Yuya Tanaka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1112-3am-01]

A Platinum-linked Polyaromatic Tube with Postsynthetic Modification and Molecular Binding Abilities

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

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1112-3am-02]

Photoinduced Platinum-Catalyzed Umpolung Allylation of α-Diketones

○Junpei Shimosato[1], Yusuke Masuda[1,2], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1112-3am-03]

Synthesis of Cyclic Platinum(II)-Acetylide Complex via Transmetallation

○Ryusei Kaneko[1], Shinichi Saito[1], Yuusuke Yoshigoe[1] (1. Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1112-3am-04]

Pt-catalyzed rearrangement reactions of *ortho*-alkynylbenzenesulfinates via consecutive S-O bond cleavage

○Keiryo Kubota[1], Masahiro Terada[1], Itaru Nakamura[1] (1. Graduate School of Science, Tohoku University.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1112-3am-05]

Lewis acid mediated amide bond cleavage of polyamides bearing directing groups

○Ryota Shiraki[1], Yu-I Hsu[1], Hiroshi Uyama[1], Mamoru Tobisu[1,2] (1. Osaka Univ., 2. ICS-OTRI)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1112-3am-06]

Copper-catalyzed cross-coupling of thiols with alcohols

○Nobukazu Taniguchi[1] (1. Osaka Metropolitan University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1112-3am-07]

Asymmetric Cu-Catalyzed Electrophilic Fluorination in Water Using Water-Soluble Helical Polymer Ligands

○Takuo Tamura[1], Takeshi Yamamoto[1], Michinori Suginome[1] (1. Kyoto University)

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Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1112-3am-08]
Copper-Catalyzed Asymmetric Coupling Utilizing Helical Macromolecular Bipyridine Ligand Based on Screw-Sense Induction by Chiral Additives

○Hiroki Shimura[1], Yukako Yoshinaga[1], Michinori Suginome[1] (1. Kyoto University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1112-3am-09]
Cu-catalyzed enantioselective conjugate addition and electrophilic trapping of enolate intermediates

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

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1112-3am-10]
Substituent effect of imidazo[1,5-*α*]pyridine carbene ligands on copper and gold-catalyzed addition reaction of alkynes

○Mayu Suganuma[1], Fumitoshi Shibahara[1] (1. GIfu University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1112-3am-11]
Synthesis and Catalytic Activity Evaluation of Triaryl Mesoionic Carbene Metal Complexes Based on Planar Chiral Ferrocene

○Kazuki Osawa[1], Shungo Shimizu[1], Shinici Fukuzawa[1] (1. Graduate School of Engineering, Chuo University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1112-3am-12]
Asymmetric Synthesis of Spirocyclopropyloxyindole Derivatives Catalyzed by Chiral Bis(imidazolidine) Pyridine-Cobalt Complex

○Takaaki Saito[1], Takayoshi Arai[1] (1. Graduate School of Science, Chiba University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1112-3am-13]
Cobalt-catalyzed reductive cross-coupling reaction of aldehydes with organohalide

○Ko Sudo[1], Takuya Kurahashi[1] (1. Kwansei Gakuin University)

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

Wed. Mar 20, 2024 3:55 PM - 4:45 PM JST | Wed. Mar 20, 2024 6:55 AM - 7:45 AM UTC
E1111(1111, Bldg. 11 [1F])

[E1111-3vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kento Ishida, Takuya Suga

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1111-3vn-01]

Disturbing continuous movement of carbon atoms in organic molecules

○Tamotsu Takahashi[1,2], Masayoshi Bando[2], Hui Chen[1], Yang Zheng[3], Zhiyi Song[2] (1. Institute of Chemistry, Henan Academy of Science, 2. Institute for Catalysis, Hokkaido University, 3. Henan Chemical Industrial Institute, Henan Academy of Science)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1111-3vn-02]

Low-Valent Titanium-Mediated Radical Substitution of Allyl Pivalates Using Aliphatic Alcohols as Carbon Radical Sources

○Tatsuto Egawa[1], Chinatsu Miki[1], Takuya Suga[1], Yutaka Ukaji[1] (1. Kanazawa University)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1111-3vn-03]

Zirconocene difluoride-catalyzed hydrosilylation of olefins

○Ryota Kanchiku[1], Keita Takahashi[1], Kento Ishida[1], Yohei Ogiwara[1], Norio Sakai[1] (1. Tokyo University of Science)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1111-3vn-04]

Allylic silylation of allyl phosphates using zinc catalysts and a silylborane

○Ami Sasaki[1], Kazuhiko Semba[1], Tetsuaki Fujihara[1] (1. Graduate School of Engineering, Kyoto University)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[E1111-3vn-05]

Synthesis of Functionalized Nitrones from Nitro Compounds and Organozinc Reagents

○Koki Yamaguchi[1], Koki Nishi[1], Takeshi Hata[1] (1. Tokyo Institute of Technology)

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

Wed. Mar 20, 2024 3:55 PM - 4:55 PM JST | Wed. Mar 20, 2024 6:55 AM - 7:55 AM UTC
E1112(1112, Bldg. 11 [1F])

[E1112-3vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Naoyuki Toriumi, Taiga Yurino

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1112-3vn-01]

Rhodium-Catalyzed Decarbonylative Coupling of Acyl Halides with Bis(pinacolato)diboron and Alkynes

○Masato Tsukahara[1], Nanako Katsurayama[1], Risako Miura[1], Yuu Kimura[1], Teruyuki Kondo[1] (1. Kyoto University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1112-3vn-02]

Highly Regio- and Enantioselective Intermolecular [2+2+2] Cycloaddition of 1,7-Enynes and Unsymmetric Alkynes

○Taichi Kishi[1], Yuto Horio[1], King Hung Nigel Tang[1], Takanori Shibata[1] (1. The Univ. of Waseda)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1112-3vn-03]

Development of a Cross Coupling Reaction Using Ketones as Aryl Sources Enabled by the Norrish Type Ⅰ Reaction and Rhodium Catalysis

○Shimizu Atsuya[1], Yuki Fujimaki[1], Jun Takaya[1] (1. Tokyo Institute of Technology)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1112-3vn-04]

Synthesis and Reactivity of Nickel–Rhodium Bimetallic Complexes

○Kouki Fujita[1], Kazuhiko Semba[1], Yoshiaki Nakao[1] (1. Kyoto Univesity)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[E1112-3vn-05]

Silver(I)–Catalyzed Intermolecular Carbofluorination of Alkynes Using Acyl Fluorides via C–F Bond Cleavage

○Tomoya Emmei[1], Mamoru Tobisu[1,2] (1. Osaka Univ., 2. ICS-OTRI)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[E1112-3vn-06]

Ag-Catalyzed Double Benzylic Isocyanation and Its Application

○Tomoko Ishikawa[1], Takuya Nakamura[1], Taiga Yurino[2,3], Takeshi Ohkuma[2,3] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
E1113(1113, Bldg. 11 [1F])

[E1113-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Seihou Jinnai, Yumi Yakiyama

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1113-3am-01]

Synthesis and photophysical properties of donor-acceptor-type triarylmethane dye etinologues

Shigeyuki Yamada[1], ○Hayato Kitaoka[1], Motohiro Yasui[1], Tsutomu Konno[1] (1. Kyoto Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1113-3am-02]

Synthesis and characterization of tetrafluorinated tolane-type ionic liquid crystals with both photoluminescence and room-temperature liquid-crystalline properties

Shigeyuki Yamada[1], ○Yuto Eguchi[1], Motohiro Yasui[1], Tsutomu Konno[1] (1. Kyoto institute of Technology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1113-3am-03]

Synthesis and Emission Color Tuning of Liquified Boron Difluoride Complexes

○Miku Ichinose[1], Masahiro Ikeshita[2], Takashi Tsuno[2] (1. Graduate School of Industrial Technology, Nihon University, 2. College of Industrial Technology, Nihon University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1113-3am-04]

Synthesis of Triptycene Derivatives for Application in Perovskite Solar Cells

○Akio Hasegawa[1], Tomoya Nakamura[1], Minh Anh Truong[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Institute of Chemical Research, Kyoto University)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1113-3am-05]

Photochromic Luminescence Derived From Photochemical Migrations of Monodentate Ligands in Group 13 Element Complexes

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

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1113-3am-06]

Luminescence properties of aza-boranils and effects of halogen atoms

○Teruki Sawada[1], Masamichi Yasui[1], Takayoshi Arai[1] (1. Graduate School of Science, Chiba University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1113-3am-07]

Development of Hole-Collecting Monolayer Materials Based on Isotriazatruxene Structure

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○Yuta Adachi[1], Minh Anh Truong[1], Tomoya Nakamura[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Institute for Chemical Research, Kyoto University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1113-3am-08]

Water-soluble pyrene-polymer conjugates that function as pressure-responsive chemosensors with distinctive uptake into human tumors.

○Yumiko HORI[1], Takao SAIKI[3], Xinyi Qi[2], Keiichi NAKAGAWA[2], Gaku FUKUHARA[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Bioengineering, The University of Tokyo, 3. Department of Precision Engineering, The University of Tokyo)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1113-3am-09]

Photo-responsive hydrogen storage using amine-B(C_6F_5)$_3$-based FLP system

○Keisuke Nakamura[1], Maki Miyamoto, Aki Okamoto, Tatsushi Imahori[1] (1. The Tokyo Univ. of Science)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1113-3am-10]

A water-soluble pressure-responsive chemosensor that exhibit thermally activated delayed fluorescence: Hydrostatic pressure effects and cellular uptake

○Kotaro Matsumoto[1], Youhei TAKEDA[2], Keiichi NAKAGAWA[3], Gaku FUKUHARA[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Applied Chemistry, Osaka University, 3. Department of Bioengineering, The University of Tokyo)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1113-3am-11]

Diphenylphosphonium-Bridged Fluorescent Dyes for Mitochondrial Imaging

○Ayato Hakamada[1], Masayasu Taki[3], Masahito Murai[2], Shigehiro Yamaguchi[2,3,4] (1. Faculty of Science, Nagoya University, 2. Graduate school of science, Nagoya University, 3. ITbM, Nagoya University, 4. IRCCS, Nagoya University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1113-3am-12]

Aggregation-Induced Emission Enhancement of tris(naphthaleneimide)-substituted benzenes

○Toshiaki Ikeda[1], Yuhei Takahashi[1], Hiro Sugawara[1], Haruki Furukoshi[1] (1. Tokai University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1113-3am-13]

Chirality Singal-amplification Sensing via a Sumanene-based Supramolecular Polymerization

○Ruipu Qi[1], Hiroaki Mizuno[1], Yumi Yakiyama[2], Hidehiro Sakurai[2], Gaku Fukuhara[1] (1. Tokyo Institute of Technology, 2. Osaka University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1113-3am-14]

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Fe^{3+}-Specific Photoluminescence by 17-Membered Macrocyclic Ligands with Amino, Amide, and Carbamate Groups in the Cyclic Skeleton Bearing Anthracene or Pyrene as Chromophores

○Izumi Sato[1], Hiroki Horita[1], Mari Ikeda[2], Shunsuke Kuwahara[1], Yoichi Habata[1] (1. Toho Univ., 2. Chiba Inst. of Tech.)

Japanese

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

[E1113-3am-15]

Synthesis and photophysical properties of ESIPT-capable 4,6-bis(phenanthroimidazol)resorcinol and its analogues.

○Shota Sugi[1], Motoko Akita[1] (1. Josai University)

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

Wed. Mar 20, 2024 9:00 AM - 11:20 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:20 AM UTC
E1121(1121, Bldg. 11 [2F])

[E1121-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Koki Ikemoto, Takuya Shimajiri

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1121-3am-01]

Synthesis and Chiroptical Properties of Radially Extended Carbazole with Chiral [2.2]Paracyclophane Core

○Masashi Hasegaw[1], Wanli Xiao[1], Yuki Ishida[1], Kazuyuki Asahi[2], Hiroyuki Nishikawa[2], Reo Ohno[3], Daisuke Hayauchi[3], Miki Hasegawa[3], Yasuhiro Mazaki[1] (1. Graduate School of Science, Kitasato University, 2. Graduate School of Science and Engineering, Ibaraki University, 3. Department ofChemistry and BiologicalScience, Aoyama GakuinUniversity)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1121-3am-02]

Synthesis of Carbon–Iodine Bond Atropisomers

○Shohei Abe[1], Jun Kikuchi[1], Naohiko Yoshikai[1] (1. Grad. Sn. Pharm. Sci., Tohoku University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1121-3am-03]

Synthesis of BODIPYs Using Phellandrene-fused Pyrrole as a Key Substance

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

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1121-3am-04]

Elucidation of structures and optical properties of (1*Z*,3*Z*,5*Z*)-heptaaryl-1,3,5-hexatriene derivatives

○Kensuke Echizen[1], Tsuyoshi Taniguchi[4], Yoko Sakata[2], Shigehisa Akine[2], Tatsuya Nishimura[2], Katsuhiro Maeda[2,3] (1. Grad. Sch. of Frontier Sci. Initiative, Kanazawa Univ., 2. Grad. Sch. of Nat. Sci, and Tech., Kanazawa Univ., 3. WPI-NanoLSI, Kanazawa Univ., 4. IRC3, AIST)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1121-3am-05]

Catalytic Enantioselective Synthesis of Figure-Eight π-System: Cyclobisbiphenylenecarbonyl

○Reiji Yoshina[1], Shunsuke Minabe[1], Muhammet Uyanik[1], Kazuaki Ishihara[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2] (1. Graduate-School-of-Engineering, Nagoya-University, 2. JST-PRESTO)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1121-3am-06]

Synthesis and Properties of Helical Oligothiophenes Anchored to Binaphthyl

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○Hikari Kawashima[1], Masashi Hasegawa[1], Yasuhiro Mazaki[1] (1. Graduate School of Science, Kitasato University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1121-3am-07]

Synthesis and circularly polarized luminescence of binaphthyl-bridged pyrenophanes

Kazuto Takaishi[1], ○Yoshihiro Sato[1], Fumiya Yoshinami[1], Chihiro Maeda[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
[E1121-3am-08]

Synthesis and Intramolecular Biarylation of Cyclic Tetraamide Obtained by Condensation of Dibromoisophthalic Acid and 1,4-Phenylenediamine

○Kazuki Uoda[1], Kenta Rakumitsu[1], Akihiro Yokoyama[1] (1. Seikei University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1121-3am-09]

Concise Synthesis of Molecular Hyperboloids by Oligomeric Macrocyclization of Octagonal Molecules

○Daiya Nagata[1], Koki Ikemoto[1], Taisuke Matsuno[1], Hiroyuki Isobe[1] (1. The Univ. of Tokyo)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1121-3am-10]

Synthesis of Belt-Shaped Cyclic Trimer by Self-Condensation of Diaminoterephthalic Acid and Its Absorption and Luminescence Properties

○Kota Matsuda[1], Kenta Rakumitsu[1], Akihiro Yokoyama[1] (1. Seikei University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1121-3am-11]

Synthesis, Structures and Properties of All-Carbon One-Dimensional Spiro-Oligomers

○Kumpei Hasebe[1], Kenichiro Itami[1], Hideto Ito[1] (1. Nagoya Univ.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1121-3am-12]

Preparation and Self-Condensation of Diaminoisophthalic Acid for the Synthesis of Belt-Shaped Macrocycles

○Shunsuke Mamiya[1], Kenta Rakumitsu[1], Akihiro Yokoyama[1] (1. Seikei University)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1121-3am-13]

Synthesis and Function of Novel Amide-Embedded Cyclic π-System

○Sho Fukuda[1], Daiki Morishita[2], Yoshimitsu Itoh[2,3] (1. Sch. Eng., The Univ. of Tokyo, 2. Grad. Sch. Eng., The Univ. of Tokyo, 3. JST PRESTO)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
E1122(1122, Bldg. 11 [2F])

[E1122-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Satoru Hiroto, Youhei Miura

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1122-3am-01]

Synthesis and Crystal Structure of Imidazo-Fused Dehydro[12]annulene

○Youhei Miura Miura[1], Kazuki Murai[1], Naoki Yoshioka[1] (1. Keio University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1122-3am-02]

Synthesis of π-extended aromatic azo compounds and their functional evaluation

○Yurina Kozu[1], Hayato Yamada[1], Kazuma Amaike[1], Kenichiro Itami[1] (1. Nagoya University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1122-3am-03]

Synthesis and properties of tetratia[8]circulene having hydrogen bon

○Takahiro Minoura[1] (1. University of Hyogo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1122-3am-04]

Synthesis and properties of cyclobutatricyclopentatetraphenylene via an unexpected 4-membered-ring formation reaction

○Soshi Hirota[1,2], Sachiko Nakano[1], Haruki Sugiyama[1,2,3], Yasutomo Segawa[1,2] (1. Institute for Molecular Science, 2. SOKENDAI, 3. CROSS)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1122-3am-05]

Synthesis and characterization of multi-electron reduced species of oligo(pentafulvalene)s bearing a 1D fragment of C_{60}

○Zhe Wang[1], Shu Takagi[2], Aiko Fukazawa[1] (1. WPI-iCeMS, Kyoto University, 2. Graduate School of Engineering, Kyoto University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1122-3am-06]

Synthesis and Characteristics of Non-Alternant Hydrocarbons Possessing a Planar Octagon

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

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1122-3am-07]

[3+2]cycloadditions for multifaced applications of molecular nanocarbons

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○Rikuou Tanase[1], Sajan Pradhan[4], Jean Bouffard[4], Kazuma Amaike[2], Kenichiro Itami[2,3] (1. School of Science, Nagoya University, 2. Graduate School of Science, Nagoya University, 3. Institute of Transformative Bio-Molecules, 4. Department of Chemisry and Nanoscience, Ewha womans University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1122-3am-08]

Synthesis of polycyclic compounds by [2+2]cyclobutene formation reaction of anthracene and DDQ

○Masahiko Fukumoto[1], Satoru HIroto[1] (1. The Univ. of Kyoto)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1122-3am-09]

Iterative synthesis of long-chain oligo(pentafulvalene)s

○Shu I. Takagi[1], Zhe Wang[1], Masahiro Hayakawa[1], Aiko Fukazawa[1] (1. Kyoto University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1122-3am-10]

One-shot Synthesis of π-Conjugated Cations by Formal C^{4+} Introduction

○Daisuke Doi[1], Masahiro Hayakawa[1], Ryosuke Sowa[1], Takuji Hatakeyama[1] (1. Kyoto University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1122-3am-11]

Synthesis and Properties of Adamantane-Annulated Molecular Nanographenes

○Miyuka Ogawa[1], Takaku Yoshihara[1], Kenichiro Itami[1], Akiko Yagi[1] (1. Nagoya University)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1122-3am-12]

Controlling the Frontier Molecular Orbitals and Photophysical Properties of Boron Tropolonate Complexes by Regioselective Functionalization

○Hikari Ogoshi Ogoshi[1], Shunichiro Ito[1], Kazuo Tanaka[1] (1. Grad.Sch. of Eng., Kyoto Univ.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1122-3am-13]

The Effect of Fused Rings on the Coordination Ability of Antiaromatic Hydrocarbons to Ni(0) Center

○Riina Kuwata[1], Takefumi Imanishi[1], Shota Hasegawa[2], Yuta Uetake[3], Junichi Usuba[2], Kosuke Yasui[2], Aiko Fukazawa[2] (1. Graduate School of Engineering, Kyoto University, 2. Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, 3. Graduate School of Engineering, Osaka University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1122-3am-14]

Synthesis of Thiazolochlorin Compounds and Their Optical Properties

○Shu Miyawaki[1], Takeo Nakano[1] (1. Shinshu University)

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

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[E1122-3am-15]

Synthesis and physical properties of thienocyclopenta-fused pyrenes

○Kenji Tsukamoto[1], Koji Takagi[2], Yasutomo Segawa[1,3] (1. Institute for Molecular Science, 2. Grad. Sch. Eng., Nagoya Institute of Technology, 3. SOKENDAI)

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

Wed. Mar 20, 2024 1:00 PM - 3:20 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:20 AM UTC
E1123(1123, Bldg. 11 [2F])

[E1123-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Gaku Fukuhara, Yuki Nagai

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1123-3pm-01]

Chiral recognition mediated by a photoresponsive dinuclear Eu(III) complex

○Midori Ishitsuka[1], Chiasa Motoki[1], Junpei Yuasa[1] (1. Tokyo University of Science)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1123-3pm-02]

Self-aggregation of bacteriochlorophyll-*d* analogs with linear and branched alkyl chains at the 17-position

○Nobuyuki Hara[1], Hitoshi Tamiaki[1] (1. Ritsumeikan University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1123-3pm-03]

Synthesis and optical properties of light-harvesting antenna models using peptide-chlorophyll conjugates

○Ryoko Nakajyo[1], Masahiro Higuchi[1], Hitoshi Tamiaki[2], Shogo Matsubara[1] (1. Grad.Sch. of Eng.,Nagoya Inst. of Tech., 2. Graduate School of Life Sciences, Ritsumeikan Univ.)

English
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1123-3pm-04]

Ion recognition ability and guest uptake/release kinetics of cobalt(III) macrocyclic metallohosts bearing bulky amine ligands

○Dejan Walter[1], Yoko Sakata[1,2], Shigehisa Akine[1,2] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1123-3pm-05]

Synthesis of a Hexabenzocoronene Radical Cation Having Double-concave Structure and Its Photophysical Properties in near-IR and IR Region

○Souta Uno[1], Shuichi Suzuki[1], Takeshi Naota (1. Osaka Univ.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1123-3pm-06]

Control of Photophysical and Magnetic Properties of Dihydrophenazine Radical Cation Salts during Solid-Liquid Phase Transitions

○Ritsuki Tanaka[1], Shuichi Suzuki[1], Takeshi Naota (1. Osaka Univ.)

Japanese

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

[E1123-3pm-07]

Synthesis and properties of salen-type cryptophane complexes that can close the aperture

○Zongjiang Yu[1], Yoko Sakata[2,3], Shigehisa Akine[2,3] (1. Grad. Sch. of Front. Sci., Kanazawa Univ., 2. Grad. Sch. of Natl. Sci. and Tech., Kanazawa Univ., 3. NanoLSI., Kanazawa Univ.)

Japanese

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

[E1123-3pm-08]

Construction of nanovesicles by self-assembly of oligoproline derivatives and its properties

○Shogo Matsubara[1], Yui Okamoto[1], Masahiro Higuchi[1] (1. Graduate School of Engineering, Nagoya Institute of Technology)

Japanese

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

[E1123-3pm-09]

Encapsulation of Multinuclear Copper Clusters by Aromatic Micelles and its Emission Enhancement

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

Japanese

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

[E1123-3pm-10]

Preparation and Self-Assembly of Dumbbell-shaped Aromatic Amphiphiles

○Aguri Sugawara[1], Kazuki Toyama[1], Lorenzo Catti[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

English

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

[E1123-3pm-11]

Oligomerization of Bent Anthracene Dimers via Imine-based Dynamic Covalent Bonds

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

Japanese

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

[E1123-3pm-12]

Minimal double-stranded β-helices formation by metal cross-linking

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

Japanese

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

[E1123-3pm-13]

Development of giant spheres using small molecules through hydrogen-bonding networks

○Shoya Ogawa[1], Ken Yamanomoto[1], Kohei Endo[1] (1. Tokyo University of Science)

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

Wed. Mar 20, 2024 1:00 PM - 3:20 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:20 AM UTC
E1131(1131, Bldg. 11 [3F])

[E1131-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Koki Ikemoto, Yoichi Sasaki

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1131-3pm-01]

Cooperative photochemical reaction and crystal shape change in dimethyl 1,4-phenylenediacrylate single crystals

○Rei Tomoda[1], Daichi Kitagawa[2,3], Seiya Kobatake[2,3] (1. Osaka City Univ., 2. Grad. School of Eng., Osaka City Univ., 3. Grad. School of Eng., Osaka Metropolitan Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1131-3pm-02]

Image-based Machine Learning Prediction for Mixing Ratio of Solids from Droplet Drying

○Taichi Sano[1], Hayato Shirakura[1], Yuki Ide[2], Sheng Hu[2], Ichigaku Takigawa[2,3], Yasuhide Inokuma[1,2] (1. Grad. Sch. Eng, Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. CIREDS, Kyoto Univ.)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1131-3pm-03]

Controlling Molecular Alignment of Perylene Chromophores in Crystals and Photon Upconversion Properties

○Hayato Shoyama[1], Naoyuki Harada[1], Yoichi Sasaki[1], Tsubasa Kashino[2], Nobuo Kimizuka[1,3] (1. Grad. Sch. Eng., Kyushu Univ., 2. Nissan Chemical Corporation, 3. CMS, Kyushu Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1131-3pm-04]

Accumulation of interaction sites for ion recognition via folded conformations of flexible molecules enforced by confinement

○Takahiro Nakagawa[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The University of Tokyo, 2. Institute for Molecular Science)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1131-3pm-05]

Optical control of diarylethene crystals that exhibit elastic and plastic deformation by mechanical stimulation

○Jun Fukuchi[1], Ryo Nishimura[1], Masakazu Morimoto[1] (1. Rikkyo University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1131-3pm-06]

Phenanthrene boronate co-crystals with long-persistence luminescence

○Natsumi Sugawara[1], Masato Ito[1], Yuji Kubo[1] (1. Tokyo Metropolitan University)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1131-3pm-07]
Crystal structure and solid state luminescent properties of pyrrole derivatives

○Toru Okawara[1], Mike Sithole[1], Yu-Hui Lim[1], Toshikazu Ono[2,3] (1. NIT KIT, 2. Kyushu Univ., 3. CMS, Kyushu Univ.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1131-3pm-08]
Creating Conductive Molecular Materials through a Hydrogen Bonding Framework in Naphthalene diimide derivatives

○yusei yamamoto[1], iguchi hiroaki[3], yu hoshino[1,2], toshikazu ono[1,2] (1. Graduate School of Engineering, Kyushu Univ., 2. Center for Molecular Systems Kyushu Univ. , 3. Graduate School of Engineering, Nagoya Univ.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1131-3pm-09]
Fluorescence observation of polymorphic precipitation process of dibenzoylmethanato boron difluoride complex

○Daichi Ito[1], Yuta Kajihara[3], Yushi Fujimoto[1], Daichi Kitagawa[2], Seiya Kobatake[2], Fuyuki Ito[1,3] (1. Grad. Sch. of Sci. and Tech., Shinshu Univ., 2. Grad. Sch. of Eng., Osaka Metropolitan Univ., 3. Inst. of Edu., Shinshu Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1131-3pm-10]
Stoichiometry Validation of Supramolecular Complexes with a Hydrocarbon Cage Host by van't Hoff Analyses

○Toshiya M. Fukunaga[1], Yuzuka Onaka[1], Takahide Kato[1], Koki Ikemoto[1], Hiroyuki Isobe[1] (1. The University of Tokyo)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[E1131-3pm-11]
Side chains vs side loops in supramolecular polymers

○Masahiro Sugiyama[1], Natsumi Fukaya[1], Kazunori Sugiyasu[1] (1. Kyoto University)

English
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1131-3pm-12]
Bio-compatible matrix development for triplet dynamic nuclear polarization of pyruvate

○Jiarui Joey SONG[1], Sakamoto Keita[2], Tateishi Kenichiro[3], Uesaka Tomohiro[3], Yanai Nobuhiro[2] (1. Sch. of Eng., Kyushu Univ , 2. Grad. Sch. of Eng., Kyushu Univ , 3. RIKEN Nishina Center for Accelerator-Based Science)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1131-3pm-13]
Phosphonic acid recognition of a diamidine having a tetraphenylethylene unit

○Kohei Matsushima[1], Hiroki MURAKAMI[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

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

Wed. Mar 20, 2024 9:00 AM - 11:10 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:10 AM UTC
E1131(1131, Bldg. 11 [3F])

[E1131-3am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Kenji Higashiguchi, Toshikazu Ono

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1131-3am-01]

Synthesis and fluorescent properties of pyridine-type BODIPY analogues

○Hideaki Hashimoto[1], Raita Goseki[1], Motoyasu Kobayashi[1] (1. Kogakuin Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1131-3am-02]

Photoexcited States and Photostabilization Mechanism of a Photostabilizer, Dioctyl 4-Hydroxy-3,5-Dimethoxybenzylidenemalonate

○Kanma Igarashi[1], Mikio Yagi[2], Azusa Kikuchi[2] (1. Yokohama National University Faculty of Science and Engineering, 2. Yokohama National University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1131-3am-03]

Spectral and structural behaviors of naphthalimide-containing spiropyran in aqueous media

○Taku Oshima[1], Yasuhiro SHIRAISHI[2], Takayuki HIRAI[2] (1. Osaka University Graduate School, 2. Osaka University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1131-3am-04]

Supramolecular Assembly of Amphiphilic Diarylethene Showing Phase Transition between LCST Hydrated Phases.

○Yodai Yoshikawa[1], Kenji Higashiguchi[1], Kenji Matsuda[1,2] (1. Kyoto University, 2. FIFC, Kyoto Univ.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1131-3am-05]

Diarylethene Dimer Showing NIR Absorption upon Stepwise Stimuli of Photoirradiation and Redox

○Kurumi Satake[1], Naoto Ootsuki[1], Kenji Higashiguchi[1], Kenji Matsuda[1,2] (1. Kyoto University, 2. FIFC, Kyoto Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1131-3am-06]

Syntheses and Spectroscopic Properties of Calixarene-Centered Pentacene Tetramers

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○Kazushi Ishikawa[1], Hayato Sakai[1], Kentaro Harada[2], Takeharu Haino[2], Taku Hasobe[1] (1. Fac. Sci. Tech., Keio Univ., 2. Adv. Sci. Eng., Hiroshima Univ.)

Japanese

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

[E1131-3am-07]

Synthesis and Energy Transfer Properties of Tetracene–Ultrasmall Au Nanocluster Dyads

○Sunao Hiramatsu[1], Mana Nakamoto[2], Aoi Akiyama[2], Hayato Sakai[1], Yuchi Negishi[2], Taku Hasobe[1] (1. Fac. of Sci. Tec., Keio Univ., 2. Fac. of Sci., Tokyo Univ. of Sci.)

Japanese

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

[E1131-3am-08]

The effect of additional hydroxy compounds on the excited state intermolecular proton transfer reaction of pyrene-urea compounds

○Leyun Huang[1], Yoshinobu Nishimura[1] (1. University of Tsukuba)

Japanese

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

[E1131-3am-09]

Synthesis and Spectroscopic Properties of Hydrophilic Acene Derivatives

○Naoya OKUBO[1], Hayato SAKAI[1], Keigo NONAKA[2], Yoshimitsu SAGARA[2], Taku HASOBE[1] (1. Keio University, 2. Tokyo Institute of Technology)

Japanese

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

[E1131-3am-10]

Synthesis of *N*,*N*-type imidazo[1,2-*a*]pyridine–BF_2 complexes and photocytotoxicity

○Itsuki Ogawa[1], Shoko Ueta[2], Keiji Minagawa[2], Fumitoshi Yagishita[2,3] (1. Tokushima Univ., 2. Grad. School, Tokushima Univ. , 3. Inst. pLED, Tokushima Univ.)

Japanese

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

[E1131-3am-11]

Near-Infrared Photosensitizer-Carbon Nanohorn Composites for the Treatment of Peri-implantitis

○Yuta Takano[1], Eri Hirata[1], Daisuke Konishi[1], Yukari Maeda[1], Natsumi Ushijima[1], Masako Yudasaka[2], Atsuro Yokoyama[1] (1. Hokkaido Univ., 2. Meijo Univ.)

Japanese

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

[E1131-3am-12]

Synthesis of Thiophene-fused Polycyclic Aromatic Hydrocarbons Using Photocyclization–Dehydrogenation Reaction

○Yusuke Tokuyama[1], Takuya Ogaki[1], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ.)

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

Wed. Mar 20, 2024 9:00 AM - 11:20 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:20 AM UTC
E1132(1132, Bldg. 11 [3F])

[E1132-3am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Hisanori Senboku, Kenta Tanaka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1132-3am-01]

Electrochemical Synthesis of Dibenzothiophene Dioxides from Biaryl Sulfonyl Hydrazides

○Yasuyuki Okumura[1], Koichi Mitsudo[1], Seiji Suga[1] (1. Division of Applied Chemistry, Graduated School of Natural Science and Technology, Okayama University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1132-3am-02]

Investigation of the Possibility of Two-step Synthesis of Firefly Luciferin from Tetrachloroethylene

○Kouichi Matsumoto[1], Emi Murai[1], Yuta Fujiki[1], Akiko Kuwabara[2], Masafumi Kobayashi[2] (1. Kindai Uni., 2. Kanto Denka Kogyo Co., Ltd.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1132-3am-03]

Kinetics study of O-C glycoside rearrangement and its synthetic application using flash electro synthesis

○Yiyue Yao[1], Yosuke Ashikari[1], Masahiro Takumi[1], Aiichiro Nagaki[1] (1. The Univ. of Hokkaido)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1132-3am-04]

α-Aminoalkylation of Sulfonylheteroarenes with Amines and Aldehydes by Cathodic Reduction

○Kyohei Yonekura[1], Kotaro Sekinishi[1], Eiji Shirakawa[1,2] (1. School of Biological and Environmental Sciences, Kwansei Gakuin University, 2. CREST, JST)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1132-3am-05]

Effect of Supporting Electrolyte on the Selective Electrochemical Decarboxylative Olefination of Carboxylic Acids

○Tasuku Ito[1], Xiongjie Jin[1], Kyoko Nozaki[1] (1. Grad. Sch. of Engineering, The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1132-3am-06]

Electrochemical Carboxylation of Benzyl Alcoholes

○Hisanori Senboku[1], Mizuki Hayama[1] (1. Hokkaido University)

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Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1132-3am-07]
Electrochemical intramolecular C-N bond formation using π-extended bromoarene mediator and its kinetic analysis

○Atsuki Hirama[1], Shohei Yoshinaga, Naoki Shida[1], Mahito Atobe[1] (1. Yokohama Natonal University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1132-3am-08]
One-step Synthesis of Diarylacetylenes from Tetrachloroethylene and Arylboronic Acids under Silica-gel by Using Suzuki Coupling Reaction

○Hiyono Suzuki[1], Akiko Kuwabara[2], Masafumi Kobayashi[2], Kouichi Matsumoto[1] (1. Kindai University, 2. KANTO DENKA KOGYO CO.,LTD.)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1132-3am-09]
Strongly Reducing Helical Phenothiazines as Recyclable Organophotoredox Catalysts

○Kenta Tanaka[1], Haru Ando[2], Hiroyoshi Takamura[2], Kadota Isao[2] (1. Okayama Univ. Research Institute for Interdisciplinary Science, 2. Okayama Univ.Department of Chemistry, Graduate School of Natural Science and Technology)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1132-3am-10]
Preparation of Au:CNT electrocatalysts and their application to the aerobic oxidation of alcohols

○Honoka Nakamura[1], Rento Yabuki[1], Yuta Uetake[1,2], Taiyo Shimizu[3], Ken Kokubo[3], Hidehiro Sakurai[1,2] (1. Osaka University, 2. ICS-OTRI, 3. Advanced Industrial Science and Technology)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1132-3am-11]
Magnesium-promoted reductive C-C bond formation of diphenylfulvene derivatives

○Ryunosuke Koyama[1], Tianyuan Zhang[1], Hirofumi Maekawa[1] (1. Nagaoka University of Technology)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1132-3am-12]
Visible-light-induced [4+2] Cycloadditions of *o*-Quinone Methides for the Synthesis of Chromanes.

○Sakura Kodaki[1], Kenta Tanaka[2], Hiroyosi Takamura[3], Isao Kadota[3] (1. School of Science, Okayama University, 2. Research Institute for Interdisciplinary Science Research Institute for Interdisciplinary Science, 3. Graduate School of Natural Science and Technology, Okayama University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1132-3am-13]
Investigation on the reaction conditions for the electrocatalytic hydrogenation of nitrogen-containing aromatic compounds in an AEM reactor

○Akizumi Yonezawa[1], Yugo Shimizu, Juri Harada[1], Naoki Shida[1], Mahito Atobe[1] (1. Yokohama National university)

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

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC
E1132(1132, Bldg. 11 [3F])

[E1132-3pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Keiichi Imato, Naoki Shida

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1132-3pm-01]

Synthesis and electrochemical characterization of biphenyl multi carboxylate derivatives as anode materials for SIBs

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

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1132-3pm-02]

Electrogenerated Acid Promoted Claisen Rearrangement of Allyl Aryl Ethers

○Yuta Niki[1], Eisuke Sato[1], Seiji Suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1132-3pm-03]

Divergent Synthesis of Benzolactones via Electrochemical C−O Bond Formation

○Yuma Hironaka[1], Koichi Mitsudo[1], Seiji suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1132-3pm-04]

Photocatalytic carbon-carbon bond forming reactions using recyclable alkyl radical precursors

○Shuta Horiuchi[1], Kenta Tanaka[2], Hiroyoshi Takamura[1], Isao Kadota[1] (1. Department of Chemistry, Graduate School of Natural Science and Technology, Okayama University, 2. Research Institute for Interdisciplinary Science, Okayama University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1132-3pm-05]

Development of the electrochemical N2 gas insertion reaction into carbonyl compounds

○Fumiya Kokudai[1], Minami Fukuhara[1], Yutaka Saga[1], Tetsuya Kambe[1], Mio Kondo[2,1,3], Shigeyuki Masaoka[1] (1. Osaka University, 2. Tokyo Institute of Technology, 3. Precursory Research for Embryonic Science and Technology)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1132-3pm-06]

Paired Electrosynthesis of β-Nitroalcohols Using an Electrogenerated Base

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○Haruka Homma[1], Ruka Hasegawa[1], Tomohiro Yokoyama[1], Toshiki Tajima[1] (1. Shibaura Inst. of Tech.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1132-3pm-07]

Anodic Fluorination of Organic Compounds Using Quaternary Ammonium Fluoride-HFIP Complexes

○Aika Mochizuki[1], Haruka Homma[1], Nobutaka Kitajima[1], Toshiki Tajima[1] (1. Shibaura Inst. of Tech.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1132-3pm-08]

Electrochemical post-functionalization of polythiophenes by using aryldiazonium salts

○Satoshi Koiso[1], Kosuke Sato[1], Shinsuke Inagi[1] (1. Tokyo Institute of Technology)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1132-3pm-09]

Polymer Synthesis by Hole Catalytic Cycloaddition Polymerization with Bifunctional Monomers Derived from Isoeugenol

○Ryo Nagaya[1], Tatsuya Seko[1], Naoki Shida[1], Mahito Atobe[1] (1. Yokohama National University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[E1132-3pm-10]

Machine Learning-Supported Reaction Condition Explolation of Cyanomethylation Using Electrochemical Microflow Reactor

○Akine Tani[1], Shunpei Kunimoto[1], Eisuke Sato[1], Seiji Suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

English
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1132-3pm-11]

Electrooxidative Dearomatization of Phenols Catalyzed by Bromine Species

○Kai Matsui[1], Muhammet Uyanik[1], Kazuaki Ishihara[1] (1. Nagoya University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1132-3pm-12]

Ritter-type Reaction of Glycosyl Bromides and Alkenes using Arylamines as Photocatalysts

○Hiryu Takinami[1], Naoya Sawada[1], Ziyi Yu[1], Norihiko Sasaki[1], Toshiki Nokami[1], Manabu Abe[2], Tsuyoshi Taniguchi[3], Takashi Koike[4] (1. Tottori University, 2. Hiroshima Univ., 3. IRC3, AIST, 4. Nippon Inst. Tech.)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[E1132-3pm-13]

Deuterodehalogenation of (hetero)aryl halides using PEM reactor

○Kyoko Mandai[1], Yosuke Ashikari[1], Yiyue Yao[1], Aiichiro Nagaki[1] (1. Hokkaido Univ.)

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1133(1132, Bldg. 11 [3F])

[E1133-3am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kei Murakami, Kohei Sekine

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1133-3am-01]

Visible-light-driven borylation of aryl halides by a phosphonium ylide organophotoredox catalyst

○Ren Yamaguchi[1], Masaya Iwasaki[1], Yasunori Toda[1], Hiroyuki Suga[1] (1. Shinshu University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1133-3am-02]

Development of Pd-catalyzed phosphonium cyclopentadienylide (PCPY) synthesis through photo-irradiation

○Takaya Tomoike[1], Shoma Chiba[1], Bumpei Maeda[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1133-3am-03]

Development of Radical Germinations Using Photocatalyst and Digermane

○Haruka Iimuro[1], Shiho Ishigaki, Tomonori Inoue[1], Yuki Nagashima[1], Ken Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1133-3am-04]

Photocatalytic 1,2-Phosphorus-Migrative [3+2] Cycloaddition of Tri(*t*-butyl)phosphine with Alkynes

○Yusuke Masuda[1], Daichi Ikeshita[2], Kosuke Higashida[3], Masaki Yoshida[1], Naoki Ishida[2], Masahiro Murakami[2], Masaya Sawamura[1,3] (1. Hokkaido University, 2. Kyoto University, 3. WPI-ICReDD)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1133-3am-05]

Synthesis of Highly Condensed Benzophosphole Derivatives by Lewis-acid-assisted, Visible-light-promoted Mallory Reaction

○Ikki Kamiyoshi[1], Xu Shibo[1], Kosuke Yasui[1], Koji Hirano[1] (1. The Univ. of Osaka)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1133-3am-06]

Photocatalyzed Construction of Indole-Fused 1,4-Diazepine Derivatives

○Tatsushi Oishi[1], Tatsuhiro Uchikura[1], Takahiko Akiyama[1] (1. Gakushuin University)

Japanese

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

[E1133-3am-07]

π-Lewis Acidic Metal Catalyzed Photochemical Flow Reaction via Activation of Alkynes

○Zen Iwasaki[1], Ryohei Yazaki[1], Ren Obayashi[1], Jun Kikuchi[2], Shigenobu Umemiya[1], Masahiro Terada[1] (1. Grad. School of Science, Tohoku Univ., 2. Grad. School of Pharmaceutical Sciences, Tohoku Univ.)

Japanese

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

[E1133-3am-08]

Synthesis of Cyclic Imides Based on Visible-Light Induced Carbamoylarylation

○Taewoo Ko[2], Di Wu[2], Kohei SEKINE[1,2], Yoichiro KUNINOBU[1,2] (1. IMCE, Kyushu Univ., 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu Univ.)

Japanese

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

[E1133-3am-09]

Aerobic Photooxidation of Alcohols Catalyzed by Azaborine

○Yuri Kikuiri[1], Peiyuan Yang[1], Hiroki Fukumoto[1], Tomohiro Agou[2], Masaru Kondo[3] (1. Ibaraki Univ., 2. Univ. of Hyogo, 3. Univ. of Shizuoka)

Japanese

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

[E1133-3am-10]

Syntheses of heteropolycyclic aromatic compounds with tetrahydro-*b*-carboline structures

○Takuma Yuba[2], Yoshimitsu Tachi[1,2], Masatoshi Kozaki[1,2] (1. Osaka Metropolitan University, 2. Osaka City University)

Japanese

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

[E1133-3am-11]

Development of organic luminescent radicals with hydrophilic-group substituted carbazole donor

○Kosuke Anraku[1], Kenshiro Matsuda[1], Satoshi Miyata[2], Takuya Hosokai[2,3], Satoshi Okada[4], Kazuhiro Nakamura[1], Kohei Nakao[5], Ken Albrecht[5] (1. Graduate School of Science and Engineering, Kyushu Univ., 2. Department of Pure and Applied Chemistry, Tokyo Univ. of Sci., 3. AIST, 4. Laboratory for Chemistry and Life Science, Tokyo Tech., 5. IMCE, Kyushu Univ.)

Japanese

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

[E1133-3am-12]

A novel conversion of ionic liquids containing a diol unit in the cationic part to alkenylammonium salts

○Runa Sasakura[1], Takuji Kawamoto[1], Akio Kamimura[1] (1. Yamaguchi University)

Japanese

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

[E1133-3am-13]

Preparation of bicyclic dihydrosiloles via radical cascade reaction of 1,6-enynes.

○Yuki Kanda[1], Kanako Ishido[1], Takuji kawamoto[1], Akio Kamimura[1] (1. Yamaguchi University)

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-3am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kohsuke Aikawa, Motohiro Yasui

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1141-3am-01]

Synthesis of 3-CF_3-indoles from HFO-1234ze *via* cross coupling and intramolecular cyclization

○Futa Yotsume[1,2], Shota Mizuno[2], Runa Kasahara[3], Takeshi Fujita[2], Munenori Inoue[2], Jyunji Ichikawa[2] (1. Kitasato University, 2. Sagami Central Resarch Institute, 3. University of Tsukuba)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1141-3am-02]

Aminofluorination of alkenes utilizing with N–F reagents under copper catalysis

○Akiya Adachi[1], Yuki Ito[1], Takuya Hashimoto[2], Kohsuke Aikawa[1], Kyoko Nozaki[1], Takashi Okazoe[1,3] (1. The School of Engineering, The University of Tokyo, 2. RIKEN, 3. AGC Inc.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1141-3am-03]

Synthesis of perfluorocycloalkyl compounds using fluorine gas and their property

○Toshiki Nakajima[1], Koji Kadota[1], Masafumi Sugiyama[1], Kohsuke Aikawa[1], Daisuke Kawaguchi[1], Takashi Okazoe[1,2] (1. Graduate School of Engineering, The University of Tokyo, 2. AGC Inc.)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1141-3am-04]

Ventures into the Sulfur-Fluorine World

○Tim Gatzenmeier[1], Yue Liu[1], Misato Akamatsu[1], Takashi Okazoe[2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. Materials Integration Laboratories, AGC Inc., Tokyo, Japan)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1141-3am-05]

Mechanochemical S_NAr fluorination

○Tetsu Makino[1], Tamae Seo[1], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1141-3am-06]

Optimization of Visible Light Induced Perfluoroalkylation of Aromatics Using Machine Learning

○Airi Yamaguchi[1], Tomoko Yajima[1] (1. Ocha. Univ)

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Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[E1141-3am-07]
Synthesis of Tetracenes with Fluoroalkyl Groups
○Moe Tasaki[1], Tsuyuka Sugiishi[1], Hideki Amii[1] (1. The Univ. of Gunma)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1141-3am-08]
Direct Addition Reactions of Fluoroform to Aldehydes with Fluoride ions as a base
○Yuki Iwataki[1], Yusuke Higashi[1], Tsuyoshi Kawai[1], Tsumoru Morimoto[1] (1. Nara Inst. Sci. Technol.)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1141-3am-09]
Synthesis of Trisubstituted Fluoroalkenes Enabled by Stereoselective Substitution of Vinyl Sulfoximine
○Masayuki Miyaoka[1], Yuichiro Tomishima[1], Kosuke Yasui[1], Koji Hirano[1] (1. Graduate School of Engineering, Osaka University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1141-3am-10]
Regioselective difluorination of dodecahydro-*closo*-dodecaborate in the presence of α-cyclodextrin
○Hayato Nakamura[1], Kazuki Kurata[2], Tomoyuki Tajima[3] (1. Faculty of environmental science and technology, Okayama University, 2. Graduate school of environmental, life, natural science and technology, Okayama University, 3. Graduate school of environmental, life, natural science and technology, Okayama University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1141-3am-11]
Combination of photoredox catalysts and borates for radicalic difluoromethylation
○Yuen Huang[1], kakeru Konagaya[1], Shigekazu Ito[1] (1. Tokyo Institute of Technology)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1141-3am-12]
Photoredox-catalyzed synthesis of tetrafluoroethylene-containing benzoindene derivatives.
○Mayuka Ukai[1], Motohiro Yasui[1], Shigeyuki Yamada[1], Tsutomu Konno[1] (1. Kyoto Institute of Technology)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1141-3am-13]
Copper-Catalyzed Cross-Coupling Reactions of Perfluoroalkylene Zinc Reagents and Aryl Halides
○Tomoya Baba[1], Daisuke Inoue[2], Kazuya Kubo[3], Tomohiro Agou[3] (1. University of Hyogo, 2. TOSOH FINECHEM CORPORATION, 3. Graduate School of Science, University of Hyogo)

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
E1133(1132, Bldg. 11 [3F])

[E1133-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Akihiro Tsurusaki, Kenichi Michigami

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1133-3pm-01]

Visible-light-induced generations of silyl radicals under neutral conditions and development of silylation reaction

○Mone Suzuki[1], Yuki Nagashima[1], Ken Tanaka[1], Antônio Junio Araujo Dias[1] (1. Tokyo Institute of Technology)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1133-3pm-02]

Synthesis and Optical Property of Dibenzobarrelene Derivatives with Boron Substituents at the Bridgehead Positions

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

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1133-3pm-03]

Synthesis and photophysical properties of new functional λ^5-phosphinines

○Ryusei Ikeda[1], Hidetoshi Ohta[1], Minoru Hayashi[1] (1. Ehime University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1133-3pm-04]

Photoracemization of axially chiral 4,4′-dimethoxy-1,1′-biphenanthrene-2,2′-diol: Inhibitory effect of its analogs and additives on racemization

○Kohei Maruyama[1], Yuya Ishiyama[1], Daiki Kanai[1], Yuichi Kitamoto[1], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1133-3pm-05]

Synthesis of Olefin-bridged Fluorenylidene Indoloindole Bis-π-polycycles Using Pd-Catalyzed Dual C-H Annulative Coupling Strategy

○Sho Aida[1], Masahiro Terada[1], Tienan Jin[1] (1. Tohoku University)

English
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1133-3pm-06]

Synthesis and electrochemical properties of indigo derivatives modified with amino acids

○Mizuha Ujita[1], Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

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

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[E1133-3pm-07]

Synthesis of Chromones via Pd-catalyzed Tandem Acyl Transposition/Intramolecular Cyclization of Enol Esters

○Yosuke Kanda[1], Yoshiki Otawa[2], Kenichi Michigami[1,2], Mitsuhiro Ueda[1,2], Masato Ohashi[1,2] (1. Department of Chemistry, Graduate School of Science, Osaka Metropolitan University, 2. Department of Chemistry, Graduate School of Science, Osaka Prefecture University)

Japanese

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

[E1133-3pm-08]

Synthesis of Silicon-containing Cyclic Compounds by Gold-catalyzed Cyclization Reaction of Aryldiynes

○Kazuto Fuji[2], Kohei Sekine[1,2], Yoichiro Kuninobu[1,2] (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

Japanese

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

[E1133-3pm-09]

Gold(I)-Catalyzed Intramolecular Hydroarylation of Biarylbis(phenylethynyl)phosphine Derivatives

○Akihiro Komura[1], Marii Kishimoto[1], Akihiro Tsurusaki[2], Ken Kamikawa[2] (1. Osaka Prefecture University, 2. Osaka Metropolitan University)

Japanese

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

[E1133-3pm-10]

Development of iridium-catalyzed C(sp^3)-C(sp^2)[1,5]-silyl rearrangement reaction and analysis of its reaction mechanism

○Keigo Watanabe[1], Juwei Qiu[1], Shinsuke Komagawa[1], Tsuyoshi Matsuzaki[2], Makoto Sako[1], Kennichi Murai[1], Takeyuki Suzuki[2], Haruta Junichi[1], Mitsuhiro Arisawa[1] (1. Graduate School and School of Pharmaceutical Sciences, Osaka University, 2. SANKEN, Osaka University)

Japanese

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

[E1133-3pm-11]

Asymmetric [3+2] cycloaddition of acetal imino esters with methyl acrylate catalyzed by chiral silver complexes

○Mizuki Katagiri[1] (1. Chuo University)

Japanese

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

[E1133-3pm-12]

Synthesis of 2,4,6-Triarylpyridines Using Flavin-Catalyzed Aerobic Oxidation of Acetophenones and Benzylamines

○Nozomi Miyazaki[1], Tatsuki Fukuda[2], Hiroki Iida[1,2] (1. Shimane University, 2. Graduate School of Natural Science and Technology,Shimane University)

Japanese

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

[E1133-3pm-13]

Aerobic Oxidative C-C Bond Formations through C-H Activation of Tetrahydroisoquinolines Using Dehydrogenative Oxidation Catalysis of Flavin

○Hazuki Miyake[1], Hiroki Iida[1] (1. Graduate School of Natural Science and Technology, Shimene University)

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Japanese

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

[E1133-3pm-14]

Organic synthesis using cationic indium catalysts-ligand synthesis for the isolation of catalysts

○Kodai Iguchi[1], Manoka Kikuchi[1], Mitsuhiro Yoshimatsu[1] (1. Gifu University)

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kensuke Kiyokawa, Okano Kentaro

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1141-3pm-01]

Hexadehydro Diels–Alder/Alkynyliodanation Cascade

○Shunya Morohashi[1], Liejin Zhou[1], Kazuya Kanemoto[1], Naohiko Yoshikai[1] (1. Tohoku University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1141-3pm-02]

Synthesis of iodinated 1,1′-spirobi[indene] derivatives via double iodocyclization reactions of tetraaryl[4]cumulenes

○Tsubasa Ito[1], Keiji Minagawa[1], Yasushi Imada[1], Fumitoshi Yagishita[1,2] (1. Dept. of Applied Chem., Tokushima Univ., 2. Inst. of pLED, Tokushima Univ.)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1141-3pm-03]

para-Selective Iodination of Phenols and *ortho*-Selective Cyclization with Azadienes

○Weijie Cao[1], Takayoshi Arai[1] (1. Chiba University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1141-3pm-04]

Stereocontrolled Halogen Dance of Bromoimidazolylmagnesium

○Nishimoto Hayato[1], Kengo Inoue[1], Kentaro Okano[1], Atsunori Mori[1,2] (1. Kobe University, 2. Kobe University Center for Membrene and Film Technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1141-3pm-05]

Haloamidation of α,β-C(sp^3)-H to the nitrogen of amide derivatives

○Chiyuki Naito[1], Satoshi Minakata[1] (1. Osaka University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1141-3pm-06]

Stereoselective Diamination of π-Conjugated Molecules utilizing *N*-halosulfonamides

○Ryo Nakajima[1], Satoshi Minakata[1] (1. Osaka University)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1141-3pm-07]

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Convenient Synthesis of Amino-λ^3-iodanes and Their Application to Oxidative Amination

○Shusuke Narita[1], Kazuki Kawanaka[1], Kensuke Kiyokawa[1], Satoshi Minakata[1] (1. Osaka University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1141-3pm-08]

Pyrrolidine-Thiazolium Conjugated Chiral Ionic Liquid Catalysts for Stetter Reaction

○Masaaki Tokunaga[1], Syunsuke Kimura[1], Yuichi Isikawa[2], Satoshi Kitaoka[3], Kaoru Nobuoka[2] (1. Graduated School of Engineering, Oita University, 2. Faculty of science and Technology, Oita University, 3. Faculty of Engineering, Kindai University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1141-3pm-09]

Development of methods for catalytic conversions of indoles via the hydrosilylation of carbon dioxide

○Sha Li[1], Shoko Nakahara[1], Reito Yasui[1], Taishin Adachi[1], Takumi Murata[1], Chihiro Maeda[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Technol., Okayama Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1141-3pm-10]

Carbamoylarylation of Alkenes with *N*-Aryl Oxamic Acids Involving 1,4-Aryl Migration via C(aryl)–N Bond Cleavage

○Akira Shiozuka[2], Di Wu[2], Kyohei Kawashima[1], Toshifumi Mori[1,2], Kohei Sekine[1,2], Yoichiro Kuninobu[1,2] (1. IMCE, Kyushu Univ. , 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu Univ.)

English
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1141-3pm-11]

Catalytic Asymmetric *exo*-Selective [3+2] Cycloaddition of Iminoesters with Nitroalkenes Using Imidazoline-Proline-*t*Butyl ester-Copper Complex

○Yan Yu[1], Takayoshi Arai[1] (1. Chiba university)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1141-3pm-12]

A mechanistic study on radical cascade reaction of 1,6-enyne precursors using cyclopropylacetylene.

○KANAKO ISHIDO[1], Yuki Kanda[2], Takuji Kawamoto[2], Akio Kamimura[2] (1. Yamaguchi-University, 2. Yamaguchi University Engineering Faculty)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[E1141-3pm-13]

Lewis acid-promoted preparation of nitrones from nitroso compound

○Masaya Maegawa[1], Takuya Suga[1], Takahiro Soeta[1], Yutaka Ukaji[1] (1. Kanazawa University)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[E1141-3pm-14]

Amination of 2-chloro-benzo[*c*]tetrazolo[2,3-*a*]cinnolinium salt

○Eri Kamiya[1], Tsunehisa Hirashita[1] (1. Nagoya Inst. of Tech.)

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-3vn] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Atsushi Ohtaka, Kohei Sekine

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1141-3vn-01]

Facile Synthesis of α-Aryl Ketones via Grignard Reaction of Benzocyclobutenones

○Yukitaka Hoshi[1], Shinya Tabata[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1141-3vn-02]

Synthesis of *ortho*-Substituted Benzotrifluorides by Deprotonative Transformations

○Yotaro Seki[1], Keisuke Nakamura[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1141-3vn-03]

Facile Synthesis of 2,7-Disubstituted 1,8-Naphthyridine Derivatives

○Takumi Hamada[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi Univ. of Tech.)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1141-3vn-04]

Simple *N*-formylation of secondary amines using DMF as a formylating reagent

○Tomoya Sakaguchi[1], Hibiki Awata[1], Yoshimasa Matsumura[1], Osamu Shimomura[1], Atsushi Ohtaka[1] (1. Osaka Institute of Technology)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[E1141-3vn-05]

Synthesis, structure, and reactivities of tetranuclear silver(I) complex with 1,8-naphtylbis(sulfane)carbon(0) ligand

○Rena Tsukamoto[1], Keiko Noguchi[1], Takayoshi Fujii[1] (1. TheThe Univ. of Nihon)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[E1141-3vn-06]

Catalytic activity and fluorescence property of pyridodipyrimidine derivatives mimicking nicotinamide coenzymes

○Eriko Ohishi[1], Taiga Mizushima[2], Marina Oka[2], Fumitoshi Yagishita[3,4], Yasushi Imada[3], Hiroki Iida[1,2] (1. Shimane University, 2. Graduate School of Natural Science and Technology, Shimane University, 3. Graduate School of Technology, Industial and Social Sciences, Tokushima University, 4. Institute of Post-LED Photonics, Tokushima University)

Japanese

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5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[E1141-3vn-07]

Synthesis and physical properties of chlorophyll derivatives with a newly fused six-membered ring

Hitoshi Tamiaki[1], ○Takuma Imuta[1], Nobuyuki Hara[1], Shin Ogasawara[1] (1. Ritsumeikan University)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
E1142(1142, Bldg. 11 [4F])

[E1142-3am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Kento Ishida, Ryosuke Haraguchi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1142-3am-01]

Enantioselective Synthesis of Triptycene Derivatives by Enzymatic Desymmetrization

○Shiina Noguchi[1], Masayuki Shigeta[1], Mio Ochiai[1], Hikaru Yanai[1], Takashi Matsumoto[1] (1. Tokyo University of Pharmacy and Life Sciences)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1142-3am-02]

Development of synthesis of thioesters from acyl fluorides and thiosilanes

○Ryuki Takeuchi[1], Kento Ishida[1], Norio Sakai[1] (1. Tokyo University of Science)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1142-3am-03]

Copper-catalyzed Aminoazidation of Alkenes with NFC

○Hiroto Kimura[1,2], Kohsuke Aikawa[3], Takuya Hashimoto[2,1] (1. Chiba Univ., 2. RIKEN, 3. Univ. of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1142-3am-04]

Conversion of Oxygenates to Alkenes by TiO_2 and Cobaloxime Dual Photocatalyst System

○Eiki Maruyama[1], Xiongjie Jin[1], Kyoko Nozaki[1] (1. School of Engineering, The University of Tokyo)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1142-3am-05]

Development of 1,3,2-Dioxaborolan-4-one Catalyst for Dehydrative Condensation toward Peptides Synthesis

○Qianchun HUANG[1], Shuhei Ohmura[1], Kazuaki Ishihara[1] (1. Nagoya University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1142-3am-06]

Diastereoselective Alkylation for Construction of 1,3-Nonadjacent Stereogenic Centers Containing a Tetrasubstituted Carbon Center

○Rihaku Ojima[1], Azusa Kondoh[1], Masahiro Terada[1] (1. Graduate School of Science, Tohoku University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1142-3am-07]

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Brønsted Base-Catalyzed Aminooxylation of Allylic- and Benzylic Compounds

○Azusa Kondoh[1], Masahiro Terada[1] (1. Tohoku University)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1142-3am-08]

Synthetic Method for *vic*-Amino Alcohol with Consecutive Tertiary Carbons

○Shiori Takashima[1], Tomoka Watanabe[1], Tomoya Wakana[1], Yu Sakano[2], Ryosuke Haraguchi[1] (1. Graduate School of Engineering, Chiba Institute of Technology, 2. Faculty of Engineering, Chiba Institute of Technology)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1142-3am-09]

Catalyst-Controlled Chemodivergence in Nucleophilic Cyanation to 1,2-Ketoimine

○Tomoka Watanabe[1], Shiori Takashima[1], Tomoya Wakana[1], Yu Sakano[2], Ryosuke Haraguchi[2] (1. Graduate School of Engineering, Chiba Institute of Technology, 2. Faculty of Engineering, Chiba Institute of Technology)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1142-3am-10]

Update of imine-anion mediated Smiles rearrangement: application to migration of electron-neutral/rich aromatic groups

○Shunki Jinno[1], Keiji Mori[1] (1. Tokyo University of Agriculture and Technology)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1142-3am-11]

Development and application of oxidative cleavage reaction of 1,2-diamine

○Wakana Ito[1], Daiki Higuchi[1], Takeshi Sugiyama[2], Kota Hashimoto[1], Satoshi Matsubara[1], Satoshi Minakata[2], Kei Murakami[1] (1. Kwansei Gakuin University, 2. Osaka University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1142-3am-12]

Visible-Light-Induced Aminodifunctionalization of Alkenes

○Asa Tagata[1], Emna Mejri[1], Yohei Shimizu[1,2], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1142-3am-13]

Synthesis and Transformation of Dynamic Chiral N-Arylamide

Yuuya Kawasaki[1,2], ○Rintaro Naoe[2], Kazunobu Igawa[3], Katsuhiko Tomooka[1,2] (1. IMCE, Kyushu Univ. , 2. IGSES, Kyushu Univ. , 3. FAST, Kumamoto Univ.)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1142-3am-14]

New Trivalent Platforms for Sequential Conjugation Methods Based on Selective Azaylide Formations

○Mayo Hamada[1], Gaku Orimoto[1], Suguru Yoshida[1] (1. Tokyo University of Science)

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

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[E1142-3am-15]

New Trivalent Platforms with Azido, Ethynyl, and Fluorosulfonyl Groups

○Takahiro Yasuda[1], Gaku Orimoto[1], Suguru Yoshida[1] (1. Tokyo University of Science)

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1143(1143, Bldg. 11 [4F])

[E1143-3am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Takuji Kawamoto, Yuto Sumida

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1143-3am-01]

Development of a radical addition/cyclization cascade reaction using photoexcited palladium for a synthesis of boronic-ester substituted hetero- and carbocycles

○Takara Fukugaichi[1], Haruki Mizoguchi[1], Haruka Ikeda[1], Akira Sakakura[1] (1. The Univ. of Okayama)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1143-3am-02]

Radical reaction using vinyl cyclic sulfonylamide and allyl bromide

○Takaaki Maejima[1], Moeri Terauchi[1], Akio Kamimura[1], Takuji Kawamoto[1] (1. Yamaguchi University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1143-3am-03]

Radical reaction using vinyl triflates and vinyl acetate

○Muramatsu Kenshin[1], Akio Kamimura[1], Takuji Kawamoto[1] (1. Yamaguchi University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1143-3am-04]

Development of Water-Soluble Caged Acetylcholine

○Rikako Nakamura[1], Yuto Sumida[2], Satoshi Arai[3], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. IBB, Tokyo Med. & Dent. Univ., 3. WPI-NanoLSI, Kanazawa Univ.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1143-3am-05]

Synthesis and Application of α-Boryl-α-Silyl Alkylamine

○Koh Watanabe[1], Kazunori Nagao[2], Hirohisa Ohmiya[2] (1. Grad. Sch. Med. Sci., Kanazawa Univ., 2. ICR, Kyoto Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1143-3am-06]

Development of Non-nucleophilic Electron Donor Catalysts and Their Applications to Photoreactions

○Airi Tanaka[1,2], Takuya Hashimoto[1,2] (1. Chiba Univ., 2. RIKEN)

English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1143-3am-07]

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Copper-Ligand-to-Metal Charge Transfer Photocatalysis Involving Halogen-Atom-Transfer in Alkene Difunctionalization

○Subrata Mukherjee[1], Shintaro Kawamura[1,2], Mikiko Sodeoka[1,2] (1. RIKEN, CSRS, 2. RIKEN, CPR)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[E1143-3am-08]

C-Glycosylation of Photo-Excitable Glycosyl Borate

○Yusuke Miyamoto[1], Sho Murakami[1], Yuto Sumida[2], Go Hirai[3], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. IBB, Tokyo Med. & Dent. Univ., 3. Grad. Sch. Phar. Sci., Kyushu Univ.)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1143-3am-09]

Synthesis of Azetidine via C(sp3)–H Activation by A Light-Driven Triple Catalysis

○Masanari Nakagawa[1], Kazunori Nagao[1], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ.)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1143-3am-10]

para-Selective Alkylation of Aromatic Carboxylic Acid Derivatives Using Organic Photoredox Catalyst and Trialkylphosphine

○Ryoto Oya[1], Kazunori Nagao[1], Hirohisa Ohmiya[1] (1. Kyoto University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1143-3am-11]

Regioselective C(sp3)-H Alkylation of Tetrahydrofuran Derivatives by Photoredox Catalysis

○Reiji Abe[1], Kazunori Nagao[1], Tomohiro Seki[2], Dai Hata[2], Yusuke Sasaki[2], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. Takeda Pharmaceutical Company Limited)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1143-3am-12]

Csp3–Csp3 Bond Cleavage of Benzyl Alcohol via Benzophenone-type Organic Photocatalysis

○Tomotoki Matsuo[1], Masaki Sano[2], Yuto Sumida[3], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. Grad. Sch. Med. Sci., Kanazawa Univ., 3. IBB, Tokyo Med. & Dent. Univ.)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1143-3am-13]

Enantioselective Radical Cation [2+2] Cycloaddition by Chiral Iron(III) Photoredox Catalysis

○Kei Katagiri[1], Shuhei Ohmura[1], Sho Miyakawa[2], Jun-ya Hasegawa[2], Kazuaki Ishihara[1] (1. Nagoya University, 2. Hokkaido University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1143-3am-14]

Development of Chiral Iron(III) Photoredox Catalysts for Enantioselective Radical Cation [4+2] Cycloaddition Toward Natural Product Synthesis

○Hayato Akao[1], Shuhei Ohmura[1], Kazuaki Ishihara[1] (1. Nagoya University)

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
E1143(1143, Bldg. 11 [4F])

[E1143-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Koji Kubota, Shinichiro Fuse

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1143-3pm-01]

Chemoselective control of arylpotassium apecies by a flow reaction system using Schlosser superbases

○Hiroki Nakayama[1], Shintaro Kamio[2], Kazuhiro Okamoto[1], Aiichiro Nagaki[1] (1. Hokkaido University, 2. Hokkaido University of Science)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1143-3pm-02]

Precise polymerization of styrenes with alkoxysilyl groups using flow microreactor

○Kyosuke Tomite[1], Yuya Yonekura[1,2], Tomoko Kawaguchi[1], Takashi Tamaki[1], Mai Furusawa[2], Yosuke Ashikari[1], Aiichiro Nagaki[1] (1. Hokkaido University, 2. TOHO CHEMICAL INDUSTRY COMPANY,LIMITED)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1143-3pm-03]

Oxidative coupling and related reactions via organocopper reagents generated in a flow microreactor

○Ruka Ebisawa[1], Kazuhiro Okamoto[1], Aiichiro Nagaki[1] (1. Hokkaido University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1143-3pm-04]

Chemoselective generation and reactions of unstable organolithium species based on flowmicro synthesis

○Masatomo Iwata[1], Yosuke Ashikari[1], Aiichiro Nagaki[1] (1. Hokkaido University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1143-3pm-05]

Synthesis of asymmetric azulenes based on controlled organolithium reactions using flow microreactors

○Ryuhei Kikuchi[1], Hiroki Soutome[1,3], Masahiro Takumi[1], Shigeharu Wakabayashi[2], Aiichiro Nagaki[1] (1. Hokkaido University, 2. Suzuka University of Medical Science, 3. AGC Inc.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1143-3pm-06]

Regioselective Mechanochemical Cyclodehydrogenation of Polycyclic Aromatics Compounds

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○Takumu Nakamura[1], Yuta Morinaka[1], Yohei Ono[1], Kenichiro Itami[2], Hideto Ito[2] (1. Tosoh Co., 2. Nagoya Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[E1143-3pm-07]

Synthesis of Arylated Aromatic Compounds by Mechanochemical Anionic Activation of Polycyclic Aromatic Hydrocarbons

○Yoshifumi Toyama[1], Akiko Yagi[1], Kenichiro Itami[1], Hideto Ito[1] (1. Nagoya University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1143-3pm-08]

Development of micro-flow synthesis of unsymmetrical *H*-phosphonate and consideration of details of the reaction

○Yuma Tanaka[1], Hiroshi Kitamura[1], Shinichiro Fuse[1] (1. Graduate School of Pharmaceutical Sciences, Nagoya University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1143-3pm-09]

Development of peptoid chain elongation avoiding diketopiperazine formation utilizing micro-flow technology

○Yuki Okura[1], Yuma Tanaka[1], Shinichiro Fuse[1] (1. Nagoya Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1143-3pm-10]

A Facile Generation of *t*-Butoxycarbonyl Chloride Equivalent and Its Use in a Micro-flow Reactor.

○Kana Miyamoto[1], Ren Okabe, Shinichiro Fuse[1] (1. Nagoya University Graduate School of Pharmacetutical Science)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[E1143-3pm-11]

Micro-flow heteroatom alkylation via TfOH-mediated rapid and in situ generation of carbocation and the following addition of nucleophiles

○Yuma Matsuura[1], Shinichiro Fuse[1] (1. The Univ. of Nagoya)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1143-3pm-12]

Sequential-flow Synthesis of Flecainide Using Continuous-flow Amidation Reaction

○Kota Takeno[1], Haruro Ishitani[1], Masahiro Sasaya[1], Shū Kobayashi[1] (1. The University of Tokyo)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1143-3pm-13]

Improved efficiency of C-H carboxylation using peroxodisulfate in triphasic continuous droplet flow

○Takahide Fukuyama[1], Riku Nagaki[1], Mariko Fuji[1], Ilhyong Ryu[1] (1. Osaka Metropolitan Univ.)

Japanese

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

[E1143-3pm-14]

Nitroxide-mediated polymerization (NMP) initiated by BlocBuilder MA in flow reactors

○Ryo Takabayashi[1], Ilhyong Ryu[1], Takahide Fukuyama[1] (1. Osaka Metropolitan University)

English

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

[E1143-3pm-15]

Catalytic continuous-flow cyclic carbonate synthesis using supercritical CO_2

○Zhibo Yu[1], Haruro Ishitani[1], Shū Kobayashi[1] (1. the University of Tokyo)

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC
E1142(1142, Bldg. 11 [4F])

[E1142-3vn] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Takatsugu Murata, Haruro Ishitani

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1142-3vn-01]

Unified concise syntheses of acyl quercitrin natural products using boronic acid-catalyzed regioselective acylation

○Toshihiro Ishida[1], Yuuki Nakamura[2], Mari Tanikawa[2], Naoyuki Shimada[1] (1. Nihon University, 2. Kitasato University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1142-3vn-02]

Improved Synthesis of a Stereoisomer of 2′-Demethyl-7′-hydroxy-2-methyltanzawaic Acid B Amide at Fused Positions

Takatsugu Murata[1], Hisazumi Tsutsui[1], Fumiya Watabe[1], Daiki Usukura[1], ○Ryo Hirata[1], Hiroki Okano[1], Yamato Kanai[1], Ryunosuke Shiogama[1], Miyuki Natsume[1], Sho Ichikawa[1], Takuma Okamoto[1], Motoyuki Shimonaka[1], Isamu Shiina[1] (1. Tokyo University of Science)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1142-3vn-03]

Synthetic Study of Eushearilide Analog

Takatsugu Murata[1], Shunsei Hiraga[1], ○Shodai Kichi[1], Rio Seki[2], Misako Ohkusu[2], Yasuko Koga[2], Katsuhiko Kamei[2], Akira Watanabe[2], Naruhiko Ishiwada[2], Isamu Shiina[1] (1. Tokyo University of Science, 2. Chiba University)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1142-3vn-04]

Synthetic Study of C_{2v}-Symmetric Violaceoid A Analog

Takatsugu Murata[1], Takuto Iwayama[1], ○Yukiho Kosaka[1], Ryo Nakayama[1], Isamu Shiina[1] (1. Tokyo University of Science)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[E1142-3vn-05]

Development of Lewis Acid Catalysts for Transesterification of P(V) compounds

○Taro Konno[1], Yuki Saito[1], Shū Kobayashi[1] (1. Synthetic Organic Chemistry Lab., Department of Chemistry, Grad. School of Science, The University of Tokyo.)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[E1142-3vn-06]

Synthesis of high-value organophosphates via catalytic phosphonylation/phosphorylation

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○Yuki Saito[1], Shū Kobayashi[1] (1. The University of Tokyo)

Japanese

4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[E1142-3vn-07]

γ-Lactam Synthesis from Cyclobutanones *via N*-Insertion Reaction

○Shota Sakakura[1], Yuhao Wu[1], Kengo Hyodo[1] (1. Kindai University)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[E1142-3vn-08]

Substituent Effects of Sulfonium Salts in The Synthesis of Fullerene Derivatives PCBM by Sulfur Ylide Method

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

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC H933(933, Bldg. 9 [3F])

[H933-3pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Hiroyoshi Takamura, Yoko Yasuno

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H933-3pm-01]

Development of a strain-promoted Diels-Alder rection of vinylated cyclic allene for the convergent construction of carbocyclic skeletons

○Obata Takumi[1], Hirai Taiki[1], Mizoguchi Haruki[1], Sakakura Akira[1] (1. The Univ. of Okayama)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H933-3pm-02]

Development of the stereoselective decarboxylative radical coupling at an angular position toward the synthesis of polycyclic terpenoid

○Naochika Matsumaru[1], Haruki Mizoguchi[1], Akira Sakakura[1] (1. Okayama University)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H933-3pm-03]

Synthesis of diverse alkaloidal scaffolds using Au(I) catalysts

○Kiyoshi Shimohata[1], Mana Moriguchi[2], Hiroki Oguri[1] (1. The University of Tokyo, 2. Tokyo University of Agriculture and Technology)

English
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H933-3pm-04]

Development of one-pot dimerization reaction of azepinoindole scaffold

○Tomohiro Yoshida[1], Nobuto Kaneko[1], Hiroki Oguri[1] (1. The Univ. of Tokyo)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H933-3pm-05]

Total Synthesis of Indolizidine Alkaloids by Reductive Synthesis of Nitrones

○Sora Iwamoto[1], Toshitaka Okamura[1], Takaaki Sato[1] (1. Keio Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[H933-3pm-06]

Development of Iridium-Catalyzed Reductive (3+2)-Annulation of Lactams

○Kento Yamada[1], Yasukazu Sugiyama[1], Daiki Kaneko[1], Yuya Kusagawa[1], Toshitaka Okamura[1], Takaaki Sato[1] (1. Keio Univ.)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H933-3pm-07]

Synthetic Study of QR Ring System of Brevisulcenal-F

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○Tomoya Sato[1], Kenta Tanaka[1], Isao Kadota[1], Hiroyoshi Takamura[1] (1. Okayama University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[H933-3pm-08]

Synthetic Studies on Loritrem B

○Tomonori Teranishi[1], Keisuke Nishikawa[1], Yosiki Morimoto[1] (1. Osaka Metropolitan University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H933-3pm-09]

Synthetic studies on a diterpene with hedgehog signaling pathway inhibitory activity

○Kazuaki Maeno[1], Yuichi Orita[1], Yuichi Ishikawa[1] (1. Graduate School of Nanobioscience, Yokohama City University)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H933-3pm-10]

Synthetic Study of the ABCDEF Ring of Maitotoxin

○Tatsuya Teshigawara[1], Kenshiro Fuse[1], Yuhei Suzuki[1], Yoko Yasuno[1], Tohru Oishi[1] (1. Kyushu University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[H933-3pm-11]

Synthetic Study of the QRSTU Ring of Maitotoxin

○Hiroshi Yamaguchi[1], Takahiro Harada[1], Keitaro Umeno[1], Yoko Yasuno[1], Tohru Oishi[1] (1. Kyushu University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[H933-3pm-12]

Synthesis and Biological Activity of the Macrolactone Moiety of Scytophycin B

○Mayu Namiki[1], Shusei Sato[1], Takayuki Ohyoshi[1], Hideo Kigoshi[1] (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[H933-3pm-13]

Evaluation of Antioxidant Activity of Humic Substances Obtained from Fermented and Aged Softwood Chip Compost

○Yuki Tsutaho[1], Yasushi Kojima[2], Hiroki Hotta[1,3], Yoshio Tsujino[3] (1. Graduate School of Maritime Sciences, Kobe University, 2. KEI TWO COMMUNICATIONS , 3. Graduate school of Science, Technology and Innovation, Kobe university)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[H933-3pm-14]

Isolation and structure determination of new polyketides containing a terminal alkyne from a marine cyanobacterium collected at Hateruma Island

○Hiroto Saima[1], Kousuke Dodo[2], Mikiko Sodeoka[2], Arihiro Iwasaki[1] (1. Chuo University, 2. RIKEN)

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC H935(935, Bldg. 9 [3F])

[H935-3pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Arihiro Iwasaki, Gosuke Hayashi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H935-3pm-01]

Isolation and structure determination of a new peptide from a marine cyanobacterium *Okeania* sp.

○Natsumi Watanabe[1], Arihiro Iwasaki[1] (1. Chuo University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H935-3pm-02]

Isolation and structure determination of a new peptide from marine cyanobacteria collected at Hateruma Island

○Kensuke Irie[1], Arihiro Iwasaki[1] (1. Chuo University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H935-3pm-03]

Isolation, Structure Determination, Total Synthesis and Biological Activity of New Lipopeptide; Ukabamide

○Masahiro Hagihara[1], Raimu Taguchi[1], Arihiro Iwasaki[2], Ghulam Jeelani[3], Tomoyoshi Nozaki[3], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. Faculty of Science and Technology, Keio Univ., 2. Faculty of Science and Engineering, Chuo Univ., 3. Graduate School of Medicine, The Univ. of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H935-3pm-04]

The structure and bioactivity of a new lipopeptide from an unidentified marine cyanobacterium

○Kazuki Wakai[1], Kairi Umeda[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. Keio university)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H935-3pm-05]

Isolation, Structure Determination, and Total Synthesis of Antimalarial Peptide, Hiyajyamine, from Marine Cyanobacterium

○Kairi Umeda[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. The Univ. of Keio)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H935-3pm-06]

Synthetic study of hedoamide, a new linear peptide from marine cyanobacteria

○Asaya Nakura[1], Naoaki Kurisawa[1], Arihiro Iwasaki[2], Kiyotake Suenaga[1] (1. Keio Univ., 2. Chuo Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

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[H935-3pm-07]

Synthetic study of iezoside-alkyne probe to identify the binding site on SERCA

○Akari Noto[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. Faculty of Science and Technology, Keio Univ.)

Japanese

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

[H935-3pm-08]

A novel uric acid production inhibitor from Okinawan marine cyanobacterium

○Sein Higa[1], Kazumasa Yagisawa[1], Noriyuki Natsume[3], Toshiaki Teruya[1,2] (1. Graduate School of Engineering and Science, University of the Ryukyus, 2. Faculty of Education, University of the Ryukyus, 3. NatuPharma Ryukyus Co., Ltd.)

Japanese

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

[H935-3pm-09]

Interspecies differences in submandibular gland components in shrews, venomous insectivorous mammals

○Nozomi Hara[1], Yusuke Yano[2], Ryo Fukuoka[2], Satoshi Ohdachi[3], Masaki Kita[2] (1. School of Agricultural Sciences, Nagoya University, 2. Graduate School of Bioagricultural Sciences, Nagoya University, 3. Institute of Low Temperature Science, Hokkaido University)

Japanese

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

[H935-3pm-10]

Concise synthesis of polyamine analogs for fluorescent labeling

○Taiga Ohnishi[1], Raku Irie[1], Masato Oikawa[1] (1. Yokohama City University)

Japanese

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

[H935-3pm-11]

Structural analysis of AcuPep, a peptide moiety of aculeines

○Raku Irie[1], Yumi Irie[2], Satoko Matsunaga[3], Ryuichi Sakai[4], Kazuhiro Irie[2], Masato Oikawa[1] (1. Yokohama City University, 2. Kyoto University, 3. National Institute of Technology, Hakodate College, 4. Hokkaido University)

Japanese

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

[H935-3pm-12]

A novel protecting group for selenocysteine applicable to Solid-phase peptide synthesis

○Fumika Yoshitomi[1], Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1] (1. Nagoya Univ.)

Japanese

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

[H935-3pm-13]

Improved synthesis of peptide thioester with α-disubstituted amino acids

○Genki Nakamura[1], Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1] (1. Nagoya Univ.)

Japanese

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

[H935-3pm-14]

Screening of peptide sequences with cell adhesion using molecular descriptors and measurement data related to fibril formation.

○Taisei Terao[1], Akira Takekawa[3], Tomohiro Umetani[2], Fumihiro Kayamori[1], Kenji Usui[1] (1. FIST, Konan Univ., 2. Konan Univ., 3. Kobe Univ.)

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Japanese

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

[H935-3pm-15]

Developing novel nucleosome ligand for expansion of histone acylation catalyst

○Yuma Takeuchi[1], Tamiko Nozaki[1], Mayu Onoda[1], Kenzo Yamatsugu[1], Shigehiro Kawashima[1], Motomu Kanai[1]
(1. The University of Tokyo)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
H931(931, Bldg. 9 [3F])

[H931-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Yasuaki Kimura, Yoshiaki Masaki

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H931-3am-01]

Chemical synthesis of rare sugar-derived nucleosides

○Yutaka Narita[1], Natsuhisa Oka[1,2,3] (1. Fac. of Eng., Gifu Univ., 2. iGCORE, Gifu Univ., 3. COMIT, Gifu Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H931-3am-02]

Post-modification of nucleic acids with amino acids via a ciano group

○Takumi Yoshida[1], Natsuhisa Oka[1,2,3] (1. Fac. of Eng., Gifu Univ., 2. iGCORE, Gifu Univ., 3. COMIT, Gifu Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H931-3am-03]

Development of chemoselective condensation reaction of nucleoside 3'-*H*-phosphonothioate

○Harumi Okutsu[1], Yuhei Takahashi[1], Kazuki Sato[1], Takeshi Wada[1] (1. Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H931-3am-04]

Development of purity assay method of boranophosphate DNAs by using PB/PO conversion reaction

○Kentaro matsumoto[1], Yuhei Takahashi[1], Kazuki Sato[1], Wada Takeshi[1] (1. Tokyo university of science)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H931-3am-05]

Photoreactivity of psoralens and trioxsalens for DNA duplexes

○Kazuhisa Fujimoto[1], Amin Md Al[2], Takanori Oyoshi[2] (1. Kyushu Sangyo University, 2. Shizuoka University)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H931-3am-06]

Interstrand Crosslinks using Oligonucleotides Containing 2’-Deoxythioguanosine

○Jamila Abbas Osman[1,2], Kazumitsu Onizuka[1,2], Yuuhei Yamano[1,2], Ahmed Mostafa Abdelhady[1,2], Fumi Nagatsugi[1,2] (1. Graduate school of science, Department of Chemistry, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H931-3am-07]

Development and Comparison of 4-Thiouridine to Cytidine Chemical Base Conversion Reaction

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○Sana Ohashi[1], Mayu Nakamura[1], Susit Archaryya[1], Masahito Inagaki[1], Naoko Abe[1], Yasuaki Kimura[1], Fumitaka Hashiya[2,3], Hiroshi Abe[1,2,3,4] (1. Graduate School of Science, Nagoya Univ., 2. Research Center for Material Science, Nagoya Univ., 3. CREST, Japan Science and Technology Agency, 4. Institute for Glyco-core Research (iGCORE), Nagoya Univ.)

English
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H931-3am-08]

Enzymatic incorporation and extension studies of the unnatural alkynylated purine-pyridazine base pair

○Wenjue Fan[1,2], Hidenori Okamura[1,2], Zhuoxin Dong[1,2], Giang Hoang Trinh[1,2], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku Univ., 2. Grad. Sch. Sci., Tohoku Univ.)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[H931-3am-09]

Synthesis and properties of antisense oligonucleotides containing 4'-*C*-(*N*-alkyl)aminoethyl thymidines.

○Kota Fujiki[1,5], Yoshihito Ueno[1,2,3,4] (1. The Graduate School of Natural Science and Technology, Gifu University, 2. Faculty of Applied Biological Science, Gifu University, 3. The United Graduate School of Agricultural Science, Gifu Univercity, 4. Center for One Medicine Innovative Translational Reseach(COMIT), Gifu university Institute for Advanced Study, Gifu University, 5. Convolution of Informatics and Biomedical Sciences on Glocal Alliances, CIBoG)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H931-3am-10]

Synthesis of 4'-*C*-aminoethoxy-2'-*O*-methyl-5-propynyluridine and its application for antisense oligonucleotide

○Yujun Zhou[1,4], Yoshihito Ueno[1,2,3,5] (1. The United Graduate School of Agriculture Science (UGSAS), Gifu University, 2. Faculty of Applied Biological Sciences, Gifu University, 3. Graduate School of Natural Sciences and Technology, Gifu Unviversity, 4. Convolution of Informatics and Biomedical Sciences on Glocal Alliances (CIBoG), Nagoya University, 5. Center for One Medicine Innovative Translational Research (COMIT), Tokai National Higher Education and Research System)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H931-3am-11]

Synthesis and evaluation of a thymidine dimer with an extended backbone at five prime position

○Shigetoshi Tachibana[1], Rie Ohnishi[1], Yoshiaki Masaki[1], Kohji Seio[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H931-3am-12]

Synthesis of 5-methyluridine derivatives with sulfonamide or sulfonate modifications on the 2´ hydroxyl group and evaluation of their ability to form duplex chains

○Shuntaro Takigawa[1], Takahito Tomori[1], Koya Uekusa[1], Yoshiaki Masaki[1], Kohji Seio[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H931-3am-13]

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Synthesis and properties of oligonucleotides having substituted 2′-*O*, 3′-*C*-bridged [3.2.0]bicycloarabinonucleoside

○Ayano P Tabira[1], Shunsuke Wakatsuki[1], Kohji Seio[1], Yoshiaki Masaki[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese

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

[H931-3am-14]

Synthesis and Evaluation of Photolabile Selenium-Modified Nucleic Acid for Intracellular Gene Expression Switching

○Yuki Yoshida[1], Haruka Hiraoka[1], Hirotaka Murase[1,2], Naoko Abe[1], Fumitaka Hashiya[3], Hiroshi Abe[1,4,5] (1. Graduate School of Science, Nagoya University, 2. Department of Pharmacy, Sojo University, 3. Research Center for Materials Science, Nagoya University, 4. JST-CREST, 5. Institute for Glyco-core Research)

Japanese

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

[H931-3am-15]

Construction of Chimeric Artificial Nucleic Acids (CANA) forward Inhibition of Pancreatic Cancer Transcription Factor BACH1 Ⅰ V: - Effects of Junction Position on Complex Stability and Cleavage Efficiency -

○Yuki Igarashi[1], Yuto Horiuchi[1], Mitsuyo Matsumoto[2], Yu Mikame[3], Masaki Nishijima[1], Yasuyuki Araki[1], Asako Yamayoshi[3], Kazuhiko Igarashi[2], Takehiko Wada[1] (1. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2. Graduate School of Medicine, Tohoku University, 3. Graduate School of Biomedical Sciences, Nagasaki University)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
H934(934, Bldg. 9 [3F])

[H934-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Takahiro Nakama, Tsuyoshi Takahashi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H934-3am-01]

Synthesis of amino acid from ammonia and pyruvate by visible-light irradiation using photo/biocatalyst

○Kyosuke Yamada[1], Yutaka Amao[2] (1. Osaka City University, 2. Osaka Metropolitan University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H934-3am-02]

Effect of catalytic reactions resulting from the network formation of cascade enzymes

○Aoi Mameuda[1], Masahiro Takinoue[2], Koki Kamiya[1] (1. Graduate School of Science and Technology, Gunma University, 2. Department of Computer Science, School of Computing, Tokyo Institute of Technology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H934-3am-03]

NMR analysis of dimerization of amyloid β hydrophobic fragments by encapsulation in a giant spherical metallo-cage

○Yuta Onodera[1], Erina Takeuchi, Takahiro Nakama[1], Maho Yagi[2], Daishi Fujita[3], Koichi Kato[2], Makoto Fujita[1,2,4] (1. Graduate School of Engineering, The University of Tokyo , 2. Institute for Molecular Science, 3. iCeMS, Kyoto University, 4. Institutes for Advanced Study, The University of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H934-3am-04]

NMR structural analysis of protein–lipid interactions by confinement in isolated space of spherical metallo-cages

○Miri Tadokoro[1], Takahiro Nakama[1], Hongkun Liu[1], Maho Yagi-Utsumi[2,3], Koichi Kato[2,3], Makoto Fujita[1,3,4] (1. Graduate School of Engineering, The University of Tokyo , 2. Graduate School of Pharmaceutical Sciences, Nagoya City University, 3. Institute for Molecular Science (IMS), 4. UTIAS, The University of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H934-3am-05]

Protein Refolding by Releasing from Nanopores

○Ko Shinohara[1], Nobuhiko Hosono[1,2], Takashi Uemura[1,2] (1. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H934-3am-06]

Analysis of the hierarchical structure of the pH-responsive piston protein assembly

○Souta Masumura[1], Koki Date[1], Thuc Toan PHAM[1], Xin Li[1], Kosuke Kikuchi[1], Takafumi Ueno[1] (1. School of Life Science and Technology, Tokyo Institute of Technology)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[H934-3am-07]
Investigation of Denaturation and Aggregation Behavior of Proteins under Microwave Irradiation

○Mizuki Yoshihara[1], Yuna Sakakibara[1], Ma Yunting[2], Yoshihiro Sasaki[2], Eito Fukushima[1], Haruya Yamaguchi[1], Hikaru Takaya[1] (1. Grad. Sch. of Teikyo Univ. of Sci., 2. Grad. Sch. of Eng., Kyoto Univ)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[H934-3am-08]
Analysis of the Effect of Phosphorylation on HP1α Dynamics by ESR spectroscopy

○Toshiki Takei[1], Kohei Muraoka[1], Toru Kawakami[1], Toshiaki Arata[2], Isao Suetake[3], Hironobu Hojo[1] (1. Institute for Protein Research, Osaka University, 2. Osaka Metropolitan University, 3. Nakamura Gakuen Universtiy)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[H934-3am-09]
Evaluation of protein splicing activities of cysteine-less intein from hyperthermophiles

○Kanta Katagiri[1], Tsuyoshi Takahashi[1] (1. Gunma University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[H934-3am-10]
Selection of proteins that recognize a specific peptide sequence using engineered split intein

○Momoka Shimizu[1], Tsuyoshi Takahashi[1] (1. The Univ. of Gunma)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[H934-3am-11]
Analysis of interactions between glycopeptides and sugar-recognizing F-box protein Fbs2

○Midori Aikyo[1], Haruka Inoue[1], Satoshi Takahashi[1], Nozomi Ishii[1], Ichiro Matsuo[1], Yukiko Yoshida[2], Tadashi Suzuki[3], Tsuyoshi Takahashi[1] (1. The Univ. of Gunma, 2. Tokyo Metropolitan Institute of Medical Science, 3. RIKEN)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H934-3am-12]
Selection of peptides that bind to Keap1 using split intein and reconstitution of kanamycin kinase

○Kana Nobusawa[1], Tsuyoshi Takahashi[1] (1. Gunma University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H934-3am-13]
Construction of cyclized Renilla Luciferase using the Catcher/Tag system

○Makoto Ichikawa[1], Kei Nishida[1], Jun Yamaguchi[1], Eiry Kobatake[1], Masayasu Mie[1] (1. Tokyo Institute of Technology)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[H934-3am-14]

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Modification of cholesterol-binding proteins by polymer grafting

○Tianjian Ma[1], Kei Nishida[1], Ikumi Sato[1], Masayasu Mie[1], Eiry Kobatake[1] (1. Tokyo Institute of Technology)

Japanese

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

[H934-3am-15]

Construction of high-secretion expression system for albumin using Pichia pastoris

○Mizuki Komori[1], Nobutaka Fujieda[2,1], Yoshitsugu Morita[2] (1. Osaka Pref. Univ., 2. Osaka Metro. Univ.)

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

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC H932(932, Bldg. 9 [3F])

[H932-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Eiji Nakata, Hiromu Kashida

English
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H932-3pm-01]

Artificial liposome compartment with DNA origami scaffold for size exclusion molecular transport

○shiwei zhang[1], Eiji Nakata[1], Peng Lin[1], Takashi Morii[1] (1. Kyoto university)

English
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H932-3pm-02]

In vitro model of RNA-Protein aggregates in myotonic dystrophy type 1

○Surachada Chuaychob[1,2], Wanqing Hou[2], Musashi Shimizu[2], Shun Nakano[2], Arivazhagan Rajendran[1,2], Eiji Nakata[1,2], Takashi Morii[1,2] (1. Integrated Research Center for Carbon Negative Science, Institute of Advanced Energy, Kyoto University, 2. Institute of Advanced Energy, Kyoto University)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H932-3pm-03]

Development of a method for simultaneous measurement of multiple factors in the intracellular local environment

○Mashal Asif[1], Eiji Nakata[1], Yuya Shibano[1], Peng Lin[1], Takashi Morii[1] (1. Institute of Advanced Energy, Kyoto University)

English
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H932-3pm-04]

Construction of an artificial CO_2 fixation compartment using DNA nanostructure as a scaffold

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

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H932-3pm-05]

Assembly of the functional proteins located on DNA nanostructures

○SHUHUI XIAN[1], Eiji Nakata[2], Peng Lin[2], Takashi Morii[2] (1. Kyoto University, 2. Institute of Advanced Energy, Kyoto University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H932-3pm-06]

Investigation of efficient amplification in ab initio DNA synthesis

○Yuka Kataoka[1], Chihiro Kubo[1], Tomoko Wariishi[1], Hiroto Fujita[1], Masayasu Kuwahara[1] (1. Grad. Sch. Integrated Basic Sci., Nihon Univ.)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H932-3pm-07]
Self-assembly of double-stranded DNA into micrometer-sized H-shaped structures
○Tetsunao Makino[1], Makiko Tanaka[1] (1. The University of Electro-Communications)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[H932-3pm-08]
Exploration of Pt complex that induce DNA coacervate
○Ryu Tashiro[1], Takuma Yamada[1], Serika Yano[1], Ayane Araki[1], Hiroki Nishihara[1], Moe Nakagawa[1], Masako Uemura[1], Seiji Komeda[1] (1. Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H932-3pm-09]
Design of template circular DNA for light-triggered activation of siRNA transcription utilizing gold nanoparticles
○Tomoki Ikemizu[1], Weijie Cheah[1], Yusuke Yonamine[2], Hideyuki Mitomo[2], Kuniharu Ijiro[2] (1. Hokkaido University Graduate School of Life Science, 2. Hokkaido University Research Institute for Electronic Science)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H932-3pm-10]
Imidazolium modified-silica support for facile DNA extraction from contaminants
○Yasuaki Kakikura[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[H932-3pm-11]
Evaluation of helical amplification ability of using SNA tethering fluorescent dyes
○Itsumi Sugiyama[1], Hiromu Kashida[1], Hiroyuki Asanuma[1] (1. Grad. Sch. Eng., Nagoya Univ.)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[H932-3pm-12]
Sequence analysis of SNA bearing artificial bases by duplex formation with DNA
○Nozomi Hibino[1], Hiroyuki Asanuma[1], Hiromu Kashida[1] (1. Grad. Sch. Eng., Nagoya Univ.)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[H932-3pm-13]
Development of a novel method to analyze PNA sequences bearing artificial bases.
○Kazuma Inagaki[1], Hiromu Kashida[1], Yuichiro Aiba[2], Osami Shoji[2], Hiroyuki Asanuma[1] (1. Grad. Sch. Eng., Nagoya Univ., 2. Grad. Sch. Sci., Nagoya Univ.)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[H932-3pm-14]
Unique homopurine parallel-type triplex structure formed by XNA
○Lao Siyuan[1], Ariyoshi Jumpei[2], Sato Fuminori[1], Asanuma Hiroyuki[1], Kamiya Yukiko[1,2] (1. Nagoya University, 2. Kobe Pharmaceutical University)

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC H936(936, Bldg. 9 [3F])

[H936-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Akimitsu Okamoto, Takashi Sera

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H936-3pm-01]

Inhibition of RNA replication of avian influenza virus using artificial RNA-cleaving enzymes

○Tomoaki Mori[1], Koichi Mori[1], Takashi Sera[1] (1. Okayama University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H936-3pm-02]

N-terminal Modification of Antibodies Using Triazolecarbaldehyde Derivatives Containing a Fluorescent Dye

○Yuya Maeda[1], Takanobu Yasuda[2], Akira Onoda[1,3] (1. Graduate School of Environmental Science, Hokkaido University, 2. Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, 3. Faculty of Environmental Earth Science, Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H936-3pm-03]

Immobilization of green fluorescent protein with an N-terminally tagged alkyl chain onto the surface of liposome

○Lisa Tara Connolly[1], Akira Onoda[1,2] (1. Grad. School Env. Sci., Hokkaido Univ., 2. Faculty of Env. Earth Sci., Hokkaido Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H936-3pm-04]

Chemical protein synthesis via peptide ligation on PNA scaffold

○Sae Suzuki[1], Shingo Mizushima[1], Yukino Takeuchi[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Nagoya Univ., 2. Institute of nano-life-systems, Nagoya Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H936-3pm-05]

Efficiency of protein translocation into HeLa cells depends on fusion sites of cell penetrating peptide sequence

○Akari Miwa[1], Koki Kamiya[1] (1. Grad. Sci. and Tech., Gunma Univ.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H936-3pm-06]

Creation of enveloped viral replicas modified with nuclear-localized signal peptide

○Mizuki Wada[1], Kentarou Sakamoto[2], Hiroto Furukawa[2], Hiroshi Inaba[2], Kazunori Matsuura[2] (1. Faculty of Engineering, Tottori University, 2. Graduate School of Engineering, Tottori University)

Japanese

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2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[H936-3pm-07]

Chemical diversification of C-terminal of proximal ubiquitin in the synthetic heterotypic polyubiquitin chain

○Takafumi Furuhata[1], Choi Bumkyu[1], Taiki Uno[1], Yusuke Sato[2], Kei Okatsu[3], Shuya Fukai[3], Akimitsu Okamoto[1] (1. The Univ. of Tokyo, 2. Tottori Univ., 3. Kyoto Univ.)

Japanese

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

[H936-3pm-08]

Structure Controlled Synthesis of Heterotypic Ubiquitin Chain using Oxime Ligation

○Ryota Shinohara[1], Takafumi Furuhata[1], Seigo Yamada[1], Akimitu Okamoto[1] (1. The University of Tokyo)

English

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

[H936-3pm-09]

GTP Responsiveness of Biomolecular Machine GroEL by Binding Pocket Engineering

○Ryotaro Toda[1], Kiyoshi Morishita[1], Takayuki Miki[1], Hideki Taguchi[2], Takuzo Aida[1,3] (1. The University of Tokyo, 2. Tokyo Institute of Technology, 3. RIKEN Center for Emergent Matter Science)

English

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

[H936-3pm-10]

Development of Self-assembling Peptide Tags That Form Intracellular Droplets in Response to Hydrogen Peroxide

○Masatoshi Shimizu[1], Takuzo Aida[1], Takayuki Miki[1] (1. The Univ. of Tokyo)

English

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

[H936-3pm-11]

Toward a near infrared (NIR) fluorescent chemigenetic indicator for Ca^{2+} based on photoactive yellow protein (PYP)-tag

○Takumi Yanagimachi[1], Takuya Terai[1], Robert E. Campbell[1] (1. Graduate School of Science, The University of Tokyo)

Japanese

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

[H936-3pm-12]

Chemigenetic red calcium indicator: improvement through directed evolution and imaging applications

○Shosei Imai[1], Wenchao Zhu[1], Takuya Terai[1], Robert Earl Campbell[1] (1. The university of Tokyo)

Japanese

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

[H936-3pm-13]

Towards the development of chemigenetic Ca^{2+} indicators based on dihydrofolate reductase

○Kenryo Sakoi[1], Takuya Terai[2], Robert Earl Campbell[2] (1. School of Science, The University of Tokyo, 2. Graduate School of Science, The University of Tokyo)

Japanese

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

[H936-3pm-14]

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Photoreaction of light-induced cluster forming protein TePixD and its downstream molecule

○Chihiro Aramoto[1], Yusuke Nakasone[1], Yusuke Masuda[1], Shunrou Tokonami[2], Masahide Terazima[1] (1. Kyoto University, 2. Gakushuin University)

Japanese

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

[H936-3pm-15]

Opto-control of protein activities utilizing dimerization of photosensor eBLUF

○Takafumi Kuno[1], Yusuke Nakasone[1], Kazuhiro Sakamaki[1], Masahide Terazima[1] (1. Kyoto Univ.)

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC H931(931, Bldg. 9 [3F])

[H931-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Masayasu Taki, Yutaro Saito

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[H931-3vn-01]

Synthesis of a Mg^{2+} Probe Consisting of a Phospha-Xanthone Dye and a Crown Ether-Type Ligand

○Yuichi Asada[1], Masayasu Taki[2], Shigehiro Yamaguchi[1,2,3] (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University, 3. Integrated Research Consortium on Chemical Science, Nagoya University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[H931-3vn-02]

Development of Aldehyde Dehydrogenase 1A1- and 1A3-responsive Turn-on Fluorescent Probes

○Yuki Nishida[1], Koki Miki[1], Huiying Mu[1], Koji Miki[1], Kouichi Ohe[1] (1. Kyoto University)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[H931-3vn-03]

Analysis of aminopeptidase using the amino acid-tethered oligodeoxynucleotide

○Reoto Mio[1], Tatsuya Nishihara[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

English
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[H931-3vn-04]

Environment-sensitive and Super-photostable Probes for Monitoring Lipid Droplets through Fluorescence Lifetime Imaging

○junwei wang[1], Masayasu Taki[1], Shigehiro Yamaguchi[1,2,3] (1. ITbM, Nagoya University, 2. Department of Chemistry, Graduate School of Science, Nagoya University, 3. IRCCS, Nagoya University)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[H931-3vn-05]

Development of ^{19}F MRI Probe labeling β-lactamase

○Hiroto Fukuda[1], Masafumi Minoshima[1,2], Kazuya Kikuchi[1,3] (1. Graduate School of Engineering, Osaka Univ., 2. JST PRESTO, 3. Immunology Frontier Research Center, Osaka Univ.)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[H931-3vn-06]

Development of ^{19}F MRI probe using gelled emulsion

○Shiho Sugiura[1], Tomoya Yamamoto[2,3], Kazuya Kikuchi[2,3] (1. Osaka University, School of Engineering, 2. Osaka University, Graduate School of Engineering, 3. Osaka University, Immunology Frontier Research Center)

Japanese

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5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[H931-3vn-07]

Evaluation of long-hyperpolarization-lifetime molecules for *in vivo* oximetry by hyperpolarized MRI

○Ruki Ashikaga[1], Yutaro Saito[2], Hiroyuki Yatabe[2], Yohei Kondo[2], Hiroshi Nonaka[2], Yoichi Takakusagi[3,4], Kazutoshi Yamamoto[5], Murali C. Krishna[5], Shinsuke Sando[2] (1. School of Engineering, The University of Tokyo, 2. Guraduate School of Engineering, The University of Tokyo, 3. National Institutes for Quantum Science and Technology, 4. Graduate School of Science, Chiba University, 5. National Institutes of Health, USA)

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC H934(934, Bldg. 9 [3F])

[H934-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Kohsuke Kuroda, Noriyuki Uchida

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[H934-3vn-01]

Development of Photo-Induced Electron Transfer Reversible Addition–Fragmentation Chain Transfer Polymerization Mediated by Calcein Acetoxymethyl as an Esterase Responsive Photocatalyst

○Kanta Ogura[1], Masahiko Nakamoto[2], Michiya Matsusaki[2] (1. Osaka University, 2. Graduate School of Engineering Osaka University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[H934-3vn-02]

Kinetics-Controlled Gel-Sol Transition and Cargo Release of Methionine-Containing peptides

○Yoshika Hara[1], Atsuya Yaguchi[1], Hirotsugu Hiramatsu[2], Takahiro Muraoka[1,3] (1. Tokyo University of Agriculture and Technology, 2. National Yang Ming Chiao Tung University, 3. KISTEC)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[H934-3vn-03]

Development of self-adjuvanting protein vaccines using gold nanoparticles as carriers

○Koki Murata[1], Naohiro Hayakawa[1], Masahiro Wakao[1], Yasuo Suda[1], Hiroyuki Shinchi[1] (1. Grad. Sch. Sci. and Eng., Kagoshima Univ.)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[H934-3vn-04]

Development of a Ratiometric Fluorescent Probe for Visualizing Lipid Peroxidation in Plasma Membrane

○Rina Tokunaga[1], Kosei Shioji[1], Hidefumi Iwashita[1] (1. Fukuoka University)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[H934-3vn-05]

Thermostability of a thermotolerant yeast by zwitterions

○Souta Uemori[1], Ayumi Hachisu[1], Kazuaki Ninomiya[2], Kosuke Kuroda[1] (1. Faculty of Biological Science and Technology, Institute of Science and Engineering, Kanazawa University, 2. Institute for Frontier Science Initiative, Kanazawa University)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[H934-3vn-06]

Synthesis of fluorescence-derivative of DHA-containing phospholipids and its behavior in lipid bilayers.

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○Kotaro Shimizu[1], Masanao Kinoshita[1], Nobuaki Matsumori[1] (1. Kyushu University)

Japanese

4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[H934-3vn-07]

Synthesis and Evaluation of β-Glucan Mimicking Polymers Assembled with β-Glucan Oligosaccharides

○Atsushi Miyagawa[1], Nami Yamamoto[1], Ayane Ohno[1], Hatsuo Yammaura[1] (1. Nagoya Inst. Tech.)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[H934-3vn-08]

Controlling the spatial arrangement of the gold nanoparticles conjugated with the peptide on the self-assembling DNA nanostructure

○Yosuke Ochi[1], Yuki Gomibuchi[1], Takuo Yasunaga[1], Junichi Taira[1] (1. Kyushu Inst. of Tech.)

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Academic Program [Oral A] | 18. Polymer：Oral A

Wed. Mar 20, 2024 9:00 AM - 11:00 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:00 AM UTC
D341(341, Bldg. 3 [4F])

[D341-3am] 18. Polymer

Chair: Ryo Sekiya, Tatsuya Nishimura

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[D341-3am-01]

Synthesis and water retention properties under the low humidity of proton-conducting covalent organic frameworks bearing with alkyl functional groups

○Takashi Sato[1], Kouji Inagaki[1], Koki Fujiu[1], Masane Kin[1], Hiroyasu Tabe[2], Ryota Shinozaki[1], Aiko Fukazawa[2], Satoshi Horike[2], Takumi Okamoto[1] (1. DENSO CORPORATION, 2. Kyoto University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[D341-3am-02]

Synthesis of sulfur-containing polymers with oligo (ethylene oxide) side chains and their properties as solid polymer electrolytes

○Takuya YOKOO[1], Akinari CHIBA[1], Kenichi OYAIZU[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[D341-3am-03]

Synthesis of Copolymers Containing TEMPO-disubstituted Fumarate and Their Electrochemical Properties

○Ryo Shirakawa[1], Kohei Ishigami[1], Kenichi Oyaizu[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[D341-3am-04]

Optical properties of nanographene materials with different kinds of photoemissive organic functional groups

○Saki Arimura[1], Ryo Sekiya[1], Takeharu Haino[1,2] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM2, Hiroshima University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[D341-3am-05]

Side-Chain Engineering of Thienothiophene-containing Polymer as Hole transporting Materials toward a Perovskite Solar Cell.

○Yu SAKAI[1], Masaki MINAI[1], Kenichi OYAIZU[1], Hiroyuki NISHIDA[1], Takeo SUGA[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[D341-3am-06]

Development of semiconducting polymers consisting of novel π-extended building unit based on benzo[1,2-*d*:4,3-*d*']bisthiazole for organic photovoltaics

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○Mayu Tomita[1], Hiroto Iwasaki[1], Kodai Yamanaka[1], Tubasa Mikie[1], Itaru Osaka[1] (1. The Univ. of Hiroshima)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[D341-3am-07]

Synthetic studies of human influenza virus inhibitors (II)
~Synthetic construction of key intermediates~

○Kaito Takanezawa[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Natsuoka[1,2,3] (1. Grad. Sch. & Sci. & Engin., Saitama University, 2. Adv. Inst. Innov. Tech., Saitama University, 3. Strategic Res. Ctr., Saitama University)

English
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[D341-3am-08]

Synthetic studies of *N*-linked glycopolymers (Ⅶ): Preparation of a glycosyl monomer with different linker lengths

○Mio Sunaga[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)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[D341-3am-09]

Development of a Highly Enantioselective Chiral Adsorbent Using a One-Handed Helical Poly(diphenylacetylene) Derivative

○Shota Sona[1], Hirose Daisuke[2], Maeda Katsuhiro[2,3] (1. Grad. Sch. of Frontier Sci. Initiative, Kanazawa Univ., 2. Grad. Sch. of Nat. Sci. and Tech., Kanazawa Univ., 3. WPI-NanoLSI, Kanazawa Univ.)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[D341-3am-10]

Synthesis of alkynyl spacer-containing chiral polyguanidines and their noncovalent modification for organocatalyst design

○Daiki Mori[1], Keiji Minagawa[1,2], Yukihiro Arakawa[1] (1. Department of Applied Chemistry, Tokushima University, 2. Institute of Liberal Arts and Sciences, Tokushima University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[D341-3am-11]

Synthesis and Photo-Plasticization of Polyurethanes Containing Azobenzene Moieties

○MARIN TAKEUCHI[1], Takenori Ikegaya[2], Shogo nobukawa[2], Yasuhiro Kohsaka[1,3,4] (1. Fac. of Textile Sci. and Tech., Shinshu Univ, 2. Grad. Sch. of Eng., NITech, 3. RISM, Shinshu Univ.,, 4. JST PRESTO)

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Academic Program [Oral A] | 18. Polymer：Oral A

Wed. Mar 20, 2024 1:00 PM - 2:50 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:50 AM UTC D341(341, Bldg. 3 [4F])

[D341-3pm] 18. Polymer

Chair: Kazuko Nakazono, Jin Hotoyanagi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[D341-3pm-01]

Synthesis and mechanical properties of hydrogels with rotaxane cross-linked structures

○Reo Onda[1], Haruka Minato[2], Daisuke Suzuki[2], Kazuko Nakazono[1] (1. Sch. of Mat and Eng., Tokyo Tech, 2. Grad. Sch. of Text Sci and Tech, Shinshu Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[D341-3pm-02]

Synthesis of hydrogen-bonded crosslinked network polymers and their decross-linking using chemical stimuli

○Keita Aoki[1], Kiyoshi Masuda[1], Haruka Minato[2], Daisuke Suzuki[2], Kazuko Nakazono[1] (1. Sch. of Mat and Eng., Tokyo Tech, 2. Grad. Sch. of Text Sci and Tech, Sinshu Univ)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[D341-3pm-03]

Synthetic studies of Glycopolymers having Porphyrin(VI) : Biological evaluation of glycopolymers having porphyrin against Hela cells

○Yuta Komano[1], Miho Suzuki[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Saitama University, 2. Advanced Institute of Innovative Technology, Saitama University, 3. Health Sciences and Technology Research Area, Strategic Research Center, Saitama University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[D341-3pm-04]

LCST-type thermo-responsiveness of *N*,*N*′-dimethylpolyurea in water

○Keitaro Matsuoka[1,2], Mio Sasaki[2], Masanori Miyoshi[2], Akari Sugano[2], Takuro Tsutsumi[1,2], Kazuki Sada[1,2] (1. Fac. of Sci., Hokkaido Univ., 2. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[D341-3pm-05]

Thermo-responsiveness of polyphenylacetylenes with hydrogen bond substituent

○Koki Takasu[1], Natsuki Inaba[2], Keitaro Matsuoka[2,3], Takuro Tsutsumi[2,3], Kazuki Sada[2,3] (1. Sch. of Sci., Hokkaido Univ., 2. Grad. Sch. of Chem. Si. and Eng., Hokkaido Univ.c, 3. Fac. of Sci., Hokkaido Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[D341-3pm-06]

Thermally-cured Anionic Polymer Coatings for Responsive Hydrophilic Surface

○Homare KUWAHARA[1], Natsumi FUJI[1], Kenichi OYAIDU[1], Takeo SUGA[1] (1. Waseda University, School of Advanced Science and Engineering)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[D341-3pm-07]
Synthesis of Lipid Bilayer Adhesion Polymers Containing Zwitterions (II) -Synthesis of Fluorescent-labeled Acrylamide Monomers-

○Hiroki Kato[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
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[D341-3pm-08]
Development of adhesive materials based on the synergy effect of the surface structure having vertically oriented pillars and electrostatic interactions

○Kaito Kishimoto[1], Jin Motoyanagi[1], Masahiko Minoda[1] (1. Grad. Sch. of Sci. and Tech., Kyoto Inst. of Tech.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[D341-3pm-09]
Creation of a composite hydrogel composed of activated carbon and hydrogelator for a spreadable adsorbent material

○Mai HIRUKAWA[1], Yutaka OHSEDO[2] (1. Faculty of Human Life and Environment, NWU, 2. Fac. Eng., NWU)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[D341-3pm-10]
Reversible Hydrogenation and Dehydrogenation of Cyclopentanone-containing Polymer

○Tomoki Oura[1], Hiroyuki Odaki[1], Yusuke Kaiwa[1], Kenichi Oyaizu[1] (1. Waseda University, School of Advanced Science and Engineering)

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Academic Program [Oral A] | 19. Colloid and Interface Chemistry：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
A1443(1443, Bldg. 14 [4F])

[A1443-3pm] 19. Colloid and Interface Chemistry

Chair: Motohiro Kasuya, Tomonori Ohba

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1443-3pm-01]

High-speed camera observation of the hydrogen evolution reaction

○Wacaco Tao[1], Daiki Sato[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. School of Science, Hokkaido University, 2. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 3. Faculty of Science, Hokkaido University)

English
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1443-3pm-02]

Effects of surface nanostructures on the oxygen evolution reaction

○Andrew Harrison Propper[1], Daiki Sato[1], Ryoji Suzuki[1], Tomohiro Fukushima[1], Kei Murakoshi[1] (1. Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1443-3pm-03]

Control of oxygen evolution reaction using structured electrodes

○Kazuma Kobashigawa[1], Daiki Ashizawa[1], Tomohiro Fukushima[2], Kei Murakoshi[2] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1443-3pm-04]

Observation and analysis of metal complex-immobilized ionic liquid-modified electrodes by surface-enhanced infrared spectroscopy

○Hiroto Wada[1], Tatsuya Kitagawa[1], Tomohiko Inomata[1], Tomohiro Ozawa[1], Hideki Masuda[2] (1. Graduate School of Engineering, Nagoya Institute of Technology, 2. Aichi Institute of Technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1443-3pm-05]

Catalyzation of Gold Surfaces by Modification with L-Proline Molecules, a naturally occurring homogeneous catalyst

○Tomoki Watanabe[1], Hidenori Noguchi[2], Mikio Ito[1,2] (1. National Institute of Technology, Tokyo College., 2. National Institute for Materials Science)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1443-3pm-06]

Temperature-dependence of CO_2 Adsorption/Reaction on $BaTiO_3$ Nano-catalyst

○Masatoshi Miyamoto[1], Smita Takawane[1], Takumi Watanabe[1], Tomonori Ohba[1] (1. Chiba University)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1443-3pm-07]

Development of a New Synthesis Method for Nanoporous Carbons Using Ionic Liquids with π-Conjugated Frameworks.

○Toshinori Seki[1], Kento Nakamura[1], Ryuta Sekiguchi[3], Taku Iiyama[2], Ryusuke Futamura[2] (1. Graduate School of Science and Technology, Shinshu University, 2. Faculty of Science, Shinshu University, 3. Faculty of Science and Technology, Hirosaki University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[A1443-3pm-08]

Synthesis and characterization of novel porous materials with temperature-responsive gels

○Tamao Sawada[1], Ryusuke Futamura[2], Taku Iiyama[2] (1. Graduate School of Science and Technology Department of Science , 2. Department of Chemistry, Faculty of Science, Shinshu University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1443-3pm-09]

Pore structure evaluation of carbon-based nanoporous materials using positron annihilation lifetime method

○Kei Kubo[1], Hayato Otsuka[1], Daisuke Saeki[1], Toshio Sakai[1], Katsumi Kaneko[1] (1. Shinshu univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1443-3pm-10]

Elucidation of the molecular mixing state in pore in liquid phase adsorption on activated carbon using X-ray scattering measurements

○Itsuki Tsubakihara[1], Kiri Sato[1], Ryusuke Futamura[1], Taku Iiyama[1] (1. Shinshu University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[A1443-3pm-11]

Water adsorption mechanism on activated carbon from the viewpoint of precise isothermal adsorption heat measurement

○Rin Iwatsuki[1], Ryusuke Futamura[2], Taku Iiyama[2] (1. Graduate School of Science and Technology, Shinshu University, 2. Faculty of Science, Shinshu University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[A1443-3pm-12]

Molecular Interactions and Adsorption Selectivity of Six-Membered Ring Alicyclic Hydrocarbons on ZIF-8 during Physisorption Process

○Takahiro Ueda[2], Yuta Yamada[1], Kota Fujii[1], Ryota Mihara[3], Taku Iiyama[3], Yasutaka Hamada[2], Mitsutaka Okumura[2] (1. Faculty of Science, Osaka University, 2. Graduate school of science, Osaka University, 3. Graduate school of science, Shinshu University)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[A1443-3pm-13]

Formation of micro-solution and figure out opposite dissolution/precipitation phenomena induced by water physisorption

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○Takeru Yokoyama[1], Yuka Matsuda[1], Takahiro Ueda[2], Ryusuke Futamura[3], Taku Iiyama[3] (1. Graduate School of Science and Technology, Shinshu University, 2. Dep. of Chem., Graduate School of Science, Osaka University, 3. Faculty of Scienece, Shinshu University)

Japanese

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

[A1443-3pm-14]

Adsorption behavior of several adsorbate under light irradiation on ZnS introduced FAU

○Saho Baba[1], Yukino Muramatsu[1], Satoshi Yamazaki[1] (1. Shizuoka Inst. of Sci. and Tech.)

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

Wed. Mar 20, 2024 10:30 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:30 AM - 2:30 AM UTC
C442(442, Bldg. 4 [4F])

[C442-3am] 20. Materials Chemistry -Basic and Application-

Chair: Miho Aizawa, Tuyoshi Fukaminato

English
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[C442-3am-01]

Synthesis of Electrochromic Supramolecular Polymers Driven by Data Science

○Aiwei Zhao[1,2], Masayoshi Higuchi[1,2] (1. National Institute for Materials Science, 2. Osaka University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[C442-3am-02]

Formation behavior of topographical surfaces on liquid-crystalline polymers by patterned cationic photopolymerization

○Yasuto Sasaki[1], Sayuri Hashimoto[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech, 2. PRESTO, JST)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[C442-3am-03]

Design of anisotropically mechanical polymer films by patterned photopolymerization of isotropic monomers

○Kyosuke Misaki[1], Yusho Kishimoto[1], Kyohei Hisano[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[C442-3am-04]

Development of Dithienonaphthobistriadiazole-Based π-Conjugated Polymers and Their Charge Transport Property

○Yuki Okazaki[1], Tsubasa Mikie[1,2], Itaru Osaka[1,2] (1. The Univ. of Hiroshima, 2. Graduate School of Advanced Science and Engineering, Hiroshima)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[C442-3am-05]

Synthesis of Hyper-branched Phthalocyanines Polymers for Photodynamic Therapy

○Chihiro Hashimoto[1], Sunnam Kim[1], Tsuyoshi Fukaminato[1] (1. Kumamoto Univ.)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[C442-3am-06]

Synthesis and properties of donor-acceptor polymers incorporating benzodichalcogenophenediones

○Shohei Wada[1], Kohsuke Kawabata[1,2], Kazuo Takimiya[1,2,3] (1. Graduate School of Science, Tohoku University, 2. Riken Center for Emergent Matter Science (CEMS), 3. Advanced Institute for Materials Research (WPI-AIMR), Thohoku University)

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

Wed. Mar 20, 2024 1:30 PM - 3:20 PM JST | Wed. Mar 20, 2024 4:30 AM - 6:20 AM UTC C443(443, Bldg. 4 [4F])

[C443-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Kenji Okada, Taichi Ikeda

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[C443-3pm-01]

Effect of electrode structure on morphology of deposition layer in Ag deposition-based electrochromic device

○Haruka Shimanuki[1], Syun Uji[2], Kazuki Nakamura[2], Norihisa Kobayashi[2] (1. Fac.Eng.,Chiba Univ., 2. Grad.Sch.Eng.,Chiba Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[C443-3pm-02]

Research on adhesion strength of fiber reinforced resin

○Tomoya Oikawa[1], Hidetoshi Hirahara[1], Jing Sang[1], Sumio Aisawa[1], Naoyuki Sekine[2], Shiori Masuda[2], Shinobu Komiyama[3] (1. Iwate Univ., 2. SUBARU Corporation, 3. Nihon Parkerizing CO.,Ltd.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[C443-3pm-03]

Luminescence properties of imidazolium acetate-based ionic liquids containing chiral Eu(III) complexes

○Arata Suzuki[1], Ziying Li[2], Norihisa Kobayashi[2], Kazuki Nakamura[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[C443-3pm-04]

Oriented growth of metal-organic framework on single crystals of copper-based mineral

○Yuka Koseki[1], Kenji Okada[1], Arisa Fukatsu[1], Masahide Takahashi[1] (1. Osaka Metropolitan University)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[C443-3pm-05]

Electrochemical control of emission color of europium ion in electrolytic solution containing crown ether.

○Genta Yoshida[1], Ryoto Yabuta[2], Norihisa Kobayashi[2], Kazuki Nakamura[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[C443-3pm-06]

Ionic Polymer-Metal Composite Actuators Consisting of Nafion and Gold Nanowire Electrodes

○Taichi Ikeda[1] (1. National Institute for Materials Science)

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Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[C443-3pm-07]
Chiroptical properties of hybrid material composed of chiral nematic liquid crystals and luminescent Eu(III) complexes

○Yusuke Sagawa[1], Takuro Kawahata[2], Norihisa Kobayashi[2], Kazuki Nakamura[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[C443-3pm-08]
Hybridization of β-detonate Eu(III) complexes and synthetic clay minerals and their luminescent properties.

○Ryota Nishiyama[1], RONG CAO[2], Kazuki Nakamura[2], Norihisa Kobayashi[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[C443-3pm-09]
Synthesis of mesostructured organosiloxane-based thin films using alkoxysilanes with an alkylammonium group

○Kazutomo Ido[1], Yuki Saito[1], Yoshiaki Miyamoto[1], Takamichi Matsuno[1,2], Atsushi Shimojima[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Kagami Memorial Research Institute for Materials Science and Technology, Waseda University)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[C443-3pm-10]
Synthesis and characterization of ionic plastic crystals with perovskite-type structure

○Hiroaki Mine[1], Hirokazu Shimooka[1], Tatsuo Okauchi[1], Mitsuru Kitamura[1] (1. Kyushu Institute of Technology)

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC C442(442, Bldg. 4 [4F])

[C442-3vn] 20. Materials Chemistry -Basic and Application-

Chair: Sachio Yoshihara, Yuta Nishina

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[C442-3vn-01]

Analysis of organic additives in metal-plating bath forby use of boron-doped diamond electrode

○Sachio Yoshihara[1] (1. Utsunomiya University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[C442-3vn-02]

Characterization of Surface of Diamond Electrodes Treated by Various Methods

○Yuki Tsuda[1], Takashi Yamamoto[1], Yasuaki Einaga[1] (1. Keio Univ.)

English
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[C442-3vn-03]

Microstructural analysis and performance evaluation of carbon hybrid electrode materials.

○HAONAN ZHANG[1], WENLIANG ZHU[1] (1. Kyoto Institute of Technology)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[C442-3vn-04]

Preparation and characterization of precisely pore-size-controlled boron-doped carbon

○Kentaro Ohkura[1], Yuta Nishina[1] (1. The Univ. of Okayama)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[C442-3vn-05]

Preparing liquid crystalline dispersion of high aspect ratio carbon nanotubes

○Nodoka Kosugi[1,2], Keiko Kojima[2], Hirokuni Jintoku[2], Kazufumi Kobashi[2], Toshiya Okazaki[2,1] (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[C442-3vn-06]

Synthesis of cationic polymer-graphene oxide composites and application for adsorbents

○Ryota Kimura[1], Yuta Nishina[1,2] (1. Okayama University, 2. RCIS)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[C442-3vn-07]

Synthesis of redox-active plastic crystal containing tetrachloroferrate ion and its application to solid refrigerant

○Takuya Ono[1], Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

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Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[C442-3vn-08]

Characterization of biomass adsorbed L-ascorbic acid and reducing ability for Fe(III)

○Ryuki Ikeda[1], Yui Igaki[1], Takumi Akinaga[1], Yuko Shikami[2], Toshiyuki Miyauchi[2] (1. Graduate of Chubu University, 2. Chubu University)

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Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral A

Wed. Mar 20, 2024 1:00 PM - 2:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:30 AM UTC
A1455(1455, Bldg. 14 [5F])

[A1455-3pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Kenya Kubo, Masahiro Goto

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1455-3pm-01]

Thermoelectric property of nanosuructured MgSiSn thin films

○Masahiro Goto[1], Michiko Sasaki[1,2] (1. NIMS, 2. The Univ. of Tokyo)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1455-3pm-02]

Dependence of thermoelectric performance of PEDOT:PSS/Graphene multilayer thin films on the amounts of Graphene

○Keito Uchida[1], Yuma Watanabe[2], Syunya Sakane[2,3], Hideki Tanaka[2] (1. Chuo University Graduate School, 2. Chuo University, 3. Ibaraki University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1455-3pm-03]

Characterization of Graphene/Copper Nanoparticle Composite Materials for Thermoelectric Conversion Application

○LIAO WEILI[1], Saitou Kouki[1], Sakane Shunya[1,2], Tanaka Hideki[1] (1. Chuo University Graduate School, 2. Ibaraki University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1455-3pm-04]

Thermoelectric properties of Ag_2Se nanowires /BBL:PEI composite films and their composition dependence

○Haruna Kasugai[1], Shunichiro Miwa, Shunya Sakane[2,3], Hideki Tanaka[2] (1. Chuo University Graduate School, 2. Chuo University, 3. Ibaraki University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1455-3pm-05]

Improvement of thermoelectric properties of α-Cu_2Se nanowires by annealing

○Yusuke Morikawa[1], Kazuki Munakata[1], Insoo Kang[2], Shunya Sakane[2,3], Hideki Tanaka[2] (1. Chuo University Graduate School, 2. Chuo University, 3. Ibaraki University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[A1455-3pm-06]

Study on amine solutions used for direct air capture using solar heat

○Ryo Murai[1], Yukio Furukawa[1], Dongmin Seo[1] (1. Waseda University)

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Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1455-3pm-07]

DFT-based Prediction of Half-Lives and Internal Conversion Spectra of ^{235m}U halide

○So Hashiba[1], Masashi Kaneko[1], Ryotaro Masuda[1], Yudai Shigekawa[2], Yoshitaka Kasamatsu[1] (1. Osaka University, 2. RIKEN)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[A1455-3pm-08]

Noise Reduction in Neutron In-beam Mössbauer Spectroscopy

○Kenya Kubo[1], Mio Yoshida[2], Yasuo Watanabe[2], Yoshio Kobayashi[2], Wataru Sato[3], Jun Miyazaki[4], Mototsugu Mihara[5], Takashi Nagatomo[7], I-Huan Chiu[6], Takahito Osawa[6] (1. ICU, 2. University of Electro-communications, 3. Kanazawa Univ., 4. Dendai, 5. Osaka Univ., 6. JAEA, 7. RIKEN)

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

Wed. Mar 20, 2024 1:00 PM - 3:10 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:10 AM UTC H937(937, Bldg. 9 [3F])

[H937-3pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Masahiro Higashi, Ryohei Kishi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H937-3pm-01]
Development of an Organic Structure-Directing Agents Design Algorithm for Zeolite Utilizing Large-Scale Language Models

○Shusuke Ito[1], Koki Muraoka[1], Akira Nakayama[1] (1. The Univ. of Tokyo)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H937-3pm-02]
Theoretical study on solvatochromism in tetracyanoquinodimethane(TCNQ)

○Sumire Tobe[1], Mikako Higa[2], Hirofumi Sato[3,4], Masahiro Higashi[5] (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering and Science University of the Ryukyus, 3. Guraduate School of Engineering, Kyoto University , 4. Fukui Institute for Fundamental Chemistry, Kyoto University, 5. Guraduate School of Informatics, Nagoya University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H937-3pm-03]
Theoretical analysis of electronic structures and reaction mechanism for NH_3-SCR reaction using binuclear Cu complexes

○Ryusei Morimoto[1], Kanami Sugiyama[2], Masahiro Higashi[3], Hirofumi Sato[2,4] (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. Graduate School of Informatics, Nagoya University, 4. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H937-3pm-04]
Analysis of a Reaction Route Network of Water Gas Shift Reaction

○Akane Emura[1], Kanami Sugiyama[2], Shin-ichi Minato[3], Masahiro Higashi[4], Hirofumi Sato[2,5] (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. Graduate School of Informatics, Kyoto University, 4. Graduate School of Informatics, Nagoya University, 5. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H937-3pm-05]
Extension of Global Area Search (GLAS) method to reactions with spin-state crossing and Application to small organic molecules

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○Takechika Kikkawa[1], Syusuke Yamanaka[1], Takashi Kawakami[1], Mitsutaka Okumura[1], Mitsuo Shoji[2] (1. Osaka University, 2. University of Tsukuba)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H937-3pm-06]

Linear response analysis of electron density in polypeptides

○Ren Oike[1], Takechika Kikkawa[1], Tomohiro Maruyama[1], Takasi Kawakami[1], Shusuke Yamanaka[1], Mitsutaka Okumura[1] (1. Osaka 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
[H937-3pm-07]

Development of *ab initio* divide-and-conquer method under periodic boundary condition

○Gen Ogawa[1], Masatsugu Nishida[2], Tomoko Akama[3], Masato Kobayashi[3,4], Tetsuya Taketsugu[3,4] (1. Sch. Sci., Hokkaido Univ., 2. Grad. School Chem. Sci. Eng., Hokkaido Univ., 3. WPI-ICReDD, Hokkaido Univ., 4. Fac. Sci., Hokkaido Univ.)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[H937-3pm-08]

Raman intensities of conformation-dependent low-frequency modes of chalcogenoanisole: analysis by singular value decomposition

○Akira Mizushina[1], Keigo Yamaguchi[2], Yoshihiro Yamakita[2] (1. School of Informatics and Engineering, University of Electro-Communications, 2. Graduate School of Informatics and Engineering, University of Electro-Communications)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H937-3pm-09]

Theoretical study on the muonium adduct structure of N-heterocyclic carbene by path integral molecular dynamics

○Satoshi Orikono[1], Kazuaki Kuwahata[1], Tomomi Shimazaki[1], Masanori Tachikawa[1] (1. Yokohama City University)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H937-3pm-10]

Theoretical study on hydrogen-bonded structures of EGFP using first principles calculations

○Mio Takakuwa[1], Tomomi Shimazaki[1], Masanori Tachikawa[1], Yukiumi Kita[1] (1. Yokohama City University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[H937-3pm-11]

Surface hopping *ab initio* molecular dynamics simulation on nonadiabatic dissociation process of OCS^{2+} induced by photo ionization

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○Ryuto Kambara[1], Takuro Tsutsumi[2], Kenji Furuya[3,4], Tetsuya Taketsugu[2,5] (1. Grad. Sch. Chem. Sci. Eng., Hokkaido Univ., 2. Fac. Sci., Hokkaido Univ., 3. Fac. Arts Sci., Kyushu Univ., 4. Dep. Mol. Mat. Sci., Kyushu Univ., 5. WPI-ICReDD, Hokkaido Univ.)

Japanese

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

[H937-3pm-12]

Heating Mechanism in Near-Infrared Laser-Induced Growth Reactions from Polyhydroxy Fullerenes to Carbon Nanotubes

○Mahiro Honkai[1], Manabu Kanno[2], Fuminori Misaizu[2], Hirohiko Kono[2] (1. Faculty of Science, Tohoku University, 2. Gradurate School of Science, Tohoku University)

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大規模言語モデルによるゼオライトの有機構造規定剤の設計

（東大院工 [1]）○伊東 周昌 [1]・村岡 恒輝 [1]・中山 哲 [1]

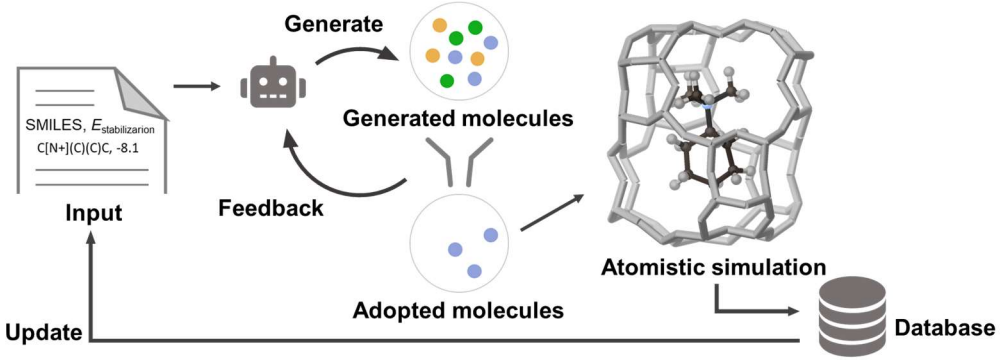
Designing Organic Structure-Directing Agents for Zeolite using Large Language Models

([1]*Graduate School of Engineering, The University of Tokyo*)
○Shusuke Ito[1], Koki Muraoka[1], Akira Nakayama[1]

Zeolites are crystalline microporous aluminosilicates that are widely used in applications such as membranes and catalysts[1]. One approach to direct the crystallization of zeolites is the use of organic structure-directing agent (OSDAs)[2], which are typically quaternary ammonium cations. While novel OSDA can lead to new zeolites, conventional trial-and-error experiments involve significant time and cost[3]. In this study, we employed Large Language Models (LLMs)[4] to facilitate human-machine collaboration in designing potent molecules. We fed feedback derived from screening and atomistic simulation to the LLM to refine subsequent suggestions, thereby continuously improving the proposed OSDAs and fostering the exploration of chemical space. The predicted molecules were compared to experimentally verified OSDAs.

Keywords: Molecular Design; Zeolite; Informatics; Organic Structure-Directing Agents; Large Language Models

ゼオライトは多孔質なアルミノケイ酸塩の総称であり、分離膜や触媒などに広く利用される [1]。ゼオライトの結晶化を導く方法の 1 つが有機構造規定剤（OSDAs）の利用である [2]。OSDA は主に四級アンモニウムカチオンである。新規 OSDA の設計は新規ゼオライトを誘導する可能性があるが、実験による試行錯誤は膨大な時間とコストを要する [3]。本研究では、大規模言語モデル（LLMs）[4] を活用し、人間と計算機の協創を実現する分子設計アルゴリズムを開発した。スクリーニングおよび原子シミュレーションによって得られる結果をフィードバックすることにより、LLM が継続的に提案分子を改善し、広大な化学空間を探索させるようにデータフローを設計した。提案された新規分子を既存の OSDAs と比較した。



1. B. M. Weckhuysen and J. Yu, *Chem. Soc. Rev.*, 2015, **44**, 7022–7024.
2. R. F. Lobo, S. I. Zones and M. E. Davis, *J. Incl. Phenom. Mol. Recognit. Chem.*, 1995, **21**, 47–78.
3. K. Muraoka, W. Chaikittisilp and T. Okubo, *Chem. Sci.*, 2020, **11**, 8214–8223.
4. OpenAI, 2023, arXiv:2303.08774v4.

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テトラシアノキノジメタン(TCNQ)のソルバトクロミズムに関する理論的研究

(京大工[1]・琉大院理工[2]・京大院工[3]・京大福井センター[4]・名大院情報[5]) ○戸部すみれ[1]・比嘉未香子[2]・佐藤啓文[3,4]・東雅大[5]

Theoretical study on solvatochromism in tetracyanoquinodimethane (TCNQ) ([1] *Faculty of Engineering, Kyoto University*, [2] *Graduate School of Engineering and Science, University of the Ryukyus,*[3] *Graduate School of Engineering, Kyoto University,* [4]*Fukui Institute for Fundamental Chemistry, Kyoto University,* [5]*Graduate School of Informatics, Nagoya University*) ○ Sumire Tobe,[1] Mikako Higa,[2] Hirofumi Sato,[3,4] Masahiro Higashi[5]

Tetracyanoquinodimethane (TCNQ) exhibits solvatochromism, in which, the excitation energy varies depending on the solvent. The absorption wavelength generally changes monotonically with the solvent polarity. However, it is known that solvatochromism of TCNQ shows complicated behavior[1)]. The reason for this property is not yet clear. In this study, we analyzed the solvent dependence of the excitation energy using the polarizable continuum model (PCM) and the QM/MM method.

The results calculated with PCM showed nonmonotonic solvent dependence. However, the calculated excitation energies were not in quantitative agreement with the experimental ones. In the QM/MM calculations with only TCNQ included in the QM region, no significant solvent dependency was observed. In contrast, inclusion of solvent molecules around TCNQ into the QM region and addition of diffuse basis functions reproduced the experimental results almost quantitatively. These results indicate that quantum chemical effects such as electronic polarization in the surrounding solvent molecules play an important role in TCNQ solvatochromism.

Keywords : Tetracyanoquinodimethane (TCNQ), QM/MM Method, Solvatochromism

テトラシアノキノジメタン(TCNQ)は、溶かす溶媒によって励起エネルギーが異なるソルバトクロミズムを示す。一般に吸収波長は溶媒の極性に対して一様に変化するが、TCNQ では複雑な挙動を示すことが知られている[1)]。この性質を示す理由についてはまだ明らかになっていない。そこで本研究では、分極連続体モデル(PCM)、QM/MM 法などを用いて励起エネルギーの溶媒依存性を解析した。

PCM 法を用いた励起エネルギー計算において、極性に対して一様にならないことがわかったが、実験結果を定量的には説明できなかった。また QM/MM 計算において TCNQ のみを QM 領域とした場合では、顕著な溶媒依存性は見られなかった。一方、QM 領域に TCNQ 周りの溶媒分子を加えて、かつ分散基底関数を加えた計算では実験結果と定量的に近い結果が得られた。これらの結果から、TCNQ のソルバトクロミズムにおいて、周辺の溶媒分子における電子分極などの量子化学的な効果が重要な役割を果たしていることを明らかにした。

1) H. Tamaya, H. Nakano, T. Iimori. *J .Lumin.*, **2017**, *192*, 203.

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詳細な電子状態解析に基づく Cu 二核錯体における NH_3-SCR 反応の検討

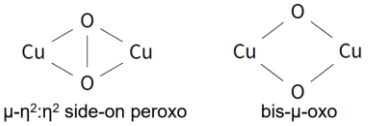
（京大工[1]・京大院工[2]・名大院情報[3]・京大福井センター[4]）○森本流星[1]・杉山佳奈美[2]・東雅大[3]・佐藤啓文[2,4]
Theoretical analysis of electronic structures and reaction mechanisms for NH_3-SCR reaction using binuclear Cu complexes ([1]*Faculty of Engineering, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*Graduate School of Informatics, Nagoya University,* [4]*Fukui Institute for Fundamental Chemistry, Kyoto University*) ○ Ryusei Morimoto,[1] Kanami Sugiyama,[2] Masahiro Higashi[3], Hirofumi Sato[2, 4]

NH_3-assisted selective catalytic reduction (NH_3-SCR) is an effective chemical reaction for NO_x removal. Cu-CHA, a zeolite catalyst, is widely used for the NH_3-SCR reaction because of its high reactivity under low temperature. The binuclear Cu complex in Cu-CHA is highly reactive in the catalytic cycle and its structure is considered to have a Cu_2O_2 structure.[1)] However, the exact structure is challenging to identify both experimentally and theoretiocally.[2)] The proposed reaction mechanisms are also diverse because they include decomposition of Cu_2O_2 and many molecules such as NH_3, NO, and H_2O.[3)]

In this work, we focused on the binuclear Cu intermediate complexes and investigated the electronic structures by using quantum chemical calculations and spin state analysis. Furthermore, the reaction pathways and the stabilities of intermediates were discussed in combination with the automated reaction path search.
Keywords : NH_3-SCR; DFT calculation; Cu-CHA; Zeolite catalyst; Binuclear Cu complex

アンモニアを還元剤とした選択的触媒還元(NH_3-SCR)は、NO_x の除去に有用な化学反応である。中でも特に、酸化物触媒の一種である Cu-CHA は、比較的低温でも高活性であることから注目されている。反応中間体である Cu 二核錯体は Cu_2O_2 骨格を持ち、触媒サイクル中において高い反応性を持つ[1)]。しかし、Cu_2O_2 の構造として bis-μ-oxodicopper(II) や μ-η^2:η^2 side-on peroxodicopper(II)を含む様々な構造が提案されており、その正確な構造は実験でも計算でも特定は困難で、スピン状態についても未解明である[2)]。加えて、SCR 機構中に Cu_2O_2 の分解や、NH_3、NO、H_2O といった様々な分子が存在するため、提案されている反応機構も多岐にわたる[3)]。

本研究では、量子化学計算を用いて Cu 二核錯体の詳細な電子状態解析を行った。bis-μ-oxodicopper(II) および μ-η^2:η^2 side-on peroxodicopper(II)のエネルギー、スピン状態、分子軌道を様々な計算レベルで得ることで安定性を議論した。また反応経路探索を用いて SCR 機構を得て、先行研究と比較しながら妥当性を検討した。



1) C. Paolucci, *et al*., *Science*, **2017**, *357*, 898.
2) L. Chen, *et al*., *Phys. Chem. Chem. Phys.*, **2019**, *21*, 10923.
3) C. Paolucci, *et al*., *Acc. Chem. Res.*, **2020**, *53*, 1881.

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水性ガスシフト反応の反応経路ネットワーク分析

(京大工[1]・京大院工[2]・京大院情報[3]・名大院情報[4]・京大福井センター[5]) ○江村 紅音[1]・杉山 佳奈美[2]・湊 真一[3]・東 雅大[4]・佐藤 啓文[2,5]

Analysis of a Reaction Route Network of Water Gas Shift Reaction ([1]*Faculty of Engineering, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*, [3]*Graduate School of Informatics, Kyoto University*, [4]*Graduate School of Informatics, Nagoya University*, [5]*Fukui Institute for Fundamental Chemistry, Kyoto University*) ○Akane Emura,[1] Kanami Sugiyama,[2] Shin-ichi Minato,[3] Masahiro Higashi,[4] Hirofumi Sato[2,5]

It is important to understand not only main reaction but also side reactions to obtain the desired product with high yield and selectivity. A reaction route network consisting of nodes (molecular structures) and edges (transition states) includes information of such reaction routes, but the analysis method has not been established. In this study, the network of the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) was constructed and analyzed.

First, a reaction route network was created by the Global Reaction Route Mapping (GRRM) program[1]. It is useful to express the route length as a sum especially for more complicated networks. Therefore, the logarithm of the rate constant k was set as the weight of each edge, and the sum of edge weights was set as the length of the route. Then the routes from reactant $CO + H_2O$ to product $CO_2 + H_2$ were enumerated and ranked. Furthermore, enumerated routes were compared with other kinetic analyses[2,3], and the influence of side reactions was discussed.
Keywords : Reaction Route Network; Path Enumeration; Water Gas Shift Reaction

化学反応において目的の生成物を高収率・高選択率で得るためには、主反応だけでなく副反応の解析も重要である。従来の計算の解析は主に主反応を対象としており、主反応以外を系統的に考慮することは難しかったが、反応経路自動探索(GRRM)プログラム[1]によって、多数の反応物・中間体・生成物の系統的探索が作成可能となった。ここで、探索結果から安定構造を頂点、構造間をつなぐ遷移状態を辺とした反応経路ネットワークが構築できる。しかしこのネットワークは非常に複雑で、解析手法は未確立である。本研究では大規模ネットワークの理解を目指し、まず小規模な水性ガスシフト反応 $CO + H_2O \rightarrow CO_2 + H_2$ の反応経路ネットワークの解析手法を検討した。

まず、GRRM プログラムを用いて、10 の安定構造と 12 の遷移状態から成る CH_2O_2 の反応経路ネットワークを構築した。膨大な数の反応経路を列挙し、それぞれの経路長を求めるとき、経路長を和であらわすと都合が良い。そこで、素過程の速度定数 k の対数$\ln k$を各辺の重み、その和を経路の長さと設定し、反応物 $CO + H_2O$ と生成物 $CO_2 + H_2$ をつなぐ経路の列挙と順序付けを行った。さらに、列挙した経路を他の速度解析手法[2,3]で得られた結果と比較して妥当性を検証しながら、副反応が主反応へ与える影響について議論した。

1) S. Maeda, *et al*., *J. Comput. Chem*., **2018**, *39*, 233.
2) Y. Sumiya, *et al*., *J. Phys. Chem. A*, **2015**, *119*, 11641.
3) Y. Nagahata, *et al*., *J. Phys. Chem. B*, **2016**, *120*, 1961.

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Global Area Search(GLAS)法のスピン状態交差を伴う反応系への拡張と有機小分子への適用

(阪大院理[1]・筑波大院工[2]) ○橘川武知[1].山中秀介[1],川上貴資[1],奥村光隆[1],庄司光男[2]

Improvement of GLobal Area Search (GLAS) algorithm and Application of GLAS approach to peptide system([1]Graduate School of Science, Osaka University,[2]Graduate School of Science and Technology, University of Tsukuba) ○Takechika Kikkawa[1],Syusuke Yamanaka[1],Takashi Kawakami[1],Mitsutaka Okumura[1], Mitsuo Shoji[2]

The analysis of intersecting spin states is important in the mechanisms of chemical reactions of transition metals. In fact, standard reaction pathway search methods were also extended to the multiple spin cases[1),2)]. In this study, we extend the Global Area Search (GLAS) method[3)] to deal with multiple spin states. The GLAS method, which was developed by Shoji et al., efficiently searches for potential surfaces within a specified energy range by repulsive interactions among all the sampling structures on the potential surface.

In the spin extended version of the GLAS (SE-GLAS) method, we apply a bias potential in order to search other spin states intersected with the initial spin state. We tested our method using B3LYP calculations on ethylene and formaldehyde molecules. For the ethylene molecule, the SE-GLAS method followed a nearly minimum energy path starting from the planar singlet state, passing through the triplet state with the perpendicularly twisted ethylene structure, and returning to the planar singlet state. For the formaldehyde molecule, the SE-GLAS method successfully searched six S_0 structures and three T_1 structures (including two dissociated structures) via several spin-crossing points. The details will be presented on the day.

Keywords: Automated Exploration of Chemical Reaction Pathway, Quantum Chemical Calculation

スピン状態が交差する状態の解明は遷移金属の化学反応のメカニズムにおいて重要である。実際，標準的な反応経路探索法でも多重スピン系への拡張は行われてきた[1),2)]。本研究では筑波大庄司らによって開発された反応経路探索法の一種であるGlobal Area Search(GLAS)法[3)]を複数のスピン状態を扱えるよう拡張した。GLAS 法は，ポテンシャル曲面上の複数のサンプリング構造間の反発によって，指定したエネルギーレンジ内のポテンシャル曲面を効率的に探索する方法である。

スピン拡張版 GLAS 法では，探索する平面にバイアスポテンシャルをかけることにより初期スピン状態と交差するスピン状態構造を探索する。検証計算には B3LYP 計算を用い，エチレン，ホルムアルデヒドで行なった。エチレン分子では平面構造の一重項から一旦ねじれた構造の三重項状態を経由し平面一重項に戻る最安定反応経路に近い経路を探索し，またホルムアルデヒドでは，複数のスピンクロッシングを経由し，一重項(S_0)状態 6 個と三重項(T_1)状態 3 個を探索した。詳細は当日発表する。

1) J. M. Anglada, J. M. Bofill, J. Comput. Chem. 18, 992-1003
2) S. Maeda, K. Ohno, K. Morokuma , J. Phys. Chem. A. 2009, 113, 1704-1710.
3) M. Shoji, M. Kayanuma, Y. Shigeta Bull. Chem. Soc. Jpn. 2018, 91, 1465–1473.

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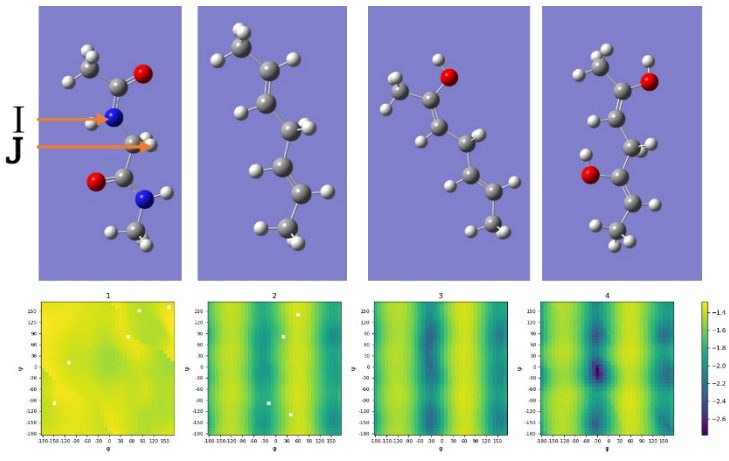
分子系の線形応答関数解析

(阪大院理[1])○尾池　蓮[1]・橘川 武知[1]・丸山 智大[1]・川上 貴資[1]・山中 秀介[1]・奥村 光隆[1]
Linear response function analysis of molecular systems ([1]*Graduate School of Science, Osaka University*) ○Ren Oike[1], Takechika Kikkawa[1], Maruyama Tomohiro[1], Takasi Kawakami[1], Shusuke Yamanaka[1], Mitsutaka Okumura[1]

The linear response function of a molecular system is defined as the density fluctuation of the Jth atom due to a virtual perturbation to the Ith atom in the molecule and can be treated as a descriptor of the reaction. In this study, we investigated the relationship between LRF and result suggests that it is possible to define the "chemical distance in polypeptide systems" as a new index for the calculation and design of protein systems.
Keywords : polypeptide, linear response function

分子系の線形応答関数は分子中の I 番目の原子への仮想摂動による J 番目の原子の密度揺らぎとして定義され、反応の記述子として扱うことができる。本研究では、ポリペプチド系との LRF と分子構造の関係を調べ、LRF の値が水素結合効果と超共役効果を介して C α 原子間の二面角に対して定量的に依存することを見出した。具体的にはポリペプチド系と、超共役構造を持つ類似の分子について LRF を調べた。結果、LRF に超共役が与える効果が見られたと同時に、選択する原子 I,J の原子種の組み合わせに対する依存性も明らかになった。この結果は, タンパク質系の計算や設計のための新たな指標となる「ポリペプチド系における化学距離」の定義が可能であることを示唆している。



[1] E. Prodan and W. Kohn, Proc. Natl. Acad. Sci. USA 102, 11635 (2005).
[2] S. Yamanaka et al., AIP Conf. Proc. 1504, 916 (2012); K. Ueda, et al. Int. J. Quantum Chem. 113, 336 (2013).;Y. Mitsuta, et al., Molecules 19, 13358 (2014); Y. Mitsuta et al., J. Phys. Soc. Conf. Proc. 5, 01105 (2015); Y. Mitsuta, et al. Mol. Phys. 114, 380 (2015); 満田他, アンサンブル 18, (2016); C. Kitagawa, et al. Molecules 24, 821(2019).

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周期境界条件を考慮した *ab initio* 分割統治(DC)法の開発

(北大理[1]・北大院総合化学[2]・北大 WPI-ICReDD[3]・北大院理[4])
○小川 紘[1]・西田 倫嗣[2]・赤間 知子[3]・小林 正人[3,4]・武次 徹也[3,4]

Development of *ab initio* divide-and-conquer method under periodic boundary condition

([1]*Sch. Sci., Hokkaido Univ.*, [2]*Grad. School Chem. Sci. Eng., Hokkaido Univ.*, [3]*WPI-ICReDD, Hokkaido Univ.*, [4]*Fac. Sci., Hokkaido Univ.*) ○Gen Ogawa,[1] Masatsugu Nishida,[2] Akama Tomoko,[3] Masato Kobayashi,[3,4] Tetsuya Taketsugu[3,4]

Accurate quantum chemical calculations for large periodic models are important for the computational elucidation of the elaborate functional manifestations of amorphous materials with complex doping. We have developed the *ab initio* divide-and-conquer (DC) method, which is a fast and accurate method for calculating large-scale systems by dividing the system into subsystems. The DC-MP2 method has also been developed, but it has not been applied to periodic systems. In this study, we developed a program that extends the *ab initio* DC method to periodic systems. This program takes advantage of the features of the DC method to solve periodic systems in real space Gauss basis. This procedure is like the method of periodic boundary conditions in the fragment molecular orbital (FMO) method. We apply this program to amorphous materials and attempt to elucidate their functional manifestations from their electronic states.

Keywords : Divide-and-conquer method; Periodic boundary condition; Amorphous; Electronic structure calculation

複合的なドーピングを含むアモルファス材料の緻密な機能発現を計算化学の見地から解明するには大規模系をユニットセルとする周期モデルに対する高精度な量子化学計算が重要である。従来の大規模周期系に対する量子化学計算手法は半経験的な強束縛近似に基づくため、精度の保証がない。我々は系を部分系に分割して計算を行い、大規模系を高精度のまま高速計算する *ab initio* 分割統治(DC)法[1,2]の開発を行ってきた。また DC-MP2 法も開発してきたが、周期系には適用できていない。本研究では *ab initio* DC 法を周期系へ拡張したプログラムを開発した。本プログラムは DC 法の特徴を活かし、Bloch 基底を用いずに実空間の Gauss 基底で周期系を解く。この手続きは、フラグメント分子軌道(FMO)法における周期境界条件の取扱い[3]に類似する。本プログラムをアモルファス材料に適用し、電子状態から機能発現の解明を試みる。

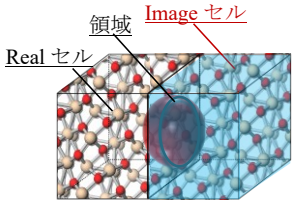

Figure 1：Real セルと Image セル

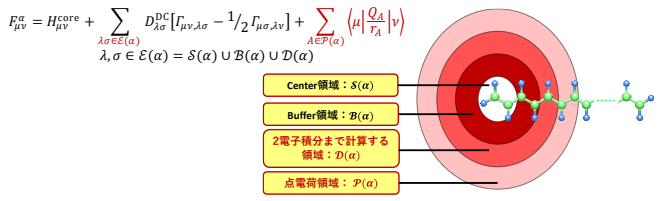

Figure 2：部分系 Fock 式と領域

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カルコゲノアニソールの立体配座に依存した低振動数モードのラマン強度：特異値分解による解析

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Raman intensities of conformation-dependent low-frequency modes of chalcogenoanisole: analysis by singular value decomposition ([1]*School of Informatics and Engineering, University of Electro-Communications,* [2]*Graduate School of Informatics and Engineering, University of Electro-Communication*) ○Akira Mizushina,[1] Keigo Yamaguchi,[2] Yoshihiro Yamakita[2]

We studied the intramolecular rotation-dependent low-frequency Raman intensities of chalcogenoanisole $C_6H_5XCH_3$ (X = O, S, Se), focusing on the interaction between the benzene ring and the substituent XCH_3. Polarizabilities were obtained from dipoles induced by electric fields, and the characters of excitation from occupied to virtual orbitals were represented as natural perturbation orbitals (NPO) using the singular value decomposition (SVD). In the vertical conformation, the values of the off-diagonal terms of the polarizability derivatives for Q_B and Q_T were found to be large and contribute to the enhancement of the Raman intensities, and the σ-π interactions between the benzene ring and the substituent were visualized using the NPOs that contributed the most to $\partial\alpha_{zx}/\partial Q_B$ and $\partial\alpha_{yx}/\partial Q_T$. The $\partial\alpha_{zx}/\partial Q_B$ and $\partial\alpha_{yx}/\partial Q_T$ for the planar conformation were small, resulting in an NPO with a distribution of σ orbitals for anisole and π orbitals for thioanisole and selenoanisole. In summary, the MOs contributing to the polarizability derivative were visualized as NPOs, elucidating the enhancement of Raman intensity as an electronic interaction between the benzene ring and the substituent.

Keywords：Chalcogenoanisole, Raman scattering, Singular value decomposition, Polarizability

カルコゲノアニソール $C_6H_5XCH_3$ (X = O, S, Se)では、ベンゼン環に対して置換基 XCH_3 が垂直な場合、面外変角振動 Q_B とねじれ振動 Q_T との低振動数ラマン強度が増大することが観測・計算されており、σ–π共役による分極率の増大が提案されている[1]。本研究では、分子内回転による垂直構造および平面構造に依存したラマン強度におけるベンゼン環と置換基の間の相互作用の寄与を研究した。分極率は電場で誘起される双極子から算出し、その際の電子分布の変化は、占有 MO から仮想 MO への励起対の重ね合わせとして表すことができる。それらの MO を特異値分解 (SVD) を用いて自然摂動軌道 (NPO) に変換すると、電子分布の変化を表現できる[2]。その結果、垂直構造では、Q_B, Q_T についての分極率微分の非対角項 $\partial\alpha_{zx}/\partial Q_B$, $\partial\alpha_{yx}/\partial Q_T$ がそれぞれラマン強度に大きく寄与することが分かった。Fig. 1(a)は、垂直構造のチオアニソールの Q_B による振動変位と 6 つの占有・仮想 NPO $(\hat{\psi}_i, \hat{\psi}_i')$の組による α_{zx} の変化を示したものであり、1 組目が最大の寄与を示した。Fig. 1(b)には 1 組目の NPO $(\hat{\psi}_1, \hat{\psi}_1')$ の振動変位前後 (Q^0, Q_B) についてそれぞれ示した。この軌道対では、ベンゼン環のπ軌道と置換基のσ軌道の間にσ–π相互作用が表れている。一方、平面構造では Q_B, Q_T による$\partial\alpha_{zx}/\partial Q_B$, $\partial\alpha_{yx}/\partial Q_T$ の値は小さい。平面構造の Q_B については、アニソールではπ軌道が分子全体に広がった NPO が、チオアニソールとセレノアニソールではσ軌道が分子全体に分布した NPO が得られたが、これらは小さな分極率微分しか与えないことが分かった。さらに平面構造の Q_T では、チオアニソールとセレノアニソールのσ軌道は置換基に局在した NPO が寄与することが分かった。

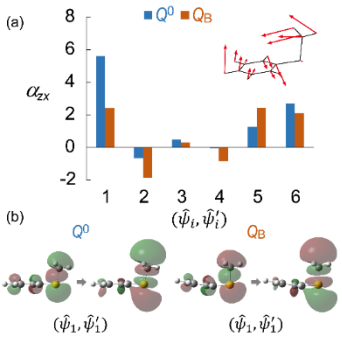

Fig. 1. (a) A comparison of polarizability α_{zx} with respect to out-of-plane bending mode Q_B and (b) NPOs with the largest change in polarizability.

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2) M. Miyamoto, M. Hada, *J. Comput. Chem.*, **2020**, 41, 1628.

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Theoretical study on the muonium adduct structure of N-heterocyclic carbene by path integral molecular dynamics

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○Satoshi Orikono,[1] Kazuaki Kuwahata,[1] Tomomi Shimazaki,[1] Masanori Tachikawa[1]
Keywords: Muon; Quantum Effects; Path Integral Molecular Dynamics; Hyperfine Coupling Constants; Carbenes

The hyperfine coupling constants (HFCC) have been experimentally measured by adsorbing muonium to N-heterocyclic carbenes.[1] However, previous theoretical studies have not fully incorporated the quantum effects of muonium, which makes it difficult to interpret the corresponding experimental HFCC values. In the present study, we have elucidated the details of the muonium adduct structure of N-heterocyclic carbene by using path integral molecular dynamics (PIMD), which can incorporate the quantum effects of muonium.

To investigate the quantum effects, PIMD simulations were performed for three different models of N-heterocyclic carbenes: the muonium addition model (QM(μ)), the hydrogen addition model (QM(H)), and the classical model (CL). Three simulations were conducted under isothermal conditions at 300 K, and the total steps are 100,000, 100,000, and 500,000 steps for QM(μ), QM(H), and CL, respectively. The number of pseudo particles representing quantum effects are 64, 16, and 1 for QM(μ), QM(H), and CL, respectively. The potentials were obtained at the HISSbPBE/6-31G(d,p) level of calculation using Gaussian16.

Fig. 1. shows the HFCC distributions and their expectation values for each simulation, where EQ is the value at the equilibrium structure. The width of the distribution is narrower for CL and wider for QM(μ). The expectation values are similar for all models. The distribution of QM(μ) is large above 500 MHz because the C-Mu bond length elongates due to quantum effects and the HFCC increases. On the other hand, the distribution of QM(μ) is found to be large below 0 MHz because the HFCC decreases as Mu tends to be on the molecular plane due to quantum effects.

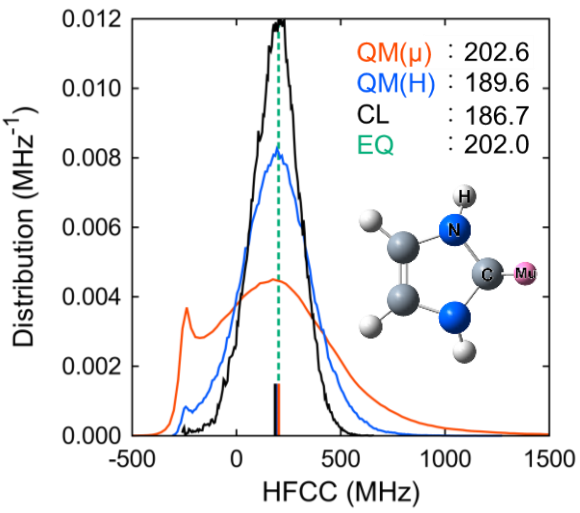

Fig. 1. Distribution of HFCC of N-heterocyclic carbene. Expectation values are also included.

1) Iain McKenzie *et al., J. Am. Chem. Soc.* **2003**, *125*, 11565-11570

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第一原理計算を用いた EGFP の水素結合構造に関する理論的研究

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Theoretical study on hydrogen-bonded structures of EGFP using first-principles calculations

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○Mio Takakuwa,[1] Tomomi Shimazaki,[1] Masanori Tachikawa,[1] Yukiumi Kita[2]

Enhanced Green Fluorescent Protein (EGFP) is a protein that exhibits stronger fluorescence than GFP, which was discovered in a jellyfish, *Aequorea victoria*. Recent neutron crystallography studies on EGFP revealed that the heavy water directly hydrogen-bonded to the chromophore (CRO), DOD323, is longer than other heavy water. This notable elongation is attributed to electrostatic potential effects inside the EGFP protein, though the detailed physicochemical origins remain not fully understood. In conventional EGFP, the structure of the CRO is greatly affected by the peripheral residues such as Arg96 and Thr203. However, it is unclear whether the peripheral residues play a similar role in EGFPs in which the mother liquor is heavy water. In this study, we aimed to elucidate the effect of peripheral residues on the hydrogen-bonded structures near the CRO in heavy water. Applying multi-component density functional theory, which can distinguish H/D quantum fluctuations, to computational models with/without Arg96 and Thr203, we found that Arg96 and Thr203 affect the bond asymmetrization of DOD323, as well as the protonation state of the CRO.

Keywords: Green fluorescent protein; Hydrogen bonded structures; Nuclear quantum effects

高感度緑色蛍光タンパク質(Enhanced Green Fluorescent Protein: EGFP) は、オワンクラゲから発見された GFP より強い蛍光を示すタンパク質である [1)]。近年、母液を重水にした EGFP の中性子結晶解析実験より、発色団(chromophore)と直接水素結合している重水(DOD323)の結合長が一般の重水より長いと報告された [2)]。これはタンパク質内部の静電ポテンシャルの関与が示唆されているが、その詳細は未解明である。従来の EGFP の発色団の構造は、周辺残基である Arg96 と Thr203 から大きな影響を受けることが知られている。しかし、母液を重水にした EGFP において周辺残基が同様の役割を果たすのかは不明である。そこで本研究では、重水環境下において周辺残基が発色団近傍の水素結合構造に与える影響の理論的解明を目的とした。

Arg96 と Thr203 を取り込んだモデルと取り込んでいないモデルを作成し、構造最適化計算を実行した。水素結合構造を詳細に解析するために、H/D の量子揺らぎを区別可能な多成分密度汎関数理論 [3)]を実装した Gaussian16 を用いた。その結果、Arg96 と Thr203 は DOD323 の結合の非対称化に影響すること、また発色団の電荷と構造にも影響を与えることが分かった [4)]。

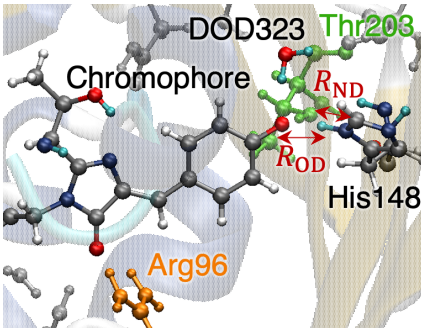

Fig. 1. The location of chromophore, DOD323, Arg96 and Thr203 in EGFP.

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2) Chie Shibazaki *et al. J. Phys.* **2020**, 11, 492.
3) T. Udagawa *et al. J. Chem. Phys.* **2006**, 125, 244105.
4) M. Takakuwa, *et al. Bull. Chem. Soc. Jpn.* **2023**, 96, 711.

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光イオン化された OCS^{2+} の非断熱解離過程の動力学シミュレーション

(北大院総化[1]・北大院理[2]・九大基幹[3]・九大院総理工[4]・北大 WPI-ICReDD[5])
○神原 龍冬[1]・堤 拓朗[2]・古屋 謙治[3,4]・武次 徹也[2,5]

Surface hopping *ab initio* molecular dynamics simulation on nonadiabatic dissociation process of OCS^{2+} induced by photoionization ([1]*Grad. Sch. Chem. Sci. Eng., Hokkaido Univ.*, [2]*Fac. Sci., Hokkaido Univ.*, [3]*Fac. Arts Sci., Kyushu Univ.*, [4]*Dep. Mol. Mat. Sci., Kyushu Univ.*, [5]*WPI-ICReDD, Hokkaido Univ.*) ○Ryuto Kambara,[1] Takuro Tsutsumi,[2] Kenji Furuya,[3,4] Tetsuya Taketsugu[2,5]

The photoion–photoion coincidence (PIPICO) spectroscopy enables us to explore ionized-dissociation products and their energy threshold levels systematically. For OCS molecule, the thresholds for S^+ or O^+ dissociation after doubly photoionization were reported[1)]. In computational chemistry, the global reaction route mapping (GRRM) strategy[2)] exhaustively exposes reaction paths including dissociative channels. To analyze the PIPICO results for OCS^{2+}, we have investigated the reaction path networks for the triplet ground state of OCS^{2+}; however, it reveals discrepancies between observed dissociation thresholds and calculated ones[3)]. This discrepancy suggested the involvement of electronically excited states in dissociation reactions. In this study, we utilized surface hopping *ab initio* molecular dynamics (AIMD) simulations on the excited OCS^{2+} to elucidate the S^+ and O^+ dissociation mechanisms.
Keywords: Nonadiabatic Transition, AIMD, Excited States, Unimolecular Dissociation, Multiply-Charged Ions

光イオン－光イオンコインシデンス（PIPICO）実験は放射光照射により分子を多重イオン化することで解離生成物の網羅的観測を可能にする。これまでに PIPICO 実験により OCS^{2+} からの S^+ および O^+ の解離閾値が報告されている[1)]。一方、計算化学分野では反応経路自動探索法[2)]によって解離経路を含む網羅的反応経路網を得ることが可能となった。我々は、OCS に対する PIPICO 実験の結果を詳細に検討するために OCS^{2+} の 3 重項基底状態における反応経路探索を行い、解離経路の活性化エネルギーが実験結果と矛盾することを見出した[3)]。この結果は電子励起状態の関与を示唆している。そこで、我々は非断熱遷移を考慮した *ab initio* 分子動力学計算を実行し、OCS^{2+} の励起状態解離反応の動力学を調査した。これにより、実験結果に矛盾しないエネルギー帯における S^+ および O^+ の解離反応を見出した(**Fig. 1**)。

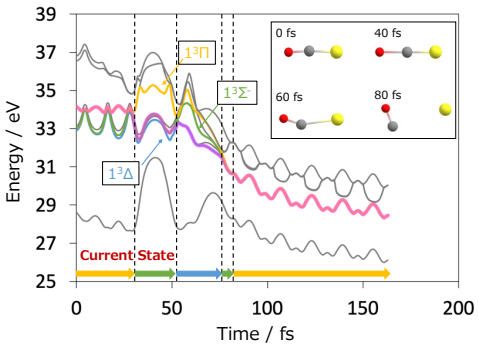

Figure 1. Variations of potential energies along a typical trajectory.

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ポリヒドロキシフラーレンからカーボンナノチューブへの近赤外光誘起成長反応における加熱機構

（東北大理[1]・東北大院理[2]）○本開 真皓[1]・菅野 学[2]・美齊津 文典[2]・河野 裕彦[2]
Heating Mechanism in Near-Infrared Laser-Induced Growth Reactions from Polyhydroxy Fullerenes to Carbon Nanotubes ([1] *Faculty of Science, Tohoku Univ.*, [2] *Graduate School of Science, Tohoku Univ.*) ○Mahiro Honkai,[1] Manabu Kanno,[2] Fuminori Misaizu,[2] Hirohiko Kono[2]

The effect of chemical modification on the structural stability of C_{60} is an intriguing topic in the field of nanocarbon chemistry. Experiments have been reported by Krishna *et al*. on the irradiation of various fullerene derivatives with low-intensity (10^2 Wcm^{-2}) near-infrared (785 nm) lasers for several 10 seconds at room temperature.[1)] Generation of carbon nanotubes and carbon onions has been observed only for the samples of polyhydroxy fullerenes (PHFs), indicating that the temperature of the system exceeds 2600 K. Krishna *et al*. explained this photoreaction in the electronic ground state. However, electronic excitation may still be possible due to long-time irradiation even with low-intensity lasers. We selected $C_{60}(OH)_{24}$ as a PHF molecule to examine the laser-induced heating mechanism using real-time TDDFTB dynamics calculations.[2)]

Since a simulation on the order of 10 seconds is difficult, we assumed that $C_{60}(OH)_{24}$ at its equilibrium structure is exposed to a linearly polarized 20-ps laser pulse with an intensity of 4.8×10^{12} Wcm^{-2} and a wavelength of 785 nm. In the real-time TDDFTB, the time-dependent Kohn-Sham equation is solved to simulate electron dynamics at time t, and then the molecular structure at $t + \Delta t$ is obtained by running a classical nuclear trajectory on the average potential formed by the electrons. Figure 1 shows a dramatic increase in the average potential (i.e., electronic energy) of $C_{60}(OH)_{24}$, which indicates a significant contribution of the electronic excitation. The nuclear kinetic energy continues increasing even after the end of the laser pulse (> 20 ps), and thus the molecule is expected to be heated through electronic relaxation. On the assumption of complete relaxation to the electronic ground state, the temperature of the system is estimated to reach about 3200 K. In contrast, the energy of pristine C_{60} hardly increases upon irradiation with the same laser pulse. This means that hydroxy groups are responsible for the heating of PHFs.

Keywords : Fullerene Derivatives, Carbon Nanotubes, Near-Infrared Laser, Real-Time TDDFTB

化学修飾が C_{60} の特異的な構造安定性に与える影響は、ナノカーボン化学の興味深い問題である。Krishna らは数種類の C_{60} 誘導体の粉末に室温で低強度 (10^2 Wcm^{-2}) の近赤外 (785 nm) レーザーを数 10 秒間照射する実験を行った[1)]。ポリヒドロキシフラーレン (PHF) でのみ、カーボンナノチューブなどの生成が確認され、系の温度は 2600 K を超えた。Krishna らはこの反応が電子基底状態で進行すると考えたが、低強度レーザーでも長時間照射することで電子励起が起こる可能性がある。本研究では $C_{60}(OH)_{24}$ を対象とし、実時間 TDDFTB 動力学計算[2)]を用いて PHF の加熱機構を調べた。

秒オーダーの計算は困難なので、光強度に対する線形応答を仮定し、$C_{60}(OH)_{24}$ の安定構造に光強度 4.8×10^{12} Wcm^{-2}、波長 785 nm、パルス長 20 ps の直線偏光パルスを照射する計算を行った。実時間 TDDFTB 法では、時間依存 Kohn-Sham 方程式を解いて時刻 t における電子ダイナミクスを求め、電子が形成する平均ポテンシャルに沿って原子核の古典軌道を走らせて $t + \Delta t$ の分子構造が得られる。Fig. 1 は $C_{60}(OH)_{24}$ の平均ポテンシャル (電子エネルギー) が急増し、電子励起の寄与が大きいことを示している。原子核の運動エネルギーはパルス消失後 (> 20 ps) も増えており、電子緩和を経て $C_{60}(OH)_{24}$ が加熱されると考えられる。電子基底状態へ完全に遷移すると、系の温度は約 3200 K に達する。C_{60} では同様の計算を行ってもエネルギーは増えず、PHF の加熱はヒドロキシ基に起因することが明らかになった。

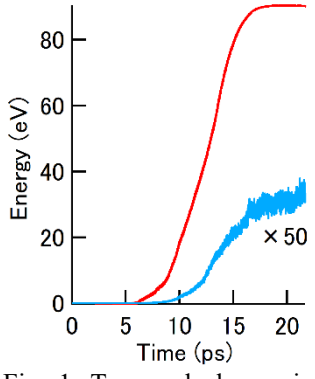

Fig. 1. Temporal change in the potential (red) and kinetic (blue) energies of $C_{60}(OH)_{24}$.

1) V. Krishna *et al*., Nat. Nanotechnol. **5**, 330 (2010).
2) F. P. Bonafé *et al*., J. Chem. Theory Comput. **16**, 4454 (2020).

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

Wed. Mar 20, 2024 1:00 PM - 3:00 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:00 AM UTC
A1452(1452, Bldg. 14 [5F])

[A1452-3pm] 03. Physical Chemistry -Structure-

Chair: Mitsuhiko Miyazaki, Toshiaki Ando

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1452-3pm-01]
Photoreactions of the C_2H_4-SO_2 complex in a low-temperature matrix (II): A pursuit of reaction pathways

○Fumiyuki Ito[1], Toshihiro Omokawa[2], Jun Miyazaki[2] (1. AIST, 2. TDU)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1452-3pm-02]
Observation of Ar Atom Migration in the Resorcinol-Ar$_n$ (n = 1, 2) Clusters by MATI-IR Spectroscopy

○Yumeno HIGO[1], Mitsuhiko MIYAZAKI[1] (1. Ochanomizu University)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1452-3pm-03]
Formation and gas-phase photoelectron spectroscopy of dimers of open-shell superatom anions $[PtAu_{24}(SC_nH_{2n+1})_{18}]^-$

○Yosuke NAKASHIMA[1], Shun ITO[1], Kiichirou KOYASU[1], Tatsuya TSUKUDA[1] (1. Graduate School of Science, The University of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1452-3pm-04]
Spectral changes in the far-ultraviolet region caused by the structure of lipid bilayers

○YOSHIKI Hanjo[1], Yusuke Morisawa[1] (1. kindai university)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1452-3pm-05]
Study of electronic structure of adamantane in condensed phase by far-ultraviolet spectroscopy

○Tomoyuki Komoto[1], Yusuke Morisawa[1] (1. kinki university)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1452-3pm-06]
Relation between solution states and electronic states of water in high concentrated lithium and sodium salt aqueous electrolyte

○Yusuke Morisawa[1], Shoichi Higashi[1], Ayano Nanba[1], Ryotarou Wake[1] (1. Kindai University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

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Break

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[A1452-3pm-07]
Construction and evaluation of optical measurement system for excitation-emission map using Fourier transform spectroscopy

○Shintaro Yamamoto[1], Takumi Ehara[1], Shuji Kimura[1], Ami Takada[1], Tomohiro Ogawa[1], Kiyoshi Miyata[1], Ken Onda[1] (1. Kyushu University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[A1452-3pm-08]
Effect of 2′-OH Group of Sugar Moiety in Nucleotides on Intermolecular Dynamics of Their Aqueous Solutions

○Masako Shimizu[1], Hideaki Shirota[1] (1. Chiba University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1452-3pm-09]
Infrared spectroscopic analysis of Ca^{2+}-coordination structure of parvalbumin: Effect on Glu at the 12th position by an amino-acid replacement

○Masayuki Nara[1], Hisayuki Morii[1], Akira Sakamoto[2], Takuya Miyakawa[3], Masaru Tanokura[4] (1. Tokyo Medical and Dental University, 2. Aoyama Gakuin Univ., 3. Kyoto Univ., 4. The Univ. of Tokyo)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1452-3pm-10]
Analysis of Conformational Change of Perfluoroalkanes by Heating Measurement

○Taisuke Araki[1], Taizo Mori[1], Takayuki Oka[1], Nobutaka Shioya[1], Takeshi Hasegawa[1] (1. Kyoto University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[A1452-3pm-11]
Free-energy analysis of the cosolvent effects on the peptide amorphous aggregation through molecular dynamics simulation

○Yudai Tagawa[1], Kento Kasahara[1], Nobuyuki Matubayasi[1] (1. Osaka University)

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C_2H_4-SO_2 錯体の低温マトリックス環境下での光化学反応

（２）反応機構の検討

（産総研 [1]、東京電機大学 [2]）○伊藤文之 [1,2]、面川駿宏 [2]、宮﨑淳 [2]
Photoreactions of the C_2H_4—SO_2 complex in a low-temperature matrix (II): A pursuit of reaction pathways ([1]*AIST*, [2]*Tokyo Denki University*) ○Fumiyuki Ito,[1,2] Toshihiro Omokawa,[2] Jun Miyazaki[2]

We explored the reaction pathways of C_2H_4—SO_2 complex following UV excitation via S_1-S_0 transition (250-300 nm) by using density functional calculations. The details will be presented in the conference.
Keywords : Matrix-isolation; density functional theory; infrared spectroscopy; T_1 state

我々は昨年の本学会において、低温アルゴンマトリックス中におけるエチレン C_2H_4 と二酸化硫黄 SO_2 の光誘起反応生成物の赤外分光と、密度汎関数法による同定について発表を行った [1)]。本研究では、光励起に伴い SO_2 が項間交差により $S_1 \rightarrow T_1$ 緩和を行ってから C_2H_4 と反応するという仮定の下に反応機構の検討を行ったので、その結果について発表する。

先ず B3LYP-D_3/6-31+G(d) レベルで S_0 状態における C_2H_4—SO_2 錯体の構造最適化を行った。得られた構造は FTMW 分光 [2)]で得られたものとよく一致した。SO_2 の $S_1(^1B_1) \rightarrow T_1(^3B_2)$緩和は数百 fs 程度で進行する事から [3)]、同錯体の T_1 状態の構造最適化を Frank-Condon 状態から行い、T_1 の安定構造を探索した。その結果、3 個の安定構造を得た（図１）。安定性の順位は分散力補正の有無に依存しなかった。C_2H_4 に SO_2 が酸素原子側で求電子付加したバイラジカルが最安定であり、我々が先に同定した反応生成物（図２）の T_1 状態と同一であることがわかった。詳細は当日発表する。

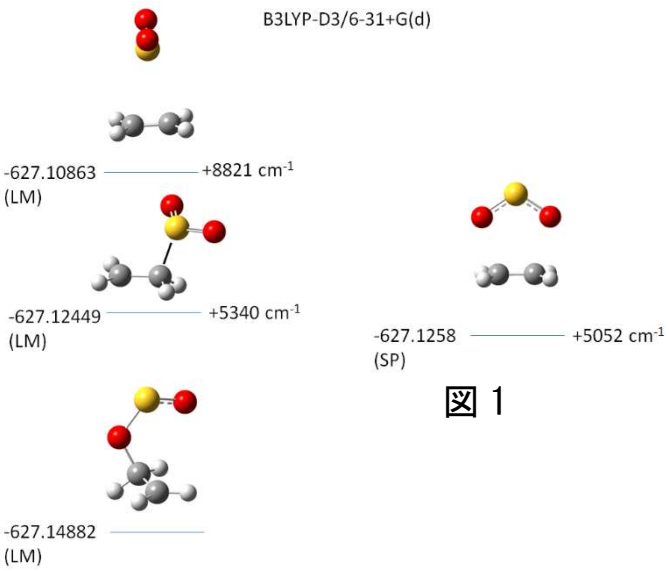

図 1

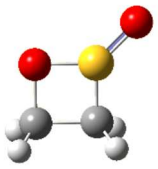

図２

1)日本化学会第 103 春季年会、K201-4am-01. 2) Andrews *et al*., J. Chem. Phys. 93, 7030 (1990). 3) Mai, Marquetand, Gonzalez, J. Chem. Phys. 140, 204302 (2014).

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MATI-IR 分光法による Resorcinol(I)–Ar$_n$ (n = 1, 2)クラスターの Ar 原子移動反応の観測

（お茶大[1]・お茶大基幹[2]）○肥後 夢乃・宮﨑 充彦
Observation of Ar Atom Migration in the Resorcinol–Ar$_n$ (n = 1, 2) Clusters by MATI-IR Spectroscopy (*Department of Chemistry, Faculty of Science, Ochanomizu University*)
○Yumeno Higo, Mitsuhiko Miyazaki

Solvation dynamics has a strong impact on mechanism of chemical reactions. Migration of Ar in the phenol–Ar$_n$ clusters from the π-ring to the OH group has attracted attention as a microscopic model of solvation dynamics by non-polar solvent. In this study, we showed that the π→OH Ar migration also occurs in the resorcinol–Ar$_n$ (n = 1, 2) clusters, though the acidity of the OH groups is lower than that of phenol. Energy dependence of the π→OH Ar migration was investigated in detail by MATI-IR spectroscopy, which utilizes the high Rydberg states.
Keywords : Infrared spectroscopy; Gas phase cluster; Intermolecular site switching; Mass-analyzed threshold ionization spectroscopy

分子の溶媒和構造変化のダイナミクスは、化学反応に大きな影響を与える。そのため、光励起に誘起される溶媒和構造変化のメカニズムが研究されている。本研究では、超音速ジェット中に生成する気相 resorcinol–Ar$_n$ (Rs–Ar$_n$, n = 1, 2)クラスターを用いて、光イオン化に誘起される溶媒和運動の振動準位依存性の観測を試みた。

Rs–Ar$_1$ の最安定構造は、中性状態では Ar 原子が π 電子雲と結合した π 結合構造、カチオン状態では OH 基の H 原子と結合した H 結合構造である。従って、イオン化により Ar 原子は π 電子雲から OH 基へ移動する π→OH 移動が起きる。本研究では、この Ar 移動反応の振動準位依存性を調べるため、イオン状態の単一振動準位からの反応性について高 Rydberg 状態を利用する MATI-IR 分光法[1]を用いて検討した。

Fig. 1 に Rs–Ar$_1$ の共鳴イオン化から生成した RsI$^+$–Ar$_1$ の赤外スペクトル（REMPI-IR）と MATI-IR スペクトルを示す。π 結合構造イオンのゼロ振動準位（IE_0）では、π 結合構造の自由 OH 伸縮振動だけが 3569 と 3581 cm^{-1} に観測され、π→OH 移動は起きないことがわかる。一方、IE_0 よりも−6.1 cm^{-1} 下にイオン化した際には、REMPI-IR スペクトルに 3540 cm^{-1} 付近にブロードな H-結合型に由来する OH 伸縮振動が観測され、Franck-Condon の垂直遷移からは困難と予想される π→OH の直接イオン化が起きているように見える。講演では、phenol–Ar$_1$ クラスターとの比較を通して Ar 移動反応の機構について議論する予定である。

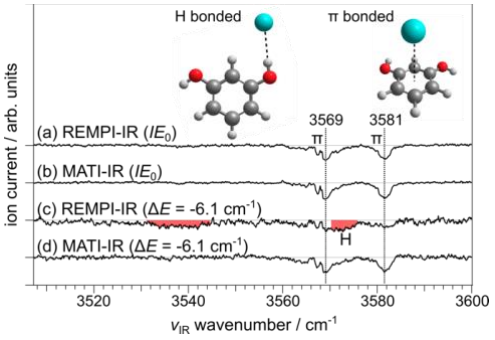

Fig. 1 Rs–Ar$_1$ の IE_0 での(a) REMPI-IR、(b) MATI-IR スペクトル、および ΔE = −6.1 cm^{-1} での(c) REMPI-IR、(d) MATI-IR スペクトル

[1] M. Miyazaki et al., *Phys. Chem. Chem. Phys.* **2015**, *17*, 2494.

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Formation and gas-phase photoelectron spectroscopy of dimers of open-shell superatom anions $[PtAu_{24}(SC_nH_{2n+1})_{18}]^-$

(*Graduate School of Science, The University of Tokyo*) ○Yosuke Nakashima, Shun Ito, Kiichirou Koyasu, Tatsuya Tsukuda

Keywords: Metal Cluster; Electrospray Ionization; Mass Spectrometry

Thiolate-protected gold clusters can be viewed as chemically modified Au superatoms. For example, $[PtAu_{24}(SC_nH_{2n+1})_{18}]^-$ ($[\boldsymbol{n}]^-$) (Figure 1 for n = 4) has an icosahedral $PtAu_{12}$ core with an open electron configuration $(1S)^2(1P)^5$. Interaction between chemically modified Au superatoms plays crucial roles in exchange processes of the ligand(s), metal atom(s), and electron and crystallization. In this work, we studied electronic structures of $([\boldsymbol{m}]\cdot[\boldsymbol{n}])^{2-}$ (m, n = 6, 8, 10, or 12) formed from $[\boldsymbol{m}]^-$ and $[\boldsymbol{n}]^-$ in gas phase and discussed the nature of the interaction.

The dimer $([\boldsymbol{m}]\cdot[\boldsymbol{n}])^{2-}$ was formed by electrospray ionization of a mixed solution of chemically synthesized $[\boldsymbol{m}]^-$ and $[\boldsymbol{n}]^-$ (m, n = 6, 8, 10, or 12). Photoelectron (PE) spectra of pulsed, mass-selected beams of $([\boldsymbol{m}]\cdot[\boldsymbol{n}])^{2-}$ were recorded using the 3rd, 4th, and 5th harmonics of Nd:YAG laser. The PE spectra of $[\boldsymbol{n}]^-$ and $[\boldsymbol{n}]^{2-}$ were also obtained as references.

As an example, a typical PE spectrum of $([\mathbf{6}]\cdot[\mathbf{8}])^{2-}$ is shown in Figure 2a. It exhibits a cutoff at high electron binding energy region by repulsive Coulomb barrier (RCB), as indicated by gray shade. The spectral onset due to electron detachment from 1P orbital of $([\mathbf{6}]\cdot[\mathbf{8}])^{2-}$ was 2.34 eV, significantly smaller than those of $[\mathbf{6}]^-$ and $[\mathbf{8}]^-$ (3.26 and 3.30 eV, respectively). The relative intensity of the metal(5*d*) band with respect to the 1P band of $([\mathbf{6}]\cdot[\mathbf{8}])^{2-}$ was more similar to that of $[\mathbf{6}]^-$ than that of $[\mathbf{6}]^{2-}$ (Figure 2b). This result indicates that $([\mathbf{6}]\cdot[\mathbf{8}])^{2-}$ is viewed as $[\mathbf{6}]^-\cdot[\mathbf{8}]^-$ rather than $[\mathbf{6}]^{2-}\cdot[\mathbf{8}]^0$ or $[\mathbf{6}]^0\cdot[\mathbf{8}]^{2-}$. The formation of dimer of open-shell superatoms $[\mathbf{6}]^-\cdot[\mathbf{8}]^-$ suggests that vdW attraction between alkyl chains exceeds the electrostatic repulsion between $[\mathbf{6}]^-$ and $[\mathbf{8}]^-$. Gas-phase PES thus enables us to distinguish the charge states of the dimers and gain experimental insights on the inter-cluster interactions.

1) Fei, W. *et al. J. Am. Chem. Soc.* **2019**, *141*, 16033. 2) Suyama, M. *et al. J. Am. Chem. Soc.* **2019**, *141*, 14048.

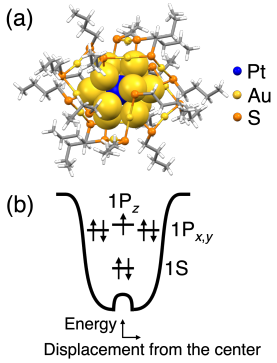

Figure 1. (a) Crystal structure of $[\mathbf{4}]^0$, and (b) schematic diagram of the electronic structure of $[\boldsymbol{n}]^-$.[1,2]

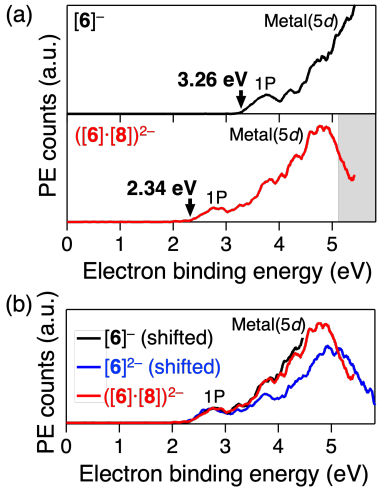

Figure 2. (a) PE spectra of $[\mathbf{6}]^-$ and $([\mathbf{6}]\cdot[\mathbf{8}])^{2-}$ at 213 nm. Black arrows and a gray shaded region indicate onset energies and a cutoff region by RCB, respectively. (b) PE spectra of $[\mathbf{6}]^-$, $[\mathbf{6}]^{2-}$, and $([\mathbf{6}]\cdot[\mathbf{8}])^{2-}$ after normalization and horizontal shift for comparing their spectral features.

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脂質において観測された二重膜構造によって生じる遠紫外領域のスペクトル変化

（近畿大学院[1]・近畿大学理工[2]）○繁昌義樹[1]・森澤勇介[1,2]

Spectral changes in the far-ultraviolet region caused by the structure of lipid bilayers

([1] Graduate School of Science and Engineering, kindai University, [2]science and engineering , Kindai University) ○Yoshiki Hanjo,[1] Yusuke Morisawa,[1,2]

We have developed a new spectroscopic technique using attenuated total reflection (ATR) in the far ultraviolet (FUV) region. This technique allows us to observe electronic transitions from the σ orbitals that form the backbone of organic molecules. Previous studies have shown that the ATR-FUV spectra of low-temperature solid n-alkanes exhibit a decrease in excitation energy, suggesting a change in the electronic state of the σ orbitals due to interactions between the alkyl chains.[1] Inspired by these findings, this study aimed to analyze the membrane structure due to intermolecular interactions between alkyl chains in lipid bilayers. Lipid bilayers were prepared by the manipulation described in the paper [2]. In this experiment, when the lipid bilayers were prepared with H_2O and D_2O, a red shift of 10 nm was observed as seen in Fig. 1b..

Keywords : Lipid Bilayer Membrane, far-ultraviolet

我々は、遠紫外（FUV）領域の減衰全反射（ATR）を用いた新しい分光技術を開発した。この技術により、有機分子の骨格を形成するσ軌道からの電子遷移を観測することができる。これまでの研究により、低温固体の n-アルカンの ATR-FUV スペクトルが励起エネルギーの減少を示すことが示されており、アルキル鎖間の相互作用によるσ軌道の電子状態の変化が示唆されている。[1]これらの知見に触発され、本研究では脂質二重膜中のアルキル鎖間の分子間相互作用による膜構造解析を目指した。脂質二重膜は[2]の論文に書かれている操作で脂質二重膜を作成した。今回の実験では脂質二重膜の中の溶液を H_20 と D_20 で作成すると H_20 では 160nm に観測されたピークが D_20 では 170nm にピークが観測されていることから 10nm のレッドシフトが観測された。この原因について考察する。

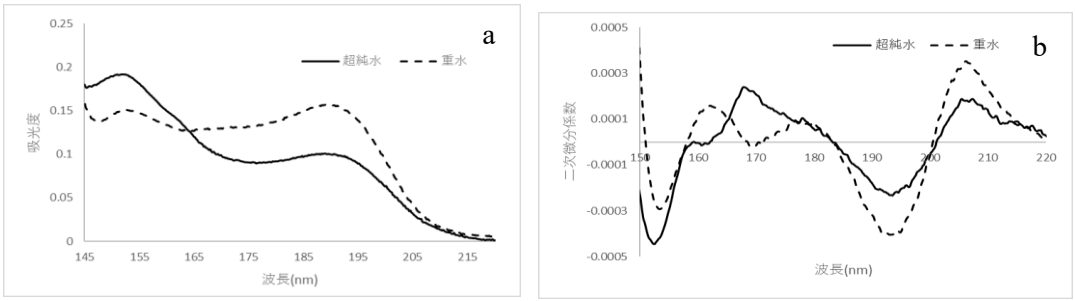

図１ monoolein の ATR-FUV スペクトル(a)と二次微分スペクトル(b)

[1] Morisawa et al. “Changes in the Electronic States of Low-Temperature Solid n-Tetradecane: Decrease in the HOMO–LUMO Gap”, *ACS Omega*, 2017, 2, 618-625

[2] Pisania M., “Nanostructured liquid crystalline particles as delivery vectors for isofuranodiene: Characterization and in-vitro anticancer activity”, *Colloids and Surfaces B: Biointerfaces* 2020, 192, 111050.

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遠紫外分光法を用いた凝縮相中のアダマンタンの電子状態の研究

（近大理工[1]）○河本 朋之[1]・森澤 勇介[1]

Study of electronic structure of adamantane in condensed phase by far-ultraviolet spectroscopy

([1]*Kindai University*) ○Tomoyuki Komoto,[1] Yusuke Morisawa,[1]

Our group measured FUV spectra of cast film of adamantane using attenuate total reflection technique. We found the FUV spectra of adamantane in the film have absorption band in the different wavelength region (140—300 nm) from the FUV spectra of adamantane in the gas phase. The origin of spectral alternation has not been elucidated. Therefore, in this study, we focus on the solution state that is thought to be in isotropic interactions and present the results and analysis of the electronic state of adamantane in solution using different solvents. I dissolved a suitable amount of adamantane (99.8%) in chloroform and hexane solvents and measured the adamantane in solution using attenuated total reflection far-infrared spectroscopy. Analyzing the acquired spectra using Kramers-Kronig relation (KK transformation) and second derivative, a blue shift was observed in the spectrum of hexane solvent compared to chloroform solvent. The Fig1 represents the second derivative spectrum of adamantane in chloroform solvent.

Keywords : FUV; adamantane; electronic transitions;

当研究室において行われた減衰全反射遠紫外分光法を用いたアダマンタンの薄膜のスペクトル測定を行った。紫外光電子分光によって得られている気相中のアダマンタンに対し、薄膜状態のアダマンタンでは異なる波長領域吸収が観測されたが，その帰属をはじめとして，スペクトル変化の原因解明には至っていない。そこで本研究では等方的な相互作用を受けていると考えられる溶液状態に注目し、異なる溶媒を用いて溶液中アダマンタンの電子状態を測定・解析を報告する。

アダマンタン(99.8%)をクロロホルム溶媒およびヘキサン溶媒に適量溶かし、減衰全反射遠視外分光法を用いて溶液状態でのアダマンタンを測定した。獲得したスペクトルを Kramers-Kroning の関係式(KK 変換)および二次微分を用いて解析したところ、クロロホルム溶媒に対しヘキサン溶媒のスペクトルのブルーシフトが観測された。Fig1 はクロロホルム溶媒におけるアダマンタンの二次微分スペクトルである。

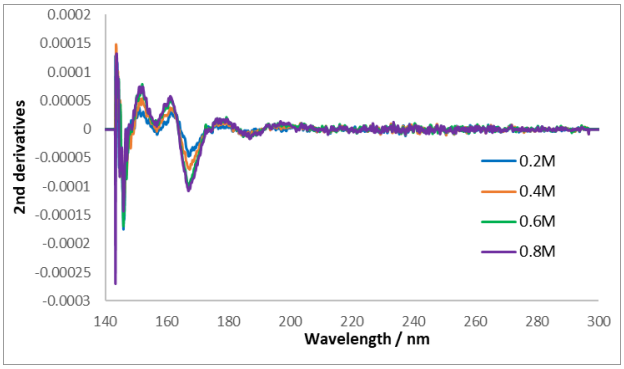

Fig1. The 2nd derivative FUV spectra of Adamantane in chloroform. The FUV spectrum was derived by the subtracted spectra using the pure chloroform spectrum multiplying by a ratio that takes into account the concentration in the solution.

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高濃度リチウムおよびナトリウム塩を用いた水系電解質における水の溶液構造と電子状態

（近畿大学[1]）○森澤 勇介[1]、東 翔一[1]、難波 綾乃[1]、和氣 諒太郎[1]

Relation between solution states and electronic states of water in high concentrated lithium and sodium salt aqueous electrolytes.

([1] *School of Science and Engineering, Kindai University*)
○Yusuke Morisawa[1], Shoichi Higashi[1], Ayano Nanba[1], Ryotarou Wake[1]

High-concentration lithium and sodium salt aqueous solutions exhibit excellent properties as electrolytes at ultra-high concentrations (m >18 mol kg^{-1}), such as hydrate-melt and water-in-salts, show a great property, for example, wide range of electrochemical stability. Changes in the electronic state of water due to cation coordination are thought to be a contributing factor to such the unique nature of this state. It is also known that the hydrogen bond structure with anions changes depending on the salt concentrations. In this study, we will observe the electronic state of water using attenuated total internal reflection far-UV spectroscopy (ATR-FUV), and examine the solution structure using near-infrared spectroscopy in the same solution. In case of the very high concentration of electrolyte in aqueous solutions, FUV spectroscopy shows that the first electron transition of water shifts to a higher energy due to the coordination of the cations to the n-electron of oxygen. On the other hand, using NIR spectroscopy, changes in the hydrogen bond structure of water were clearly observed as shifts of frequency of overtone. Regarding changes in hydrogen bonds, differences were observed between lithium and sodium salts.

Keywords : Aqueous electrolyte; hydrate melt; storage battery

高濃度のリチウムおよびナトリウム塩水溶液は、ハイドレイトメルトや water-in-solt と呼ばれるような超高濃度（m >18 mol kg^{-1}）領域では，気化学的安定性が大幅に向上するなど，電解質として優れた特性を示します。カチオン配位による水の電子状態の変化によって水の酸化が阻害されることにより，このような独特の性質に寄与する要因であると考えられています。また、陰イオンとの水素結合およびカチオンとの構造変化によって，電極表面への不動態膜の形成が進むと考えられています。本研究では、減衰全反射遠紫外分光法(ATR-FUV)を用いて水の電子状態を観察し、同じ溶液中での近赤外分光法を用いて溶液の構造を調べます。すでに，リチウムにおいて報告したように[1]，ナトリウムにおいても水溶液中の電解質の濃度が非常に高い場合、FUV 分光法は、酸素の n 電子へのカチオンの配位により、水の第一電子遷移がより高いエネルギーにシフトしたことをとらえました。一方、近赤外分光法を用いると、水の水素結合構造の変化が倍音の周波数の変化としてはっきりと観察されました。水素結合の変化については，リチウム塩とナトリウム塩で違いが見られました。

[1] Ueno N., Takegoshi M., Zaitseva A., Ozaki, Y., Morisawa Y., “Experimental verification of the increased electronic excitation energy of water in hydrate-melt via ATR-far ultraviolet spectroscopy,” *J. Chem. Phys.* **2022**, 156 (7) 074705

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フーリエ変換分光法を用いた励起-蛍光マップ測定系の構築および評価

（九大院理[1]）○山本 真太朗[1]・江原 巧[1]・木村 周慈[1]・髙田 亜美[1]・小川 知弘[1]・宮田 潔志[1]・恩田 健[1]

Construction and evaluation of excitation-emission map measurement system using Fourier transform spectroscopy ([1]*Graduate School of Science, Kyushu University*) ○ Shintaro Yamamoto[1], Takumi Ehara[1], Shuji Kimura[1], Ami Takada[1], Tomohiro Ogawa[1], Kiyoshi Miyata[1], Ken Onda[1]

Excitation-emission map (EEM) shows both excitation spectrum and emission spectrum at the same time, which is capable of detecting spectrally buried individual components and intermolecular energy transfer in heterogeneous systems at steady state. However, it takes a long time to acquire one EEM with a conventional measurement system, and instrumental limitation causes its wavelength resolution. EEM can be quickly acquired by adopting Fourier transform (FT) spectroscopy. FT spectroscopy is a widespread method in infrared region, but it is less common in ultraviolet and visible wavelength because of the requirement of severe instrumental control.

Here, we constructed a quick EEM measurement system in UV and visible range with Fourier transform spectroscopy using a high precision birefringence-based interferometer[1]. The extracted excitation spectrum from the EEM of rhodamine 6G has confirmed sufficient agreement with the results obtained by conventional methods. We also applied the EEM system to heterogeneous systems and succeeded in separating each species in heterogeneous systems as different peaks.

Keywords : Fourier transform spectroscopy; Excitation-Emission Map (EEM); Inhomogeneity; Mixture

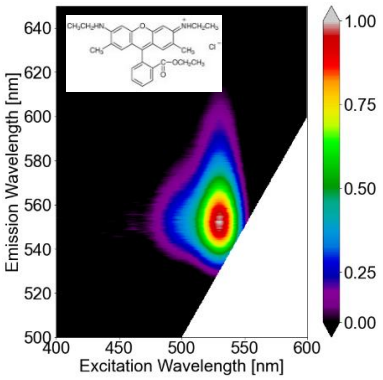

Fig.1 Acquired EEM of rhodamine 6G in methanol. (Inset: molecular structure of rhodamine 6G.)

励起-蛍光マップ（EEM）は励起スペクトルと蛍光スペクトルを同時にプロットする手法であり、不均一系の成分解析および成分間のエネルギー移動の検出に有効である。しかし従来の分散光学系を用いる方法では EEM の取得に長時間の測定を要するうえ、波長分解能は光学部品により制限される。フーリエ変換分光法は高速でスペクトル取得が可能であり、赤外領域では FT-IR として汎用化が進んでいるが、電子状態遷移に対応する紫外・可視領域においてはより精密な機器制御が要求されるため発展途上である。

そこで、複屈折性結晶を用いた高精度干渉計を用いたフーリエ変換分光法により紫外・可視領域の EEM を分散型の方法と比較して高速で取得できる光学系を構築した。結果の信頼性についてはローダミン 6G 溶液を用いて得られた EEM (Fig.1)から抽出したスペクトルを分散型の手法により得られた結果と比較することで評価した。さらに、多成分系に適用したところ各成分を別のピークとして検出することに成功した。

1. D. Brida, C. Manzoni, G. Cerullo, *Optics letters*, **2012**, 37,15, 3027-3029.

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水溶液中におけるヌクレオチドの分子間ダイナミクスに与える糖の 2’-OH 基の影響

（千葉大院理）○清水 柾子・城田 秀明

Effect of 2’-OH Group of Sugar Moiety in Nucleotides on Intermolecular Dynamics of Their Aqueous Solutions

(*Department of Chemistry, Chiba University*) ○Masako Shimizu, Hideaki Shirota

The difference in the chemical structures of ribonucleotide (rNMP) and deoxyribonucleotide (dNMP) is the presence/absence of OH group. This structural difference affects various properties including higher-order structure in RNA and DNA. Since OH group is hydrophilic, it is expected that the solvation and dynamics in aqueous solutions of rNMP are different from those of dNMP. Previously, we clarified the difference in the intermolecular dynamics of aqueous solutions of rNMP and dNMP with cytosine (C) and uracil (U) bases. Conversely, the intermolecular dynamics of aqueous solution of ribose (Rib) was similar to that of deoxyribose (dRib). In this presentation, we will discuss the intermolecular dynamics of aqueous solutions of rNMP and dNMP with purine base, adenine (A) and guanine (G). We used femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES) to observe the intermolecular dynamics. The relaxation processes in picosecond region of aqueous solutions of NMP were fitted using a triexponential function. The time constants of the intermediate relaxation processes about 20 ps for aqueous solutions of dAMP and dGMP were 1.4 and 1.1 times slower than those of rAMP and rGMP, respectively. In contrast, there was no difference in the relaxation time of aqueous solutions of Rib and dRib. Considering these facts, 2’-OH group of sugar moiety might not directly affect the intermediate relaxation. We will also discuss about the intermolecular vibration in this presentation.

Keywords : femtosecond Raman-induced Kerr effect spectroscopy, picosecond relaxation process, ribonucleotide, deoxyribonucleotide, aqueous solution

リボヌクレオチド（rNMP）とデオキシリボヌクレオチド（dNMP）の化学構造の違いは糖の 2'位の OH 基の有無であり，この差が RNA や DNA の機能および高次構造の違いに影響している。OH 基は親水性であるため，rNMP と dNMP で水溶液中の水和構造やダイナミクスに違いがあることが予想される。前回の発表において私達はピリミジン塩基であるシトシン（C），ウラシル（U）を塩基にもつ rNMP および dNMP の水溶液の分子間ダイナミクスに違いが現れることを報告した [1]。一方で糖であるリボース（Rib）およびデオキシリボース（dRib）の水溶液の分子間ダイナミクスについては違いが見られなかった。今回の発表では，プリン塩基であるアデニン（A），グアニン（G）を持つヌクレオチドにターゲットを広げ，それらの水溶液について検討した結果を報告する。分子間ダイナミクスの測定にはフェムト秒ラマン誘起カー効果分光（fs-RIKES）を用いた [2]。ピコ秒領域に観測される遅い過減衰した緩和について 2 ps 以上の領域を三成分の指数関数でフィットした。ヌクレオチド由来の緩和と考えられる 20 ps 程度の時定数は，dAMP 水溶液で約 1.4 倍，dGMP 水溶液で約 1.1 倍同じ塩基を持つ rNMP の水溶液より遅くなった。この結果は前回報告した CMP と UMP の水溶液と同じ傾向を示している。一方，Rib と dRib の水溶液の緩和時間は両者で一致することから，糖の 2'-OH 基は緩和に直接的な影響を与えているのではないと考えられる。当日は分子間振動についても議論を行う。

1) 清水柾子，城田秀明，日本化学会第 103 春季年会，K201-4am-03.
2) H. Shirota, *J. Phys. Chem. A* **2011**, *115*, 14262–14275.

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赤外分光によるパルブアルブミンの Ca^{2+}配位構造解析－配位子置換が 12 位のグルタミン酸に及ぼす影響について

（医科歯科大教養[1]・青山学院大理工[2]・京大院生命[3]・東大院農[4]）○奈良 雅之[1]・森井 尚之[1]・坂本 章[2]・宮川 拓也[3]・田之倉 優[4]

Infrared spectroscopic analysis of Ca^{2+}-coordination structure of parvalbumin: Effect on Glu at the 12th position by an amino-acid replacement ([1]*Liberal Arts and Sciences Division, Tokyo Medical and Dental University*, [2]*College of Science and Engineering, Aoyama Gakuin University*, [3]*Graduate School of Biosciences, Kyoto University*, [4]*Graduate School of Agricultural and Life Sciences, University of Tokyo*) ○Masayuki Nara,[1] Hisayuki Morii,[1] Akira Sakamoto,[2] Takuya Miyakawa,[3] Masaru Tanokura[4]

EF-hand motif (helix-loop-helix) is a Ca^{2+}-binding domain in common among many intracellular Ca^{2+}-binding proteins such as calmodulin and troponin C. Infrared spectroscopy (FTIR) was applied to analyze the Ca^{2+} coordination structures of the CD and EF sites of carp parvalbumin pI 4.25. The 17-residue synthetic peptide analog of the CD and EF sites showed a band at about 1556 cm^{-1} and 1553 cm^{-1}, respectively, which were assigned to the sidechain COO^- group of Glu at the 12th position serving as the ligand for Ca^{2+}. On the other hand, the mutated one of CD site, where Glu was replaced with Asp at the 9th position, showed the band at about 1545 cm^{-1}. This result suggests that the negative charge of Glu at the 9th position made effect on the coordination structure of Glu at the 12th position.

Keywords :Coordination Structure; Infrared Spectroscopy; Calcium Binding Protein; Synthetic Peptide Analog

EF ハンドモチーフ（helix-loop-helix）はカルモジュリン、トロポニン C などに共通する Ca^{2+}結合ドメインであるが、その名称はパルブアルブミン（Parv）の EF サイトに由来する。Ca^{2+}結合部位はアミノ酸 12 残基からなり、N 端側から 1 位、3 位、5 位、7 位、9 位、12 位のアミノ酸残基の側鎖や水分子等が Ca^{2+}の配位子に関わっている。12 位の Glu 側鎖の COO^-基は Ca^{2+}と二座配位型で配位するので、赤外分光法で調べると、その COO^-逆対称伸縮モードは 1555-1550 cm^{-1} にバンドを示す [1]。本研究では、Parv の CD サイトと EF サイトに相当する 17 残基の合成ペプチドアナログ（CD サイト：Ac-DQDKSGFIEEDELKLFL-NH_2, EF サイト：Ac-DSDGDGKIGVDEFTALV-NH_2）の Ca^{2+}配位構造について赤外分光法で解析した。EF サイトは、ペプチド凝集を避けるために、Ca^{2+}結合には関与しない 15 位の Ala を Lys に置換したものを用いた。その結果、CD サイトは 1556 cm^{-1}, EF サイトは 1553 cm^{-1} に 12 位 Glu 由来の COO^-逆対称伸縮モードのバンドが観測された。次に、CD サイトの 9 位の Glu を Asp に置換した合成ペプチドアナログを調べると、12 位 Glu の COO^-逆対称伸縮モードのバンドは 1545 cm^{-1} に観測された。CD サイトと EF サイトの Ca^{2+}配位構造の違いは、前者は 9 位の Glu の COO^-基が Ca^{2+}に直接配位するのに対し、後者は 9 位のところに水分子が Ca^{2+}に配位している点にある。CD サイトの 5 位の Ser は負電荷を帯びていないため、9 位の Glu の負電荷が 12 位 Glu の配位構造に影響を与えていることが示唆された。

1) Nara, M., Morii, H., and Tanokura, M. (2013) *Biochim. Biophys. Acta* **1828**, 2319-2327.

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パーフルオロアルカンの加熱測定によるコンフォメーション変化の解析

（京大化研）○荒木 泰介・森 泰蔵・岡 昂徹・塩谷 暢貴・長谷川 健
Analysis of Conformational Change of Perfluoroalkanes by Heating Measurement (*Institute for Chemical Research, Kyoto University*) ○Taisuke Araki, Taizo Mori, Takayuki Oka, Nobutaka Shioya, Takeshi Hasegawa

Molecular conformation change of a perfluoroalkyl compound on heating is analyzed by infrared spectroscopy. For the study, *n*-$C_{15}F_{32}$ is employed. We have found that the band progression of the symmetric CF_2 stretching vibration band decreases in absorption intensity as heated. We consider that this significant change reflects the conformational change from D_{15} to D_{2h}.

Keywords : PFAS; Infrared Spectroscopy; Raman Spectroscopy; Coupled Oscillator; Dispersion Curve

有機フッ素化合物の中でもパーフルオロアルキル(R_f)基を含む PFAS は，炭化水素にはまねのできない特異で有用な性質から産業応用が盛んな一方，環境や人体への蓄積性や毒性が懸念されている．しかし，物性の分子論的な解釈で不明な点が多く，分子構造に基づいた物性の統一的な理解が求められている．そこで，PFAS の主骨格である R_f 基の構造変化を分光学的に理解することを目指し，パーフルオロアルカンについて，赤外分光法を用いて詳しく調べた．測定には，粉末試料 *n*-$C_{15}F_{32}$ を用いた．

その結果，Fig. 1 に示すように，CF_2 対称伸縮振動(νCF_2)の近くに現れる多数のサテライトバンドが，加熱によって顕著に減衰することを見出した．これは，炭化水素鎖での CH_2 縦揺れ振動由来のバンドプログレッションが加熱により減衰する様子 [1]に似ている．本研究では，赤外およびラマン分光法により，サテライトバンドが νCF_2 のバンドプログレッションである [2]ことを突き止めた．その結果，炭化水素における D_{2h} から C_{2v} へのコンフォメーション変化と同様に，R_f 基が加熱により D_{15} から D_{2h} へ変化する [3]ことを分光学的にとらえていることがわかった．

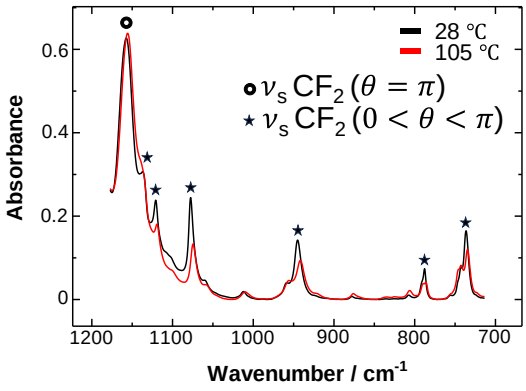

Figure 1. IR ATR spectra of *n*-$C_{15}F_{32}$ for before and after heating.

1) J. Umemura, S. Takeda, T. Hasegawa, and T. Takenaka, *J. Mol. Struct.* **1993**, 297, 57–62. 2) S.L. Hsu, N. Reynolds, S.P. Bohan, H.L. Strauss, and R.G. Snyder, *Macromolecules* **1990**, 23(21), 4565–4575 3) L. Piseri, B. M. Powell, G. Dolling, *J. Chem. Phys.* **1973**, 58, 158–171.

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ペプチドアモルファス凝集に対する共溶媒効果の MD シミュレーションによる自由エネルギー解析

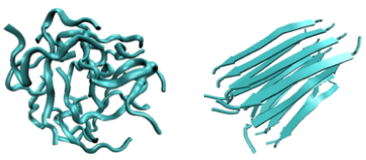
（阪大院基礎工）○田川 雄大・松林伸幸・笠原健人

Free-energy analysis of the cosolvent effects on the peptide amorphous aggregation through molecular dynamics simulation (*Graduate School of Engineering Science, Osaka University*) ○Yudai Tagawa, Nobuyuki Matubayasi, Kento Kasahara

Protein (peptide) aggregation can be malfunctional. It is thus important to develop a scheme to prevent the aggregation, and addition of a cosolvent is a promising approach to do so. The extent of aggregation is determined by the cooperation and competition among the aggregating molecules, water, and cosolvent. In this work, we analyze the cosolvent effect on the aggregation equilibrium of a peptide. We focus on the NACore peptide, the aggregation center of *a*-synuclein, and the cosolvent-induced changes in the equilibrium constants are computed all-atom MD simulation and the energy-representation theory of solvation. It is found that glycerol inhibits the aggregation more strongly than urea, while the strengths of the cosolvent effects are similar between the amyloid and amorphous structures.

Keywords : MD simulation; aggregation; cosolvent effect ; free-energy analysis

タンパク質凝集は疾患を引き起こす。したがって凝集を防ぐことが重要であり、共溶媒の添加は有効なアプローチである。凝集プロセスの初期段階に見られるオリゴマー(アモルファス凝集体)は、強い毒性を持つとして注目されている。しかし、観察が困難であることからメカニズムや溶媒効果の詳細は明らかになっていない。本研究では、全原子 MD シミュレーションからアモルファス凝集体の特性を理解する。NACore ペプチドを対象として、純水中におけるアモルファスおよびアミロイド様凝集体の構造を複数個サンプリングする(右図)。それぞれの構造に対してエネルギー表示法を用いて共溶媒添加(1.0 M)による自由エネルギー変化を計算し、その平均値を会合数(1, 4, 8, 16-mer)で比較することで、凝集阻害効果を定量的に評価する。純水中においてアモルファス凝集体はアミロイド様凝集体に比べて、多くの溶媒と相互作用によって安定化していたが、ペプチド内、ペプチド間相互作用はエネルギー的に半分程度であった。さらに、尿素、グリセリン添加によってそれぞれ凝集阻害効果が確認でき、効果はグリセリンの方が強いことがわかった。凝集阻害効果は、凝集体－溶媒間の van der Waals 相互作用による安定化効果が会合数増加につれて小さくなることが要因である。そして、アモルファス凝集体とアミロイド凝集体で効果の違いはほとんど無かった。



アモルファス（左）とアミロイド（右）の 16 量体

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

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC
A1441(1441, Bldg. 14 [4F])

[A1441-3pm] 04. Physical Chemistry -Properties-

Chair: Takashi Takeda, Tomoko Fujino

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1441-3pm-01]

Crystal Structures and Conducting Properties of Molecular Conductors Composed of an Unsymmetrical Palladium(II)-Dithiolene Complex Containing a TTF Skeleton

○Satomi Mochizuki[1], Kiyonori Takahashi[2], Takayoshi Nakamura[2], Tomohiro Agou[1], Kazuya Kubo[1] (1. Graduate School of Science, University of Hyogo, 2. Research Institute for Electronic Science, Hokkaido University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1441-3pm-02]

Theoretical studies on electronic and spin properties in trinuclear Mn complex of single molecular magnets

○Takashi Kawakami[1,2], Mizuki Otsuka[2], Koichi Miyagawa[3], Yuta Suzuki[2], Shusuke Yamanaka[2], Mitsutaka Okumura[2], Takahito Nakajima[1], Kizashi Yamaguchi[2,1] (1. RIKEN, 2. Osaka Univ., 3. Univ. Tsukuba)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1441-3pm-03]

Correlations between intermolecular interactions and FET characteristics in both carriers of d/π-conjugated ambipolar semiconductors

○Masatoshi Ito[1], Tomoko Fujino[1], Toshiki Higashino[2], Mafumi Hishida[3], Hatsumi Mori[1] (1. ISSP, the Univ. of Tokyo, 2. AIST, 3. Dept. of Chemistry, Faculty of Science, TUS)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1441-3pm-04]

Electronic and steric effects of halogen substituents on spin crossover iron(III) complexes

○Mai Hirota[1], Takahiro Sakurai[2], Hitoshi Ohta[3], Kazuyuki Takahashi[1] (1. Graduate School of Science, Kobe University, 2. Research Facility Center for Science and Technology, Kobe University, 3. Molecular Photoscience Research Center, Kobe University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1441-3pm-05]

Orbital hybridization of donor and acceptor to enhance conductivity of mixed-stack complexes

○Tomoko Fujino[1], Ryohei Kameyama[1], Kota Onozuka[1], Kazuki Matsuo[1], Shun Dekura[1], Tatsuya Miyamoto[1], Zijing Guo[1], Hiroshi Okamoto[1], Toshikazu Nakamura[2], Kazuyoshi Yoshimi[1], Shunsuke Kitou[1], Taka-hisa Arima[1,3], Hiroyasu Sato[4], Kaoru Yamamoto[5], Akira Takahashi[6], Hatsumi Mori[1] (1. The Univ. of Tokyo, 2. Institute for Molecular Science, 3. RIKEN Center for

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Emergent Matter Science, 4. Rigaku Corporation, 5. Okayama University of Science, 6. Nagoya Institute of Technology)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1441-3pm-06]

Molecular Perovskite Solid Solution $(H_2dabco,H_2hmta)(NH_4)(BF_4)_3$ Synthesized by Mechanochemical Method

○Jumpei Moriguchi[1], Atsuko Masuya-Suzuki[1], Nao Tsunoji[2], Masahiro Sadakane[2], Ryo Tsunashima[1] (1. Graduate School of Science and Technology for Innovation, Yamaguchi University, 2. Graduate School of Advanced Science and Engineering, Hiroshima University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[A1441-3pm-07]

Phase transition and dielectric behavior of rod-shaped camphor sulfonamide derivatives

○Chisato Sato[1], Dekura Shun[1,2], Tomoyuki Akutagawa[1,2] (1. Graduate School of Engineering, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

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
[A1441-3pm-08]

Structure and physical properties of $[Ni(dmit)_2]$ salts with supramolecular cations composed of 2-hydroxy-2-methylpropan-1-aminium/[18]crown-6 derivatives

○Kazuya Kanamaru[1], Kiyonori Takahashi[1,2], Rui-kang Huang[1,2], Chen Xue[1,2], Jiabing Wu[1,2], Takayoshi Nakamura[1,2] (1. Hokkaido University Graduate School of Environmental Science, 2. Research Institute for Electronic Science, Hokkaido University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[A1441-3pm-09]

Negative thermal expansion and dielectric behavior of 2,2'-disulfanediylbis(ethan-1-aminium) $([18]crown\text{-}6)_2[Ni(dmit)_2]_2$

○Masato Haneda[1], Kiyonori Takahashi[2,1], Ruikang Huang[2,1], Jiabing Wu[2,1], Chen Xue[2,1], Takayoshi Nakamura[2,1] (1. Grad. School of Env. Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[A1441-3pm-10]

Crystal Structure and Phase Transition Behaviors of Monoprotonated 1,3,5-Triaza-7-Phosphoadamantane Salts

○Yukino Ohtsubo[1], Yuki Ohishi[2], Atsuko Masuya-Suzuki[2], Ryo Tsunashima[2] (1. Yamaguchi University, 2. Graduate School of Science and Technology for Innovation)

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

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Preparation of and dielectric property of Preyssler-type polyoxometalate-LDH composite films.

○Yuta Kawamura[1], Masaru Fujibayashi[2], Atsuko Suzuki[3], Sadafumi Nishihara[4], Ryo Tsunashima[3] (1. Yamaguchi University, 2. National Institute of Technology, Ube College, 3. Graduate School of Science and Technology for Innovation, Yamaguchi University, 4. Graduate School of Advanced Science and Engineering, Hiroshima University)

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

Optical and low-temperature transport properties of an organic conductor with disordered anion structure κ''-$(ET)_2Cu[N(CN)_2]Br$

○Soichiro Yasaka[1], Yukihiro Yoshida[1], Yuto Nakamura[2], Hideo Kishida[2], Hiroshi Kitagawa[1], Mitsuhiko Maesato[1] (1. Kyoto University, 2. Nagoya University)

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

Dielectric properties related to structural transformation of basket-shaped polyoxometalate

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English
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[A1441-3pm-14]

Physical Properties and Redox Chemistry of Copper Hexahydroxytriptycene MOFs

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TTF 骨格を導入した非対称型パラジウム(II)ジチオレン錯体からなる分子性導体結晶の構造と伝導性

(兵庫県立大院理[1]・北大電子研[2]) ○望月 理美[1]・高橋 仁徳[2]・中村 貴義[2]・吾郷 友宏[1]・久保 和也[1]

Crystal Structures and Conducting Properties of Molecular Conductors Composed of an Unsymmetrical Palladium(II)-Dithiolene Complex Containing a TTF Skeleton

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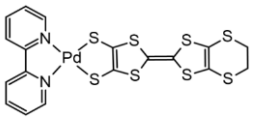
Unsymmetrical metal-dithiolene complexes are expected to be utilized for components of various functional materials such as molecular conductors.[1,2] In this study, we focused on an unsymmetrical palladium(II) complex containing a tetrathiafulvalene (TTF) moiety [(bpy)Pd($C_8H_4S_8$)] (**1**) as a new donor component. Six crystals [**1**](anion)$_n$ (anion = BF_4^-, ClO_4^-, $GaCl_4^-$, PF_6^-, AsF_6^-, TaF_6^-, $0 < n \leq 2$) were obtained by electrochemical crystallization of **1**. Isolated dimers of **1** surrounded by the anions were observed in [**1**]$(GaCl_4)_2$ crystals (Fig. 1). The donors formed one-dimensional columnar structures with a head-to-head arrangement in the radical cation crystals [**1**](anion) (anion = BF_4^-, ClO_4^-, PF_6^-, AsF_6^-), which were an isostructural for crystals of the platinum(II) derivative complex.[1] The columnar arrangements of **1** were also observed in the TaF_6^- crystals which were non-stoichiometric materials with a donor-anion ratio of 1:0.37. Temperature dependance of electrical resistivities of the crystals measured by a standard two-probe method exhibited semiconducting behaviors.

Keywords : Molecular conductor; Unsymmetrical complex; Palladium(II) complex; Dithiolene ligand; Conducting property

ジチオレン配位子とピリジン系配位子からなる非対称型金属錯体は、分子性導体など様々な機能性材料の構成分子としての応用が期待されている。[1,2] 本研究では、分子性導体の新たなドナー分子としてテトラチアフルバレン(TTF)骨格をもつ非対称型パラジウム(II)錯体[(bpy)Pd($C_8H_4S_8$)] (**1**)に着目し、この錯体を種々のアニオン存在下で電解酸化することにより 6 つの結晶[**1**](anion)$_n$ (anion = BF_4^-, ClO_4^-, $GaCl_4^-$, PF_6^-, AsF_6^-, TaF_6^-, $0 < n \leq 2$)を得ることができた。



[(bpy)Pd($C_8H_4S_8$)] (**1**)

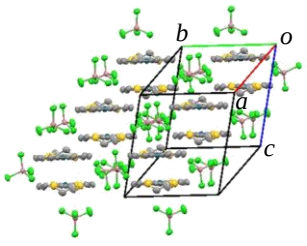


Fig. 1 Crystal structure of [**1**]$(GaCl_4)_2$ at 300 K.

図 1 に、300 K における[**1**]$(GaCl_4)_2$ の結晶構造を示す。錯体分子が head-to-tail 型の二量体を形成し、その周りの空隙に $GaCl_4^-$が存在していた。ラジカルカチオン結晶 [**1**](anion) (anion = BF_4^-, ClO_4^-, PF_6^-, AsF_6^-)では、300 K で錯体分子が head-to-head 型の一次元カラムを形成し、類似の白金錯体の 1:1 塩と同形構造であった。[1] TaF_6^-塩の結晶でも 1:1 結晶と同様に錯体分子の一次元カラムが形成されていたが、錯体とアニオンの比が 1:0.37 であった。2 端子法で測定したこれらの結晶の電気抵抗の温度変化は、半導体的な挙動を示した。

1) K. Kubo *et al.*, *Inorg. Chim. Acta* **2002**, *336*, 120. 2) K. Kubo *et al.*, *Inorg. Chem.* **2008**, *47*, 5495.

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強相関電子系としての Mn 三核錯体の単分子磁石発現に関する理論解析

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Theoretical studies on electronic and spin properties in trinuclear Mn complex of single molecular magnets ([1]*Center for Computational Science, RIKEN,* [2]*Graduate School of Science, Osaka University*, [3]*University of Tsukuba*) ○Takashi Kawakami,[1,2] Mizuki Otsuka,[2] Koichi Miyagawa,[3] Yuta Suzuki,[2] Shusuke Yamanaka,[2] Mitsutaka Okumura,[2] Takahito Nakajima,[1] Kizashi Yamaguchi[1,2]

Oxygen-evolving complex (OEC) of PSII consists of four manganese ions and one calcium ion linked by oxo (or hydroxo) bridges, i.e. Ca Mn_4O_5, and shows complicated interaction change during five oxidation states (S_0, S_1, S_2, S_3, and S_4) in Kok cycle as water-splitting reaction. In series of our studies, such electronic properties have been investigated by high accuracy MO (molecular orbital) methods. Recently, Agapie and his co-workers reported tetranuclear heterometallic *M* Mn_3O_4 cubane species as one of model complex of OEC cluster.[1)] Though Y(III) ion as well as Ca(II) ion in OEC have no magnetic spins, Dy(III) as lanthanoid elements possess 4*f* electrons and can contribute 3*d*-4*f* electron coupling. In Agapie's reports, Dy $Mn(IV)_3O_4$ complex displays single molecule magnet (SMM) properties, while the one electron reduced species (Dy $Mn(IV)_2Mn(III)O_4$) does not, despite the presence of a Mn(III) center with higher spin and single-ion anisotropy. In this study, we carried out UB3LYP method and post-HF/beyond-DFT methods to overcome limitation of hybrid-DFT methods.
Keywords : trinuclear Mn complex; single molecular magnets

天然光合成 PSII の酸素発生錯体 OEC(Ca Mn_4O_5 クラスタ)は、Kok サイクル(S_1, S_2, S_3, S_4)に従って Mn イオンの酸化数(III, IV)が変化し、また誘起される構造変化に伴って相互作用は複雑に変化していく。我々の研究では、この電子状態解析を高精度分子軌道法を駆使して行ってきた。近年 Agapie らは、この歪んだ椅子型構造に関する構造モデルとして、四核ヘテロ金属 *M* Mn_3O_4 キュバン錯体(*M* = Ca → Y, Dy)を合成し電子物性を実験的に解析した[1)]。OEC の Ca(II)イオンと同じく Y(III)イオンは非磁性であるが、Dy(III)イオンはランタノイド元素であるため 4*f* 電子を含み、Mn の 3*d* 電子との相互作用を研究する上で興味深い。彼らの実験結果によると、Dy $Mn(IV)_3O_4$ は単分子磁石特性を示したが、一電子還元種(Dy $Mn(IV)_2Mn(III)O_4$)は異方性を有する Mn(III)イオンの存在にもかかわらず単分子磁石特性を示さなかった。そこで本研究では、この実験結果を複数の磁気的相互作用経路の競合に着眼して、UB3LYP 法と高精度 post-HF, beyond-DFT 法を用いて解析した。

1) Effect of the Mn oxidation state in single-molecular-magnet properties: Mn^{III} vs Mn^{IV} in biologically inspired $DyMn_3O_4$ cubanes, P.-H. Lin, E. Y. Tsui, F. Habib, M. Murugesu, T. Agapie, *Inorg. Chem.* **2016**, *55*, 6095.

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d/π 共役系アンバイポーラ半導体の両キャリアにおける分子間相互作用と FET 特性の相関性

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Correlations between Intermolecular Interactions and FET Characteristics in Both Carriers of d/π-conjugated Ambipolar Semiconductors ([1]*ISSP, the University of Tokyo*, [2]*AIST,* [3]*Dept. of Chemistry, Faculty of Science, Tokyo University of Science*) ○Masatoshi Ito,[1] Tomoko Fujino,[1] Toshiki Higashino,[2] Mafumi Hishida,[3] Hatsumi Mori[1]

We have developed air-stable ambipolar semiconductors based on nickel bis(dithiolene) complexes. They have a herringbone-like stacking form with a two-dimensional electronic structure both in single crystals and crystalline thin films, ensuring multiple carrier conduction paths. However, interactions between frontier orbitals of neighboring molecules are not completely isotropic, and the direction in which carriers tend to conduct depends on the carrier type (hole or electron). Herein, we experimentally observed the in-plane angular dependence of hole and electron mobilities in FETs with crystalline thin films. The tendency was consistent with the predictions by theoretical calculations based on crystallographic orientation.

Keywords : Ambipolar Semiconductor; Metal Dithiolene Complex; Crystalline Thin Film; Field-effect Transistor (FET)

我々がこれまでに開発した d/π 共役系アンバイポーラ半導体材料 **C3**[1] (Fig. 1a) は、溶液塗布法により作製した結晶性薄膜においても分子がヘリングボーン様に積層し、隣接分子が複数方向で相互作用することで 2 次元的なキャリア伝導パスが確保される。しかし、分子間相互作用は完全に等方的ではなく、正孔伝導を担う隣接分子の HOMO 間と電子伝導を担う LUMO 間で、より強い相互作用を稼げる方位が異なる (Fig. 1b) ため、FET 特性にはキャリアごとに傾向の異なる異方性が生じる。本研究では、分子間相互作用とキャリア移動度の相関性を結晶学的方位に基づき議論するため、溶液塗布法により作製した **C3** の結晶性薄膜から単一の結晶性ドメインを切り出し、GIWAXS 測定により面内方向の方位を決定するとともに、当該ドメインを用いて作製した FET の方向別の特性評価を行った。その結果、正孔移動度は電子移動度に比べてより異方的になるとともに、高い正孔移動度を示すチャネル方向が積層カラム方向と一致する傾向を示し、計算によるシミュレーション結果の傾向とも合致した。

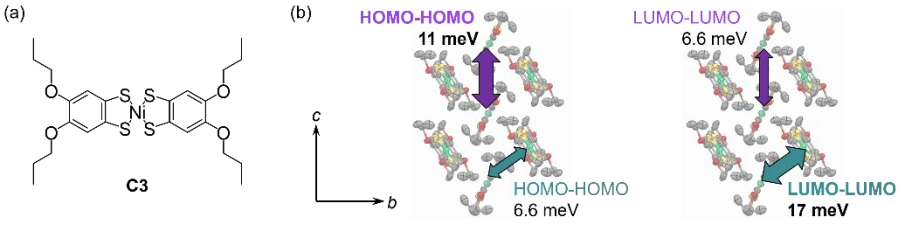

Fig. 1. (a) Structural formula of **C3**. (b) Molecular stacking form and intermolecular interactions (electron couplings calculated by the Amsterdam Density Functional, GGA:PW91/TZP) of **C3**.

1) M. Ito *et al. J. Am. Chem. Soc.* **145**, 2127 (2023).

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日本化学会 第104春季年会 (2024)

ハロゲン置換基がスピンクロスオーバー鉄(Ⅲ)錯体にもたらす電子的、立体的効果

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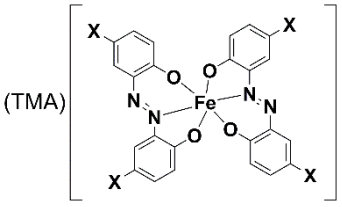
Electronic and steric effects of halogen substituents on spin crossover iron(III) complexes
([1]*Graduate School of Science, Kobe University*, [2]*Research Facility Center for Science and Technology, Kobe University*, [3]*Molecular Photoscience Research Center, Kobe University*)
○Mai Hirota[1], Takahiro Sakurai[2], Hitoshi Ohta[3], Kazuyuki Takahashi[1]

Recently we reported that the homoleptic Fe(III) complex of 2,2'-azobisphenolate ligands is a rare anionic spin crossover (SCO) complex. In this study, we prepared a series of complexes with halogen substituents on the ligands and compared their magnetic and structural properties to study the electron-withdrawing groups effect on their SCO behaviors. The magnetic susceptibility showed a gradual transition in **1**-F, while the SCO behavior changed from an abrupt transition to a gradual transition in **1**-Cl. **1**-Br was in the high spin state in the temperature range studied. These differences in magnetic behavior will be discussed by comparing their crystal structures.

Keywords : spin crossover, iron(III) complex, substituent effect

スピンクロスオーバー（SCO）とは、温度、光、圧力などの外部刺激により、遷移金属錯体のスピン状態が高スピンと低スピンの間を変化する現象である。我々は2,2’-アゾビスフェノレートの Fe(III)錯体 **1**-H (Fig. 1)がこれまでに報告例の少ないアニオン性 SCO 錯体であることを見いだした[1)]。本研究では、電子求引性基の電子的、立体的な効果を調べるために、配位子にハロゲンを導入した錯体を合成し、磁性や構造を比較した。



1-H : X = H　**1**-F : X = F
1-Cl : X = Cl　**1**-Br : X = Br
1-I : X = I

Fig. 1　錯体の分子構造

各配位子を合成した後、ナトリウムメトキシドと反応させ、無水塩化鉄(III)、臭化テトラメチルアンモニウムを加えることで、各錯体を合成した。単結晶 X 線構造解析を行った結果、**1**-F と **1**-Cl はともに $P2_1/n$ で同形であり、**1**-Br は $C2/c$ であった。磁化測定の結果 (Fig. 2)、**1**-F はほぼ高スピンからなだらかな可逆転移を示すが、完全な SCO ではなかった。一方、**1**-Cl は室温ではほぼ低スピンであり、昇温すると 330 K 付近で急激な転移を示した。続けて降温昇温するとなだらかな転移に変化した。**1**-Br は、すべての温度領域でほぼ高スピンであることがわかった。これらの磁気挙動の違いについて、結晶構造の比較から議論する。また、**1**-I についても併せて報告する。

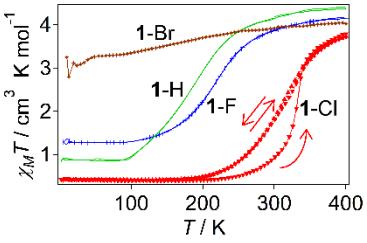


Fig. 2　錯体の磁化率の温度変化

1) K. Takahashi *et al*., *Chem. Eur. J.* **2016,** *22*, 1253.

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ドナーとアクセプターの軌道混成に基づく交互積層型錯体の高伝導化

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Orbital hybridization of donor and acceptor to enhance conductivity of mixed-stack complexes ([1]*ISSP, The Univ. of Tokyo*, [2]*Department of Advanced Materials Science, The Univ. of Tokyo*, [3]*IMS*, [4]*CEMS, RIKEN*, [5]*Rigaku Corp.*, [6]*Faculty of Science, Okayama Univ. of Science*, [7]*Department of Physical Science and Engineering, Nagoya Institute of Technology*)

○Tomoko Fujino,[1] Ryohei Kameyama,[1] Kota Onozuka,[1] Kazuki Matsuo,[1] Shun Dekura,[1] Tatsuya Miyamoto,[2] Zijing Guo,[2] Hiroshi Okamoto,[2] Toshikazu Nakamura,[3] Kazuyoshi Yoshimi,[1] Shunsuke Kitou,[2] Taka-hisa Arima,[2,4] Hiroyasu Sato,[5] Kaoru Yamamoto,[6] Akira Takahashi,[7] Hatsumi Mori[1]

Mixed-stack complexes, which comprise alternating layers of donors and acceptors, are organic conductors with typically poor electrical conductivity because they are either in a neutral or highly ionic state. In this study, mixed-stack complexes that uniquely exist at the neutral–ionic boundary were synthesized by combining donors and acceptors with similar energy levels and orbital symmetry between the donor's HOMO and the acceptor's LUMO. The orbitals were highly hybridized, endowing them with the highest room-temperature conductivity for single-crystal 1D complexes under ambient pressures. The unique electronic structures at the boundary exhibited structural perturbations between their electron-itinerant and localized states. *Keywords : Charge transfer complex; Molecular crystal; Electrical conductivity; Oligothiophene*

交互積層型の電荷移動錯体は電気伝導度が低いのが通例である．ほとんどの錯体が，キャリア数の乏しい中性かキャリアの局在化したイオン性状態にあるためである．本研究では，我々が最近開発している拡張共役系オリゴマー分子[1]をドナーに活用し，テトラシアノキノジメタン類をアクセプターとすることで，中性ーイオン性境界に位置する錯体群を開発した（図 1）．ドナーの HOMO とアクセプターの LUMO のエネルギー準位と軌道対称性に着目した分子設計に基づいたものである．1 次元電荷移動錯体単結晶のなかで最高の室温伝導度を実現し，境界領域固有の相転移現象を見出した．

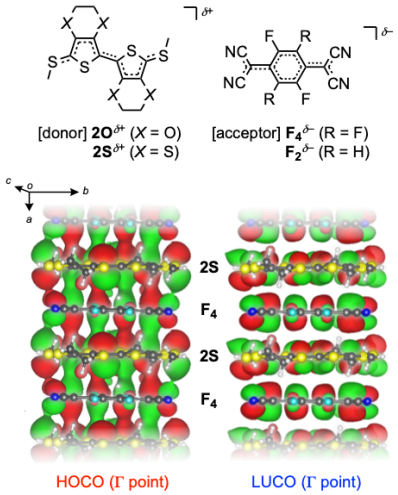

図 1. 高伝導性交互積層型錯体の構造と Γ 点での結晶軌道

[1] Kameyama, R. *et al. Chem. Eur. J.* **2021**, *27*, 6696–6700; Kameyama, R. *et al. Phys. Chem. Chem. Phys.*, **2022**, *24*, 9130–9134; Kameyama, R. *et al. J. Mater. Chem. C*, **2022**, *10*, 7543–7551; Onozuka, K. *et al. J. Am. Chem. Soc.*, **2023**, *145*, 15152–15161; Fujino, T. *et al. Faraday Discuss.* in press.

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BF_4^-を対アニオンとしたペロブスカイト分子結晶$(AA')(NH_4)(BF_4)_3$のメカノケミカル法による固溶化

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○森口 順平[1]・鈴木 敦子[1]・津野地 直[2]・定金 正洋[2]・綱島 亮[1]

Molecular Perovskite Solid Solution $(H_2dabco,H_2hmta)(NH_4)(BF_4)_3$ Synthesized by Mechanochemical Method

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We applied mechanochemical method to prepare solid solution of molecular perovskite $(H_2dabco,H_2hmta)NH_4(BF_4)_3$. By P-XRD, DSC and solid-state NMR, we revealed solution ratio dependence on phase transition temperature and morphotropic phase boundary appeared at which space group and molecular dynamics of A cation differs from end member.

Keywords: Perovskite, Solid Solution, Mechanochemical Method

固体を機械的に粉砕混合するメカノケミカル法は、溶解度や比重などの溶液・液相における性質が異なる無機化合物の固溶化に用いられている。これまで、この手法を用いて径が類似している一方で対称性の異なる dabco と hmta を固溶化したペロブスカイト分子結晶$(AA')NH_4(BF_4)_3$を作製し、溶液からの結晶化では得られない組成域での固溶化が可能となった事を報告してきた。本研究では、構造の組成・温度依存性に加え、固溶化による分子運動の影響を調査したので報告する。

$(H_2dabco_{1-x},H_2hmta_x)(NH_4)(BF_4)_3$ は HBF_4 と NH_4BF_4 の存在下で dabco と hmta を摩砕することで作製し、P-XRD と DSC より、構造の組成・温度依存性を決定した(Figure 1)。相境界である II 相は、DSC に相転移を示唆する熱異常は見られず、また disorder した分子を含む *Fm*-3*c* 相であった。これは dabco 分子が配向の自由度を獲得した dynamic disorder 相、またはランダムな配向で凍結した static disorder 相であるが結晶学的に判断することはできない。そこで、II 相($x = 0.5$)の分子運動性を固体 NMR より評価した (Figure 2)。dabco に由来するピークは 45 ppm に現れ、固溶化によって半値幅が 0.390 から 0.210 へと変化し、結晶中の dabco 分子の運動性が端成分($x = 0$)に比べて高いためと考えられた。同様に、hmta に由来するピークは 60 ~ 80 ppm に現れ、固溶化によってより鋭いピークへ変化し、hmta 分子の運動性が端成分($x = 1$)に比べ高いためだと考えられた。以上より、300 K 以上の温度域においては、分子が配向の自由度を獲得した柔軟性結晶相であると考えられる。

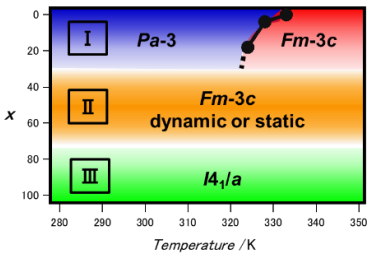

Fig 1. Phase Diagram

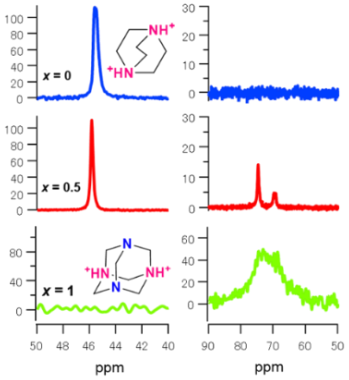

Fig 2. Solid-State ^{13}C-NMR at 300 K

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棒状カンファースルフォンアミド誘導体の相転移および誘電挙動

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Phase transition and dielectric behavior of rod-shaped camphor sulfonamide derivatives

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○Chisato Sato,[1] Shun Dekura,[1,2] Tomoyuki Akutagawa[1,2]

Plastic crystalline (PC) phase is an intermediate phase between solid and liquid phases, which exhibits molecular rotational motions while maintaining the crystal lattice. We have previously reported that a sulfonamide with adamantane (**AD**) and camphor (**CS**) moieties exhibits a PC phase despite its rod-like shape. In this presentation, we synthesized sulfonamide derivatives **NBCS**/**CHCS**, where **AD** in **ADCS** was replaced with the smaller norbornane (**NB**) or cyclohexane (**CH**), and investigated their phase transition behaviors, crystal structures, and dielectric behaviors. **NBCS** and **CHCS** exhibited various phase transition behaviors different from **ADCS**.

Keywords : Camphorsulfonamide; Molecular dynamics; Plastic crystal; Molecular rotator; Hydrogen-bond

柔粘性結晶(PC)相は、結晶格子を保ちながら分子が回転運動を示す固液中間相である。これまで、アダマンタン(**AD**)とキラルなカンファー(**CS**)を結合させたスルフォンアミド誘導体 **ADCS** が、棒状分子にもかかわらず PC 相を示すことを報告した[1]。本発表では、**AD** 部位をよりサイズの小さなノルボルナン(**NB**)とシクロヘキサン(**CH**)に置き換えた誘導体である **NBCS** と **CHCS** のキラルおよびラセミ体を合成し、それぞれの相転移挙動・結晶構造・誘電挙動を検討した（図 1）。

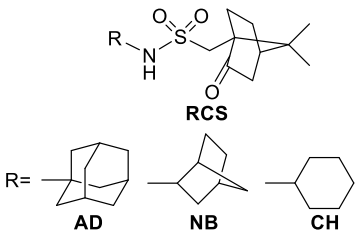

図 1. **ADCS**, **NBCS**, および **CHCS** の分子構造

DSC および PXRD 測定から、**NBCS** のラセミ体は可逆な結晶－液相転移を示した。一方、キラル体は、温度掃引速度を変化させることで、DSC のベースライン変化や新たなピークが出現した。**CHCS** のラセミ体は、2 周目以降に可逆なガラス転移を示し、キラル体は同様のガラス転移に加えて、加熱過程で結晶化および結晶－液相転移を示した（図 2 上）。誘電率の実部(ε_1)の温度－周波数依存性においても各相転移に対応する挙動が観測された（図 2 下）。**ADCS** の **AD** 部位を **NB** および **CH** に置換することで、PC 相のみならず多様な相転移挙動を発現することを見出した。

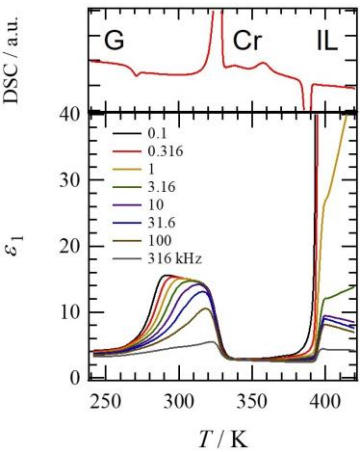

図 2. キラル **CHCS** の 2 回目の加熱過程における (上) DSC および (下) ε_1 の温度依存性

1) Sato. C., *et al.*, *Cryst. Growth Des.*, **23**, 5889 (2023).

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2-hydroxy-2-methylpropan-1-aminium/[18]crown-6 誘導体からなる超分子カチオンを導入した[Ni(dmit)$_2$]塩の構造と物性

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Structure and physical properties of [Ni(dmit)$_2$] salts with supramolecular cations composed of 2-hydroxy-2-methylpropan-1-aminium/[18]crown-6 derivatives

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○ Kazuya KANAMARU[1], Kiyonori TAKAHASHI[1,2], Rui-kang HUANG[1,2], Chen XUE[1,2], Jiabing Wu[1,2], Takayoshi NAKAMURA[1,2]

Supramolecular cations consisting of hydroxyammonium (OH-mpa$^+$) and [18]crown-6 or benzo[18]crown-6 (B[18]crown-6) were introduced to [Ni(dmit)$_2$]$^-$ salt. Within the crystal of (OH-mpa)([18]crown-6)[Ni(dmit)$_2$]•acetone (**1**), the cation and acetone exhibited dynamic disorder. B[18]crown-6 gave a partially oxidized crystal of (OH-mpa)(B[18]crown-6)[Ni(dmit)$_2$]$_3$ (**2**). Correlation between molecular motion in the crystals and conductivity is discussed. *Keywords : Supramolecular cations; crystal structure; molecular motion; conductivity; [Ni(dmit)$_2$]*

分岐鎖型アルキルアンモニウム 2-hydroxy-2-methylpropane-1-ammonium (OH-mpa) をカチオンとして用い、[18]crown-6 あるいは benzo[18]crown-6 (B[18]crown-6)との超分子カチオンを導入した結晶を合成し、結晶内分子運動と物性との相関を精査した。(OH-mpa)([18]crown-6)[Ni(dmit)$_2$]•acetone (**1**)の構造を Fig. 1a に示す。OH-mpa および acetone 分子はそれぞれ 2 サイトにディスオーダーしており、2 分子が接近している組み合わせでは分子間水素結合を形成していた(Fig. 1 a)。(OH-mpa)(B[18]crown-6)[Ni(dmit)$_2$]$_3$ (**2**)の *a* 軸投影図を Fig. 1b 示す。 結晶中で[Ni(dmit)$_2$]は 1 次元カラムを形成し、ab 面と平行な平面上に 2D 配列を形成していた。[Ni(dmit)$_2$] の 2D 配列間で OH-mpa と B[18]crown-6 が超分子を形成し、2D 層を形成していた。OH-mpa$^+$ の OH 基がゲスト分子と相互作用する向きで配列していた。当日は、結晶構造と物性の相関について詳細に報告する。

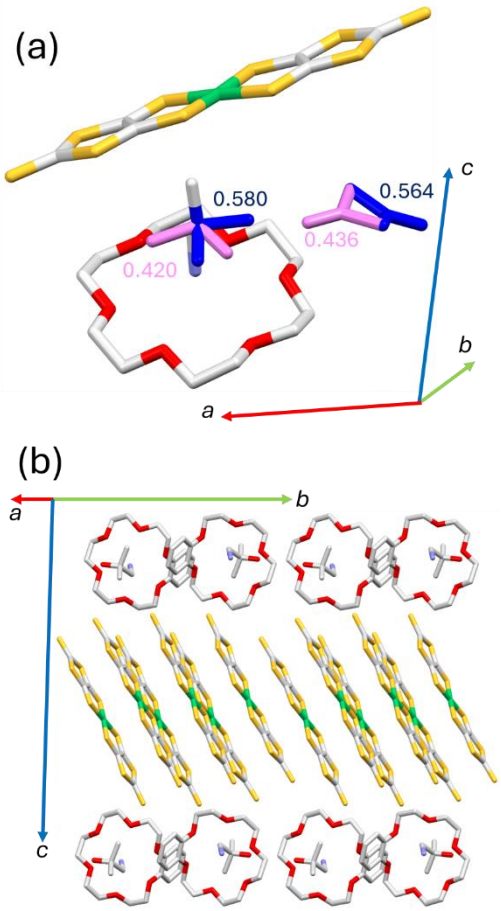

Fig. 1 (a) 93 K における結晶 **1**。図中の数字は占有率を表している。(b) 93 K における結晶 **2** の ***a*** 軸投影図。水素原子は省略してある。

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(2,2'-Disulfanediylbis(ethan-1-aminium))([18]crown-6)$_2$[Ni(dmit)$_2$]$_2$ 結晶の負の熱膨張と誘電挙動

(北大院環境科学[1]・北大電子研[2]) ○羽田 将人[1]・高橋 仁徳[1,2]・黄 瑞康[1,2]・呉 佳冰[1,2]・薛 晨[1,2]・中村 貴義[1,2]

Negative thermal expansion and dielectric behavior of 2,2'-disulfanediylbis(ethan-1-aminium)([18]crown-6)$_2$[Ni(dmit)$_2$]$_2$ ([1]*Graduate School of Environmental Science, Hokkaido Univ.*, [2]*RIES, Hokkaido Univ.*) ○Masato Haneda[1], Kiyonori Takahashi[1,2], Ruikang Huang[1,2], Jiabing Wu[1,2], Chen Xue[1,2], Takayoshi Nakamura[1,2]

A supramolecular structure consisting of the flexible cystamine dication $S_2(C_2H_4NH_3^+)_2$ and [18]crown-6 was combined with [Ni(dmit)$_2$] to develop unique physical properties based on molecular motion within the crystal. In the crystal of $(S_2(C_2H_4NH_3^+)_2)$([18]crown-6)$_2$[Ni(dmit)$_2$]$_2$ (**1**), [18]crown-6 and $S_2(C_2H_4NH_3^+)_2$ were disordered into two sites and the crystal exhibited uniaxial negative thermal expansion below 210 K. Temperature-frequency dependence of the complex permittivity showed dielectric relaxation due to molecular motion.
Keywords : Negative Thermal Expansion, Dielectric properties, Supramolecular Cation, Molecular motion in a crystal

柔軟なアルキル鎖と剛直なジスルフィドを持つ cystamine のジカチオン、 $(S_2(C_2H_4NH_3^+)_2)$ に着目し、クラウンエーテルと組み合わせた超分子カチオンを導入した$(S_2(C_2H_4NH_3^+)_2)$([18]crown-6)$_2$[Ni(dmit)$_2$]$_2$ (**1**)結晶を合成した。100 K における超分子カチオンの構造を Figure 1 に示す。超分子カチオンは隣接する[18]crown-6 間での C-H···O 相互作用により、[1 0 −1]方向に 1 次元に配列し、鎖間では[18]crown-6 と $S_2(C_2H_4NH_3^+)_2$ 間に C-H···C 相互作用が存在するため、超分子カチオンは 2 次元層を形成している。$[Ni(dmit)_2]^-$ は 2 量化し、*ac* 面と平行な平面内に 2 次元層を形成した。超分子カチオンおよび$[Ni(dmit)_2]^-$それぞれの 2 次元層は *b* 軸に沿って交互に配列していた。$S_2(C_2H_4NH_3^+)_2$ と[18]crown-6 はそれぞれ 2 サイトで等価にディスオーダーし、複素比誘電率の温度-周波数依存性は、分子運動に起因する誘電緩和を示した。210 K 以下では、$S_2(C_2H_4NH_3^+)_2$ のアルキル鎖が分子運動することで 1 次元鎖とほぼ平行な方向に負の熱膨張を示した。一方で 220 K 以上では、一軸方向に金属並に小さい熱膨張（ゼロ熱膨張）が見られた。当日は構造変化と物性の相関について詳細を報告する。

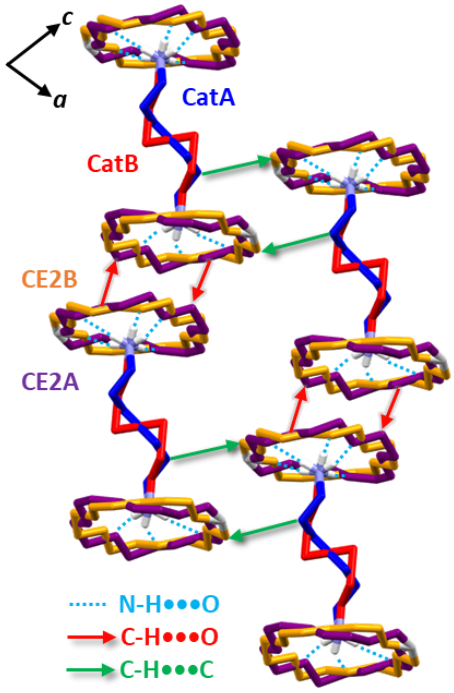

Figure 1. (a) Supramolecular structure in crystal **1**.

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日本化学会 第104春季年会 (2024)

1,3,5-トリアザ-7-ホスファアダマンタンのモノプロトン化体の結晶構造と相転移挙動

(山口大理[1]・山口大院創成科学[2]) ○大坪由季乃[1]・大石優希[2]・鈴木敦子[2]・綱島亮[2]

Crystal Structure and Phase Transition Behaviors of Monoprotonated 1,3,5-Triaza-7-Phosphoadamantane Salts ([1]*Yamaguchi University*, [2] *Graduate School of Science and Technology for Innovation*) ○Yukino Ohtsubo,[1] Yuki Ohishi,[2] Atsuko Masuya-Suzuki,[2] Ryo Tsunashima[2]

Molecular ionic crystals of hmtaH･X (X=Cl, Br, hmta=hexamethylenetetramine) exhibits ferroelectricity by rotational inversion of hmtaH[1]. Herein, similar salts with 1,3,5-triaza-7-phosphoadamantane (pta), instead of hmta, (ptaH・X ,X=Cl, Br, I) was prepared. We investigated crystal structure, phase transition behavior and, dielectricity.

Keywords : Crystal Structure, Phase Transitions, Dielectricity

hmta(ヘキサメチレンテトラミン)をモノプロトン化したハロゲン化物塩 hmtaH･X(X=Cl, Br)は、分子配向の反転による強誘電性を示すことが知られている[1]。本研究では、hmta と類似した構造を有する一方、より低対称な分子である 1,3,5-トリアザ-7-ホスファアダマンタン(pta)に着目し、ptaH･X(X=Cl, Br, I)の作製とその結晶構造、相転移挙動、誘電性を調査した。ptaH･Cl と ptaH･Br では無極性な空間群 *Pnma* をとり、ptaH あたり 6 配位と、hmtaH･Cl、hmtaH･Br とは異なる構造であった(Figure1.)。ptaH･I は極性空間群 *Cm*、8 配位構造で結晶化した。これは hmtaH･I と同形である一方、hmtaH･I では見られなかった柔粘性結晶相への相転移が示唆された。hmtaH･X とは異なり、ptaH･X では結晶構造はアニオン種に依存し、新たに構造相転移を示すことが明らかとなった。当日は、結晶構造、相転移挙動、誘電性について ptaH･X と hmtaH･X の比較による考察を行う予定である。

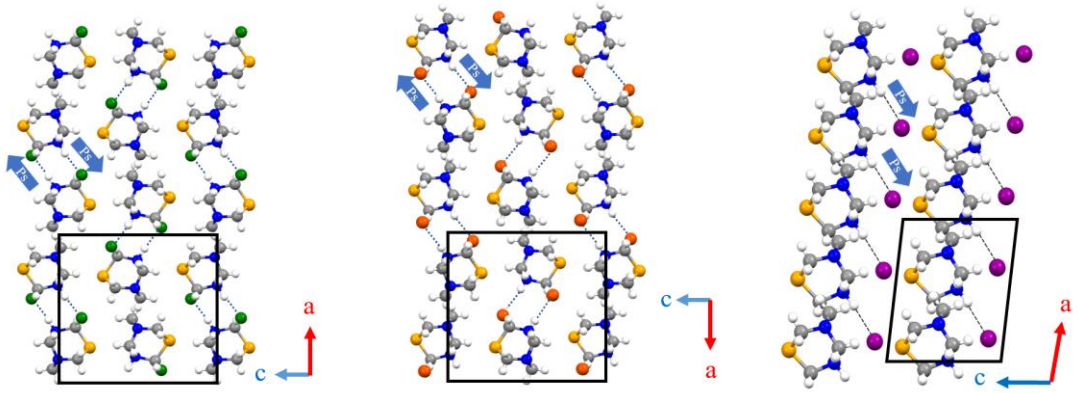

Figure1.　ptaH･Cl、ptaH･Br、ptaH･I のパッキング図（*ac* 面）

1) Yan-Xin Zhao, Kai-Ge Gao, Zi-Shuo Yao, and Jun Tao, *Inorg. Chem*., **62**, 23, 8778–8783 (2023)

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Preyssler 型ポリオキソメタレート–LDHs 複合体の作製と誘電物性評価

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Preparation of Preyssler-type polyoxometalate-LDH composite films and evaluation of their dielectric properties ([1]*Faculty of Science, Yamaguchi Univ.,* [2]*NIT, Ube Collage,* [3]*Graduate School of Sciences and Technology for Innovation, Yamaguchi Univ.,* [4]*Graduate School of Advanced Science and Engineering, Hiroshima Univ.*) ○ Yuta Kawamura[1], Masaru Fujibayashi[2], Atsuko Masuya-Suzuki[3], Sadafumi Nishihara[4], Ryo Tsunashima[3]

Preyssler-type polyoxometalates (P_5W_{30}) encapsulate a single metal ion within a cage-like molecular framework. With the aim of controlling the molecular orientation of this Tb@P_5W_{30}, hybrid materials with layered double hydroxides (LDHs) were prepared. The obtained compounds were confirmed to have a layered structure from powder X-ray diffraction (P-XRD) patterns, and impedance measurements.

Keywords : Polyoxometalates; Single-molecule electret; Layered Double Hydroxides

Preyssler 型ポリオキソメタレート(P_5W_{30})は、骨格内部に一つの金属イオンを内包し、外部電場によりこの内包イオンが上下二ヵ所の安定サイト間を移動することにより単一分子で強誘電体のような分極ヒステリシスを示す。[1] 測定試料内でイオン移動方向を揃えることでより優れた強誘電特性が期待できる。今回新たに分子配向を制御しやすいカチオン性無機酸化物シートの層状複水酸化物(LDHs)を用いることで、層間に Tb@P_5W_{30} を挿入した新たな複合体の合成を試みた。Mg_2Al-NO_3 をホルムアミド中に分散させ単層に剥離させたのち、Tb@P_5W_{30} の水溶液を加え、複合体の合成を行った。P-XRD の回折パターンにおいて面間隔 $d = 2.11$ nm と $d = 1.42$ nm に対応する回折が現れ、ラメラ構造であることを確認した。Na@P_5W_{30} の LDHs 複合体では、C_5 軸と垂直に挿入した場合は $d = 1.71$ nm となり、C_5 軸と平行に挿入した場合 $d = 2.18$ nm と報告されている(図 1)。[2] したがって、今回作製した複合体は、Tb@P_5W_{30} の配向が異なる２種類の複合体の混合物であると考えられる。当日は複合体の詳細な構造、また複素誘電率測定などの電気測定について報告する。

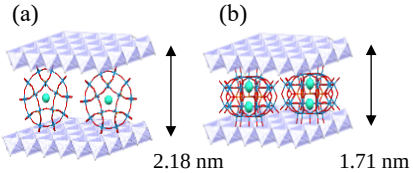

図 1. Na@P_5W_{30}-LDHs の構造

[1] C. Kato, R. Tsunashima, S. Nishihara, *et al., Angew. Chem. Int. Ed*., **2018,** 57, 13429-13432.

[2] Y. Guo *et al., International Journal of Inorganic Materials.* 3, **2001**, 347–355

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Optical and low-temperature transport properties of an organic conductor with disordered anion structure κ''-$(ET)_2Cu[N(CN)_2]Br$

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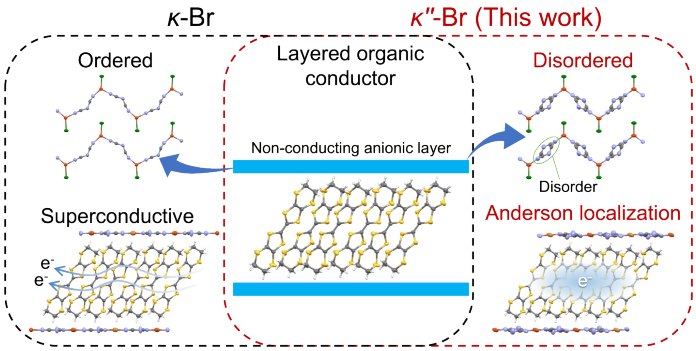
Keywords: BEDT-TTF; Organic conductor; Disorder; Conductivity; Optical properties; Electron localization

The organic conductors κ-$(ET)_2X$ have been known as highly correlated electronic systems where a superconducting phase is located in the vicinity of a Mott-insulating phase.[1] Recently, the effect of structural disorder in κ-$(ET)_2X$ has attracted much attention. For example, X-ray irradiation induces lattice defects, leading to a disorder-induced metal–insulator transition in the superconducting κ-$(ET)_2Cu[N(CN)_2]Br$ (**κ-Br**)[2] and the suppression of long-range magnetic order in the Mott-insulating κ-$(ET)_2Cu[N(CN)_2]Cl$ (**κ-Cl**).[3] However, the destructive X-ray irradiation may also induce secondary effects such as carrier doping due to ionization and local modulation of Coulomb interactions.[4] To elucidate the intrinsic effect of a random potential, a nondestructive method such as chemically-introduced/controlled disorder in the anion layer while keeping the ordered conducting ET layer is desirable.

Recently, we succeeded in synthesizing κ''-$(ET)_2Cu[N(CN)_2]Br$ (**κ''-Br**), which is the first polymorph of **κ-Br**, having very similar conducting ET layers but disordered insulating anion layers in contrast to those of **κ-Br**. It was found that the **κ''-Br** is neither a conventional superconductor nor a Mott insulator, but the detailed electronic states remained unclear. In this study, we investigated the ground state of **κ''-Br** from the results of reflectance spectroscopy, Raman scattering spectroscopy, and low-temperature resistivity behavior obtained by using a high-quality single crystal of **κ''-Br** which is free from crystal twinning or magnetic impurities. Our results suggest the occurrence of Anderson localization in **κ''-Br** due to disordered anion layers.



1) Kanoda K. *J. Phys. Soc. Jpn.* **2006**, *75*, 051007. 2) Sano K., Sasaki T., Yoneyama N., Kobayashi N. *Phys. Rev. Lett.* **2010**, *104*, 217003. 3) Furukawa T., Miyagawa K., Itou T., Ito M., Taniguchi H., Saito M., Iguchi S., Sasaki T., Kanoda K. *Phys. Rev. Lett.* **2015**, *115*, 077001. 4) Sasaki T., Yoneyama N., Nakamura Y., Kobayashi N., Ikemoto Y., Moriwaki T., Kimura H. *Phys. Rev. Lett.* **2008**, *101*, 206403.

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Basket 型ポリオキソメタレートの構造変形に伴う誘電特性

（宇部高専 [1]）○藤林 将 [1]

Dielectric Properties Related to Structural Transformation of Basket-Shaped Polyoxometalate

([1]*NIT, Ube College*) ○Masaru Fujibayashi[1]

Recently, our group reported organic-inorganic hybrids basket-shaped polyoxometalate (POM) of $[Na^{+}\subset(SO_3)_2(R\text{-}PO_3)_4Mo^{V}_4Mo^{VI}_{14}O_{49}]^{5-}$ with various organic functional groups, such as phenyl, propyl, *tert*-butyl, and *n*-butyl groups. Especially, *n*-butyl modified basket-shaped POM showed structural phase transition between symmetric and asymmetric POM frameworks. During the phase transition, encapsulated Na^{+} ion was shifted to one side of molecular frameworks, and distorted Mo-O molecular frameworks were confirmed. In this work, the effect of DC bias on structural phase transition was investigated to elucidate the details of domain structure in a single crystal.

Keywords : Dielectrics, Polyoxometalate, Phase Transition

分子性金属酸化物であるポリオキソメタレートは、多彩な電子状態や構造拡張性の面から有機無機ハイブリッド化合物における無機ホストとして活用されてきた。近年、我々は Mo18 核からなる Mo-O 骨格表面に４つの有機ホスホン酸を修飾した有機無機ハイブリッド Basket 型ポリオキソメタレート$[Na^{+}\subset(SO_3)_2(R\text{-}PO_3)_4Mo^{V}_4Mo^{VI}_{14}O_{49}]^{5-}$ を報告した [1,2]。分子骨格内部には、１つの Na イオンと２つの亜硫酸イオンが包接されており、Na イオンは分子中心軸上に位置している。有機分子として *n* ブチルホスホン酸（*R* = *n*-Bu）を用いたところ、分子骨格の変形を伴う構造相転移現象を示すことを見出した [3]。低温相では Na イオンが分子中心軸上からずれた非対称構造を形成していた（図１）。本研究では、外部電場を印加しながら相転移過程を追随することで、相転移機構におけるドメイン構造の調査、および誘電材料としての開拓を目指した。

同結晶の低温からの昇温過程について、誘電率の周波数－温度依存性評価を実施した。外部電場による影響を評価するため、DC バイアスあり／なしの両条件について評価した。DC バイアスを印加しない場合では相転移過程のみが観測された一方、DC バイアスを印加することで温度に依存した誘電異常が観測され、新たな秩序相の形成が示唆された。

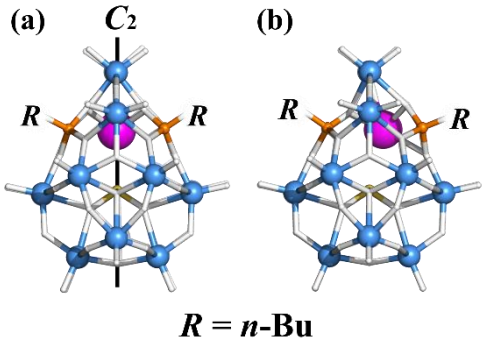

図１．（ａ）240 K、（ｂ）100 K における Basket 型ポリオキソメタレートの分子構造。

1. I. Nakamura, M. Fujibayashi, R. Tsunashima, *et al*., *J. Am. Chem. Soc.*, **2015**, *137*, 6524-6530.
2. M. Fujibayashi, R. Tsunashima, *et al*., *Bull. Chem. Soc. Jpn*., **2019**, *92*, 918-922.
3. M. Fujibayashi, R. Tsunashima, *et al*., *Angew. Chem. Int. Ed.*, **2020**, *59*, 22446-22450.

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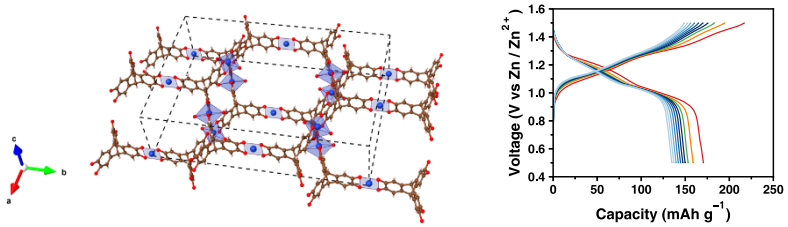
Unveiling the Physical Properties of Non-Planar Copper Hexahydroxytriptycene Metal-Organic Frameworks for High-Capacity Aqueous Zn-Ion Batteries

([1]*Graduate School of Science, Nagoya University*, [2]*International Research Organization for Advanced Science and Technology, Kumamoto University*) ○Qi Chen,[1] Zhongyue Zhang,[2] Kunio Awaga[1]

Keywords: Metal-Organic Frameworks; Zn-ion Battery; Electron Spin Resonance

Recently, the emergence of quasi two-dimensional (2D) metal-organic frameworks (MOFs) has ushered in a new platform for electronics, sensing, and electrochemical energy storage devices, owing to their tunable physical properties and high crystallinity. In our previous studies[1,2], we revealed the crucial role played by intralayer π-d conjugation and interlayer π-π interaction in the electrochemical performance of planar 2D MOFs, particularly in terms of specific capacity and cycling stability. In contrast, this work seeks to provide a comprehensive understanding of the charge storage mechanism inherent in non-planar copper hexahydroxytriptycene (Cu-HHTT) MOFs. In this unique architecture, the C_3 symmetric HHTT ligand lacks fully π conjugation, and the aromatic rings stand perpendicular to the 2D plane, resulting in the absence of interlayer π-π interaction.

The synthesis of Cu-HHTT MOFs employed both diffusion and solvothermal methods, yielding single crystals and polycrystalline powders with distinctive stacking models. Solid-state electrochemistry for Cu-HHTT MOFs were conducted in an aqueous Zn-ion battery, utilizing 1M $ZnSO_4/H_2O$ as the electrolyte. Impressively, Cu-HHTT MOF delivered a substantial reversible capacity of ~150 mAh/g, corresponding to a 1.5-electron reaction per Cu, thereby suggesting the dual redox activity of Cu ions and HHTT ligands. To delve deeper into the charge storage mechanism of non-planar Cu-HHTT MOF, electron spin resonance (ESR) and magnetic susceptibility studies of pristine MOFs and electrochemical intermediates are planned, promising further insights into the function of π conjugation and interlayer π-π interaction.



Crystal structure of Cu-HHTT MOF and charge-discharge profiles Zn/Cu-HHTT battery.

1) Q. Chen *et. al.*, *J. Am. Chem. Soc.* **2023**, *145*, *2*, 1062-1071. 2) Q. Chen *et. al.*, *J. Vis. Exp.* **2023**, *196*, e65335.

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

Wed. Mar 20, 2024 9:00 AM - 10:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 1:30 AM UTC
A1454(1454, Bldg. 14 [5F])

[A1454-3am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Muneyuki Matsuo, Nobuhiko Suematsu

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1454-3am-01]
Belousov-Zhabotinsky reaction in nonionic surfactant emulsion system

Kotarou Oda[1], ○Akiko Kaminaga[1] (1. Kagoshima University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1454-3am-02]
Self-propelled motion switching of a thymol acetate droplet depending on concentration of aqueous surfactant solutions

○Takuya Fujino[1], Muneyuki Matsuo[1,2], Satoshi Nakata[1] (1. Graduate School of Integrated Sciences for Life, Hiroshima University, 2. Graduate School of Arts and Sciences, The Unicersity of Tokyo)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1454-3am-03]
Anion effects in the aqueous phase on motion of a camphor self-propelled object

○Mai Tateishi[1], Muneyuki Matsuo[1,2], Satoshi Nakata[1] (1. Hiroshima University, 2. The Univ. of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1454-3am-04]
Effects of flow rate and solubility product in chemical gardens

○Yujin Kubodera[1], Muneyuki Matsuo[1,2], Masashi Fujii[1], Oliver Steinbock[3], Satoshi Nakata[1] (1. Hiroshima Univ., 2. The Univ. of Tokyo, 3. Florida State Univ.)

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
[A1454-3am-05]
Real-time Mode-switching of a Self-propelled Droplet
Controlled by the Photosensitive Belousov–Zhabotinsky
Reaction

○Nobuhiko J. Suematsu[1,2], Satoshi Udagawa[1] (1. Meiji University, 2. Meiji Institute for Advanced Study of Mathematical Sciences (MIMS))

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1454-3am-06]

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Droplet size dependence of chemical state in BZ droplets in oil phase

○Keigo Takeda[1], Satoshi Udagawa[2], Nobuhiko J Suematsu[2,3] (1. Meiji Univ., School of Interdisciplinary Mathematical Sciences, 2. Meiji Univ., Graduate School of Advanced Mathematical Sciences, 3. Meiji Institute for Advanced Study of Mathematical Sciences (MIMS))

Japanese

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

[A1454-3am-07]

Effects of Differences in Mixing Condition of Reaction System and Precipitation Behavior on the Chiral Asymmetry Amplification of Soai Reaction System

○Kazuma Furuya[1], Taisuke Banno[1], Ken-ichi Takao[1], Kouichi Asakura[1] (1. Keio University)

Japanese

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

[A1454-3am-08]

Propagation of precipitate bands produced by precipitation and redissolution reaction of aluminum hydroxide

○Yuhei Onishi[1], Nobuhiko J. Suematsu[1,2] (1. Graduate School of Advanced Mathematical Sciences, 2. Meiji Institute for Advanced Study of Mathematical Sciences)

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日本化学会 第104春季年会 (2024)

非イオン界面活性剤エマルション系での Belousov-Zhabotinsky 反応

（鹿児島大理）小田 虎太朗・○神長 暁子
Belousov-Zhabotinsky Reaction in Nonionic Surfactant Emulsion System (*Faculty of Science, Kagoshima University*) Kotarou Oda, ○Akiko Kaminaga

The Belousov-Zhabotinsky reaction, which exhibits patterns such as concentric circles and spirals in aqueous solution, is known to exhibit various patterns such as standing waves that are not observed in homogeneous aqueous solution when the reaction solution is dispersed as the aqueous phase of w/o type microemulsion. In previous studies, aerosol OT, an oil-soluble anionic surfactant, has been mainly used for preparation of microemulsions. In this study, emulsions were prepared using the nonionic surfactants Tween 80 and Span 20, and the BZ reaction solution with 1,4-cyclohexanedione, a reducing agent that does not produce carbon dioxide was used as the aqueous phase to observe pattern formation in Petri dishes. At higher percentages of surfactant, the solution became gelatinous and no patterns were observed. When the percentage of aqueous phase was higher, the solution became a fluid but turbid, and patterns similar to those observed in aqueous solution were observed. The induction time to pattern formation was longer and the duration of the pattern was shorter than in the aqueous solution.
Keywords : Oscillatory Reaction; Pattern Formation; Reaction-Diffusion System; Emulsion

水溶液中で同心円や渦巻き等のパターンを示す Belousov-Zhabotinsky(BZ)反応は、反応溶液を w/o 型マイクロエマルションの水相として分散させると、均一な水溶液中では観測されない定在波等の多様なパターンを示すことが知られている。これまでの研究では、マイクロエマルションの調製に油溶性のアニオン界面活性剤であるエアロゾル OT が主に用いられてきた。本研究では非イオン界面活性剤である Tween 80 および Span 20 を用いてエマルションを調製し、水相に二酸化炭素を生じない還元剤である 1,4-シクロヘキサンジオンを用いた BZ 反応溶液を用い、シャーレに展開した溶液中でのパターン形成を観察した。界面活性剤の割合が高いとゲル状になり、パターンは観測されなかった。また、水相の割合が高いほど流動性はあるが濁ったエマルションとなり、溶液中と類似したパターンが観測された。水溶液中と比べてパターンが生じるまでの誘導期間は長くなり、パターンの持続時間は短くなった。

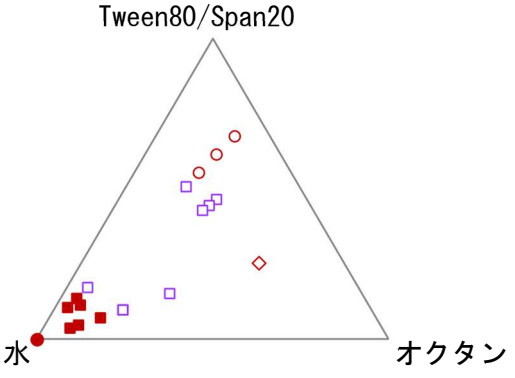

図　界面活性剤/オクタン/BZ 溶液の相図
パターン形成有（●、■）、無（○、□、◇）
透明（○）、乳濁（■、□）、乳濁から透明（◇）

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日本化学会 第104春季年会 (2024)

水中の界面活性剤濃度による酢酸チモール液滴の運動モードスイッチング

（広大院統合生命[1], 東大院総合文化[2]）○藤野 拓也[1]・松尾 宗征[1,2]・中田聡[1]
Self-propelled motion switching of a thymol acetate droplet depending on the concentration of aqueous surfactant solutions ([1]*Graduate School of Integrated Sciences for Life, Hiroshima University*, [2]*Graduate School of Arts and Sciences, The University of Tokyo*) ○Takuya Fujino,[1] Muneyuki Matsuo,[1,2] Satoshi Nakata[1]

A thymol acetate (TA) droplet exhibited self-propulsion on 15 mM sodium dodecyl sulfate (SDS) aqueous solution in couple with a production of thymol (TOH) by hydrolysis of TA[1)]. In this study, the motion of TA droplet on the aqueous phase (pH 9) at different SDS concentrations (C_{SDS}) was performed to control mode switching of self-propulsion due to the interaction between SDS and TOH. The TA droplet exhibited oscillatory motion between motion and rest (Fig. 1a) and a Marangoni flow around a droplet also oscillated when $C_{SDS} < 7$ mM. The TA droplet exhibited back-and-forth motion (Fig. 1b) and the flow was steady when $C_{SDS} \geqq 7$ mM. These results suggest that mode switching originates from the micelle formation of SDS because the critical micelle concentration of SDS is about 8 mM.
Keywords : Self-propelled object; Droplet; Surface tension; Hydrolysis; Surfactant

【緒言】私たちは最近、酢酸チモール (TA)を含む油滴がドデシル硫酸ナトリウム(SDS)水溶液上で、TA の加水分解の生成物であるチモール (TOH)を駆動因子として表面張力差により駆動することを報告した[1)]。本研究では、SDS と TOH の相互作用による TA 液滴の運動モードの制御を目指した。

【方法と結果】pH 9 で水相中の SDS 濃度 (C_{SDS})を変えて、TA 液滴運動の実験を行った。また、可視化粒子 (200μm)を用いて、水面に固定した TA 液滴周囲のマランゴニ流を可視化した。

C_{SDS} が 7 mM で運動モードがスイッチングした。$C_{SDS} < 7$ mM で TA 液滴は、運動と停止を繰り返す振動運動を示し (Fig. 1a)、マランゴニ流も振動した。一方、$C_{SDS} \geqq 7$ mM で TA 液滴は往復運動を示し (Fig. 1b, c)、マランゴニ流は一定であった。

【考察】SDS の臨界ミセル濃度 (cmc)は約 8 mM であるため、結果から運動モードと対流のスイッチングは SDS のミセル形成に由来することが示唆される。cmc 以下では水面の SDS と TOH は複合体を形成しにくい。一方、cmc 以上では SDS と TOH が複合体形成して溶解するため、水面の表面張力差が維持され一定のマランゴニ流が生じると考えられる。

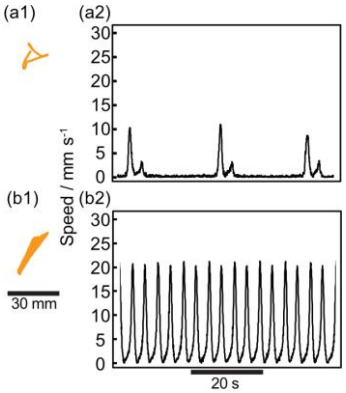

Fig. 1 (1) 60 second trajectory and (2) time-variation of speed of TA droplet on (1) 3, (2) 15 mM SDS aqueous solutions (pH 9).

1) T. Fujino *et al.*, *J. Phys. Chem. Lett.* 2023, *14*, 9279-9284.

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樟脳自己駆動体の運動様相に対する水相中の陰イオンの効果

（広島大学大学院統合生命科学研究科 [1]）○立石 舞 [1]・松尾 宗征 [1]・中田 聡 [1]
Effect of anions in the aqueous phase on motion of a camphor self-propelled object ([1]*Graduate School of Integrated Sciences for Life, Hiroshima University*) ○Mai Tateishi,[1] Muneyuki Matsuo,[1] Satoshi Nakata[1]

Maintained motion of a camphor self-propelled object requires the continuous development of camphor molecules from the camphor disk to the water surface, their dissolution into the aqueous phase, and their sublimation to the air. The purpose of this study is to experimentally elucidate the effect of dissolution of camphor molecules into the aqueous phase on the maintained motion of the camphor self-propelled object driven by differences in surface tension. In this study, anions (Cl^-, Br^-, SO_4^{2-}) in the aqueous phase were changed.
Keywords : Camphor; Self-propulsion; Difference in surface tension; Ion

水面滑走する樟脳自己駆動体は、駆動力である円板周りの表面張力差が保たれることで、運動が持続する。このためには、樟脳円板から水面に対する樟脳分子の展開、水相への溶解、および気相への昇華が連続的に進行する必要がある。本研究では、表面張力差を駆動力とする樟脳円板の運動持続性に対する、樟脳分子の水相への溶解の効果を実験的に解明することを目的とした。陽イオン (Na^+) を統一して陰イオン (Cl^-, Br^-, SO_4^{2-}) を変更し、運動の速さを解析した (Fig.1) 。また NaCl 水溶液の表面張力を測定した (Fig. 2) 。陰イオンの価数が大きいと、価数が小さい場合よりも低い塩濃度で樟脳円板の運動の速さが低下した。また 1.5 mM 樟脳を含んだ NaCl 水溶液と、樟脳を含まない NaCl 水溶液において、表面張力の NaCl 濃度依存性が異なった。以上より、塩濃度が高いと気水界面の樟脳濃度が高まり、円板周囲の表面張力差が低下すると考えられる。その結果、運動の速さが低下すると考察する。この運動の速さの低下に対する陰イオンの効果について、水相中への樟脳分子の溶けにくさと表面張力の観点から議論する。

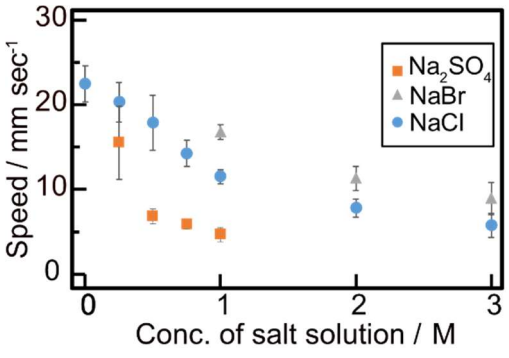

Fig 1. Speed of a camphor disk depending on the concentration of different sodium salt solutions.

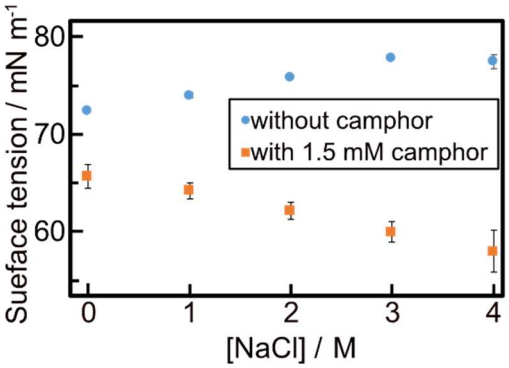

Fig 2. NaCl concentration dependence of surface tension.

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ケミカルガーデンにおける流速と溶解度積の効果

(広島大学[1]・東京大学[2]・フロリダ州立大学[3])
○久保寺 裕進[1]・松尾 宗征[1,2]・藤井 雅史[1]・Oliver Steinbock[3]・中田 聡[1]
Effects of Flow Rate and Solubility Product in Chemical Gardens ([1]*Hiroshima University*, [2] *University of Tokyo*, [3] *Florida State University*) ○Yujin Kubodera,[1] Muneyuki Matsuo,[1,2] Masashi Fujii,[1] Oliver Steinbock,[3] Satoshi Nakata,[1]

Chemical garden was a precipitation tubes growing from the metal salts soaked in Na_2SiO_3 solution. Their growth process is regarded as self-organization evolving spatio-temporally under non-equilibrium conditions. To reveal the relationship between the flow rate inside and around the tube tip F, solubility product K_{sp} of the precipitation, and the tube growth rate G_r, a metal salt solution was injected from the bottom of the vertical Hele-Shaw cell filled with Na_2SiO_3 solution. As a result, the relationship between G_r and F was found to be influenced by K_{sp}.

Keywords : Chemical Gardens; Nonequilibrium; Self-organization

ケミカルガーデンとは、$CuSO_4$、$CaCl_2$ などの金属塩を Na_2SiO_3 水溶液に浸すことで自発的に成長するチューブ状の水酸化金属とケイ酸化金属の沈殿である。著者らは、$CuSO_4$ と $CaCl_2$ が共存すると、ケミカルガーデンの成長速度が増加することを報告したが、その機構は解明されていない[1]。本研究では、成長速度に対する流速と溶解度積の関与を明らかにするために、鉛直に置いた厚さ 1 mm の Hele-Shaw セル底部に内径 0.3 mm の注射針を挿入し、可視化粒子として直径 2 μm 球体ポリマーを分散させた金属塩水溶液を注入した。結果、これまで困難であったチューブ内流速の観察に成功した（図 1a）。また、チューブ内部又は先端の流速 F を制御し、チューブ成長速度 G_r を観察した。結果、$CuSO_4$ では F と G_r は比例関係であったが、$CaCl_2$ では、G_r は F に依存しにくくなった（図 1b）。以上から、G_r は F のみならずチューブ主成分である水酸化物の溶解度積 K_{sp} にも依存すると考えられる。$Cu(OH)_2$ の K_{sp} は 2.2×10^{-22} と比較的小さいため沈殿形成が起こりやすく、F と G_r は比例関係になると考えられる。一方、$Ca(OH)_2$ の K_{sp} は 5.0×10^{-6} と沈殿形成が起こりにくいため、G_r は F に依存しにくいと考える。

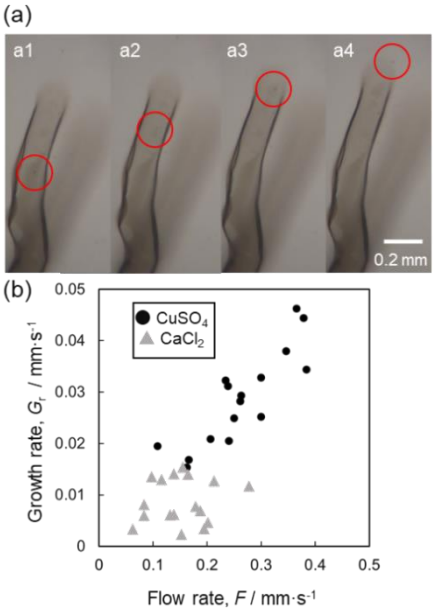

図 1 F と G_r の関係
(a) $CuSO_4$ から成るチューブ内を移動する球体ポリマー（赤丸内）．時間間隔は 1.0 s. (b) $CuSO_4$ または $CaCl_2$ からなるチューブにおける F と G_r の関係.

[1] Y. Kubodera et al., *Phys. Chem. Chem. Phys.*, **2023**, 12974-12978

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光感受性 BZ 反応を介した自己駆動液滴の運動モード制御

(明治大院先端数理[1]・明治大先端数理科学インスティテュート[2]) ○末松 J. 信彦[1,2]・宇田川 聡[1]

Real-time Mode-switching of a Self-propelled Droplet Controlled by the Photosensitive Belousov–Zhabotinsky Reaction ([1]*Graduate School of Advanced Mathematical Sciences, Meiji University*, [2]*Meiji Institute for Advanced Study of Mathematical Sciences (MIMS)*) ○ Nobuhiko J. Suematsu,[1,2] Satoshi Udagawa[1]

Spontaneous motion of oil-in-water or water-in-oil droplets driven by an interfacial chemical reaction of surfactants are reported. Additionally, varieties of functionalities are realized recently such as response to physicochemical environmental conditions. We attempted to introduce a chemical oscillatory reaction, the Belousov-Zhabotinsky (BZ) reaction, into self-propelled aqueous droplets in oil and succeeded to realize oscillation of speed or spontaneous change in movement modes; uniform and random motions. In this study, we introduced a photosensitive catalyst to the BZ reaction and observed the self-propelled motion depending on the environmental light intensity. As the results, the droplet motion was rapidly response to change in the light intensity and showed the mode-switching of self-propelled motion between uniform and oscillatory motions (Fig. 1).[1)]

Keywords : Self-propelled droplet, Chemical oscillatory reaction, Interfacial chemical reaction, Photosensitivity

界面化学反応のエネルギーを利用して自発的に運動する油中水滴や水中油滴が様々な化学物質で実現され始めている。さらに、環境条件に応じて運動の様相を変化させるような機能を付加することにも成功してきている。これまで本研究室では、代表的な非線形化学反応のひとつである Belousov-Zhabotinsky(BZ)反応を水滴中に導入することで、水滴内部の化学状態に応じた運動性を実現することに成功してきた。本研究では、光感受性の金属触媒を用いて、自己駆動 BZ 液滴の光環境応答性を確認した。界面活性剤であるモノオレインをスクアランに溶解したものを油相とし、そこに光感受性 BZ 反応の水滴を作成した。照射する光が弱いとき（1850 lx）は、BZ 反応は定常状態となり、等速直線運動を示したのに対して、光強度が強いとき（37800 lx）は振動状態となり、運動速度が時間周期的に振動する運動が現れた（Fig. 1)。このように、光条件に応じてリアルタイムで直進運動と振動運動を切り替えることのできる自己駆動油中水滴の作成に成功した。[1)]

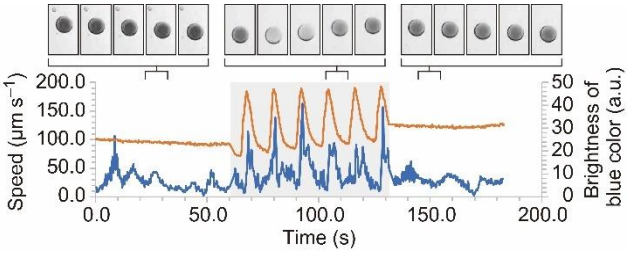

Fig. 1 Time profiles of movement speed (blue line) and blue color brightness (orange line). The Background indicates the strength of illumination and the insets are images of droplet.

1) N. J. Suematsu and S. Udagawa, *Chem. Lett.* **2023**, 52, 110–112.

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油相中の BZ 液滴における化学状態の液滴サイズ依存性

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Droplet size dependence of chemical state in BZ droplets in oil phase (1. Meiji Univ., School of Interdisciplinary Mathematical Sciences, 2. Meiji Univ., Graduate School of Advanced Mathematical Sciences, 3. Meiji Institute for Advanced Study of Mathematical Sciences (MIMS))○Keigo Takeda[1], Satoshi Udagawa[2], Nobuhiko J. Suematsu[1-3]

The Belousov-Zhabotinsky (BZ) reaction is known as a typical chemical oscillatory reaction. The oscillation is caused by the periodic oxidation and reduction of metal catalysts in the solution. The period of the oscillation depends on the concentration of the chemicals. Additionally, a steady state is also observed with some chemical condition. When the BZ reaction introduces into microdroplets, the chemical states depend on the droplet size. In this study, we observed the BZ reaction inside microdroplets prepared in an oil phase, mineral oil, with change in the droplet size. The phase diagram of the chemical state depending on the droplet size and solution concentration revealed that the chemical state becomes steady state with small droplets (Fig.1).

In order to clarify the mechanism of the droplet size dependency of the chemical state, a mathematical model was constructed by introducing a reaction term with the specific surface area as a variable, and we tried to reproduce the experimental results with numerical simulation.

Keywords: Belousov-Zhabotinsky reaction, Droplet, Interfacial dynamics, Chemical oscillatory reaction

Belousov-Zhabotinsky 反応(以下 BZ 反応)は自励振動現象を起こす化学反応として知られている。この反応は溶液内の金属触媒が周期的に酸化、還元されることで振動現象を示す。この振動の周期は溶液内の化学物質の濃度に依存して変わり、条件によっては定常状態を示す。微小液滴内で BZ 反応が進行する場合、この振動状態、定常状態のような化学状態は液滴のサイズに依存する。本研究では、油相中に作成した微小液滴内部における BZ 反応を観察し、化学状態の液滴サイズ依存性を実験的に調べた。液滴サイズと溶液組成を変数として総図を作成した結果、液滴サイズが小さいと定常状態になることが明らかになった(Fig. 1)。

さらに、化学状態の液滴サイズ依存性が現れる仕組みを明らかにするため、比表面積を変数とした反応項を導入した数理モデルを構築し、数値計算により実験結果の再現を試みた。発表ではこれらの結果をまとめて報告する予定である。

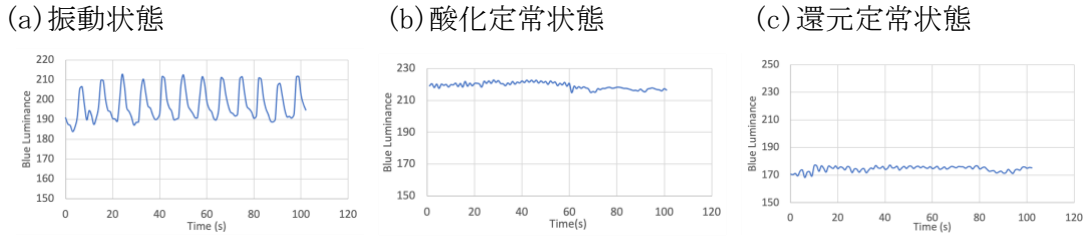

Fig.1 化学状態の時間変化のサイズ依存性。
液滴直径は(a) 0.56mm, (b) 0.40mm, (c) 0.62mm

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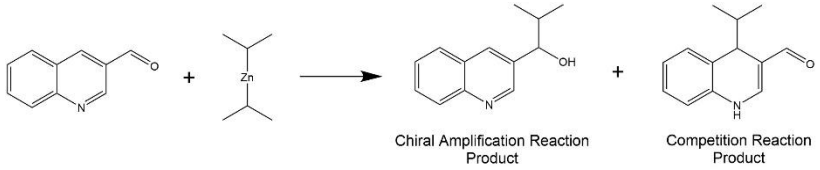
Soai 反応系の不斉増幅現象に対する化学系の混合状態および沈殿生成挙動の差異の影響

（慶大理工）○古谷 和麻・伴野 太祐・高尾 賢一・朝倉 浩一

Effects of Differences in Mixing Condition of Reaction System and Precipitation Behavior on the Chiral Asymmetry Amplification on Soai Reaction System (*Faculty of Science and Technology, Keio University*) ○Kazuma Furuya, Taisuke Banno, Ken-ichi Takao, Kouichi Asakura

The concept of chiral symmetry breaking transition was proposed as a mechanism for the generation of homochirality in living organisms. It shows the growth of fluctuation in chirality by nonlinear chemical reactions in far-from-equilibrium condition. Spontaneous generation of chiral asymmetry in the Soai system has been considered as the example of chiral symmetry breaking transition. In this study, behavior of the Soai system in which quinoline-3-carbaldehyde is the reactant was analyzed. Experiments were carried out in different mixing conditions, since we already found that not only the chiral amplification reaction but also its competition reaction is simultaneously progress in this chemical system. Time evolution of the amount of each compound in the solution and precipitate phases was monitored for each condition. It was found that precipitation of the competition reaction product associated with zinc was enhanced under vigorous mixing condition to inhibit the chiral amplification reaction.
Keywords : Chiral Symmetry Breaking Transition; Autocatalytic Reaction; Chiral Amplification; Competition Reaction; Precipitation

生命体におけるホモキラリティーの発生メカニズムとして、キラル対称性の破れ転移という概念が提唱されている[1]。この概念は、平衡から遠く離れた条件下でのキラリティーの微小なゆらぎの非線形化学反応による増幅を説明し、そのメカニズムに従うキラリティーの自発的偏りが発生したと予測される化学反応系として Soai 反応系がある。本研究では、キノリン-3-カルボアルデヒドを反応物とした Soai 反応系[2]について、その混合状態ならびに沈殿生成が化学反応挙動に与える影響を調査した。これまでの研究で、自触媒的進行が予測される不斉増幅反応に競争する反応の存在、ならびに化学系の混合状態が両反応の優劣に顕著な影響を与えることが見出されていた。そこで、異なった混合状態でこの Soai 反応を進行させ、溶液相および生成する沈殿相中の各化合物量の変化を追跡した。その結果、混合強度の上昇により、亜鉛を伴う競争反応生成物の沈殿生成の促進、ならびに不斉増幅反応の抑制が確認された。



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水酸化アルミニウムの沈殿・再溶解反応による沈殿物バンドの伝搬現象

（明大院先端数理[1]・明治大学先端数理科学インスティテュート[2]）○大西 悠平[1]・末松 信彦[1,2]

Propagation of precipitate bands produced by precipitation and redissolution reaction of aluminum hydroxide

([1]*Graduate School of Advanced Mathematical Sciences*, [2]*Meiji Institute for Advanced Study of Mathematical Sciences*) ○Yuhei Onishi,[1] Nobuhiko J. Suematsu,[2]

It is known that when an aqueous sodium hydroxide solution is dropped onto a gel containing aluminum ions, a band of precipitate propagating downward through the gel at a specific concentration is generated, forming a spiral pattern [1]. The mechanism by which this spiral pattern is formed is thought to be produced by aluminum hydroxide reacting with a large amount of hydroxide ions to form complex ions (re-dissolution) [2]. In this study, in order to clarify the physicochemical characteristics of the precipitates that form the bands that create this spiral pattern, aqueous aluminum chloride and sodium hydroxide solutions were brought into contact in a space without convection, and the precipitates formed at the interface at each concentration were observed under an optical microscope. Two types of precipitates with different physicochemical characteristics were observed at the interface where the solutions were in contact, and it was confirmed that the precipitation bands propagated as the precipitation bands were re-dissolved. It was also confirmed that the propagation speed of the precipitation bands and the state of the two types of precipitates changed as the concentration of aluminum chloride solution was changed. This suggests that the spiral patterns formed at certain concentrations are formed by the change in the state of these precipitates.

Keywords : aluminum hydroxide, precipitation reaction, space-time pattern, band propagation, mathematical modeling

アルミニウムイオンを含むゲルの上に水酸化ナトリウム水溶液を加えると、特定の濃度においてゲル中を下向きに伝播する沈殿物のバンドが生成され、そこに螺旋状のパターンが形成されることが知られている[1]。この螺旋状のパターンができるメカニズムについて、水酸化アルミニウムが多量の水酸化物イオンと反応して錯イオンを形成する（再溶解）することによるものだと考えられている[2]。

本研究では、この螺旋状のパターンを作るバンドを形成する沈殿物の物理化学的特徴を明らかにするため、塩化アルミニウム水溶液と水酸化ナトリウム水溶液を対流のない空間で接触させ、各濃度において界面で生成される沈殿物の状態を光学顕微鏡で観察した。

溶液の接触している界面では、物理化学的特徴の異なる２種類の析出物が観察され、沈殿バンドが再溶解することで沈殿バンドが伝搬していくことが確認できた。また、塩化アルミニウム溶液濃度を変えると、沈殿バンドの伝搬速度・２種類の沈殿物の状態が変化することが確認できた。このことから、特定の濃度において形成される螺旋パターンは、これらの析出物の状態が変化することにより形成されていると考えられる。

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

Wed. Mar 20, 2024 3:55 PM - 5:05 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:05 AM UTC
A1455(1455, Bldg. 14 [5F])

[A1455-3vn] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Masashi Arakawa, Sadahiro Masuo

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[A1455-3vn-01]

Observation of carrier dynamics in a quasi-two-dimensional lead halide perovskite crystal with naphthylmethylamine

○Tatsuya Fujii[1], Yuichi Ikura[1], Tetsuro Katayama[1], Akihiro Furube[1] (1. Tokushima University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[A1455-3vn-02]

Substrate dependence of carrier dynamics in $MoSe_2$ monolayer by using femtosecond transient absorption microscopy

○Sho Yamanochi[1], Akira Yamamoto[1], Naohiko Endo[2], Kenji Watanabe[3], Takashi Taniguchi[3], Yasumitsu Miyata[2], Tetsuro Katayama[1], Akihiro Furube[1] (1. Tokushima University, 2. Tokyo Metropolitan University, 3. National Institute for Materials Science(NIMS))

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[A1455-3vn-03]

Spin coherence in a spin correlated triplet pair observed by pulsed EPR

○Yasuhiro Kobori[1,2], Masaaski Fuki[1,2], Taku Hasobe[3] (1. Kobe University, 2. CREST, JST, 3. Keio University)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[A1455-3vn-04]

Observation of hydrogen bubble evolution reactions at micro-structured electrodes

○Itsuki Abe[1], Daiki Ashizawa[2], Daiki Sato[2], Kazuma Kobashigawa[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. School of Science, Hokkaido University, 2. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 3. Faculty of Science, Hokkaido University)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[A1455-3vn-05]

In situ Observation of Adsorption of Ionomers onto Pt Electrode Surface by Electrochemical Quartz Crystal Microbalance

○Kaede Takei[1], Takatoshi Noguchi[2], Katsumi Chikama[2], Toshihiro Kondo[1] (1. Ochanomizu University, 2. Nissan Chemical)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[A1455-3vn-06]

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Electric field catalyzed isomerization of di-pyridyl-tetrazine and dihydrofuran Diels -Alder adduct

○Kentaro Adachi[1], Masaki Furusawa[2], Ken Albrecht[2] (1. Interdisciplinary Graduate School of Engineering Sciences (IGSES), Kyushu University, 2. Institute for Materials Chemistry and Engineering (IMCE), Kyushu University)

English

4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[A1455-3vn-07]

Advancement of the r-BS+G electrocatalyst with high stability for the oxygen evolution reaction

○Linghui Li[1], Satoshi Hagiwara[2], Cheng Jiang[3], Haruki Kusaka[1], Norinobu Watanabe[1], Takeshi Fujita[4], Fumiaki Kuroda[2], Akiyasu Yamamoto[5], Masashi Miyakawa[6], Takashi Taniguchi[6], Hideo Hosono[6,7], Minoru Otani[2], Takahiro Kondo[8,9] (1. Graduate School of Pure and Applied Sci., Univ. of Tsukuba, Tsukuba, 2. Center for Computational Sci., Univ. of Tsukuba, Tsukuba, 3. Inst. of Technical and Macromolecular Chemistry, RWTH Aachen Univ., Aachen, 4. School of Environmental Sci. and Engineering, Kochi Univ. of Tech., Kochi, 5. Tokyo University of Agriculture and Technology, 6. Research Center for Functional Materials, National Institute for Materials Science, 7. MDX Res. Center for Element Strategy, Tokyo Inst. of Tech., Yokohama, 8. Department of Materials Sci. and Tsukuba Res. Center for Energy Materials Science, Inst. of Pure and Applied Sci., Univ. of Tsukuba, Tsukuba, 9. Advanced Institute for Materials Research, Tohoku University, Sendai)

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ナフチルメチルアミンを用いた擬二次元型ハロゲン化鉛ペロブスカイト結晶におけるキャリアダイナミクス観測

(徳大理工[1]、徳大院理工[2]、徳大 pLED 研[3]、 JST 創発[4])
○藤井 達也[1]・以倉 優一[2]・片山 哲郎[2,3,4]・古部 昭広[2,3]

Observation of Carrier dynamics in a Quasi-Two-Dimensional Lead Halide Perovskite Crystal with Naphtylmethylamine

○ Tatsuya Fujii[1], Yuichi Ikura[2] , Tetsuro Katayama[2,3,4] , Akihiro Furube[2,3] ([1]*Faculty of Science and Technology, Tokushima University,* [2]*Graduated School of Science and Technology, Tokushima University,* [3]*Institute of post-LED Photonics, Tokushima University,* [4]*JST FORES*T)

Lead halide perovskite materials have attractive properties not only for solar cells but also for light-emitting devices because of their high performance and wavelength tunability. Efficient light emission and lasing are indispensable for such applications, and the essential needs are miniaturization and low threshold. To realize lasing at room temperature and to understand the time evolution of light-matter interactions in perovskite crystal systems, it is necessary to measure the carrier dynamics in each crystal. Lead halide-based quasi-two-dimensional perovskite crystals with different organic cations were prepared and their transient absorption spectra were measured using femtosecond transient absorption microscopy.

Keywords : Femtosecond transient absorption microscope; Quasi-two-dimensional $CsPbBr_3$; Nonlinear emission phenomena;

光励起に続く誘導放出を利用した発光増幅現象は、光と物質の相互作用を理解するという基礎的な観点からだけでなく、近年急速に発展しつつある光コンピューティング、光エレクトロニクス分野における光源の微小化、省電力化の実現に向けた応用的な観点からも重要である。有機カチオンを導入したハロゲン化鉛ペロブスカイト系は室温において低閾値光学発振(レージング)を示すことが報告されており、さらにその発光波長が複数のハロゲン化物の混合比率により容易に制御可能であるため次世代ナノレーザー媒体として期待されている。このハロゲン化鉛ペロブスカイト材料系において量子とじこめの効いた数層の二次元層が結晶内に含まれる擬二次元型 $CsPbBr_3$ 試料系は高効率な発光性と室温における超蛍光生成が報告されており、これら発光現象の解明は新規発光材料設計指針を提出する観点からも重要である。本研究ではフェムト秒顕微過渡吸収分光法を用いてナフチルアミンを含有している擬二次元型 $CsPbBr_3$ 単一微結晶に対してキャリアダイナミクスを計測した。一例として顕微過渡吸収スペクトル計測例を Fig.1 に示す。励起後 0 ps 以降から 450 - 510 nm 付近に負の信号が観測され、このスペクトル形状は 100 ps 以内に大きく緩和した。このスペクトル形状変化はホットキャリアの緩和および複数層間からバルク層へのエネルギー移動を示唆している。発表ではこれらのキャリアダイナミクスについて時間分解蛍光スペクトルの結果と合わせて議論する。

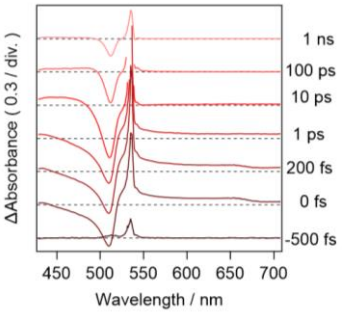

Fig.1 Transient absorption spectra of quasi-two-dimensional perovskite crystals excited by femtosecond pulse at 400 nm.

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フェムト秒過渡吸収顕微鏡を用いた単層 $MoSe_2$ におけるキャリアダイナミクスの基板依存性

(徳大理工[1]、徳大院理工[2]、徳大 pLED 研[3]、東京都立大学[4]、国立研究開発法人物質・材料研究機構[5])○山之内 捷[1]、山本 輝[2]、遠藤 尚彦[4]、渡邊 賢司[5]、谷口 尚[5]、宮田 耕充[4]、片山 哲郎[3]、古部 昭広[3]

Substrate Dependence of Carrier Dynamics in $MoSe_2$ Monolayer by using Femtosecond Transient Absorption Microscopy (Tokushima University[1], Tokyo Metropolitan University[2], National Institute for Materials Science(NIMS)[3]) ○Sho Yamanochi[1], Akira Yamamoto[1], Naohiko Endo[2], Kenji Watanabe[3], Takashi Taniguchi[3], Yasumitsu Miyata[2], Tetsuro Katayama[1], Akihiro Furube[1]

Two-dimensional materials such as graphene and transition metal dichalcogenides have attracted much attention in recent years because of their thin monatomic layers, high mobility, and the fact that their physical properties change significantly due to interactions between the monatomic layers. On the other hand, these two-dimensional materials are greatly affected by the unevenness of the substrate because the constituent atoms are exposed on the surface. In this study, we have performed spectroscopy on atomically flat hexagonal boron nitride (hBN) by using femtosecond transient absorption microscopy with time and spatial resolution for single-layer $MoSe_2$ on a flat substrate. We discuss the flat substrate dependence of carrier dynamics.

Keywords : Transition Metal Dichalcogenide, femtosecond transient absorption microscopy, carrier dynamics, Substrate dependence

グラフェンや遷移金属ジカルコゲナイドなどの二次元材料は原子レベルの薄さを有し、単原子層同士の相互作用により物性が大きく変化することから近年注目を浴びている。一方でこれら二次元材料は構成する原子が表面に露呈していることから基盤由来の凹凸に大きく影響を受ける。本研究においては、原子レベルでの平坦性を有する六方晶窒化ホウ素(hexagonal boron nitride:hBN) を基板としたセレン化モリブデン($MoSe_2$)で時・空間分解能を有するフェムト秒顕微過渡吸収分光法を用いて、分光計測を行い、そのキャリアダイナミクスの平坦基板依存性について議論する。

Fig.1a に試料透過像を示す。ラマン計測も行い hBN-$MoSe_2$ 試料の層数を評価し、黒丸線内に hBN 上の単層 $MoSe_2$ があることを確認した。この試料対して顕微過渡吸収スペクトルを計測した。Fig.1b にその結果の一例を示す。単層特有のブリーチ信号が 550 nm 付近より短波長側に現れ、820 nm 付近の誘導放出信号が 1 ps 以内に立ちあがる挙動が観測された。発表では、石英基板上の $MoSe_2$ と比較議論する。

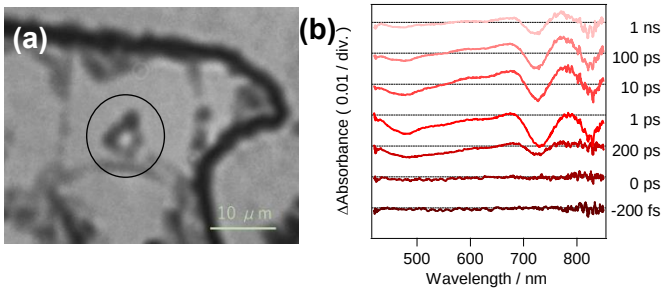

Fig.1 Transmission image(a) and Femtosecond transient absorption spectra(b) of monolayer $MoSe_2$ with excitation at 400 nm.

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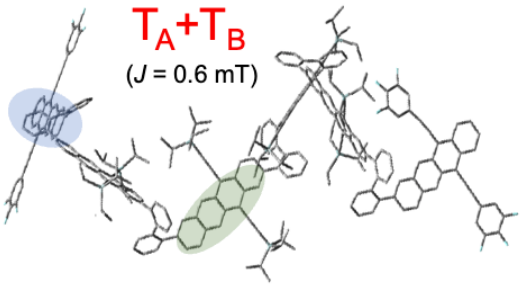
パルス EPR 法によるスピン相関三重項対のスピン量子コヒーレンス観測

(神戸大分子フォト[1]・CREST, JST[2]・慶応大理工[3]) ○小堀 康博[1,2]・婦木 正明[1,2]・羽曾部 卓[3]
Spin coherence in a spin correlated triplet pair observed by pulsed EPR ([1]*Molecular Photoscience Research Center, Kobe University*, [2]*CREST, JST,* [3] *Department of Chemistry, Faculty of Science and Technology, Keio University*) ○Yasuhiro Kobori,[1,2] Masaaki Fuki,[1,2] Taku Hasobe[3]

Singlet fission (SF) is a phenomenon that produces multiple triplet excitons (triplet pairs) from a single photon. The multiple excitons produced in this process are expected not only to improve the efficiency of organic solar cells, but also to be applied to extended molecular quantum computing by using four qubits composed of unpaired electrons that make up a triplet pair. We have observed the electron spin polarization of multiple excitons by time-resolved EPR and characterized the spin quantum states of strongly correlated quintet multiple excitons and spin correlated triplet pairs (SCTP) due to exciton dissociation.
Keywords : Singlet Fission; Qbit; Spin Correlated Triplet Pair; Pulsed EPR; Coherence

一重項励起子分裂(SF)は、単一の光子から複数の三重項励起子（三重項ペア）を生む現象として知られている。この過程で生成する多重励起子は、有機太陽電池の超高効率化にとどまらず、三重項ペアを構成する不対電子による四量子ビットを基本単位とした分子量子コンピューティングへの応用が期待される。我々は三重項ペアの電子スピン分極を時間分解 EPR 法で観測し、強相関五重項多重励起子や、励起子解離によるスピン相関三重項対のスピン量子状態を特徴づけ、1)遠隔地に互いに離れた三重項ペアによる一重項、三重項、五重項の量子重ね合わせとしてスピン波動関数が表現されること、2)スピン量子状態分布は、この量子重ね合わせによる基底関数組み換えに伴うユニタリ変換を用いた量子演算として得られることを実証した[1-4]。これらは、光照射によって遠隔地に励起子が離れた三重項ペアのスピン量子もつれ状態を準備できることを示している。本研究では、パルス電子スピン共鳴法を用い、多量体で構成される連結系分子(図)の励起子分裂による三重項ペア[2]を観測した。SF後のスピン変換ならびに解離に対する振電的機構を明らかにするとともに、パルスマイクロ波によるスピン量子コヒーレンス制御を行った。



1) A. Yamauchi, M. Fuki, Y. Kobori, K. Miyata, N. Yanai, *et. al.*, *Sci. Adv.* **2024**, *10*, eadi3147.
2) S. Nakamura, M. Fuki, Y. Kobori, T. Hasobe, *et. al. ACIE* **2023,** *62*, e202217704.
3) Y. Kobori, *et. al. Chem. Sci.* **2020,** *11*, 2934. 4) Y. Kobori, *et. al. J. Phys. Chem. B* **2020**, *124*, 9411.

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マイクロ構造電極における水素発生気泡生成の顕微観測

(北大理[1]・北大院総化[2]・北大院総化[3])
○阿部 樹[1]・芦澤 大輝[2]・佐藤 大樹[2]・小橋川 和磨[2]・福島 知宏[3]・村越敬[3]
Observation of hydrogen bubble evolution reactions at micro-structured electrodes (Department of Chemistry, Faculty of Science, Hokkaido University) ○Itsuki Abe, Daiki Ashizawa, Daiki Sato, Kazuma Kobashigawa, Tomohiro Fukushima, Kei Murakoshi

Hydrogen evolution reaction (HER) is an important reaction for the water electrolysis. The dissociation of water molecules in Volmer or Heyrovsky process can be modulated by the cation-dependent hydration structure at electrode-electrolyte interface. In this work, we discuss the structural dependence of the HER using micro-structured electrodes.
Keywords : Hydrogen evolution reaction; Cavity; Bubble observation

【序論】水素発生反応 (HER) は電気化学的に重要な反応である。電極―電解質界面における水分子の水素結合ネットワークから水素が脱離する過程が HER 触媒サイクルを律速することが知られている。当研究室の先行研究において、共振器内の水分子が強結合状態を形成することによる水和構造の変調が検証されている。[1] そのため、共振器構造を界面へ導入することにより、HER へ振動強結合状態を導入し、水素の脱離が関与する素反応の反応速度が変調することを期待している。本研究においては、HER に強結合状態を導入するために、共振器構造が配列された電極を用いて HER を変調することを目的として研究を行った。

【実験】Fig. 1 に示すように、共振器の深さ(d) 1 μm、共振器長(L)が 1.0 ~ 6.5 μm の共振器構造を有する基板をフォトリソグラフィーにより作製した。この基板に Ti を 4 nm 蒸着した後、Ni あるいは Ag を 200 nm 蒸着したものをマイクロ構造電極とした。これらを作用極とし、参照極に Ag/AgCl、対極に白金黒、溶液として 0.5 M Na_2SO_4 を用いた。このときの作用極での気泡発生の様子を、Fig. 2 に示すような正立配置カメラにて 1 秒間に 60 フレームの速度で撮影した。

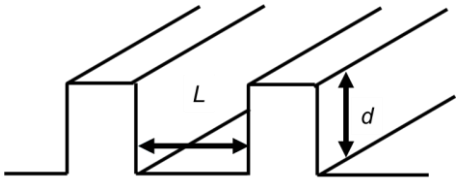

Fig. 1. An image of microelectrode. d is the cavity depth. L is the cavity length (1.0 ~ 6.5 μm).

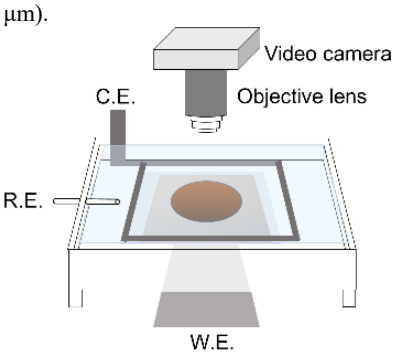

Fig. 2. A schematic image of observation of bubble evolution system that video camera above electric cell. W.E.: microelectrode C.E.: Pt, R.E.: Ag/AgCl in 0.5 M Na_2SO_4.

【結果と考察】自然電位と溶液抵抗を計測した後、掃引速度 5 mV s^{-1} で Liner sweep voltammetry を行った。この際、作用極の電気化学計測を行いながら、同時にマイクロ構造上で気泡が発生・成長・脱離する過程を観測した。気泡成長速度を電位の関数として解析することにより、構造電極における HER 触媒活性の特徴を検討した。

参考文献 1) T. Fukushima, S. Yoshimitsu, K. Murakoshi, *J. Am. Chem. Soc.* **2022**, *144* (27), 12177.

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電気化学水晶振動子マイクロバランスによる白金電極表面へのアイオノマー吸着のその場解析

（お茶女大院[1]・日産化学[2]）○武井 楓[1]・野口 貴俊[2]・近間 克己[2]・近藤 敏啓[1]
In situ Observation of Adsorption of Ionomers onto Pt Electrode Surfaces Using Electrochemical Quartz Crystal Microbalance ([1]*Graduate School of Humanities and Sciences, Ochanomizu University*, [2]*Nissan Chemical*) ○Kaede Takei,[1] Takatoshi Noguchi,[2] Katsumi Chikama,[2] Toshihiro Kondo[2]

In the polymer electrolyte fuel cells (PEFCs), a platinum catalyst is covered by an ionomer of the solid polymer electrolyte. The ionomer, which is the electrolyte for the electrode, transports protons and oxygen molecules to the surface of the platinum catalyst. Therefore, the adsorption/desorption behavior of ionomers during on/off of the PEFC is considered to affect the catalytic activity. In this study, the relationship between the adsorption/desorption of several PFSA-based ionomers and the redox behavior of Pt electrodes was investigated by in situ electrochemical quartz crystal microbalance (EQCM) technique. The EQCM is a method that can measure the potential-dependent mass changes on the electrode surface. The EQCM measurements were performed in the aqueous dispersion solutions containing two kinds of perfluorosulfonic acid ionomers, such as Nafion® and Aquivion®, to observe the mass changes during Pt oxide formation and its removal reaction and hydrogen adsorption/desorption reactions. Nafion® exhibits specific adsorption/desorption behavior during the Pt oxide formation/removal reaction process. On the other hand, Aquivion® showed adsorption/desorption behavior dependent on the reaction process of hydrogen adsorption/desorption on the Pt surface. The adsorption/desorption processes of these ionomers were modeled and discussed.
Keywords：Electrochemical Quartz Crystal Microbalance (EQCM); Perfluorosulfonic acid (PFSA) based Ionomer; Polymer Electrolyte Fuel Cells (PEFCs)

固体高分子形燃料電池（PEFC）において、白金触媒は、固体高分子電解質のアイオノマーで覆われている。電極用電解質であるアイオノマーは、白金触媒表面へプロトンや酸素分子を輸送する。そのため、PEFC の on/off 時のアイオノマーの吸脱着挙動が触媒活性を左右すると考えられている。そこで本研究では、いくつかの PFSA 系アイオノマーの吸脱着と白金電極の酸化還元挙動との関係を調べるために、電気化学水晶振動子マイクロバランス（EQCM）でその場追跡して、比較・検討した。EQCM は、電位依存的に電極表面上の微少な質量変化を測定することができる。EQCM 電極を作用電極とした電気化学セルを用いて、Nafion®分散水溶液、及び Aquivion®分散水溶液で、電気化学測定を行い、白金酸化物形成/除去及び、水素吸着/脱離反応中での質量変化を観測した。Nafion®は、白金酸化物形成/除去の反応過程に特異的な吸脱着挙動を示し、酸化上限電位に依存することがわかった。一方、Aquivion®は、白金表面への水素吸着脱離反応過程に依存的な吸脱着挙動を示した。これらの実験結果を踏まえて、アイオノマーの吸着脱離挙動をモデルをたてて考察したことを報告する。

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電極-電解液界面における電界を触媒としたジピリジルテトラジンージヒドロフラン Diels-Alder 付加体の異性化反応

（九大院総理工[1]・九大先導研[2]）○足立 健太朗[1]・古澤 将樹[2]・アルブレヒト 建[2]
Electric field catalyzed isomerization of di-pyridyl-tetrazine and dihydrofuran Diels -Alder adduct ([1]*Grad. Sch. Eng. Sci., Kyushu Univ.,* [2]*IMCE, Kyushu Univ.*) ○Kentaro Adachi,[1] Masaki Furusawa,[2] Ken Albrecht[2]

External electric fields (EEFs) have been investigated as a tool to control the reactivity and selectivity of a chemical reaction. When an electric field is applied to a reactant, it interacts with the dipole moment of the ground or transition state and changes the energy. This allows the control of the activation energy. In this talk, we report an isomerization reaction of 3,6-di(4-pyridyl)-1,2,4,5-tetrazine and 2,3-Dihydrofuran Diels-Alder adduct under an applied EEFs. The electric field was applied by utilizing the electrical double layer formed at the electrode-electrolyte interface of a standard three-electrode cell. The progress of the isomerization reaction was confirmed in the absence of a Faradaic current. When no voltage was applied, the isomerization reaction did not proceed; when voltage was applied, the isomerization rate depended on the field strength. The reaction temperature was changed and the activation energy was determined from the isomerization rate.
Keywords : External electric field; Electrostatic catalysis; Electric double layer; Isomerization reaction

電界（電場）を分子に印加すると、基底状態や遷移状態の双極子モーメントと相互作用することで反応性に影響を及ぼすと考えられている。電界を印加することで反応系の基底状態や遷移状態のエネルギーを制御することができれば、反応の速度や選択性を制御することが可能となる。近年、このような「電界」を触媒とする反応に注目が集まっている。本研究では、単分子接合中での電界による反応促進が報告されている 3,6-di(4-pyridyl)-1,2,4,5-tetrazine と 2,3-dihydrofuran の Diels-Alder (DA)付加体の OH 体への異性化反応 [1]について、電気二重層中での反応について報告する(Fig.1)。電界印加による反応速度変化を観測するため、三電極系セルを用いた電気二重層形成状態での反応の進行を追跡した。ファラデー電流の観測されない電圧を作用極に印加した状態で、無印加では進行しない異性化反応の進行を確認した。さらに、印加時の保持温度を変えて各温度における異性化率から活性化エネルギーを求め、電界が活性化エネルギーを引き下げていることを明らかとした。

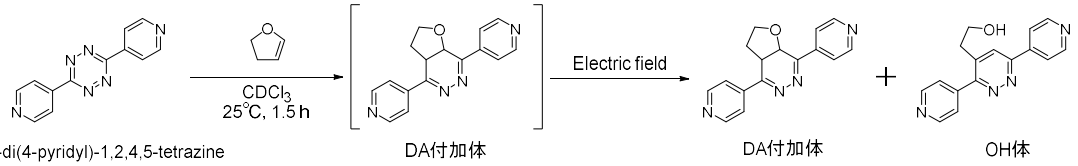

Fig. 1 Isomerization reaction of 3,6-di(4-pyridyl)-1,2,4,5-tetrazine and 2,3-dihydrofuran Diels-Alder adduct.

1) X. Huang *et al.*, *Sci Adv.* **2019**, 5, eaaw3072

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Advancement of the r-BS+G electrocatalyst with high stability for the oxygen evolution reaction

([1] *Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan.* [2] *Center for Computational Sciences, University of Tsukuba, Japan.* [3] *Institute of Technical and Macromolecular Chemistry, RWTH University, Germany.* [4] *School of Environmental Science and Engineering, Kochi University of Technology, Japan.* [5] *Tokyo University of Agriculture and Technology, Japan.* [6] *Research Center for Materials Nanoarchitectonics, NIMS, Japan.* [7] *MDX Research Center for Element Strategy, Tokyo Institute of Technology, Japan.* [8] *Institute of Pure and Applied Sciences, University of Tsukuba, Japan.* [9] *Advanced Institute for Materials Research, Tohoku University, Japan*) ○L. Li [1], S. Hagiwara [2], C. Jiang [3], H. Kusaka [1], N. Watanabe [1], T. Fujita [4], F. Kuroda [2], A. Yamamoto [5], M. Miyakawa [6], T. Taniguchi [6], H. Hosono [6,7], M. Otani [2], T. Kondo [8,9]

Keywords: rhombohedral boron monosulfide; electrocatalysts; oxygen evolution reaction; renewable energy device

Due to the sluggish four-electron path, the oxygen evolution reaction (OER) requires higher energy consumption, so designing low-cost and high-efficiency electrocatalysts for OER is necessary. Rhombohedral boron monosulfide (r-BS) is a new metal-free catalyst, it was synthesized by a previously reported high-pressure solid-state reaction [1]. Previously, we reported that r-BS mixed with graphene (r-BS+G) as a new metal-free electrocatalyst, showing promising electrocatalytic activity with much better performance than most published metal-free catalysts in 1M KOH solution [2]. Stability is very important for the application of electrocatalysts, but the electrochemical activity of r-BS+G declined after performing 2000 cyclic voltammetry cycles [2]. To solve this problem, we introduced Nickel foam (NF) as the self-supporting working electrode. After dropping the r-BS+G sample ink onto the NF, the r-BS+G-NF shows significantly enhanced OER activity with the ultralow an overpotential of 308 mV at 100 mA cm^{-2}, which is 53 mV better than commercial RuO_2 dropped on NF (RuO_2-NF). Most importantly, the r-BS+G-NF exhibited strong durability in a prolonged chronopotentiometry test at a constant current density of 100 mA cm^{-2} for 100 h (Fig. 1), which provides more possibilities for future practical applications [3].

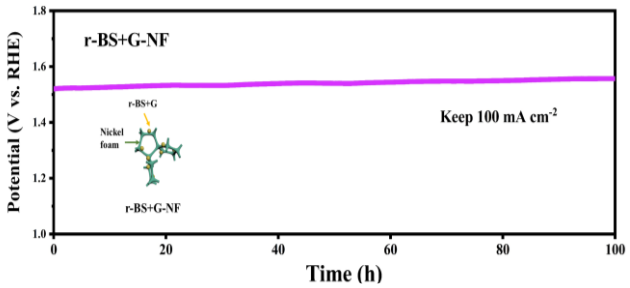

Fig. 1 A chronopotentiometry test of r-BS+G-NF for 100 h.

1) H. Kusaka, L. Li, T. Kondo, et al., *J. Mater. Chem. A*, **2021** *9*, 24631. 2) L. Li, T. Kondo, et al., Chem. Eng. J., **2023** *471*, 144489. 3) L. Li, T. Kondo, et al., *Sci. Tech. Adv. Mate.* **2023** *24*, 2277681.

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Academic Program [Oral A] | 06. Analytical Chemistry：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC
A1453(1453, Bldg. 14 [5F])

[A1453-3pm] 06. Analytical Chemistry

Chair: Atsuko Masuya-Suzuki, Tsuyoshi Minami

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1453-3pm-01]
Design of chemical nuclease for searching G4 sites on the genome

○Shigeori Takenaka[1], Shinobu Sato[1], Sanada Yukina[1], Fujii Satoshi[2] (1. Dept. Appl. Chem. Kyutech, 2. Dept. Biosci. Bioinfor. Kyutech)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1453-3pm-02]
Development of biotin-modified cyclic naphthalene diimide for detection of G4 in the genome

○Shinobu Sato[1], Satoshi Fujii[1], Ryuki Hidaka[1], Shigeori Takenaka[1] (1. Kyushu Inst. Tech.)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1453-3pm-03]
Electrochemical telomerase assay using naphthalene diimide immobilized electrode

○Yudai Higashi[1], Shinobu Sato[1], Shigeori Takenaka[1] (1. Kyushu Inst. Tech.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1453-3pm-04]
Detection of anionic surfactants using microfluidic devices with optodes as detectors

○Ryu Konno[1], ryo yamada[1], mika hanayama[1], takashi masadime[1] (1. shibaura institute of technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1453-3pm-05]
Forming of TRDF using PEG-copper ion (II) aqueous two phase system and effects of coexisting substances

○Yoshiki Hiramatsu[1], Daiki Isikawa[1], Takeshi Iharada[1], Kazuhiko Tsukagoshi[1] (1. Doshisha University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1453-3pm-06]
Investigation of analysis conditions and practical sample measurement in hydrogen peroxide analysis using reactions with hypochlorite and phenol

○Ikko Mikami[1], Takahiro Fukase[1] (1. Tokai University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

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[A1453-3pm-07]

High-speed fluorescence mode XAFS measurement in wide-energy range using the X-ray image detector CITIUS

○Tomoya Uruga[1,2], Yoshiaki Honjo[2], Takuma Kaneko[1,2], Nobuhiro Yasuda[1], Oki Sekizawa[1], Yasuhiko Imai[1,2], Kyosuke Ozaki[2], Haruki Nishino[1,2], Takaki Hatsui[2] (1. JASRI, 2. RIKEN)

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

[A1453-3pm-08]

Retention Behavior of Oligopeptides in MOF Column Chromatography

○Yosuke Higuchi[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese

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

[A1453-3pm-09]

Chemoinformatics Analysis on Retention Behavior of MOF Column Chromatography

○Akihiro Torimoto[1], Yosuke Higuchi[1], Nobuhiko Hosono[1], Takashi Uemura[1] (1. Grad. Sch. Eng., The Univ. of Tokyo)

Japanese

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

[A1453-3pm-10]

Fabrication of MOF@SiO2 Core-Shell Stationary Phases for High-Precision Polymer Separation

○Toshiaki Matsumura[1], Nobuhiko Hosono[1,2], Takashi Uemura[1,2] (1. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese

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

[A1453-3pm-11]

Cationic/anionic-exchange mode switching chromatography utilizing pH-responsive mixed charge polymer-modified silica beads

○Koichi Deura[1], Taisei Kaku[1], Tomoka Yoshii[1], Daniel Citterio[1], Yuki Hiruta[1] (1. Keio university)

Japanese

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

[A1453-3pm-12]

Mutual separation of main metal elements Fe/Nd/Dy in neodymium magnets by crystallization

○Natsuki Hasegawa[1], Atsuko Suzuki[2], Ryo Tsunashima[2] (1. Faculty of Science, Yamaguchi University, 2. Graduate School of Sciences and Technology for Innovation, Yamaguchi University)

Japanese

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

[A1453-3pm-13]

Effect of chemical enhancer on peroxidase catalyzed luminol chemiluminescence in kosmotropic salt solution

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○Hajime Karatani[1] (1. Kyoto luminous science lab.)

Japanese

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

[A1453-3pm-14]

Effect of aminopropyl sulfate-ester group in zwitterionic surfactant on the thermosensitive phase-separation

○Yuto Kusunoki[1], Taichi Nakagawa[1,2], Willie L. Hinze[3], Yoshitaka Takagai[1] (1. Fukushima Univ., 2. JAEA, 3. Wake Forest Univ.)

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日本化学会 第104春季年会 (2024)

ゲノム上のグアニン４本鎖(G4)部位検索のための化学ヌクレアーゼの設計

（九工大院工[1]・情報工[2]）○竹中繁織[1]・佐藤しのぶ[1]・眞田幸奈[1]・藤井聡[2]
Design of chemical nuclease for searching G4 sites on the genome ([1]*Deapartment of Apply Chemistry, Kyushu Institute of Technology*, [2]*Deptment of Bioscience and Bioinformatics, Kyushu Institute of Technology*,) ○Shigeori Takenaka,[1] Shinobu Sato,[1] Yukina Sanada,[1] Satoshi Fujii[2]

We attempted to design an artificial nuclease, cNDI-Cu, that selectively binds to the G-quartet (G4) structure and cleaves it in order to analyze the true G4-forming sequences. The cyclic naphthalene diimide (cNDI) developed by us as the G4 binding site was introduced with a peptide copper complex, Cu(II)-bound Gly-Gly-His, as the DNA cleavage site. The interaction of the obtained cNDI-Cu with G4 and its cleavage behavior were investigated.
Keywords : G-quartet (G4); genome; cyclic naphthalene diimide; chemical nuclease; peptide cupper complex

ヒトゲノム DNA 上の推定 G4 形成配列が多数存在することがバイオインフォマッテクス解析から明らかになっているが、本研究では真の G4 形成配列を分析するために G4 構造に選択的に結合し、その部位を切断する人工ヌクレアーゼ, cNDI-Cu（図 1A）の設計を試みた。G4 結合部位として著者らが開発した cNDI[1]。切断部位としてペプチド銅錯体 Cu(II)-bound Gly-Gly-His の導入を行った。この合成した cNDI-Cu と G4 相互作用と切断挙動に関して検討した。Gly-Gly-His は Cu^{2+}と錯形成して、H_2O_2 存在下で OH･を生成し、近傍の DNA を切断することが知られている[2]。cNDI-Cu は、cNDI のリンカー部に導入したアミノ基を介して Gly-Gly-His の導入した後、Cu^{2+}との錯体を形成させることにより合成した。cNDI-Cu はパラレル型 G4 構造を有する c-myc に 10^6 M^{-1} オーダーで結合することが明らかとなった。また、結合個数 n=2 であったことから G4 平面の上下に stacking 結合していることが示唆された(図 1 B)。これは当初予想していたように cNDI-Cu が G4 に連結している DNA 部位を二か所から切断できることが示唆される。現在、H_2O_2 存在下で G4 部位を有する DNA 断片の切断条件を検討している。講演では、cNDI-Cu の G4 結合の基礎的な検討に加え、切断挙動に関しても報告する予定である。

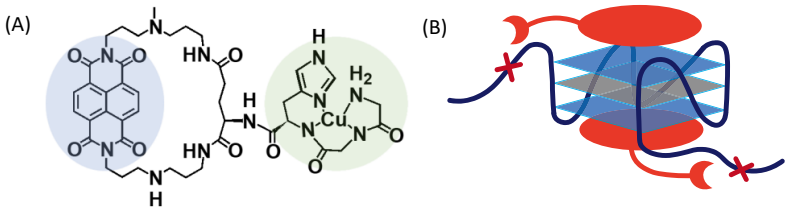

図１．(A) G4 特異的化学ヌクレアーゼ, cNDI-Cu と (B) G4 部位への結合概念図. ×の部分で DNA 切断が期待される.

1) Y. Esaki, Md. M. Islam, S. Fujii, S. Sato, S. Takenaka, *Chem. Commun.*, **2014**, *50*, 5967.
2) Z. Yu, A. L. Hendricks, J. A. Cowan, *iScience*, **2021**, *24*, 102661.

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日本化学会 第104春季年会 (2024)

ゲノム中の G4 検出を目指したビオチン修飾環状ナフタレンジイミドの開発

（九工大院工 [1]・九工大情報工 [2]）○佐藤 しのぶ [1]・藤井 聡 [2]・日高 竜希 [1]・竹中 繁織 [2]

Development of biotin-modified cyclic naphthalene diimide for detection of G4 in the genome

([1]*Department of Applied Chemistry,* [2]*Department of Bioscience and Bioinformatics, Kyushu Institute of Technology*) ○Shinobu Sato,[1]Satoshi Fujii,[2] Ryuki Hidaka,[1] Shigeori Takenaka[1]

G-quadruplex (G4) in the genome is thought to be involved in biological events. Information about true G4 forming region in genome has been detected using antibodies that recognize G4, but access to G4 is problematic due to the size of the antibodies themselves. To solve this problem, we considered the use of cyclic naphthalene diimide, which specifically binds to G4 DNA. Here, we synthesized biotinylated cyclic naphthalene diimide (biotin-cNDI) and attempted it to detect G4 by combination of streptavidin-modified magnetic beads (avidin-beads). When a 120-base synthetic oligonucleotide containing c-myc region was pulled down using biotin-cNDI and avidin-beads, this oligonucleotide was detected quantitatively by qPCR with a detection limit of 2 amol.

Keywords : cyclic naphthalene diimide, G-quadruplex, genome, pull down assay

ゲノム中の G4 は生体イベントに関与することから、ゲノム上の真の G4 形成部位の検出は重要である。G4 認識抗体は、ゲノム上の G4 形成部位の検出に利用されている。しかし、抗体自身の大きさから G4 へのアクセシビリティーに問題があった。そこで、4 本鎖 DNA に特異的に結合する小分子、環状ナフタレンジイミド [1]を利用した。まず、ビオチン化環状ナフタレンジイミド(cNDI-biotin)を合成し、Fig. 1 に従ってストレプトアビジン修飾磁気ビーズを組み合わせて G4 の検出を試みた。

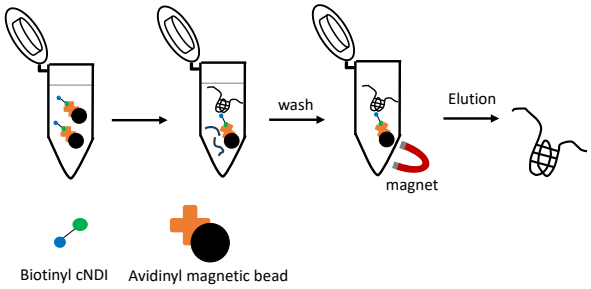

Fig. 1. Pulldown protocol to isolate G4s using biotinyl cNDI and avidin magnetic beads.

等温滴定カロリメトリー(ITC)測定より cNDI-biotin は c-myc に対して 3.9×10^{6} M^{-1}, ヒトテロメア G4 に対して 2.1×10^{6} M^{-1} の結合定数を有し、biotin を持たない他の cNDI 誘導体とほぼ同じ結合定数 [1]であった。一方、2 本鎖 DNA に対しては、優位な熱変化は観察されず、cNDI-biotin と 2 本鎖 DNA の相互作用が弱いことが示された。c-myc 領域を持つ 120mer のモデル合成オリゴヌクレオチドに対して、pull down を行い、qPCR で定量したところ、回収下限 2 amol で回収率 50%以上の回収が可能であった。

1) H. Fukuda, S. Sato, T. Zou, S. Higashi, O. Takahashi, M. Habu, M. Sasaguri, K. T., S. Takenaka, H. Takeuchi, *Bioorg. Med. Chem. Lett.*, **2021**, *50*, 128323.

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ナフタレンジイミド固定化電極による電気化学的テロメラーゼ活性検出

（九工大院工 [1]）○東 祐大 [1]・佐藤 しのぶ [1]・竹中 繁織 [1]
Electrochemical telomerase assay using cyclic naphthalene diimide immobilized electrode
(*Graduate School of Engineering, Kyushu Institute of Technology*[1]) ○ Yudai Higashi[1], Shinobu Sato[1], Shigeori Takenaka[1]

Naphthalene diimide is known as an intercalator that binds to double-stranded DNA by threading intercalating mode. We synthesized a cyclic naphthalene diimide (cNDI) derivative having an amino group to be immobilized on a gold electrode. Thus obtained this cNDI-electrode is expected to immobilize a DNA duplex and to be detect electrochemically using ferrocenyl naphthalene diimide (FND) concentrated to the DNA duplex. Here we tried to detect the PCR product from telomerase elongated teromeric DNA. We evaluated the amount of the concentrated DNA duplex using the Δi value: $\Delta i = (i\text{-}i_0)/i_o$, where i_0 and i were the current before and after treatment with PCR product. We evaluated the Δi value under the varied amount of telomerase elongation product at 5, 3, 1, or 0.5 ng/μL and obtained the correlated response of the concentration of PCR products.

Keywords : Naphthalene diimide; ferrocenyl Naphthalene diimide; Telomerase; PCR product

これまで 4 本鎖 DNA に特異的結合する環状ナフタレンジイミド誘導体(cNDI)を設計・合成してきた [1]。この分子は二本鎖 DNA への結合できないものであったが、二本鎖 DNA の末端領域へは結合することができた。そこで、cNDI 固定化電極を用いて二本鎖 DNA への電極固定化を検討し、二本鎖 DNA の末端固定化を可能にすることを明らかにした。そこで、ここでは新たにテロメラーゼ伸長産物由来の PCR 産物の検出を試みた。図 1 に示す手順によって PCR 産物の固定化と電気化学的検出を試みた。まず、FND 溶液中で cNDI 固定化電極の電流値 i_0 を測定し、PCR 産物を添加した後に再度 FND 溶液中で電流値 i 測定した。これらの値を $\Delta i\ (\%) = (i\text{-}i_0)/i_0 \times 100$ 用いて電流増加率 Δi を算出した。HeLa 細胞破砕液から抽出したテロメラーゼを用いてテロメア DNA 伸長後、さらに PCR 伸長反応を行い、PCR 産物を cNDI 電極に固定化した。得られた PCR 産物の濃度を 5, 3, 1, 0.5 ng/μL で変化させ、FND 中で電気化学測定を行ったところ濃度依存的に Δi の増加が観察された。この結果は、本電極によってテロメア PCR 産物の検出とテロメラーゼによるがん診断の可能性を示している。

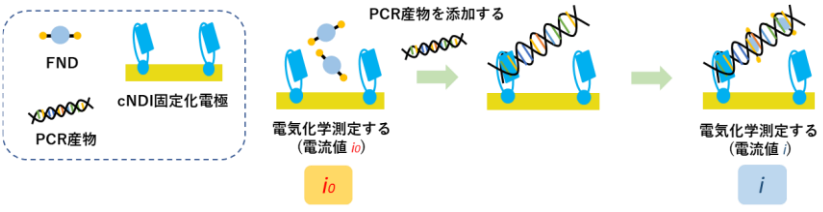

図 1.　cNDI 固定化電極による PCR 産物検出原理.

参考文献 1) R. Takeuchi, T. Zou, D. Wakahara Y. Nakano, S. Sato, S. Takenaka, *Chem. A Eur. J.*, **25**, 8691-8695 (2019).

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オプトードを検出器とするマイクロ流体デバイスを用いた陰イオン性界面活性剤の検出

(芝浦工業大学 [1])○紺野 琉 [1]・山田 凌 [1]・華山 美香 [1]・正留 隆 [1]

Detection of anionic surfactants using microfluidic devices with optodes as detectors

(1. Shibaura Institute of Technology) ○Ryu Konno[1], Ryo Yamada[1], Mika Hanayama[1], Takashi Masadome[1]

Anionic surfactant (AS) is widely used in household detergents, and its production is increasing every year. Since AS is toxic to living organisms and persistent, it is important to monitor the concentration of AS. However, conventional determination methods for AS are complicated, time-consuming, and use toxic substances. In this study, we developed a new determination method for AS using a microfluidic device with fluorescence optode detector.

The limit of detection for sodium dodecylbenzenesulfonate obtained using the 3σ rule was 0.02 mg/L (0.05 μM), which satisfied the water quality standard (0.2 mg/L) for tap water established by the Ministry of Health, Labor and Welfare in Japan.

Keywords：Optode, fluorescence spectroscopy, Anionic Surfactant, Flow Injection Analysis, Microfluidic Devices

陰イオン性界面活性剤(AS)は家庭用洗剤などに多く用いられており、生物に有害かつ難分解性であるため、その濃度監視が重要である。しかし従来の AS の定量法は、操作が煩雑、時間がかかる、有害物質の使用などの問題がある。そこで本研究では、蛍光オプトードを検出器とするマイクロ流体デバイスによる AS の新規定量法を検討した。図 1 のマイクロ流体デバイスにより得られた AS であるドデシルベンゼンスルホン酸ナトリウム(NaDBS)に対する検量線を図 2 に示す。オプトードの蛍光強度と 0-20 μM の濃度範囲の NaDBS 濃度との間には良好な直線関係が成立した。NaDBS の検出限界は 0.02 mg/L(0.06 μM)であり、厚生労働省の定める水道水の水質基準の 0.2 mg/L を満たしている。

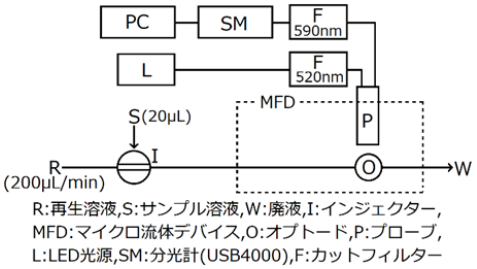

図 1 AS 測定用マイクロ流体デバイス

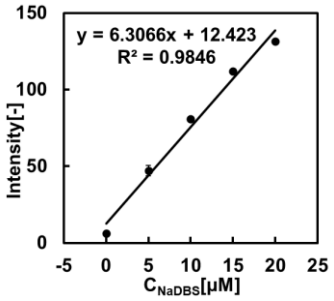

図 2 NaDBS に対する検量線

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PEG-銅(Ⅱ)イオン水性二相系を用いた TRDF の創出と共存物質の影響

（同志社大学 [1]）○平松 芳樹 [1]・石川 大暉 [1]・居原田 健志 [1]・塚越 一彦 [1]
Forming of TRDF using PEG-copper ion (Ⅱ) aqueous two phase system and effects of coexisting substances ([1]*Faculty of Science and Engineering, Doshisha University*) Yoshiki Hiramatsu,[1] Daiki Ishikawa,[1] Takeshi Iharada,[1] Kazuhiko Tsukagoshi[1]

A two-phase separated mixed solution changes from one homogeneous phase to two heterogeneous phases when the temperature and/or pressure are changed. When this homogeneous one-phase solution is fed into a microspace and the temperature and pressure are changed, phase separation occurs and a phase-separated multiphase flow is obtained. We focused on the annular flow (Tube Radial Distribution Flow (TRDF)).

In this experiment, we investigated the conditions for creating TRDF using a PEG-copper(II) ion aqueous two-phase system. Phase diagrams of the PEG-copper(II) ion-water system and the PEG-copper(II) ion-sodium hydroxide aqueous solution (pH 14) system were examined. Solutions with each composition ratio were delivered to a capillary tube (75 μm i.d.), and the fluid behavior was observed in bright field using a microscope. Capillary tubes were kept at the temperature of 25 or 50 °C respectivly. TRDF could not be observed in the PEG-copper(II) ion-water solution, but there was a composition ratio in which TRDF could be observed in the PEG-copper(II) ion-sodium hydroxide solution. Human serum albumin, triglycine, and EDTA were added to this solution to examine their effects on TRDF. Slug flow was observed in the solution containing EDTA at 5 μL/min. The interfacial tension of the solution containing EDTA was the largest (0.73 mN/m).
Keywords : Aqueous two-phase system; Tube Radial Distribution Flow; PEG-copper ion(Ⅱ)

二相分離混合溶液は、温度圧力を変化させると均一一相から不均一二相に変化する。この均一一相の溶液を微小空間に送液し、温度圧力変化させると相分離が生じ、液滴流、スラグ流、平行流、環状流といった動的液液界面を有する流れが得られる。これらの流れを相分離混相流と呼ぶ。我々は特に環状流 (管径方向分配流；Tube Radial Distribution Flow (TRDF)) に注目した。

本実験では PEG-銅(II)イオン水性二相系を用いて TRDF の創出条件を調べた。PEG-銅(II)イオン-水系および PEG-銅(II)イオン-水酸化ナトリウム水溶液 (pH 14) 系の相図を作成した。これらの溶液は銅(II)過剰相と PEG 過剰相に相分離する。各組成比の溶液をキャピラリーチューブ (75 μm i.d.) に 0.1~10 μL/min の間の流量で送液し、顕微鏡を用いて流体挙動を明視野で観察した。キャピラリーチューブは 25 および 50℃に調温した。PEG-銅(II)イオン-水系の溶液では TRDF を観察できなかったが、PEG-銅(II)イオン-水酸化ナトリウム系の溶液では 5 μL/min で TRDF が観察できる組成比があった。この溶液においてヒト血清アルブミン、トリグリシン、EDTA を添加し TRDF への影響を調べた。EDTA を添加した溶液は 5 μL/min でスラグ流、10 μL/min で TRDF が観察された。界面張力を調べると、EDTA が共存する溶液が最も大きい値 (0.73 mN/m) を示した。PEG-銅(Ⅱ)イオン水性二相系を用いた TRDF の創出条件について考察した。

1) K.Tsukagoshi, Analytical Sciences, 2023, DOI: https://doi.org/10.1007/s44211-023-00442-1

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次亜塩素酸塩・フェノールとの反応を利用した過酸化水素分析における分析条件の検討および実試料測定

（東海大理）○三上　一行・深瀬　尚宏

Investigation of analysis conditions and practical sample measurement in hydrogen peroxide analysis using reactions with hypochlorite and phenol（*School of Science, Tokai University*）○Ikko Mikami, Takahiro Fukase

A novel method for hydrogen peroxide analysis using the spectrophotometric measurement of benzoquinones produced by the reaction of hypochlorite and phenol with hydrogen peroxide was investigated. In order to determine the optimal conditions for using this detection method as a post-column reaction in HPLC, we examined the effects of reaction solution composition and measurement conditions on analytical sensitivity, measurement range, and other factors. When comparing different flow paths, the flow path where hydrogen peroxide was added after mixing hypochlorite and phenol solutions produced the largest response peak. It was observed that sensitivity and the measurable concentration range varied significantly depending on the concentration of hypochlorite. The highest sensitivity was achieved at a hypochlorite concentration of 5 mM, and the detection limit at this concentration was 0.2 μM. The linear relationship between hydrogen peroxide concentration and response peak area was observed up to about 1/5 of the hypochlorite concentration. Using this method, we successfully measured real samples such as contact lens cleaning solutions and bleach, obtaining accurate results.

Keywords : Hydrogen peroxide; Determination; Absorption spectrophotometry; Phenol; Hypochlorite

過酸化水素は、食品、医薬品、歯科製品、繊維製品等で広く使用されている。食品産業では過酸化水素は殺菌剤あるいは漂白剤として扱われることがある。過剰な残留過酸化水素は人体に有害であるため、残留する過酸化水素濃度には規制が設けられている。当研究室では次亜塩素酸塩およびフェノールと過酸化水素で生じるベンゾキノン類の吸光度測定を利用する、過酸化水素の新規測定法について検討を行っている。本研究では、この検出法を HPLC のポストカラム反応として利用する場合の最適条件を見出すために、反応液の流路、各試薬濃度等の測定条件が分析感度や測定範囲等に与える影響を調べた。また実試料の測定を行い、本法の有効性を検証した。

流路の比較を行ったところ、次亜塩素酸塩とフェノール溶液を混合してから過酸化水素が加えられる流路が最も応答ピークが大きく、次亜塩素酸塩と過酸化水素を先に混合した場合はその 3 分の 1 程度の大きさであった。次亜塩素酸塩と過酸化水素から生じる活性酸素種の寿命が短いことが原因であると推測される。次亜塩素酸塩濃度により、感度や測定可能な濃度範囲が大きく変動することがわかった。最も高い感度が得られたのは次亜塩素酸塩濃度が 5 mM のときであり、この時の検出限界は 0.2 μM であった。次亜塩素酸塩が過剰な条件では、過酸化水素と次亜塩素酸塩の反応によって生じる活性酸素種が次亜塩素酸塩と反応し、フェノールの酸化を阻害したと推測される。過酸化水素濃度と応答ピーク面積が直線的な関係となるのは、過酸化水素濃度が次亜塩素酸塩濃度の 1/5 程度までであり、それ以上の濃度では検量線の傾きが減少した。他の測定条件の検討を行ったうえで、消毒液やブリーチ剤等の実試料を測定したところ、精度や回収率において良好な結果が得られた。

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X 線画像検出器 CITIUS を用いた広エネルギー領域高速蛍光法 XAFS 計測

（JASRI/SPring-8[1]・理研[2]）○宇留賀 朋哉[1,2]・本城 嘉章[2]・金子 拓真[1,2]・安田 伸広[1]・関澤 央輝[1]・今井 康彦[1,2]・尾﨑 恭介[2]・西野 玄記[1,2]・初井 宇記[2]
High-speed fluorescence mode XAFS measurement in wide-energy range using the X-ray image detector CITIUS ([1]*JASRI/SPring-8,* [2]*RIKEN*) ○Tomoya Uruga,[1,2] Yoshiaki Honjo,[1] Takuma Kaneko,[1,2] Nobuhiro Yasuda,[1] Ouki Sekizawa,[1] Yasuhiko Imai,[1,2] Kyosuke Ozaki,[1] Haruki Nishino,[1,2] Takaki Hatsui[2]

CITIUS is a high-frame-rate, charge-integrated X-ray image detector, and has features of no counting-loss and energy resolution [1]. We are developing X-ray spectroscopy measurement system using CITIUS at the beamline BL36XU [2] at SPring-8. In this report, we show experimental results of a performance of CITIUS as a fluorescence mode XAFS detector.

The XAFS measurement was conducted under *ex-situ* conditions by quick scan XAFS (QXAFS) method using a channel-cut crystal monochromator for synchrotron radiation X-ray from a tapered undulator light source. CITIUS used was a single sensor type (280 k pixels, detection area: 28×53 mm^2) and continuous image measurements were conducted at a frame rate of 6.5 kHz. Experimental results show that the EXAFS measurement under fluorescence mode is possible in a wide energy range by using CITIUS with short measurement time (< 1 s (4.5-20 keV), < 10 s (20-30 keV)). In the presentation, the outline of measurement system and details of the experimental results will be reported. This work was supported by the Polymer Membrane Fuel Cell Project (JPNP20003) of the NEDO of Japan.
Keywords : XAFS; QXAFS; Fluorescence XAFS; X-ray image detector; High energy X-ray

CITIUS は高フレームレート・電荷積分型の X 線画像検出器であり、数え落としがない点、エネルギー分解能を有する点に大きな特徴を持つ[1]。我々は、X 線分光計測分野における CITIUS を用いた計測法の開発を進めている。本報告では、蛍光法 XAFS 計測検出器として用いた際の CITIUS の性能評価実験の結果について報告を行う。

評価実験は、SPring-8 BL36XU [2]にて実施した。XAFS 計測は、テーパーアンジュレータ光を用い、チャネルカット結晶分光器の連続角度走査による蛍光法 QXAFS 計測により、*ex-situ* 条件下で行った。CITIUS は最小構成の 280 kpixel タイプ（受光面積：28×53 mm^2）を使用し、フレームレート 6.5 kHz で連続画像計測を行った。評価実験の結果、CITIUS を用いることにより、広エネルギー領域で高速な蛍光法 EXAFS 計測（計測時間：< 1 s（4.5-20 keV）、< 10 s（20-30 keV））が可能であることが判明した。発表では、計測システムの概要と実験結果の詳細について報告する。本成果は、国立研究開発法人新エネルギー・産業技術総合開発機構（NEDO）の委託業務（JPNP20003）の結果得られた。

1) SPring-8-II Conceptual Design Report, RIKEN SPring-8 Center, 2014.
2) T. Uruga, M. Tada, O. Sekizawa, Y. Takagi, T. Yokoyama, Y. Iwasawa, *Chem. Rec*., **19**, (2019) 1444.

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MOF カラムクロマトグラフィーにおけるオリゴペプチドの保持挙動

（東大院工 [1]）○樋口 陽介 [1]・細野 暢彦 [1]・植村 卓史 [1]
Retention Behavior of Oligopeptides in MOF Column Chromatography ([1]*Graduate School of Engineering, The University of Tokyo*) ○Yosuke Higuchi,[1] Nobuhiko Hosono,[1] Takashi Uemura[1]

Peptide drugs are attracting attention as a new drug discovery modality since they have fewer side effects compared to traditional small-molecule drugs. However, peptide synthesis often entails arduous multistep reactions. This causes many problems of impurities that have close in structure to the target peptide. To remove such impurities, considerable energy and resources have been expended for the purification step. In this study, we have investigated the separation performance and retention behavior of peptides on HPLC using nanoporous metal–organic frameworks (MOFs) as the stationary phase. Two MOFs with ~1 nm pore diameter, $[La(btb)]_n$ (btb = 1,3,5-tris(4-carboxyphenyl)benzene) and Ni-MOF-74, were packed in a column and used to analyze oligopeptides (dipeptides and tripeptides) on HPLC. The MOF columns showed intriguing selectivity to the oligopeptides, discriminating the molecular weight, terminal residue, and residue sequences. The column retention is ascribed to the adsorption of peptide chain in the MOFs, in which minute difference of peptide structure is recognized plausibly by steric effect, hydrophobicity, and coordination interactions.
Keywords : Peptide; Metal-Organic Framework; Liquid Chromatography; Separation; Stationary Phase

ペプチド医薬品は、従来の低分子医薬品に比べて副作用が少ないため、新しい創薬モダリティとして近年注目を集めている。しかし、一般にペプチド鎖の合成は煩雑な多段階反応を経て行われるため、その過程において様々な不純物が混入する。これらの不純物は目的のペプチドに構造や性質が類似するものが多く、その分離の困難さ故、従来のペプチド精製工程には多大なコストが費やされているのが現状である。本研究で我々は、多孔性金属錯体（MOF）が有するナノサイズの細孔へペプチド鎖が吸着される現象を利用し、MOF を固定相としたカラムにおけるペプチドの分離能および保持挙動を調査した。水系溶離液中で安定であり、ペプチド鎖の直径と同サイズの約 1 nm の細孔径を有する MOF、$[La(btb)]_n$ および Ni-MOF-74 を固定相として使用した（Figure 1）。本 MOF を充填したカラムを作成し、数種のオリゴペプチド（ジペプチドおよびトリペプチド）を分析したところ、アミノ酸残基数、末端残基種、アミノ酸配列順序等の違いによりカラム保持時間に違いが生じ、それらの分離が可能であることを見出した。また、ジペプチドに関しては$[La(btb)]_n$ と Ni-MOF-74 の保持傾向が逆転していることも示された。本 MOF カラムのペプチド鎖の識別原理を解明し、条件を最適化することにより、従来の HPLC を凌駕する精密かつ効率的なペプチド分離技術への発展が期待される。

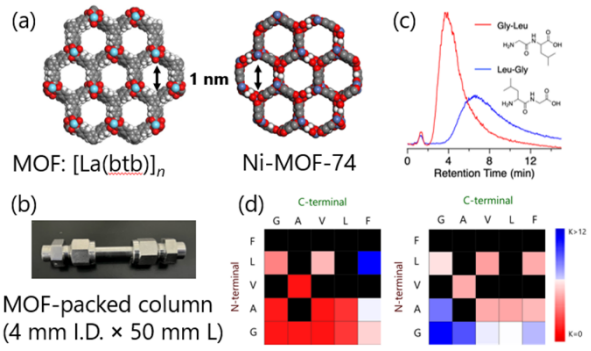

Figure 1 (a) Crystal structure of $[La(btb)]_n$ and Ni-MOF-74. (b) The MOF-packed column. (c) Representative chromatograms of dipeptides on the MOF-packed column. (d) 5×5 matrixes of retention factor (k) of dipeptides with different amino acid sequences on (left) $[La(btb)]_n$ and (right) Ni-MOF-74 columns (red < k < blue, black = N.A.).

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日本化学会 第104春季年会 (2024)

ケモインフォマティクスを用いた MOF カラムクロマトグラフィーの保持挙動解析

（東大院工 [1]）○鳥本 明大 [1]・樋口 陽介 [1]・細野 暢彦 [1]・植村 卓史 [1]

Chemoinformatics Analysis on Retention Behavior of MOF Column Chromatography

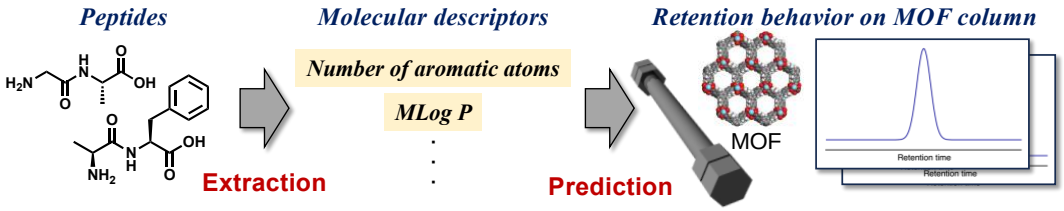
([1]*Graduate School of Engineering, The University of Tokyo*) ○Akihiro Torimoto, Yosuke Higuchi, Nobuhiko Hosono, Takashi Uemura

Synthetic peptides have been used as important substances in the field of biochemical research and pharmaceuticals. To address currently existing challenges on peptide purification, we recently developed a new liquid chromatography method employing metal–organic framework (MOF) as the stationary phase. Utilizing columns filled with MOFs, we examined the retention behavior of dipeptides on HPLC, and discovered an intriguing trend in the relationship among the retention time, dipeptide structure, and pore structure of the MOFs. In this study, we applied a chemoinformatics approach to gain insights into the recognition mechanism and construct prediction models for peptide separation on MOF column chromatography.

Keywords : Chemoinformatics; Metal-Organic Frameworks; Column Chromatography

合成ペプチドは中分子薬をはじめとした医療業界への応用が期待される化合物群である。生理活性や安定性の向上のために末端修飾や非天然アミノ酸の導入など種々の修飾がなされるが [1]、このプロセスは同時に未反応体や副生成物などの分離精製を必要とする。構造が類似した多様な不純物を含む混合物の中から、目的のペプチド鎖を高い精度で分離するためには、逆相クロマトグラフィーを主流とする既存手法とは異なる認識原理に基づいた新しい分離技術の開発が望まれる。我々はそのための認識場として、ナノ空間の自在設計が可能な多孔性材料である Metal–Organic Framework (MOF)に着目し、MOF を固定相としたカラムクロマトグラフィー法によるオリゴペプチドの分離試験を行ってきた。本研究では、二種の異なる MOF を充填したカラムを用いて数十種類のジペプチドを分離した結果に対し、ケモインフォマティクスを利用した解析を行い、その構造認識メカニズムの解明および保持挙動の予測モデルの開発に挑戦した。

保持係数を目的変数、ペプチドの構造から得られる分子記述子を説明変数とし、変数間の相関関係に基づく説明変数の絞り込みを行ったところ、疎水性や芳香族原子数などが選択された。絞り込まれた説明変数を用いて保持係数の予測モデルの構築および予測性能の評価を行った。これらで得た知見をもとに、本発表ではペプチドの構造的特徴と MOF の細孔構造および細孔内環境がどのように保持挙動に影響を与えるかについて議論する予定である。



1) B. Todaro, *et al.*, *Pharmaceutics* **2023**, *15*, 1648.

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高分子の高精度分離を志向した MOF 修飾シリカ固定相の開発

（東大工[1]・東大院工[2]）○松村 俊明[1]・細野 暢彦[1,2]・植村 卓史[1,2]
Fabrication of MOF@SiO_2 Core-Shell Stationary Phases for High-Precision Polymer Separation ([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering, The University of Tokyo*) ○Toshiaki Matsumura,[1] Nobuhiko Hosono,[1,2] Takashi Uemura[1,2]

We have previously succeeded in recognition and separation of polymers based on their minute structural differences using metal–organic framework (MOF) particles as stationary phases for HPLC.[1,2] However, peak resolution performance (number of theoretical plate) of the conventional MOF columns is considerably low because of uncontrolled size and shape of the MOF particles, slow intraparticle diffusion, and strong interaction between polymeric analytes and the MOFs. Herein, we have developed MOF@SiO_2 core-shell stationary phases to address the above-raised issues for polymer separation. Uniformly sized and shaped SiO_2 particles are coated with MOF layers by layer-by-layer method (Figure 1),[3] which allows for precise control of the MOF layer thickness and morphologies, thus provides an ideal MOF stationary phase. The separation performance of the MOF@SiO_2 column will be discussed in the presentation.
Keywords : column, metal-organic framework; separation; polymer; chromatography

我々はこれまでに多孔性金属錯体 (MOF) の粒子を固定相とした MOF カラムクロマトグラフィーを開発し、従来のカラムでは不可能であった高分子の微細な構造の違いの認識及び分離に成功してきた[1,2]。しかし、用いる MOF の粒子サイズや形状の不均一性、遅い粒子内拡散、および高分子と MOF の強い相互作用のために十分な理論段数や分離度が得られておらず、高性能化に向けた充填剤の改良が求められてきた。

本研究では、上記問題の解決に向けて MOF を球状シリカ微粒子表面に成長させたコアシェル型固定相の開発を行なった。均一なサイズかつ形状をもつシリカ微粒子に Layer-by-Layer 法を用いて MOF（$[Zn_2(ndc)_2ted]_n$,および$[Cu_2(ndc)_2ted]_n$, ndc = 1,4-naphthalenedicarboxylate, ted = triethylenediamine）を積層した。得られた MOF@SiO_2 コアシェル固定相を充填したカラムを用いて末端官能基の異なる polyethylene glycol (PEG)を分析し、分離性能について従来の MOF 充填カラムと比較検討した。

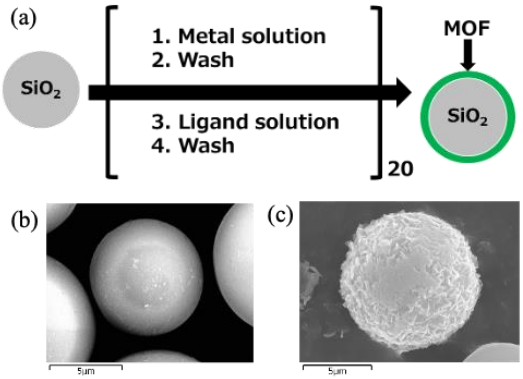

Figure 1. (a) Synthetic scheme of MOF@SiO_2 core-shell particle by layer-by-layer method. SEM images of the SiO_2 particle (b) before and (c) after MOF coating.

1) N. Hosono, T. Uemura, *Acc. Chem. Res.* **2021**, *54*, 3593.
2) N. Mizutani, *et al*., *J. Am. Chem. Soc.* **2020**, *75*, 7644.
3) K. Otsubo, T. Haraguchi, O. Sakata, A. Fujiwara, H. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 9605.

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pH 応答性混合電荷ポリマー修飾シリカビーズを用いたカチオン／アニオン交換モードスイッチングクロマトグラフィー

（慶應義塾大学 [1]）○出浦 浩一 [1]・加來 大晴 [1]・吉井 智夏 [1]・Daniel Citterio[1]・蛭田 勇樹 [1]

Catio/anion exchange mode switching chromatography using pH-responsive mixed-charge polymer-modified silica beads ([1]*Keio University*) ○Koichi Deura[1], Taisei Kaku[1], Tomoka Yoshii[1], Daniel Citterio[1], Yuki Hiruta[1]

Ion exchange chromatography is widely used for purification of biomolecules because of its high separation capacity and industrial-scale purification. However, it is necessary to select an ion exchange column that matches the separation target. We present ion-exchange mode switching chromatography using silica beads modified with pH-responsive mixed-charge polymers. pH-responsive mixed-charge polymers can change its interaction with charged substances in response to pH. The charge balance and pK_a can be adjusted by altering the monomer ratio. In this study, column packing materials modified with pH-responsive mixed-charge polymers containing cationic monomers and pH-responsive anionic monomers at 1:2 were developed. The prepared columns functioned in both cationic and anionic exchange modes by changing the pH of the mobile phase, and the separations of four basic and four acidic pharmaceuticals were achieved.

Keywords : pH-responsive mixed-charge polymer; Chromatography; Cation/anion mode switching; column packing material

イオン交換クロマトグラフィーは、分離能が高く工業スケールでの精製が可能なため、生体分子の精製に広く用いられるが、分離対象に合わせたイオン交換カラムの選択が必要である。pH 応答性混合電荷高分子は、構造内にカチオン性基とアニオン性基を有し、pH に応答して電荷を有する物質との相互作用を変化させる高分子であり、モノマー比を変化させることで電荷バランスや pK_a を調節することができる [1)]。本研究では、カチオン性モノマーと pH 応答性アニオン性モノマーを 1:2 で含む pH 応答性混合電荷高分子を修飾したシリカビーズを固定相とした、移動相の pH 変化による、イオン交換モードスイッチングクロマトグラフィーを開発した(Fig. 1)[2)]。

pH 応答性アニオン性モノマーの種類とスペーサー部位の有無を変えることで、充填剤表面の電荷が切り替わる pH は 4.9 から 5.6 まで変化した。作製したカラムを用いて、塩基性医薬品と酸性医薬品の分離を行った。いずれも 4 種類ずつの溶出ピークにおいて分離度 1.5 以上を達成し、完全分離するに至った。

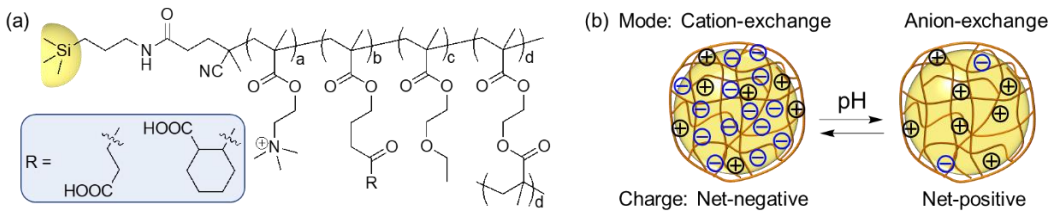

Fig. 1　pH 応答性混合電荷高分子修飾シリカビーズの(a)構造式、(b)模式図 [2)]

1) Hiruta, Y.; Sawada, K.; Mizui, Y.; Citterio, D. *Bull. Chem. Soc. Jpn.* **2020**, *75* (4), 547-552.
2) Kaku, T.; Deura, K.; Yoshii, T.; Citterio, D.; Hiruta, Y. *Mol. Syst. Des. Eng.*, **2024**, *9*, 56-62.

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ネオジム磁石に含まれる主要金属 Fe/Nd/Dy の結晶化による相互分離

（山口大理[1]・山口大院創成科学[2]）○長谷川 奈樹[1]・鈴木 敦子[2]・綱島 亮[2]
Mutual separation of the major metals Fe/Nd/Dy in neodymium magnets by crystallization ([1] Faculty of Science, Yamaguchi University, [2] Graduate School of Sciences and Technology for Innovation, Yamaguchi University)○Natsuki Hasegawa[1],Atsuko Suzuki[2] , Ryo Tsunashima[2]

As a new method for the separation of the components of neodymium magnets and recycling of the separated metals, our laboratory has been working on the selective crystallization of complexes using tripodal Schiff base ligands.

We report the results of the separation of Fe/Nd/Dy, which are main metal components of the magnet, and the factors causing the separation. The factors that cause the mutual separation of metal complexes include differences in complex formation constants, solubility and formation rates. We also report the mechanism by which such separation of metal complexes occurs.

Keywords : rare-earth complex; separation; crystallization

ネオジム磁石とは Fe や B、Dy、Nd を主成分とした永久磁石である。磁石の成分を分離し、リサイクルするための従来の分離法として、溶媒抽出やイオン交換法が挙げられるが、その分離精製過程は複雑かつ多段階である。当研究室では、より高選択的で簡素な金属分離の新たな手法として、三脚型シッフ塩基配位子(H_3L, Fig.1)を用いた金属錯体の選択的結晶化を研究し、すでに Nd^{3+}/Dy^{3+}混合溶液から Dy^{3+}錯体を選択的に結晶化できることを報告した。[1] 今回、磁石の主要金属成分である Fe^{3+}存在下でこの分離法を用いることを目指して、Fe^{3+}も含めた Fe/Nd/Dy の分離を行った。

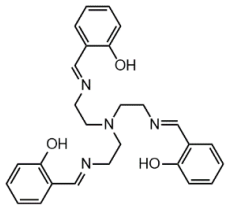

Fig. 1 三脚型シッフ塩基配位子 (H_3L).

金属塩を溶解した溶液に H_3L 及び塩基であるジイソプロピルアミン(DIEA)を加え、その溶液を 25℃で静置した。その結果、実験条件①及び③において Fe^{3+} が選択的に結晶化した(Table 1)。この結果は、Fe^{3+}が含まれた場合でもこの分離法が機能することを示唆する。この金属錯体の相互分離機構には、錯体の生成定数及び溶解度の差が関与すると考えられる。各金属錯体の生成定数を算出したところ、塩基が含まれない場合において Fe^{3+}錯体の生成定数が最も大きくなった(Table 2)。現在、塩基の有無による各錯体の生成定数の違い、各錯体の生成反応が平衡に達するまでの時間、各錯体の溶解度を調べている。当日は、これらの結果を基に分離機構を議論する。

Table 1 生成した結晶における各金属の比率

	分離前の溶液における物質量比	結晶中の比率 (%)		
	Fe:Dy:Nd:H_3L:DIEA	Fe	Dy	Nd
①	2:1:1:4:6	91.15	8.77	0.08
②	1:1:1:3:6	52.6	46.2	1.2
③	1:1:1:3:3	82.82	16.64	0.54

Table 2 条件生成定数 (log *K'*)

M^{3+}:H_3L:DIEA	FeL	DyL	NdL
1:1:0	4.54	4.16	3.95
1:1:1.5	4.77	5.07	4.92
1:1:3	5.73	6.61	5.88

[1] A. Masuya-Suzuki, *et al, Chem. Commun*., **58**, 2283 (2022)

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コスモトロープ塩水溶液におけるペルオキシダーゼを触媒とするルミノール化学発光に及ぼす化学エンハンサーの効果

（一般社団法人京都光科学研究所）○柄谷　肇
Effect of chemical enhancer on peroxidase catalyzed luminol chemiluminescence in kosmotropic salt solution (*Kyoto Luminous Science Laboratory*) ○Hajime Karatani

To date, the effect of kosmotropic salts on luminol-hydrogen peroxide-horseradish peroxidase chemiluminescence has been studied aiming at the analytical application. In particular, in the presence of high concentration ammonium sulfate as a kosmotropic salt, the detection sensitivity of peroxidase as an analyte has been increased by three orders of magnitude as compared with that in the normal peroxidase-catalyzed luminol system. This study has shown that the detection sensitivity has been further improved by combining the well-known chemical enhancers, such as *p*-substituted phenol derivatives, with the kosmotropic effect on the peroxidase-catalyzed luminol chemiluminescence. As chemical enhancer, 4-(1-imidazozolyl)phenol and *p*-iodophenol are favorably combined with the kosmotropic effect.
Keywords：Chemiluminescence; Kosmotropic Salt; Luminol; Peroxidase; Chemical Enhancer

pmol·dm^{-3}（1 mol·dm^{-3} = 1 M）およびより低濃度のペルオキシダーゼ検出用化学発光センサーとして、コスモトロピック効果に基づくルミノール化学発光の高感度化を進めてきた[1)]。今回、表題の化学発光の化学エンハンサーとして使用される物質[2)]とコスモトロピック効果を組み合わせた発光系を調べた。コスモトロピック効果は、既報[1)]の通り 3 M 近傍の硫酸アンモニウムを溶存して発現させた。ペルオキシダーゼは西洋ワサビ由来標品（HRP）を使用した。反応溶液 pH は緩衝剤および水酸化ナトリウムを用いて最終的に 8.5～9.5 とした。化学発光は、5.0 mM ルミノール溶液（0.083 M *N,N*-ビス(2-ヒドロキシエチル)グリシン (Bicine)、0.5 M 水酸化ナトリウムおよび 2.9 M 硫酸アンモニウム混合物溶液中に調製）および 100 mM 過酸化水素溶液（2.0 mM EDTA を含む 3.5 M 硫酸アンモニウム溶液中に調製）を等量ずつ混合し、この溶液 1000 μL を、色々濃度調節した HRP 溶液（2.5 μL）に添加して開始した。緩衝剤として Tris に替えて Bicine を使用することによりバックグラウンド発光は無視できる程に低減した。エンハンサー物質は少量のジメチルスルホキシドに溶解し、ルミノール溶液に添加した。エンハンサー物質として、種々の *p*-置換フェノール類[2)]を評価した結果、4-(1-イミダゾリル)フェノールあるいは *p*-ヨードフェノールの効果とコスモトロピック効果の組合せにより、特に反応初期過程において、コスモトロピック効果のみの系と比べてさらに 3 倍程度の発光増大を可能とした。最適なエンハンサー終濃度は数十μM であった。また、両効果の発現メカニズムについて検討した。

1) Luminol–hydrogen peroxide–horseradish peroxidase chemiluminescence intensification by kosmotrope ammonium sulfate. H. Karatani, *Anal. Sci.*, **2022**,*38*, 613.
2) Enhanced chemiluminescence reactions catalyzed by horseradish peroxidase. G. H. G. Thorpe, L. J. Kricka, *Methods in Enzymology*, **1986**, *133*, 331.

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熱感応性相分離における両性イオン界面活性剤のアミノプロピル硫酸エステル基の効果

（福島大理工[1]・JAEA[2]・Wake Forest Univ.[3]）○楠 裕翔[1]・中川 太一[1,2]・Willie L. Hinze[3]・高貝 慶隆[1]

Effect of aminopropyl sulfate-ester group in zwitterionic surfactant on the thermosensitive phase-separation ([1]*Faculty of Symbiotic Systems Science, Fukushima Univ.*, [2]*JAEA*, [3]*Wake Forest Univ.*) ○Yuto Kusunoki[1], Taichi Nakagawa[1,2], Willie L. Hinze[3], Yoshitaka Takagai[1]

Cloud point extraction (CPE) is a kind of extraction method utilizing the cloud point (phase-separation temperature) of surfactants and is available to extraction of coexisting substances which has a high affinity to surfactants, into the surfactant rich phase caused by phase separation. In the analytical chemistry, CPE is used as a preconcentration method and contributes the improvement to enhance the sensitivity of instrumental analysis. Aminopropyl sulfate surfactant (C_nAPSO_4), a type of zwitterionic surfactant, has a CP and is available to CPE of nanoparticles. However, the effect of molecular structure on phase separation phenomenon has been not elucidated. In this study, various series of C_nAPSO_4 was synthesized and investigated the effect on phase separation phenomenon. With the change of the structure in the quaternary ammonium side chain of C_nAPSO_4, variances were observed in the CP from low temperature (phase separation) to high temperature (homogeneous solution) and from high temperature to low temperature. This phenomenon was indicated that the structure of the quaternary ammonium side chain has a significant effect on the hydration water bound to C_nAPSO_4.

Keywords : zwitterionic surfactant; cloud point extraction; phase separation phenomenon

曇点抽出法は，界面活性剤の曇点(相分離温度)を利用し，界面活性剤と親和性の高い共存物質を相分離後の界面活性剤相に抽出する方法である。分析化学では前濃縮法として用いられ，機器分析における高感度化に貢献している。アミノプロピル硫酸エステル系両性イオン界面活性剤(C_nAPSO_4)は曇点を有し，ナノ粒子の曇点抽出に用いられている。しかし，分子構造が相分離現象に与える効果は明らかとなっていない。そこで本研究では，分子構造が異なる C_nAPSO_4 を合成し，分子構造が相分離現象に与える効果を検討した。第四級アンモニウム側鎖の構造を変化させると，低温(相分離)から高温(均一溶液)にしたときの曇点と，高温から低温にしたときの曇点に差異が生じた。これは，第四級アンモニウム側鎖の構造が，C_nAPSO_4 に結合する水和水に大きな効果を与えていると考えられる。

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
A1444(1444, Bldg. 14 [4F])

[A1444-3am] 07. Inorganic Chemistry

Chair: Soichi Kikkawa, Takamasa Tsukamoto

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1444-3am-01]
the properties of precisely synthesized metal cluster–metal oxide cluster complexes

○TAISHI Suzuki[1], Tomoki Matsuyama[1], Soichi Kikkawa[1], Naoki Nakatani[1], Seiji Yamazoe[1] (1. Tokyo Metroporitan University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1444-3am-02]
Synergistic hydrogen storage properties of POM-based porous ionic crystals with Pd nanoparticles

○Yuki Iwata[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
[A1444-3am-03]
Synthesis of crystalline proton conductors based on polyacids and polyvinyl alcohols.

○Yuta Yamada[1], Sayaka Uchida[1], Tukasa Iwano[1] (1. The Univ. of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1444-3am-04]
Hydrogen evolution reaction using porous ionic crystals composed of salen complexes and polyoxometalates

○Tsutsumi Yutaro[1], Yuto Shimoyama[1], ryota Imashioya[1], Yudai Suzuki[1], Naoki Ogiwara[1], Sayaka Uchida[1] (1. The Univ. of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1444-3am-05]
Selective synthesis and photophysical properties of two isomers of unsymmetric Pt and Pt_2Ag_3 complexes having two pyrazole derivatives

○Yiming Yang[1], Shinnosuke Horiuchi[2], Kenichiro Omoto[1], Eri Sakuda[1], Yasuhiro Arikawa[1], Keisuke Umakoshi[1] (1. nagasaki university, 2. The Univ. of Tokyo)

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
[A1444-3am-06]

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Control of structures and electronic states of silver nanoclusters within ring-shaped polyoxometalates and their properties

○Daiki Yanai[1], Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

English
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1444-3am-07]

Synthesis and property of palladium nanoclusters within a ring-shaped polyoxometalate

○Rui Xi[1], Yoshihiro Koizumi[1], Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

English
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1444-3am-08]

Synthesis of metal clusters with porous ionic crystals based on Preyssler-type polyoxometalate

○Hsinyun Lu[1], Naoya Haraguchi[1], Sayaka Uchida[1] (1. The Univ. of Tokyo)

English
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1444-3am-09]

Reduction-induced selective adsorption of Cs^+ based on Keplerate-type polyoxometalates

○Ken Wang[1], Tsukasa Iwano[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1444-3am-10]

Redox-Induced Proton Uptake Based on Polyoxometalate Capsules

○Tsukasa Iwano[1], Nanako Tamai[1], Sayaka Uchida[1] (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

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

Break

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1444-3am-11]

Development of a synthesis method of lacunary polyoxomolybdates in organic solvents

○Atsuhiro Jimbo[1], Chifeng Li, Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1444-3am-12]

Synthesis of Polyoxothiotungstates by Oxygen–Sulfur Substitution Reactions

○Kentaro Yonesato[1], Kosuke Suzuki[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[A1444-3am-13]

Developing a mild synthesis method and elucidating the physical properties of heavy metal subnanoparticles based on tungsten

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○Hiroki Tomizaki[1], Takamasa Tsukamoto[2,3], Tatsuya Moriai[1,4], Augie Atqa[1], Tetsuya Kambe[5], Wang Jae Chun[6], Takane Imaoka[1,4], Kimihisa Yamamoto[1,4] (1. Lab. Chem. Life Sci., Tokyo Tech, 2. IIS., The Univ. of Tokyo, 3. JST-PRESTO, 4. JST-ERATO, 5. Osaka Univ., 6. ICU)

Japanese

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

[A1444-3am-14]

Precise controlled synthesis of group 15 metal element subnanoparticles with hydrolysis method and exploration of their physical properties

○Hiroaki Nabe[1], Takamasa Tsukamoto[2,3], Tatsuya Moriai[1,4], Tetsuya Kambe[5], Takane Imaoka[1,4], Kimihisa Yamamoto[1,4] (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-PRESTO, 3. IIS, The Univ. of Tokyo, 4. JST-ERATO, 5. Osaka Univ.)

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クラスター複合塩の精密合成と評価

（都立大理）○鈴木 太士, 松山 知樹, 吉川 聡一, 中谷 直輝, 山添 誠司
The properties of precisely synthesized metal cluster–metal oxide cluster complexes (*Tokyo Metropolitan University*) ○Taishi Suzuki, Tomoki Matsuyama, Soichi Kikkawa, Naoki Nakatani, Seiji Yamazoe

The composite of phosphine-protected gold cluster cations and metal oxide cluster anions is a promising approach for design of multifunctional materials. Recently, we have found that metal oxide clusters of different sizes and charges can be used to control the cluster arrangement and induce structural isomerization at the nanoscale[1]. Although NO_3^- and $[PMo_{12}O_{40}]^{3-}$ salts of $[MAu_8(PPh_3)_8]^{2+}$ (**MAu8**, M = Pt, Pd) that the center Au atom was replaced to other elements have a crown-type core structure, the crystallization with the metal oxide cluster $[Mo_6O_{19}]^{2-}$ as the counter anion successfully transformed them into a butterfly-type metal core structure. In this study, the more negatively charged niobium oxide cluster $[Nb_6O_{19}]^{8-}$ (**Nb6**) was applied to the counter anion to form the complex with **Au9** and **PdAu8**, and the spectroscopic properties were evaluated.

The solid precipitates of **Au9-Nb6** and **MAu8-Nb6** (M = Pt, Pd) were obtained by the dropping of acetonitrile solution of NO_3^- salts of **Au9** and **MAu8** (M = Pt, Pd) into an aqueous solution of an excess concentration of the tetrabutylammonium salt of **Nb6**. Diffuse-reflectance UV-visible spectra of the composite cluster salts showed that there is no characteristic absorption band of the butterfly-type structure at around 700 nm. These results suggest the possibility of isomerization due to complexation with **Nb6**.

Keywords : Ligand-protected metal cluster, Metal oxide cluster, Complex materials, Nanostructure control, Sub nano meter cluster

カチオン種であるホスフィン保護金クラスターとアニオン種である金属酸化物クラスターの複合は、多元機能材料の設計において有望な手法である。最近我々は、異なるサイズ及び電荷の金属酸化物クラスターを用いることで、ナノスケールでクラスター配列を制御し、構造異性化を誘起できることを見出した [1]。ホスフィン保護金属クラスター$[Au_9(PPh_3)_8]^{3+}$（**Au9**）の中心の Au 原子を異種元素で置換した$[MAu_8(PPh_3)_8]^{2+}$（**MAu8**, M = Pt, Pd）の NO_3^-塩や$[PMo_{12}O_{40}]^{3-}$塩はクラウン型構造を有するが、対アニオンとして金属酸化物クラスターである$[Mo_6O_{19}]^{2-}$と結晶化することで、バタフライ型の金属コア構造に変形させることに成功した。本研究では、より負電荷の大きなニオブ酸化物クラスター$[Nb_6O_{19}]^{8-}$（**Nb6**）について、**Au9** や **MAu8**（M = Pt, Pd）との複合化を検討し，その物性を分光学的手法により評価した。

Au9 や **MAu8**（M = Pt, Pd）の NO_3^-塩をアセトニトリルに溶解させ、過剰濃度の **Nb6** のテトラブチルアンモニウム塩の水溶液に滴下することで固体析出物 **Au9-Nb6** や **MAu8-Nb6**（M = Pt, Pd）を得た。各複合クラスター塩の拡散反射紫外可視分光スペクトルを測定したところ、いずれの複合クラスター塩においても、700 nm 付近のバタフライ構造に特徴的な吸収帯が存在しないことを確認した．以上より、複合化による異性化の可能性が示唆された。

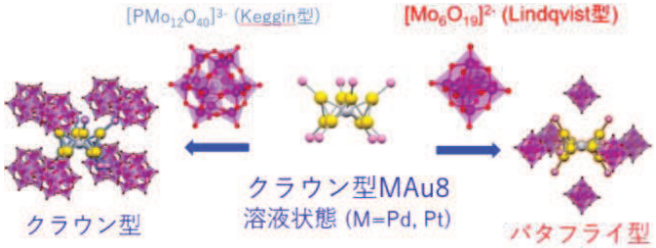

図１．クラスター配列による MAu8 クラスター(M = Pt, Pd)のコア構造制御.

1) Y Fujiki *et al.*, *Commun. Chem.* 6,129 (2023).

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日本化学会 第104春季年会 (2024)

POM を基盤とする多孔性イオン結晶とナノ Pd の複合化による相乗的な水素吸蔵特性

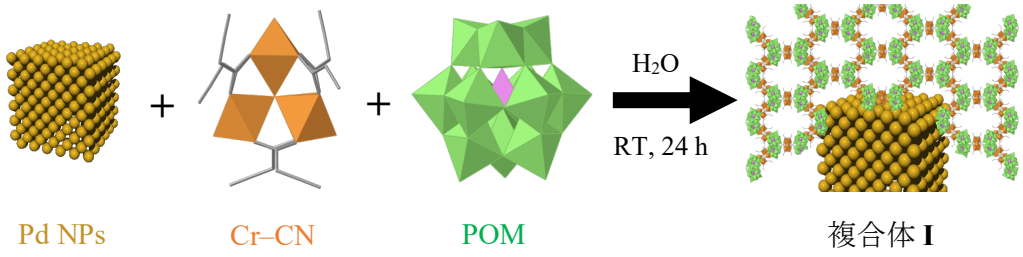
（東大院総合 [1]）○岩田 友樹 [1]・荻原 直希 [1]・内田 さやか [1]
Synergistic hydrogen storage properties of POM-based porous ionic crystals with Pd nanoparticles([1]*Grad. Sch. of Arts and Sci., The Univ. of Tokyo*)○Yuki Iwata,[1] Naoki Ogiwara,[1] Sayaka Uchida[1]

Pd nanoparticles (Pd NPs) have attracted attention as functional materials because of the hydrogen storage properties different from Pd bulk metals. Recently, it has been reported that the covering of Pd NPs with metal-organic frameworks (MOFs) has caused an enhancement in the hydrogen storage property of the Pd NPs[1)]. We focused on porous ionic crystals (PICs), $Cr[Cr_3O(OOCCH_2CN)_6(H_2O)_3]_3[PW_{12}O_{40}]_2$[2)] that has redox-active POMs as a component, to combine with PVP-protected Pd NPs (composite **I**), and studied their hydrogen storage property. The PXRD indicated that the crystal structures were retained in **I**. TEM images revealed that Pd NPs were covered with PIC, and the XPS suggested that charge transfer occurred from Pd NPs to W in POM. The hydrogen storage amount of **I** was about twice as high as that of Pd NPs alone.

Keywords : metal nanoparticle, polyoxometalate, porous ionic crystal

Pd ナノ粒子（Pd NP）は、バルクの Pd 金属とは異なる水素吸蔵特性を有し、機能性材料として注目されている。近年、Pd NP と多孔性金属錯体（MOF）からなる複合体は Pd NP を凌駕する水素吸蔵特性を発現する事が報告されている [1)]。本研究では、高いレドックス活性を有するポリオキソメタレート（POM）を構成要素にもつ多孔性イオン結晶（PIC）に着目し、Pd NP との複合化、水素吸蔵特性の調査を行った。

PVP 保護された Pd NP（粒子径：9.6 nm）と室温合成が可能な PIC[2)]、$Cr[Cr_3O(OOCCH_2CN)_6(H_2O)_3]_3[PW_{12}O_{40}]_2$ からなる複合体 **I** を合成した。複合体 I の PXRD 測定から、複合化後も PIC および Pd NP の結晶構造は保持されていると確認された。さらに、透過電子顕微鏡（TEM）像から、複合体 **I** は Pd NP が PIC 粒子で被覆されており、XPS 測定から Pd NP から POM 中の W へ電荷移動が生じていることが示唆された。また、複合体は Pd NP 単体と比較して約 2 倍の水素吸蔵量を示した。



1) G. Li, et al., *Nat. Mat.*, 2014, **13**, 802–806.
2) R. Kawahara, et al., *Dalton Trans.*, 2016, **45**, 2805–2809.

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ポリ酸とポリビニルアルコールを基盤とした結晶性プロトン伝導体の創成

○山田 裕太[1]、岩野 司[1]、内田 さやか[1] (1. 東京大学)

Synthesis of crystalline proton conductors based on polyacids and polyvinyl alcohols

○Yuta Yamada[1], Sayaka Uchida[1], Tukasa Iwano[1] (1. The Univ. of Tokyo)

Solid-state proton conductors are used as electrolyte materials in fuel cells, which have attracted much attention in recent years and are being actively studied. It is very important to improve the proton conductivity of proton conductors in the function of fuel cells.Anionic metal oxide clusters called polyoxometalates (POMs) have been widely studied as components of proton conductors because of their diverse molecular structures and elemental selectivity. In this study, we succeeded in synthesizing crystalline POM-polymer composites using polyvinyl alcohol (PVA), a polymer containing hydroxy groups in its monomer unit, and selected Preyssler-type POM as the POM. Three types of composites were successfully obtained, in which the poly(vinyl alcohol) was encapsulated within the pores of the inorganic framework with only potassium ions, only cesium ions, or a mixture of potassium and cesium ions, respectively. These composites showed high proton conductivity in the humidified medium-temperature range.

Keywords：polyoxometalate, polyvinyl alcohol, proton conductivity

近年注目を集めている燃料電池には、電解質材料として固体プロトン伝導体が用いられており、研究が積極的に進められている。燃料電池の機能においてプロトン伝導体のプロトン伝導度を向上させることが非常に重要である[1]。

ポリオキソメタレート（POM）と呼ばれるアニオン性金属酸化物クラスターは、多様な分子構造及び元素選択性を有し、プロトン伝導体の構成要素として広く研究されている[2]。本研究では、モノマーユニットにヒドロキシ基を含んでいるポリマーである、ポリビニルアルコール(PVA)を使用して 結晶性POM—ポリマー複合体を合成することに成功した。POM としては Preyssler 型 POM を選択し、対カチオンがそれぞれカリウムイオンのみ、セシウムイオンのみ、カリウムイオンとセシウムイオン混合である無機骨格の細孔内にポリビニルアルコールを内包した三種類の複合体を得ることに成功した。これらの複合体は加湿中温領域で高いプロトン伝導性を示した。

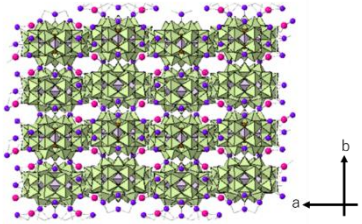

Figure 1 結晶構造

[1] Y. Sone *et al.*, *J. Electrochem. Soc.*, 143, 1254, (1996).

[2] O. Nakamura *et al.*, *Chem. Lett.*, 8, 17, (1979).

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サレン錯体とポリ酸を構成要素とする多孔性イオン結晶を用いた水素発生反応

（東大院総合[1]）○堤 由太朗[1]・下山 雄人[1]・今塩屋 亮太[1]・鈴木 雄大[1]・荻原 直希[1]・内田 さやか[1]

Hydrogen evolution using porous ionic crystals composed of salen complexes and polyacids

([1]*Graduate School of Arts and Sciences, Tokyo University*) ○ Yutaro Tsutsumi,[1] Yuto Shimoyama,[1] Ryota Imashioya,[1] Yudai Suzuki,[1] Naoki Ogiwara,[1] Sayaka Uchida[1]

Hydrogen is promising as an energy carrier in the future, and many research efforts have been devoted to developing hydrogen evolution reaction (HER) catalysts. To design efficient HER catalysts, polyoxometalates (POMs) have attracted attention due to their molecular deniability. In this study, we assembled anionic POM with cationic metal complexes to construct porous ionic crystals (PICs) with HER activity. Linear sweep voltammetry (LSV) measurements of PICs revealed that the HER activities of PICs were superior to that of pristine POMs and metal complexes. The origin of the synergistic HER for PICs will be discussed on the basis of the crystal structure of PICs and the electronic structure of POMs in PICs. *Keywords : Polyoxometalate; Salen complex; Hydrogen Evolution Reaction*

水素は次世代のエネルギーキャリアとして有望であり、水素発生反応(HER)触媒の開発が盛んである。そのなかで、HER 触媒の候補として注目されているのが、ポリオキソメタレート(POM)であり、液相中での HER 活性が報告されている[1]。

本研究では、アニオン性の POM をカチオン性の金属錯体との静電相互作用を利用し、多孔性イオン結晶(PIC)として集積化することで、固相での HER 活性の獲得を目指した。PIC の合成は、Keggin 型 POM $[\alpha\text{-}XW_{12}O_{40}]^{y-}$ ($X = Co^{2+}$, Si^{4+}, P^{5+})、および Mn サレン錯体 $[Mn(salen)]^{+}$を水溶液で反応させることにより行った(図 1,2)。LSV 測定により PIC の HER 活性を評価したところ、PIC はその構成要素である単体の POM や Mn サレン錯体を凌駕する活性を示し、特に$[\alpha\text{-}CoW_{12}O_{40}]^{6-}$の系においては約 18 倍の活性向上が観測された。当日は PIC の構築に伴う相乗的な HER 活性の起源に関して、PIC の結晶構造や、PIC 中の POM の電子状態を基に、議論する予定である。

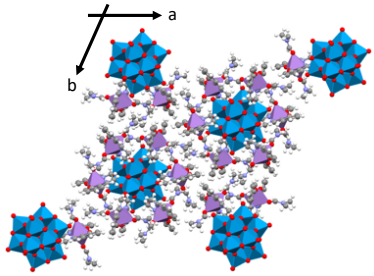

図 1 $[Mn(salen)]_6[\alpha\text{-}CoW_{12}O_{40}]$の結晶構造

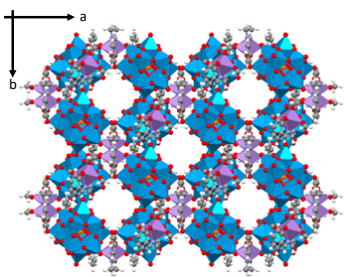

図 2 $[Mn(salen)]_4[\alpha\text{-}SiW_{12}O_{40}]$の結晶構造

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非対称 Pt 錯体の幾何異性体と Pt_2Ag_3 混合金属錯体の構造異性体の選択的合成および光物性解明

（1.長崎大，2.東大）○楊 益鳴[1]・堀内 新之介[2]・尾本 賢一郎[1]・作田 絵里[1]・有川 康弘[1]・馬越 啓介[1]

Selective synthesis and photophysical properties of two isomers of unsymmetric Pt and Pt_2Ag_3 complexes having two pyrazole derivatives

(1. *Nagasaki Univ*., 2. *The Univ. of Tokyo*) ○Yiming Yang[1], Shinnosuke Horiuchi[2], Kenichiro Omoto[1], Eri Sakuda[1], Yasuhiro Arikawa[1], Keisuke Umakoshi[1]

Mononuclear Pt(II) complex possessing two different pyrazoles and N^C chelate ligand forms two geometrical isomers. We report the reaction of the two geometrical isomers of unsymmetric Pt complexes with Ag(I) ions, resulting in two structural isomers of Pt-Ag complexes. The structures of these complexes were investigated by X-ray crystallographic analyses and ^{1}H NMR spectroscopy. Their photophysical properties were also investigated.

Keywords：*heteropolynuclear complex*; *luminescence*; *geometrical isomer*

N^C キレート配位子 ppy (2-フェニルピリジン) と異なる 2 種類のピラゾール配位子を有する単核 Pt 錯体は 2 種類の幾何異性体を与える。本研究では，3,5-ジフェニルピラゾール (Ph_2pzH) と 3-*tert*-ブチルピラゾール (^{t}BupzH) を用いて 2 つの幾何異性体を選択的に合成し，さらに Ag(I)と反応させることにより，異なる結合様式をもつ Pt_2Ag_3 錯体 (**1a** と **1b**) が生成することを見出した。それぞれの構造異性体の光物性を調べ，Pt→Ag 結合様式の違いが錯体の性質に与える影響を確かめた。

^{t}Bupz 配位子が ppy 配位子上の窒素のトランス位に配位し，Ph_2pz 配位子が窒素のシス位に配位した Pt_2Ag_2 錯体 **2a** (*SP*-4-4 異性体) と AgOTf を反応させると，Pt_2Ag_3 錯体 **3a** を生成した。また，^{t}Bupz と Ph_2pz の位置を入れ替えると錯体 **3b** (*SP*-4-3 異性体) も同様に合成した (Figure 1)。これらの非対称混合金属錯体の構造と光物性を明らかにした。

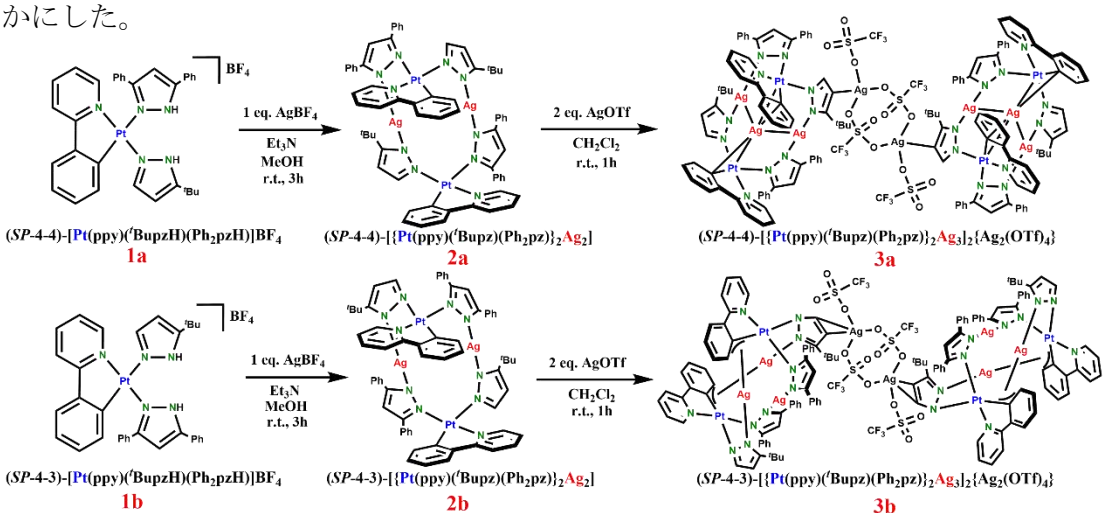

Figure 1. Synthesis of Pt-Ag complexes consisting of unsymmetric Pt complexes having two different pyrazolate ligands

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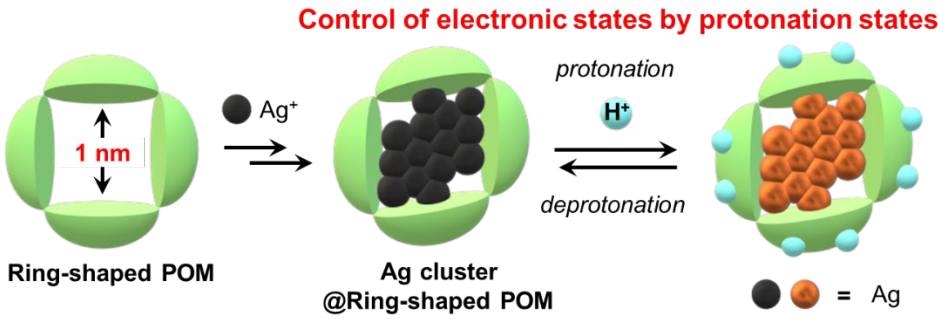
環状ポリオキソメタレートに内包された銀ナノクラスターの構造・電子状態の制御と機能

(東大院工)○屋内 大輝・米里 健太郎・鈴木 康介・山口 和也

Control of Structures and Electronic States of Silver Nanoclusters within Ring-Shaped Polyoxometalates and Their Properties (*School of Engineering, The Univ. of Tokyo*) ○Daiki Yanai, Kentaro Yonesato, Kosuke Suzuki, Kazuya Yamaguchi

Silver (Ag) nanoclusters exhibit unique properties that depend on their structures and electronic states. We have recently reported the Ag nanoclusters within a ring-shaped polyoxometalate that exhibited unique catalytic properties owing to the cooperative reactivity of Ag nanoclusters and POMs as well as the exposed Ag surface.[1] In this study, we successfully demonstrated that the structures and the electronic states of Ag nanoclusters within ring-shaped POMs could be controlled by the protonation states of the ring-shaped POM or the synthesis conditions. In addition, we investigated the photocatalytic properties of those Ag nanoclusters.
Keywords : Polyoxometalate, Ag nanocluster, Inorganic synthesis

銀ナノクラスターは構造や電子状態に依存した特異な分子機能を示す。当研究室では、環状ポリオキソメタレート (POM) に内包された銀ナノクラスターを合成し、この分子性複合体が銀ナノクラスターと POM による協働的な機能と、露出した銀表面に由来する特異な触媒活性を示すことを明らかにした [1)]。本研究では、酸や塩基の添加によって環状 POM 骨格のプロトン化状態を変えることや、銀ナノクラスターの合成条件を変えることによって、環状 POM に内包される銀ナノクラスターの構造や電子状態を制御することに成功した。さらに、それらの銀ナノクラスターの光触媒特性について検討した。



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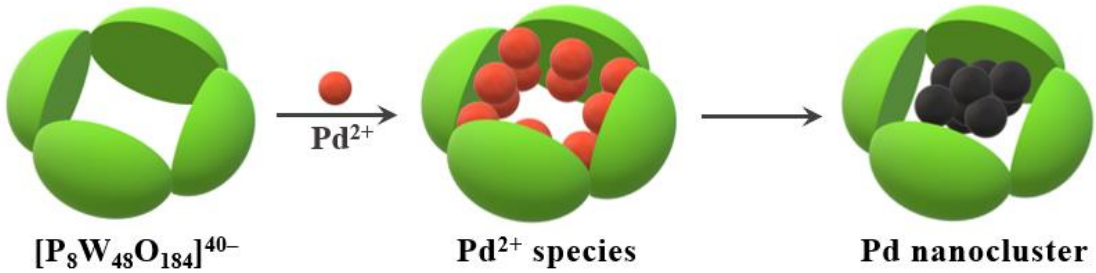
Synthesis and Property of Palladium Nanoclusters within a Ring-Shaped Polyoxometalate

(*School of Engineering, The University of Tokyo*) ○Rui Xi, Yoshihiro Koizumi, Kentaro Yonesato, Kosuke Suzuki, Kazuya Yamaguchi

Keywords: Polyoxometalates; Palladium nanoclusters; Catalysis

Metal nanoclusters have attracted great interest in the design of functional catalysts for the decades because their electronic states and designable physicochemical properties strongly relate to the sizes, compositions, and structures.[1] Despite stabilization using organic ligands or solid supports is one of the efficient strategies to synthesize metal nanoclusters, palladium (Pd) nanoclusters obtained using organic ligands sometimes suffer from decomposition or aggregation during catalytic reactions caused by ligand exchange with reactants or ligand degradation. Pd nanoclusters on metal oxide supports are generally reactive catalysts with high stability and controllable synergistic effects. Recently, by using a ring-shaped polyoxometalate (POM) as a rigid inorganic molecular metal oxide support, our group reported the synthesis of surface exposed but highly stable silver (Ag) nanoclusters that exhibit efficient catalysis for hydrogenation reaction of organic substrates through synergistic effects between Ag nanoclusters and POMs.[2]

In this work, we report the synthesis of a small Pd nanocluster within the inner cavity of a ring-shaped POM $[P_8W_{48}O_{184}]^{40-}$. By the reaction of $[P_8W_{48}O_{184}]^{40-}$ and Pd^{2+} in an organic solvent, Pd^{2+} species were incorporated within the ring-shaped POM. By solid-state reduction of Pd^{2+} species incorporated within $[P_8W_{48}O_{184}]^{40-}$, the formation of a small Pd nanocluster was confirmed by several spectroscopic studies. Notably, reversible redox property of the Pd nanocluster was observed by exposing it to air. Catalytic applications of the Pd nanocluster will also be discussed in the presentation.



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Synthesis of Metal Clusters with Porous Ionic Crystals based on Preyssler-Type Polyoxometalate

([1]*Graduate School of Arts and Sciences, the University of Tokyo*), ○Hsin-Yun Lu,[1] Naoya Haraguchi,[1] Sayaka Uchida[1]

Keywords: Metal Cluster; Porous Crystalline Materials; Polyoxometalates

In the dynamic field of materials chemistry, altering the atomic numbers in metal clusters is a pivotal factor in dictating their chemical and physical properties,[1,2] but the approach of precise size control remains challenging because of the spontaneous agglomeration. Building on this background, our group has focused on forming such components utilizing polyoxometalates (POMs), which are nano-sized anionic metal-oxygen clusters of early transition metals, known for their reversible multi-electron transfer properties. In this work, we focus on exploring the use of Co^{2+}-bridged Preyssler POM (Co-Pry, $Co_4K_{3.5}Li_{1.5}NaO_{126.5}P_5W_{30})^3$, a combination that is notable for its exceptional electronic conductivity and reduction reversibility, to synthesize Ag and Cu clusters.

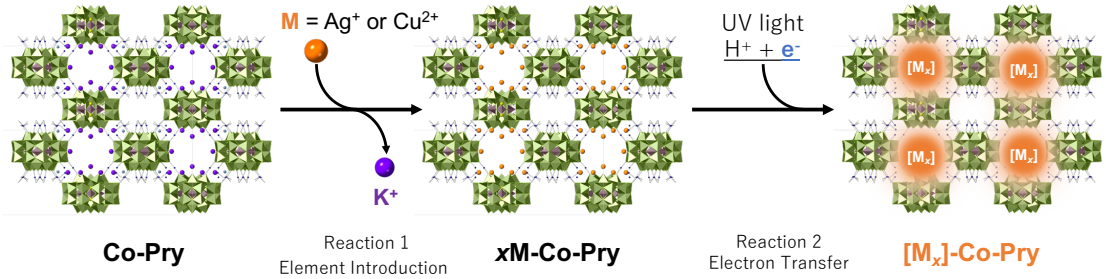
Metal clusters Mx (M = Ag^+ or Cu^{2+}) have been synthesized following two-step reactions. In the first stage, we attempted to introduce metal ion by immersing the Co-Pry scaffold into aqueous solutions of $AgNO_3$ or $CuCl_2$.

$$\mathrm{Co-Pry} + zAg^+ \rightarrow 6.5\mathrm{Ag-Co-Pry} + 1.5Li^+ + 3.5K^+ (t = 6h)$$
$$\mathrm{Co-Pry} + zCu^{2+} \rightarrow 4.2\,Cu-Co-Pry + 1.5Li^+ + 3.5K^+ \ (t = 4h)$$

Second step involves UV irradiation to reduce the oxidation state and subsequently form small metal clusters in the framework.

$$\mathrm{Ag-Co-Pry} + 3CH_3OH \xrightarrow{UV} 6.5\mathrm{AgH-Co-Pry} + 3CH_2O$$
$$\mathrm{Cu-Co-Pry} + 3CH_3OH \xrightarrow{UV} 4.2\mathrm{CuH-Co-Pry} + 3CH_2O$$

The combination use of X-ray photoelectron spectroscopy (XPS), Photoluminescence spectroscopy (PL), and X-ray absorption fine structure (XAFS) measurements verifies the formation of metal clusters inside the crystal.



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Redox-Active Keplerate Capsule Encapsulating Keggin-Type POM for Cesium Ion Uptake

([1]School of Arts and Sciences, The University of Tokyo) ○Ken Wang,[1] Tsukasa Iwano,[1] Sayaka Uchida[1]

Keywords: Keplerate; Polyoxometalate; Cation-coupled electron-transfer; Cesium uptake.

Currently, POM-based compounds for cation uptake can be categorized into three types: (1) cation exchange with POM-based ionic solids,[1] (2) cation trapping by POM molecules regarded as inorganic crown ethers or cryptands,[2] (3) cation absorption induced by redox reactions intrinsic to POM compounds.[3] Given limited reports on cation uptake via redox reactions, we explored this unique property in a charge-neutral Keplerate capsule ({$Mo_{72}Fe_{30}$}) encapsulating a Keggin-type POM ($[PMo_{12}O_{40}]^{3-}$), initially described by Müller and co-workers.[4] {$Mo_{72}Fe_{30}$} features 20 crown-ether-like pores, exhibiting selective Cs^+ uptake through a cation-coupled electron-transfer (CCET) reaction:[5] Cs^+ ions were selectively trapped into the crown-ether-like pores of {$Mo_{72}Fe_{30}$}, while electrons were located in both {$Mo_{72}Fe_{30}$} and the encapsulated POM. This property utilizes the denticity and coordination ability of {$Mo_{72}Fe_{30}$} as well as the redox property of the encapsulated POM, resulting in a unique Cs^+ uptake effect.

In the present work, we selected three structurally similar Keplerate-based compounds with different compositions of metallic elements. The compounds exhibited distinct absorption properties during the Cs^+ uptake process via CCET reaction, which I will explain in detail at the CSJ meeting. This observation is crucial for further understanding the absorption mechanism and providing new references to address environmental problems.

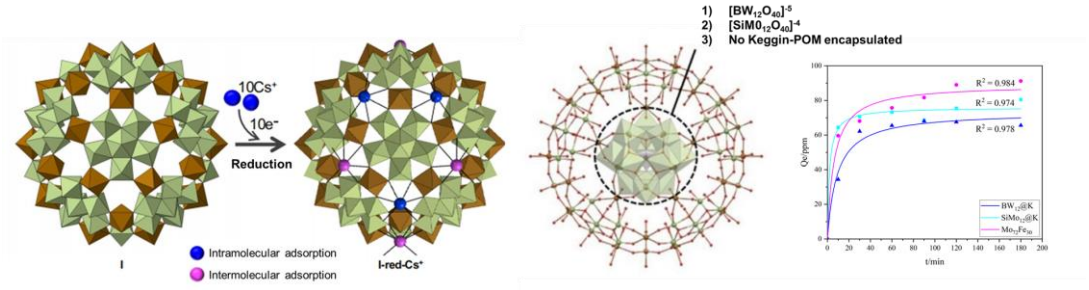

Figure 1. (left) Schematic illustration of Cs^+ uptake via CCET by a charge neutral Keplerate capsule ({$Mo_{72}Fe_{30}$}) encapsulating a Keggin-type POM, and (right) time courses of Cs^+ uptake by {$Mo_{72}Fe_{30}$} with or without the encapsulated Keggin-type POM.

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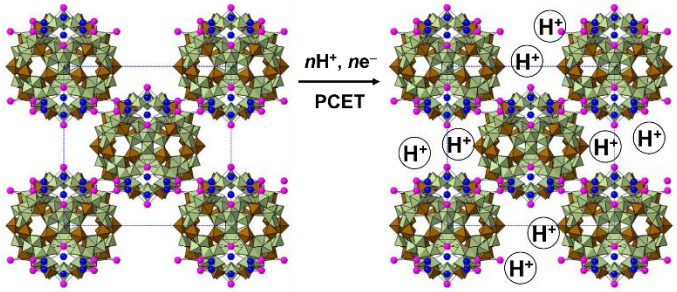
カプセル状ポリオキソメタレートを用いた還元的なプロトン導入

（東大院総合[1]） ○岩野 司[1]・玉井 奈々子[1]・内田 さやか[1]
Redox-Induced Proton Uptake Based on Polyoxometalate Capsules ([1]*School of Arts and Sciences, The University of Tokyo*) ○Tsukasa Iwano,[1] Nanako Tamai,[1] Sayaka Uchida [1]

Polyoxometalates (POMs), which is anionic metal oxide cluster, are received great attention as acid catalysts and proton conductors because POMs have high acidity and negative charge of POMs smeared over the oxygen atoms. These functions are derived from protons in the compounds and the number of protons is very associated with the higher functionality. In this work, making use of redox activity that is another feature of POMs, redox induced proton uptake by proton coupled electron transfer (PCET) was conducted. Keggin-type POMs ($[PMo_{12}O_{40}]^{3-}$) encapsulated Keplerate-type POM (**I**), which Cs^+ were successfully incorporated by cation coupled electron transfer (CCET) reaction in our previous work, was utilized to investigate the proton uptake. **I-red-H**$^+$ was obtained by stirring **I** with ascorbic acid under aqueous acetate solution. The chemical formula was determined by elemental analyses and XPS measurement. In our presentation, the acid catalytic activity and proton conduction of **I-red-H**$^+$ will be shown.
Keywords : Ionic crystal; Polyoxometalate; Cation Uptake

アニオン性金属酸化物クラスターのポリオキソメタレート(ポリ酸)は、高い酸性度を有し、表面電荷密度が小さいことから、酸触媒[1]やプロトン伝導材料[2]として注目されている。これらの機能には化合物内のプロトンが寄与しており、プロトン数の増大が機能性の向上に密接に関わると考えられる。そこで本研究ではポリ酸のもう一つの特徴である還元活性であることを活用し、プロトン共役電子移動(PCET)による還元的なプロトン導入を試みた。先行研究において、CCET 反応により還元的にセシウムを導入されることが知られる Keggin 型ポリ酸($[PMo_{12}O_{40}]^{3-}$)を内包した Keplerate 型ポリ酸($[\alpha\text{-}PMo^{VI}_{12}O_{40}]^{3-} \subset [Mo^{VI}_{72}Fe^{III}_{30}O_{252}(H_2O)_{102}(CH_3CO_2)_{15}]^{3+} \cdot 60H_2O$, **I**)[3] を化合物として用いた。**I** を酢酸水溶液中で還元剤であるアスコルビン酸とともに撹拌することで、還元体(**I-red-H**$^+$)を得た。組成式は、ICP 発行分光分析法、CHNS 有機微量分析及び XPS 測定により決定した。講演では、得られた **I-red-H**$^+$の酸触媒活性やプロトン伝導性についても報告する予定である。



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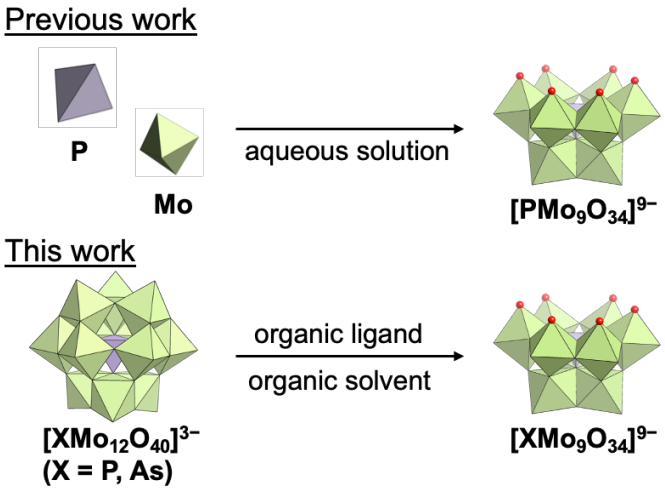
Development of a Synthesis Method of Lacunary Polyoxomolybdates in Organic Solvents

(*School of Engineering, The University of Tokyo*) ○Atsuhiro Jimbo, Chifeng Li, Kentaro Yonesato, Kosuke Suzuki, Kazuya Yamaguchi

Keywords: Polyoxometalates; Lacunary Polyoxomolybdates

Lacunary polyoxometalates (POMs) are important rigid inorganic multidentate ligands that show diverse properties by controlling structures and introducing transition metals. In particular, lacunary polyoxomolybdates are attractive POMs because of their unique electrochemical and photochemical properties; however, their low stability made it difficult to use them as ligands. We have recently reported that coordination of pyridyl ligands can stabilize lacunary polyoxomolybdates,[1] which can be further used as precursors for introducing multinuclear metal cores and synthesizing inorganic–organic hybrids.[2] However, by a conventional synthesis method in aqueous solutions, only a limited types of lacunary polyoxomolybdates can be synthesized.

In this study, we developed a new synthetic method for lacunary polyoxomolybdates in organic solvents. By treating a plenary phosphomolybdate $[PMo_{12}O_{40}]^{3-}$and several organic ligands in organic solvents, a trivacant lacunary phosphomolybdate was successfully synthesized. We also revealed that this method can be applied to the synthesis of a trivacant lacunary arsenomolybdate from plenary $[AsMo_{12}O_{40}]^{3-}$. The structures of the obtained lacunary species were determined by ESI-MS and the X-ray crystallographic analysis. Furthermore, we also report that these lacunary species can be utilized as mutidentate ligands for introducing multinuclear metal cores.



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Synthesis of Polyoxothiotungstates by Oxygen–Sulfur Substitution Reactions

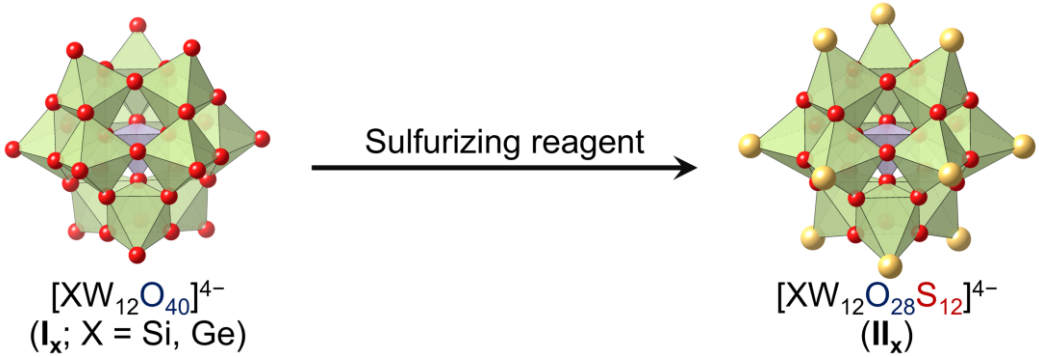
(*School of Engineering, The Univ. of Tokyo*) ○Kentaro Yonesato, Kosuke Suzuki, Kazuya Yamaguchi

Keywords: Polyoxometalates, Substitution reactions, Sulfur

Sulfur is a member of Group 16 that shares its elemental classification with that of oxygen. Nevertheless, metal sulfides exhibited unique structures, electronic states, and properties that significantly differs those of metal oxides. Therefore, the modification of metal oxides with sulfur has a great potential to develop the novel functions and applications.

Polyoxometalates (POMs) are anionic metal oxide clusters that show diverse structures, electronic states. Because their properties depend on their structures, the substitution of their constituent elements is an important approach to develop novel applications of POMs. To date, the substitution of metal sites of POMs has been widely developed, while that of oxygen sites is still limited due to the difficulty in the control of reactivity. Considering that the diverse structures of POMs have been synthesized, the development of site-selective sulfurization method of POMs has a significant importance to modify a wide variety of POMs.

In this report, we successfully developed the site-selective oxygen–sulfur substitution method that enables converting Keggin-type polyoxothiotungstates $[XW_{12}O_{40}]^{4-}$ (**I**$_X$; X = Si, Ge) into polyoxothiometalates (POTMs) $[XW_{12}O_{28}S_{12}]^{4-}$ (**II**$_X$) with retaining the original Keggin-type structures.[1] The 12 terminal oxygen atoms of **I**$_{Si}$ (i.e., W=O groups) were selectively substituted by sulfur atoms (i.e., W=S groups) thorough the reactions of **I**$_{Si}$ and sulfurizing reagents. The resultant **II**$_{Si}$ exhibited unique electronic states, optical property, and redox property owing to the introduction of sulfur atoms. This sulfurization method may be applicable to various POM types and will lead to the development of unprecedented applications in diverse fields, including catalysis, photochemistry, and electrochemistry.



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タングステンを基点とする重金属サブナノ粒子の温和合成手法の開拓と物性解明

(東工大化生研[1]・東大生研[2]・JST-さきがけ[3]・JST-ERATO[4]・阪大[5]・国際基督教大[6])
○富崎 展生[1]・塚本 孝政[2,3]・森合 達也[1,4]・Augie Atqa[1]・神戸 徹也[5]・田 旺帝[6]・今岡 享稔[1,4]・山元 公寿[1,4]

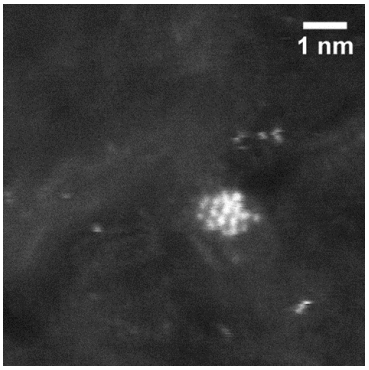
Developing a mild synthesis method and elucidating the physical properties of heavy metal subnanoparticles based on tungsten.

([1]Lab. Chem. Life Sci., Tokyo Tech, [2]IIS., The Univ. of Tokyo, [3]JST-PRESTO, [4]JST-ERATO, [5]Osaka Univ., [6]ICU) ○Hiroki Tomizaki[1], Takamasa Tsukamoto[2,3], Tatsuya Moriai[1,4], Augie Atqa[1], Tetsuya Kambe[5], Wang Jae Chun[6], Takane Imaoka[1,4], Kimihisa Yamamoto[1,4]

Subnanoparticles (SNPs) consisting of a few or few dozens of atoms are known for structures and properties varying depending on the number of atoms. In this study, we tried the precise template synthesis of tungsten SNPs by using tungsten multinuclear-complex of dendrimer with imine ligands. In the previous method, due to the strong Lewis acidity of the tungsten salts such as WCl_6, a decline in reaction temperature and an addition of some basic reagents were necessary to suppress the decomposition and aggregation of dendrimer[1)]. Therefore, by designing suitable tungsten precursors for more accurate complex formation such as $WOCl_3$(acac), we aimed to develop the new synthetic method for tungsten SNPs under milder condition. Characterizations such as XAFS and XPS were performed on the synthesized SNPs, and changes in physical properties depending on the atomicity were revealed.

Keywords: Dendrimer, Subnanoparticle, Tungsten, Multinuclear metal complex, Acetylacetonate complex

原子数個～数十個から成るサブナノ粒子はバルク物質とは異なり、その構造や物性が原子数に依存して大きく変化することが知られている。本研究では、イミン配位子を多数内包するデンドリマーに金属塩を配位集積させた「デンドリマー型多核金属錯体」を鋳型とした合成法により、W サブナノ粒子の温和かつ精密合成を試験した。これまで、WCl_6 を始めとした強力なルイス酸性を持つ W 塩の多核錯体形成には、鋳型分子の分解や凝集を防ぐために溶液の冷却や塩基性剤の添加などが必要不可欠であり、これにより温和条件下での W クラスターの精密合成は困難であった[1)]。そこで、錯体形成に最適な構造を持つ W 塩を新たに設計・合成することで、室温かつ添加剤を用いない W クラスターの新規合成法の開拓を目指した。初めに、金属塩のルイス酸性の低減と配位座の限定を目的としてアセチルアセトナート配位子を導入した W 塩を複数合成した。続いて、各金属塩の鋳型分子への配位力を確認した後、実際に W クラスターの鋳型合成を行い、HAADF-STEM 観察により粒径を制御した W クラスターの精密合成を確認した。合成したサブナノ粒子について XAFS や XPS などのキャラクタライゼーションを行い、粒径ごとの特異的な物性や原子数による性質の傾向を確認した。



1) M. Wakizaka, et al. *Inorg. Chem.*, **2020**, 59, 15690-15695.

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第 15 族金属元素サブナノ粒子の加水分解法による精密合成と物性開拓

（東工大 化生研[1]・JST-さきがけ[2]・東大生研[3]・JST-ERATO[4]・阪大）○那部 寛晃[1]・塚本孝政[1,2,3]・森合 達也[1,4]・神戸 徹也[5]・今岡 享稔[1,4]・山元 公寿[1,4]
Precise controlled synthesis of group 15 metal element subnanoparticles with hydrolysis method and exploration of their physical properties ([1]*Lab. Chem. Life Sci., Tokyo Tech.*, [2]*JST-PRESTO*, [3]*IIS, The Univ. of Tokyo*, [4]*JST-ERATO*, [5]*Osaka Univ.*) ○Hiroaki Nabe[1], Takamasa Tsukamoto[1,2,3], Tatsuya Moriai[1,4], Tetsuya Kambe[5], Takane Imaoka[1,4], Kimihisa Yamamoto[1,4]

Subnanoparticles are materials consisting of dozens of atoms with a particle diameter of approximately 1 nm, and have recently attracted attention as new materials that exhibit physical properties and functions different from those of nanoparticles. We have synthesized subnanoparticles of various metal species using dendritic phenylazomethine (DPA G4) as a template.[1)] By utilizing the stepwise complexation induced by the electron density gradient in DPA G4, we can precisely control the number of atoms (**Figure 1**).

In this study, we applied the hydrolysis method as a novel particle formation process in dendrimer template synthesis of subnanoparticles, and realized subnanoparticulation of group 15 metal elements, which was difficult to achieve with conventional methods. Next, we evaluated the physical properties of the subnanoparticles and found that they have different properties from those of nanoparticles, and also different electronic and chemical states for each number of constituent atoms.

Keywords : Subnanoparticle; Dendrimer; The hydrolysis method; Bismuth; Antimony

サブナノ粒子は原子数十個から構成される粒径約 1 nm の物質であり、ナノ粒子と異なる物性・機能を発現する新物質として近年注目されている。我々はこれまでに、フェニルアゾメチンデンドリマー(DPA G4)を鋳型として、様々な金属種のサブナノ粒子を合成してきた[1)]。DPA G4 内の電子密度勾配により誘導される段階的な錯形成を利用することで、原子数を精密に制御したサブナノ粒子合成が可能である（**Figure 1**）。

本研究では、サブナノ粒子のデンドリマー鋳型合成における新規の粒子化プロセスとして加水分解法を応用し、従来法では困難であった第 15 族金属元素のサブナノ粒子化を実現した。次にその物性を評価し、ナノ粒子と異なる物性、さらに構成原子数ごとに異なる電子状態や化学状態を見出したので報告する。

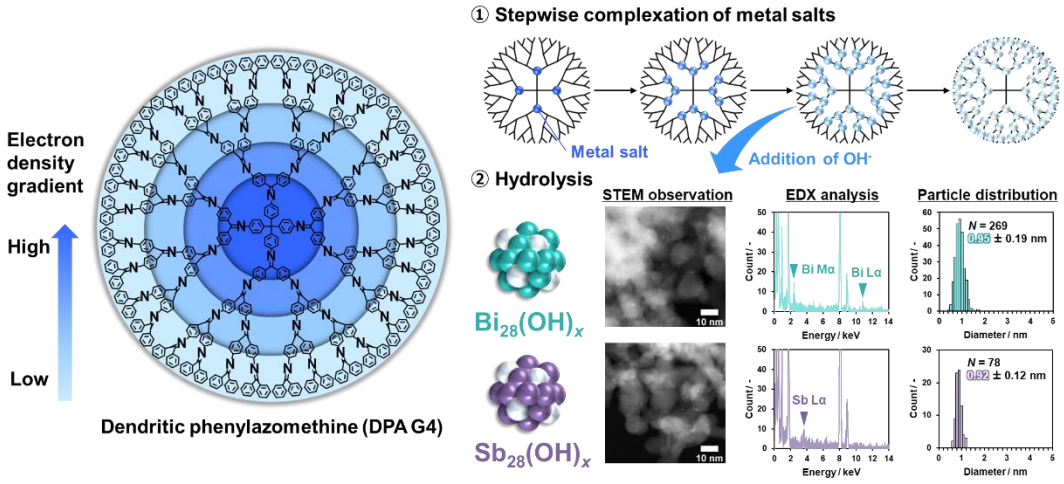

Figure 1. Electron density gradient and stepwise complexation of metal salts in DPA G4.

1) K. Yamamoto *et al.*, *Chem. Rev.*, **2020**, 120, 2, 1397-1437.

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
A1456(1456, Bldg. 14 [5F])

[A1456-3am] 08. Catalysts and Catalysis

Chair: Kosuke Beppu, Yugo Miseki

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1456-3am-01]
AFM imaging of photo-corrosion on $SrTiO_3$ wafers in $FeCl_3$ solution

○Kyohei Matsui[1], Hiroshi Onishi[1,2] (1. Kobe University, 2. Institute for Molecular Science)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1456-3am-02]
Liquid-phase chemo-selective reduction of nitrobenzenes with a photocatalytic fixed bed flow-type reactor

○Katsumi Tanimoto[1], Atsuhiro Tanaka[2], Hiroshi Kominami[2] (1. Graduate School of Science & Engineering, Kindai University, 2. Faculty of Science & Engineering, Kindai University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1456-3am-03]
Active sites for nitrate-to-ammonia photocatalytic reduction on copper-doped titanium dioxide

○Wataru Hiramatsu[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Osaka University)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1456-3am-04]
Enhanced Stability of Cu_2O Photocathode in Nitrate Solution

○Rizki Marcony Surya[1], Surya Pratap Singh[1], Takuya Okazaki[1], Kosuke Beppu[1], Fumiaki Amano[1] (1. Tokyo Metropolitan University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1456-3am-05]
Preparation of Au/AgCl catalysts by microwave-assisted reduction methodand hypochlorous acid generation

○Yoko Hiroaki[1], Yasuhiro Shiraishi[1], Takayuki Hirai[1] (1. Osaka University)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1456-3am-06]
Hydrophobic and Visible-light Responsive TiO_2 Photocatalyst for Efficient Hydrogen Peroxide Production in a Two-phase System

○Yifan Zhao[1], Yoshifumi Kondo[1], Yasutaka Kuwahara[1], Kohsuke Mori[1], Hiromi Yamashita[1] (1. Osaka University)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1456-3am-07]
Hydrogen Peroxide Synthesis from Pure Water Using rGO/$BiVO_4$ Photocatalyst

○Nozomi Suzuki[1,2], Takumi Okada[1,2], Masanori Kodera[1], Yugo Miseki[1], Takahiro Gunji[2], Kazuhiro Sayama[1,2] (1. AIST, 2. Tokyo University of Science)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1456-3am-08]
Simultaneous generation of hydrogen and chlorine from NaCl solution using TiO_2 photocatalyst

○Takumi Okada[1,2], Masanori Kodera[1], Yugo Miseki[1], Hitoshi Kusama[1], Takahiro Gunji[2], Kazuhiro Sayama[1,2] (1. AIST, 2. 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
[A1456-3am-09]
Development of a dye-sensitized molecular photocathode incorporating Ru(II)- and Os(II)-complex photosensitizers and its application to photoelectrochemical CO_2 reduction

○Jo Onodera[1], Yusuke Tamaki[2], Osamu Ishitani[1,3] (1. Tokyo Institute of Technology , 2. National Institute of Advanced Industrial Science and Technology, 3. Hiroshima University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1456-3am-10]
Photocatalytic CO_2 reduction by hybrid photocatalysts composed of organic polymer semiconductor and dinuclear Ru(II)-Re(I) complex

○Shotaro Sakamoto[1], Noriaki Sakakibara[1], Ewan McQueen[2], Sebastian Sprick[2], Osamu Ishitani[1,3] (1. Tokyo Institute of Technology, 2. Univ. of Strathclyde, 3. Hiroshima Univ.)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1456-3am-11]
Visible-light CO_2 reduction by hybrid photocatalysts consisting of soluble conjugated polymers with long alkyl chains and a Ru(II) complex

○Shunsuke Asai[1], Akinobu Nakada[2,3], Hajime Suzuki[2], Osamu Tomita[2], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1456-3am-12]
Effects of crystal phase mixture in Ga_2O_3 photocatalysts and roles of each phase on photocatalytic CO_2 reduction with water

○Naoto Ota[1], Yukie Takashiro[1], Muneaki Yamamoto[1], Tetsuo Tanabe[1], Tomoko Yoshida[1] (1. Osaka Metropolitan Univ.)

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Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1456-3am-13]

Effect of various metal dopants into $SrTiO_3$ photocatalyst on photocatalytic activity for CO_2 conversion

○Takechi Nakamoto[1], Shoji Iguchi[1], Shimpei Naniwa[1], Tsunehiro Tanaka[1,2,3], Kentaro Teramura[1,2,3] (1. Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, 2. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 3. Fukui Institute for Fundamental Chemistry, Kyoto University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[A1456-3am-14]

The effect of Zn/Ta ratio in $ZnTa_2O_6$ photocatalyst on the activity for the photocatalytic conversion of CO_2

○Kio Kawata[1,2], Masamu Nishimoto[1], Shoji Iguchi[2], Shimpei Naniwa[2], Tsunehiro Tanaka[2,3], Kentaro Teramura[2,3,4] (1. Sumitomo Metal Mining Co., Ltd., 2. Graduate School of Engineering, Kyoto University, 3. Kyoto University Elements Strategy Initiative for Catalysts and Batteries (ESCIB), 4. Kyoto University Fukui Institute for Fundamental Chemistry)

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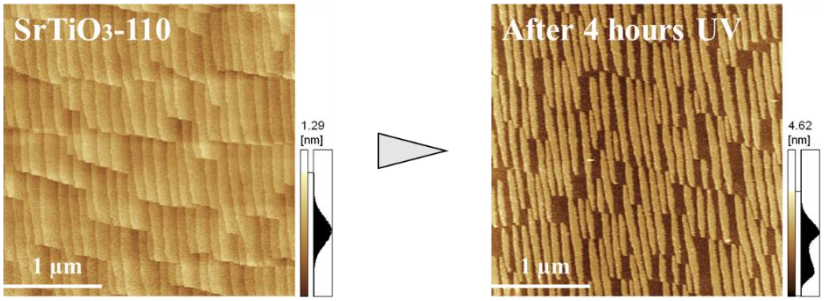
$FeCl_3$ 水溶液中における $SrTiO_3$ 光触媒基板の光腐食の AFM 計測

（神大院理[1]・分子研[2]）○松井 恭平[1]・大西 洋[1,2]
AFM imaging of photo-corrosion on $SrTiO_3$ wafers in $FeCl_3$ solution (*[1]Graduate School of Science, Kobe University*, *[2]Institute for Molecular Science*) ○Kyohei Matsui,[1] Hiroshi Onishi[1,2]

$SrTiO_3$ is a highly active semiconductor photocatalyst for the overall water splitting reaction when doped with Al and modified with co-catalysts. Domen and co-workers found that (110) and (111) oriented facets appeared on $SrTiO_3$ particles due to Al doping. On the other hand, a previous study suggested photo-corrosion on an Al-doped $SrTiO_3$ photocatalyst. In this study, we aimed to detect the surface change due to UV light irradiation on $SrTiO_3$ wafers immersed in $FeCl_3$+HCl solution adjusted to pH 1, which environment should promote photo-corrosion. Non-doped (110) oriented wafers exhibited significant photo-corrosion during UV irradiation as evidenced by 2 nm deep trenches. Trenches were not observed on Al-doped (110) wafers. (100) and (111) oriented wafers remain intact under irradiation regardless of Al doping. These results suggest that Al doping improves the durability of $SrTiO_3$ photocatalysts against photo-corrosion.
Keywords : $SrTiO_3$; AFM; Photo-corrosion; Al doping

$SrTiO_3$ は Al ドープと適切な助触媒の担持により 96%の量子収率と高い水分解活性を示す．そして Al ドープによる（110）面と（111）面の出現が水分解活性向上に寄与する可能性が報告されている[1]．さらに実用化に不可欠な指標である耐久性の議論として，高強度長時間の光照射後の $SrTiO_3$ が光腐食している可能性が報告されている[2]．本研究では光腐食を促進する環境である pH を 1 に調製した 10 mM の $FeCl_3$ 水溶液中に浸した $SrTiO_3$ 単結晶基板に 365 nm の紫外光を照射し，照射前後の表面形状を AFM を用いて検出した．Al ドープにかかわらず（100）面と（111）面では光照射による表面変化はなかったが，無ドープ（110）面では光腐食による表面変化が検出された．光照射前では 0.3 nm ほどの凹凸が照射後には 2 nm を超える凹凸となり，深さ方向への腐食が進行していることがわかった．Al ドープ（110）面では光腐食が観察されなかったことから Al ドープにより光腐食に対する耐久性が向上することがわかった．



1) Takata. T, et al., *Nature,* **581**, 411–414 (2020)
2) Kosaka. T, et al., *Phys. Chem. Chem Phys*., **23**, 19386-19393 (2021)

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日本化学会 第104春季年会 (2024)

固定床流通光触媒反応器を用いたニトロベンゼンの液相化学選択的還元

（近畿大院総合理工[1]・近畿大理工[2]）○谷本 捷倫[1]・田中 淳皓[2]・古南 博[2]
Liquid-phase chemoselective reduction of nitrobenzenes with a photocatalytic fixed bed flow-type reactor ([1]*Graduate School of Science & Engineering, Kindai University,* [2]*Faculty of Science & Engineering, Kindai University*) ○Katsumi Tanimoto,[1]Atsuhiro Tanaka,[2] Hiroshi Kominami[2]

Titanium dioxide (TiO_2) photocatalyst is known as a green catalyst that allows redox reactions to proceed under irradiation of UV light and ambient conditions. Liquid-phase photocatalytic reactions are normally carried out in butch-type reactors, such as a glass vessel, which are not suitable for continuous production of the target substance because the catalyst must be separated from the liquid phase after the reaction.

In this study, the continuous reduction of nitrobenzene to aniline was carried out in a flow-type photocatalytic reactor. As shown in Fig. 1, this reactor is a fixed bed flow-type one in which a PFA tube filled with TiO_2-coated zircon beads is suitable for continuous production of the target substance because the catalyst does not need to be separated from the liquid phase after the reaction. We examined various parameters to optimize the conditions, and we achieved an aniline production rate of 0.5 mmol h^{-1}.

Keywords : Photocatalyst; Nitrobenzene; Flow-type reactor

酸化チタン（TiO_2）光触媒は常温常圧紫外光照射下で酸化還元反応を進行させるグリーンな触媒として知られている。通常、液相光触媒反応はガラス製容器などのバッチ型反応器を用いて行われるため、反応後に触媒の分離回収が必要となり、目的物質の連続生産に適していない。

本研究では、流通型光触媒反応器を用いたニトロベンゼンからアニリンへの還元反応[1)]を実施した。本反応器は Fig. 1 に示すように、ジルコンビーズの TiO_2 塗布体を PFA チューブに充填し、ブラックライトに螺旋状に巻きつけた構造になっている[2)]。通常の不均一系触媒反応と同様に、光触媒は反応器内で固定されているため、チューブ出口から生成物と溶媒（＋未反応の基質）が回収される。光触媒失活した際の再生処理過程を除き、目的物質を連続的に生成できるとともにナンバーリングアップによる生成物の増量が容易である。支持体、TiO_2 の塗布方法や担持量、基質濃度、チューブ長、流速など種々の変数を検討した結果、単流路のワンパス条件下においてアニリン生成速度 0.5 mmol h^{-1} を達成した。

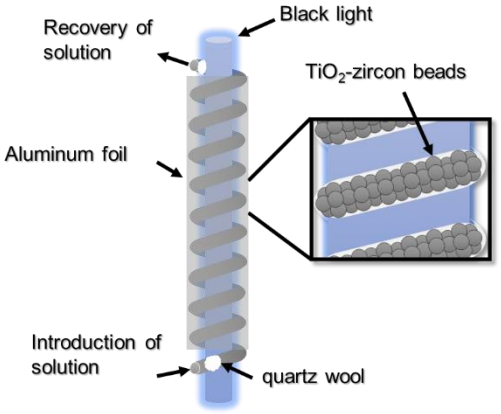

Fig. 1 Illustration of a flow-type reactor.

1) Imamura *et al., Appl. Catal. B*, **134**, 193 (2013).
2) Shiozaki *et al*., 125th CATSJ Meeting, 2P46 (2020).

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硝酸—アンモニア光触媒還元における銅イオンドープ二酸化チタンの活性点構造

（阪大院基礎工）○平松 航・白石 康浩・平井 隆之
Active sites for nitrate-to-ammonia photocatalytic reduction on copper-doped titanium dioxide (*Graduate School of Engineering Science, Osaka University*), ○Wataru Hiramatsu, Yasuhiro Shiraishi, Takayuki Hirai

We found that copper-doped titanium dioxide (Cu(II)-TiO_2) catalysts, when photoirradiated in pure water containing nitrate anions (NO_3^-), successfully produced ammonia (NH_3) with water as an electron donor. The Cu(II)-TiO_2 was synthesized by the preparation of gels using a mixture of Ti(IV) alkoxide and Cu(II) nitrate with 6% Cu followed by calcination under air flow at 650 °C. Photoreactions revealed the catalyst generated nitrite anion (NO_2^-) at the early stage, which was subsequently reduced to NH_3. The sum of the amounts of NH_3 and NO_2^- generated was identical to the amount of NO_3^- consumed, indicating that consecutive $NO_3^- \rightarrow NO_2^- \rightarrow NH_3$ reduction was promoted. XPS measurement and DFT calculations revealed that the surface oxygen vacancies created by the Cu doping behave as stable active sites for NO_3^--to-NH_3 reduction.
Keywords : Titanium dioxide; Nitrate; Ammonia; Photocatalysis

銅イオンをドープした二酸化チタン（Cu(II)-TiO_2）光触媒を、硝酸イオン（NO_3^-）を含む水溶液に懸濁させ、不活性ガス雰囲気下で光照射を行うと、水を電子源としてNO_3^-からアンモニア（NH_3）が生成することを見出した。触媒は、Ti(IV)アルコキシドと硝酸銅(II)による前駆体からゲルを調製した後、空気流通下で焼成して合成した。

Figure 1 には、Ti に対する Cu 仕込み量を 6%として調製したゲルを 650 °C で焼成することにより合成した触媒を用いて、純水中で光触媒反応を行った場合の NO_3^-の反応量、および亜硝酸イオン（NO_2^-）・NH_3 生成量の経時変化を示している。反応初期には NO_2^-が生成するが、その後 NH_3 が生成し始めることが分かる。また、NO_3^-反応量と NO_2^-・NH_3 生成量の合計はほぼ一致した。したがって、触媒上で $NO_3^- \rightarrow NO_2^- \rightarrow NH_3$ の逐次還元が進行することを示している。XPS 測定を行うと、Cu ドープにより Ti(IV)に対する Ti(III)の割合が大きくなり、表面酸素欠陥が形成されることが分かった。また、DFT 計算により、Cu ドープにより形成した表面酸素欠陥は大気中においても酸素酸化されずに安定に存在しており、$NO_3^- \rightarrow NO_2^- \rightarrow NH_3$ 還元の活性点として機能することを明らかにした。

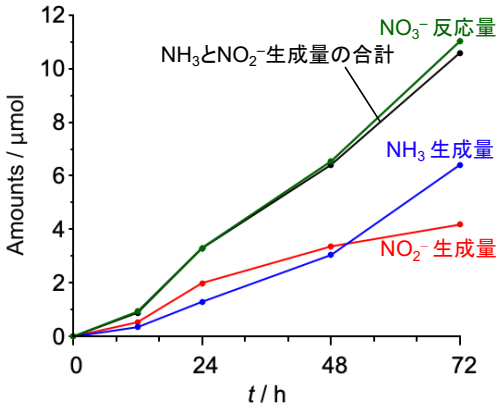

Figure 1. Change in the amounts of NO_3^- consumed and of NH_3 and NO_2^- generated during photoirradiation on Cu(II)-TiO_2.

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Enhanced Stability of Cu_2O Photocathode in Nitrate Solution

(*Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1–1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*) ○Rizki Marcony Surya, Surya Pratap Singh, Takuya Okazaki, Kosuke Beppu, Fumiaki Amano*

Keywords: Photoelectrochemistry, Photostability, Cuprous Oxide, Nitrate reduction

Cu_2O is a promising photoabsorber in solar energy conversion devices, such as photocatalytic and photoelectrochemical (PEC) cells. However, p-type Cu_2O surface is prone to photocorrosion due to sluggish electron transfers from the surface to the redox species. Consequently, self-reduction ($Cu_2O + 2H^+ + 2e^- \rightarrow 2Cu + H_2O$, +0.47 V vs RHE) is occurred, resulting in a diminished photoresponse (Fig. 1a).[1] In this study, we evaluated the photostability of the Cu_2O layer, which was electrodeposited on Ti felt,[2] in various electrolytes. We found that nitrate anions enhance its photostability at 0 V vs RHE under blue LED (470 nm). In the presence of 0.1 M $NaNO_3$, the photocurrent response remained stable (Fig. 1b and 1c) and the decrease in incident photon to current efficiency (IPCE) for 1 h of photoirradiation was minimal (0.294% h^{-1}) (Fig. 1d). In contrast, Cu_2O self-reduction was more feasible without nitrate solution, leading to the deterioration of IPCE (3.03% h^{-1}).

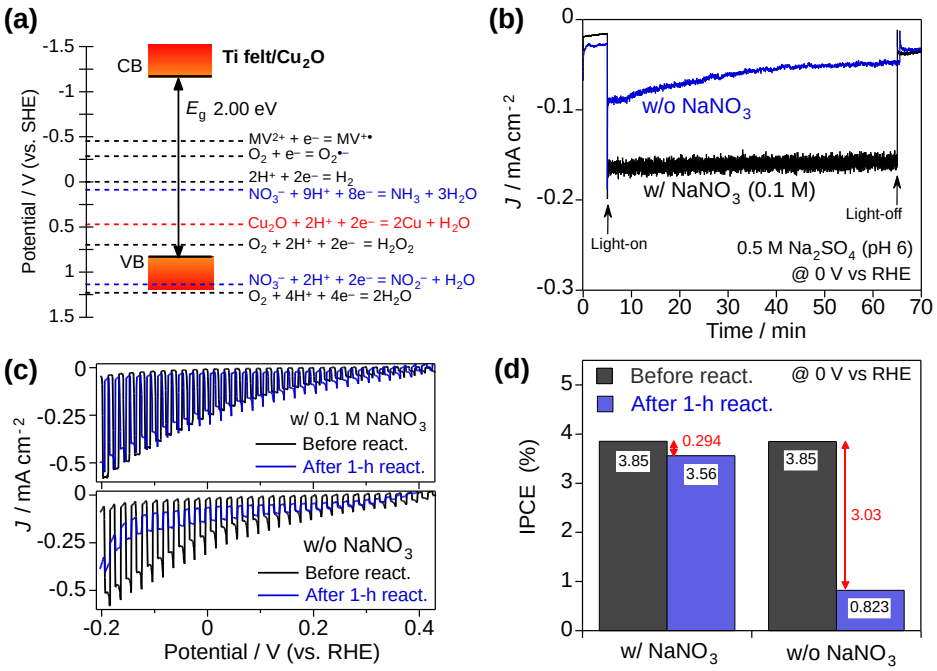

Figure 1. PEC properties of Cu_2O photocathode in 0.5 M Na_2SO_4 (pH 6) with and without 0.1 M $NaNO_3$ under blue light irradiation.

1) S. D.Tilley, *ACS Energy Lett.* **2023**, *8* (5), 2338–2344. 2) F. Amano, A. Uchiyama, Y. Furusho, A. Shintani, *J. Photochem. Photobiol. A Chem.* **2020**, *389*, 112254.

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日本化学会 第104春季年会 (2024)

マイクロ波還元法による Au/AgCl 光触媒の調製と次亜塩素酸生成反応

（阪大院基礎工）○広明 燿子・白石 康浩・平井 隆之

Preparation of Au/AgCl catalysts by microwave-assisted reduction method and hypochlorous acid generation (*Graduate School of Engineering Science, Osaka University*) ○Yoko Hiroaki, Yasuhiro Shiraishi, Takayuki Hirai

Hypochlorous acid (HClO) is usually manufactured from chlorine (Cl_2) gas generated by electrochemical oxidation of chloride anions (Cl^-) using considerable electrical energy ($2Cl^- + 1/2O_2 + 2H^+ \rightarrow Cl_2 + H_2O$; $\Delta G° = +105$ kJ mol^{-1}). Therefore, renewable energy-driven HClO generation is desirable. Recently, we have found that visible light irradiation of Au particles loaded on semiconductor AgCl powders (Au/AgCl), prepared by a deposition-precipitation (DP) method (400 °C, 2 h), successfully generates HClO in chloride solutions under air flow.[1] For further activity enhancement, it is necessary to increase the Au-AgCl interface. In the present work, we loaded Au particles onto AgCl by a microwave-assisted reduction method consisting of microwave irradiation of an ethylene glycol solution containing an Au precursor and AgCl (160 °C, 12 min). The Au/AgCl catalyst prepared by this method produced twice amount of HClO than that prepared by the DP method.

Keywords : Silver chloride; Au particle; Hypochlorous acid; Photocatalysis

次亜塩素酸（HClO）は、塩水の電解により合成した塩素ガスから製造されている（$2Cl^- + 1/2O_2 + 2H^+ \rightarrow Cl_2 + H_2O$; $\Delta G° = +105$ kJ mol^{-1}）ため、膨大な電気エネルギーを必要とする。そのため、再生可能エネルギーを用いた HClO 生成が必要である。我々のグループでは、析出沈殿（DP）法 (400 °C, 2 h)により金（Au）粒子を担持した塩化銀（AgCl）触媒（Au/AgCl）を塩化ナトリウム（NaCl）水溶液に懸濁させ、空気流通下で可視光を照射することで HClO が生成することを見出している[1]。

Au/AgCl 触媒の高活性化には、Au 粒子と AgCl の接触界面を増加させる必要がある。本研究では、マイクロ波還元法により Au/AgCl 触媒を合成した。Au 前駆体を含むエチレングリコール溶液に AgCl を懸濁させ、マイクロ波を照射した (160 °C, 12 min)。本方法は、DP 法よりも短時間かつ温和な条件下で AgCl に Au 粒子を担持することが可能である。さらに、Figure 1 に示すように、本方法で合成した触媒は DP 法で合成した触媒の約 2 倍の活性で HClO を生成した。

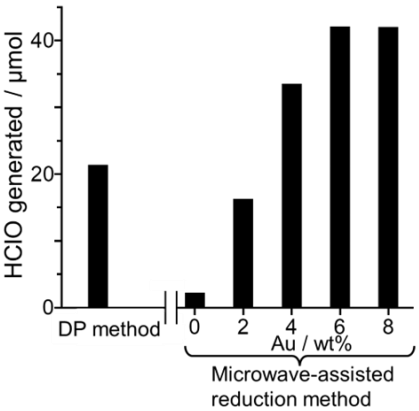

Figure 1. The amount of HClO formed. Reaction conditions; 550 mM NaCl solution (50 mL), Au/AgCl catalyst (100 mg), air flow (1.0 L/min), λ >420 nm (Xe lamp).

[1]: Y Shiraishi, Y Shimabukuro, K Shima, S Ichikawa, S Tanaka, T Hirai, *JACS Au* **2023**, 3, 1403-1412

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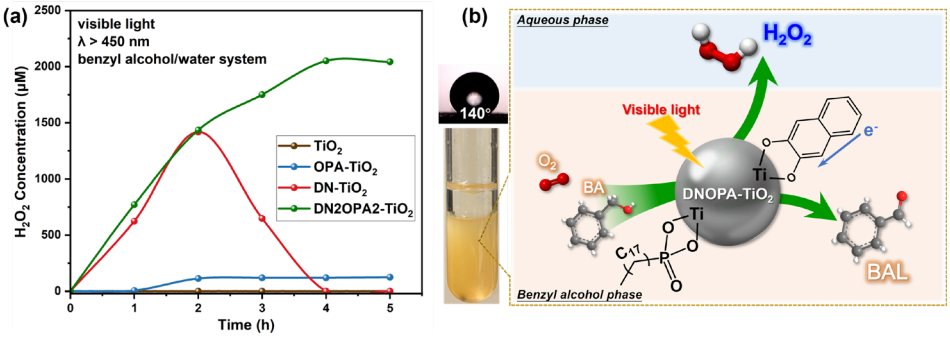
Hydrophobic and Visible-light Responsive TiO_2 Photocatalyst for Efficient Hydrogen Peroxide Production in a Two-phase System

([1]*Graduate School of Engineering, Osaka University*, [2]*Institute for Open and Transdisciplinary Research Initiatives (OTRI), Osaka University*) ○Yifan Zhao,[1] Yoshifumi Kondo,[1] Yasutaka Kuwahara,[1,2] Kohsuke Mori,[1,2] Hiromi Yamashita[1,2]

Keywords: Photocatalysis ; Hydrogen peroxide; Oxygen reduction reaction; Titanium dioxide; Surface modification

The enhancement of photocatalytic reaction using TiO_2 material has been widely investigated these years because of the high chemical stability and low cost of TiO_2. For photocatalytic H_2O_2 production, an environmentally friendly reaction using water, oxygen and solar as sources, the doping of TiO_2 with noble metals, quantum dot, etc. has been reported to improve the photocatalytic performance. However, the challenges of TiO_2 application in H_2O_2 production, particularly the formation of peroxide complexes (≡Ti-OOH) on the TiO_2 surface causing H_2O_2 decomposition, necessitate continued attention and resolution from researchers.[1] Moreover, it is preferable to combine O_2 reduction reaction (ORR) with oxidative synthesis of high value-added chemicals based on the economical consideration.

In this work,[2] we have reported 2,3-dihydroxynaphthalene (2,3-DN) and octadecylphosphonic acid (OPA) co-modified TiO_2 materials with unique hydrophobic properties applied for photocatalytic H_2O_2 production under visible light irradiation in a benzyl alcohol/water two-phase system. DN2OPA2-TiO_2 with the proper contents of surface complexes exhibited higher activity and stability for H_2O_2 production (2050 μmol/L) over a 5-hour reaction under visible light (λ > 450 nm). Enhanced activity is attributed to the addition of 2,3-DN, which enables TiO_2 to harvest visible light and provide abundant electrons for ORR for H_2O_2 synthesis. Higher stability is due to the unique hydrophobic nature of catalysts modified by OPA, which confirms the stable existence of catalysts in organic phase and inhibits H_2O_2 decomposition.



1) Y. Isaka, Y. Kawase, Y. Kuwahara, K. Mori, H. Yamashita, Angew. Chemie **2019**, 131, 5456–5460.
2) Y. Zhao, Y. Kondo, Y. Kuwahara, K. Mori, H. Yamashita, *Catal. Today* **2024**, *425*, 114350.

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rGO/$BiVO_4$ 光触媒を用いた純水からの過酸化水素合成

(産総研[1]・東理大[2]) ○鈴木 希[1,2]・岡田 拓巳[1,2]・小寺 正徳[1]・三石 雄悟[1]・郡司 天博[2]・佐山 和弘[1,2]

Hydrogen Peroxide Synthesis from Pure Water Using rGO/$BiVO_4$ Photocatalyst ([1]*AIST*, [2]*Faculty of Science and Technology, Tokyo University of Science*) ○Nozomi Suzuki,[1,2] Takumi Okada,[1,2] Masanori Kodera,[1] Yugo Miseki,[1] Takahiro Gunji,[2] Kazuhiro Sayama[1,2]

Hydrogen peroxide (H_2O_2) is an important chemical used in various industrial fields. The anthraquinone method, an industrial process for producing H_2O_2, is energy intensive and uses hazardous hydrogen gas, so there is a need to develop a safe and environmentally friendly method for producing H_2O_2. Photocatalytic H_2O_2 synthesis has attracted attention as a new method for H_2O_2 synthesis because it uses sunlight as an energy source and only water and oxygen as raw materials, but it is expensive due to its low activity and the use of precious metals as a cocatalyst. In addition, sacrificial reagents, etc., are often added to the reaction system to improve activity, making it difficult to separate the H_2O_2 from the reaction solution. In this study, $BiVO_4$ was used as a photocatalyst and reduced graphene oxide (rGO) as a nonmetal cocatalyst to investigate the formation of H_2O_2 by the reduction of oxygen. $BiVO_4$ without an auxiliary catalyst did not produce H_2O_2, whereas $BiVO_4$ loaded with rGO produced about 2 μM/h of hydrogen peroxide. The $BiVO_4$ loaded with rGO after silylation was 2.3 times more active than the $BiVO_4$ without silylation. In the presentation, we will discuss the changes in activity of rGO under different loading conditions.

Keywords : Photocatalyst; Reduced Graphene Oxide; Hydrogen Peroxide Synthesis

過酸化水素 (H_2O_2)は様々な工業分野で利用される重要な化学品である。H_2O_2 の工業的製法であるアントラキノン法は、エネルギー消費が大きく、危険な水素ガスを使用するため、安全で環境にやさしい H_2O_2 製造法の開発が求められている [1)]。光触媒を用いた H_2O_2 合成は、太陽光をエネルギー源とし、水と酸素のみを原料とすることから、新しい H_2O_2 合成法として注目を集めているが、活性が低く、助触媒に貴金属を用いることが多いため、コストが高い。また、活性向上のために反応系中に犠牲剤などを添加する場合が多く [2)]、生成した H_2O_2 との分離が困難である。本研究では、光触媒として $BiVO_4$、助触媒として非金属である還元型酸化グラフェン (rGO)を用い、純水中で酸素の還元による H_2O_2 の生成を検討した。

助触媒を担持していない $BiVO_4$ では H_2O_2 は生成しなかったのに対し、rGO を担持した $BiVO_4$ は約 2 μM/h の過酸化水素を生成した。また、$BiVO_4$ に対しシリル化を施したのち rGO を担持したものはシリル化を施さないものに比べ 2.3 倍の活性を示した。発表では、rGO の担持条件の違いによる活性の変化について議論する。

1) X. Zeng., Y. Liu, X. Hu, X. Zhang, *Green Chem.*, **2021**, *23*, 1466.
2) W. Yu, C. Hu, L. Bai, N. Tian, Y. Zhang, H. Huang, *Nano Energy*, **2022**, *104*, 107906.

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TiO_2 光触媒を用いた NaCl 水溶液からの水素と塩素の同時生成

（産総研[1]・東理大理工[2]）○岡田 拓巳[1,2]・小寺 正徳[1]・三石 雄悟[1]・草間 仁[1]・郡司 天博[2]・佐山 和弘[1,2]
Simultaneous generation of hydrogen and chlorine from NaCl solution using TiO_2 photocatalyst ([1]*AIST*, [2]*Faculty of Science and Technology, Tokyo University of Science*)
○Takumi Okada,[1,2] Masanori Kodera,[1] Yugo Miseki,[1] Takahiro Gunji,[2] Hitoshi Kusama,[1] Kazuhiro Sayama[1,2]

Water splitting with particulate photocatalysts has attracted attention as a green hydrogen production method. It would be desirable from the viewpoint of resource quantity to utilize seawater, which is abundant on the earth, instead of water. In addition, if seawater can be decomposed into hydrogen and chlorine, which has a higher value than oxygen, profitability could be expected to improve in the early stage of widespread use. In this study, we investigated the effects of modification conditions of the catalyst, pH and NaCl concentration of the reaction solution on the products and activity using Pt-loaded TiO_2 as a photocatalyst and NaCl solution. Hydrogen, chlorine, and a small amount of oxygen were stoichiometrically evolved under acidic condition,.

Keywords : Photocatalyst; Titanium dioxide; Hydrogen; Chlorine; High-value-added chemicals

粉末光触媒を用いた水分解反応はグリーン水素生成法として注目されている。その際、反応物として水の代わりに地球上に豊富に存在する海水を利用することができれば、資源量の観点から望ましいと考えられる。加えて海水を水素と、酸素より価値の大きな塩素に分解できれば普及初期には採算性の向上が期待できる。本研究では光触媒として Pt 担持 TiO_2、海水の代わりにモデル溶液として NaCl 溶液を使用し、反応溶液の pH や NaCl 濃度、助触媒の担持条件等が生成物や活性に与える影響について流通系反応装置を用いて調査した。図 1 左のように反応溶液が酸性条件下では水素、塩素および少量の酸素が光を照射している間だけ化学量論的に生成した。一方、中・塩基性条件下では水素のみが生成し、塩素ガスは確認できなかった (図 1 中央・右)。また、反応後の溶液にも次亜塩素酸や次亜塩素酸イオンは存在しなかった。イオンクロマトグラフィーにおいて、反応溶液中に塩素酸イオンの存在が確認されたことから、一度生成した次亜塩素酸が紫外光により塩素酸イオンに分解されたことが示唆された。
発表では反応溶液の pH や NaCl 濃度、助触媒の担持条件等が生成物や活性に与える影響についてより詳細に議論する。

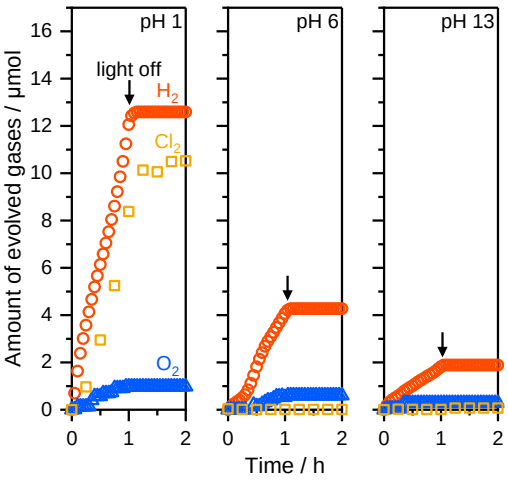

Fig. 1 Time courses of brine splitting using 0.1 wt% Pt-loaded TiO_2 under different pH conditions.

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日本化学会 第104春季年会 (2024)

Ru(II)および Os(II)光増感錯体を組み込んだ色素増感分子光カソードの開発と光電気化学 CO_2 還元への応用

（東工大理[1]・産総研[2]・広大院先進理工[2]）○小野寺 丈[1]・玉置 悠祐[2]・石谷 治[1,3]

Development of a dye-sensitized molecular photocathode incorporating Ru(II)- and Os(II)-complex photosensitizers and its application to photoelectrochemical CO_2 reduction

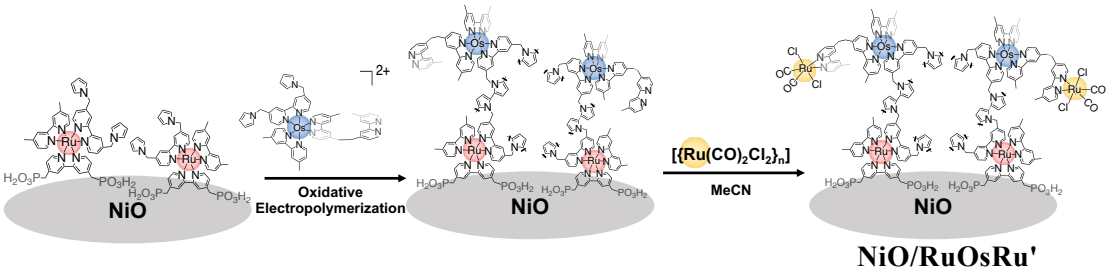
([1]*Tokyo Institute of Technology*, [2] *National Institute of Advanced Industrial Science and Technology*, [3] *Hiroshima University*) ○Jo Onodera,[1] Yusuke Tamaki,[2] Osamu Ishitani[1,3]

Photocatalytic CO_2 reduction using solar light and water is one of the promising technologies for solving global warming and the shortage of fossil resources. Recently, we developed a dye-sensitized molecular photocathode fixed a polypyrrole layer involving Ru(II)-complex photosensitizers that absorb light up to 550 nm, Ru(II)-complex catalysts, and NiO[1], which photoelectrochemically produced CO and formic acid in water. In this study, we added Os(II)-complex photosensitizers that absorb light up to 750 nm in the dye-sensitized molecular photocathode. Electropolymerization of the Os(II)-complex photosensitizers with pyrrole groups was performed on a NiO electrode on which the Ru(II)-complex photosensitizers with pyrrole groups were already immobilized. The Ru(II)-complex catalysts were synthesized on the surface of this electrode giving a new dye-sensitized molecular photocathode **NiO/RuOsRu'**.

Keywords : CO_2 reduction; Metal complex; Semiconductor; Photocathode, Os(II) complex

地球温暖化と化石資源枯渇の問題を一挙に解決する技術として、太陽光と水を利用し CO_2 を有用な炭素資源へと変換する技術は有望である。我々は、Ru(II)光増感錯体を組み込んだポリピロール膜を NiO 電極の表面に固定化し、そのポリピロール膜表面に CO_2 還元能を有する Ru(II)錯体触媒を固定化した色素増感分子光カソードを開発し、水を電子源とする CO_2 還元光電気化学システムの構築に成功した[1]。しかし、Ru(II)光増感錯体の吸収は 550 nm より短波長に限られるため、より長波長を利用できるシステムの構築が必要である。トリスジイミン Os(II)錯体は、中心金属の大きな重原子効果のため本来禁制の S-T 吸収が 750 nm まで観測される。本研究では、この Os(II) 光増感錯体の光増感機能に注目した。Ru(II)光増感錯体に加え、Os(II)光増感錯体を光カソードに組み込むことで長波長可視光の利用による活性向上を目指して研究を行った。

ピロール基を有する Os(II)光増感錯体（0.5 mM）を含むアセトニトリル溶液中に、ピロール基を有する Ru(II)光増感錯体が NiO 表面に固定された電極を保持させた。正の電位を印加し電解酸化重合を行うことで、Ru(II)および Os(II)光増感錯体が組み込まれたポリピロール膜を合成した。重合後の電極を、触媒前駆体を溶解させた溶液中に保持することで、色素増感分子光カソード **NiO/RuOsRu'**の合成に成功した（下図）。発表では **NiO/RuOsRu'**を用いた CO_2 還元反応についても報告する。



NiO/RuOsRu'

1) F. Kuttassery, O. Ishitani *et al*., *Chem. Sci.*, **2021**, *12*, 13216–13232.

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有機高分子半導体と Ru(Ⅱ)-Re(Ⅰ)二核錯体からなるハイブリッド光触媒を用いた可視光駆動 CO_2 還元反応

（東工大理[1]・ストラスクライド大[2]・広島大院先進理工[3]）○坂本翔太郎[1]・榊原教貴[1]・Ewan McQueen[2]・Reiner S. Sprick[2]・石谷 治[1,3]

Photocatalytic CO_2 reduction by hybrid photocatalysts composed of organic polymer semiconductor and dinuclear Ru(II)-Re(I) complex ([1]*School of Science, Tokyo Institute of Technology*, [2] *Department of Pure and Applied Chemistry, University of Strathclyde*, [3] *Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Shotaro Sakamoto,[1] Noritaka Sakakibara,[1] Ewan McQueen,[2] Reiner S. Sprick,[2] Osamu Ishitani[1,3]

Hybrid photocatalysts comprising of semiconductors and supramolecular photocatalysts have attracted much attention for constructing efficient CO_2 reduction system using visible light. [1)] Recently, we have developed highly efficient and durable hybrid photocatalyst using conjugated polymers and Ru(II) dinuclear supramolecular photocatalyst for formate production. [2)] In this study, we have developed hybrid photocatalysts using conjugated polymers and Ru(II)-Re(I) dinuclear supramolecular photocatalyst (**RuRe**) for efficient CO formation.

The hybrid photocatalyst (**RuRe**/Ag/P10), in which Ag is loaded onto the conjugated polymer poly(dibenzo[*b,d*]thiophenesulfone) (P10), was dispersed in CO_2-bubbled *N,N'*-dimethylacetamide/triethanolamine and was irradiated by visible light (λ_{max} = 460 nm). The hybrid photocatalyst produced CO with turnover of 116.6, and H_2 and formate were also formed as by-products., leading to the selectivity for CO formation of 0.56%. To gain better selectivity of CO formation, we are now investigating various conjugated polymers other than P10 and the optimal sacrificial reductants and proton sources for the CO_2 reduction.

Keywords : Polymer semiconductor; Supramolecular photocatalyst; CO_2 reduction

半導体と超分子光触媒を複合化したハイブリッド光触媒は、可視駆動の高効率な CO_2 還元システムの実現に向けて大変有望である。[1)]最近我々は、共役高分子と Ru(II)二核超分子光触媒から成るハイブリッド光触媒を開発し、超高効率かつ高耐久なギ酸生成を実現した。[2)]本研究では、半導体として共役高分子、超分子光触媒として高選択的な CO 生成が可能な Ru(Ⅱ)-Re(Ⅰ)二核錯体（**RuRe**）を用いることで、高効率に CO_2 を CO へと変換するハイブリッド光触媒の創製を目指した。

共役高分子に銀ナノ粒子を担持した後に、**RuRe** を固定化することでハイブリッド光触媒を得た。CO_2 を飽和させた *N,N'*-ジメチルアセトアミド／トリエタノールアミン中において光触媒粉末を懸濁させ、可視光（λ_{max} = 460 nm）を照射した。ポリジベンゾ[*b,d*]チオフェンスルホン(P10)を用いたハイブリッド光触媒(**RuRe**/Ag/P10)では、CO がターンオーバー数 116.6 で生成したものの、副生成物として H_2 とギ酸が生成し、CO 生成の選択率は 0.56%であった。そこで現在、様々な共役高分子半導体を検討すると同時に、最適な犠牲還元剤およびプロトン源についても検討することで、CO 生成の選択率向上を目指している。

1) A. Nakada, H. Kumagai, M. Robert, O. Ishitani, K. Maeda, Acc. Mater. Res. 2021, 2, 458.
2) E. McQueen, N. Sakakibara et al., submitted.

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長鎖アルキル鎖を有する可溶性共役系高分子/Ru(II)錯体複合光触媒による可視光 CO_2 還元

(京大工[1]・京大院工[2]・JST さきがけ[3]) ○浅井 俊亮[1]・中田 明伸[2,3]・鈴木 肇[2]・冨田 修[2]・阿部 竜[2]

Visible-Light CO_2 Reduction by Hybrid Photocatalysts Consisting of Soluble Conjugated Polymers with Long Alkyl Chains and a Ru(II) Complex

([1]*Fac. of Eng., Kyoto Univ.*, [2]*Grad. Sch. of Eng., Kyoto Univ.*, [3]*PRESTO/JST*) ○Shunsuke Asai,[1] Akinobu Nakada,[2,3] Hajime Suzuki,[2] Osamu Tomita,[2] Ryu Abe[2]

Recently, conjugated polymers have attracted much attention as photocatalysts due to design flexibility. We previously reported a hybrid photocatalysts consisting of linear conjugated polymers with phenylcarbazole skeleton and Ru(II) complex catalysts for visible-light-induced CO_2 reduction. Herein, we develop a soluble conjugated polymer/Ru complex hybrid by introducing blanched alkyl chains to control their polymer structure by utilizing its solubility.

Keywords : Hybrid photocatalyst; CO_2 Reduction; Conjugated Polymer; Metal Complex; Solubility

近年、共役系高分子が高い分子設計柔軟性を有する光触媒として注目されている。我々は、フェニルカルバゾール (PhCz)骨格を有する共役系高分子に Ru(II)錯体触媒を位置選択的に配位導入した複合光触媒が、可視光により CO_2 還元活性を示すことを報告している[1]。しかし、この複合光触媒は難溶性であり、合成条件により重合度や集積構造を制御することで、その光触媒性能を改良することが困難であった。そこで本研究では、カルバゾール骨格に分岐アルキル鎖を導入することで有機溶媒に可溶な共役系高分子/錯体複合体を開発し、その可溶性を活かした高分子構造変調を試みた。

異なるカルバゾール置換基を有する高分子**[X-Bpy]**$_n$ (X = PhCz or $C_{8,8}$Cz; Fig. 1)を、*o*-ジクロロベンゼン (*o*-Cl_2Ph)溶媒中における鈴木カップリング反応により合成を試みた。その結果、**[$C_{8,8}$Cz-Bpy]**$_n$ を *o*-Cl_2Ph 中で合成した場合に限り、生成物が溶解した状態で反応が進行した。拡散反射スペクトルにおいて、いずれの高分子も同様の吸収極大波長を示したが、**[$C_{8,8}$Cz-Bpy]**$_n$ では**[PhCz-Bpy]**$_n$ よりも長波長側にショルダー吸収を示した。一方で、**[$C_{8,8}$Cz-Bpy]**$_n$ の溶液吸収スペクトルではそのようなショルダー吸収は見られなかった。このことから、**[$C_{8,8}$Cz-Bpy]**$_n$ はその集積状態において、**[PhCz-Bpy]**$_n$ とは異なる構造を有していると考えられる。当日は、錯体触媒を配位導入した高分子について、その高分子構造が各種物性と光触媒特性に与える影響を報告する予定である。

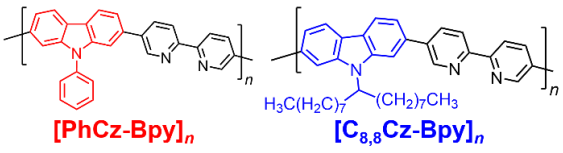

Fig. 1 Molecular structures of **[X-Bpy]**$_n$.

1) Nakada, A.; Abe R.; Chang, H.-C. *et al.*, *J. Mater. Chem. A*, **2022**, *10*, 19821.

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日本化学会 第104春季年会 (2024)

酸化ガリウム光触媒の二酸化炭素還元反応活性に及ぼす結晶相の混合と各相の役割

（大阪公大）○太田 尚人・髙城 友紀恵・山本 宗昭・田邉 哲朗・吉田 朋子

Mixing of crystalline phases and the role of each phase on the activity of gallium oxide photocatalysts for carbon dioxide reduction reaction (*Osaka Metropolitan University,*)

○Naoto Ota, Yukie Takashiro, Muneaki Yamamoto, Tetsuo Tanabe, Tomoko Yoshida

Gallium oxide (Ga_2O_3), which is well known as a photocatalyst for CO_2 reduction with water, has six different crystalline phases (α, β, γ, δ, ε, and κ). Although α, β, and γ phases have been examined well as the photocatalysts, the other phases have not. In the present work, we have synthesized α, β, γ, and κ phases and their mixed phases and examined their photocatalytic activity for CO_2 reduction with water under UV light illumination to understand the role of each phase and phase mixing.

Fig. 1 compares the production rates of H_2, CO and O_2, the main products of the CO_2 reduction. The α phase and the γ phase show higher selectivity of H_2 and CO productions, respectively, while the mixed phase of α and γ shows the highest catalytic activity. The role of each phase and the effect of phase mixing on the CO_2 reduction will be discussed in detail considering specific surface area and morphology of synthesized samples.

Keywords : Ga_2O_3; CO_2 reduction; Crystalline phase; Phase mixing

酸化ガリウム（Ga_2O_3）は CO_2 の水による還元反応を促進する光触媒として働くことが知られているが、6 種類もの結晶相（α, β, γ, δ, ε, κ）を呈する。これまでに α, β, γ の各単相について、また α と γ または β と γ との混相について触媒活性が調べられてはいるが、それ以外の相やそれらとの混相については報告例がない。本研究では、α, β, γ および κ の各単相とそれらの混相を作成し、それらを光触媒として紫外光照射下での水による CO_2 還元反応を実施し、各相の活性を比較すると共に、その混合効果について調べた。

Fig. 1 に CO_2 還元により生成する H_2、CO および O_2 の生成速度を α, β, γ, κ 各単相および α+γ と α+κ 混相について比較した。α 相では水素発生の選択性が高く、γ 相では CO 発生の選択性が高くなっており、両者を混合すると触媒活性が著しく増すことがわかった。講演では比表面積などの比較も含めて、各相の触媒としての役割を議論する。

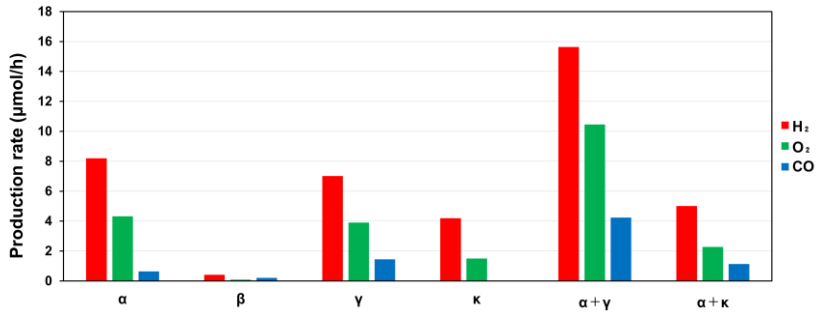

Fig1. Comparison of the production rates of H_2, O_2, and CO for different phases of Ga_2O_3

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CO_2 光還元における $SrTiO_3$ 光触媒への各種金属イオンのドープ効果

（京大院工 [1]・京大 ESICB[2]・京都大福井謙一記念研究センター[3]） ○中本 嵩市 [1]・井口 翔之 [1]・浪花 晋平 [1]・田中 庸裕 [1,2,3]・寺村 謙太郎 [1,2,3]

Effect of various metal dopants into $SrTiO_3$ photocatalyst on photocatalytic activity for CO_2 conversion ([1]*Graduate School of Engineering, Kyoto University*, [2]*ESICB, Kyoto University*, [3]*Fukui Institute for Fundamental Chemistry, Kyoto University*) ○Takechi Nakamoto,[1] Shoji Iguchi,[1] Shimpei Naniwa,[1] Tsunehiro Tanaka,[1,2,3] Kentaro Teramura[1,2,3]

We have investigated the effect of metal doping into $SrTiO_3$ photocatalyst on photocatalytic conversion of CO_2 by H_2O as an electron donor. Al, Mg, Zn, Li, Mn, W, Ca, or Y-doped $SrTiO_3$ were fabricated by a flux method, and the activities for the photocatalytic conversion of CO_2 by H_2O were evaluated under the photoirradiation by a monochromatic LED lamp at 365 nm. Al or Mg-doped $SrTiO_3$ showed significant activities for photocatalytic conversion of CO_2 by H_2O, while the others exhibited negligible activities.[1] Furthermore, it was found that Mg-doped $SrTiO_3$ showed higher formation rate of CO than Al-doped $SrTiO_3$.

SEM images of the photocatalysts revealed that Al or Mg-doped $SrTiO_3$ has edge-shaved cube particles with {110} facets in addition to {100} facets. It is reported that photogenerated electrons and holes in Al-doped $SrTiO_3$ are anisotropically distributed on the {100} and {110} facets, respectively, to promote the charge separation.[2] In the case of Zn, Li, Mn, W, Ca, or Y-doped $SrTiO_3$, the shapes of the photocatalysts were cubic particles with only {100} facets. We concluded that the suppression of charge recombination due to the particle shapes of Al or Mg-doped $SrTiO_3$ is responsible for the characteristically enhanced photocatalytic activities.

Keywords : CO_2 conversion; $SrTiO_3$ photocatalyst; Metal doping

本研究では，H_2O を電子源とする CO_2 光還元における，$SrTiO_3$ 光触媒への金属ドープの効果を検討した．Al，Mg，Zn，Li，Mn，W，Ca，Y をそれぞれフラックス法で $SrTiO_3$ にドープし，365 nm 単波長の光照射下における H_2O を電子源とする CO_2 光還元活性を評価した．Zn，Li，Mn，W，Ca，Y をドープした $SrTiO_3$ はほとんど活性を示さなかった一方で，Al や Mg をドープした $SrTiO_3$ は H_2O を電子源とする CO_2 光還元に活性を示した．[1)]また，Mg ドープ $SrTiO_3$ は Al ドープ $SrTiO_3$ よりも高い CO 生成速度を示した．

SEM 像によって光触媒粒子の形状を観察すると，Al や Mg をドープした $SrTiO_3$ は{100}面に加えて{110}面が露出した立方体形状を有することが分かった．Al ドープ $SrTiO_3$ の場合，光照射により生じた励起電子が{100}面に，正孔が{110}面に異方的に分布し，電荷分離が促進されることが報告されている．[2)]また，Al や Mg 以外をドープした場合には，光触媒粒子は{100}面のみが露出した立方体形状であった．よって，粒子形状に起因する異方的な電荷分布が，Al や Mg をドープした $SrTiO_3$ の高い CO_2 光還元活性をもたらしたと結論した．

1) T. Nakamoto, S. Iguchi, S. Naniwa, T. Tanaka, K. Teramura, *Catal. Sci. Technol*., **2023**, *13*, 4534.
2) T. Takata, J. Jiang, Y. Sakata, M. Nakabayashi, N. Shibata, V. Nandal, K. Seki, T. Hisatomi, K. Domen, *Nature*, **2020**, *581*, 411.

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$ZnTa_2O_6$ 光触媒の Zn/Ta 比が CO_2 光還元活性に及ぼす効果

（住友金属鉱山（株）[1]・京大院工[2]・京大触媒電池[3]・京大福井謙一記念研究セ[4]）
○川田稀士[1,2]，西本大夢[1]，井口翔之[2]，浪花晋平[2]，田中庸裕[2,3]，寺村謙太郎[2,3,4]
Effect of Zn/Ta ratio in $ZnTa_2O_6$ photocatalyst on the activity for the photocatalytic conversion of CO_2 ([1]*Sumitomo Metal Mining Co., Ltd.*, [2]*Graduate School of Engineering, Kyoto University,* [3]*Kyoto University ESICB,* [4]*Kyoto University FIFC*) ○Kio Kawata,[1,2] Masamu Nishimoto,[1] Shoji Iguchi,[2] Shimpei Naniwa,[2] Tsunehiro Tanaka,[2,3] Kentaro Teramura[2,3,4]

We previously reported that $ZnTa_2O_6$ photocatalyst, which was modified with appropriate Zn species and/or Ag co-catalyst, exhibited good activity for the photocatalytic conversion of CO_2 using H_2O as an electron donor. In this study, the effect of Zn/Ta ratio in $ZnTa_2O_6$ photocatalyst on the activity for the photocatalytic conversion of CO_2 in water was investigated. As shown in Fig. 1, we found that $Zn_{0.85}Ta_2O_{5.85}$ (Zn/Ta = 0.43), where the Zn content is 15% lower than the stoichiometric $ZnTa_2O_6$ (Zn/Ta = 0.5), exhibited excellent photocatalytic activity in terms of both the formation rate of CO (902 μmol h^{-1}) and the selectivity toward CO (94 %).
Keywords Photocatalyst, Photocatalytic conversion of CO_2, Zinc tantalate

近年，地球上に豊富に存在する水を電子源とする，光触媒を用いた CO_2 の光還元に大きな注目が集まっている．我々はこれまでに，$ZnTa_2O_6$ の表面を Zn 種や Ag 助触媒で適切に修飾すると水中での CO_2 光還元活性が大きく向上することを報告した[1,2]．本研究では，$ZnTa_2O_6$ 光触媒の Zn/Ta 比を変化させた種々の光触媒に Ag と Cr を助触媒として担持し，水を電子源とする CO_2 光還元に及ぼす影響を調べた．

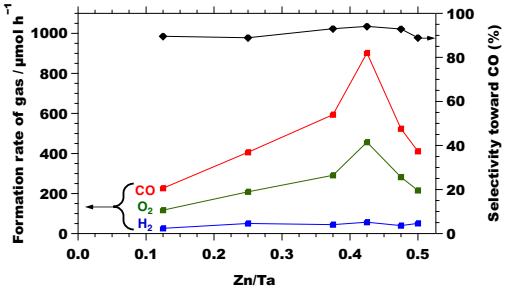

Figure 1 The activities for photocatalytic conversion of CO_2 by H_2O over $ZnTa_2O_6$ with various Zn/Ta ratio.

$ZnTa_2O_6$ は既報に従い ZnO と Ta_2O_5 を原料として固相法で合成した[3]．ZnO と Ta_2O_5 の混合比を調整し，Zn/Ta 比を 0.13～0.5 の範囲で変化させた．水を電子源とする CO_2 の光還元活性は，CO_2 流通型回分式反応装置を用いて評価した．光触媒 0.5 g を 0.1 M $NaHCO_3$ 水溶液 1.0 L に分散させ，30 mL min^{-1} の CO_2 流通下で反応管内部から 400 W 高圧水銀灯により光照射を行った．生成ガスの分析には TCD-GC 及び FID-GC を用いた．

種々の Zn/Ta 比をもつ光触媒の CO_2 光還元活性を評価したところ，CO 生成速度は Zn/Ta 比が量論比（Zn/Ta = 0.5）から減少するに伴って増大し，Zn/Ta = 0.43 を頂点とする山型の挙動を示した(Fig. 1)．Zn/Ta = 0.43 では，CO 生成速度 902 μmol h^{-1}，CO への選択率 94 %と，生成速度と選択率の両面で非常に優れた CO_2 光還元活性を示すことを見出した．化学量論組成の $ZnTa_2O_6$ (Zn/Ta = 0.5) より小さい Zn/Ta 比をもつ光触媒の X 線回折パターンには，$ZnTa_2O_6$ 相に加え，複数の Ta 酸化物に帰属される回折ピークが現れた．従って，$ZnTa_2O_6$ と Ta 酸化物の共存状態が，高い CO_2 光還元活性をもたらしていると考えられる．

1) S. Wang *et al.*, *J. Phys. Chem. C*, **2021**, *125*, 1304. 2) S. Iguchi *et al.*, *Catal. Sci. Technol.*, **2016**, *6*,4978. 3) X. Xu *et al.*, *Appl. Catal. B*, **2021**, *298*, 120508.

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
A1458(1458, Bldg. 14 [5F])

[A1458-3am] 08. Catalysts and Catalysis

Chair: Megumi Okazaki, Shoji Iguchi

English
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1458-3am-01]

Convolutional Neural Network Prediction of the photocurrent−voltage curve directly from scanning electron microscopic image for Hematite

○shinichi fujiwara[1], Yuta Hayashi[1], Yuya Nagai[1], Zhenhua Pan[1], Kenji Katayama[1] (1. Chuo Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1458-3am-02]

Arc plasma deposition for loading effective cocatalysts on water-splitting photocatalysts

○Hajime Suzuki[1], Toshiki Abe[1], Masanobu Higashi[2], Masanobu Higashi[1], Akinori Saeki[3], Ryu Abe[1] (1. Kyoto University, 2. Osaka Metropolitan University, 3. Osaka University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1458-3am-03]

Expanding visible-light absorption by bismuth substitution of perovskite layer metal species in layered oxyhalide photocatalysts

○Wataru Sato[1], Akinobu Nakada[2,3], Hajime Suzuki[2], Osamu Tomita[2], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1458-3am-04]

Flux synthesis and surface modification of an oxyiodide photocatalyst $Ba_2Bi_3Nb_2O_{11}I$ toward efficient water splitting under visible light

○Reiya Takahashi[1], Hajime Suzuki[2], Osamu Tomita[2], Akinobu Nakada[2,3], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1458-3am-05]

Development of noble-base metal composite cocatalysts for hydrogen evolution in Z-scheme water splitting systems

○Xinru Sui[1], Hajime Suzuki[2], Osamu Tomita[2], Akinobu Nakada[2,3], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate school of Eng., Kyoto Univ., 3. PRESTO/JST)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1458-3am-06]

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Z-scheme Water Splitting System Consisting of $BaTaO_2N$-Based Hydrogen Evolution Photocatalyst and Carbon-Based Electron Mediator

○LI WENPENG[1], Gu Chen[2], Hisatomi Takashi[2,3], Takata Tsuyoshi[2], Zettsu Nobuyuki [1], Domen Kazunari [2] (1. Shinshu university, 2. Research Initiative for Supra-Materials, 3. PRESTO, JST)

English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1458-3am-07]

Photocatalyst sheets employing narrow-bandgap GaN:ZnO for oxygen evolution in Z-scheme pure water splitting

○Swarnava Nandy[1], Hiroka Sandaiji[1], Natsutogi Iwasa[1], Shuji Sekimori[1], Takashi Hisatomi[1,2], Tsuyoshi Takata[1], Kazunari Domen[1,3] (1. Shinshu University, 2. PRESTO, JST, 3. The University of Tokyo)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1458-3am-08]

Synthesis of GaN:ZnO using Mg_3N_2 as a solid nitrogen source and its photocatalytic actiity

○Kosuke Ebihara[1], Shintaro Abe[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Shinshu University, 2. Graduate School of Science and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Shinshu University, 4. PRESTO, JST)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[A1458-3am-09]

Enhancement of water splitting activity of GaN:ZnO solid solutions under visible light by molten salt treatments

○Natsutogi Iwasa[1], Shintaro Abe[1], Guijun Ma[3], Takashi Hisatomi[1,2], Kazunari Domen[1] (1. Shinshu University, 2. PREST JST, 3. ShanghaiTech University)

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

Break

English
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1458-3am-10]

Non-oxide photocatalyst sheet based on metal-free conductors for Z-scheme water splitting

○Rhauane Almeida Galvao[1], Swarnava Nandy[1], Chen Gu[1], Tsuyoshi Takata[1], Takashi Hisatomi[1,2], Nobuyuki Zettsu[1], Kazunari Domen[1,3] (1. Shinshu University, 2. Presto, JST, 3. The Univ. of Tokyo)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1458-3am-11]

Synthesis and photocatalytic activity of $SrTaO_2N$ synthesized from $SrTa_2O_6$ as a starting material

○Shunya Kono[1], Takashi Hisatomi[2,3], Kazunari Domen[2] (1. Graduate School of Science and Technology, Shinshu University, 2. Research Initiative for Supra Materials , Shinshu University, 3. PRESTO, JST)

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

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[A1458-3am-12]

Synthesis of $LaTiO_2N$ Photocatalysts via Flame Spray Pyrolysis and Their Hydrogen Evolution Activity

○Mayu Inose[1,2], Shuhei Nakakura[1], Takashi Hisatomi[3], Tsuyoshi Takata[3], Kazunari Domen[3] (1. Sumitomo Metal Mining Co., Ltd., 2. Graduate School of Medicine, Science and Technology, 3. Research Initiative for Supra-Materials, Shinshu University)

Japanese

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

[A1458-3am-13]

Study on synthesis conditions and water splitting activity of gallium nitride prepared from sulfides

○Atsuto Terui[1], Shintaro Abe[2], Takashi Hisatomi[3,4], Kazunari Domen[3] (1. Department of Materials Chemistry, Faculty of Engineering, Shinshu University, 2. Department of Engineering, Graduated School of Science and Technology, Shinshu University, 3. Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4. PRESTO, JST)

Japanese

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

[A1458-3am-14]

Metal cation doping of $Y_2Ti_2O_5S_2$ photocatalytic particles intended for improvement of water splitting activity

○Riku Kumemoto[1], Yosuke Kageshima[1], Katsuya Teshima[1], Kazunari Domen[2], Hiromasa Nishikiori[1] (1. Shinshu University, 2. Tokyo University)

Japanese

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

[A1458-3am-15]

Preparation of $SrTiO_3$ particulate photoelectrodes intended for application to impedance analysis

○Yusuke Sasai[1], Yousuke Kagesima[1], Katuya Tesima[1], Kazunari Doumen[2], Hiromasa Nisikiori[1] (1. Shinshu University, 2. The University of Tokyo)

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Convolutional Neural Network Prediction of the Photocurrent−Voltage Curve directly from Scanning Electron Microscopic image for Hematite

(*Chuo University*) ○Shinichi Fujiwara, Yuta Hayashi, Yuya Nagai, Zhenhua Pan, Kenji Katayama

Keywords: CNN, Hematite

In the race for efficient and sustainable energy conversion, the development of high-performance photocatalytic devices holds great promise. The photoanodes are usually characterized by the photocurrent density vs applied voltage (J−V) curve, providing insights into their physical properties. In our previous study, using convolutional neural network (CNN), from dozens of $BiVO_4$'s scanning electron microscopy (SEM) images, we succeeded in predicting J−V curves with the match ratio for the curve agreement, 98.9%.[1] In this study, we applied this method for hematite photoanodes, another popular material as a photocatalyst.

We prepared 33 hematite photoanodes, and they were measured with SEM in various magnifications and two different modes (secondary electron image (SEI), backscattered electron image (BEI)). We used the SEM images as an input data and J−V curves (11 points in the range of 0.5−1,5 V) were predicted as an output data using the CNN network function. To increase the input data for the CNN, we cut a single SEM image into 12 images. We examined different magnification and mode data of the SEM images. By investigating the best prediction ratio, a combination of BEI and SEI with the magnification of 4000 provided the best prediction. The model achieved 99.3% curve match ratio. This result indicates that the methodology is applicable for many photocatalytic materials.

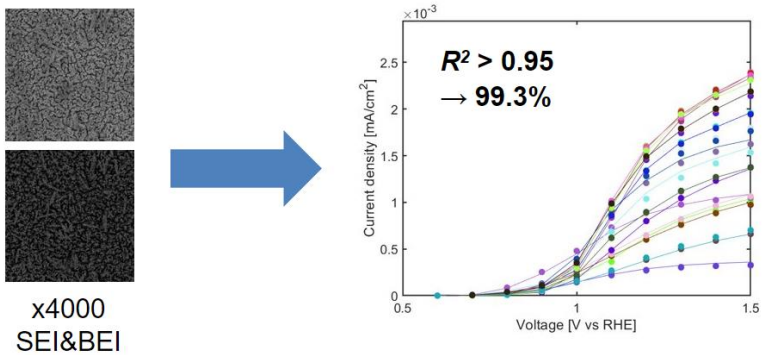

Figure Overview of the result. The SEM images (x4000, SEI and BEI) show 99.3% prediction accuracy.

[1] Y. Hayashi et al, *Journal of Materials Chemistry A*,**2023**,11,22522-22532

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アークプラズマ助触媒担持による水分解用光触媒の高活性化

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Arc plasma deposition for loading effective cocatalysts on water-splitting photocatalysts ([1]*Graduate School of Engineering, Kyoto University,* [2]*Osaka Metropolitan University,* [3]*Graduate School of Engineering, Osaka University*) ○ Hajime Suzuki,[1] Toshiki Abe,[1] Masanobu Higashi,[2] Osamu Tomita,[1] Akinori Saeki,[3] Ryu Abe[1]

Loading cocatalysts is known as an effective strategy for promoting photocatalytic reactions such as water splitting. Herein, arc plasma deposition (APD) method[1)] was applied to develop highly active photocatalyst materials for H_2 production from water via loading highly dispersed cocatalyst nanoparticles with almost uniformed size on semiconductors such as TiO_2 and TaON. We revealed that highly dispersed and similar sized Pt species nanoparticles could successfully be loaded on the photocatalysts by APD method under various atmosphere (i.e., under low-pressure gases flow such as H_2, O_2, and Ar), not only under conventional high vacuum, and that the gas component significantly affected the chemical state and particle size of Pt species deposited and thereby the resulting photocatalytic activity.
Keywords : photocatalyst, water splitting, arc plasma method, cocatalyst, nanoparticle

光触媒の高効率化において半導体上に助触媒を担持させることは最も効果的な戦略の一つである。助触媒の担持法としてはこれまで、含浸法や光析出法が一般的に用いられてきた。一方で、含浸法では担持後に熱処理が必要であること、光析出法では光触媒担体が前駆体を還元または酸化し得るバンドレベルを有する必要があることなどから、光触媒担体や担持金属種にはいくらか制限があった。一方、アークプラズマ蒸着（APD）法[1)]は、熱処理を必要とせず、あらゆる粉末光触媒粒子に種々の助触媒担持が可能であると考えられるが、その有効性は明らかになっていなかった。

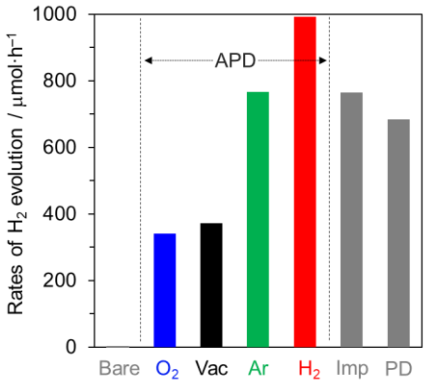

Fig. 1. Rates of H_2 evolution over Pt-TiO_2 prepared by various methods: APD, impregnation (Imp), and photodeposition (PD) from aqueous MeOH solution under UV light (λ > 300 nm). The APD was carried out under vacuum (Vac) and gases (O_2, Ar, H_2) flow.

本研究では、APD 法により、TiO_2 および TaON 光触媒上へ Pt 種を担持し、その水素生成活性を評価した。チャンバー雰囲気を制御して APD 法により TiO_2 上へ Pt 種を担持したところ、水素雰囲気下で担持した試料が最も高い水素生成活性を示した（Fig. 1）。種々の測定から、水素雰囲気下で担持することにより 0 価に近い粒径数 nm の Pt 種が担持され、効果的に電子を捕捉することで高い水素生成活性を示すことが明らかとなった。更に、従来の含浸法および光析出法を用いて Pt 種を担持した試料と比較しても同等以上の水素生成速度を示した。この手法を酸窒化物光触媒 TaON に適応したところ、TiO_2 系と同様の傾向が得られ、APD 法が助触媒担持法として有用であることが示された。

1) S. Hinokuma, S. Misumi, H. Yoshida, M. Machida, *Catal. Sci. Technol.* **2015**, *5*, 4249-4257.

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層状酸ハロゲン化物光触媒におけるペロブスカイト層金属種の Bi 置換による可視光吸収拡張

（京大工[1]・京大院工[2]・JST さきがけ[3]）○佐藤 航[1]・中田 明伸[2,3]・鈴木 肇[2]・冨田 修[2]・阿部 竜[2]

Expanding Visible-Light Absorption by Bismuth Substitution of Perovskite Layer Metal Species in Layered Oxyhalide Photocatalysts ([1]*Fac. of Eng., Kyoto Univ.*, [2]*Grad. Sch. of Eng., Kyoto Univ.*, [3]*PRESTO/JST*) ○Wataru Sato,[1] Akinobu Nakada,[2,3] Hajime Suzuki,[2] Osamu Tomita,[2] Ryu Abe[2]

Development of photocatalyst materials that can utilize wide range of visible light for water splitting is important toward achieving practical solar hydrogen production. Layered oxyhalides have attracted much attention as photocatalysts because of their high photostability, visible light responsibility, and suitable band position due to their unique band structures. In this study, we demonstrate the expansion of visible-light absorption of layered oxyhalide photocatalysts by replacing the metal species of the perovskite pentavalent metals with bismuth.
Keywords : Photocatalyst; Water splitting; Perovskite; Oxyhalide; Bismuth

太陽光水素製造の効率向上に向けて、長波長まで幅広い可視光を利用できる光触媒材料の開発が望まれている。半導体光触媒の可視光吸収帯の拡張戦略として、アニオン変調による価電子帯制御[1)]や、遷移金属由来のバンド間準位形成[2)]などが主に適用されてきた。さらに近年我々は、ビスマス系層状酸ハロゲン化物群が、その特異なバンド構造に起因する可視光吸収能と高い光安定性を兼備する光触媒として機能することを報告している[3)]。本研究では、層状酸ハロゲン化物光触媒のペロブスカイト層を構成する 5 価金属種をさらにビスマスに置換する手法により、可視光吸収帯を拡張できることを見出した。

Sillén-Aurivillius 型酸ハロゲン化物 $A_2Bi_3M_2O_{11}Cl$ (Fig. 1a; A = Sr, Ba, M = Ta, Nb) の 5 価の金属カチオン種 M^{5+}をビスマスに置換した新規化合物 $A_2Bi_{3+x}M_{2-x}O_{11}Cl$ の合成は、前駆体 $ABi_{2+x}M_{2-x}O_9$ を経由する二段階合成法により行った[3b)]。得られたビスマス置換体は、親化合物 $A_2Bi_3M_2O_{11}Cl$ に対して吸収端が長波長化し (Fig. 1b)、Ag^+や Fe^{3+}を電子受容体とする可視光 O_2 生成を進行する光触媒として機能した。

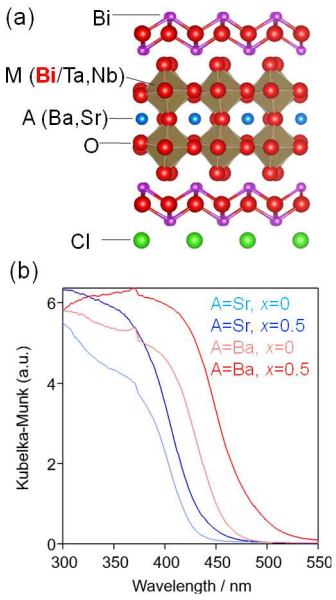

Fig. 1 (a) Crystal structure and (b) UV-vis diffuse reflectance spectra of $A_2Bi_{3+x}Ta_{2-x}O_{11}Cl$.

1) Kageyama, H.; Maeda, K. *et al*., *Nat. Commun*. **2018**, *9*, 772.
2) Kudo, A. *et al*., *Chem. Soc. Rev.* **2009,** *38*, 253.
3) a) Fujito, H.; Abe, R. *et al*., *J. Am. Chem. Soc.* **2016,** *138*, 2082. b) Nakada, A.; Abe, R. *et al., Chem. Mater*. **2019**, *31*, 3419.

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高効率可視光水分解を目的とした酸ヨウ化物光触媒 $Ba_2Bi_3Nb_2O_{11}I$ のフラックス合成と表面修飾

(京大工[1]・京大院工[2]・JST さきがけ[3]) ○高橋 怜也[1]・鈴木 肇[2]・冨田 修[2]・中田 明伸[2,3]・阿部 竜[2]

Flux synthesis and surface modification of an oxyiodide photocatalyst $Ba_2Bi_3Nb_2O_{11}I$ toward efficient water splitting under visible light ([1]*Fac. of Eng., Kyoto Univ.,* [2]*Grad. Sch. of Eng., Kyoto Univ.,* [3]*PRESTO/JST*) ○Reiya Takahashi,[1] Hajime Suzuki,[2] Osamu Tomita,[2] Akinobu Nakada,[2,3] Ryu Abe[2]

We have recently revealed that various layered oxyhalides are promising photocatalysts for visible-light-driven water splitting. Among them, Sillén-Aurivillius-type oxyiodides such as $Ba_2Bi_3Nb_2O_{11}I$ (BBNOI) can absorb a wider range of visible light than its chloride counterparts and function as efficient O_2 evolution photocatalysts[1)]. In this study, we prepared BBNOI via flux method and modified it with cocatalysts to enhance the photocatalytic performance. The BBNOI sample prepared via flux method showed a higher O_2 evolution activity than that prepared via solid state reaction (SSR).

Keywords : Photocatalyst; Water splitting; Layered oxyhalide, Flux synthesis; Cocatalyst

当研究室ではこれまでに、種々の層状酸ハロゲン化物が可視光水分解用光触媒として有望であることを見出してきた。なかでも最近、$Ba_2Bi_3Nb_2O_{11}I$ (BBNOI, Fig. 1a)をはじめとする Sillén-Aurivillius 型酸ヨウ化物が、従来の塩素体と比べてバンドギャップが小さく、長波長までの可視光利用が可能であるとともに、高い酸素生成活性を示すこと、さらには Z スキーム水分解系の安定な酸素生成用光触媒として機能することを明らかにした[1)]。本研究では、酸ヨウ化物群の更なる高性能化を目的として、BBNOI のフラックス合成と表面修飾に取り組んだ。ヨウ化物系溶融塩を用いて合成条件を精査することで、単相の BBNOI 板状粒子を得ることに成功した(Fig. 1b)。このフラックス合成で得られた BBNOI 試料は、従来の固相法により合成した試料に比べて、電子受容体 Ag^+の存在下で 10 倍以上高い可視光酸素生成活性を示した。これはフラックス合成により、粗大化・凝集することなく、高結晶性の BBNOI 粒子が得られたためと考えられる。さらに適切な条件で表面修飾を行うことで、Fe^{3+}を電子受容体とする酸素生成反応においても、固相法試料に比べて高い酸素生成活性を示した。

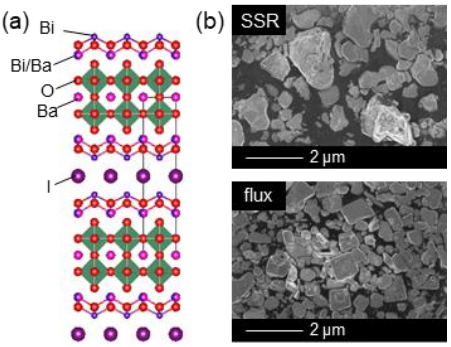

Fig. 1. (a) Crystal structure of BBNOI (b) SEM images of BBNOI prepared via solid state reaction (SSR) and flux method

1) K. Ogawa, H. Suzuki, C. Zhong, R. Sakamoto, O. Tomita, A. Saeki, H. Kageyama, R. Abe, *J. Am. Chem. Soc.* **2021**, *143*, 8446−8453.

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Z-スキーム水分解系の高効率化を目的とした貴-卑金属複合型水素生成用助触媒の開発

（京大工[1]・京大院工[2]・JST さきがけ[3]）○SUI XINRU[1]・鈴木 肇[2]・冨田 修[2]・中田 明伸[2,3]・阿部 竜[2]

Development of noble-base metal composite cocatalysts for hydrogen evolution in Z-scheme water splitting systems ([1]*Fac. of Eng., Kyoto Univ.,* [2]*Grad. Sch. of Eng., Kyoto Univ.,* [3]*PRESTO/JST*) ○Xinru Sui,[1] Hajime Suzuki,[2] Osamu Tomita,[2] Akinobu Nakada,[2,3] Ryu Abe[2]

Z-scheme water splitting system has been extensively studied as a promising technology for solar hydrogen production. Developing effective cocatalysts that can suppress various backward reactions, such as water formation from hydrogen and oxygen and reverse electron transfer to the redox couples, is indispensable for improving total efficiency. In this study, we attempted to develop noble metal-base metal composite cocatalysts that simultaneously possess the ability to suppress the backward reactions and the high activities for water reduction. CrO_x species were modified on the Pt-loaded $SrTiO_3$:Rh[1)] photocatalyst via photodeposition method using different precursors K_2CrO_4 and $CrCl_3$. The Cr species-loaded samples showed a higher photocatalytic H_2 evolution activity from aqueous NaI solution than Pt-$SrTiO_3$:Rh; especially, the use of $CrCl_3$ was more effective than that of conventional precursor K_2CrO_4.

Keywords : Photocatalyst; Z-scheme water splitting; Cocatalyst; Backward reaction

太陽光水素製造を目的として、可視光を有効に利用可能な Z-スキーム水分解系の高効率化が盛んに研究されている。本系は、２種類の異なる光触媒とその間の電子伝達を担うレドックス対により構成され、様々な光触媒が適用可能であることに加え、利用波長の長波長化も比較的容易である。高効率水分解の実証のためには、水素と酸素からの水の生成や、レドックス対への逆電子移動、といった様々な逆反応を抑制しながら、同時に正反応を促進可能な助触媒の担持が必要となる。本研究では、これら種々の逆反応を抑制し、水の還元に高い活性と選択性を示す貴金属/クロム種複合型水素生成用助触媒の開発に取り組んだ。Pt を担持した Rh ドープ $SrTiO_3$ ($SrTiO_3$:Rh)[1)]上へ、二種類の Cr 種前駆体 K_2CrO_4、$CrCl_3$ を用いて CrO_x を光析出したところ、通常用いられる６価 Cr 前駆体 K_2CrO_4[2)]よりも、３価 Cr 前駆体 $CrCl_3$ を用いた場合に、I^-を電子供与体とする可視光水素生成に高い活性を示した（Fig. 1）。種々の検討により、いずれの前駆体を用いて CrO_x を担持した場合にも、レドックス種への逆電子移動（IO_3^-の再還元）と水素と酸素からの水の生成が効果的に抑制されることが明らかとなった。当日の発表では、$CrCl_3$ 前駆体を用いた際に高い活性を示した要因についても議論する。

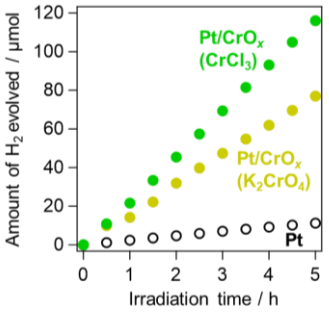

Fig. 1. H_2 evolution over Pt- or Pt/CrO_x-loaded $SrTiO_3$:Rh from NaI aq. under visible light (λ > 400 nm). Two different Cr species precursors (K_2CrO_4 and $CrCl_3$) were used.

1) R. Konta, A. Kudo *et al.*, *J. Phys. Chem. B* **2004**, *108*, 8992.
2) K. Maeda, K. Domen *et al.*, *Angew. Chem. Int. Ed.* **2006**, *45*, 7806.

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Z-scheme Water Splitting System Consisting of $BaTaO_2N$-Based Hydrogen Evolution Photocatalyst and Carbon-Based Electron Mediator

([1]*Graduate School of Medicine, Science and Technology, Shinshu University*, [2]*Research Initiative for Supra-Materials, Shinshu University*, [3]*PRESTO, JST*, [4]*Department of Materials Chemistry, Shinshu University*) ○Wenpeng Li,[1] Chen Gu,[2] Takashi Hisatomi,[2,3] Tsuyoshi Takata,[2] Nobuyuki Zettsu,[4] Kazunari Domen[2]

Keywords: *Oxynitride, Visible light, Electron transfer*

Efficient charge transfer between the hydrogen evolution photocatalyst and oxygen evolution photocatalyst is a crucial factor in realizing efficient Z-scheme water splitting for hydrogen production.[1] Carbon nanotubes (CNTs) are considered as promising electron transport mediators applicable to construct Z-scheme photocatalytic systems due to their high physicochemical stability and high axial electron mobility.[2] In this study, we designed a Z-scheme water splitting system free from homogeneous electron mediators by utilizing CNTs as a solid electron mediator. Factors governing the activity and stability of the Z-scheme system were investigated.

$BaTaO_2N$:Zr and $BiVO_4$ were employed as a hydrogen evolution photocatalyst and an oxygen evolution photocatalyst, respectively. $BaTaO_2N$:Zr was synthesized by molten salt-assisted one-step nitridation and subsequently loaded with a Cr_2O_3-coated Pt cocatalyst.[1] $BiVO_4$ was prepared via a hydrothermal method and loaded with a $FeCoO_x$/Ir cocatalyst.[3] CNTs employed as electron transfer mediators were added to a reaction suspension or loaded onto the surface of $BiVO_4$ through photodeposition method.

In the absence of CNTs, only a small amount of H_2 was evolved due to the lack of an electron transfer path from the $BiVO_4$ to $BaTaO_2N$:Zr, as illustrated in Fig. 1. The addition of CNTs facilitated electron transfer between $BaTaO_2N$:Zr and $BiVO_4$, enabling Z-scheme water splitting. The photoreduction of CNTs onto $BiVO_4$ effectively improved the contact between the components, inducing a six-fold increase in the water splitting activity. This is presumably because the CNTs were more preferentially loaded on the reductive crystal faces in $BiVO_4$, thereby extracting electrons from $BiVO_4$ and transferring them more effectively to $BaTaO_2N$:Zr.

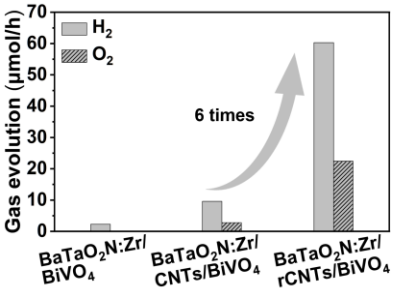

Figure 1. Z-scheme water splitting activity of the $BaTaO_2N$:Zr-$BiVO_4$ system modified with CNTs.

1) Li, W. *et al., J. Catal.* **2023**, 428, 115187. 2) Xu, Y. *et al.*, *Chem. Soc. Rev.* **2016**, *45*, 3039. 3) Qi *et al., Nat. Commun.* **2022**, 13, 484.

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Photocatalyst sheets employing narrow-bandgap GaN:ZnO for oxygen evolution in Z-scheme pure water splitting

([1]*Shinshu University,* [2]*PRESTO, JST,* [3]*The University of Tokyo*) ○Swarnava Nandy,[1] Hiroka Sandaiji,[1] Natsutogi Iwasa,[1] Shuji Sekimori,[1] Takashi Hisatomi,[1,2] Tsuyoshi Takata,[1] Kazunari Domen[1,3]

Keywords: Oxynitride; Visible light; Hydrogen production, Particle transfer

Improving the solar-to-hydrogen energy conversion efficiency (STH) of the photocatalytic water splitting reaction beyond 5% is a critical concern behind the commercialization of renewable hydrogen.[1] Some Z-scheme photocatalyst sheets, comprising particulate photocatalysts rigidly embedded on a conductive layer, can efficiently split water while maintaining performance despite scaling up. A STH of 0.41% was achieved by Z-scheme overall water splitting (ZOWS) under atmospheric pressure using a sheet composed of Mg, Al-codoped $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ (LTCA), Mo-doped $BiVO_4$ (BVO:Mo) and a gold as the hydrogen evolution photocatalyst (HEP), the oxygen evolution photocatalyst (OEP), and the conductive layer, respectively.[2] However, due to the use of BVO:Mo, the photocatalyst sheet could only utilize visible light with wavelengths of up to 520 nm. To achieve potentially higher STH, it is important to replace BVO:Mo with OEPs with n-type semiconductor character and narrower band gap.

In this study, we show that photocatalyst sheets composed of doped-LTCA, GaN:ZnO solid solution and Au (denoted as LTCA/Au/GaN:ZnO) as the HEP, OEP, and conductive layer, respectively, and coloaded with cocatalysts split water at a STH of 0.15% at 5 kPa. Notably, the photocatalytic activity of the sheet was further improved by 1.7 times by sequential deposition of high and low work function metal layers (Figure 1). This improvement is due to the reduction of energy barriers at the interface with the conductive layer, which enhanced the recombination of holes from the HEP and electrons from the OEP. The STH was found to be an order of magnitude higher than the previously studied LTCA:Ga/Au/$LaTiO_2N$[3] and $SrTiO_3$:Rh/$Fe^{3+/2+}$/GaN:ZnO[4] systems employing oxynitrides as OEP.

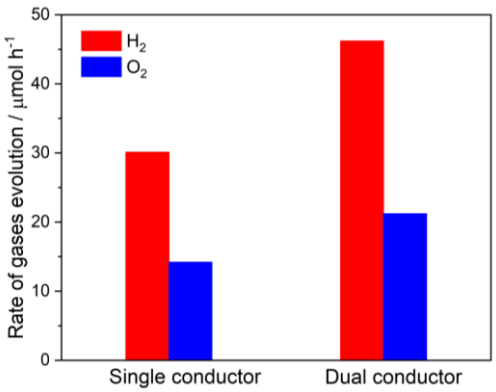

Figure 1. ZOWS activity of LTCA/Au/GaN:ZnO photocatalyst sheets with single and dual conductor layers under visible light irradiation (λ > 420 nm) at 5 kPa and 283 K.

1) Hisatomi *et al. Nat. Catal.* **2019**, *2*, 387. 2) Nandy et al. *Joule*. **2023**, *7*, 1641. 3) Hisatomi *et al. Catal. Sci. Technol.* **2018**, *8*, 3918. 4) Liu *et al. ACS Catal.* **2022**, *12*, 14637.

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Mg_3N_2を窒素源とするGaN:ZnOの合成と光触媒活性

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Synthesis of GaN:ZnO using Mg_3N_2 as a solid nitrogen source and its photocatalytic activity

([1] *Faculty of Engineering, Shinshu University*, [2] *Graduate School of Science and Technology, Shinshu University*, [3] *Research Initiative for Supra Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University*, [4] *PRESTO, JST)*
○Kosuke Ebihara,[1] Shintaro Abe,[2] Takashi Hisatomi,[3,4] Kazunari Domen[3]

GaN:ZnO was synthesized in sealed evacuated tubes using various ratios of Zn_3N_2 and Mg_3N_2 as nitriding sources, and the composition and water splitting activity of the products were investigated. The Zn/Ga ratio of the obtained GaN:ZnO decreased with increasing the ratio of Mg_3N_2 used, and the absorption edge wavelength was shortened accordingly. The GaN:ZnO prepared with a Zn_3N_2/Mg_3N_2 ratio of 1:1 exhibited the highest water splitting activity when loaded with cocatalysts.

Keywords: Oxynitride, Sealed evaluated tube, Composition control

GaN:ZnO 固溶体はウルツ鉱型の酸窒化物であり、その吸収端は ZnO 含有量によって変化する。真空封管中で原料を反応させることにより ZnO 含有量が高く高結晶性の長波長応答型 GaN:ZnO を合成することができることが 2022 年に報告された[1)]。本研究では出発原料として窒素源となる Zn_3N_2 と Mg_3N_2 を様々な比率で用いて GaN:ZnO を合成し、組成、吸収端波長及び水分解活性への影響を検討した。

Ga_2O_3、Zn_3N_2、Mg_3N_2、$ZnCl_2$ の混合物を真空封管中で焼成し、生成物を洗浄した。Zn_3N_2 と Mg_3N_2 のモル比は 4:0, 3:1, 2:2, 1:3, 0:4 と変化させた。生成物に助触媒を共担持して可視光水分解活性を計測した。いずれの条件でも GaN:ZnO が単相で生成した。EDS を用いて Zn/Ga 比を測定すると、窒素源として用いる Mg_3N_2 の比率が高くなるとともに低下し、それに伴い吸収波長も短波長化した（図 1)。従って、窒素源の組成に応じて吸収端波長を制御できることがわかった。

各種後処理の後、酸素生成助触媒、水素生成助触媒を担持すると、GaN:ZnO は水分解活性を示した。水分解活性は窒素源の組成に依存し、Zn_3N_2 と Mg_3N_2 を 1:1、1:3 で用いた時に特に見られ、1:1 の時最大となった。

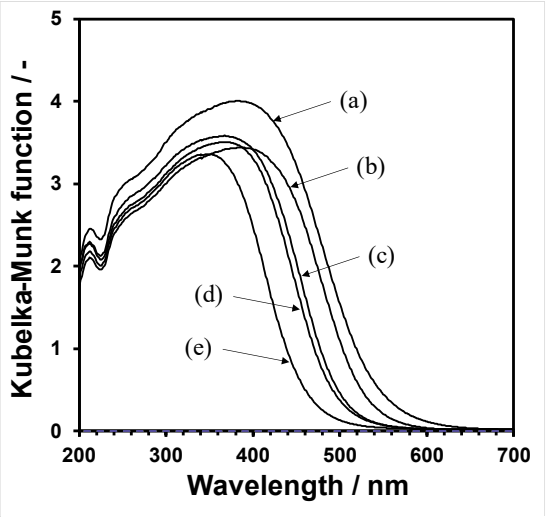

図 1 GaN:ZnO の拡散反射スペクトル Zn_3N_2:Mg_3N_2 比 (a) 4:0、(b) 3:1、(c) 2:2、(d) 1;3、(e) 0:4

1) Liu et al., *ACS* Catal., 2022, 12, 14637

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GaN:ZnO 固溶体の溶融塩処理による可視光水分解活性の向上

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Enhancement of water splitting activity of GaN:ZnO solid solutions under visible light by molten salt treatments

([1]*Shinshu University*, [2]*ShanghaiTech University*, [3]*JST-PRESTO*) ○ Natsutogi Iwasa,[1] Ma Guijun,[2] Takashi Hisatomi,[1,3] Kazunari Domen,[1]

Treatment of ZnO-rich GaN:ZnO solid solutions with molten salts containing $MgCl_2$ in sealed evacuated tubes was found to improve the water splitting activity under visible light. The absorption edge was shifted to shorter wavelengths by the molten salt treatment due to the decrease in ZnO content. By investigating the treatment conditions, it was suggested that the water splitting activity depended not only on the absorption edge wavelength, but also on the crystallinity and surface properties of GaN:ZnO after the molten salt treatments.

Keywords: oxynitride, sealed evacuated tube, solid nitrogen source

Zn_3N_2 を固体窒素源とした真空封管加熱によって、ZnO 濃度が高く長波長の可視光まで吸収可能な GaN:ZnO が合成可能である。このような手法で得られる GaN:ZnO は、犠牲剤存在下での酸素生成反応に優れた外部量子効率（波長 420 nm で 14.4%）を示す一方で、水素生成反応や水分解反応に対する活性は低かった[1)]。本研究では、真空封管中での溶融塩処理により GaN:ZnO の光触媒活性を向上させることを試みた。

出発原料として非晶質 Ga_2O_3、Zn_3N_2、ZnI_2、Zn を混合し、真空封管中で加熱することで 600 nm 付近まで可視光吸収する GaN:ZnO を得た。得られた GaN:ZnO を $MgCl_2$ 及び $BaCl_2$ と混合して真空封管加熱すると、吸収端が短波長化された。溶融塩処理によって回折ピークが高角度側（GaN 側）へシフトしたことから、ZnO 含有量の低下が示唆された。これは $MgCl_2$ が GaN:ZnO 中の ZnO 成分と反応して MgO となる一方、ZnO は $ZnCl_2$ として固溶体から排出されたためだと考えられる。

未処理の GaN:ZnO は助触媒を担持しても水分解活性を示さなかったが、溶融塩処理により水分解活性が発現した（図 1）。また、処理条件を変えると、吸収端波長はほとんど同じであるにもかかわらず、水分解活性が変化する場合がみられた。このことは、吸収端波長だけでなく結晶性や表面状態も GaN:ZnO の光触媒活性に影響していることを示唆しており、溶融塩処理条件を制御することで吸収端波長を維持したまま水分解活性を向上させることができると考えられる。

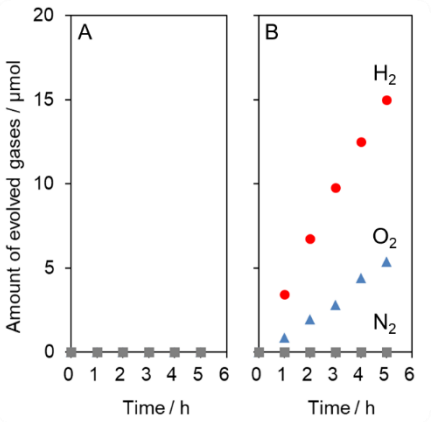

図 1 溶融塩処理前後の GaN:ZnO の可視光水分解活性、(A) 処理前、(B) 処理後

1) 三大寺ら、日本化学会第 103 回春季年会、P2-2nv-13 (2023)

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Non-oxide photocatalyst sheet based on metal-free conductors for Z-scheme water splitting

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Keywords: Oxynitride; Oxysulfide; Carbon; Charge transfer; Visible light

Z-scheme photocatalyst sheets based on an oxygen evolution photocatalyst (OEP) and a hydrogen evolution photocatalyst (HEP) immobilized on a conductive layer have been fabricated by the particle transfer (PT) method involving vacuum processes.[1] However, since it is challenging to apply this method on a large scale, it is desirable to develop a method for fabricating photocatalyst sheets without vacuum processes. In this work, we investigated a carbon nanotube (CNT) thin film supported on a porous membrane as a conductive layer for application to Z-scheme photocatalyst sheets.

$SrTaO_2N$ (STON) prepared by a flux method and doped $La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ (LTCA) prepared by a solid-state reaction were used as OEP and HEP, respectively. Prior to the sheet fabrication, CoO_x and TiN nanoparticles were loaded on STON, while Rh was loaded on LTCA. CNT was added to a solution containing the STON and LTCA just prior to the deposition onto a membrane, which is referred to as CNT_{sol}. In some experiments, CNT was also loaded onto the STON and LTCA, denoted as CNT_{STON} and CNT_{LTCA}, respectively. The resultant photocatalyst sheet was used for water splitting after photodeposition of Cr_2O_3.

Table 1. Dependence of the water splitting activity of the photocatalyst sheets on the CNT addition methods.

CNT_{STON}	CNT_{LTCA}	CNT_{sol}	H_2 (μmol h^{-1})	O_2 (μmol h^{-1})
		○	2.8	1.2
○		○	5.1	2.3
○			0.4	0.2
○	○		0.8	0.2
○	○	○	2.8	1.4

Table 1 shows the H_2 and O_2 evolution rates of the photocatalyst sheets with the different CNT addition methods. CNT_{sol} was essential for achieving a reasonable water splitting activity. Addition of CNT_{STON} could improve the activity, whereas CNT_{LTCA} was not effective. The water splitting activity was improved by changing the loading conditions of CNT at different steps of the fabrication of the STON photocatalyst and the resultant sheets. This work suggests that CNT is applicable as a conductive layer alternative to Au for the facile fabrication of large photocatalyst sheets for Z-scheme water splitting.

1 S. Nandy, T. Hisatomi, M. Nakabayashi, H. Li, X. Wang, N. Shibata, T. Takata, K. Domen, *Joule* **2023**, *7*, 1641.

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$SrTa_2O_6$を出発原料とする$SrTaO_2N$の合成と光触媒活性

(信大院工[1]、信大先鋭材料研[2]、JST さきがけ[3])○河野 駿哉[1]・久富 隆史[2,3]・堂免 一成[3]

Synthesis and photocatalytic activity of $SrTaO_2N$ synthesized from $SrTa_2O_6$ as a starting material ([1]*Graduate School of Science and Technology, Shinshu University,* [2]*Research Initiative for Supra-Materials, Shinshu University,* [3]*PRESTO, JST*) ○Shunya Kono,[1] Takashi Hisatomi,[2,3] Kazunari Domen[3]

$SrTaO_2N$ was nitrided from $SrTa_2O_6$ in the presence of NaOH-$SrCl_2$ flux and its photocatalytic activity was investigated. The $SrTaO_2N$ synthesized from $SrTa_2O_6$ had higher crystallinity than $SrTaO_2N$ synthesized from $Sr_2Ta_2O_7$ or $Sr_5Ta_4O_{15}$ and exhibited higher hydrogen evolution activity under visible light from aqueous methanol solution.

Keywords: oxynitride, precursor, hydrogen evolution, oxygen evolution

$SrTaO_2N$ はペロブスカイト構造を有する可視光応答性酸窒化物であり、2023 年に出発原料から炭酸塩を排除することで可視光水分解反応に活性な $SrTaO_2N$ が得られることが報告された [1)]。炭酸塩を出発原料とした場合には中間体として $Sr_2Ta_2O_7$ や $Sr_5Ta_4O_{15}$ が生成していたが、炭酸塩を用いなかった場合には $SrTa_2O_6$ が生成していることがわかった [2)]。そこで本研究では、$SrTa_2O_6$ を出発原料として $SrTaO_2N$ を合成し、光触媒活性を検討した。

$SrTa_2O_6$ は Ta_2O_5、NaOH、$SrCl_2$ の混合物を空気中で加熱することで合成した。得られた $SrTa_2O_6$ は単相であり、長軸径が 5 μm 以上の板状粒子が観察された。得られた $SrTa_2O_6$ を NaOH−$SrCl_2$ フラックス存在下で窒化した。比較のため、$Sr_2Ta_2O_7$ 及び $Sr_5Ta_4O_{15}$ を窒化して $SrTaO_2N$ を合成した。$SrTaO_2N$ は Pt 担持後にメタノール水溶液からの可視光水素生成活性を計測した。

$SrTa_2O_6$ から合成した $SrTaO_2N$ は粒径が 100-200 nm 程度であり、XRD 半値幅からは $Sr_2Ta_2O_7$ 及び $Sr_5Ta_4O_{15}$ から合成した $SrTaO_2N$ よりも結晶性が高いことがわかった。図 1 に各種 $SrTaO_2N$ 試料の水素生成活性を示す。出発物質として $SrTa_2O_6$ を用いた場合に最も高い水素生成活性を示し、高い結晶性が活性向上に寄与したと考えられる。また、活性はフラックスとして用いる $SrCl_2$ の量にも依存し、$SrCl_2$ 量が少ない方が高くなる傾向がみられた。

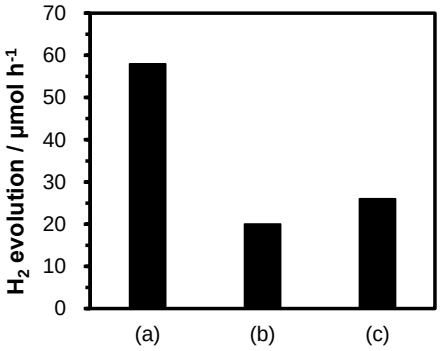

図 1 Pt/$SrTaO_2N$ の水素生成活性。出発物質：(a) $SrTa_2O_6$, (b) $Sr_2Ta_2O_7$, (c) $Sr_5Ta_4O_{15}$.

1) Chen *et al. J. Am. Chem. Soc.* **2023**, *145*, 3839.
2) 河野ら，第 132 回触媒討論会，1P07，(2023)

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火炎噴霧法を経由した $LaTiO_2N$ 光触媒の合成と水素生成活性

（住友金属鉱山（株）[1]・信大院総合医理工[2]・信大先鋭材料研[3]）
○猪瀬 真由[1,2]・中倉 修平[1]・久富 隆史[3]・高田 剛[3]・堂免 一成[3]

Synthesis of $LaTiO_2N$ Photocatalysts via Flame Spray Pyrolysis and Their Hydrogen Evolution Activity

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○Mayu Inose,[1,2] Shuhei Nakakura,[1] Takashi Hisatomi,[3] Tsuyoshi Takata,[3] Kazunari Domen[3]

$LaTiO_2N$ with a perovskite-type structure is a photocatalyst capable of absorbing visible light up to 600 nm. However, the hydrogen evolution activity of $LaTiO_2N$ photocatalysts was low due to carrier recombination, which limited their utility as water splitting photocatalysts. This work focused on the synthesis of $LaTiO_2N$ photocatalysts via flame spray pyrolysis (FSP) and their hydrogen evolution activity. The obtained LaTi oxide precursors utilizing rapid quenching of FSP were a mixture of perovskite-type LaTi oxide and $La_2Ti_2O_7$. The peak intensity of the perovskite-type LaTi oxide was increased by doping Al. The perovskite-type $LaTiO_2N$, which was obtained by heating under a flow of ammonia, loaded with Ru and IrO_x cocatalysts exhibited hydrogen evolution activity.

Keywords : Oxynitride; Visible light; Rapid quenching

$LaTiO_2N$ はペロブスカイト型構造を有し、600 nm までの可視光を吸収できる光触媒である[1)]。しかし、結晶内部での構造欠陥によりキャリア再結合が起こるため、$LaTiO_2N$ の水素生成活性は乏しく、水分解用光触媒としての利用が限られてきた。本研究では、火炎噴霧法を経由して Al ドープ $LaTiO_2N$ 光触媒を合成し、その水素生成活性を検討した。

LaTi 酸化物前駆体粒子の合成には、火炎噴霧法の急冷プロセスを利用した。通常固相法等により合成される $La_2Ti_2O_7$ と特異なペロブスカイト型酸化物が生成した（図 1(a)）。Al ドープにより、ペロブスカイト型酸化物のピーク強度は増大する一方、$La_2Ti_2O_7$ のピーク強度は減少した（図 1(b)）。得られた LaTi 酸化物前駆体粒子をアンモニア気流中で焼成すると、いずれも単相の $LaTiO_2N$ が生成した。ペロブスカイト型酸化物と $LaTiO_2N$ は結晶構造が類似することから、窒化時の構造変化が小さく、結晶中の欠陥形成が抑制されたと考えられる。得られた $LaTaO_2N$ は、助触媒として Ru や IrO_x を担持すると、水素生成活性を示した。

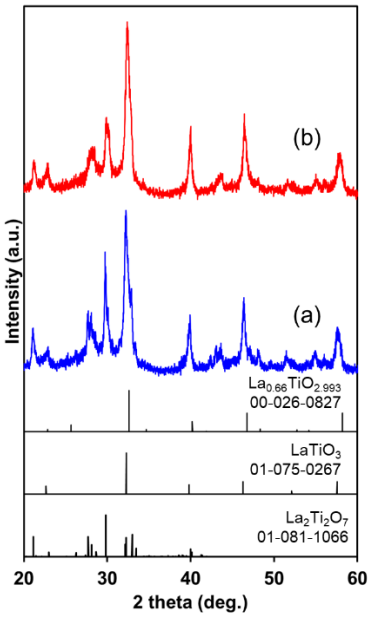

図 1. LaTi 酸化物前駆体の XRD パターン
(a) 未ドープ試料
(b) Al ドープ試料

1) A. Kasahara *et al.*, *J. Phys. Chem. A* **2002**, *106*, 6750-6753.

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硫化物を出発原料とする窒化ガリウムの合成条件と水分解活性の検討

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Study on synthesis conditions and water splitting activity of gallium nitride prepared from sulfides ([1]*Department of Materials Chemistry, Shinshu University*, [2]*Department of Engineering, Shinshu University,* [3]*Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University,* [4]*JST, PRESTO*) ○Atsuto Terui,[1] Shintaro Abe,[2] Takashi Hisatomi,[3,4] Kazunari Domen[3]

Mg-doped GaN was synthesized by nitriding mixtures of Ga_2S_3 and MgS under NH_3 stream, and the photocatalytic water splitting activity of the products under ultraviolet light was investigated. GaN:Mg showed higher activity than undoped GaN when loaded with the Cr_2O_3/Rh cocatalyst. The activity was further improved by coloading CoOOH.

Keywords: Nitride, Ultraviolet light, Cocatalyst

遷移金属元素（Ti^{4+}）を構成元素とする $SrTiO_3$ は低価数の Al^{3+}をドーピングし、水素生成助触媒（Cr_2O_3/Rh）と酸素生成助触媒（CoOOH）を共担持すると、紫外光照射下でほぼ 100%の外部量子効率で水を分解できる [1)]。一方、典型金属元素を構成元素とする光触媒の場合に、同様の試みで高効率に水を分解できるかどうかはほとんど検討されていない。GaN は紫外光照射下で水分解活性を示す光触媒として知られている。本研究では、GaN の水分解活性が低価数の Mg^{2+}のドーピングと助触媒の共担持によりどのように変化するかを検討した。

Mg ドープ GaN（GaN:Mg）は、既報をもとに、Ga_2S_3 と MgS（Mg/(Ga+Mg) = 0, 0.01）を NH_3 気流下、1273 K の温度で 15 時間加熱窒化して合成した [2)]。XRD パターンからは単相のウルツ鉱型の GaN の回折ピークが確認された。

図 1 に種々の助触媒を担持した GaN と GaN:Mg の水分解活性を示す。Mg のドーピングにより水分解活性は向上した。Mg により形成されたアクセプター準位が正孔の移動を促進したと考えられる [2)]。また、Cr_2O_3/Rh と CoOOH 助触媒を共担持することで水分解活性がいっそう向上し、水素と酸素の生成量が化学量論比に近づいた。このことは助触媒の共担持により電荷分離が促進されたためだと解釈できる。

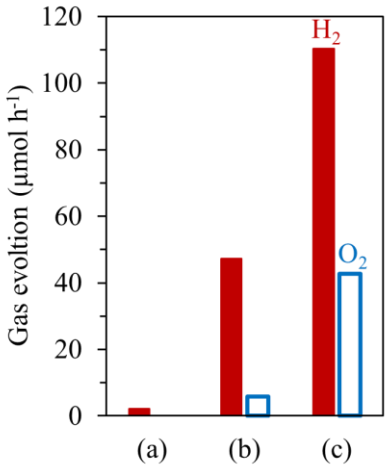

図 1 : 各種助触媒を担持した GaN 及び GaN:Mg の水分解活性.
(a) Cr_2O_3/Rh/GaN,
(b) Cr_2O_3/Rh/GaN:Mg,
(c) CoOOH/Cr_2O_3/Rh/GaN:Mg.

1) Takata *et al*. Nature **2020**, *581*, 411.
2) Arai *et al*. *Catal. Today* **2007**, *129*, 407.

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水分解活性の向上を志向した $Y_2Ti_2O_5S_2$ 光触媒粉末に対する金属カチオンドーピング

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Metal Cation Doping of $Y_2Ti_2O_5S_2$ Photocatalytic Particles Intended for Improvement of Water Splitting Activity ([1]*Faculty of Engineering, Shinshu University,* [2]*Research Initiative for Supra-Materials, Shinshu University,* [3]*The University of Tokyo*) ○ Riku Kumemoto,[1] Yosuke Kageshima,[1,2] Katsuya Teshima,[1,2] Kazunari Domen,[2,3] Hiromasa Nishikiori[1,2]

The metal oxysulfide $Y_2Ti_2O_5S_2$ (YTOS) has been reported as a photocatalytic material that responds to long wavelength light up to approximately 650 nm and is capable of driving the overall water splitting reaction. However, there remains a problem of insufficient photocatalytic activity. In this study, we investigated doping of YTOS with metal cations such as Al and Mg to improve the photocatalytic hydrogen evolution activity. The doped specimens were synthesized through a solid-state reaction using Al_2O_3 and MgO as precursors. The time courses of photocatalytic hydrogen evolution are shown in Fig. 1a. The synthesized specimens steadily generated hydrogen from aqueous solution of Na_2S/Na_2SO_3 under visible light irradiation. The hydrogen evolution rates of Al-doped YTOS as a function of doping level are summarized in Fig. 1b. It was found that 0.5% Al-doping achieved the highest hydrogen production activity, although further increasing doping level decreased the photocatalysis rate. In the presentation, the effects of dopant species and doping amount on the physical properties of the obtained photocatalytic particles will also be reported in detail.

Keywords: Photocatalysts, Powder, Water Splitting, Oxysulfide, Doping

金属酸硫化物である $Y_2Ti_2O_5S_2$ (YTOS) は 650 nm 程度までの長波長光に応答し、水の全分解反応を駆動可能な光触媒材料であると報告されている[1)]。しかし活性には改善の余地が残る。本研究では、YTOS の光触媒的水素生成活性の向上を目的とし、Al や Mg のような金属カチオンのドーピングを検討した。ドープ試料は、Al_2O_3、MgO を前駆体として用いて、固相法によって合成した。光触媒的水素生成の経時変化を Fig. 1a に示す。調整した試料は、可視光照射下で Na_2S/Na_2SO_3 水溶液から定常的に水素を生成した。ドープ量が Al ドープ YTOS の水素生成速度に及ぼす影響を Fig. 1b にまとめた。Al ドープ量 0.5%の時に最大の水素生成速度が得られるが、それ以上のドーピングは光触媒反応速度を低下させることが分かった。発表ではドーパント種やドープ量が得られる光触媒粒子の物性に与える影響についても詳細に報告する。

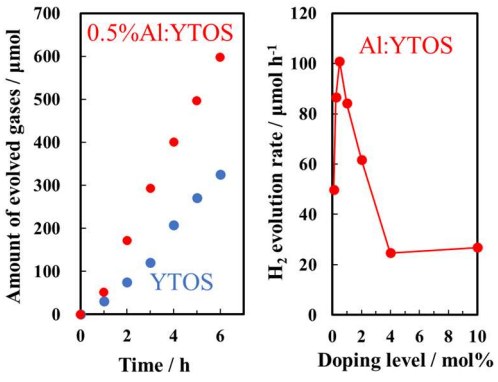

Fig. 1 (a) Time courses of hydrogen evolution and (b) effect of Al-doping level on the hydrogen evolution rate.

1) Qian Wang, *et al.*, *Nat. Mater.* **2019**, *18*, 827–832.

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インピーダンス分析への適用を志向した $SrTiO_3$ 粉末光電極の作製

(信州大工[1]・信州大先鋭材料研[2]・東大[3]) ○笹井 勇佑[1]・影島 洋介[1,2]・手嶋 勝弥[1,2]・堂免 一成[2,3]・錦織 広昌[1,2]

Preparation of $SrTiO_3$ Particulate Photoelectrodes Intended for Application to Impedance Analysis ([1]*Faculty of Engineering, Shinshu University*, [2]*Research Initiative for Supra-Materials, Shinshu University*, [3]*The University of Tokyo*) ○ Yusuke Sasai,[1] Yosuke Kageshima,[1,2] Katsuya Teshima,[1,2] Kazunari Domen,[2,3] Hiromasa Nishikiori[1,2]

Impedance analysis can be a powerful tool to obtain a variety of information about the semiconductor/electrolyte interface. However, it is not easy to reasonably interpret the results of impedance measurement for particulate electrodes because they contain many interfaces. In this study, we developed a particulate photoelectrodes applicable to precise impedance analysis by using a $SrTiO_3$/Ta/Ti film fabricated by particle transfer (PT) method. Nyquist plots obtained from single crystalline STO electrode and STO PT electrodes fixed by carbon tape or epoxy resin are summarized in Fig. 1. The impedance value of single crystal was in the order of 10^6 Ω, whereas the PT electrode fixed by carbon tape showed the significantly small value of 10^4 Ω, indicating that only the metal/electrolyte interface was detected because the backside metal of the PT electrode is exposed to the electrolyte. Meanwhile, PT electrode fixed by epoxy showed the comparable value to the single crystal, due to the backside metal being sealed by the epoxy resin. In the presentation, electrode-potential-dependence of the impedance will be discussed.
Keywords : Photocatalysts, Photoanodes, Electrochemical Impedance Spectroscopy, Powder, Oxides

インピーダンス分析は、半導体/電解液界面の様々な情報を得る強力なツールとなる。しかし、粉末材料から成る電極は多くの界面を含むため、インピーダンス測定結果を合理的に解釈することは容易ではない。本研究では、粒子転写 (PT)法により作製した $SrTiO_3$ (STO)/Ta/Ti 膜を用い、インピーダンス分析の精密解析に適用可能な粉末光電極を開発した。単結晶 STO 電極及び、カーボンテープまたはエポキシ樹脂によってガラス基板上に固定した STO PT 電極の、ナイキストプロットを Fig. 1 に示す。単結晶のインピーダンスが 10^6 Ω のオーダーであったのに対し、カーボンテープで固定した PT 電極は 10^4 Ω 程度の極端に小さな値を示した。これは、露出した裏面金属層が電解液と接触しているため、金属/電解液界面しか検出できていないものと考えられる。一方、PT 電極をエポキシ樹脂で固定すると、単結晶と同程度の大きさのインピーダンスが得られた。これは、エポキシ樹脂によって裏面金属層がシールされたためと考えられる。発表では、インピーダンスの電位依存性について議論する。

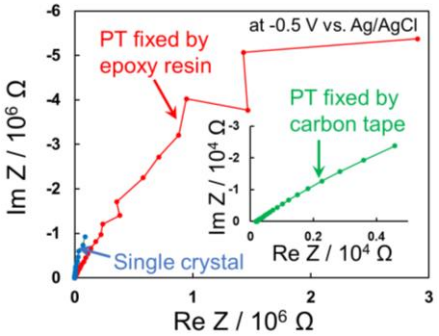

Fig. 1 Nyquist plots obtained from various STO electrodes in 0.1 M phosphate buffer electrolyte under dark condition.

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
A1457(1457, Bldg. 14 [5F])

[A1457-3pm] 08. Catalysts and Catalysis

Chair: Shingo Hasegawa, Tomohiro Yabe

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1457-3pm-01]
Selective reduction reactions of organic molecules by powdered silicon as a reducing agent

○Takuya Shiroshita[1], Yurino Sasaki[1], Shingo Hasegawa[1], Ken Motokura[1] (1. Yokohama National University.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1457-3pm-02]
Silica-immobilized Pd-base catalyst for Suzuki-Miyaura coupling without homogeneous base

○Mariko Honda[1], Shunichi Sakai[1], Shingo Hasegawa[1], Ken Motokura[1] (1. Yokohama National University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1457-3pm-03]
Selective pyrrole synthesis through oxidative dehydrogenative aromatization using a supported Au–Pd nanoparticle catalyst

○Kenshiro Sekine[1], Takafumi Yatabe[1], Yasutaka Tomiki[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1457-3pm-04]
Hydrogenation of Aromatic Compounds by Supported Ni Nanoparticle Catalysts under Ambient Pressure

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

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1457-3pm-05]
Selective acetone hydrodeoxygenation over supported polyoxometalate catalysts

○Takaaki Suzuki[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1457-3pm-06]
Ni-catalyzed Kumada–Tamao–Corriu double cross-coupling of diaryl sulfides via desulfurization

○Ikuya Sugimoto[1], Takahumi Yatabe[1], Takehiro Matsuyama[1], Kazuya Yamaguchi[1] (1. The Univ. of Tokyo)

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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

[A1457-3pm-07]

Aerobic oxidation of sulfides catalyzed by Ru-doped hexagonal perovskite oxides

○Masashi Makizawa[1], Keiju Wachi[1], Takeshi Aihara[1], Keigo Kamata[1] (1. MLS, Tokyo Tech)

Japanese

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

[A1457-3pm-08]

Sustainable aviation fuel formation by hydrocracking of *n*-heptadecane using Y-zeolite-Al_2O_3 composite-supported Pt catalyst

Shunma Mitsuoka[1], Kosuke Murata[1], Tadanori Hashimoto[1], Ning Chen[2], Yuki Jonoo[2], Sho Kawabe[2], Keita Nakao[2], ○ATSUSHI ISHIHARA[1] (1. Graduate School of Engineering, Mie University, 2. Tosoh Corporation)

Japanese

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

[A1457-3pm-09]

Cu-containing atom-hybridized subnanoparticles for catalysis

○Ryusuke Iijima[1], Makoto Tanabe[1,2], Kimihisa Yamamoto[2] (1. Fukushima Medical University, 2. Lab. Chem. Life Sci., Tokyo Tech.)

Japanese

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

[A1457-3pm-10]

Development of improved photo-responsive thiourea/DMAP combined catalyst that switches catalytic activity

○Yusuke Nakamura[1], Akihiro Kawaguti, tatsushi Imahori[1] (1. The Tokyo Univ. of Science)

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

[A1457-3pm-11]

Ti_2Ni Alloys Catalyzed β-Alkylation of Alcohols

○Itsuki Kawasaki[1], Chihiro Yamaguchi[1], Ryo Kanishi[1], Ryota Kondo[1], Yasushi Obora[1] (1. Fac. Chem. Matl. & Bioeng., Kansai Univ.)

Japanese

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

[A1457-3pm-12]

Ceria-catalyzed oxidative C-C bond cleavage of 1,2-diols

○Nakamura Yukino[1], Miura Hiroki[1], Shishido Tetsuya[1] (1. Tokyo Metropolitan University)

Japanese

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

[A1457-3pm-13]

Aerobic oxidation of alcohols with supported Pt-Bi catalysts

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○Kazuki Haruguchi[1], Hinata Yamamoto[1], Yasutaka Kawai[1], Eiji Yamamoto[1], Haruno Murayama[2], Akina Yoshizawa[1], Makoto Tokunaga[1] (1. Kyushu University, 2. Kanagawa Institute of Technology)

Japanese

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

[A1457-3pm-14]

Creation of active structure derived from Al_2O_3-supported Cu-Al LDH in ammoxidation of aldehydes

○Ryota Yodose[1], Takayoshi Hara[1], Enggah Kurniawan[1], Yessi Permana[2], Nobuyuki ichikuni[1] (1. Chiba University, 2. Institut Teknologi Bandung)

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シリコン粉末を還元剤とする有機分子の選択的還元反応

（横浜国立大学）○白下 拓哉・佐々木 ゆりの・長谷川 慎吾・本倉 健

Selective reduction reactions of organic molecules by powdered silicon as a reducing agent

（*Department of Chemistry and Life Science, Yokohama National University*）
○Takuya Shiroshita, Yurino Sasaki, Shingo Hasegawa, Ken Motokura

We have previously reported the synthesis of formic acid and formamide from CO_2 using silicon powder as a reducing agent in the presence of fluoride catalyst. In this study, we found that the reduction reaction by silicon with fluoride catalyst was also applicable to internal and terminal alkynes and carbonyl compounds. As a result of optimization of reaction conditions for the reduction of diphenylacetylene by silicon powder, *cis*-stilbene was quantitatively obtained by using tetrabutylammonium fluoride (TBAF) and acetic acid as catalyst and proton source, respectively (**Table 1**). It was found that the reaction efficiency was highly dependent on the type of proton sources; the use of water as a proton source significantly decreased the conversion and yield, whereas the reaction did not proceed with alcohols such as methanol and ethanol. Furthermore, selective reduction of terminal alkynes to corresponding alkenes was achieved by similar reaction conditions (**Table 2**). Reduction reactions of carbonyl compounds will be discussed in the presentation.

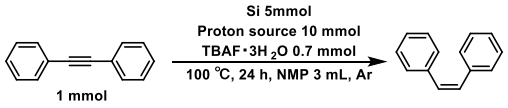
Keywords：Hydrogenation, Silicon, Reduction reaction, Alkynes

我々は以前、フッ化物触媒存在下シリコン粉末を還元剤として CO_2 からギ酸[1]やホルムアミド[2]を合成する手法を報告している。本研究では、フッ化物触媒とシリコン還元剤を用いる反応系を拡張し、内部・末端アルキンおよびカルボニル化合物の選択的還元を達成した。

シリコン粉末による diphenylacetylene の還元反応について条件検討を行なったところ、tetrabutylammonium fluoride（TBAF）を触媒、酢酸をプロトン源として、NMP 溶媒中・Ar 雰囲気下・100 ℃・24 h の反応条件によって定量的かつ選択的に *cis*-stilbene が得られることがわかった（**Table 1**）。プロトン源の種類によって反応効率が顕著に変化することが見出され、水をプロトン源とする反応では転化率・収率が大幅に低下し、メタノールあるいはエタノールをプロトン源に用いると反応は全く進行しなかった。

さらに、同様な反応条件によって末端アルキンから末端アルケンへの選択的変換を達成した（**Table 2**）。適切なプロトン源を用いることで phenylacetylene 類縁体から対応する末端アルケンが高い（>90%）選択率で得られた。講演ではカルボニル化合物の還元反応についても論ずる。

Table 1. Reduction of Diphenylacetylene



Proton source	Conversion (%)	Alkene yield (%)	Selectivity (*cis* : *trans*)
H_2O	32	21	16:5
MeOH	0	n.d.	-
EtOH	0	n.d.	-
AcOH	100	>99	99:1

Table 2. Reduction of Phenylacetylenes



R	Proton source	Conversion (%)	Alkene yield (%)	Alkane yield (%)
H	MeOH	100	90	n.d.
Me	AcOH	100	94	6
OEt	MeOH	100	98	n.d.

1) K. Motokura, K. Nakao, Y. Manaka, *Asian J. Org. Chem.*, **2022**, 11, e202200230.

2) R. Wang, K. Nakao, Y. Manaka, K. Motokura, *Commun. Chem.*, **2022**, 5, 150.

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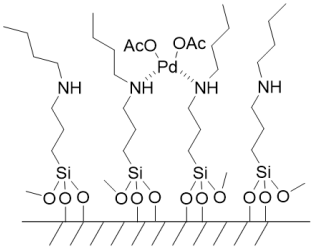
シリカ固定化 Pd-塩基触媒による均一系塩基を用いない鈴木宮浦カップリング

（横国大理工 [1]）○本田 麻里子 [1]・坂井 俊一 [1]・長谷川 慎吾 [1]・本倉 健 [1]
Silica-immobilized Pd-base catalyst for Suzuki-Miyaura coupling without homogeneous base
([1]*Department of Chemistry and Life Science, Yokohama National University*) ○ Mariko Honda,[1] Shunichi Sakai,[1] Shingo Hasegawa,[1] Ken Motokura[1]

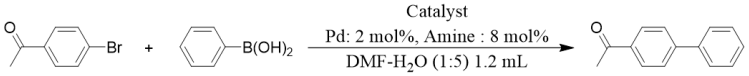
Suzuki-Miyaura coupling is a widely used C-C bond forming reaction and generally requires stoichiometric amount of base. Some methods have been developed for base-free Suzuki-Miyaura coupling. For example, reactions with stoichiometric amount of zinc complexes as an additive were reported.[1)] In this study, we developed a catalyst consisting of Pd and organic base co-immobilized on silica surface (SiO_2/NH^{n}Bu/Pd, **Scheme 1**) for the Suzuki-Miyaura coupling with the catalytic amount of base. Suzuki-Miyaura coupling of 4-bromoacetophenone and phenylboronic acid with SiO_2/NH^{n}Bu/Pd resulted in the higher product yield than those of reaction systems without co-immobilized base (**Table 1**). The amount of product was 7.5 times larger than that of immobilized base, indicating that the base acted as a catalyst.
Keywords : Suzuki-Miyaura Coupling; Palladium; Silica; Concerted Catalysis; Base

C-C 結合形成反応として広く用いられる鈴木宮浦カップリングは一般に量論量の塩基が反応進行に必要である。塩基を添加しない条件での鈴木宮浦カップリングの報告例として量論量の亜鉛錯体を添加する手法等が報告されている [1)]。本研究ではシリカ上に Pd と有機塩基を固定した触媒（SiO_2/NH^{n}Bu/Pd, **Scheme 1**）を開発し、触媒量の塩基存在下での鈴木宮浦カップリングを試みた。SiO_2/NH^{n}Bu/Pd を用いて 4-bromoacetophenone と phenylboronic acid の鈴木宮浦カップリングを実施した結果 61% の収率で目的生成物が得られ、Pd のみを固定した触媒（SiO_2/Pd, 22%）および SiO_2/Pd に有機塩基を添加した系（40%）と比較して収率が向上した（**Table 1**）。SiO_2/NH^{n}Bu/Pd を用いた場合に有機塩基に対して 7.5 倍量の生成物が得られたことから、有機塩基が触媒として機能していると考えられる。



Scheme 1. Estimated structure of SiO_2/NH^{n}Bu/Pd

Table 1. The result of heterogeneous and homogeneous catalyst of Suzuki-Miyaura Coupling



Entry	Catalyst	Yield (%)	TON (Pd^{-1})	Product /amine
1	SiO_2/NH^{n}Bu/Pd	61	30	7.5
2	SiO_2/Pd + NH(^{n}Bu)$_2$	40	20	5.0
3	SiO_2/Pd	22	11	-

1) T. Niwa, Y. Uetake, M. Isoda, T. Takimoto, M. Nakaoka, D. Hashizume, H. Sakurai, T. Hosoya, *Nat. Catal.* **2021**, *4*, 1080.

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担持 Au–Pd ナノ粒子触媒を用いた酸化的脱水素芳香環形成を経る選択的ピロール合成

（東大院工 [1]）○関根 堅志郎 [1]・谷田部 孝文 [1]・冨木 泰峻 [1]・矢部 智宏 [1]・山口 和也 [1]

Selective Pyrrole Synthesis through Oxidative Dehydrogenative Aromatization Using a Supported Au–Pd Nanoparticle Catalyst ([1]*School of Engineering, The University of Tokyo*) ○ Kenshiro Sekine,[1] Takafumi Yatabe,[1] Yasutaka Tomiki,[1] Tomohiro Yabe,[1] Kazuya Yamaguchi[1]

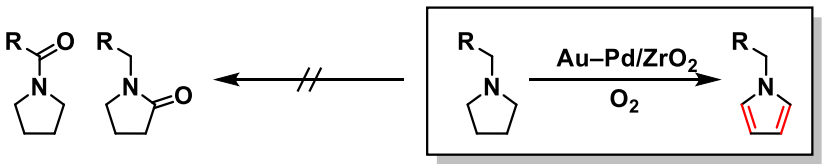
Pyrroles are widely utilized in various fields such as pharmaceuticals, semiconductors, dyes, and polymers. Dehydrogenative aromatization to pyrroles from pyrrolidines, which are also ubiquitous structures in useful compounds, is important in terms of efficient development of novel functional chemicals; however, the previously published reports have several issues such as use of (super)stoichiometric amounts of oxidants and limited substrate scopes.[1)]

In this study, we aimed at selective oxidative dehydrogenative aromatization to pyrroles in the presence of supported Au–Pd alloy nanoparticle catalysts by utilizing Au-catalyzed cyclic-α-methylene regioselective aerobic oxidation of tertiary amines[2)] and Pd-catalyzed dehydrogenative aromatization.[3)] After various investigations, we have developed to selective pyrrole synthesis from structurally diverse pyrrolidines by a ZrO_2-supported Au–Pd alloy nanoparticle catalyst whose Au/Pd ratio was suitably controlled to suppress the side reactions.

Keywords : Au–Pd Nanoparticles; Dehydrogenative Aromatization; Selective Oxidation; Pyrrolidines; Pyrroles

ピロールは医薬品・半導体・色素・高分子などの多岐にわたる分野で利用される有用な化合物であり、同様に有用化合物に遍在するピロリジンをピロールに変換する脱水素芳香環形成は、効率的な新規機能性化学品開発等の観点で重要である。しかし、既報では、化学量論量以上の酸化剤の使用、基質適用性の制限等の課題があった [1)]。

本研究では、担持 Au–Pd 合金ナノ粒子触媒を用いて、Au の環状 α 位メチレン選択的第三級アミン酸素酸化能 [2)]と Pd の脱水素芳香環形成能 [3)]を利用し、分子状酸素を酸化剤としたピロールへの選択的脱水素芳香環形成の検討を行った。種々の検討の結果、ZrO_2 担持 Au–Pd 合金ナノ粒子触媒において Au/Pd 比を適切に制御することで副反応を抑制し、様々な構造のピロリジンを基質とした選択的ピロール合成を開発した。



1) a) B. Bonnaud, D. C. H. Bigg, *Synthesis* **1994**, *5*, 465. b) D. F. Brayton, C. M. Jensen, *Chem. Commun.* **2014**, *50*, 5987. 2) a) X. Jin, K. Kataoka, T. Yatabe, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2016**, *55*, 7212. b) T. Yatabe, K. Yamaguchi, *Nat. Commun.* **2022**, *13*, 6505. 3) a) T. Oyama, T. Yatabe, X. Jin, N. Mizuno, K. Yamaguchi, *Chem. Lett.* **2019**, *48*, 517. b) W.-C. Lin, T. Yatabe, K. Yamaguchi, *Chem. Commun.* **2021**, *57*, 6530.

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担持 Ni ナノ粒子触媒を用いた常圧での芳香族化合物の水素化反応

(東大院工[1]) ○佐々木 義弘[1]・谷田部 孝文[1]・松山 剛大[1]・山口 和也[1]

Hydrogenation of Aromatic Compounds by Supported Ni Nanoparticle Catalysts under Ambient Pressure

([1]*School of Engineering, The University of Tokyo*) ○Yoshihiro Sasaki,[1] Takafumi Yatabe,[1] Takehiro Matsuyama,[1] Kazuya Yamaguchi[1]

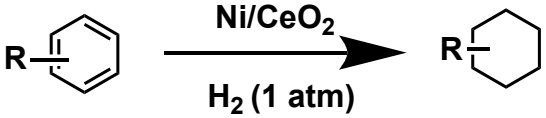
Hydrogenation of aromatic compounds represents one of the most important reactions widely utilized in various chemistry fields including hydrogen storage and transportation, fine chemical synthesis, and petroleum refinery.[1)] Hydrogenation of aromatic compounds has been developed mainly using noble metal catalysts such as palladium and platinum.[2)] On the other hand, most of previous reports on hydrogenation of aromatic compounds using non-noble metal catalysts have required harsh conditions of high H_2 pressure and/or high temperature. Although some of them were conducted under ambient H_2 pressure, the catalytic systems were limited to flow synthesis in gas phase flow at relatively high temperatures.[3)] Thus, a novel catalytic system applicable to hydrogenation of a variety of aromatic compounds in liquid phase is desired.

In this study, we have successfully developed hydrogenation of various aromatic compounds under ambient H_2 pressure and low temperature (80 ºC) in liquid phase using a CeO_2-supported nickel nanoparticle catalyst (Ni/CeO_2). Indeed, when using Ni/CeO_2 for the hydrogenation of *p*-cresol under H_2 (1 atm) at 80 ºC for 24 h, 4-methylcyclohexanol was obtained in 93% yield. In this presentation, we will discuss support effects, control experiments, the substrate scope of this reaction, and so forth in detail.

Keywords : Supported Ni Nanoparticle Catalysts; Hydrogenation; Aromatic Compounds; Heterogeneous Catalysts

芳香族化合物の水素化反応は、水素の輸送・貯蔵や精密化学品の製造、バイオマス転換、石油精製等において重要な反応である[1)]。芳香族化合物の水素化反応は主に Pd や Pt といった貴金属触媒を用いて開発されてきた[2)]。一方で、非貴金属触媒を用いた芳香環水素化反応の報告は少なく、一般に高温や高圧といった過激な反応条件を必要とする。水素 1 気圧での反応も報告されているが、比較的高温条件における気相フロー合成に限られるため[3)]、液相中での幅広い基質に適用可能な触媒反応系が望まれる。

本研究では、担持 Ni ナノ粒子触媒 (Ni/CeO_2) を用いることで、液相中で穏和な条件下における幅広い芳香族化合物の芳香環水素化反応の開発に成功した。実際、*p*-クレゾールの芳香環水素化反応を水素 1 atm、80 °C、Ni/CeO_2 存在下で 24 h 行った結果、4-メチルシクロヘキサノールが 93%の収率で得られた。本発表においては、担体効果、コントロール実験、基質適用性等についても詳しく述べる。



1) M. P. Wiesenfeldt, Z. Nairoukh, T. Dalton, F. Glorius, *Angew. Chem. Int. Ed.* **2019**, *58*, 10460.
2) S. C. Qi, X. Y. Wei, Z. M. Zong, Y. K. Wang, *RSC Adv.* **2013**, *3*, 14219.
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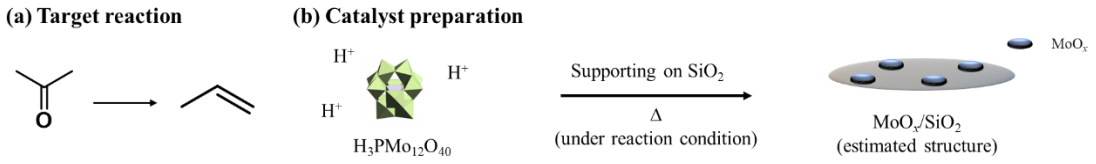
担持ポリオキソメタレート触媒を用いた選択的アセトン水素化脱酸素反応

（東大院工）○鈴木 崇哲・矢部 智宏・山口 和也
Selective acetone hydrodeoxygenation over supported polyoxometalate catalysts (*School of Engineering, The University of Tokyo*) ○Takaaki Suzuki, Tomohiro Yabe, Kazuya Yamaguchi

Propylene is an industrially important key substance, and hydrodeoxygenation (HDO) of biomass-derived acetone is a promising reaction to synthesize propylene. MoO_3 is one of the effective catalysts to produce unsaturated hydrocarbons via HDO of lignin-derived oxygenates[1]. However, the facile deactivation of MoO_3 through excessive reduction and carbon deposition is the key challenges. Noting the importance of the surface state of catalysts under reaction conditions, this study examined acetone HDO using a catalyst prepared by supporting a Keggin-type phosphomolybdate $H_3PMo_{12}O_{40}$ on SiO_2 (MoO_x/SiO_2). The highly dispersed MoO_x species on SiO_2 was found to afford propylene in high yields (> 80%), and the catalyst lifetime of MoO_x/SiO_2 was significantly improved compared to MoO_3. In addition, we investigated various catalyst precursors, pretreatment conditions, and the dispersion state of MoO_x species in order to improve the catalytic activity and lifetime of the catalysts, and various characterization were performed.

Keywords : supported polyoxometalate catalysts, acetone hydrodeoxygenation, propylene

プロピレンは工業的に重要な基幹化合物であり、バイオマス資源から入手可能なアセトンの水素化脱酸素反応 (HDO) による合成が切望されている。MoO_3 は、リグニン由来の含酸素化合物の HDO による不飽和炭化水素の合成に有効な触媒であるが[1]、反応条件下で過剰な還元を受けて HDO に不活性な MoO_2 を形成すること、および触媒表面への炭素析出によって、容易に失活することが課題であった。本研究では、反応条件下での触媒の表面状態が重要であることに着目し、Keggin 型ホスホモリブデート $H_3PMo_{12}O_{40}$ を SiO_2 に担持して調製した触媒 (MoO_x/SiO_2) を用いてアセトン HDO を検討した。MoO_x 種を SiO_2 上に高分散に担持することで、プロピレンを高収率 (> 80%)で得ることができ、さらに MoO_x/SiO_2 の触媒寿命は MoO_3 と比べて大幅に向上することも見出した。さらに触媒活性や寿命を向上するために、触媒前駆体、前処理条件の最適化や MoO_x 種の分散度の影響を検討し、合わせて触媒の各種キャラクタリゼーションを行った。



[1] T. Prasomsri *et al*., *Energy Environ. Sci*., **2013**, *6*, 1732; A. J. Kohler *et al*., *ACS Catal*., **2023**, *13*, 14813.

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Ni 触媒によるジアリールスルフィドの脱硫黄を伴う熊田・玉尾・コリューダブルクロスカップリング

（東大院工 [1]）○杉本 育矢 [1]・谷田部 孝文 [1]・松山 剛大 [1]・山口 和也 [1]
Ni-catalyzed Kumada–Tamao–Corriu double cross-coupling of diaryl sulfides via desulfurization ([1]*School of Engineering, The University of Tokyo*) ○ Ikuya Sugimoto,[1] Takafumi Yatabe,[1] Takehiro Matsuyama,[1] Kazuya Yamaguchi[1]

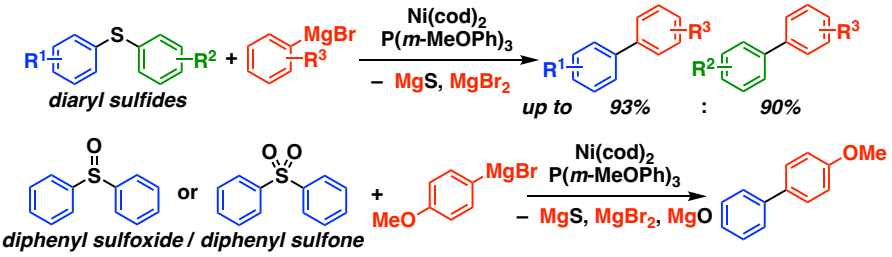
Cross-coupling reactions which involve the cleavage of inert bonds such as C–C, C–O, and C–S bonds ubiquitous in organic molecules are useful reactions that do not require pre-functionalization or produce harmful byproducts;[1)] however, the low atom economy due to the leaving groups containing carbon moieties is problematic. Recently, Kumada–Tamao–Corriu cross-coupling via scission of two C–S bonds in diaryl sulfides was reported.[2)] The reaction proceeds with high atom economy in which only sulfur atom is removed from the substrate, while the catalytic activity to unsymmetrical diaryl sulfides is insufficient.

In this study, after optimization of reaction conditions focusing on ligand effects, we found a highly efficient Kumada–Tamao–Corriu double cross-coupling reaction of diaryl sulfides via desulfurization by Ni/P(*m*-MeOPh)$_3$ catalytic system. In this reaction system, various biphenyls can be synthesized from diaryl sulfides including unsymmetrical ones in high yields, and this catalytic system can be applied to sulfoxides and sulfones. The ligand effects will be discussed based on Tolman parameters and quantum chemical calculations.

Keywords : diaryl sulfide; desulfurization; double cross-coupling; Ni catalyst; ligand effect

有機分子中に遍在する C–C、C–O、C–S 結合などの不活性結合の切断を経るクロスカップリング反応は、予備官能基化を必要とせず有害な副生成物を生じない有用な反応であるが [1)]、炭素骨格を含む脱離基により原子効率が低くなるという問題を抱えている。一方で、近年報告されたジアリールスルフィドの 2 つの C–S 結合切断を経る熊田・玉尾・コリュークロスカップリングは [2)]、基質から硫黄原子しか脱離しない高原子効率反応であるものの、非対称な基質における活性が不十分であった。

本研究では、配位子効果を中心とした条件最適化を行った結果、Ni/P(*m*-MeOPh)$_3$ 触媒により、ジアリールスルフィドの脱硫黄を伴う高効率な熊田・玉尾・コリューダブルクロスカップリングを見出した。本反応系では、非対称ジアリールスルフィドからも高収率で 2 種類のビフェニルを合成でき、スルホキシドやスルホンにも適用可能である。配位子効果については、各種パラメータ及び量子化学計算をもとに議論する。



1) Z. Qiu, C.-J. Li, *Chem. Rev.* **2020**, *120*, 10454.
2) N.-N. Ma, X.-B. Hu, Y.-S. Wu, Y.-W. Zheng, M. Ma, X.-Q. Chu, H. Xu, H. Luo, Z.-L. Shen, *Org. Lett.* **2023**, *25*, 1771.

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Ru ドープ六方晶型ペロブスカイト酸化物を触媒としたスルフィドの酸素酸化

（東京工業大学フロンティア材料研究所）○牧澤 昌史[1]・和知 慶樹[1]・相原 健司[1]・鎌田 慶吾[1]

Aerobic oxidation of sulfides catalyzed by Ru-doped hexagonal perovskite oxides ([1]*Tokyo Institute of Technology, Laboratory for Materials and Structures*) ○Masashi Makizawa,[1] Keiju Wachi,[1] Takeshi Aihara,[1] Keigo Kamata[1]

Sulfones and sulfoxides are useful compounds as ligands for asymmetric catalytic reactions and pharmaceutical intermediates. While these compounds are obtained by sulfide oxidation using activated oxidants such as hydrogen peroxide, catalytic systems using molecular oxygen (O_2) as the sole oxidant are still limited. Therefore, we focused on ruthenium in perovskite oxides because $BaRuO_3$ catalyst is highly active for sulfide oxidation with O_2. In this study, we synthesized a Ru-doped perovskite oxide catalyst with a hexagonal structure similar to $BaRuO_3$, and achieved high activity to sulfide oxidation with a small amount of Ru.

A Ru-doped perovskite oxide ($SrMn_{0.9}Ru_{0.1}O_3$) was synthesized by a sol-gel method using a dicarboxylic acid. Nitrogen sorption and powder XRD measurements revealed that the current catalyst possessed a high specific surface area and a hexagonal 4H-structure, respectively. $SrMn_{0.9}Ru_{0.1}O_3$ efficiently catalyzed the oxidation of thioanisole with only O_2, and the corresponding sulfoxides and sulfones were obtained in high yields. Furthermore, control experiments over various perovskite oxides elucidated the effectiveness of the hexagonal structure.

Keywords : Sulfide oxidation, Hexagonal perovskite, Ru doping

スルホンやスルホキシドは、不斉触媒反応のリガンドや医薬品中間体として重要な化合物である。これらはスルフィドの過酸化水素酸化等によって得られるが、分子上酸素(O_2)を酸化剤とした触媒反応系が求められている。そこで、スルフィドの酸素酸化に高い活性を示すペロブスカイト酸化物中の Ru 種に着目した[1]。本研究では、六方晶構造を有するペロブスカイト酸化物に Ru を添加した触媒を合成し、少量の Ru で高い活性を示す触媒を開発した。

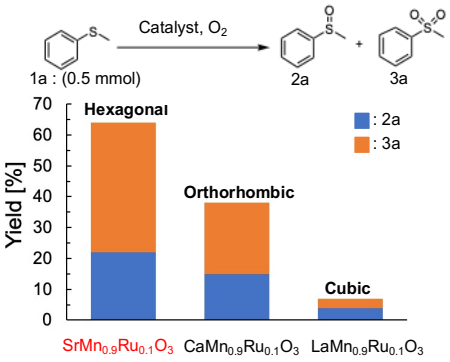

Figure.1 結晶構造と触媒活性

ジカルボン酸を用いたゾルゲル法により、Ru ドープペロブスカイト酸化物 ($SrMn_{0.9}Ru_{0.1}O_3$) を合成した。窒素吸着および粉末 XRD 測定から、本触媒が高い比表面積と 4H-六方晶構造を有することがそれぞれ明らかとなった。本触媒はチオアニソールの酸素酸化に高い活性を示し、対応するスルホキシドおよびスルホンが高収率で得られた。さらに種々の触媒比較により六方晶構造の有効性を明らかにした。(Figure.1)

1) K. Kamata *et al. ACS Appl. Mater. Interfaces* **2018**, *10*, 23792−23801

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Y-zeolite-Al_2O_3 複合担体担持 Pt 触媒を用いた *n*-ヘプタデカンの水素化分解による SAF 生成

（三重大院工[1]・東ソー（株）[2]）光岡駿真[1]・村田航佑[1]・橋本忠範[1]・○石原　篤[1]・陳　寧[2]・城之尾裕樹[2]・河部　正[2]・中尾圭太[2]

Sustainable aviation fuel formation by hydrocracking of *n*-heptadecane using Y-zeolite-Al_2O_3 composite-supported Pt catalyst (*Graduate School of Engineering, Mie University[1], Tosoh Institute of Inorganic Materials[2]*) Shunma Mitsuoka[1], Kosuke Murata[1], Tadanori Hashimoto[1], ○Atsushi Ishihara[1], Ning Chen[2], Yuki Jonoo[2], Sho Kawabe[2], Keita Nakao[2]

Into a zeolite-Al_2O_3 composite prepared by the kneading method was supported Pt using the impregnation method. The catalyst obtained was used for hydrocracking of *n*-heptadecane to produce sustainable aviation fuel (SAF). When hydrocracking of *n*-heptadecane was performed using a fixed-bed flow reactor at a H_2 pressure of 0.5MPa, H_2 flow rate of 300 mL/min, WHSV of 2.3 h^{-1}, and a catalyst weight of 2 g, 0.5Pt/Y(100)35A, where 0.5 means wt% of Pt, Y means zeolite type, 100 in a parenthesis means SiO_2/Al_2O_3 ratio and 35 means wt% of Al_2O_3, exhibited the high selectivity for jet fuel (C8-C15) of 74%, the conversion of 99% and the high yield of SAF of 73% at 295℃, which was almost an ideal maximum yield of 75%. In contrast to this, 0.5Pt/Z(110)35A, where 0.5 means wt% of Pt, Z means ZSM-5 zeolite, 110 in a parenthesis means SiO_2/Al_2O_3 ratio and 35 means wt% of Al_2O_3, exhibited the increase in gaseous products, the low selectivity for jet fuel of 22%, the conversion of 97% and the low yield of SAF of 21% at 270℃.

Keywords : Sustainable aviation fuel formation, Hydrocracking of n-heptadecane, Y-zeolite-Al_2O_3 composite-supported Pt catalyst

油脂やバイオマスを用いた Fischer-Tropsch 法から得られる長鎖炭化水素の水素化分解から Sustainable aviation fuel (SAF)を製造するプロセスが注目されている[1)]。本研究では、その長鎖炭化水素のモデルとして *n*-heptadecane を用い、水素化分解反応による SAF 製造の可能性について検討した。従来の触媒では過分解が進行し、目的生成物を選択的に得られないという欠点があった。そこで、選択性を向上させるために、水素化に寄与する活性金属種として Pt、酸機能を持つゼオライトおよび酸化物でメソ細孔を持つ Al_2O_3 を組み合わせた多元機能触媒を用いた。さらに過分解を抑制するため、適切な反応条件を検討した[1)]。

複合担体は 50wt%の Y-あるいは ZSM-5-ゼオライトと 35wt%の Al_2O_3 をバインダー(Al_2O_3 15wt%)とともに混錬・焼成して調製した。これに 0.5wt%の Pt を担持した触媒を用いて、*n*-heptadecane の水素化分解反応を、固定床流通式反応装置により H_2 0.5MPa、H_2 流量 300 mL/min, WHSV 2.3 h^{-1}, 触媒 2 g の条件で行った。0.5Pt/Y(100)35A（100 は SiO_2/Al_2O_3 比）では、反応温度 295℃で転化率が 99%に達し、Jet 燃料(SAF)の収率も 73wt%と高い値を示した。これは、2 級のカルベニウムイオンが同じ確率で分解した場合に得られる 75wt%の収率に近い値であった。一方、0.5Pt/Z(110)35A 触媒では 270℃で高い転化率を示したが、ガス生成物を含む C3～C7 留分への分解が多く、Jet 燃料を選択的に得ることは難しかった。

1) S Mitsuoka, K. Murata, T. Hashimoto, N. Chen, Y. Jonoo, S. Kawabe, K. Nakao, A. Ishihara, ACS Omega, 2024, https://doi.org/10.1021/acsomega.3c07678.

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銅を軸とする多元素ハイブリッド粒子の触媒機能

（福島県医大[1]・東工大化生研[2]）○飯島 隆輔[1]・田辺 真[1,2]・山元 公寿
Cu-containing atom-hybridized subnanoparticles for catalysis (*[1]Fukushima Medical University, [2]Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○Ryusuke Iijima,[1] Makoto Tanabe,[1,2] Kimihisa Yamamoto[2]

Subnanoparticles with ultrasmall particle sizes (<1 nm) exhibit specific geometric structures and electronic states that are different from those of common nanoparticles. Subnano alloy particles (SAPs), hybridized by two or three different metals in a subnanoparticle, are expected as novel catalytic materials to elevate catalytic performance and selectivity. The SAPs composed of noble (Pt), base (Cu), and typical (Sn) metals were prepared with atomicity using a macromolecular dendritic template, which were utilized as heterogenous catalysts by immobilization to SiO_2 support. The PtCuSn SAPs exhibited best catalytic performance and tolerance in xanthene oxidation with O_2 as an oxidant, compared to those of the bimetallic catalysts (ex. PtSn, PtCu SAPs). In addition, the PtCuSn SAPs also enhanced catalytic activity and recyclability in reductive reactions of 4-nitrophenol with excess $NaBH_4$. We will discuss unique properties of these hybridized SNPs based on the results of XAFS measurements.
Keywords : Nanoparticles; Alloy; Dendrimer; Catalytic Oxidation; Copper

粒子径が約 1 nm のサブナノ粒子は、従来のナノ粒子とは異なる特異な幾何学的構造や電子状態を示すため、それを活かした触媒反応の開発が注目されている。中でも、複数の元素が混在した多元素ハイブリッド触媒は、触媒活性、反応選択性および耐久性の要素を自在に改善できることが期待される[1]。本研究では、酸化還元活性を示す「卑金属 (Cu)」、酸素親和性が低い「貴金属 (Pt)」、酸素親和性が高い「典型金属 (Sn)」で構成される三元素サブナノ粒子を合成し、芳香族炭化水素の酸化反応と極性官能基の還元反応をモデル反応として、三元素ハイブリッド粒子の触媒機能を評価した。

三元素サブナノ合金粒子の合成には、π共役樹状高分子デンドリマーへの混合集積法を利用した。デンドリマーの内層からルイス酸性が高い金属イオンを段階的に集積させ、それを $NaBH_4$ での化学還元後、シリカ (SiO_2) 担体へ吸着させ、三元素・二元素ハイブリッド触媒を合成した。合成した触媒を用いて、キサンテンおよび 4-ニトロフェノールを基質とする触媒モデル反応を検討した結果と考察を報告する (Fig. 1)。

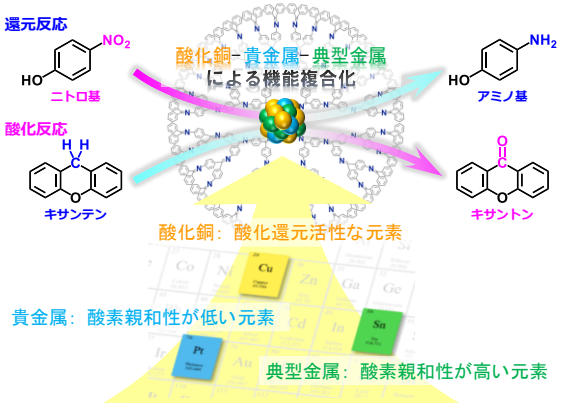

Fig. 1 本研究の概念図

1) Yamamoto, K.; Imaoka, T.; Tanabe, M.; Kambe, T. *Chem. Rev.* **2020**, *120*, 1397.

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日本化学会 第104春季年会 (2024)

触媒活性を切り替える改良型刺激応答性チオウレア・DMAP 複合触媒の開発

（東理大院工）○中村祐介・川口明裕・今堀龍志

Development of improved photo-responsive thiourea・DMAP combined catalyst that switches catalytic activity, (*Graduate school of Engineering, Tokyo University of Science*)○Yusuke Nakamura, Akihiro Kawaguchi, Tatsushi Imahori

Our group has recently developed an azobenzene based thiourea・DMAP combined catalyst and applied to Friedel-Crafts reaction of indole and ethyl pyruvate. From the result, the catalyst achieved switching of the catalytic activity by the photo-responsive structural changes through photoisomerization of the azobenzene core. Herein, we designed and developed improved azobenzene-based photo-responsive thiourea・DMAP catalyst, in which direction of the thiourea unit was modified by introducing C1-methylene tether. We envisioned that indole and pyruvate that were captured by the thiourea and DMAP units would be suitably placed closer in the active form of *cis*-azobenzene isomer, to allow enhanced switching of the catalytic activity. The improved catalyst was synthesized and evaluated for switching of the catalytic activity based on the photo-responsive structural changes.

Keywords : azobenzene, stimuli-responsive catalyst, acid-base combined catalyst

刺激応答性触媒は化学反応を時間軸で段階的に制御することで、より高度な化学変換を実現することができる。我々のグループはこれまでに、外部刺激によって構造変換するアゾベンゼンを基盤に、触媒機能を切り替える光応答性チオウレア・DMAP 複合触媒 1[1]（Figure 1a）を開発し、インドールのピルビン酸エチルに対する Friedel-Crafts 反応[2]において、光構造変換に伴う 7.4 倍の触媒活性の切り替えを実現している。しかしながら、触媒 1 は活性型の *cis*-アゾベンゼン体において、酸部位のチオウレアと塩基部位の 4-ジメチルアミノピリジンによってインドールとピルビン酸エチルが逆向きに捕捉され、反応点が接近しづらくなっていることから、効果的な触媒機能が発現していないと推定された（Figure 1b）。そこで本研究では、インドールとピルビン酸エチルがより接近しやすい形で捕捉され、より高い触媒活性が期待できる改良型光応答性チオウレア・DMAP 複合触媒 2（Figure 1a）の設計開発を行った。アゾベンゼン骨格とチオウレアユニットをメチレンを挟んで連結することで、ピルビン酸エチルをインドールと同じ向きで捕捉し、インドールとピルビン酸エチルが容易に接近できると想定した（Figure 1c）。改良型触媒 2 を合成し、Friedel-Crafts 反応において光応答性の触媒活性の切り替えを評価した。

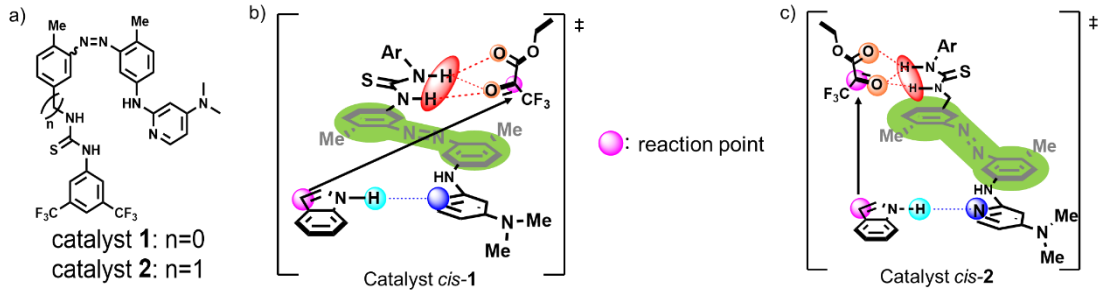

Figure 1. a) modification of catalyst, b) assumed transition state of *cis*-**1**, c) assumed transition state of *cis*-**2**

1) 平成 30 年度　川口明裕　第 7 回 CSJ 化学フェスタ 2017　P8-045
2) G. K. S. Prakash et al., *Angew. Chem. Int. Ed.* **2005**, *44*, 3086

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Ti_2Ni 触媒を用いたアルコールの β-アルキル化反応

(関西大化学生命工)○川崎 一気・山口 千尋・香西 凌・近藤 亮太・大洞 康嗣

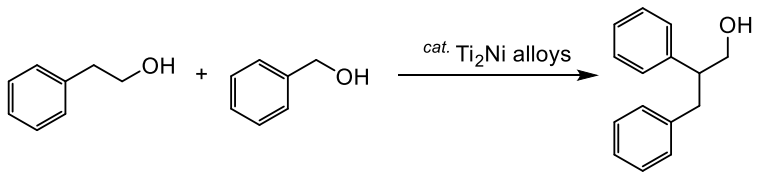
Ti_2Ni Alloys Catalyzed β-Alkylation of Alcohols

(*Faculty of Chemistry, Materials and Bioengineering, Kansai University*)
○Itsuki Kawasaki, Chihiro Yamaguchi, Ryo Kanishi, Ryota Kondo, Yasushi Obora

Heterogeneous catalysts are industrially utilized due to their stability and ease of separation and recycling. They are used for hydrogenation / dehydrogenation reactions.[1] Hydrogen auto-transfer involving these reactions is an important key-step in C-C and C-N formation process using alcohols. Our research group has reported bulk Ti-Pd alloys as a catalyst for applying the hydrogen auto-transfer.[2] Ti-Pd alloys are composed of Ti that has a high affinity for hydrogen and Pd that has a high catalytic activity. In this work, we focused on Ni contained Ti alloys for the substitution of Pd. Ni is known for having high alloying efficiency with transition metals. Furthermore, its electrical properties are similar to those of Pd and it is less expensive than Pd.[3] In this presentation, we will report Ti-Ni intermetallic compound Ti_2Ni has catalytic activity in β-Alkylation of alcohols.

Keywords : Ti-Ni alloy; β-Alkylation; hydrogen absorbing alloys; alcohols; intermetallic compound

不均一系触媒は高い安定性と分離の容易さなどの理由から工業的に広く用いられている. 不均一系触媒を用いた水素化・脱水素化反応は多く報告されている [1]. 水素化・脱水素化反応を伴う新たな C-C, C-N 結合形成反応に水素移動反応がある. 我々は水素との親和性の高い Ti に触媒活性の高い Pd を固溶させた Ti-Pd 固溶体合金を不均一系触媒として用いた水素移動反応を報告している [2]. さらに触媒活性の向上させるため Pd と類似した電子的性質を持ち, 多くの遷移金属と異なる質量比で合金化できる性質を持つ Ni に注目した [3]. Ni 不均一系触媒を用いた水素移動反応への利用は多く報告されており, Pd よりも安価であることから Pd の代替として利用を考えた. 今回, 我々は Ti と Ni の金属間化合物である Ti_2Ni が水素移動反応の一種であるアルコールの β-アルキル化反応へ触媒活性を示すことを見出したため報告する.



1) (a)X. Jiang, X. Nie, X. Guo, C. Song, J. G. Chen, *Chem. Rev.,* **2020**, *120*, 7984. (b)Y. Dai, X. Gao, Q. Wang, X. Wan, C. Zhou, Y. Yang, *Chem. Soc. Rev.,* **2021**, *50*, 55909.
2) (a) M. Utsunomiya, R. Kondo, T. Oshima, M. Safumi, T. Suzuki, Y. Obora, *Chem. Commun.*, **2021**, *57*, 5139. (b)Y. Takahashi, R. kondo, M. Utsunomiya, T. Suzuki, H. T. Takeshita, Y. Obora, *ChemCatChem*, **2019**, *11*, 2432.
3)(a)S. De, J. Zhang, R. Luque, N. Yan, *Energy Environ. Sci.,* **2016**, *9*, 3314.(b)T. Irrgang, R. Kempe, *Chem. Rev.,* **2019**, *119*, 2524.

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日本化学会 第104春季年会 (2024)

酸化セリウム触媒による 1,2-ジオールの酸化的 C-C 結合開裂

（東京都立大学）○中村 雪乃・三浦 大樹・宍戸 哲也

Ceria-catalyzed oxidative C-C bond cleavage of 1,2-diols

(*Tokyo Metropolitan University*)○Yukino Nakamura, Hiroki Miura, Tetsuya Shishido

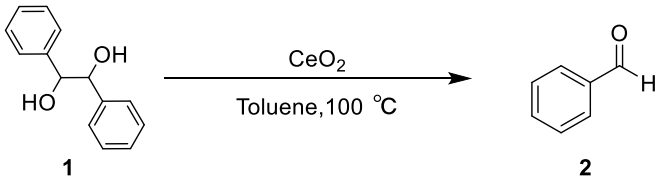
The oxidative cleavage of C–C bonds in 1,2-diols is crucial for the effective utilization of biomass feedstocks and their conversion into functional molecules. However, the activation of C–C bonds remains challenging because they are thermodynamically stable. Hence, direct and selective cleavage of C–C bonds are desired process. On the other hand, the development of reusable heterogeneous catalysts for the cleavage of C–C bonds is important from the perspectives of sustainable chemistry.

In this study, we found that the oxidative cleavage of C–C bond of 1,2-diols proceeded efficiently by the use of CeO_2 catalyst., The reaction of hydrobenzoin (**1**) in the presence of a catalytic amount of CeO_2 at 100℃ in toluene proceeded efficiently to obtain benzaldehyde (**2**) in a good yield (Scheme 1). Moreover, doping of other metallic elements into CeO_2 enhanced its activity.

Keywords : 1,2-diol; C–C bond cleavage; Ceria

1,2-ジオールの C–C 結合開裂はバイオマス原料の有効的な活用、さらには機能性分子への変換において重要である。しかし、一般的に C–C 結合は熱力学的に安定であるためその活性化は困難とされている。そのため C–C 結合の直接かつ選択的な開裂を可能にする新しい触媒系が求められている。一方、環境負荷やコストの観点から再利用可能な不均一系触媒を用いた反応の開発が望まれる。そこで本研究では、酸化セリウム（CeO_2）触媒存在下において 1,2-ジオールの酸化的 C–C 結合開裂反応が効率的に進行することを見出した。

触媒量の CeO_2 存在下でヒドロベンゾイン（**1**）の反応を Toluene 溶媒中、100℃で検討したところ、C–C 結合開裂が効率的に進行し、ベンズアルデヒド（**2**）が良好な収率で得られた（Scheme 1）。さらに、CeO_2 に他の金属元素をドープすることによって触媒活性の向上がみられたことから、その原因についても詳細に検討した。



Scheme 1. Ceria-catalyzed oxidative C–C bond cleavage of hydrobenzoin

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担持 Pt-Bi 触媒を用いたアルコール類の空気酸化

(九州大学[1]・神奈川工科大学[2]) ○春口 一騎[1]・山本 向洋[1]・河合 靖貴[1]・山本 英治[1]・村山 美乃[2]・吉澤 明菜[1]・徳永 信[1]
Aerobic oxidation of alcohols with supported Pt-Bi catalysts ([1]*Kyushu University*, [2]*Kanagawa Institute of Technology*) ○Kazuki Haruguchi[1], Hinata Yamamoto[1], Yasutaka Kawai[1], Eiji Yamamoto[1], Haruno Murayama[2], Akina Yoshizawa[1], Makoto Tokunaga[1]

Aerobic oxidation of alcohols with heterogeneous Pt-Bi catalysts is the focus of extensive study from the perspective of green chemistry because no waste other than water is generated. The reaction is generally used at substrate concentrations as low as 10 wt%, but when water is used as a solvent, energy loss due to purification via distillation is a problem. Thus, catalysts that can be used at higher substrate concentrations are required. In this study, Pt-Bi catalysts were applied to the synthesis of *β*-hydroxy *β*-methylbutyrate (HMB), which is used as a muscle-building supplement from isoprene glycol (IPG), allowing reactions at higher substrate concentrations. The reaction of IPG with Pt-Bi catalyst gave HMB in 77% yield at a low concentration of 10 wt%. Furthermore, good yields were achieved even at substrate concentrations higher than 20 wt% (Figure 1). In addition, to investigate the effects of Bi species, the catalyst was analyzed before and after the reaction by X-ray photoelectron spectroscopy (XPS). The result showed that the valence of Pt was not change, but Bi was oxidated from 0 to 3 valence.
Keywords : Aerobic oxidation, Pt-Bi NPs, Alcohol, Carboxylic acid

担持 Pt-Bi 触媒を用いたアルコールの空気酸化は、環境負荷の小さな酸素を酸化剤とすることに加え、水以外の廃棄物が発生しないためグリーンケミストリーの観点から注目されている。この反応は通常 10 wt%程度の基質濃度で行われるが、水を溶媒とした場合、蒸留精製によるエネルギーロスが問題となるため、より高い基質濃度で実施可能であることが望ましい。そこで、本研究では、工業原料のイソプレングリコール（IPG）から、空気酸化によって筋肉増強のサプリメントに用いられる *β*-hydroxy *β*-methylbutyrate（HMB）を合成する反応において、高基質濃度で実施可能な Pt-Bi 触媒系の開発に取り組んだ[1)]。

IPG を Pt-Bi 触媒下で反応させたところ、20 wt%では HMB が 77%の収率で得られた。さらに、20 wt%以上の高い基質濃度でも良好な収率を達成した（Figure 1）。また、反応前後の触媒の X 線光電子分光法（XPS）を用いた分析では、反応中に Pt は変化しなかった一方で、Bi は 0 価から 3 価に酸化されていることが確認された。

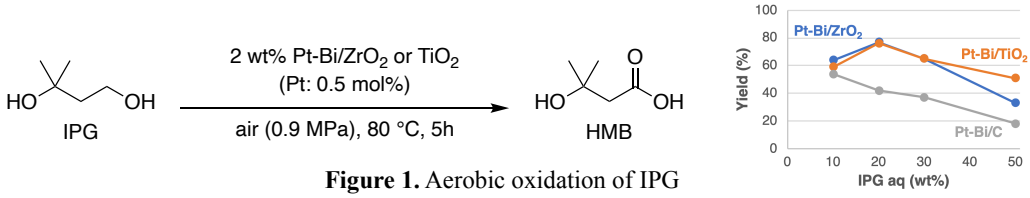

Figure 1. Aerobic oxidation of IPG

1) Kawai, Y.; Haruguchi, K.; Sumikawa, K.; Kawada, M.; Yamamoto, E.; Murayama, H.; Tokunaga M. *Appl. Catal. A Gen.*, **2022**, *643*, 118781.

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アルミナ担持 CuAl LDH のアルデヒド類のアンモ酸化反応における活性構造の創出に関する研究

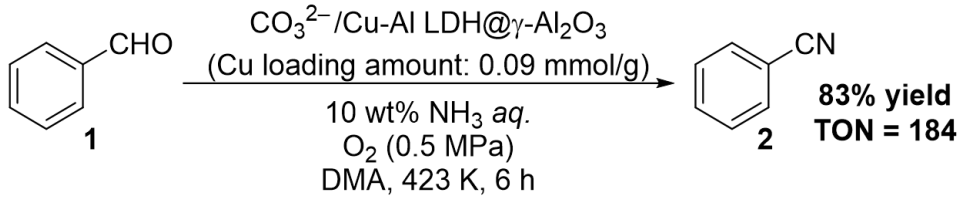
（千葉大院工[1]・バンドン工科大[2]）○淀瀬 涼太[1]・原 孝佳[1]・Enggah Kurniawan[1]・Yessi Permana[2]・一國 伸之[1]

Creation of active structure derived from Al_2O_3-supported Cu-Al LDH in ammoxidation of aldehydes ([1]*Chiba University*, [2]*Institut Teknologi Bandung*) ○Ryota Yodose,[1] Takayoshi Hara,[1] Enggah Kurniawan,[1] Yessi Permana,[2] Nobuyuki Ichikuni[1]

In this study, we found that alumina-supported Cu-Al layered double hydroxide (Cu-Al LDH@γ-Al_2O_3) acted as an effective heterogeneous catalyst toward ammoxidation of aldehydes into nitriles. The Cu-Al LDH@γ-Al_2O_3 catalyst was synthesized by simple alkaline coprecipitation method in the presence of commercially available γ-Al_2O_3 described in the literature under the condition that $Cu^{2+}/Al^{3+} = 1$.[1)] The crystallite size of Cu-Al LDH on γ-Al_2O_3 decreased with decreasing Cu loading amount, confirmed by XRD. This catalyst (Cu loading amount: 0.09 mmol/g) efficiently proceeded ammoxidation of benzaldehyde into benzonitrile with 10 wt% aqueous NH_3 under 0.5 MPa of molecular oxygen in *N,N*-dimethylacetamide (DMA) solvent, the turnover number reached up to 184 based on the Cu amount. During catalytic reaction, the Cu(II) species in the nanosheet of LDH transformed into catalytically active species.

Keywords : Cu-Al layered double hydroxide catalyst; liquid phase ammoxidation; alumina support; aqueous ammonia; molecular oxygen

本研究ではアルミナ表面に担持した層状 Cu-Al 複水酸化物 (Cu-Al LDH@γ-Al_2O_3) をアルデヒド類からニトリル類を得るアンモ酸化反応に用いると, 不均一系触媒として有効に機能することを見出した．Cu-Al LDH@γ-Al_2O_3 触媒は市販の γ-Al_2O_3 と共存させ, $Cu^{2+}/Al^{3+} = 1$ となる条件で文献記載[1)]のアルカリ共沈法により合成した. XRD 測定から Cu の担持量が減少するにつれて γ-Al_2O_3 表面の Cu-Al LDH の結晶子サイズは小さくなった. 5 気圧酸素雰囲気下，DMA 溶媒中, 10 %アンモニア水を窒素源として銅の担持量が 0.09 mmol/g の Cu-Al LDH@γ-Al_2O_3 触媒を用いるとベンズアルデヒドからベンゾニトリルへのアンモ酸化反応は効率良く進行し，銅基準の触媒回転数は 184 に達した．この反応の触媒活性種は Cu-Al LDH 基本層の Cu(II)種が反応中に構造転換されることで創出されることが分かった.



1) F. Yusniyanti, T. Hara, K. Makishima, E. Kurniawan, T. Fujimura, R. Sasai, C. Moriyoshi, S. Kawaguchi, Y. Permana, N. Ichikuni, *Chem. Asian J.*, e202300727 (2023)

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1231(1231, Bldg. 12 [3F])

[F1231-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Shun Ohta, Takashi Komuro

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1231-3am-01]

Paramagnetic one-dimensional chains with reduced Pt–Fe–Pt complex bridged by pivalamidate in trans fashion

○Iori Yoshida[1], Tomonori Adachi[2], Kazuhiro Uemura[1] (1. Faculty of Engineering, Gifu Univ., 2. Graduate School of Natural Science and Technology, Gifu Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1231-3am-02]

Crystal structures and properties of one-dimensional assembles consisting of octamolybdate-typed polyoxometalates and tetranuclear platinum complex

○Takayuki Oda[1], Momoka Oshika[2], Yuma Ito[2], Kazuhiro Uemura[1] (1. Faculty of Engineering, Gifu Univ., 2. Graduate School of Natural Science and Technology, Gifu Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1231-3am-03]

Synthesis of Anionic Pt(0) and Pd(0) Complexes Bearing Trigonal Bipyramidal Geometry

○Tokoro Miyazaki[1], Daisuke Izumi, Hajime Kameo[2], Hiroyuki Matuzaka[2] (1. Osaka Prefecture University, 2. Osaka Metropolitan University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1231-3am-04]

Synthesis and propeties of platinum complexes bearing cyclometalated ligands

○Shinnosuuke Hada[1], Satoshi Inoue[1], Katsunori Yamanishi[1], Tatsuya Kawamoto[1] (1. The Univ. of Kanagawa)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1231-3am-05]

Synthesis and Reaction of Rhodium dinuclear Sandwich Complexes Bearing Bow-shaped π-Conjugated Unsaturated Hydrocarbon Ligands

○Iori Inoue[1], Yukiho Aida[1], Koji Yamamoto[2], Tsubasa Omoda[1], Tetsuro Murahashi[1] (1. Tokyo Tech., 2. National Defense Academy)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1231-3am-06]

Reactions of chlorosilylene supported by bulky iminophosphonamido ligands with Group 9 transition metal complexes

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○Ayana Kawanishi[1], Shintaro Takahashi[2], Akihiko Ishii[2], Daisuke Hashizume[3], Norio Nakata[2] (1. Faculty of Science, Saitama Univ., 2. Graduate School of Science and Engineering, Saitama Univ., 3. Riken)

Japanese

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

[F1231-3am-07]

Ligand-induced Reversible Assembly of Rh Atoms within a Sandwich Framework

○Yukiho Aida[1], Iori Inoue[1], Koji Yamamoto[2], Tsubasa Omoda[1], Tetsuro Murahashi[1] (1. Tokyo Tech., 2. National Defense Academy)

Japanese

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

[F1231-3am-08]

Metal selectivity in the complexation using by a terpyridine-based biradical ligand

○Yota Nagumo[1], Takuya Kanetomo[1], Masaya Enomoto[1] (1. Tokyo Univ. of Sci.)

Japanese

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

[F1231-3am-09]

Synthesis of Zinc Complexes Bearing Isoindoline-based Pincer-type Polyprotic Pyrazole Ligand

○Yuki Kajitani[1], Wei-Syuan Lin[2], Kuwata Shigeki[1] (1. Ritsumeikan University, 2. Tokyo Institute of Technology)

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

[F1231-3am-10]

Reactions of iminophosphonamido-chlorosilylene with anionic transition metal carbonyl complexes

○Haruna Sato[1], Shintaro Takahashi[1], Akihiko Ishii[1], Norio Nakata[1] (1. Graduate school of science and engineering, Saitama Univ.)

Japanese

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

[F1231-3am-11]

Synthesis and Structures of First-Row Transition Metal Complexes of Amide Ligands Having Aromatic Rings as Coordinating Groups

○Kazuma Tanaka[1], Shinnosuke Otsuka[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

Japanese

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

[F1231-3am-12]

Construction of Iron-Sulfur Clusters in a Cavity of a Cage-Type Ligand

○Koki Nagamatsu[1], Kenta Ochiai[1], Keita Yamanaka[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

Japanese

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

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[F1231-3am-13]

Synthesis of nickel complexes with imidazole moieties

○Kakeru Shinkai[1], Satoshi Inoue[1], Katsunori Yamanishi[1], Tatsuya Kawamoto[1] (1. Kanagawa University)

Japanese

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

[F1231-3am-14]

Synthesis and Properties of Heterobimetallic Complexes Containing a Vanadocene Skeleton, and Their Application to Dinitrogen Activation

○Asahi Suzuki[1], Hinano Kusunose[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1] (1. Osaka Univ.)

English

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

[F1231-3am-15]

Synthesis of a Quadruple-Pyridylated Imidazo[1,5-*b*]pyridazine-7-ylidene Ligand for Aiming the Formation of Bimetallic Complexes

○Márton Nagyházi[1], Miyu Sato[2], Kosuke Higashida[1], Masaya Sawamura[1,2] (1. Hokkaido University, WPI-ICReDD, 2. Hokkaido University, Faculty of Science)

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トランス架橋 Pt-Fe-Pt 三核錯体の還元および常磁性一次元多核化

（岐阜大工[1]・岐阜大院自然科技[2]）○吉田 伊央莉[1]・安達 友教[2]・植村 一広[1]

Paramagnetic one-dimensional chains with reduced Pt–Fe–Pt complex bridged by pivalamidate in trans fashion ([1]*Faculty of Engineering, Gifu University*, [2]*Graduate School of Natural Science and Technology, Gifu University*) ○Iori Yoshida,[1] Tomonori Adachi,[2] Kazuhiro Uemura[1]

It was succeeded in obtaining a paramagnetic heterometallic one-dimentional chain complex by mixing *trans*-$[Pt_2Fe(piam)_4(NH_3)_4](ClO_4)_3$ (piam = pivalamidate), ascorbic acid, and $(Bu_4N)_2[PtCl_4]$ in MeOH. Single crystal X-ray structure analysis showed the chain structure of –[Pt–Fe–Pt]–Pt– with metal–metal bonds. The magnetic susceptibility measurement revealed that antiferromagnetic interaction of Fe(+3) through –Pt–Pt–Pt– with TN = 80 K.
Keywords : Multinuclear complex; Hetero-metal; Magnetic behavior; One-dimensional chain

我々は、第一遷移金属（M）と白金がトランス位で架橋され、Pt–M–Pt と並んだ三核錯体の *trans*-$[Pt_2M(piam)_4(NH_3)_4]^{2+}$ (piam = pivalamidate)の合成に成功している。[1] シス位で架橋されたものと違い、dz^2 軌道が不安定化し、三核錯体が多量化する傾向があり、M = Mn, Co, Ni, Cu の場合、二量化して、–Pt---Pt–の 3.8 Å の距離で、金属結合を介した反強磁性的相互作用を示す。本研究では、*trans*-$[Pt_2Fe(piam)_4(NH_3)_4]^{3+}$の還元と、一次元化多核化を検討したので、各種物性測定とともに報告する。

trans-$[Pt_2Fe(piam)_4(NH_3)_4](ClO_4)_3$ の MeOH 溶液に、アスコルビン酸を加え、$(Bu_4N)_2[PtCl_4]$とゆっくり混合すると、赤色結晶の **1** が析出した。単結晶 X 線構造解析の結果、**1** は$[\{Pt_2Fe(piam)_4(NH_3)_4\}\{PtCl_4\}]_n(ClO_4)_n$ で、*trans*-$[Pt_2Fe(piam)_4(NH_3)_4]$と$[PtCl_4]$が繰り返し並び、金属が–[Pt–Fe–Pt]–Pt–と並んだ一次元鎖錯体であった。非架橋の白金間距離は 3.0 Å で、Fe は–Pt–Pt–Pt–の 11.2 Å の距離で金属結合していた。組成を考慮すると、金属酸化数は Pt(+2)および Fe(+3)と考えられる。**1** の磁化率測定をしたところ、常温での χT 値は、3.65 $cm^3 K mol^{-1}$ で不対電子 5 個分であり、Fe(+3)は高スピン状態と考えられる。χT 値は低温になるにつれ減少し、ネール温度 80 K を示し、2 K で 0.07 $cm^3 K mol^{-1}$ となり、金属結合を介した反強磁性的相互作用を示した。

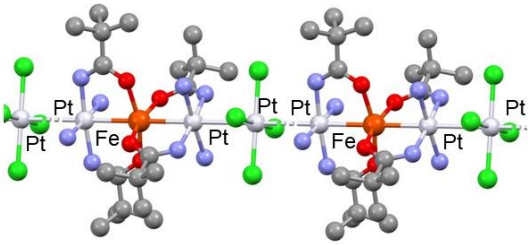

図 1. **1** の結晶構造

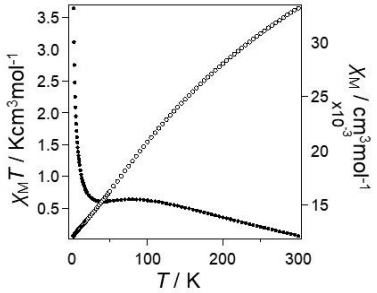

図 2. 磁化率測定結果

1) A. Takamori, K. Uemura. *Inorg. Chem.* **2022**, *61*, 5762-5778.

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Lindqvist 型からの構造変換を経たポリオキソメタレート-白金一次元集積体の構造と性質

(岐阜大工[1]・岐阜大院自然科技[2]) ○小田嵩之[1]・大鹿桃果[2]・伊藤悠真[2]・植村一広[1]
Crystal structures and properties of one-dimensional assembles consisting of octamolybdate-typed polyoxometalates and tetranuclear platinum complex ([1]*Faculty of Engineering, Gifu University,* [2]*Graduate School of Natural Science and Technology, Gifu University*) ○Takayuki Oda,[1] Momoka Oshika,[2] Yuma Ito,[2] Kazuhiro Uemura[1]

Previously, we have succeeded in obtaining one-dimensional mixed-valence assembles by mixing Keggin-typed or Dawson-typed polyoxometalate with tetranuclear platinum complex. In this study, we will show the syntheses and crystal structures of similar assembles consisting of *β*-octamolybdate-typed ones, discussing its crystal structure and physical properties.
Keywords : Polyoxometalate; *One-dimensional; Mixed-valence; Multinuclear complex*

我々は、Kegging 型および Dawson 型ポリオキソメタレートと、白金四核錯体を混合し、一次元状および二次元状の混合原子価集積体の合成に成功している。[1)] 今回、モリブデン六核の Lindqvist 型、および八核の *β*-octamolybdate 型の、内包イオンをもたないポリオキソメタレートを用いて集積化の検討をした。

既報を参考に合成した白金四核錯体の $[Pt_2(piam)_2(NH_3)_4]_2(CF_3SO_3)_4$ (piam = pivalamidate)と、Lindqvist 型の$(n\text{-}Bu_4N)_2[Mo_6O_{19}]$を、MeCN 中で 1:1 の割合で混合し、ゆっくり蒸発させると緑色結晶が析出した。単結晶 X 線構造解析の結果、$\{[Mo_8O_{26}][Pt_2(piam)_2(NH_3)_4]_2\}_n$ で、$[Pt_2(piam)_2(NH_3)_4]_2$ と *β*-$[Mo_8O_{26}]$が 1:1 で繰り返し並んだ一次元状の集積体であった（図 1)。POM は、反応の過程において、$[Mo_6O_{19}]^{2-}$から *β*-$[Mo_8O_{26}]$へと変換したと考えられる。白金四核錯体中の白金間距離は、錯体内が 2.7617(6) Å、錯体間が 2.8662(6) Å で、$Pt(+2.25)_4$ の酸化状態をもつ白金ブルーに特徴的であった。よって、白金四核錯体の電荷は+5 で、*β*-$[Mo_8O_{26}]$は−5 となる。すなわち、金属酸化数は Pt(+2.25) と Mo(+7.83) と混合原子価状態で、双方に不対電子が存在すると考えられる。当日は、一次元集積体の生成メカニズムと各種諸物性測定の結果も発表する予定である。

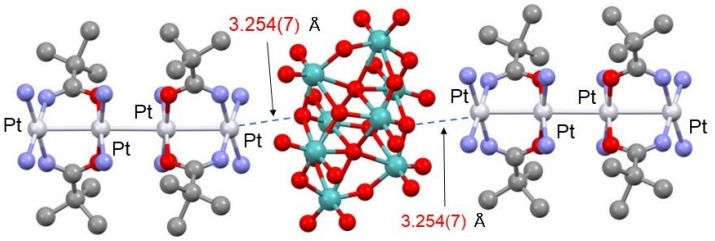

図 1. 一次元集積体の構造

1) 日本化学会第 103 春季年会 K503-1pm-13, K503-1pm-14.

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三方両錐形構造を有するアニオン性 Pt(0)および Pd(0)錯体の合成

（阪府大理[1]・阪公大院理[2]）○宮﨑 十志[1]・泉 大輔[1]・亀尾 肇[1,2]・松坂 裕之[1,2]

Synthesis of Anionic Pt(0) and Pd(0) Complexes Bearing Trigonal Bipyramidal Geometry

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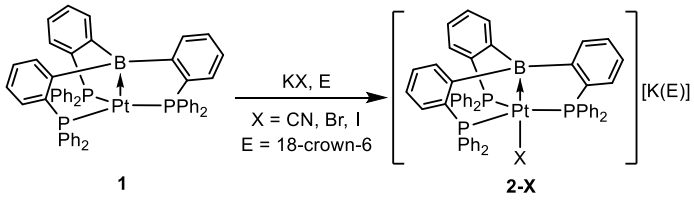
Anionic M(0) complexes (M = Group 10 metals) have been proposed as active species in a variety of coupling reactions. However, structural determinations of these highly nucleophilic species have rarely been realized. Recently, we have synthesized and structurally characterized anionic Pt(0) complexes with diphosphine-borane (DPB) ligands.[1] In this study, we report the synthesis of anionic Pt(0) complexes with TPB (triphosphine-borane) ligand and realize a new type of geometry for anionic Pt(0) complexes (Scheme 1). The desired anionic Pt(0) complex **2-CN** was synthesized by the reaction of the coordinatively unsaturated Pt(0) complex **1** with KCN in the presence of 18-crown-6. Similarly, the uses of KBr and KI also gave the corresponding anionic Pt(0) complexes **2-X** (X = Br, I) in good yields. X-ray structure analysis of **2-X** (Figure 1) revealed the first trigonal bipyramidal structure for Pt(0) anions. Furthermore, the XPS analysis on **2-X** supported d^{10} Pt(0) electron configuration.

Keywords : Pt, Anionic complexes, Trigonal Bipyramidal Geometry

アニオン性 10 族 0 価錯体は、様々なカップリング反応の活性種として提案されている。しかしながら、それら高度に求核的な化学種の構造解析はほとんど実現されていない。最近、所属グループでは、ボラン配位子の σ-電子受容性による求核的な中心金属の安定化効果に着目して、DPB（diphosphine-borane) 配位子を有するアニオン性 Pt(0) 錯体を合成し、その構造解析を実現した [1]。本研究では、アニオン性 Pt(0) 錯体の新しいタイプの幾何構造を実現するため、TPB (triphosphine-borane) 配位子を用いて、アニオン性 Pt(0) 錯体の合成を検討した (Scheme 1)。配位不飽和な Pt(0) 錯体 **1** と KCN を 18-crown-6-ether 存在下で反応させることで、アニオン性 Pt(0) 錯体 **2-CN** を合成した。同様に、錯体 **1** と KBr や KI との反応でも、対応するアニオン性 Pt(0) 錯体 **2-X** (X = Br, I) を良好な収率で得た。錯体 **2-X** の単結晶 X 線構造解析を行い (Figure 1)、Pt まわりは三方両錐 (TBP) 構造をとることを明らかにした。さらに、XPS スペクトルより錯体 **2-X** が Pt(0)の電子状態であることを確認した。



Scheme 1. Synthesis of anionic TBP Pt(0) complexes **2-X**

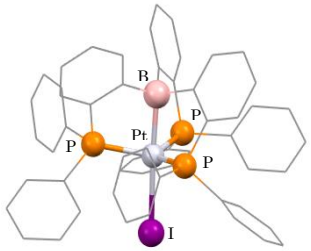


Figure 1. Structures of **2-I**

1) Kameo, H. et al. *Angew. Chem. Int. Ed.* **2023**, *63*, e202301509.

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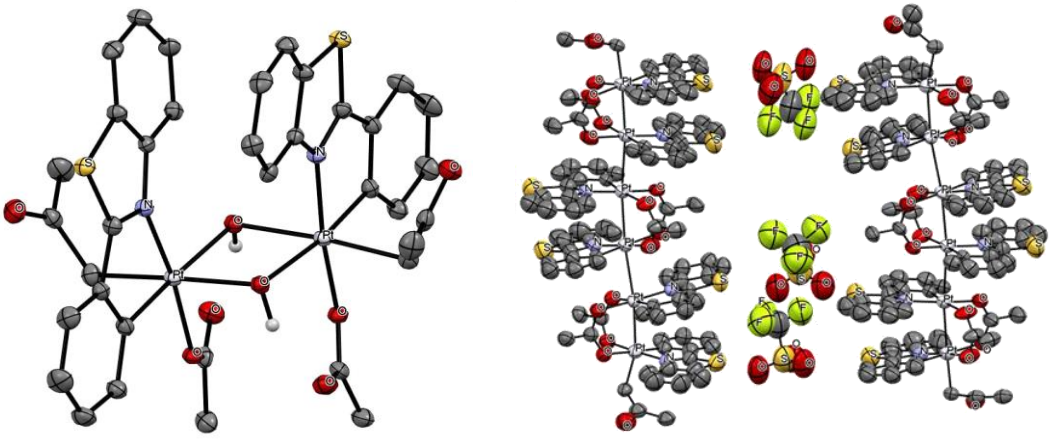
シクロメタレート型配位子を有する白金多核錯体の合成と性質

（神奈川大理）○羽田 慎之介・廣瀬 茉央・山西 克典・川本 達也
Synthesis and properties of polynuclear platinum complexes with cyclometalated ligands (*Faculty of Science, Kanagawa University*) ○Shinnosuke Hada, Mao Hirose, Katsunori Yamanishi, Tatsuya Kawamoto

The reaction of $[PtCl_2(dmso)_2]$ with 2-phenylbenzothiazole in acetic acid afforded an acetato-bridged dinuclear platinum(III) complex with chlorine atoms at the axial positions. A green powder showing photochromism in acetone solution was obtained by reacting the platinum(III) dinuclear complex with silver salt and K_2CO_3 aqueous solution. Upon crystallization of this green powder, both hydroxo-bridged platinum(IV) dinuclear complex and linear hexanuclear complex were obtained as crystals. Furthermore, when the linear hexanuclear complex was dissolved in acetone, it exhibited the same photochromic behavior as the green powder.
Keywords : platinum complex, photochromism, polynuclear complex

当研究室において、酢酸中で$[PtCl_2(dmso)_2]$と 2-phenylbenzothiazole を反応させると、軸位に塩素原子を有するシクロメタレート型白金(Ⅲ)二核錯体が合成できることを明らかにした。アセトン中、同じ白金(Ⅲ)二核錯体を銀塩およびK_2CO_3水溶液と反応させることで、アセトン溶液においてフォトクロミズムを示す緑色粉体が得られた。また、この緑色粉体を結晶化したところ、ヒドロキソ架橋白金(Ⅳ)二核錯体と直鎖状六核錯体(下図)が得られた。さらに、その直鎖状六核錯体のアセトン溶液は、緑色粉体と同じフォトクロミズムを示すことも分かった。



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弓状型 π-共役系不飽和炭化水素配位子を有する Rh 二核サンドイッチ錯体の合成と反応性

(東工大物質理工[1]・防衛大応化[2]) ○井上 伊織[1]・相田 有希歩[1]・山本 浩二[2]・重田 翼[1]・村橋 哲郎[1]

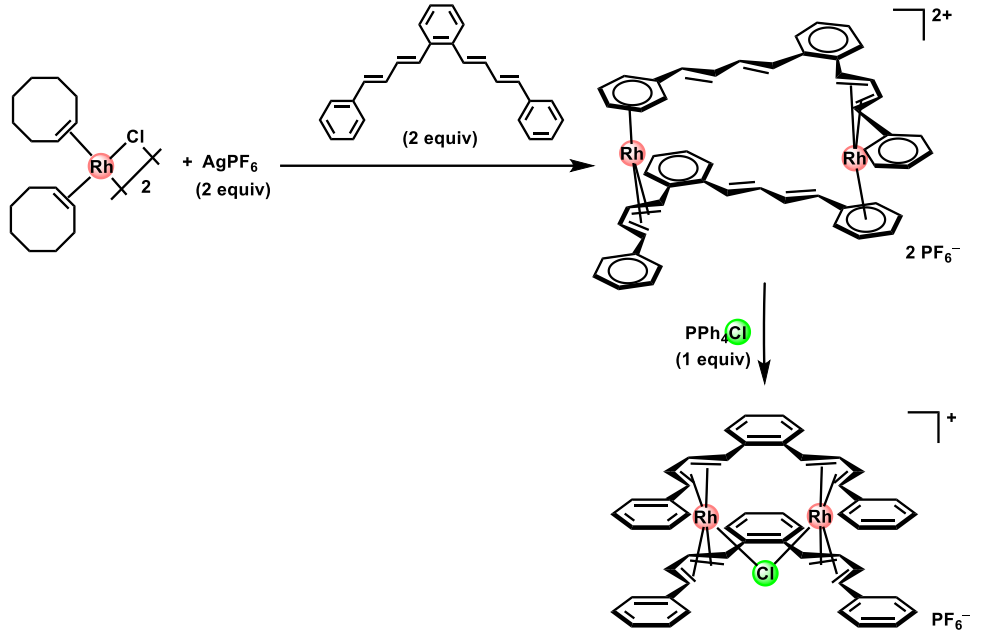
Synthesis and Reaction of Rhodium dinuclear Sandwich Complexes Bearing Bow-shaped π-Conjugated Unsaturated Hydrocarbon Ligands

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology,* [2]*Department of Applied Chemistry National Defense Academy*)
○Iori Inoue,[1] Yukiho Aida,[1] Koji Yamamoto,[2] Tsubasa Omoda,[1] Tetsuro Murahashi[1]

Although the chemistry of the dinuclear sandwich complexes has been developed with the use of group 10 metals, recently the chemistry has been also developed with group 9 metals. Here, we report synthesis of the dinuclear Rh sandwich complex by using bow-shaped unsaturated hydrocarbon ligands. This complex undergoes translocation of metal atoms upon accommodation of a chloride ligand. The structures of dinuclear sandwich complexes were determined by NMR and X-ray crystallographic analysis.

Keywords : Rhodium; Sandwich Complex

複核サンドイッチ錯体の化学は主に 10 族金属を用いて発展してきたが、最近我々のグループは、9 族金属を用いて展開している[1)]。今回、弓状型に屈曲した π-共役構造をもつ不飽和炭化水素を架橋配位子として用い、Rh 二核サンドイッチ錯体を合成した。この錯体はクロリド配位子を収容する際に金属原子移動を起こすことを明らかにした。それぞれの錯体は NMR 測定及び X 線構造解析によって同定した。



1) I. Inoue, K. Yamamoto, S. Sakaki, T. Murahashi, *Chem. Eur. J.* **2021**, *27*, 10558.

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嵩高いイミノホスホナミド配位子を有するクロロシリレンと 9 族遷移金属錯体との反応

（埼玉大理 [1]・埼玉大院理工 [2]・理化学研究所 [3]）○川西 絢菜 [1]、高橋 慎太郎 [2]、石井 昭彦 [2]、橋爪 大輔 [3]、中田 憲男 [2]

Reactions of chlorosilylene supported by bulky iminophosphonamido ligands with Group 9 transition metal complexes ([1]*Faculty of Science, Saitama Univ.*, [2]*Graduate School of Science and Engineering, Saitama Univ.*, [3]*Riken*) ○Ayana Kawawnishi,[1] Shintaro Takahashi,[2] Akihiko ishii,[2] Daisuke hashizume,[3] Norio Nakata[2]

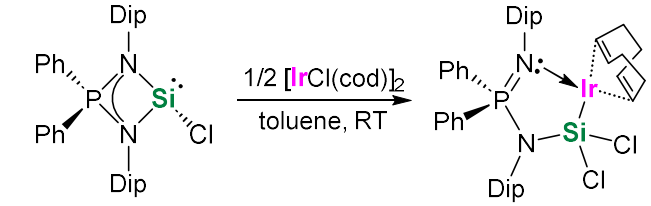
We have already succeeded in the synthesis of iminophosphonamido silylenes **1** and **2**, which exhibit strong σ-donor ability.[1,2] For example, ^{t}Bu-substituted derivative **1** acted as a typical L-type ligand in the reaction of **1** with $[RhCl(cod)]_2$, giving the corresponding silylene-Rh(I) complex **3**.[1] Here, we report the complexation of a sterically demanding Dip-substituted derivative **2** (Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$) with Group 9 transition metal complexes.

Treatment of **2** with 0.5 equivalent of $[IrCl(cod)]_2$ in toluene led to the unexpected ring-expansion reaction forming a five-membered silairidacycle **4** in 54% yield. We also present the synthesis of the corresponding silarhodacycle.

Keywords : silylene, iminophosphonamido, iridium, rhodium, ring expansion

すでに本研究室では、アミジナート配位子[RC(NR’)$_2$]のリン類縁体であるイミノホスホナミド配位子[R$_2$P(NR’)$_2$]を導入したクロロシリレン **1** および **2** を合成し、これらの強力な電子供与性と多様な配位挙動を明らかにしている [1,2]。例えば、^{t}Bu 誘導体 **1** とロジウム(I)錯体、$[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) との反応では、**1** が典型的な L 型配位子として作用し、対応するシリレン―ロジウム(I)錯体 **3** が得られている [1]。本発表では、嵩高いアリール基である Dip 基 (Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$) を有するイミノホスホナミドシリレン **2** と一連の 9 族遷移金属錯体との反応を検討したので報告する。

2 と 0.5 当量の$[IrCl(cod)]_2$との反応をトルエン中、室温で行ったところ予想外の環拡大反応が進行し、対応する 5 員環シライリダサイクル **4** を収率 54%で得た。本発表では、対応するシラロダサイクルの合成についても行ったので併せて報告する。



2 (Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$) **4** (54%)

1) Takahashi, S.; Sekiguchi, J.; Ishii, A.; Nakata, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 4055.
2) Takahashi, S.; Ishii, A.; Nakata, N. *Chem. Commun,* **2021**, *57*, 6728.

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配位子の会合・脱離による Rh 二核サンドイッチ錯体の分子内可逆的金属集合挙動

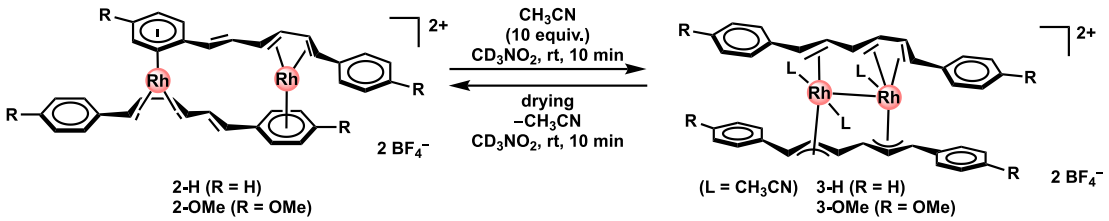
（東工大物質理工 [1]・防衛大応化 [2]）○相田 有希歩 [1]・井上 伊織 [1]・山本 浩二 [2]・重田 翼 [1]・村橋 哲郎 [1]

Ligand-induced Reversible Assembly of Rh Atoms within a Sandwich Framework ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Department of Applied Chemistry, National Defense Academy*) ○ Yukiho Aida,[1] Iori Inoue,[1] Koji Yamamoto,[2] Tsubasa Omoda,[1] Tetsuro Murahashi [1]

Here, we report that a dinuclear Rh sandwich complex of conjugated triene shows reversible assembly of Rh atoms inside the sandwich framework upon addition and elimination of acetonitrile ligands. By using a triene substituted by electron-withdrawing groups, we isolated the complex in which two Rh atoms are assembled within the sandwich framework. The structures of the dinuclear sandwich complexes were determined by NMR and X-ray crystallographic analysis.

Keywords : Rhodium; sandwich complex; dynamic behavior

2 枚のπ配位子によって 2 つ以上の金属原子を保持する複核サンドイッチ錯体は、動的挙動などの特異な反応性を示す。例えば、当研究室では、Pd 四核サンドイッチ錯体はレドックス反応によって可逆的な金属離散・集合挙動を示すことを報告している [1]。今回、鎖状共役トリエンを配位子に用いた Rh 二核サンドイッチ錯体がアセトニトリルの会合・解離によって可逆的な金属離散・集合挙動を示すことを明らかにした。また、配位子に電子求引性置換基を導入することでアセトニトリル会合体を単離し、各種 NMR 測定及び X 線構造解析によって構造を同定した。



1) T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi, H. Kurosawa, *Nat. Chem*. **2012**, *4*, 52.

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テルピリジン骨格のビラジカル配位子を用いた錯形成における金属選択性

（東理大[1]）○南雲 陽太[1]・金友 拓哉[1]・榎本 真哉[1]
Metal selectivity in the complexation using by a terpyridine-based biradical ligand ([1]*Tokyo Univ. of Sci.*) ○Yota Nagumo,[1] Takuya Kanetomo,[1] Masaya Enomoto[1]

A 4f-3d-2p heterospin system consists of a lanthanide metal (Ln, 4f spin), a 3d transition metal (3d spin), and an organic radical (2p spin). In this study, we have utilized a terpyridine-based biradical ligand, 2,2':6',2"-terpyridine-5,5"-diyl bis(*t*-butyl nitroxide) (5tpybNO), for a development of the 4f-3d-2p heterospin system (Fig. 1a). 5tpybNO coordinated to the 3d ion (a Zn^{2+} ion, in this study) via the terpyridine moiety according to the HSAB principle, yielding a 3d-2p complex $[Zn^{II}(Cl)_2(5tpybNO)]$ (**Zn-5tpybNO**). Interestingly, when **Zn-5tpybNO** and the Ln ions coexisted in the reaction mixture, 5tpybNO coordinated to the Ln ion, giving 4f-2p complexes $[Ln^{III}(hfac)_3(5tpybNO)]$ (**Ln-5tpybNO**; Ln = Ce, Nd, Gd~Er, Lu; Fig 1b). This metal selectivity of 5tpybNO seems to violate the HSAB principle, because the Ln^{3+} and Zn^{2+} ions are assigned to the hard and soft acids according to its rule. We will discuss the metal selectivity of the coordination of 5tpybNO and the physical properties of **Ln-5tpybNO**.
Keywords : Molecular Magnetism; Lanthanide Complexes

4f-3d-2p ヘテロスピン系錯体はランタノイド元素 (Ln, 4f スピン)、3d 遷移金属 (M, 3d スピン) と有機ラジカル (2p スピン) と 3 つのスピン源で構成される。本研究では、テルピリジン骨格の 5,5" 位にニトロキシドを導入したビラジカル配位子 (5tpybNO) を用いて 4f-3d-2p ヘテロスピン系錯体の形成を目指している (**Fig. 1a**)。3d 金属イオン (Zn^{2+}) と 5tpybNO の錯形成反応では、HSAB 則に従い、テルピリジン部位が配位した$[Zn^{II}(Cl)_2(5tpybNO)]$ (**Zn-5tpybNO**) が得られた。しかし、反応系に軟らかい Zn^{2+}イオンと硬い Ln^{3+}イオンが存在するとき、HSAB 則に反して、軟らかいテルピリジン部位が硬い Ln^{3+}イオンへ配位した単核 Ln 錯体 $[Ln^{III}(hfac)_3(5tpybNO)]$ (**Ln-5tpybNO**; Ln = Ce, Nd, Gd~Er, Lu) が得られた (**Fig. 1b**)。本発表では、5tpybNO で見られた金属選択的な配位能と得られた **Ln-5tpybNO** の物性について報告する。

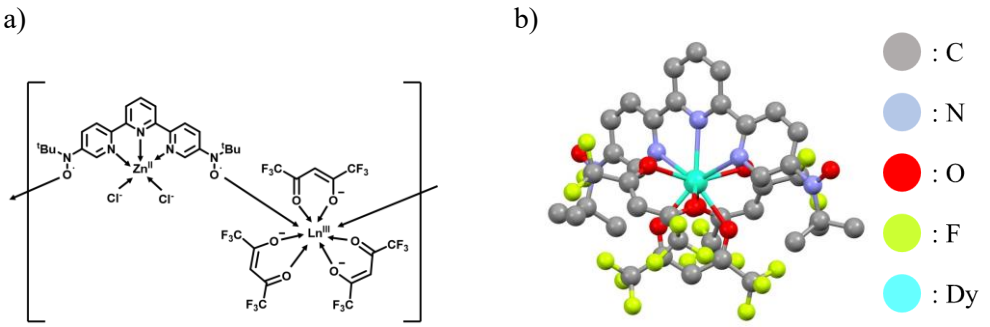

Fig. 1. (a) A molecular structure of the 4f-3d-2p heterospin system. (b) A crystal structure of **Dy-5tpybNO**.

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プロティックなピンサー型イソインドリン-ビス(ピラゾール)配位子をもつ亜鉛錯体の合成

（立命館大生命[1]・東工大物質理工[2]）○梶谷 裕樹[1]・林 暐軒[2]・桑田 繫樹[1]

Synthesis of Zinc Complexes Bearing a Protic Pincer-Type Isoindoline Bis(pyrazole) Ligand

([1]*College of Life Sciences, Ritsumeikan University*, [2]*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○ Yuki Kajitani,[1] Wei-Syuan Lin,[2] Shigeki Kuwata[1]

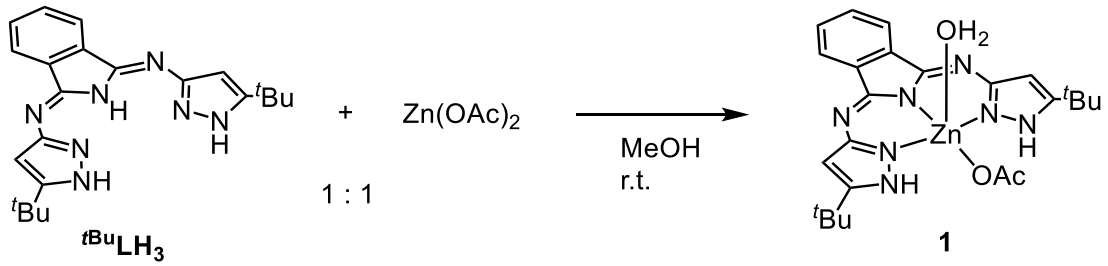
We have recently demonstrated that 1,3-bis(5-*tert*-butylpyrazol-3-ylimino)isoindoline ($^{t\mathrm{Bu}}LH_3$) with three Brønsted acidic protons undergoes stepwise deprotonation on transition metals such as iron,[1] copper,[2] and cobalt.[3] We are also interested in redox properties of $^{t\mathrm{Bu}}LH_3$ bearing a π-conjugated structure analogous to phthalocyanine. We thus chose zinc, which is a redox-inactive metal and explored its coordination chemistry to $^{t\mathrm{Bu}}LH_3$.

When zinc acetate and an equimolar amount of $^{t\mathrm{Bu}}LH_3$ were stirred in methanol at room temperature, a square-pyramidal pincer-type zinc complex [Zn(H_2O)(OAc)($^{t\mathrm{Bu}}LH_2$)] (**1**) was obtained accompanied by spontaneous deprotonation of the isoindoline NH group in $^{t\mathrm{Bu}}LH_3$. Complex **1** was identified by ^{1}H NMR and single-crystal X-ray structure analysis. The redox behavior of the complex will also be reported.

Keywords: Zinc; Pyrazole Complex; Isoindoline Complex; Redox; Non-innocent Ligand

当研究室では最近、三つの酸性プロトンをもつビス(ピラゾール-3-イルイミノ)イソインドリン（$^{t\mathrm{Bu}}LH_3$）が鉄[1]や銅[2]、コバルト[3]などの金属錯体上で逐次的に脱プロトン化を受けることを見いだした。環構造が切断されたフタロシアニンに類似したπ共役系をもつ LH_3 配位子についてはその酸化還元特性にも興味がもたれるため、本研究では中心金属として酸化還元不活性と考えられる亜鉛を選択し、$^{t\mathrm{Bu}}LH_3$ の配位挙動を検討した。

酢酸亜鉛と 1 当量の $^{t\mathrm{Bu}}LH_3$ をメタノール中、室温で撹拌したところ、イソインドリン窒素の脱プロトン化を伴ってピンサー型亜鉛錯体[Zn(H_2O)(OAc)($^{t\mathrm{Bu}}LH_2$)] (**1**)が選択的に得られた。錯体 **1** は ^{1}H NMR および単結晶 X 線構造解析によって同定した。亜鉛中心は歪んだ四角錐型構造をとっている。錯体の酸化還元挙動についても報告する。



1) T. Toda, S. Kuwata, *Z. Anorg. Allg. Chem*. **2021**, *647*, 1471.
2) T. Sugiyama, Y. Kayaki, S. Kuwata, *The 102nd Annual Meeting of CSJ*, **2022**, J403-3vn-09.
3) W.-S. Lin, S. Kuwata, *The 73rd Conference of JSCC*, **2023**, 1Aa-01.

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イミノホスホナミドクロロシリレンとアニオン性遷移金属カルボニル錯体との反応

（埼玉大院理工）○佐藤 春菜・高橋 慎太郎・石井 昭彦・中田 憲男

Reactions of iminophosphonamido-chlorosilylenewith anionic transition metal carbonyl complexes (*Graduate School of Science and Engineering, Saitama University*)

○Haruna Sato, Shintaro Takahashi, Akihiko Ishii, Norio Nakata

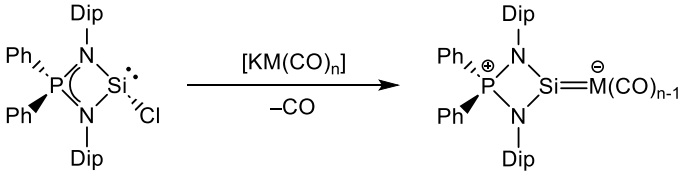
We have been investigating three-coordinated chlorosilylenes supported by an iminophosphonamide ligands, which exhibit strong σ-donating abilities compared with the related *N*-heterocyclic silylenes and carbenes. Here, we present the synthesis of novel silylidene complexes by the reactions of Dip-substituted silylene **1** (Dip ＝ 2,6-$^{i}Pr_2C_6H_3$) with anionic transition metal carbonyl complexes.

The reaction of chlorosilylene **1** with [$KMn(CO)_5$] in toluene led to the unexpected formation of silylidene-Mn(I) complex **2** accompanied with the elimination of 1 molar equivalent of CO. Similarly, the corresponding silylidene-Co(I) complex **3** was synthesized by the reaction of **1a** with [$KCo(CO)_4$].

Keywords : Silylene; Anionic transition metal carbonyl complexes; Manganese; Cobalt; Iminophosphonamide

当研究室では、*N,N*－キレート配位子であるイミノホスホナミド配位子を有する三配位のクロロシリレンに関する研究に取り組んでおり、これらが *N*－ヘテロ環状シリレンやカルベンよりも強い σ－ドナー性を有することを明らかにしている。本研究では、嵩高い Dip 基 (Dip ＝ 2,6-$^{i}Pr_2C_6H_3$) を有するイミノホスホナミドクロロシリレン **1** とアニオン性遷移金属カルボニル錯体との反応から新規なシリリデン錯体の生成を見出したので報告する。

クロロシリレン **1** に[$KMn(CO)_5$]をトルエン中で作用させたところ、1 モル当量の CO が脱離し,マンガン(I)－シリリデン錯体 **2** が黄色結晶として収率 68％で得られた。同様に、**1** と[$KCo(CO)_4$]との反応から対応するコバルト(I)－シリリデン錯体 **3** が収率 83％で得られた。本発表では、生成したシリリデン錯体 **2** および **3** の反応性についても調査したので併せて報告する。



1

2 (M = Mn, n = 5)
3 (M = Co, n = 4)

1) Takahashi, S.; Sekiguchi, J.; Ishii, A.; Nakata, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 4055–4059.
2) Takahashi, S.; Ishii, A.; Nakata, N. *Chem. Commun.* **2021**, *57*, 3203–3206.

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中心金属近傍に芳香環を配するアミド配位子を用いた第一遷移系列錯体の合成と構造

(阪大院理)○田仲 航馬・大塚 信之介・畑中 翼・舩橋 靖博

Synthesis and Structures of First-Row Transition Metal Complexes of Amide Ligands Having Aromatic Rings as Coordinating Groups (*Osaka Univ.*) ○Kazuma Tanaka, Shinnosuke Otsuka, Tsubasa Hatanaka, Yasuhiro Funahashi

In order to achieve small molecule activation mediated by first-row transition metals, we focus on coordinatively unsaturated complexes having highly electron-donating amide ligands. In this work, we performed synthesis and reactions of first-row transition metal complexes using amide ligands HL which possess aromatic rings as an auxiliary coordinating group. Desired homoleptic ML_2 (M = Cr, Mn, Fe, Co) were successfully synthesized by deprotonation of HL with $KN(SiMe_3)_2$, followed by addition of metal chlorides. Reduction of the Fe(II) and Co(II) complexes were also found to provide anionic Fe(I) and Co(I) complexes. X-ray crystallography exhibited that interaction between the metal centers and the aromatic rings becomes stronger for softer metal centers.

Keywords : First-Row Transition Metal Complexes; Coordinatively Unsaturated; Amide Complexes; Aromatic Rings; Reduction

第一遷移系列元素を用いた小分子活性化を目指して、我々は電子供与性の高いアミド配位子を導入した配位不飽和な錯体の合成と反応を行っている。通常、そのような錯体は不安定であるため、本研究では補助的な配位部位として芳香環を持つアミド配位子を用いることとした (**Figure 1**)。具体的には、配位子として N-ビフェニルアニリン誘導体 HL を用いて第一遷移系列錯体の合成と反応を行い、反応活性種の準安定化における芳香環の有効性について調査した。

配位子 HL に対して $KN(SiMe_3)_2$ を作用させ脱プロトン化した後に、0.5 当量の金属塩化物を反応させることで、ホモレプティックな ML_2 (M = Cr, Mn, Fe, Co)を合成した。また、比較対象として Zn 錯体を同様の方法により合成した。X 線構造解析により、これらの錯体では中心金属が芳香環と相互作用していることが確認できた。Fe および Co 錯体の電気化学測定の結果、還元側に可逆な酸化還元挙動が見られたため、実際に化学還元を試みたところ、対応する Fe(I)および Co(I)錯体が得られた。X 線回折により、還元によって中心金属がよりソフトになることで芳香環との相互作用が強くなることが明らかとなった。得られた錯体の反応性についても報告する予定である。

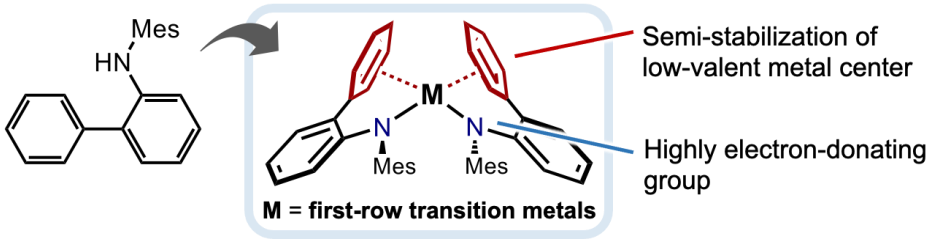

Figure 1. 錯体の合成戦略について

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籠型配位子が有する内部空間での鉄硫黄クラスターの構築

（阪大院理）○長松 幸輝・落合 建太・山中 慶太・畑中 翼・舩橋 靖博
Construction of Iron-Sulfur Clusters in a Cavity of a Cage-Type Ligand (*Osaka Univ.*) ○Koki Nagamatsu[1], Kenta Ochiai[1], Keita Yamanaka[1], Tsubasa Hatanaka[1], Yasuhiro Funahashi[1]

In order to construct iron-sulfur clusters having unique skeletons, we employed a cage-type ligand with three bis(imino)pyrrole moieties. As a result, a rare open-cubane-type [4Fe–3S] cluster was found to be obtained by addition of iron bisamide, 4-*tert*-butylbenzenethiol, and inorganic sulfur to the cage-type ligand. In addition, reaction of the [4Fe–3S] cluster with water resulted in conversion into a [2Fe–2S] cluster by protonation of one pyrrole and one imine moieties in the ligand. Structures of these clusters were determined by X-ray crystallography, and will be discussed.
Keywords : Model Complexes; Iron-Sulfur Clusters; Cage-Type Ligands; Multinuclear Complexes; Redox Behavior

生体内に存在する金属クラスターの中には特異な構造を持つものも数多く知られており、タンパク質内部の空間の形状や残基の配置により、それらのクラスターの構築や保持がなされていると予想される。我々はこれまでに、大環状配位子や籠型配位子と呼ぶクリプタンド型の配位子の内部空間を利用した第一遷移系列多核錯体の合成と反応を報告しているが、今回、天然に見られる鉄硫黄クラスターに着想を得て、籠型配位子を用いて新奇なコア構造を持つ鉄硫黄クラスターの構築を行った。

籠型配位子 $H_3\mathbf{L}^{pr}$ に対して $Fe\{N(SiMe_3)_2\}_2$、4-^{t}BuC$_6$H$_4$SH、および無機硫黄を順次作用させることにより、オープンキュバン型の[4Fe–3S]クラスター**1** が得られた（**Figure 1**）。X 線構造解析により、クラスター**1** に含まれる 4 つの鉄中心のうち、3 つはイミノピロリル部位と二座で、残り 1 つはイミン部位と単座で相互作用することで籠型配位子内に保持されていることがわかった。また、得られた構造から鉄の酸化数は $3Fe^{II}Fe^{III}$ であると推定した。クラスター**1** の骨格変換を期待して水を作用させたところ、[2Fe–2S]クラスター**2** が得られることがわかった。X 線回折から、籠型配位子のピロリル部位とイミン部位がそれぞれ 1 つプロトン化されていることがわかった。また構造から酸化数は $Fe^{II}Fe^{III}$ であると推定した。

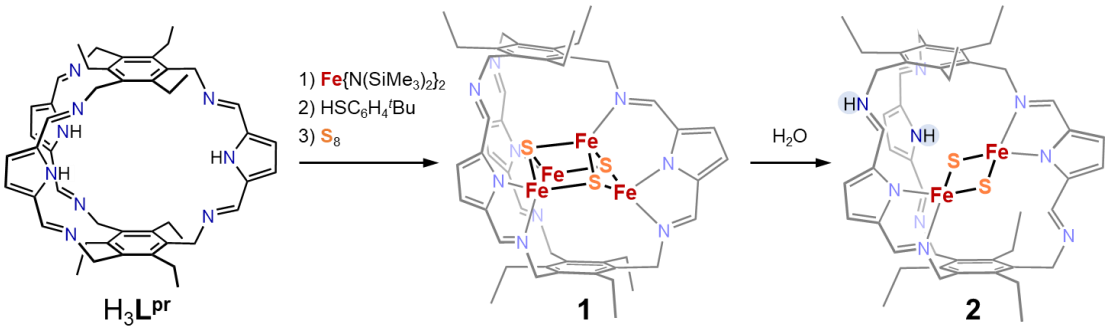

Figure 1. 錯体 **1**, **2** の合成と構造

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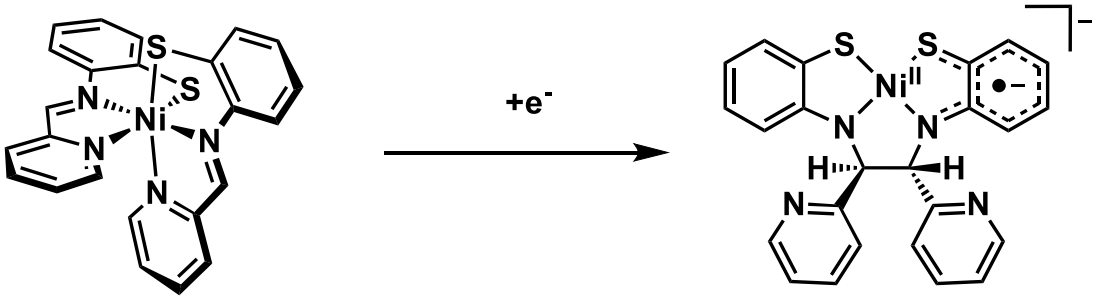
イミダゾール部位を有するニッケル錯体の合成

（神奈川大理）○新海 翔・井上 哲・山西 克典・川本 達也

Synthesis of nickel complexes with imidazole moieties(*Faculty of Science, Kanagawa University*)○Kakeru Shinkai, Satoshi Inoue, Katsunori Yamanishi, Tatsuya Kawamoto

It is known that Schiff base nickel complexes containing sulfur atoms derived from can be converted into various nickel complexes. Recently, it has been reported that an octahedral Schiff base complex with pyridine moieties in the pendant arms is a catalytic precursor for hydrogen evolution[1]. Furthermore, the catalytically active species was also found to be the one-electron reduced species of the complex, a non-innocent-type complex. Here we report on the synthesis of nickel complexes in which the pyridine moieties are replaced by imidazole.
Keywords ; Nickel; Schiff base Complex; Non-innocent-type Complex

ベンゾチアゾリン類をもつニッケル錯体からは、平面四配位の含硫シッフ塩基ニッケル錯体が得られ、その錯体から様々なニッケル錯体へと変換されることが知られている。側鎖にピリジン環を有するニッケル錯体の合成では、六配位八面体型のシッフ塩基錯体が得られ、その錯体は優れた水素生成触媒の前駆体として機能することが報告されている [1)]。また、実際の触媒の活性種はシッフ塩基錯体を 1 電子還元することで得られる。ノンイノセント型錯体の−1 価種であることも明らかにされている。本研究では、ピリジン環をイミダゾールに置き換えたベンゾチアゾリン類を配位子として用いてニッケル錯体を合成し、得られた錯体の構造を解明するとともにそのニッケル錯体の水の光還元反応における触媒作用を明らかにすることを目的とした。
そして、これまでに THF 中にて配位子と酢酸ニッケルをモル比 3:1 の割合で反応させることで六配位八面体型錯体を得ることができた。



1) Inoue, *et al., Chem. Commun.*, **2020**, *56*, 2829-2832.

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バナドセン骨格を有する異種金属二核錯体の合成と性質および窒素分子活性化への応用

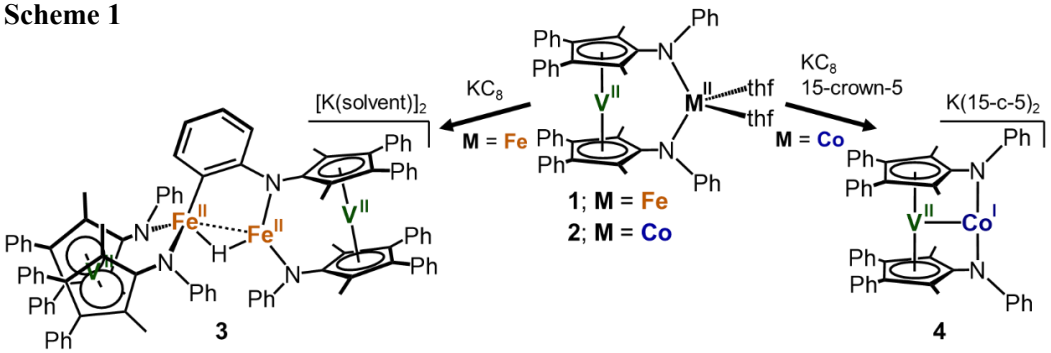
（阪大院理）○鈴木 朝陽・楠瀬 ひなの・畑中 翼・舩橋 靖博
Synthesis and Properties of Heterobimetallic Complexes Containing a Vanadocene Skeleton, and Their Application to Dinitrogen Activation (*Osaka Univ.*) ○Asahi Suzuki, Hinano Kusunose, Tsubasa Hatanaka, Yasuhiro Funahashi

We have previously synthesized heterobimetallic complexes of iron or cobalt using 1,1'-bis(mesitylamide)vanadocene ligand, and achieved dinitrogen activation. In this work, we used a vanadocene bisamide ligand having phenyl groups on nitrogen atoms, and performed synthesis and reactions of iron and cobalt complexes. The complexes **1** and **2** were synthesized by reaction of a lithium salt of N-(cyclopentadienyl)amide with $(TMEDA)_2VCl_2$, followed by addition of $FeCl_2$ or $CoCl_2$, respectively. Reduction of the iron complex **1** with KC_8 resulted in C-H activation of the phenyl group in the ligand to form a tetranuclear V_2Fe_2 complex **3**. On the other hand, reduction of the cobalt complex **2** gave a cobalt(I) complexes **4**. Catalytic dinitrogen conversion was also found to be accomplished by the complexes **1** and **2**.
Keywords : Low-Valent Complexes; Metallocene; Arylamide Ligands; Catalytic Dinitrogen Conversion; C-H Bond Activation

我々は電子供与性の高いアミド配位子を導入した第一遷移系列多核錯体の合成と基質活性化を行っている。これまでに、1,1'-ビス(メシチルアミド)バナドセン配位子を有する Fe および Co 錯体を用いて、触媒的な窒素分子変換が可能であることを見出している。[1] 今回、窒素原子上の置換基の影響を調べるため、メシチル基をフェニル基に置換した配位子を用いて、Fe および Co 錯体の合成と反応を行った。

N-(シクロペンタジエニル)アニリドのリチウム塩に対し、$(TMEDA)_2VCl_2$、$FeCl_2$ または $CoCl_2$ を順次作用させることで、Fe 錯体 **1** および Co 錯体 **2** を合成した (Scheme 1)。**1** に KC_8 を作用させ還元したところ、配位子上のフェニル基の C-H 結合活性化が進行し、四核 V_2Fe_2 錯体 **3** が得られた。一方で、**2** の還元からは Co 中心が一価に還元された錯体 **4** が得られた。**1**、**2** を触媒とする窒素分子変換を検討したところ、錯体基準でそれぞれ 12 当量、21 当量のアミンが得られることが明らかとなった。

Scheme 1



1) T. Hatanaka, H. Kusunose, H. Kawaguchi, Y. Funahashi, *Eur. J. Inorg. Chem.* **2020**, *2020*, 1449-1455.

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Synthesis of a Quadruple-Pyridylated Imidazo[1,5-*b*]pyridazine-7-ylidene Ligand for Aiming at Formation of Bimetallic Complexes

([1]*WPI-ICReDD, Hokkaido University*, [2]*Faculty of Science, Hokkaido University*) ○Márton Nagyházi,[1] Miyu Sato,[2] Kosuke Higashida,[1] Masaya Sawamura[1,2]

Keywords: *N-Heterocyclic carbene, multidentate ligand, bimetallic complex*

Multimetallic active sites are common feature of highly efficient metalloenzymes in the biological systems as well as synthetic catalysts.[1] Hence, multinuclear complexes bearing such multimetallic active sites are attractive synthetic targets for designing highly active catalysts. As a facile preparation method for the multinulear complexes, Tilley introduced a naphthyridine-based ligand with four pyridyl groups to prepare dinuclear copper complexes (Figure 1a).[2] We recently reported an imidazo-[1,5-*b*]pyridazine-7-ylidene scaffold with similar structural feature to the naphthyridine-based ligand, which was utilized to synthesize mono-*3d*-metal di-gold(I) trinuclear complexes (Figure 1b).[3] In this context, we envisioned the introduction of four pyridyl groups as coordination sites into the imidazo-[1,5-*b*]pyridazine-7-ylidene framework to realize novel dimetal complexes with multimetallic active sites. Herein we present the synthesis and complexation capability towards transition metals of a novel multidentate ligand, a quadruple-pyridylated imidazo-[1,5-*b*]pyridazine-7-ylidene scaffold (Figure 1c).

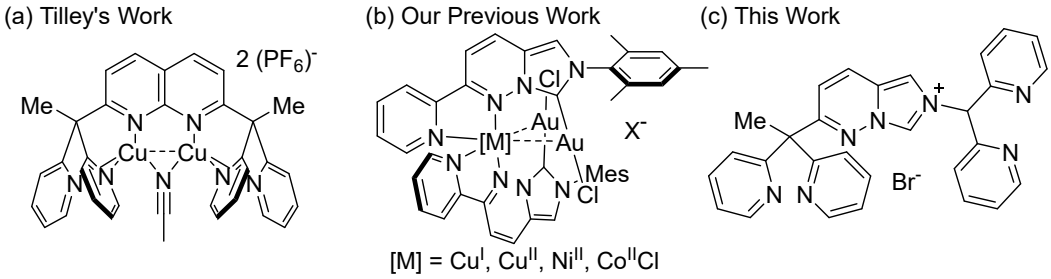

Figure 1. The structures of (a) a reported copper complex, (b) imidazo-[1,5-*b*]pyridazine-7-ylidene complexes, and (c) an quadruple-pyridylated imidazo-[1,5-*b*]pyridazine-7-ylidene precursor.

1) A. N. Desnoyer, A. Nicolay, P. Rios, M. S. Ziegler, T. D. Tilley, *Acc. Chem. Res.* **2020**, *53*, 1944-1956. 2) a) T. C. Davenport, T. D. Tilley, *Angew. Chem., Int. Ed.* **2011**, *50*, 12205-12208. Recent examples, b) A. N. Desnoyer, A. Nicolay, M. S. Ziegler, K. V. Lakshmi, T. R. Cundari, T. D. Tilley, *J. Am. Chem. Soc.* **2021**, *143*, 7135-7143. c) A. Nicolay, J. Héron, C. Shin, S. Kuramarohit, M. S. Ziegler, D. Balcells, T. D. Tilley, *Organometallics* **2021**, *40*, 1866-1873. 3) A. Kitabayashi, Y. Ono, T. Taketsugu, M. Sawamura, K. Higashida, *Chem. Eur. J.* **2023**, *29*, e202301673.

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1232(1232, Bldg. 12 [3F])

[F1232-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Takashi Matsuo, Tomoya Ishizuka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1232-3am-01]

Reactions of molybdenum nitride complexes with unsaturated compounds toward nitrogen–carbon bond formation

○Tomoyuki MIYAZAKI[1], Shun SUGINOME[1], Yoshiaki NISHIBAYASHI[1] (1. School of Engineering, The University of Tokyo)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1232-3am-02]

Molybdenum–Catalyzed Dinitrogen Borylation with Hydroboranes

○Atsushi Okochi[1], Shun Suginome[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1232-3am-03]

Capture and catalytic silylation of dinitrogen with novel molybdenum complexes bearing tripodal ligands

○Shoki Yabutani[1], Yuko Wasada[1], Tomohiko Inomata[1], Tomohiro Ozawa[1], Hideki Masuda[2] (1. Graduate School of Engineering, Nagoya Institute of Technology, 2. Aichi Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1232-3am-04]

Reaction of dioxo-ruthenium(VI) porphyrin complex with proton

○Arimi Mori[1], Yuki Honda[1], Hiroshi Fujii[1] (1. Nara Women's University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1232-3am-05]

Formation and reactivity of Ru(IV)-hydroxo complexes having N-heterocyclic carbene (NHC) ligands

○Shotaro Takeshita[1], Tomoya Ishizuka[1], Ayako Nagahara[1], Hiroto Fujisaki[1], Hiroaki Kotani[1], Takahiko Kojima[1] (1. Univ. of Tsukuba)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1232-3am-06]

Electrochemical Ammonia Oxidation Catalyzed by Ruthenium Complexes with Multidentate Ligand Containing N-Heterocyclic Carbene Moiety

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○Takuma Shimada[1], Takashi Inagaki[2], Shogo Kuriyama[1], Yoshiaki Nishibayashi[1] (1. School of Engineering, The University of Tokyo, 2. TDK Corporation)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1232-3am-07]

Photocatalytic substrate oxidation with a heteroaromatic ligand bound to a ruthenium(II) complex as an active site using dioxygen as a terminal oxidant through an Anti-Kasha mechanism

○Taichiro NISHI[1], Tomoya ISHIZUKA[1], Nanse NAMURA, Hiroaki KOTANI[1], Mamoru FUJITSUKA[2], Takahiko KOJIMA[1] (1. University of Tsukuba, 2. Osaka University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1232-3am-08]

Effects of Conjugated-Anchor Molecule Side Chain on Metal Oxide Surface Modification and Photocatalytic Hydrogen Generation

○Morihiro JO[1], Qichun JIANG[1], Atsushi KOBAYASHI[2], Hiroshi MASAI[1], Shin-ya TAKIZAWA[1], Tomohiro IWAI[1], Jun TERAO[1] (1. Graduate School of Arts and Sciences, The University of Tokyo, 2. Graduate School of Sciences, Hokkaido 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
[F1232-3am-09]

Carbazole-modified mononuclear metal complex photocatalysts workable for visible-light CO_2 reduction without the aid of external photosensitizers

○Yuya Tomiura[1], Akinobu Nakada[2,3], Hajime Suzuki[2], Osamu Tomita[2], Ryu Abe[2] (1. Faculty of Eng., Kyoto Univ., 2. Graduate School of Eng., Kyoto Univ., 3. PRESTO/JST)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1232-3am-10]

Development of machine-learning models for the ruthenium complex-catalyzed hydrogenation of ketones

○Haruno Nakajima[1], Chihaya Murata[1], Naoki Noto[2], Susumu Saito[2,1] (1. The Univ. of Nagoya, 2. IRCCS)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1232-3am-11]

Synthesis and Reactivities of Ruthenium-Porphyrin-Based Supramolecular Frameworks Constructed by Intermolecular Non-Covalent Interaction

○Akira Yoneda[1], Kento Kosugi[1], Yutaka Saga[1], Tetsuya Kanbe[1], Mio Kondo[2], Shigeyuki Masaoka[1] (1. Osaka Univ., 2. Tokyo Tech.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1232-3am-12]

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Effects of sulfur atoms in the ligand of Hoveyda-Grubbs-type complexes on their reactivities in polar solvents

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

Japanese

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

[F1232-3am-13]

Synthesis and characterization of amide-containing N2S3-type nitrosyl Ru(II) complex

○Yuya Terada[1], Yuko Wasada[1], Tomohiko Inomata[1], Tomohiro Ozawa[1] (1. Graduate School of Engineering, Nagoya Institute of Technology)

Japanese

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

[F1232-3am-14]

C-C Bond Formation between Two μ-Ethylidyne Ligands in a Diruthenium Bis(μ-ethylidyne) Complex Accompanied by the incorporation of an Iron Fragment

○Naoya Noguchi[1], Toshiro Takao[1] (1. Tokyo Institute of Technology)

Japanese

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

[F1232-3am-15]

Skeletal Rearrangement of a μ-η^2:η^4-Trienyl Ligand on a Diruthenium Site via a μ-Cyclohexadienyl Intermediate

○Taiki Taniguchi[1], Yohei Tsurumaki[1], Toshiro Takao[1] (1. Tokyo Institute of Technology)

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窒素–炭素結合形成に向けたモリブデンニトリド錯体と不飽和結合を有する化合物との反応

（東大院工）宮﨑 朋幸・杉野目 駿・西林 仁昭

Reactions of molybdenum nitride complexes with unsaturated compounds toward nitrogen–carbon bond formation (*Graduate School of Engineering, The University of Tokyo*) Tomoyuki MIYAZAKI, Shun SUGINOME, Yoshiaki NISHIBAYASHI

Our group reported stoichiometric[1] and catalytic[2] reactions to form nitrogen–carbon bonds between molybdenum nitride complexes derived from dinitrogen and carbon-centered electrophiles. For further improvement of such reactions, the use of highly reactive electrophiles should be avoided to suppress side reactions.

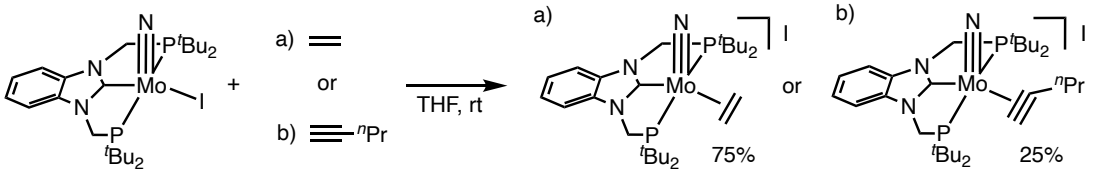
In this study, we have investigated reactivities of molybdenum nitride complexes with various unsaturated compounds toward formation of nitrogen–carbon bonds. Reactions of molybdenum nitride complexes with 10 equivalents of ethylene or 1 equivalent of 1-pentyne as substrates with carbon-carbon unsaturated bonds afforded the corresponding alkene and alkyne complexes in 75% and 25% yields, respectively. The structure and reactivity of the obtained complexes will be discussed in the presentation.

Keywords : molybdenum complex; nitride complex; organonitrogen compound; pincer-type ligand; nitrogen fixation

これまで当研究室は、窒素分子由来のモリブデンニトリド錯体と炭素求電子剤を用いて窒素－炭素結合を形成する量論反応[1]および触媒反応[2]を報告してきた。これらの反応では、強い求電子性を有する反応剤を用いることから、共存させることのできる試薬の制限が大きいことが課題であった。

今回我々は、炭素求電子剤以外の反応剤を用いた窒素－炭素結合の形成を目指し、不飽和結合を有する化合物を用いた反応を各種検討した。炭素－炭素不飽和結合を有する基質として、モリブデンニトリド錯体に対して 10 当量のエチレン(Scheme a)あるいは 1 当量の 1-ペンチン(Scheme b)を反応させたところ、不飽和結合がモリブデン中心に π 配位した新規錯体がそれぞれ収率 75%、25%で得られた。講演では、得られた錯体の構造および反応性に関して議論する予定である。

Scheme



(1) Itabashi, T.; Arashiba, K.; Kuriyama, S.; Nishibayashi, Y. *Dalton Trans.* **2022**, *51*, 1946–1954.
(2) Itabashi, T.; Arashiba, K.; Egi, A.; Tanaka, H.; Sugiyama, K.; Suginome, S.; Kuriyama, S.; Yoshizawa, K.; Nishibayashi, Y. *Nat. Commun.* **2022**, *13*, 6161.

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日本化学会 第104春季年会 (2024)

モリブデン錯体を用いたヒドロボランによる窒素分子の触媒的ホウ素化

（東大院工）○大河内 敦史・杉野目 駿・西林 仁昭

Molybdenum–Catalyzed Dinitrogen Borylation with Hydroboranes (*School of Engineering, The University of Tokyo*) ○Atsushi Okochi, Shun Suginome, Yoshiaki Nishibayashi

Dinitrogen borylation mediated by transition metal complexes under mild conditions is an attractive strategy for dinitrogen activation, considering strong driving force to form stable N–B bond and easy conversion of products to ammonia by hydrolysis. Our group previously reported the stoichiometric conversion of dinitrogen to borylamines by using molybdenum–nitride complex bearing a PNP-type pincer ligand and hydroboranes.[1]

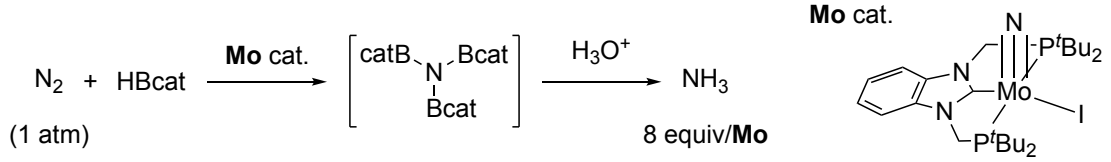
Herein, we have found that dinitrogen reacted with catecholborane in the presence of a catalytic amount of molybdenum–nitride complexes bearing a PCP-type pincer ligand to afford 8 equivalents of borylamine per the molybdenum atom (**Scheme**). This is the first example of the catalytic borylation of dinitrogen under mild condition using hydroborane as both reductant and borylating reagent.

Keywords : Molybdenum–Nitride Complex; Hydroboration; Nitrogen Fixation; Borylamine; Pincer Ligand

遷移金属錯体を用いた穏和な条件での窒素分子のホウ素化は、安定な N–B 結合の生成が熱力学的駆動力となること、また生成物を加水分解することによりアンモニアへと容易に変換できることから、窒素分子の活性化の戦略として極めて有望である。当研究室では以前、PNP 型ピンサー配位子を有するモリブデンニトリド錯体とヒドロボランを用いた、窒素分子の化学量論的なボリルアミンへの変換について報告している [1]。

今回我々は PCP 型ピンサー配位子を有するモリブデンニトリド錯体を用いることで、窒素分子とカテコールボランとの反応により、モリブデン錯体に対し最大 8 当量のボリルアミンが生成することを見出した**(Scheme)**。この結果は、ヒドロボランを還元剤かつホウ素化剤として用い、穏和な条件下での窒素分子の触媒的ホウ素化を達成した世界で初めての例である。

Scheme



(1) Itabashi, T.; Arashiba, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. *Organometallics* **2022**, *41*, 366–373.

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三脚型配位子を有する新規モリブデン錯体による窒素の捕捉および触媒的シリル化

(名工大院工[1]・愛工大工[2]) ○薮谷 翔輝[1]・和佐田祐子[1]・小澤 智宏[1]・猪股 智彦[1]・増田 秀樹[2]

Capture and catalytic silylation of dinitrogen with novel molybdenum complexes bearing tripodal ligands (*Graduate School of Engineering*, *Nagoya Institute of Technology*[1], *Aichi Institute of Technology*[2]) ○Shoki Yabutani[1], Yuko Wasada[1], Tomohiro Ozawa[1], Tomohiko Inomata[1], Hideki Masuda[2].

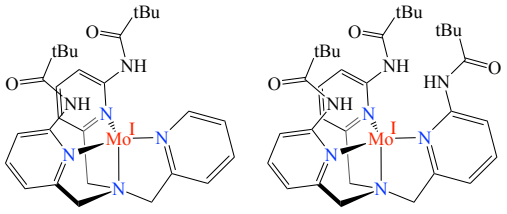
Nitrogen plays an important role in biological activities and is a constituent element of important substances for living organisms such as proteins, amino acids, and nucleic acids. The development of the Haber-Bosch process has enabled mankind to obtain unlimited amounts of organic nitrogen. However, this reaction is problematic because it consumes a large amount of energy. In this study, we developed a new complex catalyst for the synthesis of ammonia with the aim of establishing an ammonia synthesis method that consumes less energy.

In this study, we synthesized and characterized new molybdenum complexes with tripodal ligands, investigated the reaction conditions with nitrogen molecules, and evaluated the catalytic silylation reaction of nitrogen molecules. As a result, there were signs of reaction between the complexes and nitrogen molecules by UV-vis spectral measurements of the complexes, etc., and catalytic silylation reactions yielded catalytic amounts of silylamines. In addition, DFT calculations suggested that the reaction energy was negative at each step of the catalytic reaction, supporting the catalytic function of the complex.

Keywords : Complex; Dinitrogen; Ammonia; Catalyst

窒素は生命活動において重要な役割を担っており、タンパク質やアミノ酸、核酸などの生物にとって重要な物質の構成元素である。ハーバー・ボッシュ法の開発により、人類は無限の有機体窒素を得られるようになった。しかし、この反応はエネルギーを大量に消費することが問題視されている。本研究ではよりエネルギー消費の少ないアンモニア合成法の確立を目指し、アンモニア合成のための新規錯体触媒の開発を行なった。

本研究では、三脚型配位子を用いた新規モリブデン錯体の合成とその特性評価、窒素分子との反応条件の検討、および窒素分子の触媒的シリル化反応の評価を行った。その結果、錯体の UV-vis スペクトル測定などにより錯体と窒素分子が反応している兆候が見られ、触媒的シリル化反応においても触媒量のシリルアミンを得ることができた。また、DFT 計算により触媒反応の各段階で反応エネルギーが負の値を取ることが示唆され、本錯体の触媒としての機能が裏付けられた。



[Mo^{I}(BPPA)]$^{+}$ **[Mo^{I}(TPPA)]$^{+}$**

Figure 1. 今回合成した新規錯体 **[Mo^{I}(BPPA)]$^{+}$** と **[Mo^{I}(TPPA)]$^{+}$**

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ルテニウム 6 価ジオキソポルフィリン錯体とプロトンとの反応解析

（奈良女大理）○森　有美・本田　裕樹・藤井 浩

Reaction of Dioxo-Ruthenium(VI) Porphyrin Complex with Proton

(*Graduate School of Chemistry Biology and Environmental Science, Nara Women's University*)
○Arimi Mori, Yuki Honda, Hiroshi Fujii

The reactions of high-valent metal oxo complexes with proton have been proposed to be key processes for generating reactive species. Recently, we reported the generation of reactive high valent metal oxo porphyrin species from the protonation of oxoiron(IV) porphyrin and dioxo manganese(V) porphyrin complexes with proton. In this study, we examined the reaction of dioxo ruthenium(VI) porphyrin complex with proton.

We observed a new complex in the reaction of dioxo ruthenium(VI) porphyrin complex with trifluoroacetic acid (TFA). It was found to be a porphyrin-π-cation radical complex from the features of absorption signals and NMR analysis. Moreover, we studied kinetics by absorption spectroscopy to confirm the involvement of protons in the rate-limiting step. In this presentation, we report the structure expected from those results and the reactivity.

Keywords : Oxo Complexes ; Proton ; Reactive Intermediate ; Ruthenium ; Porphyrin

高原子価金属オキソ錯体は、酸化触媒として優れた機能を発揮する。鉄 4 価オキソポルフィリン錯体はプロトン存在下で不均化反応を観測でき、マンガン 5 価ジオキソポルフィリン錯体では非常に高活性なマンガンのオキソ錯体の同定に成功した。これらよりオキソ錯体とプロトンとの反応は重要であると考える。本研究ではルテニウムジオキソポルフィリン錯体において、プロトンとの反応により生成する錯体の電子構造と反応性を研究した。

ルテニウム 6 価ジオキソポルフィリン錯体にテトラフルオロ酢酸(TFA)を反応させると、今までにない新たな吸収スペクトルを持つ錯体を合成できた。吸収スペクトルの特徴と、NMR 測定の結果より、ポルフィリンカチオンラジカルが生成していることが判明した。また、擬 1 次反応条件下での速度論的実験により、律速段階にプロトンが関与していることを確認した。さらに、基質との反応性も検討した。今回の講演では、これらの結果から予想される構造や反応性について報告する。

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N-ヘテロ環状カルベン(NHC)を配位子に有する Ru^{IV}-ヒドロキソ錯体の生成とその反応性

（筑波大数物）○竹下 祥太朗・石塚 智也・永原 彩瑚・藤﨑 寛人・小谷 弘明・小島 隆彦

Formation and Reactivity of Ru^{IV}-Hydroxo Complexes Having *N*-Heterocyclic Carbene (NHC) Ligands (*Graduate School of Pure and Applied Sciences, University of Tsukuba*)

○Shotaro Takeshita, Tomoya Ishizuka, Ayako Nagahara, Hiroto Fujisaki, Hiroaki Kotani, Takahiko Kojima

Recently, besides high-valent metal-oxo complexes, high-valent metal-hydroxo complexes have attracted attention as active species for substrate oxidation.[1] In this study, introduction of strong σ-donating *N*-heterocyclic carbene and π-accepting bipyridine to Ru^{II}-aquo complexes as ancillary ligands enabled formation of unprecedented Ru^{IV}-OH complexes, showing activity in the oxidation of organic substrates (Fig. 1). In Raman spectra of a Ru^{IV}-OH complex, a vibration band for the Ru-O bond was observed at 633 cm^{-1}, indicating the single-bond character. The XANES spectrum of the Ru^{IV}-OH complex showed a 2.3 eV shift in the Ru-*K* edge compared to that of the starting Ru^{II}-OH_2 complex, suggesting an increase in the valence number by 2. The Ru^{IV}-OH complex was reactive for the oxidation of organic substrates such as benzaldehyde to afford $2e^-$-oxidized products.

Keywords : Ruthenium; Substrate Oxidation; N-Heterocyclic Carbene; Raman Spectroscopy; Hydroxo Ligand

最近、一般的に基質酸化反応の活性種として知られている高原子価金属-オキソ錯体以外にも、高原子価金属-ヒドロキソ錯体が、例は少ないながらも酸化活性種として注目を集めている。例えば、Mn^{IV}-OH 錯体は C-H 酸化反応などに活性を示すことが報告されている [1)]。本研究では、Ru 錯体の補助配位子として、強いσ供与性を持つ NHC とπ受容性を持つビピリジンを導入し、$(NH_4)_2[Ce^{IV}(NO_3)_6]$ (CAN)を酸化剤に用いることで、有機基質酸化活性を示す、前例のない Ru^{IV}-OH 錯体を合成した(Fig. 1)。得られた Ru^{IV}-OH 錯体の Raman スペクトルにおいて、633 cm^{-1} に Ru-O 結合の伸縮振動に由来するピークが観測され、従来の Ru^{IV}=O 錯体の伸縮振動 (798–833 cm^{-1})に比べて小さく、Ru-O 結合の単結合性が示された。また、Ru^{IV}-OH 錯体の XANES 測定において、*K* 吸収端が、原料の Ru^{II}- OH_2 に比べて 2.3 eV シフトしており、Ru^{IV} 錯体であることが示唆された。また、得られた Ru^{IV}-OH 錯体は、ベンズアルデヒド、シクロヘキサノール等の有機基質の酸化反応に対して活性を示し、2 電子酸化生成物を与えた。

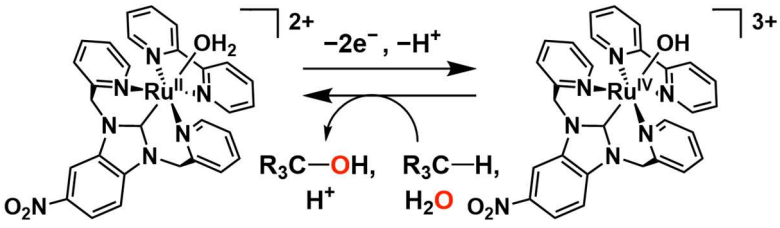

Fig. 1. Ru^{IV}-OH 錯体の生成と有機基質の酸化の反応式.

1) J. Cho and co-workers, *J. Am. Chem. Soc*. **2022**, *144*, 20752.

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N−ヘテロ環状カルベン含有多座配位子を持つルテニウム錯体を触媒とした電気化学的なアンモニア酸化反応

(東大院工[1]・TDK 株式会社[2]) ○嶌田 拓真[1]・稲垣 尭[2]・栗山 翔吾[1]・西林 仁昭[1]
Electrochemical Ammonia Oxidation Catalyzed by Ruthenium Complexes with Multidentate Ligand Containing N-Heterocyclic Carbene Moiety ([1]*The School of Engineering*, *The University of Tokyo,* [2]*TDK Corporation*) ○ Takuma Shimada,[1] Takashi Inagaki,[2] Shogo Kuriyama,[1] Yoshiaki Nishibayashi[1]

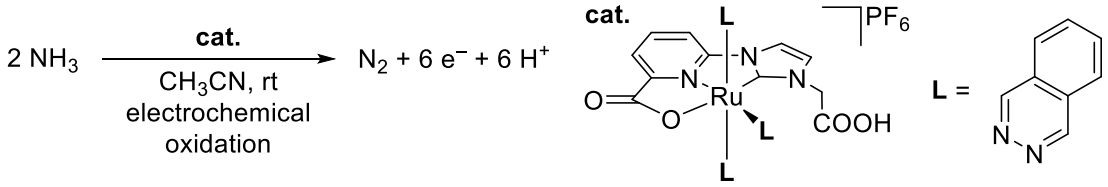
Recently, catalytic ammonia oxidation with transition metal catalysts has been actively studied. Our group previously found that ruthenium complexes bearing a 2,2'-bipyridine-6,6'-dicarboxylate ligand worked as highly effective catalysts toward electrocatalytic ammonia oxidation. In this study, we have synthesized novel ruthenium complexes with a multidentate ligand bearing an *N*-heterocyclic carbene moiety and investigated the catalytic activity of these complexes toward electrochemical ammonia oxidation.

Keywords : Ruthenium Complex; Ammonia; Oxidation; N-heterocyclic Carbene; Electrocatalytic Reaction

最近、遷移金属錯体を用いた触媒的アンモニア酸化反応の開発が活発に行われている。当研究室ではこれまでに、2,2’-ビピリジン-6,6’-ジカルボキシレート配位子を持つルテニウム錯体を用いた触媒的アンモニア酸化反応を報告してきた[1]。さらに、アキシャル位にフタラジンを有するルテニウム錯体が電気化学的アンモニア酸化反応に高い触媒活性を有することを見出した[2]。

今回我々は、より高活性なルテニウム触媒を開発することを目的に、金属と安定な結合を形成し高い電子供与性を有する *N*-ヘテロ環状カルベン配位子を有するルテニウム錯体を設計した。*N*-ヘテロ環状カルベン、ピリジン、およびカルボン酸部位を有する多座配位子を新規に合成し、この配位子とフタラジンを持つ新規ルテニウム錯体の合成に成功した。この新規ルテニウム錯体の電気化学的性質および電気化学的アンモニア酸化反応に対する触媒活性についても報告する予定である(Scheme 1)。

Scheme 1.



[1] K. Nakajima, H. Toda, K. Sakata, Y. Nishibayashi, *Nat. Chem.* **2019**, *11*, 702–709.
[2] H. Toda, K. Kuroki, R. Kanega, T. Yano, T. Yoshikawa, S. Kuriyama, Y. Himeda, K. Sakata, Y. Nishibayashi, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 980–988.

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ルテニウム(II)錯体上の複素環配位子を活性点とした anti-Kasha 型反応機構を経由する有機物の光触媒的酸素酸化反応

(筑波大院数物 [1]・阪大産研 [2]) ○西 太一朗 [1]・石塚 智也 [1]・名村 七星 [1]・小谷 弘明 [1]・藤塚 守 [2]・小島 隆彦 [1]

Photocatalytic Substrate Oxidation with a Heteroaromatic Ligand Bound to a Ruthenium(II) Complex as an Active Site Using Dioxygen as a Terminal Oxidant through an Anti-Kasha Mechanism ([1]*Graduate School of Pure and Applied Sciences, University of Tsukuba*, [2]*The Institute of Scientific and Industrial Research, Osaka University*)○Taichiro Nishi,[1] Tomoya Ishizuka,[1] Nanase Namura,[1] Hiroaki Kotani,[1] Mamoru Fujitsuka,[2] Takahiko Kojima[1]

Photocatalytic substrate oxidation using O_2 as a terminal oxidant has attracted attention, since it is environmentally benign. However, photocatalysis using O_2 as the oxidant suffers from difficulty such as competition with the formation of singlet oxygen ($^1O_2$) *via* energy transfer to $^3O_2$. In this study, we have successfully constructed a photocatalytic oxidation system of organic substrates, in which O_2 is used as the oxidant (Fig. 1). In the catalysis, the protonated form of a Ru^{II} complex **1**[1] (**1**-H^+), having a pyrazine moiety as an active site in one of the ancillary ligands, was used as a photocatalyst. The photocatalytic substrate oxidation proceeds not through the triplet MLCT excited state of **1**-H^+, but through a higher excited state, *i.e.*, the singlet π-π* excited state (^{1}π-π*) of the ligand having the pyrazine moiety, in the adduct of **1**-H^+ with a substrate. ^{1}H NMR analysis supported the association of **1**-H^+ with an organic substrate prior to the photocatalytic oxidation. Thus, **1**-H^+ in ^{1}π-π* with a short lifetime can perform the substrate oxidation in the adduct (Fig. 1). This photocatalytic reaction is an example that breaks the Kasha's rule, allowing us to use the species in ^{1}π-π* with suppressing the formation of $^1O_2$.

Keywords: Substrate Oxidation; Photocatalytic Reaction; Proton-Coupled Electron Transfer; Oxidation by Dioxygen; Transient Absorption Spectroscopy

酸素を末端酸化剤とする光触媒的基質酸化反応は、環境に優しい反応であることから近年注目されているが、$^1O_2$ の生成と競合するなどの問題点がある。本研究では、配位子内に活性点としてピラジン部位を有する Ru^{II} 錯体 **1**[1]のプロトン化体 **1**-H^+を光触媒とし、酸素を末端酸化剤とする有機基質の光触媒酸化反応系を構築することに成功した(Fig. 1)。錯体 **1**-H^+による光触媒反応は、^{3}MLCT 励起状態ではなく、さらに上の励起状態である錯体 **1**-H^+の補助配位子上の一重項π-π*励起状態(^{1}π-π*)を利用して進行することを明らかにした。^{1}H NMR 測定から基質と触媒 **1**-H^+の会合が示唆され、そのため短寿命の ^{1}π-π*にある励起種による酸化反応が可能になったと考えている。従って、この光触媒的反応は Kasha 則を破る稀有な例であると考えられる。また、補助配位子の ^{1}π-π*を利用しているために、酸素へのエネルギー移動による $^1O_2$ の生成が抑制されていると考えられる。

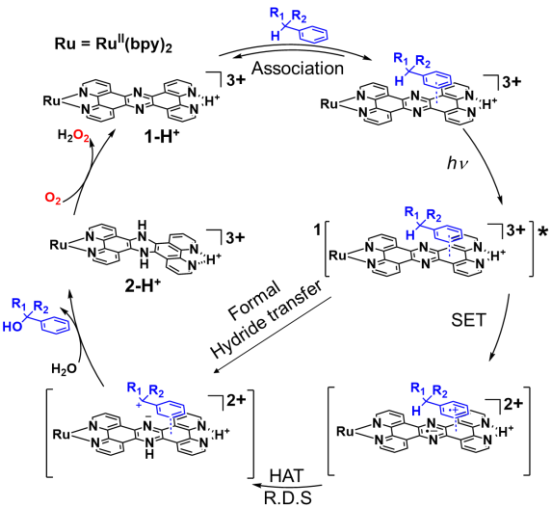

Fig. 1. **1**-H^+による光触媒的酸化反応の推定機構

[1] T. Sawaki, *et al. Dalton Trans.* **2020**, *49*, 17230.

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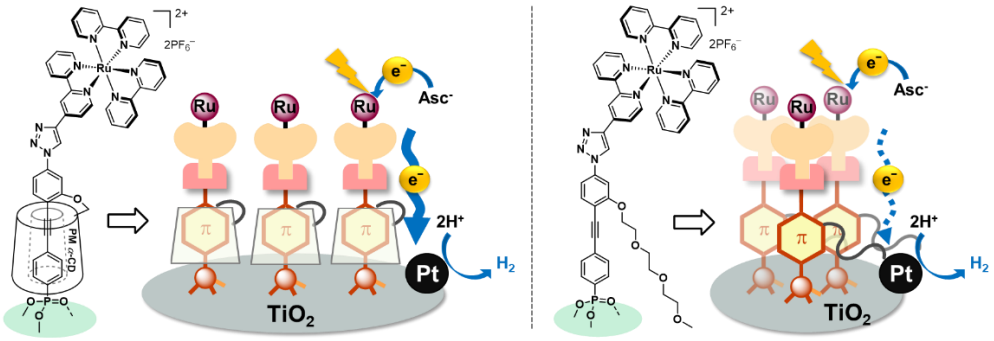
金属酸化物表面修飾と水素発生光触媒における共役アンカー分子側鎖の効果

（東大院総合文化[1]・北大院理[2]）○徐 盛浩[1]、Qichun JIANG[1]、小林 厚志[2]、正井 宏[1]、滝沢 進也[1]、岩井 智弘[1]、寺尾 潤[1]
Effects of Conjugated-Anchor Molecule Side Chain on Metal Oxide Surface Modification and Photocatalytic Hydrogen Generation ([1]*Graduate School of Arts and Sciences, The University of Tokyo*, [2]*Graduate School of Sciences, Hokkaido University*) ○Morihiro JO[1], Qichun JIANG[1], Atsushi KOBAYASHI[2], Hiroshi MASAI[1], Shin-ya TAKIZAWA[1], Tomohiro IWAI[1], Jun TERAO[1]

We recently reported aggregation-free surface modification of metal oxides using an insulated conjugated phosphonic acid anchor, in which the tolan structure was covered by covalently-linked permethylated α-cyclodextrin as a side chain. In this study, focusing on the influence of side chain structure on inorganic surface modification, we evaluated the photocatalytic hydrogen generation activity of Pt-supported TiO_2 nanoparticles containing Ru(II) photosensitizers introduced via conjugated phosphonic acid anchors bearing cyclic or linear side chains.
Keywords : Organic-inorganic hybrid materials; π-Conjugated molecule; Metal oxide; Photocatalyst; Hydrogen generation

我々は最近、トラン骨格に完全メチル化α-シクロデキストリン（PM α-CD）からなる環状被覆側鎖を導入した共役アンカー分子を開発し、金属酸化物への凝集のない表面修飾が可能なことを報告した[1)]。本研究では、共役アンカー分子の側鎖構造が表面修飾や触媒機能に与える効果に着目し、環状被覆及び鎖状側鎖を有する共役アンカーで接合した Ru(II)光増感剤含有白金担持 TiO_2 ナノ粒子の水素発生能を評価した。

水素発生光触媒は、アジド末端共役アンカーで修飾した白金担持 TiO_2 ナノ粒子と末端アルキンを有するポリピリジル Ru(II)錯体増感色素との銅触媒 Huisgen 付加環化反応により調製した。水素発生における Ru 原子当たりの触媒回転数は、環状被覆側鎖を有する光触媒の方が鎖状側鎖のものよりも高かった。修飾 ITO 膜ガラス基板の AFM 及び CV 測定から、環状被覆側鎖は、界面でのπ共役分子の凝集抑制及び分子–金属酸化物担体間の電子伝達に有効であると考えられる。



1) Chou, S.-Y.; Masai, H.; Otani, M.; Miyagishi, H. V.; Sakamoto, G.; Yamada, Y.; Kinoshita, Y.; Tamiaki, H.; Katase, T.; Ohta, H.; Kondo, T.; Nakada, A.; Abe, R.; Tanaka, T.; Uchida, K.; Terao, J. *Appl. Catal. B.* **2023**, *327*, 122373.

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光増感剤フリーで可視光 CO_2 還元を駆動するカルバゾール修飾型単核錯体光触媒

(京大工[1]・京大院工[2]・JST さきがけ[3]) ○冨浦 勇哉[1]・中田 明伸[2,3]・鈴木 肇[2]・冨田 修[2]・阿部 竜[2]

Carbazole-Modified Mononuclear Metal Complex Photocatalysts Workable for Visible-Light CO_2 Reduction without the Aid of External Photosensitizers

([1]*Fac. of Eng., Kyoto Univ.*, [2]*Grad. Sch. of Eng., Kyoto Univ.*, [3]*PRESTO/JST*) ○Yuya Tomiura,[1] Akinobu Nakada,[2,3] Hajime Suzuki,[2] Osamu Tomita,[2] Ryu Abe[2]

Most of the photocatalytic systems for CO_2 reduction using metal complexes require both photosensitizer and catalyst molecules, whereas only a few simple mononuclear complex photocatalysts have been reported so far. In this study, we found the modification of carbazole skeleton in the diimine ligand enables visible-light absorption to "visible-light inactive" mononuclear complex catalysts owing to its ligand-based donor-acceptor transition.
Keywords : Photocatalyst; CO_2 reduction; Metal complex; Mononuclear complex; Carbazole

金属錯体を光触媒として用いた CO_2 還元系が精力的に研究されているが、その多くは、触媒錯体に加えて光増感錯体を系中に添加する必要がある[1]。これら 2 元錯体系では、両者を結合した多核錯体を形成することが両者間の電子移動促進のために重要であることが知られている[1]が、多核錯体の合成が容易でない錯体系もしばしば存在する。一方で、よりシンプルな単核錯体を系中に添加するだけで進行する光触媒系は、$Re(bpy)(CO)_3L$ (L: 単座配位子)錯体[2]を用いた例などごく一部に限られている。本研究では、配位子のジイミン骨格にカルバゾールを修飾することで、本来可視光吸収能を持たない錯体触媒に配位子由来の可視光吸収能を付与できることを見出した。

ジブロモ基を有するビピリジン (Bpy)またはフェナントロリン (Phen)と、モノボロン酸エステルを有するフェニルカルバゾールを、鈴木カップリング反応により結合することで、カルバゾール修飾型配位子 **Cz_2X** (X = Bpy, Phen; Fig. 1a) を合成した。**Cz_2X** と 1 当量の$[Ru(CO)_2Cl_2]_n$ を反応させて得た Ru カルボニル錯体 (**Cz_2XRu**)は、カルバゾール未修飾の配位子を有する錯体 (**XRu**)と比べて可視光領域に強い吸収を示した (Fig. 1b)。分子軌道計算[3]により、**CzBpy** 配位錯体の最低励起状態は配位子内のドナーアクセプター遷移が支配的であることが示唆され、**Cz_2X** を配位子として用いることで中心金属種に依存せず多様な錯体触媒を可視光応答化できる可能性が示唆された。当日は、カルバゾール修飾が含む配位子が光吸収、電気化学的特性、及び光触媒活性へ与える影響について報告する予定である。

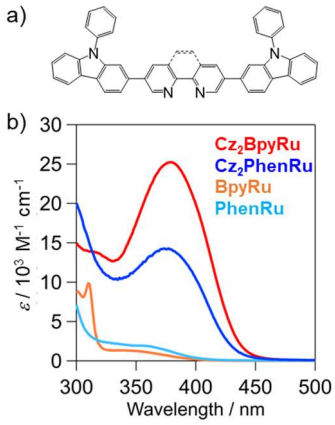

Fig. 1 (a) Molecular structure of ligand **Cz_2X** and (b) absorption spectra of their Ru carbonyl complexes.

1) Ishitani, O. *et al.*, *J. Photochem. Photobiol. C,* **2015**, *25*, 106.
2) Lehn, J.-M. *et al. J. Chem. Soc., Chem. Commun.* **1983**, *9*, 536.
3) Nakada, A.; Abe, R.; Chang, H.-C. *et al.*, *J. Mater. Chem. A*, **2022**, *10,* 19821.

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ルテニウム触媒によるケトンの水素化反応におけるデータベース構築と機械学習法の開発

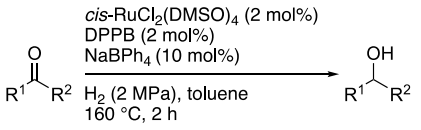
（名大院理[1]・名大 IRCCS[2]）○中島春野[1]・村田千隼[1]・納戸直木[2]・斎藤進[1,2]

Development of machine-learning models for the ruthenium-catalyzed hydrogenation of ketones ([1]*Graduate School of Science, Nagoya University,* [2]*IRCCS, Nagoya University*) ○ Haruno Nakajima,[1] Chihaya Murata,[1] Naoki Noto,[2] Susumu Saito[1,2]

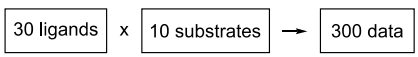
The development of machine-learning (ML) models capable of recognizing changes in reactivity, derived from factors such as used ligands and substrates, is crucial in achieving more efficient design and screening of metal catalysts. We have created a systematic database focusing on ligand- and substrate-types in the ruthenium-catalyzed hydrogenation of ketones. In addition, we have developed ML models to accurately predict the yield of products using the constructed database. Through an investigation into descriptors and ML algorithms, the combination of Mordred and histogram-based gradient boosting exhibited the best predictive performance (average R^2 = 0.83). Details on this investigation and its application will be discussed in the presentation.

Keywords : Ruthenium catalysis; Hydrogenation; Machine Learning; Ketones

金属錯体触媒の探索や設計を自動化する上で、使用する配位子や基質に応じた反応性の変化を認識できる機械学習モデルの開発は重要である[1]。本研究では、ルテニウム触媒を用いたケトンの水素化反応において、配位子と基質の種類に焦点を当てた網羅的データベースを構築し、また構築したデータベースを基に、反応収率を精度良く予測することが可能な機械学習モデルの開発に取り組んだ。その結果、mordred で算出した分子記述子と機械学習アルゴリズムの一つである勾配ブースティング法 histogram-based gradient boosting（HGB）の組み合わせが最も良好な予測精度を発揮することが明らかとなった（average R^2 = 0.83）。また、訓練データに含まれないホスフィン配位子の触媒活性を予測する「外挿型」の機械学習においても、使用するデータセットによっては、機械学習による予測が十分有効であることを見出した。その際、通常の HGB もある程度の効果を発揮したが、ドメイン適応の一種である KLIEP がより良い予測精度を発揮した（HGB：R^2 = 0.73、KLIEP：R^2 = 0.83）。



Database construction



Investigation into descriptors (with random forest)

Descriptor	MF	MK	MD	Mordred
R^2 test	0.6	0.48	0.74	0.79

MF: Morgan fingerprint, MK: MACCS Keys,
MD: RDKit 'MoleculeDescriptors'

Investigation into ML algorithms (with Mordred)

Algorithm	KNN	SVM	RF	HGB	MLP
R^2 test	0.28	0.66	0.82	0.83	0.72

KNN: k-Nearest neighbor, SVM: Support-vector machine,
RF: Random forest, MLP: Multi-layer perceptron

[1] (a) D. T. Ahneman, J. G. Estrada, S. Lin, S. D. Dreher, A. G. Doyle, *Science* **2018**, *360*, 186. (b) J. Werth, M. S. Sigman, *ACS Catal.* **2021**, *11*, 3916.

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非共有結合性相互作用により構築される Ru ポルフィリン超分子フレームワークの合成と反応性

（阪大院工[1]・東工大院理[2]・JST さきがけ[3]）○米田　暁[1]・小杉健斗[1]・神戸徹也[1]・嵯峨　裕[1]・近藤美欧[1,2,3]・正岡重行[1]

Synthesis and Reactivities of Ruthenium-Porphyrin-Based Supramolecular Frameworks Constructed by Intermolecular Non-Covalent Interaction ([1]*Graduate School of Engineering, Osaka University*, [2]*Graduate School of Science, Tokyo Institute of Technology*) ○ Akira Yoneda,[1] Kento Kosugi,[1] Tetsuya Kambe,[1] Yutaka Saga,[1] Mio Kondo,[1,2] Shigeyuki Masaoka[1]

Recently, the catalytic application of porous materials such as metal-organic frameworks (MOFs) has been actively studied using the properties of pores and constituent units. However, it is difficult to precisely design active sites in MOFs because vacant sites around the metal centers are easily capped during the construction of MOFs by coordination-bond-based assembly. Therefore, it is important to develop new type of porous materials bearing precisely designed active sites. We have found that the metal complexes with intermolecular interaction sites can form supramolecular frameworks, which have porous structures with active sites[1)].

In this work, we synthesized and characterized Ru-porphyrin supramolecular frameworks by introducing pyrene unit, which is capable of intermolecular interaction, into the *meso* position of Ru-porphyrin. In our presentation, we will report on electro- and photochemical properties and catalytic activity of the newly synthesized supramolecular frameworks.

Keywords : Supramolecular complex, Self-assembly, Porphyrin

近年、細孔や構成ユニットの性質を利用して有機金属構造体（MOF）などの多孔性材料の触媒への応用が盛んに研究されている。しかしながら、これらの材料は構造体構築のために配位結合を用いるために金属イオン周りが配位飽和となり、触媒活性サイトとなる置換活性サイトの設計に制限がある。よって、置換活性サイトを持つ新たな多孔性材料の開発は重要である。我々はこれまでに高い対称性を有するパドルホイール錯体やポルフィリンのメソ位に分子間相互作用可能な官能基を導入することで触媒活性中心となる置換活性サイトを緻密に配列した結晶性多孔体、超分子フレームワークが形成できることを見出している[1)]。

本研究では、Ru ポルフィリン錯体のメソ位に分子間相互作用可能なピレン部位を導入することで、超分子フレームワークを合成し、分光学的に同定した。発表では、得られた超分子フレームワークについて電気・光化学的特性、触媒活性の検討結果についても報告する。

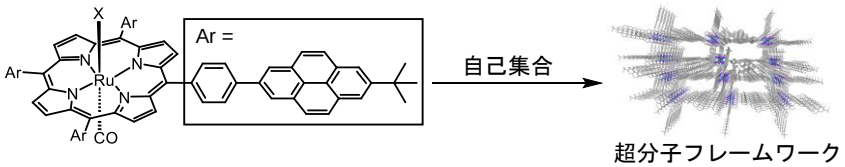

Figure 1. Formation of a Ru-porphyrin supramolecular framework.

1) K. Kosugi, C. Akatsuka, H. Iwami, M. Kondo, S. Masaoka., *J. Am. Chem. Soc.* **2023**, *145*, 10451.

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極性溶媒中における Hoveyda-Grubbs 型錯体の反応性に対する配位子上の硫黄原子効果

（奈良先端大・物質創成 [1]）○光定　誠修 [1]、衣川　翼 [1]、松尾 貴史 [1]、廣田 俊 [1]

Effects of sulfur atoms in the ligand of Hoveyda-Grubbs-type complexes on their reactivities in polar solvents.

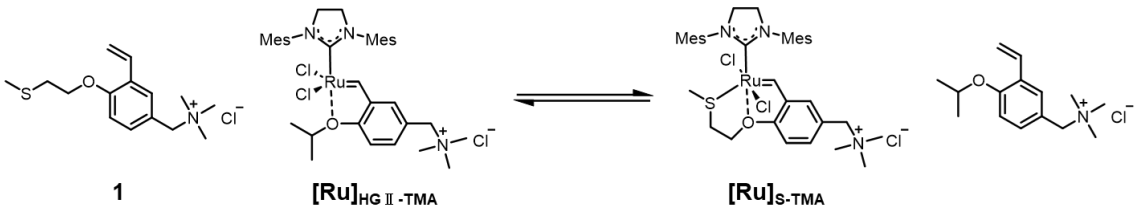
([1]*Division of Materials Science, Nara Institute of Science and Technology*)
○Seishu Mitsusada, [1] Tsubasa Kinugawa,[1] Takashi Matsuo,[1] Shun Hirota[1]

Hoveyda-Grubbs 2nd generation catalyst (HG-II) are expected as a tool of biomolecules modification because of its high stability and olefinic specificity. However, HG-II is hydrophobic and its reactivities decrease in aqueous media, indicating the necessity of structural optimization. We previously reported that an HG-type complex with a sulfur atom in the ligand enhances the stability because of the Ru–S interaction. In this study, we synthesized an HG-type complex with a cationic moiety and sulfur atom in the ligand and investigated the occurrence of the sulfur-coordination to the Ru center in polar solvents, using the ligand exchange strategy. The ^{1}H-NMR spectral change showed the up-field shift of *S*-Me protons in methanol, proving the sulfur-coordination to the Ru center also in polar solvents.

Keywords : Transition Metal, Sulfur Atom, Olefin Metathesis, Polar Solvents, Hoveyda-Grubbs Complex

オレフィンメタセシスは、オレフィンに対して高い官能基選択性を示すことから、多様な官能基を有する生体分子の化学修飾への応用が期待されている。しかし、オレフィンメタセシス触媒の多くは、疎水性が高く、水系溶媒で熱的安定性が低下するため、構造最適化が必要である。我々は、以前に、ホベイダグラブス第２世代錯体(HG-Ⅱ)のフェノキシ末端部位に硫黄原子を持つ錯体において、Ru–S 相互作用によって、触媒活性を保ちながらも、熱的安定性が向上することを報告した [1)]。そこで、本研究では、配位子に親水性置換基と硫黄原子を導入した錯体(**[Ru]$_{S\text{-}TMA}$**)において、極性溶媒中でも Ru-S 間の相互作用によって錯体が安定に存在しているかを配位子交換反応によって検討した。

重メタノール中で、カチオン性ホベイダグラブス第２世代錯体(**[Ru]$_{HGII\text{-}TMA}$**)に対して、フェノキシ末端部位に硫黄原子を有するカチオン性配位子 **1** を 1:1 で混合し、**[Ru]$_{S\text{-}TMA}$** の生成反応を ^{1}H-NMR で追跡した。その結果、硫黄原子に隣接するメチル基のプロトンの化学シフトが 1.57 ppm に観測され、配位子 **1** における化学シフトよりも高磁場シフトしていた。この高磁場シフトは、Ru–S 間の相互作用に起因するものであり、**[Ru]$_{S\text{-}TMA}$** において、極性溶媒中でも Ru–S 間の相互作用が機能することが確認された。



1　　**[Ru]$_{HG\,II\text{-}TMA}$**　　**[Ru]$_{S\text{-}TMA}$**

1) Kinugawa, T.; Matsuo, T. *Dalton Trans*. **2023**, *52*, 9499

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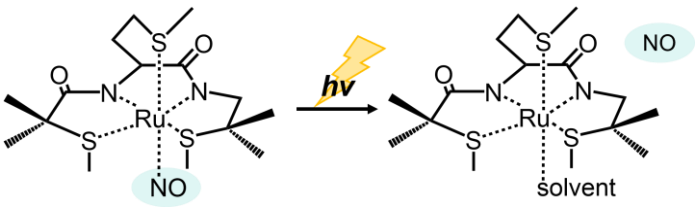
アミド含有 N2S3 型ニトロシル Ru(II)錯体の合成と性質

（名工大院工）○寺田 侑矢・和佐田 祐子・猪股 智彦・小澤 智宏
Synthesis and characterization of amide-containing N2S3-type nitrosyl Ru(II) complex (*Graduate School of Engineering, Nagoya Institute of Technology*) ○Yuya Terada, Yuko Wasada, Tomohiko Inomata, Tomohiro Ozawa

Nitric oxide (NO) is an essential molecule to maintain the human life; regulation of blood vessel, immune response, and so on. Therefore, unusual concentration of NO leads to some diseases. So development of NO quantification method and application as a drag using NO are required. In nature, nitrile hydratase (NHase), which has a hexacoordinated octahedral Fe(III) complex with specific amidato-coordination at the active center, keeps a NO molecule in the resting state. The NO molecule releases by light irradiation. Such a photoactivity has been reported for Ru(II) complexes. In this study, we prepared a nitrosyl Ru(II) complex with amidato-coordination and investigated the spectrochemical and photochemical properties. FT-IR spectrum of the Ru(II) complex prepared showed an absorption band at 1878 cm^{-1}, which can be assigned as NO stretching vibration based on the one of free NO (1848 cm^{-1}). When xenon light was irradiated for 1h on the mixed DMF solution of the complex and Fe-$(DTCS)_2$ as a NO trapping agent, a EPR spectrum characteristic for a NO trapping agent (g = 2.03) could be observed.
Keywords : Ruthenium complex; NO sensing; Photorelease of NO

一酸化窒素(NO)は血圧調整・免疫作用等生命維持に必要不可欠な分子であるが、異常濃度では病気の原因となる。そのため NO の定量や薬剤としての利用が期待されている。自然界には、NO との相互作用が確認されている金属酵素ニトリルヒドラターゼ(NHase)が存在する。NHase は活性中心に六配位八面体の Fe(III)錯体をもち、特異的なアミド窒素配位を有するとともに軸位に NO が配位している。この NO 分子は可視光により可逆的に脱着可能である。このような光応答性は、Ru(II)錯体で多く報告されている。我々はこの性質が NO センシングおよび光解離に利用できると考え、N2S3 型ニトロシル Ru(II)錯体を合成して、分光化学的性質を調べるとともに光応答性を検討することにした。

合成した N2S3 型ニトロシル Ru(II)錯体の FT-IR スペクトルでは、NO の伸縮振動に由来する吸収が 1878 cm^{-1}（Free NO: 1840 cm^{-1}）に確認されたことから、NO が配位していることが確認できた。また DMF 溶液中において、錯体及び NO トラップ剤（Fe-$(DTCS)_2$）を混合しキセノンランプを 1 時間照射すると、g = 2.03 にトラップ剤由来の特徴的な EPR シグナルが現れた。



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日本化学会 第104春季年会 (2024)

二核ルテニウムビス架橋エチリジン錯体への鉄フラグメントの導入に伴う炭素-炭素結合形成反応

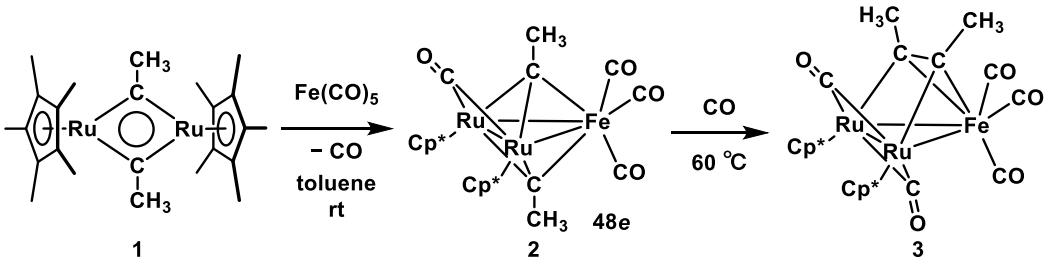
（東工大物質理工院）○野口 尚弥・高尾 俊郎

C-C Bond Formation between Two μ-Ethylidyne Ligands in a Diruthenium Bis(μ-ethylidyne) Complex Accompanied by the Incorporation of an Iron Fragment (*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Naoya Noguchi, Toshiro Takao

Despite its unsaturated nature, diruthenium bis(μ-ethylidyne) complex **1** is highly stable owing to the aromaticity of the Ru_2C_2 core. While **1** did not react with H_2 and ethylene even under harsh conditions, complex **1** reacted with $Fe(CO)_5$ yielding trinuclear heterobimetallic complex **2**. Although **2** adopts a saturated 48-electron configuration, it reacted with CO at 60 °C yielding 2-butyne complex **3**. The introduced Fe unit increased the flexibility of the trinuclear skeleton, which may be responsible for the facile C-C bond formation between the μ-ethylidyne ligands across the trinuclear plane.

Keywords : Bis(μ-alkylidyne) Complex, Diruthenium Complex, C-C Bond Formation

二核ルテニウムビス架橋エチリジン錯体 **1** は配位不飽和であるが、Ru_2C_2 コア部分の σ と π の二重の芳香族性によって高い安定性を示す[1]。この電子豊富な Ru_2C_2 コア部分へ求電子性の金属フラグメントを導入することで芳香族性が低下し、活性を示すものと期待される。**1** と $Fe(CO)_5$ との反応から Ru_2C_2 骨格へ鉄フラグメントを導入し、異種金属三核錯体 **2** を合成した。さらに **2** と CO との反応ではエチリジン配位子がカップリングすることで 2-ブチン錯体 **3** が得られた。鉄フラグメントの導入することでクラスター骨格の柔軟性が増加し、2 つのエチリジン配位子が 4 電子供与の 2-ブチン配位子へと変化することで、CO を取り込んだものと考えられる。



1) T. Takao; K. Seki *Eur.J. Inorg.Chem.* **2021**, 2505

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日本化学会 第104春季年会 (2024)

μ-ルテナシクロヘキサジエニル中間体を経由する二核ルテニウム上での μ-η^2:η^4-トリエニル配位子の骨格変換反応

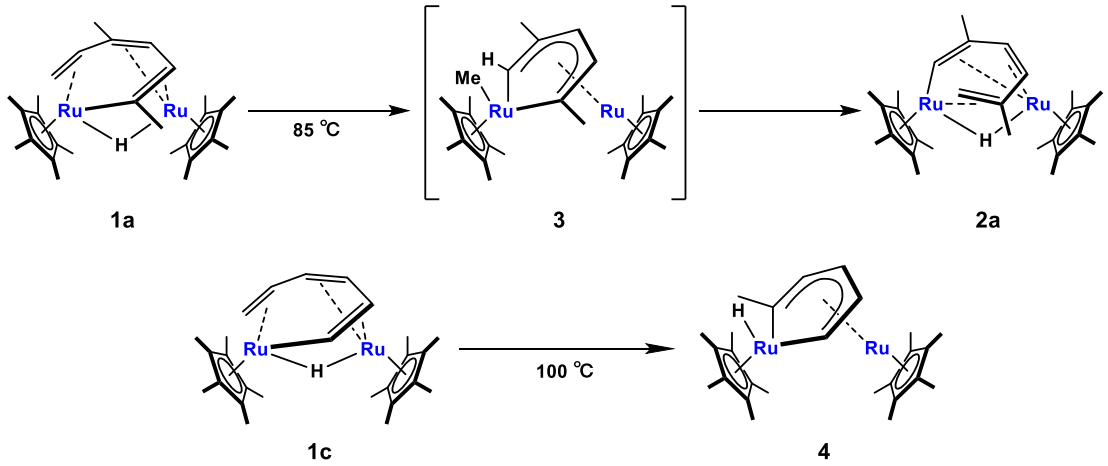
（東工大物質理工院）○谷口泰輝・弦牧洋平・高尾俊郎

Skeletal Rearrangement of a μ-η^2:η^4-Trienyl Ligand on a Diruthenium Site via a μ-Ruthenacyclohexadienyl Intermediate (*School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Taiki Taniguchi, Yohei Tsurumaki, Toshiro Takao

A diruthenium complex having a μ-η^2:η^4-1,4-dimethylhexatrienyl ligand, [(Cp*Ru)$_2$(μ-η^2:η^4-CMe=CHCH=CMeCH=CH$_2$)(μ-H)] (**1a**), isomerized to a 2,5-dimethyl isomer, [(Cp*Ru)$_2$(μ-η^2:η^4-CH=CMeCH=CHCMe=CH$_2$)(μ-H)] (**2a**), upon heating above 85 °C. The reaction employed ^{13}C-labelled ethylene demonstrated that the terminal C=C bond was selectively broken in the rearrangement. DFT calculations suggested the mechanism via a μ-η^5-ruthenacyclohexadienyl intermediate, [(Cp*Ru)$_2$(μ-η^5-CMeCHCHCMeCH-)(Me)] (**3**). On the other hand, an unsubstituted μ-η^2:η^4-hexatrienyl complex, [(Cp*Ru)$_2$(μ-η^2:η^4-CH=CHCH=CHCH=CH$_2$)(μ-H)] (**1c**), was converted into a μ-η^5-ruthenacyclohexadienyl complex, [(Cp*Ru)$_2$(μ-η^5-CHCHCHCHCMe-)(H)] (**4**), without C–C bond cleavage.

Keywords : Diruthenium Complex; C–C Bond Cleavage/Formation; Skeletal Rearrangement; DFT Calculation

二核ルテニウム μ-η^2:η^4-1,4-ジメチルヘキサトリエニル錯体 **1a** は、加熱によってメチル基の転位を伴う異性化反応を起こし、2,5-ジメチル体の錯体 **2a** に変化した。^{13}C 標識実験から、5, 6 位の C=C 結合が選択的に切断されることを明らかにした。さらに DFT 計算からは μ-η^5-ルテナシクロヘキサジエニル中間体 **3** を経由する機構が示唆された。無置換のヘキサトリエニル錯体 **1c** の加熱反応では、μ-ルテナシクロヘキサジエニル錯体 **4** が得られた。



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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1233(1233, Bldg. 12 [3F])

[F1233-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaki Yoshida, Tomohiro Ogawa

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1233-3am-01]

Proton Control of Emission Behaviors in Heteroleptic Copper(I) Dinuclear Complex and Development of Transparent Emissive Material

○Naoki Takaishi[1], Hajime Kamebuchi[1], Zhou Biao[1], Chihiro Shibuya[1] (1. Nihon Univercity)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1233-3am-02]

Synthesis of novel macrocyclic molecular gears using NHC Cu(Ⅰ) complex and the solid-state emission property

○Ryunosuke Tomita[1], Rempei Ando[1], Hajime Ito[2,3], Mingoo Jin[3] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Graduate School of Engineering, Hokkaido University, 3. WPI-ICReDD, Hokkaido University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1233-3am-03]

Development of crystalline molecular rotors using asymmetric NHC metal complexes and the solid-state emissive properties

○Yusuke Fujisawa[1], Rempei Ando[1], Motohiro Mizuno[2], Hajime Ito[3,4], Mingoo Jin[4] (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. NanoMaterials Research Institute, Kanazawa University, 3. Graduate School of Engineering, Hokkaido University , 4. WPI-ICReDD, Hokkaido University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1233-3am-04]

Crystal structures and photoluminescence vapochromism of multinuclear copper(I) complexes in hydrogen-bonding network assemblies

○Rin Suhara[1], Syun Fujioka[1], Yoshiki Ozawa[1], Masaki Abe[1] (1. University of Hyogo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1233-3am-05]

Photophysical property of tetrahedral copper(I) complexes with dibenzophenanthroline ligands

○Shun Yamamura[1], Ayano Okuda, Shinichi Saito[1], Yusuke Yoshigoe[1] (1. Tokyo University of Science)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1233-3am-06]

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Vapor-induced photoluminescence switching response of crystalline-state hexanuclear copper(I) and silver(I) complexes

○Yuki Takenaka[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. Graduate School of Science, University of Hyogo)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1233-3am-07]

Crystal structures and thermo/piezochromic photoluminescence of silver(I) coordination polymers with N-heterocyclic ligands

○Itaru Tsuchiya[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. University of Hyogo)

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
[F1233-3am-08]

Structural and Luminescent Changes Induced by the Exposure of acid vapor in 0-Dimensional Organic-Inorganic Hybrids Metal Halides

○Takumi Ide[1], Sotaro Kusumoto[1], Yoshihiro Koide[1] (1. Kanagawa University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[F1233-3am-09]

Exciton Transfer in Photoluminescent Dipyrrin-Zn(II) Molecular Wires in Polymer Films

○Haru Taniguchi[1], Ryojun Toyoda[1], Shinya Takaishi[1], Ryota Sakamoto[1] (1. Tohoku University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1233-3am-10]

Luminescent-Property Variations Based on Assembled Structures of Cationic Terpyridine Platinum(II) Complexes Having Alkynyl Ligands

○Rina Hiura[1], Shuichi Suzuki[1], Takeshi Naota[1] (1. Osaka University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1233-3am-11]

Synthesis and optical properties of pincer-type Pt complex linked by chiral isocyanide ligand

Kohei Yamada[1], Takaki Kanbra[1], ○Junpei Kuwabara[1] (1. University of Tsukuba)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1233-3am-12]

Polymorphism-Dependent Crystalline-State Photoluminescence of a Tetranuclear Au(I) Complex with Iminothiolato Bidentate Ligands

○Syumpei Semba[1], Kenji Nakauchi[1], Yoshiki Ozawa[1], Masaaki Abe[1] (1. University of Hyogo)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1233-3am-13]

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Theoretical study on substituent effects on phosphorescent emission wavelengths of Ir(III) complexes with phenylpyridine ligands

○Naoya Nakayama[1], Yasutaka Kitagawa[1,2,3,4,5], Ryohei Kishi[1,2,3,4] (1. Osaka University, 2. QIQB, Osaka University, 3. ICS-OTRI, Osaka University, 4. RCSEC, Osaka University, 5. ICS-SRN, Osaka University)

Japanese

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

[F1233-3am-14]

Luminescence behavior of the helicate Eu complexes with two independent π-electronic systems

○Fuuto Kojima[1], Yuki Murata[1], Hitomi Ohmagari[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

Japanese

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

[F1233-3am-15]

Circularly polarized luminescence of chiral Eu(III) complex with aromatic ring functionalized camphor-type ligands

○Ryohei Takizawa[1], Makoto Tsurui[2], Mengfei Wang[3,4], Yuichi Kitagawa[3,4], Yasuchika Hasegawa[3,4] (1. Sch. Eng., Hokkaido Univ., 2. Grad. Chem. Sci. Eng., Hokkaido Univ., 3. Fac. Eng., Hokkaido Univ., 4. WPI-ICReDD, Hokkaido Univ.)

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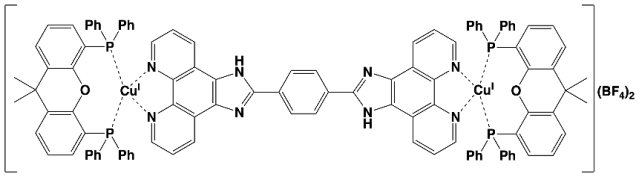
プロトン応答性ヘテロレプティック銅(I)2 核錯体における発光挙動の制御と透明発光体の開発

（日大文理）○高石直輝・渋谷知宙・亀渕 萌・周 彪
Proton Control of Emission Behaviors in Heteroleptic Copper(I) Dinuclear Complex and Development of Transparent Emissive Material
(*College of Humanities and Sciences, Nihon University*) Naoki Takaishi, Chihiro Shibuya, Hajime Kamebuchi, Biao Zhou

Transparent emissive materials are expected to be a promising candidate for advanced products as they can emit light efficiently due to low optical absorption and scattering properties of the material itself. In particular, functional materials that allow multiple emission colors and mechanisms from a single luminophore are desired, where the emission behaviors can be controlled by external stimuli. In this presentation, a heteroleptic copper(I) dinuclear complex $[(Xantphos)_2Cu^I_2(H_2bpib)](BF_4)_2$ (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, H_2bpib = 1,4-bis([1,10]phenanthroline[5,6-*d*]-imidazol-2-yl)benzene) (**1·H₂**) has been synthesized and investigated for changes in emission wavelength, TADF and other emission behaviors as well as deprotonated (**1**) and protonated (**1·H₄**) forms. In addition, we will report the preparation of transparent films in which **1·H₂** is introduced into a highly-proton conductive membrane Nafion and the control of the emission behavior by pH, keeping in mind that the emission behavior of the Cu(I) complex would be controlled by an electric field.[1]

Keywords : Heteroleptic Complex; Cu(I) Dinuclear Complex; Thermally Activated Delayed Fluorescence; Proton Sensitive; Transparent Emitter

透明発光体は材料自身の光吸収や散乱が少なく、効率よく発光を取り出せることから次世代発光材料として期待されている。特に、単一の発光団を用いて複数の発光色や、複数の発光メカニズムを外部刺激で制御できるような機能性材料が求められている。今回は 1,4-bis([1,10]phenanthroline[5,6-*d*]-imidazol-2-yl)benzene (H_2bpib)を有するヘテロレプティック銅(I)2 核錯体 $[(Xantphos)_2Cu^I_2(H_2bpib)](BF_4)_2$ (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) (**1·H₂**)を合成し、脱プロトン化体(**1**)およびプロトン化体(**1· H₄**)と併せて発光色および TADF 等の発光挙動の変化を調べた。また、この銅(I)錯体の発光挙動を電場で制御することを念頭に置き、[1] **1·H₂** をプロトン伝導膜 Nafion へ導入した透明フィルムの作成、および pH による発光挙動の制御を行ったので報告する。



[1] H. Kamebuchi et al., *Mater. Adv.* **2020**, *1*, 569.

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NHC 銅(I)錯体を用いた大環状分子ギアの合成と固体発光物性

（北大院総化[1]・北大院工[2]・北大 WPI-ICReDD[3]）○富田 龍ノ介[1]・安藤 廉平[1]・伊藤 肇[2,3]・陳 旻究[3]
Synthesis of novel macrocyclic molecular gears using NHC Cu(I) complex and the solid-state emission property ([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Graduate School of Engineering, Hokkaido University*, [3]*WPI-ICReDD, Hokkaido University*) ○Ryunosuke Tomita,[1] Rempei Ando,[1] Hajime Ito,[2,3] Mingoo Jin[3]

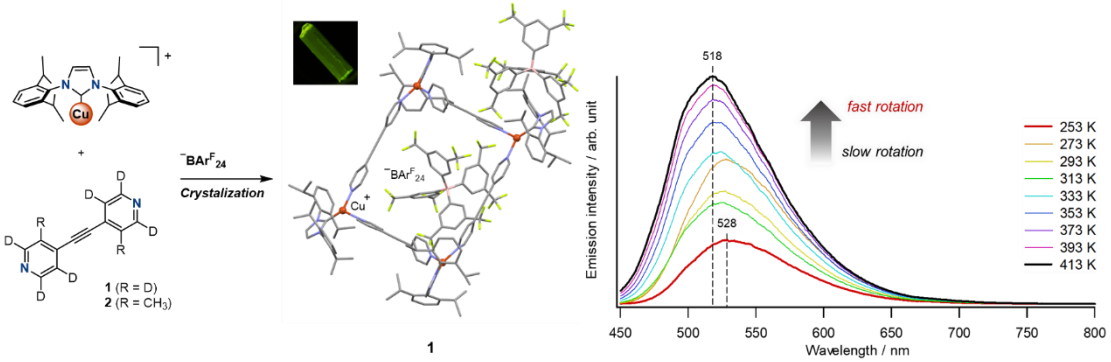
Amphidynamic crystals, exhibiting molecular rotation in the crystalline solid, have attracted many interests because the molecular rotational motion in solid state can work for key factor for fine control of solid-state emission properties.[1,2] We have previously developed luminescent crystalline molecular rotors, passing emission quenching process by molecular rotation.[1,2] In this study, we synthesized macrocyclic molecular gears using NHC Cu(I) complex, exhibiting emission enhancement and measured its rotational behavior and solid-state emission properties.

Single crystal X-ray diffraction measurement revealed that crystal **1** using bis(4-pyridyl)acetylene-d_8 as a rotator moiety form macrocycle with $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$ ($BAr^F{}_{24}$) anions in the ring. We will describe the crystal structure, molecular motions, and their emission properties of **1** and its analogue **2** at the presentation.

Keywords: Organic Crystal; Solid-state Emission; Molecular Gear; NHC Metal Complex

発光を示すアンフィダイナミック結晶は、固体中の分子回転を介して固体発光特性を制御できる因子として、分子センサーなどへの応用が期待されている[1,2]。我々はこれまでに、回転によって消光のプロセスを経る発光性結晶分子ローターを開発してきた[1,2]。本研究では、回転によって発光が強化される NHC 銅(I)錯体を用いた大環状分子ギアを合成し、その回転挙動と固体発光特性を調査した。

単結晶 X 線構造解析の結果、回転部位にビス（4-ピリジル）アセチレン-d_8 を用いた結晶 **1** は環状構造を形成しており、環内にはテトラキス（3,5-ビス（トリフルオロメチル）フェニル）ホウ酸イオンが存在することが明らかとなった。本発表では、**1** およびアナログ **2** の結晶構造、回転運動および発光特性について詳細を述べる。



1) Jin, M.; Chung, T. J.; Seki, T.; Ito, H.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2017**, *139*, 18115–18121.
2) Jin, M.; Ando, R.; Jellen, M. J.; Garcia-Garibay, M. A.; Ito, H. *J. Am. Chem. Soc.* **2021**, *143*, 1144–1153.

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非対称な NHC 金属錯体を用いた結晶性分子ローターの開発と固体発光物性

（北大院総化[1]・金沢大ナノマリ[2]・北大院工[3]・北大 WPI ICReDD[4]）○藤澤 優輔[1]・安藤 廉平[1]・水野 元博[2]・伊藤 肇[3,4]・陳 旻究[4]

Development of crystalline molecular rotors using asymmetric NHC metal complexes and the solid-state emissive properties ([1]*Graduate School of Chemical Science and Engineering, Hokkaido University*, [2]*NanoMaterials Research Institute, Kanazawa University*, [3]*Graduate School of Engineering, Hokkaido University*, [4]*WPI-ICReDD, Hokkaido University*)○Yusuke Fujisawa,[1] Rempei Ando,[1] Motohiro Mizuno,[2] Hajime Ito,[3,4] Mingoo Jin[4]

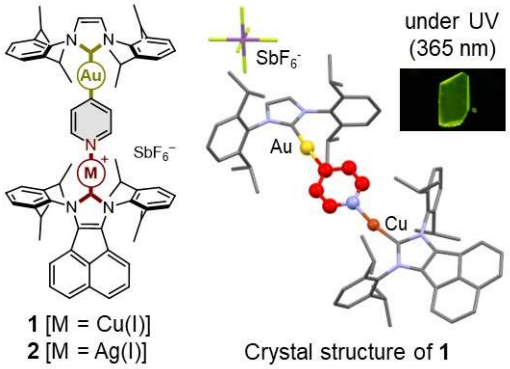
Crystalline molecular rotors, showing high crystallinity and fast molecular dynamics, have attracted much attention in luminescent solid-state materials because molecular rotation can play a key role in controlling the emission properties. Recently, we have developed luminescent crystalline molecular rotors in which a rotational moiety is introduced into a copper(I) or gold(I) complex bearing a bulky *N*-heterocyclic carbene (NHC) as the ligand. Here, we report the development of crystalline molecular rotors in which different metals and NHC ligands are introduced above and below a rotational moiety and the rotational motion in the solid-state with the emission properties.

Single crystal XRD measurement revealed that crystals **1** and **2** have a relatively vacant environment around the pyridine, which is the rotator, and can exhibit rotational motion in the crystal. In addition, crystal **1** was shown to emit yellow luminescence under UV light. In this presentation, we describe the rotational motion in the solid-state with the emission properties of crystals **1** and **2**.

Keywords: Crystalline molecular rotor, NHC metal complex, Emission in solid-state

結晶性分子ローターは、高い結晶性を有しながらその構造の一部が結晶中で回転運動を示す。この結晶性材料は、結晶内での分子回転を用いて固体発光性を制御できるため注目を集めている[1]。最近我々は、嵩高い *N*-ヘテロ環式カルベン(NHC)配位子を有する銅(I)または金(I)錯体に回転部位を導入した発光性結晶分子ローターを見出した[2]。本研究では、回転部位の上下に異なる金属および NHC 配位子を導入した結晶性分子ローターの開発を報告する。

単結晶 X 線構造解析により、分子ローター**1**, **2** ともに回転部位であるピリジンの周辺環境が比較的空いており、結晶中で回転運動を示しうることが示唆された。また、**1** の結晶は UV 照射によって黄色発光を示した。本発表では、分子ローター**1**, **2** の回転運動および固体発光特性について述べる。



1) Jin, M.; Chung, T. S.; Seki, T.; Ito, H.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2017**, *139*, 18115.
2) Jin, M.; Ando, R.; Jellen, M. J.; Garcia-Garibay, M. A.; Ito, H. *J. Am. Chem. Soc.* **2021**, *143*, 1144.

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銅(I)多核錯体に基づく水素結合ネットワーク結晶構築と溶媒蒸気による発光ベイポクロミズム

（兵庫県立大学院理）○須原 凜・藤岡 舜・小澤 芳樹・阿部 正明

Crystal structure and photoluminescence vapor chromism of multinuclear copper(I) complexes in hydrogen-bonding network polymer crystalline states (*Graduate School of Science, University of Hyogo*) ○Rin Suhara, Syun Fujioka, Yoshiki Ozawa, Masaaki Abe

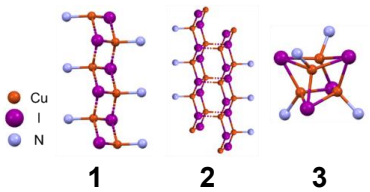
External stimuli-responsive photoluminescent compounds have recently attracted much attention because of their potential applications for sensing and optical switching materials. In this study, we have focused on the photoluminescent multinuclear iodo-copper(I) complexes and herein we report their luminescence vapochromic behavior to volatile organic compounds.

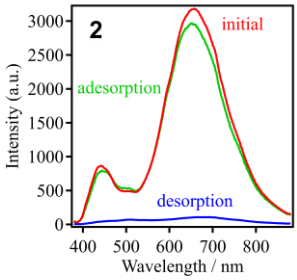
The multinuclear Cu(I) complexes with nicotinamide (na) or isonicotinamide (ina) ligands form coordination polymer networks through intermolecular hydrogen bonds between amide groups of the ligands with guest inclusion of polar solvent molecules in the crystalline lattice (Fig. 1). Single-crystal X-ray crystallography revealed that ladder-type network $\{[CuI(na)]\cdot MeCN\}_\infty$ (**1**) and double-ladder-type network $\{[Cu_2I_2(na)]\cdot DMF\}_\infty$ (**2**) were prepared by using ligands ina and na, respectively, and show remarkable emission enhancement under guest-adsorption process (Fig. 2). The network structure containing cubane-type $[Cu_4I_4(na)_4]\cdot DMF$ (**3**) exhibit vapochromism on the guest removal (Fig. 3).

Keywords: *Multinuclear iodo-copper(I) complexes, Hydrogen-bonding network, Photoluminescence vapochromism*

外部刺激に応答する発光性化合物は、スイッチング材料、分子センサーへと展開できる可能性を有することから近年注目を浴びている。本研究ではピリジン誘導体を配位子とする発光性ヨウ化銅(I)多核錯体に基づき、水素結合を可能とする官能基導入により、主に極性溶媒蒸気を取り込み、発光応答する化合物に着目した。

配位子としてニコチンアミド及びイソニコチンアミド配位子を用いた多核銅(I)錯体をもちい、アミド基による水素結合ネットワークを構築し極性溶媒をネットワークに組み込んだゲスト包接結晶 **1**-**3** を (Fig. 1) 溶媒蒸気との相互作用について検討したところ、新奇ラダー型錯体 **2** ではゲスト吸着によって発光強度が約 30 倍変化する発光スイッチング現象 (Fig. 2) を示した。また新奇キュバン型錯体 **3** では脱溶媒によって発光色がレッドシフトした (Fig. 3)。





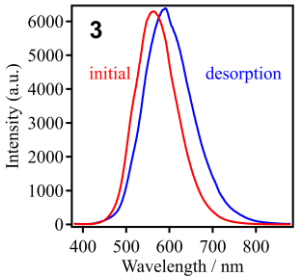


Fig. 1. Network structures **1** to **3**.
Fig. 2. Vapochromic behavior of **2**.
Fig. 3. Vapochromic behavior of **3**.

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ジベンゾフェナントロリン誘導体を配位子とする四面体型銅(I)錯体の光学的特性

（東理大理[1]）○山村　駿[1]・奥田　綾乃[1]・斎藤　慎一[1]・吉越　裕介[1]
Photophysical property of tetrahedral copper(I) complexes with dibenzophenanthroline derivatives as ligands ([1]*Faculty of Science, Tokyo University of Science*) ○Shun Yamamura,[1] Ayano Okuda,[1] Shinichi Saito,[1] Yusuke Yoshigoe [1]

The tetrahedral copper(I) complex,[1] whose structure leads to attractive properties, has been synthesized for decades. In this study, we have synthesized dibenzophenanthroline derivatives, **1** and **2**. Copper salts were initially reacted with bidentate phosphine ligands **3** or **4,** followed by a subsequent reaction with phenanthroline ligands **1** or **2**. This synthetic approach led to the formation of heteroleptic tetrahedral copper(I) complexes **5a-d** (Figure 1). The photophysical properties of these complexes have been studied. We found that copper(I) complexes exhibited a broad absorption band at 460 nm (**5a**), 460 nm (**5b**), 488 nm (**5c**), or 487 nm (**5d**) with long wavelength owing to the metal-to-ligand charge transfer (MLCT). Moreover, each complex displayed a weak red fluorescence.
Keywords : dibenzophenanthroline; bidentate phosphine ligand; heteroleptic complex; copper(I) complex; metal-to-ligand charge transfer (MLCT)

四面体型銅(I)錯体は，その構造と電子状態を反映した多様な物性[1]を示す．本研究では，ジベンゾフェナントロリン誘導体 **1** および **2** を新たに合成した．銅塩をまず二座ホスフィン配位子 **3** あるいは **4** と反応させ，さらにフェナントロリン配位子 **1** あるいは **2** と反応させることによりヘテロレプティックな四面体型銅(I)錯体 **5a-d** を合成し，その光学的特性を精査した (Figure 1)．銅(I)錯体はそれぞれ 460 nm (**5a**)，460 nm (**5b**)，488 nm (**5c**)，487 nm (**5d**) に，金属-配位子電荷移動（MLCT）に基づく長波長かつ幅広な吸収帯を示した．また，それぞれが弱い赤色発光を示した．

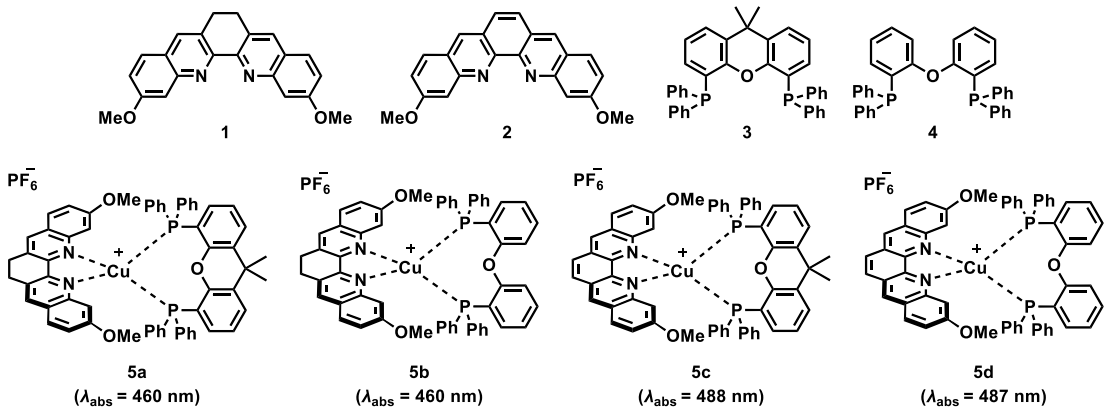

Figure 1. Structures of ligands **1-4** and Cu(I) complexes **5a-d**.

(1) McMillin, D. R.; Buckner, M. T.; Ahn, B. T., *Inorg. Chem*. **1977**, *16*, 943—945.

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銅(I)および銀(I)六核錯体結晶の溶媒蒸気による発光スイッチング応答

(兵庫県立大院理[1])○竹中 裕紀[1]・小澤 芳樹[1]・阿部 正明[1]
Vapor-induced photoluminescence switching response of crystalline-state hexanuclear copper(I) and silver(I) complexes ([1]*Graduate School of Science, University of Hyogo*) ○Yuki Takenaka,[1] Yoshiki Ozawa[1], Masaaki Abe[1]

Copper(I) and silver(I) hexanuclear complexes with 2-pyridinethiolato bidentate ligands show strong luminescence in the visible region under UV light. By introducing a carboxyl and amide group into the ligand, we found remarkable photoemission ON-OFF switching phenomena by adsorption or desorption of polar solvent molecules in the crystalline state[1)]. We report here the structure and vapochromic behavior of novel copper(I) and silver(I) complexes with ester groups (Fig. 1). The new complex shows vapochromic behavior on the adsorption of chloroform as a guest molecule in the crystalline state (Fig. 2). We will discuss guest selectivity and compare photoemission response with that of hexanuclear analogs with carboxyl and amide pendants reported previously.
Keywords: Paddlewheel-type hexanuclear complex; Vapor-induced emission enhancement; Solvent adsorption / Desorption; Hydrogen bond; Crystal structure

外部刺激に対して物質の発光色が可逆的に変化する発光クロミック現象は、スイッチング、センサー材料への応用が期待されている。我々はこれまで配位子にカルボキシ基およびアミド基といった水素結合形成が可能な官能基を導入した発光性銅(I)および銀(I)多核錯体を合成し、結晶状態で極性溶媒分子の吸着によって発光強度が脱離状態と比べ 100 倍以上に増大する発光スイッチング現象を見出した[1)]。本発表では、メチルエステル基を導入した 2-ピリジンチオラトを二座配位子とする銅(I)および銀(I)パドルホイール型六核錯 $[M_6(mmn)_6]$ (M = Cu, Ag) (Fig. 1)について報告する。

新規の銀(I)錯体結晶は、UV 照射により黄緑色の強い発光を示し、クロロホルム蒸気吸蔵により発光色の変化が見られた (Fig. 2)。本発表では新規錯体とカルボキシ基錯体のゲスト選択性および発光応答性の違いについても比較する。

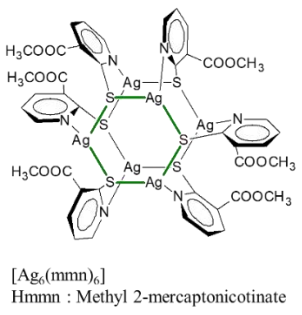

Fig. 1. 錯体の構造模式図

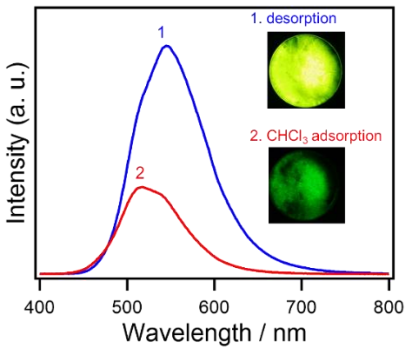

Fig. 2. 固体発光ベイポクロミズム

1) H. Inoue, Y. Ozawa, M. Abe *et al.*, *Molecules*, **2021**, *26*, 6731-6745.

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含窒素芳香族配位子を含む銀(I)配位高分子の結晶発光とサーモ・ピエゾクロミズム

（兵庫県立大院理 [1]）○土谷 到 [1]・小澤 芳樹 [1]・阿部 正明 [1]
Crystal structures and thermo/piezochromic photoluminescence of silver(I) coordination polymers with *N*-heterocyclic ligands ([1]*Graduate School of Science, University of Hyogo*)
○Itaru Tsuchiya[1], Yoshiki Ozawa[1], Masaaki Abe[1]

Though many examples exist in literatures for the synthesis of cationic 1D coordination polymers (CPs) $[Ag(\mu\text{-BL})]_nX_n$, where BLs (Fig. 1) and X^- represent bridging ligands and counter anions, respectively, surprisingly few reports are available to date on their solid-state photoluminescence (PL) properties. Herein we describe the first systematic study on the solid-state PL of a series of 1D silver(I) CPs with the emphasis on their thermochromic and piezochromic solid-state response. Single-crystal X-ray diffraction study revealed that the CP chains form, in general, 2D sheet-like and 3D stacking structures, among which interchain Ag(I)•••Ag(I) contacts are seen for the bpy complex. Depending on BLs employed, the CPs are found to be emissive or non-emissive upon UV irradiation (λ_{ex} = 365 nm). The bpy complex, for example, is faintly emissive in yellow (λ_{em} = 550 nm) in air, but is strongly luminescent upon cooling (78 K) or under high pressure (1.1 GPa) accompanied with the redshift of the PL peak by *ca*. 60 or 30 nm, respectively. The PL lifetimes, PLQYs, and band assignments will also be discussed.
Keywords: Silver, Coordination polymers, Photoluminescence, Thermochromism, Piezochromism

銀(I)イオンが二座の架橋配位子(BL)で架橋されたカチオン性一次元配位高分子 $[Ag(\mu\text{-BL})]_nX_n$ は、BL と対アニオン X^- の多様な組み合わせから成る合成例が多いが、その固体発光特性に関して報告は少ない。本研究では、数種の BL (図 1) と X^-を用いて配位高分子$[Ag(\mu\text{-BL})]_nX_n$ を合成、構造決定し、その固体発光スペクトルの温度依存性および静水圧依存性について検討した。結晶中、各錯体の高分子鎖はシート配列化し、それらがスタックしたパッキング構造を有する。bpy 錯体には鎖間に弱い Ag•••Ag 接触が見られた。UV 照射下(λ_{ex} = 365 nm)、各錯体は BL により発光性または無発光性のグループに分かれた。このうち発光性錯体として、bpy 錯体は常温常圧で弱い黄色発光 (λ_{em} = 550 nm) を示すが、冷却および昇圧により強発光化し、ピーク波長はそれぞれ約 60 nm (78 K)および 30 nm (1.1 GPa)レッドシフトした。本発表では、各錯体の発光寿命と発光量子収率および固体発光への温度・静水圧効果、光励起状態の帰属について議論する。

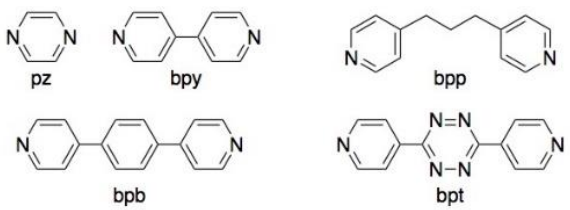

Fig. 1. BLs used for the 1D silver(I) CPs.

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0 次元有機無機ハイブリッドを用いた酸蒸気曝露による構造及び発光変化

（神奈川大工 [1]）○井手 拓美 [1]・楠本 壮太郎 [1]・小出 芳弘 [1]

Structural and Luminescent Changes Induced by the Exposure of acid vapor in 0-Dimensional Organic-Inorganic Hybrids Metal Halides ([1]*Department of Engineering, Kanagawa University*,) ○Takumi Ide,[1] Sotaro Kusumoto,[1] Yoshihiro Koide[1]

In recent years, organic-inorganic hybrid metal halides (OIMHs) materials have attracted attention as functional materials. Although halogen elements in metal halide moieties cause significant changes in functionality, few attempts have been made to control the physical properties associated with their replacement by acid vapors. In this study, halogen substitution in metal halides by exposure to hydrobromic and hydrochloric acid vapors is demonstrated using new zero-dimensional Zn(II) hybrids (Fig. 1a, b). As a result, both photoluminescence and structure were altered upon exposure to acid vapors (Fig. 1c).

Keywords : Organic-Inorganic Metal Halides (OIMHs); Vapochromism; Ligand substitution

有機無機ハイブリッド材料は有機カチオンと金属ハライドアニオンによって構成され、その組み合わせの多様さから様々な機能性材料として注目を集めている。ハイブリッド材料における金属ハライド部位のハロゲン元素は機能性に大きな変化をもたらすが、蒸気によって直接的に置換および物性制御させる試みはほとんどない[1]。

本研究では、4’-(3-pyridyl)-2,2’;6’,2”-terpyridine(3N-terpy)と ZnX_2(X=Cl,Br)をそれぞれ塩酸中および臭化水素酸中で反応させることで得た 0 次元の新規 Zn(II)ハイブリッド(Fig. 1a, b)を用いて、臭化水素酸や塩酸蒸気曝露による金属ハライドにおけるハロゲンの置換を試みた。蒸気曝露後には、それぞれ発光色の変化が確認された(Fig. 1c)。酸蒸気曝露前後における構造および物性を PXRD, 蛍光スペクトルをもとに比較、検討を行った結果、メタルハライドにおけるハロゲンが塩素から臭素、臭素から塩素への可逆的な変化が示唆された。

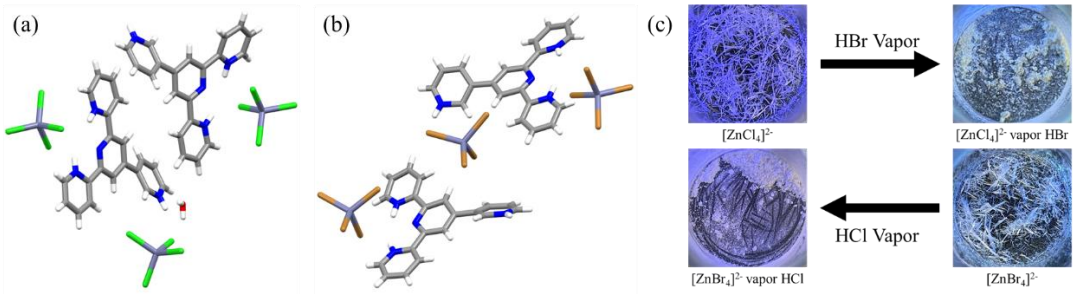

Fig. 1(a) 新規$[ZnCl_4]^{2-}$ハイブリッドの構造 (b) 新規$[ZnBr_4]^{2-}$ハイブリッドの構造 (c)酸蒸気曝露による発光色の変化

1) S. He, J. Zhao, Q. Liu, et. al., *Adv. Optical Mater.*, **2023**, *15*, 2300218

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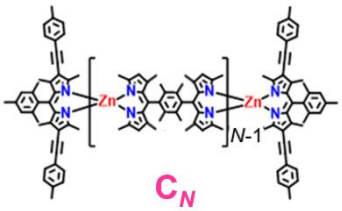
高分子固体中における発光性ジピリン亜鉛(II)分子ワイヤー内励起子移動

（東北大院理 [1]）○谷口 晴 [1]・豊田 良順 [1]・高石 慎也 [1]・坂本 良太 [1]
Exciton Transfer in Photoluminescent Dipyrrin-Zn(II) Molecular Wires in Polymer Films ([1]*Graduate School of Science, Tohoku University*)○Haru Taniguchi,[1] Ryojun Toyoda,[1] Shinya Takaishi,[1] Ryota Sakamoto[1]

Dipyrrin-Zn(II) molecular wires have unique features such as efficient photoluminescence based on the constituent complexes and their rigid molecular structures. These properties have been mainly investigated in solution. However, in terms of applications in molecular devices, acquiring knowledge of their properties in the solid state is required for future developments. In this study, size-defined dipyrrin-Zn(II) molecular wires were prepared and encapsulated in polymer films such as polystyrene, and their photoluminescence properties were measured. By comparing the absorption and photoluminescence spectra of wires, exciton transfer in the wires in the solid state was validated. In addition, changes in fluorescence quantum yield depending on the polarity of the polymer was observed as well as in solution. The effect of the length and concentration of the wire in the polymer on the fluorescence quantum yield was also measured, leading to an understanding of the fluorescence properties of these molecules in the solid polymer film.
Keywords : Solid-state Photoluminescence; Multinuclear Complexes; Coordination Polymer; Dipyrrin-metal Complexes; Exciton Transfer

ジピリン亜鉛(II)分子ワイヤーは、構成要素錯体に基づく鮮やかな蛍光特性や剛直な分子構造といったユニークな特徴をもつ。これらの特性は主に溶液中で観測されてきたが、分子デバイスへの応用など今後の展開を見据え、固体状態での知見が必要である。本研究ではジピリン亜鉛(II)分子ワイヤーを核数ごとに調製してポリスチレンをはじめとした高分子固体に封入し蛍光特性を測定した。異なる吸収・蛍光波長をもつ配位子を混合したワイヤーの吸収および蛍光スペクトルを比較することで、固体状態におけるワイヤー内の励起子移動を実証した。加えて、固体高分子の極性によって蛍光量子収率が変化するといった、溶液中で確認されている現象 [1]も同様に観測された。また、高分子中におけるワイヤーの核数や濃度が蛍光量子収率に及ぼす影響についても測定した結果、これらの分子の固体高分子状態における蛍光特性の理解に繋がった。



1) Toyoda, R. *et al. Sci. Adv.* **5**, eaau0637 (2019).

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カチオン性アルキニル白金テルピリジン錯体の集積構造に基づく発光特性変化

（阪大院基礎工 [1]）○日浦 里奈 [1]・鈴木 修一 [1]・直田 健 [1]

Luminescent-Property Variations Based on Assembled Structures of Cationic Terpyridine Platinum(II) Complexes Having Alkynyl Ligands ([1]*Graduate School of Engineering Science, Osaka University*) ○Rina Hiura,[1] Shuichi Suzuki,[1] Takeshi Naota[1]

In this session, we will describe, "Luminescent-Property Variations Based on Assembled Structures of Cationic Terpyridine Platinum(II) Complexes Having Alkynyl Ligands".

Keywords : Platinum Complexes; Solid State Emission

平面構造をもつ白金錯体や金錯体は非共有性の分子間相互作用によって発光特性を制御できることから、魅力的な分子モチーフである[1–3]。特に我々は、各種対アニオンを導入可能なカチオン性金属錯体に注目して研究を進めている[3]。これまでに大きな対アニオンであるビス(トリフルオロメタンスルホニル)イミドイオン (NTf_2^-) を導入した発光性金属錯体塩が結晶状態で強い発光性を示すことを明らかにしてきた。今回、アルキルアセチリド部位をもつテルピリジン白金錯体塩において、アセチリド部位の構造が結晶での発光特性に与える影響を明らかにするため錯体 **1-C*n*** および錯体 **2** を合成したところ、様々な発光色を示すことを明らかとした (Figure 1)。

錯体 **1-C*n*** および錯体 **2** は黄緑色から赤色までアルキル基の違いにより発光色が大きく変化した。結晶構造解析の結果からテルピリジン白金錯体部の集積構造が異なっており、分子間相互作用に起因して発光波長が大きく変化することが示唆された。

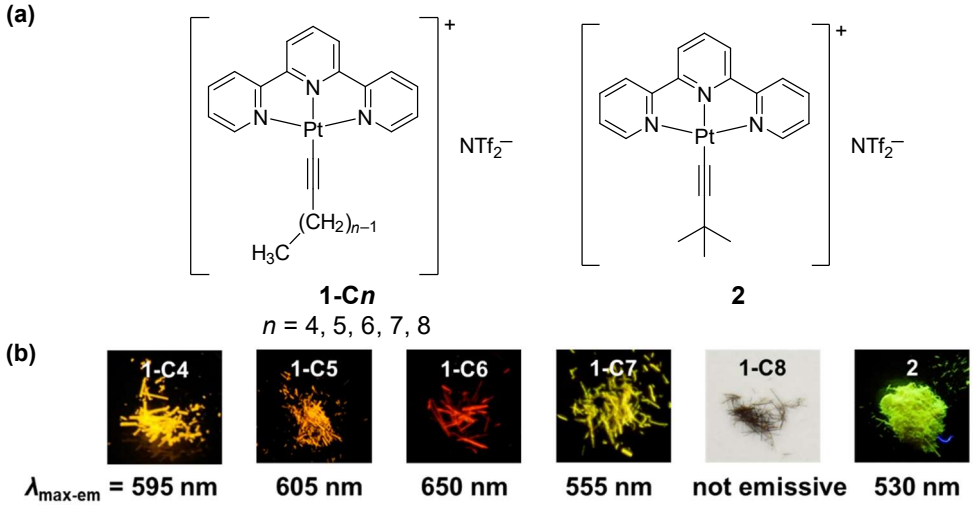

Figure 1. (a) Structures of **1-C*n*** and **2**, (b) photographs of their luminescence in crystalline state under UV lamp at 298 K.

1) Kato, M. et al. *Angew. Chem., Int. Ed*. **2002**, *41*, 3183. 2) Eisenberg, R. et al. *J. Am. Chem. Soc*. **2004**, *126*, 16841. 3) Zhang, D.; Suzuki, S.; Naota, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 19701.

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キラルなイソシアニド配位子によって連結されたピンサー型 Pt 錯体の合成と光学特性

(筑波大院数理物質 [1]) 山田 康平 [1]・神原 貴樹 [1]・○桑原 純平 [1]

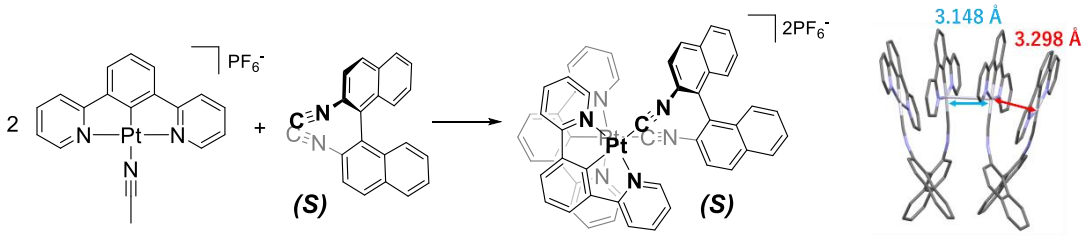
Synthesis and optical properties of pincer-type Pt complex linked by chiral isocyanide ligand

([1]Univ. of Tsukuba) Kohei Yamada[1], Takaki Kanbara[1], ○Junpei Kuwabara[1]

Pincer Pt complexes with high planarity are known to have high luminescence quantum yields and to exhibit unique long-wavelength emission when stacking structures are formed by Pt-Pt interactions. In this study, we newly synthesized dinuclear pincer Pt complexes linked by a chiral isocyanide ligand to evaluate their optical and chiral properties. Single crystal X-ray structure analysis has confirmed the dinuclear structure and revealed that the dinuclear complexes form further stacked structures. The dinuclear Pt complexes show long-wavelength dimer emission (584 nm) even in diluted solution state. In a 1:9 mixture of acetonitrile and water (10 μM), a new absorption band appeared around 530 nm and the emission shifted to a longer wavelength of 784 nm. The dinuclear complexes would form further stacked aggregates as observed in the crystal structure. CD spectra and other chiral properties will also be discussed.

Keywords : Pt complex; Pincer complex; Chiral ligand; Pt-Pt interaction

高い平面性を有するピンサー型 Pt 錯体は高い発光量子収率を有し、Pt-Pt 間の相互作用を駆動力に積層構造を形成すると長波長シフトした発光を示すことが知られている。[1)] 本研究では、キラルなジイソシアニド配位子によって連結された二核ピンサー型 Pt 錯体の合成と構造解析、光学特性およびキラル特性の評価を目的に研究を行った。カチオン性 Pt 錯体とビナフチル骨格を有するキラルなジイソシアニド配位子 (*S* 体) の反応により、Pt 二核錯体を合成した (Scheme 1)。単結晶 X 線構造解析によって、Pt 同士が近接した二核構造であること、二核錯体がさらに積層構造体を形成することを明らかにした。*R* 体も同様に合成と構造解析を行った。Pt 二核錯体は、希薄溶液中においてブロードな長波長発光 (584 nm) を示した。この発光は原料の単核 Pt 錯体の 483 nm の発光とは大きく異なり、Pt-Pt 相互作用を有する励起状態を経由したダイマー発光であると考えられる。アセトニトリル:水=1:9 の混合溶媒中 (10 μM) では、530 nm 付近に新たな吸収帯が発現し、発光が 784 nm にまで長波長シフトした。結晶構造で見られるような二核錯体がさらに積層した凝集体を形成しているものと考えられる。CD スペクトルなど、キラル特性についても発表する。



Scheme 1. キラルな配位子で連結された二核ピンサー型 Pt 錯体の合成と結晶構造

1 M. H.-Y. Chan and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2022, **144**, 22805–22825.

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イミノチオラト架橋 Au(I)四核錯体結晶の固体発光とその多形依存外部刺激応答性

（兵庫県立大院理）○仙波 舜平・中内 健司・小澤 芳樹・阿部 正明
Polymorph-dependent crystalline-state photoluminescence of tetranuclear gold(I) complex with iminothiolato bidentate ligands (*Graduate School of Science*, *University of Hyogo*)
○Syumpei Semba, Kenji Nakauchi, Yoshiki Ozawa, Masaaki Abe

Gold(I) complexes show photoluminescence based on interatomic Au···Au interactions in the solid state. The emission energy can be varied by external stimuli, exhibiting the photoemission chromism. Herein we have synthesized a new tetranuclear Au(I) complex with bidentate iminothiolato ligands [Au_4(Et-bimt)$_4$] (Et-bimtH = Ethylbenzimidazolethiol), having Au···Au contacts in the molecule. We obtained three crystals by recrystallization under the condition of kinds of solvent, which show different emission colors under UV illumination. Also, We discovered decomposition or polymerization of the [Au_4(Et-bimt)$_4$] cluster in solution by ^{1}HNMR.
Keywords : Multinuclear metal complex; Gold-gold interaction; Photoluminescence thermochromism; Photoluminescence piezochromism; Polymorphism

金(I)錯体は固体中で分子間の Au···Au 相互作用に基づくフォトルミネッセンスが観測され、外部刺激に対し発光エネルギーが変化するクロミック現象が報告されている。我々は Au· · · Au 相互作用を分子内部にもつイミノチオラト架橋 Au(I)四核錯体 [Au_4(Et-bimt)$_4$] (Et-bimtH = Ethylbenzimidazolethiol)を合成した。得られた[Au_4(Et-bimt)$_4$]を溶媒の条件を変えて再結晶により単結晶作製を行った結果、UV 照射時の発光色の異なる 3 種の多形および擬多形結晶 (Form I–III) が得られた。Form I は直方晶で 464 nm に発光極大を持つ水色発光、Form II は三斜晶で赤色の発光 (λ_{em} = 690 nm)を示した。またトルエン溶媒を含む擬多形 Form III は三斜晶で青色発光 (λ_{em}= 443 nm) を示した。$CDCl_3$ 中の ^{1}HNMR スペクトルは、[Au_4(Et-bimt)$_4$]錯体に相当するピークの他に、時間経過とともに核数が異なると思われるピークが 5 種類以上現れ、その強度が増大することから、溶液中で分解／重合反応が起こることが示唆された。

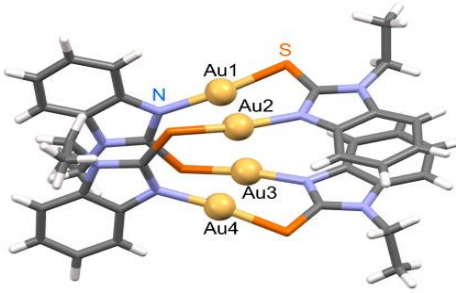
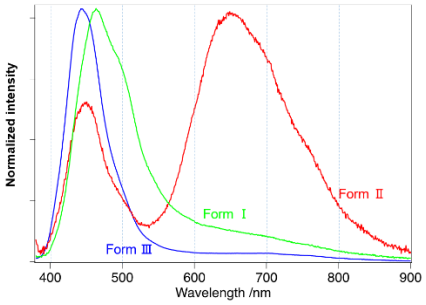


Fig.1 [Au_4(Et-bimt)$_4$]の分子構造



Fig, 2 多形 I–III の発光スペクトル

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フェニルピリジンを配位子としたIr(III)錯体のリン光発光波長における置換基効果に関する理論研究

（阪大院基礎工[1],阪大 QIQB[2],阪大 ICS-OTRI[3],阪大 RCSEC[4], 阪大 ICS-SRN[5]）
○中山直哉[1]・岸亮平[1,2,3,4]・北河康隆[1,2,3,4,5]

Theoretical study on substituent effects on phosphorescent emission wavelengths of Ir(III) complexes with phenylpyridine ligands ([1]Osaka University Engineering Science, [2]QIQB, [3]ICT-OTRI, [4]RCSEC, [5]ICS-SRN)○Naoya Nakayama[1], Ryohei Kishi[1,2,3,4], Yasutaka Kitagawa[1,2,3,4,5]

In recent years, the organic electroluminescence (OLED) has been widely used as a thin-film display materials and illuminations. The organic electroluminescence (OLED) materials can be classified into fluorescent and phosphorescent emitting materials, but the exciton generation efficiency, i.e. the ratio of excitation and emission photons, is 25% in the case of fluorescent emitting materials, while it increases up to 100% when the phosphorescence is used together with fluorescence. From those points of view, the development of phosphorescent materials is expected, and especially, Ir(III) complexes such as *fac*-Ir(ppy)$_3$, which show high luminescence yields have attracted much attention. A change in the phosphorescence emission energy by the various substituents into *fac*-Ir(ppy)$_3$ flamework can be estimated using quantum chemical calculations. In this study, we aim to obtain a designing guideline for the blue phosphorescence, which is an important issue for the organic electroluminescence (OLED). The calculated results indicate that the complex exhibits the blue-shift in the phosphorescence when fluorine atoms are introduced as substituents. In the presentation, we discuss its mechanism and the combination effects with other substituents.

Keywords : phosphorescence, Iridium complexes, Substituent Effects, Organic electroluminescence (OLED), Quantum Chemical Calculations

近年、薄膜型ディスプレイ材料や照明として、有機エレクトロルミネッセンス(EL)の利用が広まりつつある。有機 EL 材料は蛍光性発光材料とリン光性発光材料に分けられるが、生成された励起子のうち、発光として利用することが可能な励起子の割合である励起子生成効率は、蛍光性発光材料では最大 25%であるのに対し、リン光性発光材料は、項間交差により最大 100%を実現できることが知られている。このような観点から、リン光性発光材料の開発が期待されており、中でも高い発光収率を示す *fac*-Ir(ppy)$_3$ 錯体などのIr(III)錯体が注目されている[1-3]。*fac*-Ir(ppy)$_3$ 錯体の骨格に様々な置換基を導入することで生じる、リン光発光エネルギーの変化は量子化学計算を用いて求めることができる。そこで本研究では、リン光の色を青色に近づけるための分子設計の構築を目的とした。計算の結果、フッ素を置換基として導入した際、リン光がブルーシフトすることが示され、その原因を明らかにするとともに、その他の置換基との組み合わせによる影響も議論した。

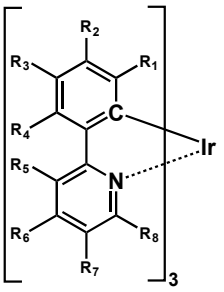

Fig.1 The structure of *fac*-Ir(ppy)$_3$

1) M. A. Baldo *et al.*, *Appl. Phys. Lett.,***1999**, 75, 4-6.
2) J. M. Younker *et al.*, *J. Phys. Chem. C,* **2013**, 117, 48, 25714-25723.
3) A. Endo *et al., Chem. Phys. Lett.,* **2008,** 460, 155–157.

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独立した二種のπ電子系を有するヘリカルな Eu 錯体の発光挙動

（青山学院大理工）○兒嶋 風人・村田 雄貴・大曲 仁美・長谷川 美貴
Luminescence behavior of the helicate Eu complexes with two independent π-electronic systems (*Coll. Sci & Eng., Aoyama Gakuin University*) ○Fuuto Kojima, Yuki Murata, Hitomi Ohmagari, Miki Hasegawa

In this study, we focus on Eu complexes with ligands which have different π-electronic systems at the equatorial and axial positions. Previously, we have reported a helical complex EuL with a hexadentate ligand L having two bipyridine moieties bridged by an ethylenediamine at the equatorial position[1]. Two nitrate ions are coordinated to the axial position of EuL. They can be substituted with aromatic carboxylic acids such as 1,4-benzenedicarboxylic acid[2]. Here, we aim to synthesize complexes with various aromatic carboxylic acids at the axial position of EuL and discuss the changes in luminescence behavior by binding of various aromatic carboxylic acids. The complex *R*-EuL-2PA [2PA = 2-phenylpropionic acid] was synthesized by coordinating a chiral carboxylic acid *R*-2PA to EuL and it exhibits Circularly Polarized Luminescence (CPL) in solution. This result indicates that the addition of a chiral molecule in the axial position of the complex impart circular polarization to the ff luminescence.
Keywords : Lanthanide Complex; Luminescence; Excitation Wavelength Dependence; Circularly Polarized Luminescence

本研究では、Eu 錯体のエカトリアル位とアキシャル位に異なるπ共役系を有する配位子を導入し、それらを直交するように配位させた系に着目している。これまで、2 個のビピリジンをエチレンジアミンで架橋した 6 座配位子 L をエカトリアル位に有するヘリカルな錯体 EuL を報告している [1]。EuL の軸位には 2 個の硝酸イオン(NO_3^-)が結合しており、これは 1,4-ベンゼンジカルボン酸などの芳香族カルボン酸と置換可能である [2]。本研究では、EuL の軸位に種々の芳香族カルボン酸を導入した錯体を合成し、軸配位子の導入による発光挙動の変化について議論することを目的とする。

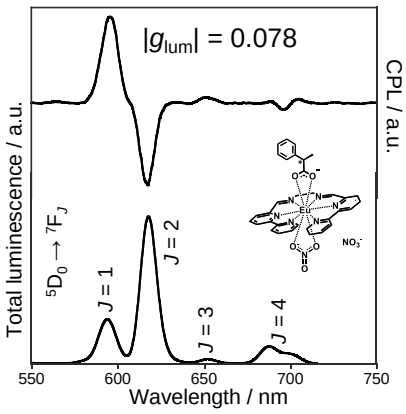

Fig. CPL spectra of *R*-EuL-2PA in CH_3CN (λ_{ex} = 340 nm)

EuL にキラルなカルボン酸 *R*-2PA を配位させた錯体 *R*-EuL-2PA を合成した。*R*-EuL-2PA は、溶液中で CPL を示し、錯体の軸方向にキラル分子を導入するのみで中心金属の発光に円偏光性を付与できることが見出された。

CPL 測定は北里大学長谷川真士先生に御助力いただきました。この場をお借りして御礼申し上げます。

1) M. Hasegawa, H. Ohtsu, D. Kodama, T. Kasai, S. Sakurai, A. Ishii, K. Suzuki, *New J. Chem*. **2014**, *38*, 1225.
2) S. Sato, I. Ayumi, C. Yamada, J. Kim, C. H. Song, A. Fujiwara, M. Takata, M. Hasegawa, *Polymer J*. **2015**, *47*, 195.

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カンファー型配位子に芳香環を導入したキラル Eu(III)錯体の円偏光発光特性

(北大工,[1] 北大院総化,[2] 北大院工,[3] 北大 WPI-ICReDD[4]) ○滝沢 諒平,[1] 鶴井 真,[2] Wang Mengfei,[3,4] 北川 裕一,[3,4] 長谷川 靖哉 [3,4]

Circularly polarized luminescence of chiral Eu(III) complex with aromatic ring functionalized camphor-type ligands

([1]School of Engineering, Hokkaido University, [2]Graduate School of Chemical Sciences and Engineering, Hokkaido University, [3]Faculty of Engineering, Hokkaido University, [4]WPI-ICReDD, Hokkaido University) ○ Ryohei Takizawa,[1] Makoto Tsurui,[2] Mengfei Wang,[3,4] Yuichi Kitagawa,[3,4] Yasuchika Hasegawa[3,4]

Keywords: *Europium, Circularly Polarized Luminescence, Lanthanide Complex, Chiral*

Chiral Eu(III) complexes exhibit circularly polarized luminescence (CPL)[1]. In particular, Eu(III) complexes with four chiral β-diketonato ligands show relatively large dissymmetry factor, g_{CPL}[2]. Introduction of aromatic group in the chiral β-diketonato ligand leads to control of the electronic and steric environments around the Eu(III) ion. In this study, we report on synthesis and CPL property of novel chiral tetrakis-typed Eu(III) complex, $NEt_4^+[Eu(+bzc)_4]^-$ (+bzc: (+)-3-benzoylcamphorate, Figure 1).

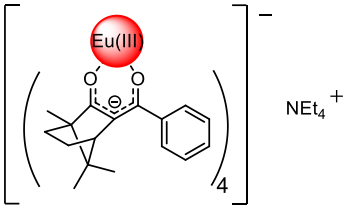

Figure 1. Chiral Eu(III) complex with aromatic ring functionalized camphor-type ligands.

The chiral ligand +bzc was prepared by the reaction of (+)-camphor with ethyl benzoate. The emission spectrum of $NEt_4^+[Eu(+bzc)_4]^-$ showed 4f-4f transition bands with narrow FWHM related to Eu(III) ion. The 4f-4f emission quantum yield was estimated to be more than 30%. We also observed that the g_{CPL} value of $NEt_4^+[Eu(+bzc)_4]^-$ in KBr pellet was larger than those of previous chiral Eu(III) complexes[3].

キラル配位子を有する Eu(III)錯体は左右の円偏光強度に差が生じる円偏光発光（CPL）を示す[1]。特にキラル型β-ジケトナト配位子が 4 つ配位したテトラキス型の Eu(III)錯体は比較的高い CPL の異方性因子(g_{CPL})を示す[2]。キラル型β-ジケトナト配位子に芳香環を導入することで Eu(III)イオン周りの電子構造と立体構造を制御することができる。本研究ではテトラキス型の新規キラル Eu(III)錯体 $NEt_4^+[Eu(+bzc)_4]^-$ (+bzc: (+)-3-benzoylcamphorate, Figure 1) の合成および CPL 特性について報告する。

キラル配位子+bzc は(+)-カンファーと安息香酸エチルを用いて合成した。$NEt_4^+[Eu(+bzc)_4]^-$の発光スペクトルは Eu(III)イオンに特徴的な半値幅の狭い発光バンドを示した。4f-4f 遷移の発光量子収率は 30%以上と見積もられた。また、KBr ペレット中での g_{CPL} 値はこれまでのキラル Eu(III)錯体よりも高いことが分かった[3]。

[1] Y. Kitagawa et al., *Commun. Chem.* **2020**, 3, 119. [2] J. Yuasa et al., *Chem. Commun*. **2016**, 52, 9885. [3] M. Tsurui, Y. Hasegawa et al., *Dalton Trans.* **2023**, 52, 796.

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
F1234(1234, Bldg. 12 [3F])

[F1234-3am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaaki Sadakiyo, Yuki Wada

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[F1234-3am-01]

The luminescence and heat-responsive properties of NDI-based MOF with biphenyl derivatives as guest

○Shoto Yamashita[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2] (1. Graduate School of Faculty of Frontiers of Innovative Research in Science and Technology, Konan University, 2. Konan University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[F1234-3am-02]

Unique photodimerization behavior of Cd coordination polymer with 4-styrylpyridine ligands

○ARATA TATEISHI[1], Yun Chen[1], Yunya Zhang[1], Yuki Saito[1,2], Xin Zheng[1,2], Shin-ichiro Noro[1,2] (1. Grad. Sch. of Env. Sci.,Hokkaido Univ., 2. Fac. of Env.Earth Sci., Hokkaido Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[F1234-3am-03]

Quantum sensing by persistent radicals photo-generated in metal-organic frameworks

○Miku Inoue[1], Akio Yamauchi[1], Bhavesh Parmar[1], Orihashi Kana[1], Mizue Asada[2], Toshikazu Nakamura[2], Nobuhiro Yanai[1,3] (1. Kyushu University, 2. Institute for Molecular Science, 3. CREST, JST)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[F1234-3am-04]

Structural Analysis of Low-boiling Compounds by Soaking in the Gas Phase State Using the Crystalline Sponge Method

○Kazuhiko Sakaguchi[1], Nao Tamaki[1], Akihiro Kawaraya[1], Satoru Moriya[1], Yoshihiro Yaguchi[1] (1. Takasago international corporation)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[F1234-3am-05]

Structural analysis using microcrystal sponges with hierarchical clustering analysis as the key.

○Satoshi Yoshida[1], Seiki Baba[2], Yuki Nakamura[2], Sota Sato[1,3], Makoto Fujita[1,3,4] (1. School of Engineering, TheUniv. of Tokyo, 2. JASRI, 3. IMS, 4. UTIAS, The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[F1234-3am-06]

A series of adaptable porous frameworks constructed from different positional isomers of tris-pyridyl hexaazaphenalene for crystalline sponge method

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○Tomoki Nakagawa[1,2], Yuki wada[2], Pavel M Usov[2], Yiying Zhu[2], Makoto Tadokoro[1], Masaki Kawano[2] (1. Tokyo Institute of Technology, 2. Tokyo University of Science)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[F1234-3am-07]

Effects of defect and particle size on the structural transformation properties of Al-based MOFs

○Shintaro Tanaka[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2] (1. Konan graduate school , 2. Konan University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[F1234-3am-08]

Rational synthesis of hierarchical metal-organic framework using structual transformation reaction

○Reon Teramoto[1], Yohei Takashima[1], Takaaki Tsuruoka[1], Kensuke Akamatu[1] (1. Konan 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
[F1234-3am-09]

Morphology-controlled synthesis of a metal-organic framework generated from sphere amorphous precursor

○Takumi Kakuchi[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2] (1. Konan graduate school, 2. Konan University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[F1234-3am-10]

Fabrication of metal-organic framework composite membranes for CO_2 separation

○Jieru CHEN[1], Xin ZHENG[2], Yuki SAITO[2], Shin-ichiro NORO[1,2] (1. Grad. Sch. of Env. Sci., Hokkaido Univ., 2. Fac. of Env. Earth Sci., Hokkaido Univ.)

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[F1234-3am-11]

Removal of Perchlorate Anion from Water Using Coordination Polymers

○Umme Fariha Tasnim[1], Aditya Irfan Witono[1], Xin Zheng[1], Shin-ichiro Noro[1] (1. Hokkaido University)

English
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[F1234-3am-12]

Substituent introduction effect on CO_2 adsorption properties in three-dimensional SiF_6-bridged porous coordination polymers

○Zhongjie Gu[1], Jia-bing Wu[2,3], Xin Zheng[2], Yuki Saito[2], Shin-ichiro Noro[1,2] (1. Grad. Sch. of Env. Sci., Hokkaido Univ., 2. Fac. of Env. Earth Sci., Hokkaido Univ., 3. Res. Ins. for Ele. Sci., Hokkaido Univ.)

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Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[F1234-3am-13]
Separation of Amino Acids by a Zirconium Metal–Organic Framework Having Small-Sized Pores and High Acid Tolerance

○Kyoko Shiraishi[1], Masaaki Sadakiyo[1] (1. Tokyo Univ. of Sci.)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[F1234-3am-14]
Synthesis of novel phosphoramide ligand and their application in metal-organic frameworks

○Sho KOBAYASHI[1], Koh SUGAMATA[1], Natsuki AMANOKURA[1,2], Akihiro SHIRAI[1,2], Mao MINOURA[1] (1. Rikkyo Univ., 2. Nippon Soda Co., Ltd.)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[F1234-3am-15]
Reversible structural change of a cyano-bridged coordination polymer with Zn^{2+} ion induced by water adsorption and desorption

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

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ビフェニル誘導体ゲストと NDI ベース MOF からなる複合体が示す発光特性と熱応答特性

(甲南大院 FIRST[1]・甲南大 [2])○山下 翔斗 [1]・髙嶋 洋平 [2]・鶴岡 孝章 [2]・赤松 謙祐 [2]

The luminescence and heat-responsive properties of NDI-based MOF with biphenyl derivatives as guest

([1]*Graduate School of Faculty of Frontiers of Innovative Research in Science and Technology, Konan University*, [2]*Konan University*) ○Shoto Yamashita[1], Yohei Takashima[2], Takaaki Tsuruoka[2], Kensuke Akamatsu[2]

Luminescent metal-organic frameworks (MOFs) can be obtained by using the organic linkers with luminescent moiety and their luminescent properties were further tuned by the accommodations of guest molecules. We have previously showed that one NDI-based MOF($[Zn_2(bdc)_2dpNDI]_n$) with biphenyl derivatives as guest showed different luminescence properties depending not only on the difference of accommodated guests but also on their accommodation conditions. In this presentation, we show more details about the unique luminescent properties and their interesting thermal response.

Keywords : Metal-Organic Frameworks, naphthalenediimide, luminescence

金属イオンと有機配位子からなる多孔性金属錯体(Metal-Organic Frameworks: MOFs)は用いる金属イオンと有機配位子の組み合わせに応じたさまざまな機能を付与することが可能である。特に発光部位を導入した場合は、ゲスト分子との相互作用によって発光特性の制御が可能であることからセンサー材料などへの応用研究が盛んに行われている。我々はこれまで、ナフタレンジイミド(NDI)含有MOF($[Zn_2(bdc)_2dpNDI]_n$)にベンゼン誘導体やビフェニル誘導体がゲスト分子として導入されると NDI とゲスト分子の相互作用に由来した発光を示すことが明らかにしている。さらに、4-シアノビフェニル(Biph-CN)がゲスト分子の場合、導入条件によって発光挙動が異なるという興味深い現象を見出している。そこで本研究では、その現象の理解を目的とし種々の実験を行った。発光メカニズムを明らかにするために Biph-CN@MOF の時間分解発光スペクトルを測定したところ、Biph-CN@MOF の発光には NDI と Biph-CN との相互作用に由来する発光と NDI と bdc との相互作用に由来する発光の両方が含まれており、それらの発光強度は、細孔内での Biph-CN の導入状態によって変化していることが強く示唆された(Figure a)。また、加熱処理をした直後の Biph-CN@MOF の発光スペクトルを測定したところ、加熱処理をしていないものと比べて、発光強度の増大と発光波長の短波長シフトが観測された(Figure b)。本発表では、これらの特異な発光挙動の詳細、及び Biph-CN 以外のビフェニル誘導体を導入したサンプルの熱応答特性についても報告する予定である。

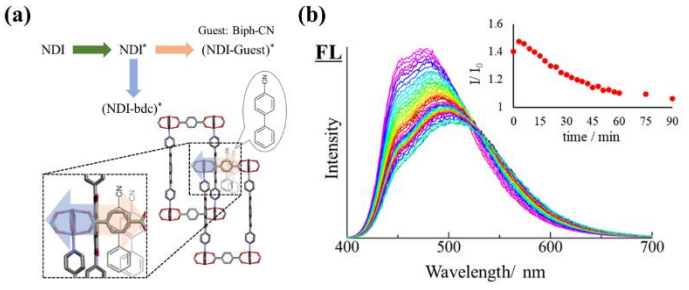

Figure. (a) Schematic illustration of two types of luminescent species in Biph-CN@MOF. (b) Fluorescence spectra of Biph-CN@MOF after heating. Inset: I/I_0 vs. time.

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4-スチリルピリジン配位子を有する Cd 配位高分子の特異な光二量化挙動

(北大院環境[1]・北大院地球環境[2]) ○立石 新[1]・陳 ユン[1]・張 雲雅[1]、齋藤 結大[1,2]、鄭 キン[1,2]、野呂 真一郎[1,2]

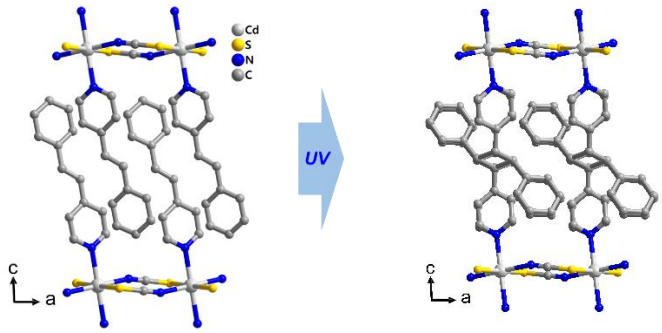
Unique photodimerization behavior of Cd coordination polymer with 4-styrylpyridine ligands

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Arata Tateishi[1], Yun Chen[1], Yunya Zhang[1], Yuki Saito[1,2], Xin Zheng[1,2], Shin-ichiro Noro[1,2]

A [2+2] photodimerization is a reaction in which two C=C double bonds become a cyclobutane upon UV irradiation. 4-styrylpyridine (4-spy) is a ligand showing the [2+2] photodimerization and has been used for synthesizing photoreactive coordination polymers (CPs). We synthesized new photoreactive one-dimensional CP $[Cd(SCN)_2(4\text{-spy})_2]$ (**1**) in which SCN anions bridge between Cd ions. The shortest distance between C=C double bonds of 4-spy ligands is 4.6 Å, longer than Schmidt's threshold distance (4.2 Å) for the [2+2] photodimerization reaction. Nevertheless, **1** was found to undergo 4-spy photodimerization with a 100% reaction rate and convert to a two-dimensional CP. The details will be discussed in this presentation.

Keywords : Coordination Polymer, Photodimerization, 4-Styrylpyridine

[2+2]光二量化は、2 つの C=C 二重結合が紫外線照射によってシクロブタン環を形成する反応である。4-スチリルピリジン(4-spy)は光二量化を示す配位子であり、これまで光応答性配位高分子を合成するために用いられてきた [1]。本研究では、4-spy 配位子を有する一次元配位高分子$[Cd(SCN)_2(4\text{-spy})_2]$ (**1**)を新規に合成した。**1** は SCN アニオンによって Cd 間が一次元状に架橋された配位高分子である。**1** で観測された 4-spy 間の C=C 二重結合間距離は約 4.6 Å であり、これはシュミットが報告した[2+2]光二量化反応の閾値 4.2 Å より長い [2]。それにも関わらず、**1** は 100%の反応率で 4-spy 間光二量化を起こし、一次元配位高分子から二次元配位高分子へ構造変化することがわかった。本発表ではその詳細について説明する。



1) R. Medishetty, A. Husain, Z. Bai, T. Runcevski, R. E. Dinnebier, P. Naumov, J. J. Vittal, *Angew. Chem., Int. Ed.* **2014**, *53*, 5907.
2) G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647.

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多孔性金属錯体に光発生した持続性ラジカルによる量子センシング

（九州大学[1]・分子科学研究所[2]・JST CREST[3]）○井上 魅紅[1]・山内 朗生[1]・Bhavesh Parmar[1]・折橋 佳奈[1]・浅田 瑞枝[2]・中村 敏和[2]・楊井 伸浩[1,3]
Quantum sensing by persistent radicals photo-generated in metal-organic frameworks ([1]*Kyushu University*, [2]*Institute for Molecular Science,* [3]*CREST, JST*) ○Miku Inoue,[1] Akio Yamauchi,[1] Bhavesh Parmar,[1] Kana Orihashi,[1] Mizue Asada,[2] Toshikazu Nakamura,[2] Nobuhiro Yanai[1,3]

Quantum sensing is one of the applications of qubits. It is a method of measuring physical quantities using quantum effects and is expected to be highly sensitive. The qubits used for quantum sensing must maintain the superposition state for a long time, corresponding to the long coherence time (T_2) of the electron spin. Recently, metal-organic frameworks (MOFs) have attracted much attention as a platform due to their ability to sense guest molecules in the pores. We observed persistent radicals in a MOF with diazatetracene derivative (DAT) after photoirradiation[1]. However, the unstable structure of this MOF made it difficult to introduce various guest molecules. In this study, we have synthesized a new UiO-type MOF with a DAT-based ligand into which guest molecules can be stably introduced. The change in coherence time depending on the guest species was evaluated by pulse ESR measurements.
Keywords :Quantum sensing; Coherence time; Metal-organic frameworks; Radical; Molecular qubits

量子センシングは量子ビットの応用先の一つであり、量子効果を利用した物理量の測定手法のことである。量子センシングに利用する量子ビットは量子重ね合わせ状態を長時間保持できることが必要とされ、これは電子スピンのコヒーレンス時間 (T_2) が長いことに対応する。また、近年細孔中のゲスト分子のセンシングが可能なことから多孔性金属錯体 (MOF) が有用なプラットフォームとして注目されている。当研究室ではジアザテトラセン (DAT) の誘導体を配位子として用いた MOF に光照射を行うことにより長いコヒーレンス時間を持つラジカルを観測している[1]。しかしながら、MOF の構造が不安定であったため多様なゲスト分子の導入が困難であるという課題があった。そこで本研究ではゲスト分子の安定な導入が可能な UiO 型の新規 MOF を合成し、様々なゲスト分子を導入した際のコヒーレンス時間の変化をパルス ESR 測定によって評価した。

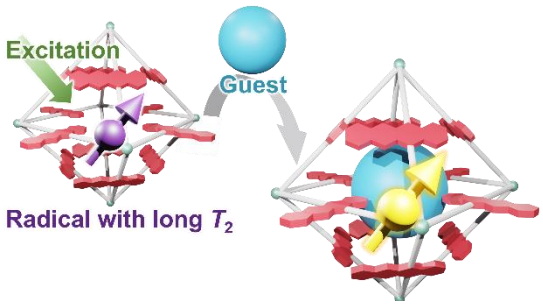

Fig. 1 Schematic illustration of quantum sensing with long coherence time radical

1) K. Orihashi et al., *J. Am. Chem. Soc.* **2023**, *145*, 27650–27656.

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結晶スポンジ法を用いた気相状態でのソーキングによる低沸点化合物の分子構造解析

（高砂香料工業株式会社　研究開発本部）○坂口　和彦・玉城　奈和・瓦谷　明宏・守屋　理・矢口　善博

Structural Analysis of Low-boiling Compounds by Soaking in the Gas Phase State Using the Crystalline Sponge Method (*Takasago international Corporation, Corporate Research & Development Division*) ○Kazuhiko Sakaguchi, Nao Tamaki, Akihiro Kawaraya, Satoru Moriya, Yoshihiro Yaguchi

The crystalline sponge (CS) method is an innovative technique that enables structure determination by X-ray crystal structural analysis without crystallization of samples [1]. In the CS method, the process of inclusion of samples in the CS pores is most important. However, applying the CS method to a volatile compound in the standard way may result in vaporizing the sample away before it is encapsulated in the CS. Therefore, we have developed a method for inclusion of very small amounts of sample in the gas phase state by separating the solution containing 10 μg of the sample and the CS in a sealed vial (Figure 1). Furthermore, the temperature during soaking was found to be an important factor in the inclusion process and following X-ray structure determination.

Keywords : the Crystalline Sponge Method; Structure Determination; Single Crystal X-ray Structure Analysis, Coordination Complex

結晶スポンジ（CS）法は試料を結晶化せずに X 線結晶構造解析による構造決定を可能とする革新的な手法である [1]。CS 法において細孔性の結晶に試料を包接させるプロセスが最も重要であるが、標準的な方法で揮発性化合物に CS 法を適用しても CS に包接される前に試料が揮散してしまうことがある。そこでわれわれは、密閉したバイアル中で 10 μg の試料を含む溶液と CS を隔離して静置することにより、極微量の試料を気相状態で包接させる手法を開発した（Figure 1）。さらにソーキング時の温度が構造決定の重要な要因であることを明らかにした。

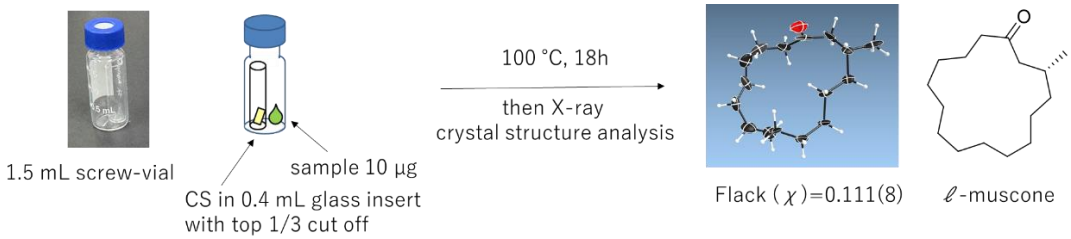

Figure 1. CS への気相ソーキング法

1) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita, *Nature* **2013**, *495*, 461-466.

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階層的クラスタリング解析を鍵とするマイクロ結晶スポンジを用いた構造解析

（東大院工[1]・JASRI[2]・分子研[3]・東大 UTIAS[4]）○吉田 知史[1]、馬場 清喜[2]、仲村 勇樹[2]、佐藤 宗太[1,3]、藤田 誠[1,3,4]
Structural analysis using microcrystalline sponge with hierarchical clustered analysis as the key ([1]*Graduate School of Engineering, Tokyo University*, [2] *JASRI,* [3] *IMS,* [4]*UTIAS*, The Univ. of Tokyo) Satoshi Yoshida,[1] Seiki Baba,[2] Yuki Nakamura,[2] Sota Sato,[1,3] Makoto Fujita[1,3,4]

Crystalline Sponge(CS) method is a powerful structural analysis method by introducing an analyte into the pore of MOF. Previously, we succeeded in observing analytes in CS more clearly and improving the inclusion speed by using small crystals(5-10 μm) and synchrotron radiation sources. However, It is usually difficult to prepare uniform sample crystals and this problem hinders the observation of the analyte structure after merging partial data. Here, we prepared a test dataset by mixing two sub-datasets of similar analytes (Flavone and Flavanone) and tried to separate them. Flavone datasets can be extracted by the hierarchical clustering method using intensity correlation between each dataset as a distance.

Keywords : Crystalline Sponge Method, Single Crystal X-ray Diffraction, Coordination Complex, Structure Determination,

結晶スポンジ(CS)法は、錯体結晶の細孔中に試料分子を導入することで、微量な試料分子構造を、その絶対配置も含めて決定できる強力な手法である。しかしながら、従来法で用いられる一辺 100-200 μm の結晶では、試料分子が細孔中に十分に拡散せず、試料分子が規則的に配列しない場合がある。これまでに、5-10 μm 程度のマイクロ CS を用いることで、拡散律速が解消され、調製時間が大きく短縮できることを見出した。この手法では、高輝度な放射光 X 線源を用いて複数個のマイクロ CS から得た単結晶 X 線回折データを統合するが、均一なマイクロ CS を調製できないケースが多く、解析できない場合もある。そこで、本研究では、モデルケースとして、似ているが異なる試料分子（フラボンおよびフラボノン）をそれぞれ包接した 2 種類のデータセットを混合し、データセットを分離することを試みた。データ間の回折強度の相関から算出される距離に基づき、階層的クラスタリングによるデータ統合を行ったところ、フラボンに対しては、回折データ抽出して構造解析できることを見出した。

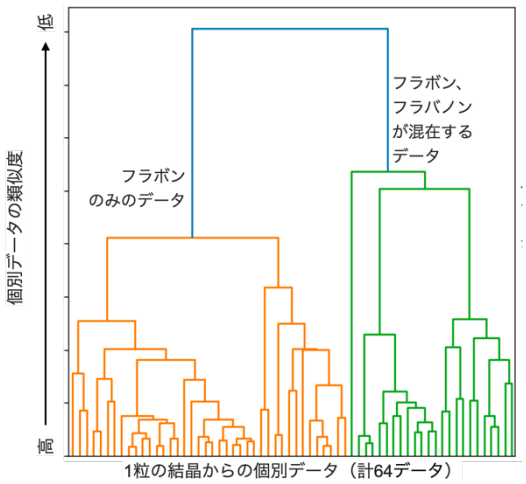

図 1 強度相関によるデータ統合

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MOF 中におけるピリジル配位子の N 位置異性体の効果と結晶スポンジ法への応用

(東京理科大学[1]・東京工業大学[2]) ○中川 智暉[1,2]・和田 雄貴[2]・ユーソフ パベル[2]・祝 伊穎[2]・田所 誠[1]・河野 正規[2]

A series of adaptable porous frameworks constructed from different positional isomers of tris-pyridyl hexaazaphenalene for crystalline sponge method.

([1]*Tokyo University of Science*, [2]*Tokyo institute of Technology*) ○Tomoki Nakagawa,[1] Yuki Wada,[2] Pavel M Usov,[2] Yiying Zhu,[2] Makoto Tadokoro,[1] Masaki Kawano[2]

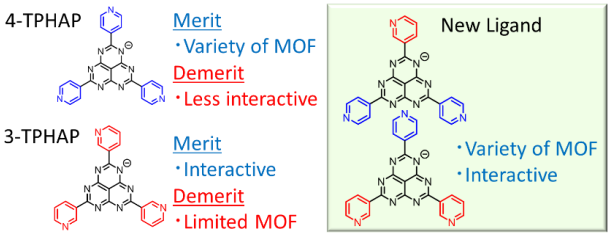
The crystal sponge method visualizes the structure of molecules by encapsulating them in the pores of an organometallic framework (MOF). We have succeeded in synthesizing two types of ligands that can produce MOFs. These MOFs can be used in the crystalline sponge method. The two types of ligands respectively possess 3-pyridyl group or 4-pyridyl group as a coordination site. While the 4-pyridyl ligand can produce many various types of MOFs, it has weak interactions with guests. Conversely the 3-pyridyl ligand can produce only one type of MOF, it has rich interactions mediated by water.

We found that the newly synthesized ligand, containing 3- and 4-pyridyl group, can produce four types of MOFs. Additionally, the guest molecules encapsulated in the pores were clearly visualized by single crystal X-ray diffraction. These findings suggest that this new ligand possesses both properties effectively.

Keywords : Metal Organic Frameworks; Single Crystal X-ray Diffraction; Host Guest Interaction

結晶スポンジ法は金属有機構造体(MOF)の細孔中に分子を包接することで、対象物の構造を決定する方法である。特に、結晶化が困難な化合物や、サンプル量が微量な化合物の構造決定に有力な手法である。我々の研究室では、現在までに 2 種類の配位子で結晶スポンジ法を行える MOF の合成に成功しており、この配位子はそれぞれ 4 位または 3 位のピリジル基のみを持つ配位子である。4 位ピリジル配位子はホストーゲスト間相互作用に乏しいが多数の MOF を構築できる一方で、3 位ピリジル配位子は MOF の多様性に乏しいが水を介した強力なホストーゲスト間相互作用を持つ。

今回、新規に合成された 3 位と 4 位の両方のピリジル基を持つ配位子は、現在までに 4 種の MOF の合成に成功しており、さらにゲスト包接を行ったところ、水を介したホスト—ゲスト間相互作用によってゲスト分子が単結晶 X 線回折により明瞭に確認できた。従って、今回合成された新規分子は 3 位と 4 位のピリジル配位子両方の長所を併せ持つ配位子であると考えられる。



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Al-MOF が示す特異な構造変換反応における欠陥と粒子サイズの影響

（甲南大院[1]・甲南大[2]）田中 進太郎[1]・髙嶋 洋平[2]・鶴岡 孝章[2]・赤松 謙祐[2]
Effect of defect and particle size on the structural transformation properties of Al-based MOFs
(Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology, Konan University) ○Shintaro Tanaka, Yohei Takashima, Takaaki Tsuruoka, Kensuke Akamatsu

Metal-Organic Frameworks (MOFs) that are composed of metal ions and organic linkers have the defined structures with permanent porosity, high specific surface areas and flexibility. Many flexible MOFs have been reported until now, but very few MOFs showed the structural flexibility accompanied with bond switching. In this work, we have succeeded in controlling the structural transformation phenomenon from MIL-53 to MIL-68 by tuning the number of defects and particle size in their structures.
Keywords : Metal-Organic Frameworks; Structural Transformation; Defect; Particle Size

ある構造から別の構造へと可逆的に構造が変換する材料は、スイッチング材料やメモリ材料などへの応用が可能でありこれまで精力的に研究が行われてきているが、新たな変換モジュールを合理的に構築することは未だ困難である。そこで本研究では、新たな変換モジュールとして多孔性金属錯体(MOF)に着目する。MOF は金属イオンと有機配位子が配位結合することで形成される結晶性のハイブリッド材料であり、多孔性、高い構造設計性および柔軟性などの特徴を有しているが、構造変換可能な MOF は少ない上、その設計指針についても明らかになっていない。我々はこれまでアルミニウムベースの多孔性金属錯体(MOF)の一つである MIL-53-OH を遊離配位子共存下にて加熱することにより構造異性体の関係にある MIL-68-OH へと変換させることに成功している。しかしながら、そのメカニズムを含めた詳細についてはまだわかっていないため、本研究では、フレームワーク上の欠陥量と粒子サイズに注目し、構造変換挙動に与える影響について詳しく調べた。

配位子量に対して X 等量(X=0, 10, 50)のモジュレーターを合成時に加え反応させることにより、配位子欠陥が導入された一連の MOF (MIL-53-OH(X)) を合成した。合成した MOF の配位子欠損率を TGA 測定より算出した結果、モジュレーターの導入量が多いものほどその欠損率も高くなり、粒子サイズも大きくなることが明らかとなった(**Figure a**)。得られたサンプルを用いて構造変換を試みたところ、MIL-53-OH(10)において MIL-68-OH へと変換することがわかった(**Figure b**)。このような結果より、MIL-53 から MIL-68 への構造変換反応において欠陥と粒子サイズが重要であることが示唆された(**Figure c**)。より詳細な結果については本発表にて報告する。

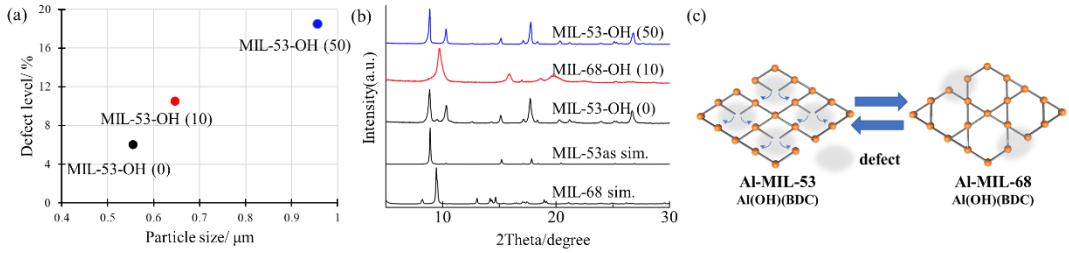

Figure. (a) Defect level and particle size of MIL-53-OH(X) (b) XRD patterns of MIL-53-OH(X) after heating (c) Schematic image of reversible structural transformation between MIL-53 and MIL-68.

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構造変換反応を用いた階層型 MOF の合理的合成

（甲南大）○寺元 玲音・髙嶋 洋平・鶴岡 孝章・赤松 謙祐

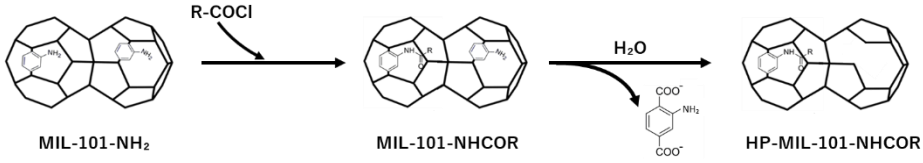
Rational synthesis of hierarchical metal—organic framework using structural transformation reaction

(Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology, Konan University) ○Reon Teramoto, Yohei Takashima, Takaaki Tsuruoka, Kensuke Akamatsu

Metal-Organic Frameworks (MOFs) have been used in various research fields including gas adsorption/separation, catalysis and so on. To further improve their functionalities, some methods have been developed to introduce hierarchical structures that can accommodate larger number of guests or improve their catalytic activities. In this work, we introduce new synthetic methodology to generate hierarchical structure of MOF by structural transformation reaction, in which one of the two ligands embedded onto a MOF scaffold is selectively removed without losing its skeleton.

Keywords : Metal-Organic Frameworks; Hierarchical structure; Structural transformation

新規多孔性ナノ材料である金属有機構造体(MOF)は、高い表面積、孔容積を有しており、ガスの吸着・分離、触媒分野への応用に向けた研究が精力的に展開されている。また近年では、MOF のさらなる機能化を指向した階層型 MOF の合成にも注目が集まっている。階層型 MOF とは本来の細孔とは異なるサイズの細孔が導入された MOF のことであり、大きな細孔が導入されたことによるガス吸着量の増加や反応基質の拡散性向上に伴う触媒性能の向上などの効果がこれまで報告されている。本研究では、我々が近年見出した構造変換反応を用いることによる階層型 MOF の合理的合成を目標としている。我々はこれまで、アルミニウムベースの MIL-101 が水と反応することでアモルファスへと構造変換すること、また、用いる配位子によってその変換速度が大きく異なることを明らかにしている。そこで、反応速度の異なる 2 種類の配位子を導入した MIL-101 固溶体を水と作用させることにより、反応速度の速い配位子部位のみを選択的にアモルファス化し MOF 骨格内から除去することで、本来の細孔よりも大きな細孔を導入できるのではないかと考えた。（**Scheme**）



Scheme. Generation of hierarchical porous MOF by structural transformation reaction.

MIL-101-NH₂（$[Al_3OCl(bdc\text{-}NH_2)_3]_n$;bdc-$NH_2$= 2-aminoterephthalate)を合成し、骨格内の配位子の一部を一連のカルボン酸塩化物（**R-COCl**）を用いて後修飾した。NMR 測定から修飾後の MOF（**MIL-101-NHCOR**）内には元々の bdc-NH_2と後修飾された bdc-NHCOR の 2 種類の配位子が存在していることを確認した。続いて試料を水条件下で加熱し、構造変換させることで階層型 MOF（**HP-MIL-101-NHCOR**）を合成した。XRD 測定と NMR 測定から、構造変換後も MIL-101 の構造を維持していることおよび bdc-NH_2が選択的に MIL-101 骨格内から除去されていることが明らかになった。また、N_2吸着測定結果から、階層構造を有していることも確認された。これより、本手法を用いることで階層型 MOF の合成が可能であることが示唆された。

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球状アモルファス前駆体を用いた MOF の形態制御合成

（甲南大 FIRST）○覚知 匠・髙嶋 洋平・鶴岡 孝章・赤松 謙祐
Morphology-controlled synthesis of a metal-organic framework generated from sphere amorphous precursor (*Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology, Konan University*) ○Takumi Kakuchi, Yohei Takashima, Takaaki Tsuruoka, Kensuke Akamatsu

Metal-organic frameworks (MOFs) are a class of porous materials composed of metal ions and organic linkers, and many synthetic methodologies have been developed until now. In this work, we have succeeded in synthesizing MOF crystals from sphere amorphous, in which their crystal morphologies were drastically changed depending on the sizes of sphere amorphous. In this presentation, we will report in detail their crystal growth mechanisms from the results of time-course observations with TEM.
Keywords : Metal-Organic Frameworks; Structural Transformation; Amorphous

多孔性金属錯体（Metal-Organic Frameworks: MOFs）は、金属イオンと有機配位子からなる結晶性の多孔体であり、金属イオンと有機配位子の選択により様々な細孔構造を有する MOF が合成されてきている。また、MOF をさまざまな環境下で利用していく上においては、MOF 結晶のサイズおよび形態の制御も重要であり、そのような観点からの MOF 合成法の開発に関する研究も同時に進行している。本研究では、球状化アモルファスを MOF 前駆体として用いることにより、MOF 結晶の形態制御を目指した。

我々はこれまで、MIL-101-NO_2 と名付けられたニトロ基を有した Al ベースの MOF と水を反応させることで球状アモルファスが得られること、および、得られた球状アモルファスが MIL-53-NO_2 と名付けられた別の MOF へと変換可能であることを明らかにしている。また、球状アモルファスのサイズによって得られる MIL-53-NO_2 結晶の形態が変化することも分かっている。そこで、異なる置換基を有する MIL-101 を用いて同様の実験を行ったところ、ブロモ基を有した MIL-101-Br において同様に球状アモルファスが得られることがわかった。さらに、球状アモルファスのサイズが MIL-53-Br の形態に与える影響について調べたところ、大きな球状アモルファス(約 100 nm)の場合は針状、中程度のサイズ(約 70 nm)の場合はロッド状、小さいサイズ(約 50 nm)の場合はコーン状の MIL-53-Br 結晶がそれぞれ得られた（**Figure**）。本発表では、本変換メカニズムの詳細について報告する予定である。

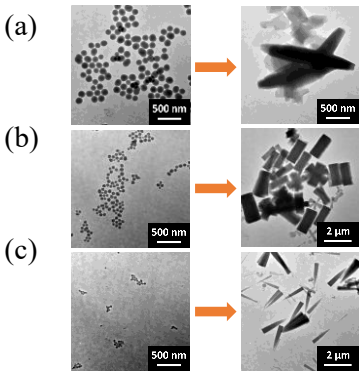

Figure. TEM images before and after the structural transformations to MIL-53-Br with (a) large, (b) medium, and (c) small spherical amorphous.

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二酸化炭素分離を目指した金属有機構造体複合膜の作製

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Fabrication of metal-organic framework composite membranes for carbon dioxide separation

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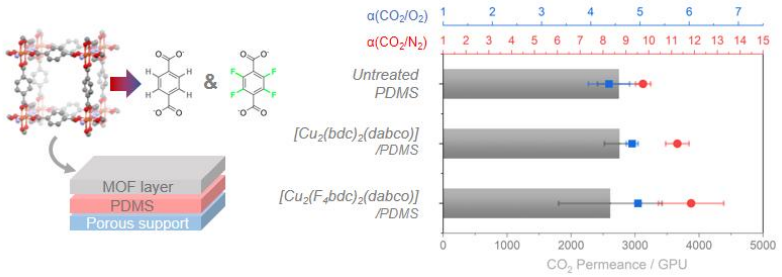
The membrane-based separation process is a promising means of reducing CO_2 emissions with energy saving. Organic polymer membranes face limitations in CO_2 separation due to permeability-selectivity trade-offs. In this study, we fabricated composite membranes consisting of organic polymers and metal-organic frameworks (MOFs)[1] and evaluated their CO_2 separation performance to simultaneously improve CO_2 permeance and selectivity. The composite membranes were prepared by alternately dipping polydimethylsiloxane (PDMS) gutter layers into metal salt and ligand solutions. The obtained composite membranes, $[Cu_2(bdc)_2(dabco)]$/PDMS and $[Cu_2(F_4bdc)_2(dabco)]$/PDMS (bdc = 1,4-benzenedicarboxylate, F_4bdc = tetrafluoro-1,4-benzenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane), were evaluated for gas permeability. Both composite membranes were found to have improved CO_2/N_2 and CO_2/O_2 selectivity with less reduction in CO_2 permeance compared to an untreated PDMS membrane.

Keywords : Metal-Organic Framework, Carbon Dioxide Separation, Composite Membranes

膜分離プロセスは省エネで二酸化炭素排出量を削減することができる有力な手段である。従来の有機高分子膜は二酸化炭素透過性と選択性のトレードオフのため実用化が困難であった。本研究では、二酸化炭素透過性と選択性の同時向上を目的に、有機高分子と金属有機構造体（MOF）からなる複合膜を作製し、その二酸化炭素分離能を評価した。

複合膜は、ポリジメチルシロキサン（PDMS）ガター層を金属塩溶液と配位子溶液に交互に浸漬させることによって作製した。得られた複合膜、$[Cu_2(bdc)_2(dabco)]$/PDMS と$[Cu_2(F_4bdc)_2(dabco)]$/PDMS のガス透過性を評価したところ、両複合膜は未処理の PDMS 膜と比べて CO_2 ガス透過速度の減少を抑えながら CO_2/N_2 および CO_2/O_2 選択性が向上することが分かった。



1) X. Yu, Y. Xian, C. Wang, H. Mao, M. Kind, T. Abu-Husein, Z. Chen, S. Zhu, B. Ren, A. Terfort, J. Zhuang, *J. Am. Chem. Soc.* **2019**, *141*, 18984.

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Removal of Perchlorate Anion from Water Using Coordination Polymers

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Keywords: Perchlorate Anion, Coordination Polymer, Water Purification

Perchlorate anion is an emerging environmental contaminant easily transferred to groundwater and surface water. Developing new materials with perchlorate-selective adsorption or ion exchange properties is necessary to remove perchlorate from water. Coordination polymers constructed from metal ions and organic bridging ligands can be applied to treat wastewater because of their high structural tunability and diversity. Our study aims to find coordination polymers that show efficient removal of perchlorate anion from water. In this study, we report the perchlorate removal performances of several coordination polymers that have already been reported.

We synthesized two coordination polymers, a two-dimensional $[Cu_3Cl_2(p\text{-bbiteb})_6]\cdot 4Cl$ (**1**, *p*-bbiteb = 1,4-bis(benzimidazol-1-yl)-2,3,5,6-tetramethylbenzene)[1] and a three-dimensional porous UiO-66 $[Zr_6O_4(OH)_4(bdc)_6]$ (**2**, bdc = 1,4-benzenedicarboxylate) with some Cl-including defect units.[2] The perchlorate removal capacity of **1** was higher than that of **2,** and the saturated amount of **1** was similar to that of the anion exchange resin Purolite A530E (Figure 1). The removal of perchlorate anion possibly proceeds by an anion-exchange process between chloride and perchlorate anions.

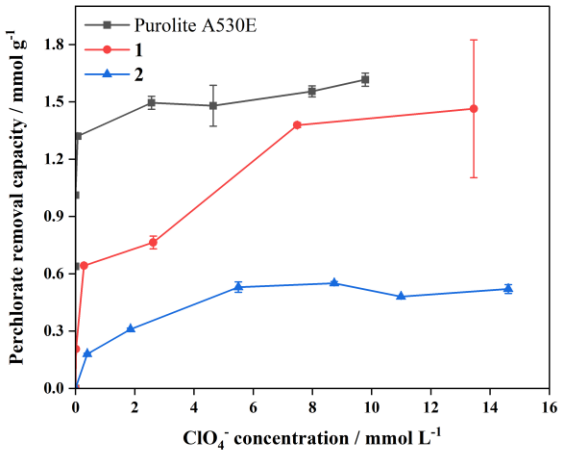

Figure 1. Perchlorate removal capacity of Purolite A530E, **1**, and **2** at 30 °C.

1) E. Sone, M. Sato, K. Yamanishi, C. Kamio, H. Takemoto, M. Kondo, *Dalton Trans.* **2016**, *45*, 894. 2) G. Ye, D. Zhang, X. Li, K. Leng, W. Zhang, J. Ma, Y. Sun, W. Xu, S. Ma, *ACS Appl. Mater. Interfaces* **2017**, *9*, 34937.

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Substituent introduction effect on CO_2 adsorption properties in three-dimensional SiF_6-bridged porous coordination polymers

([1]*Graduate School of Environmental Science, Hokkaido Univ.*, [2]*Faculty of Environmental Earth Science, Hokkaido Univ.*, [3]*Research Institute for Electronic Science, Hokkaido Univ.*) ○Zhongjie Gu,[1] Jia-bing Wu,[2,3] Xin Zheng,[2] Yuki Saito[2], Shin-ichiro Noro[1,2]

Keywords: Porous Coordination Polymer; SiF_6; CO_2 Adsorption Properties; Substituent Introduction Effect

In recent years, global warming caused by the emission of greenhouse CO_2 gas has become a widespread concern. Porous coordination polymers (PCPs) have recently attracted strong interest from researchers as adsorption-based CO_2 separation materials. [Cu(SiF_6)(4,4′-bipyridine)$_2$] (**1**) is a three-dimensional PCP that shows excellent CO_2 separation properties.[1,2] To investigate the substituent introduction effect on CO_2 adsorption properties in **1**, we synthesized the PCP derivatives with the substituents (F, CH_3, and NH_2) on the 4,4′-bipyridine ligand (Figure 1). The synthesized PCPs, [Cu(SiF_6)(L)$_2$] (L = 3-methyl-4,4′-bipyridine (**2**), 3-fluoro-4,4′-bipyridine (**3**) and 3-amino-4,4′-bipyridine (**4**)), had similar three-dimensional porous structures as **1** (Figure 2). CO_2 adsorption properties are discussed on the day.

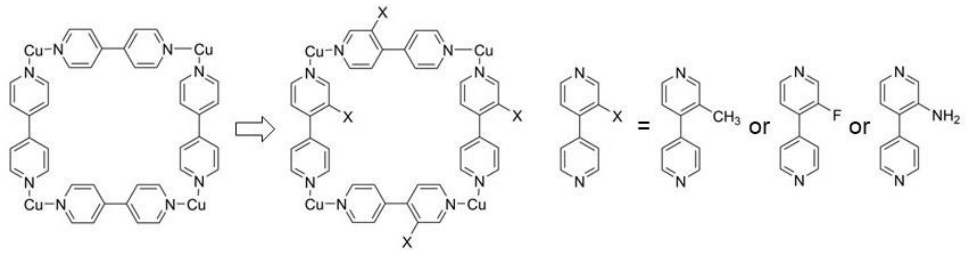

Figure 1

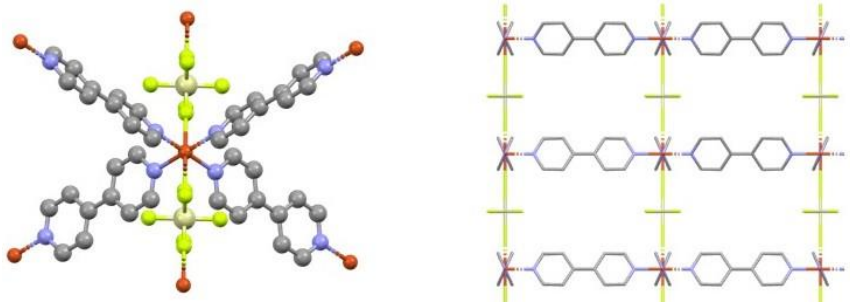

Figure 2

1) S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568. 2) P. Nugent, Y. Belmabkhout, S. Burd, A. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. Zaworotko, *Nature* **2013**, *495*, 80.

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小細孔径と耐酸性を併せ持つジルコニウム配位高分子を用いたアミノ酸の分離

（東理大[1]）○白石 恭子[1]・貞清 正彰[1]
Separation of Amino Acids by a Zirconium Metal–Organic Framework Having Small-Sized Pores and High Acid Tolerance ([1]*Tokyo University of Science*) ○Kyoko Shiraishi,[1] Masaaki Sadakiyo[1]

Meta–Organic Frameworks (MOFs) have been used for selective adsorption or separation materials due to their designable pores. On the other hand, separation of amino acids has been important for food or pharmaceutical industries. Although there are many reports of separation of neutral molecules by MOFs, the number of examples of amino acid separation with solid materials is still limited. Previously, we have succeeded in synthesizing a novel MOF, Zr-BPT ($[Zr_{12}O_8(OH)_8(HCOO)_{15}(BPT)_3]$, BPT^{3-} = [1,1'-biphenyl]-3,4',5-tricarboxylate), having small-sized pores (<5.6 Å) and high acid tolerance. In this study, we focused on Zr-BPT as the adsorbents for the amino acids and evaluated separation ability of Zr-BPT for various amino acids with different functional groups in aqueous solution by ^{1}H NMR. As the result, we found that Zr-BPT selectively adsorbs L-Phenylalanine that has an aryl group.
Keywords : Metal-Organic Framework; Amino Acid; Acid Separation

配位高分子または金属有機構造体(MOF)は結晶性の多孔性固体であり、その細孔を用いた選択的吸着能は盛んに研究されてきた。MOF を用いた中性分子の分離の報告例は多い一方で、酸性基を持つ分子の分離の報告例は未だ少ない。特に、アミノ酸の水溶性物質からの分離は重要となっているが、未だ固体の吸着剤を用いた効率的な回収技術は確立されていない。我々は最近、高い耐酸性と小細孔径を併せ持つジルコニウム配位高分子である Zr-BPT ($[Zr_{12}O_8(OH)_8(HCOO)_{15}(BPT)_3]$, BPT^{3-} = [1,1'-biphenyl]-3,4',5-tricarboxylate)の合成に成功している [1]。本研究では、小さな酸性分子の分離に適すると考えられる Zr-BPT に着目し、水溶液中での Zr-BPT のアミノ酸に対する選択的吸着能と分離能を明らかにすることを目的とした。溶液中において、異なる側鎖を持つ複数のアミノ酸の吸着実験を行い、^{1}H NMR により、その吸着特性と分離能を評価した。その結果、Zr-BPT が芳香族アミノ酸である L-フェニルアラニンを選択的に吸着し(図 1)、混合溶液中においても L-フェニルアラニンを分離可能であることを明らかにした。

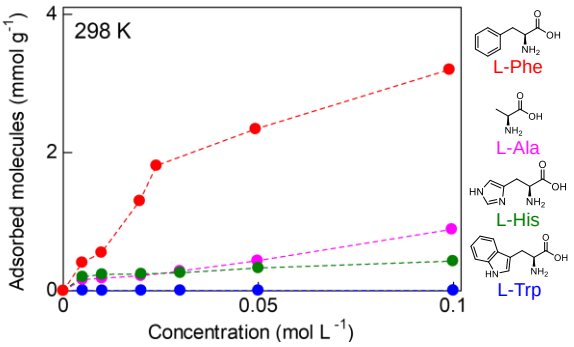

図 1. Zr-BPT のアミノ酸吸着等温線

1) K. Shiraishi, K. Otsubo, K. Kato, M. Sadakiyo, *Chem. Sci*. **2024**, in press

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新規ホスホラミド配位子の合成と金属有機構造体への応用

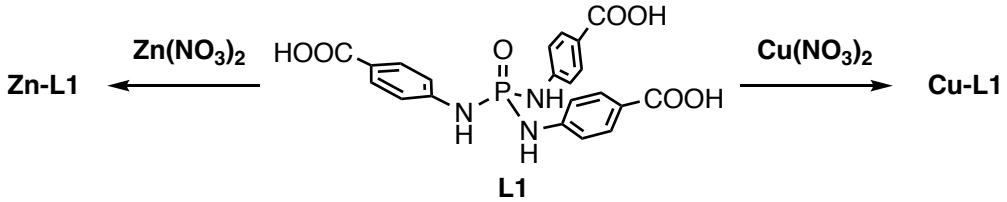
（立教大理[1]・日本曹達株式会社[2]）○小林　翔[1]・菅又　功[1]・天野倉 夏樹[1,2]・白井 昭宏[1,2]・箕浦 真生[1]

Synthesis of Novel Phosphoramide Ligands and Their Application in Metal-organic frameworks ([1]*Department of Chemistry, College of Science, Rikkyo University* [2]*Nippon Soda Co., LTD*) ○Sho Kobayashi,[1] Koh Sugamata,[1] Natsuki Amanokura,[1,2] Akihiro Shirai,[1,2] Mao Minoura[1]

Metal-organic frameworks (MOFs) are formed through the self-assembly of metal ions and organic ligands. Among them, triarylphosphine oxide-based MOFs showed high H_2 gas adsorption properties due to their interaction between H_2 molecules and P=O moieties. In this presentation, we report on the facile synthesis of novel organophosphoramide ligands and their application to MOFs. The structures and gas adsorption properties of the synthesized Zn- and Cu-MOFs will be discussed.

Keywords : Metal-organic Frameworks; Organophosphoramide Ligands; X-ray Crystallographic Analysis; Layered Structure; Gas Adsorption

金属イオンと有機配位子との自己集合によって形成される金属有機構造体(MOF)は分子内に多数の細孔を有することからガス分子の貯蔵・分離材料への応用が期待されている。MOF のガス貯蔵能向上のため、特定のガスと相互作用する原子や官能基の有機配位子への導入が行われている。例えば、トリアリールホスフィンオキシドを配位子とする MOF は、P=O 部位が水素分子と相互作用することで高い水素ガス吸着特性を発現することが報告されている[1,2)]。我々はより高いガス貯蔵能を有する MOF の合成を目的として、P=O 結合と芳香環を窒素で連結した新規ホスホラミド配位子の開発を行った。配位子中の窒素原子も水素や二酸化炭素の吸着サイトとして働くことが期待されている。新規ホスホラミド配位子と亜鉛および銅イオンとの反応により合成した MOF は、擬 3 次元構造を有することを明らかにした。それらの構造の詳細およびガス吸着特性について報告する。



1) X.-J. Li, F.-L. Jiang, M.-Y. Wu, L. Chen, J.-J. Qian, K. Zhou, D.-Q. Yuan, M.-C. Hong, *Inorg. Chem.,* **2014**, *53*, 1032-1038.

2) L. H. Song, G. Lee, J. H. Yoon, J. Jang, D. Choi, H. Yun, K. Kwon, H. Kim, C. S. Hong, Y. Kim, H. Han, K. S. Lim, W. R. Lee, *Chem. Eur. J.,* **2020**, *26*, 11767-11775.

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亜鉛を含むシアノ架橋配位高分子への水の吸脱着による可逆構造変化

（阪公大院工[1]・阪公大人工光合成セ[2]）○八田 浩紀[1]・中薗 孝志[2]・山田 裕介[1,2]

Reversible Structural Transformation of a Cyano-bridged Coordination Polymer with Zn^{2+} Ion Induced by Water Adsorption and Desorption ([1]*Graduate School of Engineering, Osaka Metropolitan University*, [2]*Research Center for Artificial Photosynthesis, Osaka Metropolitan University*) ○Hiroki Hatta,[1] Takashi Nakazono,[2] Yusuke Yamada[1,2]

Adsorption and desorption of small molecules onto and from porous coordination polymers sometimes induce their structural deformation. For example, the crystals of a cyano-bridged coordination polymer, $\{[Zn^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]\}_n$ (**Zn^{II}-Co^{III}**), have been reported to transform by heat treatment due to removal of coordinating water molecules from Zn^{II} ions.[1,2] However, the structural transformation by re-adsorption of water molecules to Zn^{II} ions has yet to be examined. In this study, the structural transformation of heat-treated **Zn^{II}-Co^{III}** was investigated by exposure to water. Powder X-ray diffraction (XRD) measurements confirmed the re-coordination of water molecules to Zn^{II} ions when heat-treated **Zn^{II}-Co^{III}** was immersed in water. In addition, immersion of **Zn^{II}-Co^{III}** without heat treatment in hexane or toluene resulted in the desorption of water molecules from Zn^{II} ions.

Keywords : Prussian blue analogue; Porous structure; Coordination structure

吸着剤として用いられる多孔性配位高分子の中には、種々のイオンや分子が吸着すると金属イオンまわりの配位構造が変化し、その骨格や細孔構造が大きく変化するものがある。プルシアンブルー類縁体である$\{[Zn^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]\}_n$ (**Zn^{II}-Co^{III}**) は加熱により水が除かれることで Zn^{II} に配位子した水分子が脱離し、配位構造が八面体型 (O_h) から四面体型 (T_d) へと変化することが報告されている[1,2]。しかしながら、加熱処理により生じた T_d 構造の Zn^{II} が再び O_h 構造に戻るのかについては、明らかにされていない。そこで本研究では、**Zn^{II}-Co^{III}** の加熱処理および溶媒吸着による Zn^{II} イオンまわりの配位構造変化の可逆性について検討した。

Zn^{II}-Co^{III} を 80℃に加熱する前後で粉末 X 線回折 (XRD) 測定を行ったところ、配位水が脱離することによる結晶構造変化が確認された (Fig. 1)。加熱後の **Zn^{II}-Co^{III}** を水に分散させ XRD 測定を行ったところ、加熱前と同じ回折パターンが得られたことから、水分子が Zn^{II} に再び配位したことが確認された。次に、非極性溶媒であるヘキサンまたはトルエン中に浸漬させ XRD 測定を行ったところ、加熱後と同じ回折パターンが現れ、Zn^{II} イオンから水分子が脱離することが確認された。

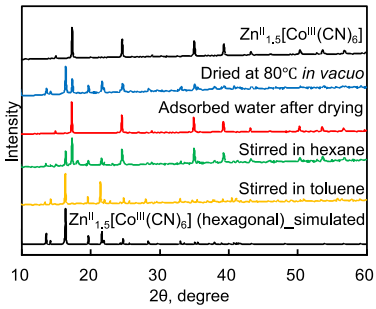

Fig.1 Powder X-ray diffraction patterns of $[Zn^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$, after drying at 80 ℃ *in vacuo*, water adsorption, stirring in hexane or toluene and simulated pattern.

1) J. R. Hernández et al., *J. Phys. Chem. Solids*, **2007**, *68*, 1630.
2) P. K. Thallapally et al., *Inorg. Chem.*, **2010**, *49*, 4909.

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1111(1111, Bldg. 11 [1F])

[E1111-3am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kazuhiko Semba, Tetsuya Satoh

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1111-3am-01]

A Strategy for Modulating the Lewis Acidity of Triarylboranes by Remote Back Strain

○Taichi Morishita[1], Mahiro Sakuraba[1], Taiki Hashimoto[1], Sensuke Ogoshi[1], Yoichi Hoshimoto[1,2] (1. Osaka University, 2. Center for Future Innovation)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1111-3am-02]

Mechanistic Study on Hydrogenation of *N*-Heteroaromatics Using H_2/CO/CO_2 Mixed Gas

○Taiki Hashimoto[1], Yu Harabuchi[4,5], Sensuke Ogoshi[1], Satoshi Maeda[3,4,5], Yoichi Hoshimoto[1,2] (1. Faculty of Engineering, Osaka University, 2. Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University, 3. Faculty of Science, Hokkaido University, 4. WPI-ICReDD, Hokkaido University, 5. JST-ERATO)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1111-3am-03]

Introduced Position Effect of Pyrenes affecting on the Lewis Acidity and Catalytic Activity of Cage-shaped Boron Complexes

Yuya Tsutsui[1], ○Yuta Uchiyama[1], Akihito Konishi[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
[E1111-3am-04]

Synthesis of Multi-substituted Allyl Boronates from Cyclic Allylborates and Allyl Halides

○Hiroki Murata[1], Go Yamagiwa[1], Kazuhiko Semba[1], Tetsuaki Fujihara[1] (1. Kyoto University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1111-3am-05]

Boron-catalyzed Michael Reaction between Carboxylic Acid Donors and α,β-Unsaturated Carboxylic Acid Acceptors

○Yukiho Yoshida[1], Yohei Shimizu[1,2], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1111-3am-06]

Lewis acidity-controlled aryl oxazaborolidinones for iterative Heck reactions

○Takaki Nojiri[1], Takashi Nishikata[1] (1. Yamaguchi University)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1111-3am-07]
Palladium-Catalyzed Direct Suzuki–Miyaura Cross-Coupling of Lewis Acidity-Diminished Organoboron Reagents with Weak Bases

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

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

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1111-3am-08]
Development of the methods for direct functionalization of anthracenes

○Haruki Katayama[1], Yoshinosuke Usuki[1], Tetsuya Satoh[1] (1. Osaka Metropolitan University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1111-3am-09]
Pd-catalyzed oxidative arylation of alkenes with aryltrimethylsilanes

○Tetsu Uemura[1], Miyu Takato[1], Shinya Tanaka[1], Shuichi Oi[1] (1. Tohoku University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1111-3am-10]
Palladium-catalyzed *anti*-Michael-type hydroalkoxylation

○Yuya Denda[1], Hirotugu Suzuki[1] (1. University of Fukui)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1111-3am-11]
Computational Analysis of Relative Stability of Cationic 1,10-Phenanthroline Alkylpalladium Complexes

○Kazuma Muto[1], Miho Hatanaka[1], Fumitoshi Kakiuchi[1], Takuya Kochi[1] (1. Keio University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1111-3am-12]
L-Region Selective Annulative π-Extension of Aromatic Compounds

○Kanami Nakata[1], Kou Kawahara[1], Wataru Matsuoka[1], Hideto Ito[1], Kenichiro Itami[1] (1. Nagoya Univ.)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1111-3am-13]
Catalytic Synthesis of Vinylic Isonitriles and Transformation into Bioactive Disubstituted Pyrroles

○Ryota Saeki[1], Asuka Hachiya[1], Taiga Yurino[2,3], Takeshi Ohkuma[2,3] (1. The Univ. of Hokkaido, 2. Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center)

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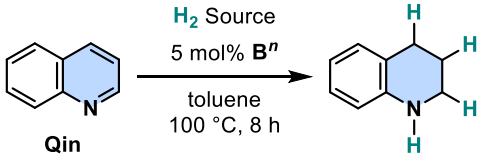
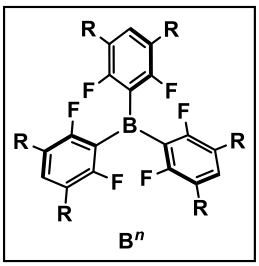
トリアリールホウ素における遠隔位置換基間の立体反発に着目したルイス酸性度制御法

（阪大院工[1]・阪大 CFi[2]）○森下 泰地[1]・櫻羽 真熙[1]・橋本 大輝[1]・生越 専介[1]・星本 陽一[1,2]
A Strategy for Modulating the Lewis Acidity of Triarylboranes by Remote Back Strain
([1]*Faculty of Engineering, Osaka University*, [2]*Center for Future Innovation (CFi), Faculty of Engineering, Osaka University*) ○Taichi Morishita,[1] Mahiro Sakuraba,[1] Taiki Hashimoto,[1] Sensuke Ogoshi,[1] Yoichi Hoshimoto[1,2]

Herein, we report the synthesis of B[2,6-F_2-3,5-$(TMS)_2$-C_6H]$_3$ (**B^1**) and B[2,6-F_2-3,5-$(allyl)_2$-C_6H]$_3$ (**B^2**) to assess the impact of remote back strain on Lewis acidity. Both the steric repulsion and noncovalent interactions generated between the *meta*-substituents of BAr_3 are essential for modulating remote back strain. Furthermore, **B^2**-catalyzed hydrogenation of quinoline using a 1:1:1 molar gaseous mixture of H_2, CO, and CO_2 was achieved.
Keywords : Triarylboranes; Crude H_2; Frustrated Lewis Pairs; Catalytic Hydrogenation; Noncovalent Interaction

一般的にトリアリールホウ素 (BAr_3) のルイス酸性度は、アリール基上の置換基を変更し、ホウ素中心の求電子性を制御する手法[1]や、ホウ素に対してオルト位の置換基を大きくし、ルイス塩基の配位を妨げる手法により制御される。[2] 当研究室では、BAr_3 のルイス酸性度を制御する手法として、ホウ素に対してメタ位の置換基間の分子内立体反発、すなわち remote back strain に注目した。本研究では、B(2,6-F_2-3,5-R_2-C_6H)$_3$ (**B^1**: R = TMS; **B^2**: R = Allyl) を新たに合成し、幾何学的、分光学的な観点から **B^1**–**B^3** (**B^3**: R = H) を比較することで BAr_3 のルイス酸性度に影響する因子を考察した。[3] 結果、メタ位の置換基間の分子内立体反発と非共有結合性相互作用が BAr_3 のルイス酸性度を調節する重要な因子であると見出した。次に、**B^1**–**B^3** を用いてキノリン (**Qin**) の触媒的水素化反応を検討した。H_2 加圧下において、**B^1** は既存の **B^3** より高い触媒活性を示し、**B^2** を用いた場合、最も効率よく反応が進行した。さらに、**B^2** を用いることで、粗水素条件下での **Qin** の水素化反応を世界で初めて達成した。





H_2 Source	B^1 (R = TMS)	B^2 (R = Allyl)	B^3 (R = H)
H_2 (10 atm)	42%	>99%	20%
H_2/CO/CO_2 (20 atm each)	–	>99%	–

1) J. L. Carden, A. Dasgupta, R. L. Melen, *Chem. Soc. Rev.* **2020**, *49*, 1706. 2) P. A. Chase, L. D. Henderson, W. E. Piers, M. Parvez, W. Clegg, M. R. J. Elsegood, *Organometallics* **2006**, *25*, 349. 3) M. Sakuraba, T. Morishita, T. Hashimoto, S. Ogoshi, Y. Hoshimoto, *Synlett* **2023**, *34*, 2187.

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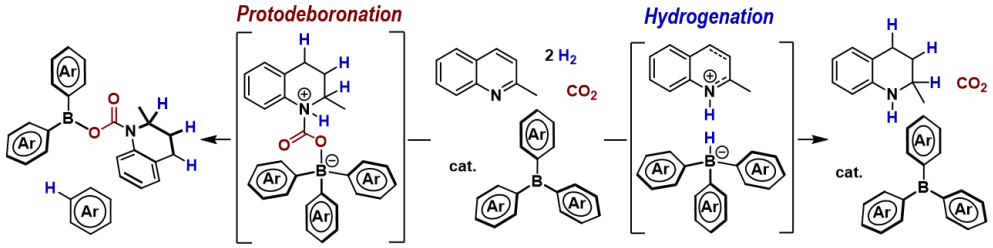
粗水素を用いた複素環化合物の水素化における反応機構

（阪大院工[1]・阪大 CFi[2]・北大院理[3]・北大 WPI-ICReDD[4]・JST-ERATO[5]）○橋本 大輝[1]・原渕 祐[4,5]・生越 専介[1]・前田 理[3,4,5]・星本 陽一[1,2]
Mechanistic Study on Hydrogenation of *N*-Heteroaromatics Using $H_2/CO/CO_2$ Mixed Gas ([1]*Faculty of Engineering, Osaka University,* [2]*Center for Future Innovation (CFi), Division of Applied Chemistry, Faculty of Engineering, Osaka University,* [3]*Faculty of Science, Hokkaido University,* [4]*WPI-ICReDD, Hokkaido University,* [5]*JST-ERATO*) Taiki Hashimoto,[1] Yu Harabuchi,[4,5] Sensuke Ogoshi,[1] Satoshi Maeda,[3,4,5] Yoichi Hoshimoto[1,2]

A frustrated Lewis pair (FLP) concept has represented a fundamental and emerging strategy to develop main-group catalysis, especially for catalytic hydrogenation. Nevertheless, their reaction mechanisms have largely remained under investigation, e.g., the detailed mechanism of the catalytic hydrogenation of *N*-heteroaromatics, while some mechanistic studies were reported. Herein, we report the details on the reaction mechanism for the FLP-mediated hydrogenation of 2-methylquinoline (**Qin**) based on the artificial force induced reaction (AFIR) method. Moreover, we also evaluate the influence of the contamination of CO and CO_2, which should shed light on the overall mechanistic picture of the triarylborane-catalyzed hydrogenation of **Qin** using a gaseous mixture of $H_2/CO/CO_2$.[3]
Keywords : Boranes; N-heteroaromatics; hydrogenation; Quantum chemical calculation; AFIR method

Frustrated Lewis pair (FLP) は、典型元素化学種を活用した触媒的分子変換反応を開発するための新たな戦略として利用されており、とりわけ触媒的水素化反応が数多く報告されてきた[1)]。しかしながら、その反応機構には未解明の部分が多く、特に含窒素芳香族化合物の触媒的水素化反応について機構研究を行った例は数例に限られる[2)]。我々は触媒量のトリアリールホウ素 (BAr_3) 存在下、$H_2/CO/CO_2$ 混合ガスをキノリン誘導体の水素化反応に直接利用できることを報告してきた[3)]。本研究では、夾雑ガス系における 2-メチルキノリン水素化の機構解明を目的とし、AFIR 法を活用した反応機構研究に取り組んだ。その結果、当該水素化反応機構および BAr_3 触媒のプロトデボロネーションによる分解機構を明らかにした。



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カゴ型ホウ素錯体の励起状態におけるルイス酸性および触媒能に対するピレンの導入位置効果

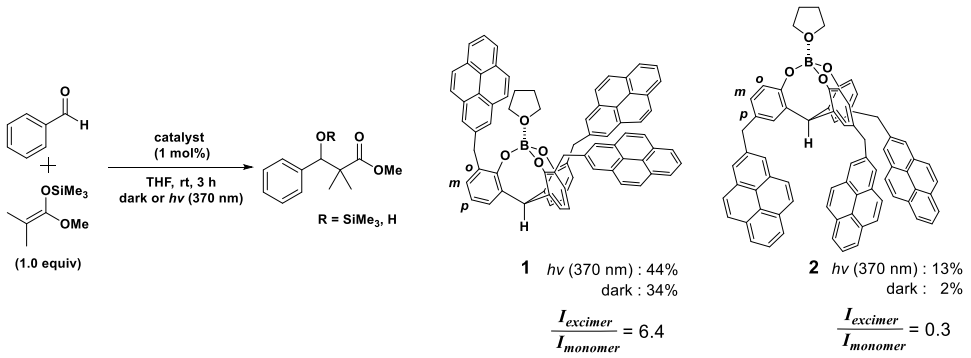
（阪大院工 [1]）筒井 裕哉 [1]・○内山 雄太 [1]・小西 彬仁 [1]・安田 誠 [1]

Introduced Position Effect of Pyrenes affecting on the Lewis Acidity and Catalytic Activity of Cage-shaped Boron Complexes ([1]*Graduate School of Engineering, Osaka University*) Yuya Tsutsui,[1] ○Yuta Uchiyama,[1] Akihito Konishi,[1] Makoto Yasuda[1]

Lewis acid is an important reagent in organic synthesis. Recently, we found that the formation of intramolecular excimer in cage-shaped boron complex **1** with pyrenes under light irradiation enhanced the Lewis acidity and promoted the Mannich-type reaction. To comfirm the role of the excimer in activating the reaction, we designed a complex **2** in which pyrenes are substituted at the *para*-positions instead of the *ortho*-positions of the oxygen atoms. The complex **2** showed a lower efficiency of the excimer formation and catalytic turnover than the complex **1** under light irradiation. The observation indicates that the intramolecular excimer changes the structure of the complex and contributes significantly to the Lewis acidity and catalytic ability of the complexes.

Keywords : Lewis acid; Boron; Photoactivation; Pyrene; Excimer

有機合成においてルイス酸は重要な試剤であり、最近では光によって活性化されるルイス酸触媒が求められているが、その例は非常に少ない。当研究室ではピレンを導入したカゴ型ホウ素錯体 **1** が、光照射下での分子内エキシマー形成を駆動力としてルイス酸性が向上し、マンニッヒ型反応を促進することを見出した [1)]。今回、光励起相互作用の変化が錯体の物性や反応性に与える効果について調べるため、ピレンの導入位置を酸素原子のオルト位からパラ位に変更した錯体 **2** を設計した。錯体 **2** では錯体 **1** に比べエキシマー形成能が低く、光照射下での活性化されにくい結果となった。これにより発色団のエキシマー形成が錯体の構造を変化させ、錯体のルイス酸性と触媒能に大きく寄与していることが分かった。また、その他の錯体のデザインの検討も報告する。



1) Y. Tsutsui, D. Tanaka, Y. Manabe, Y. Ikinaga, K. Yano, K. Fukase, A. Konishi, M. Yasuda, *Chem. Eur. J.* **2022**, *28*, e202202284.

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・環状アリルボレートのアリル化反応による多置換アリルボロン酸エステルの合成

（京大院工）○村田 紘基・山極 剛・仙波 一彦・藤原 哲晶
Synthesis of Multi-substituted Allyl Boronates from Cyclic Allylborates and Allyl Halides (*Graduate School of Engineering, Kyoto University*) ○ Hiroki Murata, Go Yamagiwa, Kazuhiko Semba, Tetsuaki Fujihara

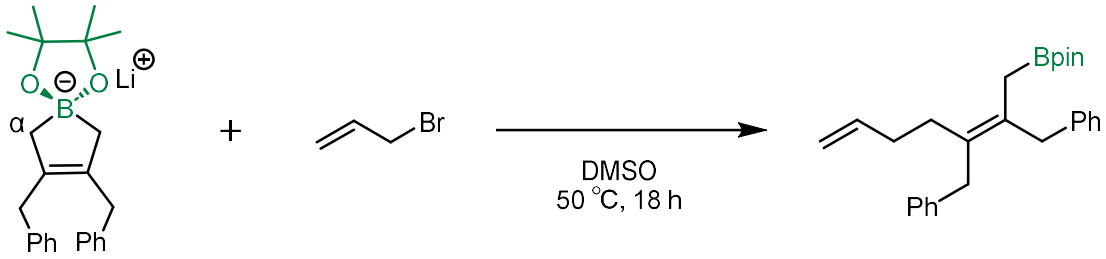
Allyl boronates are useful intermediates in organic synthesis due to their high applicability to construct carbon–carbon bonds through cross-coupling reactions. We previously revealed that cyclic allylborates, which were synthesized from 1,3-dienes and a diboron in the presence of copper catalysts, reacted with carbonyl compounds such as aldehydes and esters[1]. In this study, we found that the cyclic allylborates could react with allyl bromides to afforded multi-substituted allyl boronates (Scheme 1).

Keywords : Allyl Boronates, Allyl Halides, Borates

アリルボロン酸エステルはクロスカップリング反応などの炭素―炭素結合形成反応に適用できるため、有用な合成中間体である。我々は、銅触媒を用いた 1,3-ジエンとジボロンとの反応により得られる環状アリルボレートがアルデヒドやエステルといったカルボニル化合物と反応することを見出した[1]。本研究では、環状アリルボレートとハロゲン化アリルを反応させたところ、多置換アリルボロン酸エステルが得られることを見出した。

環状アリルボレート **1** と臭化アリル (**2**) を DMSO 溶媒中 50 ℃で反応させたところ、**1** のα位でのアリル化反応が位置選択的に進行し、三置換アリルボロン酸エステル **3** が良好な収率で得られた (スキーム 1)。

Scheme 1.



1 **2** **3**

GC Yield: 77%

1) S. Sakuragi, T. Akiba, T. Tanahashi, T. Fujihara, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202226.

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ホウ素触媒によるカルボン酸ドナーとα,β-不飽和カルボン酸アクセプターのマイケル反応

（北大院理[1]・WPI-ICReDD[2]）○吉田　薫穂[1]・清水　洋平[1,2]・澤村　正也[1,2]
Boron-catalyzed Michael Reaction between Carboxylic Acid Donors and α,β-Unsaturated Carboxylic Acid Acceptors ([1]*Department of Chemistry, Faculty of Science, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*,) ○ Yukiho Yoshida,[1] Yohei Shimizu,[1,2] Masaya Sawamura[1,2]

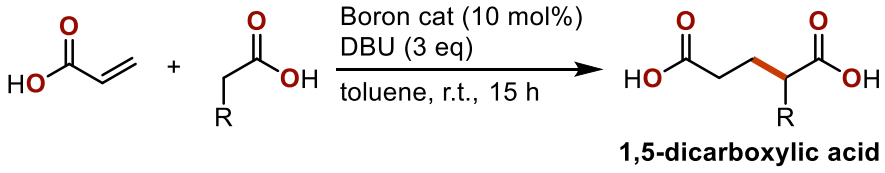
Catalytic Michael addition reaction is a powerful C-C bond forming reaction. Naturally abundant and synthetically versatile carboxylic acids, however, have been rarely applied in Michael addition reaction either as donors or acceptors. In this context, we undertook the development of catalytic Michael addition reaction using carboxylic acids as both donors and acceptors by applying boron-catalyzed carboxylic acid enolate formation.[1]

A boron catalyst smoothly promoted Michael addition of carboxylic acid donors and α,β-unsaturated carboxylic acid acceptors in the presence of DBU as a base, giving 1,5-dicarboxylic acids. No product was obtained without the boron catalyst. In addition, Michael addition reaction barely proceeded when using the corresponding methyl esters as the donor or the acceptor. These results indicated that both the donor and the acceptor were activated by the boron catalyst to facilitate the reaction.

Keywords : boron catalysis; Michael addition; carboxylic acid; dual activation; dicarboxylic acid

触媒的マイケル付加反応は、強力な炭素—炭素結合形成反応である。しかし、酸性度の高い CO_2H 基を有するカルボン酸は、天然に豊富に存在し広く利用されるビルディングブロックであるにも関わらず、その特有の反応性からマイケルドナーとしてもアクセプターとしても適用が進んでいない。今回我々は、ホウ素触媒による温和なエノラート生成法[1]を用いることで、カルボン酸をドナーかつアクセプターとしたマイケル付加反応を開発した。

ホウ素触媒の存在下、塩基として DBU を用いることでカルボン酸を基質としたマイケル付加反応が円滑に進行し、1,5-ジカルボン酸が得られた。ホウ素触媒の非存在下では全く生成物が得られず、ドナーまたはアクセプターとしてメチルエステルを用いると収率が大幅に低下した。これらの結果から、ホウ素触媒がドナーとアクセプター双方の活性化を担っていると示唆された。



[1] Shimizu, Y.; Kanai, M. *Chem. Rec.* **2023**, *23*, e202200273.

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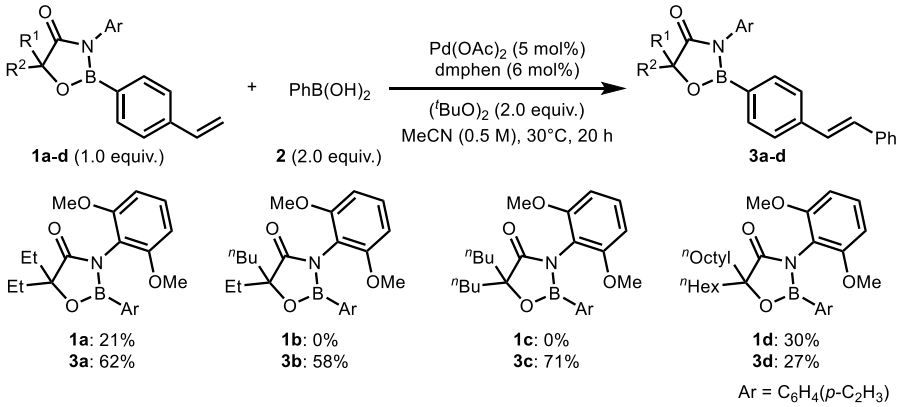
ホウ素ルイス酸性を制御した有機ホウ素試薬の Heck 反応への応用

（山大院工 [1]）○野尻 貴樹 [1]・西形孝司 [1]
Lewis acidity-controlled aryl oxazaborolidinones for iterative Heck reactions ([1] *Graduate School of Sciences and Technology, Yamaguchi University*) ○ Takaki Nojiri,[1] Takashi Nishikata,[1]

Control of boron Lewis acidity is important for the iterative coupling of organoboron with aryl halides to olefins. To date, the reactivity of organoboron has been achieved by electronic control, and control based on steric effects is not known. In this study, we found that oxazaborolidinones, which possess both steric effects derived from tertiary α-hydroxyamides and electronic effects derived from amide functional groups, can be used in iterative Heck reactions.
Keywords : cyclic borone reagents, Heck reaction, iterative coupling

ハロゲン化アリールを有する有機ホウ素とオレフィンの反復的カップリングには、ホウ素ルイス酸性の制御が重要である。これまでの有機ホウ素の反応性は電子的な制御で達成されており、立体効果に基づいた制御は知られていない。今回我々は、第三級α-ヒドロキシアミド由来の立体的な効果かつアミド官能基由来の電子的な効果を併せ持つオキサザボロリジノンを使用し、反復型 Heck 反応に応用できることを見出した。

オキサザボロリジノン **1a** とフェニルボロン酸 **2** をパラジウム触媒存在下、酸化条件で Heck 反応を試みた結果、C-B 結合部位を損なうことなく目的生成物を 62%の収率で得た。またアルキル鎖の炭素数を増加させたオキサザボロリジノン **1c** を使用して検討を行った結果、原料がすべて消費され、反応効率の改善が見られた。



1) (a) Gillis, E. P.; Burke, M. B. *J. Am. Chem. Soc.* **2007**, 129, 6716-6717. (b) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc.* **2007**, *129*, 758−759. (c) Ihara, H.; Koyanagi, M.; Suginome, M. *Org. Lett.* **2011**, *13*, 2662−2665. (d) Molander, G. A.; Ellis, N. M. *Acc. Chem. Res.* **2007**, *40*, 275−286.

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パラジウム触媒によるルイス酸性抑制有機ホウ素反応剤の弱塩基直接鈴木―宮浦クロスカップリング反応

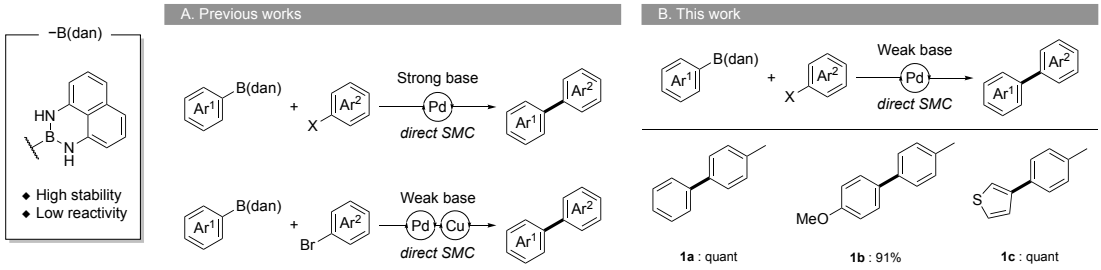
（広島大院先進理工）○友田 和希・中本 真晃・対馬 拓海・吉田 拡人

Palladium-Catalyzed Direct Suzuki–Miyaura Cross-Coupling of Lewis Acidity-Diminished Organoboron Reagents with Weak Bases (*Hiroshima University*) ○Kazuki Tomota, Masaaki Nakamoto, Takumi Tsushima, Hiroto Yoshida

Some boronic acids [−B(OH)$_2$] and their pinacol esters [−B(pin)] commonly used in Suzuki−Miyaura cross-coupling (SMC) are unstable due to the Lewis acidity, making their use in the reaction extremely difficult. The introduction of a substituent that diminishes Lewis acidity is effective for the stabilization of reagents, albeit reducing reactivity, and thus solving this dilemma would be the only remaining challenge in SMC. Actually, extremely stable Ar–B(dan) compounds, whose Lewis acidity is strongly diminished, have previously been believed to be inactive toward SMC. We have recently achieved the direct SMC of Ar–B(dan) using a strong base (*t*-BuOK)[1] or a palladium/copper cocatalyst[2] and disclose herein that Ar–B(dan) undergo the reaction under weak base conditions only with a palladium catalyst.

Keywords : Lewis acidity-diminished organoboron reagents; weak bases; direct Suzuki–Miyaura cross-coupling

鈴木−宮浦クロスカップリング（SMC）に用いられるボロン酸［−B(OH)$_2$］やピナコールエステル［−B(pin)］の中には，そのルイス酸性ゆえに不安定で，反応利用が未だ至難なものも存在する．反応剤の安定化には，ルイス酸性を抑制する置換基の導入が有効であるが，反応性低下と背中合わせであり，このジレンマの解決が SMC に唯一残された課題といってもよい．実際，1,8-ジアミノナフタレン置換によりホウ素部位のルイス酸性が強力に抑制された Ar–B(dan)化合物は極めて安定な一方，SMC 不活性とされてきた．我々はこれまで，強塩基（*t*-BuOK）[1]や，パラジウム／銅協働触媒 [2]を用いることで，Ar–B(dan)の直接 SMC を達成してきた．今回，弱塩基下，パラジウム触媒のみで Ar–B(dan)の直接 SMC が進行することを明らかにした．



1) (a) H. Yoshida, M. Seki, H. Andoh, T. Tsuchimoto, et al. *ACS. Catal.* **2020**, *10*, 346; (b) Y. Mutoh, K. Yamamoto, S. Saito, *ACS. Catal.* **2020**, *10*, 352; (c) K. Tomota, H. Yoshida, et al. *Adv. Synth. Catal.* **2023**, *365*, 682.
2) K. Tomota, H. Yoshida, et al. *Chem Rxiv.* **2023**, DOI: 10.26434/chemrxiv-2023-hgw0g.

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アントラセンへの直接置換基導入法の開発

（阪公立大院理） ○片山温貴・臼杵 克之助・佐藤 哲也

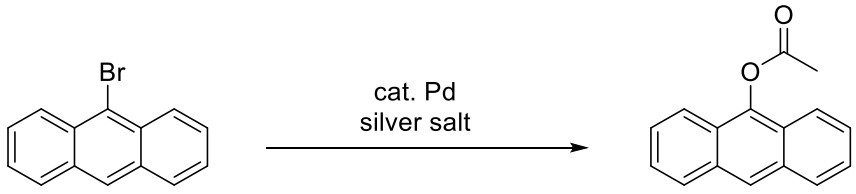
Development of the Methods for Direct Functionalization of Anthracenes (*Graduate School of Science, Osaka Metropolitan University*) ○ Haruki Katayama, Yoshinosuke Usuki, Tetsuya Satoh

Transition-metal-catalyzed C–H functionalization reactions have been recognized as atom and step-economical tools in organic synthesis field. In particular, the reactions utilizing a directing group lead to regioselective functionalization at neighboring positions. Although direct functionalization methods on benzene and naphthalene rings have been developed, those for anthracene have been less explored. Our group recently reported that 9-anthracenecarboxylic acids undergo cyclization through carboxyl-directed *peri* C–H bond cleavage in the presence of a rhodium catalyst and a silver salt oxidant to produce fused lactone derivatives. During our further studies on anthracene functionalization, we succeeded in finding that 9-bromoanthracene reacts with acetic acid under palladium catalysis to give 9-acetoxyanthracene. Related anthracene functionalization reactions will also be presented.

Keywords: palladium; anthracene; acetoxylation; silver salt; C-O coupling

遷移金属触媒を用いる C–H 誘導体化は、アトムおよびステップエコノミーの点で優れた合成手法である。特に配向基を利用すると、その近傍での位置選択的置換基導入が可能となり、精密合成にも用いられる。ベンゼンやナフタレン環上への直接置換基導入法が開発され、発展する一方で、これらの手法がアントラセン環へ適用された例は非常に限られている [1]。我々のグループでは最近、ロジウム触媒存在下、銀塩を酸化剤として用いる条件で 9-アントラセンカルボン酸を反応させると、カルボキシ基を配向基としてペリ位の C–H 結合が切断され、縮合ラクトン環が形成されることを報告している [2]。

アントラセン環への置換基導入について検討を続ける中で今回、パラジウム触媒ならびに銀塩を用いる条件で 9-ブロモアントラセンを酢酸とともに反応させると、9-アセトキシアントラセンが得られることを見出した。関連するアントラセン類の誘導体化についても検討を行ったので報告する。



1) For example, see: J. Karthikeyan, N. Yoshikai, *Org. Lett.* **2014**, *16*, 4224-4227.
2) A. Nishida, Y. Inai, Y. Usuki, T. Satoh, *Asian J. Org. Chem.* **2023**, *12*, e2023001.

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Pd 触媒を用いたアリールトリメチルシランによるアルケンの酸化的アリール化

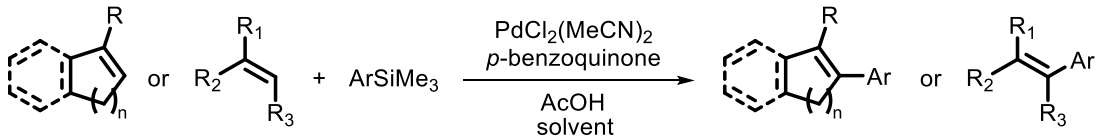
（東北大院工 [1]）○植村哲 [1]・高藤実結 [1]・田中信也 [1]・大井秀一 [1]
Pd-catalyzed oxidative arylation of alkenes with aryltrimethylsilanes ([1]*Graduate School of Engineering, Tohoku University*) ○Tetsu Uemura,[1] Miyu Takato,[1] Shinya Tanaka,[1] Shuichi Oi[1]

The oxidative Mizoroki-Heck reaction is a potent C–C bond formation reaction to construct arene–alkene skeltons which are often found in pharmaceuticals and functional materials[1)]. The use of aryl trialkylsilanes is very limited because of their low activity[2)], and the reaction with alkenes has not been achieved. We previously reported oxidative arylation reactions of aromatic hydrocarbons or benzothiophenes with aryltrimethylsilanes[3,4)]. In this study, we investigated the oxidative coupling reaction of alkenes with aryltrimethylsilanes.

The reaction of 3-phenyl-*1H*-indene with phenyltrimethylsilane in the presence of *p*-benzoquinone and acetic acid in dichloromethane at 40 °C using $PdCl_2(MeCN)_2$ as a catalyst gave the phenylated product in 89%. Moreover, when cyclohexene was used as a substrate, the phenylation proceeded at a vinyl position selectively, which is not consistent with the conventional oxidative Mizoroki-Heck reaction.
Keywords : Alkene; Palladium; Arylation

酸化的溝呂木-Heck 反応は C–C 結合形成に有効な反応であり，医薬品や機能性材料に見られるアレーン–アルケン結合を形成できる [1)]．アリールトリアルキルシランは活性が低いことから触媒反応に用いた例は少なく [2)]，またアルケンとの反応にはまだ適用されていない．当研究室ではこれまで，芳香族炭化水素やベンゾチオフェンのアリールトリメチルシランによる酸化的アリール化反応を見出している [3,4)]．本研究では，アリールトリメチルシランによるアルケンの酸化的カップリング反応の開発に取り組んだ．

$PdCl_2(MeCN)_2$ を触媒とし，*p*-ベンゾキノンおよび酢酸存在下，3-フェニル-*1H*-インデンとフェニルトリメチルシランをジクロロメタン中で反応させると，対応するフェニル化体が 89%で得られた．また，本反応でシクロヘキセンを基質とした際には，従来の酸化的溝呂木-Heck 反応の傾向とは異なり，ビニル位選択的にフェニル化が進行した．



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4) K. Funaki, T. Sato, S. Oi, *Org. Lett.* **2012**, *14*, 6186–6189.

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パラジウム触媒による *anti*-Michael 型ヒドロアルコキシ化反応

（福井大工）○伝田 裕也・鈴木 弘嗣

Palladium-Catalyzed *anti*-Michael-type Hydroalkoxylation

（*School of Engineering, University of Fukui*）○Yuya Denda, Hirotsugu Suzuki

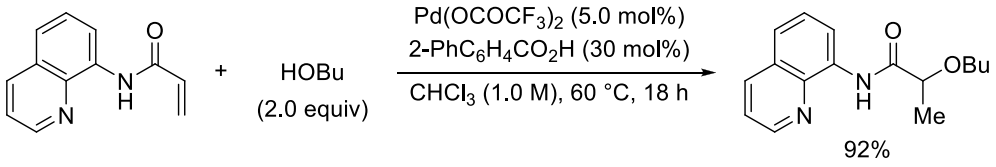
The *anti*-Michael type addition reaction represents the α-addition of nucleophiles to α,β-unsaturated carbonyl compounds, featuring the direct synthesis of α-substituted carbonyl compounds in a single step with a high atom economy. Previous reports on the *anti*-Michael-type addition reactions suffer from the limitation of substrate structures. Herein, we report a novel *anti*-Michael-type α-alkoxylation of simple acrylamides bearing no substituent on the β-position. Forming a five-membered palladacycle is crucial for controlling the regioselectivity beyond the electronic bias of the alkene moiety. This process represents the direct synthesis of α-alkoxypropionamides in atom- and step-economical manners.

N-(quinolin-8-yl)acrylamide reacted with 1-butanol in the presence of $Pd(OCOCF_3)_2$ at 60 °C for 18 h, delivering the α-alkoxypropionamides in 92% yield. Notably, this process did not undergo an undesired β-hydrogen elimination.

Keywords : Palladium-catalysts; Hydroalkoxylation; Directing group

anti-Michael 型反応とは、α,β-不飽和カルボニル化合物への求核剤の α 位付加をさし、医薬品に広くみられる α-置換カルボニル化合物を一段階かつ高原子効率で与える。しかし従来の *anti*-Michael 型反応は、特殊な構造をもつ α,β-不飽和カルボニル化合物により位置選択性を制御する基質依存的な方法であった [1]。そこで演者らは α,β-不飽和カルボニル化合物の β 位に置換基を必要としない単純なアルケンへの *anti*-Michael 型反応の開発を目指した。本研究では求核付加後に生じる五員環パラダサイクルによる反応中間体の安定化効果に着目し、単純なアクリルアミドに対する *anti*-Michael 型ヒドロアルコキシ型反応を達成した。これにより基質依存性の問題を解決し、かつ高原子効率で α-アルコキシプロピオンアミドを合成できるようになった。

8-アミノキノリンを配向基にもつアクリルアミドと 1-ブタノールを、パラジウム触媒の存在下で、クロロホルム中、60 °C で 18 時間加熱することで、α-ヒドロキシプロピオンアミドを 92%収率で得た。またこの反応では、副反応である β-水素脱離の進行は確認されていない。



1) (a) Ferreira, M.; Sá, M, M. *Adv. Synth. Catal.* **2015**, *357*, 829–833; (b) Ballini, R.; Bazán, N, A. Bosica, G. Palmieri, A. *Tetrahedron Lett.* **2008**, *49*, 3865–3867.

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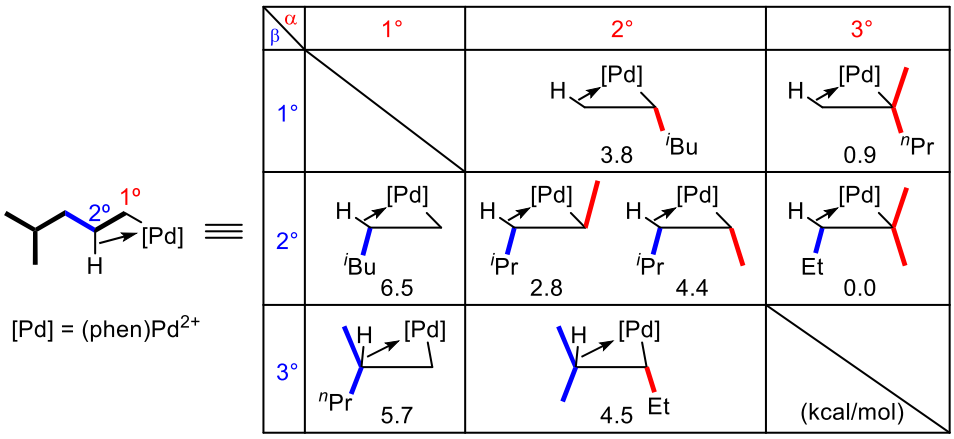
カチオン性 1,10-フェナントロリンアルキルパラジウム錯体の安定性の計算化学的解析

（慶大理工）○武藤 一馬・畑中 美穂・垣内 史敏・河内 卓彌
Computational Analysis of Relative Stability of Cationic 1,10-Phenanthroline Alkylpalladium Complexes (*Faculty of Science and Technology, Keio University*) ○Kazuma Muto, Miho Hatanaka, Fumitoshi Kakiuchi, Takuya Kochi

Our group has been studying catalytic reactions proceeding via chain walking of 1,10-phenanthroline palladium catalysts. While stability of cationic alkylpalladium complexes as intermediate of chain walking process had been studied previously,[1,2] 1,10-phenanthroline palladium complex had not been studied. Here we report computational analyses of the relative stability of 1,10-phenanthroline palladium complexes bearing a 5-methylhexyl group and its isomers possibly formed via chain walking. As a result, it was suggested that the complexes are relatively more stable, when the α-carbon and the agostic β-carbon of the alkyl group are more substituted.
Keywords : DFT Calculation; Palladium Complex; Alkyl Complex; β-Agostic Interaction

当研究室では 1,10-フェナントロリンパラジウム触媒によるチェーンウォーキングを含む反応の研究を行っている。チェーンウォーキング過程における中間体であるカチオン性アルキルパラジウム種の安定性について種々の錯体で研究されているが [1,2]、フェナントロリンパラジウム錯体については検討されていなかった。そこで今回我々は、パラジウム上に 5-メチルヘキシル基を有する錯体とそのチェーンウォーキングにより生成しうる異性体の安定性を DFT 計算により比較した。α位炭素、ならびにアゴスティック相互作用をしているβ炭素における級数が異なる錯体を比較すると、各炭素がより多置換であるほど安定性が高い傾向がみられることが分かった。



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2) Harvey, J. N. *Organometallics* **2001**, *20*, 4887-4895.

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芳香環の *L* 領域選択的縮環 π 拡張反応

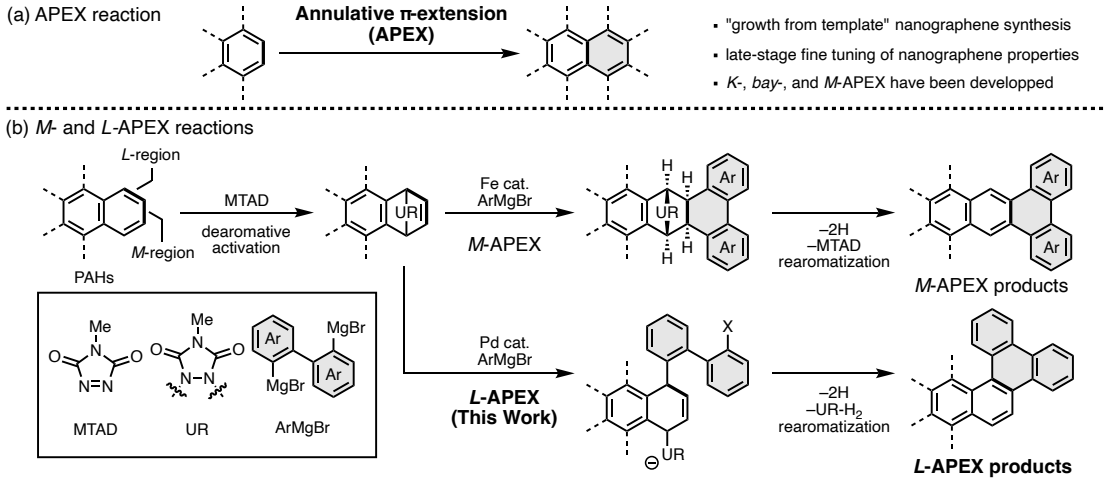
(名大院理[1]・名大 ITbM[2]) ○中田 奏未[1]・川原 巧[1]・松岡 和[1]・伊藤 英人[1]・伊丹 健一郎[1,2]

L-Region Selective Annulative π-Extension of Aromatic Compounds ([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules, Nagoya University*) ○Kanami Nakata,[1] Kou P. Kawahara,[1] Wataru Matsuoka,[1] Hideto Ito,[1] Kenichiro Itami[1,2]

Nanographenes and polycyclic aromatic hydrocarbons (PAHs) have attractive photophysical and electronic properties and are expected to be applied to organic electronic materials. Previously, we have developed annulative π-extension (APEX) reactions for more efficient synthesis of nanographenes. In addition to APEX reactions of PAHs in a site selective fashion at *K*- and *bay*-regions, we have recently achieved formal *M*-region-selective APEX reaction by dearomative activation of PAHs using *N*-methyltriazolinedione (MTAD), followed by arylation using iron catalysts and Grignard reagents, and rearomatization.[1] Herein, we have developed unexplored *L*-region-selective APEX reaction for the first time by further developing this dearomative APEX reaction.

Keywords : Dearomatization; Polycyclic aromatic hydrocarbon; Annulative π-extension (APEX); Nanographene; Allylic substitution

ナノグラフェンや多環芳香族炭化水素 (PAHs) は、魅力的な電子的・光学的特性から、有機電子材料への応用が期待されている。このような背景のもと、当研究室ではナノグラフェンのより効率的な合成を目指し、PAH に対する縮環 π 拡張 (APEX) 反応が開発されてきた。これまでに開発された *bay* 領域、*K* 領域選択的 APEX 反応のほかに、我々は最近、*N*-methyltriazolinedione (MTAD) を用いた PAH の脱芳香族化、鉄触媒と Grignard 反応剤によるアリール化、再芳香族化を行うことで、形式的な *M* 領域選択的 APEX 反応を実現した[1]。本研究では、発展途上である脱芳香族的 APEX 反応をさらに発展させることで、これまで達成できなかった *L* 領域選択的 APEX 反応の開発に成功した。発表ではその詳細について報告する。



[1] (a) W. Matsuoka, H. Ito, D. Sarlah, K. Itami, *Nature Commun.,* **2021**,*12,* 4940. (b) W. Matsuoka, K. P. Kawahara, H. Ito, D. Sarlah, K. Itami, *J. Am. Chem. Soc.* **2023***, 145,* 658.

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ビニルイソニトリルの触媒的合成法と生理活性二置換ピロールへの変換

（北大院総化[1]・北大院工[2]・フロンティア化学教育研究センター[3]）○佐伯 瞭太[1]・八谷 明日香[1]・百合野 大雅[2,3]・大熊 毅[2,3]
Catalytic Synthesis of Vinylic Isonitriles and Transformation into Bioactive Disubstituted Pyrroles ([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University,* [2] *Division of Applied Chemistry and Frontier Chemistry Center, Faculty of Engineering, Hokkaido University*) ○Ryota Saeki,[1] Asuka Hachiya,[1] Taiga Yurino,[2] Takeshi Ohkuma[2]

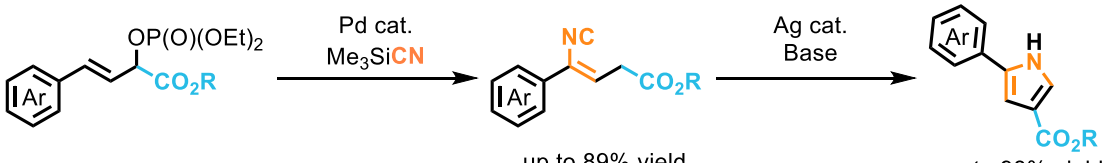
Vinylic isonitriles are unique and attractive compounds, because a transformable alkene moiety is directly connected with the isocyano group, and these two functional groups can react either individually or cooperatively. However, current synthetic procedures of vinylic isonitriles are limited.[1–3] Direct introduction of isocyano group on the alkenyl moiety is a highly desirable synthetic methodology for the preparation of this class of compounds.[4]

Herein, we succeeded in the preparation of vinylic isonitriles **2** by kinetic γ-selective substitution of isocyano group followed by thermodynamic olefin isomerization using an allylic phosphate **1** bearing an electron-withdrawing ester moiety at the α-position of the leaving phosphate group. Efficient conversion to 2,4-disubstituted pyrroles **3** using vinylic isonitrile **2** was also achieved. Formal synthesis of vonoprazan was investigated.

Keywords : Vinylic isocyanation; Pd catalysis, Pyrrole formation; Vonoprazan

ビニルイソニトリルはオレフィンとイソシアノ基が直結した二官能性化合物であり、双方を活かした多様な変換反応が期待される。このような有用性にも関わらず、その合成法は、特異な含窒素化合物からビニルイソニトリルへの変換反応、イソシアノ基を有する化合物上にオレフィン部位を構築する方法等に限られており、汎用性に乏しかった[1–3]。一方、当研究室ではアリルリン酸エステルを求電子剤とする触媒的アリル位イソシアノ化反応の開発に成功している[4]。

本研究では、脱離基であるリン酸エステルのα位に電子求引性のエステル基を導入することで、速度論的なγ位選択的イソシアノ化反応と続く熱力学的なオレフィンの異性化により、ビニルイソニトリルを良好な収率で合成することに成功した。得られたビニルイソニトリルに対しAg触媒存在下、適切な塩基を作用させることで分子内環化反応が円滑に進行し、2,4-二置換ピロールへと変換できることも見出した。



1) a) A. M. van Leusen *et al. Recl. Trav. Chim. Pays-Bas.* **1991**, *110*, 402. b) I. Ichimoto et al. *Biosci. Biotech. Biochem.* **1993**, *57*, 659. c) F. F. Fleming *et al. Angew. Chem. Int. Ed.* **2016**, *55*, 14770. 2) M. C. Pirrung *et al. J. Am. Chem. Soc.* **2006**, *128*, 11772. 3) J. Zhu *et al. Org. Lett.* **2016**, *18*, 1622. 4) T. Yurino, R. Tani, T. Ohkuma *ACS Catal.* **2019**, *9*, 4434.

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1112(1112, Bldg. 11 [1F])

[E1112-3am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Yusuke Yoshigoe, Yuya Tanaka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1112-3am-01]

A Platinum-linked Polyaromatic Tube with Postsynthetic Modification and Molecular Binding Abilities

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

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1112-3am-02]

Photoinduced Platinum-Catalyzed Umpolung Allylation of α-Diketones

○Junpei Shimosato[1], Yusuke Masuda[1,2], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1112-3am-03]

Synthesis of Cyclic Platinum(II)-Acetylide Complex via Transmetallation

○Ryusei Kaneko[1], Shinichi Saito[1], Yuusuke Yoshigoe[1] (1. Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1112-3am-04]

Pt-catalyzed rearrangement reactions of *ortho*-alkynylbenzenesulfinates via consecutive S-O bond cleavage

○Keiryo Kubota[1], Masahiro Terada[1], Itaru Nakamura[1] (1. Graduate School of Science, Tohoku University.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1112-3am-05]

Lewis acid mediated amide bond cleavage of polyamides bearing directing groups

○Ryota Shiraki[1], Yu-I Hsu[1], Hiroshi Uyama[1], Mamoru Tobisu[1,2] (1. Osaka Univ., 2. ICS-OTRI)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1112-3am-06]

Copper-catalyzed cross-coupling of thiols with alcohols

○Nobukazu Taniguchi[1] (1. Osaka Metropolitan University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1112-3am-07]

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Asymmetric Cu-Catalyzed Electrophilic Fluorination in Water Using Water-Soluble Helical Polymer Ligands

○Takuo Tamura[1], Takeshi Yamamoto[1], Michinori Suginome[1] (1. Kyoto University)

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

Break

Japanese

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

[E1112-3am-08]

Copper-Catalyzed Asymmetric Coupling Utilizing Helical Macromolecular Bipyridine Ligand Based on Screw-Sense Induction by Chiral Additives

○Hiroki Shimura[1], Yukako Yoshinaga[1], Michinori Suginome[1] (1. Kyoto University)

Japanese

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

[E1112-3am-09]

Cu-catalyzed enantioselective conjugate addition and electrophilic trapping of enolate intermediates

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

Japanese

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

[E1112-3am-10]

Substituent effect of imidazo[1,5-*a*]pyridine carbene ligands on copper and gold-catalyzed addition reaction of alkynes

○Mayu Suganuma[1], Fumitoshi Shibahara[1] (1. GIfu University)

Japanese

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

[E1112-3am-11]

Synthesis and Catalytic Activity Evaluation of Triaryl Mesoionic Carbene Metal Complexes Based on Planar Chiral Ferrocene

○Kazuki Osawa[1], Shungo Shimizu[1], Shinici Fukuzawa[1] (1. Graduate School of Engineering, Chuo University)

Japanese

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

[E1112-3am-12]

Asymmetric Synthesis of Spirocyclopropyloxyindole Derivatives Catalyzed by Chiral Bis(imidazolidine) Pyridine-Cobalt Complex

○Takaaki Saito[1], Takayoshi Arai[1] (1. Graduate School of Science, Chiba University)

Japanese

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

[E1112-3am-13]

Cobalt-catalyzed reductive cross-coupling reaction of aldehydes with organohalide

○Ko Sudo[1], Takuya Kurahashi[1] (1. Kwansei Gakuin University)

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白金架橋芳香環チューブの合成後修飾と分子捕捉能

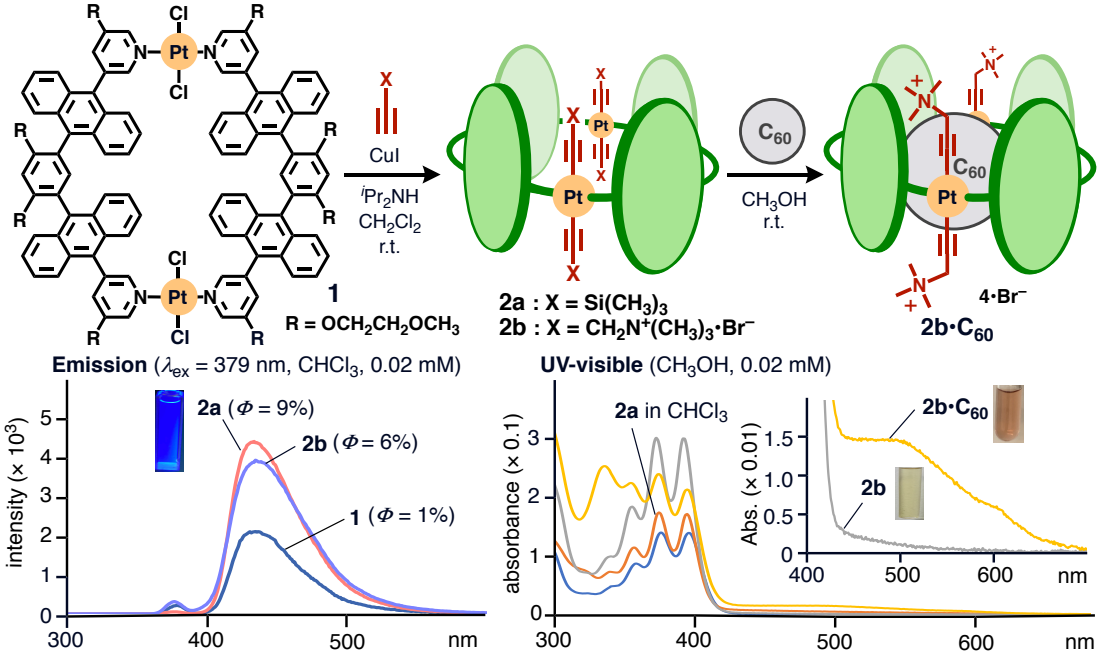
（東工大 化生研）○互井孔貴・田中裕也・吉沢道人

A Platinum-linked Polyaromatic Tube with Postsynthetic Modification and Molecular Binding Ability (*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Koki Tagai, Yuya Tanaka, Michito Yoshizawa

Here we report the postsynthetic modification and molecular binding abilities of a Pt(II)-linked polyaromatic tube, prepared from the combination of $PtCl_2$ salts and bent bispyridine ligands with anthracene rings. The chloro groups on the Pt(II) hinges were facilely replaced with various alkynyl groups to give modified polyaromatic tubes. The resultant tubes with TMS and ammonium alkynyl groups showed improved emission properties and host abilities toward fullerene derivatives, respectively.
Keywords: polyaromatic tube, postsynthetic modification, host ability, fullerene, emission properties

金属架橋芳香環チューブは金属イオンとビスピリジン配位子を混ぜることで簡便に合成できる（*Angew. Chem. Int. Ed.*, **2014**, *53*, 3604-3607）。今回、塩化白金を架橋部位とする芳香環チューブ **1** に着目し、アセチレン配位子との交換反応による合成後修飾法の開発とその分子捕捉能を明らかにした。

チューブ **1** の４つのクロロ基は、銅触媒により様々なアセチレン置換基に選択的に交換できることを見出した（下図上）。置換基の種類によりチューブの性質が変化した。例えば、トリメチルシリルアセチレンを導入した芳香環チューブ **2a** は **1** に比べて、発光性が９倍向上した（下図左）。また、４級アンモニウム基を持つチューブ **2b** は水系溶媒に溶解し、フラーレン C_{60} とその誘導体を定量的に捕捉することをUV-visible（下図右）および ESI-TOF MS 分析により明らかにした。



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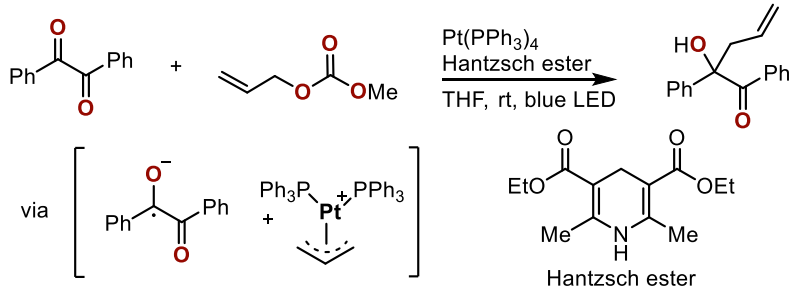
可視光と白金触媒によるα-ジケトンの極性転換型アリル化反応

(北大理[1]、WPI-ICReDD[2]) ○下里 絢平[1]・増田 侑亮[1]・澤村 正也[1,2]
Photoinduced Platinum-Catalyzed Umpolung Allylation of α-Diketones ([1]*Hokkaido University*, [2]*WPI-ICReDD*) ○ Junpei Shimosato,[1] Yusuke Masuda,[1] Masaya Sawamura[1,2]

Reductive allylation of carbonyl compounds with allylic electrophiles such as allylic halides and carboxylates is a practical way to synthesize homoallylic alcohols, dispensing with the use of allylic metal compounds that are generally unstable and need to be prepared. Recent progress of photoinduced transition metal catalysis has enabled use of stable and readily available amines as reductants, while these catalytic systems were only applied to allylation of aldehydes.[1)] We have developed photoinduced platinum-catalyzed reductive allylation of α-diketones with allyl carbonates. Allylation of α-diketones with allylic carbonates proceeded in the presence of $Pt(PPh_3)_4$ and Hantzsch ester under blue LED irradiation to afford homoallylic alcohols. Mechanistically, a photoexcited α-diketone is reduced by Hantzsch ester to give a ketyl radical, which reacts with an allylplatinum(II) complex generated from the platinum(0) catalyst and the allyl carbonate.
Keywords : Platinum catalyst, α-diketone, Allylation, Visible light, Umpolung

ハロゲン化アリルや炭酸アリルエステルのようなアリル求電子剤を用いたカルボニル化合物の還元的アリル化反応は、不安定なアリル金属試薬を調製する必要のない実用的なホモアリルアルコールの合成手法である。近年の光誘起遷移金属触媒反応の発展により、アミンを還元剤とするカルボニル化合物のアリル化反応が達成されているが、これらの反応では基質がアルデヒドに制限されていた[1)]。本研究では白金触媒を用いることで、可視光の照射下炭酸アリルエステルによるα-ジケトンの還元的アリル化反応が進行することを見出した。すなわち、α-ジケトンと炭酸アリルエステルの混合物に対して、青色 LED 光の照射下でテトラキス(トリフェニルホスフィン)白金(0)触媒前駆体と還元剤であるハンチュエステルを作用させたところ、ホモアリルアルコールが高収率で得られた。この反応は光励起されたα-ジケトンが還元剤によって還元されケチルラジカルを生じ、これが白金触媒と炭酸アリルエステルから生成したアリル白金(II)錯体と反応することで進行すると想定している。



1) For selected examples, see: a) P. G. Cozzi *et al. ACS Catal.* **2020**, *10*, 3857–3863. b) L. Shi *et al. ACS Catalysis* **2021**, *11*, 2992–2998. c) P. G. Cozzi *et al. Angew. Chem. Int. Ed.* **2022**, *61*, e202114981.

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トランスメタル化を利用した環状白金(II)-アセチリド錯体の合成

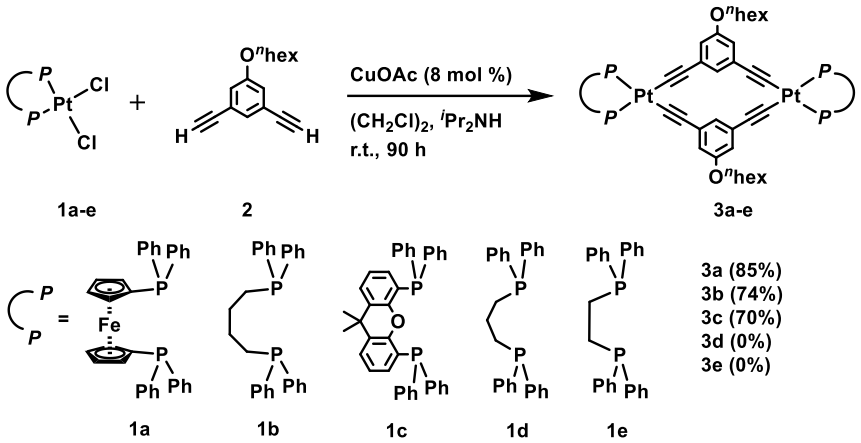
（東理大理[1]）○金子　龍星[1]・斎藤　慎一[1]・吉越　裕介[1]

Synthesis of Cyclic Platinum(II)-Acetylide Complex *via* Transmetallation ([1]*Faculty of Science, Tokyo University of Science*) ○Ryusei Kaneko,[1]Shinichi Saito,[1] Yusuke Yoshigoe[1]

Macrocyclic platinum(II)-acetylide complex, which can be a host molecule for some guests, have been synthesized in multi-steps in general. In this study, cyclic platinum(II)-acetylide complexes **3a-e** were synthesized in a single step using transmetallation (Scheme 1). The reaction of a dichloroplatinum(II) complexes, **1a-c**, and 1,3-diethynyl-5-(hexyloxy)benzene (**2**), in the presence of copper(I) acetate and diisopropylamine led to the formation of the desired cyclic complex **3a-c** in 70-85% yields. In the reaction of **1d-e**, we obtained a complex mixture and could not isolate the complexes **3d-e**, probably due to the distorted cyclic structure by ancillary ligand with bite angle of 94° or less.

Keywords : Cyclization; Transmetallation; Platinum complex; Acetylide; Bidentate phosphine ligand.

白金(II)-アセチリド構造を含む環状錯体は，分子包接などの有用な機能をもつ一方で，その合成には多段階を要する[1]．従って，短段階での合成法は有用である．本研究では，トランスメタル化反応を用いることで環状白金(II)-アセチリド錯体を単工程で合成した (Scheme 1)．二座リン配位子をもつジクロロ白金(II)錯体 **1a-c** と，ベンゼン環の 1,3 位に 2 つの末端アルキンが結合したジエチニルアレーン **2** を，酢酸銅とジイソプロピルアミンの存在下で反応させ，環状白金(II)錯体 **3a-c** を収率 70-85%で合成した．一方で，**1d-e** を用いた場合には，複雑な混合物が生成し，環化生成物 **3d-e** を単離できなかった．この要因は，配位挟角[2]が 94° 以下の支持配位子の場合，環化生成物 **3d-e** の歪みが大きくなり，**3d-e** が生成しにくくなったためであると考察した．



Scheme 1. Synthesis of cyclic platinum(II) complexes 3a-e.

(1) Li, Z. -Y.; Xu, Lin.; Wang C. -H.; Zhaoa X. -L.; Yang, H, -B. *Chem Commun.*, **2013**, *49*, 6194; (2) Birkholz, M, N.; Freixa, Z.; Piet, W. N. M. L., *Chem. Soc. Rev*. **2009**, *38*, 1099.

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白金触媒によるオルトアルキニルベンゼンスルフィン酸エステルの連続的 S-O 結合を経由する転位反応

（東北大院理）○久保田　圭亮・寺田　眞浩・中村　達

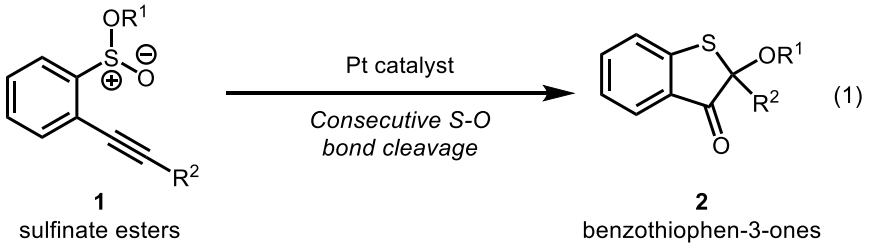
Pt-catalyzed rearrangement reactions of *ortho*-alkynylbenzenesulfinate ester via consecutive S-O bond cleavage

(*Graduate School of Science, Tohoku University*)
○Keiryo Kubota, Masahiro Terada, Itaru Nakamura

Previously, we reported that gold-catalyzed cyclization-rearrangement reactions of alkynes, which have a sulfinyl imine as nucleophilic functional groups, proceeded via consecutive cleavage of S-O and N-S bonds. In this context, we envisioned that sulfinate esters exhibit similar reactivity to sulfinyl imines in π-Lewis acidic metal catalyzed cyclization-rearrangement reaction. In this presentation, we report that the platinum-catalyzed cyclization-rearrangement reaction of *ortho*-alkynylbenzenesulfinate esters **1** produced benzothiophen-3-ones **2** via consecutive cleavage of two S-O bonds (Eq. 1).

Keywords : platinum catalyst; alkyne; sulfinate ester; sulfur containing heterocycle; rearrangement reaction

分子内に求核性官能基を有するアルキンのπルイス酸金属触媒を用いた触媒的環化-転位反応は多置換化されたヘテロ環を一段階で構築できる有用な反応である。以前当研究室は求核性官能基としてスルフィニルイミンを有するアルキンの金触媒を用いた連続的 S-O/N-S 結合の開裂を経由する触媒的環化-転位反応を報告した[1]。今回、我々はスルフィニルイミンの S-N 結合に代わり S-X 結合を有する求核性官能基を本反応に適応することで新規複素環の構築に繋がると考え、スルフィニルイミンの類縁体であるスルフィン酸エステルに着目して検討を行った。その結果、オルト位にアルキニル基を有するスルフィン酸エステル **1** に対し白金触媒を作用させることで連続的な S-O 結合の開裂を伴う触媒的環化-転位反応が進行しベンゾチオフェン-3-オン **2** が合成できることを明らかにした(式 1)。



参考文献

1) H. Tashiro, M. Terada, I. Nakamura, *Angew. Chem. Int. Ed.* **2021**, *60*, 12248.

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ルイス酸による配向基を持つポリアミドのアミド結合切断反応

（阪大院工[1]・阪大 ICS-OTRI[2]）○白木 椋大[1]・徐 于懿[1]・宇山 浩[1]・鳶巣 守[1,2]
Lewis acid mediated amide bond cleavage of polyamides bearing directing groups ([1]*Osaka Univ.*, [2]*ICS-OTRI Osaka Univ.*) ○Ryota Shiraki,[1] Yu-I Hsu,[1] Hiroshi Uyama,[1] Mamoru Tobisu[1,2]

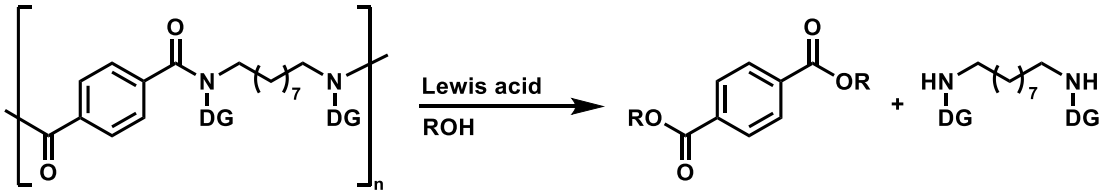
The development of new polymers that can be selectively depolymerized to monomers is an important research subject from the viewpoint of resource recycling. A common strategy to this end is to introduce easily cleavable chemical bonds, such as an ester group, to the main chain. In fact, chemical recycling of polyethylene terephthalate by depolymerization through hydrolysis has been put to practical use. On the other hand, amides are more difficult to hydrolyze than esters, and efficient depolymerization methods are limited.[1]

In this study, we synthesized polyamides with directing groups in the main chain. This polymer can be depolymerized to the corresponding diester and diamine by the reaction with alcohol in the presence of a Lewis acid. Since the corresponding polyamides without directing groups are not depolymerized under the same conditions, the interaction between the Lewis acid catalyst and the directing groups is essential for the depolymerization reaction.

Keywords : Polyamide; Depolymerization; Directing Group; Lewis acid

資源循環の観点から、モノマーへと選択的に分解可能な新規高分子材料の開発は重要な研究課題である。主鎖を効率よく分解するためには、エステル基のような切断されやすい化学結合を主鎖に導入することが一般的な戦略となる。実際、汎用エンジニアリングプラスチックであるポリエチレンテレフタレートは、解重合によるケミカルリサイクルが実用化されている。一方、エステル結合に比べアミド結合はより加水分解されにくく、効率的な分解手法は限られている[1]。

本研究では主鎖に配向基を導入したポリアミドを設計・合成した。このポリマーはルイス酸存在下、アルコールと反応させることで、対応するジエステルとジアミンへと分解可能であることを明らかにした。配向基持たないポリアミドは本条件下では分解されないため、ルイス酸触媒と配向基との相互作用が分解反応には重要である。



DG: directing group

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Copper-catalyzed cross-coupling of thiols with alcohols

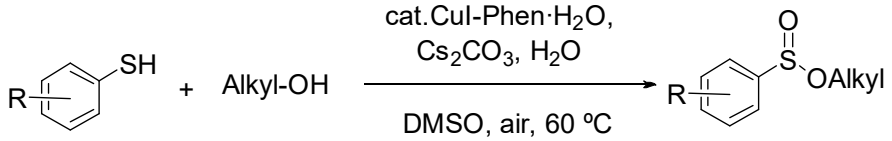
(*Department of Chemistry, Faculty of Liberal Arts and Sciences, Osaka Metropolitan University*) ○Nobukazu Taniguchi

Keywords: Sulfinic Ester; Thiol; Alcohol; Copper Catalyst; Oxidative Cross Coupling

A transition metal-catalyzed carbon-sulfur bond formation is important methodology for organic synthesis. Numerous reactions have been developed. Many sulfur-heteroatom bond formations have been also researched to date.

In particular, sulfinic esters having sulfur-oxygen bond are well investigated. To prepare sulfinic esters, esterifications of sulfinic acids or its derivatives are usually performed. On the contrary, the synthesis of sulfinic esters from thiols or disulfides is the most efficient method. It is well known that oxidation of disulfides by using NBS, Br_2 or $PhI(OCOCF_3)_2$.[1] These reactions require for using excess oxidants. Regrettably, a transition metal-catalyzed coupling of thiols with alcohols is very restricted. Only a few reactions using cat.CuI-TBD or cat.Co/N-SiO_2-AC under oxygen atmosphere are reported.[2] Therefore, a development of a convenient method is required now.

To solve the problem, a transition metal-catalyzed coupling of thiols with alcohols is the most efficient method. Therefore, a transition metal-catalyzed sulfur-oxygen bond formation was investigated. Fortunately, I found that the corresponding sulfinic esters could be produced in good yields. I would like to describe the developed methodology.



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水溶性キラルらせん高分子配位子を用いた銅触媒水中不斉求電子フッ素化反応

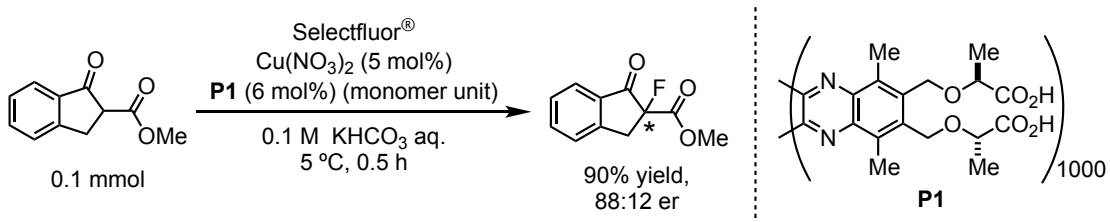
（京都大学）○田村 拓夫・山本 武司・杉野目 道紀

Asymmetric Cu-Catalyzed Electrophilic Fluorination in Water Using Water-Soluble Helical Polymer Ligands (*Kyoto University*) ○ Takuo Tamura, Takeshi Yamamoto, Michinori Suginome

Much interest is focused on asymmetric catalytic synthesis in water with particular attention to the use of macromolecular scaffolds to construct hydrophobic asymmetric environment around the catalytically active sites.[1,2] We have achieved highly stereoselective Cu-catalyzed asymmetric Diels-Alder reaction in water, employing helical poly(quinoxaline-2,3-diyl)-based water-soluble ligands bearing chiral carboxylic acid pendants derived from L-lactic acid (**P1**).[3] In this work, we utilized **P1** as a chiral ligand for the Cu-catalyzed asymmetric electrophilic fluorination of β-ketoesters in water. The reaction proceeded quantitatively at 5 °C, affording an α-fluorinated product with 88:12 er. In contrast, the use of a monomeric model ligand resulted in significantly lower enantioselectivity. These results indicate that helical polymer scaffold of **P1** provides efficient asymmetric reaction environment.

Keywords : Helical Polymer, Chiral Ligand, Asymmetric Synthesis in Water, Electrophilic Fluorination, Enolate

水を反応媒体とする不斉触媒反応では、基質が拡散できる疎水的な不斉反応場を構築することで触媒の活性と立体選択性が向上することが知られており、DNA のキラル高次構造を不斉反応場に利用した水中不斉銅触媒反応などが報告されている[1,2]。当研究室では、L-乳酸由来のキラルカルボン酸側鎖を有する水溶性ポリ（キノキサリン-2,3-ジイル）（**P1**）を配位子に用いることで、銅触媒水中不斉 Diels-Alder 反応が高収率かつ高立体選択的に進行することを報告している[3]。本研究では、**P1** を配位子に用いてβ–ケトエステルの銅触媒水中不斉求電子フッ素化反応をおこなった。5 mol%の触媒存在下、5 ºC においても反応は定量的に進行し、α位がフッ素化された生成物が 88:12 の鏡像体比で得られた。一方、単量体モデル配位子を用いた場合ではエナンチオ選択性が発現しなかったことから、**P1** が有する高分子らせん構造が不斉反応場の形成に重要な役割を果たしていることが示された。



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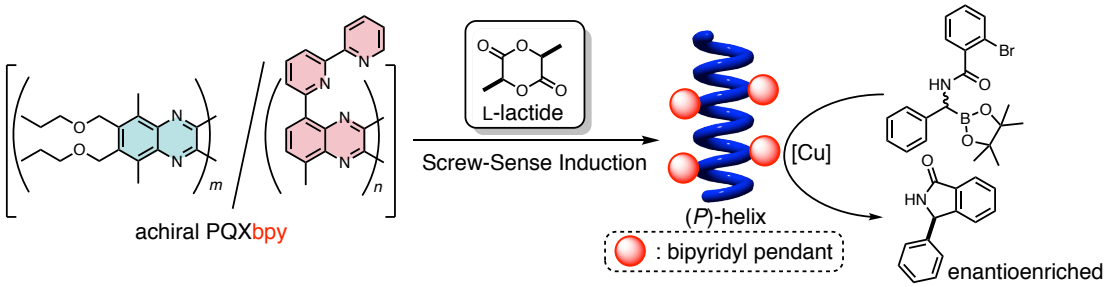
キラル添加剤による不斉らせん誘起を利用したアキラルらせん高分子ビピリジンを配位子とする不斉銅触媒反応

（京大院工）○志村 紘基・良永 裕佳子・杉野目 道紀
Copper-Catalyzed Asymmetric Coupling Utilizing Helical Macromolecular Bipyridine Ligand Based on Screw-Sense Induction by Chiral Additives *(Graduate School of Engineering, Kyoto University*) ○Hiroki Shimura, Yukako Yoshinaga, Michinori Suginome

Helical chirality of achiral poly(quinoxaline-2,3-diyl) bearing 2,2′-bipyridyl pendants was induced through the addition of L-lactide as a nonbonding chiral source. The obtained single-handed poly(quinoxaline-2,3-diyl) acted as an asymmetric ligand in the copper-catalyzed intramolecular coupling of α-aminoalkylboronic esters.
Keywords: polyquinoxaline; macromolecular catalyst; lactic acid; enantioconvergent reaction; noncovalent interaction

近年、動的らせん構造を有する高分子のらせん構造制御と機能性キラル材料としての利用に注目が集まっている。当研究室では、入手容易なキラル化合物との弱い分子間相互作用により、アキラルなエーテル側鎖を有するポリ（キノキサリン-2,3-ジイル）（PQX）に完全な片巻きらせん不斉を誘起することに成功している。[1)]また触媒部位を導入したアキラル PQX を用いることで、アミノ酸誘導体を非結合性不斉源とする高選択的不斉反応への応用も報告している。[1b)]今回我々はプロポキシ側鎖を持つ PQX にビピリジン部位を導入したアキラルらせん高分子配位子 **PQXbpy** を開発した。**PQXbpy** に対して、*t*-ブチルメチルエーテル溶液中で乳酸の二量体である L-ラクチドを添加することで主鎖に完全な右巻きらせん不斉が誘起された。L-ラクチド存在下、**PQXbpy** を用いて α-アミノアルキルボロン酸誘導体の銅触媒分子内カップリング反応[2)]を行ったところ、誘起されたらせん不斉に由来するエナンチオ選択性が発現した。



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銅触媒を用いる不斉共役付加反応により生じる亜鉛エノラート誘導体の求電子剤による捕捉

（東理大院化学）○下里 歩夢・山野本 健・遠藤 恆平

Cu-catalyzed enantioselective conjugate addition and electrophilic trapping of enolate intermediates

（*Department of Chemistry, Graduate School of Science, Tokyo University of Science*）
○Ayumu Shimozato, Ken Yamanomoto, Kohei Endo

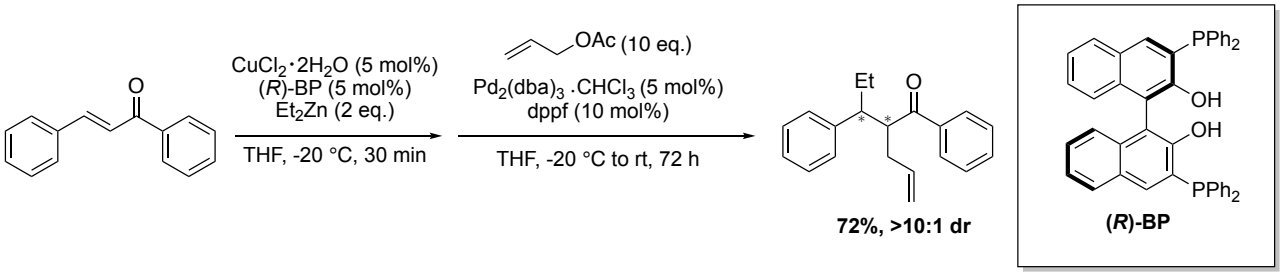
The copper-catalyzed asymmetric conjugate addition reactions of organometallic reagents to give metal enolate intermediates show high functional group tolerance, high regioselectivity, and stereoselectivity. However, there is only a several examples for the tandem reaction using metal enolate intermediates with electrophiles via Cu-catalyzed conjugate addition of organometallic reagents. A few examples use cyclic enones as starting materials for tandem electrophilic trapping via the Cu-catalyzed conjugate addition. In this study, we develop the enantioselective conjugate addition to acyclic enones and diastereoselective allylation reaction. The desired products are obtained in high yields, high diastereoselectivities, and enantioselectivities.

Chalcone was treated with Et_2Zn (2 equiv) in THF (0.1 M) at −20 ℃ in the presence of $CuCl_2 \cdot 2H_2O$ (5 mol%) and **BP** (5 mol%). The subsequent Pd-catalyzed electrophilic allylation of zinc enolate derivative with allyl acetate (10 equiv) in THF (0.1 M) took place at −20 ℃ to room temperature. The desired product was obtained in high yield and high diastereoselectivity (72%, >10:1 dr).

Keywords : asymmetric synthesis; organometallic catalysts; diastereoselectivity

銅触媒による有機金属試薬の不斉共役付加反応は，高い官能基共存性と位置選択性，立体選択性を示すことが利点である．生成物の金属エノラート中間体を利用する反応例は少なく，環状化合物を出発原料とすることが多い．本研究では，非環状エノンであるカルコン誘導体への不斉共役付加反応後に生じる亜鉛エノラートのアリル化反応について立体選択性などを調べた．その結果，高いジアステレオ選択性で目的化合物を得ることに成功した．

カルコンに対して配位子として **BP**（5 mol%），銅塩として $CuCl_2 \cdot 2H_2O$（5 mol%）を用い，THF（0.1 M）溶媒中，−20 ℃で Et_2Zn（2 当量）と反応させた．これにより生じる亜鉛エノラート誘導体に対して配位子として dppf（10 mol%），Pd 触媒として $Pd_2(dba)_3 \cdot CHCl_3$（5 mol%）を用い，THF（0.1 M）溶媒中，−20 ℃から室温条件で酢酸アリル（10 当量）と反応させたところ，目的とする生成物が 72%，>10:1 dr と高収率かつ高ジアステレオ選択的に得られた．



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銅・金触媒によるアルキンへの付加反応におけるイミダゾ[1,5-*a*]ピリジンカルベン配位子の置換基効果

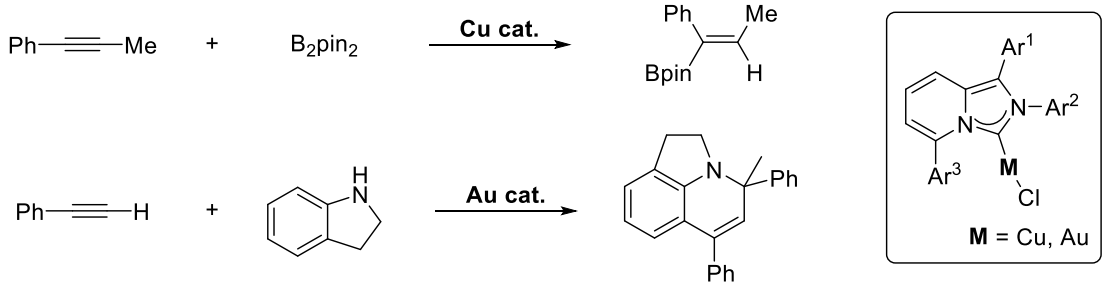
（岐阜大工）○菅沼 真由・芝原 文利
Substituent effect of imidazo[1,5-*a*]pyridine carbene ligands on copper and gold-catalyzed addition reaction of alkynes (*Faculty of Engineering, Gifu University*) ○Mayu Suganuma, Fumitoshi Shibahara

N-heterocyclic carbenes (NHCs) derived from imidazo[1,5-*a*]pyridines have non-negligible π-accepting character with maintaining σ-donating character as conventional NHCs. The π-accepting character can be controlled by simple introduction of substituent on C1 position of the skeleton. Also, introduction of that on N2 and C5 positions significantly exhibits steric effects on their transition metal catalysts. With these features, we investigated the effects on several catalytic reaction catalyzed by Cu and Au complexes.

In the case of Cu-catalyzed hydroboration of alkyne with diboron, introduction of electron withdrawing substituent on C1-position, and sterically less-hindered substituents on N2 and C5 positions indicated better results. Also, in the case of Au-catalyzed reaction of alkyne and indoline, significant steric effect was found on the catalytic activity.
Keywords : N-Heterocyclic Carbene; Cu Catalyst; Au Catalyst

イミダゾ[1,5-*a*]ピリジンから導かれるカルベン IPC は、従来の NHC が持つ σ 供与性を維持しつつ、高いπ受容性を持つ化学種である。また、1 位の置換基の導入によりその電子的性質を制御することができ、さらに 2 位や 5 位への置換基の導入は金属中心へ立体的な影響を与えることが明らかになっている [1)]。本研究では、これらの置換基効果が触媒反応へ与える影響を調査するため、IPC を配位子とする銅・金錯体を用いるアルキンへの付加反応を検討した。

銅触媒存在下のアルキンとビスピナコラートジボロンの付加反応 [2)]では、1 位の置換基が電子求引性であるほど、2 位と 5 位の置換基の立体が小さいほど収率が向上した。また、金触媒存下のアルキンとインドリンの付加反応 [3)]でも同様に 2 位と 5 位の置換基が小さいほど収率が向上した。



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面不斉フェロセンに基づくトリアリールメソイオンカルベン金属錯体の合成と触媒性能評価

（中大院理工）○大澤 一輝・清水 駿吾・福澤 信一

Synthesis and Catalytic Activity Evaluation of Triaryl Mesoionic Carbene Metal Complexes Based on Planar Chiral Ferrocene (*Graduate School of Science and Engineering, Chuo University*) ○Kazuki Osawa, Shungo Shimizu, Shinichi Fukuzawa

Mesoionic carbenes (MICs) have a carbon anion at the adjacent position of the carbene carbon and do not have a neutral resonance structure. Therefore, they are known for their high electron-donating ability to transition metals. Because of this uniqueness, catalyst development using MICs has been actively pursued in recent years.[1)]

In our laboratory, we have been developing MICs complexes that are stereocontrolled by planar chirality. In particular, palladium complexes with chiral MICs have been reported to exhibit good stereoselectivity in the asymmetric Suzuki-Miyaura cross-coupling reaction. On the other hand, the synthesis of the complexes requires other reaction steps.[2)]

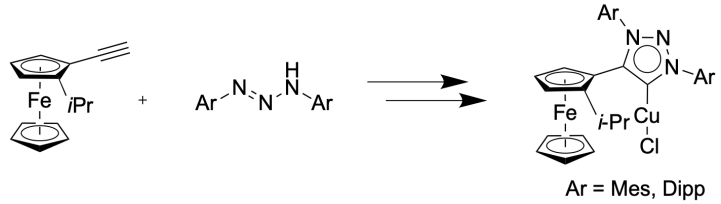
Against this background, we have synthesized chiral MICs complexes by oxidative cycloaddition of planar chiral ferrocenylalkynes with triazenes, and evaluated their catalytic and electrochemical properties.

Keywords : Copper ; Triazolylidene; Mesoionic Carbene

メソイオンカルベン(MICs)はカルベン炭素の隣接位に炭素アニオンを有し、中性の共鳴構造を持たない。そのため、遷移金属に対する電子供与能が高いことで知られており，近年 MICs を用いた触媒開発が盛んに行われている [1)]。

当研究室では、面不斉フェロセンによって立体制御を行う NHC 錯体の開発を行ってきた。特にキラル MICs パラジウム錯体は不斉鈴木宮浦クロスカップリング反応において、良好な立体選択性を示すことが報告されている。一方で、その錯体合成には多段階の反応を要することが課題として挙げられる [2)]。

このような背景から、今回我々は面不斉フェロセニルアルキンとトリアゼンを用いた酸化的環化付加反応を用いることで、トリアゾール環 3 位の窒素に面不斉フェロセンの自由回転を制御するためのアリール基の導入を達成したことに加え，従来の MICs 錯体に比べ少ない反応数でキラル MICs 錯体の合成に成功した．また，合成した MICs 錯体の触媒活性および電気化学的特性の評価を行った。



Ar = Mes, Dipp

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光学活性ビスイミダゾリジンピリジン-コバルト触媒を用いる立体選択的なスピロシクロプロピルオキシインドール誘導体の合成

(千葉大院理)○齋藤　孝明・荒井　孝義

Asymmetric Synthesis of Spirocyclopropyloxindole Derivatives Catalyzed by Chiral Bis(imidazolidine) Pyridine

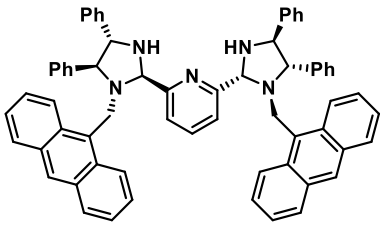
(*Graduate School of Science, Chiba University*) ○Takaaki Saito, Takayoshi Arai

Spirooxindole is an important structure found in various bioactive natural alkaloids and pharmaceutical candidates and has attracted much attention in the field of drug discovery.[1] We have developed reactions using a chiral bisimidazolidine pyridine (PyBidine) [2] as a ligand for benzalmalononitrile substrates. In this study, we synthesized chiral spirocyclooxindole derivatives using benzalmalononitriles and 3-chlorooxindoles.

We obtained desired products in high yield and selectivity using a *N*-9-Anth-PyBidine-$Co(OAc)_2$ catalyst, in which an anthracenyl methyl functionality was introduced on the nitrogen of the imidazolidine ring of PyBidine.

Keywords : Asymmetric Synthesis, Chiral Catalyst, Spiro Compound, Chlorine, Cobalt

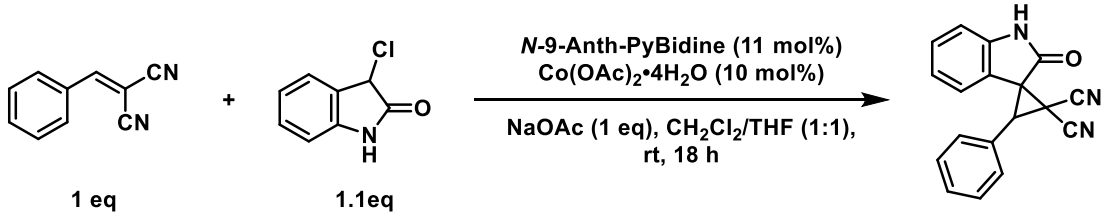
スピロオキシインドール骨格は様々な生理活性アルカロイドや医薬品候補に含まれる重要な構造であり、創薬領域において注目されている。当研究室では、独自に開発した光学活性ビスイミダゾリジンピリジン(PyBidine)[2]を配位子として用いて、ベンジリデンマロノニトリルを基質とする反応を開発してきた。本研究では、光学活性スピロシクロプロピルオキシインドール誘導体をベンジリデンマロノニトリルと 3-クロロオキシインドールを用いて合成した。



***N*-9-Anth-PyBidine**

PyBidine is abbreviation of bis(imidazolidine)pyridine.

配位子の検討を行ったところ、PyBidine のイミダゾリジン観の窒素上にアントラセニルメチル基を導入した *N*-9-Anth-PyBidine を配位子として用いた際に、高い収率・選択性で目的物を得ることができた。



1 eq　　**1.1eq**

90% yield
dr = 96:4
98% ee

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日本化学会 第104春季年会 (2024)

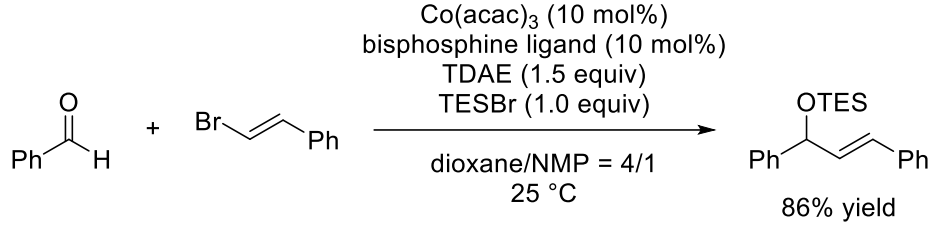
コバルト触媒によるアルデヒドと有機ハロゲン化物の還元的クロスカップリング反応

（関西学院大院理工）○首藤航・倉橋拓也
Cobalt-catalyzed reductive cross-coupling reaction of aldehydes with organohalide (*Graduate School of Science and Engineering, Kwansei Gakuin University*) ○ Ko Sudo, Takuya Kurahashi

Allyl alcohols are the basic skeleton found in many pharmaceuticals and other products, and their synthesis has been widely conducted. Among them, the coupling reaction of aldehydes with alkenyl halides using a stoichiometric amount of chromium(II) chloride reductant in the presence of nickel catalyst (NHK reaction) is known as one of the most efficient synthetic methods.) While it has high substrate acceptability, the use of a stoichiometric amount of chromium(II) chloride reductant has been problematic. Although some studies have been reported to reduce the amount of chromium(II) chloride reductant to a catalytic amount), no method has yet been reported to eliminate the use of chromium(II) chloride reductant altogether. In this study, a cobalt-catalyzed reductive cross-coupling reaction of aldehydes and alkenyl halides using TDAE as reductant was successfully developed.

Keywords : Cobalt catalyst; Nickel catalyst; Reductive coupling; Alkenyl halide; Aldehyde

アリルアルコールは医薬品などに多く含まれる基本骨格であり、その合成は広く行われてきた。中でも、効率的な合成法としてニッケル触媒存在下で量論量の塩化クロム（II）還元剤を用いたアルデヒドとアルケニルハライドのカップリング反応（NHK反応）が知られている[1)]。高い基質許容性を持つ一方で、塩化クロム（II）還元剤を量論量使用することが問題とされてきた。塩化クロム（II）還元剤を触媒量に低減させる研究が報告されているが[2)]、全く使用しない方法は未だ報告されていない。そこで本研究ではコバルト触媒による、還元剤として TDAE を用いるアルデヒドとアルケニルハライドの還元的クロスカップリング反応を開発した。



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

Wed. Mar 20, 2024 3:55 PM - 4:45 PM JST | Wed. Mar 20, 2024 6:55 AM - 7:45 AM UTC
E1111(1111, Bldg. 11 [1F])

[E1111-3vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kento Ishida, Takuya Suga

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1111-3vn-01]

Disturbing continuous movement of carbon atoms in organic molecules

○Tamotsu Takahashi[1,2], Masayoshi Bando[2], Hui Chen[1], Yang Zheng[3], Zhiyi Song[2] (1. Institute of Chemistry, Henan Academy of Science, 2. Institute for Catalysis, Hokkaido University, 3. Henan Chemical Industrial Institute, Henan Academy of Science)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1111-3vn-02]

Low-Valent Titanium-Mediated Radical Substitution of Allyl Pivalates Using Aliphatic Alcohols as Carbon Radical Sources

○Tatsuto Egawa[1], Chinatsu Miki[1], Takuya Suga[1], Yutaka Ukaji[1] (1. Kanazawa University)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1111-3vn-03]

Zirconocene difluoride-catalyzed hydrosilylation of olefins

○Ryota Kanchiku[1], Keita Takahashi[1], Kento Ishida[1], Yohei Ogiwara[1], Norio Sakai[1] (1. Tokyo University of Science)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1111-3vn-04]

Allylic silylation of allyl phosphates using zinc catalysts and a silylborane

○Ami Sasaki[1], Kazuhiko Semba[1], Tetsuaki Fujihara[1] (1. Graduate School of Engineering, Kyoto University)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[E1111-3vn-05]

Synthesis of Functionalized Nitrones from Nitro Compounds and Organozinc Reagents

○Koki Yamaguchi[1], Koki Nishi[1], Takeshi Hata[1] (1. Tokyo Institute of Technology)

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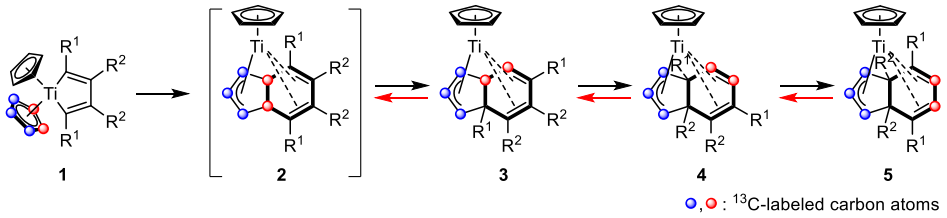
有機分子内を連続して移動する炭素原子を妨害するファクター

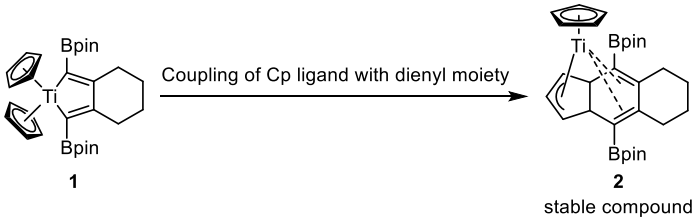
(河南化学研[1]・北大触媒研[2]・河南化工研[3]) ○高橋 保[1,2]・坂東 正佳[2]・陳 輝[1]・鄭 洋[3]・宋 志毅[2]
Disturbing continuous movement of carbon atoms in organic molecules ([1]*Institute of Chemistry, Henan Academy of Sciences,* [2]*Institute for Catalysis, Hokkaido University,* [3]*Henan Chemical Industrial Institute, Henan Academy of Science*) ○Tamotsu Takahashi,[1,2] Masayoshi Bando,[2] Hui Chen,[1] Yang Zheng,[3] Zhiyi Song [2]

We have developed continuous movement of carbon atoms in organic molecules. Titanacyclopentadiene **1** can be converted to dihydroinedenyltitaniumu compound **2**. However, compound **2** is readily transferred to compound **3**. In this research we found that compound **2** was obtained as stable compounds when titanacyclopentadiene **1** has pinacolboryl substituents at α–positions.
Keywords : Continuous movement of carbon atoms in organic compounds; Dihydroindenyl titanium

我々は有機化合物中の炭素原子を連続して移動させることができれば、有機化学において画期的な方法を開発できると考え、平衡を利用した新しい概念を提案し、いくつかの炭素原子の有機化合物内での移動反応を開発して報告してきた。



チタナシクロペンタジエン **1** を加熱反応させると、化合物 **2** が収率良く生成するが、すぐに次の炭素原子の移動反応が進行して化合物 **3** が生成するため通常化合物 **2** の段階で反応を止めることが難しい。そこで化合物 **2** の段階で安定に止めるファクターを検討したところ、チタナシクロペンタジエン **1** のα位の置換基にピナコールボリル基を用いると安定に化合物 **2** を得ることに成功したので報告する。



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低原子価チタン試薬を用いた脂肪族アルコールを炭素ラジカル源とするアリルピバレートの置換反応

（金沢大院自然[1]）○江川 巽翔[1]・三木 稚夏[1]・菅 拓也[1]・宇梶 裕[1]

Low-Valent Titanium-Mediated Radical Substitution of Allyl Pivalates Using Aliphatic Alcohols as Carbon Radical Sources

([1]*Graduate School of Natural Science & Technology, Kanazawa University*) ○Tatsuto Egawa,[1] Chinatsu Miki,[1] Takuya Suga,[1] Yutaka Ukaji[1]

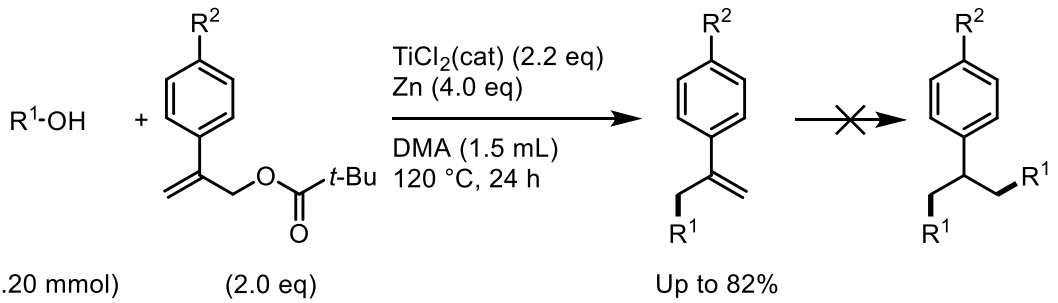
Our group has discovered homolytic cleavage of alcohol C(sp^3)-OH bonds facilitated by low-valent titanium reagents. In the present study, we applied this method for a radical coupling reaction between alcohols and allyl pivalates. When an alcohol was treated with $TiCl_2$(cat) (cat = catecholate) and Zn in the presence of an allyl pivalate having an aryl group at the 2-position, the carbon radical reacted at the alkene terminus of the allyl pivalate, and subsequent elimination of the pivaloxy group afforded a formal substitution product. Interestingly, even though both starting material and product are 1,1-di-substituted alkenes, the further reaction of the radical with the product did not occur.

The substrate scope covers a wide range of primary, secondary and tertiary alcohols, and allyl pivalates.

Keywords : Titanium; Carbon radical; Alcohols; Substitution reaction

当研究室は既に、低原子価チタン試薬を利用してアルコールの C(sp^3)-OH 結合を切断し、対応する炭素ラジカルを直接発生させることに成功している。本研究では、この炭素ラジカル発生法を応用して、アルコールとアリルピバレートとのラジカルカップリング反応を開発した。アルコールに対し、2 位にアリール基を有するアリルピバレート存在下で $TiCl_2$(cat) (cat = catecholate) と Zn を作用させたところ、炭素ラジカルがアリルピバレートのアルケン部位に付加し、さらにピバロキシ基の脱離が進行した生成物が得られることが判明した。興味深いことに、出発物質・生成物ともに 1, 1-二置換アルケンであるにも関わらず、炭素ラジカルが生成物にさらに付加した化合物は得られなかった。

この知見をもとに反応の基質一般性を検討したところ、様々な第 1〜3 級アルコールやアリルピバレートにおいて一般性があることがわかった。



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フッ化ジルコノセンを触媒とするオレフィンのヒドロシリル化反応

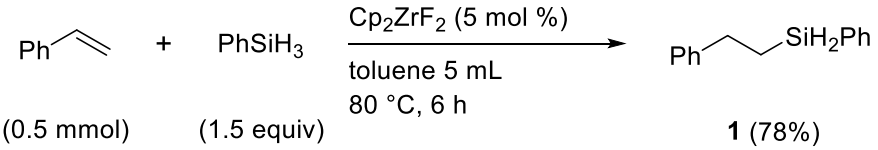
（東理大創域理工）○寒竹 亮太・髙橋 慶多・石田 健人・荻原 陽平・坂井 教郎
Zirconocene difluoride-catalyzed hydrosilylation of olefins (*Faculty of Science and Technology, Tokyo University of Science*) ○Ryota Kanchiku, Keita Takahashi, Kento Ishida, Yohei Ogiwara, Norio Sakai

Hydrosilylation of olefins is a powerful synthetic methodology for organosilicon compounds. Platinum catalysts are known as the most practical catalyst for hydrosilylation. However, because of the rarity and environmental concerns of platinum, the other transition metal catalysts, especially earth-abundant transition metals, have attracted attention. So far, some hydrosilylation reactions using group 4 transition metal complexes have been reported. In this study, we investigated hydrosilylation of olefins using zirconocene difluoride (Cp_2ZrF_2).

As a result, the reaction of styrene and phenylsilane in the presence of catalystic amount of Cp_2ZrF_2 in toluene at 80 °C afforded the desired hydrosilylation product **1** in 78% yield. We also examined the generality of this reaction and found that a variety of substrates could be applied to the reaction. Details of the reaction will be presented in the meeting.
Keywords : Alkene; Hydrosilane; Zirconocene; Hydrosilylation

オレフィンのヒドロシリル化は、有機ケイ素化合物の強力な合成法である。白金触媒は、ヒドロシリル化の最も実用的な触媒として知られている。しかし、白金の希少性や環境負荷の懸念のため、他の遷移金属触媒を用いたヒドロシリル化反応の開発に注目が集まっている[1)]。これまでに、第 4 族遷移金属錯体を用いたヒドロシリル化反応がいくつか報告されている[2)]。本研究では、フッ化ジルコノセンを触媒に用いて、オレフィンのヒドロシリル化反応を検討した。

検討の結果、スチレンとフェニルシランを触媒量のフッ化ジルコノセン存在下、トルエン溶媒中、80℃で反応させると、目的のヒドロシリル化体 **1** が 78%の収率で生成することが分かった。また、基質一般性について検討した結果、様々な反応基質で本反応が進行することが分かった。講演では、本反応の詳細について報告する。



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亜鉛触媒とシリルボランを用いたアリルリン酸エステルのアリル位ケイ素化反応

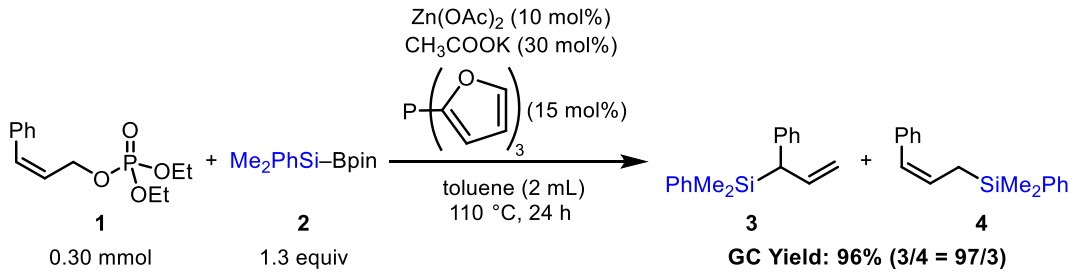
（京大院工）○佐々木 麻朱・仙波 一彦・藤原 哲晶
Allylic silylation of allyl phosphates using zinc catalysts and a silylborane (*Graduate School of Engineering, Kyoto University*) ○Ami Sasaki, Kazuhiko Semba, Tetsuaki Fujihara

Allylsilanes are useful intermediates in organic synthesis. For the catalytic synthesis of allylsilanes, palladium-catalyzed reactions[1] or copper-catalyzed reactions[2] have been reported to date. In the present study, we found that the allylic silylation of allyl phosphates proceeded by using a silylborane as a silicon source in the presence of cost-effective and low-toxic zinc catalysts.
Employing zinc acetate as a catalyst, with tri(2-furyl)phosphine as a ligand in the presence of potassium acetate as an additive, the reaction of (*Z*)-allyl phosphate having a phenyl group at the γ-position **1** with dimethylphenylsilylboronic acid pinacol ester (**2**) in toluene afforded a branched allylsilane **3** in high yield with high selectivity (**Scheme 1**).

Keywords：Allylic silylation; Zinc; Silylborane; Allyl phosphate; Phosphine ligand

アリルシランは精密有機合成における有用な合成中間体である。これまで、触媒的なアリルシラン合成反応にはパラジウム触媒[1]や銅触媒[2]によるアリル位ケイ素化反応が報告されている。本研究では安価で低毒性の亜鉛を触媒、シリルボランをケイ素源として用いることでアリルリン酸エステルのアリル位ケイ素化反応が進行することを見出した。
触媒として酢酸亜鉛、添加剤として酢酸カリウム、配位子としてトリ（2-フリル）ホスフィンを用い、γ位にフェニル基をもつ*Z*体のアリルリン酸エステル **1** とジメチルフェニルシリルボロン酸ピナコールエステル (**2**) をトルエン溶媒中で反応させたところ、分岐構造のアリルシラン **3** が高収率かつ高選択的に得られた（スキーム 1）。

Scheme 1



1) Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. *J. Org. Chem.* **1996**, *61*, 5779.
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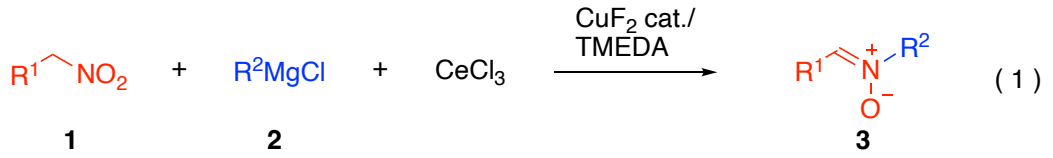
ニトロ化合物と有機亜鉛反応剤からの官能性ニトロン合成

（東工大生命理工）西 晃希・○山口功貴・秦 猛志
Synthesis of Functionalized Nitrones from Nitro Compounds and Organozinc Reagents (*School of Life Science and Technology, Tokyo Institute of Technology*) Koki Nishi, ○Koki Yamaguchi, Takeshi Hata

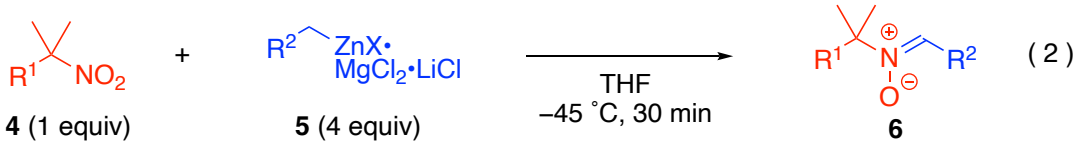
We have already reported that the treatment of nitro compound **1** with Grignard reagent in the presence of $CeCl_3$ and a catalytic amount of CuF_2 gave nitrone **2** as single isomers. This time, treatment of nitro compound **3** with organozinc reagent **4** afforded functionalized nitrones **5**. Some products obtained by this reaction are shown below.
Keywords : *Organozinc Reagents; Nitro Compounds; Nitrones; Reductive Coupling Reaction*

既に我々は、CuF_2 触媒および $CeCl_3$ 共存下、ニトロ化合物 **1** にグリニャール反応剤 **2** を作用させると、ニトロン **3** が単一の異性体として得られることを見出し報告している（式 1）。[1)]

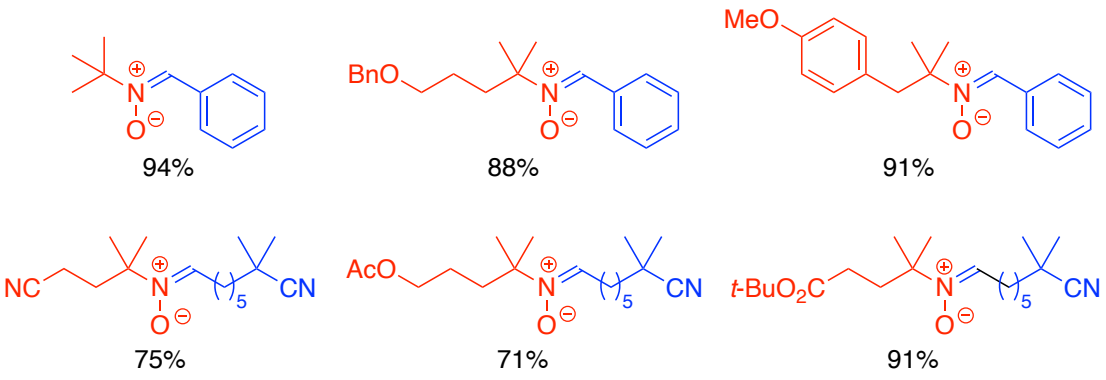


(1)

今回、式 2 に示すように、ニトロ化合物 **4** に対し、有機亜鉛反応剤 **5** を用いたところ、官能性ニトロン **6** を収率良く得ることができた。式 2 の下には、得られた生成物の例を示す。



(2)



1) 日本化学会第 95 春季年会、1E4-52（2015 年）.

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

Wed. Mar 20, 2024 3:55 PM - 4:55 PM JST | Wed. Mar 20, 2024 6:55 AM - 7:55 AM UTC
E1112(1112, Bldg. 11 [1F])

[E1112-3vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Naoyuki Toriumi, Taiga Yurino

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1112-3vn-01]

Rhodium-Catalyzed Decarbonylative Coupling of Acyl Halides with Bis(pinacolato)diboron and Alkynes

○Masato Tsukahara[1], Nanako Katsurayama[1], Risako Miura[1], Yuu Kimura[1], Teruyuki Kondo[1] (1. Kyoto University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1112-3vn-02]

Highly Regio- and Enantioselective Intermolecular [2+2+2] Cycloaddition of 1,7-Enynes and Unsymmetric Alkynes

○Taichi Kishi[1], Yuto Horio[1], King Hung Nigel Tang[1], Takanori Shibata[1] (1. The Univ. of Waseda)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1112-3vn-03]

Development of a Cross Coupling Reaction Using Ketones as Aryl Sources Enabled by the Norrish Type Ⅰ Reaction and Rhodium Catalysis

○Shimizu Atsuya[1], Yuki Fujimaki[1], Jun Takaya[1] (1. Tokyo Institute of Technology)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1112-3vn-04]

Synthesis and Reactivity of Nickel–Rhodium Bimetallic Complexes

○Kouki Fujita[1], Kazuhiko Semba[1], Yoshiaki Nakao[1] (1. Kyoto Univesity)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[E1112-3vn-05]

Silver(I)–Catalyzed Intermolecular Carbofluorination of Alkynes Using Acyl Fluorides via C–F Bond Cleavage

○Tomoya Emmei[1], Mamoru Tobisu[1,2] (1. Osaka Univ., 2. ICS-OTRI)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[E1112-3vn-06]

Ag-Catalyzed Double Benzylic Isocyanation and Its Application

○Tomoko Ishikawa[1], Takuya Nakamura[1], Taiga Yurino[2,3], Takeshi Ohkuma[2,3] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Engineering, Hokkaido University, 3. Frontier Chemistry Center)

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ロジウム触媒存在下、酸ハロゲン化物の脱カルボニル化を経るジボロンおよびアルキンとのカップリング反応

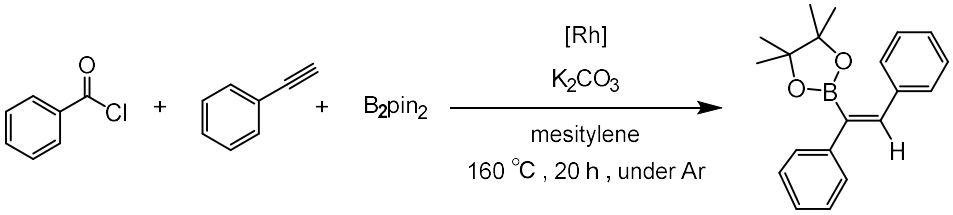
（京都大学）○塚原 雅人・桂山 菜々子・三浦 理紗子・木村 祐・近藤 輝幸

Rhodium-Catalyzed Decarbonylative Coupling of Acyl Halides with Bis(pinacolato)diboron and Alkynes (*Kyoto University*) ○Masato Tsukahara, Nanako Katsurayama, Risako Miura, Yu Kimura, Teruyuki Kondo

Organoboronic acids, which are stable in the presence of water and/or air, were highly effective boron compounds for Suzuki-Miyaura cross-coupling reactions, which was used to synthesis of valuable compounds such as fine chemicals and several drugs in various fields. Organoboronic acids have been prepared mainly by the reaction of electrophilic boron species with Grignard reagents or organolithium as well as hydroboration. In this study, Rh-catalyzed reaction of benzoyl chloride (PhCOCl) with bis(pinacholato)diboron (B_2pin_2) in the presence of K_2CO_3 was examined in mesitylene at 160 ºC for 20 h under an argon atmosphere, which gave 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (PhBpin) was obtained in 83% yield with high selectivity through the catalytic decarbonylation of PhCOCl. When the same catalytic reaction was carried out in the presence of phenylacetylene (PhC≡CH), decarbonylative coupling reaction occurred to give in (E)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 71% yield, in which concomitant addition of a phenyl group and Bpin to carbon-carbon triple bond of alkynes proceeded in one-pot.

Keywords: Rhodium; Catalyst; Organoboronic acid; Acyl halide; Alkyne

水や空気に安定な有機ボロン酸は、鈴木ー宮浦クロスカップリング反応の基質として極めて有効であり、ファインケミカルズ合成や創薬等の広範な分野で利用されている。一般に有機ボロン酸は、求電子性のホウ素化合物と Grignard 試薬および有機リチウム試薬との反応、およびヒドロホウ素化反応により合成されてきた[1)]。本研究では、ロジウム錯体触媒および K_2CO_3 存在下、塩化ベンゾイル（PhCOCl）とビス（ピナコラート）ジボロン（B_2pin_2）との反応を、アルゴン雰囲気下、メシチレン溶媒中、160 ℃で 20 時間行った結果、塩化ベンゾイルの脱カルボニル化反応を経る B_2pin_2 とのカップリング反応が良好に進行し、PhBpin が収率 83％で高選択的に得られた。そこで、同様の反応を、アルキンとしてフェニルアセチレン（PhC≡CH）共存下で行った結果、アルキンの炭素ー炭素三重結合にフェニル基と Bpin 基が cis–付加した生成物が、ワンポットで、収率 71％で得られることを見出した。



1) Yang, C.-H. *Org. Chem. Front.* **2023**, *10*, 6010.

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1,7-エンインと非対称アルキンの高位置選択的かつエナンチオ選択的分子間[2+2+2]付加環化反応

（早大先進理工）○岸 大智、堀尾 優斗、King Hung Nigel Tang、柴田 高範

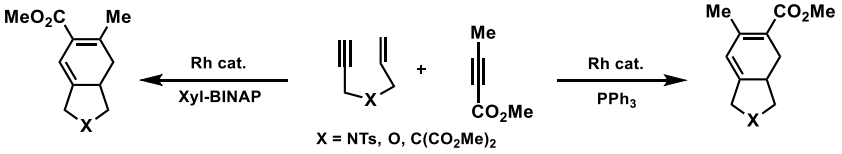
Highly Regio- and Enantioselective Intermolecular [2+2+2] Cycloaddition of 1,7-Enynes and Unsymmetric Alkynes (*School of Advanced Science and Engineering, Waseda University*)

○Taichi Kishi, Yuto Horio, King Hung Nigel Tang, Takanori Shibata

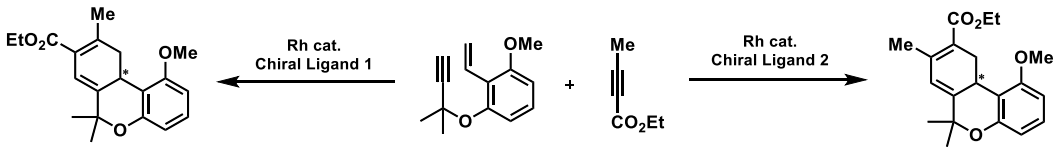
[2+2+2] Cycloaddition is a highly atomically efficient reaction that gives six-membered ring products. Various cycloadducts can be obtained by inter- and intramolecular reactions using alkynes and alkenes as C2 sources. For example, intermolecular reactions of heteroatom-tethered enynes and alkynes can be used to synthesize heteroatom-containing fused bicyclic compounds. Evans *et al*. achieved a regioselective intermolecular [2+2+2] cycloaddition of 1,6-enynes with unsymmetrical alkynes in the presence of cationic Rh catalysts.[1] The regioselectivity was controlled by the proper choice of the phosphine ligand. We here investigated a Rh-catalyzed intermolecular [2+2+2] cycloaddition using ortho-phenylene-tethered 1,7-enynes and unsymmetric alkynes. As a result, two regioisomers were selectively obtained with high enantiomeric excesses by the proper choice of chiral ligands and reaction conditions.

Keywords : Intermolecular [2+2+2] Cycloaddition, Rh Catalyst, Regioselective Synthesis, Enantioselective Synthesis

[2+2+2]付加環化は、高い原子効率で 6 員環生成物を与える反応であり、アルキン、アルケンを C2 源として、分子間、分子内反応により、種々の環化体が得られる。例えば、エンインとアルキンの分子間反応が挙げられ、エンインの架橋部位に窒素や酸素を導入することで含ヘテロ原子縮合二環式化合物を合成できる。Evans らは、カチオン性 Rh 触媒存在下、1,6-エンインと非対称アルキンの位置選択的な分子間[2+2+2]付加環化反応を達成した [1)]。本反応では、配位子の選択により、両位置異性体の選択的合成を達成した。



今回、我々はカチオン性 Rh 触媒存在下、オルトフェニレン架橋 1,7-エンインと非対称アルキンの分子間[2+2+2]付加環化反応を検討した。その結果、不斉配位子と反応条件の選択により、2 つの位置異性体が選択的かつ高鏡像体過剰率で得られた。



1) P. A. Evans, J. R. Sawyer, P. A. Inglesby, *Angew. Chem. Int. Ed.* **2010**, *49*, 5746.

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Norrish I 型反応とロジウム触媒を利用したケトンをアリール源とするクロスカップリング反応の開発

（東工大理）○清水 敦也・藤巻 友樹・鷹谷 絢
Development of a Cross Coupling Reaction Using Ketones as Aryl Sources Enabled by the Norrish Type I Reaction and Rhodium Catalysis (*Department of Chemistry, Tokyo Institute of Technology*) ○Atsuya Shimizu, Yuki Fujimaki, Jun Takaya

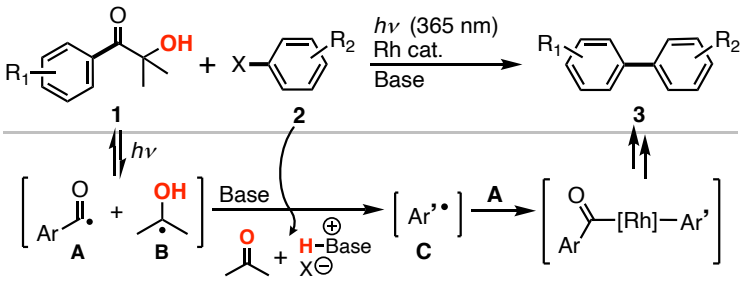
Development of cross-coupling reactions using aryl ketones without directing groups as aryl sources is challenging due to the difficulty of cleaving the strong carbon-carbon σ-bond. We have recently developed the borylation reaction of aryl ketones via cleavage of the carbon-carbon σ-bond by cooperation of the Norrish type I reaction and Rh-catalysis.

In this presentation, we applied this cooperative system to a cross-coupling reaction using aryl ketones as aryl sources. As a result, we have found that the reaction of *α*-hydroxy ketones **1** and aryl halides **2** in the presence of a rhodium catalyst and a base under photoirradiation conditions affords biaryl compounds **3** in moderate yields. This reaction is initiated by the Norrish type I reaction of the ketone to produce an aroyl radical **A** and an alkyl radical **B**. The latter acts as a one-electron reductant for the aryl halide to generate an aryl radical **C**, and the former provides another aryl group via decarbonylation with the rhodium catalyst.

Keywords : Rhodium; Norrish type I reaction; Cross coupling; Decarbonylation

配向基を持たないアリールケトンをアリール源として用いるクロスカップリング反応は、その不活性な炭素–炭素 σ 結合を切断する必要があることから極めて困難である。一方我々は以前、Norrish I 型反応と Rh 触媒作用を協働的に用いることで、アリールケトンのカルボニル基 *α*-位の炭素–炭素 σ 結合を切断し、ホウ素化する新反応を見出し報告した[1]。

今回我々は、ロジウム触媒及び塩基存在下、*α*-ヒドロキシケトン **1** とハロゲン化アリール **2** に対して 365 nm の光照射を行うと、ビアリール化合物 **3** が中程度の収率で得られることを見出した。本反応では、ケトンの Norrish I 型反応により生じる *α*-ヒドロキシアルキルラジカル **B** が、ハロゲン化アリール **2** に対する一電子還元剤として働くことでアリールラジカル **C** が生じる。また同時に発生したアロイルラジカル **A** がロジウム上で脱カルボニルすることでもう一方のアリール源となり、分子間クロスカップリング反応が進行すると考えている。



1) Y. Fujimaki, N. Iwasawa, J. Takaya, *Chem Sci.* **2023**, *14*, 1960–1965.

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ニッケルーロジウム複核錯体の合成と反応性

（京大院工）○藤田 航輝・仙波 一彦・中尾 佳亮
Synthesis and Reactivity of Nickel–Rhodium Bimetallic Complexes (*Graduate School of Engineering, Kyoto University*) ○Kouki Fujita, Kazuhiko Semba, Yoshiaki Nakao

Metalloligands have received considerable attention due to their unique electronic properties. For instance, metallloligands derived from group 13 metals exhibit unique reactivity due to their high σ-donicity resulting from low electronegativity and Lewis acidity arising from an empty p orbital. In contrast, metalloligands based on transition-metals exert electronic perturbation to coordinating transition-metals by σ-, π-, and/or δ-bonding through their d orbitals, allowing for precise control of reactivity compared to main group metals.

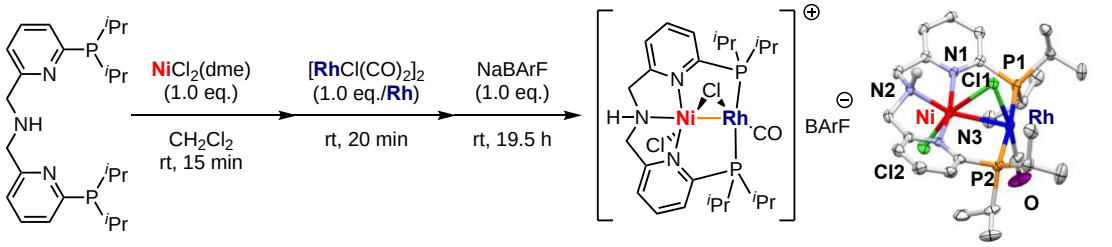
Here we report the synthesis and reactivity of rhodium complexes bearing a nickel ligand.

Keywords : metalloligand; rhodium; nickel; bimetallic complexes

金属配位子は，電気陽性な金属元素に由来するユニークな電子的性質を有するため注目されている [1]。例えば，13 族金属配位子は低い電気陰性度に由来する強い σ 電子供与性と，空の p 軌道に由来する Lewis 酸性を示すため，それを有する遷移金属錯体は特異な触媒活性を示すことが知られている。一方，遷移金属配位子は典型金属配位子と比べて，d 軌道を通じた電子的摂動により，配位した遷移金属の反応性を精密に制御することが期待される [2]。今回我々は，ニッケル含有配位子を有するロジウム錯体を合成し，ニッケル配位子がロジウム中心に与える電子的効果や，複核錯体の反応性について調査した。

PNNNP 配位子 **1** に対して，等量の $NiCl_2$(dme) (dme: 1,2-dimethoxyethane)，0.50 当量の $[RhCl(CO)_2]_2$，等量の NaBArF (BArF: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)を，CH_2Cl_2 中で順次反応させることによって，ニッケル含有配位子を有するロジウム錯体を収率 79%で得た (スキーム 1)。**2** は常磁性を示したため，その構造は単結晶 X 線構造解析および ESI-HRMS により同定した。

Scheme 1



1 **2**, 79%

crystal structure of **2**; counter anion and H atoms except for N2H are omitted for clarity.

1) a) J. Takaya *Chem. Sci.* **2021**, *12*, 1964. b) Y. Nakao *et al*. *ACS Catal.* **2022,** *12,* 1626.
2) a) C. Uyeda *et al*. *ACS Catal.* **2017,** *7*, 936. b) J. Takaya, N. Iwasawa *et al*. *The 67th Symposium on Organometallic Chemistry, Japan,* PC-29. c) T. Nakajima, T. Tanase *et al. Eur. J. Inorg. Chem.* **2023**, *26*, e202200648. d) E. Bill, L. Gagliardi, C. C. Lu *et al. Inorg. Chem.* **2012**, *51*, 728. f) L. Gagliardi, C. C. Lu *et al. J. Am. Chem. Soc.* **2015**, *137,* 4638.

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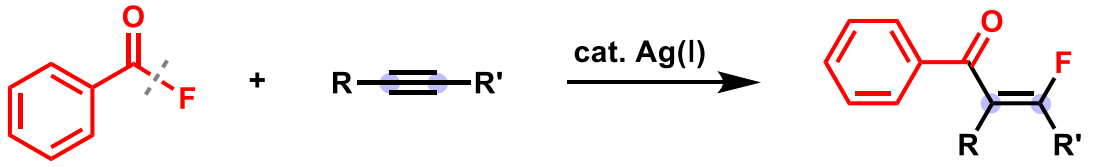
Ag(I)触媒による酸フッ化物の C–F 結合切断を経るアルキンの分子間カルボフルオロ化反応

（阪大院工[1]・阪大 ICS-OTRI[2]）○延命 友哉[1]・鳶巣 守[1,2]
Silver(I)–Catalyzed Intermolecular Carbofluorination of Alkynes Using Acyl Fluorides via C–F Bond Cleavage ([1]*Osaka Univ.*, [2]*ICS-OTRI, Osaka Univ.*) ○Tomoya Emmei,[1] Mamoru Tobisu[1,2]

Organic fluorine compounds play an important role in diverse fields including pharmaceutical, agrochemical, and material sciences. Therefore, the development of catalytic reactions that allows for the synthesis of complex fluorine compounds in an efficient manner is strongly desired. If a carbon–fluorine bond in fluorinated molecules is cleaved and an alkene or alkyne can be inserted in a catalytic manner, it would offer a powerful tool for the synthesis of new organic fluorine compounds with a 100% atom economy. However, such an insertion reaction requires a catalyst that can mediate both cleavage and formation of a C–F bond, which is a challenging problem. In fact, catalytic carbofluorination reactions of unsaturated bonds via C–F bond activation reported so far are limited.[1] Herein, we report on intermolecular carbofluorination of alkynes using acyl fluorides via C–F bond cleavage, which is catalyzed by a silver(I) salt.

Keywords : Silver(I); Carbofluorination, Organic Fluorine Compounds; Acyl Fluorides; C–F Bond Cleavage

有機フッ素化合物は薬学、農学、材料化学を含む多様な分野で重要な役割を果たしている。そのため、複雑なフッ素化合物を効率よく合成する触媒反応の開発が強く求められている。なかでも炭素–フッ素結合を切断してアルケンやアルキンを挿入する反応の開発は、原子効率 100%での新たな有機フッ素化合物の合成を可能とする強力な手法となる。しかし、そういった挿入反応には C–F 結合の切断と形成を担うことのできる触媒が必要であり、困難な課題となっている。実際、これまで報告されてきた C–F 結合への挿入を経る不飽和結合のカルボフルオロ化反応は置換基や基質に制限をともなう限定的なものである。[1)]本研究では、Ag(I)触媒存在下、酸フッ化物とアルキンとを反応させることで C–F 結合の切断をともなう新規分子間カルボフルオロ化反応を達成した。



1) (a) Fujimoto, H.; Kodama, T.; Yamanaka, M.; Tobisu, M. *J. Am. Chem. Soc*. **2020**, *142*, 17323-17328; (b) Yu, X.; Meng, Q.-Y.; Daniliuc, C. G.; Studer, A. *J. Am. Chem. Soc*. **2022**, *144*, 7072–7079; (c) McKnight, E. A.; Arora, I. R.; Pradhan, E.; Fujisato, H. Y.; Ajayi, A. J.; Lautens, M.; Zeng, T.; Le, C. M. *J. Am. Chem. Soc*. **2023**, *145*, 11012; (d) Yoshida,T.; Ohta, M.; Emmei, T.; Kodama, T.; Tobisu, M. *Angew. Chem. Int. Ed*. **2023**, *62*, e202303657.

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銀触媒を用いた二重ベンジル位イソシアノ化反応の開発とその応用

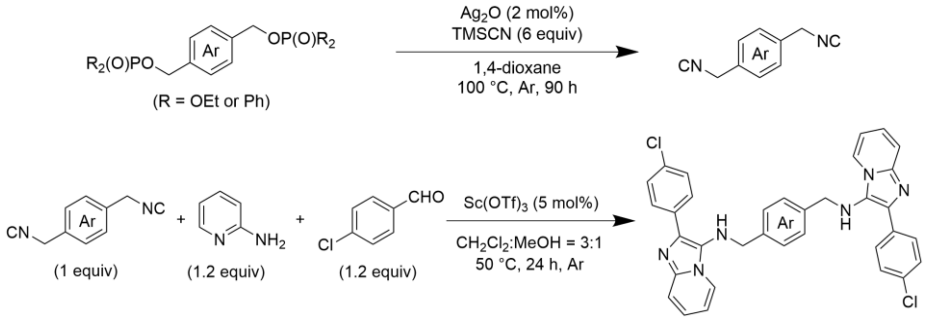
(北大院総化[1]・北大院工[2]・フロンティア化学教育研究センター[3]) ○石川 智子[1]・中村 拓也[1]・百合野 大雅[2,3]・大熊 毅[2,3]

Ag-Catalyzed Double Benzylic Isocyanation and Its Application ([1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [2]*Faculty of Engineering, Hokkaido University*, [3]*Frontier Chemistry Center*) ○Tomoko Ishikawa,[1] Takuya Nakamura,[1] Taiga Yurino,[2,3] Takeshi Ohkuma[2,3]

Isonitriles are chemical equivalents of carbon monoxide with both nucleophilic and electrophilic properties. They are useful reagents in the construction of heteroaromatic compounds with appropriate reactants. Bisisonitriles having two benzylic isocyano groups in the molecular structure can be used as intermediates of fluorescent azole-containing oligoarenes bearing two 3-aminoimidazo[1,2-α]pyridine groups. In this study, we have established the Ag-catalyzed formation of a wide variety of bisisonitriles and their transformation to afford azole-containing oligoarene derivatives.

Keywords : Nucleophilic Isocyanation; Bisisonitrile; Ag Catalysis; Heterocyclization; Multi-Component Reaction

イソニトリルは求核性と求電子性を併せ持つ一酸化炭素等価体であり、適切な反応剤と組み合わせることで多彩なヘテロ芳香族化合物を合成できる。なかでもベンジルイソニトリルと 2-アミノピリジン、アルデヒドとの多成分縮合反応では、生理活性物質や発色団として用いられる 3-アミノイミダゾ[1,2-*a*]ピリジンが 1 段階で合成される[1)]。分子内に二つのベンジルイソシアノ基を有するビスイソニトリルを用いれば、二つの 3-アミノイミダゾ[1,2-*a*]ピリジン骨格を構造中に含む含アゾールオリゴアレーンを一挙に構築することが可能となる。本研究では、基質の母骨格に対して、適切な脱離基をそれぞれ選択することで、中程度から良好な収率で目的のビスイソニトリルが得られることを明らかにした。また、得られた各種ビスイソニトリルに対し、触媒として 5 mol%の $Sc(OTf)_3$ 存在下、それぞれ 1.2 当量の 2-アミノピリジン、*p*-クロロアルデヒドをジクロロメタン/メタノール混合溶媒中 50 ºC において 24 時間反応させた。その結果、目的の含アゾールオリゴアレーンを良好な収率で得ることに成功した。



[1] C. Blackburn, B. Guan, P. Fleming, K. Shiosaki, S. Tsai *Tetrahedron Lett.*, **1998**, *39*, 3635–3638.

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
E1113(1113, Bldg. 11 [1F])

[E1113-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Seihou Jinnai, Yumi Yakiyama

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1113-3am-01]
Synthesis and photophysical properties of donor-acceptor-type triarylmethane dye etinologues

Shigeyuki Yamada[1], ○Hayato Kitaoka[1], Motohiro Yasui[1], Tsutomu Konno[1] (1. Kyoto Institute of Technology)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1113-3am-02]
Synthesis and characterization of tetrafluorinated tolane-type ionic liquid crystals with both photoluminescence and room-temperature liquid-crystalline properties

Shigeyuki Yamada[1], ○Yuto Eguchi[1], Motohiro Yasui[1], Tsutomu Konno[1] (1. Kyoto institute of Technology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1113-3am-03]
Synthesis and Emission Color Tuning of Liquified Boron Difluoride Complexes

○Miku Ichinose[1], Masahiro Ikeshita[2], Takashi Tsuno[2] (1. Graduate School of Industrial Technology, Nihon University, 2. College of Industrial Technology, Nihon University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1113-3am-04]
Synthesis of Triptycene Derivatives for Application in Perovskite Solar Cells

○Akio Hasegawa[1], Tomoya Nakamura[1], Minh Anh Truong[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Institute of Chemical Research, Kyoto University)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1113-3am-05]
Photochromic Luminescence Derived From Photochemical Migrations of Monodentate Ligands in Group 13 Element Complexes

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

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1113-3am-06]
Luminescence properties of aza-boranils and effects of halogen atoms

○Teruki Sawada[1], Masamichi Yasui[1], Takayoshi Arai[1] (1. Graduate School of Science, Chiba University)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1113-3am-07]
Development of Hole-Collecting Monolayer Materials Based on Isotriazatruxene Structure

○Yuta Adachi[1], Minh Anh Truong[1], Tomoya Nakamura[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Institute for Chemical Research, Kyoto 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
[E1113-3am-08]
Water-soluble pyrene-polymer conjugates that function as pressure-responsive chemosensors with distinctive uptake into human tumors.

○Yumiko HORI[1], Takao SAIKI[3], Xinyi Qi[2], Keiichi NAKAGAWA[2], Gaku FUKUHARA[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Bioengineering, The University of Tokyo, 3. Department of Precision Engineering, The University of Tokyo)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1113-3am-09]
Photo-responsive hydrogen storage using amine-B(C_6F_5)$_3$-based FLP system

○Keisuke Nakamura[1], Maki Miyamoto, Aki Okamoto, Tatsushi Imahori[1] (1. The Tokyo Univ. of Science)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1113-3am-10]
A water-soluble pressure-responsive chemosensor that exhibit thermally activated delayed fluorescence: Hydrostatic pressure effects and cellular uptake

○Kotaro Matsumoto[1], Youhei TAKEDA[2], Keiichi NAKAGAWA[3], Gaku FUKUHARA[1] (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Applied Chemistry, Osaka University, 3. Department of Bioengineering, The University of Tokyo)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1113-3am-11]
Diphenylphosphonium-Bridged Fluorescent Dyes for Mitochondrial Imaging

○Ayato Hakamada[1], Masayasu Taki[3], Masahito Murai[2], Shigehiro Yamaguchi[2,3,4] (1. Faculty of Science, Nagoya University, 2. Graduate school of science, Nagoya University, 3. ITbM, Nagoya University, 4. IRCCS, Nagoya University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1113-3am-12]
Aggregation-Induced Emission Enhancement of tris(naphthaleneimide)-substituted benzenes

○Toshiaki Ikeda[1], Yuhei Takahashi[1], Hiro Sugawara[1], Haruki Furukoshi[1] (1. Tokai University)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1113-3am-13]

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Chirality Singal-amplification Sensing via a Sumanene-based Supramolecular Polymerization

○Ruipu Qi[1], Hiroaki Mizuno[1], Yumi Yakiyama[2], Hidehiro Sakurai[2], Gaku Fukuhara[1] (1. Tokyo Institute of Technology, 2. Osaka University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[E1113-3am-14]

Fe^{3+}-Specific Photoluminescence by 17-Membered Macrocyclic Ligands with Amino, Amide, and Carbamate Groups in the Cyclic Skeleton Bearing Anthracene or Pyrene as Chromophores

○Izumi Sato[1], Hiroki Horita[1], Mari Ikeda[2], Shunsuke Kuwahara[1], Yoichi Habata[1] (1. Toho Univ., 2. Chiba Inst. of Tech.)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[E1113-3am-15]

Synthesis and photophysical properties of ESIPT-capable 4,6-bis(phenanthroimidazol)resorcinol and its analogues.

○Shota Sugi[1], Motoko Akita[1] (1. Josai University)

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ドナー-アクセプター型トリアリールメタン系色素エチノローグの合成と光学特性評価

（京工繊大工芸）山田 重之・○北岡 勇人・安井 基博・今野 勉
Synthesis and photophysical properties of donor-acceptor-type triarylmethane dye ethynologues (*Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology*) Shigeyuki Yamada, ○Hayato Kitaoka, Motohiro Yasui, Tsutomu Konno

Recently, our group discovered that fluorinated tolanes, which are composed of a julolidine skeleton as an electron-rich aromatic ring and a tetrafluorobenzonitrile skeleton as an electron-poor aromatic ring, emit red light in the crystalline state. Using a carbocation as an electron-accepting site instead of a fluorinated aromatic ring can further improve donor-acceptor (D-A) properties and is expected to offer interesting photophysical properties. Therefore, we developed a D-A-type triarylmethane dye ethynologue **1** with julolidine as a donor moiety, and aimed to elucidate their photophysical properties and the structure-property relationship.
Keywords : Dye; Triarylmethane dye ethynologue; Carbocation; Donor-Acceptor

近年、当研究室ではドナー–アクセプター (D-A) 型フッ素化トランを開発し、ジュロリジンを電子供与部位とした誘導体が結晶中で赤色発光することを見出した。フッ素化トランによる電子受容部位をカルボカチオンに変更することでさらに大きな D-A 性を誘起し、興味深い光学特性の発現が期待できる。そこで本研究では、**Figure 1** に示す D-A 型トリアリールメタン系色素エチノローグの合成と、その光学特性評価を検討した。

化合物 **1a** は紫色の粉末でジクロロメタンに溶解すると青色に呈色した。希薄溶液中、624 nm に極大吸収波長 (λ_{abs}) を、732 nm に極大発光波長 (λ_{PL}) を示すことがわかった (**Figure 2a**)。しかし、蛍光量子収率は、0.01 以下と非常に小さい値となった。また固体状態では 750 nm 付近まで強い吸収を示すことがわかった。本発表では、カルボカチオンに結合した芳香環上の置換基を種々変化させた誘導体 **1b** および **1c**、さらに対アニオンも変更させた誘導体の合成を検討し、それらの光学特性評価についても述べる予定である。

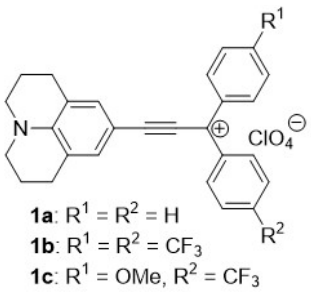

Figure 1. Chemical Structures of **1a-c**

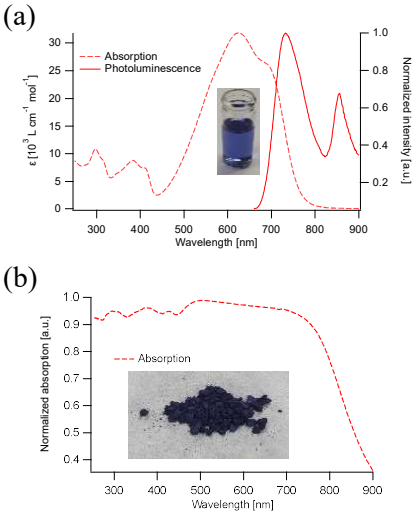

Figure 2. Photophysical properties of **1a** (a) in DCM and (b) in solid states.

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四フッ素化トランをメソゲンとした発光性室温イオン液晶分子の合成および物性評価

（京工繊大工芸）山田 重之・○江口 優人・安井 基博・今野 勉

Synthesis and characterization of tetrafluorinated tolane-type ionic liquid crystals with both photoluminescence and room-temperature liquid-crystalline properties (*Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology*) Shigeyuki Yamada, ○Yuto Eguchi, Motohiro Yasui, Tsutomu Konno

Recently, our interest has been directed toward the development of multifunctional molecules that possess both efficient photoluminescence and room-temperature liquid-crystalline (LC) characteristics, which would have potential applications in optical devices. Our group has developed a series of difluorinated tolane-based LC molecules with flexible chains with imidazolium ions at the ends, which exhibit room-temperature LC properties when they have a large counteranion. On the other hand, the PL efficiency has not yet reached a satisfactory result. Aiming to improve PL efficiency by inducing multiple intermolecular H···F hydrogen bond formation to suppress non-radiative deactivation, we attempted the development of tetrafluorinated tolanes with flexible chains with imidazolium ions at the ends, and investigated their LC and PL properties.

Keywords : Fluorine; Ionic liquid crystals; Photoluminescence; Fluorinated tolane; Counter anion

近年、次世代ディスプレイ材料として液晶性と発光特性を併せもつ有機分子の開発が求められている。当研究室では、トラン骨格にフッ素原子を導入することで H-F 水素結合により分子軸回転を阻害し発光特性の向上を報告している。そこで、フッ素化トランの凝集構造に注目し、その骨格をメソゲンとした液晶分子の開発を試みた。本研究では四フッ素化トランをメソゲンかつ発光部位とし、柔軟鎖末端にイオン部位を有する新規な液晶性発光分子を設計・合成し液晶性および光学特性について調査した。

本研究で新たに開発した **4FCF$_3$-OTf** **(Fig. 1)** の液晶性を評価したところ、室温にて扇状の光学組織が確認され、SmA 相の発現を確認した **(Fig. 2, inset)**。しかし、加熱により最安定構造である結晶状態に最配列したため、第一冷却過程以降には液晶相の発現は確認されなかった。また、**4FCF$_3$-OTf** は液晶状態で 415 nm に極大発光波長をもつ青色蛍光が観察された **(Fig. 2)**。蛍光量子収率は 57 %であり，非常に高い発光効率であった。これは H-F 水素結合により無輻射失活が抑制されたためであると推察している。本発表では、その他の誘導体の液晶特性ならびに光学特性についても併せて発表する。

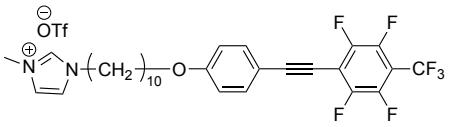

Fig. 1 Chemical structure of **4FCF$_3$-OTf**.

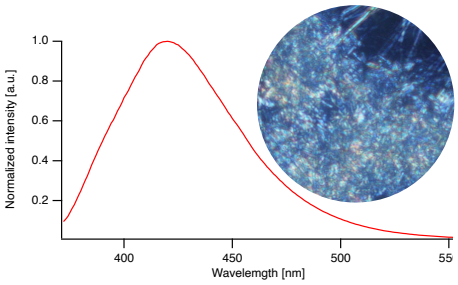

Fig. 2 PL spectrum of **4FCF$_3$-OTf** and POM image in liquid crystal.

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液状化二フッ化ホウ素錯体の合成と発光色調制御

（日大院生産工[1]・日大生産工[2]）○一ノ瀬 未来[1]・池下 雅広[2]・津野 孝[2]
Synthesis and Emission Color Tuning of Liquified Boron Difluoride Complexes ([1]*Graduate School of Industrial Technology, Nihon University*, [2]*College of Industrial Technology, Nihon University*) ○Miku Ichinose,[1] Masahiro Ikeshita,[2] Takashi Tsuno[2]

Solvent-free luminous molecular liquids (LMLs) have an advantage that ease of fabrication, processing under solvent-free conditions and non-volatility. They are potentially applicable to flexible optical devices and recognized as next-generation soft-materials. In this study, we developed room-temperature liquefied boron difluoride complexes **1a−4a** with polyethylene glycol chains. These complexes exhibited blue to yellow luminescence in the solvent-free liquid state. Furthermore, we have succeeded in luminescence color tuning by dissolving luminescent organic solid in **1a**. As the molar ratio of luminescent organic solids increases, the emission color of the composite changed from blue to yellowish-white.

Keywords : *Solvent-free luminous molecular liquids; Boron complexes; Shiff-base ligands Polyethylene glycol chains*

無溶媒発光性分子液体材料(LMLs)は成形の容易さや不揮発性、溶媒を使用せずに他の物質と攪拌できるといった利点から、フレキシブルな光学デバイスへの応用が期待されており、次世代のソフトマテリアルとして様々な化合物が報告されている [1)]。我々の研究グループでは、キラルな分子骨格を有したシッフ塩基配位子のベンゼン環上にポリエチレングリコール(PEG)鎖を導入することで、常温で液体状態を保持する円偏光発光性キラルホウ素錯体の合成に成功している [2)]。本研究ではシッフ塩基配位子の窒素上に PEG 鎖を導入した二フッ化ホウ素錯体の合成 **1a−4a** の合成を行った。ホウ素錯体 **1a−4a** は室温下で液体状態を保持し、紫外線ライト照射下では青から黄色の発光を示した。さらに、**1a** に赤色発光性の rubrene と緑色発光性の Alq_3(tris(8-hydroxyquinolinato)aluminium を溶解させることにより、発光色調を制御することに成功した。複合体の発光色は、複合体中の固体色素の混合モル比を増加させることで青から黄白色へと調整できた。

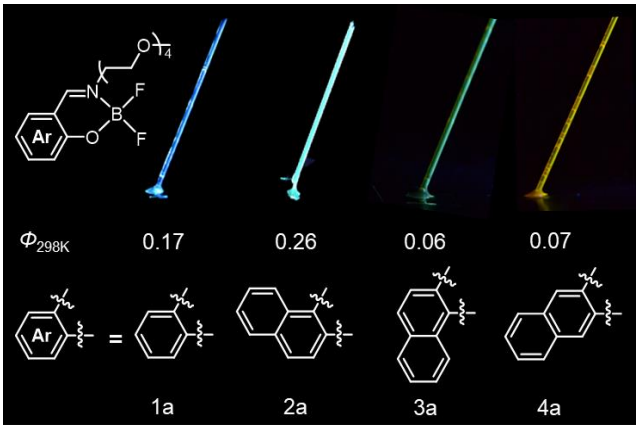

図 1. 錯体 **1a−4a** の液体状態における紫外線照射下での発光挙動

1) F. Lu, T. Nakanishi, *Adv. Opt. Mater.* **2019**, *7*, 1900176.
2) M. Ikeshita, T. Oka, M. Kitahara, S. Suzuki, Y. Imai, T. Tsuno, *Chem. Lett.* **2023**, *52*, 556.

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ペロブスカイト太陽電池への応用を指向したトリプチセン誘導体の合成

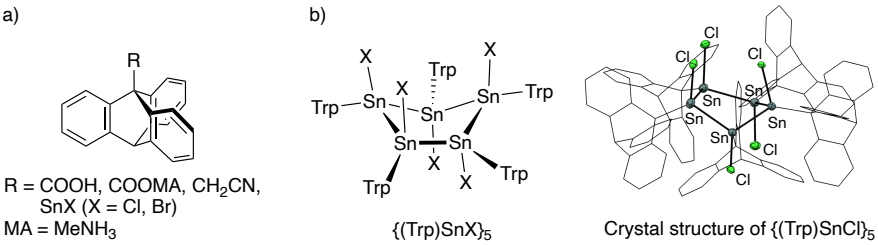
（京大化研）○長谷川 晃央・中村 智也・ミンアン チョン・リチャード マーディー・若宮 淳志

Synthesis of Triptycene Derivatives for Application in Perovskite Solar Cells (*Institute of Chemical Research, Kyoto University*) ○Akio Hasegawa, Tomoya Nakamura, Minh Anh Truong, Richard Murdey, Atsushi Wakamiya

Due to their high efficiencies, ABX_3-type perovskite soler cells recently have attracted huge research interest. Surface modification and control of crystal orientation are promising ways to improve their performance. In this study, halostannylene derivative that possesses 9-triptycyl (Trp) groups was synthesized. Containing Sn, the B-site atom in perovskite, and Trp group, which has the ability of self-assembly, this compound can be used to passivate the surface of perovskites. As revealed by XRD and NMR, this compound is pentamerized in the solid state and exists as a monomer in dimethyl sulfoxide solution.

Keywords : Perovskite; Hetero Atoms; Triptycene; Molecular Self-assembly; X-ray Crystallographic Analysis

ABX_3 型ペロブスカイト半導体を用いた太陽電池が注目を集めている。その高性能化には表面修飾や結晶方位の制御が重要とされている。最近、シクロヘキシルアミンやフェネチルアンモニウムをパッシベーション材料として用いることで結晶方位が制御され、安定性が向上することが報告された[1]。本研究では、トリプチセン骨格の入れ子状に自己集合する特性に着目し、これをペロブスカイト表面に導入することで、結晶方位の制御が可能になると期待した。まず、ペロブスカイトの鍵前駆体となるトリプチセン誘導体の合成をするため、9-ブロモトリプチセン（TrpBr）を出発原料としてリチオ化後、ABX_3 の各サイトに対応する置換基を導入した（Figure 1a）。B サイトに対応すると考えられる二価のスズハライドとして合成した (Trp)SnX (X = Cl, Br)の X 線結晶構造解析の結果、環状に五量化した構造を示した（Figure 1b）。^{119}Sn NMR において、ペロブスカイトの前駆体溶液に用いる DMSO 溶媒中では、単量体として存在することが確認され、パッシベーション材料として機能することが期待できる。発表では、それらの構造とペロブスカイト太陽電池への応用について議論する予定である。



1) (a) S. J. Kwon, M. Grätzel, N.-G. Park et al., *Science* **2023**, *379*, 173. (b) S. J. Kwon, C.-W. Yang, Y. Yang, N.-G. Park, et al., *J. Am. Chem. Soc.* **2023**, *145*, 24349.

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Photochromic Luminescence Derived From Photochemical Migrations of Monodentate Ligands in Group 13 Element Complexes

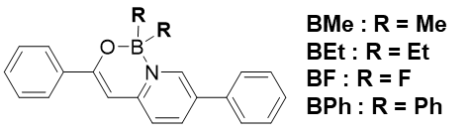
(*Graduate School of Engineering, Kyoto University*) ○Yuto AOYAMA, Shunichiro ITO, Kazuo TANAKA

Keywords: Group 13 Complex; Stimuli Responsiveness; Emission; Boron; Photochemical Reactions

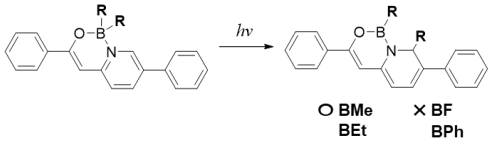
Stimuli-responsive luminescent materials change the emission color or intensity in response to various external stimuli. Due to their fruitful functions, the materials have attracted great attention for their applications in light-sensing technology. We have reported that various pyridylenolate boron complexes show stimuli-responsive luminescence.[1,2] Herein, we found that the pyridylenolate complexes exhibited a photochromic luminescence derived from unprecedented photochemical migrations of monodentate ligands (Schemes 1 and 2).

We synthesized the boron pyridylenolate complexes with various monodentate ligands (Scheme 1). Among them, **BMe** and **BEt** showed photochemical migration of monodentate ligands in their solution states and irreversible photochromic luminescence (Scheme 2 and Figure 1). Interestingly, the degree of photochromic luminescence depended on temperature (Figure 1). Utilizing the synergetic responsiveness to light and temperature, we demonstrated the applicability of the complexes to luminescence thermography, which can qualitatively and quantitatively memorize the temperature when and where they are irradiated by UV light (Figure 2). In addition, since the photochromic change occurred only at the bulk surface, the materials can be reused by scratching the powder and exposing the unchanged bulk (Figure 1).

Scheme 1. Chemical structures of boron pyridylenolate complexes



Scheme 2. Photochemical migrations of monodentate ligands



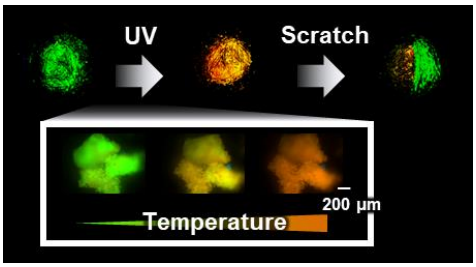


Figure 1. Photochromic luminescent behaviors of **BMe**.

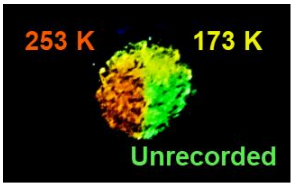


Figure 2. Luminescence thermography utilizing the powder of **BMe**.

1) Tanaka, K. *et al*. *Mater. Chem. Front.* **2020**, *4*, 1781. 2) Chujo, Y. *et al. EJOC*. **2017**, 5191.

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アザボラニル類の発光特性とハロゲン原子置換の効果

（千葉大院理）○澤田 輝貴・安井 将満・荒井 孝義
Luminescence properties of aza-boranils and effects of halogen atoms
(Graduate School of Science, Chiba University) ○Teruki Sawada・Masamichi Yasui・Takayoshi Arai)

Boranils, organoboron complexes based on salicylaldimine ligands, have garnered significant attention owing to their potential applications in organic light-emitting materials.[1)] In this study, we developed aza-boranil and haologenated aza-boranils in which the aniline moieties of boranils were replaced with aminopyridines (Figure 1).

Aza-Boranils **1**, parent **1a** and **1b-e** with halogen atoms, were easily prepared in excellent yields by a similar procedure to the synthesis of boranils. Upon the photoluminescence measurement of **1a-e**, the electron-withdrawing substituent induced a redshift in the emission maxima (Table). Furthermore, the crystal of **1c** bearing a chlorine atom exhibited mechano- and vapochromic properties (Figure 2).

Keywords : Organic Luminescent Materials; Halogen Atoms; Mechanochromism; Boranils

サリチリデンアニリンとジフルオロホウ素から形成される有機ホウ素錯体、ボラニル類は、その優れた発光特性から、有機発光材料へ応用が期待されている[1)]。今回我々は、新たなボラニル類縁体として、サリチリデンアニリンのアニリン部位がアミノピリジンに置換された、アザボラニル **1** を設計した (Figure 1) 。

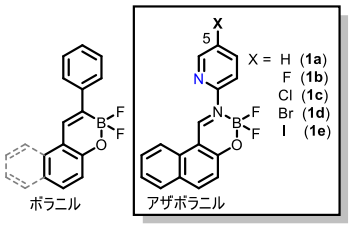

Figure 1. Boranils and Aza-Boranils

アザボラニル **1** は一般的なボラニルと同様の手法により合成でき、いずれも良好な収率で得た。これらの発光特性を明らかにすべく、ジクロロメタン溶液および結晶状態における発光スペクトルを測定した (Table) 。溶液状態においてアザボラニル **1a-e** の極大発光波長は、置換基の種類によってほとんど変化しなかったものの、置換基の導入により発光量子収率が改善し、特にフッ素体 **1b** では 30%まで向上した。一方、**1b-e** の結晶は、置換基の電子求引性が増すにつれ、発光波長が長波長シフトした。また、ジエチルエーテルから得た塩素体 **1c** の結晶に対し機械的刺激を与えると、発光色が緑色から黄色へ変化した (Figure 2) 。また、**1c** のジクロロメタン溶液から溶媒を急速に留去すると、橙色の発光を示す結晶が得られた。

本発表ではアザボラニル **1a-e** やその類縁体の発光特性、および塩素体 **1c** のクロミズム特性について、粉末 X 線回折、単結晶 X 線構造解析、(TD-)DFT 計算などを用い議論する。

Table. Photophysical properties of **1**

Compound	x	DCM solution λ_{em} /nm	DCM solution Φ_{PL}	Solid States[1] λ_{em} /nm	Solid States[1] Φ_{PL}
1a	**H**	457	0.20	493	0.35
1b	**F**	458	0.30	498	0.68
1c	**Cl**	463	0.27	502	0.37
1d	**Br**	465	0.26	512	0.15
1e	**I**	463	0.16	525	0.020

[1]recrystallized from diethy ether

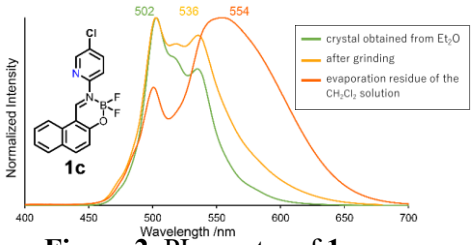

Figure 2. PL spectra of **1c**

1) Boranils: Versatile Multifunctional Organic Fluorophores for Innovative Applications. J. Massue, D. Jacquemin, G. Ulrich, *Organics* **2021**, *2*, 365.

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イソトリアザトルキセン骨格を有する正孔回収単分子膜材料の開発

（京大化研[1]）○足立 裕太[1]・チョン ミンアン[1]・中村 智也[1]・マーディー リチャード[1]・若宮 淳志[1]

Development of Hole-Collecting Monolayer Materials Based on Isotriazatruxene Structure

([1]*Institute for Chemical Research, Kyoto University*) ○Yuta Adachi,[1] Minh Anh Truong,[1] Tomoya Nakamura,[1] Richard Murdey,[1] Atsushi Wakamiya[1]

The development of efficient charge-collecting materials is important to further improve the performance of perovskite solar cells (PSCs). Recently, PSC devices using hole-collecting monolayers (HCMs) have been reported to show superior efficiency and stability.[1,2]

In this study, a series of isotriazatruxene derivatives bearing three phosphonic anchoring groups (**iso-PATAT**) was designed as hole-collecting monolayer materials. By using commercially available indole derivatives as starting materials, target molecules were successfully synthesized via three steps, including Cu-catalyzed cyclization, nucleophilic substitution, and deprotection reactions (Figure 1). In this presentation, molecular design and characterization as well as device fabrication and evaluation will be discussed in detail.

Keywords : Perovskite Solar Cell; Monolayer; Hole-Collecting Material; Isotriazatruxene; Chemisorption

ペロブスカイト太陽電池の高性能化には、光吸収により生成する電荷を効率的に回収する半導体材料の開発は重要となっている[1]。最近、当研究室でも、トリアザトルキセン誘導体を単分子膜を正孔回収材料に用いることで、高い光電変換効率と優れた安定性を示すペロブスカイト太陽電池が得られている[2]。

本研究では、新たな正孔回収単分子膜材料として、イソトリアザトルキセン骨格に金属酸化物表面への吸着力を有するホスホン酸基を三つ導入した一連の化合物の設計をした。入手容易なインドール誘導体から、銅触媒による環化反応、求核置換反応および脱保護反応を用いて標的分子群を合成した（図 1）。本発表では、これらの分子設計と基礎特性と、これらの単分子膜を正孔回収層に用いたペロブスカイト太陽電池の作製と特性について詳細に報告する。

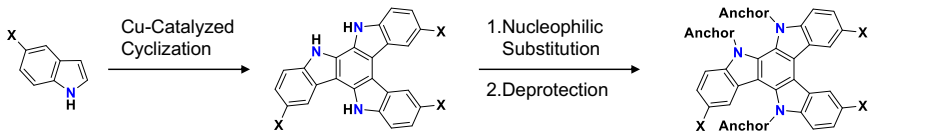

Figure 1. Synthesis route for target molecules.

1) A. Al-Ashouri, V. Getautis, S. Albrecht et al., *Science* **2020**, *370*, 1300.
2) M. A. Truong, A. Wakamiya et al., *J. Am. Chem. Soc.* **2023**, *145*, 7528.

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水溶性感圧化学センサー：ピレン修飾ポリマーの光学特性および細胞導入

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Water-soluble pyrene-polymer conjugates that function as pressure-responsive chemosensors with distinctive uptake into human tumors. ([1]*Department of Chemistry, Tokyo Institute of Technology*, [2]*Department of Precision Engineering, The University of Tokyo*, [3]*Department of Bioengineering, The University of Tokyo*) ○Yumiko Hori,[1] Takao Saiki,[2] Xinyi Qi,[3] Keiichi Nakagawa,[2,3] Gaku Fukuhara[1]

Mechanical properties in living systems become an attractive alternative to conventional biomarkers. In the present study, we synthesized the pressure-responsive biocompatible chemosensors such as pyrene-polystyrene, pyrene-polylysine, and pyrene-rhodamine-polystyrene conjugates, and then investigated their fluorescence properties upon the hydrostatic pressurization and uptake behavior into HeLa cells. The fluorescence properties and conformational changes of the polymer chemosensors under hydrostatic pressures and biocompatibility will be discussed.

Keywords : Chemosensor; Pyrene; Polymer; HeLa cell

がん細胞と正常細胞の弾性率の差に基づき、細胞の力学的性質が新たなバイオマーカーとして注目されている[1]。当研究室では、静水圧（溶液中の等方的な圧力）下のコンフォメーション変化や発色団の分子間相互作用の変化に着目し、種々の感圧化学センサーの開発を行っている[2]。本研究では、細胞内の音響波（動圧）イメージングのため、静水圧への応答を調査し、圧力と光学特性の相関を取得した。

発色団としてピレンを修飾したポリスチレン（**PSpyr**, Fig. 1a）とポリリシン（**PLLpyr**, Fig. 1b）、さらなる圧力感受性が期待できる FRET（蛍光共鳴エネルギー移動）を示すポリマー（**PSpyr-Rhod**, Fig. 1c）を合成した。静水圧下での光学特性を比較した結果、主鎖構造によって異なる静水圧応答性を示すことがわかった。本発表では、静水圧下における主鎖のコンフォメーションや置換度が及ぼす影響、細胞導入実験に基づく生体への適用可能性について検討したので報告する。

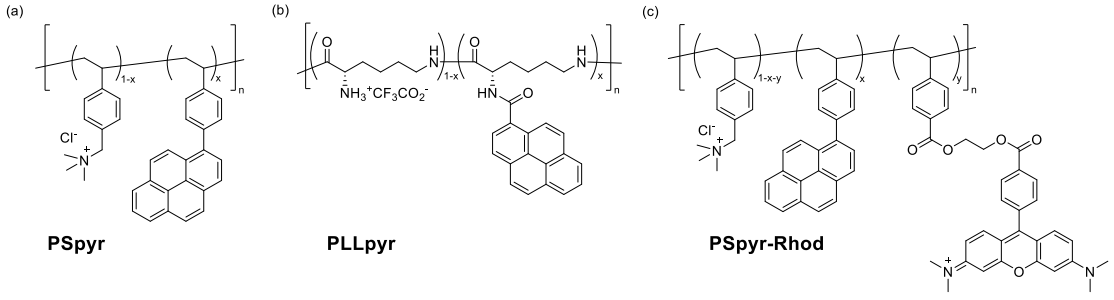

Figure 1. Chemical structures of (a) pyrene-polystyrene (**PSpyr**), (b) pyrene-polylysine (**PLLpyr**), and (c) pyrene-rhodamine-polystyrene (**PSpyr-Rhod**) conjugates, respectively.

1) Cross, S. E.; Jin, Y. S.; Rao, J.; Gimzewski, J. K. *Nat. Nanotech.* **2007**, 2, 780–783.
2) Mizuno, H.; Fukuhara, G. *Acc. Chem. Res.* **2022**, 55, 12, 1748–1762.

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光による水素貯蔵技術を目指したアゾベンゼンアミン-$B(C_6F_5)_3$ 系 FLP システムの開発

（東理大院工 [1]）○中村圭佑 [1]・宮本真希・岡本暁・今堀龍志 [1]

FLP system with azobenzene-amine and $B(C_6F_5)_3$ for Photo-responsive hydrogen storage

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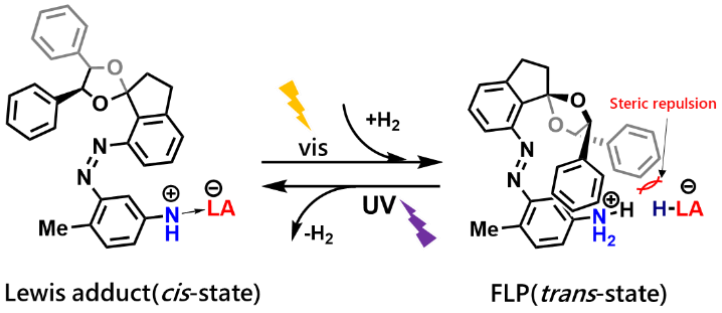
Since hydrogen is attracting attention as a next-generation energy, development of sustainable storage system for hydrogen is need. To develop the sustainable storage system, we focused on Frustrated Lewis Pair (FLP), which is a useful chemical absorption method of hydrogen. By combining FLP and photo-isomerization of azobenzene, we designed and developed a new hydrogen storage system that absorbs and releases hydrogen using light. We envisioned that combination of the azobenzene-based Lewis base and $B(C_6F_5)_3$ would switch the function as FLP by controlling bulkiness of the Lewis base through photo-responsive structural changes of the azobenzene core, which would change hydrogen absorption and release by light. The designed FLP system was synthesized and evaluated.

Keywords : Hydrogen storage material; Photo-responsive molecule; Frustrated Lewis Pair

次世代エネルギーとして注目される水素の持続可能な貯蔵技術が必要であり、本研究では水素の有用な化学吸収法である Frustrated Lewis Pair（FLP）に着目した新たな水素貯蔵システムの開発を行なった。FLP はともに嵩高い Lewis 酸・塩基の組み合わせであり、水素のような小分子を不均一に開裂させて吸収し、加熱により放出可能な反応系である [1]。FLP による水素貯蔵と放出に加熱を行わずに光で制御することができれば、クリーンな水素貯蔵技術を実現できると考え、光エネルギーを利用した FLP システムを設計した（右下図）。可逆的な光異性化を行うアゾベンゼンを骨格にもつ Lewis 塩基分子を開発し、その光構造変換により、Lewis 塩基活性点周辺の嵩高さを調節することで、FLP としての機能を切り替えることを想定した。具体的には、*trans*-アゾベンゼン体では嵩高いアセタール部位が Lewis 塩基活性点であるアミノ基の周辺の嵩高さを増大させて FLP として機能すると仮定した。一方、*cis*-アゾベンゼン体ではアミノ基周辺の嵩高さが減少し、FLP の形成が困難になると推定した。

設計した Lewis 塩基分子を合成し、$B(C_6F_5)_3$ を Lewis 酸に用いて光応答性の FLP の機能を評価した。



1) “Frustrated Lewis pairs”: a concept for new reactivity and catalysis. Douglas W. Stephan, *Org. Biomol. Chem.*, **2008**, 6, 1535-1539

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熱活性化遅延蛍光を示す水溶性感圧化学センサー：静水圧効果および細胞導入

（東工大理[1]・阪大院工[2]・東大院工[3]）○松本 晃太朗[1]・武田 洋平[2]・中川 桂一[3]・福原 学[1]

A water-soluble pressure-responsive chemosensor that exhibit thermally activated delayed fluorescence: Hydrostatic pressure effects and cellular uptake ([1]*Department of Chemistry, Tokyo Institute of Technology*, [2]*Department of Applied Chemistry, Osaka University*, [3]*School of Engineering, The University of Tokyo*) ○Kotaro Matsumoto,[1] Youhei Takeda,[2] Keiichi Nakagawa,[3] Gaku Fukuhara[1]

Mechanical probes are powerful tools for checking living systems, which will lead to further health promotion. In the present study, we focused on a chemosensor that shows thermally activated delayed fluorescence. The fluorescence properties under hydrostatic pressures and cellular uptake of the chemosensor will be discussed.

Keywords : Chemosensor; Thermally Activated Delayed Fluorescence; Hydrostatic Pressure

がん細胞の弾性率は正常細胞よりも小さい（異なる）ことから、細胞の力学的性質はバイオマーカーとして利用できる[1]。当研究室では、静水圧（溶液中に等方的にかかる圧力）下のコンフォメーション変化や発色団の分子間相互作用の変化に着目し、感圧化学センサーの開発を行っている[2]。本研究では、細胞内のリアルタイムな圧力（動圧や衝撃波）伝播イメージングのため、はじめに静水圧への応答を調査した。

熱活性化遅延蛍光（Thermally Activated Delayed Fluorescence, TADF）が活性な D-A-D triad を親水性のデンドリマーで修飾した **Dend-MCM**（Fig. 1）について静水圧下での光学特性を調査した[3]。静水圧の増加に伴い蛍光強度の変化が観測された。静水圧が **Dend-MCM** のコンフォメーションに及ぼす影響や細胞導入について検討したので報告する。

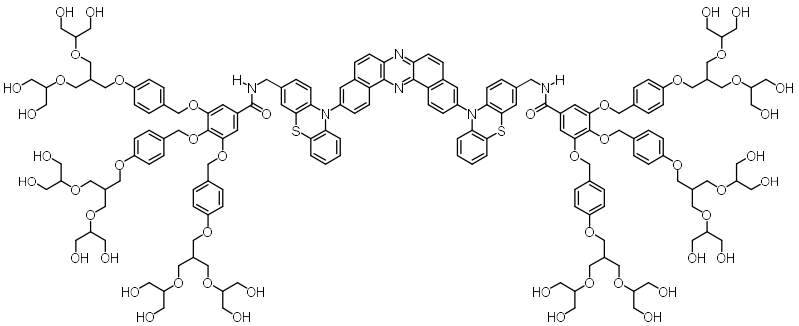

Figure 1. Chemical structure of **Dend-MCM**.

1) Cross, S. E.; Jin, Y. S.; Rao, J.; Gimzewski, J. K. *Nat. Nanotech.* **2007**, 2, 780–783.
2) Mizuno, H.; Fukuhara, G. *Acc. Chem. Res.* **2022**, 55, 12, 1748–1762.
3) Takeda, Y.; Mizuno, H.; Okada, Y.; Okazaki, M.; Minakata, S.; Penfold, T.; Fukuhara, G. *ChemPhotoChem* **2019**, *3*, 1203–1211.

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ミトコンドリアイメージングを志向したジフェニルホスホニウム架橋型蛍光色素の開発

（名大理[1]・名大院理[2]・名大 ITbM[3]・名大 IRCCS[4]）○袴田 彩仁[1]・多喜 正泰[3]・村井 征史[2]・山口 茂弘[2,3,4]

Development of Diphenylphosphonium-Bridged Fluorescent Dyes for Mitochondrial Imaging

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Most dyes employed for mitochondrial imaging possess a lipophilic cationic moiety such as triphenylphosphonium, resulting in considerable molecular weights and limited functional expandability. Herein, a novel ladder-type fluorescent dye **1** containing a cationic diphenylphosphonium as a bridging entity was synthesized. This compound exhibited absorption and emission maxima at 460 nm and 575 nm, respectively, in an aqueous solution containing 10% DMSO. Notably, it showed almost no dependence on solvent polarity, maintaining a consistently high fluorescence quantum yield of 60% in aqueous environments.

Fluorescence imaging of HeLa cells stained with this compound demonstrated mitochondria specific localization. Remarkably, it allowed mitochondrial staining at concentrations as low as 50 nM. Moreover, super-resolution STED imaging exhibited clear cristae structures, indicating that the dye selectively localized within the inner mitochondrial membrane.

Keywords : cationic π conjugating molecule; ladder-type skeleton; phosphonium; mitochondria labeling; organic fluorescent dye

ミトコンドリアイメージングに使用される蛍光色素は，トリフェニルホスホニウムに代表される脂溶性のカチオン性基を連結させたものが多い．そのため，分子量が大きくなってしまうことに加え，機能の拡張性も制限されていた．本研究では，カチオン性のジフェニルホスホニウムを架橋基として有する新たなラダー型蛍光色素 **1** を開発した．**1** は，10%DMSO を含む水溶液中で 460 nm および 575 nm にそれぞれ吸収および発光極大を示した．溶媒の極性依存性はほとんど示さず，蛍光量子収率は水溶液中においても 60%と高い値を保っていた．

本化合物を用いて HeLa 細胞の蛍光イメージングを行なったところ，ミトコンドリアが選択的に染色される様子が確認された．特筆すべきことに，本化合物は 50 nM という低い濃度でミトコンドリアを染色することが可能であった．また，STED 顕微鏡を用いて蛍光イメージングを行なったところ，図のようなミトコンドリアのクリステ構造が観察され，本化合物はミトコンドリア内膜に保持されていることが推測された．

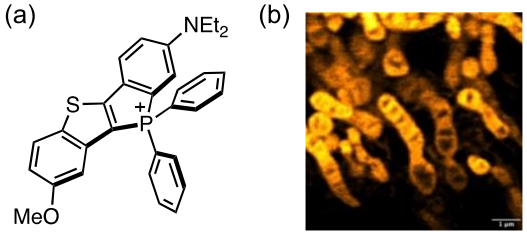

Figure. (a) Structure of diphenylphosphonium-bridged fluorescent dye **1**. (b) STED image of inner mitochondrial membrane with **1**.

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ナフタレンイミドで三置換されたベンゼンの凝集誘起発光増強

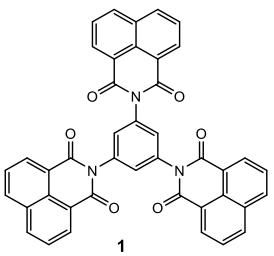
（東海大院理）○池田 俊明・高橋 侑平・菅原 嘉・古越 悠樹
Aggregation-Induced Emission Enhancement of Tris(naphthaleneimide)-substituted Benzenes (*Graduate School of Science, Tokai University* ○Toshiaki Ikeda, Yuhei Takahashi, Hiro Sugawara, Haruki Furukoshi

The luminescence of organic dyes is frequently quenched due to their stacked structure in the condensed phase, which is called as aggregation caused quenching (ACQ). Introduction of the non-planar structure is a promising approach to avoid ACQ, and that gives aggregation-induced emission enhancement (AIEE). In this study, benzens equipping three naphthaleneimide moieties **1-3** were synthesized. The benzene ring and the naphthaleneimide moieties of these molecules take non-planar configuration due to the steric repulsion between the hydrogen atom of benzene and the oxygen atom of imide.

Optical properties of these molecules were investigated using UV-vis absorption and emission spectroscopies. In THF, these molecules displayed only weak emissions. The addition of water to the THF solution caused enhancement of emission; the emission was increased 130-fold in THF-water (2:8) solution. The molecules form aggregates with increasing the content of water, resulting in the emission enhancement. In this presentation, the AIEE properties and host-guest chemistry of **1-3** will be reported.

Keywords : Aggregation-Induced Emission Enhancement, Naphthaleneimide, Luminescent Dye

発光性色素が凝集することで強い発光を示す凝集誘起発光増強（Aggregation-Induced Emission Enhancement, AIEE）が近年注目を集めている。AIEE の実現のためには、凝集状態で積層しないかさ高い構造と、溶液中で熱運動する置換基が必要である。本研究では、ベンゼン環にナフタレンイミドを三置換した色素 **1-3** を合成した。これらの色素は中央のベンゼン環の水素原子とナフタレンジイミドのカルボニル基との立体反発によってベンゼン環とナフタレン環が非平面となる。そのため、積層構造を形成することが難しく、AIEE を示すことが期待される。



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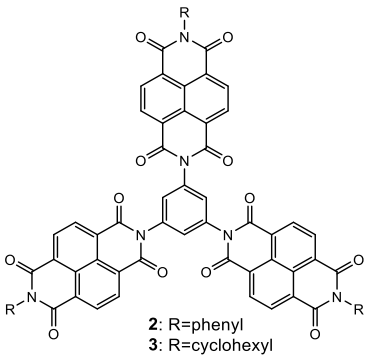

2: R=phenyl
3: R=cyclohexyl

紫外可視吸収および蛍光スペクトルを用いて光学特性について検討した。THF と水の混合溶媒において、THF のみを溶媒とした場合は弱い発光が観察された一方で、水の比率が増加すると長波長シフトした強い発光が観察された。これは水の割合が増えることによって凝集体を形成した結果であり、これらの色素が AIEE 特性を有することが示唆された。。本発表では、**1-3** の光学特性およびホスト―ゲスト錯体形成について報告する。

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キラリティー修飾スマネンをモノマーとする超分子ポリマー形成及びシグナル増幅センシング

（東工大理[1]・阪大院工[2]）○戚 瑞璞[1]・水野 裕彬[1]・燒山 佑美[2]・櫻井 英博[2]・福原 学[1]

Chirality Singal-amplification Sensing via a Sumanene-based Supramolecular Polymerization

([1]*Department of Chemistry, Tokyo Institute of Technology*, [2]*Department of Applied Chemistry, Osaka University*) ○Ruipu Qi,[1] Hiroaki Mizuno,[1] Yumi Yakiyama,[2] Hidehiro Sakurai,[2] Gaku Fukuhara[1]

We synthesized indole-modified sumanene as a chemosensor, which was then mixed with pristine sumanene to afford a sumanene-based hetero supramolecular polymer. When testosterone as a steroid was added to the solution containing the heteromer, an extremely large Cotton effect was observed. This finding indicates the potential application of this hero-supramolecular polymer system to chiral-amplification sensing. Therefore, we synthesized a chirally-modified sumanene chemosensor (**CSC**), which may selectively recognize chiral compounds. In this presentation, the signal-amplification mechanism via the hetero-supramolecular polymerization based on the DFT calculation and the chiroptical properties of **CSC** upon the complexation of steroids will be discussed.

Keywords: Chemosensor；Sumanene；Supramolecular Polymer；Chiral Amplification

我々は、溶液中でも超分子ポリマー形成が可能なスマネン（**sumenene**, Figure 1a）[1), 2)]に着目し、超分子ポリマーに基づくシグナル増幅系の構築へと展開した。合成したスマネン化学センサー（**SC**, Figure 1a）[3)]を用いて標的分子であるテストステロンをセンシングする際、スマネンの添加によって形成される超分子ポリマーの吸収帯に大きな正の誘起円二色性の変化が観測された（Figure 1bの青線）。この結果から、**SC**をキラル増幅可能なセンサーに応用できると考えた。本研究では、キラル化合物を選択的に認識できる化学センサーの開発を目指して、スマネンにキラリティーを有する側鎖を修飾した化学センサー（**CSC**, Figure 1a）を合成した。本発表では、**CSC** の分子軌道計算および光学特性について報告する。

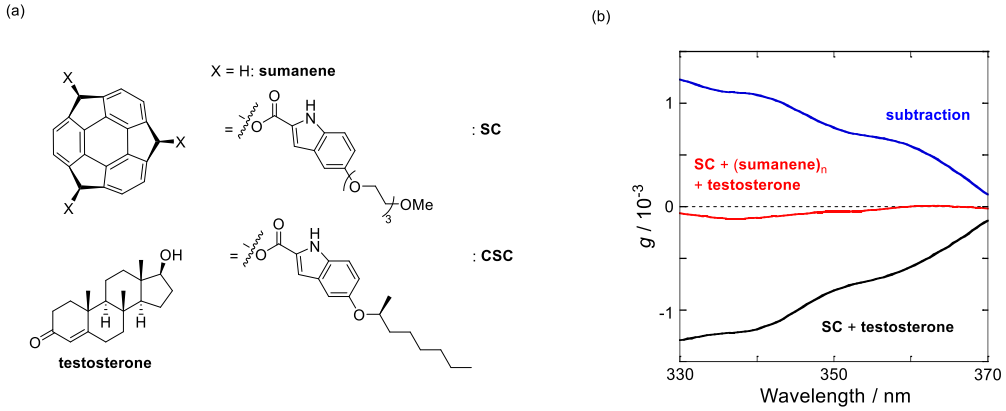

Figure 1. (a) Chemical structures of sumanene, sumanene chemosensor (**SC**) and chiral sumanene chemosensor (**CSC**). (b) Anisotropy ($g = \Delta\varepsilon/\varepsilon$) spectra of **SC** (black) or **SC** + **sumanene** (heteromer) upon the complexation of testosterone in CH_2Cl_2.

1) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878.
2) Mizuno, H.; Nakazawa, H.; Harada, M.; Yakiyama, Y.; Sakurai, H.; Fukuhara, G. *Chem. Commun*. **2023**, *59*, 9595.
3) Mizuno, H.; Nakazawa, H.; Miyagawa, A.; Yakiyama, Y.; Sakurai, H.; Fukuhara, G. submitted.

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アントラセンまたはピレンを発色団として導入したアミド，アミノ，カルバメート基を含む 17 員環大環状化合物の Fe^{3+}に対する発光挙動

（東邦大理 [1]・東邦大複合物性研究セ [2]・千葉工大工 [3]）○佐藤 泉美 [1]・堀田 拓希 [1]・池田 茉莉 [3]・桑原 俊介 [1,2]・幅田 揚一 [1,2]

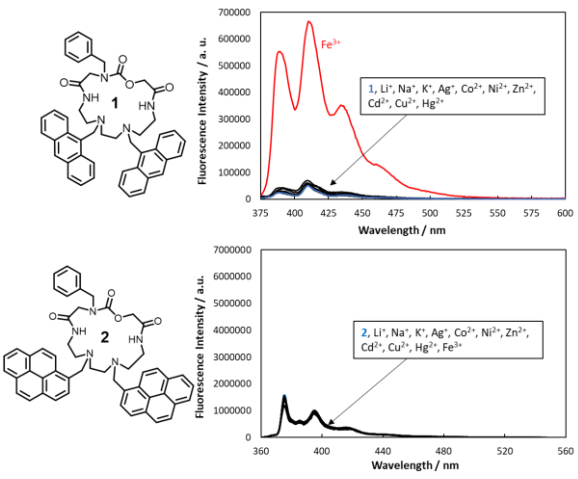
Fe^{3+}-Specific Photoluminescence by 17-Membered Macrocyclic Ligands with Amino, Amide, and Carbamate Groups in the Cyclic Skeleton Bearing Anthracene or Pyrene as Chromophores

([1]*Department of Chemistry and* [2]*Research Center for Materials with Integrated Properties, Toho University,* [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*)
○Izumi Sato,[1] Hiroki Horita,[1] Mari Ikeda,[3] Shunsuke Kuwahara,[1,2] Yoichi Habata[1,2]

Recently, we reported the unexpected formation of macrocyclic compounds containing amide, amino, and carbamate groups in the ring during the synthesis of dioxocyclen. In this study, we synthesized two compounds, **1** and **2**, incorporating anthracene and pyrene, respectively, with the aim of detecting specific metal ions through fluorescence spectra. Fluorescence spectra of these compounds were recorded with the addition of 30 equivalents of various metal ions. Interestingly, the fluorescence intensity exhibited a specific increase when Fe^{3+} was added to compound **1**. In contrast, ligand **2** did not display such spectral changes. These findings suggest that the fluorescence characteristics towards Fe^{3+} vary depending on the chromophore type present in the 17-membered macrocycle.
Keywords : Maclocycle; Anthracene; Pyrene; Fluorescence; Metal ions

最近我々は，ジオキソサイクレンを合成した際に予期せぬ副生成物として環内にアミド，アミノ，カルバメート基を有する大環状化合物が形成されることを報告した [1]．今回，これらの官能基を有する 17 員環大環状化合物にアントラセンおよびピレンを導入した化合物 **1** および **2** を合成し，蛍光スペクトルを用いて特定の金属イオンに対して選択性を示すかどうか検討した．

1 および **2** に様々な金属イオンを 30 当量添加して蛍光スペクトルを測定したところ，アントラセンを導入した **1** に Fe^{3+}を添加した時に特異的に蛍光強度が増大した．一方，ピレンを導入した **2** では蛍光強度の増大は見られなかった．これらの結果から，この大環状化合物アミド，アミノ，カルバメート基を含む 17 員環大環状化合物では，導入する発色団の種類によって金属イオンに対する蛍光特性が異なることが示唆された．



1) H. Horita, I. Sato, *et al. J. Org. Chem.,* **2023**, *88*, 9381–9387.

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ESIPT 可能なフェナントロイミダゾール置換レゾルシノールおよびその類縁体の合成と発光特性

（城西大院理）○杉 翔太・秋田 素子

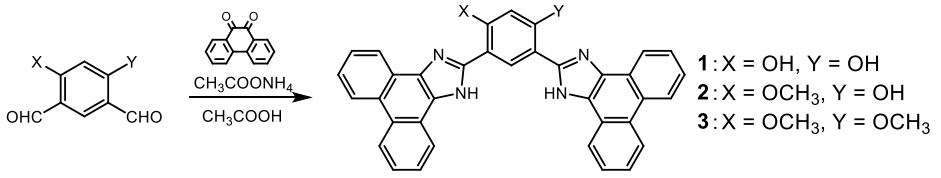
Synthesis and Photophysical Properties of ESIPT-capable 4,6-bis(phenanthroimidazol)resorcinol and Its Analogues. (*Graduate School of Science, Josai University*) ○Shota Sugi and Motoko Akita

Organic solid-state luminescent materials have been of great interest in both fundamentals and application. We have synthesized 2-arylphenanthroimidazoles, which emit strong luminescence in the solid state, and have studied their structures and luminescence properties in solution and in the solid state. Excited-state intramolecular proton transfer (ESIPT) fluorescence is the emission from a proton-transfer species generated by the photoexcitation of intramolecularly hydrogen bonded molecule and characterized by a large Stokes shift, which improve the efficiency of fluorescence and result in longer emission wavelength. We present here synthesis and luminescence properties of a new ESIPT-capable imidazole-based compound **1** and its methoxy analogues **2**, **3**. Compound **1-3** were obtained by condensation of phenanthrenequinone with ammonium acetate and corresponding aldehyde which was synthesized from resorcinol. Among them, **1** and **2** exhibited emission at longer wavelength than **3** both in the solid state and solution.

Keywords : ESIPT; 2-Arylphenanthroimidazole; Intramolecular Hydrogen bond; Fluorescence

固体で高効率発光する有機化合物の創出は学術・応用の両面から興味を持たれている。一般的な発光性化合物は溶液中で強い発光を示すが、固体中では濃度消光により発光強度が減少する。我々は固体で強い発光を示す 2-アリールフェナントロイミダゾール類を合成し、その構造と溶液および固体での発光性について検討してきた。本研究では固体での発光強度の増大のため、ストークスシフトを拡大させる励起状態分子内プロトン移動(Excited-State Intramolecular Proton Transfer ; ESIPT)を伴う発光を期待して、フェナントロイミダゾール置換レゾルシノールおよびその類縁体 **2**, **3** を合成しそれらの発光特性について比較検討した。

化合物 **1-3** はレゾルシノールを原料として前駆体のアルデヒドを合成し、それらと、9,10-フェナントレンキノン、酢酸アンモニウムを酢酸中で縮合させることにより得た。固体状態で UV ランプの 365 nm の光を照射すると、**1** は弱い緑色、**2** は緑色、**3** は強い緑色の発光を示した。また DMSO 溶液では **1**, **2** は水色、**3** は青紫色の発光を示した。



Scheme 1

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

Wed. Mar 20, 2024 9:00 AM - 11:20 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:20 AM UTC
E1121(1121, Bldg. 11 [2F])

[E1121-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Koki Ikemoto, Takuya Shimajiri

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1121-3am-01]

Synthesis and Chiroptical Properties of Radially Extended Carbazole with Chiral [2.2]Paracyclophane Core

○Masashi Hasegaw[1], Wanli Xiao[1], Yuki Ishida[1], Kazuyuki Asahi[2], Hiroyuki Nishikawa[2], Reo Ohno[3], Daisuke Hayauchi[3], Miki Hasegawa[3], Yasuhiro Mazaki[1] (1. Graduate School of Science, Kitasato University, 2. Graduate School of Science and Engineering, Ibaraki University, 3. Department ofChemistry and BiologicalScience, Aoyama GakuinUniversity)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1121-3am-02]

Synthesis of Carbon–Iodine Bond Atropisomers

○Shohei Abe[1], Jun Kikuchi[1], Naohiko Yoshikai[1] (1. Grad. Sn. Pharm. Sci., Tohoku University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1121-3am-03]

Synthesis of BODIPYs Using Phellandrene-fused Pyrrole as a Key Substance

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

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1121-3am-04]

Elucidation of structures and optical properties of (1*Z*,3*Z*,5*Z*)-heptaaryl-1,3,5-hexatriene derivatives

○Kensuke Echizen[1], Tsuyoshi Taniguchi[4], Yoko Sakata[2], Shigehisa Akine[2], Tatsuya Nishimura[2], Katsuhiro Maeda[2,3] (1. Grad. Sch. of Frontier Sci. Initiative, Kanazawa Univ., 2. Grad. Sch. of Nat. Sci, and Tech., Kanazawa Univ., 3. WPI-NanoLSI, Kanazawa Univ., 4. IRC3, AIST)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1121-3am-05]

Catalytic Enantioselective Synthesis of Figure-Eight π-System: Cyclobisbiphenylenecarbonyl

○Reiji Yoshina[1], Shunsuke Minabe[1], Muhammet Uyanik[1], Kazuaki Ishihara[1], Hiroshi Shinokubo[1], Norihito Fukui[1,2] (1. Graduate-School-of-Engineering, Nagoya-University, 2. JST-PRESTO)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1121-3am-06]

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Synthesis and Properties of Helical Oligothiophenes Anchored to Binaphthyl

○Hikari Kawashima[1], Masashi Hasegawa[1], Yasuhiro Mazaki[1] (1. Graduate School of Science, Kitasato University)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1121-3am-07]
Synthesis and circularly polarized luminescence of binaphthyl-bridged pyrenophanes

Kazuto Takaishi[1], ○Yoshihiro Sato[1], Fumiya Yoshinami[1], Chihiro Maeda[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
[E1121-3am-08]
Synthesis and Intramolecular Biarylation of Cyclic Tetraamide Obtained by Condensation of Dibromoisophthalic Acid and 1,4-Phenylenediamine

○Kazuki Uoda[1], Kenta Rakumitsu[1], Akihiro Yokoyama[1] (1. Seikei University)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1121-3am-09]
Concise Synthesis of Molecular Hyperboloids by Oligomeric Macrocyclization of Octagonal Molecules

○Daiya Nagata[1], Koki Ikemoto[1], Taisuke Matsuno[1], Hiroyuki Isobe[1] (1. The Univ. of Tokyo)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1121-3am-10]
Synthesis of Belt-Shaped Cyclic Trimer by Self-Condensation of Diaminoterephthalic Acid and Its Absorption and Luminescence Properties

○Kota Matsuda[1], Kenta Rakumitsu[1], Akihiro Yokoyama[1] (1. Seikei University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1121-3am-11]
Synthesis, Structures and Properties of All-Carbon One-Dimensional Spiro-Oligomers

○Kumpei Hasebe[1], Kenichiro Itami[1], Hideto Ito[1] (1. Nagoya Univ.)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1121-3am-12]
Preparation and Self-Condensation of Diaminoisophthalic Acid for the Synthesis of Belt-Shaped Macrocycles

○Shunsuke Mamiya[1], Kenta Rakumitsu[1], Akihiro Yokoyama[1] (1. Seikei University)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1121-3am-13]
Synthesis and Function of Novel Amide-Embedded Cyclic π-System

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○Sho Fukuda[1], Daiki Morishita[2], Yoshimitsu Itoh[2,3] (1. Sch. Eng., The Univ. of Tokyo, 2. Grad. Sch. Eng., The Univ. of Tokyo, 3. JST PRESTO)

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キラルな[2.2]パラシクロファンから放射状にπ拡張したカルバゾールとキラル光学特性

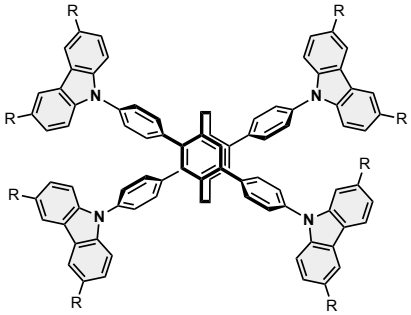
（北里大院理[1]・茨城大院理[2]・青山学院大院理工[3]）○長谷川　真士[1]・肖　万里[1]・石田　雄規[1]・朝日　宗将[2]・西川　浩之[2]・大野　礼雄[3]・早内　大介[3]・長谷川　美貴[3]・真崎　康博[1]

Synthesis and Chiroptical Properties of Radially Extended Carbazole with Chiral [2.2]Paracyclophane Core ([1]*Graduate School of Science, Kitasato University*, [2]*Graduate School of Science, Ibaraki University*, [3]*Department of Chemistry and Biological Science, Aoyama Gakuin University*) ○Masashi Hasegawa,[1] Xiao Wanli,[1] Yuki Ishida,[1] Kazuyuki Asahi,[2] Hiroyuki Nishikawa,[2] Reo Ohno,[3] Daisuke Hayauchi,[3] Miki Hasegawa,[3] and Yasuhiro Mazaki[1]

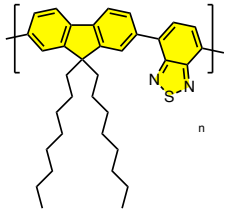
Herein, we have established an effective π-extension method for chiral [2.2]PC with four substitutions, using chiral 4,7,12,15-tetrabromo[2.2]PC as a starting material. This has led to TMS-protected tetraphenyl-[2.2]PC that serves as a versatile building resource for radial-type chiral π-conjugated compounds with a [2.2]PC core. In this study, we further succeeded in synthesizing compounds with the introduction of carbazole (**Cbz$_4$-[2.2]PC** and **^{t}BuCbz$_4$-[2.2]PC**) and investigated their chiroptical properties and chiral induction ability in achiral π-conjugated polymers. A thin film of F8BT with 3wt% **Cbz$_4$-[2.2]PC** prepared by spin-coating exhibited circularly polarized luminescence (CPL) properties with a high dissymmetry factor ($|g_{lum}|$ = 0.01), which was much higher than that of **Cbz$_4$-[2.2]PC** in CH_2Cl_2 solution. By contrast, the doped film of F8BT with 3wt% **^{t}BuCbz$_4$-[2.2]PC** exhibited only weak CPL properties.

Keywords : [2.2]Paracyclophane, Carbazole, Planar Chirality, Circularly Polarized Luminescence, Chiral dopant

[2.2]パラシクロファンの 4,7,12,15-位の４箇所に同じ置換基を導入した分子は、面不斉を持ち特徴あるキラル光学特性 [円二色性スペクトル(CD)、円偏光発光スペクトル(CPL)]を示す。本研究では、テトラブロモシクロファンを出発物質としてカルバゾールを放射状に導入した **Cbz$_4$-[2.2]PC** および **^{t}BuCbz$_4$-[2.2]PC** を合成した。光学分割後のこれらの化合物は、溶液中にてカルバゾールユニットに由来したキラル光学特性を示した($|g_{lum}|$ = 3.2-4.7 x 10^{-4})。また、これらを F8BT にドープし、薄膜を作製したところ、**Cbz$_4$-[2.2]PC** をドープした薄膜の CPL スペクトルにて、非対称性因子が大きく増大した ($|g_{lum}|$ = 1.1 x 10^{-2}) 。



Cbz$_4$-[2.2]PC: R = H
^{t}BuCbz$_4$-[2.2]PC: R = ^{t}Bu



F8BT

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日本化学会 第104春季年会 (2024)

炭素－ヨウ素結合アトロプ異性体の合成

（東北大院薬 [1]）○阿部 将平 [1]・菊池 隼 [1]・吉戒 直彦 [1]

Synthesis of Carbon–Iodine Bond Atropisomers ([1]*Graduate School of Pharmaceutical Sciences, Tohoku University*) ○Shohei Abe,[1] Jun Kikuchi,[1] Naohiko Yoshikai[1]

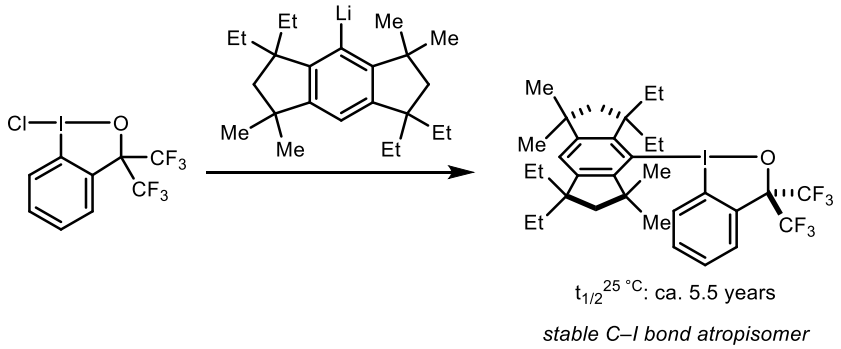
Atropisomerism, which arises from restricted rotation around single bonds, is an important aspect of organic stereochemistry and is commonly found in chiral catalysts, pharmaceutical drugs, and optoelectronic materials. While numerous compounds with atropisomerism around a bond between second-row elements, including optically active biaryls, have been reported, studies on atropisomerism around longer chemical bonds containing third-row or heavier elements are extremely rare.

We report here on the synthesis of a hitherto unprecedented hypervalent iodine compound that exhibits stable atropisomerism around the bond between iodine, a fifth-row element, and carbon. The compound, featuring a cyclic benziodoxole moiety and a rigid and sterically crowded xMEInd group, was synthesized by nucleophilic aryl transfer to an appropriate iodine(III) electrophile and was optically resolved at room temperature. The optically resolved sample displayed a racemization half-lifetime of ca. 5.5 years at room temperature, demonstrating highly restricted rotation around the bulky aryl–iodine bond.

Keywords： Hypervalent Iodine Compounds; Atropisomers; Axial Chirality

アトロプ異性は，単結合の自由回転が制限されることにより生じる立体異性であり，不斉触媒，医薬品，材料などの立体化学要素として重要である．これまでにビアリール化合物をはじめとした第二周期元素間の結合にアトロプ異性を持つ化合物が多数知られているが，第三周期以降の元素を含む長い結合のアトロプ異性に関する研究はわずかである．

このような背景の下，本研究で我々は第五周期元素であるヨウ素と炭素の結合に安定なアトロプ異性を示す初の超原子価ヨウ素化合物を合成した．環状のベンズヨードキソール骨格と剛直かつ立体的に混雑した xMEInd 基を有するその化合物は，三価ヨウ素求電子剤とアリール求核剤との反応によって合成でき，室温下で光学分割可能であった．解析の結果，本化合物は室温下で約 5 年半のラセミ化寿命を持ち，かさ高いアリール–ヨウ素結合周りの回転が大きく抑制されていることが明らかとなった．



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フェランドレン縮合ピロールを鍵物質とする BODIPY 類の合成

(愛媛大院理工[1]・ADRES[2])○一柳累[1]・森重樹[2]・髙瀬雅祥[1]・奥島鉄雄[1]・宇野英満[1]

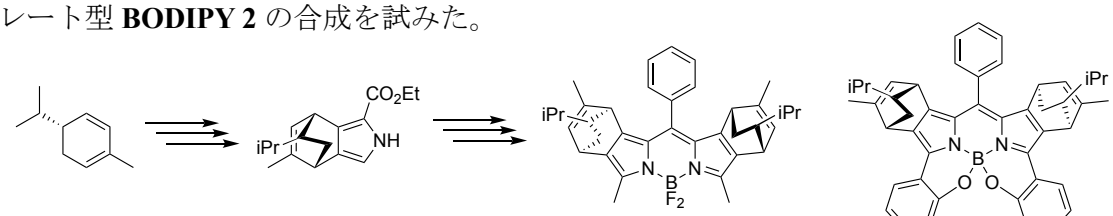
Synthesis of BODIPYs Using Phellandrene-fused Pyrrole as a Key Substance ([1]Graduate School of Science and Engineering, [2]Advanced Research Support Center (ADRES), Ehime University) ○Rui Ichiryu[1], Shigeki Mori[2], Masayoshi Takase[1], Tetsuo Okujima[1], Hidemitsu Uno[1]

Compounds exhibiting circularly polarized luminescence (CPL) have attracted much attention as elements for 3D displays and other applications. In particular, the realization of CPL in small organic molecules is in demand due to high fluorescence quantum yield, low cost, and easy modification. BODIPY, one of the research targets, is characterized by high fluorescence quantum yield and photostability. BODIPYs with CPL properties have been synthesized so far and required chiral columns for optical resolution due to their enantiomers. In this study, using diastereopure pyrrole as a starting material, we have started the synthesis of new chiral BODIPYs without chiral chromatography. The target compound **BODIPY 1** was synthesized from phellandrene-fused pyrrole, which was found to be diastereopure by ^{1}H-NMR and CD spectral analysis. In addition, to enhance the g-value, we attempted to form **BODIPY 2** is an oxygen-chelated BODIPY with a twisted skeleton in addition to the chirality derived from phellandrene.

Keywords : Chirality; Pyrrole; BODIPY;

円偏光発光(CPL)を示す化合物は、3D ディスプレイなどの要素として注目されている。中でも、高い蛍光量子収率、低コスト、容易な化学修飾などの観点から有機小分子での実現には注目が集まっている。研究対象のひとつである BODIPY は特徴として高い蛍光量子収率・光安定性を有しており、これまでにもさまざまな CPL 特性を示す BODIPY が合成されてきた。しかし、その多くはエナンチオマーであり、光学分割にキラルカラムが必要である[1]。本研究ではジアステレオマーなピロールを合成、光学分割することでジアステレオピュアな BODIPY の合成に取り組んだ。

ジアステレオピュアなピロールを得るために天然有機化合物である(-) α フェランドレンを用いてピロールの合成・光学分割を行った。得られたフェランドレン縮合ピロールを原料として **BODIPY 1** を合成した。また、偏り強度(g 値)増強を目指し、フェランドレン由来のキラリティーに加え BODIPY 骨格が捻れた構造を有する酸素キレート型 **BODIPY 2** の合成を試みた。



(-) α フェランドレン　フェランドレン縮合ピロール　**BODIPY 1**　**BODIPY 2**

1) R. B. Alnoman *et al*., *Chem. Eur. J.*, **2016**, *22*, 93.

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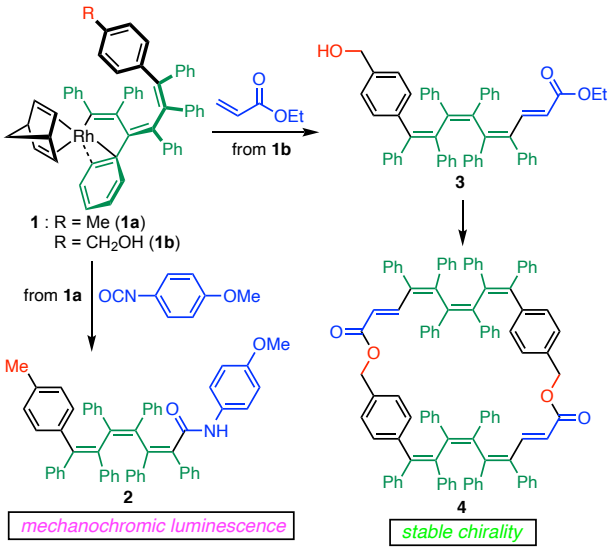
(1*Z*,3*Z*,5*Z*)-ヘプタアリール-1,3,5-ヘキサトリエン誘導体の構造と光学特性の解明

（金沢大院新学術[1]・金沢大院自然[2]・金沢大 WPI-NanoLSI[3]・産総研触媒 RC[4]）○越前 健介[1]・谷口 剛史[4]・酒田 陽子[2]・秋根 茂久[2]・西村 達也[2]・前田 勝浩[2,3]
Elucidation of structures and optical properties of (1*Z*,3*Z*,5*Z*)-heptaaryl-1,3,5-hexatriene derivatives ([1]*Grad. Sch. of Frontier Sci. Initiative, Kanazawa Univ.*, [2]*Grad. Sch. of Nat. Sci, and Tech., Kanazawa Univ.*, [3]*WPI-NanoLSI, Kanazawa Univ.*, [4]*IRC3, AIST*) ○Kensuke Echizen,[1] Tsuyoshi Taniguchi,[4] Yoko Sakata,[2] Shigehisa Akine,[2] Tatsuya Nishimura,[2] Katsuhiro Maeda[2,3]

We have recently reported bench-stable (1*Z*,3*Z*,5*Z*)-heptaaryl-1,3,5-hexatrienylrhodium(I) complexes **1** bearing various functional groups. Complexes **1** were found to have chirality based on their twisted triene backbone, while they showed no fluorescence. In this study, we synthesized novel 1,3,5-hexatriene derivatives by replacing the rhodium center of **1** with a variety of structures using appropriate electrophiles. We found that they showed the aggregation-induced emission due to their triene structure densely substituted by aromatic groups. The fluorescence color of the derivative **2** having an amide group changed from cyan to yellow upon grinding its crystals, which is known as mechanochromic luminescence. In addition, the cyclic dimer **4** derived from **3** was found to have stable helical chirality.
Keywords : rhodium complexes; hexatriene compounds; chirality; aggregation-induced emission; mechanochromic luminescence

最近、我々は、さまざまな官能基を有する(1*Z*,3*Z*,5*Z*)-ヘプタアリール-1,3,5-ヘキサトリエニルロジウム(I)錯体 **1** が、水や空気に安定な固体として得られることを見出した[1]。錯体 **1** は、ねじれたトリエン骨格に由来するキラリティーを有しているが、蛍光を示さないことが明らかになっている。本研究では、**1** に適切な求電子剤を作用させることにより、ロジウム部分をさまざまな構造で置き換えた 1,3,5-ヘキサトリエン誘導体を合成した。これらの誘導体は、高密度に置換されたトリエン構造に起因する凝集誘起発光を示した。そのうち、アミド基を導入したトリエン **2** は、メカノクロミック発光を示し、青白色の蛍光を発する結晶をすりつぶすと発光色が黄色に変化した。また、テトラエン **3** を経由して得られた環状二量体 **4** が、トリエン骨格に由来する安定なキラリティーを有していることを見出した。



1) S. Sakamoto et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 22201–22206.

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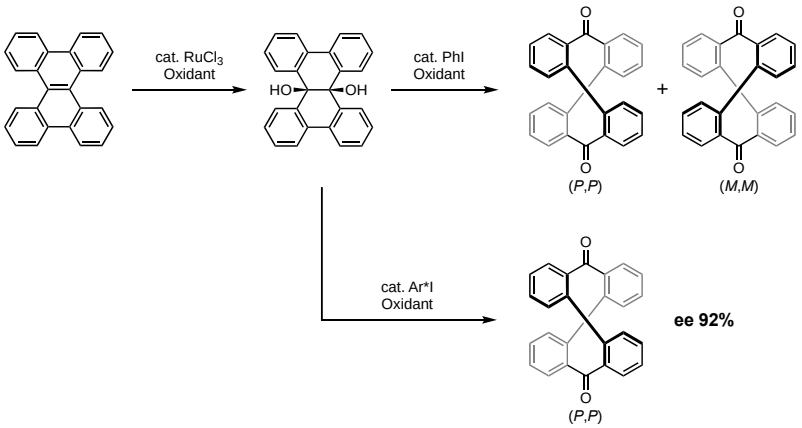
８の字型分子シクロビスビフェニレンカルボニルの触媒的不斉合成

（名大院工[1]・JST さきがけ[2]）○用品 伶時[1]・三鍋 駿介[1]・ウヤヌク ムハメット[1]・石原 一彰[1]・忍久保 洋[1]・福井 識人[1,2]
Catalytic Enantioselective Synthesis of Figure-Eight π-System: Cyclobisbiphenylenecarbonyl (*[1]Graduate School of Engineering, Nagoya University, [2]JST PRESTO*) ○Reiji Yoshina[1], Shunsuke Minabe[1], Muhammet Uyanik[1], Kazuaki Ishihara[1], Hiroshi Shinokubo[1], and Norihito Fukui[1,2]

Cyclobisbiphenylenecarbonyl (CBBC) represents a chiral figure-eight π-system. Previously, CBBC was obtained as a racemic mixture through the oxidative cleavage of an inner double bond of dibenzo[*g*,*p*]chrysene (DBC) with an excess amount of sodium dichromate in refluxed acetic acid. Here, we report a catalytic protocol via stepwise oxidation: ruthenium-catalyzed *cis*-dihydroxylation of DBC and subsequent glycol cleavage with a hypervalent iodine reagent. The use of a chiral hypervalent iodine reagent in the second step resulted in kinetic resolution, which afforded CBBC in 92% ee.
Keywords: Asymmetric synthesis, Hypervalent iodine, Nonplanar π-system, Figure-eight molecule, Cyclobisbiphenylenecarbonyl

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キラルなπ共役分子である。過去の報告では、CBBC はジベンゾ[*g*,*p*]クリセンに量論量以上の二クロム酸ナトリウムを酢酸溶媒中加熱還流下で作用させ、骨格内部の二重結合を酸化的に開裂することでラセミ体として合成された[1,2]。今回我々は、この酸化的開裂をルテニウム触媒によるジヒドロキシ化と超原子価ヨウ素触媒によるグリコール開裂の二段階の変換に分けることで、CBBC を穏和な条件下で合成することに成功した。さらに後半の反応にキラル超原子価ヨウ素触媒を用いると速度論的光学分割が進行し、92% ee で CBBC が得られることを見いだした。



1. Suszko, J.; Schillak, R., *Roczniki Chem.* **1934**, *14*, 1216.
2. N. Fukui, *et al. ChemRxiv* **2023**. (DOI: 10.26434/chemrxiv-2023-f1djk)

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軸不斉ユニットに組み込まれた環状ヘリカルオリゴチオフェンの合成と性質

（北里大院理[1]）○川島 光[1]・長谷川 真士[1]・真崎 康博[1]
Synthesis and Properties of Helical Oligothiophenes Anchored to Binaphthyl ([1]*Graduate School of Sciense, Kitasato University*) ○Hikari Kawashima,[1] Masashi Hasegawa,[1] Yasuhiro Mazaki[1]

Chiral molecules with twisted π-conjugated units have attracted much interest due to their unique structure-property relationships. As a model compound for *all-cis*-helical oligothiophenes (Fig. 1a), we designed a macrocyclic compound (*R*)/(*S*)-**1** consisting of an oligothiophene linked to an axially chiral binaphthyl (Fig. 1b).

The precursor containing the 1,3-butadiyne moiety was synthesized by Eglinton coupling under highly dilute conditions, followed by Na_2S conversion to thiophene to form **1**.

Subsequent optical resolution by chiral HPLC gave (*R*)/(*S*)-**1**. The absolute conformation of (*R*)-**1** was deduced by comparison of CD spectra and TD-DFT calculations, and X-ray structural analysis showed that (*R*)-**1** has a sulfur atom inside of the macrocycle and *M*-helicity (Fig. 2). Both the CD and CPL spectra of (*R*)-**1** showed the negative first-cotton effects (g_{CD} = –5.8, g_{CPL} = -3.5×10^{-3}).

Keywords : Macrocycle; Chiroptical properties; Helical oligothiophenes; Circularly dichroism; Circularly polarized luminescence

ねじれたπ共役系ユニットを持つ分子は、そのユニークな構造と物性の相関に興味がもたれている。*all-cis*-ヘリカルオリゴチオフェン(Fig. 1a)のモデル化合物として、軸不斉のビナフチルにオリゴチオフェンを連結した大環状化合物(*R*)/(*S*)-**1**を設計した(Fig. 1b)。高希釈条件下でEglintonカップリングにより1,3- ブタジイン骨格を含む前駆体を合成し、続くNa_2Sによるジイン部のチオフェン環への変換反応により**1**を合成した。その後キラルHPLCにより光学分割を行い(*R*)/(*S*)-**1**を得た。(*R*)-**1**の絶対立体配置は、CDスペクトルとTD-DFT計算の比較により推定された。X線構造解析より、(*R*)-**1**は硫黄が大員環の内側に向いた構造を持ち、オリゴチオフェン部は*M*-ヘリシティーを持つことがわかった(Fig 2)。また、(*R*)-**1**のCDとCPLスペクトルの第一コットン効果は共に負を示した(g_{CD} = –5.8, g_{CPL} = -3.5×10^{-3})。これらの酸化還元特性についても調査したためあわせて報告する。

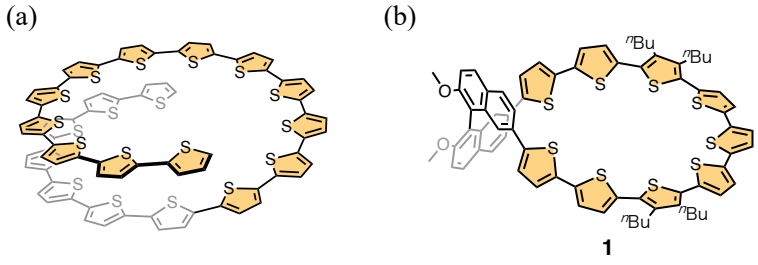

Fig. 1 (a) *all-cis*-helical oligothiophene (b) **1** の分子構造

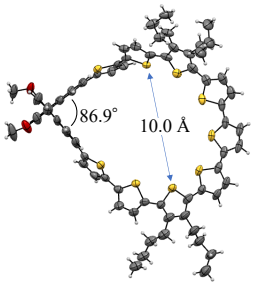

Fig. 2 (*R*)-**1** の X 線構造解析

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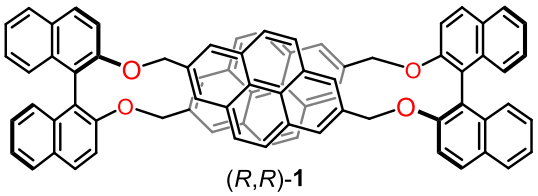
ビナフチル架橋ピレノファンの合成と円偏光発光性

（岡山大院自然）高石 和人・○佐藤 嘉洋・由浪 史也・前田 千尋・依馬 正
Synthesis and Circularly Polarized Luminescence of Binaphthyl-bridged Pyrenophanes (*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) Kazuto Takaishi, ○Yoshihiro Sato, Fumiya Yoshinami, Chihiro Maeda, Tadashi Ema

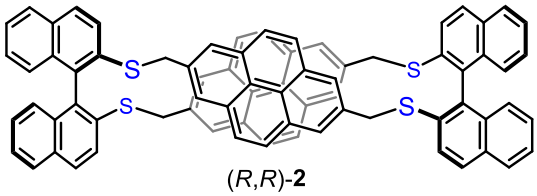
We synthesized macrocycles consisting of pyrene and axially chiral binaphthyl moieties (pyrenophanes) with ether or thioether linkers. These pyrenophanes exhibited intense CPL: g_{lum} values of -5.3×10^{-2} for the ether and -1.3×10^{-2} for the thioether. The thioether exhibited temperature-dependent CPL with sign inversion. DFT calculations indicate that the pyrenes form a kinetically trapped left-handed twist excimer at low temperatures, while they form a thermodynamically favored right-handed twist excimer at high temperatures.
Keywords: circularly polarized luminescence; excimer; binaphthyl; pyrene

本研究では優れた円偏光発光 (CPL) を示す有機色素の開発を目指し、ピレンと軸性キラルビナフチルがエーテル結合 [1] またはチオエーテル結合を介して交互に連結した環状体 (ピレノファン) (*R*,*R*)-**1** と (*R*,*R*)-**2** を設計した。

まず、(*R*)-BINOL または (*R*)-BINAS と 2,7-ビス(クロロメチル)ピレンを反応させ、(*R*,*R*)-**1** および (*R*,*R*)-**2** をそれぞれ収率 18% と 15% で合成した。(*R*,*R*)-**1** と (*R*,*R*)-**2** はいずれも分子内ピレンエキシマーに由来した強い CPL を示し、20 ºC での g_{lum} 値はそれぞれ -5.3×10^{-2} と -1.3×10^{-2} であった。次に、CPL の温度依存性を調査した。その結果、(*R*,*R*)-**1** では大きな変化は見られなかったが、興味深いことに (*R*,*R*)-**2** は温度によって強度が大きく変化し、符号の反転も確認された。この温度依存性の有無は、エーテル結合とチオエーテル結合の結合長の差に由来する構造的自由度の違いに起因していると考えている。DFT 計算により、(*R*,*R*)-**2** のピレン環は低温では速度論的に安定な左回りにねじれたエキシマーを形成し (−)-CPL を、高温では熱力学的に安定な右回りにねじれたエキシマーを形成し (+)-CPL を示すことが導かれた。



(*R*,*R*)-**1**
g_{lum}: -4.4×10^{-2} (90 °C)
-5.3×10^{-2} (20 °C)



(*R*,*R*)-**2**
g_{lum}: $+6.0 \times 10^{-3}$ (90 °C)
-1.3×10^{-2} (20 °C)

1) Takaishi, K.; Murakami, S.; Yoshinami, F.; Ema, T. *Angew. Chem. Int. Ed*. **2022**, *61*, e202204609.

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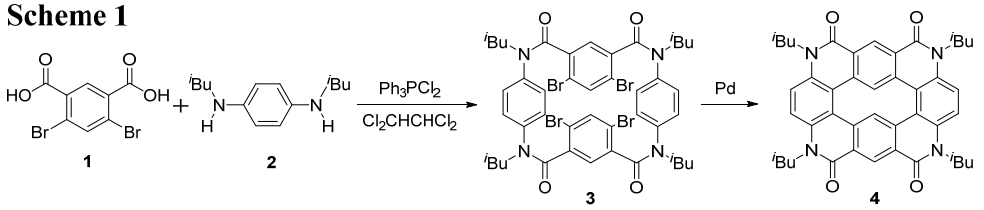
ジブロモイソフタル酸と 1,4-フェニレンジアミンの縮合による環状テトラアミドの合成と分子内ビアリール化

（成蹊大理工）○魚田 和希・楽満 憲太・横山 明弘
Synthesis and Intramolecular Biarylation of Cyclic Tetraamide Obtained by Condensation of Dibromoisophthalic Acid and 1,4-Phenylenediamine (*Faculty of Science and Technology, Seikei University*) ○Kazuki Uoda, Kenta Rakumitsu, Akihiro Yokoyama

The synthesis of strained polycyclic aromatic hydrocarbons is difficult, but the introduction of heteroatoms would often decrease the strain to facilitate the synthesis. We have reported the synthesis of the coronene analogues using Pd-catalyzed intramolecular biarylation of the cyclic triamide prepared by the self-condensation of 4-aminobenzoic acid derivatives. This study aims to synthesize a disk-shaped cyclic molecule with stacked benzene units at the central part via Pd-catalyzed intramolecular biarylation of the cyclic tetraamide (Scheme 1). For the synthesis of the cyclic tetraamide **3**, the condensation of **1** and **2** was carried out using dichlorotriphenylphosphorane as a condensation reagent. According to Scheme 2, the synthesis of **3** using the acid chloride was also investigated. We will report the Pd-catalyzed intramolecular biarylation of **3** to synthesize **4**.
Keywords: Isophthalic Acid; Phenylenediamine; Amide; Biarylation

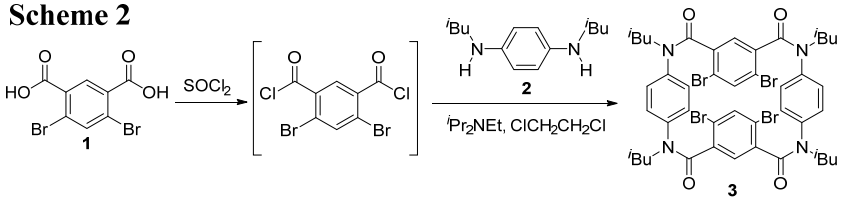
歪みがある多環芳香族炭化水素は合成が困難であるが、ヘテロ原子の導入により合成が容易になる場合がある。当研究室では、4-アミノ安息香酸誘導体の自己縮合で得られる環状アミドに対してパラジウム触媒を用いた分子内ビアリール化を行うことで、コロネン類似体の合成を報告している[1)]。本研究ではこのアミド縮合と分子内ビアリール化を利用し、ジブロモイソフタル酸 **1** と 1,4-フェニレンジアミン **2** の縮合で得られる環状テトラアミド **3** から、中央部分のベンゼン環の一部が重なったディスク型環状分子 **4** を合成することが目的である (スキーム 1)。本発表では、縮合剤としてジクロロトリフェニルホスホランを用いた **1** と **2** の反応による **3** の合成や、

Scheme 1



スキーム 2 に示したように酸クロリドと **2** の反応による **3** の合成、さらにパラジウム触媒を用いた **3** の分子内ビアリール化について報告する。

Scheme 2



1) K. Rakumitsu, *et al.*, *RSC Adv.*, **2022**, *12*, 24611.

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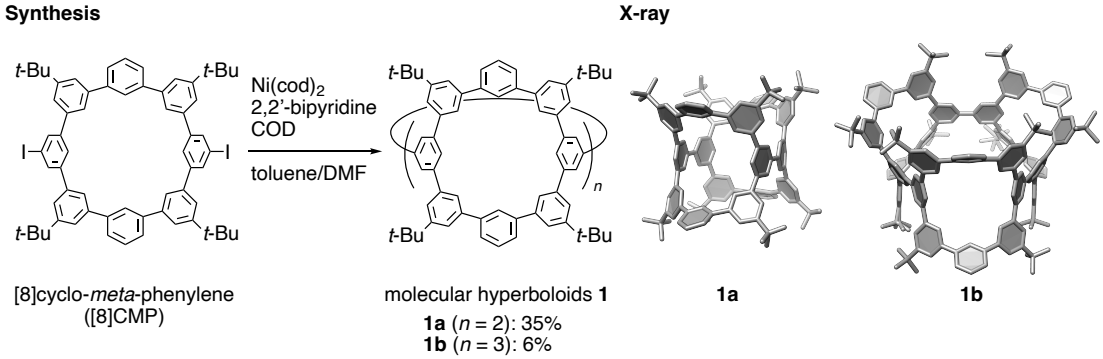
八角形分子の大環状多量化反応による分子性ハイパーボロイドの簡便合成

（東大院理[1]）○永田 大也[1]・池本 晃喜[1]・松野 太輔[1]・磯部 寛之[1]
Concise Synthesis of Molecular Hyperboloids by Oligomeric Macrocyclization of Octagonal Molecules ([1]*Department of Chemistry, The University of Tokyo*) ○Daiya Nagata,[1] Koki Ikemoto,[1] Taisuke Matsuno,[1] Hiroyuki Isobe[1]

Molecular hyperboloids were designed and synthesized. The synthesis was accomplished by oligomeric macrocyclization of an octagonal molecule with a saddle shape. The saddle-shaped molecule, [8]cyclo-*meta*-phenylene ([8]CMP), was decorated with two iodo linkers for the oligomeric macrocyclization and was assembled by Ni-mediated Yamamoto coupling. Three cyclic congeners of the molecular hyperboloids were obtained. X-ray crystallographic structures of **1a** and **2a** were successfully obtained. Crystal structures of the molecular hyperboloids revealed their nanometer-sized hyperboloidal structures with 96π and 144π electrons, which also possessed nanopores on the curved molecular structures. Structures of [8]CMP cores of the molecular hyperboloids were compared with those of saddle-shaped phenine [8]circulene with a negative Gauss curvature to confirm their structural resemblance, which suggests further explorations of expanded networks of molecular hyperboloids.
Keywords : Nanocarbon; Hyperboloid; Macrocyclization; Curvature

分子性ハイパーボロイドを設計・合成した[1]．分子性ハイパーボロイドは，鞍型形状の八角形分子のオリゴマー大環状化の開発によって合成を達成した．2 つのヨード基で装飾された鞍型分子[8]シクロメタフェニレン ([8]CMP) を合成し, 山本カップリングによる大環状多量化反応に付すことで分子性ハイパーボロイドを得た. 分子性ハイパーボロイド **1a** と **1b** について，単結晶 X 線構造解析に成功した．結晶構造解析により，96 π と 144 π の電子を持つナノメートルサイズのハイパーボロイド構造と，湾曲した分子構造上のナノ孔の存在を確認した. 分子性ハイパーボロイドと負のガウス曲率を持つ鞍型フェナイン[8]サーキュレンの[8]CMP 部分を比較した結果，両者の構造類似性が確認され，分子性ハイパーボロイドの双曲面構造が明らかとなった.



1) Ikemoto, K.; Nagata, D.; Matsuno, T.; Isobe, H. *Chem. Asian J.* **2023**, *18*, e202300046.

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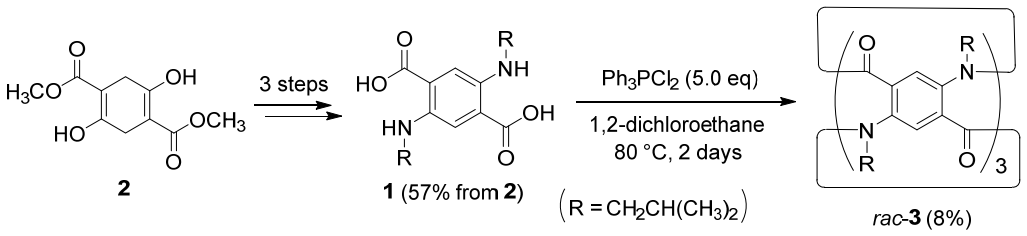
ジアミノテレフタル酸の自己縮合によるベルト型環状 3 量体の合成と光吸収および発光特性

（成蹊大理工）○松田 皓太・楽満 憲太・横山 明弘
Synthesis of Belt-Shaped Cyclic Trimer by Self-Condensation of Diaminoterephthalic Acid and Its Absorption and Luminescence Properties (*Faculty of Science and Technology, Seikei University*) ○Kota Matsuda, Kenta Rakumitsu, Akihiro Yokoyama

The condensation of a low nucleophilic aromatic secondary amine and a carboxylic acid can be carried out using dichlorotriphenylphosphorane (Ph_3PCl_2). We expected that belt-shaped cyclic compounds with a repeating structure consisting of one benzene rings and two amide linkages could be synthesized by the self-condensation of 2,5-di(isobutylamino)terephthalic acid (**1**) using Ph_3PCl_2. The compound **1** was synthesized from **2** by three steps, and the self-condensation of **1** using Ph_3PCl_2 gave a belt-shaped cyclic trimer *rac*-**3** in 8% yield. We will report the absorption and fluorescence properties of *rac*-**3**. The CD spectra of the enantiomers obtained by the optical resolution of *rac*-**3** will be reported.
Keywords: Belt-Shaped Cyclic Compound; Amide; Absorption; Luminescence

ジクロロトリフェニルホスホラン (Ph_3PCl_2) を用いると、求核性の低い芳香族第二級アミンをカルボン酸と縮合させてアミドにすることができる。この反応を利用し、2,5-ジ(イソブチルアミノ)テレフタル酸 (**1**) を自己縮合させることで、2 つのベンゼン環を 2 本のアミド結合でつなげた繰り返し構造を有するベルト型環状分子が得られると考えた。ベルト型環状分子は剛直な構造で分子内部に空洞を有することから、ホスト-ゲスト化学への利用が数多く報告されている。また、アミドを導入することにより、特異的な電子特性を示すことが期待される。そこでスキーム 1 に示すように、市販の **2** から 3 工程で **1** を合成し、Ph_3PCl_2 を用いた **1** の自己縮合を検討したところ、ベルト型環状 3 量体 *rac*-**3** を最高収率 8% で得ることができた。

Scheme 1



得られた *rac*-**3** の UV-vis 吸収測定および蛍光測定の結果を報告する。さらに、*rac*-**3** の光学分割で得られたエナンチオマー (図 1) の CD 測定についても報告する。

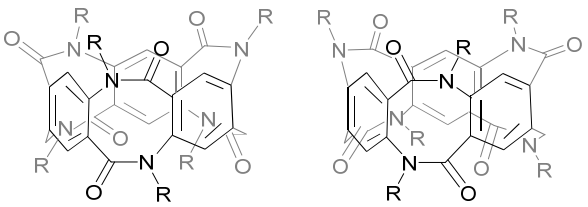


Figure 1

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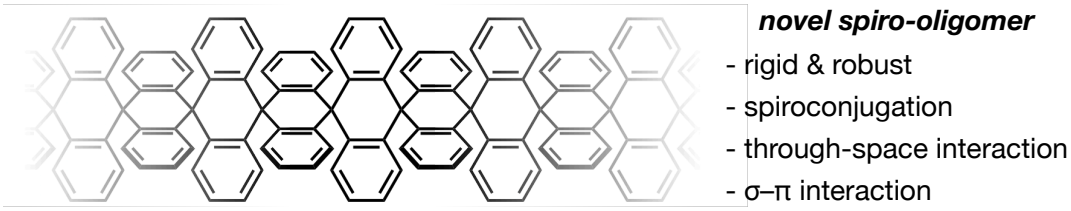
全炭素一次元スピロオリゴマーの合成・構造・物性

（名大院理[1]・名大 ITbM[2]）○長谷部 薫平[1]・伊丹 健一郎[1,2]・伊藤 英人[1]
Synthesis, Structure and Properties of All-Carbon One-Dimensional Spiro-Oligomers
([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules, Nagoya University*) ○Kumpei Hasebe,[1] Kenichiro Itami,[1,2] Hideto Ito[1]

Spiro-oligomers consisting of sequential spiro skeletons are anticipated to exhibit high rigidity and toughness due to the constrained conformation, chirality in sp^3 spiro-carbon stereocenter, microporosity arising from twisted structure and so on. While there are examples of spiro-oligomers containing heteroatoms in the main chain,[1] examples of all-carbon spiro-oligomers are highly limited.[2] In this work, we have developed the stepwise synthetic method for the creation of "dibenzo-annulated all-carbon spiro-oligomer" consisting of dihydroanthracene skeleton as a monomer unit. The synthesized spiro-oligomers are expected to have spiro-conjugation, through-space interaction, σ–π interaction, and other properties based on their rigidity and one-dimensional structures with the annulated benzene rings. In the presentation, we will report the synthesis, structural analyses by X-ray diffraction, and photophysical and electronic properties of synthesized spiro-oligomers.
Keywords : Spiro Compound; Spiro-Oligomer; Spiro-conjugation; X-ray Crystallography

スピロオリゴマーとは、モノマー同士がスピロ骨格を介して複数個連なった分子である。これらは、剛直で固定化されたスピロ骨格による強靭性や、sp^3 不斉炭素中心によるキラリティー、ねじれた高次構造に起因した微細孔性などが期待されている。しかしながら、これまでに報告されているスピロオリゴマーは主鎖にヘテロ原子を含むものがほとんどであり[1]、炭化水素のみからなる全炭素スピロオリゴマーの合成例は限られていた[2]。本研究では、ジヒドロアントラセン骨格をモノマーにもつ「ジベンゾ縮環全炭素スピロオリゴマー」の逐次的合成法の開発を行った。これらオリゴマーは縮環したベンゼン環と、剛直で固定化された一次元状の骨格に基づくスピロ共役やスルースペース相互作用、σ－π相互作用などを有することが示唆された。発表ではスピロオリゴマーの合成、X 線回折による構造解析、光・電子物性などについて報告する。



[1] Bailey W. J.; Volpe A. A. *J. Polym. Sci. Part A-1 Polym. Chem.* **1970**, *8*, 2109.
[2] Jia, L.; Yang, X.; Seyam, A. M.; Albert, I. D. L.; Fu, P-F.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 7900.

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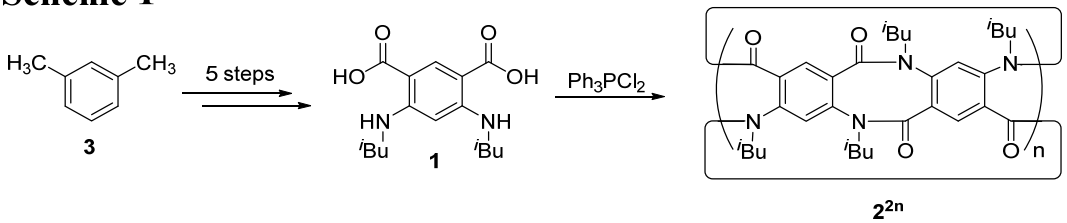
ベルト型環状分子を目指したジアミノイソフタル酸の合成と自己縮合の検討

（成蹊大理工）○間宮 俊介・楽満 憲太・横山 明弘
Preparation and Self-Condensation of Diaminoisophthalic Acid for the Synthesis of Belt-Shaped Macrocycles (*Faculty of Science and Technology, Seikei University*) ○Shunsuke Mamiya, Kenta Rakumitsu, Akihiro Yokoyama

Belt-shaped macrocycles have been used as host molecules in the field of supramolecular chemistry by taking advantage of their rigidity. We have reported the synthesis of a belt-shaped cyclic trimer with two amide bonds between monomeric units by the self-condensation of 2,5-di(alkylamino)terephthalic acid using dichlorotriphenylphosphorane as a dehydrative condensation agent. In this presentation, we report the synthesis and self-condensation of 4,6-di(alkylamino)isophthalic acid **1** as shown in Scheme 1. We expected that a belt-shaped cyclic tetramer $\mathbf{2^4}$ would be obtained as the smallest ring-size product. The compound **1** was synthesized from *m*-xylene (**3**) by five steps, and its self-condensation for the synthesis of $\mathbf{2^{2n}}$ was studied using dichlorotriphenylphosphorane.
Keywords : Belt-Shaped Macrocycle, Amide, Condensation

ベルト型環状分子は、その剛直性を活用してホスト分子として用いられるなど、超分子化学における様々な応用が報告されている。我々の以前の研究において、2,5-ジ(アルキルアミノ)テレフタル酸に脱水縮合剤であるジクロロトリフェニルホスホランを作用させることで、モノマーユニット間に 2 つのアミド結合を形成したベルト型環状 3 量体の合成を達成している。そこで本研究ではスキーム 1 に示したように、アミノ基とカルボキシ基の位置を変えた 4,6-ジ(アルキルアミノ)イソフタル酸 **1** の合成と、その自己縮合によるベルト型環状分子 $\mathbf{2^{2n}}$ の合成を検討した。アミノ基とカルボキシ基の位置を変更することで偶数個のモノマーユニットで構成されたベルト型環状分子を選択的に合成でき、最小のベルト型環状分子が 3 量体ではなく 4 量体 $\mathbf{2^4}$ になると考えた。*m*-キシレン (**3**) を出発物質として 5 工程で **1** を合成した。次にジクロロトリフェニルホスホランなどの脱水縮合剤を用いて **1** を自己縮合させ、$\mathbf{2^{2n}}$ の合成を検討した。

Scheme 1



3 **1** $\mathbf{2^{2n}}$

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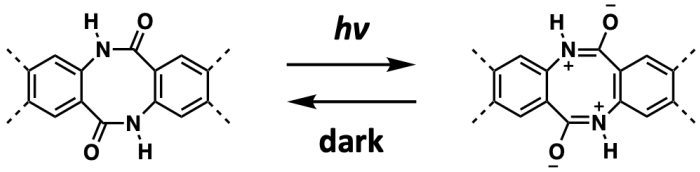
Synthesis and Function of Novel Amide-Embedded Cyclic π-System

([1]*School of Engineering The University of Tokyo*, [2]*Graduate School of Engineering The University of Tokyo*, [3]*PRESTO, JST*) ○Sho Fukuda,[1] Daiki Morishita,[2] Yoshimitsu Itoh,[2,3]
Keywords Amide; π Conjugation; Aromaticity; Photofunction

Amides have the double-bond character of the C−N bond due to the contribution of resonance structure.[1] Although their characteristics, such as chemical stability and planarity, have been widely recognized, their π-conjugation capability has not been focused on. In our research group, we have been focusing on this aspect of amides and designed molecules in which the amide bonds are embedded in a cyclic conjugation system.[2]

Here, we report that an amide-embedded cyclic framework can exhibit cyclic conjugation even in a photo-excited state. We have synthesized a series of molecules with an eight-membered cyclic structure embedded with two amide bonds. These molecules exhibit photo-responsiveness, likely due to the incorporation of the amide groups into the 8π cyclic conjugation, leading to aromatic stabilization.[3,4]



1) L. Pauling, The Nature of the Chemical Bond; Cornell University Press: Ithaca, NY, 1960.
2) D. Morishita, Y. Itoh, *submitted* for publication.
3) The 33rd Symposium on Physical Organic Chemistry, Okayama, 2023.
4) S. Fukuda, D. Morishita, Y. Itoh, *to be submitted*.

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
E1122(1122, Bldg. 11 [2F])

[E1122-3am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Satoru Hiroto, Youhei Miura

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1122-3am-01]
Synthesis and Crystal Structure of Imidazo-Fused Dehydro[12]annulene

○Youhei Miura Miura[1], Kazuki Murai[1], Naoki Yoshioka[1] (1. Keio University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1122-3am-02]
Synthesis of π-extended aromatic azo compounds and their functional evaluation

○Yurina Kozu[1], Hayato Yamada[1], Kazuma Amaike[1], Kenichiro Itami[1] (1. Nagoya University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1122-3am-03]
Synthesis and properties of tetratia[8]circulene having hydrogen bon

○Takahiro Minoura[1] (1. University of Hyogo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1122-3am-04]
Synthesis and properties of cyclobutatricyclopentatetraphenylene via an unexpected 4-membered-ring formation reaction

○Soshi Hirota[1,2], Sachiko Nakano[1], Haruki Sugiyama[1,2,3], Yasutomo Segawa[1,2] (1. Institute for Molecular Science, 2. SOKENDAI, 3. CROSS)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1122-3am-05]
Synthesis and characterization of multi-electron reduced species of oligo(pentafulvalene)s bearing a 1D fragment of C_{60}

○Zhe Wang[1], Shu Takagi[2], Aiko Fukazawa[1] (1. WPI-iCeMS, Kyoto University, 2. Graduate School of Engineering, Kyoto University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1122-3am-06]
Synthesis and Characteristics of Non-Alternant Hydrocarbons Possessing a Planar Octagon

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

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1122-3am-07]

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[3+2]cycloadditions for multifaced applications of molecular nanocarbons

○Rikuou Tanase[1], Sajan Pradhan[4], Jean Bouffard[4], Kazuma Amaike[2], Kenichiro Itami[2,3] (1. School of Science, Nagoya University, 2. Graduate School of Science, Nagoya University, 3. Institute of Transformative Bio-Molecules, 4. Department of Chemisry and Nanoscience, Ewha womans 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

[E1122-3am-08]

Synthesis of polycyclic compounds by [2+2]cyclobutene formation reaction of anthracene and DDQ

○Masahiko Fukumoto[1], Satoru HIroto[1] (1. The Univ. of Kyoto)

Japanese

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

[E1122-3am-09]

Iterative synthesis of long-chain oligo(pentafulvalene)s

○Shu I. Takagi[1], Zhe Wang[1], Masahiro Hayakawa[1], Aiko Fukazawa[1] (1. Kyoto University)

Japanese

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

[E1122-3am-10]

One-shot Synthesis of π-Conjugated Cations by Formal C^{4+} Introduction

○Daisuke Doi[1], Masahiro Hayakawa[1], Ryosuke Sowa[1], Takuji Hatakeyama[1] (1. Kyoto University)

Japanese

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

[E1122-3am-11]

Synthesis and Properties of Adamantane-Annulated Molecular Nanographenes

○Miyuka Ogawa[1], Takaku Yoshihara[1], Kenichiro Itami[1], Akiko Yagi[1] (1. Nagoya University)

English

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

[E1122-3am-12]

Controlling the Frontier Molecular Orbitals and Photophysical Properties of Boron Tropolonate Complexes by Regioselective Functionalization

○Hikari Ogoshi Ogoshi[1], Shunichiro Ito[1], Kazuo Tanaka[1] (1. Grad.Sch. of Eng., Kyoto Univ.)

Japanese

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

[E1122-3am-13]

The Effect of Fused Rings on the Coordination Ability of Antiaromatic Hydrocarbons to Ni(0) Center

○Riina Kuwata[1], Takefumi Imanishi[1], Shota Hasegawa[2], Yuta Uetake[3], Junichi Usuba[2], Kosuke Yasui[2], Aiko Fukazawa[2] (1. Graduate School of Engineering, Kyoto University, 2. Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, 3. Graduate School of Engineering, Osaka University)

Japanese

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

[E1122-3am-14]

Synthesis of Thiazolochlorin Compounds and Their Optical Properties

○Shu Miyawaki[1], Takeo Nakano[1] (1. Shinshu University)

Japanese

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

[E1122-3am-15]

Synthesis and physical properties of thienocyclopenta-fused pyrenes

○Kenji Tsukamoto[1], Koji Takagi[2], Yasutomo Segawa[1,3] (1. Institute for Molecular Science, 2. Grad. Sch. Eng., Nagoya Institute of Technology, 3. SOKENDAI)

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イミダゾールが縮環したデヒドロ[12]アヌレンの合成と結晶構造

（慶大理工）○三浦 洋平・村井 一貴・吉岡 直樹
Synthesis and Crystal Structure of Imidazo-Fused Dehydro[12]annulene (*Faculty of Science and Technology, Keio University*) ○Youhei Miura, Kazuki Murai, Naoki Yoshioka

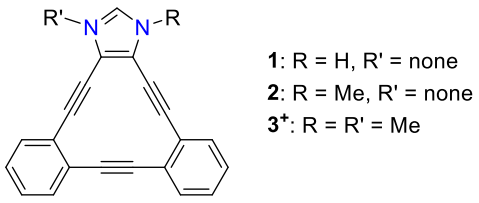
Dehydrobenzo[12]annulene(DBA) derivatives have been studied as the model of antiaromatic compounds and supramolecular synthon due to their 12π cyclic structure. Because BDA is composed of hydrogen and carbon atoms, only weak intermolecular interactions such as π-π and CH-π interactions are available to form the supramolecular structure. However, to use DBA as the supramolecular synthon, introduction of the strong intermolecular forces such as hydrogen bond and coulomb interaction are necessary for controlling the supramolecular structure. In this study, the DBA derivatives **1**, **2**, and **3** (Scheme 1) with a various structurally transformable imidazole ring were prepared, and their crystal structures were investigated.

Compound **1** formed a dimeric structure by π-π interactions and a 1D chain structure by hydrogen bonding in the crystal, reflecting its structure with both imidazole and annulene rings. (Figure 1) Compound $\mathbf{3}^{+}\mathbf{PF_6}^{-}$ formed a stacked structure to cancel their large dipole moments derived from imidazolium skeleton.

Keywords : Hydrogen bond; Annulene; Imidazole; Organic crystal

デヒドロベンゾ[12]アヌレン(DBA)は平面性の高い 12π系の環状構造を持つため、反芳香族のモデル化合物や超分子の構成要素として研究が行われている。DBA は炭素と水素のみから成る化合物であるため、π-π、CH-π 相互作用などの比較的弱い分子間相互作用のみを超分子形成に利用できる。しかし、それらは方向性を制御することが難しく、高度に制御された構造を構築するには水素結合やクーロン相互作用などのより強い相互作用を利用することが必要である。本研究では強い分子間相互作用を利用するため、様々な構造変換が可能なイミダゾール環を導入した DBA 類縁体 **1**, **2**, **3**(Scheme 1)を合成し、イミダゾール部位の化学修飾による結晶構造の変化を調査した。

化合物 **1** は結晶中でアヌレン環同士のπ-π相互作用による二量体形成と、イミダゾール同士の水素結合による一次元構造を形成しており、**1** の構造を反映した分子配列が見られた。(Figure 1) また、$\mathbf{3}^{+}\mathbf{PF_6}^{-}$はイミダゾリウム構造に由来する大きな双極子モーメントを持ち、それを打ち消すように分子が反平行に重なる構造を形成した。



1: R = H, R' = none
2: R = Me, R' = none
3^{+}: R = R' = Me

Scheme 1. Molecular structures of **1**, **2**, and **3**.

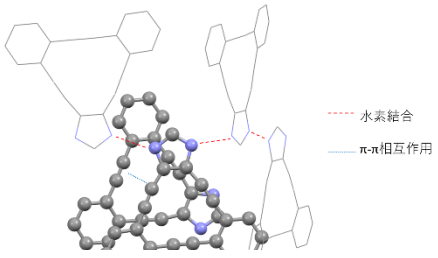


Figure 1. Molecular arrangement of **1**.

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π拡張芳香族アゾ化合物の合成と機能評価

(名大理[1]・名大院理[2]・IRCCS[3]・ITbM[4])○神頭優理菜[1]・山田早人[2,3]・天池一真[2]・伊丹健一郎[2,4])

Synthesis of π-extended aromatic azo compounds and their functional evaluation

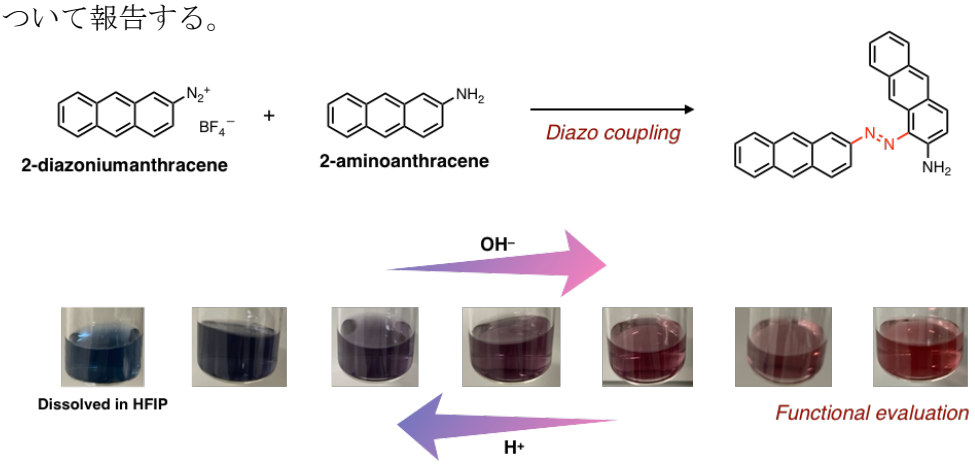
([1]School of Science, Nagoya University, [2]Graduate School of Science, Nagoya University, [3]Integrated Research Consortium on Chemical Sciences, Nagoya University, [4]Institute of Transformative Bio-Molecules, Nagoya University) ○ Yurina Kozu,[1] Hayato Yamada,[2,3] Kazuma Amaike,[2] Kenichiro Itami[2,4]

Aromatic azo compounds are a group of molecules that have long been used as dyes. Recently, they have been widely applied to not only photochemical and electrochemical fields as optical sensors and electronic devices, but also biological field due to their antibacterial and antiviral properties. On the other hand, most of the aromatic azo compounds have simple structures such as phenyl and naphthyl groups, and there are few reports of the synthesis of azo compounds with large π conjugated structures. In this work, we have unexpectedly synthesized a novel π-extended aromatic azo compound consisting of two anthracene structures and evaluated its function.

Key words: diazo coupling, azo compounds, molecular nanocarbon

芳香族アゾ化合物は、古くから色素として用いられてきた分子群である。最近では、光センサーや電子デバイスなど、光化学、電気化学分野へ幅広く応用されている。さらには、抗菌性や抗ウイルス性などの特性も見出されており、生物分野への応用も進んでいる。一方で、これまで合成されてきた芳香族アゾ化合物の大半は、フェニル基やナフチル基といった単純な構造を有する分子であり、大きなπ骨格を有するナノカーボンを用いたアゾ化合物の合成は限定的である。

今回、ジアゾニウムアントラセンとチロシンとのジアゾカップリング反応を行なっていたところ、偶然にも二つのアントラセン骨格からなる新規π拡張芳香族アゾ化合物が選択的に得られた。本発表では、π拡張芳香族アゾ化合物の合成とその機能評価について報告する。



[1] Mughal, E.; Ahmed, S. *et al*. *Dyes and Pigments* **2022**, *199*, 110050.

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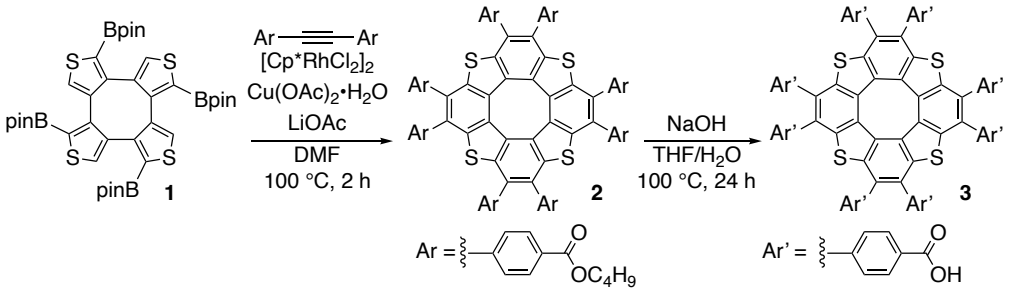
外周部に水素結合部位を持つテトラチア[8]サーキュレンの合成と性質

（兵庫県大院理）○箕浦 貴大・三宅 由寛
Synthesis and Properties of Tetrathia[8]circulenes with Hydrogen-Bonding Moieties (*Graduate School of Science*, *University of Hyogo*) ○Takahiro Minoura, Yoshihiro Miyake

Disk-shaped π-conjugated molecules with hydrogen-bonding moieties are known to exhibit liquid crystalline and charge transport properties derived from their stacking structure. Recently, we have synthesized planar tetrathia[8]circulenes and have evacuated their properties such as charge transport properties. Here, we report the successful synthesis of tetrathia[8]circulene with hydrogen-bonding moieties. In this presentation, we will also describe their structures and properties.
Keywords : circulene, hydrogen-bonding

ディスク状π共役分子に水素結合性官能基を導入し、分子間にわたる秩序構造を形成させる試みはさかんに行われている。導入した官能基に応じて多孔性骨格を構築することや積層構造に由来した液晶性および電荷移動特性が発現することが知られている。その電子的性質は用いるディスク状π共役骨格によって大きく変化する。当研究グループではディスク状分子であるテトラチア[8]サーキュレンの系統的合成に成功し、積層構造に由来した自己会合挙動や電荷輸送特性などの性質を明らかにしている[1-3]。本研究では水素結合部位をもつテトラチア[8]サーキュレンを合成し、その性質を調べた。

既報の方法を利用し、ロジウム触媒存在下、テトラボリルテトラチエニレン **1** とエステル部位をもつジフェニルアセチレン誘導体との縮環反応を行うと、対応するテトラチア[8]サーキュレン **2** が収率 18%で得られた。続いてエステル部位を加水分解することで外周部にカルボンキシ基をもつサーキュレン **3** が収率 14%で得られた。発表では誘導体の合成や得られた化合物の構造および性質をあわせて報告する予定である。



[1] Miyake, Y.; Shinokubo, H. *Chem. Commun*. **2020**, *56*, 15605-15614.
[2] Kato, S.; Serizawa, Y.; Sakamaki, D.; Seki, S. Miyake, Y.; Shinokubo, H. *Chem. Commun*. **2015**, *51*, 16944-16947.
[3] Kato, S.; Akahori, S.; Serizawa, Y.; Lin, X.; Yamauchi, M.; Yagai, S.; Sakurai, T.; Matsuda, W.; Seki, S.; Shinokubo, H.; Miyake, Y. *J. Org. Chem*. **2020**, *85*, 62-69.

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予期しない4員環形成反応によるシクロブタトリシクロペンタテトラフェニレンの合成とその性質

（分子科学研究所[1]・総合研究大学院大学[2]・総合科学研究機構[3]）○廣田 宗士[1,2]・中野 さち子[1]・杉山 晴紀[1,2,3]・瀬川 泰知[1,2]

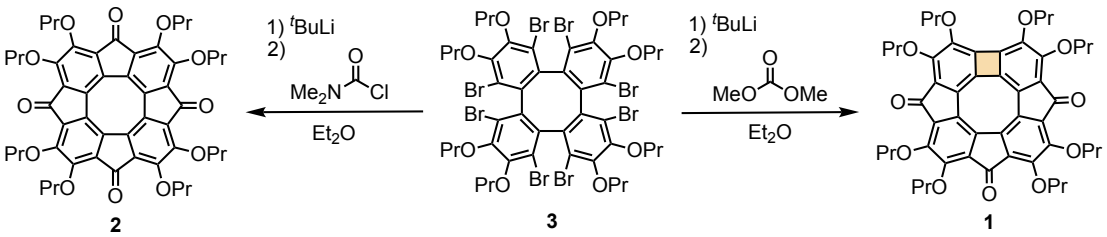
Synthesis and properties of cyclobutatricyclopentatetraphenylene via an unexpected 4-membered-ring formation reaction ([1]*Institute for Molecular Science*, [2]*SOKENDAI*, [3]*Comprehensive Research Organization for Science and Society*) ○Soshi Hirota,[1,2] Sachiko Nakano,[1] Haruki Sugiyama,[1,2,3] Yasutomo Segawa[1,2]

Aromatic compounds having 4-membered rings attract considerable interest owing to their unique structural and physical properties. However, most of the biphenylene-containing aromatic compounds reported so far consist of 4- and 6-membered rings, and the synthesis of more complex aromatic ring systems is still challenging. Herein we report the synthesis of polycyclic arenes composed of 4-, 5-, 6-, and 8-membered rings via an unexpected 4-membered ring formation reaction. The carbonylation of an octalithiated tetraphenylene yielded a tricarbonylated arene containing a 4-membered ring or a tetracarbonylated one, depending on the carbonyl reagents. The structures were determined by X-ray crystallography, and their electronic properties were examined using absorption spectroscopy and cyclic voltammetry. The antiaromaticity of the 4-, 5-, and 8-membered rings of these compounds was studied by theoretical calculations.

Keywords : 4-membered ring formation reaction; polycyclic aromatic compounds; antiaromaticity

多環芳香族化合物は、剛直な構造をもち、興味深い性質をもつ。しかし、4員環を有する多環芳香族化合物の合成例は限られており、特に4員環の他に多様な環構造を有するものは報告例が少ない。今回我々は、テトラフェニレン誘導体**3**のカルボニル化反応において、カルボニル化剤に炭酸ジメチルを使用すると、4員環を有するシクロブタトリシクロペンタテトラフェニレン**1**が得られることを見出した。また、異なるカルボニル化剤を用いた反応条件では、テトラカルボニル体**2**が得られた[1]。

各種スペクトル測定およびDFT計算により、**1**は**2**と比較して狭いHOMO–LUMOギャップをもつことがわかった。発表では、化合物**1**,**2**の合成法や構造的・電子的性質、それぞれの環の芳香族性・反芳香族性について述べる。



1) Hirota, S.; Nakano, S.; Sugiyama, H.; Segawa, Y. *Org. Lett.* **2023**, *25*, 8062–8606.

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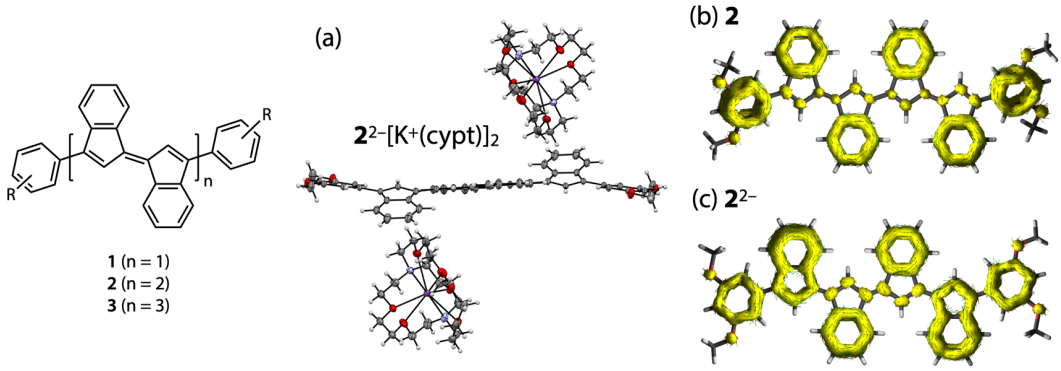
Synthesis and Characterization of Multi-Electron Reduced Species of Oligo(pentafulvalene)s Bearing a 1D Fragment of C_{60}

([1]*WPI-iCeMS, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*)
○Zhe Wang,[1] Shu I. Takagi,[2] Aiko Fukazawa[1]
Keywords: Pentafulvalene; Oligomer; Anion; Chemical Reduction; Aromaticity

Conjugated polymers consisting solely of an unsaturated hydrocarbon backbone, such as polyacetylene and poly(*p*-phenylenevinylene), are generally p-type semiconductors with relatively high-lying frontier molecular orbitals. Consequently, they exhibit low oxidation resistance and lack of stability under reductive conditions by alkali metals, impeding their applications as negative electrode materials for battery applications. On the other hand, we have recently reported the synthesis of oligo(pentafulvalene)s **1**–**3**, a series of 1D conjugated hydrocarbons that are composed of a 1D fragment structure of C_{60}, and revealed their exceptional stability toward multi-electron reductions unlike conventional 1D conjugated hydrocarbons.[1] In this study, to gain experimental insights into the origins of the high stability toward multi-electron reductions as well as the electronic structures of their reduced species, we synthesized and characterized the anionic species of **1**–**3**.

The ^{1}H and ^{13}C NMR spectroscopy revealed that the chemical reduction of pentafulvalene monomer **1** and dimer **2** in anhydrous THF using alkali metal-based reductants such as LiNaph and KC_8 proceeded cleanly. As a result of exhaustive optimization of experimental conditions, we have succeeded in the isolation of the dianionic species $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ as potassium salts (Figure a). HOMA, NICS, and ACID analyses based on the X-ray crystal structures revealed that dianion $\mathbf{2}^{2-}$ acquires 10π aromaticity in two terminal indene moieties (Figure c), while neutral dimer **2** exhibits local aromaticity at each benzene ring (Figure b). These results demonstrate their ability for multi-electron storage. Further studies on the chemical reduction of the longer-chain oligomers as well as the characterization of higher reduced species are currently underway.



1) M. Hayakawa, N. Sunayama, S. I. Takagi, Y. Matsuo, A. Tamaki, S. Yamaguchi, S. Seki, A. Fukazawa, *Nat. Commun*. **2023**, *14*, 2741.

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中央に平面八員環を含む非交互炭化水素類の合成と性質解明

（阪大院工 [1]）小西 彬仁 [1]・○徳山 はるか [1]・安田 誠 [1]

Synthesis and Characteristics of Non-Alternant Hydrocarbons Possessing a Planar Octagon

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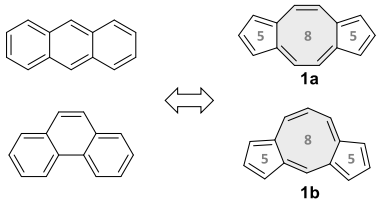
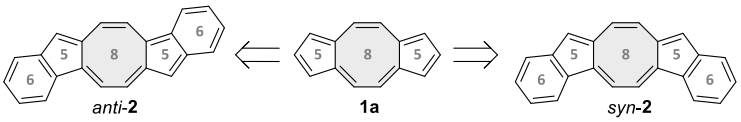
Non-alternant hydrocarbons have been studied for a long time because they have interesting properties. Recently, their chemistry has experienced a resurgence thanks to the development of efficient synthetic methodologies. Many molecules replaced their hexagons with a pair of pentagon and heptagon were designed and synthesized. In the case of tricyclic benzenoid compounds, non-alternant isomers having an octagon are possible structural isomers. Herein, we design the molecules consisting of 6-5-8-5-6 membered rings to identify π electron delocalization manner. The target molecules were synthesized via the dimerization of a diyne precursor using a Ni catalyst. X-ray crystallographic analysis revealed that one isomer has a planar structure with C_{2v} symmetry despite having a conjugated octagon.

Keywords : Non-Alternant Hydrocarbons; Conjugated Octagon; Biradical Character

非交互炭化水素は古くから研究されてきたが、効率的な合成法の開発を背景に近年再び注目を集めている [1]。特にベンゼノイド化合物の六員環を五員環や七員環で置き換えた分子は奇数員環の導入による電子物性の変化やπ電子の非局在化様式に興味が持たれ盛んに研究されてきた。三環性化合物では非交互異性体として八員環を含む分子 **1** が知られ [2,3]、いずれも周辺 14π系の寄与が明らかにされたが、更なるπ拡張による電子の非局在様式への影響に興味が持たれる。





本研究では分子 **1a** の両端にさらにベンゾ縮環を施した *anti*-**2** 及び *syn*-**2** に着目した。*syn*-**2** は閉殻、*anti*-**2** は開殻分子と予想され、縮環位置の違いが基底状態に大きな影響を与えると考えられる。Ni 触媒を用いた付加環化反応によりジイン前駆体から共役八員環骨格を構築した。*syn*-**2** は安定な赤橙色固体として合成・単離できた。X 線単結晶構造解析からほぼ平面構造を持つことが明らかとなった。本発表では分子 **2** の合成と性質の詳細について紹介する。

1) A. Konishi; M. Yasuda, *Chem. Lett.* **2021**, *50*, 195. 2) K. Hafner, G. F. Thiele; C. Mink*, Angew. Chem. Int. Ed*. **1988**, *27,* 1191. 3) M. Oda, Y. Sakamoto, T. Kajioka, T. Uchiyama, R. Miyatake; S. Kuroda, *Angew. Chem. Int. Ed*. **2001**, *40,* 2660.

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分子ナノカーボンの多方面応用を指向した[3+2]付加環化反応

(名大理[1]・名大院理[2]・名大 WPI-ITbM[3]・梨花女子大[4]) ○棚瀬陸王[1]・Pradhan Sajan[4]・Jean Bouffard[4]・天池一真[2]・伊丹健一郎[2,3]

[3+2]cycloadditions for multifaced applications of molecular nanocarbons ([1]*School of Science, Nagoya University*, [2]*Graduate School of Science, Nagoya University*, [3]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*, [4]*Department of Chemistry and Nanoscience, Ewha Womans University*), ○ Rikuo Tanase,[1] Pradhan Sajan,[4] Jean Bouffard,[4] Kazuma Amaike,[2] Kenichiro Itami[2,3]

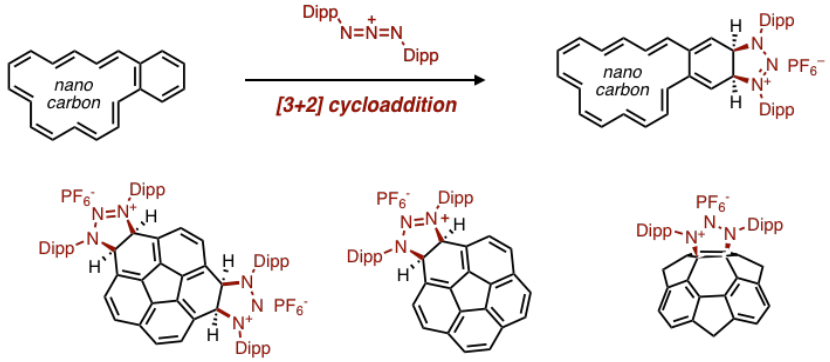
Molecular nanocarbons are a group of compounds that are expected to be applied not only in the field of materials chemistry but also in the biological field. On the other hand, application-oriented nanocarbon synthesis such as functionalized and π-expanded nanocarbons remains issue of multi-step synthesis and difficulty in synthesis, requiring development of new reactions.

To realize a new reaction in the field of molecular nanocarbons, we focused on a report by Bouffard's group in 2023, [3+2] cycloaddition of diazaanoniaallene (DAAA) cations with benzene derivatives followed by [4+2] cycloaddition with alkynes and benzynes. This transformation not only allows derivatization of the benzene derivatives in two steps, but also provides a handle for functionalization in a single step. In this presentation, we applied the [3+2] cycloaddition reaction to molecular nanocarbons, obtaining mono- or di-DAAA cation adduct.

Keywords; Molecular nanocarbon; [3+2] cycloaddition

分子ナノカーボンは材料化学分野のみならず生物分野への応用が期待されている化合物群である。一方で応用展開を指向した分子ナノカーボンを合成するにあたり、ナノカーボンの官能基化やπ拡張を行うには、合成が多段階になることや合成の困難さが依然として課題である。

分子ナノカーボン分野における新反応の開発に向け、2023 年に Bouffard グループらにより報告された diazaanoniaallene(DAAA)カチオンとベンゼン誘導体との[3+2]付加環化反応と続くアルキンやベンザインとの[4+2]付加環化反応に注目した[1]。本反応は 2 段階でベンゼン誘導体の官能基化が可能であるだけでなく、1 段階で機能化のためのハンドルを付与できるものである。本発表では、この[3+2]付加環化反応を分子ナノカーボンへ応用し、条件によって DAAA カチオンが一つないしは二つ付加した分子が得られることを見出した。



1. Pradhan, S.; Mohammadi, F.; Bouffard, J. *J. Am. Chem. Soc.* **2023**, *145*, *22*, 12214–12223.

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アントラセンと DDQ の［2+2］シクロブテン形成反応による多環式化合物の合成

（京大院人環）○福元政彦・廣戸 聡
Synthesis of polycyclic compounds by [2+2] cyclobutene formation reaction of anthracene and DDQ (*Graduate School of Human and Environmental Studies, Kyoto University*)
○Masahiko Fukumoto, Satoru Hiroto

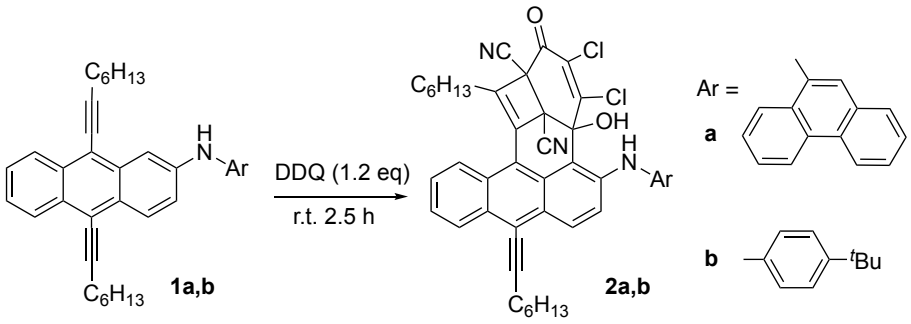
Cyclobutene has been utilized as an important reaction precursor due to its high reactivity originated by its distorted double bond. The synthesis has usually been carried out by a [2 + 2] photocyclization reaction, and has also been reported using the [2 + 2] cyclization reaction of alkynes and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Here, we report the successful synthesis of a cyclobutene-containing compound through the reaction of 2-*N*-arylamino-9,10-dialkynylanthracene and DDQ.

The reaction of 1.2 equivalents of DDQ and compounds **1a** in a methylene chloride solution produced compounds **2a** in moderate yields (Scheme 1). X-ray structural analysis indicated that the DDQ and alkyne substituent form a cyclobutene ring, and the anthracene ring also forms a six-membered ring, forming a distorted structure. In this presentation, we will report on the study of reaction conditions, details of structural analysis, and analysis of the reaction mechanism.

Keywords : Cyclobutene, DDQ, Polycyclic compound

シクロブテンは歪んだ二重結合の高い反応性を活かして重要な反応前駆体として利用されてきた[1),2)]。[2 + 2]光環化反応によって合成されるのが一般的だが[3)]、アルキンと 2,3-dichloro-5,6-dicyano-1,4-benzoquinone(DDQ)の[2 + 2]環化反応でも合成が報告されている[4)]。今回、2-*N*-arylamino-9,10-dialkynylanthracene と DDQ の反応により、シクロブテンを含む化合物の合成に成功したので報告する。

化合物 **1a** に DDQ を 1.2 当量加え、塩化メチレン溶媒中室温で 2.5 時間攪拌したところ、中程度の収率で DDQ が付加した化合物が得られた（Scheme 1）。X 線構造解析の結果、DDQ と alkyne 置換基で cyclobutene を形成しつつ、anthracene とも六員環を形成し、歪んだ構造を形成していることがわかった。本発表では、反応条件の検討と構造解析の詳細、反応機構についての解析について報告する。



Scheme 1.

1) K. B. Wiberg, J. E. Hiatt, *J. Am. Chem. Soc.* **1968**, *90*, 6495.
2) J. M. Hoyt, V. A. Schmidt, A. M. Tondreau, *Science* **2015**, *349*, 960.
3) Y.-B. Bai, Z. Luo, Y. Wang, *J. Am. Chem. Soc.* **2018**, *140,* 5860.
4) K. Shin-ichiro, T. Marten, D. Francois, *Angew. Chem. Int. Ed.* **2010**, *49,* 6207.

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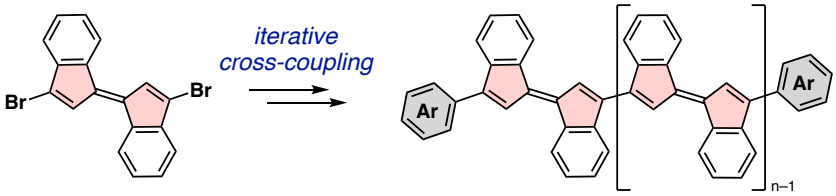
長鎖オリゴペンタフルバレンの逐次合成

（京大院工[1]・京大 WPI-iCeMS[2]）○髙木 周[1]・王 哲[2]・早川 雅大[2]・深澤 愛子[2]
Iterative synthesis of long-chain oligo(pentafulvalene)s ([1]*Graduate School of Engineering, Kyoto University*, [2]*WPI-iCeMS, Kyoto University*) ○Shu I. Takagi,[1] Zhe Wang,[2] Masahiro Hayakawa,[2] Aiko Fukazawa[2]

Electron-accepting π-electron systems are essential components for organic optoelectronic materials. We have recently reported the synthesis of oligo(pentafulvalene)s **1** up to trimer, and demonstrated their high electron affinity as well as robustness toward multi-electron reduction even without having electron-withdrawing groups.[1] However, despite the greater potential of the longer oligomers as electron-accepting materials, the low efficiency of the functional group transformation and inter-unit bond formation of dibenzopentafulvalene impeded their synthesis. Herein we report the improved synthesis of **1** based on the Pd-catalyzed stannylation and the Kosugi-Migita-Stille cross-coupling. The iterative synthesis of a tetramer as well as their electrochemical and photophysical properties will also be presented.
Keywords: electron-acceptor, pentafulvalene, cross-conjugation, oligomer, cross-coupling reaction

電子受容性 π 共役系は有機光・電子機能性材料に必要不可欠な構成要素である．我々は最近，電子求引基の導入に依存しない電子受容性炭化水素として，フラーレンの一次元部分構造であるオリゴペンタフルバレン **1** を設計し，三量体までの合成を達成した[1]．これらはフラーレンに迫る高い電子親和性と多電子還元への堅牢性，強い光吸収をもち，その性質は鎖長の伸長に伴い向上することから，より長鎖のオリゴマーの物性に興味がもたれる．一方で，酸化還元活性なペンタフルバレンの官能基変換や結合形成には困難が伴い，従来の合成法の収率の低さがさらなる研究の障害となっていた．そこで本研究では，ペンタフルバレンの官能基化およびクロスカップリング反応の収率向上を目的に種々の反応を比較した結果，パラジウム触媒を用いたトリアルキルスタンニル基の導入，および続く小杉·右田·Stille カップリングの組み合わせが最良の結果を与えることを明らかにした．可溶化のため片側末端に置換アリール基を導入したペンタフルバレンを用い，スタンニル化およびクロスカップリング反応を逐次的に行うことで，従来法では合成できなかった長鎖オリゴマーである四量体の合成を達成した．本研究では，四量体の電気化学特性や光物性についても報告する．



Oligo(pentafulvalene)s
1
(n = 1–4)

1) M. Hayakawa, N. Sunayama, S. I. Takagi, A. Tamaki, Y. Matsuo, S. Yamaguchi, S. Seki, A. Fukazawa. *Nat. Commun.*, **2023**, *14*, 2741.

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形式的 C^{4+}導入による π 共役カチオンの one-shot 合成

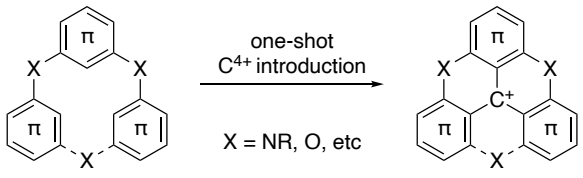
（京大院理）○土井 大輔・早川 雅大・曽和 亮佑・畠山 琢次

One-shot Synthesis of π-Conjugated Cations by Formal C^{4+} Introduction (*Graduate School of Science, Kyoto University*) ○Daisuke Doi, Masahiro Hayakawa, Ryosuke Sowa, Takuji Hatakeyama

π-Conjugated cations have potential applications in organic dyes[1] and photoredox catalysts[2] owing to their characteristic photophysical and redox properties. Among them, cationic triangulenes and helicenes exhibit high stability due to the delocalization of the positive charge, and have attracted considerable interest.[3] However, their chemical space remains limited on account of the lack of a versatile method for their synthesis. Therefore, in this study, we have developed a new synthetic method to expand the accessible chemical space. This method allows the one-shot construction of a variety of π-conjugated cations, including unexplored skeletons, by formal C^{4+} introduction and ring condensation. In this presentation, we will report details of the reaction as well as the structures and physical properties of the compounds thus obtained.

Keywords : π-Conjugated Cations; Formal C^{4+} Introduction; Ring Condensation; Chemical Space

π 共役カチオンは，特徴的な光物性や酸化還元特性をもつことから，有機染料 [1]やフォトレドックス触媒 [2]へ応用がなされている分子群である。なかでも，カチオン性トリアンギュレン・ヘリセンは，正電荷の効果的な非局在化により高い安定性を示すことから，π 共役カチオンの代表的な骨格として興味を集めてきた [3]。しかし，汎用性に優れた合成手法が乏しいために，アクセス可能な化学空間は限られている。今回我々は，その拡張のため，π 共役カチオンの新たな合成法を開発した。本手法は，形式的 C^{4+}導入と縮環を同時に行うことで，既存の手法では合成困難な構造を含む多様な π 共役カチオンを one-shot で構築することができる。本講演では，反応の詳細と得られた化合物の構造・物性について報告する予定である。



1) D. F. Duxbury, *Chem. Rev.* **1993**, *93*, 381. 2) (a) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075, (b) S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen, *J. Am. Chem. Soc.* **2004**, *126*, 1600. 3) J. Bosson, J. Gouin, J. Lacour, *Chem. Soc. Rev.* **2014**, *43*, 2824.

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アダマンタン縮環ナノグラフェン分子の合成と性質

（名大院理[1]・名大 WPI-ITbM[2]）○小川 実侑香[1]・吉原 空駆[1]・伊丹 健一郎[1,2]・八木 亜樹子[1,2]

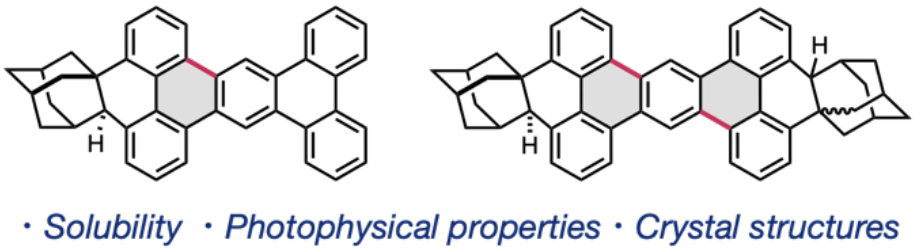
Synthesis and Properties of Adamantane-Annulated Molecular Nanographenes ([1]*Graduate School of Science, Nagoya University,*[2]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*) ○Miyuka Ogawa[1], Takaku Yoshihara[1], Kenichiro Itami[1,2], Akiko Yagi[1,2]

Adamantane ($C_{10}H_{16}$) is a tricyclic saturated hydrocarbon used in a wide variety of materials. In 2023, we developed a method for annulation of the adamantane moiety to arenes.[1] More than 30 kinds of adamantane-annulated arenes (AAAs) can be synthesized from lithiated biaryls and 4-protoadamantanone. The properties of AAAs have been revealed, such as high solubility in organic solvents in contrast to the corresponding arenes. We have also discovered that stable carbocation species can be obtained by oxidation of AAAs. In this work, we developed intramolecular cyclodehydrogenation of AAAs to synthesize adamantane-annulated molecular nanographenes. Two kinds of adamantane-annulated tetrabenzoanthracene were synthesized to reveal that their solubility in organic solvents and crystal packing structure depends on the number of adamantane units.

Keywords : adamantane; molecular nanographenes; annulation; solubility

アダマンタンは $C_{10}H_{16}$ で表される三環式飽和炭化水素であり、歪みのない剛直な構造や嵩高さをもつことから多様な材料に用いられている。2023 年に我々は、アレーン類に対してアダマンタン骨格を縮環させる反応を開発した[1]。リチオ化されたビアリール骨格と 4-プロトアダマンタノンを用いる一連の反応によって、30 種類以上のアダマンタン縮環アレーンを合成することができた。得られるアダマンタン縮環アレーン類は対応するアレーンよりも有機溶媒に対する溶解性が高いことや吸収および蛍光波長が長波長側に観測されることを明らかにした。さらに、酸化させることで安定なカルボカチオン種が得られることも分かった。

今回我々は、アダマンタン縮環芳香族分子における脱水素環化反応を検討することで、より広いπ共役骨格をもつアダマンタン縮環ナノグラフェン分子の合成を行った。具体的には、2 種類のアダマンタン縮環テトラベンゾアントラセンを合成し、それらの性質を調査した。アダマンタンユニットの個数によって有機溶媒に対する溶解性が変化することや、結晶におけるパッキング構造が異なることなどを明らかにした。



1) Yoshihara, T.; Shudo, H.; Yagi, A.: Itami, K. *J. Am. Chem. Soc.*, **2023**, *145*, 11754.

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Controlling the Frontier Molecular Orbitals and Photophysical Properties of Boron Tropolonate Complexes by Regioselective Functionalization

(*Graduate School of Engineering, Kyoto University*) ○Hikari Ogoshi, Shunichiro Ito, Kazuo Tanaka

Keywords: Tropolone; Boron Complexes; Frontier Molecular Orbital; Photophysical properties

Tropolone, a cyclic α-hydroxyketone with unsaturated seven-membered ring, shows polarized aromaticity derived from the delocalization of 6-π electrons on its seven-membered ring. Because this structure is often found in natural products, a lot of studies about synthesis and biological activities of tropolone has been reported so far. Recently, we found that tropolone shows enhanced photoluminescence by boron complexation.[1] However, despite the unique electronic structure such as polarized aromaticity, few studies focusing on their electronic structure and photophysical properties have been reported.

In this study, we conducted theoretical calculations of tropolone and its derivatives to gather insight into the relationship between structure and physical properties of tropolone-based compounds. It was found that π conjugation of frontier molecular orbitals (FMO) of tropolone differ from each other. Herein, we synthesized boron complexes based on tropolone derivatives obtained from regioselective substitution. Significantly, it was revealed that FMO energy levels and photophysical properties are tunable by introducing various kinds of functional groups.

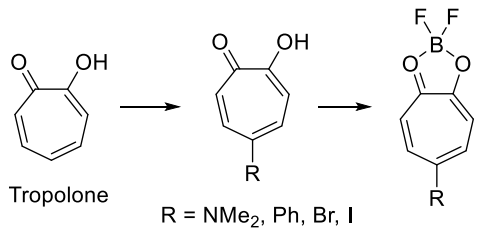

Figure 1. Chemical structures of synthesized compounds based on tropolone.

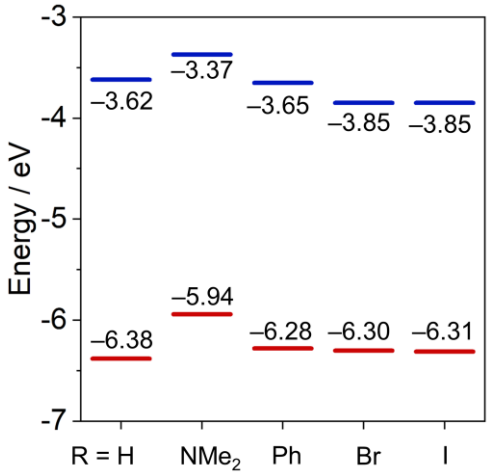

Figure 2. Energy diagram of synthesized boron complexes estimated from the results of cyclic voltammetry using the following empirical formula: E_{LUMO} / eV = –5.1 – V_{red}^{onset} / V and E_{HOMO} / eV = –5.1 – V_{ox}^{onset} / V.

1) H. Ogoshi, S. Ito, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 452–460

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反芳香族炭化水素の縮環部位がニッケル(0)への配位能に及ぼす効果

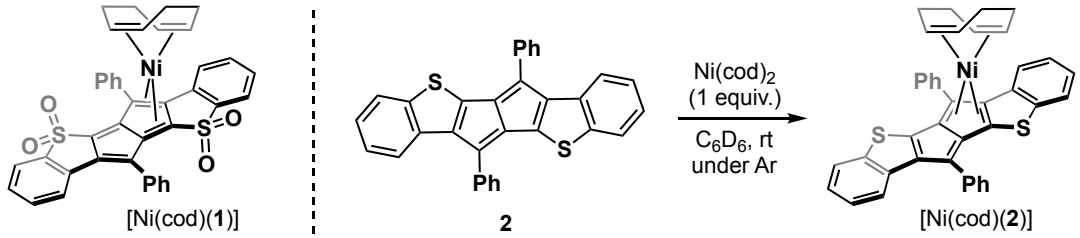
（京大院工 [1]・京大 iCeMS[2]・阪大院工 [3]）○鍬田 梨衣奈 [1]・今西 勇文 [1]・長谷川 翔大 [2]・植竹 裕太 [3]・薄葉 純一 [2]・安井 孝介 [2]・深澤 愛子 [2]

The Effect of Fused Rings on the Coordination Ability of Antiaromatic Hydrocarbons to Ni(0) Center ([1]*Graduate School of Engineering, Kyoto University*, [2]*Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University,* [3]*Graduate School of Engineering, Osaka University*) ○Riina Kuwata,[1] Takefumi Imanishi,[1] Shota Hasegawa,[2] Yuta Uetake,[3] Junichi Usuba,[2] Kosuke Yasui,[2] Aiko Fukazawa[2]

We have recently reported that a nickel (0) complex coordinated by antiaromatic benzothiophene-*S,S*-dioxide-fused pentalene (**1**), [Ni(cod)(**1**)], exhibited exceptional stability even under exposure to air.[1] To gain further insights into the origin of the stability of this Ni-pentalene complex, we investigated a complexation reaction between nickel and benzothiophene-fused pentalene (**2**). The resulting complex, [Ni(cod)(**2**)], exhibited notably lower stability compared to that of [Ni(cod)(**1**)], indicating that structural difference in the fused rings affects the strength of the coordination bond between pentalene and nickel. In this presentation, the results of the analysis on the coordination bond of these complexes will be discussed from two perspectives; loss of antiaromatic character due to the coordination to nickel and the LUMO level of pentalene ligands.

Keywords : nickel, antiaromaticity, electronic effect, frontier molecular orbital, π-back donation

ペンタレンやシクロブタジエンなどの反芳香族炭化水素を配位子にもつ遷移金属錯体は，反芳香族化合物を安定化する目的で古くから研究されてきた．一方で，金属中心の電子状態や，配位子の反芳香族性が配位結合の強さに及ぼす効果は不明な点が多く残されている．このような背景のもと，当研究室では最近，ベンゾチオフェン-*S,S*-ジオキシド縮環ペンタレン (**1**) が配位した 0 価ニッケル錯体 [Ni(cod)(**1**)] の単離に成功し，これが空気中常温でも安定に存在することを見出した[1]．今回，この錯体の安定性の起源についてさらなる知見を得るために，ベンゾチオフェン縮環ペンタレン (**2**) とニッケルとの錯形成反応をおこなった．その結果，生じた錯体 [Ni(cod)(**2**)] の安定性は [Ni(cod)(**1**)] と比べて顕著に低く，縮環部位の構造の差異がペンタレンとニッケルの配位結合の強さに影響を及ぼすことがわかった．本発表では，ニッケルの配位に伴う反芳香族性の喪失と，ペンタレンの電子受容性の 2 つの視点から，これらの錯体の配位結合を検証した結果を併せて議論する．



[1] 今西，薄葉，安井，植竹，深澤，日本化学会第 103 回春季年会，K504-2pm-05.

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チアゾロクロリン化合物の合成と光物性

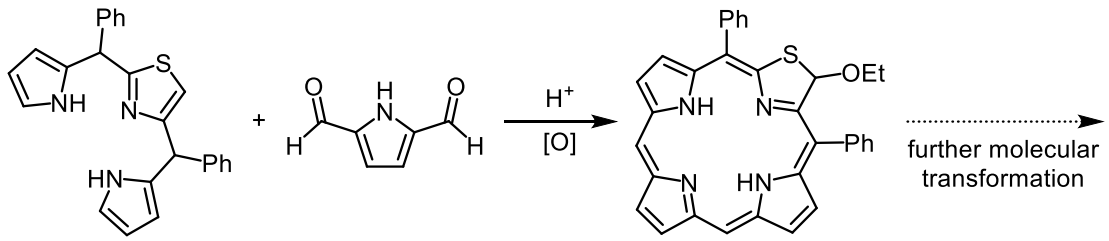
（信州大理）○宮脇脩・中野健央

Synthesis of Thiazolochrolin Compounds and Their Optical Properties (*Fac. Sci.*, *Shinshu Univ.*) ○Shu Miyawaki, Takeo Nakano

Porphyrin compounds exhibit unique absorption spectrum, which could be useful for various fields, such as biological and material chemistry. However, improvement of absorption intensity in longer wavelength region is still challenging. On the other hand, chlorins, in which their π-conjugated system is partially reduced, show distinct bathochromically shifted absorption band with increasing intensity, which is derived from asymmetric π-structure. Additionally, the introduction of hetero atom could be a powerful approach for the further precision control of the energy level and absorption wavelength. In the present work, we synthesized thiazolochlorin and its analogs, which contain sulfur atom at peripheral position. Further, their optical properties were measured.

Keywords : chlorin; thiazole; sulfur atom; photoabsorption

ポルフィリンは特異な吸収スペクトルを持つことから医療や機能性材料への応用が期待される化合物群である[1]。しかし、長波長領域における吸収強度の向上という点において課題が残されている。一方で、ポルフィリンのπ共役系の一部が還元されたクロリンは、骨格の非対称化によって、強度の増大を伴い吸収ピークが長波長化することが知られている。そこで、今回は共役系の変化と共に、ヘテロ原子を組み込んだ骨格の合成を目指した。ヘテロ原子の導入は、化合物のエネルギー準位の変化による、さらなる吸収波長の制御が見込める[2]。本研究では、クロリン骨格にチアゾール環を導入し、分子周縁部に硫黄原子を含むクロリン環の合成と、さらなる分子変換について検証した。得られた化合物の光物性についても併せて報告する。



1) S. Kim, Y. Rhee, J. Kim, *Anticancer Res*. **2017**, *37*, 6251-6258.
2) T. Nakano, H. Imoto, K, Naka, *Org*. *Lett*. **2021**, *23*, 7996-8000.

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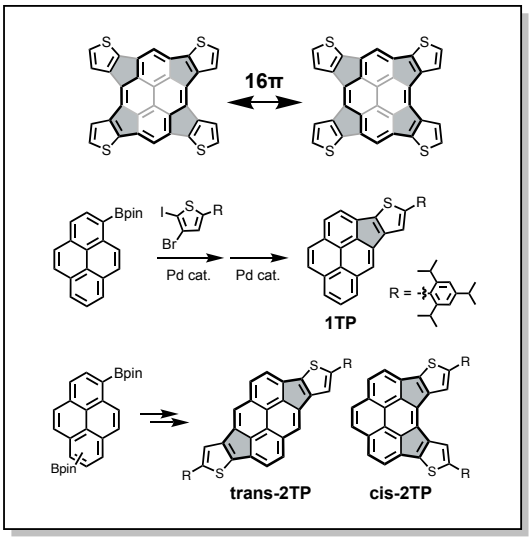
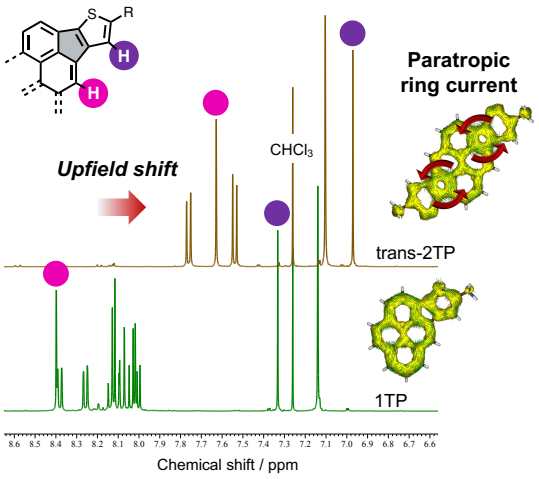
チエノシクロペンタジエン環を縮環したピレン誘導体の合成と物性

（分子研[1]・名工大院工[2]・総研大[3]）○塚本 兼司[1]・高木 幸治[2]・瀬川 泰知[1,3]
Synthesis and physical properties of thienocyclopenta-fused pyrenes ([1]*Institute for Molecular Science*, [2]*Grad. Sch. Eng., Nagoya Institute of Technology*, [3]*SOKENDAI*) ○ Kenji Tsukamoto,[1] Koji Takagi,[2] and Yasutomo Segawa[1,3]

In this work, we designed and synthesized thienocyclopenta-fused pyrenes. These molecules have different electron structures depending on the number and position of the cyclopentane rings, such as the presence or absence of a unique 16π anti-aromatic structure. The compounds were synthesized by Suzuki–Miyaura coupling of borylpyrenes with dihalothiophenes followed by Pd-catalyzed intramolecular C–H arylation. Upfield shifts were observed in the ^{1}H NMR spectra of **trans-2TP** and **cis-2TP** compared with that of **1TP** owing to the contribution of the16π anti-aromatic property of **trans-2TP** and **cis-2TP**. In addition, we carried out X-ray structural analysis, photophysical measurements, and DFT calculations for these compounds and clarified the relationship between the structures and their physical properties.
Keywords : π-conjugated compound; anti-aromaticity; thiophene

本研究では、ピレンの周囲にチエノシクロペンタジエン環が縮環した分子の設計および合成を行った。これらは、縮環の数や位置によって16π反芳香族の有無といった異なる興味深い電子状態をもつ。合成は、ボリルピレンとジハロチオフェンの鈴木カップリング反応に続く分子内C–Hアリール化反応によって達成した。16π反芳香族を伴う縮環数が2つの**trans-2TP**および**cis-2TP**のNMRスペクトルは、縮環数が1つの**1TP**と比較して高磁場シフトすることが確認された。また、これらの化合物に対しX線構造解析、光物性測定、量子化学計算を行い、分子構造が物性に及ぼす影響を詳細に調査した。





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

Wed. Mar 20, 2024 1:00 PM - 3:20 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:20 AM UTC
E1123(1123, Bldg. 11 [2F])

[E1123-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Gaku Fukuhara, Yuki Nagai

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1123-3pm-01]
Chiral recognition mediated by a photoresponsive dinuclear Eu(III) complex

○Midori Ishitsuka[1], Chiasa Motoki[1], Junpei Yuasa[1] (1. Tokyo University of Science)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1123-3pm-02]
Self-aggregation of bacteriochlorophyll-*d* analogs with linear and branched alkyl chains at the 17-position

○Nobuyuki Hara[1], Hitoshi Tamiaki[1] (1. Ritsumeikan University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1123-3pm-03]
Synthesis and optical properties of light-harvesting antenna models using peptide-chlorophyll conjugates

○Ryoko Nakajyo[1], Masahiro Higuchi[1], Hitoshi Tamiaki[2], Shogo Matsubara[1] (1. Grad.Sch. of Eng.,Nagoya Inst. of Tech., 2. Graduate School of Life Sciences, Ritsumeikan Univ.)

English
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1123-3pm-04]
Ion recognition ability and guest uptake/release kinetics of cobalt(III) macrocyclic metallohosts bearing bulky amine ligands

○Dejan Walter[1], Yoko Sakata[1,2], Shigehisa Akine[1,2] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1123-3pm-05]
Synthesis of a Hexabenzocoronene Radical Cation Having Double-concave Structure and Its Photophysical Properties in near-IR and IR Region

○Souta Uno[1], Shuichi Suzuki[1], Takeshi Naota (1. Osaka Univ.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1123-3pm-06]
Control of Photophysical and Magnetic Properties of Dihydrophenazine Radical Cation Salts during Solid-Liquid Phase Transitions

○Ritsuki Tanaka[1], Shuichi Suzuki[1], Takeshi Naota (1. Osaka 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

[E1123-3pm-07]

Synthesis and properties of salen-type cryptophane complexes that can close the aperture

○Zongjiang Yu[1], Yoko Sakata[2,3], Shigehisa Akine[2,3] (1. Grad. Sch. of Front. Sci., Kanazawa Univ., 2. Grad. Sch. of Natl. Sci. and Tech., Kanazawa Univ., 3. NanoLSI., Kanazawa Univ.)

Japanese

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

[E1123-3pm-08]

Construction of nanovesicles by self-assembly of oligoproline derivatives and its properties

○Shogo Matsubara[1], Yui Okamoto[1], Masahiro Higuchi[1] (1. Graduate School of Engineering, Nagoya Institute of Technology)

Japanese

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

[E1123-3pm-09]

Encapsulation of Multinuclear Copper Clusters by Aromatic Micelles and its Emission Enhancement

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

Japanese

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

[E1123-3pm-10]

Preparation and Self-Assembly of Dumbbell-shaped Aromatic Amphiphiles

○Aguri Sugawara[1], Kazuki Toyama[1], Lorenzo Catti[1], Michito Yoshizawa[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech)

English

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

[E1123-3pm-11]

Oligomerization of Bent Anthracene Dimers via Imine-based Dynamic Covalent Bonds

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

Japanese

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

[E1123-3pm-12]

Minimal double-stranded β-helices formation by metal cross-linking

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

Japanese

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

[E1123-3pm-13]

Development of giant spheres using small molecules through hydrogen-bonding networks

○Shoya Ogawa[1], Ken Yamanomoto[1], Kohei Endo[1] (1. Tokyo University of Science)

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光応答性二核 Eu(III)錯体をメディエーターとするキラル認識

（東理大理）○石塚美登利・元木千朝・湯浅順平
Chiral recognition mediated by a photoresponsive dinuclear Eu(III) complex
(*Fac. Sci, TUS*) ○Midori Ishitsuka, Chiasa Motoki, Junpei Yuasa

Here, we prepared a photo-responsive Eu(III) complex ($Eu_2(\mathbf{L_{Az}})_3$) as a mediator of long-range chirality recognition of chiral (bis)oxazoline ligands ((*R*/*S*)-Pybox). The $Eu_2(L_{Az})_3$ complex was synthesized by the reaction of Eu(III) ion and azobenzene-centered ligands ($\mathbf{L_{Az}}$). The mediator ($Eu_2(\mathbf{L_{Az}})_3$)-used chirality recognition of (*R*/*S*)-Pybox obeyed narcissistic chiral self-sorting mechanism both before and after UV irradiation, while the degree of the narcissistic chiral self-sorting character was diminished after the UV irradiation.
Keywords : Lanthanide complex; β-diketonte ligand; Circular dichroism; Azobenzene

鏡像異性体間の分子認識は不斉自己触媒反応やホモキリティー発現の重要な素過程であると考えられている。鏡像異性体は鏡像性以外の違いを持たないお互いに類似性の高い分子対であるため、分子間の強い相互作用と直接の分子接触を前提としてきた。一方で我々は最近、鏡像異性体間の分子認識のメディエーターとして二核 Eu(III)錯体を用いることで、分子間の直接の接触を必要としない長距離のキラル分子認識を達成している[1]。この長距離キラル分子認識機構を光などの簡便な外部刺激によって制御することができれば、鏡像異性体間の分子認識を素過程として含む様々な不斉反応系への応用展開が可能である。

本研究ではメディエーターである二核 Eu(III)錯体に光応答性部位としてアゾベンゼンを導入し、光刺激によるキラル分子認識機構の制御を目的に研究をおこなった。アゾベンゼンを導入した新規β-ジケトン配位子($\mathbf{L_{Az}}$)は薗頭カップリング反応及びクライゼン縮合により合成し、^{1}H NMR と精密質量分析によって生成を確認した。アセトン溶液中で酢酸ユーロピウムと $\mathbf{L_{Az}}$ とを 2:3 のモル比で反応させることで、メディエーターEu_2 ($\mathbf{L_{Az}}$)$_3$ を合成した。$Eu_2(\mathbf{L_{Az}})_3$ のアセトン溶液中、キラルゲスト分子の鏡像体過剰率(*ee*)を連続的に変化させ、円二色性(CD)スペクトルを測定した(**Figure**)。光照射前後で、CD 強度は *ee* に対してシグモイド曲線を示したことから、ホモキラル認識の機構が優勢であることがわかった。一方で、シグモイド性の強さは UV 照射後に弱まったことから、ホモキラル認識の選択性が光によって制御され減少することがわかった。

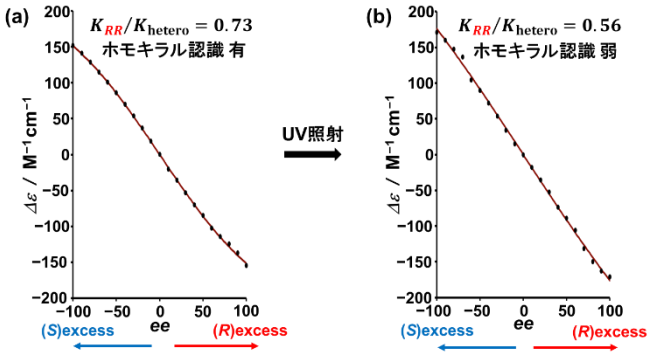

Figure. Plots of $\Delta\varepsilon$ at 360 nm versus *ee* of $Eu_2(\mathbf{L_{Az}})_3$ [(a) 9.60×10^{-6} M, (b) 1.04×10^{-5} M] in the presence of different *ee* of *R* or *S* chiral guests [total concentrations: (a) 8.30×10^{-4} M, (b) 8.30×10^{-4} M] before UV irradiation (a) and after UV irradiation (b) in acetone at 298 K.

1) Suko, N.; Itamoto, H.; Okayasu, Y.; Okura, N.; Yuasa, J. *Chem. Sci.* **2021**, *12*, 8746–8754.

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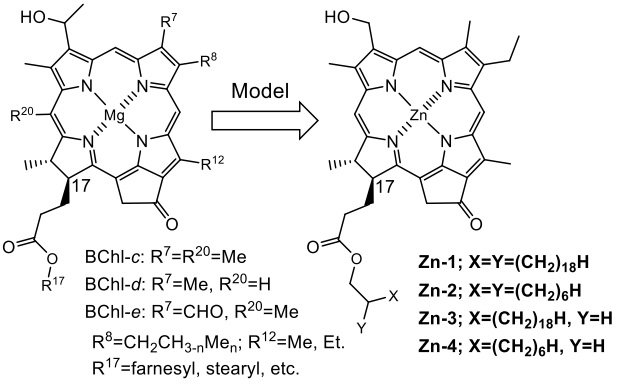
17 位に直鎖および枝分かれアルキル鎖を導入したバクテリオクロロフィル *d* 類の自己会合

（立命館大院生命科学）○原　伸行・民秋　均
Self-aggregation of bacteriochlorophyll-*d* analogs with linear and branched alkyl chains at the 17-position (*Graduate School of Life Sciences, Ritsumeikan University*) ○Nobuyuki Hara, Hitoshi Tamiaki

Chlorosomes with a large amount of bacteriochlorophyll(BChl)-*c*, *d*, or *e* molecules were composed of their well-ordered *J*-aggregates by specific intermolecular interactions without supporting from any proteins. In addition, these natural pigments have several alkyl chains including linear and branched hydrocarbon chains. In this work, we investigated the aggregation behavior of four synthetic BChl-*d* analogs possessing linear and branched alkyl chains in the 17-propionate residue. Their self-aggregation in methylcyclohexane (MCH) containing a small amount of tetrahydrofuran (THF) was measured by CD and UV–Vis–NIR spectroscopy as well as atomic force microscopy (AFM).
Keywords : Atomic force microscopy; Chlorophyll; Circular dichroism; Self-assembly; Supramolecule



長鎖アルキル鎖だけでなく枝分かれしたアルキル鎖も有しているバクテリオクロロフィル(BChl)-*c*/*d*/*e* 分子は(左図)、蛋白質の補助なしで水素結合や配位結合などの分子間相互作用により規則正しく配列した *J* 型会合体のクロロゾームを構築している[1]。また、この天然産 BChl 分子の 17 位のアルキル鎖も超分子構造の安定性へ寄与しているが、どのような超分子構造を形成するのかは判明していない。本研究では、17 位上に直鎖および枝分かれアルキル基を有する BChl-*d* 類縁体を合成することにより、17 位上のアルキル鎖が超分子構造に及ぼす影響を、UV–Vis–NIR スペクトルおよび AFM により検討したので報告する。

今回、2 種の枝分かれアルキル基と 2 種の直鎖アルキル基を有する計 4 種の BCl-*d* 類縁体 **Zn-1～4**(上右図)を合成した。全ての化合物において、1%(*v*/*v*) THF/MCH 溶液中では、730 nm 付近に *J* 型会合体由来の吸収が UV–Vis–NIR スペクトルから観測された。一方、AFM により超分子構造を観測すると、直鎖アルキル種 **Zn-3/4** では濃度に問わずロッド上の会合体が観測されたのに対し、枝分かれアルキル種 **Zn-1/2** では濃度に依存した会合体が観測された。特に **Zn-2** は、低濃度下ではロッド上の会合体であったが、高濃度下ではシート状の会合体となった。

1) S. Matsubara, H. Tamiaki, H. *J. Photochem. Photobiol. C: Photochem. Rev.* **2020**, *45*, 100385.

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ペプチド-クロロフィル複合体を用いた光捕集アンテナモデルの合成と光物性

（名工大院工[1]・立命館大院生命科学[2]）○中條 涼子[1]・樋口 真弘[1]・民秋 均[2]・松原 翔吾[1]

Synthesis and optical properties of light-harvesting antenna models using peptide-chlorophyll conjugates ([1]*Graduate School of Engineering, Nagoya Institute of Technology*, [2]*Graduate School of Life Sciences, Ritsumeikan University*) ○Nakajyo Ryoko,[1] Masahiro Higuchi,[1] Hitoshi Tamiaki,[2] Shogo Matsubara[1]

Light-harvesting antennas have important roles in the primary photosynthesis, including sunlight absorption and energy transfer into a reaction center. Green photosynthetic bacteria possess a specific light-harvesting antenna called “chlorosome” which is constructed by self-aggregates of composite chlorophylls. In this study, we constructed the chlorosome models by mimicking the supramolecular structure of the chlorophyll aggregates. We synthesized cyclic peptide-chlorophyll conjugates. The cyclic peptide-chlorophyll conjugates in 10% (v/v) DMF-H_2O could be formed tubular aggregates. We report the nanostructure of chlorophyll aggregates and its optical properties.

Keywords : Self-assembly; Supramolecule; Photosynthesis; Biomimetics

光捕集アンテナでは、光合成の初期過程における太陽光エネルギーの吸収・集約を担っている。この器官があることで、照射光強度に左右されず効率的に光エネルギーを集めて光合成を行うことができている。本研究では、色素分子を規則正しく配列することで高効率な光捕集を行っている緑色光合成細菌の「クロロゾーム」と呼ばれるアンテナ器官に着目した[1]。本研究では、クロロゾーム型の秩序だったチューブ状超分子構造の構築を目指し、環状ペプチドの自己集積性とクロロフィルの光捕集能力を組み合わせて環状ペプチド-クロロフィル複合体を合成した。合成した環状ペプチド-クロロフィル複合体を DMF に溶解させ、90% (*v*/*v*)の水で希釈することで自己集積させ、クロロゾームアンテナモデルを調製した。この水溶液の UV-vis 吸収および CD スペクトル測定より、クロロフィル類の自己集積を確認し、AFM 測定によって構造観察を行なった。またドナーからアクセプターへの FRET 過程を追うために光物性の評価を行ったので報告する。

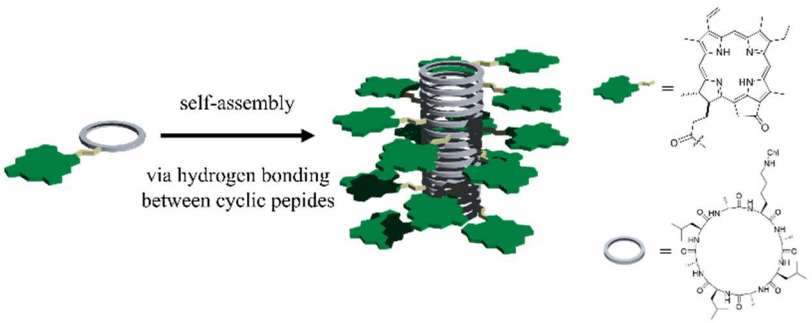

Figure 1. ペプチド-クロロフィル複合体の化学構造とチューブ状集積体のモデル図.

1) S. Matsubara, H. Tamiaki, *J. Photochem. Photobiol. C: Photochem. Rev.* **2020**, *45*, 100385.

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Ion recognition ability and guest uptake/release kinetics of cobalt(III) macrocyclic metallohosts bearing bulky amine ligands

(1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa University) ○ Dejan Walter[1], Yoko Sakata[1,2], Shigehisa Akine[1,2]

Keywords : Ion Recognition, Guest Uptake and Release Kinetics, Cobalt, Host-Guest Complex, Alkali Metal

Crown ethers are a series of ring-shaped polyethers, which are able to recognize a suitable guest according to their cavity size, such as potassium or sodium ions. Due to the usually very fast and reversible nature of the guest binding kinetics, it is difficult to permanently keep the guest species inside the cavity. However, if the apertures of the host molecules are narrow, the guest uptake/release is expected to be effectively slowed or blocked. Previously, our group has reported a unique metal-containing host molecule, $[LCo_2(MeNH_2)_4]^{2+}$, which exhibits varying exchange behavior for various guest ions. [1] Based on these observations, we sought to investigate if the bulkiness of the amines can also affect the guest binding strength and exchange kinetics of this macrocycle.

We synthesized a series of cobalt(III) macrocyclic metallohosts $[LCo_2(A)_4](OTf)_2$ by treating the macrocycle H_4L with cobalt(II) acetate and the desired amines under aerobic conditions. The increased bulkiness of the amine groups resulted in a notable decrease in the association constants, coupled with an enhancement in the exchange kinetics. Crystal structures of sodium complexes containing ethyl- and benzylamine groups showed the guest inside of the recognition cavity. As the binding cavities are alike within each host, the alteration in the binding affinities is not only attributed to the size of the amine ligands; instead, they are also affected by the electronic effects of the phenyl groups.

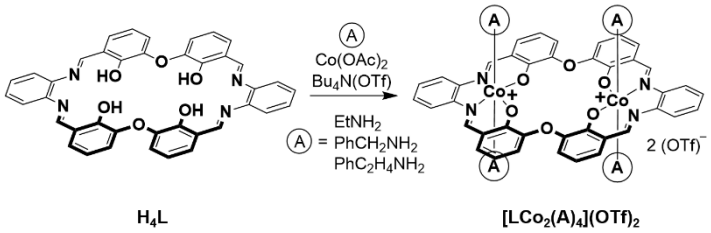

Figure 1. Synthesis of the host species $[LCo_2(A)_4](OTf)_2$

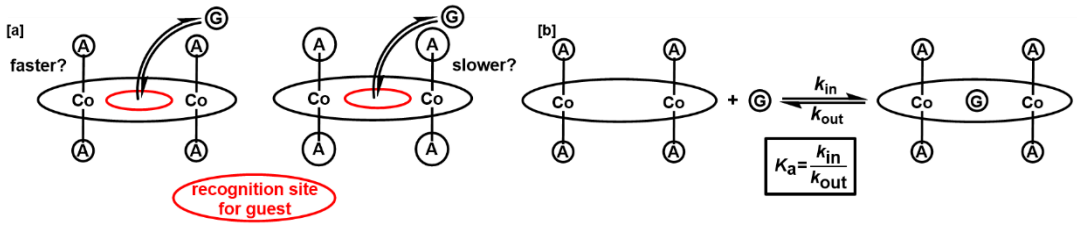

Figure 2. [a] Principle of influencing the guest uptake and release through bulky amine ligands. [b] reversible guest uptake and release.

[1] Sakata, Y.; Murata, C.; Akine, S. *Nat. Commun*. **2017**, *8*, 16005.

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二重凹面構造をもつヘキサベンゾコロネンラジカルカチオンの合成と近赤外-赤外光吸収特性

（阪大院基礎工）○宇野颯汰・鈴木修一・直田 健

Synthesis of a Hexabenzocoronene Radical Cation Having Double-concave Structure and Its Photophysical Properties in near-IR and IR Region (*Department of Chemistry, Graduate School of Engineering Science, Osaka University*) ○Souta Uno, Shuichi Suzuki, and Takeshi Naota

In this session, we will describe, “Synthesis of a Hexabenzocoronene Radical Cation Having Double-concave Structure and Its Photophysical Properties in near-IR and IR Region”.

Keywords : Hexabenzocoronene, Radical Cation, Near-infrared Absorption

開殻 π 電子系分子は特異な磁気特性、酸化還元特性や光物性を示すことから近年、注目を集めている。最近我々は、柔軟な π 電子構造や集積構造をもつラジカルカチオンに注目し、それらを利用した近赤外吸収特性や磁気特性の新奇制御法を開拓している [1-3]。今回、周辺置換基により二重凹面型の曲面 π 電子構造をもつラジカルカチオン **1**$^{\bullet+}$ を設計、合成し、赤外領域付近まで電子吸収帯を有することがわかった (Figure 1)。

化合物 **1** は既報に従って合成した [4]。化合物 **1** のサイクリックボルタモグラムでは +0.26 V vs Fc/Fc$^+$ で可逆的な一電子酸化波を示し、ラジカルカチオン **1**$^{\bullet+}$ は安定であると予想された。実際、**1**$^{\bullet+}$•**SbF$_6^-$** が化学酸化によって安定な化学種として単離された。ジクロロメタンとヘキサフルオロベンゼン (HFB) から得られた結晶を用いた **1**$^{\bullet+}$•**SbF$_6^-$** の XRD 解析では、二重凹面型構造に二つの HFB が包摂することがわかった (Figure 1b)。また、化合物 **1**$^{\bullet+}$•**SbF$_6^-$** は固体の状態において赤外領域に及ぶ 2400 nm 付近に吸収帯が存在することが明らかになり、さらにゲスト分子の影響により、吸収波長が 600 nm 程度長波長シフトすることが見出された (Figure 1c)。

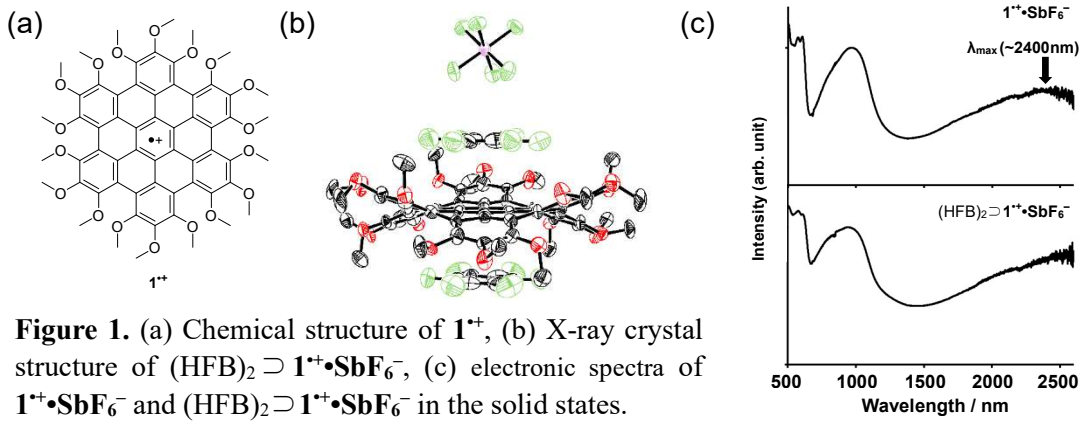

Figure 1. (a) Chemical structure of **1**$^{\bullet+}$, (b) X-ray crystal structure of (HFB)$_2$ ⊃ **1**$^{\bullet+}$•**SbF$_6^-$**, (c) electronic spectra of **1**$^{\bullet+}$•**SbF$_6^-$** and (HFB)$_2$⊃**1**$^{\bullet+}$•**SbF$_6^-$** in the solid states.

1) Suzuki, S.; Maya, R.; Uchida, Y.; Naota, T. *ACS Omega* **2019**, *4*, 10031.
2) Suzuki, S.; Yamaguchi, Y.; Uchida, Y.; Naota, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 8284.
3) 浅野翔壱朗, 鈴木修一, 直田 健, 日本化学会第 102 春季年会, K3-3pm-11.
4) Wang, Z.; Dötz, F.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1247.

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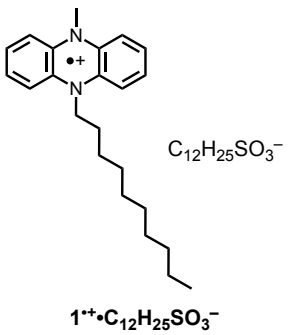
ジヒドロフェナジンラジカルカチオン塩の固液相転移における光学および磁気特性制御

（阪大院基礎工）○田中　律起・鈴木　修一・直田　健
Control of Photophysical and Magnetic Properties of Dihydrophenazine Radical Cation Salts during Solid-Liquid Phase Transition (*Graduate School of Engineering Science, Osaka University*) ○Ritsuki Tanaka, Shuichi Suzuki, Takeshi Naota

Open-shell molecules exhibit a variety of electronic and magnetic properties based on their aggregate structures. Especially in radical cation salts, the counter ions affect the aggregate structures. We have investigated novel physical properties by controlling the aggregation structures of radicals. In this study, we synthesized dihydrophenazine radical cation with linear alkylsulfonate ion and investigate its physical properties. Radical cation salt **1**$^{\bullet+}$•$C_{12}H_{25}SO_3^-$ melted at relatively low temperature, and it showed drastic change in optical and magnetic properties during solid–liquid phase transition.
Keywords : Radical cation; Dihydrophenazine; Counteranion; Dimer

開殻化合物は集合体の構造に基づいて種々の電子・磁気物性を示す。特に電荷をもつラジカルカチオン塩では対イオンが集合化構造に影響を与える。今回、デシル基を導入したジヒドロフェナジンラジカルカチオンのスルホン酸塩を合成し、その物性を調査した。ラジカルカチオン塩は比較的低い温度で融解し、固液相転移に伴い光学特性および磁気特性が劇的に変化することがわかった (Figure 1)。



1$^{\bullet+}$•$C_{12}H_{25}SO_3^-$

緑色固体である **1**$^{\bullet+}$•$C_{12}H_{25}SO_3^-$ は 120 ˚C で融解し緑色液体へと変化した。ESR スペクトルにおいて、固体状態では強い信号が観測されるのに対し、液体状態では信号が弱くなることがわかった。また、液体状態では 950 nm 付近に幅広い吸収が観測された。これらの結果から、**1**$^{\bullet+}$•$C_{12}H_{25}SO_3^-$ は常磁性的な固体状態から強い反強磁性的相互作用を示す液体状態に変化することが支持された。さらに他のアルキル鎖をもつスルホン酸塩においても液体状態でπダイマーの形成が示唆された。これらは我々が以前に報告した、ビス(トリフルオロメタンスルホニル)イミド塩と逆の傾向を示している [1]。

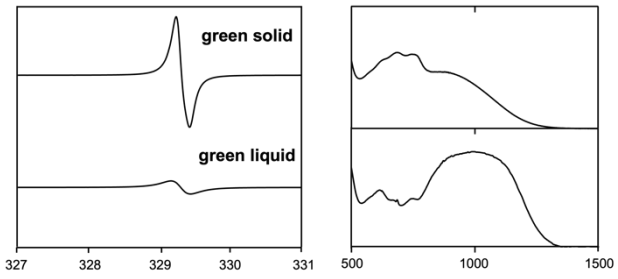


Figure 1. ESR and absorption spectra of **1**$^{\bullet+}$•$C_{12}H_{25}SO_3^-$ in the solid and liquid states.

1) Suzuki S.; Yamaguchi, D.; Uchida, Y.; Naota, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 8284.

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開口部を閉じられる salen 型クリプトファン錯体の合成と性質

（金沢大院新学術 [1]・金沢大院自然 [2]・金沢大 NanoLSI[3]）○于　宗江 [1]・酒田陽子 [2,3]・秋根茂久 [2,3]

Synthesis and properties of salen-type cryptophane complexes that can close the aperture

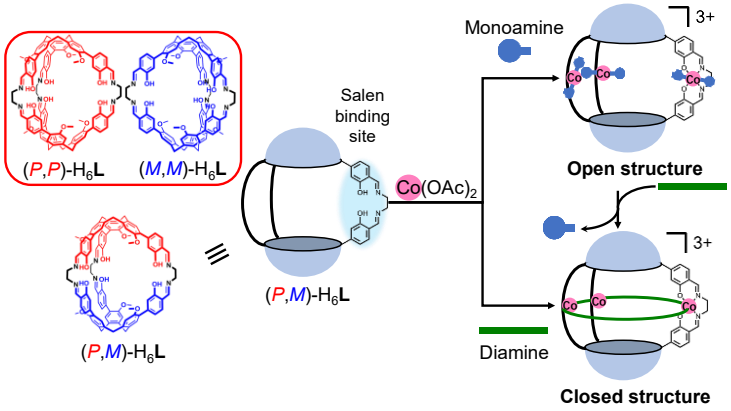
([1] *Grad. Sch. of Front. Sci., Kanazawa Univ.*, [2] *Grad. Sch. of Natl. Sci. and Tech., Kanazawa Univ.*, [3] *NanoLSI, Kanazawa Univ.*) ○Zongjiang Yu,[1] Yoko Sakata,[2,3] Shigehisa Akine[2,3]

If the aperture of cage-shaped molecules is opened and closed depending on the situation, guest uptake and release can be controlled as desired. We have previously synthesized various macrocyclic and cage-shaped hosts with oligo-salen structures, and have investigated their opening/closing behavior for guest uptake control[1]. In this study, we designed a new salen-type cryptophane cage that can incorporate larger guest molecules. The cage molecule H_6**L** was synthesized by the reaction of a precursor trialdehyde with ethylenediamine. The open and closed metal-containing cage molecules were synthesized by introducing cobalt(III) into the cage molecules H_6**L**, followed by the introduction of monoamines or diamine. The formation efficiency of the closed cage molecules depends on the chain length of diamine H_2N-$(CH_2)_n$-NH_2, and the closed-type cage molecules were efficiently formed when n = 8, 9, or 10. The open-to-close conversion of the cage molecules will also be presented.

Keywords : Cobalt complex; Cryptophane; Molecular Cage; Host-guest complex

三次元的な内部空間を持つかご型分子の開口部を状況に応じて開閉できれば、より積極的にゲストの出入りを制御することができる。当研究室では、オリゴ salen 構造を有するさまざまな大環状ホストやかご型ホストの合成を行い、その開閉機構とゲスト取り込み制御について研究してきた [1]。本研究では、この機構の応用を広げ、より大きな分子を取り込める架橋配位子によって開口部を閉じることができる新しい salen 型クリプトファンケージを設計した。

ケージ分子 H_6**L** については、前駆体のトリアルデヒドとエチレンジアミンの反応により合成した。このケージ分子 H_6**L** にコバルト(III)を導入した後、モノアミンやジアミンを導入することにより、Open 型と Closed 型の含金属ケージ分子を合成した。Closed 型ケージ分子の生成率はジアミン H_2N-$(CH_2)_n$-NH_2 の鎖長によってかわり、n = 8,9,10 の時に効率的に-Closed 型ケージ分子が生成すること見出した。Open 型から Closed 型への変換についても検討したので報告する。



1) S. Akine, M. Miyashita, T. Nabeshima *J. Am. Chem. Soc.* **2017**, *139*, 4631–4634

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オリゴプロリン誘導体の自己集積によるナノベシクルの構築とその物性

（名工大院工）○松原 翔吾・岡本 有生・樋口 真弘
Construction of nanovesicles by self-assembly of oligoproline derivatives and its properties (*Graduate School of Engineering, Nagoya Institute of Technology*) ○Shogo Matsubara, Yui Okamoto, Masahiro Higuchi

Oligoproline has unique properties such as rod-like structure and cell membrane permeability, which is expected to be applicated for drug delivery carriers as well as several nanomaterials. Here, we report the construction of supramolecular nanovesicles by self-assembly of oligoproline derivatives **PL4/6** as a novel drug carrier. Peptide nanovesicles of **PL4/6** maintained the spherical structure under dry and/or high-vacuum conditions, indicating that the vesicles have high mechanical strength. In addition, the vesicles could encapsulated fluorophores as a model for drug.

Keywords : Supramolecule; Drug delivery system (DDS); Nanomaterial; Biomaterial; Peptide

オリゴプロリンは水素結合を介さない棒状の二次構造を構築するペプチドであり、この特殊な二次構造に着目することで、様々なナノマテリアルがこれまでも報告されている [1,2]。構造的な特徴に加え、オリゴプロリンは細胞膜透過性といった性質も有しており [3]、薬物担体としての応用にも期待されている。本研究では、細胞膜透過性を有するオリゴプロリン誘導体を自己集積させることでナノキャリアとして有効なベシクル状超分子カプセルを構築したので報告する。

ナノベシクルの構成分子にはオリゴロイシンとオリゴプロリンを含む両親媒性ペプチド **PL4/6** を用い(Figure 1, left)、固相合成法によって調製した。これらのペプチドを水中で自己集積させ、電子顕微鏡および原子間力顕微鏡で構造観察を行ったところベシクル状超分子集積体を形成していることが確認できた(Figure 1, right)。一般に、ベシクルは機械強度が低く、乾燥および真空状態では球状構造を維持できないにもかかわらず、ペプチドナノベシクルは球状構造を維持した状態で観察されたことより、高い機械強度を有していることが示唆された。また、ベシクル内部への物質内包実験も行い、薬剤モデルとして用いた蛍光物質の内包が可能であることが示された。

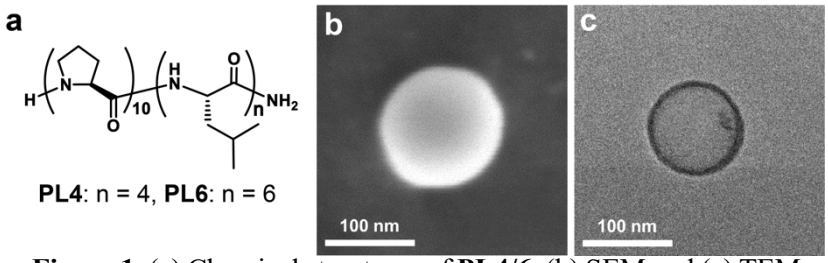

Figure 1. (a) Chemical structures of **PL4/6**. (b) SEM and (c) TEM images of assembled **PL4**.

1) S. Bobitz, *et al.*, *Acc. Chem. Res.* **2017**, *50*, 2420; 2) S. Matsubara, *et al.*, *Bioconjugate Chem.* **2022**, *33*, 1785; 3) E. Böhmová, *et al.*, *Physiol. Res.* **2018**, *67*, S267.

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芳香環ミセルによる多核銅クラスターの内包と発光増強

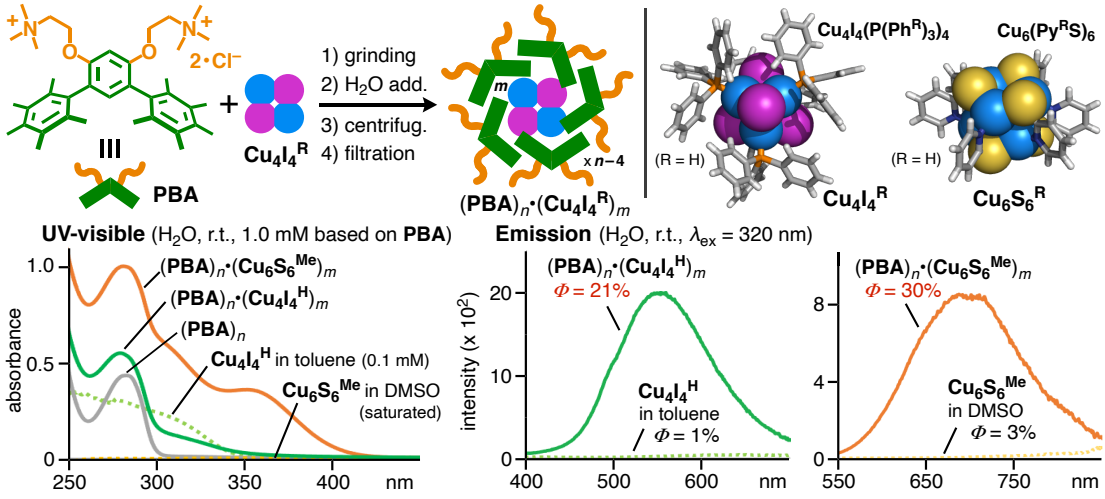
（東工大 化生研）○遠山和希・田中裕也・吉沢道人

Encapsulation of Multinuclear Copper Clusters by Aromatic Micelles and its Emission Enhancement (*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Kazuki Toyama, Yuya Tanaka, Michito Yoshizawa

Photophysical properties of multinuclear copper clusters remain elusive in solution, due to their poor solubility and/or stability. Here we report the efficient water-solubilization and emission enhancement of multinuclear copper clusters upon encapsulation by aromatic micelles. Cu_4I_4 and Cu_6S_6 clusters were efficiently incorporated by aromatic micelles in water through a grinding protocol. The UV-visible spectra showed new absorption bands derived from the clusters. Within the micelle, Cu_4I_4 clusters displayed efficient green emission (ϕ = 21%) in water, whereas the cluster is non-emissive in organic solvent. The encapsulated Cu_6S_6 clusters showed enhanced red emission (ϕ = 30%), compared to that in the solid state.
Keywords: Multinuclear Copper Cluster, Aromatic Micelle, Encapsulation, Water-Solubilization, Emission

多核銅クラスターは、溶解性や安定性が低いため、溶液中での分光学的性質は十分に調査されていない。これまで、芳香環ミセルが有機分子や単核錯体を内包し、水溶化できることを明らかにしてきた（*Acc. Chem. Res.* **2019**, *52*, 2392）。今回、芳香環ミセルにより、難溶性の４核銅-ヨウ素および６核銅-硫黄クラスターを内包することで水溶化を達成し、その発光増強に成功したので報告する。

グラインディング法により、芳香環ミセル$(PBA)_n$はホスフィン配位子を持つ$Cu_4I_4^R$クラスターを水中で効率良く内包した（下図上）。同様の操作により、2-ピリジンチオレート配位子を持つ $Cu_6S_6^R$ クラスターも効率良く内包することができた。UV-visible 測定から、それらの多核銅クラスターに由来する吸収帯が 300~420 nm に新たに出現したことから、内包を確認した（下図左下）。溶液中で非発光な $Cu_4I_4^H$ は、内包により効率的な緑色発光（ϕ = 21%）を示し、また、$Cu_6S_6^{Me}$ では固体状態より 1.5 倍向上した赤色発光（ϕ = 30%）を示した（下図右下）。



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ダンベル型の芳香族両親媒性分子の合成とその自己集合

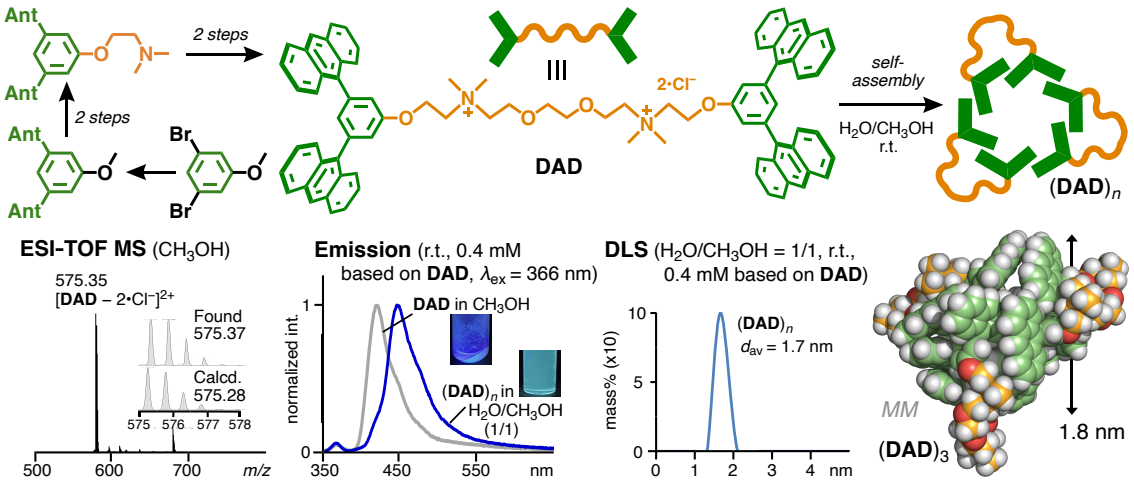
（東工大 化生研）○菅原有・遠山和希・Lorenzo Catti・吉沢道人

Preparation and Self-Assembly of Dumbbell-shaped Aromatic Amphiphiles (*Lab. for Chem. & Life Sci., Tokyo Tech*) ○Aguri Sugawara, Kazuki Toyama, Lorenzo Catti, Michito Yoshizawa

Here we report the synthesis and self-assembly of dumbbell-shaped aromatic amphiphiles, composed of two molecules of a bent anthracene dimer connected by a flexible hydrophilic spacer at the convex part. The dumbbell-shaped amphiphile is synthesized through a five-step reaction sequence in 26% yield and found to self-assemble in a 1:1 water-methanol mixture via the hydrophobic effect and π-stacking interactions. NMR, UV-visible, emission, DLS, and molecular modeling studies indicate the formation of a spherical aromatic micelle with an average diameter of 1.7 nm.
Keywords: Bent anthracene dimer, Dumbbell-shaped amphiphile, Hydrophilic spacer, Self-assembly, Water

V型アントラセン２量体を含む両親媒性分子は、水中で芳香環ミセルを定量的に形成する（*Acc. Chem. Res.* **2019**, *52*, 2392）。この芳香環ミセルのさらなる多様な集合構造の展開を期待して、今回、２つのアントラセン２量体の凸部を１つの親水性スペーサーで連結した、ダンベル型の芳香族両親媒性分子 DAD を合成した。また、その自己集合挙動を明らかにした。

DAD の合成は、全５段階の反応により総収率 26%で達成したことを、NMR と MS 測定で確認した（下図左）。DAD は 1:1 の水/メタノール混合溶媒中で、疎水効果とπ-π相互作用を駆動力に自己集合し、芳香環ミセル$(DAD)_n$が定量的に形成することを NMR、UV-visible、発光、DLS 分析により明らかにした（下図右上）。発光スペクトルでは、メタノール中の DAD と比較して、発光帯が 40 nm 長波長シフトした。また$(DAD)_n$の DLS 分析では、平均直径 1.7 nm の集合体に由来するピークが観測された（下図中央下）。以上の結果と分子モデリングにより、水系溶媒中において、球状の芳香環ミセル$(DAD)_3$が、主要な生成物と示唆された（下図右下）。



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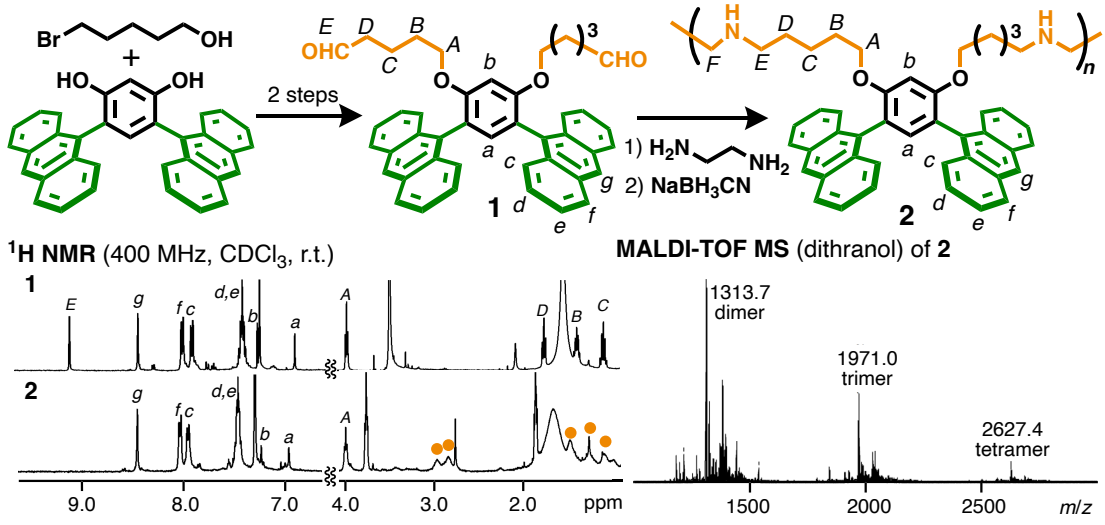
Oligomerization of Bent Anthracene Dimers via Imine-based Dynamic Covalent Bonds

(Lab. for Chem. & Life Sci., Tokyo Tech) Que Zhou, Yuya Tanaka, Michito Yoshizawa
Keywords: facile preparation; dynamic covalent bond; formyl group; oligomer; bent anthracene dimer

Imine is one of the representative dynamic covalent bonds (DCBs), formed efficiently from aldehyde and amine, and irreversibly generates amine via reduction. Such a DCB is a powerful tool for facile preparation of oligomeric compounds from dialdehyde and diamine. We have reported that amphiphilic compounds **AA**, bearing a bent anthracene dimer and two hydrophilic ammonium groups, form an aromatic micelle in water.[1,2] Trimeric amphiphiles **AT**, where three bent anthracene dimers are covalently linked by hydrophilic spacers in a step-by-step fashion, form an aromatic micelle with a higher host ability and structural stability in water.[3] Further oligomerization of the amphiphiles, however, has not been achieved, owing to the necessity of elaborate synthetic steps.

Here we present the efficient linking of bent anthracene dimers via imine-based dynamic covalent bonds toward the preparation of oligomeric amphiphiles. Diformyl compound **1** was prepared from a bent anthracene dimer with two hydroxyl groups in 2 steps (85% yield). Imine oligomers were formed via DCBs from **1** with ethylene diamine at room temperature and the subsequent reduction by $NaBH_3CN$ gave amine derivates **2** (14% yield) as revealed by ^1H NMR and MALDI-TOF MS analyses.



[1] K. Kondo, A. Suzuki, M. Akita, M. Yoshizawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 2308.
[2] M. Yoshizawa, L. Catti, *Acc. Chem. Res.* **2019**, *52*, 2392.
[3] Y. Tsuchida, K. Aratsu, S. Hiraoka, M. Yoshizawa, *Angew. Chem. Int. Ed.* **2021**, *60*, 12754.

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金属架橋を利用した最小の β ヘリックス二重鎖の誘起

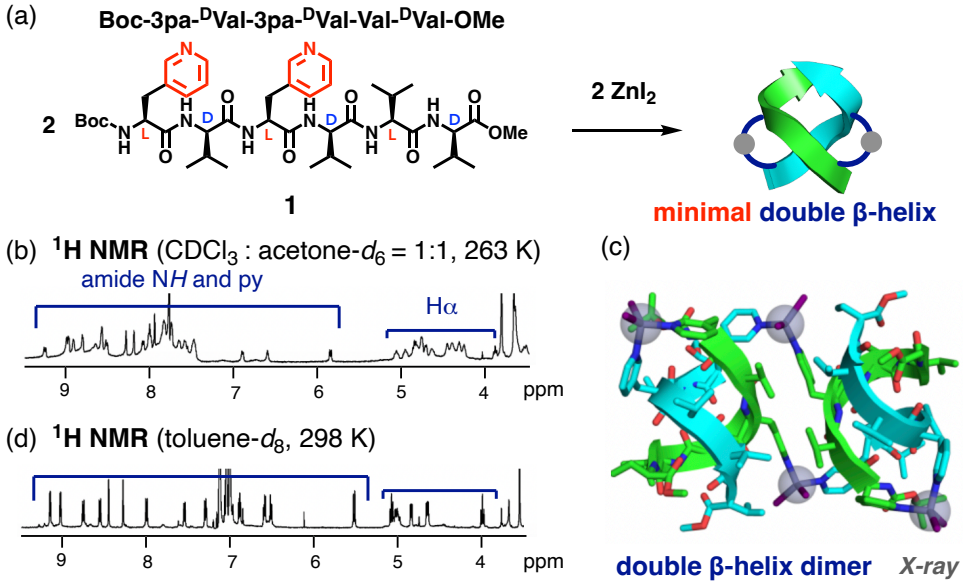
（東工大化生研[1]・JST さきがけ[2]）○遠藤祐生[1]・吉沢道人[1]・澤田知久[1,2]

Minimal double-stranded β-helices formation by metal cross-linking

([1]*Lab. for Chem. & Life Sci., Tokyo Tech*, [2]*JST PRESTO*) ○Masaki Endo,[1] Michito Yoshizawa,[1] Tomohisa Sawada[1,2]

β-Helical duplexes can be quantitatively constructed via folding and assembly of L/D alternating octapeptides and ZnI_2 salts (*Nat. Sci.* **2021**, *1*, e10008). Here, by using this method, we attempted to construct minimal β-helical duplexes from hexapeptides (Fig. a). We synthesized ligand **1** having coordinating sidechains at the 1st and 3rd residues from the N-terminus, and examined its complexation behavior with ZnI_2 in organic solvents. The ^{1}H NMR spectrum of the mixture at 263 K in $CDCl_3$/Acetone-d_6 showed a widely dispersed pattern of pyridine and amide protons, suggesting a duplex formation, though it was complicated (Fig. b). Crystallization of the product was succeeded, confirming a dimeric structure of parallel β-helical duplexes (Fig. c). On the other hand, in toluene-d_8, widely dispersed sharp signals converged at 298 K (Fig. d), and the formation of a single duplex structure was revealed by COSY and ROESY.
Keywords: double helix, β-sheet, self-assembly, folding, hydrogen bond

L/D 交互配列のオクタペプチド配位子と ZnI_2 のフォールディング集合により、8 残基の β ヘリックス二重鎖を定量的に構築できる（*Nat. Sci.* **2021**, *1*, e10008）。本研究では、この手法をヘキサペプチド配位子に適用することで最小の二重鎖の形成を試みた（図 a）。N 末端から 1、3 残基目に配位性側鎖を導入した配位子 **1** を合成し、有機溶媒中での ZnI_2 との錯形成挙動を調査した。重クロロホルム/重アセトンの混合溶媒中では、263 K での ^{1}H NMR 測定において、二重鎖形成を示唆する芳香族・アミドプロトンのシグナルの幅広い分散が観測されたが、複雑なシグナルパターンとなった（図 b）。結晶化に成功し、平行型 β ヘリックスの二量化構造が確認された（図 c）。一方、重トルエン中では、298 K において広く分散したシャープなシグナルが確認され（図 d）、COSY および ROESY 測定より、単一の二重鎖構造の形成が確認された。



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水素結合ネットワークによるサイズ制御可能な球状膜の創成

(東京理大院化学) ○小川 翔也、山野本 健、遠藤 恆平

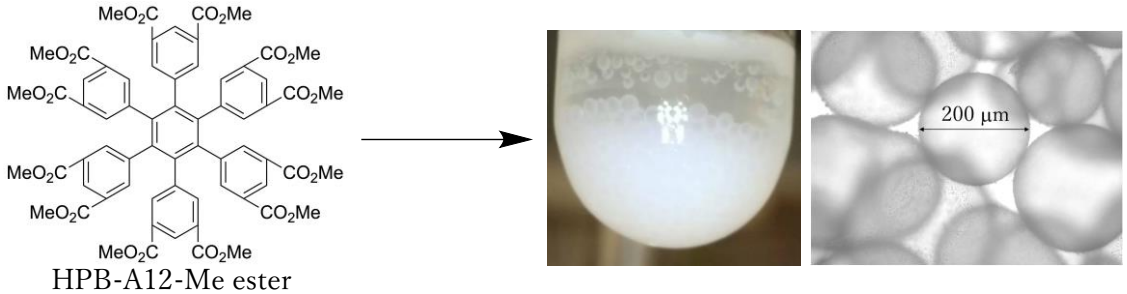
Development of giant spheres using small molecules through hydrogen-bonding networks

(*Department of Chemistry, Graduate School of Science, Tokyo University of Science*) ○ Shoya Ogawa, Ken Yamanomoto, Kohei Endo

Hydrogen-bonded networks have been utilized not only in organic chemistry but also in materials chemistry in recent years. In particular, Hydrogen-Bonded Organic Framework (HOF) is attracted much attention as a new material like Metal Organic Framework (MOF). Bulk HOF can give nanofilms as crystalline solids via exfoliation but the exfoliation of bulk HOF for the generation of spheres is rarely reported to date. We developed a unique method for the formation of nanofilms via hydrogen-bonded networks by using HPB-A12-Me ester. These nanofilms selectively take in the aqueous solution and form spheres like vesicles. The size of spheres is approximately 100-1500 μm and varied depending on the conditions. We confirmed that the present spheres incorporated water-soluble guest molecules.

Keywords : spheres; size-control; hydrogen-bonded networks; huge supramolecules

水素結合ネットワークは生体だけではなく近年は材料化学においても活用されている．特に Hydrogen-Bonded Organic Framework（HOF）は空孔を有する構造体として，近年，精力的に研究されている Metal-Organic Framework（MOF）と同様に新たな材料として注目を集めている．それら HOF の薄膜化も試みられており数 nm レベルの結晶の剥離が達成されているが，その膜から球状物質を作成した例は限定的である．我々は HPB-A12-Me ester を用いて，水素結合ネットワークによる独自の薄膜の形成法を開発した．この薄膜は水溶液を選択的に内部に取り込み球状膜を生成する．この球状膜のサイズは調製条件により変化し 100 から 1500 μm 程度であり，水溶性ゲスト分子を取り込むことを確認した．



HPB-A12-Me ester

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

Wed. Mar 20, 2024 1:00 PM - 3:20 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:20 AM UTC
E1131(1131, Bldg. 11 [3F])

[E1131-3pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Koki Ikemoto, Yoichi Sasaki

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1131-3pm-01]

Cooperative photochemical reaction and crystal shape change in dimethyl 1,4-phenylenediacrylate single crystals

○Rei Tomoda[1], Daichi Kitagawa[2,3], Seiya Kobatake[2,3] (1. Osaka City Univ., 2. Grad. School of Eng., Osaka City Univ., 3. Grad. School of Eng., Osaka Metropolitan Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1131-3pm-02]

Image-based Machine Learning Prediction for Mixing Ratio of Solids from Droplet Drying

○Taichi Sano[1], Hayato Shirakura[1], Yuki Ide[2], Sheng Hu[2], Ichigaku Takigawa[2,3], Yasuhide Inokuma[1,2] (1. Grad. Sch. Eng, Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ., 3. CIREDS, Kyoto Univ.)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1131-3pm-03]

Controlling Molecular Alignment of Perylene Chromophores in Crystals and Photon Upconversion Properties

○Hayato Shoyama[1], Naoyuki Harada[1], Yoichi Sasaki[1], Tsubasa Kashino[2], Nobuo Kimizuka[1,3] (1. Grad. Sch. Eng., Kyushu Univ., 2. Nissan Chemical Corporation, 3. CMS, Kyushu Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1131-3pm-04]

Accumulation of interaction sites for ion recognition via folded conformations of flexible molecules enforced by confinement

○Takahiro Nakagawa[1], Hiroki Takezawa[1], Makoto Fujita[1,2] (1. The University of Tokyo, 2. Institute for Molecular Science)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1131-3pm-05]

Optical control of diarylethene crystals that exhibit elastic and plastic deformation by mechanical stimulation

○Jun Fukuchi[1], Ryo Nishimura[1], Masakazu Morimoto[1] (1. Rikkyo University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1131-3pm-06]

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Phenanthrene boronate co-crystals with long-persistence luminescence

○Natsumi Sugawara[1], Masato Ito[1], Yuji Kubo[1] (1. Tokyo 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

[E1131-3pm-07]

Crystal structure and solid state luminescent properties of pyrrole derivatives

○Toru Okawara[1], Mike Sithole[1], Yu-Hui Lim[1], Toshikazu Ono[2,3] (1. NIT KIT, 2. Kyushu Univ., 3. CMS, Kyushu Univ.)

Japanese

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

[E1131-3pm-08]

Creating Conductive Molecular Materials through a Hydrogen Bonding Framework in Naphthalene diimide derivatives

○yusei yamamoto[1], iguchi hiroaki[3], yu hoshino[1,2], toshikazu ono[1,2] (1. Graduate School of Engineering, Kyushu Univ., 2. Center for Molecular Systems Kyushu Univ. , 3. Graduate School of Engineering, Nagoya Univ.)

Japanese

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

[E1131-3pm-09]

Fluorescence observation of polymorphic precipitation process of dibenzoylmethanato boron difluoride complex

○Daichi Ito[1], Yuta Kajihara[3], Yushi Fujimoto[1], Daichi Kitagawa[2], Seiya Kobatake[2], Fuyuki Ito[1,3] (1. Grad. Sch. of Sci. and Tech., Shinshu Univ., 2. Grad. Sch. of Eng., Osaka Metropolitan Univ., 3. Inst. of Edu., Shinshu Univ.)

Japanese

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

[E1131-3pm-10]

Stoichiometry Validation of Supramolecular Complexes with a Hydrocarbon Cage Host by van't Hoff Analyses

○Toshiya M. Fukunaga[1], Yuzuka Onaka[1], Takahide Kato[1], Koki Ikemoto[1], Hiroyuki Isobe[1] (1. The University of Tokyo)

Japanese

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

[E1131-3pm-11]

Side chains vs side loops in supramolecular polymers

○Masahiro Sugiyama[1], Natsumi Fukaya[1], Kazunori Sugiyasu[1] (1. Kyoto University)

English

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

[E1131-3pm-12]

Bio-compatible matrix development for triplet dynamic nuclear polarization of pyruvate

○Jiarui Joey SONG[1], Sakamoto Keita[2], Tateishi Kenichiro[3], Uesaka Tomohiro[3], Yanai Nobuhiro[2] (1. Sch. of Eng., Kyushu Univ , 2. Grad. Sch. of Eng., Kyushu Univ , 3. RIKEN Nishina Center for Accelerator-Based Science)

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Japanese

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

[E1131-3pm-13]

Phosphonic acid recognition of a diamidine having a tetraphenylethylene unit

○Kohei Matsushima[1], Hiroki MURAKAMI[1], Takahiro KUSUKAWA[1] (1. Kyoto Institute of Technology)

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1,4-フェニレンジアクリル酸ジメチルの単結晶における協同的光化学反応と結晶形状変化

（阪市大工[1]・阪市大院工[2]・阪公大院工[3]）○友田 怜[1]・北川 大地[2,3]・小畠 誠也[2,3]

Cooperative Photochemical Reaction and Crystal Shape Change in Dimethyl 1,4-Phenylenediacrylate Single Crystals

([1]*Fac. of Eng., Osaka City Univ.*, [2]*Grad. School of Eng., Osaka City Univ.*, [3]*Grad. School of Eng., Osaka Metropolitan Univ.,*) ○Rei Tomoda,[1] Daichi Kitagawa,[2,3] Seiya Kobatake[2,3]

Recently, we found that the photochemical reaction of 2,5-distyrylpyrazine (**DSP**) proceeds from the edges to the center in single crystals. In this study, we focused on dimethyl 1,4-phenylenediacrylate (*p*-**PDAMe**), which has a similar structure to **DSP**, and investigated the photochemical reaction in single crystals. When a single crystal of *p*-**PDAMe** was irradiated with 365 nm light, it was confirmed that the reaction proceeded from the edges to the center as well as the case of **DSP**. From a change in transmitted light intensity with respect to light irradiation time, it was found that the photoreaction proceeded along a sigmoidal curve with an induction period. Moreover, it was found that the shape of the crystal changed from rhombus to rectangle associated with the progress of the photoreaction. When the change in the acute angle of the crystal was plotted against the light irradiation time, it also showed a sigmoidal curve.

最近、我々は 2,5-ジスチリルピラジン (**DSP**) 単結晶において、その光反応が結晶の端から中心に向かって進行することを見出した[1]。本研究では、**DSP** と類似の分子構造を持つ 1,4-フェニレンジアクリル酸ジメチル (*p*-**PDAMe**) の単結晶を研究対象とし、その光反応について検討した。

p-**PDAMe** の単結晶に 365 nm の光を照射したところ、**DSP** の場合と同様に結晶の端から中心へと反応が進行していくことがわかった。光照射時間に対する透過光強度変化から、光反応は誘導期を有するシグモイド曲線に沿って進行することがわかった。また、光反応の進行に伴い、結晶の形状が菱形から長方形へと変化することを見出した。結晶の鋭角の角度変化を光照射時間に対してプロットしたところ、同様のシグモイド曲線を描くことがわかった。

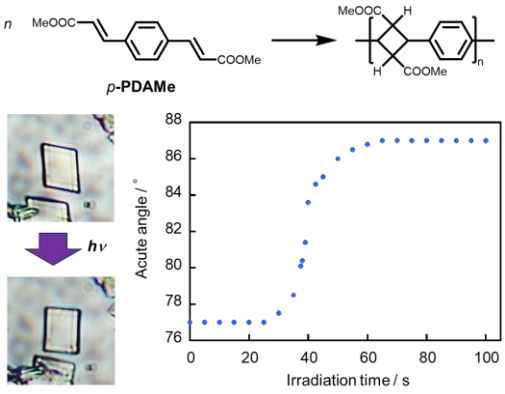

Fig. 1 Photopolymerization reaction of *p*-**PDAMe** and acute angle change of single crystal upon irradiation with 365 nm light.

1) K. Morimoto, D. Kitagawa, H. Sotome, S. Ito,H. Miyasaka, and S. Kobatake, *Angew. Chem. Int. Ed.* **2022**, *61*, e202212290.

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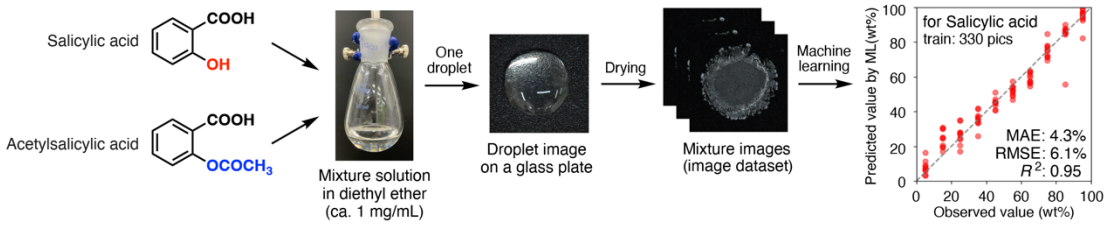
液滴乾燥から得られる固体画像と機械学習を利用した混合比率予測

（北大院工[1]・北大 WPI-ICReDD[2]・京大 CIREDS[3]）○佐野 太一[1]・白倉 逸人[1]・井手 雄紀[2]・Sheng Hu[2]・瀧川 一学[2,3]・猪熊 泰英[1,2]
Image-based Machine Learning Prediction for Mixing Ratio of Solids from Droplet Drying
([1]*Grad. Sch. Eng., Hokkaido Univ.*, [2]*WPI-ICReDD, Hokkaido Univ.*, [3]*CIREDS Kyoto Univ.*)
○Taichi Sano,[1] Hayato Shirakura,[1] Yuki Ide,[2] Sheng Hu,[2] Ichigaku Takigawa,[2,3] Yasuhide Inokuma[1,2]

We have developed a system that instantly predicts the mixing ratio from solid mixture images using machine learning[1)]. This system requires more than 300 images of mixtures with 200 mg of pure solid compounds to achieve a prediction with a mean absolute error (MAE) of around 5%, making it difficult to apply to chemical reaction analysis. In this research, using the images of solid mixtures obtained by drying droplets of 1 mg/mL diethyl ether solutions of salicylic acid and acetylsalicylic acid, the mixing ratio prediction was achieved with 4.3% of MAE.
Keywords : Solution drying; Trace amount of solids; Image-based machine learning; Salicylic acid; Acetylsalicylic acid

有機化学の研究では、溶媒を使った溶液反応により化合物を合成し、NMR や HPLC, MS などで分析するプロセスが一般的である。しかし、精度の高い分析には分析サンプルの調製が必須であり、特に大量の試料分析には非常に長い時間を必要とする。当研究室では、固体混合物画像からその混合比率を機械学習によって瞬時に予測するシステムを開発した[1)]。この予測システムは化学反応を迅速に分析できる可能性がある。絶対平均誤差 (MAE)が 5%程度で予測を達成するためには 200 mg の純粋な固体化合物を使用した混合物画像が 300 枚以上必要であり、実際の化学反応分析へ直接適用することは困難であった。本研究では溶液の液滴を乾燥させて得られる微量な固体混合物の画像を用いて機械学習による混合比率予測を行った。

任意の割合で秤量したサリチル酸とその誘導体であるアセチルサリチル酸の混合物から約 1 mg/mL の濃度のジエチルエーテル溶液を調製した。その混合溶液をガラスプレート上に 1 滴滴下し、約 10 分放置して乾燥させた画像を収集した。330 枚の混合物画像を使用して混合比率の予測を行ったところ、MAE = 4.3%と高い精度で混合比率の予測を達成した。予測に必要な化合物量は従来の方法では画像 1 枚あたり 200 mg であったのに対し、約 10 µg まで削減することができた。この手法の適用可能性を確認するために、鏡像異性体を利用した混合割合比の検討も進めている。



1) Y. Ide, H. Shirakura, T. Sano, M. Murugavel, Y. Inaba, S. Hu, I. Takigawa, Y. Inokuma, *Ind. Eng. Chem. Res.* **2023**, *62*, 13790-13798.

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イオン結晶系におけるペリレンの配列制御とフォトン・アップコンバージョン特性

（九大院工[1]・日産化学株式会社[2]・九大 CMS[3]）○庄山 隼斗[1]・原田 直幸[1]・佐々木 陽一[1]・菓子野 翼[2]・君塚 信夫[1,3]

Controlling Molecular Alignment of Perylene Chromophores in Crystals and Photon Upconversion Properties

([1]*Grad. Sch. Eng., Kyushu Univ.,* [2]*Nissan Chemical Corporation,* [3]*CMS, Kyushu Univ.*) ○ Hayato Shoyama,[1] Naoyuki Harada,[1] Yoichi Sasaki,[1] Tsubasa Kashino,[2] Nobuo Kimizuka[1,3]

Triplet-triplet annihilation-based photon upconversion (TTA-UC) has attracted much interest as a methodology for efficient use of sunlight. Solid-state TTA-UC materials are desirable from the viewpoint of practical use, but in condensed systems, acceptor emission is generally quenched by intermolecular interactions. To develop efficient solid-state UC systems, it is necessary to control the intermolecular distance and orientation of acceptors in molecular crystals. In this study, we designed ionic crystal systems composed of perylene disulfonate and countercations with varied sizes and shapes to tune the fluorescence properties based on the controlled molecular arrangements of perylene chromophores for solid-state TTA-UC.

Keywords : Photon Upconversion; Triplet-triplet Annihilation; Energy Migration; Self-Assembly; Ionic Crystals

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) は太陽光エネルギーの高効率活用に資する手法として注目されている。ペリレン発色団は溶液中で優れた TTA-UC 特性を示すことが知られているが、固体系では発色団間相互作用により消光され、固体系 UC 材料への展開にはペリレン基間の距離・配向を精密に制御する技術が重要である。本研究では、アニオン性ペリレンとかさ高い対カチオンで構成されたイオン結晶系をデザインし、発色団間の配列制御による発光特性制御と固体系で高効率な TTA-UC の実現を目指す (Fig. 1)。

アニオン性ペリレンとトリフェニルメチルアミンカチオン・テトラフェニルホスフィンカチオンからなる有機結晶において、635 nm 光照射下緑色の UC 発光を確認した。発表では対イオンとペリレンの TTA-UC 特性の関係性について系統的に議論する。

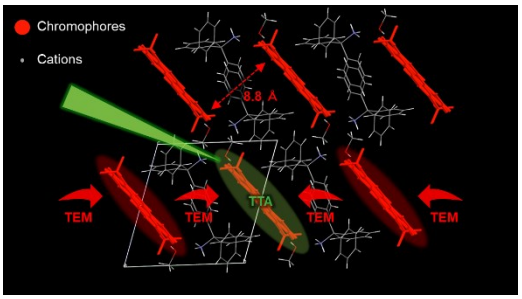

Fig. 1. Single crystal X-ray structure of an ionic crystal and schematic illustration of TTA-UC in the ionic crystal.

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空孔包接による柔軟分子の折りたたみ配座を利用した相互作用点の集積とイオン認識

(東大院工[1]・分子研[2]・東大国際高等研[3]) ○中川崇弘[1]・竹澤浩気[1]・藤田誠[1,2,3]

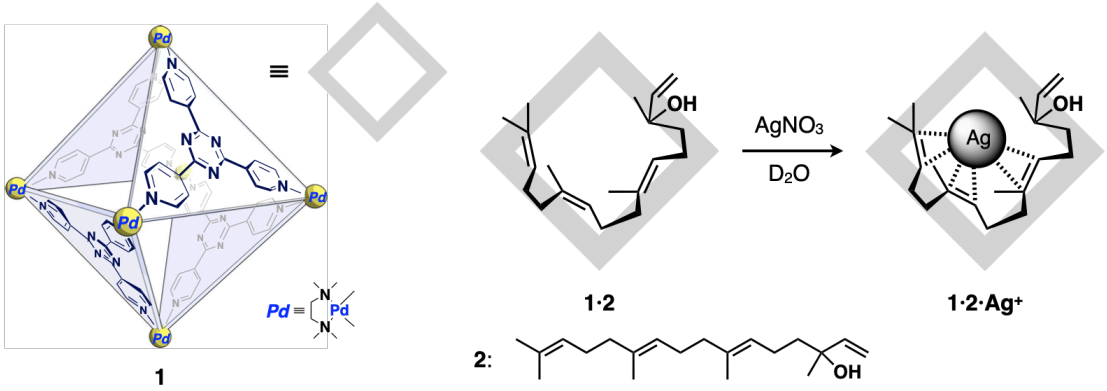
Accumulation of interaction sites for ion recognition via folded conformations of flexible molecules enforced by confinement ([1]*Grad. School of Engineering, The University of Tokyo*, [2]*IMS*, [3]*UTIAS, The University of Tokyo*) ○Takahiro Nakagawa[1], Hiroki Takezawa[1], Makoto Fujita[1,2,3]

2D or 3D arrangement of interaction sites enables sophisticated ion recognition, as observed in enzymes and artificial hosts. In contrast, due to their conformational freedom, linear flexible molecules have low ion recognition ability. In this study, we achieved enhancement of ion recognition abilities of flexible molecules via confinement in a hollow cage. Linear terpenoid **2** adopts a U-shaped conformation via encapsulation into cage **1**. When silver nitrate was added, peaks from guests shifted and broadened in ^{1}H NMR, indicating complexation. A linear polyether compound was also encapsulated in cage **1**, resulting in enhanced ion recognition.

keywords : Self-Assembly, Host-Guest, Conformational Fixation, Inclusion Complex, Ion Recognition

様々な酵素・ホストに見られるように、環状・かご状に相互作用点を並べると高度なイオン認識が可能になる。一方、直鎖柔軟分子上に官能基を並べても、大きな配座自由度のため有効なイオン認識が行えない。本研究では、中空錯体への包接によりテルペノイドやポリエーテルなどの直鎖分子に折りたたみ配座を誘起し、相互作用点を集積することでイオン認識能を高めた。

かご型錯体 1 に直鎖テルペノイド 2 を加えると、U 字型に折り畳まれて内部空孔へ包接される。これに対して硝酸銀(I)を加えると、^{1}H NMR においてゲスト由来のピークのシフトとブロード化が観測され、溶液中での錯形成が示唆された。直鎖状のポリエーテル分子に対しても包接による配座固定を介したイオン認識能の変化を確認した。



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機械刺激で弾性・塑性変形を示すジアリールエテン結晶の光制御

（立教大理[1]）○福地 純[1]・西村 涼[1]・森本 正和[1]
Optical control of diarylethene crystals that exhibit elastic and plastic deformation by mechanical stimulation ([1]*Rikkyo University*) ○Jun Fukuchi,[1] Ryo Nishimura,[1] Masakazu Morimoto[1]

Some organic crystals exhibit visible elastic[1)] or plastic[2)] deformation by mechanical stimulation. Diarylethene is a photochromic molecule and reversibly changes its color and crystal structure upon ultraviolet and visible light irradiation. In this study, we discovered a diarylethene crystal that exhibits visible elastic and plastic deformation depending crystal face, and its deformability can be reversibly switched by photoisomerization. This crystal showed elastic deformation when the (001) plane was poked with a needle and showed plastic deformation when the (100) plane was poked. Additionally, this crystal could be twisted. When the crystals were irradiated with ultraviolet light (λ = 365 nm), the crystals lost elasticity and plasticity, and were easily broken by mechanical stimulation. When irradiated with visible light (λ = 590 nm), the mechanical deformability was recovered by photoisomerization.
Keywords : Photochromism; Diarylethenes; Organic Crystals

有機結晶には機械的刺激によって弾性変形[1)]や塑性変形[2)]を示すものがある。また、ジアリールエテンは紫外光と可視光の照射により可逆的に色や結晶構造が変化するフォトクロミック分子である。本研究では、1 つの結晶で面依存的に弾性変形および塑性変形を示すジアリールエテン結晶を見出し、さらに光照射によって可逆的にその変形の ON-OFF スイッチが可能であることを見出した (**Fig. 1**)。

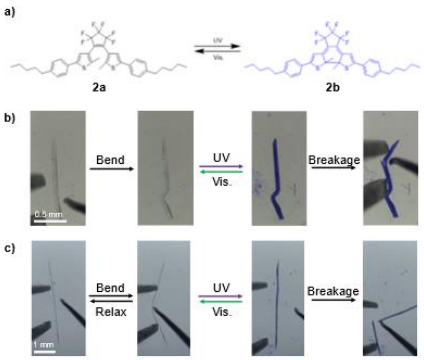

Fig. 1 a) **2a** の分子構造、b) **2a** の塑性変形と結晶フォトクロミズムによる柔軟性の低下、c) **2a** の弾性変形と結晶フォトクロミズムによる柔軟性の低下。

この単結晶は(001)面を針で突くと弾性変形、(100)面を突くと塑性変形を示し、さらにねじることができた。この単結晶に紫外光（λ = 365 nm）を照射すると無色透明から青色に着色し、光異性化反応が進むにつれて結晶に亀裂が入ることで弾性・塑性が失われ、力を加えることで容易に崩壊した。続いて可視光（λ = 590 nm）を照射すると青色から無色透明に退色し、生じていた亀裂が修復する様子が確認された。それに伴い、弾性変形及び塑性変形の柔軟性が回復し、崩壊せずに再び変形させることが可能であった。

1) N. P. Thekkeppat, M. Lakshmipathi, A. S. Jalilov, P. Das, A. M. P. Peedikakkal, S. Ghosh, *Cryst. Growth Des*. **2020**, *20*, 3937.
2) Y. Liu, P. Yang, K. Zhang, J. Xu, S. Wu, J. Gong, *Cryst. Growth Des.* **2022**, *22*, 1312.

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長寿命残光特性を有するフェナントレンボロネート共結晶

（都立大院都市環境 [1]）○菅原 なつみ [1]・伊藤 正人 [1]・久保 由治 [1]
Phenanthrene boronate co-crystals with long-persistence luminescence ([1]*Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*)○Natsumi Sugawara,[1] Masato Ito,[1] Yuji Kubo[1]

Our ongoing subject to developing afterglow materials has led us to investigate room-temperature phosphorescence (RTP) properties of aryl boronic acids. In this study, we have focused on polycyclic aromatic hydrocarbons (PAHs). Although PAHs with no heavy- or hetero-atoms have almost no RTP properties, the interplay between boronic acid and PAHs in terms of RTP properties is interesting to be investigated. Subsequently, we discovered that 9-phenanthreneboronic acid (**P-BA**) exhibited long-lived yellow phosphorescence with the quantum yield of 16.5 % at room temperature through co-crystallization with di trimethylolpropane (Di TMP) as a host material.
Keywords : Room-temperature phosphorescence; Boronic acid; Phenanthrene; Polyhydric alcohol; Co-crystals

室温りん光（RTP）は，大きなストークスシフトを伴う可視光領域に比較的寿命の長い残光現象として観測されることから，バイオイメージングを含む種々の応用が検討されている．我々はアリールボロン酸から誘導される分子系の RTP 特性に注目し，その機能化研究をおこなっている．最近，1.4-フェニルジボロン酸ドープ型共結晶の目視可能なサーモクロミック現象を見出した [1]．しかしながら，高い発光量子収率と長寿命特性との両立は，依然として挑戦的な課題である．本研究では，重元素やヘテロ原子を持たない縮合多環芳香族分子からなるボロン酸に着目し，多価アルコールとの共結晶を作成した．その結果，Di trimethylolpropane（Di TMP）をホストマトリックスとした共結晶化のアプローチ（Fig. 1a）により，その燐光量子収率が 16.5 %と比較的高い値を示した．この燐光量子収率増大は Di TMP を用いることによって，項間交差速度定数 k_{ISC} が促進されたものと考察した．

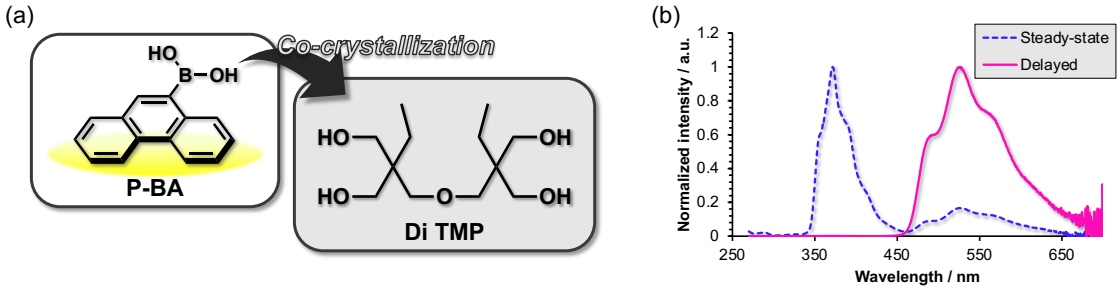

Fig. 1. (a). Chemical structures of **P-BA** and Di TMP, (b) steady-state and delayed emission spectra of **P-BA** /Di TMP co-crystal (λ_{ex} = 254 nm, delay time: 50 ms, [**P-BA**] = 0.01 mol%, r.t., solid-

1) K. Kawaguchi, N. Sugawara, M. Ito, and Y. Kubo, *Chem. Eur. J.*, accepted.

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ピロール誘導体の結晶構造と固体発光挙動の評価

（北九州高専[1]・九大院工[2]・九大 CMS[3]）○大川原 徹[1]・マイク シットホール[1]・ユフィ リム[1]・小野 利和[2,3]
Crystal structure and solid state luminescent properties of pyrrole derivatives ([1]*Department of Creative Engineering, National Institute of Technology, Kitakyushu College*, [2]*Graduate School of Engineering, Kyushu University,* [3]*Center for Molecular Systems*, *Kyushu University*)
○Toru Okawara,[1] Mike Sithole,[1] Yu Hui Lim,[1] Toshikazu Ono[2,3]

Solid state luminescent organic compounds have been attracting great attention due to its importance in materials and biochemistry. Aggregation induced emission (AIE) dye, which is one of the solid-state luminescent materials, is virtually non-luminescent in solution state, but highly luminescent in solid state or aggregated state. We have developed pyrrol-2-yl methylene derivatives that show AIE properties. Despite the growing interest of the novel AIE chromophore, structure-emission property relationships have rarely been explored. Here, we report crystal structure and solid-state luminescent properties of some pyrrol-2-yl methylene derivatives.
Keywords : Pyrrole, Fluorescence, Crystal

固体発光性を有する有機化合物は、材料化学や生化学の観点から、大きな注目を集めている。固体発光性を示す材料の一種である凝集誘起発光生色素は、溶液状態では発光を示さず、固体状態や凝集状態など、分子運動が抑制された状態において高い発光生を示す物質である。我々は、新規凝集誘起発光性色素として電子不足ビニル基を側鎖に有するピロール誘導体を見出した（図１）。この化合物群は、ビニル基末端の電子求引基の共役及び立体的な構造により、固体発光の波長や量子収率などの特性が異なることがわかっている。一方、その結晶構造と発光特性の関係に焦点を当てた研究はまだない。そこで本研究では、種々の置換基を有するピロール誘導体を合成し、結晶構造と発光特性の関係について評価を行った。

ピロール環側鎖としては、アルキル基、エステル基などを導入し、ビニル基末端にはエステル基、アミド基などを使用した。今回評価した化合物は全て、溶液状態では強い発光を示さなかった。一部の化合物は単結晶 X 線構造解析に成功し、いずれもピロール環からビニル基末端までが共平面構造を有していることがわかった。分子間相互作用に注目すると、分子の配列パターンによって複数種類に分類することができ、分子が同一方向を向く配向や、2 分子が逆向きに配列したダイマー構造を形成する配向などあることがわかった。

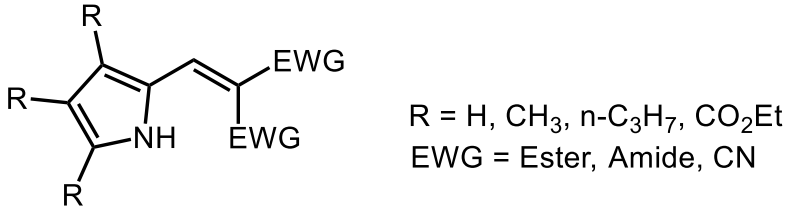

図１ 本研究で用いたビニルピロールの構造

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ナフタレンジイミド誘導体における水素結合フレームワークを活用した導電性分子材料の創製

（九大院工[1]・九大 CMS[2]・名大院工[3]）○山本 雄世[1]・井口 弘章[3]・星野 友[1,2]・小野 利和[1,2]

Creating Conductive Molecular Materials through a Hydrogen Bonding Framework in Naphthalene diimide derivatives ([1]*Graduate School of Engineering, Kyushu University*, [2]*Center for Molecular Systems (CMS), Kyushu University*, [3]*Graduate School of Engineering, Nagoya University,*) ○Yusei Yamamoto[1], Hiroaki Iguchi[3], Yu Hoshino[1,2], Toshikazu Ono[2]

Aromatic imide compounds have excellent chemical stability and electrical properties, and they are used in promising candidates for conductive materials. In this study, we synthesized various naphthalene diimide (NDI) derivatives with hydroxyl groups in their side chains and created single-crystalline materials through hydrogen bonding and π-stacking. After immersing with hydrazine-methanol solution, NDI radical anions were partially formed through chemical reduction, as indicated by diffuse reflectance and ESR measurements. Electrical conductivity measurements revealed that the value of the crystal before reduction was below the detection limit of 10^{-10} S/cm. However, the crystal after reduction achieved a very high electrical conductivity of the order of 10^{-2} S/cm. We evaluated the electrochemical properties in their reduced states and investigated the correlation between the structure of the side chains, hydrogen bonding, and electrical conductivity.

Keywords : Naphthalene Diimide; Hydrogen-bonded Framework; Electrical Conductivity; Radical anion; Infrared absorption

芳香族ナフタレンジイミドは優れた化学的安定性と電気化学的安定性を有し、導電性材料として応用が期待されている [1)]。本研究では、ナフタレンジイミド（NDI）の側鎖に種々のヒドロキシ基を含む NDI 誘導体を合成し、水素結合とπスタックを介した単結晶材料の創製を行った。ヒドラジンを用いた化学還元の結果、還元後の結晶の色が黒く変化した。拡散反射測定から NDI ラジカルアニオン由来の吸収が確認され、ESR 測定から NDI ラジカルアニオンの生成が示唆された。電気伝導度測定の結果、還元前の結晶では検出限界以下の値であったが、還元後の結晶では 10^{-2}S/cm オーダーと非常に高い電気伝導度を達成した。この値は、NDI 系結晶において非常に高い値である。本発表では、種々のヒドロキシ基を含む NDI 誘導体の還元状態における電気化学的評価を行うとともに、側鎖の構造及び電気伝導性の相関について議論を行う。

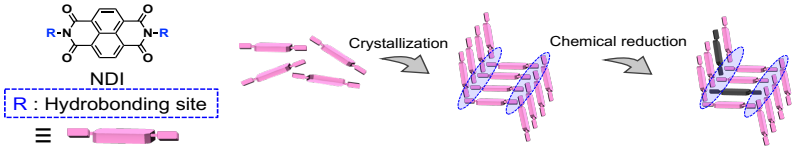

図 1. NDI 結晶における化学還元の概念図

1) H. Iguchi, *et al.*, *J. Am. Chem. Soc.*, **2019**, *141*, 6802.

This study is supported by MEXT Program: Data Creation and Utilization-Type Material Research and Development Project Grant Number JPMXP1122714694.

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結晶多形を有するジベンゾイルメタンフッ化ホウ素錯体誘導体の多形析出過程の蛍光観測

(信州大院総合理工[1]・阪公大院工[2]・信州大教育[3]) ○伊藤 大智[1]・梶原 佑太[3]・藤本 悠史[1]・北川 大地[2]・小畠 誠也[2]・伊藤 冬樹[1,3]
Fluorescence observation of polymorphic precipitation process of dibenzoylmethanato boron difluoride complex. ([1]*Graduate School of Science and Technology, Shinshu University*, [2]*Graduate School of Engineering, Osaka Metropolitan University,* [3]*Institution of Education, Shinshu University.*) ○Daichi Ito,[1] Yuta Kajihara,[3] Yushi Fujimoto,[1] Daichi Kitagawa,[2] Seiya Kobatake,[2] Fuyuki Ito[1,3]

Slight differences in crystallization conditions cause crystal polymorphism of organic fluorescent molecules. Therefore, it is necessary to clarify the crystallization mechanism for controlling the polymorphism. In this study, we focused on a dibenzoylmethanato boron difluoride complex derivative (*p*-a2bBF$_2$) with two crystal polymorphs showing different fluorescent properties and evaluated the crystal polymorph precipitation process based on fluorescence observation and fluorescence image analysis using a hyperspectral camera that can spatially resolve spectral information.

Keywords : Dibenzoylmethanato Boron Difluoride Complex; Polymorph; Hyperspectral Camera; Fluorescence Observation

有機蛍光分子の結晶多形は，結晶化条件のわずかな差により発現する．多形制御に関する知見を得るためには結晶化機構の理解が重要である．本研究では，異なる蛍光特性を示し 2 つの結晶多形をもつジベンゾイルメタナト二フッ化ホウ素錯体誘導体 (*p*-a2bBF$_2$，図 1) に着目し，結晶多形析出過程の蛍光変化ならびに画像解析から多形の生成比の溶媒依存性について検討した．

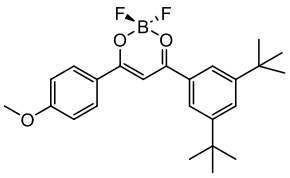

図 1　*p*-a2bBF$_2$ の分子構造．

p-a2bBF$_2$ の結晶多形は，青色蛍光を示す Form I (λ_{em} : 480 nm) と黄緑色蛍光を示す Form II (λ_{em} : 550 nm) があり，それぞれジクロロメタン (DCM) : ヘキサン=1 : 3 (v/v) 混合溶媒からの再結晶，および Form I 析出溶液への DCM 添加による溶媒媒介転移により得られる．図 2 に，*p*-a2bBF$_2$ の溶媒蒸発により得られた析出物の蛍光像の溶媒組成依存性を示す．結晶化は，溶液中のモノマーからアモルファス様中間体 (λ_{em} : 550 nm) を経由して進行する．DCM のみでは，析出物はアモルファス相のみであった．ヘキサンの増加にともない，Form I の結晶生成の割合は増加した．また，蒸発過程における液滴の重量変化から溶媒蒸発速度を見積もった．溶媒蒸発速度はヘキサンの増加により低下した．つまり，蒸発速度の低下にともない，アモルファス様な液滴状クラスターの保持時間が確保される．以上に基づいて，溶媒蒸発過程での結晶化機構は，析出したアモルファスからの相転移ではなく，溶媒を含んだ液滴状クラスター内での核形成とその後の Form I への結晶化によるものであると考えられる[1)]．当日は，分光情報を空間分解可能なハイパースペクトルカメラを用いた Form I から Form II への溶媒媒介転移過程の蛍光可視化も議論する．

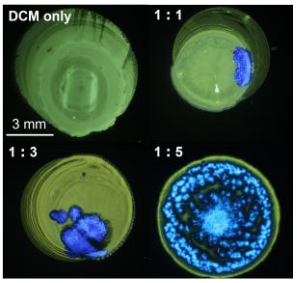

図 2 析出物の蛍光像の溶媒組成依存性．

1) S. Katsumi, M. Saigusa, F. Ito, *J. Phys. Chem. B*, **2022**, 126, (4), 976-984.

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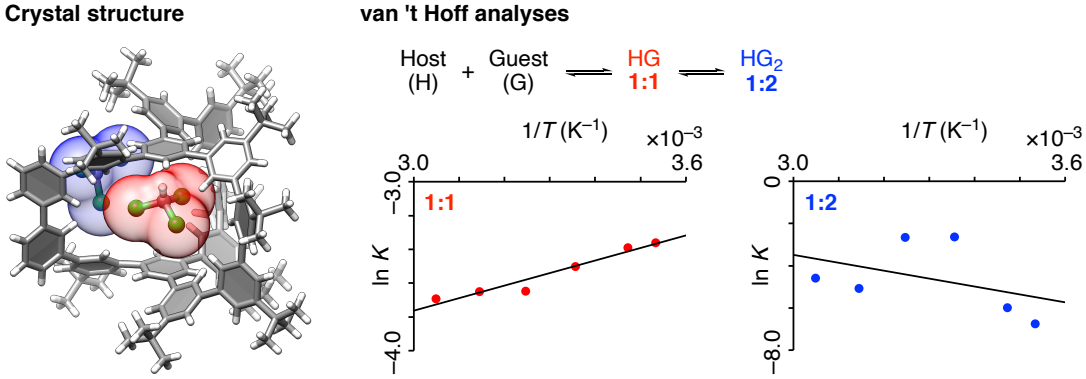
ファントホッフ解析による超分子錯体の会合比の決定法

（東大院理[1]）○福永 隼也[1]・尾仲 柚香[1]・加藤 昂英[1]・池本 晃喜[1]・磯部 寛之[1]
Stoichiometry Validation of Supramolecular Complexes with a Hydrocarbon Cage Host by van 't Hoff Analyses ([1]*Department of Chemistry, The University of Tokyo*) ○ Toshiya M. Fukunaga,[1] Yuzuka Onaka,[1] Takahide Kato,[1] Koki Ikemoto,[1] Hiroyuki Isobe[1]

Defining chemical processes with equations is the first important step in characterizing equilibria for the assembly of supramolecular complexes, and the stoichiometry of the assembled components must be defined to generate the equation. Recently, this subject has attracted renewed interest, and statistical and/or information-theoretic measures were introduced to examine the validities of the equilibrium models used during curve fitting analyses of titration. The present study shows that these measures may not always be appropriate for credibility examinations and that further reformation of the protocols used to determine the overall stoichiometry is necessary. Hydrocarbon cage hosts and their chloroform complexes formed via weak CH-π hydrogen bonds were studied, which allowed us to introduce van 't Hoff analyses for effective validation of the stoichiometries of supramolecular complexes.
Keywords : Supramolecular Chemistry, Stoichiometry, van 't Hoff Analysis, Cage

超分子錯体の会合比を決定することは，その化学平衡を理解する上で重要である．会合比の決定法は近年再注目されている課題であり，統計学や情報理論などを活用したいくつかの指標が提案されてきた．本研究では，これまでの指標では会合比が正しく推定できないことを見いだし，会合比の推定での新手法を導入した[1]．会合比を検討する具体的な例としては，かご状のナノカーボン分子「フェナインポルクセン」とクロロホルムとの超分子錯体を対象とした．当初，*F* 検定法や赤池情報量規準などの最近の評価指標によりホスト・ゲスト比の推定を試みたところ 1:2 モデルが支持されたが，そこから得られた会合定数に極めて大きな誤差が見られた．そこで，会合定数の温度依存をファントホッフプロットにより解析し，会合比推定を行うと，1:1 モデルが支持され，会合定数や誤差も無理のない値となった．この結果は，ファントホッフ解析が会合比の新しい推定法として有効であることを示すものである．



1) Fukunaga, T. M.; Onaka, Y.; Kato, T.; Ikemoto, K.; Isobe, H. *Nat. Commun.* **2023**, *14*, 8246.

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超分子ポリマーの側鎖と側環の効果

（京大院工）○杉山 雅弘・深谷 菜摘・杉安 和憲
Side chains vs side loops in supramolecular polymers
(*Graduate School of Engineering, Kyoto University*) ○Masahiro Sugiyama, Natsumi Fukaya, Kazunori Sugiyasu

Supramolecular polymers are constructed by reversible non-covalent bonds, and their states of the aggregations are significantly affected by solvents, temperature, and concentration. While they have attracted attention as stimuli-responsive materials, improving their poor thermodynamic stability has remained a challenge. We envisioned that the topological effects of cyclic structures would affect thermodynamic stability of supramolecular polymers. In this study, we introduced cyclic alkyl chains, or side loops, into a monomer (Fig. 1a). We will discuss the difference between side chains and side loops in supramolecular polymers with measurement of the sol-gel transition temperature, AFM/SEM and so on (Fig. 1b).
Keywords : Supramolecular polymer; Cyclic; Thermodynamic stability; Morphology; Supramolecular gel

超分子ポリマーは可逆的な非共有結合で形成されており、溶媒の種類や温度、濃度によって会合状態が大きく変化する。そのため外部刺激応答型の新しい材料として注目されている一方で、熱力学的な安定性の乏しさが材料として課題となる。本研究では、熱力学的に安定な超分子ポリマーの合成を行うために、環状分子の特異な自己集合挙動に着目した。

先行研究[1]で報告した 4 回対称性のポルフィリン骨格に対して、環状アルキル基である「側環」を導入した (Fig. 1a)。種々の実験から、側鎖と側環の構造の違いによる超分子ポリマーの熱力学的な安定性やモルフォロジーの違いを見いだした。発表では、ゾル-ゲル転移温度や AFM・SEM の測定結果などを示し、側環の効果を報告する (Fig. 1b)。

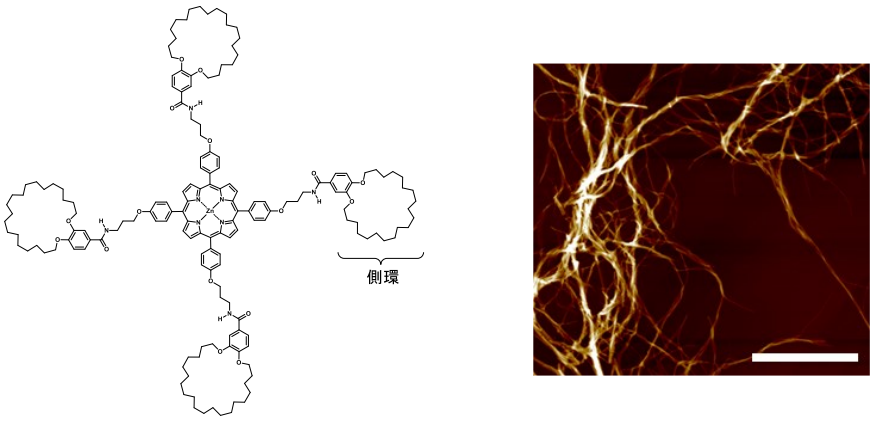

Fig. 1. (a) Monomer design (b) AFM image of the supramolecular polymers consisting of a monomer with side loops; scar bar, 2 μm.

1) S.-H. Jung *et al.*, *J. Am. Chem. Soc.*, **2018**, *140*, 10570.

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Bio-compatible matrix development for triplet dynamic nuclear polarization of pyruvate

(*[1]School of Engineering, Kyushu University, [2]Graduate School of Engineering, Kyushu University, [3]RIKEN Nishina Center for Accelerator-Based Science)* ○Jiarui Joey SONG[1], Sakamoto Keita[2], Tateishi Kenichiro[3], Uesaka Tomohiro[3], Yanai Nobuhiro[2]

Keywords: Dynamic nuclear polarization, Triplet excited state, Nuclear magnetic resonance

Triplet-DNP is a promising technique that enhances NMR intensity by transferring the polarization of the photo-excited triplet electron spins to probe nuclear spins.[1] In particular, the tracing of the metabolic pathway of [1-^{13}C] pyruvate can be utilized for MRI cancer diagnosis. Hence, the hyperpolarization of [1-^{13}C] pyruvate is a critical step toward the practical use of triplet-DNP. In the previous research, we have reported the first triplet-DNP of [1-^{13}C] pyruvate with a water-soluble supramolecular polarizing agent. However, achieving nuclear polarization at practical level remains challenging.[2] The difficulty arises from the short spin-lattice relaxation time (T_1) of matrix material. In previous studies, there are few examples of biocompatible matrices that can mix with [1-^{13}C] pyruvate, and their short T_1 (~46 s) cause rapid relaxation from a polarized state to a thermal equilibrium state.

In this study, we aim to develop biocompatible matrix materials which can disperse [1-^{13}C] pyruvate and exhibit long T_1 (~ min). We screened different types of biocompatible compounds with T_1 measurements using the saturation recovery method. Mixtures of long T_1 molecules and pyruvate were prepared by the melt quenching method. We optimized the mixing combinations and ratios, as well as the deuteration ratios, and investigated the preparation method for practical matrices.

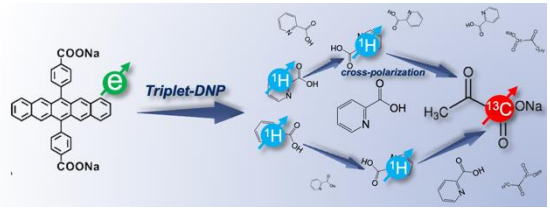

Figure 1 Schematic illustration of polarization transfer from matrix to pyruvate in triplet-DNP

1). Wenckebach, W. T. et al., *Phys. Lett. A*., **1988,** *134* (2), 134-136.
2). Hamachi, T. et al., *Chem. Sci*., **2023**, *14*, 13842-13850.

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テトラフェニルエチレン骨格を有するジアミジンのホスホン酸認識

（京工繊大院・工芸科学）○松嶋 航平・村上 弘樹・楠川 隆博
Phosphonic acid recognition of a diamidine having a tetraphenylethylene unit (Kyoto Institute of Technology) Kohei Matsushima, Hiroki Murakami, and Takahiro Kusukawa

Organophosphorous chemical weapons are highly volatile and are easily decomposed by moisture in the air, but if phosphonic acid derivatives are detected in the decomposition products, traces of chemical weapon use can be evidenced. We found that tetraphenylethylene-based diamidine **1** acts as a sensor to selectively detect phosphonic acid derivatives **2** and **3** in DMSO/CH_3CN mixed solvents. The mixed solution of diamidine **1** and monophosphonic acid **2** showed a green fluorescent color, while the mixed solution of phosphonic acid monoester **3** showed a blue fluorescent color, indicating that both can be distinguished by their fluorescent color. In this presentation, the reasons for the difference in both fluorescent colors will be discussed.
Keywords: diamidine; fluorescence; phosphonic acid

有機リン系化学剤の VX やサリンは容易に揮発や分解を起こすため、直接の検出は困難である。これらの化学剤は加水分解により、メチルホスホン酸エステル **3** へと変化したのち、メチルホスホン酸 **2** (R^1 = Me)へと変化することが知られている。そのため、ホスホン酸誘導体 **2** および **3** を検出することで、化学剤の使用痕跡を検出することができる。本研究では、テトラフェニルエチレン骨格を有するジアミジン **1** が、DMSO/CH_3CN (1:6)混合溶媒中で **2** および **3** を選択的に検出する turn-on 型の蛍光発光センサーとして機能することを見出した。さらに、ジアミジン **1** は、モノホスホン酸 **2** と混合した際には緑色の蛍光発光を示し、メチルホスホン酸エステル **3** と混合した際には青色の蛍光発光を示したことから、**2** と **3** とを蛍光発光色により識別可能であることが明らかになった(Figure 1)。DLS 測定およびレーザー顕微鏡観察から、これらの発光色の違いは、異なる形状の凝集体の生成に由来することを示唆する結果が得られたため、併せて報告する予定である。

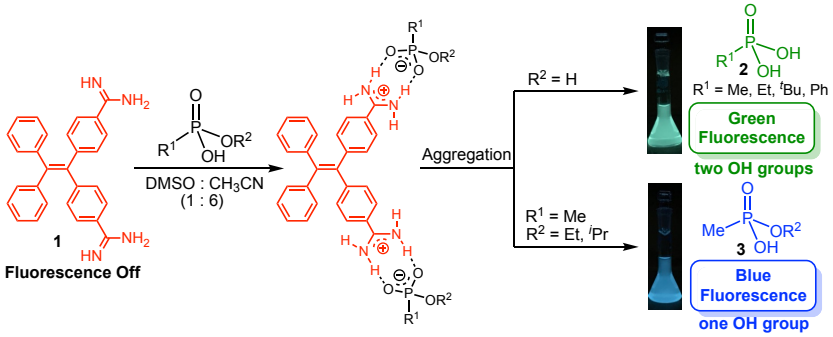

Figure 1. Fluorescence properties of diamidine **1** after the addition of monophosphonic acids **2** and phosphonic acid monoesters **3**.

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

Wed. Mar 20, 2024 9:00 AM - 11:10 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:10 AM UTC
E1131(1131, Bldg. 11 [3F])

[E1131-3am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Kenji Higashiguchi, Toshikazu Ono

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1131-3am-01]
Synthesis and fluorescent properties of pyridine-type BODIPY analogues

○Hideaki Hashimoto[1], Raita Goseki[1], Motoyasu Kobayashi[1] (1. Kogakuin Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1131-3am-02]
Photoexcited States and Photostabilization Mechanism of a Photostabilizer, Dioctyl 4-Hydroxy-3,5-Dimethoxybenzylidenemalonate

○Kanma Igarashi[1], Mikio Yagi[2], Azusa Kikuchi[2] (1. Yokohama National University Faculty of Science and Engineering, 2. Yokohama National University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1131-3am-03]
Spectral and structural behaviors of naphthalimide-containing spiropyran in aqueous media

○Taku Oshima[1], Yasuhiro SHIRAISHI[2], Takayuki HIRAI[2] (1. Osaka University Graduate School, 2. Osaka University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1131-3am-04]
Supramolecular Assembly of Amphiphilic Diarylethene Showing Phase Transition between LCST Hydrated Phases.

○Yodai Yoshikawa[1], Kenji Higashiguchi[1], Kenji Matsuda[1,2] (1. Kyoto University, 2. FIFC, Kyoto Univ.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1131-3am-05]
Diarylethene Dimer Showing NIR Absorption upon Stepwise Stimuli of Photoirradiation and Redox

○Kurumi Satake[1], Naoto Ootsuki[1], Kenji Higashiguchi[1], Kenji Matsuda[1,2] (1. Kyoto University, 2. FIFC, Kyoto Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1131-3am-06]
Syntheses and Spectroscopic Properties of Calixarene-Centered Pentacene Tetramers

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○Kazushi Ishikawa[1], Hayato Sakai[1], Kentaro Harada[2], Takeharu Haino[2], Taku Hasobe[1] (1. Fac. Sci. Tech., Keio Univ., 2. Adv. Sci. Eng., Hiroshima Univ.)

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

[E1131-3am-07]

Synthesis and Energy Transfer Properties of Tetracene–Ultrasmall Au Nanocluster Dyads

○Sunao Hiramatsu[1], Mana Nakamoto[2], Aoi Akiyama[2], Hayato Sakai[1], Yuchi Negishi[2], Taku Hasobe[1] (1. Fac. of Sci. Tec., Keio Univ., 2. Fac. of Sci., Tokyo Univ. of Sci.)

Japanese

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

[E1131-3am-08]

The effect of additional hydroxy compounds on the excited state intermolecular proton transfer reaction of pyrene-urea compounds

○Leyun Huang[1], Yoshinobu Nishimura[1] (1. University of Tsukuba)

Japanese

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

[E1131-3am-09]

Synthesis and Spectroscopic Properties of Hydrophilic Acene Derivatives

○Naoya OKUBO[1], Hayato SAKAI[1], Keigo NONAKA[2], Yoshimitsu SAGARA[2], Taku HASOBE[1] (1. Keio University, 2. Tokyo Institute of Technology)

Japanese

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

[E1131-3am-10]

Synthesis of *N*,*N*-type imidazo[1,2-*a*]pyridine–BF_2 complexes and photocytotoxicity

○Itsuki Ogawa[1], Shoko Ueta[2], Keiji Minagawa[2], Fumitoshi Yagishita[2,3] (1. Tokushima Univ., 2. Grad. School, Tokushima Univ. , 3. Inst. pLED, Tokushima Univ.)

Japanese

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

[E1131-3am-11]

Near-Infrared Photosensitizer-Carbon Nanohorn Composites for the Treatment of Peri-implantitis

○Yuta Takano[1], Eri Hirata[1], Daisuke Konishi[1], Yukari Maeda[1], Natsumi Ushijima[1], Masako Yudasaka[2], Atsuro Yokoyama[1] (1. Hokkaido Univ., 2. Meijo Univ.)

Japanese

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

[E1131-3am-12]

Synthesis of Thiophene-fused Polycyclic Aromatic Hydrocarbons Using Photocyclization–Dehydrogenation Reaction

○Yusuke Tokuyama[1], Takuya Ogaki[1], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ.)

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ピリジン型 BODIPY 類縁体の合成と蛍光特性

（工学院大先進工[1]）○橋本 英明[1]・後関 頼太[1]・小林 元康[1]
Synthesis and fluorescent properties of pyridine-type BODIPY analogues ([1]*School of Advanced Engineering, Kogakuin university*) ○ Hideaki Hashimoto,[1] Raita Goseki,[1] Motoyasu Kobayasi[1]

Boron-dipyrromethene (BODIPY) is well-known as an excellent fluorescent dye exhibiting high molar extinction coefficient, high fluorescence quantum yield, and narrow Stokes shift. In addition, it has recently reported that boron difluoride dipyridylmethenes, BODIPY-like structure with pyridine skeleton, also have luminescent properties. Therefore, the research on these optical properties is extremely limited. In this study, we synthesized the *meso*-phenyl-substituted pyridine-BF_2 complex and evaluated its luminescent properties. When BF_2 complexation was carried out in the presence of triethylamine, the obtained **1** showed luminescence property under UV irradiation (λ = 365 nm) in chloroform solution and solid state. While no luminescence was observed from the methanol solution of **2**. The precursor compound of **2** was first reacted with an equal amount of *tert*-BuOK and then $BF_3{\cdot}Et_2O$ was added, a chloroform-soluble compound **3** was obtained. In addition, it was found that the resultant compound exhibits luminescence under UV irradiation.
Keywords : BODIPY analogues, fluorescent dye, pyridine-BF_2 complex.

Boron-dipyrromethene (BODIPY)類は高いモル吸光係数・高い蛍光量子収率・狭いストークスシフトを示す優れた蛍光色素であることが知られている。また、ピリジン骨格からなるジピリジルメテン類も発光性物質であることが最近確認されている[1]。それゆえ、その光物性に関する研究は限定的である。そこで本研究では、**Figure 1** に示す *meso*-フェニル置換ピリジン-BF_2 錯体の合成とその発光特性を調査した。

トリエチルアミン存在下で BF_2 錯体化を行うことにより得られた **1** からは、クロロホルム溶液および固体状態において UV 照射下 (λ = 365 nm)で発光が確認された。一方、ピリジニウム塩型になる **2** のメタノール溶液からは発光が観測されなかった。これに対して、**2** の前駆体となる化合物に等量の *tert*-BuOK を反応させた後に $BF_3{\cdot}Et_2O$ を添加するとクロロホルムに可溶な化合物 **3** が得られ、UV 照射下で黄色発光を示した。

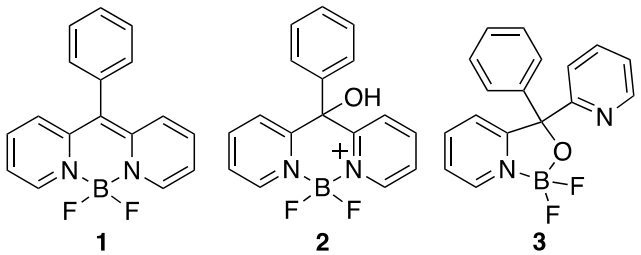

Figure 1. Chemical structure of pyridomethene-BF_2 complexes.

1) Boron Dipyridylmethene (DIPYR) Dyes: Shedding Light on Pyridine-Based Chromophores. Golden, J., Facendola, J.; Sylvinson M. R., D.; Baez, C. Q.; Djurovich, P. I.; Thompson, M. E. *J. Org. Chem*, **2017**, *82*, 7215.

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光安定化剤ジオクチルヒドロキシジメトキシベンジリデンマロネートの光励起状態と光安定化機構

(1 横浜国大理工，2 横浜国大院理工）○五十嵐 寛真 1・八木 幹雄 2・菊地 あづさ 2

Photoexcited States and Photostabilization Mechanism of a Photostabilizer, Dioctyl 4-Hydroxy-3,5-Dimethoxybenzylidenemalonate ([1]*College of Engineering Science, Yokohama National University,* [2]*Graduate School of Engineering Science, Yokohama National University*)
○Kanma Igarashi,[1] Mikio Yagi,[2] Azusa Kikuchi[2]

4-*tert*-Butyl-4'-methoxydibenzoylmethane (BMDBM) is the most widely used UV-A absorber in the world. Unfortunately, BMDBM is well known for its photoinstability. Dioctyl 4-hydroxy-3,5-dimethoxybenzylidenemalonate (diethylhexyl syringylidenemalonate, DESM) is known as an effective photostabilizer for BMDBM. Although many studies proposed that the energy transfer from BMDBM to DESM is responsible for the observed stabilization, the direct evidence of the energy transfer has not been reported. In the present study, the triplet–triplet energy transfer from BMDBM to DESM has been observed by measuring the phosphorescence decay of the energy donor, BMDBM, in rigid solutions at 77 K.

Keywords: Dioctyl 4-hydroxy-3,5-dimethoxybenzylidenemalonate; 4-tert-Butyl-4'-methoxydibenzoylmethane; Triplet–triplet energy transfer

ブチルメトキシジベンゾイルメタン（BMDBM，商標名 Parsol 1789，Figure 1）は UV-A 吸収剤として世界的に汎用されているが光安定性が低い。ジオクチル 4-ヒドロキシ-3,5-ジメトキシベンジリデンマロネート（ジエチルヘキシルシリンジリデンマロネート，DESM，商標名 Oxynex ST，Figure 1）は BMDBM の光安定化剤として知られている。BMDBM から DESM へのエネルギー移動が光安定化機構であると推定されているが，実際にエネルギー移動を観測した報告はない[1)]。本研究では，りん光スペクトルを 77 K 剛性溶媒中で測定し，DESM の最低励起三重項状態のエネルギー準位は BMDBM よりも低いことを明らかにした。続いてパルスレーザー励起による BMDBM のりん光減衰曲線に及ぼす DESM 添加効果を測定し，BMDBM から DESM への三重項－三重項エネルギー移動を直接観測した。

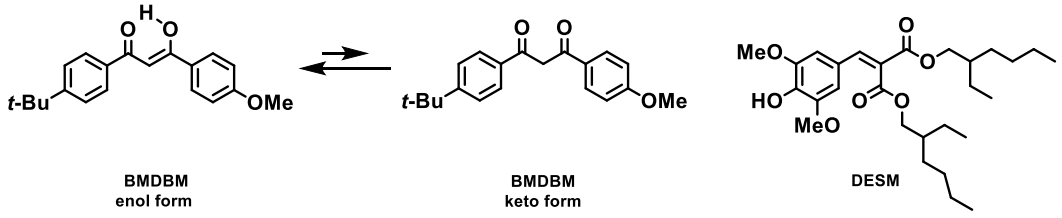

Figure 1. Molecular structures of BMDBM and DESM.

1) C. Mendrok-Edinger, K. Smith, A. Janssen, J. Vollhardt, *Cosmet. Toiletries* **2009**, *124*, 47.

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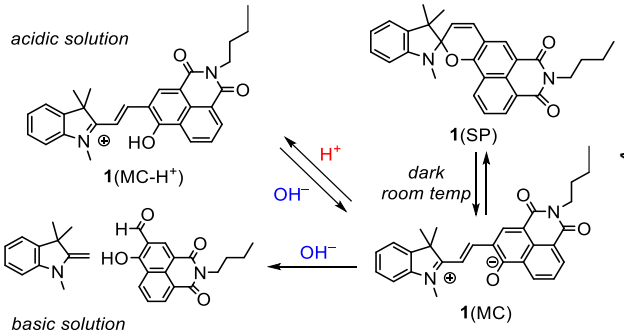
ナフタルイミド含有スピロピランの水溶液中におけるスペクトル挙動と構造変化

（阪大院基礎工）○大島 拓・白石 康浩・平井 隆之
Spectral and structural behaviors of naphthalimide-containing spiropyran in aqueous media (*Graduate School of Engineering Science, Osaka University*), ○Taku Oshima, Yasuhiro Shiraishi, Takayuki Hirai

A napthalimide-containing spiropyran molecule (**1**), when dissolved in high polarity solvents, exhibits spontaneous coloration under the dark and room temperature conditions, by stabilization of the ring-opened form[1]. In this work, we studied the spectral behavior of this molecule in aqueous media. NMR, equilibrium experiments, and DFT calculations revealed that addition of water to the solution further stabilizes the ring-opened form, accelerating the ring-opening reaction and increasing the equilibrium concentration of the form. In acidic media, the protonation of the naphthol moiety creates a shorter-wavelength absorption. In contrast, in basic media, irreversible hydrolysis of the alkene moiety leads to decomposition of the molecule.
Keywords : spiropyran; aqueous solution; naphthalimides; stabilization

ナフタルイミドを導入したスピロピラン分子（**1**）は、暗所・室温下において、溶媒極性の増加による開環体の安定化により、溶媒極性に応じて閉環（SP）体から開環（MC）体への自発的な開環挙動を示す[1]。本研究では、本分子の水溶液におけるスペクトル挙動を調べた。^{1}H NMR 測定により、水を添加した場合には、開環体由来の等価なメチル基の強度がより大きくなり、開環体がさらに安定化されることが分かった。これは、開環体のフェノレート部位へ水分子が付加することにより開環体の基底エネルギーが安定化されるためであることが DFT 計算によって確認された。平衡吸収実験の結果、水の添加により開環体の平衡濃度が増加することが分かった。また、本分子は、中性条件では MC 体として存在するが、酸性 pH においてはフェノレート部位のプロトン化により短波長吸収が出現した。一方、塩基性 pH においては、アルケン部位が不可逆的に加水分解することが分かった。



Scheme 1. Behavior of compound **1**.

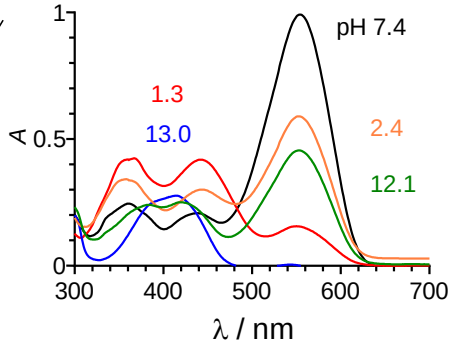


Figure 1. Absorption spectra of **1** (20 μM) measured in solvents with different pH values at 20 °C.

1) Y. Shiraishi, K. Yomo, T. Hirai, *ACS Phys. Chem. Au.* **3**, 290-298 (2023)

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2 種類の LCST 水和相を持つ両親媒性ジアリールエテン超分子構造体

（京大院工[1]・京大福井セ[2]）○吉川 陽大[1]・東口 顕士[1]・松田 建児[1,2]

Supramolecular Assembly of Amphiphilic Diarylethene Showing Phase Transition between LCST Hydrated Phases ([1]*Grad. School of Eng, Kyoto Univ*, [2]*FIFC, Kyoto Univ*) ○Yoshikawa Yodai,[1] Higashiguchi Kenji,[1] Matsuda Kenji[1,2]

Amphiphilic diarylethene (DAE) formed supramolecular assembly showing reversible morphological change in nanostructure by external stimuli. In this study, we found a system showing phase transition between LCST hydrated phases upon temperature change. The observed nanostructure were fiber and toroid when the open-ring isomer was used. The transition temperature fell drastically with the slight increase of the closed-ring isomer. The resulting assembly containing a small amount of the closed-ring isomer had a phase-separated structure in which a looped fiber and amorphous core were separated. Therefore, the toroid structure is considered to be comprised of a pure open-ring isomer.

Keywords : Diarylethene; Supramolecular assembly; LCST transition; Toroid

Oligo(ethylene glycol) 鎖を持つ両親媒性ジアリールエテン（DAE）分子は水中で超分子構造体を形成し、そのナノ構造は外部刺激により変化する。本研究では LCST 水和相において二段階で相転移をする系を発見した。Tetra(ethylene glycol) 鎖を有する **DAE 1** の超分子構造体（開環体 100%）のナノ構造は、低温領域ではファイバー、中間温度領域である 17 – 21°C の狭い温度範囲ではトロイド、高温領域では脱水和状態のコアセルベートを形成した。閉環体分率の増加に伴い中間温度領域が急激に狭く、また低下していくことからトロイドを形成しているのはほぼ開環体のみであることが示唆された。

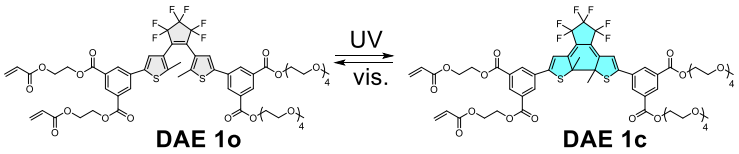

Figure 1. Photochromic reaction of **DAE 1**.

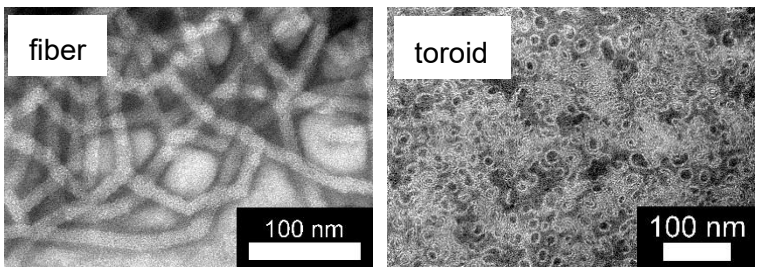

Figure 3. TEM images of the supramolecular architectures.

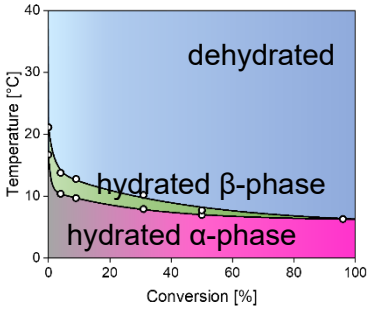

Figure 2. Phase diagram of the LCST transition in aqueous suspension.

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光と酸化・還元の段階的刺激で近赤外吸収を示すジアリールエテン二量体

（京大院工[1]・京大福井セ[2]）○佐竹 来実[1]・大月 直人[1]・東口 顕士[1]・松田 建児[1,2]
Diarylethene Dimer Showing NIR Absorption upon Stepwise Stimuli of Photoirradiation and Redox ([1]*Graduate School of Engineering, Kyoto University*, [2]*FIFC, Kyoto Univ.*) ○Kurumi Satake,[1] Naoto Ootsuki,[1] Kenji Higashiguchi,[1] Kenji Matsuda[1,2]

A linearly fused diarylethene dimer is expected to show NIR absorption. However, the isomer in which both diarylethene units are ring-closed has not been obtained due to the excitation energy transfer in photoreaction. Therefore, we focused on electrochemical ring-closure using oxidation. In this work, we synthesized a linearly fused diarylethene dimer to realize controlling absorption among UV-visible-NIR region by a combination of photo- and oxidative stimuli. An absorption band originated from **1-co** appeared at visible region upon irradiation with UV light. Subsequent oxidation and reduction resulted in the appearance of a new band originated from **1-cc** at NIR region. Furthermore, irradiation of NIR and visible light to **1-cc** resulted in a return to **1-oo**, confirming that the switching occurred reversibly.
Keywords : Diarylethene; Photochromism; Electrochromism; NIR absorption

二つのジアリールエテンを縮環させると、剛直な平面 π 共役が広がることから、原理上は長い有効共役長が得られ、近赤外域に吸収帯を有することが期待される。しかし、両方のジアリールエテンユニットが閉環した異性体は、一般には励起エネルギー移動のため形成されない。そこで酸化閉環反応に着目した。本研究では縮環型のジアリールエテン二量体を用い、光と酸化刺激の組み合わせによる、紫外－可視－近赤外域間での段階的な吸収波長スイッチングを目指した。二量体 **1-oo** のジクロロメタン溶液に紫外光を照射したところ、可視域に **1-co** 由来の吸収帯が現れた。続く酸化および還元により 950 nm 付近に **1-cc** 由来の吸収帯が現れた。さらに、**1-cc** へ近赤外光を照射すると **1-co** へと、その後の可視光照射により **1-oo** へと戻り、スイッチングが可逆に起こることが確認できた。

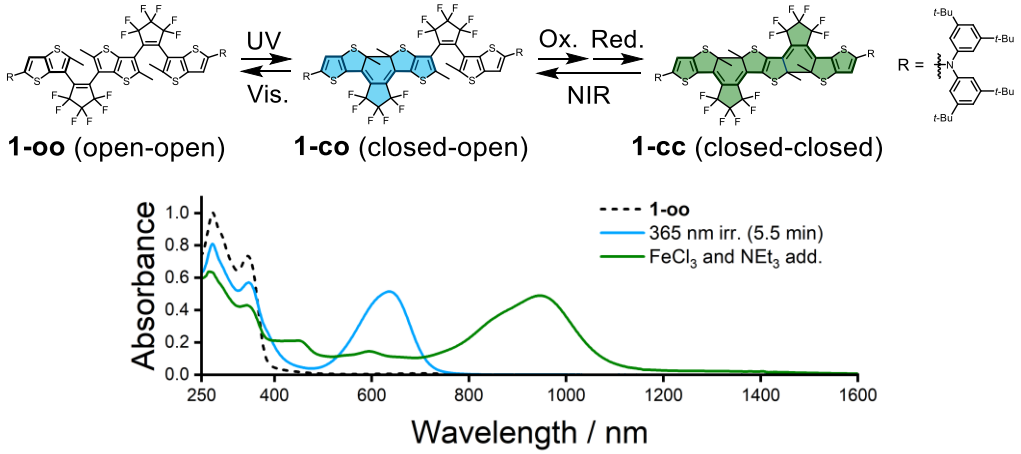

Figure 1. Change in absorption spectra of **1** upon UV irradiation and subsequent oxidation and reduction in CH_2Cl_2.

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カリックスアレーンを中心骨格としたペンタセン四量体の合成と分光特性

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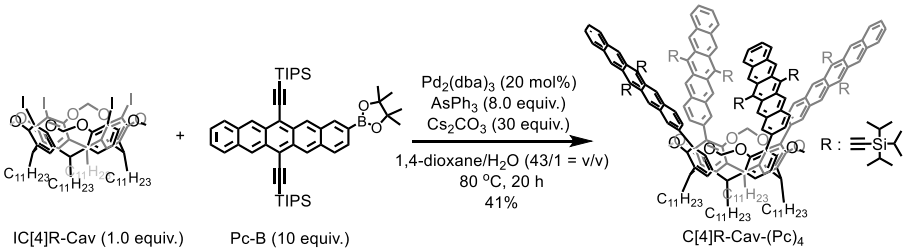
Syntheses and Spectroscopic Properties of Calixarene-Centered Pentacene Tetramers ([1]*Faculty of Science and Technology, Keio University*, [2] *Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kazushi Ishikawa,[1] Kentaro Harada,[2] Hayato Sakai[1], Takeharu Haino,[2] Taku Hasobe[1]

Calix[*n*] resorcinarene cavitand (C[*n*]R-Cav) is one of the representative molecules in the field of molecular recognition chemistry, serving as a fundamental scaffold for host molecules. On the other hand, pentacene is a typical chromophore for occurrence of singlet fission, generating two triplet excited states from one-photon absorption. In this study, we synthesized a series of C[*n*]A-centered pentacene tetramers and evaluated the structure and spectroscopic properties.

Keywords : Calix[4]resorcinarene cavitand; Singlet Fission; Pentacene

カリックス[*n*]レゾルシンアレーンキャビタンド(C[*n*]R-Cav) は、分子認識化学におけるホスト分子の基本骨格として精力的に研究されている分子の一つである。C[*n*]R-Cav は、官能基修飾が容易であり、様々な機能の付与が報告されている。一方、ペンタセンは一光子吸収から二つの三重項励起子を生成する一重項分裂 (SF) を発現する分子として知られている。本研究では、C[*n*]R-Cav を中心骨格としたペンタセン四量体 (C[4]R-Cav-$(Pc)_4$) を合成し、その構造及び分光特性の検討を行った。



Scheme 1. Synthesis of C[4]R-Cav-$(Pc)_4$

C[4]R-Cav-$(Pc)_4$ の合成は、Scheme 1 に従って行った。既報のカリックス[4]レゾルシンアレーンキャビタンド誘導体 (IC[4]R-Cav)[1)] とペンタセン誘導体 (Pc-B) から $AsPh_3$ をリガンドに用いて鈴木宮浦クロスカップリング反応を行うことで、収率 41% で目的物を合成した。C[4]R-Cav-$(Pc)_4$ の蛍光スペクトルを測定したところ、参照化合物のペンタセンモノマーに対して蛍光消光が確認され、さらに、過渡吸収測定において項間交差より速い三重項励起状態の生成が確認できたことから SF の発現が示唆された。

1) Haino, T. et al., *Chem. Eur. J.* **2006**, *12*, 3310.

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テトラセン–微小金ナノクラスター連結体の合成と励起エネルギー移動特性

(慶大理工[1]・東理大理[2]) ○平松 直[1]・中本 真奈[2]・秋山 葵[2]・酒井 隼人[1]・根岸 雄一[2]・羽曾部 卓[1]

Synthesis and Energy Transfer Properties of Tetracene-Ultrasmall Au Nanocluster Dyads

([1]*Faculty of Science and Technology, Keio University,* [2]*Faculty of Science, Tokyo University of Science*) ○Sunao Hiramatsu,[1] Mana Nakamoto,[2] Aoi Akiyama,[2] Hayato Sakai,[1] Yuichi Negishi,[2] Taku Hasobe[1]

Ultrasmall Au nanoclusters [Au_n (n: number of atoms)] such as Au_{25} and Au_{38} exhibit the characteristic molecular behaviors associated with the discrete orbital levels. Although singlet excited states and triplet excited states of Au_n have been studied by theoretical calculation and luminescence measurement, so far, there is no example of assignment of triplet-triplet absorption spectra derived from Au_n. Based on the above contents, we evaluated the intermolecular and intramolecular excitation energy transfer between Au_n and π-conjugated molecules such as tetracene.

Keywords: Au Nanocluster; Energy Transfer; Tetracene

金ナノクラスターとは数個から数百個の金原子の集合体であり、構成原子数や配位子種に依存した特性と構造を示す。中でも直径 2 nm 以下のクラスターは微小金ナノクラスター [Au_n (n: 構成原子数)] と定義され、軌道準位の離散化に伴う分子性を示す。一例としてフェニルエタンチオレート修飾金 25 原子体 (Au_{25}) では励起一重項状態 [$E(S_1)$ = ~1.5 eV] および三重項状態 [$E(T_1)$ = ~1.3 eV] [1]が定常発光測定により決定されている。また、Au_{38} は $E(S_1)$ = ~1.1 eV, $E(T_1)$ = ~0.95 eV [2]という励起エネルギー条件を示すことが予測されており、一般的な有機分子と比較して小さな一重項–三重項 (S-T) エネルギーギャップを示す。しかしながら、Au_n の T_1 は燐光や一重項酸素の測定に基づく報告だけであり、過渡吸収測定による三重項–三重項吸収スペクトルの直接的な帰属例はない。一方、テトラセン (Tc) は 4 つのベンゼン環が縮環したπ共役分子である。特に、トリイソプロピルシリルアセチレン導入 Tc は $E(S_1)$ = 2.3 eV, $E(T_1)$ = 1.2 eV という大きな S-T ギャップを有し [3]、上述の Au_n とは対照的である。

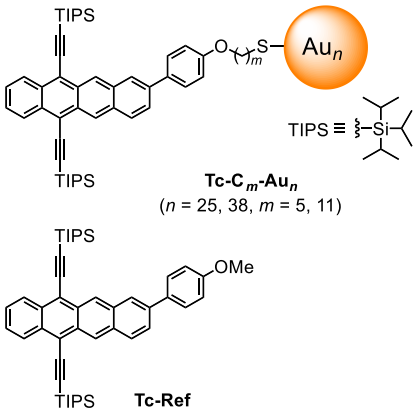

Fig. 1 Tc-C_m-Au_{25}, Tc-C_5-Au_{38} (m = 5,11) の化学構造

本研究では Au_n の分子性を評価するため、アルキル鎖を介した Tc-Au_n 連結体 [Tc-C_m-Au_{25}, Tc-C_5-Au_{38} (m = 5, 11)] を合成した (Fig. 1)。本発表では連結体における Au_n の S_1 および T_1 に関連する励起ダイナミクスの詳細を明らかにする。

1) Xu, W.; Xie, J. et al. *Angew. Chem. Int. Ed*. **2020**, *59*, 9934.
2) Day, P. N.; Pachter, R.; Nguyen, K. A.; Jin, R. *J. Phys. Chem. A* **2019**, *123*, 6472.
3) Kobori, Y.; Hasobe, T. et al. *Angew. Chem. Int. Ed*. **2023**, *62*, e202217704.

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ピレンーウレア化合物の励起状態分子間プロトン移動反応に対するヒドロキシ化合物添加の影響

(筑波大[1]) ○黄 楽耘[1]・西村 賢宣[1]

The effect of additional hydroxy compounds on the excited state intermolecular proton transfer reaction of pyrene-urea compounds ([1]*Graduate School of Pure and Applied Science, University of Tsukuba*) ○Leyun Huang,[1] Yoshinobu Nishimura[1]

The ESPT (excited state intermolecular proton transfer) reaction is a phenomenon in which a molecule, whose acidity increases in the excited state as a hydrogen bond-donating site, undergoes intermolecular proton transfer to give a tautomer species. Pyrene-urea derivatives and acetate anions were used to investigate the ESPT reaction. Since the ESPT reaction takes place when intermolecular hydrogen bonds exist between urea compounds and acetate species, we assume that this reaction might be affected by compounds with hydroxy groups. In this study, we used cyclodextrins, sugars, and ethanol to examine the effect of hydroxy groups on the ESPT reaction using kinetic methods.

After adding hydroxy compounds to the *m*-CF_3-1PUP–Acetate system in DMSO and DMF, we found solvent dependence in the fluorescence spectra and fluorescence decay curves. This phenomenon indicated different interactions between the hydroxy compounds and complexes (N) in DMSO and DMF. Owing to the higher reactivity of the hydroxy groups than the urea group of *m*-CF_3-1PUP, we attributed the relatively low reactivity observed in DMSO to the formation of a unique structure with the solvent molecules.

Keywords : ESPT reaction, rate constants, tautomer fluorescence, pyrene-urea compounds, hydroxy compounds

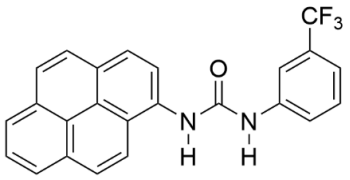

Fig. 1. The structure of *m*-CF_3-1PUP.

我々はピレンーウレア誘導体と酢酸アニオンを用いて励起状態分子間プロトン移動（ESPT）反応を調べた。ESPT 反応はウレア化合物と酢酸アニオンとの間に分子間水素結合が存在する状態で起こることから、この反応はヒドロキシ基を持つ化合物の影響を受ける可能性があると考えられる。本研究では、シクロデキストリン、糖類とエタノールを用いて、ESPT 反応に対するヒドロキシ基の影響を速度論的手法により検討した。

DMSO と DMF 中において、*m*-CF_3-1PUP-TBAAc (Fig. 1)にヒドロキシ化合物を添加したところ、蛍光スペクトルと蛍光減衰曲線に溶媒依存性があることを見出した。この現象は、DMSO と DMF 中でのヒドロキシ化合物と会合体(N)の相互作用の違いを示している。ヒドロキシ基は *m*-CF_3-1PUP のウレア基よりも反応性が高いため、DMSO 中で反応性が比較的低いのは、溶媒分子との間で特異な構造が形成されたためと考えられる。

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親水性アセン誘導体の合成と分光特性

(慶大理工[1]・東工大物質理工[2])
○大久保 尚弥[1]・酒井 隼人[1]・野中 慧悟[2]・相良 剛光[2]・羽曾部 卓[1]

Synthesis and Spectroscopic Properties of Hydrophilic Acene Derivatives ([1]*Fac. Sci. Tech., Keio Univ.,* [2]*Sch. Mat. Chem. Tech., Tokyo Inst. of Tech*)
○Naoya Okubo,[1] Hayato Sakai,[1] Keigo Nonaka,[2] Yoshimitsu Sagara,[2] Taku Hasobe[1]

Singlet fission (SF) is a multi-exciton generation process, where two triplet excitons (T_1) are generated from one-photon absorption in two neighboring chromophores. Acene derivatives such as tetracene and pentacene are well-known for occurrence of SF. However, the solubility of these derivatives in water is extremely low. In this study, we synthesized a series of acene derivatives substituted with hydrophilic groups and evaluated the structural and photophysical properties in monomeric and aggregate forms.
Keywords : Acene Derivatives; Singlet Fission; Molecular Assembly; Hydrophilic Compound

通常、π 共役系分子は水に対する溶解性は極めて乏しいが、多環芳香族炭化水素の基本骨格に対して親水性置換基を導入することで、水中における分子集合体の形成だけでなく、可溶化も実現できる。一方、π 共役系分子の一つであるテトラセンやペンタセンなどのアセン系分子は近接二分子間で一つの最低励起一重項状態 (S_1) から二つの最低励起三重項状態 (T_1) を生成する多励起子生成の一重項分裂 (SF) の発現が報告されている。発エルゴン的に SF が進行するペンタセン (Pc) に対して、テトラセン (Tc) は吸エルゴン的に SF が進行するものの、高い T_1 エネルギーを有しているため、光エネルギー変換への展開が期待できる。

本研究では上記に基づいて、アセン骨格に対してエチレングリコール鎖を基盤とした複数種の置換基導入を試みている。[1,2] その一例としてアセン誘導体の化学構造を Fig. 1 に示す。本発表では一連の化合物合成および分子集合体の分光特性を議論する。

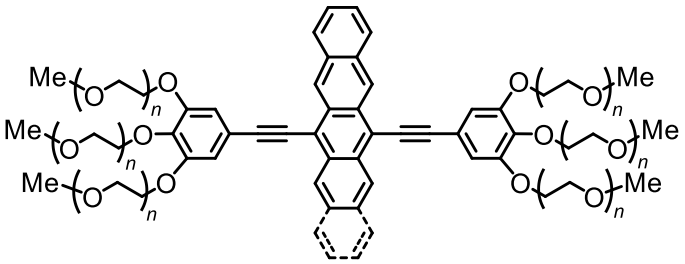

Fig. 1 本研究で用いる化合物の一例

1) Yoshino, K.; Sakai, H.; Shoji, Y.; Kajitani, T.; Anetai, H.; Akutagawa, T.; Fukushima, T.; Tkachenko, V. N.; Hasobe, T. *J. Phys. Chem. B* **2020**, *124*, 11910.
2) Sagara, Y.; Komatsu, T.; Ueno, T.; Hanaoka, K.; Kato, T.; Nagano, T. *J. Am. Chem. Soc.* **2014**, *136,* 4273.

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N,*N*-型イミダゾ[1,2-*a*]ピリジン配位子のフッ化ホウ素錯体の合成と光細胞傷害性

(徳島大理工[1]・徳島大理工院[2]・徳島大 pLED[3]) ○小川　樹[1]・上田　昭子[2]・南川 慶二[2]・八木下　史敏[2,3]

Synthesis of *N*,*N*-type imidazo[1,2-*a*]pyridine-BF_2 complexes and photocytotoxicity

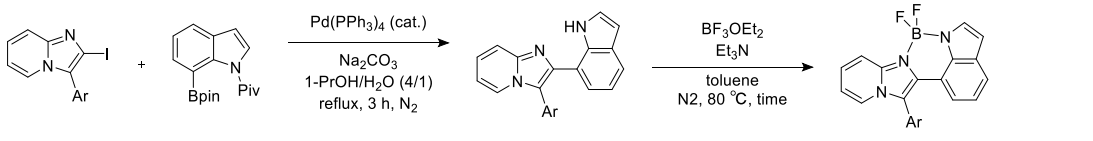
([1]*Tokushima University,* [2]*Graduate School , Tokushima University ,* [3]*Inst. pLED , Tokushima University*) ○Itsuki Ogawa,[1] Shoko Ueta,[2] Keiji Minagawa,[2] Fumitoshi Yagishita[2,3]

The introduction of boron atoms into a π-conjugate system is recognized as an effective strategy for improving photophysical properties. Thus, many efforts have been devoted to developing boron complexes based on various aromatic ligands. Although the boron complexes based on imidazo[1,2-*a*]pyridine ligands have been developed, they are limited to the use of *N*,*O*-type ligands. In this study, we synthesized *N*,*N*-type imidazo[1,2-*a*]pyridine ligands and their boron complexes and evaluated their photophysical properties. The PL quantum yields of boron complexes **1** were approximately 0.30. Notably, the synthesized boron complexes **1** were found to work not only as blue emitters but also as heavy-atom-free mitochondria-targeted photosensitizers for photodynamic therapy.

Keywords : Imidazo[1,2-a]pyridines; Boron complexes; Fluorescence; Photodynamic therapy

BODIPY 色素をはじめとし，有機ホウ素錯体は優れた発光特性を示すことが知られており，多様な分子デザインが報告されている。イミダゾ[1,2-*a*]ピリジンを窒素配位子として活用した発光性ホウ素錯体は知られているものの，イミダゾ[1,2-*a*]ピリジン環に *o*-ヒドロキシフェニル基を置換した *N*,*O*-型配位子に限られていた。そこで本研究では，イミダゾ[1,2-*a*]ピリジンの 2 位にインドール骨格を導入した *N*,*N*-型配位子 **1** をデザインし，そのホウ素錯体の合成と発光特性評価を行った。

鈴木―宮浦クロスカップリング反応をヨウ素化したイミダゾ[1,2-*a*]ピリジンと 7 位をホウ素化したインドールで行った後、三フッ化ホウ素を用いて **1** を合成した。合成したホウ素錯体 **1** は 450 nm 付近の青色発光を示し，その量子収率はおよそ 0.30 程度であった。一方，ホウ素錯体 **1b** を HeLa 細胞の蛍光染色剤として利用したところ，ミトコンドリアに集積することを見出した。興味深いことに， UVA-LED の連続照射下において HeLa 細胞の生存率低下が確認され, **1b** は重原子フリーなミトコンドリア標的型光線力学療法薬剤の候補物質として機能することを見出した。



1a: Ar = H; 43% yield (4 h)
1b: Ar = Ph; 74% yield (3 h)
1c: Ar = *p*-$MeOC_6H_4$; 59% yield (4 h)

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歯科インプラント周囲炎治療に向けた近赤外光増感剤-カーボンナノホーン複合体の開発

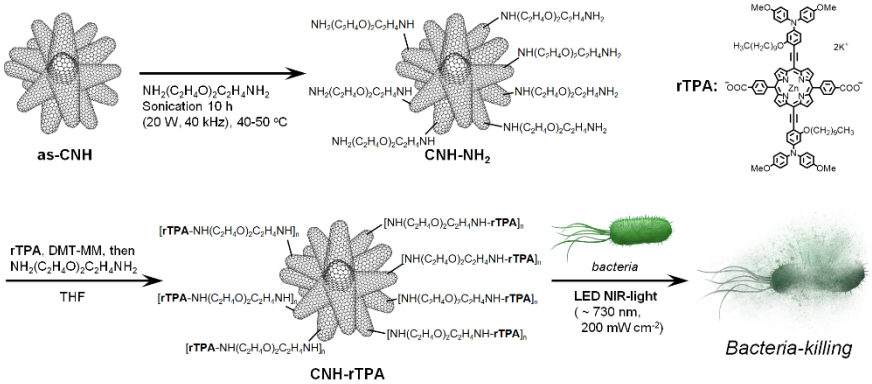
（北大電子研[1]・北大歯学[2]・名城大[2]）○高野 勇太[1]・平田 恵理[1]・小西 大輔[1]・前田 由佳利[1]、牛島 夏未[1]・湯田坂 雅子[2]・横山 敦郎[1]

Near-Infrared Photosensitizer-Carbon Nanohorn Composites for the Treatment of Peri-implantitis ([1]*RIES, Hokkaido University*, [2]*Graduate School of Dental Medicine, Hokkaido University*, [3]*Graduate School of Sci. and Tech., Meijo University*) ○Yuta Takano[1], Eri Hirata[1], Daisuke Konishi[1], Yukari Maeda[1], Natsumi Ushijima[1], Masako Yudasaka[2], Atsuro Yokoyama[1]

Carbon-based nanomaterials have attracted significant attention due to their unique chemical and physical properties. Among carbon nanomaterials, the large surface area and spherical morphology of carbon nanohorn (CNH) provide biological functionality and biocompatibility. In this study, we developed a new composite material based on carbon CNHs that exhibits bactericidal effects under near-infrared light irradiation against the bacteria that cause peri-implantitis, an inflammatory disease around implants that can lead to the failure of implants due to bone loss around implants. The near-infrared photosensitized-CNH composite showed much better photodurability than the commonly used Indocyanine Green, and showed a remarkable bactericidal effect under near-infrared light irradiation.

Keywords : NIR; Phototherapy; Porphyrin; singlet oxygen

炭素系ナノ材料は、そのユニークな化学的・物理的特性から大きな注目を集めている。カーボンナノ材料の中でも、カーボンナノホーン(CNH)は大きな表面積と球状形態を有し、種々の生物学的機能性と高い生体適合性を持つことが知られている[1]。本研究では、インプラント周囲の炎症性疾患であり、インプラント周囲の骨欠損によるインプラント喪失につながる周囲炎の原因菌に対して、近赤外光照射下で殺菌効果を示す、CNH をベースとした新しい光機能性複合材料を開発した（下図）。近赤外光増感剤-CNH 複合体は、一般的に使用されるインドシアニングリーンに比べ、光耐久性に優れ、近赤外光照射下で顕著な一重項酸素の生成効果を発揮し、光殺菌効果を示した[2]。



1) S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai and K. Takahashi, *Chem. Phys. Lett.* 1999, **309**, 165.
2) E. Hirata, Y. Takano, D. Konishi, Y. Maeda, N. Ushijima, M. Yudasaka, A. Yokoyama, *Chem. Commun.* 2023, **59**, 11000.

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光環化–脱水素化反応を利用したチオフェン縮環多環芳香族炭化水素の合成

（阪公大院工）○渡久山 裕亮・大垣 拓也・松井 康哲・池田 浩
Synthesis of Thiophene-fused Polycyclic Aromatic Hydrocarbons Using Photocyclization–Dehydrogenation Reaction (*Grad. Sch. of Eng., Osaka Metro. Univ.*) ○Yusuke Tokuyama, Takuya Ogaki, Yasunori Matsui, Hiroshi Ikeda

Thiophene-fused polycyclic aromatic hydrocarbons have attracted much attention as organic semiconductor materials because of their highly-planar π-skeleton and strong intermolecular interactions in solid states. In this work, we synthesized novel thiophene-fused phenanthrene **2** (Fig. a) by using a photocyclization–dehydrogenation reaction of a precursor **1** with a hexatriene structure.

Photoirradiation of a CH_2Cl_2 solution of **1** in the presence of *p*-chloranil (*p*-CA, 1 eq.) with a 310-nm LED lamp afforded **2** in 82% yield. The results of X-ray crystallographic analysis (Fig. b) show that **2** forms antiparallel π-stacking dimers with an interplanar distance of 3.60 Å to avoid the steric hindrance between triisopropylsilyl groups, forming a sandwich herringbone structure. In the presentation, we will give the details of the photophysical and electrochemical properties of **2** and the related π-extended derivative.

Keywords: Thiophene; Photoreaction; Mallory Reaction; Phenanthrene; π-Conjugation

チオフェン縮環多環芳香族炭化水素は，平面性の高いπ骨格と固体中での強い分子間相互作用をもつことから，有機半導体材料として注目されている．本研究では，ヘキサトリエン構造をもつ前駆体 **1**（Fig. a）の光環化–脱水素化反応を利用して，新規チオフェン縮環フェナントレン **2** を合成した．

p-クロラニル（*p*-CA，1 当量）共存下，**1** の CH_2Cl_2 溶液に 310 nm LED 灯で光照射したところ，**2** が収率 82%で得られた．X 線結晶構造解析の結果（Fig. b）から，**2** はトリイソプロピルシリル基同士の立体反発を避けるようアンチパラレル型のπ積層二量体（面間距離 3.60 Å）を形成し，それがヘリンボーン状に配列して最終的にサンドウィッチヘリンボーン構造を形成していることが分かった．発表では，**2** および関連するπ拡張誘導体の光物理特性および電気化学特性についても議論する．

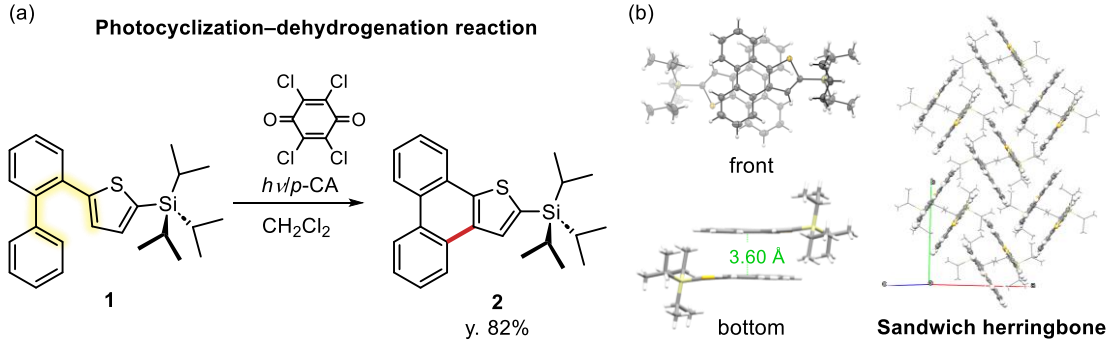

Fig. (a) Synthesis of **2** using photoreaction of **1** and (b) the π-stacking dimer (left) and the crystal structure (right) of **2**.

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

Wed. Mar 20, 2024 9:00 AM - 11:20 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:20 AM UTC
E1132(1132, Bldg. 11 [3F])

[E1132-3am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Hisanori Senboku, Kenta Tanaka

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1132-3am-01]
Electrochemical Synthesis of Dibenzothiophene Dioxides from Biaryl Sulfonyl Hydrazides

○Yasuyuki Okumura[1], Koichi Mitsudo[1], Seiji Suga[1] (1. Division of Applied Chemistry, Graduated School of Natural Science and Technology, Okayama University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1132-3am-02]
Investigation of the Possibility of Two-step Synthesis of Firefly Luciferin from Tetrachloroethylene

○Kouichi Matsumoto[1], Emi Murai[1], Yuta Fujiki[1], Akiko Kuwabara[2], Masafumi Kobayashi[2] (1. Kindai Uni., 2. Kanto Denka Kogyo Co., Ltd.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1132-3am-03]
Kinetics study of O-C glycoside rearrangement and its synthetic application using flash electro synthesis

○Yiyue Yao[1], Yosuke Ashikari[1], Masahiro Takumi[1], Aiichiro Nagaki[1] (1. The Univ. of Hokkaido)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1132-3am-04]
α-Aminoalkylation of Sulfonylheteroarenes with Amines and Aldehydes by Cathodic Reduction

○Kyohei Yonekura[1], Kotaro Sekinishi[1], Eiji Shirakawa[1,2] (1. School of Biological and Environmental Sciences, Kwansei Gakuin University, 2. CREST, JST)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1132-3am-05]
Effect of Supporting Electrolyte on the Selective Electrochemical Decarboxylative Olefination of Carboxylic Acids

○Tasuku Ito[1], Xiongjie Jin[1], Kyoko Nozaki[1] (1. Grad. Sch. of Engineering, The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1132-3am-06]
Electrochemical Carboxylation of Benzyl Alcoholes

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○Hisanori Senboku[1], Mizuki Hayama[1] (1. Hokkaido University)

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

[E1132-3am-07]

Electrochemical intramolecular C-N bond formation using π-extended bromoarene mediator and its kinetic analysis

○Atsuki Hirama[1], Shohei Yoshinaga, Naoki Shida[1], Mahito Atobe[1] (1. Yokohama Natonal University)

Japanese

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

[E1132-3am-08]

One-step Synthesis of Diarylacetylenes from Tetrachloroethylene and Arylboronic Acids under Silica-gel by Using Suzuki Coupling Reaction

○Hiyono Suzuki[1], Akiko Kuwabara[2], Masafumi Kobayashi[2], Kouichi Matsumoto[1] (1. Kindai University, 2. KANTO DENKA KOGYO CO.,LTD.)

Japanese

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

[E1132-3am-09]

Strongly Reducing Helical Phenothiazines as Recyclable Organophotoredox Catalysts

○Kenta Tanaka[1], Haru Ando[2], Hiroyoshi Takamura[2], Kadota Isao[2] (1. Okayama Univ. Research Institute for Interdisciplinary Science, 2. Okayama Univ.Department of Chemistry, Graduate School of Natural Science and Technology)

Japanese

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

[E1132-3am-10]

Preparation of Au:CNT electrocatalysts and their application to the aerobic oxidation of alcohols

○Honoka Nakamura[1], Rento Yabuki[1], Yuta Uetake[1,2], Taiyo Shimizu[3], Ken Kokubo[3], Hidehiro Sakurai[1,2] (1. Osaka University, 2. ICS-OTRI, 3. Advanced Industrial Science and Technology)

Japanese

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

[E1132-3am-11]

Magnesium-promoted reductive C-C bond formation of diphenylfulvene derivatives

○Ryunosuke Koyama[1], Tianyuan Zhang[1], Hirofumi Maekawa[1] (1. Nagaoka University of Technology)

Japanese

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

[E1132-3am-12]

Visible-light-induced [4+2] Cycloadditions of *o*-Quinone Methides for the Synthesis of Chromanes.

○Sakura Kodaki[1], Kenta Tanaka[2], Hiroyosi Takamura[3], Isao Kadota[3] (1. School of Science, Okayama University, 2. Research Institute for Interdisciplinary Science Research Institute for

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Interdisciplinary Science, 3. Graduate School of Natural Science and Technology, Okayama University)

Japanese

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

[E1132-3am-13]

Investigation on the reaction conditions for the electrocatalytic hydrogenation of nitrogen-containing aromatic compounds in an AEM reactor

○Akizumi Yonezawa[1], Yugo Shimizu, Juri Harada[1], Naoki Shida[1], Mahito Atobe[1] (1. Yokohama National university)

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スルホニルヒドラジドの電解酸化によるジベンゾチオフェンジオキシドの合成

（岡山大院自然[1]）○奥村 恭之[1]・光藤 耕一[1]・菅 誠治[1]
Electrochemical Synthesis of Dibenzothiophene Dioxides from Biaryl Sulfonyl Hydrazides
([1]*Graduated School of Environmental Life, Natural Science and Technology, Okayama University* ○Yasuyuki Okumura,[1] Koichi Mitsudo,[1] Seiji Suga[1]

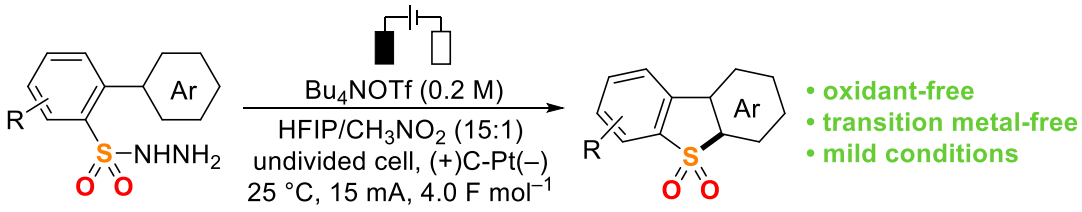
Dibenzothiophene dioxides are used for organic light-emitting materials and pharmaceuticals. However, the synthesis of dibenzothiophene dioxides usually requires rare transition metal catalysts or stoichiometric amounts of chemical oxidants. Meanwhile, electrochemical oxidation enables the oxidation reaction under mild conditions without the use of chemical oxidants, as electricity is a powerful oxidant.

Herein, we report the electrochemical synthesis of dibenzothiophene dioxides without using transition metals or chemical oxidants. Using Bu_4NOTf as an electrolyte in HFIP/CH_3NO_2, several biaryl sulfonyl hydrazides were applied to constant current electrolysis to afford dibenzothiophene dioxides efficiently.

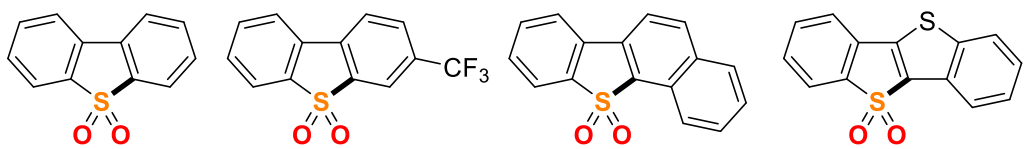
Keywords : electrochemical synthesis, dibenzothiophene dioxide, sulfonyl hydrazide, sulfonyl radical

ジベンゾチオフェンジオキシドは、有機発光素子や医薬品に用いられる重要な骨格である。しかし、従来のジベンゾチオフェンジオキシドの合成には、希少な遷移金属触媒や化学両論量以上の酸化剤が必要であった。一方、電解酸化では、化学酸化剤を使わずとも温和な条件下酸化反応を進行させることができる。

今回我々は、遷移金属や酸化剤を用いない電気化学的なジベンゾチオフェンジオキシドの合成法を開発したので報告する[1]。種々のビアリールスルホニルヒドラジドを基質とし、Bu_4NOTf 存在下、HFIP/CH_3NO_2 混合溶媒中にて定電流電解することで、様々なジベンゾチオフェンジオキシドが効率的に得られた。



Representative scope



1) Okumura, Y.; Sato, E.; Mitsudo, K.; Suga, S. *Electrochemistry* **2023**, *91*, 112007.

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テトラクロロエチレンから 2 工程でのホタルルシフェリン合成の可能性の検討

(近畿大[1]・関東電化工業（株）[2]) ○松本 浩一[1]・村井 絵美[1]・藤木 裕太[1]・桑原 晶子[2]・小林 政史[2]

Investigation of the Possibility of Two-step Synthesis of Firefly Luciferin from Tetrachloroethylene ([1]*Kindai University*, [2]*KANTO DENKA KOGYO CO., LTD.*) ○Kouichi Matsumoto,[1] Emi Murai,[1] Yuta Fujiki,[1] Akiko Kuwabara,[2] Masafumi Kobayashi[2]

Tetrachloroethylene is an inexpensive chemical product, which was used in the area such as dry cleaning and a metal cleaner. We have focused on the utilization of tetrachloroethylene as a platform, in the view pint of a highly oxidized C2 carbon unit.

During the course of our study, the possibility of the two-step synthesis of firefly luciferin was investigated using tetrachloroethylene, the aminobenzenethiol derivative and *D*-cysteine as starting materials (Figure 1). Preliminary findings were obtained, and the details will be presented (Japanese Patent No. 7194404.)[1]

Keywords : Tetrachloroethylene, Firefly Luciferin, D-Cysteine, Aminobenzenethiol Derivatives

テトラクロロエチレンはドライクリーニングや金属洗浄剤として利用されている安価な化学製品である。当研究室では、テトラクロロエチレンを高度に酸化された C2 炭素ユニットと見なすことで、これをプラットホームとする分子変換反応の開発を行ってきた。

この度、テトラクロロエチレンとアミノベンゼンチオール誘導体、および、*D*－システインを原材料に用いて、短工程でのホタルルシフェリン合成の可能性について検討を行った（図 1)。予備的な知見が得られたので、その詳細を発表する（特許 7194404）[1]。

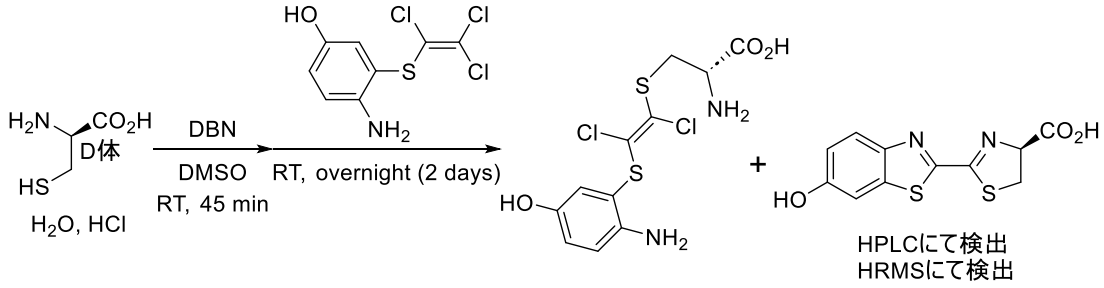

図 1. テトラクロロエチレン、アミノベンゼンチオール誘導体、および、*D*－システインを用いた短工程でのホタルルシフェリン合成の検討（特許明細より引用）

1) 特許 7194404，発明者　松本浩一，小林政史（出願人 学校法人近畿大学，関東電化工業（株））

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高速電解フロー法を基軸とする O-C グリコシド転位反応の速度研究および合成利用

（北大院理）姚弋越・○芦刈洋祐・宅見正浩・永木愛一郎
Kinetic study of *O*-*C* glycoside rearrangement and its synthetic application using flash electro synthesis (*Faculty of Science, Hokkaido University*) Yiyue Yao, ○Yosuke Ashikari, Masahiro Takumi, Aiichiro Nagaki

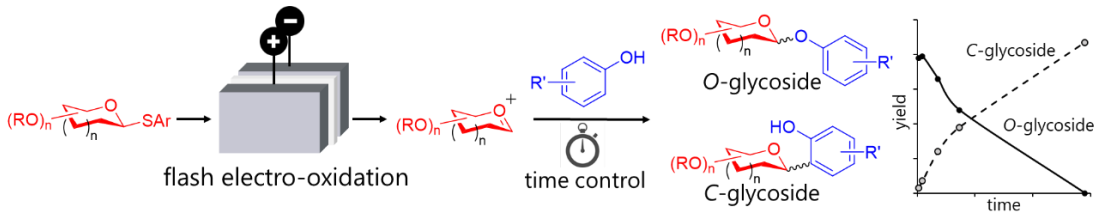
Phenolic *O*-glycosides and *C*-glycosides, which are structural isomers, are common structure in natural compounds and pharmaceuticals. Their syntheses have been widely studied, particularly *O*-*C* rearrangement.[1)] In this process, the glycosyl donner reacts with phenols catalyzed by Lewis acid to generate the *O*-glycoside, which was converted to the *C*-glycoside by raising the temperature,

We have recently reported that flash electrosynthesis[2)] and the precise control of the residence time in the flow microreactors enabled the time-control of the *O*-*C* rearrangement.[3)] Herein, we report a time-course study for *O*-*C* glycosyl rearrangement based on the precise time-controllability of flow microreactors, enabling the kinetic study, as well as a selective generation of *O*- and *C*-glycosides.

Keywords : flow electrosynthesis; O-C glycoside rearrangement; electrochemical glycosydation

糖のアノマー位にフェノール類が置換した化合物群では、フェノールの結合位置の異なる *O*-グリコシドと *C*-グリコシドの構造異性体が存在し、それぞれ天然物や生理活性物質によく見られる。これらの合成法はよく研究されており、特にグリコシルドナーに Lewis 酸触媒を作用させて *O*-グリコシドを合成し、その後の昇温により対応する *C*-グリコシドへ変換する *O*-*C* グリコシド転位がよく知られている [1)]。

一方我々は最近、独自に開発した高速電解フローリアクターを用い、不可逆的にグリコシルカチオンを発生可能であることを報告している [2)]。さらにフローマイクロリアクターの精密な時間制御能を活用することにより、*O*-*C* グリコシド転位反応を制御できることを見出している [3)]。今回、フローマイクロリアクターの精密な時間分解能の活用により、*O*-*C* グリコシド転位の反応速度研究を行い、さらに選択的な *O*-および *C*-グリコシド合成へと展開したため、これを報告する。



[1)] Suzuki, K. *J. Synth. Org. Chem., Jpn.* **2007**, *65*, 175.
[2)] Takumi, M.; Sakaue, H.; Nagaki, A. *Angew. Chem. Int. Ed.* **2022**, *61*, e202116177.
[3)] 姚弋越、芦刈洋祐、宅見正浩、永木愛一郎　日本化学会第 103 春季年会 K602-3am-05

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アミンおよびアルデヒドを用いる陰極還元によるスルホニルヘテロアレーンのα-アミノアルキル化反応

（関西学院大生命環境[1]・JST CREST[2]）○米倉 恭平[1]・関西 光太郎[1]・白川 英二[1,2]

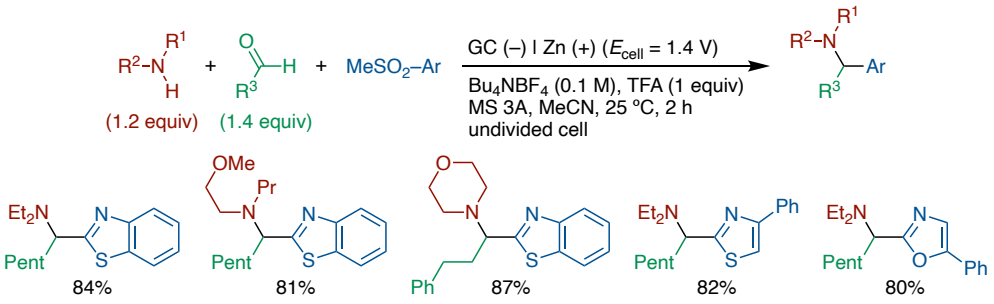
α-Aminoalkylation of Sulfonylheteroarenes with Amines and Aldehydes by Cathodic Reduction ([1]*School of Biological and Environmental Sciences, Kwansei Gakuin University*, [2]*CREST, JST*) ○Kyohei Yonekura,[1] Kotaro Sekinishi,[1] Eiji Shirakawa[1,2]

α-Aminoalkylation of sulfonylheteroarenes with amines and aldehydes in the presence of a Brønsted acid was found to proceed under electrolysis conditions. The reaction is considered to proceed through radical–radical coupling between an α-aminoalkyl radical and an anion radical of a sulfonylheteroarene, generated at a cathode by single-electron reduction of an iminium salt and the sulfonylarene, respectively.

Keywords: Radical Mechanism; Carbon–Carbon Bond Formation; Cathodic Reduction; Three-Component Reaction

α-アリールアルキルアミンは，α-アミノアルキルラジカルと芳香族化合物（Ar–Y）のアニオンラジカルの間のラジカル–ラジカルカップリングに続くアニオン種（Y^-）の脱離によって合成できるが，利用できる芳香族化合物がシアノアレーン（Y = CN）に限られていた[1]．今回，芳香族化合物としてスルホニルアレーン（Y = SO_2Me）が利用可能であり，この Ar–SO_2Me と系中で生じるイミニウム塩のそれぞれを陰極還元することで発生するラジカル種同士のカップリングを経る機構で，アミンとアルデヒドによるスルホニルアレーンの電気化学的 α-アミノアルキル化が進行することを見つけたので報告する．

陰極と陽極にそれぞれグラッシーカーボン電極と亜鉛電極を備えた非分離型セル中，Bu_4NBF_4 (0.1 M) を支持電解質として含む，ジエチルアミン（1.2 当量）とヘキサナール（1.4 当量），2-メタンスルホニルベンゾチアゾールのアセトニトリル溶液に，トリフルオロ酢酸（TFA, 1 当量）と MS 3A を加え 25 ºC で 2 時間 1.4 V の電圧を掛けると，対応する α-アリールアルキルアミンが収率 84 % で得られた．本反応は，例えば，メトキシ基を持つ非対称アミンや環状アミンに加え，フェニル基を持つアルデヒドや単環式のアゾールにも適用できる．



1) For an example, see: D. Lehnherr, Y.-h. Lam, M. C. Nicastri, J. Liu, J. A. Newman, E. L. Regalado, D. A. DiRocco, T. Rovis, *J. Am. Chem. Soc.* **2020**, *142*, 468.

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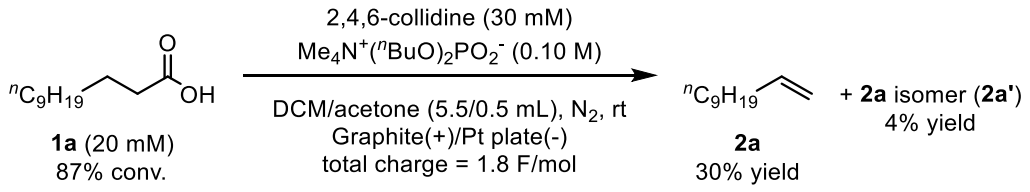
Effect of Supporting Electrolyte on the Selective Electrochemical Decarboxylative Olefination of Carboxylic Acids

(*Graduate School of Engineering, The University of Tokyo*) ○Tasuku Ito, Xiongjie Jin, Kyoko Nozaki

Keywords: Electrochemistry; Carboxylic Acids; Supporting Electrolyte; Selective Synthesis; Kolbe Electrolysis

Electrochemical decarboxylative conversion of carboxylic acids to alkenes is of great importance for the efficient utilization of renewable sources such as waste oils or fats. In particular, the Non-Kolbe process, which utilizes carboxylic acids as carbocation sources by anodic oxidation coupled with decarboxylation, has received much attention.[1] While the addition of nucleophiles (Hofer-Moest reaction) has been explored, deprotonation from the carbocation intermediate to form C=C double bond still leaves room for further development.[2] Particularly, the regioselective synthesis of terminal alkenes from primary carboxylic acids is still challenging due to the easy rearrangement of the highly active carbocation intermediates. In this work, we found that using $Me_4N^+(^nBuO)_2PO_2^-$ as the supporting electrolyte resulted in higher selectivity to terminal alkenes than internal ones in the electrochemical decarboxylative olefination of carboxylic acids.

For the electrochemical conversion of lauric acid in dichloromethane, employing $Me_4N^+(^nBuO)_2PO_2^-$ as a supporting electrolyte gave the corresponding terminal alkene **2a** in 30% yield and internal alkenes **2a'** in 4% yield. This high selectivity would be derived from the high donor number of dibutyl phosphate anion stabilizing the primary cationic intermediate.



1) a) C. Stang, F. Harnisch, *ChemSusChem* **2016**, *9*, 50. b) F. J. Holzhäuser, J. B. Mensah, R. Palkovits, *Green Chem.* **2020**, *22*, 286. 2) a) A. F. Garrido-Castro, Y. Hioki, Y. Kusumoto, K. Hayashi, J. Griffin, K. C. Harper, Y. Kawamata, P. S. Baran, *Angew. Chem. Int. Ed.* **2023**, e202309157. b) J. Yu, T. Liu, W. Sun, Y. Zhang, *Org. Lett.* **2023**, *25*, 7816.

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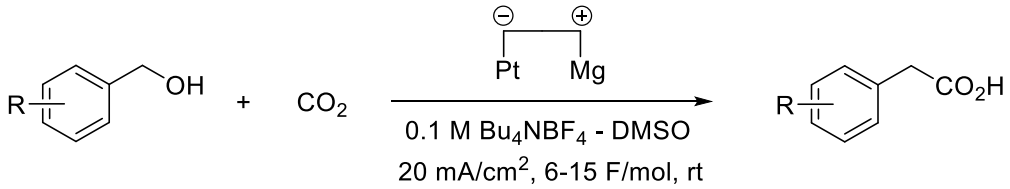
ベンジルアルコール類の電解カルボキシル化反応

（北大院工[1]・北大院総合化学[2]）○仙北 久典[1]・葉山 瑞希[2]
Electrochemical Carboxylation of Benzyl Alcohols ([1]*Faculty of Engineering, Hokkaido University*, [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*)
○Hisanori Senboku,[1] Mizuki Hayama[2]

Electrochemical reduction of organic compounds in the presence of carbon dioxide results in fixation of carbon dioxide with a carbon-carbon bond forming reaction to give carboxylic acids. It was reported that electrochemical carboxylation of benzyl alcohols having an electron-withdrawing group at the *ortho* or *para* position on the phenyl ring proceeded efficiently in DMF while a similar carboxylation using other benzyl alcohols did not proceed in DMF. Recently, we found that DMSO, instead of DMF, as a solvent was effective for electrochemical carboxylation of such benzyl alcohols. Constant current electrolysis of benzyl alcohols **1** in DMSO containing 0.1 M Bu_4NBF_4 using a one-compartment cell equipped with a Pt cathode and an Mg anode resulted in direct substitution of a hydroxyl group by a carboxyl group at the benzylic position to give the corresponding phenylacetic acids **2** in moderate yields.
Keywords : Electrochemical Carboxylation; Benzyl Alcohols; Carbon Dioxide; Electrochemical Reduction; Carboxylic Acids

二酸化炭素存在下に有機化合物を電解還元すると電解カルボキシル化反応が進行し、二酸化炭素を炭素源としてカルボン酸を合成することができる。例えば、DMF 中芳香環上のオルト位あるいはパラ位に電子求引性置換基を有するベンジルアルコールの電解カルボキシル化反応により、ベンジル位水酸基のカルボキシル基への直接置換反応が進行し、相当するフェニル酢酸類が得られるが、それ以外の置換ベンジルアルコールを用いてもカルボン酸はほとんど得られなかった。[1] 今回、反応溶媒を DMF から DMSO に変えることにより無置換のベンジルアルコールでも中程度の収率で電解カルボキシル化が進行することを見出した。[2]

白金陰極ならびにマグネシウム陽極を備えた一室型セルを用いてベンジルアルコール **1** を 0.1 M の Bu_4NBF_4 を含む DMSO を溶媒として二酸化炭素存在下定電流電解を行った。その結果、目的のフェニル酢酸 **2** が 32～39%の単離収率で得られた。



R = H, 38%; R = 2-Me, 39%; R = 3-OMe, 32%

1) H. Senboku, K. Yoneda, S. Hara, *Tetrahedron Lett.* **2015**, *56*, 6772.
2) M. Hayama, H. Senboku, *Electrochemistry* **2023**, *91*, 112011.

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π拡張構造を有するブロモアレーン電極メディエータを用いた分子内 C-N 結合生成とその速度論的解析

（横浜国立大学大学院[1]・JST さきがけ[2]）○平間 暁月[1]・吉永昌平・信田 尚毅[1,2]・跡部 真人[1]

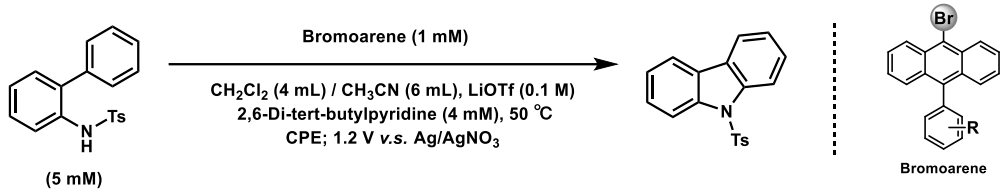
Electrochemical intramolecular C-N bond formation using π-extended bromoarene mediator and its kinetic analysis

([1]*Yokohama National University,* [2]*JST PRESTO*) ○Atsuki Hirama[1], Shohei Yoshinaga, Naoki Shida[1,2], Mahito Atobe[1]

Despite an extensive library of compounds, bromoarenes have yet to be employed as mediators for electrochemical oxidation reactions. In this study, we developed a novel electrocatalytic system using various bromoarenes based on the design concept of extending the π-system. By using various 9-bromoanthracene-derivatives as mediators and *N*-tosyl biphenyl amines as substrates, electrochemical intramolecular C-N bond formation has successfully proceeded and obtained target carbazoles in high yields. We also found that a bromo group in the catalyst plays an essential role in the desired reaction. In the presentation, in addition to the details of these studies, the evaluation of the mediators by kinetic analysis will also be reported.

Keywords: electrosynthesis, mediator, C-N bond formation, carbazole, kinetic analysis

電解合成の選択性や反応速度を向上させるため、幅広い酸化電位を網羅する電極メディエータが開発されてきたが[1]、化合物ライブラリが豊富なブロモアレーン類の利用例はほとんど報告されていない。本研究では、π系の拡張による高酸化状態の安定化を設計指針[2]とし、ブロモアレーンを用いる新規メディエータ反応系を開拓した。アントラセン骨格を有するブロモアレーンをメディエータに用い、*N*-トシルビフェニルアミン類を反応基質として電解酸化に供することで分子内 C-N 結合生成が進行することを確認し、目的物のカルバゾール類を高収率で得ることに成功した。また、本触媒にはブロモ基の存在が重要な役割を果たしていることも見出した。発表においては、これらの検討の詳細に加え、速度論的な解析による電極メディエータの評価についても併せて報告する。



1) R. Francke, R. D. Little, *Chem. Soc. Rev.* **2014**, *43*, 2492-2521.

2) S Yoshinaga, M. Atobe, N.Shida, *ChemRxiv*. **2022,** DOI: 10.26434/chemrxiv-2022-sggqd.

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日本化学会 第104春季年会 (2024)

テトラクロロエチレンとアリールボロン酸からのシリカゲル添加条件下での鈴木カップリング反応によるジアリールアセチレンの1段階合成

（近畿大[1]・関東電化工業（株）[2]）○鈴木 ひよの[1]・桑原 晶子[2]・小林 政史[2]・松本 浩一[1]

One-step Synthesis of Diarylacetylenes from Tetrachloroethylene and Arylboronic Acids under Silica-gel by Using Suzuki Coupling Reaction ([1]*Kindai University*, [2]*KANTO DENKA KOGYO CO., LTD.*) ○ Hiyono Suzuki,[1] Akiko Kuwabara,[2] Masafumi Kobayashi,[2] Kouichi Matsumoto[1]

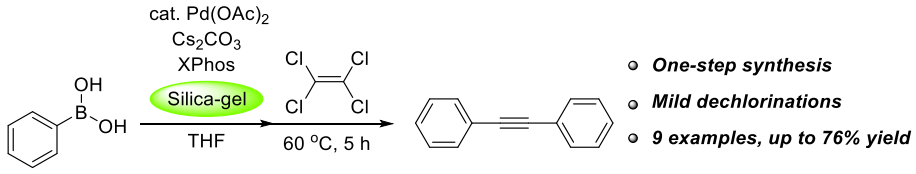
Diarylacetylenes are one of the important materials, and the synthesis of diarylacetylenes mainly depends on the Sonogashira coupling reactions. In contrast, we have found that the Suzuki coupling reaction of tetrachloroethylene and arylboronic acids followed by the reaction of *n*-BuLi for crude products gave the formation of diarylacetylene compounds in good yields (WO/2023/157909).[1]

In the present study, Suzuki coupling reaction of tetrachloroethylene and arylboronic acids in the presence of transition metal catalysts such as $Pd(OAc)_2$ with silica-gel directly gave the corresponding diarylacetylene compounds. The results of reaction optimization and the scope and limitations for substrates, as well as the plausible reaction mechanism will be discussed.

Keywords : Tetrachloroethylene; Suzuki Coupling Reaction; Silica-gel; Dechlorinations; Diarylacetylenes

ジアリールアセチレン類は、π共役系化合物の分野や有機合成のビルディングブロックなど、重要な化合物である。一般に、ジアリールアセチレン類は薗頭カップリング反応を利用して調製されることが多い。我々はテトラクロロエチレンとアリールボロン酸からの鈴木カップリング反応により生じる粗生成物に対して、*n*-BuLi を作用させると脱塩素化を経て、ジアリールアセチレンが得られることを見出している（WO/2023/157909）[1]。

今回、テトラクロロエチレンとアリールボロン酸に対して、シリカゲル存在下、$Pd(OAc)_2$ 等の遷移金属触媒を用いて鈴木カップリング反応を行ったところ、ジアリールアセチレンを1段階にて得られることを見出した。条件検討、適用範囲、機構解明などの実験結果を発表する。



1) WO/2023/157909，発明者　松本浩一，小林政史（出願人　学校法人近畿大学，関東電化工業（株））

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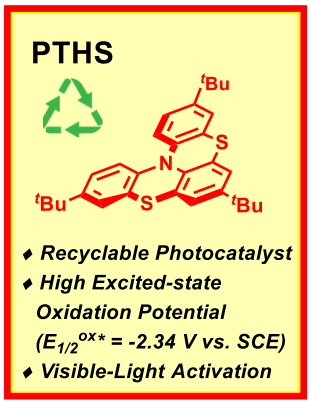
リサイクル可能な高い還元力を有する螺旋型フェノチアジン有機フォトレドックス触媒の開発

（岡山大基礎研[1]・岡山大院自然[2]）○田中健太[1]・安藤早春[2]・髙村浩由[2]・門田功[2]
Strongly Reducing Helical Phenothiazines as Recyclable Organophotoredox Catalysts
([1]*Research Institute for Interdisciplinary Science, Okayama University,* [2]*Department of Chemistry, Graduate School of Natural Science and Technology, Okayama University*)
○ Kenta Tanaka,[1] Haru Ando,[2] Hiroyoshi Takamura,[2] Isao Kadota[2]

Recycling photocatalysts has attracted much attention as a critical factor in emerging chemical technologies in terms of environmental concerns and economic benefits. 10-Aryl phenothiazines are widely used as photocatalysts for photoredox reactions in organic chemistry. Due to their high excited-state oxidation potentials ($E_{1/2}^{ox}$* ≈ −2.10 V vs. SCE), a number of 10-aryl-phenothiazine-catalyzed photoredox reactions that proceed via oxidative quenching cycles have been developed. However, the high reactivity of the *p*-position relative to the nitrogen atom on 10-aryl phenothiazines renders these prone to react with electrophiles. Thus, several modified 10-aryl phenothiazine catalysts have recently been explored. Despite these advances, the development of more stable and sustainable photoredox catalysts remains highly desirable. To explore the recyclability of organophotoredox photocatalysts, we have designed and synthesized recyclable phenothiazine organophotoredox catalysts. When the recycling performance was evaluated in the cross-coupling reaction between an aryl halide and triethylphosphite, PTHS can be recovered at least four times without loss of its catalytic activity.
Keywords : Photoredox; Phenothiazine; Visible light; Photocatalyst; Recycle

近年、可視光をエネルギー源として利用できるフォトレドックス触媒反応が注目されている。フェノチアジン誘導体は様々なフォトレドックス触媒反応に広く利用されている有用な有機分子である。[1] その一方で、フェノチアジンは窒素原子の *p* 位の反応性が高いことから、たびたび求電子剤と反応してしまう課題点があった。[2]



当研究室ではこれまでに種々の有機フォトレドックス触媒を独自に設計・開発することに成功している。[3] そこで本研究では、窒素原子の *p* 位を ^{t}Bu などの嵩高い置換基で保護した螺旋構造を特徴とする新規フェノチアジン有機フォトレドックス触媒(PTHS)を設計・開発し、光触媒反応へ応用することを目的とした。その結果、シクロヘキサン誘導体を基質とした環化三量化反応により、PTHS 触媒を合成することに成功した。さらに、青色光照射下アリルハライドと亜リン酸トリエチルのクロスカップリング反応に PTHS 触媒を応用したところ、良い収率で目的物が得られた。また、PTHS 触媒を回収・再利用した際にも活性が落ちることなく望みの生成物が得られることが分かった。

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金ナノ粒子修飾 CNT 電極触媒の作成とアルコールの空気酸化反応への応用

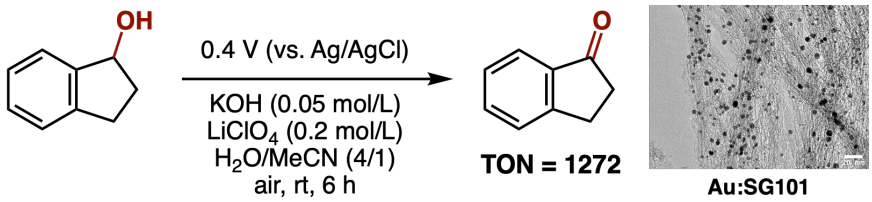
（阪大院工[1]・阪大 ICS-OTRI[2]・産総研[3]）○中村 帆花[1]・矢吹 澪斗[1]・植竹 裕太[1,2]・清水 太陽[3]・小久保 研[3]・櫻井 英博[1,2]

Preparation of Au:CNT electrocatalysts and their application to the aerobic oxidation of alcohols ([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka University,* [3]*AIST*) ○Honoka Nakamura[1], Yabuki Rento[1], Yuta Uetake[1,2], Taiyo Shimizu[3], Ken Kokubo[3], Sakurai Hidehiro[1,2]

Electrochemical synthesis is increasingly recognized as a clean and powerful method for organic synthesis. Meanwhile, the use of electrocatalyst having nanometals have not been investigated in the fields of organic synthesis. Gold nanoparticles were immobilized on a single-walled CNT (SG101) using $HAuCl_4$ and $NaBH_4$ to give a water dispersion of Au:SG101 (3.4±0.6 nm). An electrocatalyst paper was fabricated through several simple processes such as filtration, drying and pressing, affording Au:SG101 buckypaper. This was applied for an aerobic oxidation of benzyl alcohol under electrochemical conditions, yielding corresponding ketone.

Keywords : electrochemical synthesis; electrocatalysts; carbon nanotube; gold nanoparticle; aerobic oxidation

有機電解合成は、酸化剤や還元剤を必要としないクリーンかつ強力な化学合成法として近年再注目されている。ナノサイズの金属微粒子で修飾された電極触媒は燃料電池分野で広く研究されているが、有機電解合成におけるその活用は限定的である[1,2]。本研究では、単層 CNT 固定化金ナノ粒子触媒を用いた電極触媒の作成と、アルコールの空気酸化反応における電極触媒の役割について検討した。単層 CNT として SG101（Zeonano®SG101）[3,4] を用い、$NaBH_4$ 還元を行うことで Au:SG101（particle size: 3.4 ± 0.6 nm）の水分散液を調製し、得られた分散液を濾過・乾燥・加圧成形することで Au:SG101 バッキーペーパーを作成した。作成した Au:SG101 ペーパーをカソードに用いてアルコールの空気酸化反応を行ったところ、0.4 V (Ag/AgCl)の電圧印加条件で反応が進行し対応するケトンが得られた。



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ジフェニルフルベン誘導体のマグネシウム還元による炭素-炭素結合形成反応

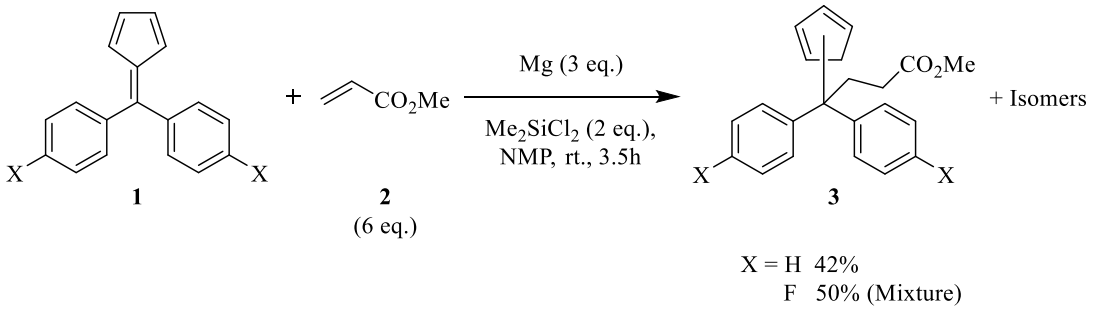
（長岡技科大院工）○小山　竜之介・張　田原・前川　博史
Magnesium-promoted reductive C-C bond formation of diphenylfulvene derivatives (*Nagaoka University of Technology*) ○Ryunosuke Koyama, Tianyuan Zhang, Hirofumi Maekawa

We have already reported that magnesium-promoted silylation of diphenylfulvenes gave disilylated products on the five-membered ring. In this study, magnesium-promoted reduction of diphenylfulvene in the presence of methyl acrylate brought about the formation of a new C-C bond at the 6-position in moderate yield.
Keywords : Reductive Coupling; Electron Transfer Reaction; Magnesium; Diphenylfulvene; Methyl Acrylate

本研究室では、ジフェニルフルベン誘導体のマグネシウム還元シリル化反応を行うと、5 員環がジシリル化された化合物が得られることを報告している [1]。

そこで本研究では、ジクロロジメチルシラン存在下、ジフェニルフルベンとアクリル酸メチルのマグネシウム還元カップリング反応を行った結果、ジフェニルフルベンにアクリル酸メチルが還元的に付加した生成物が得られることを見出した。溶媒として NMP を用いて反応を行った場合、ジフェニルフルベンの 6 位にアクリル酸メチルが付加した単一構造の生成物が得られた。溶媒を DMI に変えて反応を行ったところ、収率が低下した。また、DMF や CH_3CN で反応を行ったところ、異性体の量が増加し、反応の選択性が低下した。THF を用いた場合では、反応の進行は確認されたが、生成物の量が少ないため単離には至らなかった。

芳香環の 4 位にフッ素が置換した基質を用いて、NMP 溶媒中、同様の条件下で反応を行った結果、収率が増えた一方、異性体の比率も増加した。



Scheme Mg-promoted reductive C-C bond formation between diphenylfulvene **1** and methyl acrylate **2**

1) 森章裕、張田原、前川博史、第 83 回有機合成化学協会関東支部シンポジウム講演予稿集、B20(2022).

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可視光による *o*-キノンメチドの [4+2]環化付加反応を経由したクロマンの合成

(岡山大理[1]・岡山大基礎研[2]・岡山大院自然[3]) ○小滝 咲[1]・田中 健太[2]・髙村 浩由[3]・門田 功[3]

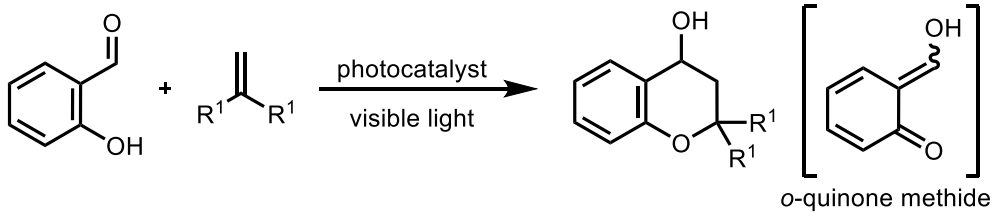
Visible-light-induced [4+2] Cycloadditions of *o*-Quinone Methides for the Synthesis of Chromanes ([1]*School of Science, Okayama University.* [2]*Research Institute for Interdisciplinary Science.* [3]*Graduate School of Natural Science and Technology, Okayama University.*) ○ Sakura Kodaki,[1] Kenta Tanaka,[2] Hiroyoshi Takamura[3] and Isao Kadota[3]

Chromanes are important structural motifs in a wide range of natural products and materials., it is important to develop an efficient method for synthesizing this skeleton. One of the representative methods for the synthesis of chromanes is known to be the cycloaddition of *o*-quinone methides under photo irradiation. On the other hand, they require high-energy light sources such as ultraviolet light. Therefore, the development of milder synthetic routes to chromanes remain highly desirable. Recently, we have reported the visible-light-induced photocatalytic cycloaddition reactions. Based on these backgrounds, herein, we report visible-light-induced [4+2] cycloadditions of *o*-quinone methides for the synthesis of chromanes.

Keywords : o-Quinonemethide; [4+2] Cycloaddition; Visible light; Photocatalyst; Chromane

クロマンは様々な天然物や機能性材料に広くみられる化学構造であることから、この骨格を効率的に合成する手法の開発は重要である。クロマンを合成する代表的な手法の一つとして光エネルギーを用いた *o*-キノンメチド中間体の発生を伴うクロマンの合成法が知られている。一方で、紫外光を光源とした合成法が多く報告されており、より穏和な可視光を利用した例は限られている。[1)]当研究室ではこれまでに、光触媒と可視光を利用した[2+2]環化付加反応を始めとした様々な環化付加反応の開発に成功している。[2)]

このような背景から、本研究では光触媒と可視光を利用した *o*-キノンメチドの発生を基盤とする[4+2]環化付加反応によりクロマンを合成することを目的として研究を行なった。



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AEM 型リアクターを用いた含窒素芳香族化合物の電解水素化における条件検討と基質探索

(横国大理工[1]・JST さきがけ[2]) ○米澤 明純[1]・清水 勇吾[1]・原田 珠里[1]・信田 尚毅[1,2]・跡部 真人[1]

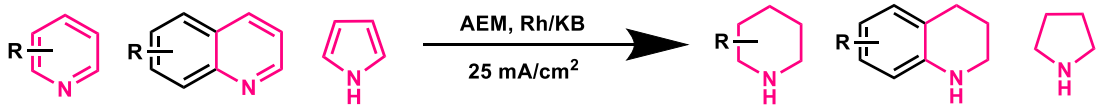
Investigation on the reaction conditions for the electrocatalytic hydrogenation of nitrogen-containing aromatic compounds in an AEM reactor (*College of Engineering Science, Yokohama National University,* [2]*JST PRESTO*) ○Akizumi Yonezawa[1], Yugo Shimizu[1], Juri harada[1], Naoki Shida[1,2], Mahito Atobe[1]

Cyclic amines obtained by hydrogenation of nitrogen-containing aromatic compounds are widely used as building blocks of pharmaceuticals. Such reactions have been performed by energy-consuming hydrogenation processes with high temperature and pressure conditions. For sustainability, replacing such thermal processes with energy-efficient electrochemical processes is an urgent issue. In this study, we report the effect of current density on current efficiency and substrate scope with respect to the electrocatalytic hydrogenation of nitrogen-containing aromatic compounds using an anion exchange membrane (AEM) reactor. When pyridine was used as a model substrate, electrochemical hydrogenation of pyridine proceeded quantitatively by using a carbon-supported rhodium catalyst with excellent current efficiency. Hydrogenation proceeded well with substituted pyridines, and the hydrogenation reaction also proceeded with quinoline-derivatives and pyrrole to selectively obtain the target product.

Keywords : Electrocatalytic hydrogenation; AEM Reactor; Metal-supported catalyst; Chemoselective; Pyridine

含窒素芳香族化合物の水素化によって得られる環状アミン類は、医薬品の部分骨格に多用されており[1)]、これらを化学選択的かつクリーンに得る合成手法の開発が望まれている。このような反応は、これまで高温高圧での接触水素化により行われてきたが[2)]、エネルギー効率や持続可能性の観点から、温和な条件での反応が見込まれ再エネ利用が可能な電気化学反応への転換が期待される。本研究では、アニオン交換膜(AEM)型リアクターを用いた含窒素芳香族化合物の電解水素化に関して、電流密度が電流効率に与える特異的な影響と、基質汎用性について報告する。

ピリジンを AEM 型リアクターのカソード側に流通させ、電流密度など様々な条件検討を行ったところ、炭素担持ロジウム触媒を電極触媒に用いることで、定量的かつ効率よくピペリジンを得ることに成功した。置換基を有するさまざまなピリジン類においても良好に反応が進行し、また、キノリン類やピロールにおいても水添反応が進行し、選択的に水素化体を得ることに成功した。



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

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC
E1132(1132, Bldg. 11 [3F])

[E1132-3pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Keiichi Imato, Naoki Shida

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1132-3pm-01]
Synthesis and electrochemical characterization of biphenyl multi carboxylate derivatives as anode materials for SIBs

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

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1132-3pm-02]
Electrogenerated Acid Promoted Claisen Rearrangement of Allyl Aryl Ethers

○Yuta Niki[1], Eisuke Sato[1], Seiji Suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1132-3pm-03]
Divergent Synthesis of Benzolactones via Electrochemical C−O Bond Formation

○Yuma Hironaka[1], Koichi Mitsudo[1], Seiji suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1132-3pm-04]
Photocatalytic carbon-carbon bond forming reactions using recyclable alkyl radical precursors

○Shuta Horiuchi[1], Kenta Tanaka[2], Hiroyoshi Takamura[1], Isao Kadota[1] (1. Department of Chemistry, Graduate School of Natural Science and Technology, Okayama University, 2. Research Institute for Interdisciplinary Science, Okayama University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1132-3pm-05]
Development of the electrochemical N2 gas insertion reaction into carbonyl compounds

○Fumiya Kokudai[1], Minami Fukuhara[1], Yutaka Saga[1], Tetsuya Kambe[1], Mio Kondo[2,1,3], Shigeyuki Masaoka[1] (1. Osaka University, 2. Tokyo Institute of Technology, 3. Precursory Research for Embryonic Science and Technology)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1132-3pm-06]

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Paired Electrosynthesis of β-Nitroalcohols Using an Electrogenerated Base

○Haruka Homma[1], Ruka Hasegawa[1], Tomohiro Yokoyama[1], Toshiki Tajima[1] (1. Shibaura Inst. of Tech.)

2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC

Break

Japanese

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

[E1132-3pm-07]

Anodic Fluorination of Organic Compounds Using Quaternary Ammonium Fluoride-HFIP Complexes

○Aika Mochizuki[1], Haruka Homma[1], Nobutaka Kitajima[1], Toshiki Tajima[1] (1. Shibaura Inst. of Tech.)

Japanese

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

[E1132-3pm-08]

Electrochemical post-functionalization of polythiophenes by using aryldiazonium salts

○Satoshi Koiso[1], Kosuke Sato[1], Shinsuke Inagi[1] (1. Tokyo Institute of Technology)

Japanese

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

[E1132-3pm-09]

Polymer Synthesis by Hole Catalytic Cycloaddition Polymerization with Bifunctional Monomers Derived from Isoeugenol

○Ryo Nagaya[1], Tatsuya Seko[1], Naoki Shida[1], Mahito Atobe[1] (1. Yokohama National University)

Japanese

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

[E1132-3pm-10]

Machine Learning-Supported Reaction Condition Explolation of Cyanomethylation Using Electrochemical Microflow Reactor

○Akine Tani[1], Shunpei Kunimoto[1], Eisuke Sato[1], Seiji Suga[1] (1. Graduate School of Environmental, Life, Natural Science and Technology, Okayama University)

English

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

[E1132-3pm-11]

Electrooxidative Dearomatization of Phenols Catalyzed by Bromine Species

○Kai Matsui[1], Muhammet Uyanik[1], Kazuaki Ishihara[1] (1. Nagoya University)

Japanese

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

[E1132-3pm-12]

Ritter-type Reaction of Glycosyl Bromides and Alkenes using Arylamines as Photocatalysts

○Hiryu Takinami[1], Naoya Sawada[1], Ziyi Yu[1], Norihiko Sasaki[1], Toshiki Nokami[1], Manabu Abe[2], Tsuyoshi Taniguchi[3], Takashi Koike[4] (1. Tottori University, 2. Hiroshima Univ., 3. IRC3, AIST, 4. Nippon Inst. Tech.)

Japanese

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

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[E1132-3pm-13]

Deuterodehalogenation of (hetero)aryl halides using PEM reactor

○Kyoko Mandai[1], Yosuke Ashikari[1], Yiyue Yao[1], Aiichiro Nagaki[1] (1. Hokkaido Univ.)

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ビフェニルマルチカルボキシレートの合成と SIB 用負極材料評価

（東電大院工[1]・横国大院[2]）○高橋 海七太[1]・藪内 直明[2]・宮坂 誠[1]

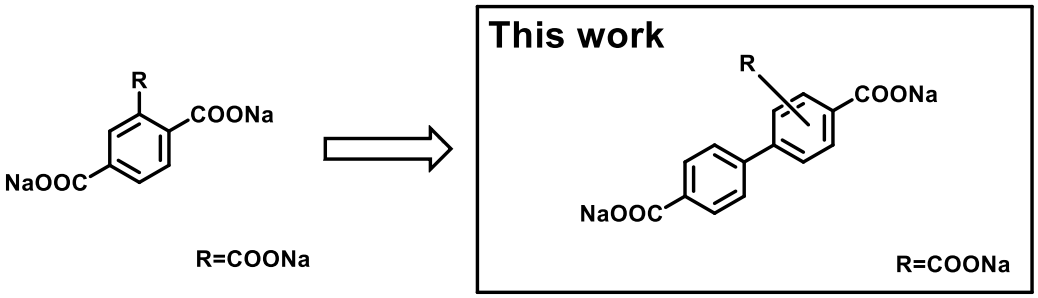
Synthesis and electrochemical characterization of sodium biphenyl-carboxylate derivatives as anode materials for SIBs ([1]*Graduate School of Engineering, Tokyo Denki University*, [2]*Department of Chemistry and Life Science, Yokohama National University*)
○Kanata Takahashi,[1] Yabuuchi Naoaki,[2] Makoto Miyasaka[1]

Sodium ion batteries (SIB) are expected to be an alternative candidate to lithium ion batteries (LIB) because they have a similar voltage range and operating principle to LIB and can utilize the wealth of knowledge accumulated in LIB. Na_2TP as an anode material for SIB[1)], organic anode materials utilizing the interaction between conjugated structure and carboxylate groups have attracted much attention. Recently, it has been reported that Na_2TP exhibits superior electrochemical performance to Na_2TP by building salt structures[2)].

In this study, conjugated carboxylate derivatives with biphenyl moieties were synthesized and evaluated as anode materials for SIBs based on the knowledge that conjugated low molecular weight carboxylates have lower potentials due to conjugate extension. In this presentation, we will report on the synthesis method and electrochemical characterization.
Keywords : Sodium Ion Battery; Organic Electrode Materials; Organic Anode Materials

ナトリウムイオン電池(SIB)は、リチウムイオン電池(LIB)と電圧範囲や動作原理が類似しており、LIB で培われた豊富な知見を活用することができるため、LIB の代替候補として期待されている。SIB の負極材料としては、Hu らによりテレフタル酸二ナトリウム(Na_2TP)が報告されたことで [1)]、共役構造とカルボキシレート基の相互作用を利用した有機負極材料が注目されている。最近では、Na_2TP に塩構造を構築することで Na_2TP よりも優れた電気化学的性能を示すことが報告されている [2)]。

本研究では、共役拡張低分子カルボキシレートが共役拡張に伴う低電位化の知見をもとに [3)]、ビフェニル骨格を持つ種々の共役カルボキシレート誘導体を合成し、SIB 用負極材料として評価した。当日は、合成方法ならびに電気化学的特性評価について報告する。



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2) Luo, C. *et al*., *J. Power Sources*, **2020**, *453*, 227904.
3) Miyasaka, M. *et al*., *Polymer J*., **2022**, *54*, 1111-1118.

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電解発生酸を用いたアリルアリールエーテルの Claisen 転位反応

（岡山大院自然[1]）○仁木 祐太[1]・佐藤 英祐[1]・菅 誠治[1]

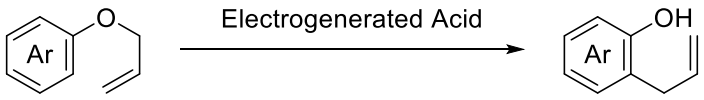
Electrogenerated Acid Promoted Claisen rearrangement of Allyl Aryl Ethers ([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Yuta Niki,[1] Eisuke Sato,[1] Seiji Suga[1]

The aromatic Claisen Rearrangement is a promising reaction, widely utilized in natural product synthesis. This reaction generally requires heating and long reaction time. Although variety of Lewis acids have been recognized as catalysts enabling relatively mild reaction conditions, in many cases, the reaction remains sluggish[1,2]. A Brønsted acid is also known as a catalyst, exhibiting better catalytic activity. However, trifluoroacetic acid has to be used as a solvent leading to multiple side products[3]. In this study, we introduce an electrogenerated acid-catalyzed aromatic Claisen rearrangement. We expected that the highly active nature of this *in situ* generated acidic proton would promote the aromatic Claisen rearrangement effectively. Indeed, pre-electrolysis of $LiClO_4/CH_3NO_2$, followed by the addition of allyl-4-methoxyphenyl ether, gave the rearrangement product in 43% yield, with 52% of starting material recovered in just 20 min at room temperature.

Keywords : Electrogenerated acid; Claisen rearrangement; Electro-organic synthesis

芳香族 Claisen 転位は天然物合成においても広く用いられる有用な化学反応である。反応の進行には一般的に高温条件下、長い反応時間を要していた。本反応は主に Lewis 酸により触媒されるが、依然として、長い反応時間を要していた[1,2]。一方で、Brønsted 酸はこの反応において、より優れた触媒活性を示すことが知られている。しかし、トリフルオロ酢酸を溶媒として使用するなどの条件が必要があり、多くの副生成物が生じることが課題であった[3]。

本研究では、電解発生酸が芳香族 Claisen 転位を効果的に触媒できることを見出した。支持電解質および溶媒に含まれる微量の水を陽極酸化して生じる電解発生酸は、溶媒和の影響を大きく受けないため、非常に活性が高いと考えられている。実際に、$LiClO_4/CH_3NO_2$ を陽極酸化したのちに、アリル-4-メトキシフェニルエーテルを加えると、室温下 20 分で芳香族 Claisen 転位が進行し、転位生成物が 43% (原料回収率 52%) 得られた。



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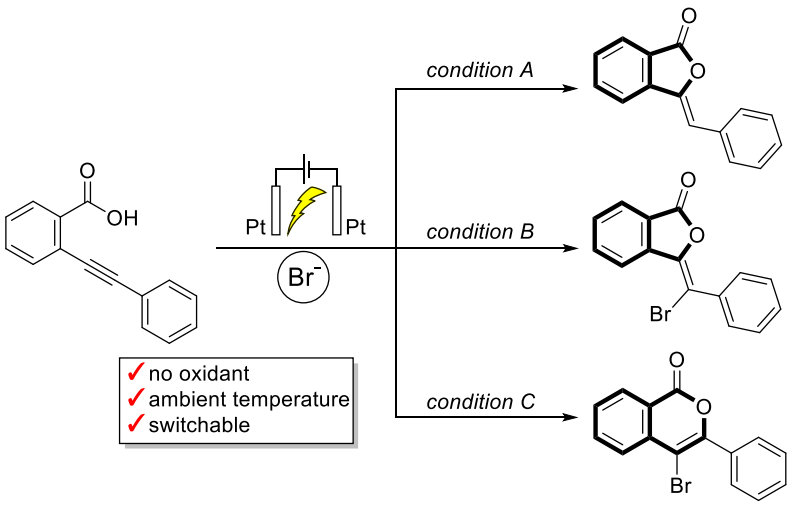
電気化学的な C–O 結合形成によるベンゾラクトン類の選択的合成

(岡山大院自然[1]) ○廣中 祐馬[1]・光藤 耕一[1]・菅 誠治[1]
Divergent Synthesis of Benzolactones via Electrochemical C–O Bond Formation ([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Yuma Hironaka[1], Koichi Mitsudo[1], Seiji Suga[1]

Benzolactones such as isocoumarins and isobenzofuranones are important molecular skeletons contained in various pharmaceuticals and bioactive molecules. The acid or base catalyzed intermolecular C–O bond formation of a benzoic acid derivative bearing an alkyne tether is of the useful methods for synthesis of benzolactones[1,2]. Electro-organic synthesis offers environmentally friendly methods which enable organic transformations under the mild and ambient conditions. In this work, we developed the divergent synthesis of benzolactones under mild conditions using electrochemical methods. Three different benzolactones were selectively obtained by choosing appropriate conditions for each.
Keywords : Benzolactone, divergent synthesis, electrolysis, C–O bond formation, halogen mediator

イソクマリン及びイソベンゾフラノンは様々な医薬品や生物活性分子に含有される重要なベンゾラクトンである。有用なベンゾラクトン合成の手法として、アルキンテザーをもつ安息香酸誘導体の酸や塩基を触媒とする分子内 C–O 結合形成反応が挙げられる[1,2]。一方で、有機電解合成は、化学反応剤を必要としない温和な条件で反応を進行させることができる手法として注目を集めている。今回我々は、電気化学的手法を用いた温和な条件下でのベンゾラクトン合成を達成したので報告する。わずかに条件を変えるだけで、3種類のベンゾラクトン類を選択的に作り分けることに成功した。

Scheme 1. ベンゾラクトン類の選択的合成



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リサイクル可能なアルキルラジカル前駆体を利用した光触媒による炭素-炭素結合形成反応

（岡山大院自然[1] ・岡山大基礎研[2]） ○堀内 柊汰[1]・田中 健太[2]・髙村 浩由[1]・門田 功[1]

Photocatalytic carbon-carbon bond forming reactions using recyclable alkyl radical precursors

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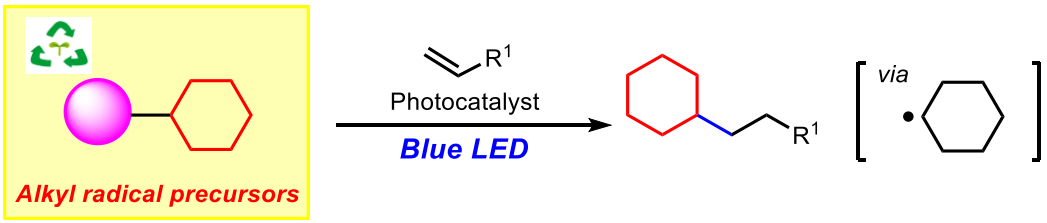
○ Shuta Horiuchi,[1] Kenta Tanaka,[2] Hiroyoshi Takamura,[1] Isao Kadota[1]

The development of carbon-carbon bond forming reactions is important for the synthesis of natural products and materials. Alkyl radical precursors are useful reagents for carbon-carbon bond formation and are widely used in various organic synthetic reactions. However, since these reagents give the quantitative byproducts derived from alkyl radical precursors in the reactions, development of sustainable alkyl radical precursors are highly desirable from the viewpoint of "atom economy". Meanwhile, we have developed organophotoredox catalyzed various synthetic reactions via single electron transfer. Based on the back ground, herein, we report the photocatalytic carbon-carbon bond forming reactions using recyclable alkyl radical precursors via single electron transfer.

Keywords : Photoredox; Alkyl radical precursors; Photocatalyst; Recyclable reagent; C-C bond formation

二つの炭素原子を連結する手法の開発は天然物や機能性材料といった有用化合物を合成する上で非常に重要である。アルキルラジカル前駆体は炭素-炭素結合を形成させることのできる有用な反応試薬であり、様々な有機合成反応に広く利用されている。その一方で、これまでに開発されたものの多くがアルキルラジカル前駆体由来の副生成物が化学量論量生成しており廃棄物となっているため、atom economy の観点から改良の余地が残されている。[1)] 当研究室ではこれまでに有機フォトレドックス触媒を利用した一電子移動を経由する様々な合成反応の開発に成功している。[2)]

このような背景から、本発表ではリサイクル可能な新規アルキルラジカル前駆体の開発と光触媒による一電子移動を鍵とする炭素-炭素結合形成反応を開発することを目的として研究を行った。



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カルボニル化合物への電気的化学的窒素ガス挿入反応の開発

(阪大院工[1]・東工大院理[2]・JST さきがけ[3]) ○石代　史哉[1]・福原　みなみ[1]・嵯峨　裕[1]・神戸　徹也[1]・近藤　美欧[1,2,3]・正岡　重行[1]

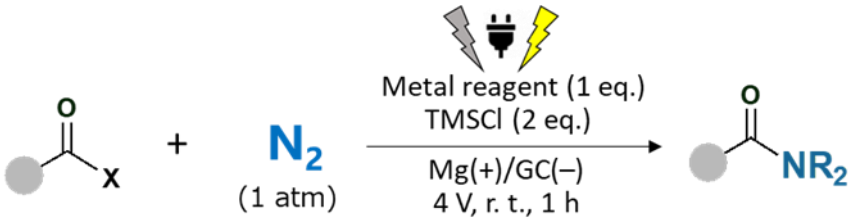
Development of the electrochemical N_2 gas insertion reaction into carbonyl compounds

(*[1]Graduate School of Engineering, Osaka Univ.; [2]School of Science, Tokyo Institute of Technology; [3]JST PRESTO*) ○Fumiya Kokudai,[1] Minami Fukuhara,[1] Yutaka Saga,[1] Tetsuya Kambe,[1] Mio Kondo,[1,2,3] Shigeyuki Masaoka[1]

Nitrogen gas is a ubiquitous gas that accounts for about 78% of the atmosphere, and its effective utilization for transformations of organic molecules is highly attractive in terms of both energy problem-solving and synthetic organic chemistry. However, there are only a few examples to achieve the direct insertion reaction of nitrogen gas into organic molecules. In this study, we aim to develop a new electrochemical method to directly insert nitrogen gas into organic molecules under mild conditions (at room temperature and atmospheric pressure of nitrogen gas). Details of the reaction development will be given in the presentation.

Keywords : Nitrogen Insertion; Group IV Metals ; Electrochemical Organic Synthesis

窒素ガスは大気中の約 78 %を占める遍在小分子であり、これを窒素源として有機分子変換反応に有効活用することはエネルギー問題の解決、及び有機合成化学の両方の側面から魅力的である。しかしながら、極めて安定な窒素ガスを、有機分子に直接挿入した報告例[1]は極めて少ない。またそれら先駆的報告例においても、高温・高圧といった過酷条件や、過剰量の危険な化学還元剤(Li, Mg 等)を必要としており、穏和条件における反応の開発が希求されている。そこで本研究では、室温・常圧かつ化学還元剤フリーの反応を実現しうる電気化学的手法に着目し、窒素ガスの有機分子への電気化学的直接挿入反応の開発を検討した。
種々検討の結果、適切な金属試薬を用いることで、カルボニル化合物への電気化学的窒素ガス挿入反応が進行することを見出した。当日は、反応開発の詳細について発表する予定である。



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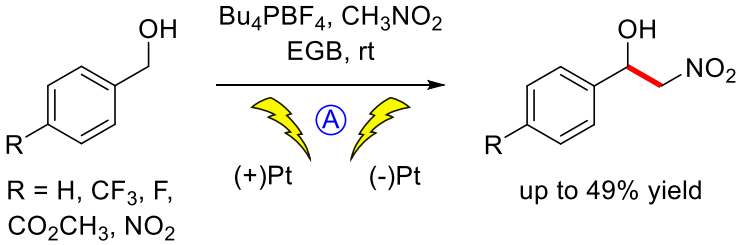
電解発生塩基を利用したβ-ニトロアルコールの両極電解合成

（芝浦工大工[1]・芝浦工大院理工[2]）○本間 晴香[1]・長谷川 瑠夏[1]・横山 智大[2]・田嶋 稔樹[1,2]
Paired Electrosynthesis of β-Nitroalcohols Using an Electrogenerated Base ([1]*College of Engineering, Shibaura Institute of Technology*, [2]*Graduate School of Engineering and Science, Shibaura Institute of Technology*)○Haruka Homma,[1] Ruka Hasegawa,[1] Tomohiro Yokoyama,[2] Toshiki Tajima[1,2]

Convergent paired electrosynthesis of β-nitroalcohols using an undivided cell was successfully demonstrated by combining anodic generation of benzaldehydes from benzyl alcohols and cathodic formation of nitromethyl anion from CH_3NO_2 via an electrogenerated base (EGB). Linear sweep voltammetry measurements in 0.1 M Bu_4NBF_4/CH_3NO_2 and 0.1 M Bu_4PBF_4/CH_3NO_2, and the electrolysis in the absence of a substrate using a divided cell suggested that CH_3NHOH may be formed as an EGB. Paired electrolysis of various benzyl alcohols was carried out to provide the corresponding β-nitroalcohols in moderate yields except for *p*-nitrobenzyl alcohol.
Keywords : Paired Electrosynthesis; Electrogenerated Base; β-Nitroalcohol

陽極でのベンジルアルコールの電解酸化に基づくベンズアルデヒドの生成と陰極での電解発生塩基 (EGB) を介したニトロメタンからのニトロメチルアニオンの生成を組み合わせることで、無隔膜セルを用いたβ-ニトロアルコールの収束型両極電解合成に成功した。0.1 M の Bu_4NBF_4/CH_3NO_2 および 0.1 M の Bu_4PBF_4/CH_3NO_2 中でのリニアスイープボルタンメトリー測定および隔膜付きセルを用いた基質非存在下での電解の結果から、EGB として *N*-メチルヒドロキシルアミンが生成している可能性が示唆された。種々のベンジルアルコールの両極電解を行ったところ (Scheme 1)、*p*-ニトロベンジルアルコールを除いて対応するβ-ニトロアルコールが中程度の収率で得られた。



Scheme 1. Paired electrosynthesis of β-nitroalcohols using an electrogenerated base

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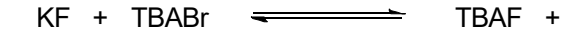
第四級アンモニウムフルオリド-HFIP 錯体を用いる電解フッ素化

（芝浦工大工[1]・芝浦工大院理工[2]）○望月 愛華[1]・本間 晴香[1]・北島 庸貴[2]・田嶋 稔樹[1,2]

Anodic Fluorination of Organic Compounds Using Quaternary Ammonium Fluoride-HFIP Complexes ([1]*College of Engineering, Shibaura Institute of Technology*, [2]*Graduate School of Engineering and Science, Shibaura Institute of Technology*) ○Aika Mochizuki,[1] Haruka Homma ,[1] Nobutaka Kitajima,[2] Toshiki Tajima[1,2]

Based on the ion exchange reaction between KF and TBABr in HFIP, we synthesized TBAF from KF. ^{1}H and ^{19}F NMR measurements of the obtained product revealed that it is not TBAF but TBAF(HFIP)$_3$ with three molecules of HFIP coordinated to TBAF. Anodic fluorination of a sulfide using TBAF(HFIP)$_3$ as not only the fluorinating reagent but also the supporting electrolyte was carried out to provide the corresponding fluorinated product in good yield.
Keywords : Anodic Fluorination; TBAF; KF; Ion Exchange Reaction

最も安全かつ安価なフッ素化剤の一つとしてフッ化カリウム（KF）が知られているが、ほとんどの有機溶媒に難溶であることから、一般的な有機溶媒中での使用にはクラウンエーテルなどの相間移動触媒が必要である。これに対し、1,1,1,3,3,3-ヘキサフルオロ-2-プロパノール（HFIP）は KF を高濃度に溶解すること[1]が知られている。一方、テトラブチルアンモニウムフルオリド（TBAF）は有機溶媒に可溶なフッ素化剤として知られているが、吸湿性が高く、水和物として扱われるのが一般的である。しかしながら、TBAF の水和物はフッ素化だけではなくヒドロキシ化が進行するなど、無水の TBAF と比較して多くの問題点を有している。これに対し、無水の TBAF を合成する方法[2]や TBAF のアルコール錯体を合成する方法[3]などが知られている。これに対し、本研究では HFIP 中での KF と TBABr のイオン交換反応に基づき、KF から TBAF を合成した（式 1）。



得られた生成物の ^{1}H および ^{19}F NMR を測定した結果、TBAF ではなく、TBAF に 3 分子の HFIP が配位した TBAF(HFIP)$_3$ であることが明らかになった。TBAF(HFIP)$_3$ をフッ素化剤兼支持電解質として用いてスルフィドの電解フッ素化を行ったところ、対応するフッ素化体が良好な収率で得られた。

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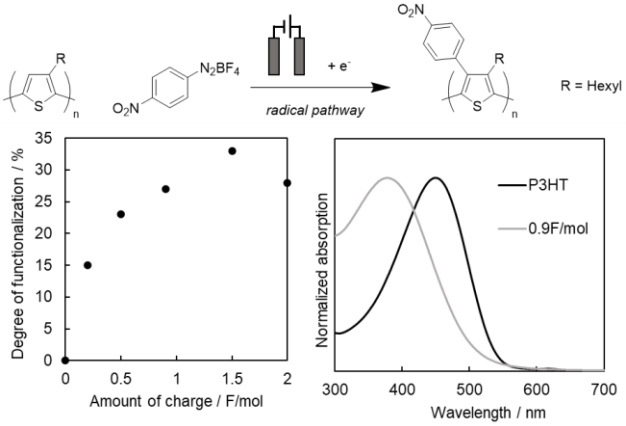
アリールジアゾニウム塩を用いるポリチオフェン類の電解ポスト機能化

（東工大物質理工 [1]）○小磯　聡士 [1]・佐藤　宏亮 [1]・稲木　信介 [1]
Electrochemical post-functionalization of polythiophenes by using aryldiazonium salts ([1]School of Materials and *Chemical Technology, Tokyo Institute of Technology*) ○Satoshi Koiso,[1] Kosuke Sato,[1] Shinsuke Inagi[1]

Polythiophenes with an aryl group in the side chain can be used for sensors and other applications.[1] Arylation of brominated poly(3-hexylthiophene) (P3HT) by transition metal-catalyzed coupling reactions is a known post-functionalization method,[2] but the residual catalyst affects the electrochemical properties of the resultant polymers. Therefore, it is necessary to develop a transition metal catalyst-free method. In this study, we investigated the C–H arylation reaction of P3HT using aryl radicals generated by electrochemical reduction of aryl diazonium salts, and successfully introduced an aryl group at the 4-position of the thiophene rings. The degree of functionalization was successfully controlled by changing the amount of charge. Furthermore, the electrochemical and optical properties of the obtained polymers were evaluated in detail.
Keywords : π-Conjugated polymer; Electrochemical post-functionalization; Electrolytic reduction; Aryldiazonium salts; C–H arylation

側鎖にアリール基が導入されたポリチオフェン類はセンサー応用などが期待される [1]。ポリ(3-ヘキシルチオフェン) (P3HT) をアリール化する手法として、ブロモ基を有する P3HT に対する遷移金属触媒カップリング反応を用いる方法が知られているが [2]、残留する触媒が電気化学的特性等に影響を与えてしまうため、遷移金属触媒を用いない手法の開発が求められている。本研究では、アリールジアゾニウム塩の電解還元によって生じるアリールラジカルを用いて P3HT の C-H アリール化反応を検討したところ、チオフェン環 4 位にアリール基を導入することに成功した。また、通電量を変えることによるアリール基の導入率の制御に成功した。さらに、得られた高分子の電気化学的特性および光学的特性について詳細に評価した。



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イソオイゲノール由来の二官能性モノマーを用いた正孔触媒的環化付加重合による高分子合成

(横国大院工[1]・JST さきがけ[2]) ○長屋 亮[1]・瀬古 達矢[1]・信田 尚毅[1,2]・跡部 真人[1]

Polymer Synthesis by Hole Catalytic Cycloaddition Polymerization with Bifunctional Monomers Derived from Isoeugenol

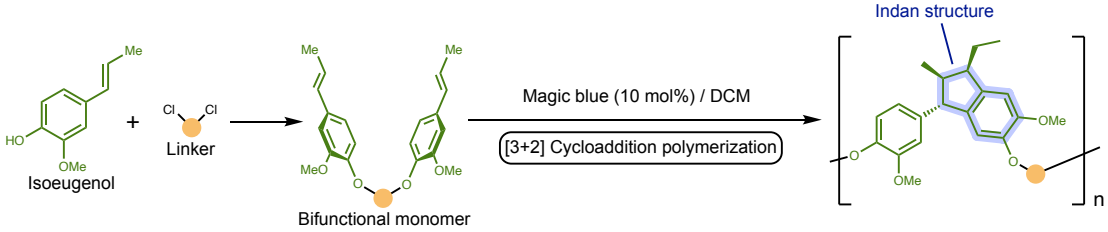
([1]*Departmentof Chemistry and Life Science, Yokohama National University,* [2]*JST PRESTO*) ○Ryo Nagaya,[1] Tatsuya Seko,[1] Naoki Shida,[1,2] Mahito Atobe[1]

Isoeugenol, an aromatic biomass resource, is expected to be a renewable raw material for polymers due to its availability and economic cost. However, the poor reactivity of isoeugenol in cationic/radical polymerization hinders its direct use as a renewable monomer resource.[1] In this study, we focused on a catalytic [3+2] cycloaddition reaction triggered by one-electron oxidation and attempted to develop it into a polymerization reaction that forms an indan structure. Bifunctional monomers composed of two isoeugenol molecules bonded by silicon or phosphorus were designed, respectively, targeting an efficient cycloaddition polymerization by a catalytic amount of oxidative electron transfer. The bifunctional monomer with siloxane-linkage was reacted with 10 mol% of tris(4-bromophenyl) ammoniumyl hexafluoroantimonate (magic blue) as a one-electron oxidant/initiator and stirred for 60 min to afford the corresponding polymer in 40% yield. The addition of Bu_4NF to the polymer cleaved the silyl ether bonds, demonstrating facile degradability under mild conditions. Polymerization of thiophosphonate-linked isoeugenol-monomer has also been demonstrated in similar manner.

Keywords: Isoeugenol; Phenylpropanoid; Cycloaddition Polymerization; Hole Catalysis; Biomass

含芳香族バイオマス資源であるイソオイゲノールは、入手容易性や価格の観点から持続可能なポリマー原料として期待されている。一方でβ置換スチレン構造を有するため、カチオン/ラジカル重合等における反応性が乏しく、直接重合が困難である[1)]。そこで本研究では、一電子酸化をトリガーとしたイソオイゲノールの触媒的[3+2]環化付加反応[2)]に着目し、インダン骨格の形成を伴う重合を報告する。具体的には、イソオイゲノール2分子をケイ素またはリンにより結合した2官能性モノマーを設計することで、触媒量の酸化的電子移動を駆動力とした効率的な環化付加重合を目指した。

シロキサン結合を有する2官能性モノマーに対し、一電子酸化剤兼開始剤として10 mol%の tris(4-bromophenyl) ammoniumyl hexachloroantimonate (magic blue)を添加し60分間反応を行った結果、所望のポリマーが収率40%, $M_n = 5800$, $M_w = 94400$ で得られた。その後、得られたポリマーのシリルエーテル結合に対して2当量の Bu_4NF を添加したところ、シリルエーテル結合が切断されインダン骨格含有ビスフェノールが得られたことから、ポリマーの可分解性が実証された。発表ではチオホスホン酸モノマーを用いた検討結果についても併せて報告する。



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マイクロフロー電解リアクターによるシアノメチル化反応の機械学習を活用した条件探索

（岡山大院自然[1]）○谷 明音[1]・國本俊平[1]・佐藤英祐[1]・菅 誠治[1]

Machine Learning-Supported Reaction Condition Exploration of Cyanomethylation Using Electrochemical Microflow Reactor ([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Akine Tani,[1] Shunpei Kunimoto,[1] Eisuke Sato,[1] Seiji Suga[1]

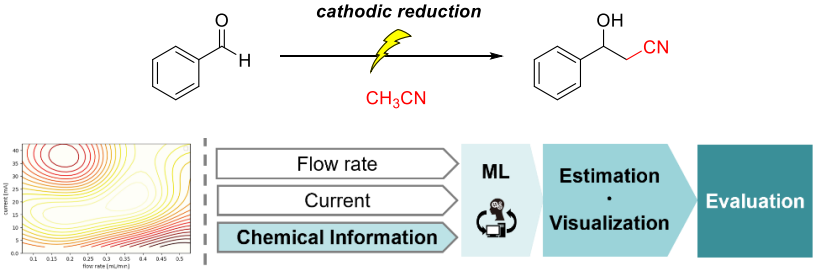
Cyanomethylation of carbonyl compounds is one of the powerful methods to introduce a cyano group, which can be converted various useful functional groups. We have already developed the efficient system for cyanomethylation of carbonyl compounds using an electrochemical microflow reactor, which give the target compounds in good yields. In this reaction, the best condition for each starting materials are different. For the efficient reaction condition optimization, we constructed the machine learning models which contain chemical information of starting materials as one of the explanatory parameters.

We herein report the machine learning model construction that makes estimation for multiple substrates, visualization and experimentally evaluation of estimated results, which gave us good estimation of reaction yields.

Keywords : Electro Chemical Organic Synthesis, Electrochemical Microflow Synthesis, Cyanomethylation, Machine Learning, Gaussian process regression

シアノ基は様々な官能基に変換可能であることから、有機合成において重要な置換基である。我々はこれまでにマイクロフロー電解リアクターを用いてアセトニトリル中でカルボニル化合物を陰極還元すると、シアノメチル化反応が良い収率で再現性良く進行することを見出した[1]。一方で、本反応では出発原料によって最適条件が異なることも明らかとなった。

そこで我々はガウス過程回帰という機械学習法[2]を用いた異なる出発原料に対する最適条件の合理的な探索に取り組んだ。今回は、構築した機械学習モデルの予測性能の実験的検証に加え、統計学的なモデルの妥当性の評価を行ったので発表する。



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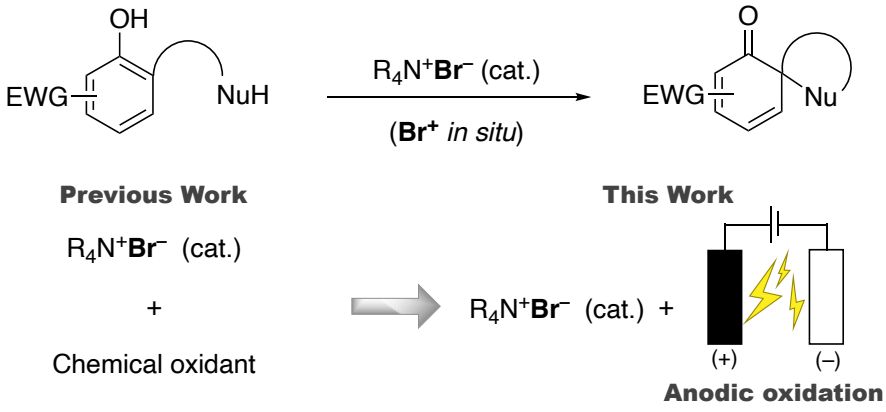
臭素種を触媒とするフェノール類の電気酸化的脱芳香族化反応

（名大院工）○松井 開・ウヤヌク ムハメット・石原 一彰
Electrooxidative Dearomatization of Phenols Catalyzed by Bromine Species (*Graduate School of Engineering, Nagoya University*) ○Kai Matsui, Muhammet Uyanik, Kazuaki Ishihara

We have already developed a hypobromite-catalyzed oxidative dearomative coupling reaction of phenols.[1] Although this method can be applied to electron-deficient phenols, which were difficult to oxidize with conventional hypoiodite catalysts,[2] the use of potentially explosive chemical oxidants is required. Here, we developed the bromine-based catalytic active species from bromide ions using anodic oxidation[3] instead of chemical oxidants. By using quaternary ammonium bromides as catalysts under the optimized conditions, the electrooxidation dearomative coupling of the electron-deficient arenols proceeded to give the corresponding spirocyclohexadienones in good yields.
Keywords : Anodic oxidation; Bromide; Electron-deficient phenols; Dearomatization; Oxidative coupling

当研究室ではこれまでに、次亜臭素酸塩触媒を用いるフェノール類の酸化的脱芳香族型カップリング反応を開発している[1)]。本手法は、従来の次亜ヨウ素酸塩触媒[2)]では適用が困難であった電子不足フェノールの酸化を可能にしたものの、依然として潜在的に爆発性を有する化学酸化剤を用いる点で課題が残されている。今回、我々は化学酸化剤の代わりに陽極酸化[3)]を用いることで臭化物イオンから臭素酸化種を発生させる手法を開発した。最適化された条件下、第四級アンモニウム臭化物を触媒として用いることで、電子不足フェノール類の電気酸化的脱芳香族型カップリング反応が進行し、目的のスピロシクロヘキサジエノンを良好な収率で得ることに成功した。



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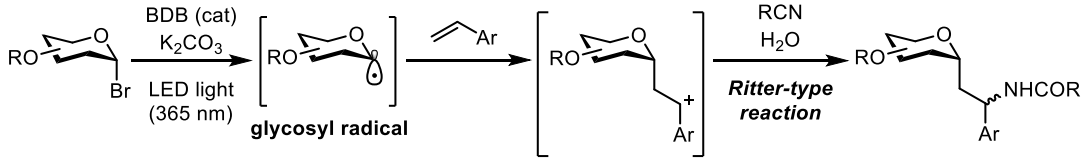
芳香族アミンを光触媒とするグリコシルブロミドとアルケンによる Ritter 型反応

（鳥取大学[1]・広島大学[2]・産総研触媒 RC[3]・日本工業大学[4]）○滝浪 飛龍[1]・澤田 直哉[1]・于 子怡[1]・佐々木 紀彦[1]・野上 敏材[1]・安倍 学[2]・谷口 剛史[3]・小池 隆司[4]
Ritter-type Reaction of Glycosyl Bromides and Alkenes using Arylamines as Photocatalysts
([1]*Tottori University*, [2]*Hiroshima University,* [3]*IRC3, AIST,* [4]*Nippon Institute of Technology*) ○ Hiryu Takinami,[1] Naoya Sawada,[1] Ziyi Yu,[1] Norihiko Sasaki,[1] Toshiki Nokami,[1] Manabu Abe[2] Tsuyoshi Taniguchi,[3] Takashi Koike[4]

C-Glycosides have been synthesized as metabolically stable analogues of glycosides.[1] Their synthesis via glycosyl radicals is a promising approach, however, generation of glycosyl radicals has been performed by using sophisticated precursors, activators, and catalysts. Recently, Koh and co-workers developed a novel photochemical method using Hantzsch ester as an activator of glycosyl sulfones.[2] Here we report a practical method to generate glycosyl radicals from glycosyl bromides using 1,4-bis(diphenylamino)benzene (BDB) as an organic photocatalyst. Glycosyl bromides served as glycosyl radical precursors by LED light (365 nm) irradiation in the presence of potassium carbonate and BDB. The generated glycosyl radicals were coupled with alkenes to afford radical-polar crossover (RPCO)-type products via the Ritter-type reaction.
Keywords : Organic Electron Transfer Chemistry; Ritter-type Reaction; Photocatalyst; Glycosyl Bromide; Arylamine

グリコシド結合（C－O 結合）の酸素原子を炭素原子に置き換えた *C*-グリコシドは、代謝安定性に優れるだけでなく、天然の配糖体よりも高い生物活性を示すことも報告されている[1)]。このような *C*-グリコシドの合成にはグリコシルラジカル中間体の発生が鍵となり、これまで、光触媒や金属触媒を用いる合成例が報告されているが、温和かつ金属フリー条件で進行する例は少ない[2)]。今回、1,4-ビス（ジフェニルアミノ）ベンゼン（BDB）を有機光触媒として用いたグリコシルブロミドからグリコシルラジカルを生成する実用的な方法を報告する。グリコシルブロミドは、炭酸カリウムおよび有機光触媒の存在下で光照射によりグリコシルラジカル前駆体として機能した。生成したグリコシルラジカルのアルケンへの付加を経て、ラジカル極性クロスオーバー型生成物と考えられる Ritter 型反応生成物を得た。



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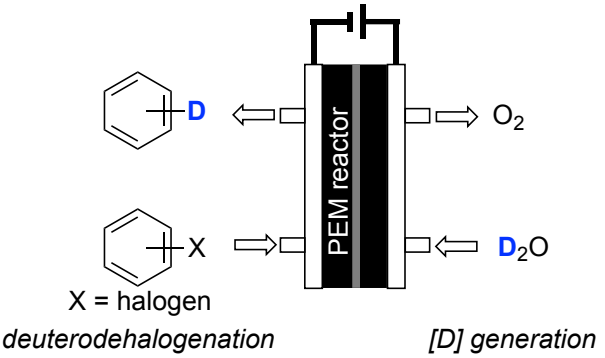
PEM 型リアクターを用いた脱ハロゲン型芳香族重水素化反応の開発

(北大院理[1]) ○萬代 恭子[1]、芦刈 洋祐[1]、姚 弋越[1]、永木 愛一郎[1]
Deuterodehalogenation of (hetero)aryl halides using PEM reactor ([1]*Graduate School of Science, Hokkaido University*) ○Kyoko Mandai[1], Yosuke Ashikari[1], Yiyue Yao[1], Aiichiro Nagaki[1]

In order to efficiently create substances that are useful for human life in a sustainable manner, organic syntheses that provide such compounds with reduced amount of reactants and wastes are highly desired. Furthermore, improving the reaction scale for large-scale synthesis is an important issue that must be realized immediately. By using our flow electrocatalytic reaction device (PEM reactor), the hydrodehalogenation reaction using water as the hydrogen source proceeds without the help of a chemical reducing agent to find that reduced compounds can be obtained from various aromatic and heteroaromatic halides chemoselectively. Particularly, using heavy water as the deuterium source, the reaction system allows monodeuteration of various aromatic systems. We report that, while a large number of reaction conditions can be considered, the number of trials can be minimized by optimizing the reaction conditions using Bayesian optimization to find the optimal reaction conditions that give both high current efficiency and deuteration rate.
Keywords : electrocatalytic reduction, hydrodehalogenation, PEM reactor, deuteration

我々人類の生活に有用な物質を持続可能な方法で効率よく創生するため、そのような化合物を合成する有機合成反応においては、反応に必要な反応剤と反応後に排出される廃棄物の低減、さらには大規模合成のための反応スケールの向上は、早急に実現すべき重要な課題である。我々が開発したフロー型電解反応装置（PEM リアクター）を用いることにより、化学的な還元剤を用いる必要なく、水を水素源としたヒドロ脱ハロゲン化反応が進行し、様々な芳香族、ヘテロ芳香族ハロゲン化物から化学選択的に還元された化合物が得られることを見出した[1)]。特に、本反応系では重水を重水素源としたモノ重水素化が可能であり、数多の反応条件が考えられる中で、ベイズ最適化を用いた反応条件最適化により、非常に少ない試行回数で、最も高い電流効率と重水素化率の両方を与える最適な反応条件を見つけることができたので報告する。



1) Yosuke Ashikari, Kyoko Mandai, Yiyue Yao, Yuta Tsuchihashi, Aiichiro Nagaki, *ChemElectroChem*, **2023**, e202300315.

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1133(1132, Bldg. 11 [3F])

[E1133-3am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kei Murakami, Kohei Sekine

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1133-3am-01]
Visible-light-driven borylation of aryl halides by a phosphonium ylide organophotoredox catalyst

○Ren Yamaguchi[1], Masaya Iwasaki[1], Yasunori Toda[1], Hiroyuki Suga[1] (1. Shinshu University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1133-3am-02]
Development of Pd-catalyzed phosphonium cyclopentadienylide (PCPY) synthesis through photo-irradiation

○Takaya Tomoike[1], Shoma Chiba[1], Bumpei Maeda[1], Kei Murakami[1] (1. Kwansei Gakuin University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1133-3am-03]
Development of Radical Germinations Using Photocatalyst and Digermane

○Haruka Iimuro[1], Shiho Ishigaki, Tomonori Inoue[1], Yuki Nagashima[1], Ken Tanaka[1] (1. Tokyo Institute of Technology)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1133-3am-04]
Photocatalytic 1,2-Phosphorus-Migrative [3+2] Cycloaddition of Tri(*t*-butyl)phosphine with Alkynes

○Yusuke Masuda[1], Daichi Ikeshita[2], Kosuke Higashida[3], Masaki Yoshida[1], Naoki Ishida[2], Masahiro Murakami[2], Masaya Sawamura[1,3] (1. Hokkaido University, 2. Kyoto University, 3. WPI-ICReDD)

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
[E1133-3am-05]
Synthesis of Highly Condensed Benzophosphole Derivatives by Lewis-acid-assisted, Visible-light-promoted Mallory Reaction

○Ikki Kamiyoshi[1], Xu Shibo[1], Kosuke Yasui[1], Koji Hirano[1] (1. The Univ. of Osaka)

Japanese

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

[E1133-3am-06]

Photocatalyzed Construction of Indole-Fused 1,4-Diazepine Derivatives

○Tatsushi Oishi[1], Tatsuhiro Uchikura[1], Takahiko Akiyama[1] (1. Gakushuin University)

Japanese

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

[E1133-3am-07]

π-Lewis Acidic Metal Catalyzed Photochemical Flow Reaction via Activation of Alkynes

○Zen Iwasaki[1], Ryohei Yazaki[1], Ren Obayashi[1], Jun Kikuchi[2], Shigenobu Umemiya[1], Masahiro Terada[1] (1. Grad. School of Science, Tohoku Univ., 2. Grad. School of Pharmaceutical Sciences, Tohoku Univ.)

Japanese

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

[E1133-3am-08]

Synthesis of Cyclic Imides Based on Visible-Light Induced Carbamoylarylation

○Taewoo Ko[2], Di Wu[2], Kohei SEKINE[1,2], Yoichiro KUNINOBU[1,2] (1. IMCE, Kyushu Univ., 2. Interdisciplinary Graduate School of Engineering Sciences, 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

[E1133-3am-09]

Aerobic Photooxidation of Alcohols Catalyzed by Azaborine

○Yuri Kikuiri[1], Peiyuan Yang[1], Hiroki Fukumoto[1], Tomohiro Agou[2], Masaru Kondo[3] (1. Ibaraki Univ., 2. Univ. of Hyogo, 3. Univ. of Shizuoka)

Japanese

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

[E1133-3am-10]

Syntheses of heteropolycyclic aromatic compounds with tetrahydro-*b*-carboline structures

○Takuma Yuba[2], Yoshimitsu Tachi[1,2], Masatoshi Kozaki[1,2] (1. Osaka Metropolitan University, 2. Osaka City University)

Japanese

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

[E1133-3am-11]

Development of organic luminescent radicals with hydrophilic-group substituted carbazole donor

○Kosuke Anraku[1], Kenshiro Matsuda[1], Satoshi Miyata[2], Takuya Hosokai[2,3], Satoshi Okada[4], Kazuhiro Nakamura[1], Kohei Nakao[5], Ken Albrecht[5] (1. Graduate School of Science and Engineering, Kyushu Univ., 2. Department of Pure and Applied Chemistry, Tokyo Univ. of Sci., 3. AIST, 4. Laboratory for Chemistry and Life Science, Tokyo Tech., 5. IMCE, Kyushu Univ.)

Japanese

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

[E1133-3am-12]

A novel conversion of ionic liquids containing a diol unit in the cationic part to alkenylammonium salts

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○Runa Sasakura[1], Takuji Kawamoto[1], Akio Kamimura[1] (1. Yamaguchi University)

Japanese

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

[E1133-3am-13]

Preparation of bicyclic dihydrosiloles via radical cascade reaction of 1,6-enynes.

○Yuki Kanda[1], Kanako Ishido[1], Takuji kawamoto[1], Akio Kamimura[1] (1. Yamaguchi University)

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ホスホニウムイリドを可視光レドックス触媒として用いる芳香族ハロゲン化物のホウ素化反応

（信州大工）○山口 礼・岩崎 将也・戸田 泰徳・菅 博幸
Visible-light-driven borylation of aryl halides by a phosphonium ylide organophotoredox catalyst (*Department of Materials Chemistry, Faculty of Engineering, Shinshu University*) ○ Ren Yamaguchi, Masaya Iwasaki, Yasunori Toda, Hiroyuki Suga

Aryl boronic esters are used as useful building blocks in organic synthesis. Recently, photoredox-catalyzed borylation reactions have been intensively studied and borylation reactions of aryl halide are well-known. Photoredox catalysts having strong reducing abilities can efficiently reduce aryl halides. The corresponding aryl radicals generated by the photoreduction undergo C−B bond formation to afford aryl boronic esters. Our group reported that phosphonium ylide **1** serves as a visible-light photoredox catalyst with a strong reducing power, enabling reductive transformations. In this study, we investigated the borylation of aryl halides by phosphonium ylide photoredox catalysis. At the outset of our study, the reaction of *p*-iodoanisole (**2**) with bis(pinacolato)diboron was carried out in the presence of **1** under visible light irradiation. As a result, we found that the desired aryl boronic ester **3** was obtained in relatively good yield.
Keywords : Phosphonium ylide; Photoredox catalyst; Aryl halide; Borylation; Radical

芳香族ボロン酸エステルは合成化学的に有用なビルディングブロックである。近年、光レドックス触媒を利用した芳香族化合物のホウ素化反応が活発に研究されている[1]。その一つとして、芳香族ハロゲン化物のホウ素化反応がよく知られている。強い還元力をもつ光レドックス触媒を用いると、芳香族ハロゲン化物を還元することができ、これにより生じたアリールラジカルがホウ素化試薬と反応して、芳香族ボロン酸エステルを与える。

一方、当研究室では、独自に開発したホスホニウムイリド **1** が還元的過程を担う可視光レドックス触媒として機能することを明らかにしている[2]。本触媒の特長は強い還元力（−2.38 V vs. SCE）をもつことである。今回、本触媒系による芳香族ハロゲン化物のホウ素化反応を検討した。

初期検討では *p*−ヨードアニソール（**2**: −2.25 V vs. SCE）を基質として、触媒 **1** および CsF 存在下、B_2pin_2 を可視光照射下で反応させた。その結果、望むホウ素化反応が進行し、芳香族ボロン酸エステル **3** が比較的良好な収率で得られることを見出した。



1) Tian, Y.-M.; Guo, X.-N.; Braunschweig, H.; Radius, U.; Marder, T. B. *Chem. Rev.* **2021**, *121*, 3561−3597.
2) Toda, Y.; Kobayashi, T.; Hirai, F.; Yano, T.; Oikawa, M.; Sukegawa, K.; Shimizu, M.; Ito, F.; Suga, H. *J. Org. Chem.* **2023**, *88*, 9574−9578.

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可視光照射と Pd 触媒が駆動するホスホニウムシクロペンタジエニリド合成法の開発

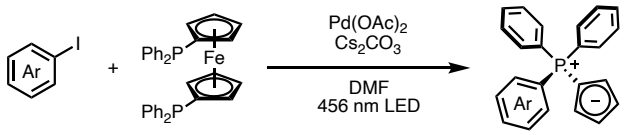
（関西学院大理工[1]）○友池天哉[1]・千葉将真[1]・前田文平[1]・村上慧[1]

Development of Pd-catalyzed phosphonium cyclopentadienylide (PCPY) synthesis through photo-irradiation ([1]*Department of Chemistry, Graduate School of Science and Engineering, Kwansei Gakuin University*) ○ Takaya Tomoike[1], Shoma Chiba[1], Bumpei Maeda[1], Kei Murakami[1]

Phosphonium cyclopentadienylides (PCPYs) are known as stable ylides that contain a phosphonium cation and a cyclopentadienyl anion moieties. They are attractive compounds due to coordinating ability and unique reactivities derived from cyclopentadienyl anion. However, the synthetic methods of PCPYs have been limited. Consequently, the investigation of the properties and reactivities of PCPYs has been hindered by synthetic challenges. Herein, we report a new palladium-catalyzed synthesis of PCPYs that proceeds with blue light irradiation. Notably, the reaction enables the one-step synthesis of PCPYs from commercially available 1,1'-bis(diphenylphosphino)ferrocene (dppf) and iodoarene under mild conditions. Thus, the reaction tolerated various functional groups.

Keywords: Ylide, Palladium, Visible light irradiation, Phosphonium, Cyclopentadienyl anion

ホスホニウムシクロペンタジエニリド(PCPYs)は、ホスホニウムカチオンとシクロペンンタジエニルアニオンの構造を有する安定イリドである。PCPYs はシクロペンタジエニルアニオンに由来する金属への配位能と特異な反応性を併せもつ興味深い化合物である[1]。しかし従来の合成手法では、PCPYs を合成するために複数の合成段階が必要となるため、PCPYs の合成例も限られており、その物性や反応性についてはいまだ十分な調査がなされていない[2]。このように、PCPYs の研究を加速するためにより簡便な合成法の開発が望まれている。今回我々は、パラジウム触媒と可視光照射を用いた PCPYs の新規合成反応の開発に成功した。本反応は 1,1'-ビス（ジフェニルホスフィノ）フェロセン（dppf）とヨードアレーンといった入手容易な原料を用いたカップリング反応であり、青色光照射のみといった穏和な条件下で反応が進行する。そのため本反応は様々なヨードアレーンが適用可能である。



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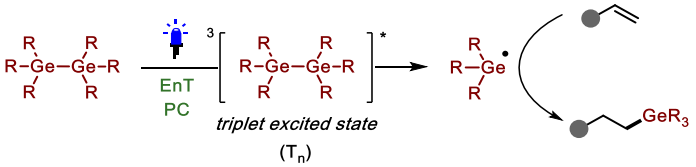
光増感剤とジゲルマニウムを用いたラジカル的ゲルミル化反応の開発

（東工大物質理工[1]）○飯室遥香[1]・石垣信穂[1]・井上智仁[1]・永島佑貴[1]・田中健[1]
Development of Radical Germylations Using Photocatalyst and Digermane ([1]*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Haruka Iimuro,[1] Shiho Ishigaki,[1] Tomonori Inoue,[1] Yuki Nagashima,[1] Ken Tanaka[1])

Germanium, a homologous element to carbon (Group 14), is a high-period element that can form stable bonds with carbon. Organogermanium compounds have attracted attention as bioactive compounds and building blocks. Therefore, synthetic methods for diverse organic germanium compounds are required. Recently, diverse germylation reactions via in situ generations of germyl radicals were developed for synthesis of organogermanium compounds under mild conditions. On the other hand, we have developed photoinduced silylation reactions through photolysis of Si–B and B–B bonds by appropriate reaction designs[1,2]. Based on our previous research, we herein reported a new method for in situ generation of germyl radicals using digermane (Ge–Ge). This protocol enabled the visible-light-induced hydrogermylation reaction of alkenes under mild conditions through photolysis of digermane with a photocatalytic energy transfer process.
Keywords : germyl radical; hydrogermylation; photolysis; organogermane compound; photoinduced reaction

炭素と同じ第 14 族元素であるゲルマニウムは、高周期元素でありながら炭素と安定な結合を形成できる。また極めて毒性が低く、炭素元素と置き換えることで脂溶性・分子体積・3 次元構造を変化させることができるので、生理活性物質の部分構造として注目されてきた。さらに、炭素–ゲルマニウム結合はビルディングブロックとして有用であり、より多様な有機ゲルマニウム化合物の開発法が求められている。

有機ゲルマニウム化合物の温和な合成法として、ゲルミルラジカルを用いる方法は有用であり、これまでに様々な前駆体を用いたラジカル発生法が報告されてきた。一方、我々はこれまでに Si–B / B–B といった元素間結合を光励起により開裂させ、有機反応に利用してきた[1,2]。本研究ではこの知見を応用し、ジゲルマン (Ge–Ge) を前駆体としたゲルミルラジカルの新規発生法に取り組んだ。種々検討の結果、光増感剤によるエネルギー移動を利用することで、可視光照射下 Ge–Ge 結合の光開裂が進行し、ゲルミルラジカルが生成することを見出した。また本反応をアルケンに適用することで、幅広い基質に対し高収率でヒドロゲルミル化体が得られることを見出した。



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リン原子の 1,2-転位を伴うトリ(*t*-ブチル)ホスフィンとアルキンの光触媒的[3+2]付加環化反応

（北大理[1]・京大院工[2]・WPI-ICReDD[3]）○増田侑亮[1]・池下大智[2]・東田皓介[3]・吉田真樹[1]・石田直樹[2]・村上正浩[2]・澤村正也[1,3]

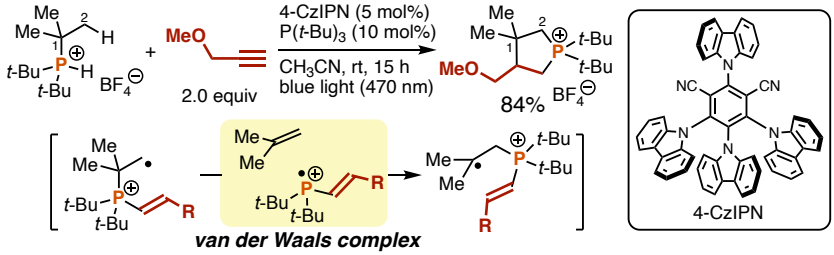
Photocatalytic 1,2-Phosphorus-Migrative [3+2] Cycloaddition of Tri(*t*-butyl)phosphine with Alkynes ([1]*Hokkaido University,* [2]*Kyoto University,* [3]*WPI-ICReDD*) ○ Yusuke Masuda,[1] Daichi Ikeshita,[2] Kosuke Higashida,[3] Masaki Yoshida,[1] Naoki Ishida,[2] Masahiro Murakami,[2] Masaya Sawamura[1,3]

Tri(*tert*-butyl)phosphine and terminal alkynes undergo 1,2-phosphorus-migrative [3+2] cycloaddition under photocatalytic conditions. The reaction exhibits broad functional group tolerance and affords substituted cyclic phosphonium salts, which are amenable to further derivatization by Wittig olefination. Experimental and theoretical studies suggest that the 1,2-phosphorus migration of a β-phosphonioalkyl radical proceeds through a phosphine radical cation–alkene van der Waals complex as a pseudointermediate.

Keywords : 1,2-migration, phosphonium salt, alkyne, cycloaddition, photoredox catalyst

アルキルラジカルはβ位原子の1,2-転位によって熱力学的により安定なアルキルラジカルを生成することが知られている[1)]。アリール基やカルボニル基といった炭素原子のラジカル1,2-転位反応が広く研究されている一方で、ヘテロ原子の転位反応については報告例が限られている。中でもリン原子のラジカル1,2-転位反応はこれまでに報告されていない。

本研究では、トリ（*t*-ブチル）ホスホニウムテトラフルオロボレート、トリ（*t*-ブチル）ホスフィン、および末端アルキンの混合物に対して光酸化還元触媒(4-CzIPN)の存在下可視光を照射することで、リン原子の1,2-転位を伴う[3+2]付加環化反応が進行し、５員環ホスホニウム塩が得られることを見出した[2)]。実験と計算による反応機構解析の結果、β−ホスホニオアルキルラジカルの1,2-リン原子転位は、ホスフィンラジカルカチオンとアルケンのファンデルワールス錯体を経由して進行することが示唆された。



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ルイス酸を利用した可視光駆動型 Mallory 反応による縮環ベンゾホスホール誘導体の合成

（阪大院工）○神吉 一輝・Shibo Xu・安井 孝介・平野 康次
Synthesis of Highly Condensed Benzophosphole Derivatives by Lewis-acid-assisted, Visible-light-promoted Mallory Reaction (*Graduate School of Engineering, Osaka University*)
○Ikki Kamiyoshi, Shibo Xu, Kosuke Yasui, Koji Hirano

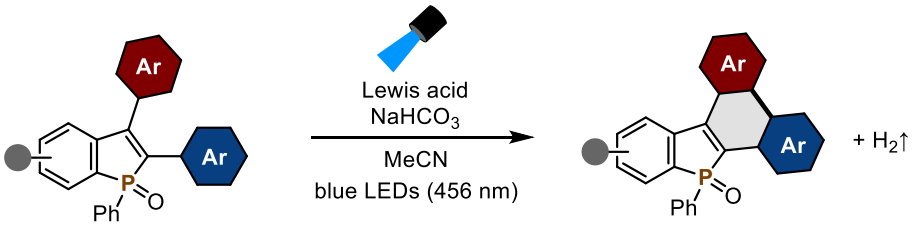
A benzophosphole is one of heterocycles with unique optical and electronic properties and has received much attention as a key skeleton for various organic functional materials such as photoelectric conversion materials. In particular, highly condensed phospholes with extended π-conjugated systems constitute an attractive class of compounds. One of representative synthetic methods for their preparation is Mallory reaction of aryl-substituted phospholes by UV light irradiation.

On the other hand, we recently found that the Mallory reaction of some specific 2,3-diarylbenzophosphole oxide derivatives proceeded even under visible light irradiation to give the corresponding condensed benzophosphole derivatives. In the present study, we developed the visible-light (456 nm blue LEDs)-promoted Mallory reaction of more general 2,3-diarylbenzophospholes with the assistance of an appropriate Lewis acid to form the corresponding dehydrogenative cyclized products, highly condensed benzophosphole derivatives, in good yields.

Keywords : Benzophospholes, Dehydrogenative cyclization, Mallory reaction, Visible light

ホスホールは特異な光学的および電子的特性を持つ複素環の一つであり、光電変換材料を始め様々な有機機能性材料の鍵骨格として注目されている。[1] 特に、パイ共役系が拡張された縮環ホスホール類は、魅力的な分子群である。その合成法の一つとして、アリール置換ホスホールに対し紫外光を照射する Mallory 反応が挙げられる。[2]

一方最近我々は、いくつかの 2,3-ジアリールベンゾホスホールオキシド誘導体の Mallory 反応が、紫外光ではなく可視光照射によっても進行し、対応する縮環ベンゾホスホール誘導体を与えることを報告している。[3] 本研究ではこの反応の一般化を目的とし、検討をおこなった。その結果、2,3-ジアリールベンゾホスホールオキシドに対し、適切なルイス酸を添加すると、可視光（青色、456 nm）であっても Mallory 反応が進行し、対応する脱水素環化生成物である縮環ベンゾホスホール誘導体が良好な収率で得られることを見出した。



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光触媒を用いたインドール縮合 1,4-ジアゼピン誘導体の合成

（学習院大理）○生石 達士・内倉 達裕・秋山 隆彦

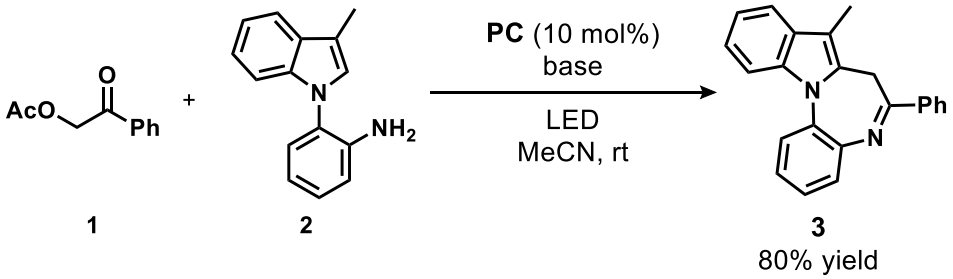
Photocatalyzed Construction of Indole-Fused 1,4-Diazepine Derivatives

(*Faculty of Science, Gakushuin University*) ○Tatsushi Oishi, Tatsuhiro Uchikura, Takahiko Akiyama

Indole-fused diazepines have attracted much attention because of their unique biological activities and development of efficient synthetic method is desired. Although the photo-induced C-H alkylations of indole are well-studied, its application to synthesis of indole-fused diazepines is underdeveloped. In this study, we synthesized indole-fused 1,4-diazepine derivatives by a photoredox-catalyzed radical addition of phenacyl radical to *N*-arylindole, followed by cyclization. Upon treatment of *N*-(2-aminophenyl)indole **2** with *α*-acetoxy acetophenone (**1**) in the presence of PC and sodium carbonate under blue LED irradiation conditions, the desired indole-fused 1,4-diazepine derivatives **3** were obtained in good yields.
Keywords: Photocatalyst; Indole; Diazepine

インドール縮合ジアゼピンは、その特異的な薬理活性から注目を集めており、優れた合成法の開発は重要な研究課題とされている。近年、光酸化還元触媒（PC）の発展に伴い、可視光駆動型ラジカル付加によるインドール 2 位の C−H アルキル化反応の開発が活発に進められている。一方、本手法によるインドール縮合ジアゼピン化合物の合成例は限られている。本研究では PC を用いて、窒素上に *o*−アミノフェニル基を有するインドール誘導体に対するフェナシルラジカルの付加反応および、連続的な環化反応によるインドール縮合 1,4−ジアゼピン誘導体の合成を行った。

PC、炭酸ナトリウム存在下、*α*−アセトキシアセトフェノン(**1**)とインドール誘導体 **2** をアセトニトリル中、紫外光照射下で反応させたところ、1,4−ジアゼピン誘導体 **3** が良好な収率で得られた。発表では基質一般性、推定反応機構についても報告する。



1 **2** **3**
80% yield

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πルイス酸性金属触媒によるアルキンの活性化を起点とする光フロー反応

(東北大院理[1]・東北大院薬[2]) ○岩崎 然[1]・矢﨑 亮平[1]・大林 蓮[1]・菊池 隼[2]・梅宮 茂伸[1]・寺田 眞浩[1]

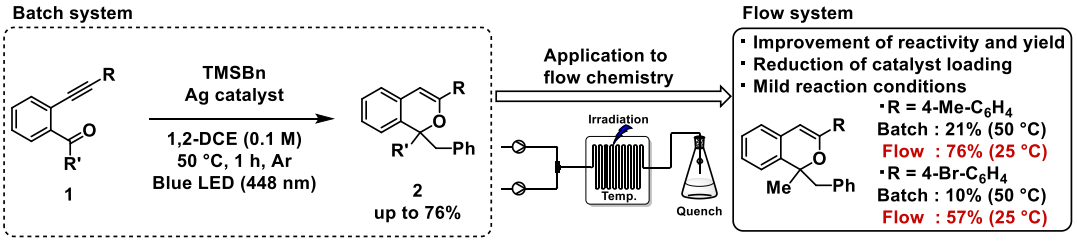
π-Lewis Acidic Metal Catalyzed Photochemical Flow Reaction via Activation of Alkynes

([1]*Graduate School of Science, Tohoku University*, [2]*Graduate School of Pharmaceutical Sciences, Tohoku University*) ○Zen Iwasaki,[1] Ryohei Yazaki,[1] Ren Obayshi,[1] Jun Kikuchi,[2] Shigenobu Umemiya,[1] Masahiro Terada[1]

Recently, the development of catalytic radical reactions by using excited cation species catalytically generated from organic cation intermediates via light irradiation has attracted much attention.[1] An efficient method to generate organic cation species is an intramolecular cyclization reaction by activation of alkynes using π-Lewis acidic metal catalysts.[2] Herein, we have developed a cyclization and successive intermolecular radical addition reaction of alkyne **1** with TMSBn, which is nonpolar prenucleophile under light irradiation conditions. The reaction of alkyne **1** and TMSBn in 1,2-DCE as a solvent at 50 °C for 1 h in the presence of Ag catalysts under blue light irradiation afforded the desired 2-benzopyran derivative **2** in good yield. Furthermore, the application to a flow reaction successfully improved the yield of the desired products due to suppress the decomposition of the products observed in the batch system.

Keywords : Radical Reaction; One-pot Reaction; Flow Chemistry; Excited Cation; C-C bond forming reaction

近年、有機カチオンを光励起することで励起カチオン種へと変換し、これを利用したドナー分子の一電子酸化を起点とするラジカル反応が注目を集めている[1]。有機カチオン種を効率的に発生させる方法の一つとして、πルイス酸性金属触媒を用いたアルキンの活性化による分子内環化反応が挙げられる[2]。我々は、銀触媒により発生させた 2-ベンゾピリリウムカチオンを光励起することで強い酸化力を有する励起カチオン種へと変換し、これと TMSBn の一電子酸化を起点とするラジカル反応を開発した。これにより、非極性化合物である TMSBn の直接的な変換をワンポットで行うことに成功した。実際に、アルキン **1** と TMSBn、及び、銀触媒存在下、1,2-DCE を溶媒に用いて 50 ℃で 1 時間、青色光を照射した場合、目的の 2-ベンゾピラン誘導体 **2** が最高収率 76%で得られた。さらに、フロー反応へと展開することにより、反応時間の短縮のみならず、バッチ系で見られた生成物の分解が抑えられ、収率を改善することができた。



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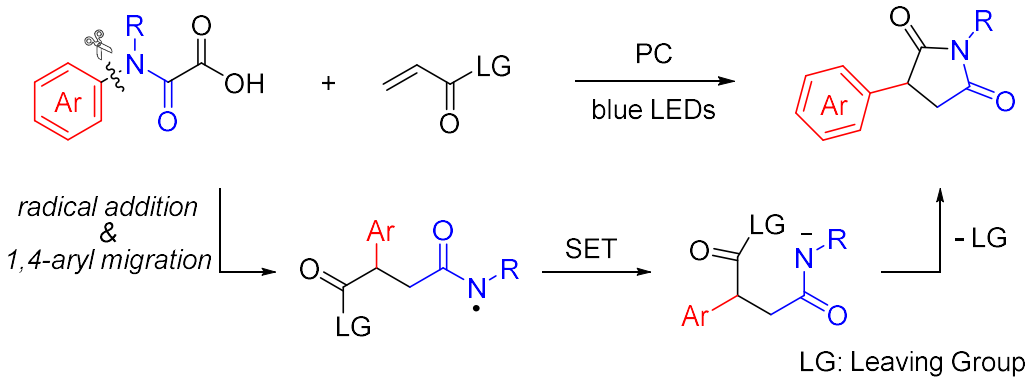
可視光駆動型カルバモイルアリール化反応を利用した環状イミドの合成

（九大先導研[1], 九大院総理工[2]）○高 汰佑[2]・呉 迪[2]・関根 康平[1,2]・國信 洋一郎[1,2]
Synthesis of Cyclic Imides Based on Visible-Light Induced Carbamoylarylation ([1]*IMCE, Kyushu University*, [2]*IGSES, Kyushu University*) ○Taewoo Ko,[2] Di Wu,[2] Kohei Sekine,[1,2] Yoichiro Kuninobu[1,2]

We have recently developed visible-light induced carbamoylarylation of alkenes. In the reaction, it is assumed that the addition of carbamoyl radicals to alkenes, resulting in 1,4-aryl migration with the cleavage of C(aryl)–N bond proceeded to afford the corresponding arylpropanamides. In this study, it was expected that when alkenes which have a leaving group at an appropriate position were used, cyclic imides could be obtained by the cyclization of amidates which were produced after the addition of carbamoyl radicals to alkenes, 1,4-aryl migration, and single electron transfer. In fact, when *N*-aryl oxamic acid and phenyl acrylate were used as starting materials, the desired reaction proceeded under visible-light irradiation using potassium carbonate and organic photocatalyst (PC) to give the corresponding 3-aryl succinimide in high yield.

Keywords : C–N Bond Cleavage; Carbamoylarylation; Aryl Migration; Cyclic Imide; Organic Photochemical Reaction

我々は、最近、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－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と想定した。今回、適切な位置に脱離基を導入したアルケンを用いれば、カルバモイルラジカルのアルケンへの付加、1,4-アリール転位、一電子移動後に生じるアミダートが環化反応を起こすことで、環状イミドが得られると考えた。実際に、*N*-アリールオキサミン酸とアクリル酸フェニルに対して、有機光触媒（PC）と炭酸カリウム存在下、可視光照射すると、目的の反応が進行し、3-アリールスクシンイミドが高収率で得られた。



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アザボリン光触媒を用いたアルコールの空気酸化反応の開発

（茨大工 [1]・茨大院理工 [2]・兵庫県大理 [3]・静岡県大薬 [4]）○菊入　優里 [1]・楊　沛源 [2]・福元　博基 [2]・吾郷　友宏 [3]・近藤　健 [4]

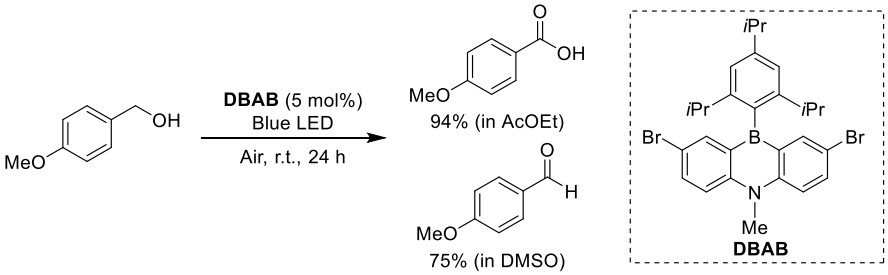
Aerobic Photooxidation of Alcohols Catalyzed by Azaborine ([1]*College of Engineering, Ibaraki University,* [2]*Graduate School of Science and Engineering, Ibaraki University,* [3]*Graduate School of Science, University of Hyogo,* [4]*School of Pharmaceutical Sciences, University of Shizuoka*) ○Yuri Kikuiri,[1] Peiyuan Yang,[2] Hiroki Fukumoto,[2] Tomohiro Agou,[3] Masaru Kondo[4]

Although selective oxidation of alcohols to aldehyde or carboxylic acids is one of fundamental reactions, highly toxic metal oxidants or explosive peroxides are often used. In recent, aerobic catalytic photooxidation of alcohols has attracted attention as a safe and inexpensive method. However, an expensive transition-metal photocatalyst and/or toxic solvent have been conventionally utilized for this transformation. Thus, aerobic organocatalytic photooxidation in a greener solvent is highly demanded. In our previous work, we reported aerobic photooxidation of phosphines and sulfides by dibenzo-fused 1,4-azaborine (DBAB), which is one of the useful light-emitting compounds[1)]. Here, we develop the aerobic photooxidation of alcohols using the DBAB catalyst and a greener solvent. Under irradiation by blue LED, the photooxidation of *p*-anise alcohol in AcOEt afforded *p*-anise acid in 94% yield and in DMSO afforded *p*-anise aldehyde in 75% yield, respectively.

Keywords : Photocatalyst; Green Solvent; Selective Oxidation

アルコールの酸化によるアルデヒドやカルボン酸の選択的合成は重要な反応であるものの、従来の合成プロセスでは高毒性の金属酸化剤や爆発性の高い過酸化物が用いられることも多い。そのため、安全で安価な手法として、光触媒によるアルコールの空気酸化が注目を集めている。しかし、既存の方法では金属触媒や毒性の高い溶媒が用いられることが多く、環境低負荷溶媒中で有機分子触媒を用いる酸化反応の開発が求められている。

最近、我々は有機発光体の一つである Dibenzo-fused-1,4-azaborine を光触媒に用いることで、ホスフィンやスルフィドの空気酸化が温和な条件下で進行することを報告した [1)]。本研究では、アザボリン光触媒と環境低負荷溶媒を用いたアルコールの空気酸化反応の開発を行った。青色光照射下、酢酸エチル中、室温で *p*-アニスアルコールの空気酸化を行ったところ、94%収率で *p*-アニス酸が得られた。また、DMSO 中、75%収率で *p*-アニスアルデヒドが得られた。



1) M. Kondo, T. Agou, *Chem. Commun.* **2022**, *58*, 5001.

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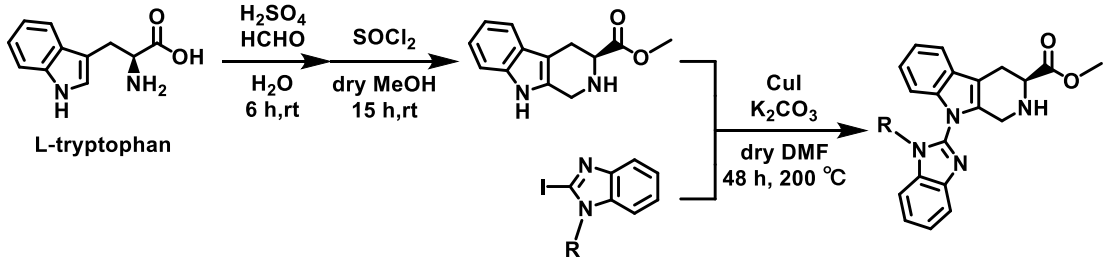
テトラヒドロ-β-カルボリン構造を有するヘテロ含有縮合多環芳香族化合物の合成

（阪公大院理[1]・阪市大理[2]）○弓場 拓真[2]・舘 祥光[1,2]・小嵜 正敏[1,2]
Syntheses of heteropolycyclic aromatic compounds with tetrahydro-β-carboline structures ([1]Graduate School of Science, Osaka Metropolitan University, [2]Faculty of Science, Osaka City University) ○Takuma Yuba,[2] Yoshimitsu Tachi,[1,2] Masatoshi Kozaki[1,2]

Tetrahydro-β-carboline skeletons are types of nitrogen-containing tricyclic compounds, and they are important compounds in medical or pharmaceutical fields because of their biological activities[1]. On the other hand, they are less studied in material chemistry. We have conducted on the synthesis of polycyclic aromatic compounds using natural amino acids as starting materials. In this study, we focused on the β-carboline skeleton derived from L-tryptophan and designed extended π-conjugated systems with the β-carboline skeleton. We synthesized compounds with β-carboline structures from L-tryptophan by the Pictet-Spengler reaction[1]. We attempted to synthesize π-extended β-carbolines by bonding heteroatom-rich aromatic compounds such as imidazole, benzimidazole, and their analogues at the 9-position of carbolines by Ullmann coupling[2]. We report the syntheses and physical properties of these compounds.

Keywords: Natural amino acid; Fused ring system; Heterocycles; β-carboline; Heteroatom rich

テトラヒドロ-β-カルボリン類は含窒素三環式化合物の一種で、その生理活性から、医学・薬学分野において重要な化合物である[1]。一方、これらの化合物を機能性材料として応用する研究はほとんどない。本研究では、天然アミノ酸を出発物質とした多環芳香族化合物の合成を目指し、L-tryptophan から誘導されるβ-カルボリン構造に注目した。Pictet-Spengler 反応によって、L-tryptophan からβ-カルボリン構造を有する化合物を合成した[2]。β-カルボリンの 9 位にイミダゾール、ベンズイミダゾールやその類縁体等のヘテロ原子豊富な芳香族化合物を Ullmann カップリング[3]により導入することで、π 共役系を拡張した機能性化合物の設計･合成を試みた。これらの化合物の合成と物性について報告する。



1) Ohta, Y. et. al. *Org. Lett.* **2009**, *11*, 1979-1982.
2) Singh, D. et. al. *ChemistrySelect* **2018**, *3*, 4859-4864.
3) Fang, Z. et. al. *J. Mater. Chem*. **2012**, *22*, 15397-15404.

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親水性置換基を導入したカルバゾールドナーを有する水溶性有機発光ラジカルの創製

(九大院総理工[1]・東理大院創域理工[2]・産総研[3]・東工大化生研[4]・九大先導研[5]) ○安楽 滉允[1]・松田 健志郎[1]・宮田 哲[2]・細貝 拓也[2,3]・岡田 智[4]・中村 和宏[1]・中尾 晃平[5]・アルブレヒト 建[5]

Development of organic luminescent radicals with hydrophilic-group substituted carbazole donor ([1]*Graduate School of Science and Engineering, Kyushu Univ.*, [2]*Department of Pure and Applied Chemistry, Tokyo Univ. of Sci.*, [3]*AIST*, [4]*Laboratory for Chemistry and Life Science, Tokyo Tech.*, [5]*IMCE, Kyushu Univ.*) ○Kosuke Anraku[1], Kenshiro Matsuda[1], Satoshi Miyata[2], Takuya Hosokai[2,3], Satoshi Okada[4], Kazuhiro Nakamura[1], Kohei Nakao[5], Ken Albrecht[5]

Air-stable organic luminescence radicals have potential applications in bioimaging due to their red to near-infrared photoluminescence and paramagnetic properties. Their actual use in bioimaging applications is rarely reported because they are hydrophobic materials. A limited number of reports demonstrated that amphiphilic polymers can make *tris*(2,4,6-trichlorophenyl)methyl (TTM) radical derivatives water-soluble. However, intrinsically water-soluble organic luminescence radicals have not been reported. In this study, we developed and evaluated a water-soluble TTM radical derivative that consists of a carbazole donor with polyethylene glycol (PEG) chain. An aqueous solution of the water-soluble TTM radical showed fluorescence, and the longitudinal relaxation time (T_1) of the water was shorter than that of pure water.

Keywords : Trityl radical; Polyethylene glycol (PEG); Luminescent radical; Carbazole

大気下で安定な有機発光ラジカルは赤-近赤外域の発光が得やすく常磁性分子であるという点からバイオイメージングへの応用が期待されている。TTM ラジカルのドナー・アクセプター型誘導体である TTM-Cz はその優れた発光特性と光耐久性から特に注目されているが、本質的に疎水性であることから水系での使用が必要となるバイオイメージングへの応用が難しく、その誘導体を界面活性剤で内包して水溶化する手法のみ報告されている[1)2)]。本研究で合成した TTM-Cz 誘導体である TTM-PEG3 は界面活性剤等を用いずに分子単独で水溶性を示す有機発光ラジカルであることを見出した(Fig. 1)。TTM-PEG3 は水中で近赤外発光を示し、H_2O のプロトンの縦緩和時間（T_1）を短縮する効果があることを確認した。

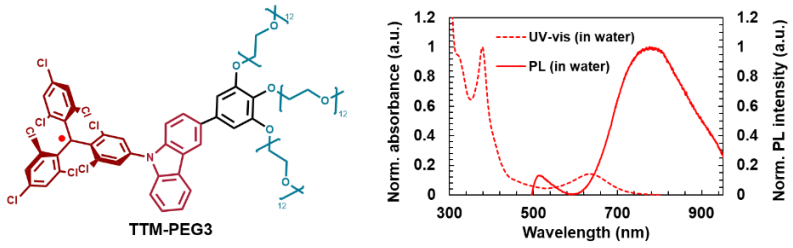

Fig.1. Chemical structure of water-soluble organic luminescent radical (left), UV-vis absorption and PL spectra of TTM-PEG3 in water (right).

1) X. Bai, W. Tan, A. Abdurahman, X. Li, and F. Li, *Dyes Pigm.*, **2022**, *202*, 110260.
2) Y. Xu, C. Teng, H. Dang, D. Yin, and L. Yan, *Talanta*, **2024**, *266*, 124948.

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カチオン部にジオールを持つイオン液体からアルケニルアンモニウムへの新規変換反応

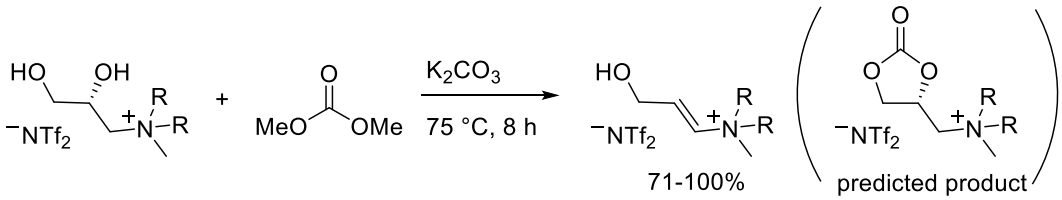
(山口大工) ○笹倉瑠那・川本拓治・上村明男
A novel conversion of ionic liquids containing a diol unit in the cationic part to alkenylammonium salts (*Department of Applied Chemistry, Yamaguchi University*) ○Runa SASAKURA, Takuji KAWAMOTO, Akio KAMIMURA

During the course of our study on solubility-switchable ionic liquids, we coincidentally found a novel conversion of the diol unit in the cation part to alkenylammonium salt. We will discuss on this novel reaction from the viewpoint of mechanism and optimization of the reaction.

Keywords : Ionic liquids, Alkenylammonium salts, Diol, Carbonate ester, Mechanistic study

イオン液体はカチオンとアニオンからなる常温で液体である塩であり，水や有機溶媒とは異なった物性や化学性を有する第三の液体として多くの化学者から興味が持たれている。一方でイオン液体の分離除去は困難であり，この問題に対する解決法が必要とされてきた。最近我々は，簡単かつ穏和な条件でイオン液体の脂溶性と水溶性の変換が可能となれば，その分離除去に新たな方法論を展開できると考えた。そしてアセタールとジオールの保護基の脱着によって溶解性を劇的に変化できるイオン液体を開発し，これをスイッチングイオン液体と名付けた。この化学は他の保護基を活用することでさらなる展開ができると考え，ジオール-環状炭酸エステルの変換を検討したところ，予想外にもジオールからの脱水反応が進行し合成しづらいアルケニルアンモニウム塩の新規合成法を見出したので報告する。

カチオン部位に 1,2-ジオールを有するアンモニウム型イオン液体 **1** に対して，グリセリンを環状炭酸エステルに変換する一般的条件である炭酸ジメチル–炭酸カリウム条件で反応を検討したところ，期待した環状炭酸エステルは得られず，代わりにアルケニルアンモニウム **2** が高収率で単一の生成物として得られた。アルケニルアンモニウムは付加環化やカップリング反応で興味が持たれている化合物群であるが，その合成方法は限られており新規な合成方法となると期待できる。発表ではこの脱水の反応機構についても述べる。



1 **2**

1) A. Kamimura, Y. Shiramatsu, K. Murata, T. Kawamoto, *Chem. Lett.* **2018**, *47*, 1079; A. Kamimura, K. Yanagisawa, N. Kaneko, T. Kawamoto, K. Fujii, *ACS Omega* **2022**, *7*, 48540.

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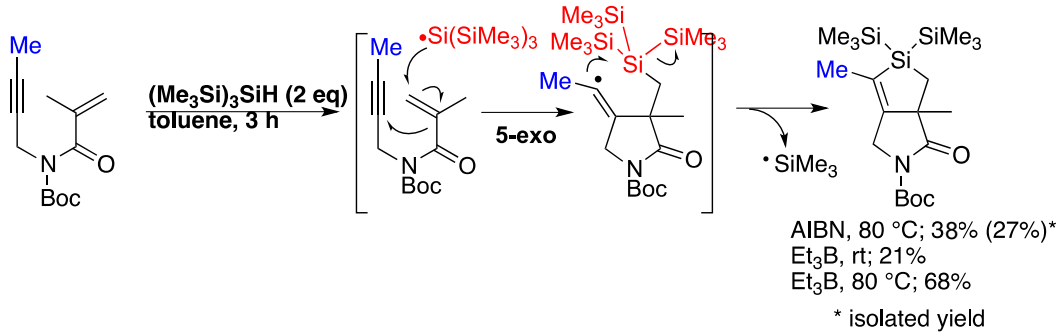
1,6-エンイン化合物のラジカルカスケード反応による二環性ジヒドロシロールの合成

（山口大工）○神田裕樹・石堂加奈子・川本拓治・上村明男
Preparation of bicyclic dihydrosiloles via radical cascade reaction of 1,6-enynes (*Department of Applied Chemistry, Yamaguchi University*) ○Yuki KANDA, Kanako ISHIDO, Takuji KAWAMOTO, Akio KAMIMURA

The reaction between 1,6-enyen and tris(trimethylsilyl)silane (TTMSS) progressed smoothly to give bicyclic dihydrosiloles in good yields. Use of AIBN as an initiator produced the desired bicyclic dihydrosilole, but the yield was low. Et3B worked as a good initiator of the reaction and the product was obtained in 80% yield. We will discuss about the details of the reaction.
Keywords : Radical reaction, Mechanistic study, 1,6-enyne, Silyl radical, Dihydrosiloles

アミド型 1,6-アザエンインはラジカル環化を経て種々の複素環に変換できる有用な前駆体である。最近我々はスズラジカルを用いることで、アルケンとアルキンの置換様式によって、二環性ジヒドロスタノール、ピペリジン、アゼピンがそれぞれ生じることを見いだした [1]。この反応はスズラジカルがアルケン末端を攻撃することで進行すると考えられる。同様のヘテロ原子中心ラジカルとして$(Me_3Si)_3SiH$ から発生できるシリルラジカルがある。我々は過去にこのラジカルも同様のラジカルカスケード反応を進行させて二環性ジヒドロシロールを与えることを見いだしている [2]。そこで今回アミド型 1,6-アザエンインに対して$(Me_3Si)_3SiH$ を作用させたところ、二環性ジヒドロシロールが得られたので報告する。

環化前駆体 **1** はこれまでに報告した方法で合成した [1]。前駆体 **1** に対してスズラジカルでの反応でよい結果を与えた AIBN を開始剤として反応させたところ、期待通りに環性ジヒドロシロール 2 が得られることがわかった。しかし収率が低かったので開始剤を Et_3B に変更して反応させたところ、目的のシロールが高収率で得られることがわかった。



1) A. Kamimura, K. Kohno, K. Ishido, N. Kamohara, T. Kawamoto, *Asian J. Org. Chem.* **2023**, e202300223
2) K. Miyazaki, Y. Yamane, R. Yo, H. Uno, A. Kamimura, *Beilstein J. Org. Chem.* **2013**, *9*, 1326.

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-3am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kohsuke Aikawa, Motohiro Yasui

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1141-3am-01]

Synthesis of 3-CF_3-indoles from HFO-1234ze *via* cross coupling and intramolecular cyclization

○Futa Yotsume[1,2], Shota Mizuno[2], Runa Kasahara[3], Takeshi Fujita[2], Munenori Inoue[2], Jyunji Ichikawa[2] (1. Kitasato University, 2. Sagami Central Resarch Institute, 3. University of Tsukuba)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1141-3am-02]

Aminofluorination of alkenes utilizing with N–F reagents under copper catalysis

○Akiya Adachi[1], Yuki Ito[1], Takuya Hashimoto[2], Kohsuke Aikawa[1], Kyoko Nozaki[1], Takashi Okazoe[1,3] (1. The School of Engineering, The University of Tokyo, 2. RIKEN, 3. AGC Inc.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1141-3am-03]

Synthesis of perfluorocycloalkyl compounds using fluorine gas and their property

○Toshiki Nakajima[1], Koji Kadota[1], Masafumi Sugiyama[1], Kohsuke Aikawa[1], Daisuke Kawaguchi[1], Takashi Okazoe[1,2] (1. Graduate School of Engineering, The University of Tokyo, 2. AGC Inc.)

English
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1141-3am-04]

Ventures into the Sulfur-Fluorine World

○Tim Gatzenmeier[1], Yue Liu[1], Misato Akamatsu[1], Takashi Okazoe[2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. Materials Integration Laboratories, AGC Inc., Tokyo, Japan)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1141-3am-05]

Mechanochemical S_NAr fluorination

○Tetsu Makino[1], Tamae Seo[1], Koji Kubota[1,2], Hajime Ito[1,2] (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC

Break

Japanese

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

[E1141-3am-06]

Optimization of Visible Light Induced Perfluoroalkylation of Aromatics Using Machine Learning

○Airi Yamaguchi[1], Tomoko Yajima[1] (1. Ocha. Univ)

Japanese

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

[E1141-3am-07]

Synthesis of Tetracenes with Fluoroalkyl Groups

○Moe Tasaki[1], Tsuyuka Sugiishi[1], Hideki Amii[1] (1. The Univ. of Gunma)

Japanese

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

[E1141-3am-08]

Direct Addition Reactions of Fluoroform to Aldehydes with Fluoride ions as a base

○Yuki Iwataki[1], Yusuke Higashi[1], Tsuyoshi Kawai[1], Tsumoru Morimoto[1] (1. Nara Inst. Sci. Technol.)

Japanese

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

[E1141-3am-09]

Synthesis of Trisubstituted Fluoroalkenes Enabled by Stereoselective Substitution of Vinyl Sulfoximine

○Masayuki Miyaoka[1], Yuichiro Tomishima[1], Kosuke Yasui[1], Koji Hirano[1] (1. Graduate School of Engineering, Osaka University)

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

[E1141-3am-10]

Regioselective difluorination of dodecahydro-*closo*-dodecaborate in the presence of α-cyclodextrin

○Hayato Nakamura[1], Kazuki Kurata[2], Tomoyuki Tajima[3] (1. Faculty of environmental science and technology, Okayama University, 2. Graduate school of environmental, life, natural science and technology, Okayama University, 3. Graduate school of environmental, life, natural science and technology, Okayama University)

Japanese

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

[E1141-3am-11]

Combination of photoredox catalysts and borates for radicalic difluoromethylation

○Yuen Huang[1], kakeru Konagaya[1], Shigekazu Ito[1] (1. Tokyo Institute of Technology)

Japanese

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

[E1141-3am-12]

Photoredox-catalyzed synthesis of tetrafluoroethylene-containing benzoindene derivatives.

○Mayuka Ukai[1], Motohiro Yasui[1], Shigeyuki Yamada[1], Tsutomu Konno[1] (1. Kyoto Institute of Technology)

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Japanese

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

[E1141-3am-13]

Copper-Catalyzed Cross-Coupling Reactions of Perfluoroalkylene Zinc Reagents and Aryl Halides

○Tomoya Baba[1], Daisuke Inoue[2], Kazuya Kubo[3], Tomohiro Agou[3] (1. University of Hyogo, 2. TOSOH FINECHEM CORPORATION, 3. Graduate School of Science, University of Hyogo)

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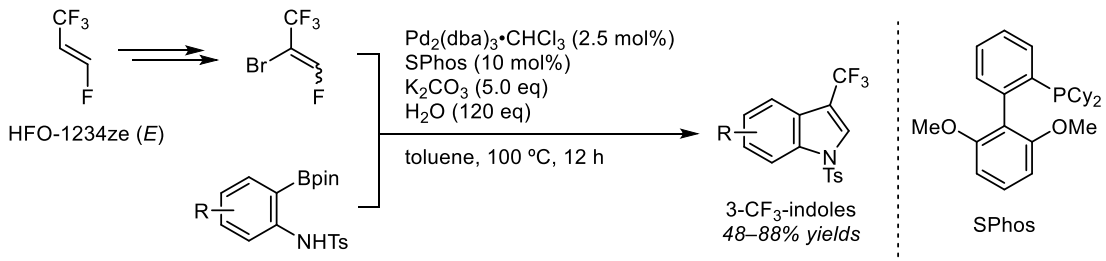
HFO-1234ze を出発物質としたクロスカップリングと分子内環化による 3-CF_3-インドールの合成

（相模中研 [1]・北里大理 [2]・筑波大数理 [3]）○四ツ目 楓太 [1,2]・水野 翔太 [1]・笠原 留奈 [3]・藤田 健志 [1]・井上 宗宣 [1]・市川 淳士 [1]

Synthesis of 3-CF_3-indoles from HFO-1234ze *via* cross coupling and intramolecular cyclization ([1]*Sagami Chemical Research Institute*, [2]*School of Science, Kitasato University* [3]*Faculty of Pure and Applied Sciences, University of Tsukuba*) ○Futa Yotsume,[1,2] Shota Mizuno,[1] Runa Kasahara,[3] Takeshi Fujita,[1] Munenori Inoue,[1] Junji Ichikawa[1]

Because of their bioactivities, 3-CF_3-indoles have attracted immense attention in the fields of pharmaceuticals and agrochemicals. However, there are few effective methods for synthesizing 3-CF_3-indoles. As part of our research on upcycling of HFOs, we envisioned a method for constructing the indole ring through Suzuki–Miyaura cross coupling of a brominated HFO-1234ze (CF_3CH=CHF) and *o*-boryl aniline derivatives, followed by nucleophilic 5-*endo-trig* cyclization at the vinylic position of fluoroalkenes.[1)] On the basis of this approach, we found that a $Pd_2(dba)_3$/SPhos catalyst system in the presence of water and K_2CO_3 in toluene gave the corresponding 3-CF_3-indoles in high yields.
Keywords : Fluorine, Hydrofluoroolefin, Upcycle, Trifluoromethyl group, 5-endo-trig cyclization

3-CF_3-インドールは，種々の生物活性を示すために医農薬としての利用が期待される．しかし，3-CF_3-インドールの効率的な合成例は少ない．そこで我々は，ヒドロフルオロオレフィン(HFO)のアップサイクルに向けた研究の一環として，ビニル位フッ素を脱離基とするビニル求核置換(S_NV)反応を分子内に適用し，CF_3 化したインドール環の構築を考えた [1)]．具体的には，フルオロアルケンである HFO-1234ze (CF_3CH=CHF)を臭素化後，*o*-ボリルアニリン誘導体との鈴木–宮浦クロスカップリングと続く 5-*endo-trig* 環化により，3-CF_3-インドールを合成する手法である．実際に両基質を，$Pd_2(dba)_3$ 触媒，SPhos 配位子および水の存在下，K_2CO_3 を塩基としてトルエン溶媒中 100 °C に加熱したところ，3-CF_3-インドールを収率良く得ることに成功した．



1) Ichikawa, J.; Wada, Y.; Fujikawa, M.; Sakoda, K. *Synthesis* **2002**, 1917–1936.

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N–F 反応剤を用いた銅触媒によるアルケンのアミノフッ素化反応

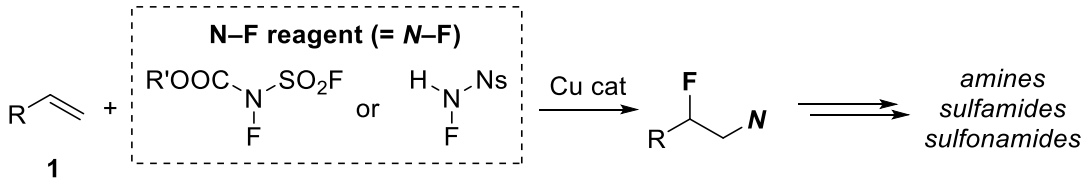
（東大院工[1]、理研[2]、AGC[3]）○足立 晶哉[1]、伊藤 悠貴[1]、橋本 卓也[2]、相川 光介[1]、野崎 京子[1]、岡添 隆[1,3]

Copper-catalyzed aminofluorination of alkenes using N–F reagents ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*RIKEN,* [3]*AGC Inc.*) ○Akiya Adachi,[1] Yuki Ito,[1] Takuya Hashimoto,[2] Kohsuke Aikawa,[1] Kyoko Nozaki,[1] Takashi Okazoe[1,3]

β-Fluoroamines, which possess an amino and a fluoro group at a vicinal position, have become more prevalent in medicinal chemistry. As one of the synthetic methodologies of such compounds, the direct aminofluorination of alkenes is a convenient one, because both a nitrogen and a fluorine atom can be introduced at the same time. In this context, NFSI is one of the most attractive molecules as an aminofluorinating reagent. However, the transformation of the corresponding products remains problematic because deprotection of the benzenesulfonyl group originating from NFSI requires harsh acidic reaction conditions. Herein, we have developed the copper-catalyzed aminofluorination of alkenes using N-F reagents with easily transformable substituents and application to transformations of the products. Indeed, we achieved the efficient transformations of amino moieties into amines, sulfamides, and sulfonamides under the mild reaction conditions.

Keywords : Aminofluorination; β-Fluoroamine; NFSI; N-F reagent; Nosyl Group

β-フルオロアミンはアミノ基とフルオロ基が隣接した化合物で、含フッ素医薬品で用いられる化合物群の一つである。その合成法の中でアルケンへ両官能基を一挙に導入できるアミノフッ素化反応は合成化学上魅力的である。特に、NFSI をアミノフッ素化剤として用いた反応は有用だが、一般的に導入したベンゼンスルホニル基の脱保護に過激な酸性条件などを必要とするため、アミノフッ素化生成物からの分子変換は最近の我々の研究報告[1]以外は報告例がない[2][3]。このような背景のもと、本研究では分子変換容易な置換基を有する N-F 反応剤を設計・合成し、それらを用いた銅触媒によるアミノフッ素化反応を開発するとともに生成物からアミンなどへの様々な分子変換に成功した。実際、我々が開発した N–F 反応剤[1][4]を用いて Cu 触媒存在下アルケン **1** を反応させたところ、Pd 触媒を用いた際の生成物とは位置異性体の関係にある、目的のアミノフッ素化体が良好な収率で得られた。続く脱保護や分子変換反応にて、第一級・第二級アミンやスルファミド、スルホンアミドへと変換することができた。



[1] Y. Ito, A. Adachi, K. Aikawa, K. Nozaki, T. Okazoe *Chem. Commun.* **2023**, *59*, 9195; [2] S. Qiu, T. Xu, J. Zhou, Y. Guo, G. Liu *J. Am. Chem. Soc.* **2010**, *132*, 2856; [3] H. Zhang, Y. Song, J. Zhao, J. Zhang, Q. Zhang *Angew. Chem. Int. Ed.* **2014**, *53*, 11079; [4] Y. Oe, R. Yoshida, A. Tanaka, A. Adachi, Y. Ishibashi, T. Okazoe, K. Aikawa, T. Hashimoto *J. Am. Chem. Soc.* **2022**, *144*, 2107.

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フッ素ガスを用いた環状ペルフルオロアルキル化合物の合成とその性質

（東大院工[1]、AGC[2]）○中島 稔喜[1]、門田 晃司[1]、杣山 真史[1]、相川 光介[1]、川口 大輔[1]、岡添 隆[1,2]

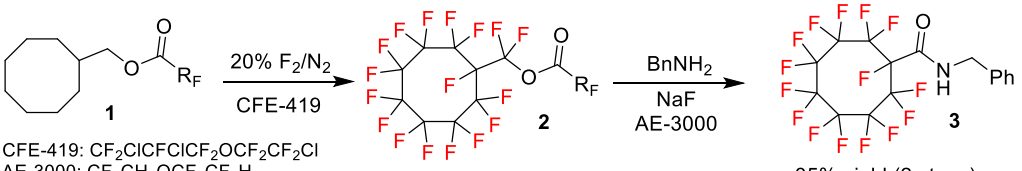
Synthesis of perfluorocycloalkyl compounds using fluorine gas and their property ([1]*Graduate School of Engineering, The University of Tokyo,* [2]*AGC Inc.*) ○Toshiki Nakajima[1], Koji Kadota[1], Masafumi Sugiyama[1], Kohsuke Aikawa[1], Daisuke Kawaguchi[1], Takashi Okazoe[1,2]

The properties of perfluoroalkyl (R_F) compounds are explained by the theory[1] associated with the aggregation structure. Dipole moment of the R_F chain is canceled by packing, and thus the aggregating properties appear. However, this theory is only applicable to linear R_F compounds.

In order to deeply understand the properties of R_F compounds, we focused on perfluorocycloalkyl (cyclo R_F) compounds. Compared to linear R_F compounds, the conformation of cyclo R_F compounds is restricted, and the aggregation property is assumed to be different from that of linear R_F compounds. However, there are only few reports of cyclo R_F compounds[2], and there are no reports of syntheses of functionalized cyclo R_F compounds. Based on this background, we synthesized the functionalized cyclo R_F compounds using fluorine gas[3] and investigated their properties.

Keywords : Fluorine; Fluorine gas; Fluorination; Perfluoroalkyl compounds; SDA theory

高度にフッ素化された化合物は特異な性質を示す。例えば、ペルフルオロアルキル（R_F）化合物は高い熱安定性、撥水撥油性、低誘電率および低屈折率を示すことが知られている。R_F 化合物の物理的性質は、凝集構造と関連付けた理論（階層双極子アレー(SDA)理論）[1]により説明されている。SDA 理論によると、R_F 鎖の炭素数が 7 以上の場合、らせん構造を形成した R_F 鎖は双極子モーメントに起因する配向力により自己集合する。R_F 鎖の双極子モーメントはパッキングにより相殺されるため、前述の特性が発現する。しかしながら、これらは鎖状 R_F 化合物に基づく知見である。そこで、R_F 化合物の性質をさらに深く理解するため、環状 R_F 化合物に着目した。環状 R_F 化合物は鎖状 R_F 化合物と比較して取りうるコンフォメーションが制限され、その凝集性も鎖状 R_F と異なると想定される。しかし、環状 R_F 化合物の報告例は極めて限られており[2]、中でも官能基化されたものの合成例はない。このような背景のもと、本研究では、化合物 **1** からフッ素ガスによる C–H 結合のラジカルフッ素化[3]を用いて、官能基化された環状 R_F 化合物 **3** の合成を行い、その性質に関する調査を行った。



CFE-419: $CF_2ClCFClCF_2OCF_2CF_2Cl$
AE-3000: $CF_3CH_2OCF_2CF_2H$
R_F: -$CF(CF_3)$-$OCF_2CF(CF_3)$-$OCF_2CF(CF_3)$-$OCF_2CF_2CF_3$

[1] T. Hasegawa, *Chem Rec.* **2017**, *17*, 903. [2] R. Lagow, H. Huang, *Bull. Soc. Chim. Fr.* **1986**, 6, 993. [3] T. Okazoe, *et al*. *Adv. Synth. Catal.* **2001**, *323*, 215.

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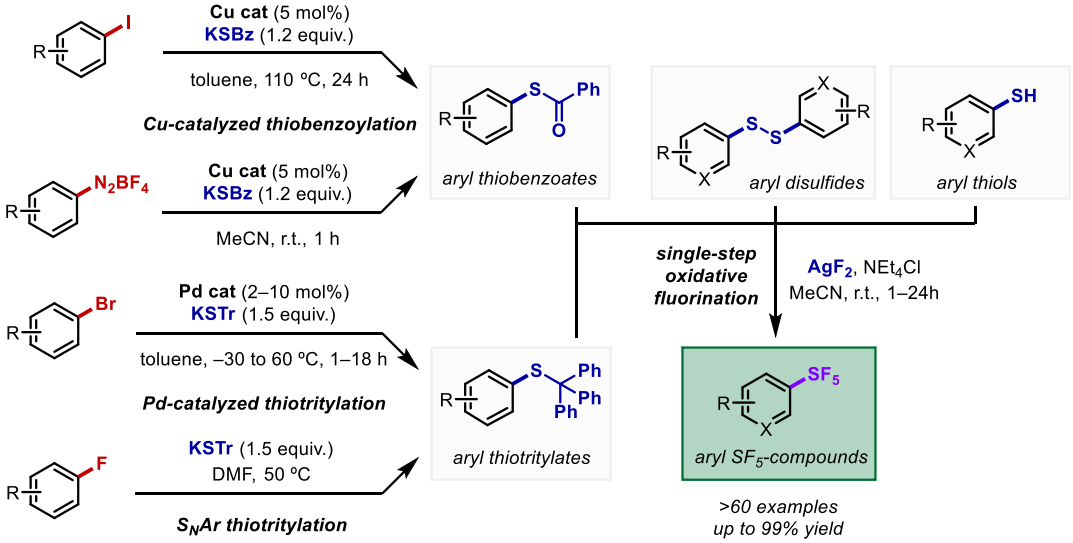
Ventures into the Sulfur-Fluorine World

([1]*The University of Tokyo*, [2]*AGC Inc.*, [3]*Itsuu Research Institute*) ○Tim Gatzenmeier[1,3], Yue Liu[1], Misato Akamatsu[1], Takashi Okazoe[2], Kyoko Nozaki[1]

Keywords: pentafluorosulfanylation, non-PFAS, thiolation cross-coupling, oxidative fluorination, sulfur-fluorine functional groups

Sulfur-fluorine functional groups, such as the pentafluorosulfanyl group (SF_5) feature many attractive properties such as increased size, electronegativity, lipophilicity and alternative molecular geometries.[1] Importantly, their favorable degradation to inorganic fluoride in the soil and their classification as non-PFAS underline their high potential for future applications in agro- and medicinal chemistry. We report here how the discovery of a direct pentafluorosulfanylation of thiolated arenes led to a generalized synthetic approach toward aryl– and heteroaryl SF_5-compounds from various common building blocks, such as aryl fluorides, bromides, iodides and diazonium salts.[2] The combination of onium halides with silver(II) fluoride (AgF_2) provided drastically enhanced oxidative fluorination conditions that enabled the single-step conversion of various thiophenol derivatives to SF_5-compounds in high yields and broad scope. Additionally, we found that aryl thiotritylates are convenient intermediates to also access the rest of the aryl sulfur-fluorine functional group family, such as SF_4Cl, SO_2F and others. This led us to a novel comprehensive synthetic approach to these compounds from various common building blocks through a thiolation cross-coupling and oxidative fluorination strategy. Many the obtained products have applications for pharmaceuticals, crop protection, materials and catalysts demonstrating the prospect for future applications.



1) M. F. Sowaileh, R. A. Hazlitt, D. A. Colby *ChemMedChem* **2017**, *12*, 1481 2) T. Gatzenmeier, Y. Liu, M. Akamatsu, T. Okazoe, K. Nozaki, **2023** *submitted* doi:10.26434/CHEMRXIV-2023-JZN11.

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メカノケミカル芳香族求核的フッ素化反応

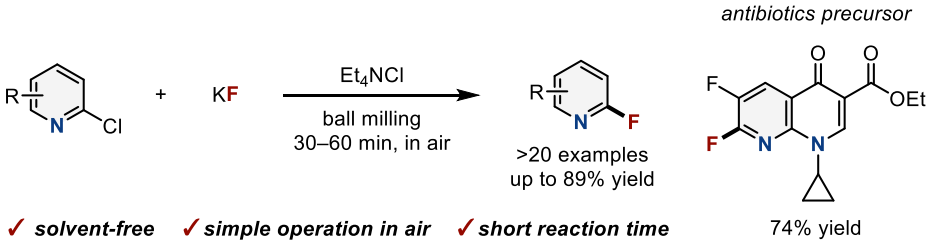
（北大院工[1]・北大 WPI-ICReDD[2]）○牧野 哲[1]・瀬尾 珠恵[1]・久保田 浩司[1,2]・伊藤 肇[1,2]

Mechanochemical nucleophilic aromatic fluorination ([1]*Graduate School of Engineering, Hokkaido University*, [2]*WPI-ICReDD, Hokkaido University*) ○Tetsu Makino,[1] Tamae Seo,[1] Koji Kubota,[1,2] Hajime Ito[1,2]

Aromatic fluorine compounds play an important role in the development of pharmaceuticals and agrochemicals. Nucleophilic aromatic fluorination reaction represents one of the most efficient synthetic methods to access a wide range of aromatic fluorides. However, the previously developed solution-based conditions require high-boiling point solvents that are difficult to remove, long reaction times and strictly dehydrated conditions, greatly reducing the practical utility.[1] In this study, we found that solvent-free mechanochemical conditions[2] using KF as a fluorination reagent and Et_4NCl as an additive enabled highly efficient fluorination of heteroaryl chlorides. This reaction is fast and completed within 60 min. Notably, the developed mechanochemical protocol does not require high-boiling point reaction solvents and all synthetic operation can be carried out in air.

Keywords : Mechanochemistry; Ball mill; Solid state reaction; Fluorination; Phase transfer

芳香族フッ素化合物は、医薬品や農薬の開発において重要な役割を担っている。それらの代表的な合成法として、芳香族求核置換反応によるフッ素化が挙げられる。しかし、従来の溶液条件の方法では、除去が困難な高沸点溶媒や長い反応時間および厳密な脱水条件が必要であり、実用性の観点から改善の余地がある[1]。本研究では、ボールミルを用いた無溶媒メカノケミカル条件下[2]、フッ素化試薬として KF および添加剤として Et_4NCl を用いるとヘテロアリールクロリドの固体フッ素化が効率良く進行することを見出した。本反応は速やかに進行し、60 分以内で完結する。また、高沸点の反応溶媒が不要な上、すべての実験操作を空気下で行うことができる。



1) See, Y. Y.; Morales-Colón, M. T.; Bland, D. C.; Sanford, M. S. *Acc. Chem. Res.* **2020**, *53*, 2372.

2) Kubota, K.; Seo, T.; Koide, K.; Hasegawa, Y.; Ito, H. *Nat. Commun.* **2019**, *10*, 111.

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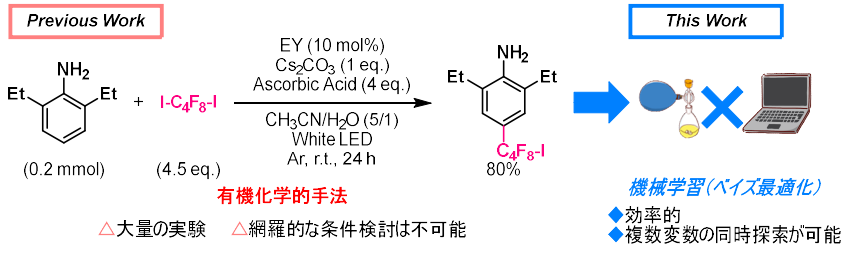
機械学習を利用した芳香族化合物の可視光ペルフルオロアルキル化反応の最適化

（お茶女大院理）○山口 愛織・矢島 知子
Optimization of Visible Light Induced Perfluoroalkylation of Aromatics Using Machine Learning (*Graduate School of Chemistry, Ochanomizu University*) ○ Airi Yamaguchi, Tomoko Yajima

Fluorinated organic compounds are widely used in our daily lives, owing to specific properties of fluorine. However, few of fluorinated organic compounds exist in nature, thus, the synthetic route development for those compounds is important. However, synthetic route development necessitates many experiments, and a comprehensive examination of all conditions is impossible. To solve those problems, in study, we introduced Bayesian optimization, one of the types of machine learning, into the investigation of visible-light-induced perfluoroalkylation of aromatics catalyzed by Eosin Y. *Keywords : Photo Perfluorolakylation; Optimization Using Machine Learning; Diiodoperfluoroalkylation; Radical Reaction; Fluorinated Aromatics*

含フッ素有機化合物は、代謝安定性や疎水性の向上などのフッ素原子に由来する特異的な性質を有することから、医農薬品などの生理活性物質や機能性材料として、その有用性が幅広く注目されており、その合成法の開発は重要な課題である。しかしながら、有機化学的手法での合成経路開発では、最適条件を得るために大量の実験が必須である。これらの課題を解決するために、有機化学への機械学習の導入が期待されている。そこで、本研究では、機械学習を芳香族化合物のパーフルオロアルキル化に導入することで、条件研究の効率を向上させることを目指した。



これまでに当研究室では、2,6-ジエチルアニリン (0.2 mmol) 、1,4-ジヨードペルフルオロブタン (4.5 eq.) 、EY (10 mol%) 、Cs_2CO_3 (1eq.) 、アスコルビン酸 (4 eq.) を CH_3CN (5 mL) および水 (1 mL) で可視光照射することで、目的生成物を 80%の収率で得ることを報告している。[1] そこで、本研究ではこの反応に機械学習の一種であるベイズ最適化を適用することとした。ベイズ最適化は、複数の変数を同時に探索することに優れた機械学習手法であり、最小限の実験で反応を最適化することが可能となる。本研究では、フッ素源、塩基、還元剤の当量およびアセトニトリルの添加量を変数として、それぞれの変数を標準化した後に異なる基質に対してベイズ最適化を行った結果について報告する。

1) 山口愛織、神原將、矢島知子、第 13 回 CSJ 化学フェスタ、P2-047、2023 年 10 月

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フルオロアルキル基を有するテトラセンの合成

（群馬大院理工）○田﨑萌愛、杉石露佳、網井秀樹

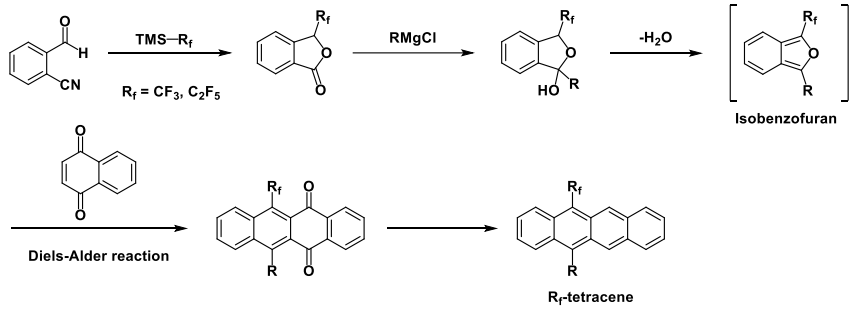
Synthesis of Tetracenes with Fluoroalkyl Groups

(*Graduate School of Science and Technology, Gunma University*) ○Tasaki Moe, Tsuyuka Sugiishi, Hideki Amii

Acene compounds such as pentacene, which have a linearly fused structure of benzene rings, are expected to have excellent properties as organic semiconductor materials, and their functions improve as the number of rings increases. However, acenes without substituents have low solubility in organic solvents, and those with more rings than pentacene are considered insoluble in organic solvents. To solve this problem, we aim to introduce fluorine-containing substituents into acene compounds by a simple method, taking advantage of the solubility enhancement and oxidation resistance of fluorine. Furthermore, when fluorine-containing substituents are introduced into π-conjugated compounds, it is possible to obtain acene compounds that are stable to oxygen in air by controlling the electron transition energy of the acene skeleton through the electron-withdrawing effect by fluorine atoms. In this presentation, we will introduce the synthesis of fluoroalkyl tetracenes using fluoroalkyl isobenzofurans with an *o*-quinodimethane skeleton.

Keywords : Fluorine; Acene; Isobenzofuran; Nucleophilic perfluoroalkylation; Diels-Alder reaction

ベンゼン環が直鎖状に縮環した構造をもつアセン化合物は、有機半導体材料として優れた機能が期待され、環の数が増えるその機能は向上する。しかし、置換基を持たないアセン化合物は有機溶媒への溶解度が低く、ペンタセンよりも環数が多いものは不溶とされている。この問題を解決するため、フッ素の溶解性向上や耐酸化性などの特性を活かし、簡便な方法で含フッ素置換基をアセン化合物に導入することを目指す。さらに、π共役系化合物に含フッ素置換基を導入した場合、電子求引効果によりアセン骨格の電子遷移エネルギーを制御することで、空気中の酸素に対して安定なアセン化合物を得ることが可能である。本発表では、*o*-キノジメタン構造をもつイソベンゾフランを用いたテトラセンの合成について紹介する。



Scheme 1 Synthesis of Trifluoromethyl and Pentafluoroethyl Tetracenes.

1) Inaba, M.; Sakai, T.; Shinada, S.; Sugiishi, T.; Nishina, Y.; Shibata, N.; Amii, H. *Beilstein J. Org. Chem.* **2018**, *14*, 182.

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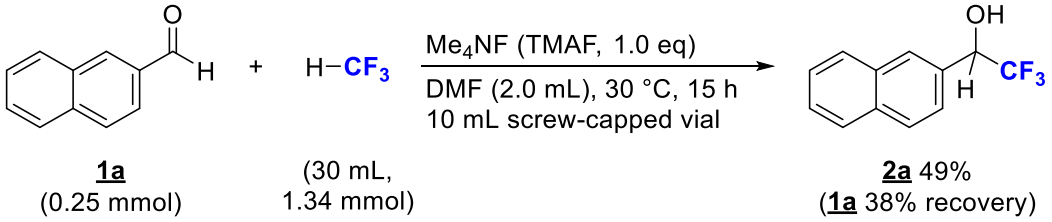
フッ化物イオンを塩基としたフルオロホルムのアルデヒドへの直接付加反応

（奈良先端大物質）○岩滝 裕基・東 裕亮・河合 壯・森本 積
Direct Addition Reactions of Fluoroform to Aldehydes with Fluoride ions as a Base (*Division of Materials Science, Nara Institute of Science and Technology (NAIST)*) ○Yuki Iwataki, Yusuke Higashi, Tsuyoshi Kawai, Tsumoru Morimoto

We have developed a direct addition reaction of fluoroform HCF_3 with aldehydes using fluoride ions as a triggering base. The reaction of HCF_3 with naphthaldehyde in the presence of the strong base tetramethylammonium fluoride under nonaqueous conditions afforded an alcohol by nucleophilic addition of CF_3 to the aldehydic carbon.
Keywords : Fluoroform, Ammonium Fluoride, Trifluoromethylation, Aldehyde

フルオロホルム HCF_3 は、含フッ素樹脂やポリビニリデン、冷媒など様々なフッ素系材料の製造過程で生じ、年産 20,000 トンのペースで副生する。そのため、HCF_3 を含フッ素官能基の原料とした直接的な分子変換法（トリフルオロメチル化反応）が数多く研究例が報告されている。今回我々は、HCF_3（pK_a 31）よりもはるかに塩基性の小さいフッ化アンモニウム類（例：TMAF、pK_b 15）を用いても、系中で CF_3 陰イオンを発生させ、それを求核剤として利用する反応を見出した。

ナフトアルデヒド（**1a**）と HCF_3 とを、1.0 当量のテトラフルオロアンモニウムフルオリド（TMAF）存在下で無水 DMF 中 30°C、15 時間反応させたところ、未反応の **1a** 38%とともに、**1a** がトリフルオロメチル化されたアルコール誘導体 **2a** が収率 49%で得られた（図）。**2a** の生成は使用する溶媒の極性に大きく影響を受け、上記 DMF 以外に DMSO や DMAc 中では生成が観測されるが、THF、CH_3CN、$PhCH_3$ 中では全く生成しなかった。これまでに報告されている類似の反応と比べて、本反応は、固体塩基である TMAF の取り扱いの容易さ、室温付近での反応温度、から簡便に実施できる手法となる。



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スルホキシイミンを脱離基とした立体選択的な置換反応を鍵とする 3 置換フルオロアルケンの合成

(阪大院工[1]・阪大工学部[2]) ○宮岡 真之[1]・富島 佑一郎[2]・安井 孝介[1]・平野 康次[1]
Synthesis of Trisubstituted Fluoroalkenes Enabled by Stereoselective Substitution of Vinyl Sulfoximine ([1]*Graduate School of Engineering, Osaka University,* [2]*School of Engineering, Osaka University*) ○Masayuki Miyaoka[1], Yuichiro Tomishima,[2], Kosuke Yasui,[1] Koji Hirano[1]

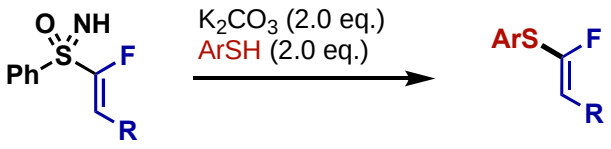
(Thio)ethers or amines bearing a 1-fluorovinyl group are intriguing bioisosteres of the (thio)carbamate and urea groups widely found in pharmaceutical and agrochemical molecules. Among various synthetic methods, substitution reactions of *gem*-difluoroalkenes are the most versatile.[1)] However, the poor stereoselectivity of the product often remains a challenge.

In this study, the compound **1**, in which one of the fluorines of *gem*-difluoroalkene is replaced with a sulfoximine, was synthesized as an alternative, and its reactivity was investigated. We found that the reaction of **1** with thiophenol, in the presence of a base, provided sulfide **2** in high yield and with complete stereoselectivity through the substitution of the sulfoximine. Since, in stark contrast, the corresponding sulfone could not efficiently provide **2**, which suggested that sulfoximine is a better leaving group than sulfone.

Keywords : sulfoximine; substitution reaction; trisubstituted alkene; C–S bond cleavage

1-フルオロビニル基をもつ (チオ)エーテルやアミンは医農薬分子に広く見られる(チオ)カルバメート基やウレア基の生物学的等価体である。様々な合成法のうち、*gem*-ジフルオロアルケンの置換反応が最も汎用される[1)]一方、この反応では生成物の立体選択性の低さがしばしば課題となる。

本研究では、*gem*-ジフルオロアルケンのフッ素の一つをスルホキシイミンで置き換えた化合物 **1** をフルオロアルケン代替物として合成し、その反応性を調査した。その結果、塩基の存在下に **1** とチオフェノールとを反応させると、スルホキシイミンと置換したスルフィド **2** が良好な収率、かつ完全な立体選択性で得られることを見出した。対応するスルホンをこの反応条件にさらすと **2** は低収率にとどまった。このことから、スルホキシイミンの脱離能がスルホンよりも高いことが示唆された。



1 **2**

1) (a) Lu, M.-Z.; Goh, J.; Maraswami, M.; Jia, Z.; Tian, J.-S.; Loh, T.-P. *Chem. Rev*. **2022**, *122*, 17479. (b) Review: Drouin, M.; Hamel, J.-D.; Paquin, J.-F. *Synthesis* **2018**, *50*, 881.

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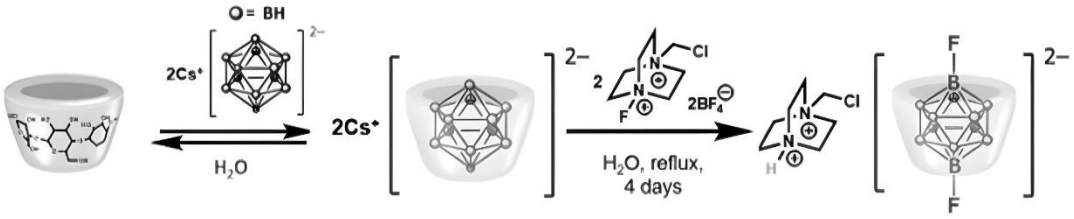
α-シクロデキストリン存在下におけるドデカハイドロ-*closo*-ドデカボレートの位置選択的ジフルオロ化反応

(岡山大環境理工[1]・岡山大院環境生命自然科学[2]・岡山大学術研究院環境生命自然科学[3]) ○中村 駿斗[1]・倉田 一輝[2]・田嶋 智之[3]
Regioselective difluorination of dodecahydro-*closo*-dodecaborate in the presence of α-cyclodextrin ([1]*Faculty of environmental science and technology, Okayama University*, [2,3]*Graduate School of environmental, life, natural science and technology, Okayama University*) ○Hayato Nakamura[1], Kazuki Kurata[2], Tomoyuki Tajima[3]

Dodecahydro-*closo*-dodecaborate dianion ($[B_{12}H_{12}]^{2-}$) is a molecular cluster with an icosahedral structure composed of 12 borons and hydrogens. There are few examples of regioselective substitution reactions of dodecahydro-*closo*-dodecaborates. Moreover, fluorination is required molecular fluorine or hydrogen fluoride, whose notorious toxicity and explosive tendencies limit its application in research[1)]. In this study, it was found that the regioselective difluorination reaction proceeds by the reaction of dodecahydro-*closo*-dodecaborate with Selectfluor™ in the presence of α-cyclodextrin[2)].

Keywords : Boron cluster; Cyclodextrin; Fluorination

ドデカハイドロ-*closo*-ドデカボレートジアニオン ($[B_{12}H_{12}]^{2-}$) は、12 個のホウ素と水素から構成される分子クラスターである。この分子クラスターの位置選択的な置換反応の例は稀で、フッ素化についてはフッ化水素やフッ素ガスのような取り扱いが難しいフッ素化剤を用いた例に限られている[1)]。本研究では、α-シクロデキストリン存在下[2)]、ドデカハイドロ-*closo*-ドデカボレートに 2 当量の Selectfluor™ を加えると、位置選択的なジフルオロ化反応が進行することを明らかとした。



1) A. A. Popov *et. al*. *J. Am. Chem. Soc*. **2009**, *131*, 18393.
2) K. Rissanen, D. Gabel, W. M. Nau *et. al. Angew. Chem. Int. Ed*. **2015**, *54*, 6852.

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光レドックス触媒とボレートを組み合わせたラジカル的ジフルオロメチル化反応

（東工大物質理工）○黄 宇恩・小長谷 翔・伊藤 繁和
Combination of Photoredox Catalysts and Borates for Radicalic Difluoromethylation (*School of Materials and Chemical Technology, Tokyo Institute of Technology*)○Yu-En Huang, Kakeru Konagaya, Shigekazu Ito

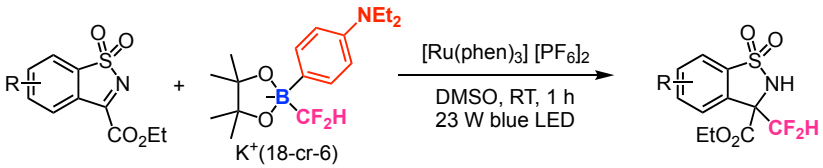
Previously we reported the synthesis of a difluoromethylborate [pinB$^-$(Ph)CF_2H][K$^+$(18-cr-6)] as an air-stable crystalline compound. The preliminary DFT calculations indicated that one-electron oxidation of the difluoromethylborate could generate difluoromethyl radical (·CF_2H) which could be useful for synthesizing various difluoromethylated compounds. Recently, we demonstrated the isonitrile insertion of 2-isocyano-1,1'-biphenyls affording 6-(difluoromethyl)phenanthridines by using a chemical oxidation condition.

To develop more efficient synthetic procedures with the difluoromethylborates, we examined difluoromethylation reactions with imines by using photoredox catalysts. The most appropriate borate **1** was allowed to react with cyclic sulfonyl imines **2** in the presence of photocatalyst $[Ru(phen)_3][PF_6]_2$, and the corresponding difluoromethylated cyclic sulfonamides were obtained in up to 88% isolated yield and >99% NMR yield within one hour reaction time. The details including the reaction conditions and the substrate scope will be presented and discussed.

Keywords : Fluorine; Borates; Photoredox Catalysts; Heterocycles

当研究室では以前、ジフルオロメチルボレート[pinB$^-$(Ph)CF_2H][K$^+$(18-cr-6)]を大気中安定な固体として合成単離している [1]。このボレートについて DFT 計算を行ったところ、1 電子酸化することで新規なラジカル的ジフルオロメチル化試薬として利用できる可能性が見出された。実際に化学酸化を用いることで、イソシアノビフェニルからジフルオロメチルフェナントリジンの合成をデモンストレーションしている [2]。

本研究では、光レドックス触媒を用いたラジカル的なジフルオロメチル化反応に着目して検討を行った。すなわち、最適化されたジフルオロメチルボレート **1** と環状スルホンイミン **2** を基質として使用し、光触媒として$[Ru(phen)_3][PF_6]_2$ を用いてジメチルスルホキシド溶媒中、1 時間反応させた。その結果、目的のジフルオロメチル化された環状スルホンアミド **3** を最大 88%の単離収率と>99%の NMR 収率で得ることができた。反応の条件検討などの詳細については当日報告する。



2 **1** **3**

1) A. Yokawa, S. Ito, *Chem. Asian J.* **2020**, *15*, 3432.
2) K. Konagaya, Y.-E. Huang, K. Iwami, T. Fujino, R. Abe, R. Parchment-Morrison, K. M. Kojima, I. McKenzie, S. Ito, S. *J. Org. Chem.* **2023**, *88*, 8042.

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光レドックス触媒によるテトラフルオロエチレン基を有するベンゾインデン誘導体の合成

（京工繊大工芸）○鵜飼茉由佳、安井基博、山田重之、今野勉

Photoredox-catalyzed synthesis of tetrafluoroethylene-containing benzoindene derivatives (*Kyoto Institute of Technology, Faculty of Molecular Chemistry and Engineering*) ○Mayuka Ukai, Motohiro Yasui, Shigeyuki Yamada, Tsutomu Konno

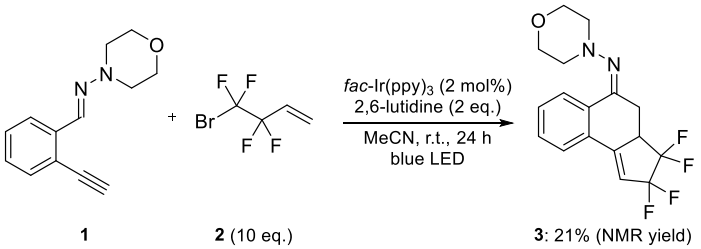
o-Ethynylbenzaldehyde hydrazone **1** and 4-bromo-3,3,4,4-tetrafluoro-1-butene (BTFB) (**2**) were treated with a photoredox catalyst, *fac*-Ir(ppy)$_3$ and 2,6-lutidine under blue LED irradiation at room temperature for 24 hours to give benzoindene derivatives including a tetrafluoroethylene (CF_2CF_2) group **3** in the ring skeleton.

Keywords: Tetrafluoroethylene, Photoredox, Hydrazone, Benzoindene, BTFB

テトラフルオロエチレン (CF_2CF_2) 基を有する化合物はフッ素原子に起因する特異な性質を持つことから医薬品化学を中心に注目を集めているが、CF_2CF_2 基を環骨格内に導入する方法は限られている [1]。そこで、CF_2CF_2 基を有する新規化合物を効率的に合成する方法を開発することで、医薬品シードの創製につながると考えた。

これまでに、エチニルベンズアルデヒドヒドラゾンとアルケニル基をもつα-ブロモジカルボニル化合物から、光レドックス触媒としてIr錯体を用いたラジカルカスケード反応による縮合三環式化合物の合成が報告されている[2]。我々は、CF_2CF_2基の導入ユニットとして安価に入手可能な4-ブロモ-3,3,4,4-テトラフルオロ-1-ブテン (BTFB) (**2**) の性質に着目した。すなわち、CF_2CF_2基による電子求引性誘起効果を受けたBTFBのC-Br結合が、光レドックス触媒により化学選択的に一電子還元を受けることで、同様のラジカルカスケード反応が進行し、CF_2CF_2基含有三環式化合物の合成が可能になると考えた。

アセトニトリル溶媒中、2 mol%の光レドックス触媒 *fac*-Ir(ppy)$_3$ 存在下、市販原料から 3 工程で合成可能な *o*-エチニルベンズアルデヒドヒドラゾン **1** に、2 当量の 2,6-lutidine と 10 当量の BTFB (**2**) を作用させ、LED 照射下、室温で 24 時間撹拌することで、環骨格内に CF_2CF_2 基を有するベンゾインデン誘導体 **3** が得られた。本検討から、BTFB と光レドックス触媒から生成するフルオロアルキルラジカルが首尾よく末端アルキンと反応し、カスケード反応が進行することが示唆された。



1 **2** (10 eq.) **3**: 21% (NMR yield)

1) B. Linclau, *et al. Org. Lett*. **2008**, *10,* 3673-3676.
2) C. Zhou, *et al. Chem. Commun.* **2017**, *53*, 2036-2039.

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銅触媒を用いたペルフルオロアルキレン亜鉛反応剤とアリールハライド類とのクロスカップリング反応

(兵庫県立大理[1]・兵庫県立大院理[2]・東ソー・ファインケム(株)[3]）○馬場智也[1]・久保和也[2]・井上大輔[3]・吾郷友宏[2]
Copper-Catalyzed Cross-Coupling Reactions of Perfluoroalkylene Zinc Reagents and Aryl Halides ([1]Department of science, *University of Hyogo*, [2]*Graduate School of Science, University of Hyogo,* [3]*TOSOH FINECHEM CORPORATION*) ○Tomoya Baba,[1] Kazuya Kubo,[2] Daisuke Inoue,[3] Tomohiro Agou[2]

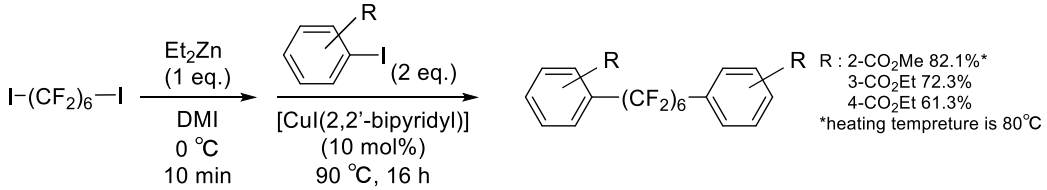
Fluoropolymers have been applied in many fields because of their various properties such as heat and chemical resistances. Fluorinated copolymers consisting of perfluoroalkylene and arylene groups are expected to be applied to functional polymeric materials including anion exchange membranes for fuel cell. However, their synthesis relies on reductive coupling reactions between haloarenes and perfluoroalkylene diiodides using stoichiometric amounts of copper, which hampers the industrial applications of these fluoropolymers.

In this study, we investigated the cross-coupling reaction between perfluoroalkylene zinc reagents and iodoarenes using [CuI(2,2'-bipyridyl)] as catalysts, referring to Uchiyama *et al*..[1] We found that bisarylated perfluoroalkylene compounds were obtained in good yields by utilizing CuI and 2,2'-bipyridine as the catalyst (Scheme 1).

Keywords : perfluoroalkylation

含フッ素高分子は耐熱性や耐薬品性など様々な特性を有することから、多方面へ応用されている。中でも、ペルフルオロアルキレン基とアリーレン基からなる交互共重合体は陰イオン交換膜などへの応用が期待されているが、その合成に化学量論量の銅を用いた還元的カップリング反応が必要であり、高分子材料として実用化における障害となっている。内山らによって銅触媒を用いたペルフルオロアルキレンアルキル亜鉛反応剤とハロアレーン類とのクロスカップリング反応が報告されていたが[1)]、ペルフルオロアルキレン化合物への展開はされていなかった。

本研究では内山らの報告[1)]を参考に、銅触媒を用いたペルフルオロアルキレン亜鉛反応剤とヨードアレーンとのクロスカップリング反応を検討した[2)]。特願種々条件を探索したところ、DMI 溶媒中で[CuI(2,2'-bipyridyl)]を触媒とすることで、ビスアリール化されたペルフルオロアルキレン化合物が良好な収率で得られることを見出したので報告する（Scheme 1）。



Scheme 1
Cross-Coupling Reactions of Perfluoroalkylene Zinc Reagents and Aryl Halides

1) M. Uchiyama *et al*., *Chem. Eur. J.,* **2015**, *21*, 3895. 2) 特願 2023-216689.

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
E1133(1132, Bldg. 11 [3F])

[E1133-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Akihiro Tsurusaki, Kenichi Michigami

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1133-3pm-01]
Visible-light-induced generations of silyl radicals under neutral conditions and development of silylation reaction

○Mone Suzuki[1], Yuki Nagashima[1], Ken Tanaka[1], Antônio Junio Araujo Dias[1] (1. Tokyo Institute of Technology)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1133-3pm-02]
Synthesis and Optical Property of Dibenzobarrelene Derivatives with Boron Substituents at the Bridgehead Positions

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

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1133-3pm-03]
Synthesis and photophysical properties of new functional λ^5-phosphinines

○Ryusei Ikeda[1], Hidetoshi Ohta[1], Minoru Hayashi[1] (1. Ehime University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1133-3pm-04]
Photoracemization of axially chiral 4,4′-dimethoxy-1,1′-biphenanthrene-2,2′-diol: Inhibitory effect of its analogs and additives on racemization

○Kohei Maruyama[1], Yuya Ishiyama[1], Daiki Kanai[1], Yuichi Kitamoto[1], Tetsutaro Hattori[1] (1. Graduate School of Engineering, Tohoku University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1133-3pm-05]
Synthesis of Olefin-bridged Fluorenylidene Indoloindole Bis-π-polycycles Using Pd-Catalyzed Dual C-H Annulative Coupling Strategy

○Sho Aida[1], Masahiro Terada[1], Tienan Jin[1] (1. Tohoku University)

1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
Break

English
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

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[E1133-3pm-06]

Synthesis and electrochemical properties of indigo derivatives modified with amino acids

○Mizuha Ujita[1], Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

Japanese

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

[E1133-3pm-07]

Synthesis of Chromones via Pd-catalyzed Tandem Acyl Transposition/Intramolecular Cyclization of Enol Esters

○Yosuke Kanda[1], Yoshiki Otawa[2], Kenichi Michigami[1,2], Mitsuhiro Ueda[1,2], Masato Ohashi[1,2] (1. Department of Chemistry, Graduate School of Science, Osaka Metropolitan University, 2. Department of Chemistry, Graduate School of Science, Osaka Prefecture University)

Japanese

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

[E1133-3pm-08]

Synthesis of Silicon-containing Cyclic Compounds by Gold-catalyzed Cyclization Reaction of Aryldiynes

○Kazuto Fuji[2], Kohei Sekine[1,2], Yoichiro Kuninobu[1,2] (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

Japanese

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

[E1133-3pm-09]

Gold(I)-Catalyzed Intramolecular Hydroarylation of Biarylbis(phenylethynyl)phosphine Derivatives

○Akihiro Komura[1], Marii Kishimoto[1], Akihiro Tsurusaki[2], Ken Kamikawa[2] (1. Osaka Prefecture University, 2. Osaka Metropolitan University)

Japanese

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

[E1133-3pm-10]

Development of iridium-catalyzed C(sp^3)-C(sp^2)[1,5]-silyl rearrangement reaction and analysis of its reaction mechanism

○Keigo Watanabe[1], Juwei Qiu[1], Shinsuke Komagawa[1], Tsuyoshi Matsuzaki[2], Makoto Sako[1], Kennichi Murai[1], Takeyuki Suzuki[2], Haruta Junichi[1], Mitsuhiro Arisawa[1] (1. Graduate School and School of Pharmaceutical Sciences, Osaka University, 2. SANKEN, Osaka 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

[E1133-3pm-11]

Asymmetric [3+2] cycloaddition of acetal imino esters with methyl acrylate catalyzed by chiral silver complexes

○Mizuki Katagiri[1] (1. Chuo University)

Japanese

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

[E1133-3pm-12]

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Synthesis of 2,4,6-Triarylpyridines Using Flavin-Catalyzed Aerobic Oxidation of Acetophenones and Benzylamines

○Nozomi Miyazaki[1], Tatsuki Fukuda[2], Hiroki Iida[1,2] (1. Shimane University, 2. Graduate School of Natural Science and Technology,Shimane University)

Japanese

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

[E1133-3pm-13]

Aerobic Oxidative C-C Bond Formations through C-H Activation of Tetrahydroisoquinolines Using Dehydrogenative Oxidation Catalysis of Flavin

○Hazuki Miyake[1], Hiroki Iida[1] (1. Graduate School of Natural Science and Technology, Shimene University)

Japanese

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

[E1133-3pm-14]

Organic synthesis using cationic indium catalysts-ligand synthesis for the isolation of catalysts

○Kodai Iguchi[1], Manoka Kikuchi[1], Mitsuhiro Yoshimatsu[1] (1. Gifu University)

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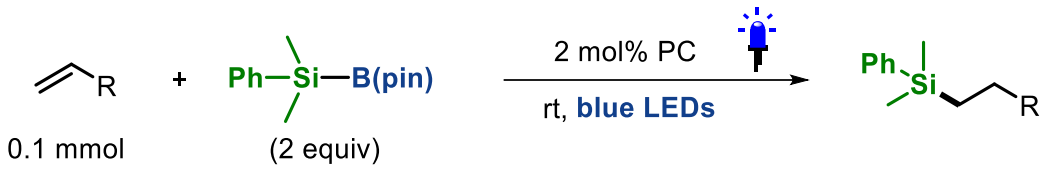
中性条件における可視光を用いたケイ素ラジカルの発生とケイ素化反応の開発

（東工大物質理工[1]）○鈴木萌音[1]・Antônio Junio Araujo Dias[1]・永島佑貴[1]・田中健[1]
Visible-light-induced generations of silyl radicals under neutral conditions and development of silylation reaction ([1]*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Mone Suzuki,[1] Antônio Junio Araujo Dias,[1] Yuki Nagashima,[1] Ken Tanaka[1]

Organosilicon compounds are useful as functional materials, bioactive compounds, and building blocks in organic synthesis. Recently, visible-light-induced in situ generations of silyl radicals have been developed for synthesis of organosilicon compounds under mild conditions. They are classified into HAT and SET strategy by combining photocatalysts with HAT catalysts or basic/acidic conditions. However, in situ generation of silyl radicals under neutral conditions has not fully developed. Based on the new mechanisms, we present here the silyl radical generation with a single photocatalyst under neutral condition. Employing a single organophotocatalyst (2 mol%) for the reaction of diverse alkenes with silylboranes at room temperature afforded the hydrosilylation product up to 93% yield.
Keywords : silyl radical, hydrosilylation, organophotocatalyst, organosilicon compound, photoinduced reaction

炭素と同じ第 14 族の元素であるケイ素を含んだ有機ケイ素化合物は、合成中間体としてのみならず、医農薬品候補化合物の部分構造としても注目されている。有機ケイ素化合物の温和な合成法として、可視光を用いたケイ素ラジカルによるシリル化反応が近年盛んに研究されてきた。これらは、光増感剤に対して水素引き抜き (HAT) 触媒や、塩基性または酸性条件を組み合わせた手法が多く[1)]、単一触媒・中性条件下によるケイ素化反応の報告例は限られている。

そこで本研究では、これまでとは異なる新規反応機構に基づいて光触媒を探索することにより、単一触媒・中性条件下でのアルケンのケイ素化反応を達成した。具体的には、アルケンとシリルボランの混合溶液を、有機光触媒 2 mol%存在下で青色光照射すると、ヒドロシリル化体が最大収率 93%で位置選択的に得られることを見出した。



1) a) R. Zhou, Y. Y. Goh, H. Liu, H. Tao, L. Li, and J. Wu, *Angew. Chem. Int. Ed.* **2017,** *56*, 16621; b) M. Zhong, X. Pannecoucke, P. Jubault, T. Poisson, *Chem. Eur. J.* **2021**, *27*, 11818; c) N. Takemura, Y. Sumida, H. Ohmiya, *ACS Catal*. **2022**, *12*, 7804; d) R. Arai, Y. Nagashima T. Koshikawa, K. Tanaka**,** *J. Org. Chem.* **2023**, *88*, 10371.

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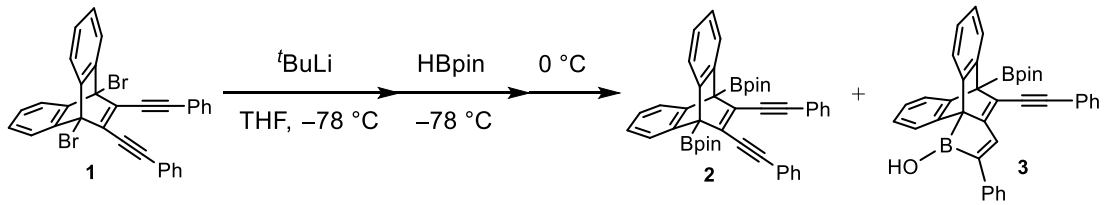
橋頭位にホウ素置換基を有するジベンゾバレレン誘導体の合成と光物性

（埼玉大院理工）○内藤 潤・中田 憲男・石井 昭彦
Synthesis and Optical Property of Dibenzobarrelene Derivatives with Boron Substituents at the Bridgehead Positions (*Graduate School of Science and Engineering, Saitama University*)
○Jun Naito, Norio Nakata, Akihiko Ishii

We have been studying the synthesis of the π-conjugated compounds fused with a dibenzobarrelene having heteroatom substituents at bridgehead positions. In this study, we report the synthesis of such derivatives having boron substituents at the bridgeheads and their optical properties. The bis(pinacolboryl) derivative **2** was synthesized by the lithiation of **1** with ^{t}BuLi followed by the treatment with pinacolborane (HBpin) in THF at −78 °C and then warming the reaction mixture to 0 °C; in this reaction, trans-hydroborated product **3** was obtained as a byproduct. Compounds **2** and **3** are fluorescent.
Keywords : Dibenzobarrelene; Boron; Optical property; Fluorescence

ホウ素原子を含む多環式芳香族炭化水素化合物は、電子不足の 3 配位ホウ素中心によって特異な電子特性や光物性を示すことが報告されており、有機発光材料としての応用が注目されている [1]。当研修室では、橋頭位にヘテロ原子置換基を有する剛直なジベンゾバレレン骨格と融合した π 共役系化合物の合成とそれらの光物性に関する研究を行っている。本研究では、ホウ素置換基を橋頭位に有する誘導体の合成と光物性について検討したので報告する。

ジブロモビス(フェニルエチニル)体 **1** を、^{t}BuLi を用いて THF 中、–78 °C でジリチオ化し、次いでピナコールボラン（HBpin）を加え、0 °C に昇温したところ、両橋頭位がピナコールボリル基で置換された誘導体 **2** が白色結晶として収率 39%で得られた。また、片側のフェニルエチニル基がトランス–ヒドロホウ素化されることで形成された含ホウ素 5 員環を有する誘導体 **3** も黄色結晶として収率 17%で得られた。**2** および **3** は室温で青色の蛍光を示した。



1) V. M. Hertz, M. Bolte, H. W. Lerner, M. Wagner, *Angew. Chem., Int. Ed*., **2015**, *54*, 8800.

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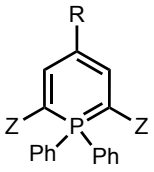
新規官能性λ^5-ホスフィニンの合成と光物性

（愛媛大院理工）○池田 流星・太田 英俊・林 実
Synthesis and Photophysical Properties of New Functional λ^5-Phosphinines (*Graduate School of Science and Engineering, Ehime University*) ○ Ryusei Ikeda, Hidetoshi Ohta, Minoru Hayashi

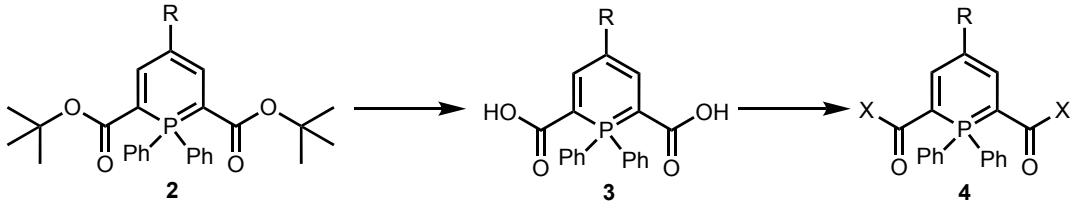
In recent years, fluorescent dyes containing heteroatoms in their conjugate system have attracted much attention. Among them, phosphorus-containing fluorescent compounds become one of the major research topics. We have reported the synthesis and optical properties of fluorescent λ^5-phosphinines, which showed bright emission in solution and solid-state. Their emission wavelengths can be successfully tuned from light-blue to near-infrared region by modifying their substituents. Herein, we wish to report the successful syntheses of the λ^5-phosphinine derivatives with carbonyl functional groups. The optical properties of the obtained λ^5-phosphinine derivatives will also be reported.
Keywords : Phosphinine, Fluorescent dye, Heterocyclic compounds, Phosphacycle, Phosphorus ylide

近年、ヘテロ原子、特にリン原子を共役系に含む蛍光色素が注目を集めている。演者らは、小さい骨格で溶液および固体状態で高効率発光を示す蛍光性λ^5-ホスフィニン **1** の合成と光物性を既に報告しており、ホスフィニンの 2, 4, 6 位を修飾することでこれまでに水色から近赤外領域までの光物性チューニングに成功している。



1
(Z = CN, CO_2Me, thiazole)

今回、2,6 位に *t*-ブチルエステル基を導入したホスフィニン誘導体 **2** を合成し、その加水分解により、2,6 位カルボン酸ホスフィニン **3** の合成を行った。カルボン酸ホスフィニン **3** を経由することで、ホスフィニンの 2,6 位に様々なカルボニル官能基を有する新たなホスフィニン誘導体 **4** の合成に成功したので、その光物性と併せて報告する。



2 **3** **4**
(X = Ar, OR, NR'R")

1) Hashimoto, N., Umano, R., Ochi, Y., Shimahara,K., Nakamura, J., Mori, S., Ohta, H., Watanabe, Y., Hayashi, M. *J. Am. Chem. Soc.,* **2018**, *140*, 2046.
2)米田 聖英・太田 英俊・林 実、第 46 回有機典型元素化学討論会(2019)、ポスター P-51.

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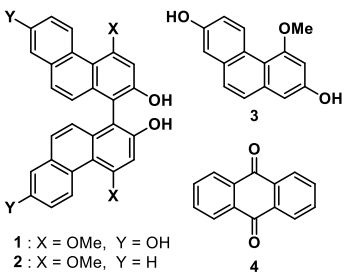
軸不斉 4,4'-ジメトキシ-1,1'-ビフェナンスレン-2,2'-ジオールの光ラセミ化：構造類縁体または添加剤によるラセミ化抑制効果

（東北大院工）○丸山 晃平・石山 友也・金井 大樹・北本 雄一・服部 徹太郎
Photoracemization of axially chiral 4,4′-dimethoxy-1,1′-biphenanthrene-2,2′-diol : Inhibitory effect of its analogs and additives on racemization (*Graduate School of Engineering, Tohoku University*) ○ Kohei Maruyama, Yuya Ishiyama, Daiki Kanai, Yuichi Kitamoto, Tetsutaro Hattori

Axially chiral 1,1′-biphenanthrenes including blestriarene C (**1**) are found in *Bletilla striata* and are used as a crude drug for pulmonary tuberculosis. Yamaki *et al*. have successfully isolated **1** as an optically active form from the tuber.[1] During the course of total synthesis for **1** and its analog (e.g., **2**) and determination of their absolute stereochemistry, we found that enantiopure **1** and **2**, upon exposure to ambient light, undergo racemization under air.[2,3] Since then, we have been trying to control a photochromic reaction for racemization of 1,1′-biphenanthrenes. In this study, we investigated the photoracemization behavior of **2** in the presence of synthetic precursors (e.g., **3**) and anthraquinone (**4**) which is an analog of extracted compound from the tuber of *Bletilla striata*.
Keywords : Axially chirality; Blestriarene C; Photoracemization; Redox; Radical cation

Blestriarene C (**1**)などの 1,1′-ビフェナンスレン類は、肺結核の生薬として用いられる *Bletilla striata* の塊茎などに含まれる軸不斉化合物であり、山木らによって単離と旋光度が報告されている [1]。一方で、当研究室では、**1** や類縁体 **2** などの全合成および絶対配置決定の過程で、それらが日常的な光の照射下で容易にラセミ化するフォトクロミズム挙動を見出している [2,3]。我々は、この類例の少ないフォトクロミズム反応に興味をもち、その制御方法について研究を行っている。本発表では、合成前駆体であるフェナンスレン誘導体や、塊茎からの抽出化合物の存在下における **2** の光ラセミ化挙動について検討した。



7-ヒドロキシ-4-メトキシフェナンスレン-2-オール(**3**)や塊茎からの抽出物の類縁体であるアントラキノン(**4**)存在下、**2** のトルエン溶液に 27 W 蛍光灯を照射したところ、添加剤存在下では 120 分照射後でも **2** のラセミ化が明確に抑制されることがわかった（Fig. 1）。

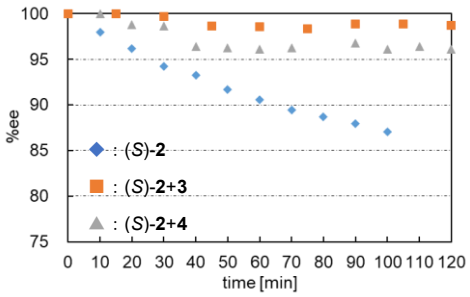


Figure 1 Photoracemization of **2** in the presence of **3** and **4** (light: 27 W fluorescent light, solvent: toluene, [(*S*)-**2**] = [**3**] = [**4**] = 0.1 mM).

1) Yamaki, M.; Bai, L.; Inoue, K.; Takagi, S. *Phytochemistry* **1989**, *28*, 3503. 2) Hattori, T.; Shimazumi, Y.; Yamabe, O.; Morohashi, N.; Kawai, W.; Miyano, S. *J. Org. Chem*. **2003**, *68*, 2099. 3) Kitamoto, Y.; Ishiyama, Y.; Kanai, D.; Hattori, T. *Symposium on Molecular Chirality 2021*, PP-55.

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Pd 触媒を用いた二重 C-H 環化カップリング反応によるオレフィン架橋型ビス-π-多環化合物フルオレニリデンインドロインドールの合成

（東北大院理）○会田 翔・寺田 眞浩・金 鉄男

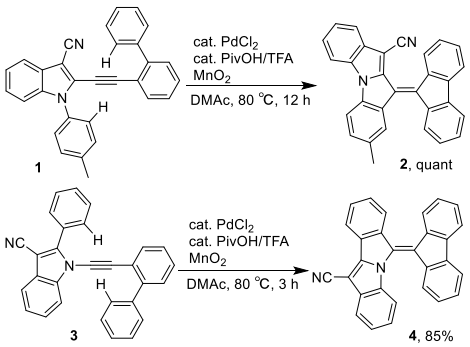
Synthesis of Olefin-bridged Fluorenylidene Indoloindole Bis-π-polycycles Using Pd-Catalyzed Dual C-H Annulative Coupling Strategy (*Graduate School of Science, Tohoku University*) ○Sho Aida, Masahiro Terada, Tienan Jin

Olefin-bridged bis-polycyclic structures (OBPs), in which two polycyclic structures are linked by a carbon-carbon double bond, have a unique twisted molecular structure as overcrowded olefins and have been shown to exhibit diverse functions such as n-type semiconductors, functional dyes, mechanochromism and molecular motors. On the basis of our previous Pd(II)-catalyzed 99'BF synthetic method via dual aromatic C-H activation of bis-biaryl alkynes, we report here a Pd(II)-catalyzed dual aromatic C-H activation of indole-incorporated bis-biaryl alkynes to access a new D-A type of π-extended OBP molecules. The new OBP molecules showed narrow HOMO-LUMO energy gaps and lower LUMO energy levels compared to the electron-accepting OBP molecule of 99'BF.

Keywords: dual C-H activation, Pd-catalyzed, Olefin-bridged Bis-π-polycycles, alkyne carbopalladation

二つの多環構造を炭素－炭素二重結合で連結したオレフィン架橋型ビス多環構造（OBP）は、混みすぎたオレフィンとしてユニークなねじれた分子構造を有しており、ｎ型半導体、機能性色素、メカノクロミズム、ロータリ分子モーターなどの多様な構造特異的な機能と現象を示すことから大きな注目が集まっている。一方、近年我々は、bis-biphenyl alkyne 分子が Pd(II)触媒を用いた芳香環の二重 C-H 結合切断反応を経て、一挙に二つのフルオレン骨格が構築され、電子アクセプター性 OBP 分子 99'BF が合成できることを報告した [1]。本研究では、Pd(II)触媒的芳香環の二重 C-H 結合活性化により電子ドナー性（D）インドール骨格とメチレンフルオレンのアクセプター（A）骨格からなる新規 D-A 型π拡張 OBP 化合物の効率的合成に成功した。

インドールの 2 位及び 1 位にビフェニルアルキン置換基を有する基質 **1** 及び **3** に $PdCl_2$ 触媒と触媒量の PivOH および TFA 添加剤、MnO_2 酸化剤を用いると、高収率で目的生成物 **2** 及び **4** が得られた。得られた新規 D-A 型 OBP 分子は電子アクセプター材料 99'BF より狭い HOMO-LUMO エネルギーギャップ、高い HOMO と低い LUMO エネルギー準位を有することを明らかにした。



1) J. Zhao, N. Asao, Y. Yamamoto, T. Jin, *J. Am. Chem. Soc*. **2014**, *136*, 9540.

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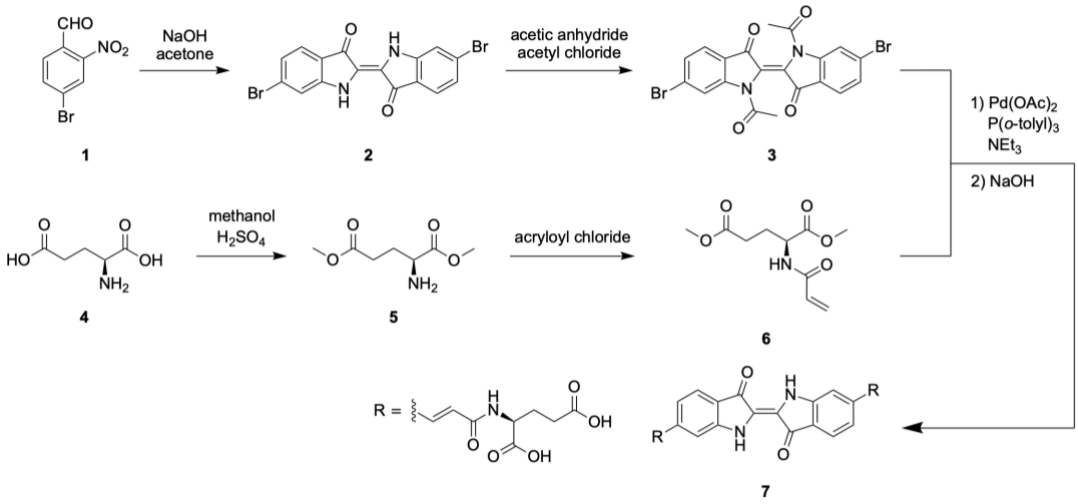
Synthesis and electrochemical properties of indigo derivatives modified with amino acids

(*Graduate School of Science, Department of Chemistry, The University of Tokyo*)
○Mizuha Ujita, Hongyao Zhou, Teppei Yamada
Keywords: Indigo; Amino acid; Electrochemistry; Redox reaction

Redox-responsive hydrogels are a promising class of materials for the construction of an electrically controllable functional soft matter or a biomimetic material. Previous research on supramolecular hydrogels showed that amino acids such as glutamic acid can form a gel material through hydrogen bonding.[1] Indigo is known to exhibit a two-step reversible redox reaction, and its hydrophilicity can be drastically turned by its redox state within the electrochemical potential window of water.[2] In this work, we attempt the synthesis of an indigo derivative attached with two glutamic acids on the aromatic rings as the gelator group (**7**, Scheme 1) and evaluate the electrochemical properties of **7**.

The synthetic scheme of **7** is shown in Scheme 1. First, brominated indigo **2** was synthesized from trisubstituted benzene **1** based on the reported method.[3] To improve the solubility of **2** in organic solvents, nitrogen atoms of **2** were acetylated to form **3**.[4] Esterification of L-glutamic acid **4** was carried out to produce **5**, which became soluble in the organic solvent.[5] A glutamic acid derivative with a double bond **6** was synthesized by amidation of **5** with acryloyl chloride. Finally, **3** was modified with **6** by the Mizoroki-Heck reaction, and the methoxy groups and the acetyl groups were removed by hydrolysis with base to obtain **7**.



Scheme 1. Synthesis of an indigo derivative modified with glutamic acids **7**.

1) T. Wang et al. *Langmuir*, **2010**, *26*, 18694–18700. 2) J. He et al. *Electrochim. Acta*, **2010**, *55*, 4845–4850. 3) P. Imming et al. *Synth Commun*, **2001**, *31*, 3721–3727. 4) M. A. Kolaczkowski et al. *Org. Lett.* **2016**, *18*, 5224–5227. 5) A. M. Benedetti et al. *Chembiochem*, **2020**, *21*, 938–942.

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Pd 触媒を用いたエノールエステルのアシル転位と分子内環化の連続反応を経由するクロモン誘導体の合成

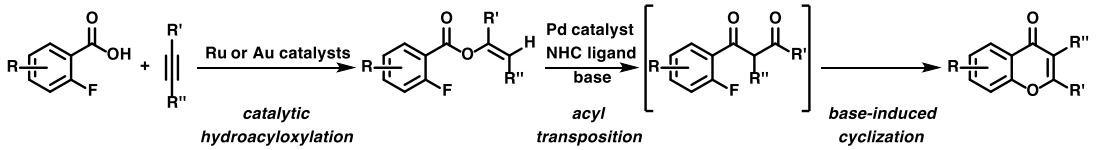
（阪公大院理 [1]・阪府大院理 [2]）○神田 洋輔 [1]・大多和 良紀 [2]・道上 健一 [1,2]・植田 光洋 [1,2]・大橋 理人 [1,2]

Synthesis of Chromones via Pd-catalyzed Tandem Acyl Transposition/Intramolecular Cyclization of Enol Esters ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*Graduate School of Science, Osaka Prefecture University*) ○ Yosuke Kanda,[1] Yoshiki Otawa,[2] Kenichi Michigami,[1,2] Mitsuhiro Ueda,[1,2] Masato Ohashi[1,2]

Chromones are one of the ubiquitous structural motifs found in diverse bioactive compounds. The Pd-catalyzed carbonylative cyclization reactions often facilitate the construction of chromone frameworks. However, the requirement of harmful carbon monoxide gives rise to a safety issue in the process. To address this concern, we focused on our recent advancements in the synthesis of 1,3-diketones through the Pd-catalyzed acyl transposition of enol esters, prepared by the catalytic alkyne hydroacyloxylation using carboxylic acid with 100% atom economy. The *ortho*-leaving group-substituted α-aroylketones can be converted into chromone derivatives through the S_NAr cyclization. We thus envisaged a tandem Pd-catalyzed acyl transposition/intramolecular cyclization of enol 2-fluoroarenoates as a strategy to furnish chromone derivatives. The investigation of the reaction conditions unveiled that *N*-heterocyclic carbene-Pd complexes efficiently catalyzed the desired transformation.

Keywords : Chromones; Palladium; Tandem Reactions; Enol Esters; C–O Bond Scission

クロモン骨格は多様な天然物および生物活性化合物に見られる構造であることから、その合成法の拡充は有機合成化学における重要な課題の一つである。効率的なクロモン誘導体の合成法として、Pd 触媒と一酸化炭素を用いたカルボニル化を伴う環化反応が近年数例報告されているが [1)]、これらの反応は毒性の高い一酸化炭素を必要とするため、安全性の観点から課題が残る。ところで、当研究室では最近、Pd 触媒を用いたエノールエステルのアシル転位反応を開発し、カルボン酸とアルキンから触媒的かつ高い原子効率にて 1,3-ジケトンを合成することに成功した [2)]。生じるα-アロイルケトンのオルト位に芳香族求核置換反応の優れた脱離基であるフッ素を導入すれば、さらなる分子内環化を経てクロモン骨格の構築が可能になると企図し、2-フルオロ安息香酸由来のエノールエステルを原料とするクロモン誘導体の高効率合成法を検討した。その結果、種々の 2-フルオロ安息香酸由来のエノールエステルに対し、塩基存在下、Pd 触媒と含窒素ヘテロ環状カルベン (NHC) 配位子を作用させたところ、対応するクロモン誘導体を高収率で得ることに成功した。



1. Shen, C.; Li, W.; Yin, H.; Spannenberg, A.; Skrydstrup, T.; Wu, X.-F. *Adv. Synth. Catal.* **2016**, *358*, 466.
2. 神田 洋輔、大多和 良紀、道上 健一、植田 光洋、大橋 理人、日本化学会第 103 春季年会 P4-2am-10.

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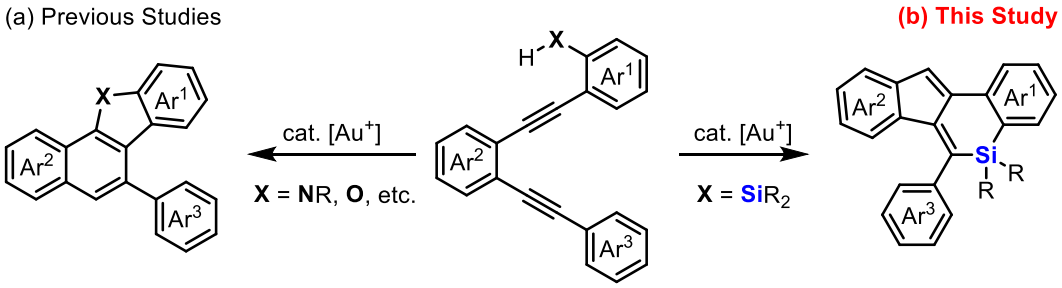
金触媒を用いたアリールジイン化合物の環化反応による含ケイ素環状化合物の合成

（九大先導研[1]・九大院総理工[2]）○藤 和人[2]・関根 康平[1,2]・國信 洋一郎[1,2]
Synthesis of Silicon-containing Cyclic Compounds by Gold-catalyzed Cyclization Reaction of Aryldiynes ([1]*IMCE, Kyushu University*, [2]*IGSES, Kyushu University*) ○Kazuto Fuji,[2] Kohei Sekine,[1,2] Yoichiro Kuninobu[1,2]

Gold catalysts act as π-Lewis acids for alkynes and facilitate various cyclization reactions. In particular, cascade cyclization of 1,5-diynes have greatly contributed to the synthesis of heterocyclic compounds[1] which have potentials for organic functional materials.[2] For example, in the case of aryl diynes having a nucleophile, such as amino or hydroxy group, gold-catalyzed cascade cyclization reactions proceeded to afford the corresponding heterocyclic compounds such as π-extended carbazole or benzofuran derivatives (Scheme a).[1] In contrast, there are few examples of the synthesis of silicon-containing cyclic compounds using gold catalysts. We herein report the cascade cyclization of aryl diynes involving a hydrosilyl group, affording *5H*-benzo[*b*]indeno[2,1-*d*]siline derivatives (Scheme b).

Keywords : Gold Catalyst; Diyne; Cyclization; Silylation; Silicon-containing Cyclic Compound

金触媒はアルキンに対してπ-Lewis酸として作用し、様々な環化反応を促進することが知られている。特に、1,5-ジイン化合物の連続的な環化反応は、含ヘテロ環状化合物の合成[1)]や、有機機能性材料の創出[2)]に大きく貢献してきた。例えば、アミノ基やヒドロキシ基などを置換基にもつアリールジイン化合物に対して金触媒を作用させると、連続的な環化反応が進行し、対応するπ拡張型のカルバゾールやベンゾフランが生成物として得られる（図a）。その一方で、金触媒を用いる含ケイ素環状化合物の合成は数例に限られる。今回の発表では、ヒドロシリル基をもつアリールジインの連続的な環化反応によって*5H*-ベンゾ[*b*]インデノ[2,1-*d*]シリン誘導体を与えることを新たに見出したため、その検討内容について報告する（図b）。



1) A. M. Asiri, A. S. K. Hashmi, *Chem. Soc. Rev*. **2016**, *45*, 4471.
2) C. H. Hendrich, K. Sekine, T. Koshikawa, K. Tanaka, A. S. K. Hashmi, *Chem. Rev.* **2021**, *121*, 9113.

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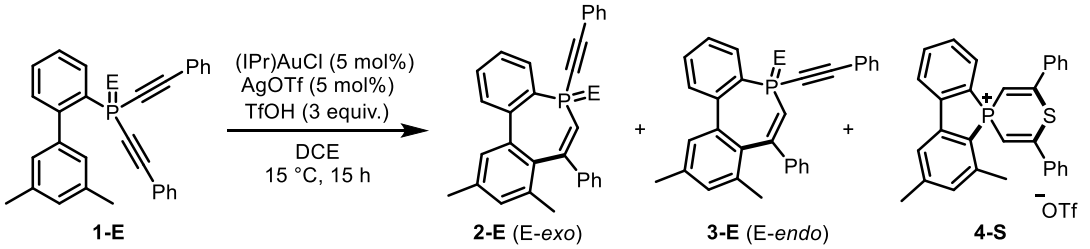
金(I)触媒を用いたビアリールビス(フェニルエチニル)ホスフィン誘導体の分子内ヒドロアリール化反応

（阪府大理[1]・阪公大院理[2]）○小村 明寛[1]・岸本 真理衣[2]・津留崎 陽大[2]・神川 憲[2]
Gold(I)-Catalyzed Intramolecular Hydroarylation of Biarylbis(phenylethynyl)phosphine Derivatives ([1]*Faculty of Science, Osaka Prefecture University,* [2]*Graduate School of Science, Osaka Metropolitan University*) ○Akihiro Komura,[1] Marii Kishimoto,[2] Akihiro Tsurusaki,[2] Ken Kamikawa[2]

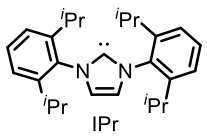
Development of a new synthetic method of π-conjugated phosphacycles would be important. We recently reported that the gold(I)-catalyzed intramolecular hydroarylation of diaryl(*o*-ethynylaryl)methylphosphonium salts gave phosphepin derivatives.[1] In this study, we carried out similar reactions of biarylbis(phenylethynyl)phosphine derivatives **1-E**. The reaction of phosphine oxide **1-O** and methylphosphonium salt **1-Me** gave phosphepins **2-E** (E = O, Me) in 77% and 93% yields, respectively, in which oxygen and a methyl group are located at the *exo* position of phosphepin. On the other hand, S-*endo* isomer of phosphepin **3-S** and phosphonium salt with a dibenzophosphole **4-S** were obtained in 22 and 31% yields, respectively, by the reaction of phosphine sulfide **1-S**.
Keywords : Phosphepin; Hydroarylation Reaction; Gold(I) Catalyst; Alkyne

含リンπ共役化合物は機能性分子の観点から広く研究されており、これらの新規合成手法の開拓は重要である。最近、ジアリール(*o*-エチニルアリール)メチルホスホニウム塩に対して、金(I)触媒を用いた分子内ヒドロアリール化反応を適用すると、ジベンゾ[*b*,*f*]ホスフェピニウム塩が得られることを報告した[1]。今回、ビアリールビス(フェニルエチニル)ホスフィン誘導体 **1** に対するヒドロアリール化反応により、ジベンゾ[*b*,*d*]ホスフェピン誘導体の合成を検討した。

(IPr)AuCl を用いてホスフィンオキシド **1-O** の反応を行ったところ、酸素原子が環外に位置したホスフェピン **2-O** (O-*exo*)が 77%の収率で得られた。一方ホスフィンスルフィド **1-S** では、硫黄原子が環内に位置したホスフェピン **3-S** (S-*endo* 体)とジベンゾホスホール骨格を有するホスホニウム塩 **4S** がそれぞれ 22%, 31%で得られた。メチルホスホニウム塩 **1-Me** からは **2-Me** (Me-*exo*)が 93%で得られた。



1-E → **2-E** (E-*exo*) + **3-E** (E-*endo*) + **4-S**



E = O	77%	8%	–
E = S	trace	22%	31%
E = Me(OTf)	93%	–	–

1) A. Tsurusaki, H. Shimatani, K. Kamikawa, *Asian J. Org. Chem.* **2021**, *10*, 154-159.

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イリジウム触媒を用いる炭素(sp^3)−炭素(sp^2) [1, 5]−シリル転位反応の開発とその反応機構解析

(阪大院薬[1]・阪大産研[2]) ○渡邉 慶悟[1]・仇 稼イ[1]・駒川 晋輔[1]・松崎 剛[2]・佐古 真[1]・村井 健一[1]・鈴木 健之[2]・春田 純一[1]・有澤 光弘[1]

Development of iridium-catalyzed Carbon(sp^3)-Carbon(sp^2) [1,5]-silyl rearrangement reaction and analysis of its reaction mechanism

([1]*Graduate School of Pharmaceutical Sciences, Osaka University*, [2]*SANKEN, Osaka University*) ○Keigo Watanabe,[1] Juwei Qiu,[1] Shinsuke Komagawa,[1] Tsuyoshi Matsuzaki,[2] Makoto Sako,[1] Kenichi Murai,[1] Takeyuki Suzuki,[2] Junichi Haruta,[1] Mitsuhiro Arisawa[1]

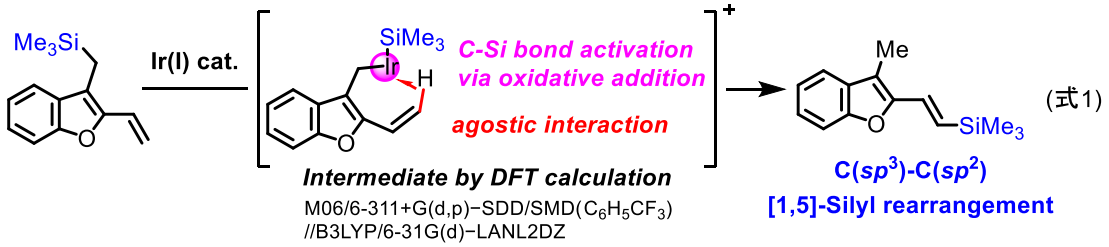
Silyl rearrangement reactions play a crucial role in the synthesis of natural products and functional molecules[1]. While many silyl rearrangements from carbon to oxygen have been reported[2], those from carbon to carbon remain underdeveloped. In a previous study, we reported the iridium (Ir)-catalyzed C(sp^3)-C(sp^2) [1,5]-silyl rearrangement (Equation 1); however, the reaction mechanism was unclear at the time[3].

This study employs computational chemistry to investigate the reaction mechanism. The results indicate that the activation of the benzylic carbon-silicon bond by the oxidative addition of the substrate to Ir is the rate-limiting step in this reaction. The presentation also includes a report on the details of the silyl rearrangement and hydride transfer catalyzed by the Ir complex.

Keywords : Iridium Catalysis; Silyl Rearrangement Reaction; Heterocyclic Compounds; Computational Chemistry

シリル基転位反応は、天然有機化合物や機能性分子などの合成において重要な反応[1] であり、新たな方法論の開発が盛んに行われている。炭素から酸素へのシリル基転位は多く報告されている[2]が、炭素から炭素へのシリル基転位反応は、未開拓な状況である。以前我々は、イリジウム（Ir）触媒を用いるシリル基の C(sp^3)-C(sp^2)[1,5]-転位反応（式 1）を報告しているが、その反応機構は不明であった[3]。

今回我々は、計算化学を用いて本反応の反応機構を解析した。その結果、本反応は反応基質の Ir への酸化的付加によるベンジル位炭素－ケイ素結合の活性化が律速段階であることが示唆された。本発表では Ir を介したシリル基転位やヒドリド移動の詳細についても報告する。



1) A. B. Smith Ⅲ *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 1740.
2) For a review, see: H. M. Huang *et al.*, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202205671.
3) 仇 稼イ他, 日本化学会 第 103 春季年会, 千葉, **K703-1pm-04**

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キラル銀錯体触媒を用いるアセタールイミノエステルとアクリル酸メチルとの不斉[3+2]環化付加反応

(中大理工 [1]) ○片桐 美月 [1]・細野 兼矢 [1]・福澤 信一 [1]
Asymmetric [3+2] cycloaddition of acetal imino esters with methyl acrylate catalyzed by chiral silver complexes ([1] *Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*), ○Mizuki Katagiri[1], Kenya Hosono[1], Shin-ichi Fukuzawa[1]

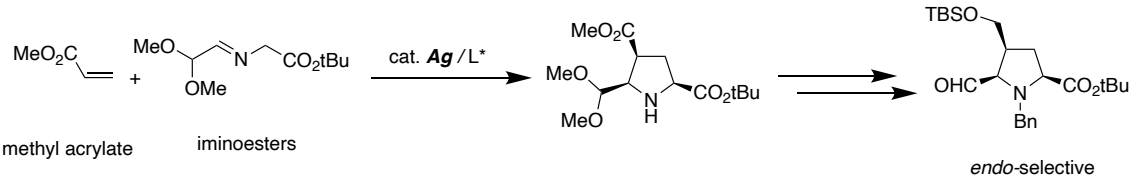
Stereoselective synthesis of pyrrolidine compounds has been sought because pyrrolidine skeleton is an important structure in many biologically active substances. The common approach is the metal complex-catalyzed asymmetric [3+2] cycloaddition of active alkenes with azomethine ylides. However, enantioselective synthesis of neuraminidase inhibitors by this method has not been achieved.[1)]

In this work, we report the asymmetric [3+2] cycloaddition reaction of methyl acrylate with imino esters. As a result, the corresponding pyrrolidine derivatives were obtained diastereo- and enantioselectively under silver complex conditions. The conversion to neuraminidase inhibitor intermediates was further investigated.

Keywords : Cycloaddition; Azomethine Ylide; Pyrrolidine: Silver Catalyst; Asymmetric Synthesis

ピロリジン骨格は多くの生物活性物質に含まれる重要な構造であることから、その立体選択的な合成が求められている。その一般的な手法として、金属錯体触媒を用いた活性アルケンとアゾメチンイリドによる不斉[3+2]環化付加反応が挙げられる。しかし、本手法によるノイラミニダーゼ阻害剤のエナンチオ選択的な合成は未達成である。[1)]

このような背景のもと今回我々は、アクリル酸メチルとイミノエステルとの不斉[3+2]環化付加反応に取り組んだ。検討の結果、銀錯体条件下で対応するピロリジン誘導体をジアステレオかつエナンチオ選択的に得た。さらにノイラミニダーゼ阻害剤中間体への変換を検討した。



1) J. Galvez, M. Diaz-de-Villegas, M. Alias, R. Badorrey *J. Org. Chem.* **2013**, 78, 11404-11413

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フラビン触媒によるアセトフェノンとベンジルアミンの酸素酸化を利用する 2,4,6-トリアリールピリジンの合成

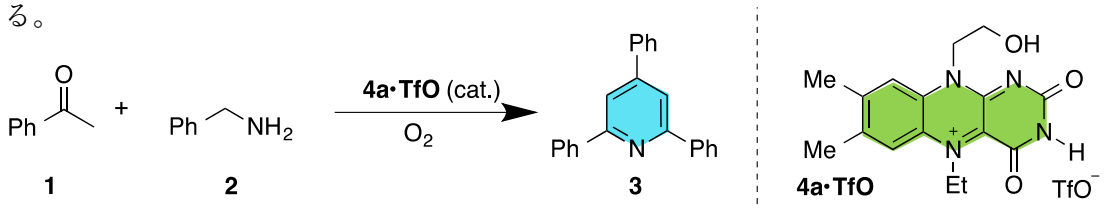
（島根大総合理工[1]・島根大院自然科学[2]）○宮崎望実[1]・福田竜己[2]・飯田 拡基[1,2]

Synthesis of 2,4,6-Triarylpyridines using Flavin-Catalyzed Aerobic Oxidation of Acetophenones and Benzylamines ([1]*Interdisciplinary Faculty of Science and Engineering, Shimane University,* [2]*Graduate School of Natural Science and Technology, Shimane University*) ○Nozomi Miyazaki[1], Tatsuki Fukuda[2], Hiroki Iida[1,2]

2,4,6-Triarylpyridines are one of the intriguing aromatic rings included in the key framework of various functional organic molecules such as phosphorescent materials and anticancer drugs. Among their various synthetic methods have been reported, the synthesis from readily available acetophenones (**1**) and benzylamines (**2**) is the simple and atom-economical approach. The flavin catalysts are known as redox organocatalysts activating molecular oxygen which is recognized as an ideal green oxidant. In this study, we developed the flavin-catalyzed aerobic oxidative reaction between **1** and **2** to synthesized 2,4,6-triphenylpyridines (**3**). By consuming only molecular oxygen, the oxidative C–C and C–N bond formations proceeded atom economically under metal-free conditions.

Keywords：Flavin; 2,4,6-Triarylpyridines; Aerobic Oxidation; Organocatalyst; Oxidative Aromatization

2,4,6-トリアリールピリジンは、りん光材料や抗がん剤など様々な機能性有機分子の鍵骨格に含まれる芳香族環の一種で、その有用性から盛んに研究が行われてきた。中でも入手容易なアセトフェノン(**1**)とベンジルアミン(**2**)から 2,4,6-トリフェニルピリジン(**3**)を合成する手法は簡便かつ高原子効率な手法であり、これまでに光触媒や酸触媒、金属触媒を用いる例などが報告されている[1)]。一方、フラビン化合物は、分子状酸素活性化能を有し、酸素添加反応や脱水素酸化反応を進行させる機能性有機分子として知られている[2)]。また我々の研究室では、このフラビン化合物を触媒として利用することで、テトラヒドロイソキノリンと種々の炭素求核剤の酸素酸化的 C–C 結合形成反応が進行することを最近見出している[3)]。これらの背景をもとに、本研究では、フラビン触媒(**4a•TfO**)を用いることで **1** と **2** から簡便に **3** を合成できることを見出した。本手法は、理想的な酸化剤である分子状酸素のみを消費することで C–C および C–N 結合形成反応が進行し、廃棄物が水だけとなる環境負荷の低い合成法である。



1 **2** **3** **4a•TfO**

1) a) S. R. Rohokale, B. Koenig, D.D. Dhavale, *J. Org. Chem*., **2016**, *81*, 7121; b) X. Zhang, Z. Wang, K. Xu, Y. Feng, W. Zhao, X. Xu, Y. Yan, W. Yi, *Green Chem*., **2016**, *8*, 2313; c) H. Huang, X. Ji, W. Wu, L. Huang, H. Jiang, *J. Org. Chem*., **2013**, *78*, 3774

2) H. Iida, Y. Imada, S.-I. Murahashi, *Org. Biomol. Chem.* **2015**, *13*, 7599.

3) H. Miyake, H. Iida, *Adv. Synth. Catal.* **2023**, DOI: 10.1002/adsc.202301427.

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フラビン触媒の脱水素化能を活用したテトラヒドロイソキノリンの C-H 活性化による酸素酸化的 C-C 結合形成反応

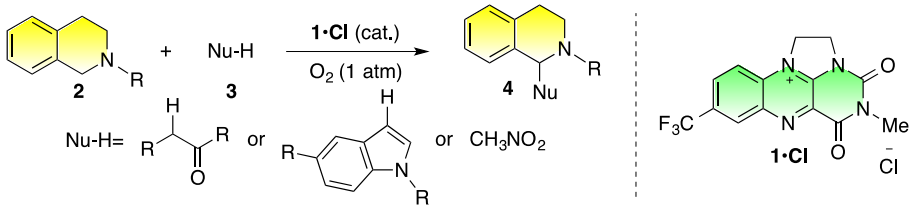
（島根大院自然科学）○三宅 葉月・飯田 拡基

Aerobic Oxidative C-C Bond Formations through C-H Activation of Tetrahydroisoquinolines using Dehydrogenative Oxidation Catalysis of Flavin (*Graduate School of Natural Science and Technology, Shimane University*) ○Hazuki Miyake, Hiroki Iida

Tetrahydroisoquinoline derivatives are often found in many pharmacologically active substances, thus various methods for their synthesis and modification using cross-dehydrogenative coupling (CDC) have been developed. Flavin compounds have attracted much attention as organocatalysts that activate molecular oxygen, an ideal oxidant, to perform two types of oxidations: oxygenation and dehydrogenation. This study demonstrated that a cationic flavin catalyst (**1•Cl**) efficiently promoted C-C bond formation reactions by CDC between tetrahydroisoquinoline **2** and carbon nucleophile **3** under an oxygen atmosphere (1 atm), resulting in the production of the corresponding product **4**.
Keywords : Flavin; Dehydrogenative oxidation; Cross-dehydrogenative coupling; Tetrahydroisoquinoline; Organocatalyst

テトラヒドロイソキノリン骨格を有する化合物は、多くの薬理活性物質に含まれるため、脱水素型カップリング（CDC）による様々な合成･修飾法が開発されてきた。フラビン化合物は分子状酸素を活性化し、酸素添加及び脱水素反応という 2 種類の酸化反応を行う有機分子触媒として注目を集めている。最近我々の研究室では、フラビン触媒を電解反応や光反応に応用するとともに、ヨウ素触媒とハイブリッド化させた二成分触媒系を開発し、これを用いた種々の酸素酸化による C–S 結合や C–N 結合形成反応を報告している [1)]。これらの背景をもとに本研究では、フラビン触媒の脱水素酸化能によりテトラヒドロイソキノリンの C-H を活性化し、炭素求核剤との CDC による C-C 結合形成反応が達成できるのではないかと考え、検討を行った [2)]。

その結果、触媒量のカチオン性フラビン触媒(**1•Cl**)存在下で、テトラヒドロイソキノリン **2** と炭素求核剤 **3** との CDC 反応が、酸素雰囲気下(1 atm)で効率良く進行し、対応する生成物 **4** が良好な収率で得られることを見出した。



1) a) T. Ishikawa, M. Kimura, T. Kumoi, H. Iida, *ACS Catal*., **2017**, *7*, 4986; b) R. Ohkado, T. Ishikawa, H. Iida, *Green Chem.*, **2018**, *20*, 984; c) H. Okai, K. Tanimoto, R. Ohkado, H. Iida, *Org. Lett*., **2020**, *22*, 8002; d) M. Oka, D. Katsube, T. Tsuji, H. Iida, *Org. Lett.*, **2020**, *22*, 9244; e) T. Mizushima, M. Oka, Y. Imada, H. Iida, *Adv. Synth. Catal.*, **2022**, *364*, 2443.
2) H. Miyake, H. Iida, *Adv. Synth. Catal.*, DOI: 10.1002/adsc.202301427

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カチオン性インジウムを用いた有機合成－触媒単離のためのリガンド合成

(1.岐阜大学)○井口 滉大[1]、菊池 真歌[1]、吉松 三博[1]

Organic synthesis using cationic indium catalysts－ligand synthesis for the isolation of catalysts

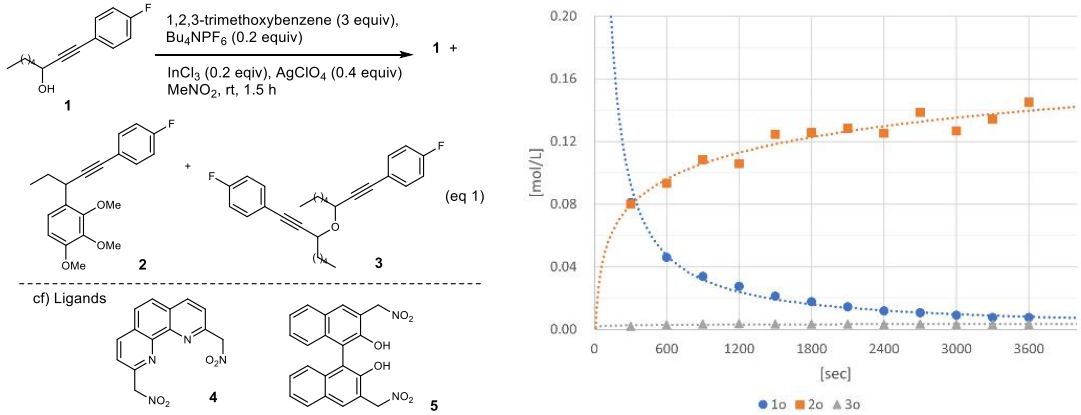
(1.Gifu University)○Kodai Iguchi[1], Manoka Kikuchi[1], Mitsuhiro Yoshimatsu[1]

Previously, we reported the cationic indium-catalyzed propargylation and unsymmetric ethers formation. We next performed the time course experiments of propargylations using the ^{19}F NMR spectrum. In order to isolate the cationic catalysts, the preparation of two types of ligands such as 1,10-phenanthroline and 1,1'-bi-2-naphthol was examined.

Keywords : Indium, Ligands

【緒言】アルコールの脱水反応は副生成物が水のみであり、持続可能な開発のためになくてはならない化学プロセスである。近年、脱水反応を利用した C-C、C-O、C-N 結合形成の開発および生理活性物質の合成研究が活発に行われている。以前我々は、カチオン性インジウム触媒がプロパルギルアルコールの脱水過程を良好に進めることを見出した。カチオン性インジウム触媒は、今までのπ酸性のものと大きく性質が異なり、オキソフィリシティーが高く、不安定中間体を経由する S_N1 反応に対して有効に作用することを報告[1]した。今回我々は、従来のカチオン性インジウムとの違いを明らかにするため、反応の経時変化を ^{19}F NMR を用いて観察した。更に、触媒の単離を目的としたリガンド合成を検討した。

【結果】^{19}F NMR 測定を利用したアルコール **1** 及び生成物 **2** の経時変化を下グラフに示した。**1** の消失と共に **2** が生成するなか、エーテル **3** の生成が常時観察できた。エーテル **3** の生成は、不安定カチオン種を回避するために自己縮合した結果であると予測できた。次に我々は、カチオン性インジウムの強いルイス酸性を調べる目的で 1,1'-ビ-2-ナフトールや 1,10-フェナントロリンにニトロ基を導入したリガンド **4**, **5** の合成を検討した。これらの結果の詳細を報告する。



(1) M. Yoshimatsu et al. *Communications Chemistry* 2023, 6, 279.

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-3pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Kensuke Kiyokawa, Okano Kentaro

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1141-3pm-01]
Hexadehydro Diels–Alder/Alkynyliodanation Cascade

○Shunya Morohashi[1], Liejin Zhou[1], Kazuya Kanemoto[1], Naohiko Yoshikai[1] (1. Tohoku University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1141-3pm-02]
Synthesis of iodinated 1,1′-spirobi[indene] derivatives via double iodocyclization reactions of tetraaryl[4]cumulenes

○Tsubasa Ito[1], Keiji Minagawa[1], Yasushi Imada[1], Fumitoshi Yagishita[1,2] (1. Dept. of Applied Chem., Tokushima Univ., 2. Inst. of pLED, Tokushima Univ.)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1141-3pm-03]
para-Selective Iodination of Phenols and *ortho*-Selective Cyclization with Azadienes

○Weijie Cao[1], Takayoshi Arai[1] (1. Chiba University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1141-3pm-04]
Stereocontrolled Halogen Dance of Bromoimidazolylmagnesium

○Nishimoto Hayato[1], Kengo Inoue[1], Kentaro Okano[1], Atsunori Mori[1,2] (1. Kobe University, 2. Kobe University Center for Membrene and Film Technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1141-3pm-05]
Haloamidation of α,β-C(sp^3)-H to the nitrogen of amide derivatives

○Chiyuki Naito[1], Satoshi Minakata[1] (1. Osaka 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
[E1141-3pm-06]
Stereoselective Diamination of π-Conjugated Molecules utilizing *N*-halosulfonamides

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○Ryo Nakajima[1], Satoshi Minakata[1] (1. Osaka University)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[E1141-3pm-07]

Convenient Synthesis of Amino-λ^3-iodanes and Their Application to Oxidative Amination

○Shusuke Narita[1], Kazuki Kawanaka[1], Kensuke Kiyokawa[1], Satoshi Minakata[1] (1. Osaka University)

Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[E1141-3pm-08]

Pyrrolidine-Thiazolium Conjugated Chiral Ionic Liquid Catalysts for Stetter Reaction

○Masaaki Tokunaga[1], Syunsuke Kimura[1], Yuichi Isikawa[2], Satoshi Kitaoka[3], Kaoru Nobuoka[2] (1. Graduated School of Engineering, Oita University, 2. Faculty of science and Technology, Oita University, 3. Faculty of Engineering, Kindai University)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[E1141-3pm-09]

Development of methods for catalytic conversions of indoles via the hydrosilylation of carbon dioxide

○Sha Li[1], Shoko Nakahara[1], Reito Yasui[1], Taishin Adachi[1], Takumi Murata[1], Chihiro Maeda[1], Kazuto Takaishi[1], Tadashi Ema[1] (1. Grad. Sch. Nat. Sci. Technol., Okayama Univ.)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[E1141-3pm-10]

Carbamoylarylation of Alkenes with *N*-Aryl Oxamic Acids Involving 1,4-Aryl Migration via C(aryl)–N Bond Cleavage

○Akira Shiozuka[2], Di Wu[2], Kyohei Kawashima[1], Toshifumi Mori[1,2], Kohei Sekine[1,2], Yoichiro Kuninobu[1,2] (1. IMCE, Kyushu Univ. , 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu Univ.)

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

Break

English
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[E1141-3pm-11]

Catalytic Asymmetric *exo*-Selective [3+2] Cycloaddition of Iminoesters with Nitroalkenes Using Imidazoline-Proline-*t*Butyl ester-Copper Complex

○Yan Yu[1], Takayoshi Arai[1] (1. Chiba university)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[E1141-3pm-12]

A mechanistic study on radical cascade reaction of 1,6-enyne precursors using cyclopropylacetylene.

○KANAKO ISHIDO[1], Yuki Kanda[2], Takuji Kawamoto[2], Akio Kamimura[2] (1. Yamaguchi-University, 2. Yamaguchi University Engineering Faculty)

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Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[E1141-3pm-13]
Lewis acid-promoted preparation of nitrones from nitroso compound
○Masaya Maegawa[1], Takuya Suga[1], Takahiro Soeta[1], Yutaka Ukaji[1] (1. Kanazawa University)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[E1141-3pm-14]
Amination of 2-chloro-benzo[*c*]tetrazolo[2,3-*a*]cinnolinium salt
○Eri Kamiya[1], Tsunehisa Hirashita[1] (1. Nagoya Inst. of Tech.)

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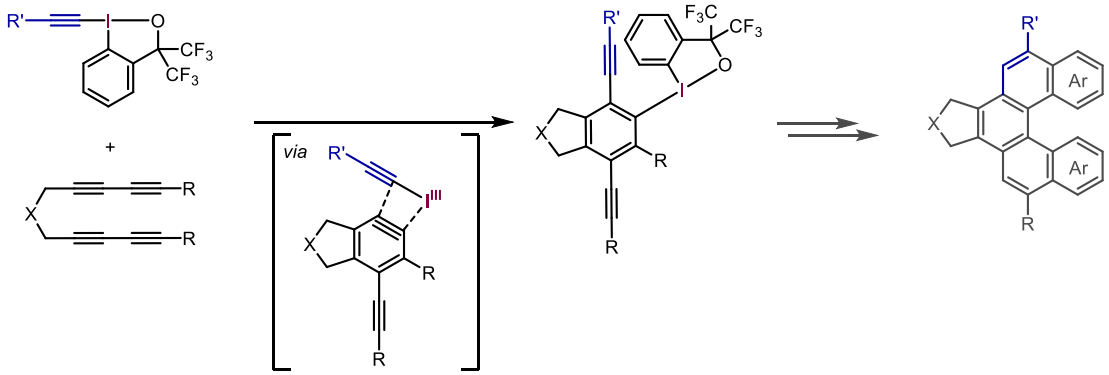
ヘキサデヒドロ Diels–Alder・アルキニルヨウ素(III)化カスケード反応

（東北大院薬）○諸橋 駿矢・周 列錦・金本 和也・吉戒 直彦
Hexadehydro Diels–Alder/Alkynyliodanation Cascade (*Graduate School of Pharmaceutical Sciences, Tohoku University*) ○Shunya Morohashi, Liejin Zhou, Kazuya Kanemoto, Naohiko Yoshikai

A cascade process comprised of hexadehydro Diels–Alder (HDDA) reaction of tetrayne compounds and interception of the resulting aryne intermediates provides an attractive strategy for the synthesis of multisubstituted aromatic compounds. Meanwhile, we recently discovered that organoiodine(III) compounds undergo nucleophilic addition (carboiodanation) across the highly electrophilic C≡C bond of arynes. In this study, we have successfully combined HDDA and carboiodanation reactions to afford novel multisubstituted aryliodine(III) compounds. These products feature the iodanyl group and the alkynyl groups exploitable for cross-coupling and cyclization reactions, respectively, and thus are expected to serve as versatile building blocks for the synthesis of polycyclic aromatic compounds such as helicenes.

Keywords: hypervalent iodine compound; aryne; cycloaddition reaction

テトライン化合物のヘキサデヒドロ Diels–Alder（HDDA）反応によるアラインの生成とその捕捉からなるカスケードプロセスは，多置換芳香族化合物の合成手法として魅力的である．一方で，我々は最近，高い求電子性を持つアラインに対して，ベンズヨードキソール骨格をもつ三価の有機ヨウ素化合物が求核的に作用し付加反応（カルボヨウ素(III)化）を起こすことを見出している.[1] 本研究では，テトラインの HDDA 反応とアルキニルヨウ素(III)化合物によるカルボヨウ素(III)化を組み合わせることにより，様々な多置換アリールヨウ素(III)化合物が得られることを明らかにした．本生成物は，クロスカップリング反応の優れた脱離基となるヨウ素(III)基に加え，そのオルト位とメタ位に環化反応に利用可能なアルキニル基を備えており，ヘリセンをはじめとする多環性芳香族化合物合成のための有用なビルディングブロックとなることが期待される．



1) C. Arakawa, K. Kanemoto, K. Nakai, C. Wang, S. Morohashi, E. Kwon, S. Ito, N. Yoshikai, *ChemRxiv*, 2023, DOI: 10.26434/chemrxiv-2023-knrnb-v2.

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テトラアリール[４]クムレンの二重ヨード環化反応によるヨウ素置換 1,1’-スピロビ[インデン]誘導体の合成

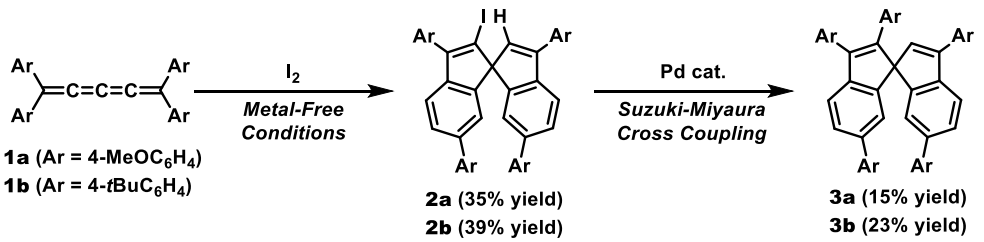
（徳島大院理工[1]・徳島大 pLED 研[2]）○伊藤 翼[1]・南川 慶二[1]・今田 泰嗣[1]・八木下史敏[1,2]
Synthesis of iodinated 1,1’-spirobi[indene] derivatives via double iodocyclization reactions of tetraaryl[4]cumulenes ([1]*Dept. of Applied Chem., Tokushima Univ.,* [2]*Inst. of pLED, Tokushima Univ.*) ○Tsubasa Ito[1], Keiji Minagawa[1], Yasushi Imada[1], Fumitoshi Yagishita[1,2]

Spirocyclic compounds have drawn considerable attention owing to their potential applications in pharmaceuticals and organic electronic devices. Therefore, many efforts have been devoted to developing synthetic methods to construct spirocyclic skeletons. Recently, we have found the reaction of tetraaryl[3]cumulene with NIS, providing benzofulvene derivatives via iodocyclization. On the basis of the results, we considered that the double iodocyclization reactions of tetraaryl[4]cumulenes would afford the corresponding 1,1’-spirobi[indene] skeleton. As a result, we found that the reaction of tetraaryl[4]cumulene with iodine provided iodinated 1,1’-spirobi[indene] derivatives via double iodocyclization. In addition, the obtained iodinated spirobi[indene] was successfully converted to the poly-arylated spirobi[indene] by Suzuki–Miyaura cross-coupling reactions.

Keywords : cumulene; Spirocycle; Iodocyclization

スピロ環骨格は医薬品や有機エレクトロニクス材料など幅広い分野で注目される分子構造であり，近年グリーンケミストリーの観点から金属を用いない温和な条件での骨格構築法の開発が求められている。一方，当研究室では最近，テトラアリール[3]クムレンのヨード環化反応がベンゾフルベン骨格を与えることを見出した。[1] そこでテトラアリール[4]クムレンのヨード環化がテトラアリール[3]クムレンと同様の反応機構で二重に進行した場合，1,1’-スピロビ[インデン]骨格の構築が可能であると予想した。

テトラアリール[4]クムレン **1** を，トルエン中，2.2 等量のヨウ素存在下で反応させたところ，二度のヨード環化過程を経て対応する 1,1’-スピロビ[インデン]誘導体が最大 39%収率で得られた。さらに、**2** は Suzuki-Miyaura クロスカップリングにおけるヨウ化アリールとして利用することが可能であり，対応する多置換 1,1’-スピロビ[インデン]**3** を構築することを見出した。



1) F. Yagishita, *et al. Eur. J. Org. Chem*. **2021**, 235–238.

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フェノールのパラ位選択的ヨウ素化とアザジエンとのオルト位環化反応

（千葉大院理）○Cao Weijie・荒井 孝義

para-Selective Iodination of Phenols and *ortho*-Selective Cyclization with Azadienes

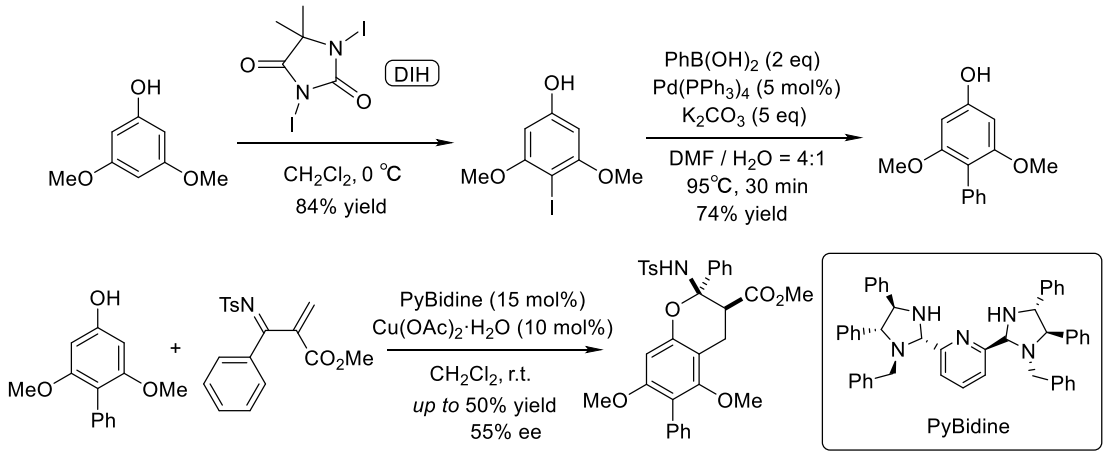
(Graduate School of Science, Chiba University) ○Cao Weijie, Takayoshi Arai

Halogenation of phenol substrates, important reaction for getting synthetically useful compounds, requires the control of regioselectivity with avoiding the multiple halogenations. We have reported a highly *para*-selective iodination of electron-rich phenols using 1,3-diiodo-5,5-dimethylhydantoin (DIH). [1]

Cross-coupling reactions of the *para*-iodophenols were demonstrated to extend the carbon framework. Furthermore, a bis(imidazoline)pyridine-$Cu(OAc)_2$ catalyst promoted Friedel-Crafts reaction of the *para*-phenylphenol with azadiene substrates at the *ortho* position, and following cyclization of phenol gave a novel chromane compounds with moderate enantiomeric excess.

Keywords : Phenol; Iodination; Cross-coupling; Friedel-Crafts Reaction; Asymmetric Catalyst

オルト位とパラ位に反応が進行しやすいフェノール基質のハロゲン化では、位置選択性の制御や多重ハロゲン化の制御など解決すべき課題が残されている。我々は、ヨウ素化剤に 1,3-ジヨード-5,5-ジメチルヒダントイン（DIH）を用いる電子豊富なフェノール基質のパラ位置選択的なヨウ素反応を報告している[1]。本ヨウ素置換化合物は、クロスカップリング反応により、パラ位から炭素骨格を拡張することできた。さらに、研究室にて独自に開発したビス（イミダゾリン）ピリジン - 銅触媒を用いて、パラ - フェニルフェノールとアザジエン基質とのフリーデル・クラフツ反応を行い、引き続くフェノール性水酸基からの環化反応により、新規クロマン化合物が中程度のエナンチオ選択性で得られることを見出した。



[1] Cao Weijie、荒井 孝義 日本化学会 第 103 春季年会 (2023)

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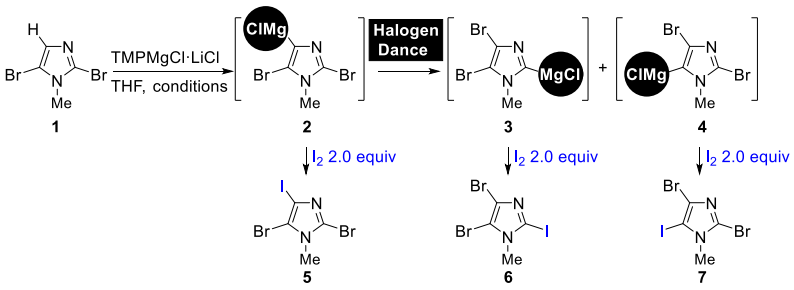
Stereocontrolled Halogen Dance of Bromoimidazolylmagnesium

([1]*Department of Chemical Science and Engineering, Kobe University*, [2]*Research Center for Membrane and Film Technology, Kobe University*) ○Hayato Nishimoto,[1] Kengo Inoue,[1] Kentaro Okano,[1] Atsunori Mori[1,2]

Keywords: Halogen Dance; Divergent Synthesis; Organomagnesium

A halogen transfer reaction, is a useful method for synthesizing a series of constitutional isomers.[1] Despite its synthetic potential, this reaction has not been a "first choice", due to the difficulty in controlling the reactivity of the organolithium intermediate. In addition, the examples of halogen dance of less reactive organomagnesium are limited.[2] Herein, we report halogen dance of bromoimidazolylmagnesium, whose migratory aptitude is controlled by heating or additive, allowing the selective synthesis of three constitutional isomers after electrophilic functionalization.

First, we investigated the halogen dance reaction of dibromoimidazole **1** using a magnesium amide base. Treatment of imidazole **1** with TMPMgCl·LiCl at –20 °C followed by iodine gave iodinated imidazole **5** in 96% yield. The result indicates that intermediate **2** is stable at –20 °C. Next, the reaction was carried out at elevated temperature to promote the halogen dance reaction. Upon heating at 80 °C, the halogen dance reaction proceeded smoothly to provide imidazole **6** in 68% yield. Moreover, the formation of another organomagnesium species **4** was also tested. Among the additives screened, HMPA proved efficient to give imidazole **7** in 76% yield. The use of other electrophiles allowed to introduce a range of functional groups. This strategy was also applicable to the synthesis of *N*-SEM and *N*-PMB imidazoles. The rationale for the switchable migratory aptitude will be discussed.



temperature	additive	**5** [%]	**6** [%]	**7** [%]
–20 °C	–	96	–[a]	–
80 °C	–	–[a]	68	–[a]
–20 °C	HMPA 14 equiv	21	3	76

[a] Not detected.

1) Inoue, K.; Feng, Y.; Mori, A.; Okano, K. *Chem. Eur. J.* **2021**, *27*, 10267. 2) Yamane, Y.; Sunahara, K.; Okano, K.; Mori, A. *Org. Lett.* **2018**, *20*, 1688.

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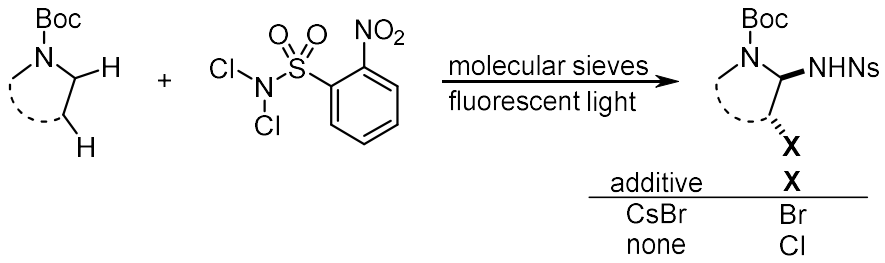
アミド誘導体の N のαおよびβ位 C(sp^3)−H ハロアミド化

（阪大院工）○内藤 智由希・南方 聖司
Haloamidation of α,β-C(sp^3)−H to the Nitrogen of Amide Derivatives
(*Graduate School of Engineering, Osaka University*) ○Chiyuki Naito, Satoshi Minakata

Direct functionalization of C(sp^3)-H bonds should be an ideal methodology for organic synthesis, which enables to provide complex compounds in short steps from readily available starting materials. Especially, stereoselective and regioselective bifunctionalization of the vicinal C(sp^3)-H bonds is useful to create such highly valuable molecules. However, only a few methods of such transformations have been reported, and those methods suffer from the use of excess amount and strong oxidants. We have already found that when amide derivatives were treated with *N,N*-dichloro-2-nitrobenzenesulfonamide (dichloramine-Ns) and cesium bromide, nosylamide and bromo groups were simultaneously introduced into α- and β-positions to the amide nitrogen. We report herein stereoselective and regioselective chloroamidation of α,β-C(sp^3)−H to the nitrogen of amide derivatives without the addition of cesium bromide by investigating various reaction conditions. The functionalization of double C(sp^3)−H would be a highly advanced method for synthesizing complex molecules.
Keywords : Double C(sp^3)-H Functionalization; Haloamidation; Amide Derivatives; N,N-dichloro-2-nitorobenzenesulfonamide

C(sp^3)−H 結合の直接的な官能基化は、入手容易な原料から短工程で複雑な化合物へ導けることから有機合成の理想的な方法論である。特に、C(sp^3)−H 結合の立体選択的かつ位置選択的なビシナル二官能基化は、高付加価値な分子を構築するために有用な手法である。しかし、それらの反応は数例報告されているのみであり、過剰量の強力な酸化剤の使用が課題となっている[1)]。我々は既に、アミド誘導体に対して、*N,N*-ジクロロ-2-ニトロベンゼンスルホンアミド（ジクロラミン-Ns）と臭化セシウムを作用させることにより、窒素原子のα位にノシルアミド基、β位にブロモ基が導入された化合物が得られることを見出している。本研究では、種々反応条件を検討することにより、臭化セシウムを添加しなくても、同様のハロアミド化が進行し、β位にクロロ基が導入された化合物を合成することが出来た。二つの C(sp^3)−H 結合のダブル官能基化は、より複雑な分子の合成に有用な方法となりうる。



1) (a) Barluenga, J. et al. *Angew. Chem. Int. Ed.* **2002**, *41*, 2556. (b) Nagib, D. A. et al. *J. Am. Chem. Soc.* **2020**, *142*, 5429. (c) Lambert, T. H. et al. *Science* **2021**, *371*, 620.

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N-ハロスルホンアミド類を活用するπ共役分子の立体選択的ジアミノ化

（阪大院工）○中嶋 遼・南方 聖司

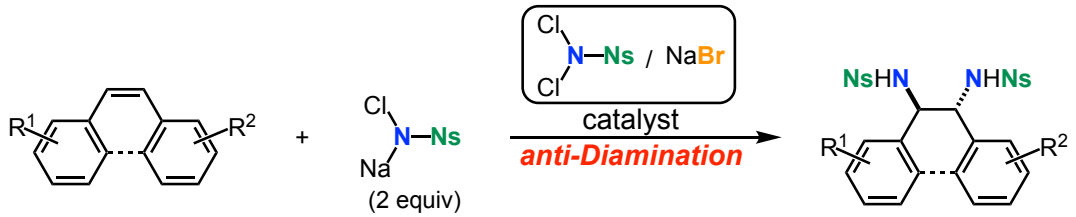
Stereoselective Diamination of π-Conjugated Molecules Utilizing *N*-Halosulfonamides

(*Graduate School of Engineering, Osaka University*) ○Ryo Nakajima, Satoshi Minakata

Diarylethylenediamine skeleton has been recognized as an important structural motif in asymmetric ligands and organocatalysts[1]. The most direct method of synthesizing diarylethylenediamine should be the diamination reaction of the carbon-carbon double bond moiety in the π-conjugated molecules. A few examples of diazidation of stilbenes have been reported so far. Since the diazidations are involved in radical pathway, it is difficult to control the stereochemistry. There are no examples of direct diamination of phenanthrenes. Therefore, the development of a simple and stereocontrolled diamination method of π-conjugated molecules is desired. We present herein *anti*-selective diamination of π-conjugated molecules with two equivalents of *N*-chloro-*N*-sodio-2-nitrobenzenesulfonamide as a nitrogen source in the presence of a catalytic amount of *N*,*N*-dichloro-2-nitrobenzenesulfonamide and NaBr. The reaction selectively proceeds with *anti*-stereochemistry, and is an unprecedented method for the synthesis of various diarylethylenediamine derivatives from π-conjugated molecules in a single step.

Keywords : Diamination; anti-Addition; π-Conjugated Molecules; N-Halosulfonamides; Diarylethylenediamine Derivatives

ジアリールエチレンジアミン骨格は、不斉配位子や有機触媒などに含まれる重要な部分構造であり、様々な合成手法が開発されている[1]。最も直接的なジアリールエチレンジアミンの合成法として、π共役分子に含まれている炭素-炭素二重結合のジアミノ化反応が考えられる。これまでにスチルベンのジアジド化は数例報告されているが、いずれもラジカル反応であるため、立体化学の制御は困難である。また、フェナントレン類に関しては、一段階でジアミノ化する例はない。従って、より簡便かつ立体制御が可能なπ共役分子のジアミノ化法の開発が望まれている。本研究では、*N*,*N*-ジクロロ-2-ニトロベンゼンスルホンアミドと臭化ナトリウムを組み合わせた触媒系を活用することにより、2 当量の *N*-クロロ-*N*-ソジオ-2-ニトロベンゼンスルホンアミドを窒素源とした、様々なπ共役分子に対する立体選択的なジアミノ化反応の開発に成功した。本反応は選択的にアンチの立体化学で進行し、π共役分子から一段階で様々なジアリールエチレンジアミン誘導体が合成できる他に類をみない手法である。



1）(a) C. Biaggi, M. Benaglia, S. Rossi, S. Proto, R. Annunziata, *Tetrahedron Lett.* **2007**, *48*, 8521. (b) F. Liu, G. Zhao, W. Cai, D. Xu, B. Zhao, *Org. Biomol. Chem.* **2018**, *16*, 7498.

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アミノ-λ^3-ヨーダンの簡便合成と酸化的アミノ化への利用

（阪大院工）○成田 修佑・川中 一輝・清川 謙介・南方 聖司

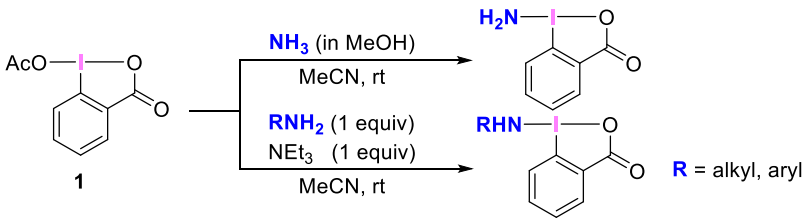
Convenient Synthesis of Amino-λ^3-iodanes and Their Application to Oxidative Amination

(*Graduate School of Engineering, Osaka University*) ○Shusuke Narita, Kazuki Kawanaka, Kensuke Kiyokawa, Satoshi Minakata

Hypervalent iodine compounds containing nitrogen functional groups (amino-λ^3-iodanes) are useful reagents that can be used as an oxidant and an aminating reagent, and have been widely used for various amination reactions. However, reagents containing an NH_2 group have never been synthesized, and there are only few examples of the synthesis of primary amine-derived reagents. Although, we recently found that amino-λ^3-iodines containing various amino groups (−NH_2, −NHR) can be synthesized by the reaction of acetoxybenziodoxolone with disilazanes, this method requires the preparation of disilazanes. Therefore, the use of readily available amines was investigated for the preparation of amino-λ^3-iodanes. As a result, amino-λ^3-iodanes containing an NH_2 group could be synthesized by the reaction of **1** with a methonolic solution of ammonia. In addition, the use of primary amines with NEt_3 as a base enabled the effective formation of the target compounds. The iodine reagents synthesized could be used for the electrophilic amination of boronic acids in the presence of Cs_2CO_3.

Keywords : Amination; Amines; Hypervalent Iodine; Boronic Acids

ヨウ素上に窒素官能基を有する超原子価ヨウ素化合物（アミノ-λ^3-ヨーダン）は、酸化剤かつアミノ化剤として作用し得る有用な反応剤であり、これまでに種々のアミノ化に利用されてきた[1]。しかし、NH_2 基を有する反応剤は合成例がなく、また第一級アミン由来の反応剤においても極めて限定的であった。最近、当研究室では、アセトキシベンズヨードキソロン（**1**）に対してジシラザンを作用させることで、種々のアミノ基 (−NH_2, −NHR) を有するアミノ-λ^3-ヨーダンが合成できることを見出した。しかし、本手法はジシラザンの調製が必要であるため、入手容易なアミンを直接利用できる簡便な合成法の開発に取り組んだ。その結果、**1** に対してアンモニア（メタノール溶液）を作用させることで、NH_2 基を有するアミノ-λ^3-ヨーダンを合成できることが判った。また、第一級アミンを作用させる場合には、塩基としてトリエチルアミンを添加することで目的化合物を簡便に合成することができた。合成したヨウ素反応剤は、炭酸セシウム存在下、ボロン酸の求電子的アミノ化に利用できることが判った。



1) a) A. Yoshimura, A. Saito, V. V. Zhdankin, *Adv. Synth. Catal.* **2023**, *365*, 2653. b) J. Macara, C. Caldeira, D. L. Poeira, M. M. B. Marques, *Eur. J. Org. Chem.* **2023**, *26*, e202300109.

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ピロリジン-チアゾリウム接合型キラルイオン液体のステッター反応への応用

（大分大院工[1]・大分大理工[2]・近畿大工[3]）○徳永 真陽[1]・木村 駿介[1]・石川 雄一[2]・北岡 賢[3]・信岡かおる[2]

Pyrrolidine-Thiazolium Conjugated Chiral Ionic Liquid Catalysts for Stetter Reaction

([1]*Graduated School of Engineering, Oita University*, [2]*Faculty of Science and Technology, Oita University,* [3]*Faculty of Engineering, Kindai University*) ○Masaaki Tokunaga,[1] Syunsuke Kimura,[1] Yuichi Ishikawa,[2] Satoshi Kitaoka,[3] Kaoru Nobuoka[2]

We have synthesized a chiral ionic liquid catalyst with thiazolium cation using proline as a starting material. This chiral ionic liquid catalyzed Michael addition reactions and showed the substrate selectivity. On the other hand, the thiazolium salts can catalyze the Stetter reaction. Therefore this ionic liquid catalyst could be used as a catalyst for cascade reaction. In this study, we present its catalytic ability in the Stetter reaction.

Keywords : L-proline; thiazolium; ionic liquids; stetter reaction

我々はこれまで天然アミノ酸であるプロリンを原料にカチオン性含窒素複素環部位を接合したキラルイオン液体触媒を開発し、マイケル付加反応への適用を検討してきた。一方、チアゾリウム塩は、塩基を添加することで脱プロトン化が起こりカルベンを形成し、ステッター反応を触媒する。そこで、不斉マイケル付加反応の触媒となるピロリジン部位と、ステッター反応の触媒となるチアゾリウム部位を組み合わせたピロリジン-チアゾリウム接合型キラルイオン液体触媒(*Fig.1*)を合成し、二種類の反応を一つの触媒で連続して行うカスケード反応へ展開する事を着想した。

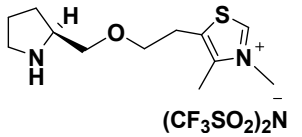
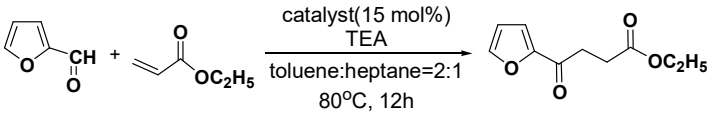
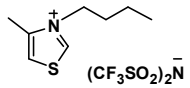
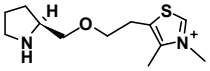


Fig.1 Thiazolium conjugated catalyst

これまでに不斉マイケル付加反応における基質選択性について見出しているが、本研究ではステッター反応への応用を検討した。チアゾリウム部位のみからなる触媒を用いて得られた最適条件を基にピロリジン-チアゾリウム接合型触媒を用いたステッター反応を行った(*Table1*)。基質にフルフラールとアクリル酸エチルを用いたところ、チアゾリウム部位のみからなる触媒を用いた場合、収率は 17%であったが(entry1)、ピロリジン-チアゾリウム接合型触媒を用いることで、42%と高い収率で目的物が得られた(entry4)。

Table1 Stetter reaction using chiral ionic liquid catalysts[a]



Entry	Catalyst	TEA (mol%)	Furfural: Ethyl acrylate (v/v)	Yield (%)
1		15	1:1	17
2		20	1:1	20
3		20	3:1	39
4		20	4:1	42

[a]Conditions:furfural(5.0 mmol, 15.0 mmol, 20 mmol), ethyl acrylate(2.5 mmol)

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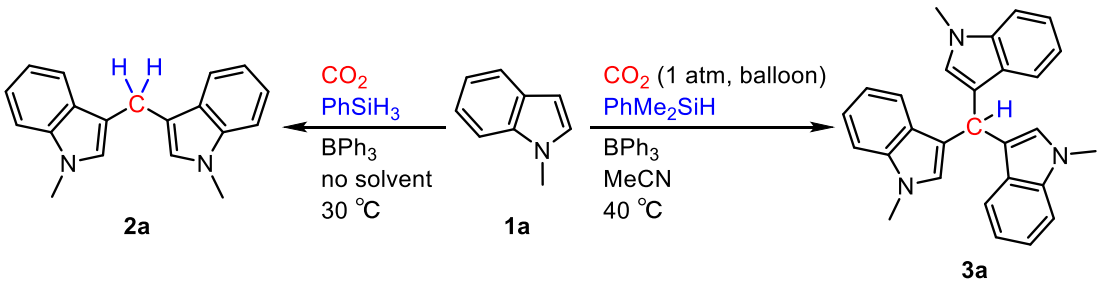
二酸化炭素のヒドロシリル化を経由するインドールの触媒的変換反応の開発

（岡山大院自然）○Sha Li・中原祥子・保井伶斗・足立泰紳・村田拓巳・前田千尋・高石和人・依馬 正
Development of methods for catalytic conversions of indoles via the hydrosilylation of carbon dioxide (*Graduate School of Natural Science and Technology, Okayama University*) ○Sha Li, Shoko Nakahara, Reito Yasui, Taishin Adachi, Takumi Murata, Chihiro Maeda, Kazuto Takaishi, Tadashi Ema

We have previously reported the synthesis of diindolylmethane **2a** from 1-methylindole (**1a**), CO_2 (1 atm, balloon), and phenylsilane using triphenylborane as a catalyst at 30 °C under solvent-free conditions. In this study, the deoxygenative CO_2 reduction coupled with the derivatization of indoles was further studied. For example, in the presence of triphenylborane and dimethylphenylsilane, the reaction of **1a** proceeded in acetonitrile at 40 °C under CO_2 atmosphere to give tris(1-methyl-3-indolyl)methane (**3a**).

Keywords : carbon dioxide, hydrosilylation, indole

当研究室では以前に、トリフェニルボランを触媒として用い、無溶媒下 30 ℃で、1-メチルインドール (**1a**)、CO_2 (1 気圧、風船) およびフェニルシランからジインドリルメタン **2a** を合成した。[1] 本研究では、このような CO_2 の脱酸素的還元反応を経由してインドールを誘導体化する触媒反応についてさらに詳しく研究した。例えば、アセトニトリル中トリフェニルボラン存在下で、ジメチルフェニルシランを還元剤として用い、CO_2 雰囲気下 40 ℃で **1a** を反応させるとトリス(1-メチル-3-インドリル)メタン (**3a**) が得られた。**2a** の合成と同様に CO_2 の脱酸素的還元反応と炭素–炭素結合形成反応が連続的に進行しているにもかかわらず異なる生成物が得られた点は大変興味深い。反応条件を種々検討した結果を報告する。



1) Murata, T.; Hiyoshi, M.; Maekawa, S.; Saiki, Y.; Ratanasak, M.; Hasegawa, J.; Ema, T. *Green Chem.* **2022**, *24*, 2385.

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N-アリールオキサミン酸の芳香族炭素－窒素結合切断を鍵とするアルケンのカルバモイルアリール化反応

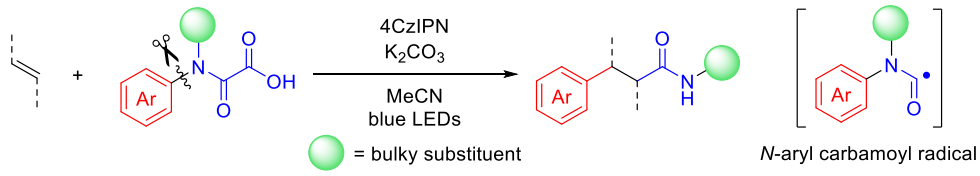
（九大先導研 [1]・九大院総理工 [2]）○塩塚 朗 [2]・呉 迪 [2]・川島 恭平 [1]・森 俊文 [1,2]・関根 康平 [1,2]・國信 洋一郎 [1,2]

Carbamoylarylation of Alkenes with *N*-Aryl Oxamic Acids Involving 1,4-Aryl Migration via C(aryl)–N Bond Cleavage ([1]*IMCE, Kyushu University*, [2]*IGSES, Kyushu University*) ○Akira Shiozuka,[2] Di Wu,[2] Kyohei Kawashima,[1] Toshifumi Mori,[1,2] Kohei Sekine,[1,2] Yoichiro Kuninobu[1,2]

The difunctionalization of alkenes using bifunctional reagents is a variable transformation in terms of step economy because it enables the direct synthesis of various complex organic molecules from readily available feedstock chemicals. The purpose of this research is developing the carbamoylarylation of alkenes, which was hitherto unknown. We recently reported that the deaminative borylation reaction of aromatic amines proceeded via *ipso*-attack of a boryl radical and C(aryl)–N bond cleavage.[1] Based on the plausible reaction mechanism, it was expected that if *N*-aryl carbamoyl radicals were used as a bifunctional reagent, the radical addition of carbamoyl radicals to alkenes, resulting in 1,4-aryl migration via the cleavage of C(aryl)–N bond could proceed. We found that the carbamoylarylation of alkenes with *N*-aryl-oxamic acids proceeded in the presence of an organic photocatalyst and K_2CO_3 in acetonitrile upon visible-light irradiation, affording arylpropanamides in high yields.

Keywords : C–N Bond Cleavage; Carbamoylarylation; Aryl Migration; Alkene; Organic Photochemical Reaction

二官能基化反応剤によるアルケンの官能基化は、入手容易な原料から機能性分子に含まれる複雑な骨格を短工程で構築できるため、ステップエコノミーの観点から有用である。今回、報告例のないアルケンのカルバモイルアリール化反応の開発を目指した。以前我々は、芳香族アミンの炭素－窒素結合の切断を伴うボリル化反応が、ホウ素ラジカルのイプソ攻撃および芳香族炭素－窒素結合の切断を経由して進行すると報告した [1]。この推定反応機構から着想を得て、*N*-アリールカルバモイルラジカルを官能基化剤として用いれば、カルバモイルラジカルのアルケンへの付加、それに引き続く芳香族炭素－窒素結合の切断を伴う 1,4-アリール転位が進行し、カルバモイルアリール化反応を達成できると考えた。実際に、アルケン、*N*-アリールオキサミン酸、有機光触媒および炭酸カリウムをアセトニトリル溶媒中で可視光照射すると、目的のカルバモイルアリール化反応が進行し、対応するアリールプロパンアミドが高収率で得られた。



1. Shiozuka, A.; Sekine, K.; Toki, T.; Kawashima, K.; Mori, T.; Kuninobu, Y. *Org. Lett.* **2022**, *24*, 4281.

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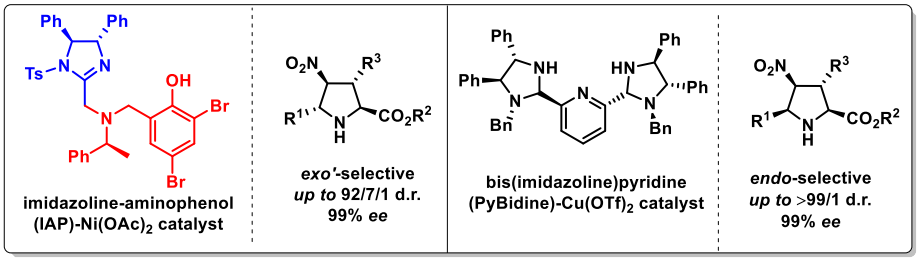
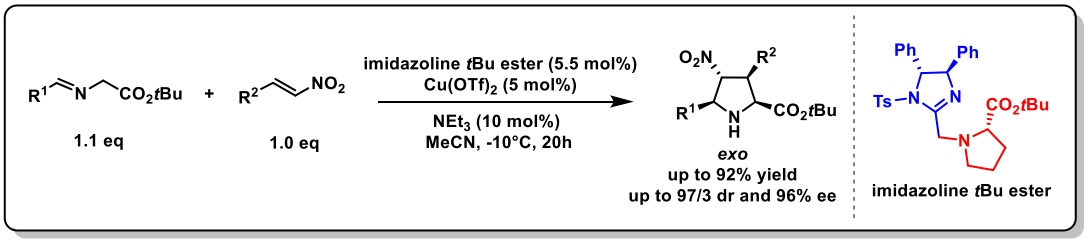
Catalytic Asymmetric *exo*-Selective [3+2] Cycloaddition of Iminoesters with Nitroalkenes Using Imidazoline-*t*Butyl ester-Copper Complex

(*Graduate School of Science and Engineering, Chiba University*) ○Yan Yu, Takayoshi Arai
Keywords: Asymmetric Synthesis; Chiral Catalyst; 1,3-Dipolar Cycloaddition Reaction

1,3-dipolar cyclization reaction has been a powerful method for the synthesis of multisubstituted pyrrolidines. Cycloaddition of iminoester and nitroalkene has the ability to introduce a nitro functionality onto the pyrrolidine. So far, our laboratory has developed novel catalytic systems of imidazoline amino phenol ligand (IAP)-Ni(II) and bis(imidazoline)pyridine ligand (PyBidine)-Cu(II), and respectively achieved asymmetric synthesis of *exo'* and *endo*- nitro functional pyrrolidines.[1)]



In this work, we designed a new catalyst derived from IAP ligand, the imidazoline center is modified by proline ester. This imidazoline *t*butyl ester ligand has shown well catalytic activity in *exo*-selective 1,3-dipolar cyclization reaction of *t*butyl iminoesters and nitroalkenes, affording products with high diastereo- and enantioselectivity.



(1) a) Arai, T.; Yokoyama, N.; Mishiro, A.; Sato, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 7895-7898;
b) Arai, T.; Mishiro, N.; Yokoyama, K. Suzuki, H.; Sato, H. *J. Am. Chem. Soc*. **2010**, *132*, 5338-5339.

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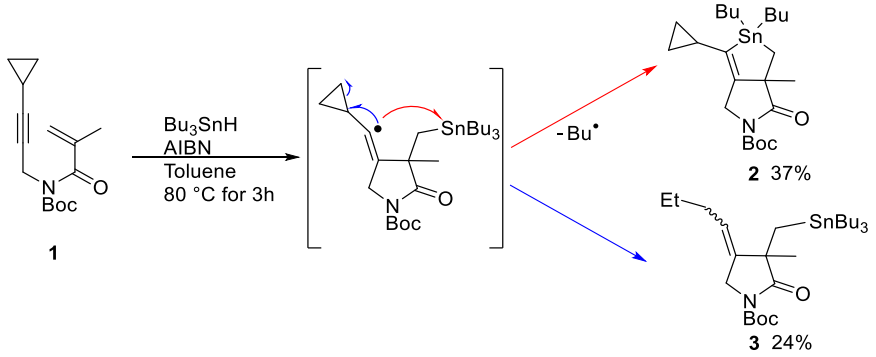
シクロプロピルアセチレンを用いた1,6-エンイン化合物のラジカルカスケード反応の機構的研究

（山口大院[1]・山口大工[2]）○石堂香奈子[1]・神田裕樹[2]・川本拓治[2]・上村明男[2]
A mechanistic study on radical cascade reaction of 1,6-enyne precursors using cyclopropylacetylene ([1]Graduate School of Engineering, Yamaguchi University, [2]Yamaguchi University) ○Kanako ISHIDO[1], Yuki KANDA[2], Takuji KAWAMOTO[2], Akio KAMIMURA[2]

We have reported that amide-type 1,6-enyne compounds are potentially useful precursors for the synthesis of various heterocyclic compounds via radical reaction induced by Bu_3SnH. We investigated kinetic parameters of the direct radical substitution on a tin atom using a cyclopropylacetylene-attached precursor. The cyclopropylvinyl intermediate undergoes either the ring-opening to give allenyethylradical or the attack on the tin to give cyclization products. In the presentation, the details of our kinetic investigation will be discussed based on the products distribution under various cnditions.
Keywords : radical reaction, mechanistic study, 1,6-enyne, tin radical, cyclopropylacetylene

我々は容易に合成できるアミド型1,6-エンイン化合物にBu_3SnHを作用させることで様々な複素環を合成できることを報告してきた[1]。この反応は中間に生じるビニルラジカル中間体がスズ原子を攻撃して進行している。そこで、我々はこの反応がビニルラジカルの化学的挙動を調べるための極めてよいプラットフォームを与えると気付いた。そこで、今回、1,6-エンインへのスズラジカルのラジカル反応によるカスケードプロセスにおけるスズ原子上への直接置換反応の反応速度の見積もりを目指して、シクロプロピルアセチレンを有する前駆体との反応を検討した。

アルキン末端にシクロプロピル基を有すると、反応途中に生じるシクロプロピルビニルラジカル中間体がスズ原子を攻撃して環化するか、ビニルシクロプロパンの開環するか、いずれかの反応が進行することがわかっている。そこでこれらを用いて種々の条件下でのこれら2つの生成物分布を通じて，速度定数の見積もりを目指した反応経路の詳細について議論する。



1) A. Kamimura, K. Kohno, K. Ishido, N. Kamohara, T. Kawamoto, Asian J. Org. Chem. **2023**, e202300223.

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ルイス酸活性化によるニトロソ化合物からのニトロン合成

（金沢大理工）○前川 優弥、菅 拓也、添田 貴宏、宇梶 裕

Lewis acid-promoted preparation of nitrones from nitroso compounds

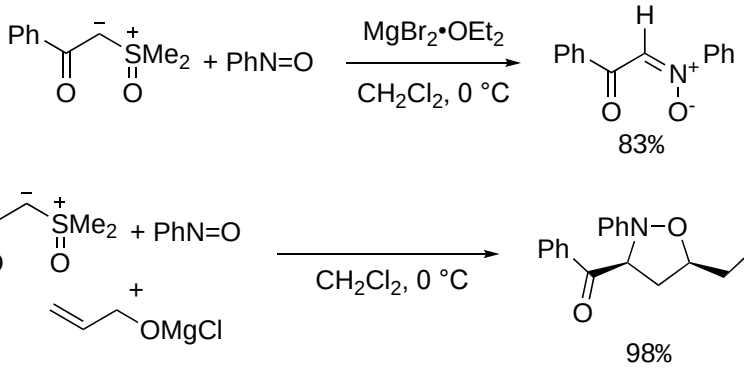
(*College of Science and Engineering, Kanazawa University*)○Masaya Maegawa, Takuya Suga, Takahiro Soeta, Yutaka Ukaji

Nitrone is an important chemical species as a 1,3-dipole and usually prepared form carbonyl compound and hydroxylamine. On the other hand, the reaction between nitroso benzene and sulfur ylides was reported to give the corresponding nitrones under relatively high temperature conditions. In this study, we investigated activation of the above reaction by Lewis acid and magnesium salts were found to activate the reaction. Furthermore, by use of the magnesium salt of allyl alcohol, the successive 1,3-dipolar cycloaddition to ally alcohol moiety smoothly proceeded after the formation of the nitrone.

Keywords: Lewis acid; Nitrone; Sulfur ylide

ニトロンは有用な 1, 3−双極子であり，アルケンと[3＋2]付加環化を起こしイソオキサゾリジンが得られる。ニトロンは，一般にカルボニル化合物とヒドロキシルアミンより合成される。一方，ニトロソベンゼンと硫黄イリドより合成する方法も報告されたが，加熱条件が必要である [1)]。今回，上述の反応がルイス酸により活性化可能かを検討した。その結果，マグネシウム塩が有効であることが明らかになった。

実際に、ベンゾイルスルホキソニウムイリドとニトロソベンゼンを臭化マグネシウム存在下で 0 ℃で混合すると、目的のニトロンが 83%収率で得られた。さらにアリルアルコールのマグネシウム塩を用いると，アリルアルコールとの[3＋2]付加環化まで一挙に進行し、対応するイソオキサゾリジンがジアステレオ選択的に生成することも明らかになった。



1) X. Li, P. Zhai, Y. Fang, W. Li, H. Chang, W. Gao, *Org. Chem. Front.* **2021**, *8*, 988.

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2-クロロ-ベンゾ[*c*]テトラゾロ[2,3-*a*]シンノリニウム塩のアミノ化反応

(名工大院工)　○神谷 恵理・平下 恒久

Amination of 2-chloro-benzo[*c*]tetrazolo[2,3-*a*]cinnolinium salt (*Graduate School of Engineering, Nagoya Institute of Technology*) ○Eri Kamiya, Tsunehisa Hirashita

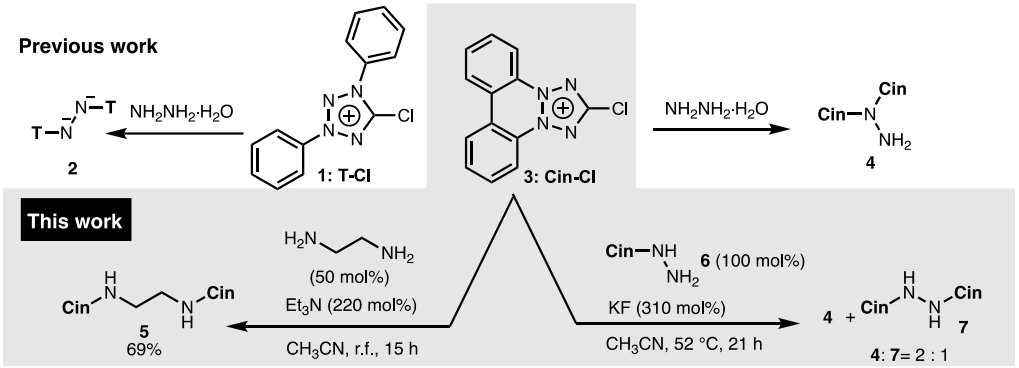
5-Chloro-1,3-diphenyltetrazolium salt **1** was reacted with hydrazine hydrate to afford the corresponding *N,N'*-disubstituted hydrazine **2**.[1)] 5-Chloro-2,3-diphenyltetrazolium salt yields triazole via successive ring-opening and recyclization upon the reaction with amines, whereas chlorocinnolinium salt **3** cross-linked at the *ortho*-position of the 2- and 3- positions of the aryl groups reacts with amines to give the corresponding tetrazolium by the substitution reaction of the chlorine atom. [3)] When hydrazine was applied to **3**, *N,N*-disubstituted amine **4** was formed in contrast to **1** [4)]. Here, we studied reactions of **3** with a series of diamines.

Chlorocinnolinium **3** was reacted with ethylenediamine to afford the corresponding *N,N'*-disubstituted amine **5**. The reaction of **3** with hydrazinocinnolinium salt **6** formed *N,N*-disubstituted hydrazine **4** and *N,N'*-disubstituted hydrazine **7** in the presence of KF.

Keywords :Mesoionic Compound; ethylenediamine; hydrazine; amination

5-クロロ-1,3-ジフェニルテトラゾリウム塩 **1** にヒドラジンを作用させると *N,N´*-ジ置換体 **2** が生成する [1)]。一方，クロロ-2,3-ジアリールテトラゾリウム塩はアミンと作用させると 2 位窒素-3 位窒素結合の開裂と再環化を経てトリアゾールが生成するが [2)]，2,3-アリール基のオルト位を架橋したクロロシノリニウム塩 **3** はアミンとの反応で塩素原子の置換によって対応するテトラゾリウムアミンが生成する [3)]。ヒドラジンを作用させると **1** とは対象的に *N,N*-ジ置換アミノ化体 **4** が生成する [4)]。今回、**3** と種々のジアミンとの反応について検討した。

3 にエチレンジアミンを反応させると，*N,N´*-ジ置換アミノ化体 **5** が得られた。KF 存在下で **3** とヒドラジノシンノリニウム塩 **6** を反応させると *N,N*-ジ置換ヒドラジン **4** に加え，*N,N´*-ジ置換ヒドラジン **7** が生成した。



1) S. Araki, *et al.*, *J. Chem. Soc. Perkin Trans. 2*, **1999**, 985-995; 2) S. Araki, *et al.*, *Beilstein J. Org. Chem.*, **2009**, *5*, 8; 3) M. Nakata, *et al.*, *Org. Biomol. Chem.*, **2023**, *21*, 4282-4289; 4) N. Nakata, T. Hirashita, 99th Annual Meeting of Union of Chemistry-Related Societies in Chubu Area, Japan, 2PB-177, **2019**.

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC
E1141(1141, Bldg. 11 [4F])

[E1141-3vn] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Atsushi Ohtaka, Kohei Sekine

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1141-3vn-01]
Facile Synthesis of α-Aryl Ketones via Grignard Reaction of Benzocyclobutenones
○Yukitaka Hoshi[1], Shinya Tabata[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1141-3vn-02]
Synthesis of *ortho*-Substituted Benzotrifluorides by Deprotonative Transformations
○Yotaro Seki[1], Keisuke Nakamura[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1141-3vn-03]
Facile Synthesis of 2,7-Disubstituted 1,8-Naphthyridine Derivatives
○Takumi Hamada[1], Kento Iwai[1], Nagatoshi Nishiwaki[1] (1. Kochi Univ. of Tech.)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1141-3vn-04]
Simple *N*-formylation of secondary amines using DMF as a formylating reagent
○Tomoya Sakaguchi[1], Hibiki Awata[1], Yoshimasa Matsumura[1], Osamu Shimomura[1], Atsushi Ohtaka[1] (1. Osaka Institute of Technology)

4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
Break

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[E1141-3vn-05]
Synthesis, structure, and reactivities of tetranuclear silver(I) complex with 1,8-naphtylbis(sulfane)carbon(0) ligand
○Rena Tsukamoto[1], Keiko Noguchi[1], Takayoshi Fujii[1] (1. TheThe Univ. of Nihon)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[E1141-3vn-06]
Catalytic activity and fluorescence property of pyridodipyrimidine derivatives mimicking nicotinamide coenzymes

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○Eriko Ohishi[1], Taiga Mizushima[2], Marina Oka[2], Fumitoshi Yagishita[3,4], Yasushi Imada[3], Hiroki Iida[1,2] (1. Shimane University, 2. Graduate School of Natural Science and Technology, Shimane University, 3. Graduate School of Technology, Industial and Social Sciences, Tokushima University, 4. Institute of Post-LED Photonics, Tokushima University)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[E1141-3vn-07]

Synthesis and physical properties of chlorophyll derivatives with a newly fused six-membered ring

Hitoshi Tamiaki[1], ○Takuma Imuta[1], Nobuyuki Hara[1], Shin Ogasawara[1] (1. Ritsumeikan University)

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ベンゾシクロブテノン類の Grignard 反応を経る α-アリールケトン類の簡便合成法の開発

(東理大先進工) ○星幸崇・田端慎也・吉田優

Development of a Simple Synthesis Method for α-Aryl Ketones via Grignard Reaction of Benzocyclobutenones

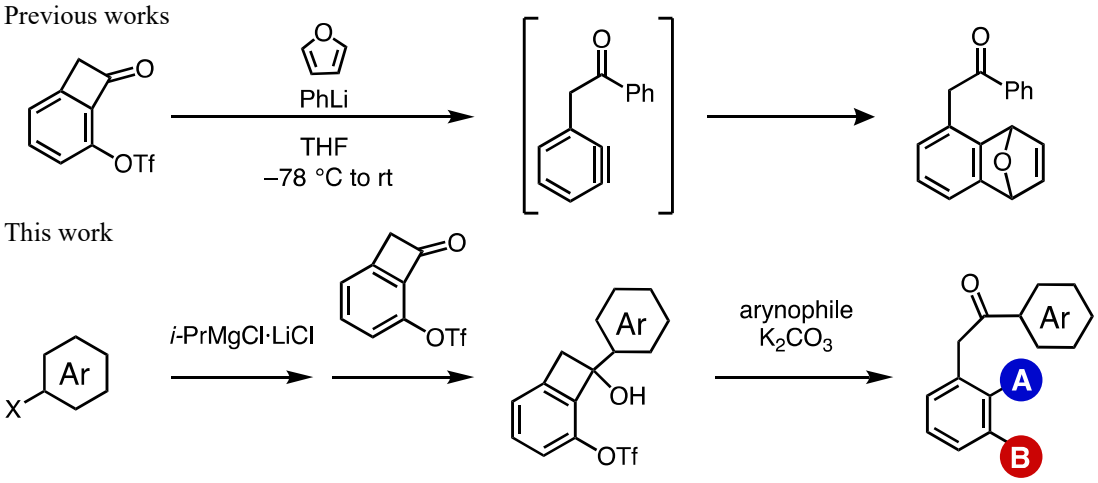
(*Faculty of Advanced Engineering, Tokyo University of Science*) ○Yukitaka Hoshi, Shinya Tabata, Suguru Yoshida

Recently, we found that treatment of ketones with phenyllithium in the presence of furan afforded cycloadducts via 1,2-addition to the carbonyl group and following generation of arynes. Herein, we succeeded in the synthesis of benzocyclobutenols with a variety of functional groups through a reaction of ketones with organomagnesiums prepared using turbo-Grignard reagent. A wide range of α-aryl-substituted ketones were synthesized through the generation of arynes from the resulting benzocyclobutenols using a base.

Keywords : Arynes, α-Aryl ketones, Ester, Turbo Grignard reagent, 1,2-Addition

最近、私たちはアライン前駆体であるベンゾシクロブテノンに対してフェニルリチウムを作用させると、カルボニル基への 1,2-付加と続くアラインの発生を経て変換できることを報告している。今回、ターボ Grignard 試薬を用いて調製した求核剤をケトンに対して反応させることによって、幅広い官能基を有するベンゾシクロブテノールを合成できることを明らかにした。次に、塩基を用いたアライン発生により、多彩な α-アリールケトン類の合成に成功した。

実際に、ベンゾシクロブテノンとエステルを持ったグリニャール試薬との反応を、トルエン溶媒中、-20 ℃の条件で行った場合、目的のアルコール体を良好な収率で得ることに成功した。さらに、得られたアルコールに対して、炭酸カリウムを加えることでアラインを発生させることができ、多様性に富んだα-アリールケトン類を合成できることを明らかにした。



1) K. Uchida, S. Yoshida, T. Hosoya, *Org. Lett.* **2017**, *19*, 1184

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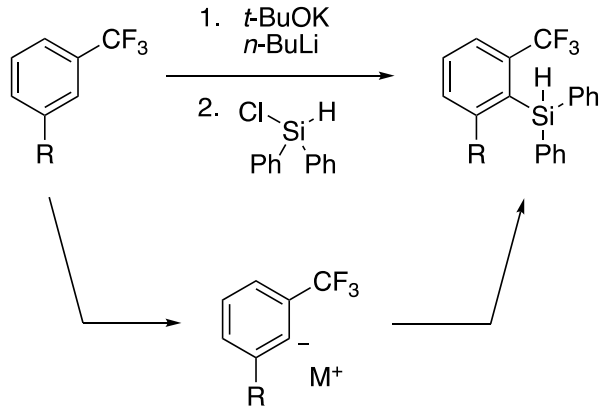
脱プロトンを経るオルト置換ベンゾフルオリド類の合成

(東理大先進工) ○関 陽太郎・中村 圭佑・吉田 優
Synthesis of *ortho*-Substituted Benzotrifluorides by Deprotonative Transformations
(*Tokyo University of Science*) ○Yotaro Seki, Keisuke Nakamura, Suguru Yoshida

Recently, we developed a range of transformations through C–F cleavage of trifluoromethyl groups. Herein, we report that deprotonation of benzotrifluorides followed by reactions with electrophiles afforded a broad range of *ortho*-substituted benzotrifluorides.
Keywords: Trifluoromethyl group; Schlosser base; Directing group; Silylation; C–F cleavage

最近我々は、トリフルオロメチル基における炭素−フッ素結合の切断を経る変換を開発してきた [1,2]。これまで、トリフルオロメチル基のオルト位での脱プロトンを経て変換できることが明らかにされているものの、本手法で合成できるトリフルオロメチルベンゼン類は限定的であった。今回我々は、ベンゾトリフルオリドに *n*-ブチルリチウムと *t*-ブトキシカリウムを作用させた後、クロロシランなどを作用させることでオルト位にヒドロシリル基を有するベンゾトリフルオリド類の合成に成功した。



1) a) S. Yoshida, *Chem. Rec.* **2023**, *23*, e202200308. b) R. Idogawa, A. Kobayashi, Y. Kim, K. Shimomori, T. Hosoya, S. Yoshida, *Chem. Commun.* **2022**, *58*, 3521. c) R. Idogawa, Y. Kim, K. Shimomori, T. Hosoya, S. Yoshida, *Org. Lett.* **2020**, *22*, 9292. d) Y. Kim, K. Kanemoto, K. Shimomori, T. Hosoya, S. Yoshida, *Chem. Eur. J.* **2020**, *26*, 6136. e) S. Yoshida, K. Shimomori, Y. Kim, T. Hosoya, *Angew. Chem., Int. Ed.* **2016**, *55*, 10406.
2) a) S. Hamada, S. Yoshida, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 401. b) M. Ikeda, T. Matsuzawa, T. Morita, T. Hosoya, S. Yoshida, *Chem. Eur. J.* **2020**, *26*, 12333.

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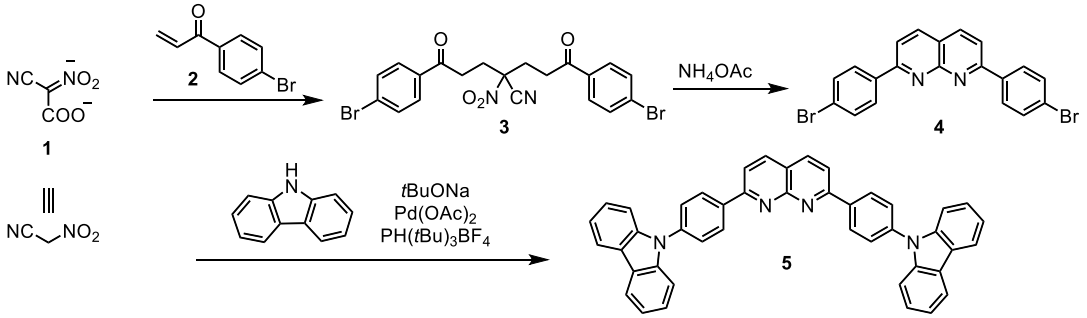
2,7-ジ置換 1,8-ナフチリジンの簡便な合成

（高知工大理工）○濱田 拓実・岩井 健人・西脇 永敏
Facile Synthesis of 2,7-Disubstituted 1,8-Naphthridine Derivatives (*School of Engineering Science, Kochi University of Technology*) ○ Takumi Hamada, Kento Iwai, Nagatoshi Nishiwaki

1,8-Naphthyridine scaffold are widely used as luminescent bioimaging and sensor; however, versatile naphthyridine derivatives are not easily available by conventional synthetic methods because of limited substrate-scope and using strong acid. To overcome these disadvantages, a new synthetic method was developed using cyano-*aci*-nitroacetate **1** as a cyano(nitro)methylation reagent. Double Michael addition of **1** with vinyl ketones **2** efficiently proceeded to afford **3** in high yields. Subsequent heating of **3** in the presence of NH_4OAc furnished 2,7-disubstituted 1,8-naphthyridines **4**. Modification at the 2 and 7-positions was readily performed by only altering the vinyl ketone **2**. Indeed, successive introduction of *p*-bromophenyl and carbazolo groups was also achieved.
Keywords: 1,8-naphtydine; cyano(nitro)methylation reagents; fluorescence

1,8-ナフチリジンを基本骨格とする分子は発光性を活かした生体イメージングやセンシングなどに幅広く利用されている。しかし、その合成方法は 2,6-ジアミノピリジンとリンゴ酸の縮合を起点としたものがほとんどであり、骨格修飾するには基質の入手が困難などの問題もあり、制限が多い。また、強酸性条件を用いることも改善すべき点の 1 つである。そのような問題を解決するために、当研究室で開発したシアノ(ニトロ)メチル化剤 [1] を利用することにより、骨格修飾が容易なナフチリジン誘導体の合成法を開発した。

シアノアシニトロ酢酸塩 **1** に対して 2 当量のビニルケトン **2** を作用させたところ、ダブルマイケル付加が効率良く進行した。次いで、酢酸アンモニウムの共存下で **3** を加熱することにより、2,7 位が修飾された 1,8-ナフチリジン **4** を得た。本法の特長は基質を変えることにより簡便に 2,7 位を修飾できることである。その結果、多様なナフチリジン骨格の分子設計と合成を行なうことが可能になる。この特長を活かして、パラブロモフェニル基およびカルバゾリル基を連続的に導入することに成功した。



1 *J. Org. Chem.* **2021**, *86*, 13177; *Tetrahedron* **2014**, *70*, 6522.

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DMF をホルミル化剤とする簡便な 2 級アミンの *N*-ホルミル化

（阪工大工）○坂口 智哉・粟田 響・松村 吉将・下村 修・大高 敦
Simple *N*-formylation of secondary amines using DMF as a formylating reagent (*Faculty of Engineering, Osaka Institute of Technology*) ○Tomoya Sakaguchi, Hibiki Awata, Yoshimasa Matsumura, Osamu Shimomura, Atsushi Ohtaka

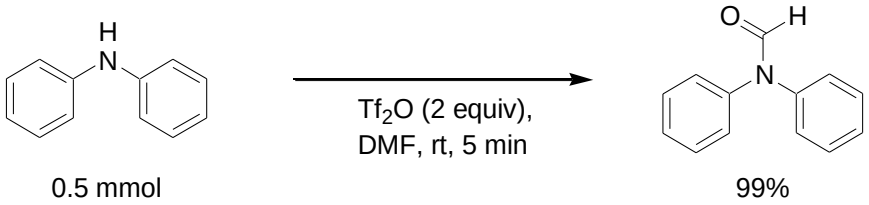
Tertiary formamides are important structures contained in various synthetic intermediates. Various direct *N*-formylations of secondary amines with formic acid derivatives have been reported. However, in many cases, metal catalysts or harsh reaction conditions are required.[1)] In recent years, *N*-formylation reactions using DMF as a formylation reagent have been reported, but they require high temperature and long reaction time.[2)]

On the other hand, Vilsmeier-Haack reaction which is formylation of aromatic rings using $POCl_3$ is known as a typical reaction with DMF as a formylating reagent. Hanack *et al.* was achieved the formylation of inert aromatic rings using Tf_2O instead of $POCl_3$.[3)] In this study, we developed a milder *N*-formylation of secondary amines by using Vilsmeier reagent from DMF and Tf_2O than previously reports.

Keywords : N-Formylation; DMF; Secondary amines; Tf_2O.

第三級ホルムアミド骨格は様々な合成中間体に含まれる重要な構造である．これまでに，ギ酸誘導体による二級アミンの直接 *N*-ホルミル化が種々報告されている．しかし，多くの場合，金属触媒や高温条件などが必要となる [1)]．また近年，安価な溶媒である DMF をホルミル化剤とする *N*-ホルミル化反応が報告されているものの，高温条件や長時間の反応時間が必要である [2)]．

一方で，DMF をホルミル化剤とする代表的な反応例として，$POCl_3$ を用いた芳香族求電子置換反応（Vilsmeier-Haack 反応）が知られている．Hanack らは，この反応の添加剤を Tf_2O に変更することで，不活性な芳香環のホルミル化が進行することを報告している [3)]．本研究では DMF と Tf_2O からなる Vilsmeier 試薬を用いることで，これまでの報告例よりも簡便な条件で，二級アミンの *N*-ホルミル化が可能となることを確認した．



0.5 mmol　　99%

1) (a) Lu, M. *et al. RSC Adv.* **2014**, *4*, 1234. (b) Yu, H.; Han, S.; Wei, Y. e*t al. Green Chem.* **2020**, *22*, 737. (c) Vries, J. G. de. e*t al. ChemSusChem* **2022**, *15*, e202201264.
2) (a) Jagtap, S. V. *et al. Org. Lett.* **2017**, *19*, 2078. (b) Kihara, N. *et al. Tetrahedron Lett.* **2019**, *60*, 1291.
3) Martinez, A. G.; Hanack, M.; *et al. J. Chem. Soc. Chem. Commun.* **1990**, 1571.

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1,8-ナフチルビス(スルファン)カーボン(0)を配位子とした 4 核銀(I)錯体の合成，構造および反応性

(日大生産工) ○塚本 玲奈・野口 桂子・藤井 孝宜

Synthesis, structure, and reactivities of tetranuclear silver(I) complex with 1,8-naphtylbis(sulfane)carbon(0) ligand (*College of Industrial Technology, Nihon University*)

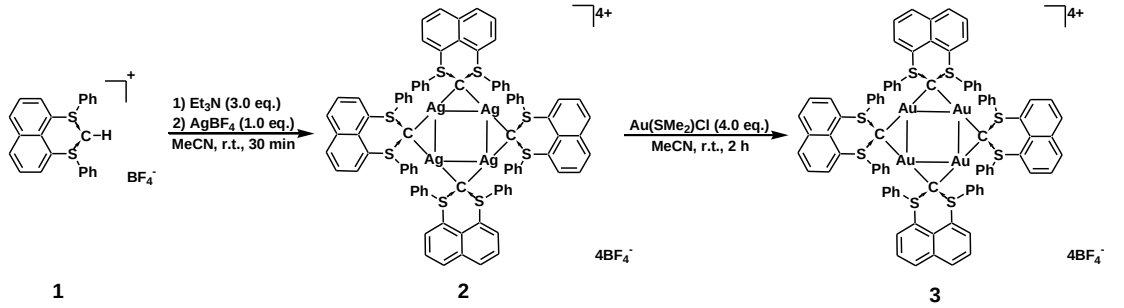
○Rena Tsukamoto, Keiko Noguchi, Takayoshi Fujii

Divalent carbon (0) species, also known as carbone are all four valence electrons in σ- and π- type lone pair (LP) orbitals and are stabilized by two ligands (L). We have presented successfully synthesized tetranuclear silver(I) complex **2**, and gold(I) complex **3**. **2** was prepared by the reaction of **1** with silver tetrafluoroborate in the presence of triethylamine. Subsequent transmetalation reaction with chloro(dimethylsulfide)gold(I), led to the formation of **3**. The molecular structure **2** and **3** was determined by X-ray crystallography.

Keywords : Divalent carbon (0) species, Cyclic carbone, Tetranuclear silver(I) complex, Main group elements chemistry

カルボンは中心炭素が 4 電子供与性を示すため，銀(I)イオンとのジェミナル配位が可能な配位子である [1]。当研究室では硫黄配位子を有する非環状型カルボンを用いた多核銀(I)錯体の合成に成功している。中でも，4 核銀(I)錯体において，ビス(イミノスルファン)カーボン(0)は κ^3C,C',N 配位型となることを報告している [2]。本研究では環状型カルボンである 1,8-ナフチルビス(スルファン)カーボン(0)と銀(I)イオンとの反応を試みたので報告する。

モノカチオン体 **1** とテトラフルオロホウ酸銀をトリエチルアミン存在下，アセトニトリル中，室温で 30 分反応させることで 4 核銀(I)錯体を得た(Scheme 1)。さらに，錯体 **2** とジメチルスルフィド金(I)クロリドをアセトニトリル中，室温で 2 時間反応させることで 4 核金(I)錯体 **3** が得られた。錯体 **2** 及び **3** の分子構造は単結晶 X 線構造解析により明らかにしたところ，これらの多核錯体は金属イオンクラスター中心に 4 つの μC,C 配位型カルボンが取り囲む構造であることが分かった。



Scheme 1. Synthesis of **3**

1) R. Tonner, F. Öxler, B. Neumüller, W, Petz, and G. Frenking, *Angew. Chem. Int. Ed.*, **45**, 8038 (2006).
2) T. Morosaki, T. Suzuki, and T. Fujii, *Organometallics*, **35**, 2715 (2016).

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ニコチンアミド補酵素を模倣したピリドジピリミジン誘導体の触媒能と蛍光特性

（島根大総合理工[1]・島根大院自然科学[2]・徳島大院理工[3]・徳島大 pLED 研[4]）○大石 恵理子[1]・水嶋 大雅[2]・岡 真里奈[2]・八木下 史敏[3,4]・今田 泰嗣[3]・飯田 拡基[1,2]

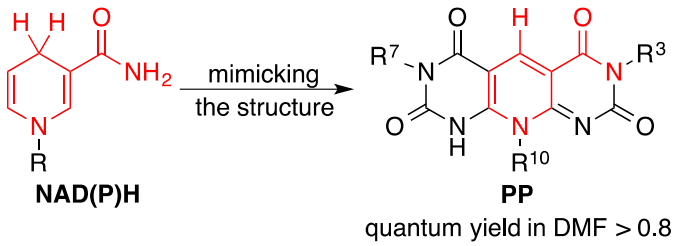
Catalytic Activity and Fluorescence Property of Pyridodipyrimidine Derivatives Mimicking Nicotinamide Coenzymes

([1]*Interdisciplinary Faculty of Science and Engineering, Shimane University*, [2]*Graduate School of Natural Science and Technology, Shimane University*, [3]*Graduate School of Technology, Industial and Social Sciences, Tokushima University*, [4]*Institute of Post-LED Photonics, Tokushima University*) ○Eriko Ohishi,[1] Taiga Mizushima,[2] Marina Oka,[2] Fumitoshi Yagishita,[3,4] Yasushi Imada,[3] Hiroki Iida[1,2]

Nicotinamide adenine dinucleotide (phosphate), **NAD(P)H**, are known as coenzymes responsible for redox reactions in vivo. Pyridodipyrimidine derivatives (**PP**s) have been developed to mimic these functions in vitro, and have been reported to catalyze the dehydrogenation of alcohols. In this study, we synthesized a series of **PP**s bearing various substituents and investigated their catalytic activity and optical properties. The study revealed that they exhibited fluorescence in both solid and solution states with the quantum yields in solution states exceeding 0.8. The fluorescence maximum wavelengths in solid states were dependent on the substituents at the 3,7-positions.

Keywords : Nicotinamide Coenzyme; Pyridodipyrimidine; Organocatalyst; Dehydrogenation; Fluorescence Property

ニコチンアミドアデニンジヌクレオチド (**NADH**) やニコチンアミドアデニンジヌクレオチドリン酸 (**NADPH**) は、一般的に生体内の酸化還元反応を行う補酵素として知られている。この機能を生体外で模倣するために、ニコチンアミド骨格を有するピリドジピリミジン誘導体 (**PP**) が開発されてきた。**PP** は触媒的にアルコールの脱水素酸化を進行させることが報告されているが[1)]、物性等についてはほとんど研究されていない。そこで本研究では、種々の置換基を有する **PP** を合成し、その触媒能について検討を行うとともに、固体および溶液状態での光学特性についても調査した。その結果、**PP** は DMF 中で青色の強い蛍光を示すことが明らかとなった。溶液状態での蛍光量子収率を測定した結果、0.8 を超える高い値を示した。また、**PP** は固体状態でも紫外光照射下で蛍光を示し、その蛍光極大波長は、3,7 位の置換基によって変化することが分かった。これらの **PP** をアルコールなどの酸化反応における触媒として用いたところ、触媒活性を示したのであわせて報告する。



1) a) F. Yoneda, H. Yamato, M. Ono, *J. Am. Chem. Soc.* **1981**, 103, 5943. b) T. Nagamatsu, H. Yamato, M. Ono, S. Takarada, F. Yoneda, *J. Chem. Soc. Perkin Trans. 1.* **1992**, 2101.

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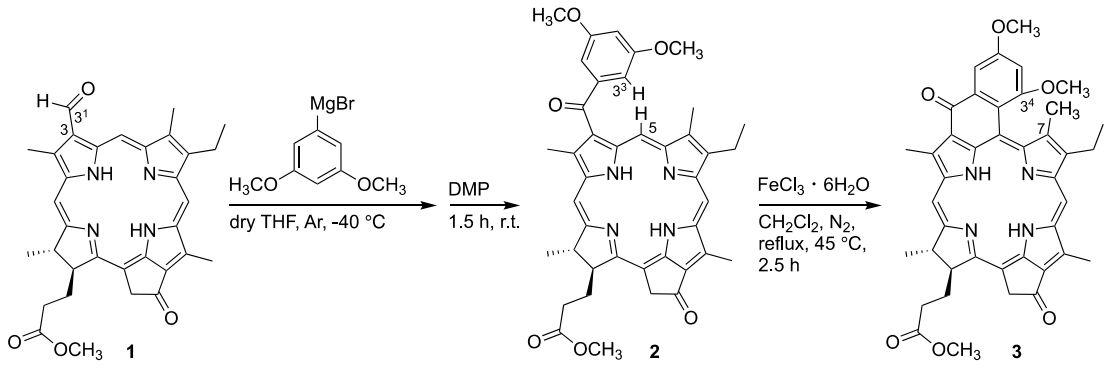
新たに六員環が縮環したクロロフィル誘導体の合成と物性

（立命館大生命科学）民秋 均・○薗牟田 拓磨・原 伸行・小笠原 伸
Synthesis and physical properties of chlorophyll derivatives with a newly fused six-membered ring (*Faculty of Life Sciences, Ritsumeikan University*) Hitoshi Tamiaki, ○Takuma Imuta, Nobuyuki Hara, Shin Ogasawara

Chlorophyll-*a* derivatives with an arylcarbonyl group at the 3-position were synthesized by Grignard reaction of the 3-formyl group and successive oxidation of the resulting alcohols. Intramolecular Scholl reactions of the synthetic 3-arylcarbonyl-chlorins gave chlorophyll derivatives with a fused six-membered ring through the C–C bonding between the *ortho*-position of the aryl group and the 5-position of the chlorin moiety, and their physical properties in a solution will be discussed.
Keywords : Chlorophyll; Grignard reaction; Scholl reaction; Stereochemistry; UV-Vis-NIR absorption

天然色素分子の一種として知られるクロロフィル(Chl)は、大環状共役系であるクロリン環を有しており、特異な光吸収スペクトルを示す[1)]。本研究では、酸化的アリール-アリールカップリングの Scholl 反応を用いて、新たに六員環が縮環した Chl 誘導体の合成に成功したので、その物性とあわせて報告する。

シアノバクテリア(*Spirulina*)から抽出された Chl-*a* を既報に従って化学修飾し、3 位にホルミル基を有する methyl pyropheophorbide-*d* (**1**)を合成した。次に Grignard 反応によって 3,5-ジメトキシフェニル基を 3^1位に導入し、Dess–Martin 酸化によって化合物 **2** を合成した。化合物 **2** をジクロロメタンに溶解させ、5 当量の $FeCl_3 \cdot 6H_2O$ を加え、遮光しながら 45 ℃、N_2 気流下で 2.5 時間加熱還流すると、3^3位と 5 位での C–C 結合形成によって、六員環が縮環した化合物 **3** が得られた。化合物 **3** は 3^4位メトキシ基と 7 位メチル基の立体反発によって、2 つの立体異性体が存在しており、それぞれの異性体を単離精製し、それらの光物性を検討した。



1) H. Tamiaki, Chlorophylls, in *Fundamentals of Porphyrin Chemistry: A 21st Century Approach*, Chapter 17, 743–776 (2022). Doi: 10.1002/9781119129301.ch17

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
E1142(1142, Bldg. 11 [4F])

[E1142-3am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Kento Ishida, Ryosuke Haraguchi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1142-3am-01]
Enantioselective Synthesis of Triptycene Derivatives by Enzymatic Desymmetrization

○Shiina Noguchi[1], Masayuki Shigeta[1], Mio Ochiai[1], Hikaru Yanai[1], Takashi Matsumoto[1] (1. Tokyo University of Pharmacy and Life Sciences)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1142-3am-02]
Development of synthesis of thioesters from acyl fluorides and thiosilanes

○Ryuki Takeuchi[1], Kento Ishida[1], Norio Sakai[1] (1. Tokyo University of Science)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1142-3am-03]
Copper-catalyzed Aminoazidation of Alkenes with NFC

○Hiroto Kimura[1,2], Kohsuke Aikawa[3], Takuya Hashimoto[2,1] (1. Chiba Univ., 2. RIKEN, 3. Univ. of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1142-3am-04]
Conversion of Oxygenates to Alkenes by TiO_2 and Cobaloxime Dual Photocatalyst System

○Eiki Maruyama[1], Xiongjie Jin[1], Kyoko Nozaki[1] (1. School of Engineering, The University of Tokyo)

English
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1142-3am-05]
Development of 1,3,2-Dioxaborolan-4-one Catalyst for Dehydrative Condensation toward Peptides Synthesis

○Qianchun HUANG[1], Shuhei Ohmura[1], Kazuaki Ishihara[1] (1. Nagoya University)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1142-3am-06]
Diastereoselective Alkylation for Construction of 1,3-Nonadjacent Stereogenic Centers Containing a Tetrasubstituted Carbon Center

○Rihaku Ojima[1], Azusa Kondoh[1], Masahiro Terada[1] (1. Graduate School of Science, Tohoku University)

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Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1142-3am-07]
Brønsted Base-Catalyzed Aminooxylation of Allylic- and Benzylic Compounds
○Azusa Kondoh[1], Masahiro Terada[1] (1. 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
[E1142-3am-08]
Synthetic Method for *vic*-Amino Alcohol with Consecutive Tertiary Carbons
○Shiori Takashima[1], Tomoka Watanabe[1], Tomoya Wakana[1], Yu Sakano[2], Ryosuke Haraguchi[1] (1. Graduate School of Engineering, Chiba Institute of Technology, 2. Faculty of Engineering, Chiba Institute of Technology)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1142-3am-09]
Catalyst-Controlled Chemodivergence in Nucleophilic Cyanation to 1,2-Ketoimine
○Tomoka Watanabe[1], Shiori Takashima[1], Tomoya Wakana[1], Yu Sakano[2], Ryosuke Haraguchi[2] (1. Graduate School of Engineering, Chiba Institute of Technology, 2. Faculty of Engineering, Chiba Institute of Technology)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1142-3am-10]
Update of imine-anion mediated Smiles rearrangement: application to migration of electron-neutral/rich aromatic groups
○Shunki Jinno[1], Keiji Mori[1] (1. Tokyo University of Agriculture and Technology)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1142-3am-11]
Development and application of oxidative cleavage reaction of 1,2-diamine
○Wakana Ito[1], Daiki Higuchi[1], Takeshi Sugiyama[2], Kota Hashimoto[1], Satoshi Matsubara[1], Satoshi Minakata[2], Kei Murakami[1] (1. Kwansei Gakuin University, 2. Osaka University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1142-3am-12]
Visible-Light-Induced Aminodifunctionalization of Alkenes
○Asa Tagata[1], Emna Mejri[1], Yohei Shimizu[1,2], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1142-3am-13]
Synthesis and Transformation of Dynamic Chiral N-Arylamide

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Yuuya Kawasaki[1,2], ○Rintaro Naoe[2], Kazunobu Igawa[3], Katsuhiko Tomooka[1,2] (1. IMCE, Kyushu Univ. , 2. IGSES, Kyushu Univ. , 3. FAST, Kumamoto Univ.)

Japanese

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

[E1142-3am-14]

New Trivalent Platforms for Sequential Conjugation Methods Based on Selective Azaylide Formations

○Mayo Hamada[1], Gaku Orimoto[1], Suguru Yoshida[1] (1. Tokyo University of Science)

Japanese

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

[E1142-3am-15]

New Trivalent Platforms with Azido, Ethynyl, and Fluorosulfonyl Groups

○Takahiro Yasuda[1], Gaku Orimoto[1], Suguru Yoshida[1] (1. Tokyo University of Science)

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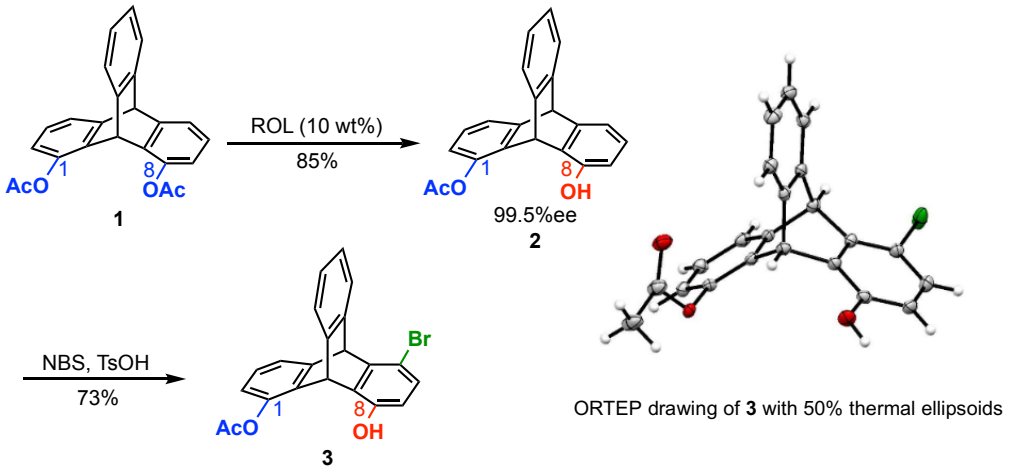
不斉非対称化反応による光学活性トリプチセン誘導体の合成

（東薬大薬）○野口汐夏・重田雅之・落合美緒・矢内光・松本隆司
Enantioselective Synthesis of Triptycene Derivatives by Enzymatic Desymmetrization (*Tokyo University of Pharmacy and Life Sciences*) ○Shiina Noguchi, Masayuki Shigeta, Mio Ochiai, Hikaru Yanai, Takashi Matsumoto

Enantioselective synthesis of chiral triptycene derivatives was investigated based on an enzyme promoted desymmetrization. 1,8-Diacetoxytriptycene underwent hydrolysis by the treatment with *Rhizopus oryzae* lipase to give the corresponding mono-acetate highly enantioselectively. The reaction profiles and detailed experimental procedure will be reported.
Keywords : Triptycene; Enantioselective desymmetrization; Lipase

トリプチセンは，3 つのベンゼン環が 2 つの sp^3 炭素原子を介してプロペラ状に配置した構造をもち，置換基同士の距離やそのなす角度の定まった明確な三次元構造をもつ誘導体を設計することが可能である。そのため，機能創出のための土台分子として興味深いが，キラルな誘導体を光学活性体として合成するための有効な手法に欠ける。今回我々は，リパーゼによる不斉非対称化の応用を試みたところ有望な結果を得たので報告する。

下にその一例を示す。C1 位と C8 位にアセトキシ基をもつ化合物 **1** に適切な条件下，*Rhizopus oryzae* 由来のリパーゼを作用させたところ，エナンチオトピックな 2 つのアセタートのうちの一方が選択的に加水分解を受け，対応するキラルなモノアセタート **2** を単離収率 85%，鏡像異性体過剰率 99.5%で得ることに成功した。また，この化合物を臭素化体 **3** へと誘導して単結晶 X 線解析することによって，絶対立体配置を図のように決定することができた。本講演では単離・精製における工夫や反応速度論的考察について述べる。



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フッ化アシルとチオシランからのチオエステル合成法の開発

（東理大創域理工）○竹内 隆貴・石田 健人・坂井 教郎
Development of synthesis of thioesters from acyl fluorides and thiosilanes (*Faculty of Science and Technology, Tokyo University of Science*) ○Ryuki Takeuchi, Kento Ishida, Norio Sakai

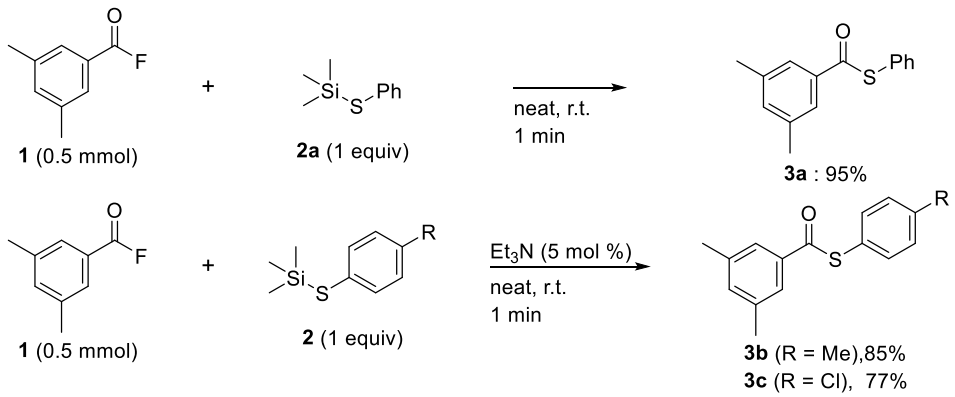
Thioesters are important compounds in a wide range of fields such as biochemistry. Thioesters are generally synthesized from carboxylic acid derivatives and thiol or thiosilanes. However, acyl chlorides which are frequently used in the synthesis, are generally unstable, and cares are required to handle them. In contrast, acyl fluorides are generally stable and easy to handle. Herein, we report the synthesis of thioesters from acyl fluorides and thiosilanes.

Reaction of 3,5-dimethylbenzoyl fluoride **1** and trimethyl(phenylthio)silane **2a** in the absence of a solvent gave thioester **3a** in 95% yield. On the other hand, when a substituted trimethyl(arylthio)silane was used, the desired product thioester was not obtained. We found that the desired reaction proceeded effiently in the presence of Et_3N.

Keywords : Acyl fluorides; thiosilanes; thioesters; trimethylsilyl fluoride

チオエステルは、医薬品などにも見られる構造であり、その簡便な合成法の開発が望まれている。チオエステルは一般に、ハロゲン化アシルとチオールまたはチオシランから合成される。[1,2]ここで、多用されるハロゲン化アシルである塩化アシルは、反応性が高く、取り扱いが困難な側面がある。一方、フッ化アシルは空気中において安定であり取り扱いが容易なため、近年その利用が注目されている。今回我々は、フッ化アシルとチオシランからチオエステルが収率よく合成できることを見出した。

3,5-ジメチルベンゾイルフルオリド(**1**)とトリメチル(フェニルチオ)シラン(**2a**)を基質とし、無溶媒条件下、室温で混合したところ、目的のチオエステル **3a** が 95%の収率で得られた。一方、芳香環に置換基をもつチオシランを用いた場合、上記と同様の条件では反応が進行しなかったが、触媒量のトリエチルアミンを添加することで良好に反応が進行することがわかった。



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2) Talley, J. J. *Synthesis* **1981**, *7*, 549.

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NFC を用いたアルケンの銅触媒アミノアジド化反応

（千葉大[1]・理研[2]・東大院工[3]）○木村 碩斗[1,2]・相川 光介[3]・橋本 卓也[1,2]
Copper-catalyzed Aminoazidation of Alkenes with NFC ([1]*Chiba University*, [2]*RIKEN* [3]*Graduate School of Engineering, The University of Tokyo*) ○Hiroto Kimura,[1,2] Kohsuke Aikawa,[3] Takuya Hashimoto[1,2]

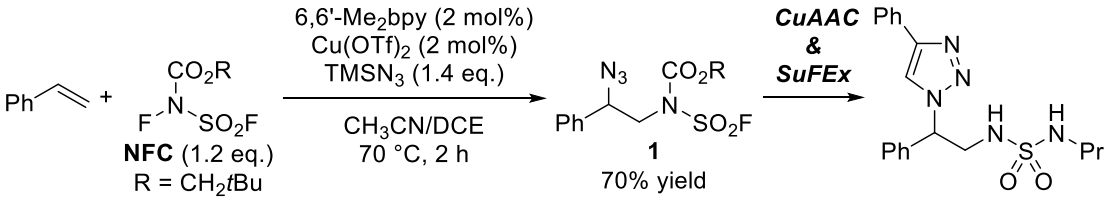
Our laboratory has developed N-fluoro-N-(fluorosulfonyl)carbamate (NFC) as a practical aminating agent to replace NFSI and applied it to the copper-catalyzed aminocyanation of alkenes. In this study, we applied NFC to perform the copper-catalyzed aminoazidation of alkenes, a reaction originally reported by Studer et al. using NFSI. This extension allowed us to achieve the previously challenging aminoazidation of aliphatic alkenes. Additionally, we successfully achieved a quick structural diversification of alkenes by independently functionalizing the azide moiety through CuAAC reaction and the carbamate moiety through SuFEx reaction.

The aminoazidation reaction of styrene was executed using 2 mol% $Cu(OTf)_2$/6,6'-dimethyl-2,2'-bipyridyl complex in the presence of NFC and trimethylsilyl azide in an acetonitrile/1,2-dichloroethane mixture at 70 °C. Consequently, the corresponding aminoazide **1** was obtained in a 70% yield.

Keywords : copper, aminoazidation, NFC, CuAAC, SuFEx

当研究室では、生成物の誘導化が困難な NFSI に代わる実用的なアミノ化剤として、N-フルオロ-N-(フルオロスルホニル)カルバメート（NFC）を開発し、同試薬を用いたアルケンの銅触媒アミノシアノ化反応を報告している[1)]。本研究では、Studer らによって報告された NFSI を用いた芳香族アルケンの銅触媒アミノアジド化反応を[2)]、我々の開発した NFC を用いて実施した。本反応では Studer らの前報では適用できなかった脂肪族アルケンのアミノアジド化反応も実現した。さらに、アミノアジド化体のアジド部位を CuAAC 反応で、カルバミン酸部位を SuFEx 反応で、互いに独立に誘導化することでアルケンを短工程で構多様化することに成功した[3)]。

実際にスチレンのアミノアジド化反応を 2 mol%のトリフルオロメチルスルホン酸銅(II)/6,6'-ジメチル-2,2'-ビピリジル錯体を用いて NFC、トリメチルシリルアジド存在下、アセトニトリル/1,2-ジクロロエタン混合溶媒中、70 ℃で行ったところ、対応するアミノアジド化体 **1** が 70%収率で得られた。



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3) H. Kimura, K. Aikawa, T. Hashimoto, *Asian J. Org. Chem.* **2023**, e202300522.

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酸化チタン/コバロキシム二元光触媒系による含酸素化合物からアルケンへの変換反応

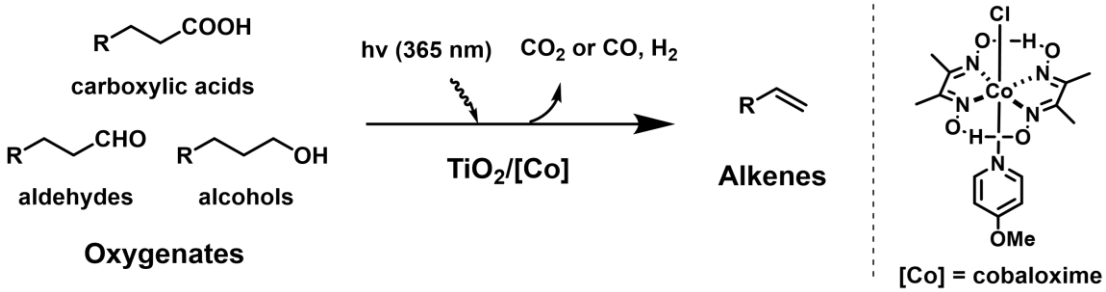
（東大院工）○丸山 詠生・金 雄傑・野崎 京子
Conversion of Oxygenates to Alkenes by TiO_2 and Cobaloxime Dual Photocatalyst System (*Graduate School of Engineering, The University of Tokyo*) ○Eiki Maruyama, Xiongjie Jin, Kyoko Nozaki

Conversion of oxygenates, such as carboxylic acids, aldehydes, and alcohols, to alkenes is of importance for utilization of renewable resources. Here, we report the conversion of various oxygenates to the corresponding one-carbon shorter alkenes using a catalyst system composed of cobaloxime and the cheap and readily available TiO_2 photocatalyst. This catalyst system enables the conversion of primary aldehydes to terminal alkenes, which was difficult to achieve in the previous reports.[1,2]

When the reaction of dodecanal was performed with TiO_2 and [Co] as catalysts under irradiation of 365 nm LED light, 1-undecene was obtained in 46% yield. Gas phase analysis suggested that the reaction mainly proceeds through the oxidation of aldehydes to carboxylic acids, followed by decarboxylation and dehydrogenation to give alkenes. The catalyst system can also be applied to the conversion of carboxylic acids and alcohols to the corresponding alkenes.
Keywords : Heterogeneous Photocatalyst; Photoredox Catalysis

カルボン酸、アルデヒド、あるいはアルコールなどの含酸素化合物からアルケンへの変換反応は再生可能資源の有効な活用法として重要である。本研究では、安価で入手容易な不均一系光触媒である酸化チタンとコバロキシムの二元光触媒系を用いることにより、種々の含酸素化合物から減炭を伴うアルケンへの変換を達成した。本触媒系を用いると、従来系 [1,2] では困難であった第一級アルデヒドから末端アルケンへのアクセプターレス変換反応が進行した。

酸化チタンと[Co]を触媒として、波長 365 nm の LED 光照射下でドデカナールの変換反応を行うと、1-ウンデセンが収率 46%で得られた。気体生成物の解析より、反応は主にアルデヒドからカルボン酸への酸化、続く脱炭酸脱水素により進行することが示唆された。加えて、本触媒系はカルボン酸あるいはアルコールを基質とするアルケンへの変換にも適用可能であった。



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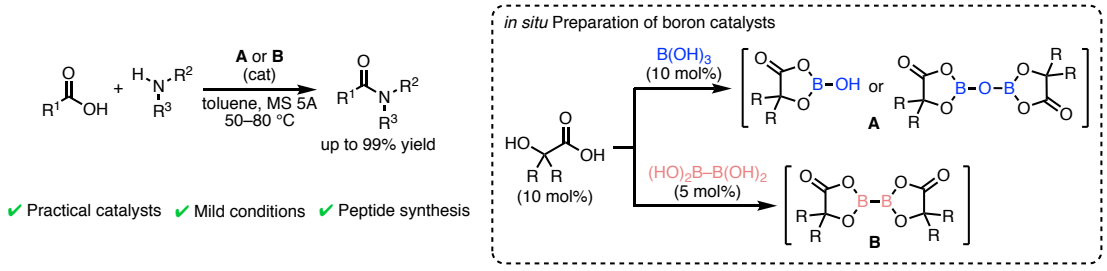
Development of 1,3,2-Dioxaborolan-4-one Catalyst for Dehydrative Condensation toward Peptides Synthesis

(*Graduate School of Engineering, Nagoya University*) ○Qianchun Huang, Shuhei Ohmura, Kazuaki Ishihara

Keywords: Boric Acid; Hypoboric Acid; Amide; Peptide; Dehydrative Condensation

Dehydrative condensation of carboxylic acids with amines is one of the most straightforward methods to synthesize amides including peptides, which are present in various pharmaceuticals. Compared with the traditional methods using coupling reagents, catalytic methods are more environmentally friendly and atom-economic because they generate water as a sole byproduct. Since Yamamoto and Ishihara's pioneering work using boronic acids as catalysts,[1] great progress has been made in developing several highly effective boron catalysts for direct amidation. However, their involvements in peptide synthesis were limited due to high reaction temperature.[2] Recently, some innovative multi-boron catalysts were reported to perform high activities in catalytic peptide coupling, but they still suffer from increasing complexities and cost.[3] Therefore, with a target of practical boron catalysts for mild amide bond formation, our strategy is to enhance the catalytic efficiency of commercially available and simple $B(OH)_3$[4] and $(HO)_2B–B(OH)_2$[5] by using an appropriate additive.

Here, we developed practical dehydrative condensations catalyzed by 1,3,2-dioxaborolan-4-one that could be generated *in situ* from $B(OH)_3$ or $(HO)_2B–B(OH)_2$ with α,α-disubstituted α-hydroxycarboxylic acid as an additive. Under relatively mild conditions, carboxylic acids and amines were condensed to provide the corresponding amides in high yield, which also finds a potential application in direct peptide synthesis.



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ジアステレオ選択的アルキル化による 四置換炭素を含む 1,3-非連続不斉炭素中心の構築

（東北大院理）○小嶋 理白・近藤 梓・寺田 眞浩

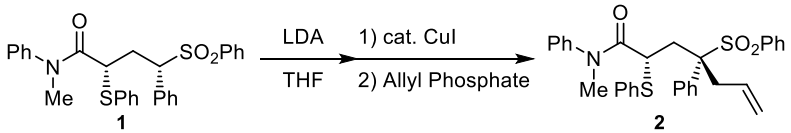
Diastereoselective Alkylation for Construction of 1,3-Nonadjacent Stereogenic Centers Containing a Tetrasubstituted Carbon Center (*Graduate School of Science, Tohoku University*)

○Rihaku Ojima, Azusa Kondoh, Masahiro Terada

Recently, we have developed the enantioselective addition reaction of α-thioacetamides as less acidic pronucleophiles with α-substituted sulfones catalyzed by a chiral strong Brønsted base, accomplishing the construction of 1,3-nonadjacent stereogenic centers, both of which were trisubstituted carbons.[1] On the other hand, Koert and coworkers reported the LDA-mediated diastereoselective alkylation of α-bromosulfones for the construction of 1,3-nonadjacent stereogenic centers including a tetrasubstituted carbon.[2] Based on these previous works, we envisioned the development of a new method for the diastereo- and enantioselective construction of 1,3-nonadjacent stereogenic centers including a tetrasubstituted carbon. Specifically, we designed the two-step reaction consisting of the enantioselective addition of α-thioacetamides with α-substituted sulfones and the subsequent diastereoselective alkylation at the α-position of sulfonyl group using LDA. As a result of our investigation, a catalytic amount of CuI was found to facilitate diastereoselective allylation, and 1,3-nonadjacent stereogenic centers including a tetrasubstituted carbon were successfully constructed.

Keywords : Base Catalysis; Enantioselective Reaction; Protonation; Stereogenic Center; Organocatalyst

我々は最近、強塩基性キラルブレンステッド塩基触媒を用いた α-チオアセトアミドと α 位に種々の置換基を有するビニルスルホンの不斉付加反応を開発した[1]。この反応は、共に三置換炭素である 1,3-非連続不斉炭素中心を有する光学活性スルホンを高立体選択性で与える。一方、Koert らは α-ブロモスルホンを基質として用い、LDA を用いたスルホニル基 α 位の脱プロトン化と続くアルキル化によって、四置換炭素を含む 1,3-非連続不斉炭素中心のジアステレオ選択的な構築に成功している[2]。今回、これらの先行研究に基づいて、四置換炭素を含む 1,3-非連続不斉炭素中心のジアステレオ選択的かつエナンチオ選択的な構築法の開発に取り組んだ。すなわち、我々が開発した不斉付加反応によって得られる光学活性スルホン **1** のスルホニル基 α 位でのアルキル化がジアステレオ選択的に進行すれば、四置換炭素を含む 1,3-非連続不斉炭素中心を二段階の反応によって立体選択的に構築できると考えた。検討の結果、LDA を用いて **1** を脱プロトン化したのち、触媒量のヨウ化銅存在下アリルホスフェートを作用させることで、アリル化が高ジアステレオ選択性で進行することを見いだした。



1 92% ee　　**2** 92% ee, 83:17 dr

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日本化学会 第104春季年会 (2024)

ブレンステッド塩基触媒による アリル化合物およびベンジル化合物のアミノオキシ化反応

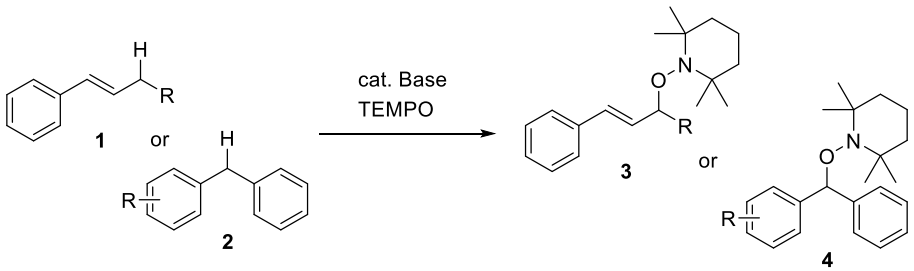
（東北大院理）○近藤 梓・寺田 眞浩

Brønsted Base-Catalyzed Aminooxylation of Allylic- and Benzylic Compounds (*Graduate School of Science, Tohoku University*) ○Azusa Kondoh, Masahiro Terada

The direct sp^3 C-H aminooxylation is a useful reaction for the synthesis of *N*-alkoxyamines which are widely employed as building blocks in organic synthesis as well as initiators in the radical polymerization. During the course of our study on the development of new molecular transformations under Brønsted base catalysis, we have serendipitously found that Brønsted bases efficiently catalyzed the aminooxylation of allylic compounds and benzylic compounds. Specifically, treatment of allylic compounds and diarylmethane derivatives with TEMPO in the presence of a catalytic amount of a Brønsted base resulted in the aminooxylation at the allylic position and the benzylic position, respectively, and the corresponding *N*-alkoxyamines were obtained in good yields.

Keywords : Base Catalysis; Aminooxylation; Oxidation; Radical; Organocatalysis

sp^3 炭素-水素結合の直接的なアミノオキシ化反応は、有機合成におけるビルディングブロックおよびラジカル重合の開始剤として利用可能な *N*-アルコキシアミン類を直接的に与える有用な反応である。代表的な触媒的アミノオキシ化反応として、銅触媒を用いた反応が報告されている [1)]。この反応では水素原子の引き抜きによって炭素ラジカルが触媒的に発生し、TEMPO によって捕捉されることで生成物が得られる。また関連する触媒的アミノオキシ化反応として、光レドックス触媒を用いたカルボニル化合物の α 位アミノオキシ化反応も報告されている [2)]。一方、我々はブレンステッド塩基触媒を用いた新たな分子変換反応の開発を行っている。その中で今回、アリル化合物およびベンジル化合物の新たな触媒的アミノオキシ化反応を見いだした。すなわち、アリル化合物 **1** またはジアリールメタン **2** に対し TEMPO 存在下で触媒量のブレンステッド塩基を作用させると、アリル位またはベンジル位がアミノオキシ化された化合物 **3** および **4** が良好な収率で得られた。



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連続三級炭素を有する *vic*-アミノアルコールの合成法の開発

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Synthetic Method for *vic*-Amino Alcohol with Consecutive Tertiary Carbons ([1]*Graduate School of Engineering, Chiba Institute of Technology,* [2]*Faculty of Engineering, Chiba Institute of Technology*) ○Shiori Takashima,[1] Tomoka Watanabe,[1] Tomoya Wakana,[1] Yu Sakano,[2] Ryosuke Haraguchi[1]

vic-Amino alcohols, in which a hydroxy group and an amino group are adjacent to each other, are an important group of compounds used in various fields such as medicinal chemistry and organometallic chemistry. Thus, the development of synthetic methods for *vic*-amino alcohols has been studied for decades. On the other hand, the synthesis of multisubstituted *vic*-amino alcohols with consecutive tertiary carbons has not yet been achieved because their steric hindrance makes it difficult to apply conventional methods to them.

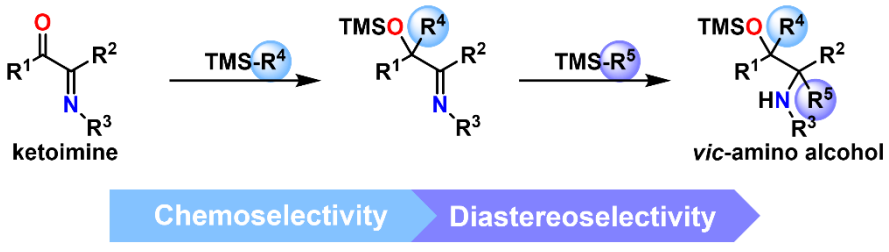
Herein, we describe a novel synthetic method for multisubstituted *vic*-amino alcohols through consecutive nucleophilic addition of organosilicon compounds to 1,2-ketoimines. This method enables the synthesis of *vic*-amino alcohols containing continuous tertiary carbons, which was challenging to synthesize using conventional methods.

Keywords：*vic-Amino Alcohol; Chemoselectivity; Diastereoselectivity*

ヒドロキシ基とアミノ基が隣接した *vic*-アミノアルコールは、医薬品化学や有機金属化学など様々な分野で用いられているため、その合成法の開発は長年研究されてきた[1)]。一方、連続三級炭素を有する多置換 *vic*-アミノアルコールは、その立体障害から従来法を適用することは難しく、その合成は未だに達成されていない。この立体障害の影響を避ける方法として我々は、極性二重結合への求核付加反応に着目した。この反応は平面性の sp^2 炭素に対する静電相互作用を駆動力とするため、立体障害の影響を比較的受けにくいと考えた。

このコンセプトに基づき我々は、連続三級炭素を有する *vic*-アミノアルコールの合成法として、1,2-ケトイミンに対する連続的な求核付加反応を開発した(Scheme 1)。本合成法では、1 段階目で化学選択性、2 段階目でジアステレオ選択性を発現するが、これらを完全な選択性で制御できる分子性触媒を見出すことに成功した。本発表では、触媒検討の結果や本合成法の適用範囲について詳述する。

Scheme 1. *vic*-アミノアルコールの新規合成法



1) S. C. Bergmeier, *Tetrahedron*, **2000**, *56*, 2561.

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1,2-ケトイミンの触媒制御型ケモダイバージェントシアノ化反応

（千葉工大院工[1]・千葉工大工[2]）○渡邉 朋香[1]・高嶋 しおり[1]・若菜 倫弥[1]・坂野 有[2]・原口 亮介[2]

Catalyst-Controlled Chemodivergence in Nucleophilic Cyanation to 1,2-Ketoimine ([1]*Graduate School of Engineering, Chiba Institute of Technology*, [2]*Faculty of Engineering, Chiba Institute of Technology*) ○Tomoka Watanabe,[1] Shiori Takashima,[1] Tomoya Wakana,[1] Yu Sakano,[2] Ryosuke Haraguchi[2]

The chemodivergent reaction can produce different products from a single molecule. Such reactions can rapidly expand chemical space, and the development of methods for switching chemoselectivity has been gaining attention in the field of organic synthetic chemistry in recent years. There have been numerous reports on switching chemoselectivity by temperature or solvents, whereas there are still a few reports in which switching chemoselectivity was achieved simply by changing the catalyst used.

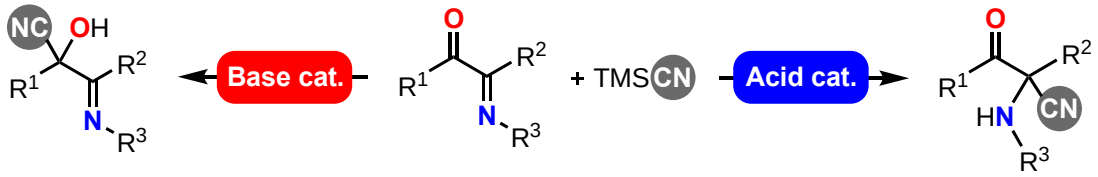
Herein, we achieved catalyst-controlled chemodivergence in nucleophilic cyanation to 1,2-ketoimine. When 1,2-ketoimines was reacted with trimethylsilyl cyanide (TMSCN) in the presence of Lewis base as a catalyst, the cyanation proceeded selectively at the keto group. In contrast, the use of a Lewis acid catalyst promoted the cyanation at the imino group selectively. In this presentation, we will discuss the mechanisms of controlling this chemoselectivity, the catalysts effect, and the substrate scope for this chemodivergent reaction.

Keywords : Chemoselectivity; Switching; Lewis Base; Lewis Acid; Cyanation

同一分子内に複数ある官能基をそれぞれ化学選択的に変換するケモダイバージェント反応は、同一分子から異なる生成物を作り分けることが可能である。このような反応はケミカルスペースを迅速に拡大できるため、化学選択性をスイッチングする手法の開発が、有機合成化学分野で近年注目を集めている。これまでに、温度や溶媒でその選択性を制御した例が多数報告されている一方、用いる触媒を変えるだけで化学選択性のスイッチングを実現した例はまだ少ない[1)]。

今回我々は、触媒制御による1,2-ケトイミンのケモダイバージェント型シアノ化反応を達成した。具体的には、1,2-ケトイミンとトリメチルシリルシアニド(TMSCN)との反応が、ルイス塩基触媒を用いるとケトン選択的に、ルイス酸触媒を用いるとイミン選択的に進行した。本発表では、これらの化学選択性制御に関するメカニズムの考察や、触媒検討、基質適用範囲について詳述する。

Scheme 1. 触媒制御による1,2-ケトイミンのケモダイバージェント型シアノ化反応



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イミンアニオン型 Smiles 転位の新展開：電子求引性基を持たない芳香環の転位によるオルトヒドロキシフェニルケチミン合成

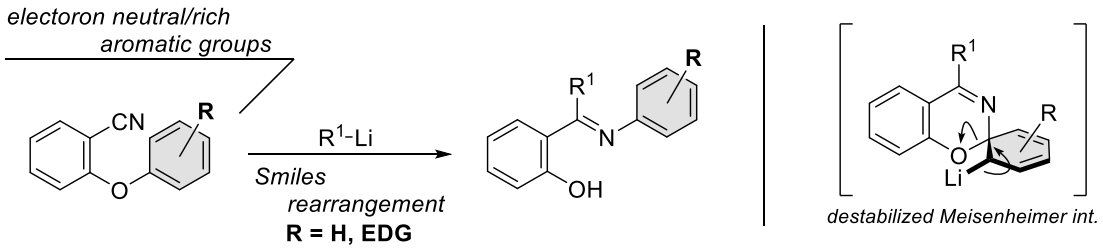
(東農工大院工) ○神野 峻輝・森 啓二

Update of imine-anion mediated Smiles rearrangement: application to migration of electron-neutral/rich aromatic groups (*Graduate School of Engineering*, *Tokyo University of Agriculture and Technology*) ○Shunki Jinno, Keiji Mori

Recently, we developed a synthetic method of *ortho*-hydroxyphenylketimines via imine anion-mediated Smiles rearrangement. Since a nucleophilic aromatic substitution reaction was involved in this system, ketimines having electron-withdrawing substituents were only accessible compounds. Detailed examinations revealed that migration of various aromatic groups, represented as unsuited for S_NAr-type reactions, such as electron-rich aromatic groups besides, sterically hindered aromatic groups was accomplished by introducing the bulky anthryl-lithium as a nucleophile. Among the aromatic groups examined, naphthyl groups exhibited excellent performance, and their migration ability was well showcased by the reaction with less bulky nucleophiles.

Keywords: Smiles Rearrangement, Nucleophilic Aromatic Substitution, Imine Synthesis

当研究室では、イミンアニオン中間体を経由する Smiles 転位を利用したケチミン合成法の開発に成功している[1]。生物活性物質や配位子などの有用な化合物の部分構造として散見されるオルトヒドロキシフェニルケチミン類を与える有用な合成法だが、芳香族求核置換反応を介するために窒素原子上に電子不足芳香環を持つケチミン類の合成に限定的であった。今回、求核剤の検討を進める中で、不安定な Meisenheimer 中間体を経由する、電子求引基を持たない芳香環での Smiles 転位によるケチミン合成が可能となることを見出した。その鍵はアントリル基のような立体的に嵩高い求核剤を導入することであり、フェニル基やオルトトリル基をはじめとする電子豊富、さらには立体的に嵩高い芳香環での転位反応を達成できた。さらに検討を進めた結果、ナフチル基は優れた転位能を示すことも見出したので併せて報告する[2]。



1) Jinno, S.; Senoo, T.; Mori, K. *Org. Lett.* **2022**, *24*, 4140.
2) Jinno, S.; Kawasaki-Takasuka, T.; Mori, K. *Synlett*, *accepted*.

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1,2-ジアミンの酸化開裂反応の開発と応用

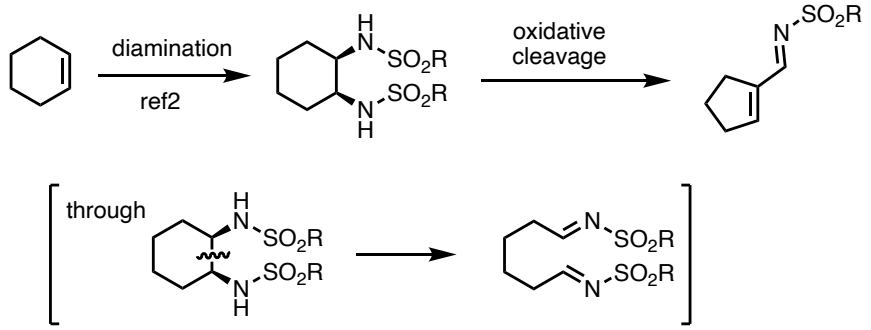
(関西学院大理工[1], 阪大院工[2]) ○伊藤 新菜[1]・樋口 大騎[1]・杉山 孟[2]・橋本 康汰[1]・松原 聡志[1]・南方 聖司[2]・村上 慧[1]

Development and application of oxidative cleavage reaction of 1,2-diamine ([1]*Department of Chemistry, Kwansei Gakuin University*, [2]*Graduate School of Engineering, Osaka University*)
○Wakana Ito,[1] Daiki Higuchi,[1] Takeshi Sugiyama,[2] Kota Hashimoto,[1] Satoshi Matsubara,[1] Satoshi Minakata,[2] Kei Murakami[1]

The oxidative cleavage reaction is a useful method for the synthesis of carbonyl compounds. However, the oxidative cleavage of the corresponding 1,2-diamine has been unexplored and leaving room for further development. Previously, we discovered the oxidative cleavage of 1,2-diamine with hypervalent iodine that forms imine. In this study, we aimed to extend the synthetic utility of this reaction. By performing a diamination reaction of cycloalkenes, diaminocycloalkanes were obtained. Then, applying oxidative cleavage conditions to these substrates resulted in the cleavage of C–C bonds to form dehomologated cycloalkenes with imine moiety. The diamination/oxidative cleavage sequence is applicable to cyclohexene, cycloheptene, and dihydronaphthalenes to furnish cyclopentene, cyclohexene, and indene, respectively. The imine moiety of the resulting product can be utilized as a foothold for further transformation.

Keywords : ethylenediamine; oxidative cleavage; imine

酸化開裂反応は 1,2-ジオールの開裂に代表されるカルボニル類の合成に有用な反応である。しかし、対応する 1,2-ジアミンの酸化開裂反応は報告例や応用例が少ないため、いまだ発展の余地を残している。これまでに我々は、1,2-ジアミン誘導体に対して超原子価ヨウ素を用いることで、酸化開裂反応が進行しイミンが合成できることを見つけている [1)]。本研究ではこの反応の合成応用性の拡張を目指した。シクロアルケン類に対し、ジアミノ化反応 [2)]を行うことにより、1,2-ジアミン骨格を有するシクロアルカンが得られる。この基質に対して、酸化的開裂反応を適用すると炭素–炭素結合の開裂を経て、1 炭素減炭したシクロアルケンが得られた。このジアミノ化／酸化開裂はシクロヘキセン、シクロヘプテン、そして、ジヒドロナフタレンに適用可能であり、それぞれ対応するシクロペンテン、シクロヘキセン、インデンが得られる。得られたシクロアルケンはイミン部位を有しており、更なる変換が可能である。



1) 樋口大騎、松原聡志、村上慧 日本化学会第 103 春季年会 K406-4am-04.
2) Minakata, S.; Miwa, H.; Yamamoto, K.; Hirayama, A.; Okumura, S. *J. Am. Chem. Soc.* **2021**, *143*, 4112–4118.

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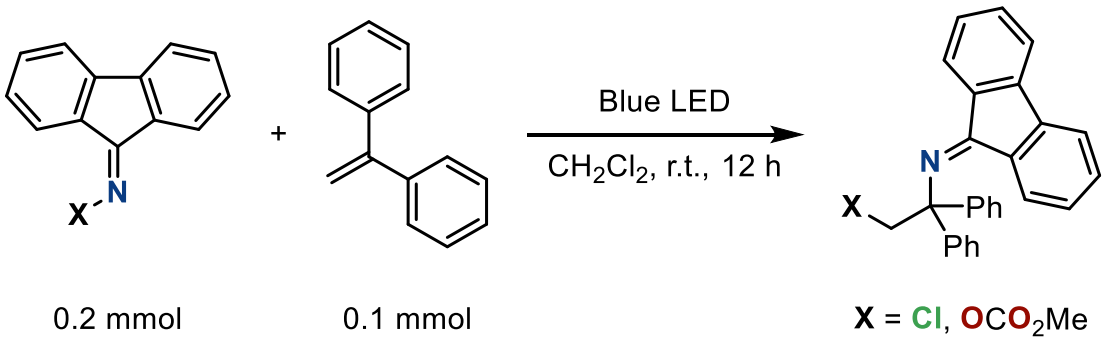
可視光が駆動するアルケンの窒素導入型二官能基化反応

（北大理[1]・WPI-ICReDD[2]）○田方　朝[1]・Emna Mejri[1]・清水　洋平[1,2]・澤村　正也[1,2]

Visible-Light-Induced Aminodifunctionalization of Alkenes ([1] *Department of Chemistry, Faculty of Science, Hokkaido University*, [2]*WPI-ICReDD*) ○Asa Tagata,[1] Emna Mejri,[1] Yohei Shimizu,[1,2] Masaya Sawamura[1,2]

Difunctionalization of alkenes that incorporates a nitrogen atom is versatile transformation rapidly providing value-added nitrogen-containing compounds from feed stock materials. We developed aminochlorination[1] and oxyamination of alkenes by taking advantage of visible-light-induced N－X bond homolysis of *N*－X-fluorenone imines (X = Cl or OCO_2R). In this reaction, electrophilic Cl radical or O radical, generated by the homolysis of the N－X bond, attacks terminal alkenes. Resulting internal C radical forms C－N bond regioselectively. The introduced imine moiety could be hydrolyzed under mild conditions to provide corresponding primary amines.
Keywords : Primary amine; Regioselective addition; Fluorenone imine; Photo-induced reaction; Difunctionalization

アルケンの両端に官能基を導入する二官能基化反応、特に窒素導入を伴う反応は、単純な原料から一挙に含窒素化合物を合成できる魅力的な反応である。我々は *N*-X－フルオレノンイミン（X = Cl or OCO_2R）の N－X 結合が可視光照射によって 均等開裂することを見出し、これを利用したアルケンのクロロアミノ化反応[1]およびオキシアミノ化反応を開発した。本反応では均等開裂により生じた電子不足な Cl ラジカルもしくは O ラジカルが末端アルケンに付加し、より安定な内部炭素ラジカルが生じて C－N 結合形成が進行するため、位置選択的にイミノ基を導入することができる。導入されたイミノ基は加水分解によって簡便に１級アミンへと変換可能である。



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動的キラルな N-アリールアミドの合成と変換

(九大先導研[1]，九大院総理工[2]，熊大院先端[3])
河崎 悠也[1,2]・○直江 倫太朗[2]・井川 和宣[3]・友岡 克彦[1,2]

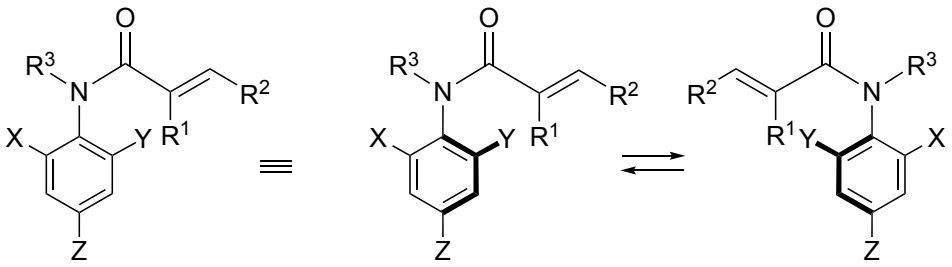
Synthesis and Transformation of Dynamic Chiral *N*-Arylamide

([1]*IMCE, Kyushu Univ.*, [2]*IGSES, Kyushu Univ.*, [3]*FAST, Kumamoto Univ.*)
Yuuya Kawasaki,[1,2] ○Rintaro Naoe,[2] Kazunobu Igawa,[3] Katsuhiko Tomooka[1,2]

As a part of our research on dynamic chiral molecules, we have synthesized *N*-arylamide having dynamic chirality at ambient temperature and revealed the substituent effect on the stereochemical stability. Herein, we wish to report the details of synthesis, stereochemical behavior, and transformation.

Keywords : Axial Chirality; N-Arylamides; Dynamic Chiral Molecule

動的キラル分子に関する研究[1-3]の一環として今回，動的キラルな *N*-アリールアミド **1**[4]の立体化学挙動の精査と合成化学的応用について検討した．多様な置換基を有する **1** を合成し，それらの各種スペクトル分析及びキラル固定相を用いた HPLC 分析の結果，**1** が室温下に動的なキラリティーを有していることが，またその立体化学的安定性はベンゼン環オルト位の置換基 X,Y 及びアミド α 位の置換基 R^1 によって大きく変化することが明らかになった．講演時には **1** の立体化学挙動の詳細，及び合成化学的応用に関して議論する．



1

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2) K. Tomooka, *J. Synth. Org. Chem. Jpn.* **2017**, *75*, 449.
3) K. Igawa, K. Uehara, Y. Kawasaki, K. Tomooka, *Chirality* **2022**, *34*, 824.
4) Q. Cass, A. L. G. Degani, M. Elizabeth, S. A. Matlin, D. P. Curran, A. Balog, *Chirality* **1997**, *9*, 109.

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選択的アザイリド形成にもとづく 3 分岐プラットフォームの合成

（東理大院先進工）〇濱田 真代・織本 雅久・吉田 優
New Trivalent Platforms for Sequential Conjugation Methods Based on Selective Azaylide Formations (*Tokyo University of Science*) 〇Mayo Hamada, Gaku Orimoto, Suguru Yoshida

Recently, trivalent platform molecules with three clickable functional groups have gained attention in pharmaceutical sciences. Previously, we succeeded in the selective azaylide formation by defferentiating two azides based on reaction rate difference. Herein, we developed a trivalent platform with terminal alkyne and two types of azides, and achieved the construction of a multifunctional molucule.
Keywords : Click Chemistry; Azide; Phosphine; Iminophosphorane; Platform

有機化学だけでなく、生命科学をはじめとする幅広い分野において 2 分子を連結できる反応が大きな役割を果たしている。これまで、高度な機能性分子を創製するために、複数の機能性部位を繋ぎ合わせる手法が利用されてきた。以前に、幅広い機能性分子同士の連結に利用できる手法として、嵩高く、電子求引性のクロロ基やフルオロ基を両オルト位に有する芳香族アジドがトリアリールホスフィンと速やかに反応し、安定なアザイリドを形成することが明らかになった[1,2]。以前に我々は、2 種の芳香族アジドを用いて、安定アザイリド形成における反応速度の違いを利用することで 2 種のアジドを区別できることを明らかにし、ジアジドの 2 度のアザイリド形成が逐次的に進行することに成功した(図 1)。今回私たちは、これらの反応と CuAAc 反応を併用でき、ジアジドとアルキンを併せ持つ 3 分岐プラットフォームを用いて、3 成分を効率的に集積できることを明らかにした。実際に本手法を利用することで、3 つの機能性分子の集積に成功した(図 2)。

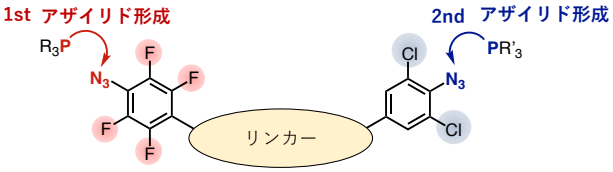

図 1

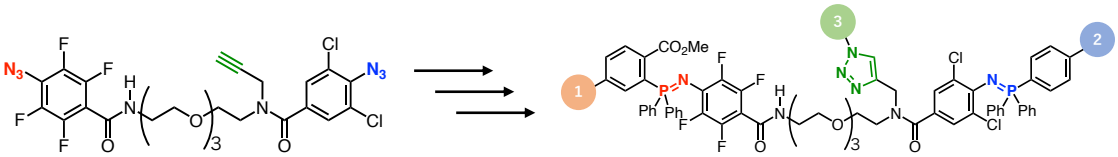

図 2

1) T. Meguro, N. Terashima, H. Ito, Y. Koike, I. Kii, S. Yoshida, T. Hosoya, *Chem. Commun.* **2018**, *54*, 7904.
2) M. Sundhoro, S. Jeon, J. Park, O. Ramström, *Angew. Chem. Int. Ed.* **2017**, *56*, 12117

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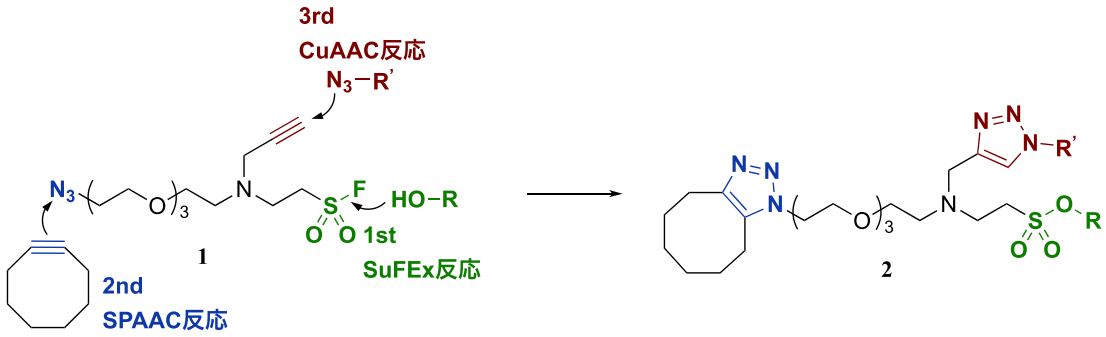
アジド基・エチニル基・フッ化スルホニル基を有する 3 分岐プラットフォーム分子の開発

（東理大先進工）〇安田 貴裕・織本 雅久・吉田 優
New Trivalent Platform with Azido, Ethynyl, and Fluorosulfonyl Groups (*Tokyo University of Science*) 〇Takahiro Yasuda, Gaku Orimoto, Suguru Yoshida

Multicomponent assembling methods with platform molecules are awaited. Herein, we succeeded in assembling three components by selective click reactions using trivalent platforms with azido, ethynyl, and fluorosulfonyl groups. Also, we achieved selective CuAAC reactions of terminal alkynes realizing efficient synthesis of diverse multi(triazole)s.
Keywords : Click reaction; Azide; Platform; CuAAC reaction; SuFEx reaction

プラットフォーム分子を用いて、多成分を短工程で集積させる手法が強く望まれている [1]。特に、クリック反応用の官能基を複数配置したプラットフォーム分子を用いて、幅広いモジュールを効率的に集積できれば、多様性に富んだ化合物ライブラリーを簡便に合成できると期待される。これに対して、今回我々は、アジド基、エチニル基、フッ化スルホニル基を併せ持った 3 分岐プラットフォーム **1** を開発し、SuFEx 反応、SPAAC 反応、CuAAC 反応を連続的に行うことで、3 成分を効率的に集積できることに成功した。さらに、プラットフォーム **1** におけるアジド基の保護 [2]を経て、末端アルキン選択的な CuAAC 反応にも成功した。このとき、続く脱保護を経て、再生したアジド基でも CuAAC 反応を行えたことから、多彩なマルチ（トリアゾール）を合成できることを明らかにした。



1) D. Sato, Z. Wu, H. Fujita, Jon S. Lindsey, *Organics* **2021**, *2* ,161.
2) T. Meguro, S. Yoshida, K. Igawa, K. Tomooka, T. Hosoya, *Org. Lett.* **2018**, *20,* 4126.

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

Wed. Mar 20, 2024 9:00 AM - 11:30 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:30 AM UTC
E1143(1143, Bldg. 11 [4F])

[E1143-3am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Takuji Kawamoto, Yuto Sumida

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[E1143-3am-01]

Development of a radical addition/cyclization cascade reaction using photoexcited palladium for a synthesis of boronic-ester substituted hetero- and carbocycles

○Takara Fukugaichi[1], Haruki Mizoguchi[1], Haruka Ikeda[1], Akira Sakakura[1] (1. The Univ. of Okayama)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[E1143-3am-02]

Radical reaction using vinyl cyclic sulfonylamide and allyl bromide

○Takaaki Maejima[1], Moeri Terauchi[1], Akio Kamimura[1], Takuji Kawamoto[1] (1. Yamaguchi University)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[E1143-3am-03]

Radical reaction using vinyl triflates and vinyl acetate

○Muramatsu Kenshin[1], Akio Kamimura[1], Takuji Kawamoto[1] (1. Yamaguchi University)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[E1143-3am-04]

Development of Water-Soluble Caged Acetylcholine

○Rikako Nakamura[1], Yuto Sumida[2], Satoshi Arai[3], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. IBB, Tokyo Med. & Dent. Univ., 3. WPI-NanoLSI, Kanazawa Univ.)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[E1143-3am-05]

Synthesis and Application of α-Boryl-α-Silyl Alkylamine

○Koh Watanabe[1], Kazunori Nagao[2], Hirohisa Ohmiya[2] (1. Grad. Sch. Med. Sci., Kanazawa Univ., 2. ICR, Kyoto Univ.)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[E1143-3am-06]

Development of Non-nucleophilic Electron Donor Catalysts and Their Applications to Photoreactions

○Airi Tanaka[1,2], Takuya Hashimoto[1,2] (1. Chiba Univ., 2. RIKEN)

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English
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[E1143-3am-07]
Copper-Ligand-to-Metal Charge Transfer Photocatalysis Involving Halogen-Atom-Transfer in Alkene Difunctionalization

○Subrata Mukherjee[1], Shintaro Kawamura[1,2], Mikiko Sodeoka[1,2] (1. RIKEN, CSRS, 2. RIKEN, CPR)

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
[E1143-3am-08]
C-Glycosylation of Photo-Excitable Glycosyl Borate

○Yusuke Miyamoto[1], Sho Murakami[1], Yuto Sumida[2], Go Hirai[3], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. IBB, Tokyo Med. & Dent. Univ., 3. Grad. Sch. Phar. Sci., Kyushu Univ.)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[E1143-3am-09]
Synthesis of Azetidine via C(sp3)–H Activation by A Light-Driven Triple Catalysis

○Masanari Nakagawa[1], Kazunori Nagao[1], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ.)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[E1143-3am-10]
para-Selective Alkylation of Aromatic Carboxylic Acid Derivatives Using Organic Photoredox Catalyst and Trialkylphosphine

○Ryoto Oya[1], Kazunori Nagao[1], Hirohisa Ohmiya[1] (1. Kyoto University)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[E1143-3am-11]
Regioselective C(sp3)-H Alkylation of Tetrahydrofuran Derivatives by Photoredox Catalysis

○Reiji Abe[1], Kazunori Nagao[1], Tomohiro Seki[2], Dai Hata[2], Yusuke Sasaki[2], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. Takeda Pharmaceutical Company Limited)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[E1143-3am-12]
Csp3–Csp3 Bond Cleavage of Benzyl Alcohol via Benzophenone-type Organic Photocatalysis

○Tomotoki Matsuo[1], Masaki Sano[2], Yuto Sumida[3], Hirohisa Ohmiya[1] (1. ICR, Kyoto Univ., 2. Grad. Sch. Med. Sci., Kanazawa Univ., 3. IBB, Tokyo Med. & Dent. Univ.)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[E1143-3am-13]
Enantioselective Radical Cation [2+2] Cycloaddition by Chiral Iron(III) Photoredox Catalysis

○Kei Katagiri[1], Shuhei Ohmura[1], Sho Miyakawa[2], Jun-ya Hasegawa[2], Kazuaki Ishihara[1] (1. Nagoya University, 2. Hokkaido University)

Japanese

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

[E1143-3am-14]

Development of Chiral Iron(III) Photoredox Catalysts for Enantioselective Radical Cation [4+2] Cycloaddition Toward Natural Product Synthesis

○Hayato Akao[1], Shuhei Ohmura[1], Kazuaki Ishihara[1] (1. Nagoya University)

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光活性化パラジウムを用いるラジカル付加ー環化カスケード反応による環式ボロン酸エステル合成法の開発

(岡山大院環境生命自然[1]) ○福垣内 尭良[1]・池田 遥香[1]・溝口 玄樹[1]・坂倉 彰[1]

Development of a radical addition/cyclization cascade reaction using photoexcited palladium for a synthesis of boronic-ester substituted hetero- and carbocycles

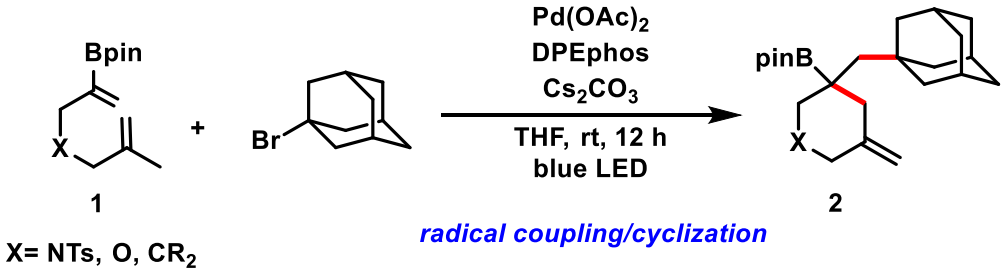
([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Takara Fukugaichi,[1] Haruka Ikeda,[1] Haruki Mizoguchi,[1] Akira Sakakura[1]

To develop a concise synthetic method for a construction of boron-substituted heterocycles and carbocycles, we devised a radical coupling/cyclization cascade reaction between alkyl halide and vinyl boronate containing 1,6-dienes using photoexcited palladium complex as a SET catalyst. Irradiation of blue LED to a THF solution contained substrate **1**, adamanthyl bromide, palladium(II) acetate, DPEphos and cesium carbonate induced a radical addition/ 6-*endo* cyclization to afford six-membered carbocyclic and heterocyclic boronic esters. The detail for the optimization of catalysts, conditions and substrates would be presented.

Keywords : Palladium Catalyst ; Radical; Blue LED; Boronic acid; Cyclization

多種多様な結合へと変換できるボロン酸構造を有する炭素環やヘテロ環は医薬品や天然物など複雑な構造を持つ化合物への合成中間体として有用である。我々は、光励起パラジウムが温和な条件下でアルキルハライドからラジカルを発生できることに着目し、これとビニルボロン酸エステルを含む 1,6−ジエン **1** とのカップリングを伴うラジカル環化をおこなうことで、アルキル基の導入された環状ボロン酸エステル **2** を合成しようと計画した。

ビニルボロン酸エステル **1** を基質とし、アダマンチルブロミド、酢酸パラジウム(II)、DPEphos、炭酸セシウム存在下で青色 LED を照射したところ、アダマンチルラジカルの位置選択的な付加と、6-*endo* 型環化が進行したと考えられるエキソアルケンをもつ環式ボロン酸エステル **2** が得られた。2 つのアルケン間のリンカー部位を変えることで、ピペリジン、テトラヒドロピラン、およびシクロヘキサン誘導体を合成できたため、その詳細を報告する。



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ビニル環状スルホニルアミドと臭化アリルを用いたラジカル反応

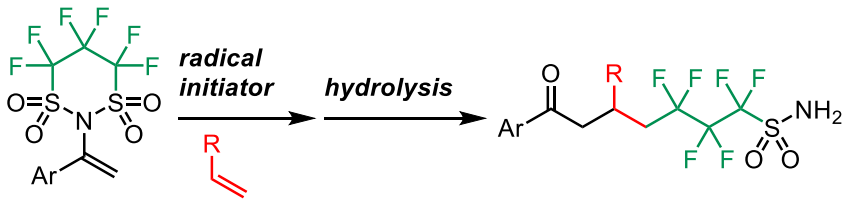
（山口大院創成科学）○前島 貴昭・寺内 萌里・上村 明男・川本 拓治
Radical reaction using vinyl cyclic sulfonylamide and allyl bromide (*Yamaguchi University*)
○Takaaki Maejima, Moeri Terauchi, Akio Kamimura, Takuji Kawamoto

Our laboratory has been actively developing the synthesis of vinyl cyclic sulfonylamides and their transformation reactions with radical species. In this study, we examined the radical reaction of vinyl cyclic sulfonylamides with allyl bromide.
Keywords : Radical Reaction, Vinyl Cyclic Sulfonyl Amide, Fluoroalkyl Compounds

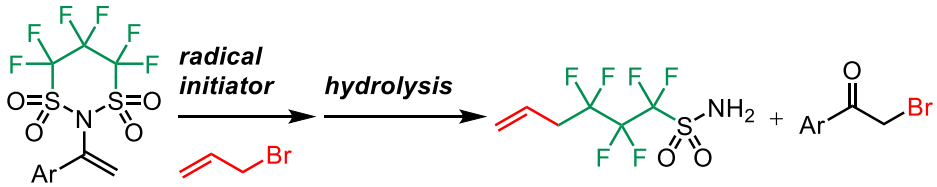
ジフルオロメチレン基（−CF_2−）はエーテル（−O−）やチオエーテル（−S−）の生物学的等価体として，創薬において注目されている。より長鎖の 1,1,2,2-テトラフルオロエチレン基（−CF_2CF_2−）や 1,1,2,2,3,3-ヘキサフルオロプロピレン基（−$CF_2CF_2CF_2$−）も創薬への応用が期待できるが，合成法は限定的である。

最近，当研究室では，ビニル環状スルホニルアミドに対してアルケン共存下でラジカル開始剤を作用させ，加水分解することで，1,1,2,2,3,3-ヘキサフルオロプロピレンアミド基を有するケトンが得られることを報告している [1)]。本研究では，アルケンを臭化アリルに置き換えることで，1,1,2,2,3,3-ヘキサフルオロプロピレンアミド基を有するアリル化合物が得られることを見いだした。

Our Previous work



This work



1) 寺内萌里，川端崇裕，山崎哲志，川本拓治，上村明男，日本化学会第 103 春季年会 2023, K704-3vn-05

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ビニルトリフラートと酢酸ビニルを用いるラジカル反応

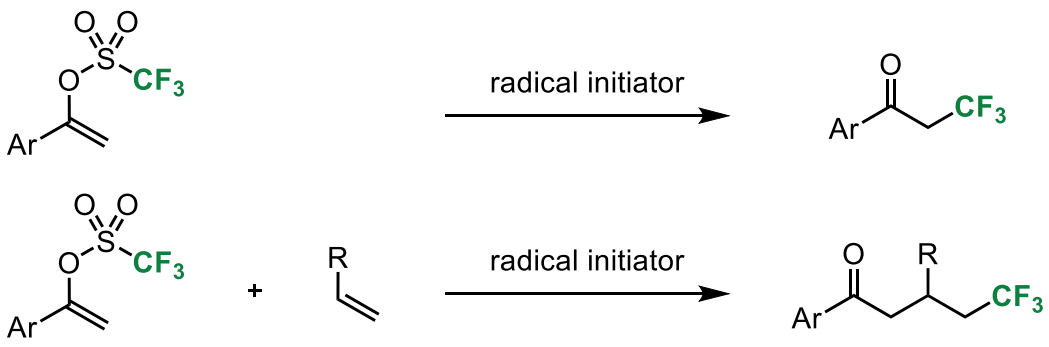
（山口大院創成科学）○村松 憲伸・上村 明男・川本 拓治
Radical reaction using vinyl triflates and vinyl acetate (*Yamaguchi University*) ○Kenshin Muramatsu, Akio Kamimura, Takuji Kawamoto

Previously, we have reported that the reaction of vinyl triflates with a radical initiator gave alpha-trifluoromethylated ketones. We have also reported synthesis of gamma-trifluoromethylated ketones from vinyl triflates with alkenes. In this study, we investigated radical reactions of vinyl triflate with vinyl acetate followed by various transformation reactions.

Keywords : Radical reaction; Vinyl triflates; Intermolecular reaction

フッ素原子は特異的な性質を有しており，フッ素原子を有機分子に導入することで化合物の性質を大きく変化させることが可能である。そのため，有機分子にフッ素原子を効率よく導入する手法の開発は重要となる。当研究室はビニルトリフラートに対してラジカル開始剤を作用させるとα位にトリフルオロメチル基が置換したケトンが得られ[1]，アルケン共存下でラジカル開始剤を作用させることで，γ位にトリフルオロメチル基が置換したケトンが得られることを報告した[2]。本研究ではビニルトリフラートと酢酸ビニルとのラジカル反応に続く脱離反応を検討した。

Our previous work



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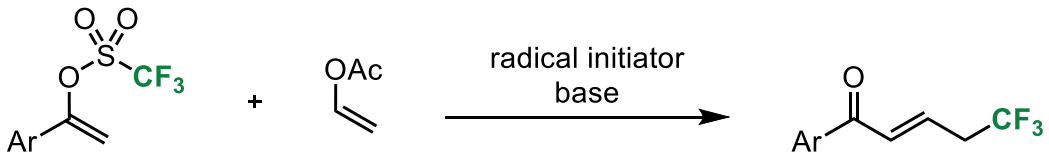

1) Kawamoto, T.; Sasaki, R.; Kamimura, A. *Angew. Chem. Int. Ed.* **2017**, *55*, 1342.
Kawamoto, T.; Noguchi, K.; Sasaki, R.; Matsubara, H.; Kamimura, A. *Chem. Eur. J.* **2021**, *27*, 9529.
2) Kawamoto, T.; Kawabata, T.; Noguchi, K.; Kamimura, A. *Org. Lett.* **2022**, *24*, 324.

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水溶性ケージドアセチルコリンの開発

（京大化研[1]・医科歯科大生材研[2]・金沢大 WPI-NanoLSI[3]）◯中村梨香子[1]・隅田有人[2]・新井敏[3]・大宮寛久[1]

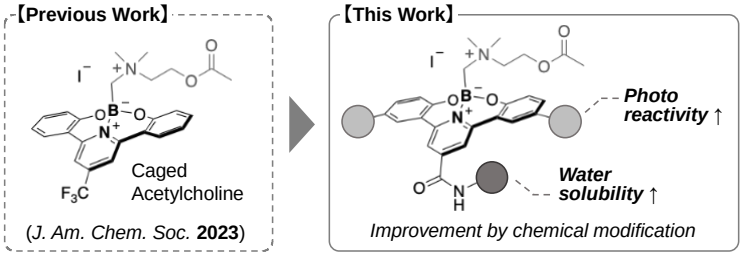
Development of Water-Soluble Caged Acetylcholine ([1]*Institute of Chemical Research, Kyoto University*, [2]*Institute of Biomaterials Bioengineering, Tokyo Medical and Dental University*, [3]*WPI-NanoLSI, Kanazawa University*) ◯Rikako Nakamura[1], Yuto Sumida[2], Satoshi Arai[3], Hirohisa Ohmiya[1]

Caged compounds are temporarily inactivated probes conjugated with a photoremovable unit to a bioactive compound. We have previously reported a radical caging strategy with boron-ate complexes enabling the generation of alkyl radicals by visible light excitation.[1] This method allows the biomolecule caging without nucleophilic heteroatoms as the binding site, and we succeeded the synthesis of caged acetylcholine, a neurotransmitter that has been difficult by conventional methods.

On the other hand, the biological concentration of acetylcholine is generally very high, which required the development of water-soluble caged acetylcholine. In this study, we designed and developed a highly water-soluble and expeditiously cleavable caged acetylcholine by chemical modification of the photoremovable unit's skeleton.

Keywords : Caged compound, Acetylcholine, Water-soluble, Boron-ate complex, Carbon-boron bond cleavage

ケージド化合物は、生理活性物質に光で除去可能なユニットを連結して一時的に不活化した分子である。我々は、可視光励起によってアルキルラジカル種を生じるホウ素アート錯体を用いることで、「炭素上での脱着」を可能とするケージド化法を報告している。[1] 本手法では、生理活性物質との連結に求核性の含ヘテロ原子官能基を必要とせず、従来法では合成困難であったアセチルコリンのケージド化に成功した。一方で、アセチルコリンは内在性神経伝達物質のため、その生体内濃度は一般的に非常に高く、質の高いイメージングの達成には、100 μM 程度の高濃度が求められる。また、神経応答イメージングにはその性質上、高効率な脱ケージド化が望ましい。このような背景のもと、我々は、ホウ素アート錯体の性能向上を目指して、光物性解析や量子化学計算による評価に基づいた分子設計を行なった。その結果、高い水溶性や光応答性を示すケージドアセチルコリンを開発した。



1) Nakamura, R.; Yamazaki, T.; Kondo, Y.; Tsukada, M.; Miyamoto, Y.; Arakawa, N.; Sumida, Y.; Kiya, T.; Arai, S.; Ohmiya, H. *J. Am, Chem. Soc.*, **2023**, *145*, 10651–10658.

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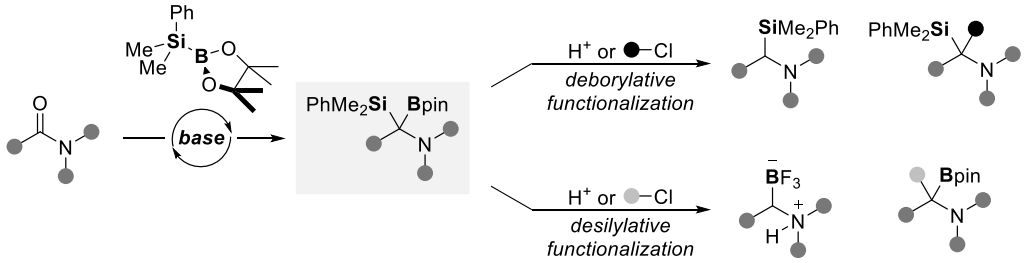
α-ボリル-α-シリルアルキルアミンの合成と応用

（金沢大院医薬保[1]・京大化研[2]）○渡邊 航[1]・長尾 一哲[2]・大宮 寛久[2]
Synthesis and Application of α-Boryl-α-Silyl Alkylamine ([1]*Grad. Sch. Med. Sci., Kanazawa Univ.,* [2]*ICR, Kyoto Univ.*) ○Koh Watanabe,[1] Kazunori Nagao,[2] Hirohisa Ohmiya[2]

We found that deoxygenative silylboration of amides using Lewis base catalyst and silylboronate ester proceeded to afford α-boryl-α-silylalkylamines. This reaction consists of 1) Lewis base-promoted silyl addition to amides, 2) 1,2-Brook rearrangement of α-silyl alkoxide generating α-amino carbanion, 3) α-amino carbene generation through elimination of silanolate group on the α-amino carbanion and 4) Si–B insertion to the α-amino carbene. The silyl and boryl groups could be utilized to chemoselective transformations, respectively.
Keywords : α-Boryl-α-silyl alkylamines, Deoxygenative functionalization, Silylboration, Amides

アルキルアミン類の窒素α位にケイ素およびホウ素基をもつ化合物は、ケイ素とホウ素がそれぞれ炭素およびカルボン酸の生物学的等価体であるとともに、官能基変換可能な合成中間体であることから魅力的である。しかし、ケイ素とホウ素基の両方を有するα-ボリル-α-シリルアミンの合成例はほとんど知られていない[1)]。今回我々は、シリルボロン酸エステルと塩基触媒を用いることで、第三級アミドの脱酸素型ジェミナルシリルホウ素化反応を見出した。本反応では、シリルボロン酸エステルからのシリルアニオンの発生と、系中で生じたα-アミノカルベンのシリルボロン酸エステルへの挿入を経ることで、窒素α位にケイ素とホウ素基が置換したα-ボリル-α-シリルアミンが得られる。

得られたα-ボリル-α-シリルアミンにおいて、ケイ素およびホウ素基を化学選択的に変換することが可能であった。α-ボリル-α-シリルアミンにアルコキシド塩基を作用させることで、脱ボリルプロトン化および脱ボリルアルキル化に適用することができた。一方で、フッ素アニオンを塩基として用いた場合、脱シリルプロトン化が進行し、α-アミノトリフルオロボレート塩が得られた。また、可視光照射下、光酸化還元触媒を用いて、α-ボリル-α-シリルアミンと塩化ベンジルを反応させたところ、脱シリルアルキル化が進行し、第四級炭素をもつα-ボリルアミンが得られた。



1) Ansorge, A.; Brauer, D. J.; Bürger, H.; Hagen, T.; Pawelke, G. *Angew. Chem. Int. Ed.* **1993**, *32*, 384–385.

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非求核性電子ドナー触媒の開発と光反応への応用

（千葉大[1]・理研[2]）○田中 愛梨[1,2]・橋本 卓也[1,2]

Development of Non-nucleophilic Electron Donor Catalysts and Their Applications to Photoreactions ([1]*Chiba University*, [2]*RIKEN*) ○Airi Tanaka,[1,2] Takuya Hashimoto[1,2]

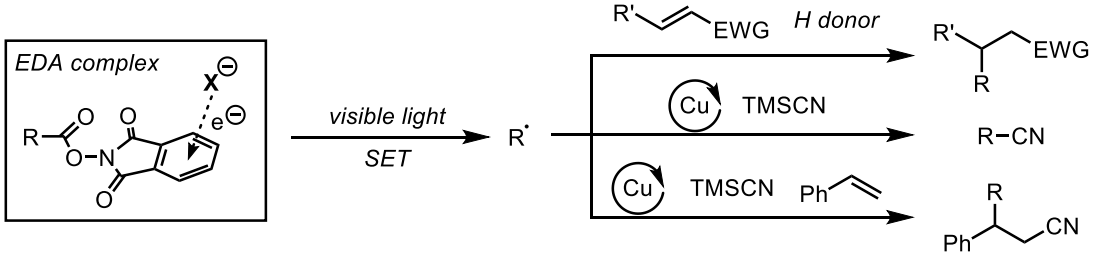
Organic electron donor catalysts, which form EDA complexes with electron acceptor substrates such as *N*-hydroxyphthalimide esters and generate reactive radicals via photoactivation of the complexes, have attracted much attention as a new class of organocatalysts. However, most of the reported catalysts are innately basic and nucleophilic, making expansion of substrate scope or reduction of catalyst loading difficult. We report here in the development of a new organic electron donor catalyst which solves these problems. Furthermore, by taking advantage of its stability and low coordination ability to metals, we developed a copper catalyst incorporating this electron donor catalyst as a counteranion.

As applications of these catalysts to photoreactions, we achieved Giese-type alkylations of electron deficient alkenes with low catalyst loading, copper-catalyzed cyanations and three-component cyanoalkylations of styrenes.

Keywords : Charge Transfer Complex; Electron Donor Acceptor Complex; Giese Reaction; Cyanation; Copper Catalysis

有機電子ドナー触媒は、*N*-ヒドロキシフタルイミドエステルなどの電子アクセプター基質との相互作用により EDA 錯体を形成し、錯体の光励起を介して反応性ラジカルを生成する、新しいタイプの有機触媒として最近注目を集めている。しかし、そのほとんどは触媒自身が塩基性や求核性を有しているため、基質適用範囲の拡大や触媒量の低減が困難であった[1,2]。そこで今回、我々はこれらの問題を解決する新しい有機電子ドナー触媒の開発に取り組んだ。さらに、この触媒の安定性及び金属への低い配位能力活かして、本電子ドナーを対アニオンとして組み込んだ銅触媒を生成した。

これら触媒を実際に用いた光反応への応用として、低触媒量での電子不足アルケンの Giese 型アルキル付加反応、また銅触媒によるシアノ化反応及びスチレンを組み合わせた三成分シアノアルキル化反応[3,4]を達成した。



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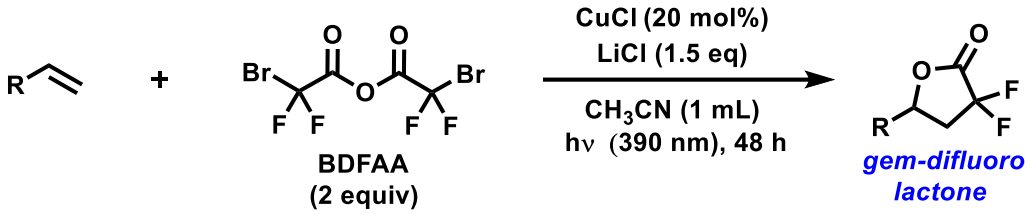
Copper Ligand-to-Metal Charge Transfer Photocatalysis Involving Halogen-Atom-Transfer in Alkene Difunctionalization

([1]*RIKEN CSRS*, [2]*RIKEN CPR*) ○Subrata Mukherjee,[1] Shintaro Kawamura,[1,2] Mikiko Sodeoka,[1,2]

Keywords: Ligand-to-metal charge transfer; Fluoroalkyaltion; Halogen-atom transfer; Difunctionalization of alkenes; Copper photocatalyst

Ligand-to-metal charge transfer (LMCT) photocatalysis enables the generation of radical species that cannot be formed through intermolecular electron transfer. For instance, LMCT of $CuCl_2$ is known to generate chlorine radical, effectively catalyzing various synthetic transformations.[1] However, the previous methods necessarily involve hydrogen atom transfer (HAT) by the chlorine radical for generating carbon centered radical intermediate and usually require addition of a strong oxidant for catalytic turnover. In particular, developing a catalytic net oxidative transformation using copper LMCT photocatalysis is still challenging without terminal oxidants.

Herein, we present an LMCT-driven $CuCl_2$-photocatalytic α,α-difluoro-γ-lactonization of alkenes using bromodifloroacetic anhydride (BDFAA) without addition of an external oxidant.[2] To the best of our knowledge, this reaction, for the first time, involves halogen-atom transfer (XAT), instead of HAT, with a chlorine radical by using BDFAA. The reaction involves halogen atom transfer (XAT) from bromodifloroacetic anhydride (BDFAA) with chlorine radical, instead of an HAT event, resulting the formation of a reactive fluoroalkyl radical and Cl–Br as an oxidant. This unprecedent approach involving XAT, affording the desired product and enabling catalytic turnover without an external oxidant. We believe this study will uncover novel application of catalytic process using LMCT, contributing to the advancement of synthetic chemistry.



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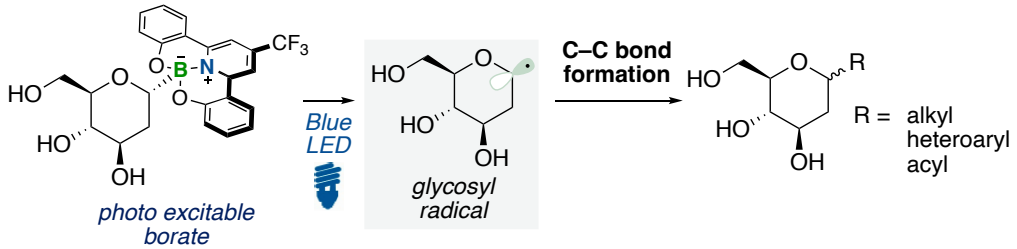
光励起グリコシルホウ素アート錯体を用いた C–グリコシル化反応

（京大化研[1]・医科歯科大生材研[2]・九大院薬[3]）○宮本 祐輔[1]・村上 翔[1]・隅田 有人[2]・平井 剛[3]・大宮 寛久[1]
C-Glycosylation of Photo-Excitable Glycosyl Borate ([1]*ICR, Kyoto Univ.*, [2]*IBB, Tokyo Med. & Dent. Univ.*, [3]*Grad. Sch. Phar. Sci., Kyushu Univ.*) ○Yusuke Miyamoto,[1] Sho Murakami,[1] Yuto Sumida,[2] Go Hirai,[3] Hirohisa Ohmiya[1]

We designed and synthesized 2,2′-(pyridine-2,6-diyl)diphenol-based glycosyl borate generating unprotected anomeric radical under visible light irradiation. The borate could be applied to carbon-carbon bond formation without photoredox catalysts enabling the introduction of sp^2 or sp^3 carbon fragments at an anomeric position.
Keywords : glycosylation; boron-ate complex; radical; direct excitation; visible light

C-グリコシドは、天然に普遍的に存在する *O*-グリコシドと比較して高い代謝安定性を有するため、医薬品開発において重要な標的分子である。したがって、*C*-グリコシド合成に利用可能なグリコシル供与体が数多く報告されている。それらグリコシル供与体のうち、アノマー炭素－金属結合をもつグリコシル金属（Li, Sn, B など）化合物は、金属元素由来の特徴的な反応性をもつことから、*C*-グリコシド合成に汎用されている。一方で、糖水酸基の保護・脱保護プロセスの減少に繋がる *C*-グリコシド合成に活用できる“無保護グリコシル金属化合物”は、合成の煩雑さや反応制御の難しさから、ほとんど知られていない。具体的には、Walczak らが報告した、無保護グリコシルスズ化合物を用いた遷移金属触媒クロスカップリング反応による *C*-グリコシド合成の例に限られる[1]。

今回、我々は、無保護グリコシルホウ素アート錯体[2]を活用した *C*-グリコシル化反応を見出した。可視光を照射することで、無保護グリコシルホウ素アート錯体の直接励起、続くアノマー炭素－ホウ素結合の均等開裂により、アノマー炭素ラジカル（グリコシルラジカル）を与える。得られたグリコシルラジカルを炭素－炭素結合形成反応に適用することで、さまざまな *C*-グリコシドを構築することができた。本反応は、触媒や添加剤を必要とせず、非熱的かつ温和な条件下にて実施可能である。



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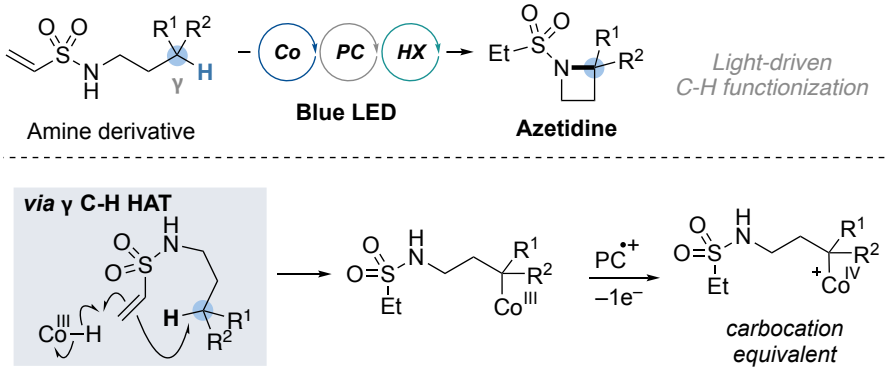
光駆動型協働触媒を用いた sp^3 炭素－水素結合活性化型アゼチジン合成

（京大化研 [1]）○中川 雅就 [1]・長尾 一哲 [1]・大宮 寛久 [1]
Synthesis of Azetidine via C(sp^3)–H Activation by A Light-Driven Triple Catalysis ([1] *Institute for Chemical Research, Kyoto University*) ○ Masanari Nakagawa,[1] Kazunori Nagao,[1] Hirohisa Ohmiya[1]

Due to the unique skeletal rigidity and polarity, azetidine has been gained much attention from medicinal chemistry. The synthesis of azetidines from simple aliphatic amines is ideal in the views of the abundance of aliphatic amines and the straightforwardness of process. Herein, we developed a new synthetic approach to azetidines from N-vinyl sulfonamides utilizing a triple photoredox/cobalt/Brønsted acid catalytic system. The catalysis entails generation of a carbon-centered radical at γ-amino position through selective hydrogen atom abstraction and oxidative radical-polar crossover of the carbon-centered radical to the carbocation equivalent. The reaction could convert the simple aliphatic amines to azetidines in single step.
Keywords : Photoredox Catalyst, Cobalt catalyst, Brønsted acid catalyst, Hydrogen atom transfer, Azetidine

アゼチジンは歪んだ構造に起因して独特な極性や剛直性を示すため、創薬科学の分野で注目を集めてきた。今回我々は、光酸化還元触媒/コバルト触媒/ブレンステッド酸触媒の協働触媒系 [1]とビニルスルホニル配向基を活用することで、アルキルアミンからアゼチジンを合成する手法を開発した。本手法は、次の 3 つの過程を経て窒素γ位炭素－水素結合をカルボカチオン等価体に変換する。1）系中で発生したコバルトヒドリド種が、窒素上に導入されたスルホニル基のアルケンに対して水素原子移動（HAT）を引き起こす、2）生成した炭素ラジカルが窒素γ位炭素－水素結合に対して HAT を引き起こす、3）光酸化還元触媒により、窒素γ位に発生した炭素ラジカル種はカルボカチオン等価体に一電子酸化される。生成物に含まれるスルホニル配向基は、容易に取り外すことができるため、入手容易なアルキルアミンから複雑かつ高度に官能基化されたアゼチジンを一挙に合成することができた。



1) Nakagawa, M.; Matsuki, Y.; Nagao, K.; Ohmiya, H. *J. Am. Chem. Soc.* **2022**, *144*, 7953.

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有機光酸化還元触媒とトリアルキルホスフィンを用いた芳香族カルボン酸誘導体のパラ位選択的アルキル化反応

（金沢大院医薬保[1]・京大化研[2]）○大谷亮人[1]・長尾一哲[2]・大宮寛久[2]

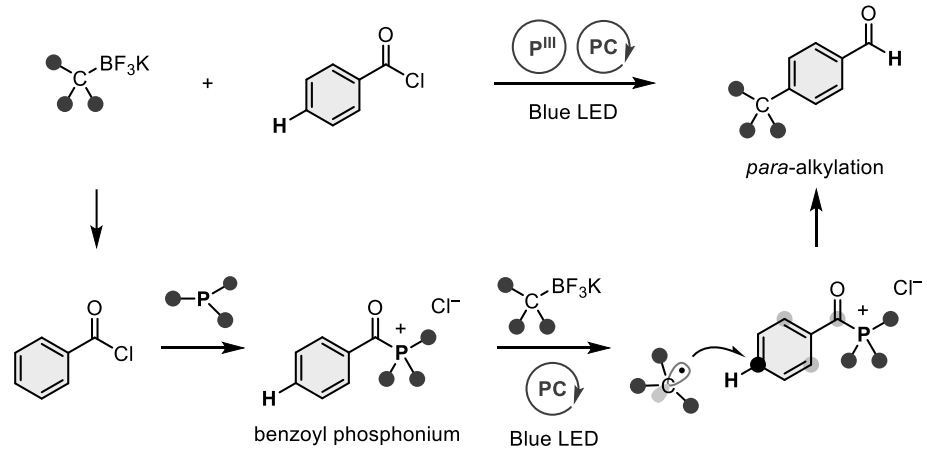
Para-Selective Alkylation of Aromatic Carboxylic Acid Derivatives Using Organic Photoredox Catalyst and Trialkylphosphine ([1]*Grad. Sch. Med. Sci., Kanazawa Univ,* [2]*ICR, Kyoto Univ.*) ○Ryoto Oya,[1] Kazunori Nagao,[2] Hirohisa Ohmiya[2]

We found that the reaction between alkylborons and benzoyl chlorides proceeded in the presence of an organic photoredox catalyst and a trialkylphosphine, providing *para*-alkylated aromatic aldehydes. The reaction would involve the addition of an alkyl radical from alkylborons to benzoyl trialkylphosphonium intermediates from benzoyl chlorides and trialkyl phosphine.

Keywords : Photoredox Catalyst, Acyl trialkylphosphonium, Alkylation, Para-selective functionalization

芳香族炭化水素の位置選択的な sp^2 炭素－水素結合の直接官能基化は、入手容易な化学原料の高付加価値化や医薬品の後期修飾化に繋がるため、その手法の開発が精力的に進められてきた。その中で、オルト位やメタ位選択的な官能基化と比較して、パラ位選択的な官能基化の報告例は少ない。既存のパラ位選択的官能基化は、高い位置選択性を担保するために遷移金属触媒の利用が必須であった。

我々は、有機光酸化還元触媒とトリアルキルホスフィンを活用することで、アルキルトリフルオロボレート塩と芳香族カルボン酸誘導体の反応が進行し、パラ位がアルキル化された芳香族アルデヒドを与えることを見出した。本手法は遷移金属触媒を用いることなく、完全なパラ位選択性を示した。反応機構実験と量子化学計算の結果から、1）ベンゾイルクロリド誘導体とトリアルキルホスフィンから生成したベンゾイルトリアルキルホスホニウム中間体に対して、アルキルラジカル種がパラ位選択的に付加反応を起こすこと、2）パラ位由来の水素原子がカルボニル炭素へと水素原子移動を起こすことが明らかとなった。



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光酸化還元触媒を用いたテトラヒドロフラン環の位置選択的 C(sp^3)-H アルキル化反応

（京大化研[1]・武田薬品工業[2]）○阿部 玲士[1]、長尾 一哲[1]、関 倫宏[2]、秦 大[2]、佐々木 悠祐[2]、大宮 寛久[1]

Regioselective C(sp^3)–H Alkylation of Tetrahydrofuran Derivatives by Photoredox Catalysis

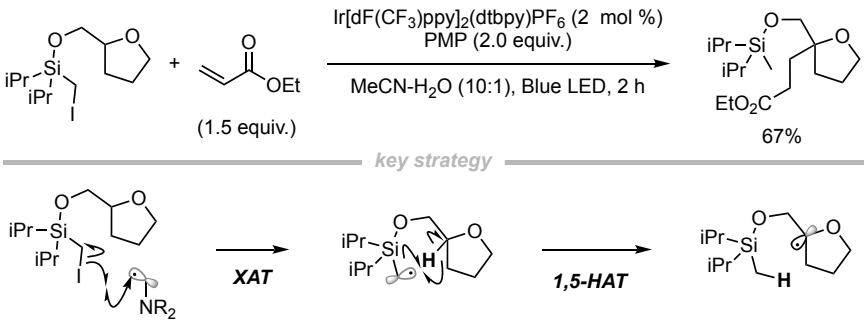
(ICR, Kyoto Univ.[1], Takeda Pharmaceutical Company Limited[2]) ○Reiji Abe[1], Kazunori Nagao[1], Tomohiro Seki[2], Dai Hata[2], Yusuke Sasaki[2], Hirohisa Ohmiya

We found C2-selective C(sp^3)–H alkylations of tetrahydrofurfuryl alcohol derivatives using a photoredox catalyst and iodomethylsilyl group capable of 1,5-hydrogen atom transfer. The reactions would involve 1) C2 selective generation of carbon-centered radicals through 1,5-hydrogen atom transfer by α-silylmetyl radical generated on hydroxy group of the tetrahydrofurfuryl alcohol and 2) addition of the resultant radicals to alkenes. This protocol allows to access chemically modified nucleotides in single step.

Keywords : Photoredox Catalyst, Chemically modified nucleotides, Tetrahydrofuran, Hydrogen atom transfer

核酸は新たな創薬モダリティとして注目されている。したがって、代謝安定性や体内動態の改善を目的とした、化学修飾核酸の合成が積極的に検討されている。核酸の構成要素であるテトラヒドロフラン環は化学修飾の標的とされているが、位置選択的に官能基化するには複数の合成工程を必要とする。今回我々は、光酸化還元触媒と位置選択的な水素原子移動を可能にする配向基を活用することで、テトラヒドロフリルアルコール類の 2 位選択的 C(sp^3)–H アルキル化反応を見出した。

可視光照射下、光酸化還元触媒とペンタメチルピペリジン（PMP）を用いて、ヨードメチルシリル基で保護されたテトラヒドロフルフリルアルコール誘導体とアクリル酸エステルを反応させたところ、所望の C2-アルキル化体が 67%収率で得られた。本反応では、光酸化還元触媒による一電子酸化により PMP から生じたα-アミノラジカルが、シリル基上のヨウ素原子を引き抜く［ハロゲン原子移動（XAT）］。その後、生成したα-シリル炭素ラジカルが 1,5-水素原子移動（HAT）を引き起こし、C2 位に炭素ラジカルを与える。本手法は、核酸誘導体にも適用可能であり、テトラヒドロフラン環の化学修飾を短工程化した。



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ベンゾフェノン型光酸化還元触媒を用いたベンジルアルコールの炭素-炭素結合開裂反応

（京大化研 [1]・金沢大院医薬保 [2]・医科歯科大生材研 [3]）○松尾 朋信 [1]・佐野 仁紀 [2]・隅田 有人 [3]・大宮 寛久 [1]

Csp^3–Csp^3 Bond Cleavage of Benzyl Alcohol via Benzophenone-type Organic Photocatalysis

([1] *Institute of Chemical Research, Kyoto University.* [2] *Graduate School of Medical Science, Kanazawa University.* [3] *Institute of Biomaterials Bioengineering, Tokyo Medical and Dental University*) ○Tomotoki Matsuo,[1] Masaki Sano,[2] Yuto Sumida,[3] Hirohisa Ohmiya[1]

In great success of photoredox chemistry, not only photocatalysts based on transition metals such as iridium and ruthenium, but also organic photocatalysts have been developed. In this study, we found carbon–carbon bond cleavage of electron-rich benzyl alcohol affording the corresponding aldehyde and alkyl radical in the presence of a weak base, via silicon-bridged benzophenone derivatives as organic photocatalyst (Figure 1). This process initiates the formation of alkoxy radicals via oxidative proton-coupled single-electron transfer of benzyl alcohol. Furthermore, we applied this catalytic system to degradation of a lignin model to obtain the corresponding aromatic aldehyde and phenol as highly value-added products in single step.

Keywords : Photoredox catalyst; Benzophenone; Single-electron transfer; Proton-coupled electron transfer; Carbon-carbon bond cleavage

近年、光酸化還元触媒化学の飛躍的な発展を背景に、Ir や Ru といった後周期遷移金属を中心元素とした光酸化還元触媒だけでなく、金属元素を含まない有機光酸化還元触媒の開発が盛んに行われている [1)]。今回我々は、ケイ素架橋型ベンゾフェノン誘導体（Figure 1）を有機光酸化還元触媒として活用することで、電子豊富なベンジルアルコール誘導体から炭素–炭素結合開裂を経て芳香族アルデヒドとアルキルラジカルを与えることを見出した。本反応は、ベンジルアルコールのプロトン共役電子移動（PCET）機構を介した一電子酸化によるアルコキシラジカル形成、続く β-開裂を経て進行する。本触媒系をリグニンモデル **1** に適用することで、対応する芳香族アルデヒド **2** とフェノール **3** を与えた（Scheme 1）。

Scheme 1

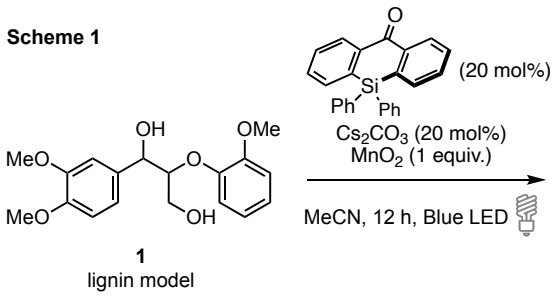
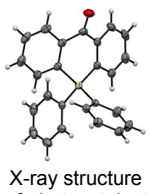


Figure 1



X-ray structure of photocatalyst

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キラル鉄(III)光レドックス触媒を用いるエナンチオ選択的ラジカルカチオン[2+2]環化付加反応

(名大院工[1]・北大触媒研[2]) ○片桐 佳[1]・大村 修平[1]・宮川 翔[2]・長谷川 淳也[2]・石原 一彰[1]

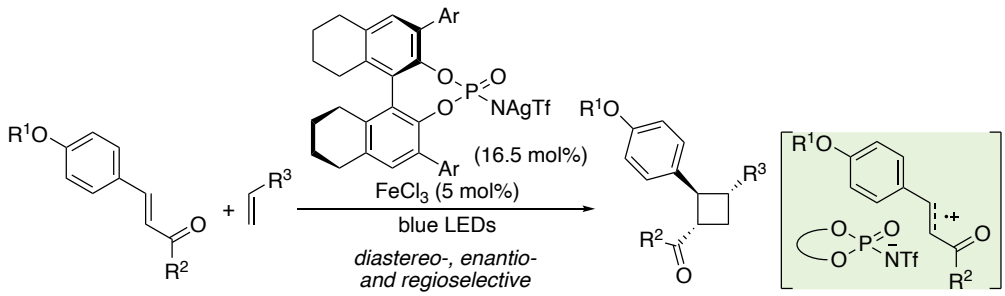
Enantioselective Radical Cation [2+2] Cycloaddition by Chiral Iron(III) Photoredox Catalysis

([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute for Catalysis, Hokkaido University*) Kei Katagiri,[1] Shuhei Ohmura,[1] Sho Miyakawa,[2] Jun-ya Hasegawa,[2] Kazuaki Ishihara[1]

Radical cation [2+2] cycloadditions have received increased attention as an alternative method to synthesize cyclobutane derivatives, which are present in various natural products and pharmaceuticals. The reaction generally proceeds with high diastereoselectivity in contrast to most of the conventional [2+2] photocycloaddition,[1] and a variety of effective methods for generating radical cation intermediates have been developed.[2] However, the development of the enantioselective reactions has been still highly challenging because they require precise control of a labile radical cation intermediate in an asymmetric fashion. Here, we developed enantio-, diastereo-, and regioselective [2+2] cycloadditions using a chiral iron(III) photoredox catalyst which could be prepared *in situ* from $FeCl_3$ and chiral silver salts.[3]

Keywords : Radical Cation; [2+2] Cycloaddition; Chiral Iron(III) Photoredox Catalysis; Chiral Counter Anion; Photoirradiation

数々の天然物や医薬品に含まれるシクロブタン骨格を構築する手法として、ラジカルカチオン[2+2]環化付加反応が近年注目を集めている。多くの光[2+2]環化付加反応と比較して[1)]、反応が高ジアステレオ選択的に進行する有用性から、ラジカルカチオン中間体を効率的に生成するための様々な手法がこれまでに開発されてきた[2)]。しかし、不安定なラジカルカチオン中間体の反応性を立体的に制御するのが難しいため、エナンチオ選択的反応の開発例はほとんどない。今回、我々は触媒量の $FeCl_3$ とキラル銀塩から反応系中で調製可能なキラル鉄(III)光レドックス触媒を用いることで、アネトール類とスチレン類から対応する[2+2]環化付加体をエナンチオ、ジアステレオ、および位置選択的に得ることに成功した[3)]。



1) Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 3.
2) Horibe, T.; Ishihara, K. *Chem. Lett.* **2020**, *49*, 107.
3) Ohmura, S.; Katagiri, K.; Kato, H.; Horibe, T.; Miyakawa, S.; Hasegawa, J.; Ishihara, K. *J. Am. Chem. Soc.* **2023**, *145*, 15054.

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エナンチオ選択的ラジカルカチオン[4+2]環化付加反応に有効なキラル鉄(Ⅲ)光レドックス触媒の開発と天然物合成への応用

（名大院工）○赤尾 颯斗・大村 修平・石原 一彰

Development of Chiral Iron(Ⅲ) Photoredox Catalysts for Enantioselective Radical Cation [4+2] Cycloaddition Toward Natural Product Synthesis (*Graduate School of Engineering, Nagoya University*) ○Hayato Akao, Shuhei Ohmura, Kazuaki Ishihara

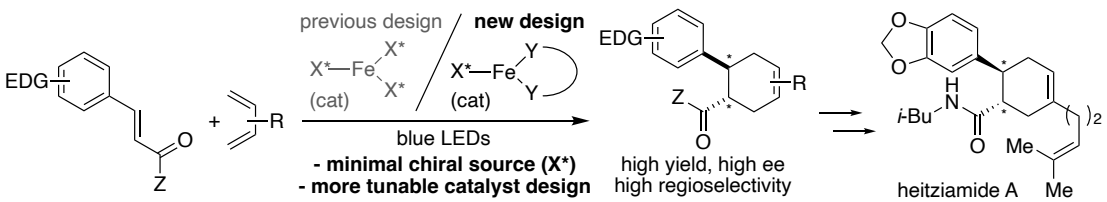
Radical cation [4+2] cycloaddition has attracted great attention as a method to afford unusual regioisomers that can be hardly obtained under thermal conditions.[1] Our group recently succeeded in enantioselective radical cation [4+2] cycloaddition using a chiral iron(III) photoredox catalyst.[2] However, the use of excess amounts of chiral sources was necessary to achieve the high enantioselectivity, although some of them were not involved in the enantio-determining step.

Here, we report a new chiral iron(III) photoredox catalyst consisting of a chiral anion and an appropriate achiral dianion, whereby the amount of chiral source can be reduced to one-third of the previous method. This strategy was applied to [4+2] cycloadditions of α,β-unsaturated carbonyl compounds with dienes to provide the products in high yield with high enantio- and regioselectivity. Furthermore, the obtained enantioenriched cycloadduct was used as a key intermediate for unprecedented asymmetric total synthesis of heitziamide A.

Keywords: Radical Cation;[4+2] Cycloaddition; Chiral Iron(Ⅲ) Photoredox Catalyst; Chiral Counter Anion; Natural Product Synthesis

ラジカルカチオン[4+2]環化付加反応は、熱条件とは異なる位置異性体を与える有用性から、数々の手法がこれまでに報告されている [1]。当研究室では、最近、キラル鉄(Ⅲ)光レドックス触媒を用いるエナンチオ選択的ラジカルカチオン[4+2]環化付加反応の開発に成功した [2]。しかし、不斉誘起に関与しない過剰のキラル源を用いている点に改善の余地が残されていた。

今回、我々はキラルアニオンと適切なアキラルなジアニオンから成る新たなキラル鉄(Ⅲ)光レドックス触媒を開発した。本触媒を用いることでキラル源の使用量を従来法の 1/3 に削減することに成功し、α,β-不飽和カルボニル化合物とジエンから対応する[4+2]環化付加体を高収率、高エナンチオ選択的、かつ高レジオ選択的に得た。さらに、得られた[4+2]環化付加体を鍵中間体に用いる heitziamide A の不斉合成を行った。



1) T. Horibe, K. Ishihara, *Chem. Lett.* **2020**, *49*, 107.
2) S. Ohmura, K. Katagiri, H. Kato, T. Horibe. S. Miyakawa, J. Hasegawa, K. Ishihara, *J. Am. Chem. Soc.* **2023**, *145*, 15054.

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
E1143(1143, Bldg. 11 [4F])

[E1143-3pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Koji Kubota, Shinichiro Fuse

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[E1143-3pm-01]
Chemoselective control of arylpotassium apecies by a flow reaction system using Schlosser superbases

○Hiroki Nakayama[1], Shintaro Kamio[2], Kazuhiro Okamoto[1], Aiichiro Nagaki[1] (1. Hokkaido University, 2. Hokkaido University of Science)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[E1143-3pm-02]
Precise polymerization of styrenes with alkoxysilyl groups using flow microreactor

○Kyosuke Tomite[1], Yuya Yonekura[1,2], Tomoko Kawaguchi[1], Takashi Tamaki[1], Mai Furusawa[2], Yosuke Ashikari[1], Aiichiro Nagaki[1] (1. Hokkaido University, 2. TOHO CHEMICAL INDUSTRY COMPANY,LIMITED)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[E1143-3pm-03]
Oxidative coupling and related reactions via organocopper reagents generated in a flow microreactor

○Ruka Ebisawa[1], Kazuhiro Okamoto[1], Aiichiro Nagaki[1] (1. Hokkaido University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[E1143-3pm-04]
Chemoselective generation and reactions of unstable organolithium species based on flowmicro synthesis

○Masatomo Iwata[1], Yosuke Ashikari[1], Aiichiro Nagaki[1] (1. Hokkaido University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[E1143-3pm-05]
Synthesis of asymmetric azulenes based on controlled organolithium reactions using flow microreactors

○Ryuhei Kikuchi[1], Hiroki Soutome[1,3], Masahiro Takumi[1], Shigeharu Wakabayashi[2], Aiichiro Nagaki[1] (1. Hokkaido University, 2. Suzuka University of Medical Science, 3. AGC Inc.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[E1143-3pm-06]

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Regioselective Mechanochemical Cyclodehydrogenation of Polycyclic Aromatics Compounds

○Takumu Nakamura[1], Yuta Morinaka[1], Yohei Ono[1], Kenichiro Itami[2], Hideto Ito[2] (1. Tosoh Co., 2. Nagoya Univ.)

Japanese

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[E1143-3pm-07]

Synthesis of Arylated Aromatic Compounds by Mechanochemical Anionic Activation of Polycyclic Aromatic Hydrocarbons

○Yoshifumi Toyama[1], Akiko Yagi[1], Kenichiro Itami[1], Hideto Ito[1] (1. Nagoya University)

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

[E1143-3pm-08]

Development of micro-flow synthesis of unsymmetrical *H*-phosphonate and consideration of details of the reaction

○Yuma Tanaka[1], Hiroshi Kitamura[1], Shinichiro Fuse[1] (1. Graduate School of Pharmaceutical Sciences, Nagoya University)

Japanese

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

[E1143-3pm-09]

Development of peptoid chain elongation avoiding diketopiperazine formation utilizing micro-flow technology

○Yuki Okura[1], Yuma Tanaka[1], Shinichiro Fuse[1] (1. Nagoya Univ.)

Japanese

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

[E1143-3pm-10]

A Facile Generation of *t*-Butoxycarbonyl Chloride Equivalent and Its Use in a Micro-flow Reactor.

○Kana Miyamoto[1], Ren Okabe, Shinichiro Fuse[1] (1. Nagoya University Graduate School of Pharmacetutical Science)

Japanese

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

[E1143-3pm-11]

Micro-flow heteroatom alkylation via TfOH-mediated rapid and in situ generation of carbocation and the following addition of nucleophiles

○Yuma Matsuura[1], Shinichiro Fuse[1] (1. The Univ. of Nagoya)

Japanese

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

[E1143-3pm-12]

Sequential-flow Synthesis of Flecainide Using Continuous-flow Amidation Reaction

○Kota Takeno[1], Haruro Ishitani[1], Masahiro Sasaya[1], Shū Kobayashi[1] (1. The University of Tokyo)

Japanese

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

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[E1143-3pm-13]

Improved efficiency of C-H carboxylation using peroxodisulfate in triphasic continuous droplet flow

○Takahide Fukuyama[1], Riku Nagaki[1], Mariko Fuji[1], Ilhyong Ryu[1] (1. Osaka Metropolitan Univ.)

Japanese

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

[E1143-3pm-14]

Nitroxide-mediated polymerization (NMP) initiated by BlocBuilder MA in flow reactors

○Ryo Takabayashi[1], Ilhyong Ryu[1], Takahide Fukuyama[1] (1. Osaka Metropolitan University)

English

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

[E1143-3pm-15]

Catalytic continuous-flow cyclic carbonate synthesis using supercritical CO_2

○Zhibo Yu[1], Haruro Ishitani[1], Shū Kobayashi[1] (1. the University of Tokyo)

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Schlosser 塩基を用いるアリールカリウム種の化学選択的なフロー反応制御

（北大院理[1]・北海道科学大[2]）○中山大輝[1]・神尾慎太郎[2]・岡本和紘[1]・永木愛一郎[1]

Chemoselective Control of Arylpotassium Species by a Flow Reaction System Using Schlosser Superbases

([1]*Graduate School of Science, Hokkaido University*, [2]*Hokkaido University of Science*)
○Hiroki Nakayama[1], Shintaro Kamio[2], Kazuhiro Okamoto[1], and Aiichiro Nagaki[1]

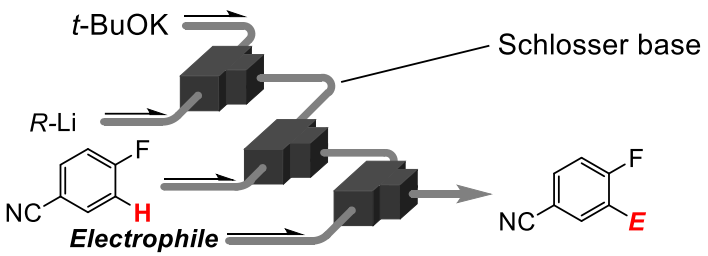
Direct and chemoselective transformation reactions of aromatic compounds bearing various functional groups have been recognized as useful synthetic methods, but the utilization of strong bases as deprotonation reagents often causes selectivity problems. We have recently developed the flow generation methods of organopotassium species in the absence of reaction substrates and their application to the reactivity studies. Herein, we have achieved the chemoselective deprotonation reactions of substrates bearing reactive functional groups, which was impossible in the previous approaches because of the competitive side reactions.

Initially, we have optimized the reaction temperature and the residence time in the series of flow reaction system. In this system, Schlosser bases were generated by the rapid mixing of alkyllithium reagent and potassium alkoxide base, and then deprotonated the substrate followed by the trapping with various electrophilic reagents. By using this system, the flow reaction of a fluoroarene with cyano group as a reactive functional group successfully reacted to undergo the selective deprotonation reaction. Moreover, changing the starting organolithium species from *n*-BuLi to PhLi remarkably improved the selectivity for deprotonation.

Keywords: Flow Microreactor; Organopotassium Species; Schlosser Bases

様々な官能基によって修飾された芳香族化合物の化学選択的な直接的変換反応は有用な合成手法として認識されているが、強塩基を用いる脱プロトン化を伴う変換手法においてそのような反応の選択性はしばしば問題となる。我々は以前より有機カリウム種の基質非共存下における発生法の開発と、その反応性について研究を行ってきた。今回、従来の方法では競合的副反応が原因で不可能であった、反応性官能基を有する基質の化学選択的な脱プロトン化を可能にした。

まず、有機リチウム試薬とカリウムアルコキシド溶液をフロー中で高速混合することで Schlosser 塩基を発生させ、その後含フッ素芳香族分子を短い滞留時間で速やかに反応させることで選択的な脱プロトン化を行った後、求電子剤で捕捉する一連のフロー反応系を組み、最適な温度・滞留時間の条件を探索した。図のように、シアノ基を有する基質と反応を行ったところ、選択的な脱プロトン化に伴う生成物が確認された。また、Schlosser 塩基の発生源である有機リチウム種を PhLi に変更することで、脱プロトン化の選択性をさらに向上させることに成功した。



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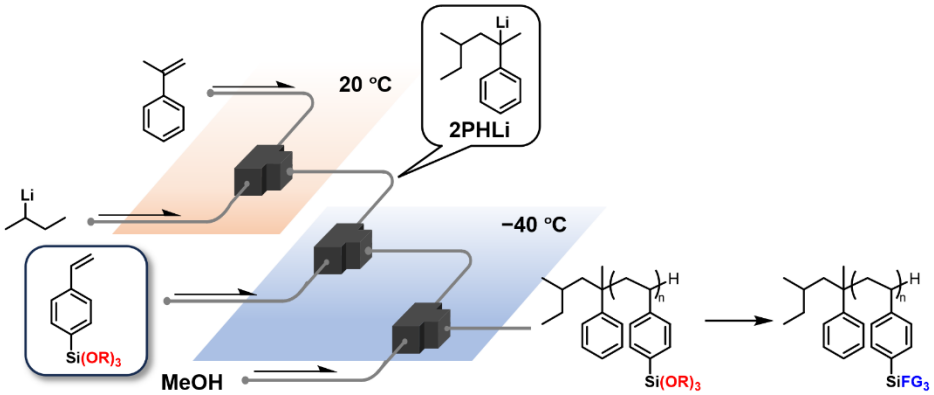
アルコキシシリル基を有するスチレンのフロー精密重合

(北大院理[1]・東邦化学工業[2]) ○冨手 響介[1]・米倉 裕哉[1,2]・川口 倫子[1]・玉木 孝[1]・古澤 真維[2]・芦刈 洋祐[1]・永木 愛一郎[1]
Precise polymerization of styrenes with alkoxysilyl groups using flow microreactor ([1]*Hokkaido University*, [2]*TOHO CHEMICAL INDUSTRY CO.,LTD.*) ○ Kyosuke Tomite[1], Yuya Yonekura[1,2], Tomoko Kawaguchi[1], Takashi Tamaki[1], Mai Furusawa[2], Yosuke Ashikari[1], Aiichiro Nagaki[1]

In anionic polymerization of styrenes with highly reactive functional groups using organolithiums as initiators, the initiators react not only with vinyl groups but also with highly reactive functional groups, making it difficult to control polymerization in conventional batch reactors. Flow microreactors, with their features of fast mixing, precise temperature and residence time control, have successfully controlled various reactions that are difficult to control in batch reactors. In this study, the chemoselectivity of the initiation reaction was improved by using 2-phenyl-4-methylhex-2-yl lithium (2PHLi) generated from *sec*-butyllithium and α-methylstyrene, and controlled anionic polymerizations of alkoxysilylstyrenes were achieved by fast mixing and precise temperature and residence time control in flow microreactors. In addition, conversions of methoxy groups to various functional groups were successfully achieved after synthesis of these polymers.
Keywords : flow microreactor, anionic polymerization, organolithium

有機リチウム種を開始剤とした高反応性官能基を有するスチレンのアニオン重合では、開始剤がビニル基だけではなく高反応性官能基とも反応してしまうため、従来のバッチ型反応器による重合制御は困難である。フローマイクロリアクターは、高速混合、温度及び滞留時間の精密制御といった特徴をもち、バッチ型反応器では困難であった高速反応の化学選択性制御に成功している。本研究では、フローマイクロリアクターを用いて、*sec*-butyllithium と α-methylstyrene から 2-phenyl-4-methylhex-2-yl lithium (2PHLi)を発生させ、高速混合、温度及び滞留時間の精密制御によって、開始剤のビニル基選択的な反応を可能とし、アルコキシシリル基を有するスチレン類のアニオン重合制御を達成した。また、これらポリマーの合成後にケイ素上官能基を様々な官能基に変換することにも成功した。



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フローマイクロリアクター中における有機銅試薬を鍵とする酸化的カップリングおよび関連反応

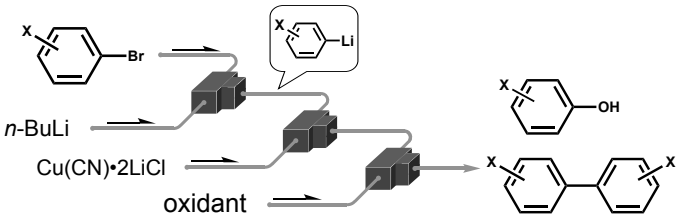
(北大院理) ○蛯澤 瑠架・岡本 和紘・永木 愛一郎

Oxidative coupling and related reactions via organocopper reagents generated in a flow microreactor (*Graduate School of Science, Hokkaido University*) ○Ruka Ebisawa, Kazuhiro Okamoto, Aiichiro Nagaki

Various carbon-carbon bond-forming reactions using organocopper reagents, exemplified by Ullman and Glaser reactions, have been developed for a wide range of applications including the synthesis of natural products or pharmaceutical compounds, utilizing their high selectivity and mild reaction conditions. However, the preparation of organocopper reagents generally involves transmetallation with strong nucleophiles such as organolithium reagents, which greatly limits the functional group acceptability due to the high reactivity of the precursor reagents. In this study, we have developed a new flow generation method for organocopper reagents, taking advantage of our synthetic methodology[1] that allows generation of functionalized organolithium species, which are extremely difficult to handle in batch reactors, through precise temperature and residence time control using flow microreactors. Transmetallation with unstable organolithium species, which can be generated with only a short residence time, leads to organocopper reagents with functional groups. Thus, functionalized organocopper reagents subsequently react with oxidants in flow to give biaryl compounds and phenols under different conditions, respectively.

Keywords: Flow microreactor; Oxidative coupling; Biaryl compounds; Organocopper compounds; Transmetalation

Ullman 反応や Glaser 反応などに代表される有機銅試薬を用いる種々の炭素–炭素結合形成反応は、その高い選択性や温和な反応条件ゆえに天然物や医薬品関連分子の合成など、幅広い用途へと展開されてきた。しかしながら有機銅試薬の調製には有機リチウム試薬のような強い求核剤とのトランスメタル化が一般的に用いられるため、前駆体となる試薬の反応性の高さゆえに官能基許容性が大きく制限される。本研究では、バッチ型反応器では扱うことが難しい官能基化された有機リチウム種を、フローマイクロリアクターを用いた精密な温度・滞留時間制御により発生できるという我々の独自技術[1]を活かして、新たな有機銅試薬のフロー発生法の開発を行った。結果として、わずかな滞留時間でのみ発生しうる不安定な有機リチウム種とのトランスメタル化により、官能基を有する有機銅試薬を発生させ、続くフロー中での酸化剤との反応により、ビアリール化合物やフェノール類をそれぞれ異なる条件で与えた。



1) A. Nagaki, Y. Ashikari, M. Takumi, T. Tamaki, *Chem. Lett.*, **50**, 485–492 (2021).

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フローマイクロリアクターを用いた芳香族リチウム種の基質共存型反応

（北大院理）○岩田 真朋・芦刈 洋祐・永木 愛一郎
Chemoselective generation and reactions of unstable organolithium species based on flowmicro synthesis (*Faculty of Science, Hokkaido University*) ○Masatomo Iwata, Yosuke Ashikari, Aiichiro Nagaki

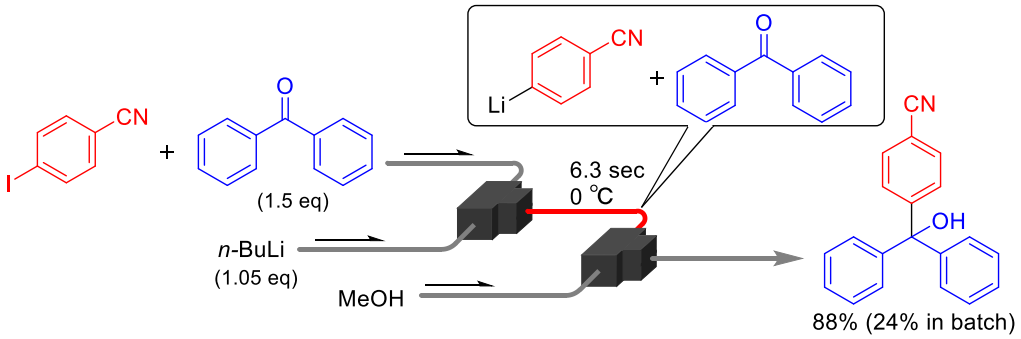
Although, the high reactivity of organolithiums is beneficial for organic synthesis, it limits the functionality tolerance, reducing their synthetic usability. We have developed “flash chemistry,” where unstable organolithiums are generated instantaneously, and are reacted with electrophiles before decomposing,[1] as well as highly chemoselective reactions even with reactive reagents.[2] Based on this high chemoselectivity, we herein report the chemoselective generation and reaction of unstable organolithiums in the presence of multiple electrophiles.

Using the flow microreactor, a solvent dissolving 4-iodobenzonitrile and benzophenone was mixed with *n*-butyllithium at 0 °C, affording the desired compound, 4-cyanotritylalcohol in a high yield. This indicates that the chemoselective generation and reaction of 4-cyanophenyl lithium proceeded even if there were multiple electrophiles.

Keywords : flowmicro reactor; chemo selectivity; organo lithium species

有機リチウム種は高い反応性から広く有機合成に用いられるが、官能基許容性が低いという課題があった。これに対し我々は、瞬間的に不安定リチウム種を発生させ、その分解前に求電子剤で捕捉するフラッシュケミストリーを展開してきた[1]。一方でフローマイクロリアクターは有機リチウム種のような高反応性化学種の反応を化学選択的に進行可能である[2]。今回我々は、この高化学選択性を活用し、複数の求電子剤が共存する条件における有機リチウム反応の開発を目的として研究を行った。

4-ヨードベンゾニトリルとベンゾフェノン（1.5 当量）の混合溶液をフローマイクロリアクター中、0 °C で *n*-ブチルリチウム（1.05 当量）と混合したところ、4-シアノトリチルアルコールが高収率で得られた。これはヨード基、シアノ基、ケトカルボニル基が共存する中、ヨード基が選択的に反応して 4-シアノフェニルリチウムが発生し、これがベンゾフェノンと選択的に反応したためだと考えられる。



1. Nagaki, A. *Tetrahedron Lett.* **2019**, *60*, 150923.
2. Nagaki, A.; Imai, K.; Ishiuchi, S.; Yoshida, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 1914.

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フローマイクロリアクターを用いた有機リチウム反応制御を基軸とする非対称アズレンの合成

(北大理[1]・鈴鹿医療科学大保健衛生[2]・AGC 株式会社[3])
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Synthesis of Asymmetric Azulene Based on Controlled Organolithium Reaction using Flow Microreactors (*Faculty of science, Hokkaido University*[1], *Suzuka University of Medical science*[2], *AGC Inc.*[3]) ○Ryuhei Kikuchi[1], Hiroki Soutome[1,3], Masahiro Takumi[1], Shigeharu Wakabayashi[2], Aiichiro Nagaki[1]

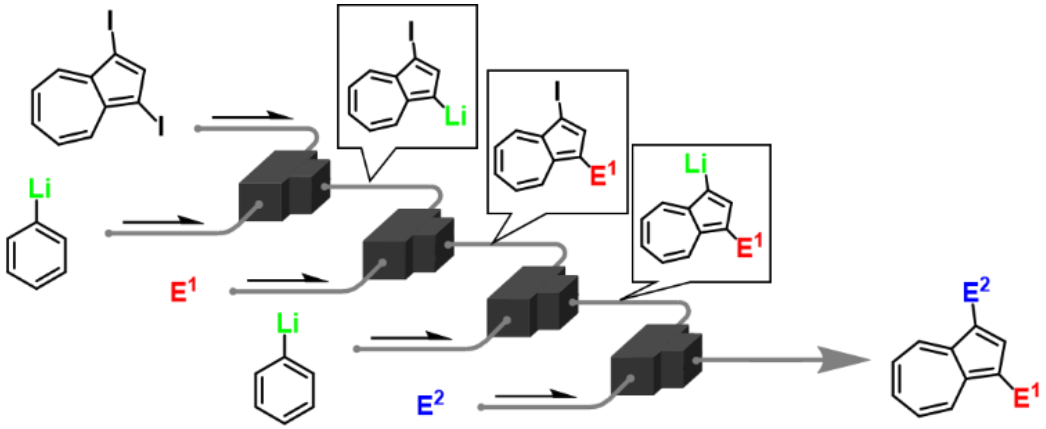
Azulene is an isomer of naphthalene with a fused structure of a seven- and five-membered ring, and has a strong dipole moment in this molecule, giving it a deep blue color. Azulene derivatives are attractive compounds with physiological activities such as anti-inflammatory effects in addition to fascinating photophysical properties, however, their synthetic methods are limited. For example, since the azulene skeleton is a highly symmetric, many reactions are known to simultaneously convert multiple substituents with close reactivity, making it difficult to convert substituents asymmetrically.

In this study, we synthesized asymmetric azulenes by sequential reactions using flow microreactors for 1,3-dihaloazulenes, which can be synthesized from azulenes in a single step.

Keywords : flow microreactor, asymmetric azulene, UV-Vis absorption spectrum, lithiation reaction

アズレンはナフタレンの異性体で七員環と五員環の縮環構造をもち、強い双極子モーメントを分子内に有することから深い青色を示す。アズレン誘導体は光機能に加えて抗炎症作用をはじめとした生理活性を有する魅力的な化合物群であるが、その合成法には制限がある。特にアズレン骨格は対称性が高く、複数の異なる置換基を導入した非対称アズレンの合成は困難である。

本研究では、フローマイクロリアクターの高い反応制御能により逐次的なアズレンへの置換基導入による非対称化を行った。アズレンから一段階で合成できる 1,3-ジハロアズレンに対して連続的にハロゲン—リチウム交換反応および求電子剤との反応を行うことにより、非対称アズレン合成を達成した。



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メカノケミカル脱水素環化反応による多環芳香族化合物の位置選択的合成

（東ソー株式会社[1]・名大院理[2]・名大 ITbM[3]）○中村拓夢[1]・森中裕太[1]・小野洋平[1]・伊丹健一郎[2,3]・伊藤英人[2]

Regioselective Mechanochemical Cyclodehydrogenation of Polycyclic Aromatic Compounds

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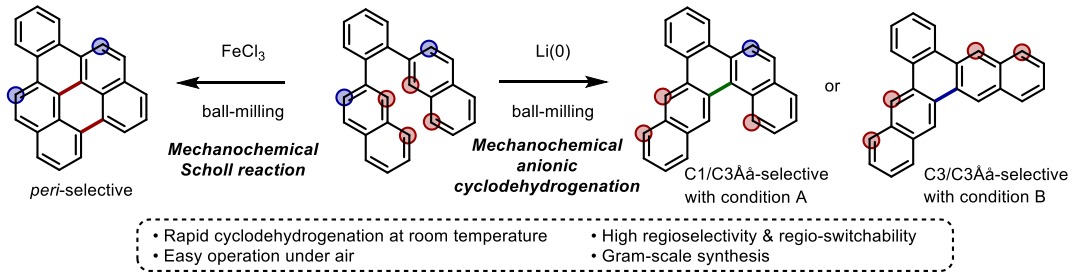
Polycyclic aromatic compounds are expected to be applied in a wide range of fields because of their unique optoelectronic properties. In general, polycyclic aromatic compounds are synthesized via cyclodehydrogenation of polyarylene precursors, but in many cases, it is difficult to control the cyclization positions of substrates having multiple reaction sites. Thus, the development of efficient and regioselective method to construct fused ring structures has been highly required. Herein, we report a regioselective synthesis of polycyclic aromatic compounds from various π-extended *o*-terphenyl derivatives under mechanochemical cyclodehydrogenation conditions. Furthermore, in the cyclization of *o*-di-(2-naphthyl)-benzene, it was found that structural isomers with different fused structures can be synthesized in high selectivity depending on the reaction conditions.

Keywords : Nanographene; Mechanochemistry; Polycyclic aromatic compound; Cyclodehydrogenation; Ball-milling

多環芳香族化合物は、特異な光・電子物性をもつことから、幅白い分野での応用が期待される。一般的に多環芳香族化合物は芳香環連結分子の脱水素環化反応によって合成されるが、反応点が複数存在する基質の反応では、環化位置の制御が困難となる問題点があった。そのため、多様な縮環構造を短工程かつ高選択的に合成する手法の開発が求められている。

本研究では、反応点が複数存在する種々のπ拡張 *o*-ターフェニル類縁体に対して金属リチウムを用いたメカノケミカル脱水素環化反応[1]を行うことで、多環芳香族化合物の位置選択的な合成を達成した。また、*o*-ジ(2-ナフチル)ベンゼンにおいては、反応条件に応じて環化位置が異なる３つの構造異性体をそれぞれ高選択的に合成できることを見出した。発表ではその詳細について報告する。



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多環芳香族化合物のメカノケミカルアニオン活性化による芳香環連結分子合成

(名大院理[1]・名大 ITbM[2]) ○遠山祥史[1]・八木亜樹子[1,2]・伊丹健一郎[1,2]・伊藤英人[1]

Synthesis of Arylated Aromatic Compounds by Mechanochemical Anionic Activation of Polycyclic Aromatic Hydrocarbons

([1]*Graduate School of Science, Nagoya University,* [2]*Institute of Transformative Bio-Molecules, Nagoya University*) ○Yoshifumi Toyama,[1] Akiko Yagi,[1,2] Kenichiro Itami,[1,2] Hideto Ito[1]

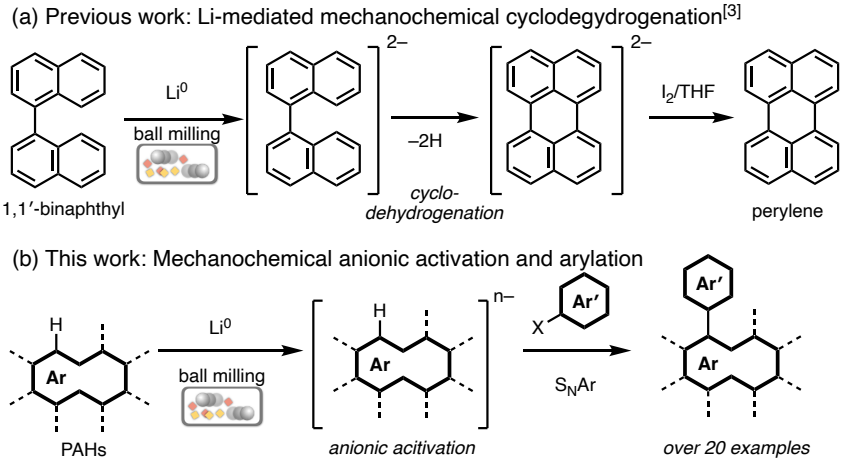
Birch/Benkeser reduction performed in the presence of alkali metals in liquid ammonia or amines is a well-known transformation for aromatic compounds. The recent reports demonstrated a mechanochemical Birch reduction[1] and a solution-state Birch-type functionalization with sodium(0) dispersion.[2] We have also reported a lithium(0)-mediated mechanochemical cyclodehydrogenation that proceed through the formation of 1,1′ -binaphthyl anion, cyclization and dehydrogenation.[3]

Herein, we report a novel C–C bond forming reaction through a similar mechanochemical anionic activation of polycyclic aromatic compounds with lithium(0) by a ball-milling machine followed by reaction with aryl electrophiles. The reaction is expected proceed in a fashion of S_NAr reaction of aromatic anions with aryl electrophiles, which has not been reported yet. In the presentation, we will present the rapid synthesis of various arylated polyaromatics by this method as well as substate scope and reaction mechanism.

Keywords: nucleophilic aromatic substitution (S_NAr), mechanochemical reaction, ball-milling, polycyclic aromatic hydrocarbons, arylation

アンモニア中あるいはアミン存在化でアルカリ金属を作用させて行う Birch/Benkeser 還元、および、生じた芳香環アニオン種と求電子剤との反応は、古くから知られる芳香族化合物の変換反応である。最近の報告例では、溶媒を用いないメカノケミカル Birch 還元[1]や金属ナトリウム分散体とさまざまな求電子剤を用いた Birch 型官能基化反応などが開発されている[2]。 一方、当研究室ではボールミルを用いたメカノケミカル脱水素環化反応による多環芳香族化合物の新規合成法を開発している（図 a)。本反応では、通常溶液中では反応性が低い金属リチウム片をメカノケミカル反応で混和することによって 1,1′-ビナフチルのジアニオン種が効率的に発生し、続く環化と脱水素化が進行すると考えられている[3]。

今回我々は、これまでと同様な金属リチウムによる多環芳香族化合物のメカノケミカルアニオン活性化に加えて、逐次的に芳香族求電子剤を作用させることで、新しい炭素−炭素結合形成反応の開発に成功した（図 b)。本反応は多環芳香族化合物のアニオン種と芳香族求電子剤との芳香族求核置換型の反応であることが予想され、同種の反応はこれまで報告されていない。発表では、本手法を用いた様々な構造のアリール化多環芳香族化合物の迅速合成と基質適用範囲、反応機構などについて報告する。



[1] Gao, Y.; Kubota, K.; Ito, H. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217723.
[2] (a) Fukazawa, M.; Takahashi, F.; Yorimitsu, H. *Org. Lett.* **2021**, *23*, 4613. (b) Miwa, K.; Aoyagi, S.; Amaya, T.; Sasamori, T.; Morisako, S.; Kurogi, T.; Yorimitsu, H. *Chem. Eur. J.* **2023**, *29*, e202301557.
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非対称 *H*-ホスホネートのマイクロフロー合成法の開発と反応の詳細

（名大院創薬）○田中 裕真・北村 宙士・布施 新一郎

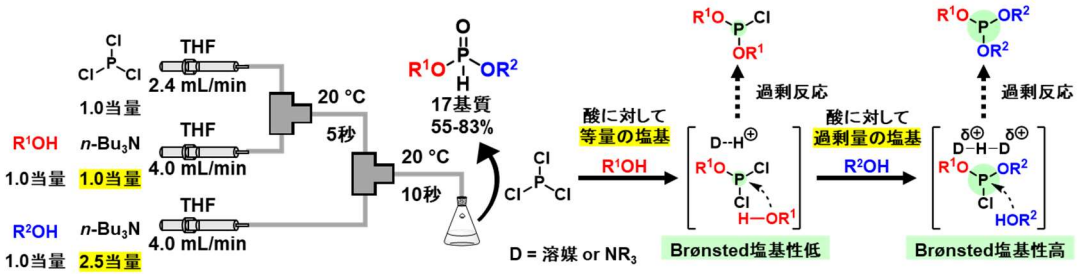
Development of Micro-Flow Synthesis of Unsymmetrical *H*-Phosphonate and Consideration of Details of the Reaction

(*Graduate School of Pharmaceutical Science, Nagoya University*) ○Yuma Tanaka, Hiroshi Kitamura, Shinichiro Fuse

H-phosphonates are important synthetic precursors for syntheses of oligonucleotide-based drugs, however the synthesis of asymmetrical *H*-phosphonates requires multiple synthetic steps. In order to overcome this problem, we developed one-flow sequential introduction of two different alcohols into inexpensive phosphorus trichloride. The key to suppress overreactions was the use of a solvent with high Lewis basicity and proper control of the amount of amine. To elucidate the mechanism of suppression of overreactions, we estimated Gibbs free energy of protonated intermediates by DFT calculation and conducted various verification experiments.

Keywords : Micro-flow; H-Phosphonate; Phosphorus Trichloride; Organophosphorus Compounds; DFT calculation

H－ホスホネートは核酸医薬などの合成前駆体として有用であるが [1]、非対称 *H*－ホスホネートの合成には多段階を要する。我々は、本問題を解決するため安価な三塩化リンに対して、異なる 2 種のアルコールを連続導入するマイクロフロー合成法を開発した [2]。本手法では高配位性溶媒の使用と適切な量のアミンの添加が過剰反応抑制のために重要であった。この理由を解明するために種々の検証実験、DFT 計算を行った結果、各段階における中間体のブレンステッド塩基性の違いにより、アミンの添加量が副反応の速度に大きく影響するためであることがわかった。本発表では、詳細な条件検討結果に加え、検証実験、DFT 計算の結果についても報告する。



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マイクロフローリアクターを用いたペプトイド合成におけるジケトピペラジン形成の回避

（名大院創薬）〇大倉 優輝・田中 裕真・布施 新一郎

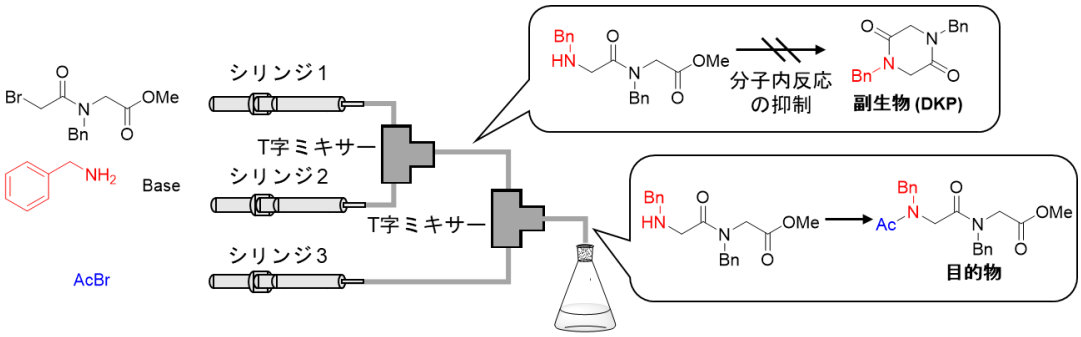
Development of peptoid chain elongation avoiding diketopiperazine formation utilizing micro-flow technology

(*Graduate School of Pharmaceutical Sciences, Nagoya University*) 〇Yuki Okura, Yuma Tanaka, Shinichiro Fuse

In organic chemistry, it is often difficult to suppress undesired intramolecular reactions competing with desired intermolecular reactions. The formation of diketopiperazine (DKP) by intramolecular cyclization during peptoid chain elongation is one example of this problem. Peptoids prefer *cis*-amide conformation compared to peptides, therefore avoidance of DKP formation in peptoid synthesis is challenging. We successfully performed the peptoid chain elongation avoiding the undesired DKP formation using micro-flow technology that can precisely control reaction time and temperature. In addition, we also demonstrated scale-up synthesis.

Keywords: *continuous-flow; peptoid; diketopiperazine; acylation; N-alkylation*

有機合成化学において望む分子間反応に対する望まない分子内反応の抑制には困難が伴うことが多い。ペプトイド鎖伸長時の分子内環化によるジケトピペラジン（DKP）形成はこの実例の一つであり、ペプトイドは *cis*-アミド配座を取りやすく、環化に有利な配座であるため、その抑制は困難である。我々は、マイクロフロー合成法を用い、反応時間、温度を精密に制御することで望まない DKP 形成を抑制しつつペプトイド鎖を伸長することに成功した。また、容易にスケールアップできることも確かめたので併せて報告する。



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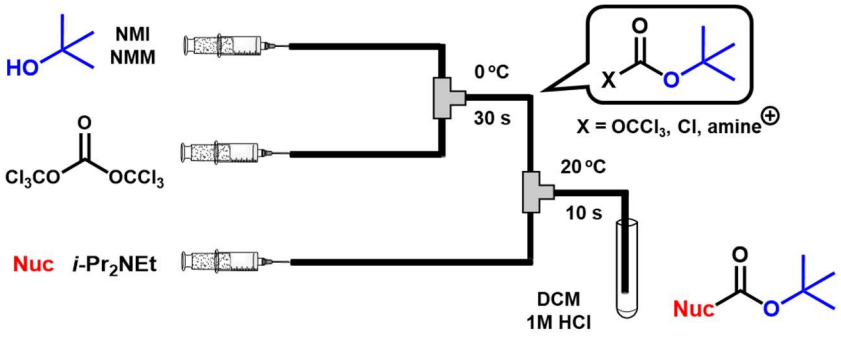
マイクロフローリアクターを用いた *t*-ブチルオキシクロリドおよびその等価体の迅速合成と利用法開発

（名大院創薬）○宮本 佳奈・岡部 蓮・布施 新一郎
A Facile Generation of *tert*-Butoxycarbonyl Chloride Equivalent and Its Use in a Microflow Reactor. (*Graduate School of Pharmaceutical Sciences, Nagoya University*) ○ Kana Miyamoto, Ren Okabe, Shinichiro Fuse

t-Butyl-carbamates and carbonates have been utilized as bioactive compounds, functional materials, and synthetic intermediates. The most conventional method includes the nucleophilic acyl substitution reaction using readily available and stable di-*t*-butyl dicarbonate (Boc_2O) as an electrophile. However, this method usually requires long reaction time and high temperature conditions due to the mild electrophilicity of Boc_2O. Herein, we report rapid and mild *in situ* generation of highly electrophilic Boc-Cl equivalent from triphosgene, *t*-BuOH, and two different types of bases, and its use for formation of carbamates and carbonates in a micro-flow reactor. The developed method was effective for the carbamate formation using less reactive amines.
Keywords : continuous-flow, Boc, nucleophilic acyl substitution, carbamate, carbonate

t-ブチルカルバマートやカルボナートは生物活性化合物、機能性材料、合成中間体として利用されている。これらを合成する際のアミンやアルコールの *t*-ブトキシカルボニル化においては、入手容易な二炭酸ジ-*t*-ブチル（Boc_2O）が Boc 化剤として汎用されている。しかし Boc_2O の温和な求電子性のため、長時間かつ高温条件を必要とする場合がある [1)]。我々は、トリホスゲンを用いる有用化合物のマイクロフロー合成法を報告してきた [2,3)]。本研究では、マイクロフローリアクターを用い、トリホスゲン、*t*-BuOH、異なる 2 種の塩基を組み合わせることによって、短時間かつ温和な条件でアミンやアルコールを Boc 化することに成功したので、報告する。



1) Basel, Y.; Hassner, A. *J. Org. Chem.*, **2000**, *65*, 6368.
2) Otake, Y.; Nakamura, H.; Fuse, S. *Angew. Chem. Int. Ed.*, **2018**, *57*, 11389.
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マイクロフロー合成法を駆使したトリフルオロメタンスルホン酸によるカルボカチオン生成と続く求核付加反応の開発

（名大院創薬）○松浦 祐真・布施 新一郎
Micro-flow heteroatom alkylation via TfOH-mediated rapid and in situ generation of carbocation and the following addition of nucleophile (*Department of Basic Medicinal Sciences, Graduate School of Pharmaceutical Sciences, Nagoya University*) ○ Yuma Matsuura, Shinichiro Fuse

One-pot/one-flow nucleophilic substitution reactions via carbocations generated from corresponding alcohols are valuable because they allow single-step and less wasteful synthesis of a variety of useful compounds. The most conventional approach involves weak Brønsted acid-mediated gradual generation of carbocations from the alcohols in the presence of nucleophiles. The coexistence of alcohols and cations often causes undesired ether formation, in addition, the use of basic nucleophiles is difficult due to the deactivation of the nucleophiles by trapping protons. Herein, we report rapid (0.5 s) and mild (25 °C) generation of carbocation using strong Brønsted acid and its rapid use for the following nucleophilic addition using basic nucleophiles. The use of micro-flow technology successfully suppressed side reactions. Generally good to high yields were observed when highly basic nucleophiles such as aliphatic amines were used. Therefore, the developed approach complements the conventional approach that is suitable for the use of less basic nucleophiles such as amides.
Keywords : continuous-flow; nucleophilic substitution; S_N1; acid; carbocation

アルコールから対応するカルボカチオンを調製し、求核剤を付加させるワンポット／ワンフロー反応は、廃棄物が少なく単段階で目的物が得られるため有用である。従来法は弱酸条件下でアルコールから反応系中で少しずつカルボカチオンを生じさせて、共存させた求核剤を付加するものである。しかしながら、アルコールとカルボカチオンの共存が引き起こす副反応や塩基性度の高い求核剤使用時のプロトン捕捉による失活が問題であった。我々は最近、インドール誘導体のマイクロフロー高速求核置換反応による合成法を発表した[1]。本発表では溶液の高速混合が可能なマイクロフロー合成法を用い、強酸によりアルコールから迅速にカルボカチオンを調製し、求核剤と段階的かつ速やかに反応させることで副反応を抑制したので報告する（図1）。なお、本反応では従来法で利用困難であった塩基性度の高い求核剤の利用にも成功した。

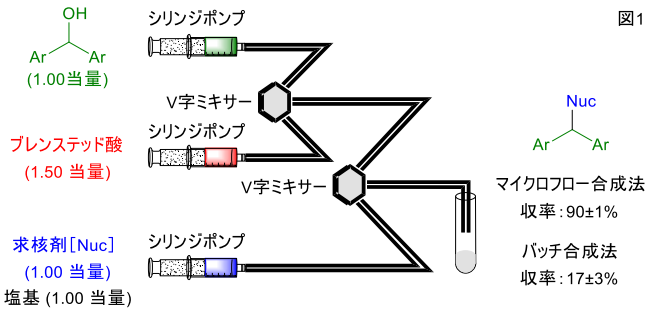

図1

1 a) Masui, H.; Kanda, S.; Fuse, S. *Commun. Chem.* **2023**, *6*, 47; b) Fuse, S.; Kanda, S.; Masui, H. *Chem. Asian. J.* **2023**, e202300909.

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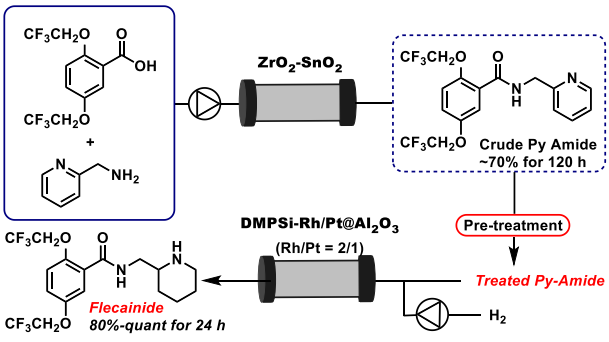
連続フローアミド化を利用する不整脈治療薬フレカイニドの連結合成

（東大院理[1]・東大院 GSC 社会連携講座[2]）○武野晃太[1]・笹谷将洋[1]・石谷暖郎[2]・小林 修[1,2]
Sequential-flow Synthesis of Flecainide Using Continuous-flow Amidation Reaction
(*School of Science[1] and GSC Social Cooperation Laboratory[2], The Univ. of Tokyo*)
○Kota TAKENO[1], Masahiro SASAYA[1], Haruro ISHITANI[2], Shū KOBAYASHI[1,2]

Sequential-flow synthesis is an effective method for next-generation fine chemical manufacturing, particularly for active pharmaceutical ingredients (APIs) involving amides as their main skeleton. This study explores a two-step sequential-flow synthesis of flecainide, an anti-arrhythmic drug, through our developed flow amidation combined with flow aromatic ring hydrogenation using a Rh/Pt bimetallic catalyst. In the amidation step, Zr-Sn mixed oxides demonstrated superior activity compared to previously reported Mo-modified oxide catalyst. In the ring hydrogenation step, moderate yield was obtained using the crude solution from the amidation flow. On the other hand, by washing the crude solution with a basic aqueous solution and using it for hydrogenation, the target drug could be obtained in high yield. Based on these results, a two-step sequential flow synthesis of the API was finally established.
Keywords: *Solid Acid, Direct amidation, Continuous-flow reaction, Sequential-flow synthesis, APIs synthesis*

医薬品原体合成に連結フロー合成を適用することができれば、効率性の向上のみならず、少量多品種・オンデマンド製造など、様々な利点が期待できる。その実現には、前段の反応と後段の反応を適切に連結することが必要であるが、前段からの不純物による阻害がしばしば問題となる。アミドは、医薬品を含む機能性化学品に多く含まれる重要な構造の一つであるが、縮合剤などを利用して合成されることが多く、多量の共生成物を排出するため、上記のような連結には困難が伴う。演者らはすでに、複合金属酸化物を用いたカルボン酸とアミン間の脱水的連続フローアミド化を報告している[1)]。本法は水のみが副生成物であるため、連結には好適な反応である。本研究では、フローアミド化と、独自に開発したポリシラン－アルミナ担持 Rh/Pt 触媒を用いたフロー芳香族水素化反応とを組合わせ、不整脈治療薬フレカイニドの二段階連結合成を検討した。アミド化は Zr/Sn 複合酸化物が優れた触媒効果を示したが、芳香族水素化との連結に際して収率が顕著に低下することが判明した。種々の検討により阻害要因を特定し、後処理工程を組み込むことにより高収率が実現できることを見出した。この結果を基に、オフライン操作を必要としないフレカイニドの二段階連結合成を達成した。



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ペルオキソ二硫酸塩を用いた C-H カルボキシル化の連続ドロップレットフロー法による効率化

（阪公大院理 [1]）○福山高英 [1]・長木 陸 [1]・冨士 万梨子 [1]・柳 日馨 [1]

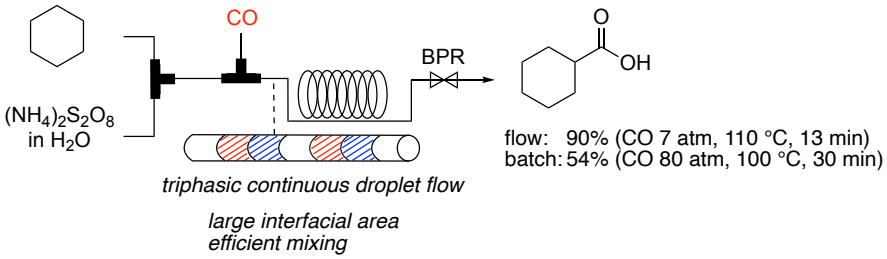
Aziridination of Styrene Derivatives Using Iminoiodinane Catalyzed by Iodine and Ammonium Iodide ([1]*Graduate School of Engineering, Osaka University*, [2]*Graduate School of Engineering, Kyoto University*) Kensuke Kiyokawa,[1] ○Tomoki Kosaka,[1] Satoshi Minakata,[1] Teruyuki Kondo[2]

Peroxodisulfate-mediated C-H carboxylation was investigated in a continuous triphasic droplet flow system. When cyclohexane was reacted with ammonium peroxodisulfate and carbon monoxide in the flow system, the reaction proceeded efficiently, and cyclohexanecarboxylic acid was obtained in high yield without any additives. Although the batch reaction required a high pressure of CO, the pressure could be reduced to 7 atm, adopting the continuous droplet flow system.

Keywords : Flow synthesis, C-H Carboxylation, Peroxodisulfate, Triphasic reaction, Continuous droplet flow

C(sp^3)-H 結合の直接官能基化反応の開発は、有機化学における最も重要な研究課題の 1 つである。C(sp^3)-H 結合を直接かつ効率的にカルボン酸に変換できれば、カルボン酸を合成する有効な方法となる。Sen らはペルオキソ二硫酸塩を用いたメタンおよびエタンのカルボキシル化反応による酢酸およびプロピオン酸合成を報告しているが収率は中程度であった[1]。

本研究ではフロー法を活用し、ペルオキソ二硫酸塩を用いたアルカンの C-H カルボキシル化の効率化を検討した。シクロヘキサンの反応をフローリアクターを用いて検討したところ、一酸化炭素圧 7 気圧、滞留時間 13 分で 90%の収率でシクロヘキサンカルボン酸が得られた。一方、バッチ反応では、一酸化炭素圧 80 気圧で収率 54%に留まった。フロー系での優れた結果は、高い気/液/液の接触界面積および内部循環流による高効率混合に起因すると考えられる。



謝辞:この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構(NEDO)の委託業務の結果得られたものです。

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フローリアクター中での BlocBuilder MA 開始ニトロキシド媒介ラジカル重合 (NMP)

(阪公大院理 [1]) ○高林 亮 [1]・柳 日馨 [1]・福山 高英 [1]

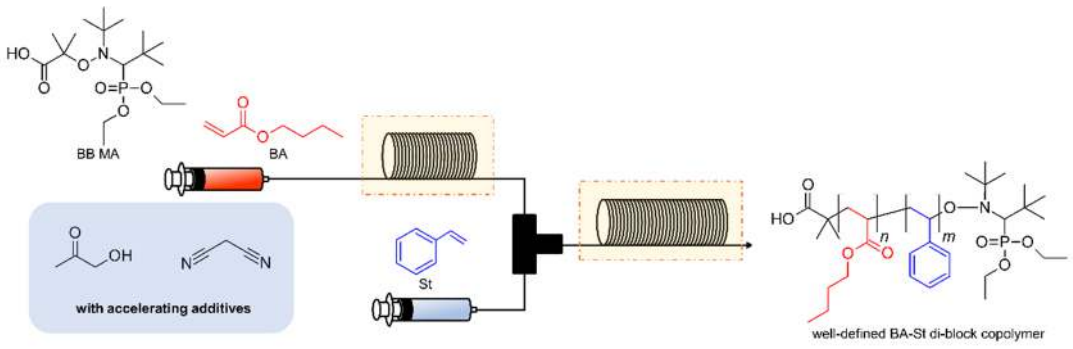
Nitroxide-mediated polymerization (NMP) initiated by BlocBuilder MA in flow reactors

([1]*Graduate School of Science, Osaka Metropolitan University*) ○Ryo Takabayashi,[1] Ilhyong Ryu,[1] Takahide Fukuyama[1]

Since flow reactors have advantages such as high-speed mixing, accurate reaction temperature and time control, many applications have been reported for polymer synthesis as well as organic synthesis. However, there are few reports on nitroxide-mediated radical polymerization (NMP), one of the precision polymerizations, in flow reactors. NMP has been reported to be accelerated by adding α-hydroxycarbonyl compounds or active methylene compounds, but no examples have been reported using the industrially available NMP initiator BlocBuilder MA (BBMA). In this study, NMP of styrene and butyl acrylate using BB MA under continuous flow reaction conditions showed higher conversions and lower polydispersity index values compared to batch reaction conditions. Furthermore, we found that highly controlled butyl acrylate-styrene di-block copolymers could be obtained in a relatively short time in flow reactors.

Keywords : Polymer, di-block copolymer, Nitroxide-mediated radical polymerization (NMP), flow reactors

フローリアクターは、高速撹拌や正確な反応温度と時間の制御などの利点があることから、有機合成のみならずポリマー合成への応用例も多く報告されている。しかしながら、精密重合の一つであるニトロキシド媒介ラジカル重合 (NMP)のフローリアクター中での報告例は限られている。α-ヒドロキシカルボニル化合物や活性メチレンを持つ化合物を添加することにより NMP が加速させることが報告されているが [1),2)]、工業的に利用可能な NMP 開始剤の BlocBuilder MA (BBMA) と組み合わせた例はまだ報告されていない。本研究では、連続フロー反応条件下で BB MA を開始剤としたスチレンおよびアクリル酸ブチルの NMP を検討した。その結果、バッチ反応条件下と比べ高いモノマー転化率と分子量分布(Đ)が小さいポリマーが得られた。また、アクリル酸ブチルとスチレンのブロック共重合を検討したところ、高度に制御されたジブロックコポリマーが比較的短時間で得られることを見出した [3)]。



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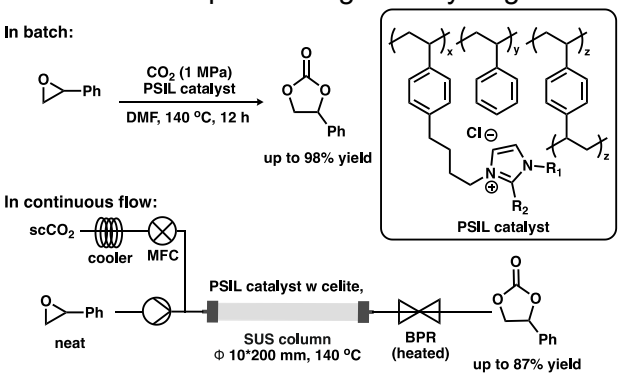
Catalytic Continuous-flow Cyclic Carbonate Synthesis Using Supercritical CO_2

([1] Department of Chemistry, School of Science, The Univ. of Tokyo, [2] GSC Social Cooperation Laboratory, Graduate School of Science, The Univ. of Tokyo)
○Zhibo YU,[1] Haruro ISHITANI,[2] Shū KOBAYASHI[1, 2]

Keywords: Polymer-supported catalyst; Ionic liquid; Supercritical CO_2: Cyclic carbonate; Continuous-flow reaction

Supercritical CO_2 ($scCO_2$) exhibits characteristics which make it juxtapose with but also differentiate from liquid and gaseous CO_2. It has been widely utilized in organic synthesis, especially CO_2 conversions where it can function as both reactant and solvent. As well as nontoxicity and incombustibility, both its high thermal conductivity enabling systems free from the interference from reaction heat and the powerful capability on mass transfer ascribed to its low viscosity in porous solid catalysts along with high solubility to substrates also products, consequently make it surpass conventional organic solvents[1,2]. As one of its well-developed applications, the synthesis of cyclic carbonates from epoxides has been drawing increasing interest due to their promising industrial uses, such as aprotic polar solvents, benign intermediates for polymer synthesis, etc. In view of the high energy barriers of the reaction between CO_2 and epoxides, efficient catalyst design allowing the activation of cycloaddition is the essence of the work. Polymer-supported ionic liquids (PSILs), with exceptional chemical stability, strong designability and high reactivity, have been testified efficient on cyclic carbonate synthesis by facilitating both the capture and activation of epoxides, and synergistical ring-opening process.

In this study, we synthesized and utilized a series of Imidazolium-based PSIL catalysts in a continuous-flow cyclization of epoxides with $scCO_2$. According to our prior research, 4-bromobutyl linker was introduced onto polymers for the immobilization of imidazolium as active site. In addition, hydroxyl groups demonstrated to be beneficial, attributing to their activation with epoxide rings via hydrogen bond effect. Based on those findings, we further modified the structure to obtain the optimal PSIL catalyst, which guaranteed an over 98% yield in the titled batch cycloaddition reaction and 87% yield under optimized continuous-flow conditions. In the presentation, we will discuss the latest progress of this research project.



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2) Baiker, A. *et al., Catal. Rev.* **2003**, 45, 1-96.

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC
E1142(1142, Bldg. 11 [4F])

[E1142-3vn] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Takatsugu Murata, Haruro Ishitani

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[E1142-3vn-01]

Unified concise syntheses of acyl quercitrin natural products using boronic acid-catalyzed regioselective acylation

○Toshihiro Ishida[1], Yuuki Nakamura[2], Mari Tanikawa[2], Naoyuki Shimada[1] (1. Nihon University, 2. Kitasato University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[E1142-3vn-02]

Improved Synthesis of a Stereoisomer of 2′-Demethyl-7′-hydroxy-2-methyltanzawaic Acid B Amide at Fused Positions

Takatsugu Murata[1], Hisazumi Tsutsui[1], Fumiya Watabe[1], Daiki Usukura[1], ○Ryo Hirata[1], Hiroki Okano[1], Yamato Kanai[1], Ryunosuke Shiogama[1], Miyuki Natsume[1], Sho Ichikawa[1], Takuma Okamoto[1], Motoyuki Shimonaka[1], Isamu Shiina[1] (1. Tokyo University of Science)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[E1142-3vn-03]

Synthetic Study of Eushearilide Analog

Takatsugu Murata[1], Shunsei Hiraga[1], ○Shodai Kichi[1], Rio Seki[2], Misako Ohkusu[2], Yasuko Koga[2], Katsuhiko Kamei[2], Akira Watanabe[2], Naruhiko Ishiwada[2], Isamu Shiina[1] (1. Tokyo University of Science, 2. Chiba University)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[E1142-3vn-04]

Synthetic Study of C_{2v}-Symmetric Violaceoid A Analog

Takatsugu Murata[1], Takuto Iwayama[1], ○Yukiho Kosaka[1], Ryo Nakayama[1], Isamu Shiina[1] (1. Tokyo University of Science)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[E1142-3vn-05]

Development of Lewis Acid Catalysts for Transesterification of P(V) compounds

○Taro Konno[1], Yuki Saito[1], Shū Kobayashi[1] (1. Synthetic Organic Chemistry Lab., Department of Chemistry, Grad. School of Science, The University of Tokyo.)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC

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[E1142-3vn-06]

Synthesis of high-value organophosphates via catalytic phosphonylation/phosphorylation

○Yuki Saito[1], Shū Kobayashi[1] (1. The University of Tokyo)

Japanese

4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[E1142-3vn-07]

γ-Lactam Synthesis from Cyclobutanones *via N*-Insertion Reaction

○Shota Sakakura[1], Yuhao Wu[1], Kengo Hyodo[1] (1. Kindai University)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[E1142-3vn-08]

Substituent Effects of Sulfonium Salts in The Synthesis of Fullerene Derivatives PCBM by Sulfur Ylide Method

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

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ボロン酸触媒による位置選択的アシル化反応を利用したアシルケルシトリン天然物群の網羅的簡便合成

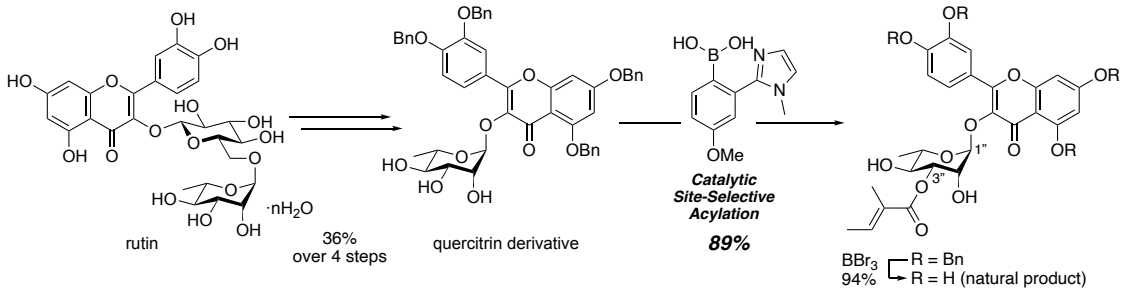
（日本大文理[1]・北里大薬[2]）○石田 俊宏[1]・中村 優生[2]・谷川 真梨[2]・嶋田 修之[1]
Unified Concise Syntheses of Acyl Quercitrin Natural Products Using Boronic Acid-Catalyzed Regioselective Acylation ([1]*Department of Chemistry, Nihon University*, [2]*Department of Pharmaceutical Sciences, Kitasato University*) ○Toshihiro Ishida,[1] Yuki Nakamura,[2] Mari Tanikawa,[2] Naoyuki Shimada[1]

The chemical transformation of carbohydrates requires multi-step protection and deprotection processes. Therefore, a development of a methodology for catalytic regioselective functionalization of the specific hydroxy group is highly demand. Previously, we have found that *N*-methyl imidazole-containing boronic acid can be applied to the regioselective acylation of unprotected carbohydrates as a highly active catalyst.[1)] In this study, we hypothesized that our catalytic reaction could be used for the unified concise syntheses of a series of 3"-*O*-acyl quercitrin natural products.
Keywords : Natural Product Synthesis; Regioselective Acylation; Flavonol; Boronic Acid Catalysis; Quercetin Glycoside

複数のヒドロキシ基を有する糖鎖関連化合物の化学変換には，多段階の保護・脱保護の工程が伴う。そのため，望みとするヒドロキシ基のみを触媒的かつ位置選択的に官能基化する技術の開発が求められている。当研究室では，*N*-メチルイミダゾール含有ボロン酸が無保護糖の位置選択的アシル化反応において，高活性な触媒として機能することを見出している[1)]。そこで今回我々は,本触媒反応を利用することで，3-*O*-アシルケルシトリン天然物群の網羅的簡便合成が可能であると考え，研究に着手した。

安価で入手容易なルチン水和物を出発原料とし，アシル化反応前駆体となるケルシトリン誘導体を 4 工程収率 36%で合成した。次にボロン酸触媒存在下，チグリン酸クロリドとの位置選択的アシル化反応を検討したところ，目的とする 3 位アシル化体が 89%の高収率で得られた。最後に三臭化ホウ素を用いた脱保護を行うことで，所望とするケルセチン-3"-*O*-チグロイルラムノピラノシド天然物[2)]の初の全合成を達成した (Scheme 1)

Scheme 1. Unified Concise Syntheses of Acyl Quercitrin Natural Product



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2’-デメチル-7’-ヒドロキシ-2-メチルタンザワ酸Ｂアミド縮環部異性体の改良合成

（東理大理）村田 貴嗣・筒井 久澄・渡部 史也・臼倉 大輝・○平田 諒・岡野 宙輝・金井 大和・塩釜 龍之介・夏目 美祐希・市川 翔・岡本 卓真・下仲 基之・椎名 勇

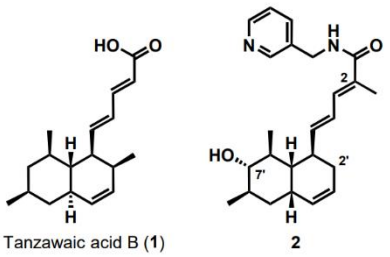
Improved Synthesis of a Stereoisomer of 2’-Demethyl-7’-hydroxy-2-methyltanzawaic Acid B Amide at Fused Positions (*Faculty of Science*, *Tokyo University of Science*)

Takatsugu Murata, Hisazumi Tsutsui, Fumiya Watabe, Daiki Usukura, ○Ryo Hirata, Hiroki Okano, Yamato Kanai, Ryunosuke Shiogama, Miyuki Natsume, Sho Ichikawa, Takuma Okamoto, Motoyuki Shimonaka, Isamu Shiina

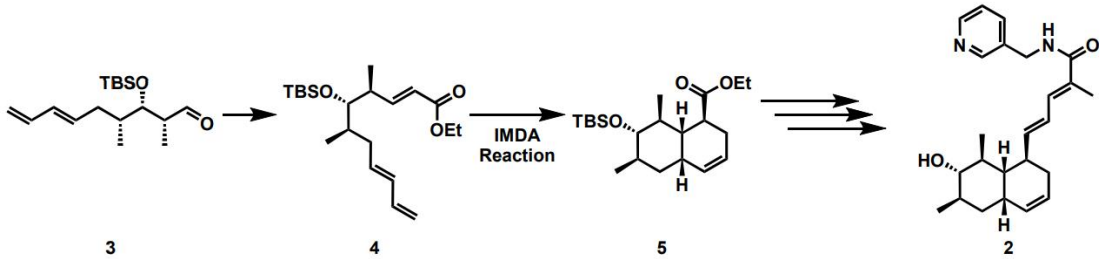
Tanzawaic acids, which are natural products, mostly have pentadienoic acid moiety and octalin skeleton. We had already reported a stereoselective total synthesis of stereoisomer of 2’-demethyl-7’-hydroxy-2-methyltanzawaic acid B amide at fused positions. In this study, we accomplished the improved synthesis of it 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・シトリナ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]。また既に我々は、タンザワ酸Ｂの類縁化合物である 2’-デメチル-7’-ヒドロキシ-2-メチルタンザワ酸Ｂアミド縮環部異性体(**2**)の合成を報告している。今回我々はその合成の改善を行い、がん細胞株に対する細胞増殖阻害活性について調査した。



予め調製したアルデヒド **3** の Wittig 反応により IMDA 反応[4]前駆体 **4** を合成した。条件検討の結果、熱的条件下で **4** の IMDA 反応を行うことにより、シス縮環した成績体 **5** が選択的に得られた。また、Wittig 反応と IMDA 反応をワンポットで行うことにより、合成の効率化を達成した。その他の工程についても検討を行い合成収率の改善も達成した。得られた合成品のがん細胞株に対する細胞増殖阻害活性を評価し、その薬理活性に関する新たな知見を入手した。



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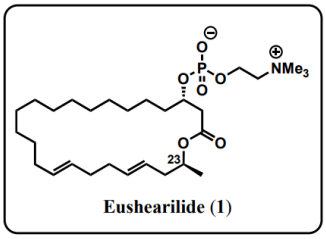
抗真菌活性化合物ユーシェアリライドの類縁物質の合成検討

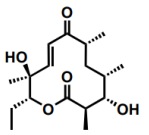
（東理大理[1]・千葉大[2]）村田 貴嗣[1]・平賀 駿星[1]・○木地 翔大[1]・関 里亜[2]・大楠 美佐子[2]・古賀 育子[2]・亀井 克彦[2]・渡辺 哲[2]・石和田 稔彦[2]・椎名 勇[1]
Synthetic Study of Eushearilide Analog
([1]*Faculty of Science, Tokyo University of Science,* [2]*Chiba University*)
Takatsugu Murata,[1] Shunsei Hiraga,[1] ○Shodai Kichi,[1] Rio Seki,[2] Misako Ohkusu,[2] Yasuko Koga,[2] Katsuhiko Kamei,[2] Akira Watanabe,[2] Naruhiko Ishiwada,[2] Isamu Shiina[1]

Eushearilide, which bears 24-membered lactone moiety and phosphorylcholine moiety, has an antifungal activity. We had already reported the total synthesis of eushearilide. In this study, we report the synthetic studies on eushearilide congeners through effective lactonization using 2-methyl-6-nitrobenzoic anhydride (MNBA).
Keywords : Eushearilide; Phosphorylcholine; Lactonization

Eushearilide (**1**)は 2006 年に糸状菌 *Eupenicillium shearii* より単離された 24 員環ラクトンを主骨格とするマクロライドである [1]。我々はこれまでに **1** の不斉全合成を達成し、その構造活性相関研究を進めてきた [2,3]。本研究を通じて、**1** は種々の病原性菌類に対する抗菌活性を有することを明らかにしている。さらに、23 位のメチル基が欠損した類縁体を合成し薬理活性調査を行ったところ、抗菌活性が維持されることを見出した [3]。今回、Methynolide (**2**)を模倣した Eushearilide 類縁体(**EU-N1**)を考案し、合成及び薬理活性調査を行った。

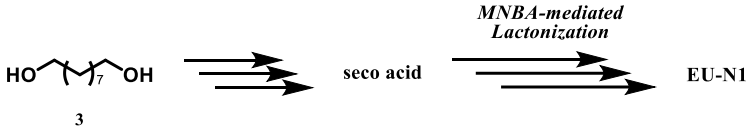


Eushearilide (1)



Methynolide (2)

ノナン-1,9-ジオール(**3**)より数工程を経てセコ酸を入手した。次いで、2-メチル-6-ニトロ安息香酸無水物(MNBA)を用いたラクトン化反応によりセコ酸を環状化合物へと導き、構造修飾を施すことで **EU-N1** を合成した。本講演では合成の詳細と合成品の抗菌活性について報告する。



3

1) T. Hosoe, K. Fukushima, K. Takizawa, T. Itabashi, N. Kawahara, V. Vidotto, K. Kawai, *J. Antibiot.,* **2006**, *59*, 597–600.
2) T. Tonoi, T. Inohana, T. Sato, T. Yoshida, I. Shiina, *J. Org. Chem*., **2018**, *83*, 7886–7899.
3) T. Tonoi, T. Inohana, T. Sato, Y. Noda, M. Ikeda, M. Akutsu, T. Murata, Y. Maekawa, A. Tanaka R. Seki, M. Ohkusu, K. Kamei, N. Ishiwada, I. Shiina, *Molecules*, **2019**, *24*, 3437–3448.

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C_{2v} 対称性を有する Violaceoid A 類縁体の合成研究

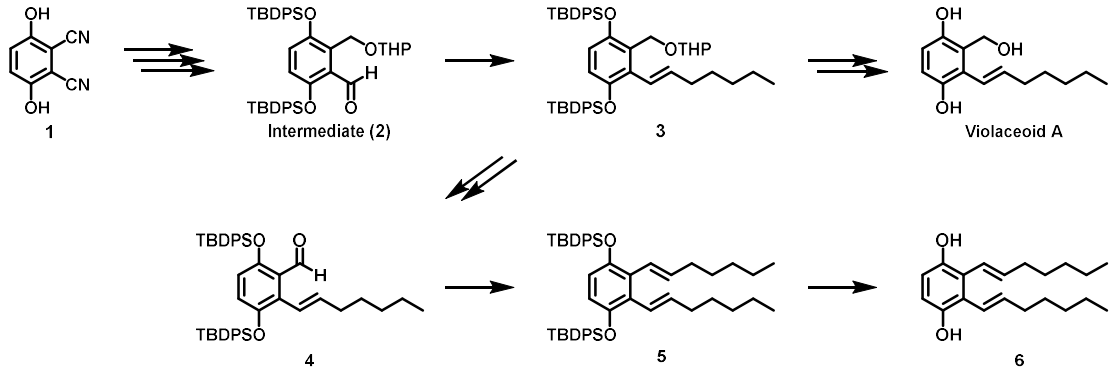
（東理大理）村田 貴嗣・岩山 拓翔・○小坂 幸穂・中山 諒・椎名 勇
Synthetic Study of C_{2v}-Symmetric Violaceoid A Analog (*Faculty of Science*, *Tokyo University of Science*) Takatsugu Murata, Takuto Iwayama, ○Yukiho Kosaka, Ryo Nakayama, Isamu Shiina

Violaceoid A, which composes of quinol moiety and directly connected heptenyl moiety, is isolated from a culture broth of *Aspergillus violaceofuscus* Gasperini coexisting with moss. We had already reported the total synthesis of violaceoid A. In this study, we accomplished the synthesis of C_{2v}-symmetric violaceoid A analog.
Keywords : Violaceoid; Quinol; Desymmetrization; Symmetric molecule

Violaceoid A は京都市嵐山に生息する苔と共生する菌の培養物から、菅原らにより単離された、キノール構造と 1-ヘプテニル基が直結した構造を有する天然物である[1]。

我々は既に、中間体(**2**)を経由した Violaceoid A の全合成を報告している[2]。今回我々は、構造活性相関研究を目的に、ヘプテニル基を 2 つ持つ C_{2v} 対称性を有する Violaceoid A 類縁体(**6**)の合成に取り組んだ。**2** から **3** を経由し **4** へと誘導し、**5** を *E* 選択的に得たのちに **6** を合成した。

本講演では、C_{2v} 対称性を有する Violaceoid A 類縁体の合成の詳細について報告する。



1) Y. Myobatake, K. Takemoto, S. Kamisuki, N. Inoue, A. Takasaki, T. Takeuchi, Y. Mizushina, F. Sugawara, *J. Nat. Prod.*, **2014**, *77*, 1236−1240.
2) T. Murata, T. Kuboki, R. Ishikawa, T. Saito, S. Taguchi, K. Takeuchi, E. Hatano, M. Shimonaka, I. Shiina, *J. Nat. Prod.*, **2018**, *81*, 2364−2370.

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ルイス酸触媒を用いる五価リン化合物のエステル交換反応

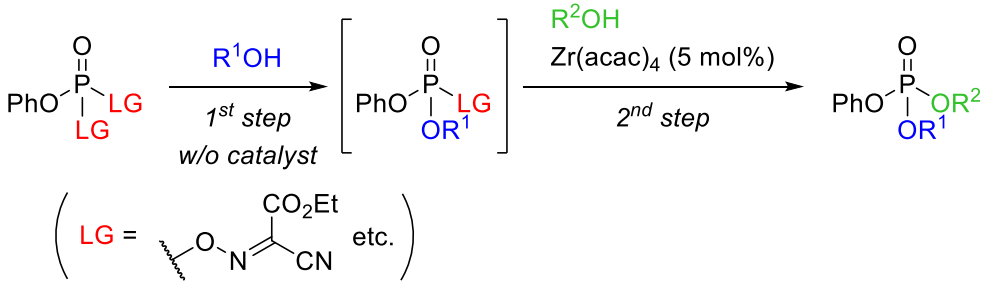
（東大理化） ○今野 太郎・齋藤 由樹・小林 修
Development of Lewis Acid Catalyst for Transesterification of P(V) compounds (School of Science, The Univ. of Tokyo) ○Taro KONNO, Yuki SAITO, Shū KOBAYASHI

Oligonucleotide therapeutics are increasingly gaining attention as one of a new modality. The synthesis of these molecules commonly involves constructing the phosphate triester moiety via solid-phase synthesis; however, this process generates significant waste due to excess reagents. This research focuses on the activation of P=O bonds in P(V) compounds by using Lewis acid catalysts to develop efficient transesterification reactions for phosphate triester synthesis. We found that, by using oxime-type leaving group, the first phosphorylation proceeded under catalyst-free conditions. While the second phosphorylation did not proceed without catalysts, $Zr(acac)_4$ and $Hf(acac)_4$ proved to be highly effective catalysts, and the use of 5 mol% of these facilitated the production of desired phosphate triester in high yield. We further investigated the effects of other leaving groups and ligand for the Lewis acids, and tried to expand substrate scope. The presentation will delve into these detailed findings and discuss the potential of this approach for sustainable oligonucleotide synthesis.

Keywords: Phosphorus compound, Lewis acid catalyst, Zirconium complex, Transesterification, Nucleic acid synthesis

近年、新たな創薬モダリティとしてオリゴヌクレオチド類などの核酸医薬が注目されている。これらの分子の合成には、リン酸トリエステル結合の形成が鍵となる。現在の工業的生産法としては、三価リン化合物を用いる固相合成により分子骨格を形成したのちに酸化的にトリエステルへと誘導する方法が主流であるが、過剰量の試薬に起因する大量の廃棄物が問題である。今回発表者らは、五価リン化合物の P=O 二重結合を触媒的に活性化することによるエステル交換反応の可能性に着目し、ルイス酸触媒を用いる効率的なリン酸トリエステル類合成反応の開発を行った。

検討の結果、オキシムを脱離基とした場合には、1 段階目のリン酸エステル化が無触媒で進行するが、2 段階目のリン酸エステル化は進行しないことが明らかになった。2 段階目のリン酸エステル化において、様々なルイス酸触媒を用いた検討の結果、$Zr(acac)_4$ または $Hf(acac)_4$ を用いることで反応が効率的に進行し、5 mol%の触媒量で目的物が良好な収率で得られることを見出した。その他の脱離基の反応性、ルイス酸に対する配位子の効果についても検討するとともに、基質適用範囲の拡大を試みた。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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触媒的亜リン酸化/リン酸化反応を活用する高付加価値リン酸化合物の合成

（東大院理） ○齋藤　由樹・小林　修

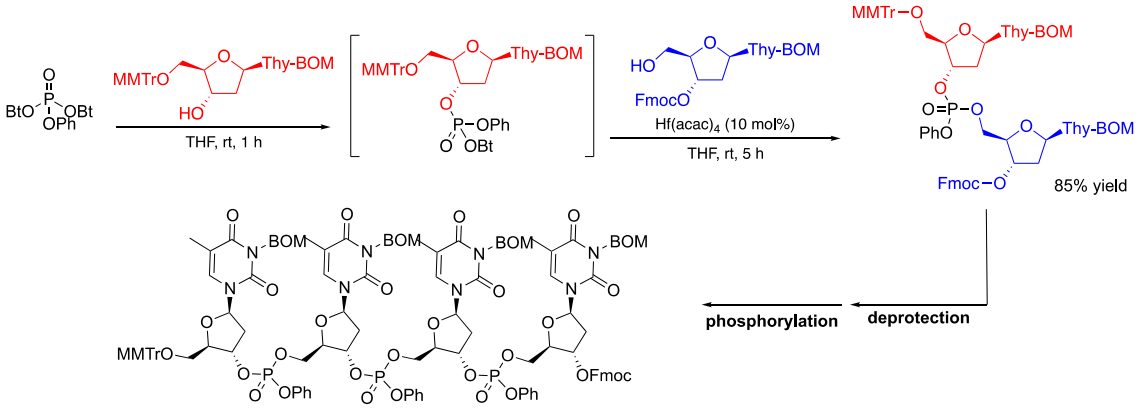
Synthesis of High-value Organophosphates via Catalytic Phosphonylation/Phosphorylation

(School of Science, The Univ. of Tokyo) ○Yuki SAITO, Shū KOBAYASHI

Phosphate triesters are present in many valuable compounds. To address the limitations of conventional synthesis methods, we have developed catalytic phosphonylation/phosphorylation using minimal activating reagents. Our previous work focused on Lewis acid/base catalyzed phosphite diester synthesis with P(III) reagents. In this study, we discovered that P(V) reagents, which were considered to be less reactive, can be effectively applied to the reactions through the uses of tailored leaving groups and catalysts. In this presentation, we explore the application of this method for oligonucleotide synthesis. Using HOBt derivatives as leaving groups and $Hf(acac)_4$ as a catalyst, we demonstrate efficient synthesis of a di-thymidine phosphate. Furthermore, selective deprotection of the resulting phosphate followed by [2+2] chain elongation affords thymidine 4-mer in good yield.

Keywords: Phosphate ester, oligonucleotide therapeutic, Lewis acid catalyst, phosphorylation, phosphonylation

リン酸トリエステルは、核酸医薬に代表される高付加価値化合物の構造に含まれる。従来の化学量論量の活性化剤を用いる合成法は、原料や活性化剤のコストが高く、環境負荷も大きいため、触媒を活用する新規合成法の開発が重要である。最近我々は、三価の亜リン酸試薬と Lewis 酸触媒や有機触媒を用いる効率的な亜リン酸ジエステル合成法を見出している。本研究においては、従来反応性が低いとされていた五価のリン酸試薬による直接的なリン酸トリエステル合成法の確立を目指し、五価リン酸試薬の脱離基の構造や Lewis 酸の効果を検討した。本手法を核酸医薬に適用するため、リン酸化剤の構造と、原料として用いるヌクレオシドの保護基に関して詳細に検討し、リン酸化剤の脱離基として HOBt 類縁体を、触媒として $Hf(acac)_4$ を用いることで、保護チミジン 2 量体が高収率で得られることを明らかにした。また、得られた生成物の 3'-位、5'-位アルコールの保護基を選択的に脱保護した後、次反応の基質とすることで、2+2 反応によりヌクレオチド 4 量体の合成を達成した。



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・シクロブタノン類からの窒素導入型 γ–ラクタムの合成

(近大理工) ○阪倉　翔太・武　宇浩・兵藤　憲吾

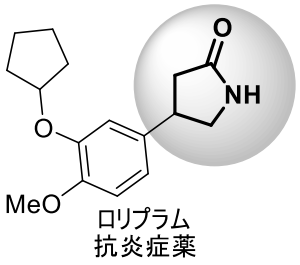
γ-Lactam Synthesis from Cyclobutanones via *N*-Insertion Reaction. (*Faculty of Science and Engineering, Kindai University*)○Shota Sakakura, Yuhao Wu, Kengo Hyodo

γ-Lactams are biologically active and have the effect of enhancing learning and memory abilities. Thus the γ-lactams structure are widely used in pharmaceuticals such as Rolipram. As one of representative synthetic methods, cyclobutanones were converted to cyclobutanone oximes, which were transformed to γ-lactams *via* Beckmann rearrangement.

On the other hand, we have previously developed oxime reagent that could be treated as equivalents of explosive hydroxylamine derivatives and achieved direct and catalytic secondary amide synthesis form ketone using the reagent under acidic conditions *via* transoximation and Beckmann rearrangement.[1] In this work, we attempted to synthesize γ-lactams from cyclobutanones directly.

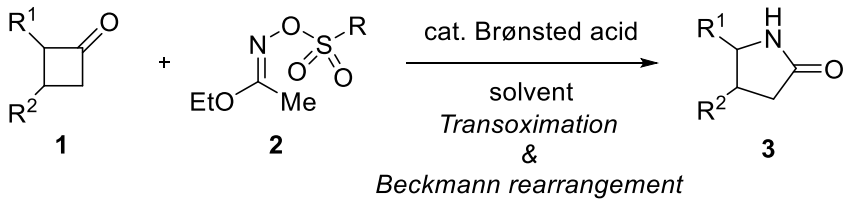
Keywords : γ-Lactam, Beckmann rearrangement, Transoximation.

γ–ラクタムは生物学的に活性があり，学習能力や記憶能力を高める効果があるとされている．また γ–ラクタム構造は抗炎症薬ロリプラムなどの医薬品にもみられる非常に有用な骨格である. その合成法として，シクロブタノン類からオキシムを経て，ベックマン転位によってラクタムを合成する方法が知られる．



ロリプラム
抗炎症薬

一方で，当研究室で開発されたオキシム化合物 **2** は，爆発性があるとされているヒドロキシルアミン誘導体の等価体として，比較的安全に扱うことができ，酸性条件下ケトン化合物との反応からオキシム転移およびベックマン転位によって一気に二級アミドへと変換することができる [1]．本研究では，本法を応用してシクブタノン類 **1** とオキシム化合物 **2** を用いて触媒的かつ直接的に γ-ラクタム **3** の合成を図った (Scheme 1)．そして，溶媒や酸触媒，オキシム反応剤 **2** を種々検討することによって良好な収率で目的物であるラクタム **3** を得ることに成功した．



Scheme 1. 環状ケトンから γ-ラクタム合成

1) K. Hyodo, G. Hasegawa, N. Oishi, K. Kuroda, K. Uchida, *J. Org. Chem.* **2018**, *83,* 13080-13087.

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硫黄イリド法によるフラーレン誘導体（PCBM）合成におけるスルホニウム塩の置換基効果

（阪工大工[1]・大阪技術研[2]）○河合 笙[1]・村田 理尚[1]・隅野 修平[2]・松元 深[2]・岩井 利之[2]伊藤 貴敏[2]

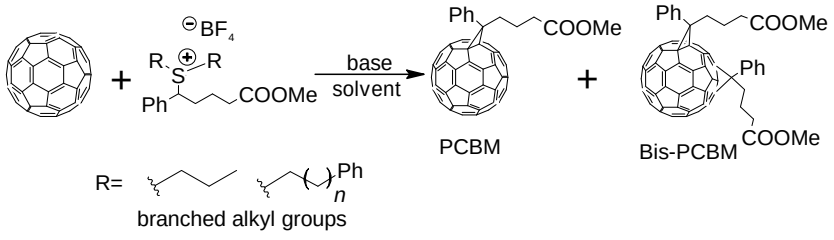
Substituent Effects of Sulfonium Salts in The Synthesis of Fullerene Derivatives PCBM by Sulfur Ylide Method ([1]*Faculty of Engineering, Osaka Institute of Technology,* [2]*ORIST*) ○Sho Kawai,[1] Michihisa Murata,[1] Shuhei Sumino,[2] Fukashi Matsumoto,[2] Toshiyuki Iwai,[2] Takatoshi Ito[2]

A soluble fullerene derivative PCBM is used for electron acceptors in organic photovoltaics. Most of the reported yields of PCBM are not so high, because it is difficult to control sequential reactions when the substituents are introduced to fullerenes. We have developed a synthetic method of PCBM using the sulfur ylide. In this presentation, the effect of substituents on sulfur atom of sulfonium salt was investigated to control the sequential reaction, and to improve the yield and selectivity of PCBM.

Keywords : Fullerene; Substituent Effect; PCBM; Sulfonium Salt; Sulfur Ylide

フラーレン誘導体 PCBM は有機薄膜太陽電地の電子受容体として用いられる。フラーレンへの置換基導入に際しては逐次反応制御が困難なため、PCBM 合成時の収率は高いものではない。我々は以前に硫黄イリド法による PCBM の合成法を報告しているが[1]、さらなる収率・選択性の向上を目指し検討を行っている。硫黄イリド法を用いた[70]PCBM の合成の際には、硫黄上の置換基がモノアダクトのα体とβ体の選択性に影響を与えることを見出した[2]。この知見をもとに、スルホニウム塩の硫黄上の置換基が PCBM の逐次反応の制御にも影響を与える可能性があると考え検討を行うこととした。硫黄上の置換基としては、芳香環の有無、アルキル基の長さ、分岐の有無などについて検討を行った。また、付加原料と C_{60} が反応した中間体を安定化することによっても逐次反応を制御できるのではないかと考え、溶媒などの効果についても検証することとした。本発表ではこれらの検討結果について報告する。

Scheme 1. Comparison of sulfonium salts with different substituents



1) T. Ito, T. Iwai, F. Matsumoto, K. Hida, K. Moriwaki, Y. Takao, T. Mizuno, T. Ohno, *Synlett,* **2013**, *24*, 1988.

2) T. Ito, Y. Inoue, T. Iwasawa, S. Sumino, F. Matsumoto, T. Iwai, K. Moriwaki, Y. Takao, T. Mizuno, T. Ohno, *Synlett*, **2017**, *28*, 1457.

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC H933(933, Bldg. 9 [3F])

[H933-3pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Hiroyoshi Takamura, Yoko Yasuno

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H933-3pm-01]
Development of a strain-promoted Diels-Alder rection of vinylated cyclic allene for the convergent construction of carbocyclic skeletons

○Obata Takumi[1], Hirai Taiki[1], Mizoguchi Haruki[1], Sakakura Akira[1] (1. The Univ. of Okayama)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H933-3pm-02]
Development of the stereoselective decarboxylative radical coupling at an angular position toward the synthesis of polycyclic terpenoid

○Naochika Matsumaru[1], Haruki Mizoguchi[1], Akira Sakakura[1] (1. Okayama University)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H933-3pm-03]
Synthesis of diverse alkaloidal scaffolds using Au(I) catalysts

○Kiyoshi Shimohata[1], Mana Moriguchi[2], Hiroki Oguri[1] (1. The University of Tokyo, 2. Tokyo University of Agriculture and Technology)

English
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H933-3pm-04]
Development of one-pot dimerization reaction of azepinoindole scaffold

○Tomohiro Yoshida[1], Nobuto Kaneko[1], Hiroki Oguri[1] (1. The Univ. of Tokyo)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H933-3pm-05]
Total Synthesis of Indolizidine Alkaloids by Reductive Synthesis of Nitrones

○Sora Iwamoto[1], Toshitaka Okamura[1], Takaaki Sato[1] (1. Keio Univ.)

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
[H933-3pm-06]
Development of Iridium-Catalyzed Reductive (3+2)-Annulation of Lactams

○Kento Yamada[1], Yasukazu Sugiyama[1], Daiki Kaneko[1], Yuya Kusagawa[1], Toshitaka Okamura[1], Takaaki Sato[1] (1. Keio Univ.)

Japanese

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

[H933-3pm-07]

Synthetic Study of QR Ring System of Brevisulcenal-F

○Tomoya Sato[1], Kenta Tanaka[1], Isao Kadota[1], Hiroyoshi Takamura[1] (1. Okayama University)

Japanese

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

[H933-3pm-08]

Synthetic Studies on Loritrem B

○Tomonori Teranishi[1], Keisuke Nishikawa[1], Yosiki Morimoto[1] (1. Osaka Metropolitan University)

Japanese

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

[H933-3pm-09]

Synthetic studies on a diterpene with hedgehog signaling pathway inhibitory activity

○Kazuaki Maeno[1], Yuichi Orita[1], Yuichi Ishikawa[1] (1. Graduate School of Nanobioscience, Yokohama City University)

Japanese

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

[H933-3pm-10]

Synthetic Study of the ABCDEF Ring of Maitotoxin

○Tatsuya Teshigawara[1], Kenshiro Fuse[1], Yuhei Suzuki[1], Yoko Yasuno[1], Tohru Oishi[1] (1. Kyushu 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

[H933-3pm-11]

Synthetic Study of the QRSTU Ring of Maitotoxin

○Hiroshi Yamaguchi[1], Takahiro Harada[1], Keitaro Umeno[1], Yoko Yasuno[1], Tohru Oishi[1] (1. Kyushu University)

Japanese

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

[H933-3pm-12]

Synthesis and Biological Activity of the Macrolactone Moiety of Scytophycin B

○Mayu Namiki[1], Shusei Sato[1], Takayuki Ohyoshi[1], Hideo Kigoshi[1] (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

Japanese

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

[H933-3pm-13]

Evaluation of Antioxidant Activity of Humic Substances Obtained from Fermented and Aged Softwood Chip Compost

○Yuki Tsutaho[1], Yasushi Kojima[2], Hiroki Hotta[1,3], Yoshio Tsujino[3] (1. Graduate School of Maritime Sciences, Kobe University, 2. KEI TWO COMMUNICATIONS , 3. Graduate school of Science, Technology and Innovation, Kobe university)

Japanese

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

[H933-3pm-14]

Isolation and structure determination of new polyketides containing a terminal alkyne from a marine cyanobacterium collected at Hateruma Island

◯Hiroto Saima[1], Kousuke Dodo[2], Mikiko Sodeoka[2], Arihiro Iwasaki[1] (1. Chuo University, 2. RIKEN)

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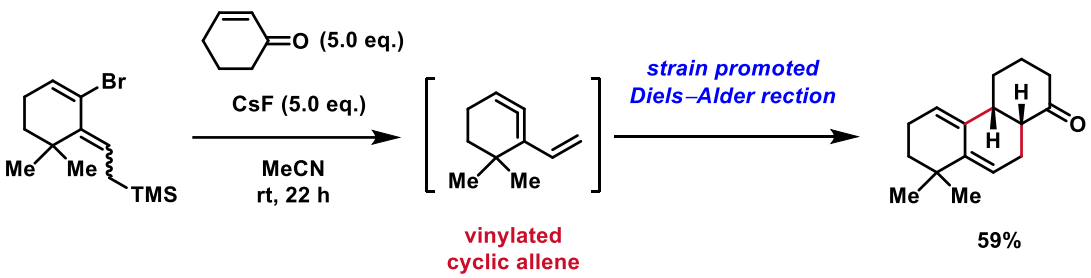
ビニル環状アレンを新規歪みジエンとして用いた Diels-Alder 反応の開発と炭素環骨格の構築

（岡山大院環境生命自然[1]）○小幡 匠[1]・平井 大貴[1]・溝口 玄樹[1]・坂倉 彰[1]

Development of a strain-promoted Diels–Alder rection of vinylated cyclic allene for the convergent construction of carbocyclic skeletons ([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Takumi Obata[1], Taiki Hirai[1], Haruki Mizoguchi[1], Akira Sakakura[1]

Intermolecular Diels–Alder reaction is useful for a convergent construction of polycyclic frameworks, but often requires harsh reaction conditions which result in a limitation of applicable substitutes. In this study, we developed a new strain-promoted Diels–Alder reaction by designing a vinyl conjugated cyclic allene as the new type of strained diene to realize a versatile carbocyclic skeleton synthesis. Activation of silyl-substituted vinyl bromide with cesium fluoride resulted in a generation of the designed diene. Planed Diels–Alder reaction of the fleeting diene successfully proceeded at room temperature with variety of dienophiles to give fused cyclic systems including 6/6/6 tricycles which are often found in natural products. The reactivity and selectivity trend of the new strained diene would be discussed.
Keywords：Terpene, Diels-Alder reaction, Cyclic allene, Natural product

環状ジエンやジエノフィルを用いた分子間 Diels–Alder 反応は、テルペンなどの多環性骨格の収束的構築法として有用であるが、反応性は必ずしも高いとは言えず、適用可能な基質に制限が多い。本研究では、ビニル基を共役させた環状アレンを新規歪みジエンとして設計することで、温和な条件下での分子間 Diels–Alder 反応に取り組んだ。シリル基を有するビニルブロミドに対し、シクロヘキセノン存在下でフッ化セシウムを作用させ、ビニル環状アレンの発生と環化付加を試みた。その結果、室温条件下で位置選択的な Diels–Alder 反応が進行し、6/6/6 縮環骨格の構築に成功した。本反応は、様々なジエンおよびジエノフィルに対して利用可能である。これらの基質適用範囲の検討から得られた、この新たな歪みジエンの反応性や選択性についての知見も併せて報告する。



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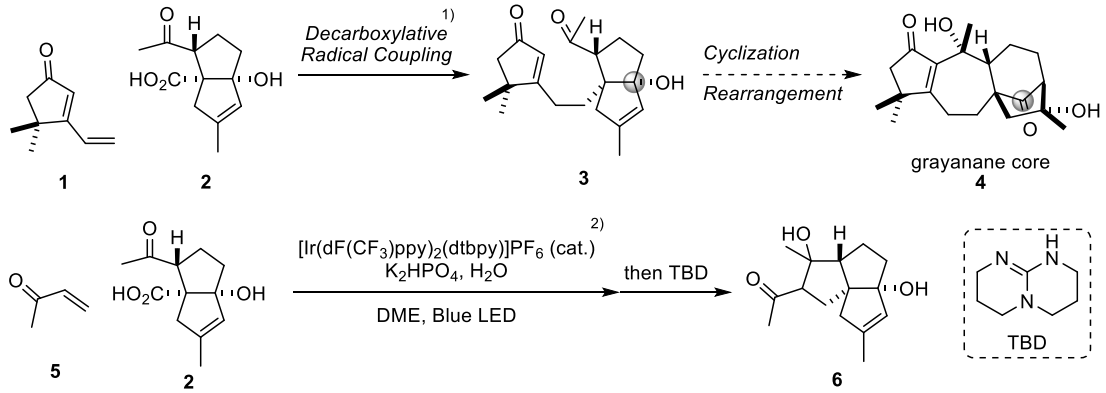
多環性テルペン骨格構築のための核間位ラジカルカップリング反応の開発

（岡山大院環境生命自然）○松丸 直睦・溝口 玄樹・坂倉 彰
Development of the stereoselective decarboxylative radical coupling at an angular position toward the synthesis of polycyclic terpenoid (*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*) ○Naochika Matsumaru, Haruki Mizoguchi, Akira Sakakura

Natural products bearing bicyclo[3.2.1]octane moiety are known to possess unique bioactivities. Toward a concise and convergent synthesis of these molecules, we devised a synthetic method based on i) decarboxylative fragment coupling at the angular position of bicyclo[3.3.0]octane core, and ii) pinacol-type skeletal rearrangement of bicyclo[3.3.0]octane to bicyclo[3.2.1]octane (**1**+**2**→**3**→**4**). This time, we conducted a detailed optimization of the decarboxylative coupling of the bicyclo[3.3.0]octane fragment. During the course exploring the scope of radicalophiles, we found that the coupling of **2** with methyl vinyl ketone **5** followed by a base-promoted aldol cyclization produced triquinane-type skeleton **6** in a one-pot procedure.
Keywords : terpenoid, convergent synthesis, decarboxylative radical coupling, quaternary carbon center

当研究室では、ビシクロ[3.3.0]オクタン骨格 **2** をビルディングブロックに用いた二成分連結反応と骨格転位を鍵とするビシクロ[3.2.1]オクタン骨格含有天然物の収束的合成法の開発を目指し、研究を行っている (**1**+**2**→**3**→**4**)。昨年度は、ビシクロ[3.3.0]オクタン環核間位での脱炭酸的ラジカルカップリングを報告したが、詳細な条件検討や適応可能な求ラジカル剤の調査を行えていなかった [1]。条件検討の結果、用いる塩基によって原料の消費と生成物に変化が生じることが分かった。また、メチルビニルケトン **5** を求ラジカル剤とする脱炭酸的ラジカルカップリングを行った後、塩基による環化を試みたところ、ワンポットにてトリキナン型の三環性化合物 **6** を合成することに成功した。



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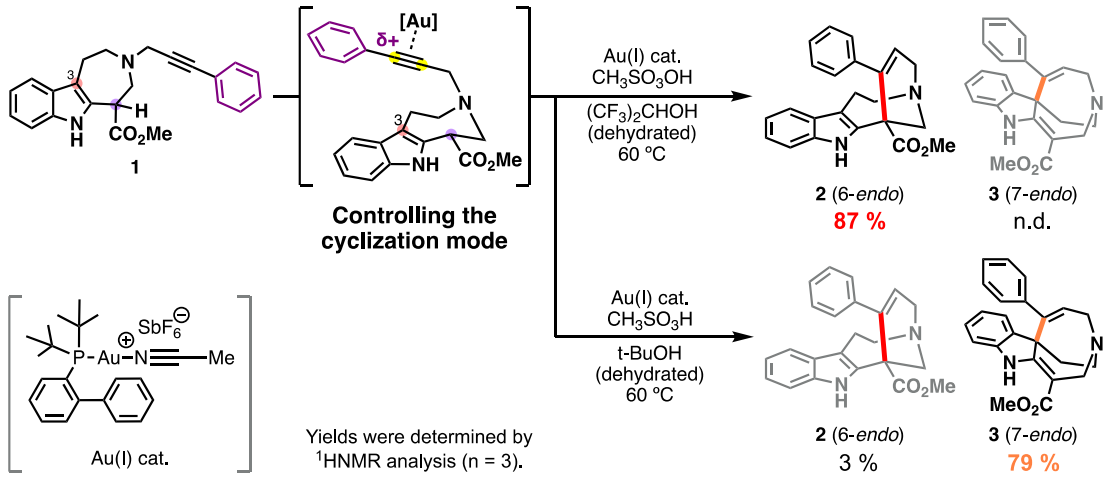
Synthesis of diverse alkaloidal scaffolds using Au(I) catalysts

([1]*Graduate school of Science, The University of Tokyo*, [2]*Graduate School of Engineering, Tokyo University of Agriculture and Technology*) ○Kiyoshi Shimohata,[1] Mana Moriguchi,[2] Hiroki Oguri[1]

Keywords: Indole Alkaloids; Divergent Synthesis; Gold(I) catalysts; Azepinoindole Scaffold; Conia-ene reaction

Our research group has been developing a rapid and divergent synthetic platform through Lewis acid-catalyzed activation of alkynes in common intermediates to generate a variety of skeletally diverse alkaloidal scaffolds.[1)] In this study, we designed the tricyclic intermediate **1**, consisting of an azepinoindole framework bearing both an alkyne moiety and a methyl ester group. To achieve the divergent gold(I)-catalyzed cyclization between the two nucleophilic sites (indole C3 position and ester α position) and internal and peripheral sp carbon centers in the alkyne, we synthesized the common intermediate **1** with a phenyl group as the alkyne substituent to modulate the reactivity of the triple bond, yielding products **2** (6-*endo*) and **3** (7-*endo*) with the formation of a quaternary center either at the ester α position or the indole C3 position, respectively.

Upon treatment of **1** with a cationic gold(I) catalyst and methanesulfonic acid using hexafluoroisopropanol (HFIP) as a solvent, the cyclization proceeded site-selectively at the ester α position to afford **2** (6-*endo*) in high yield of 87 %. On the other hand, the use of *t*-BuOH drastically altered the mode of annulation. The corresponding cyclization preferentially proceeded at the indole C3 position to furnish **3** (7-*endo*) in 79 % yield. Further investigation to verify the effects of solvents, additives, and alkyne substituents will also be reported.



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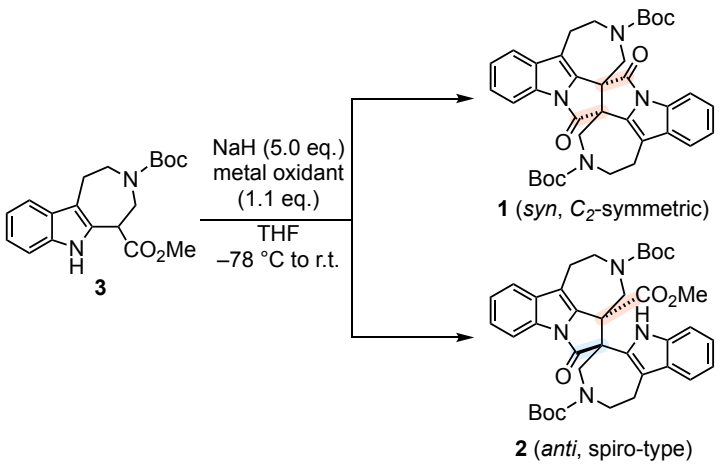
Development of one-pot dimerization reaction of azepinoindole scaffold

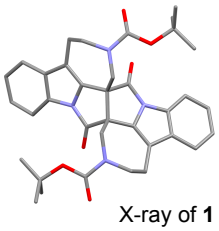
([1]*School of Science, The University of Tokyo*, [2]*Graduate School of Science, The University of Tokyo*) ○Tomohiro Yoshida,[1] Nobuto Kaneko,[2] Hiroki Oguri,[2]

Keywords: Azepinoindole Alkaloids; Dimeric Natural Products; Oxidative Dimerization of Enolates; Radical Coupling; Diastereoselective Synthesis

Dimeric indole alkaloids, represented by vinblastine, exhibit potent biological activities by inhibiting protein–protein interactions. In this study, we developed a one-pot dimerization reaction of the azepinoindole skeleton for stereo-divergent synthesis of dimeric alkaloidal scaffolds, yielding C_2-symmetric octacyclic dimer **1** (*syn*) and septacyclic **2** (*anti*).

Azepinoindole **3** bearing a methyl ester group was prepared from tryptamine in 4 steps. Treatment of **3** with NaH and an alkyl bromide serendipitously resulted in the formation of dimerized products **1** and **2** in 3.2:1.0 ratio, with a combined yield of 35%. With the aims of both improving the yield and diastereo-selectivity of the dimerization and elucidating the reaction mechanisms lead to the formation of vicinal quaternary carbon centers, various reaction conditions were investigated. The use of NaH to generate the corresponding dianion intermediate resulted in optimal conversions. The choice of metal oxidants was found to be important for the diastereoselectivity of this dimerization. $Fe(acac)_3$ slightly favored the formation of **1** (*syn*) in 43% yield over **2** (*anti*) in 31% yield. Meanwhile, $Ti(OiPr)_4$ led to the predominant formation of the spiro dimer **2** in 40% yield, while the yield of dimer **1** (*syn*) was approximately 8%. Based on these preliminary results, further investigations aimed at improving the stereo-divergent dimerization reactions and elucidating the reaction mechanism will be reported.





X-ray of **1**

Oxidants	Yields [%]	
	1	**2**
$Fe(acac)_3$	43	31
$Ti(OiPr)_4$	8	40

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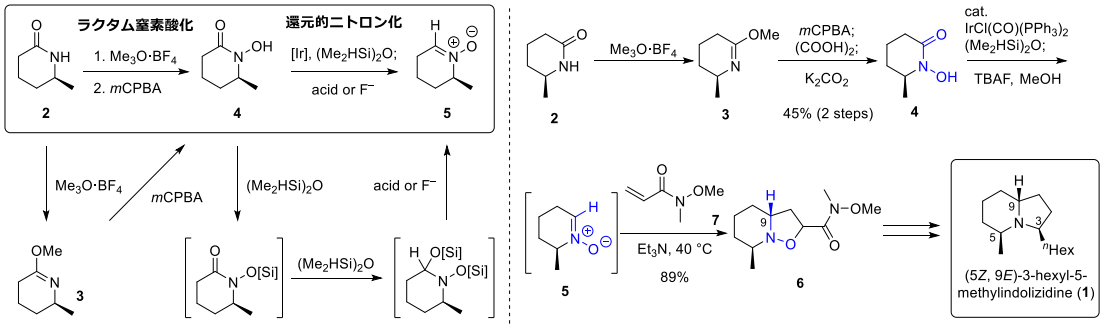
還元的ニトロン合成法を用いたインドリジジンアルカロイドの全合成

（慶大理工）○岩本 青空・岡村 俊孝・佐藤 隆章
Total Synthesis of Indolizidine Alkaloids by Reductive Synthesis of Nitrones (*Keio Univ.*)
○Sora Iwamoto, Toshitaka Okamura and Takaaki Sato

Nitrone is known to be the most extensively studied 1,3-dipole in organic synthesis. This functional group can undergo a variety of reactions to give access to key intermediates for the synthesis of biologically active alkaloids and pharmaceuticals. For example, [3+2] cycloaddition of nitrones has been studied due to the synthetic versatility of the resulting isoxazolidines. In this study, we show the total synthesis of 3-hexyl-5-methylindolizidine (**1**) by using two methods: oxidation of secondary lactams (**2**→**3**→**4**) and reductive synthesis of nitrones (**4**→**5**).
Keywords : indolizidine alkaloids; nitrone; [3+2] cycloaddition

ニトロンは、[3+2]環化付加反応や、衣笠反応による β-ラクタムの構築などに利用できるため、アルカロイドをはじめとした含窒素複素環の合成に広く用いられている。特に、光学活性な環状ニトロン **5** は、多環性化合物の有用な合成中間体として期待されているが、その合成法は非常に限られている。当研究室ではこれまでに、ラクタム窒素酸化反応[1]と還元的ニトロン化[2]を利用した、入手容易なラクタムを原料とする光学活性な環状ニトロン合成法の開発に成功しており、本戦略を 3-Hexyl-5-methylindolizidine (**1**)の全合成に応用した。

キラルなラクタム **2** を出発原料とし、Meerwein 試薬を作用させイミデート **3** へと変換し、*m*CPBA・シュウ酸・K_2CO_3 で段階的に処理すると、*N*-ヒドロキシラクタム **4** が得られた。Vaska 錯体と$(Me_2HSi)_2O$ による環状ニトロン **5** 形成後に、オレフィン **7** を加えて加熱すると、光学活性を損なうことなく[3+2]環化付加反応が進行し、9 位の立体が制御されたイソオキサゾリジン **6** を良好な収率で与えた。その後、**6** を用いた Weinreb ケトン合成によるアルキル側鎖の導入と、5 員環の形成により 3-Hexyl-5-methylindolizidine (**1**)の全合成を達成した。



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2) T. Sato, N. Chida *et al. J. Am. Chem. Soc.* **2016**, *138,* 5246.

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イリジウム触媒を用いたラクタムの還元的(3+2)環化付加反応の開発

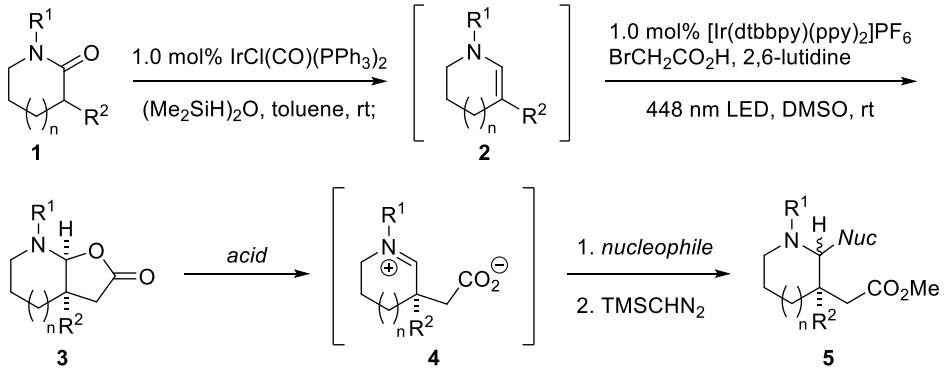
（慶大理工）○山田健人、杉山靖和、金子大輝、草川裕哉、岡村俊孝、佐藤隆章

Development of Iridium-Catalyzed Reductive (3+2)-Annulation of Lactams (*Keio Univ.*) ○ Kento Yamada, Yasukazu Sugiyama, Daiki Kaneko, Yuya Kusagawa, Toshitaka Okamura, Takaaki Sato

Nucleophilic addition to amides is an effective method for synthesis of biologically active alkaloids. In this study, we developed a reductive (3+2) annulation by taking advantage of Ir-catalyzed hydrosilylation of lactam **1** to give einamine and subsequent photoredox reaction with α-bromoacetic acid. The developed reaction showed the high functional group tolerance, providing cyclic *N,O*-acetal **3** with a quaternary carbon center. The resulting *N,O*-acetal **3** could be converted to substituted cyclic amine **5** by acid-mediated nucleophilic addition to iminium ion **4**.

Keywords : lactam, photoredox reaction, iridium, quaternary carbon center, (3+2)-annulation

アミド基への求核付加反応は、入手容易なアミド基から多置換アミンを一挙に与えるため、生物活性アルカロイドの供給法として精力的に研究されている。本研究では、Ir 触媒を用いたラクタム **1** のヒドロシリル化によるエナミン生成と [1]、α-ブロモ酢酸との光酸化還元反応を組み合わせ [2]、還元的な(3+2)環化反応を開発した。ラクタム **1** に Vaska 錯体と $(Me_2SiH)_2O$ を作用させエナミン **2** とした後、ワンポット反応にて光触媒、塩基、および α-ブロモ酢酸存在下で 448 nm の波長の光を照射すると、光酸化還元反応が進行し、*N,O*-アセタール **3** が得られた。開発した反応は、官能基許容性が高く、第四級炭素を有する環状 *N,O*-アセタール **3** を与えた。得られた *N,O*-アセタール **3** は、酸によって生じたイミニウムイオン **4** に対する求核付加反応にて、多置換環状アミン **5** へと変換できた。



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ブレビスルセナール-F の QR 環部の合成研究

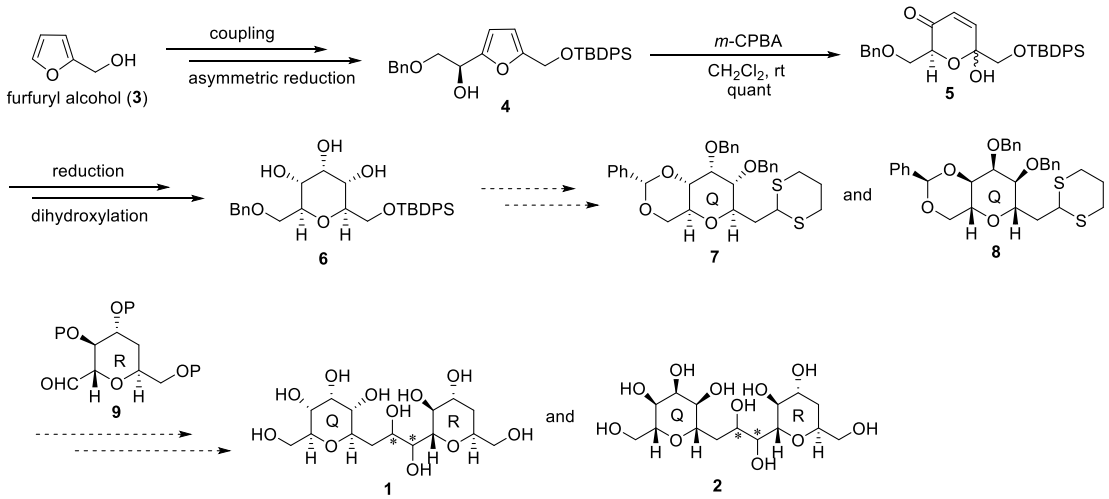
（岡山大院自然科学 [1]・岡山大基礎研 [2]）○佐藤　智也 [1]・田中　健太 [2]・門田　功 [1]・髙村　浩由 [1]

Synthetic Study of QR Ring System of Brevisulcenal-F ([1]*Graduate School of Natural Science and Technology, Okayama University,* [2]*Research Institute for Interdisciplinary Science, Okayama University*) ○Tomoya Sato,[1] Kenta Tanaka,[2] Isao Kadota,[1] Hiroyoshi Takamura[1]

The absolute configuration of the entire molecule of polycyclic ether natural product brevisulcenal-F has not been determined. In this study, the synthesis of eight possible diastereomers of the QR ring system, **1** and **2**, was investigated toward stereostructure determination of this part. Alcohol **4** was synthesized from starting material **3** by coupling and asymmetric reduction. The resulting alcohol **4** was converted to enone **5** by Achmatowicz reaction. Q ring system **6** was then synthesized by Luche reduction and dihydroxylation. Q ring system **6** will be converted to coupling precursors **7** and **8**, and the desired QR ring system **1** and **2** will be synthesized from coupling precursors **7** and **8** with R ring system **9**.

Keywords : Brevisulcenal-F; Stereostructural Elucidation; Stereoselective Synthesis; Luche Reduction; Dihydroxylation

ポリ環状エーテル天然物ブレビスルセナール-F の分子全体の絶対立体配置は未解明である。本研究では本天然物の QR 環部の立体構造を決定することを目的とし、QR 環部の考えうる 8 つのジアステレオマー**1** および **2** を合成標的とした。出発原料である furfuryl alcohol（**3**）に対するカップリングおよび不斉還元によりアルコール **4** を得た。得られたアルコール **4** に対してアフマトヴィッチ反応を行うことでエノン **5** を得た。続いて、ルーシェ還元およびジヒドロキシ化を行うことで Q 環部 **6** を合成した。今後は得られた Q 環部 **6** をカップリング前駆体 **7** および **8** へと変換し、R 環部 **9** とのカップリングにより目的の QR 環部 **1** および **2** を合成する予定である。



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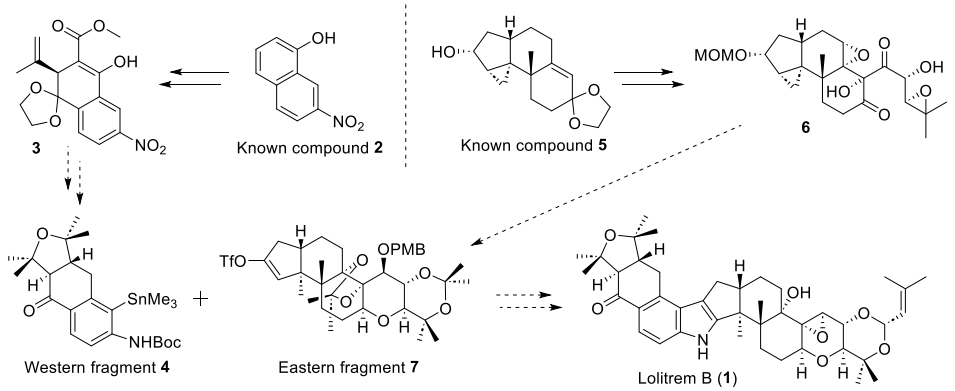
ロリトレム B の合成研究

（阪公大院理）○寺西智徳・西川慶祐・森本善樹
Synthetic studies on lolitrem B (*Graduate School of Science, Osaka Metropolitan University*)
○Tomonori Teranishi, Keisuke Nishikawa, and Yoshiki Morimoto

Lolitrem B (**1**) is a kind of indole alkaloid toxin isolated from fine perennial ryegrass[1]. Toxin **1** has been reported to possess potent insect feeding inhibition activity and neurotoxicity. However, since only a small amount of **1** has been isolated from nature and no examples of total synthesis of **1** have been reported to date, its detailed biological studies have not been conducted. Therefore, synthetic studies on it were initiated with the aim of establishing its quantitative supply for its biological studies. Toward the total synthesis of toxin **1**, we embarked on the synthesis of Western fragment **4** and Eastern fragment **7**. Indeed, the synthesis of enol **3** and diepoxide **6** was achieved from known compounds **2**[2] and **5**[3], respectively.

Keywords : Natural product synthesis, Convergent synthesis, Endophytic toxin, Wieland–Miescher ketone

Lolitrem B（**1**）は細麦ペレニアルライグラスから単離されたインドールアルカロイド毒素の一種である。毒素 **1** は、強力な昆虫摂食阻害活性および神経毒性を有することが報告されている。しかし、天然からの単離量は僅少であり、**1** の全合成例は現在までに未報告であるため、詳細な生物学的研究は行われていない。そこでlolitrem B（**1**）の量的供給法の確立を目的とし、合成研究に着手した。毒素 **1** の全合成に向けて、Western fragment **4** および Eastern fragment **7** の合成に着手した。実際に、既知化合物 **2** および **5** からそれぞれエノール **3** およびジエポキド **6** の合成を達成した。



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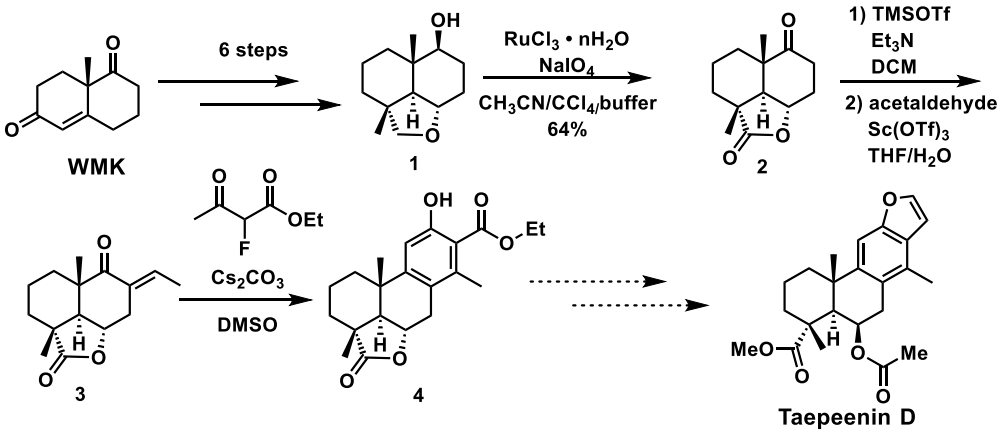
ヘッジホッグシグナル伝達経路の阻害活性を有するジテルペンの合成研究

（横浜市大院生命ナノ）○前野和明・折田悠一・石川裕一
Synthetic studies on a diterpene with hedgehog signaling pathway inhibitory activity (*Graduate School of Nanobioscience, Yokohama City University*) ○Kazuaki Maeno, Yuichi Orita, Yuichi Ishikawa

Taepeenin D has inhibitory activity against Hedgehog signaling pathway and is expected as a novel anticancer lead compound. In this study, we aimed to accomplish the syntheses of Taepeenin D and its analogs to elucidate the mechanism of its biological activity by structure-activity relationship studies and to develop new anti-cancer drugs and apply them to the biological studies. First, by using WMK as the starting material, **1** was obtained in 6 steps. Ruthenium oxidation of **1** under basic conditions yielded **2**, which was converted to **3** by Mukaiyama aldol reaction. Next, introduction of aromatic ring structure to **3** gave **4**. Now, we attempt to construct a furan structure against **4** to obtain Taepeenin D.
Keywords：*Taepeenin D, Hedgehog signaling pathway, diterpene*

ヘッジホッグシグナル伝達経路は、細胞増殖や分化などの重要なプロセスに関与している。その異常な活性化は、がんの発生、増殖などに深くかかわっており、がんの一種は、この伝達経路の異常な活性化によって引き起こされる。Taepeenin D は、この伝達経路の阻害剤であり、新たなメカニズムによる新規抗がん剤リード化合物として注目を集めている。[1] 本研究では、Taepeenin D 及びそのアナログの合成を行い、構造活性相関の解明と新規抗がん剤の創製を目指している。

まず合成経路の確立を目的に、ラセミ体の WMK を出発物質として 6 段階の工程を経て化合物 **1** を得た。次に、**1** を pH 8.5 の塩基性条件下でルテニウム酸化に付することにより、化合物 **2** を得ることに成功した。さらに、**2** に対して向山アルドール反応を行い化合物 **3** へと誘導したのちに、芳香環部分の構築を行うことによって、化合物 **4** を得ることができた。現在、**4** に対してフラン環部分の構築の検討を行っており、Taepeenin D の合成を目指している。



1) Rifai, Y. *et al*. *J. Nat. Prod*. **2010**, *73*, 995-997.

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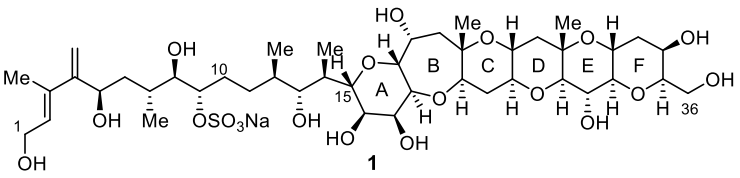
マイトトキシンの ABCDEF 環部の合成研究

（九大院理）○勅使川原 樹弥・布施 賢志朗・鈴木 悠平・保野 陽子・大石 徹
Synthetic Study of the ABCDEF Ring of Maitotoxin (*Graduate School of Science, Kyushu University*) ○Tatsuya Teshigawara, Kenshiro Fuse, Yuhei Suzuki, Yoko Yasuno, Tohru Oishi

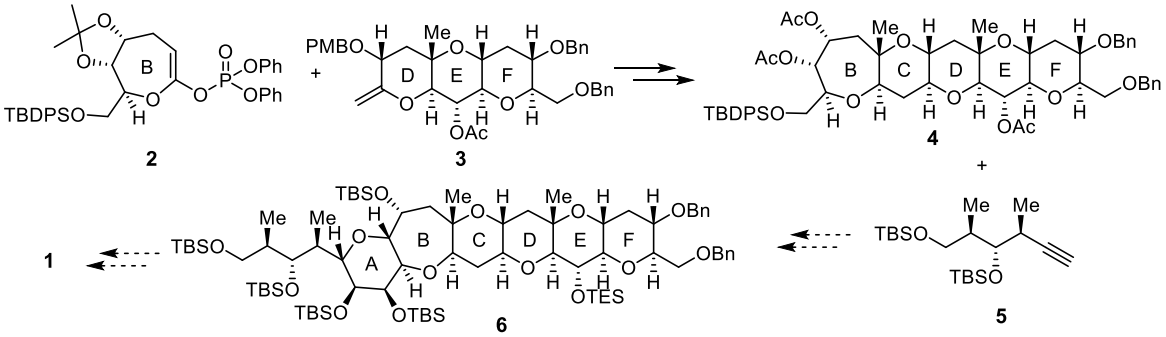
Maitotoxin (MTX) is a ladder-shaped polyether isolated from the dinoflagellate *Gambierdiscus toxicus*. Partial structures of MTX were synthesized and their biological activities were evaluated in our laboratory. In this study, synthesis of the ABCDEF ring of MTX was examined for further structure-activity relationship studies on the hydrophilic part. The BCDEF ring was synthesized via Suzuki–Miyaura coupling of the B ring enol phosphate and the DEF ring *exo*-olefin followed by hydroboration/oxidation, *O,S*-acetal formation, and methylation. Synthesis of the ABCDEF ring from the BCDEF ring via introduction of the side chain and construction of the A ring is in progress.
Keywords : Maitotoxin; Synthetic Study; ABCDEF Ring

マイトトキシン（MTX）は渦鞭毛藻 *Gambierdiscus toxicus* から単離された梯子上ポリエーテルである。当研究室では, MTX の部分構造を合成し, その生物活性を評価してきた。本研究では, 親水性部分に関するさらなる構造活性相関研究を目的とし, MTX の ABCDEF 環部 **1** の合成を検討した。



1

MTX の B 環部に相当するエノールホスフェート **2** と, DEF 環部に相当するエキソオレフィン **3** [1]との鈴木–宮浦カップリング, ヒドロホウ素化–酸化, および *O,S*-アセタールのメチル化を経由して BCDEF 環部 **4** を合成した（Scheme 1）。アルキン **5** とのカップリングを経由した A 環部の構築, および **6** から ABCDEF 環部 **1** への変換法の開発を検討中である。



Scheme 1. Synthetic scheme of the ABCDEF ring of MTX

1) T. Yasudomi, H. Yakushiji, K. Torikai, M. Ebine, T. Oishi, *Chem. Lett.* **2019**, *48*, 1156.

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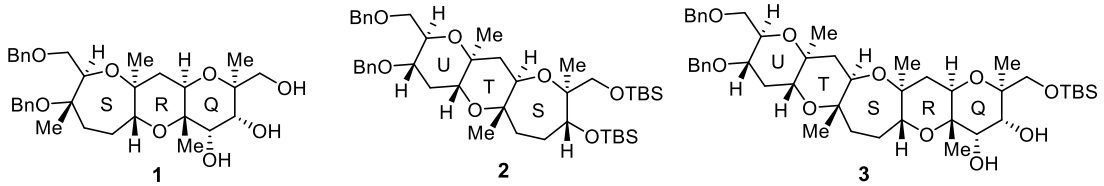
マイトトキシンの QRSTU 環部の合成研究

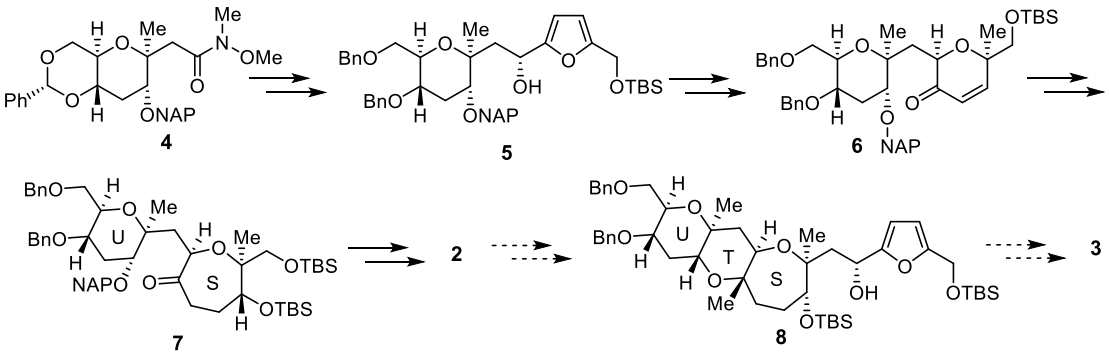
（九大院理）○山口 寛史・原田 陽光・梅野 圭太郎・保野 陽子・大石 徹
Synthetic Study of the QRSTU Ring of Maitotoxin (*Graduate School of Science, Kyushu University*) ○Hiroshi Yamaguchi, Takahiro Harada, Keitaro Umeno, Yoko Yasuno, Tohru Oishi

Maitotoxin (MTX) is a ladder-shaped polyether produced by the dinoflagellate *Gambierdiscus toxicus*. As a part of our structure–activity relationship study of MTX, synthesis of the QRS ring of MTX was reported. In this study, synthesis of the QRSTU ring was examined via iterative utilization of the furan based strategy. The common intermediate for synthesizing the QRS ring was prepared from a Weinreb amide via Achmatowicz reaction of a furfuryl alcohol derivative and methylation of an acetal. The resulting enone was converted to the STU ring via β-borylation/oxidation, ring expansion, and methylation of an *O,S*-acetal. Synthesis of the QRSTU ring from the STU ring via a furfuryl alcohol derivative is in progress.
Keywords : Maitotoxin; Synthetic Study; QRSTU Ring

マイトトキシン(MTX)は，渦鞭毛藻 *Gambierdiscus toxicus* によって産生される梯子状ポリエーテルである。当研究室では，フラン誘導体を基盤とする三環性エーテルの合成戦略を開発し，MTX の QRS 環部 **1** を合成した[1]。そこで，この方法を繰り返し用いることにより，STU 環部 **2** を経由して QRSTU 環部 **3** を合成する計画を立てた。



Weinreb アミド **4** から調製したフラン誘導体 **5** から，Achmatowicz 反応およびメチルアセタール化のメチル化を経由してエノン **6** を合成した。さらに，β-ボリル化/酸化と環拡大反応によってケトン **7** へと変換し，*O,S*-アセタールのメチル化を経由して STU 環部 **2** を合成した。現在，**8** を経由した QRSTU 環部 **3** の合成を検討中である。



1) H. Onoue, T. Baba, K. Konoki, K. Torikai, M. Ebine, T. Oishi, *Chem Lett.* **2014**, *43*, 1904.

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サイトファイシン B マクロラクトン部の合成と生物活性

（筑波大院数理物質 [1]）○並木 真悠 [1]・佐藤 秀成 [1]・大好 孝幸 [1]・木越 英夫 [1]

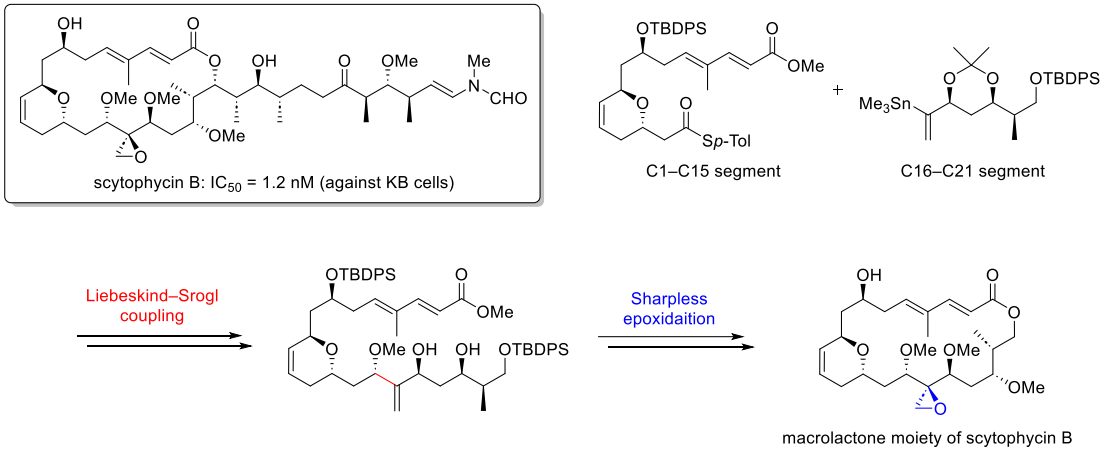
Synthesis and Biological Activity of the Macrolactone Moiety of Scytophycin B

([1]*Degree Programs in Pure and Applied Sciences, University of Tsukuba*) ○[1]Mayu Namiki, [1]Shusei Sato,[1] Takayuki Ohyoshi,[1] Hideo Kigoshi

Scytophycin B is a 22-membered macrolide with potent actin-depolymerizing activity and cytotoxicity. It consists of a macrolactone moiety containing an epoxide and a side chain moiety with a terminal enamide group. We have synthesized its side chain moiety and evaluated the actin-depolymerizing activity. Therefore, we attempted to investigate the contribution of the macrolactone moiety to the biological activity of scytophycin B itself. We established the synthetic method of the macrolactone moiety of scytophucin B using a Liebeskind–Srogl coupling and a Sharpless epoxidation as key reactions (Scheme 1). The biological activity of the synthesized macrolactone moiety of scytophycin B was evaluated. Herein, we report the details of the synthesis and biological activity of the macrolactone moiety of scytophycin B.

Keywords : Scytophycin B; macrolide; epoxide

サイトファイシン B[1]は強力なアクチン脱重合活性と細胞毒性を有する 22 員環のマクロライドであり、エポキシドを含むマクロラクトン部と末端にエナミド基を有する側鎖部からなる。これまでに、当研究室ではその側鎖部を合成し、アクチン脱重合活性を示すことを明らかにした。そこで、未だ明らかになっていないマクロラクトン部の生物活性への寄与を明らかにすることにした。そこで、Liebeskind–Srogl カップリングと Sharpless エポキシ化を鍵反応としてマクロラクトン部の合成法を確立した (Scheme 1)。さらに、合成したサイトファイシン B マクロラクトン部の生物活性試験を行った。今回はその合成と生物活性の詳細について報告する。



Scheme 1. synthesis of macrolactone moiety of scytophycin B

1) Moore, R. E. *et al*. *Pure Appl. Chem*. **1986**, *58*, 263.

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針葉樹チップ発酵熟成堆肥より得た腐植物質の抗酸化活性評価

(神戸大院海事[1]・(株)ケーツーコミュニケーションズ[2]・神戸大院科学技術イノベ[3])
○蔦保 侑樹[1]・小嶋 康詞[2]・堀田 弘樹[1,3]・辻野 義雄[3]

Evaluation of Antioxidant Activity of Humic Substances Obtained from Fermented and Aged Softwood Chip Compost

([1]*Graduate School of Maritime Sciences, Kobe University*, [2]Keitwo Communications Co., Ltd., [3]*Graduate School of Science, Technology and Innovation, Kobe University*) ○Yuki Tsutaho,[1] Yasushi Kojima,[2] Hiroki Hotta,[1,3] Yoshio Tsujino[3]

In general, when industrially refining humic substances (HS), extraction is performed using strong acids or bases from materials such as sub-bituminous coal or peat. Conversely, "HS-2®Pro" that demonstrated its effectiveness in this study uses coniferous wood chips as raw material and employs no chemicals such as strong acids or bases during the extraction process. We examined the characteristics of HS-2®Pro compared to commercially available HSs refined by conventional methods. HS-2®Pro has a large amount of phenolic hydroxyl groups per weight, suggesting that it exhibits strong redox properties. However, since HS is a relatively high-molecular compound, it was not possible to directly observe the electron transfer at a typical disk electrode. Therefore, we observed indirect electron transfer using ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic Acid) radical as electron transfer mediator [1)]. Based on the digital simulation analysis of cyclic voltammetry (CV), this study revealed that HS-2®Pro demonstrates faster electron transfer compared to other HSs.

Keywords : Humic Substances, Antioxidant Activity, Cyclic Voltammetry, ABTS

一般的に、腐植物質を工業的に製造する際には、亜炭や泥炭等を原料として強酸や強塩基による抽出が行われる。対照的に、本研究で検証された「HS-2®プロ」は、針葉樹チップを原料とし、強酸や強塩基を一切使用せずに抽出している。本研究では、HS-2®プロの官能基評価およびサイクリックボルタンメトリー（CV）を用いた酸化還元特性の評価を行い、一般的な精製法によって得られた腐植物質（今回は富士フィルムー和光純薬、アルドリッチ、ナカライ各社製試薬を用いた）と比較した。HS-2®プロは重量当たりのフェノール性水酸基量が多く、強い酸化還元特性を示すことが示唆された。しかし、高分子化合物であることから一般的な電極での直接の電子移動反応を観察することはできなかった。そこで電子移動メディエータとして ABTS ラジカルを用いた間接的電子移動反応を観察した。得られた CV をデジタルシミュレーションにより解析し、腐植物質と ABTS ラジカルとの電子移動速度定数を評価した[1)]。その結果、HS-2®プロが一般的な腐植物質と比較して、迅速にラジカル消去反応を行っていることが明らかとなった。

1) Olga I. Klein et al. *J Soils Sediment*s **2018**, 18, 1355.

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波照間島産海洋シアノバクテリア由来、新規末端アルキン含有ポリケチド化合物の単離と構造決定

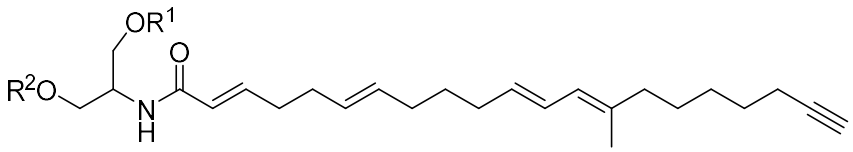
(中大理工[1]・理研 CPR[2]) ○齊間広人[1]・闥闥孝介[2]・袖岡幹子[2]・岩崎有紘[1]

Isolation and structure determination of new polyketides containing a terminal alkyne from a marine cyanobacterium collected at Hateruma Island. ([1]*Faculty of Science and Engineering, Chuo University,* [2]*RIKEN Cluster for Pioneering Research*) ○Hiroto Saima,[1] Kousuke Dodo,[2] Mikiko Sodeoka,[2] Arihiro Iwasaki[1]

To discover novel natural products possessing remarkable structures and biological activities, we have investigated secondary metabolites of a marine *Moorena* sp. cyanobacterium collected at Hateruma Island. As a result, we discovered a new polyketide with a terminal alkyne and named it budumaryne A (**1**). Considering that this cyanobacterium possesses a gene for synthesizing a terminal alkyne group, we purified other fractions by direct alkyne enrichment method and successfully discovered other analogs, budumarynes B (**2**) and C (**3**). In this annual meeting, we report the isolation and structure determination of budumarynes (**1**-**3**).

Keywords : marine natural products, terminal alkyne, direct alkyne enrichment method

特異な構造や生物活性を示す新規天然物を発見することを目的として、波照間島で採集した *Moorena* 属海洋シアノバクテリアに含まれる二次代謝物の探索を行った。その結果、末端アルキンを有する新規ポリケチド化合物を単離し budumaryne A (**1**) と名付けた 。さらに本シアノバクテリアが末端アルキン生合成遺伝子をもつことに着目し、周辺画分に対して直接的アルキン濃縮法 [1)] を用いることで、新規類縁体 (budumaryne B (**2**) および C (**3**)) の発見に成功した。本化合物群の単離、構造決定について報告する。



Budumaryne A (**1**) : R^1 = H, R^2 = H
Budumaryne B (**2**) : R^1 = Ac, R^2 = H
Budumaryne C (**3**) : R^1 = Ac, R^2 = Ac

1) 日本化学会 第 100 春季年会 1H6-20, 誌上開催, 2020 年 3 月

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Academic Program [Oral A] | 16. Natural Products Chemistry, Chemical Biology：Oral A

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC H935(935, Bldg. 9 [3F])

[H935-3pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Arihiro Iwasaki, Gosuke Hayashi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H935-3pm-01]
Isolation and structure determination of a new peptide from a marine cyanobacterium *Okeania* sp.

○Natsumi Watanabe[1], Arihiro Iwasaki[1] (1. Chuo University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H935-3pm-02]
Isolation and structure determination of a new peptide from marine cyanobacteria collected at Hateruma Island

○Kensuke Irie[1], Arihiro Iwasaki[1] (1. Chuo University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H935-3pm-03]
Isolation, Structure Determination, Total Synthesis and Biological Activity of New Lipopeptide; Ukabamide

○Masahiro Hagihara[1], Raimu Taguchi[1], Arihiro Iwasaki[2], Ghulam Jeelani[3], Tomoyoshi Nozaki[3], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. Faculty of Science and Technology, Keio Univ., 2. Faculty of Science and Engineering, Chuo Univ., 3. Graduate School of Medicine, The Univ. of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H935-3pm-04]
The structure and bioactivity of a new lipopeptide from an unidentified marine cyanobacterium

○Kazuki Wakai[1], Kairi Umeda[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. Keio university)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H935-3pm-05]
Isolation, Structure Determination, and Total Synthesis of Antimalarial Peptide, Hiyajyamine, from Marine Cyanobacterium

○Kairi Umeda[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. The Univ. of Keio)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H935-3pm-06]
Synthetic study of hedoamide, a new linear peptide from marine cyanobacteria

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○Asaya Nakura[1], Naoaki Kurisawa[1], Arihiro Iwasaki[2], Kiyotake Suenaga[1] (1. Keio Univ., 2. Chuo Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[H935-3pm-07]

Synthetic study of iezoside-alkyne probe to identify the binding site on SERCA

○Akari Noto[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1] (1. Faculty of Science and Technology, Keio Univ.)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H935-3pm-08]

A novel uric acid production inhibitor from Okinawan marine cyanobacterium

○Sein Higa[1], Kazumasa Yagisawa[1], Noriyuki Natsume[3], Toshiaki Teruya[1,2] (1. Graduate School of Engineering and Science, University of the Ryukyus, 2. Faculty of Education, University of the Ryukyus, 3. NatuPharma Ryukyus Co., Ltd.)

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
[H935-3pm-09]

Interspecies differences in submandibular gland components in shrews, venomous insectivorous mammals

○Nozomi Hara[1], Yusuke Yano[2], Ryo Fukuoka[2], Satoshi Ohdachi[3], Masaki Kita[2] (1. School of Agricultural Sciences, Nagoya University, 2. Graduate School of Bioagricultural Sciences, Nagoya University, 3. Institute of Low Temperature Science, Hokkaido University)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H935-3pm-10]

Concise synthesis of polyamine analogs for fluorescent labeling

○Taiga Ohnishi[1], Raku Irie[1], Masato Oikawa[1] (1. Yokohama City University)

Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[H935-3pm-11]

Structural analysis of AcuPep, a peptide moiety of aculeines

○Raku Irie[1], Yumi Irie[2], Satoko Matsunaga[3], Ryuichi Sakai[4], Kazuhiro Irie[2], Masato Oikawa[1] (1. Yokohama City University, 2. Kyoto University, 3. National Institute of Technology, Hakodate College, 4. Hokkaido University)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[H935-3pm-12]

A novel protecting group for selenocysteine applicable to Solid-phase peptide synthesis

○Fumika Yoshitomi[1], Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1] (1. Nagoya Univ.)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[H935-3pm-13]

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Improved synthesis of peptide thioester with α-disubstituted amino acids

○Genki Nakamura[1], Koki Nakatsu[1], Gosuke Hayashi[1], Hiroshi Murakami[1] (1. Nagoya Univ.)

Japanese

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

[H935-3pm-14]

Screening of peptide sequences with cell adhesion using molecular descriptors and measurement data related to fibril formation.

○Taisei Terao[1], Akira Takekawa[3], Tomohiro Umetani[2], Fumihiro Kayamori[1], Kenji Usui[1] (1. FIST, Konan Univ., 2. Konan Univ., 3. Kobe Univ.)

Japanese

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

[H935-3pm-15]

Developing novel nucleosome ligand for expansion of histone acylation catalyst

○Yuma Takeuchi[1], Tamiko Nozaki[1], Mayu Onoda[1], Kenzo Yamatsugu[1], Shigehiro Kawashima[1], Motomu Kanai[1] (1. The University of Tokyo)

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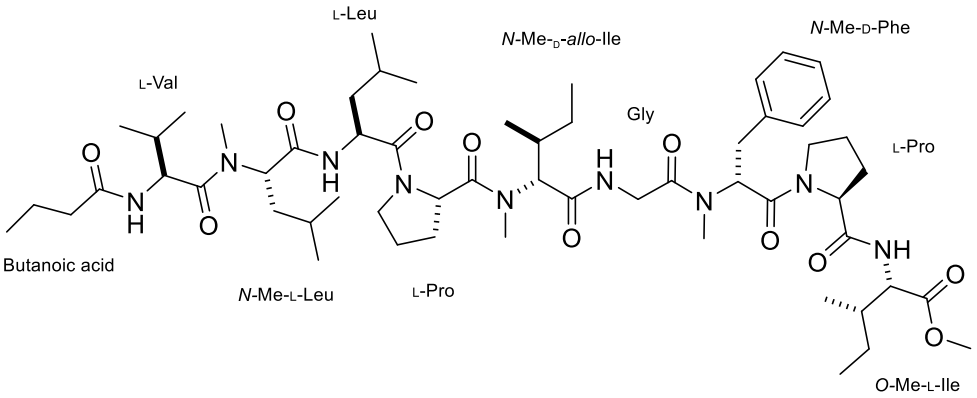
海洋シアノバクテリア *Okeania* sp. 由来新規ペプチド化合物の単離及び構造決定

（中大理工）○渡邉 夏海・岩崎 有紘
Isolation and structure determination of a new peptide from a marine cyanobacterium *Okeania* sp. (*Chuo University*) ○Natsumi Watanabe, Arihiro Iwasaki

To discover new natural products with peculiar structures and biological activities, we have investigated secondary metabolites of an *Okeania* sp. marine cyanobacterium collected at Tonaki Island. As a result, we isolated a new liner lipopeptide composed of nine amino acid residues including an *O*-methyisoleucine and *N*-methyl-D-amino acid moiety. The planar structure was clarified by the analyses of several NMR spectra and tandem mass spectra. The absolute configuration of all amino acid residues was determined by chiral-phase HPLC analyses of the acid hydrolysate. Evaluation of biological activities of fugimiamide is ongoing. In this annual meeting, we report the isolation, structure determination, and biological activities of fugimiamide.
Keywords : Marine natural products, Cyanobacteria, Peptide

特異な構造や生物活性を有する新規天然物の発見を目的として、渡名喜島産 *Okeania* 属海洋シアノバクテリアのもつ二次代謝産物の探索を行った。その結果、*O*-メチルイソロイシンや *N*-メチル-D-アミノ酸を含む、9 残基のアミノ酸からなる新規鎖状リポペプチドを単離した。本化合物の平面構造は、各種 NMR スペクトルの解析とタンデム質量スペクトルの解析によって決定した。各アミノ酸残基の絶対立体配置は、酸加水分解物から単離したアミノ酸に対してキラルカラム HPLC 分析を行い、保持時間を標品と比較することで決定した。現在は fugimiamide のもつ生物活性の評価を進めている。本化合物の単離、構造決定、生物活性について報告する。



Structure of fugimiamide

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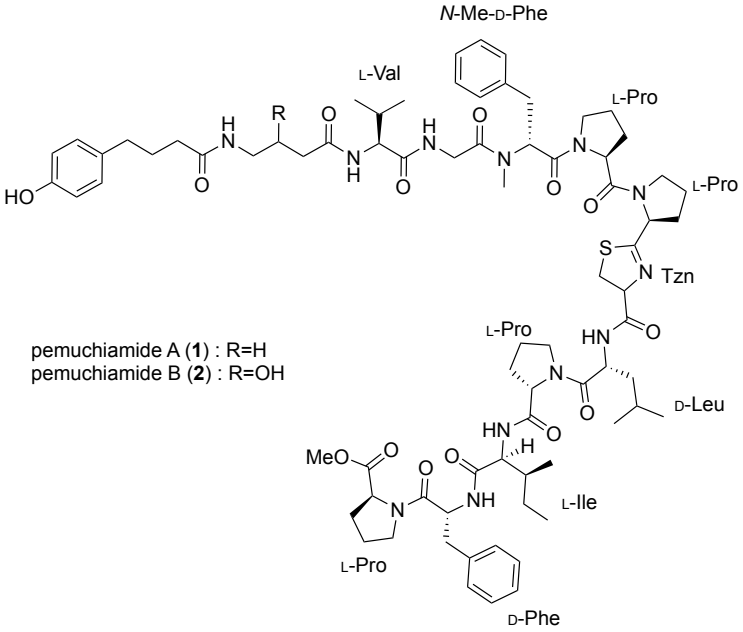
日本化学会 第104春季年会 (2024)

波照間島産海洋シアノバクテリア由来，新規ペプチドの単離と構造決定

（中大理工）○入江　健介・岩崎　有紘
Isolation and structure determination of a new peptide from marine cyanobacteria collected at Hateruma Island. *(Faculty of Science and Engineering, Chuo University*) ○Kensuke Irie, Arihiro Iwasaki

To discover novel natural products possessing interesting structure and biological activity, we have investigated secondary metabolites of a marine cyanobacterium collected at Hateruma Island. As a result, we isolated two linear peptides possessing many unnatural amino acid moieties and named them pemuchiamides A (**1**) and B (**2**). The planar structures of **1** and **2** were estimated by analyses of NMR data and tandem mass spectrometry data. The clarification of the absolute configuration is ongoing mainly by amino acid analyses using chiral column HPLC against acid hydrolysate of **1** and **2**. In this annual meeting, we report the isolation, structure determination, and biological activities of pemuciamides A (**1**) and B (**2**).
Keywords : marine natural products, cyanobacteria, isolation

特異な構造や生物活性をもつ新規天然物の発見を目的として、波照間島産海洋シアノバクテリアに含まれる二次代謝産物の探索を行なった。その結果、多数の異常アミノ酸残基を含む鎖状ペプチドを 2 種単離し、pemuchiamide A (**1**) および B (**2**) と命名した。本化合物の平面構造は NMR 測定とタンデム質量分析によって推定した。また絶対立体配置については、酸加水分解物に対するキラルカラム HPLC アミノ酸分析を中心に決定を進めている。本化合物の単離、構造決定、生物活性について報告する。



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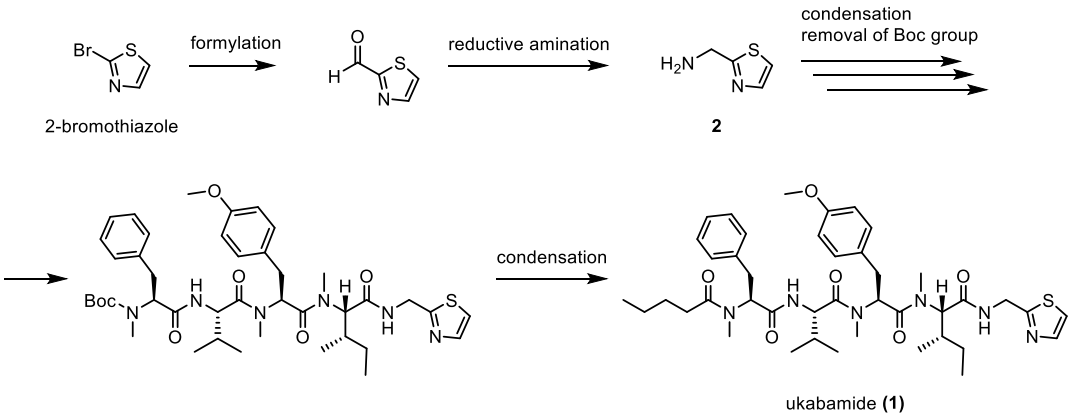
沖縄県産海洋シアノバクテリア由来新規リポペプチド ukabamide の単離、構造決定、全合成および生物活性

(慶大理工[1]・中央大理工[2]・東大院医[3]) ○萩原大尋[1]・田口黎武[1]・岩﨑有紘[2]・Ghulam Jeelani[3]・野崎智義[3]・栗澤尚瑛[1]・末永聖武[1]
Isolation, Structure Determination, Total Synthesis and Biological Activity of New Lipopeptide; Ukabamide ([1] *Faculty of Science and Technology, Keio University,* [2] *Faculty of Science and Engineering, Chuo University,* [3] *Graduate School of Medicine, The University of Tokyo*) ○ Masahiro Hagihara,[1] Raimu Taguchi,[1] Arihiro Iwasaki,[2] Ghulam Jeelani,[3] Tomoyoshi Nozaki,[3] Naoaki Kurisawa,[1] Kiyotake Suenaga[1]

Our group isolated a new linear lipopeptide ukabamide (**1**) from an unidentified marine cyanobacterium collected in Nanjo, Okinawa, Japan. The planar structure was determined by a combination of 2D NMR and MS/MS analyses. The absolute configurations were determined by chiral HPLC analyses of acid hydrolysate of **1**. In addition, we achieved the total synthesis of ukabamide (**1**). We firstly synthesized the amine **2** via formylation and following reductive amination from 2-bromothiazole. We completed the synthesis of **1** by repeating the condensation of each amino acid derivative and valeric acid to **2**. Regarding the biological activities, ukabamide (**1**) exhibited potent growth-inhibitory activity against *Trypanosoma brucei rhodesiense* (IC_{50} 91 ± 48 nM).
Keywords: Natural Products; Cyanobacteria; Lipopeptide; Total Synthesis; Biological activity

沖縄県南城市で採集した海洋シアノバクテリアより、新規リポペプチド ukabamide (**1**)を単離した。平面構造は二次元 NMR と MS/MS を解析することで決定した。構成アミノ酸の絶対立体配置は、天然物を酸加水分解しキラルカラム分析することですべて L 体であると決定した。合成経路の確立と創薬への応用を見据えた量的供給のため、**1** の全合成を行った。まず、2-bromothiazole を出発原料とし、ホルミル化に続く還元的アミノ化によりアミン **2** を得た。**2** に対して適切にメチル化したアミノ酸誘導体と吉草酸を順次縮合することによって、**1** の全合成を達成した。Ukabamide (**1**) はアフリカの一部地域の風土病「アフリカ睡眠病」の病原生物 (トリパノソーマ原虫) に対して、強力な増殖阻害活性 (IC_{50} 91 ± 48 nM) を示すことが明らかとなった。



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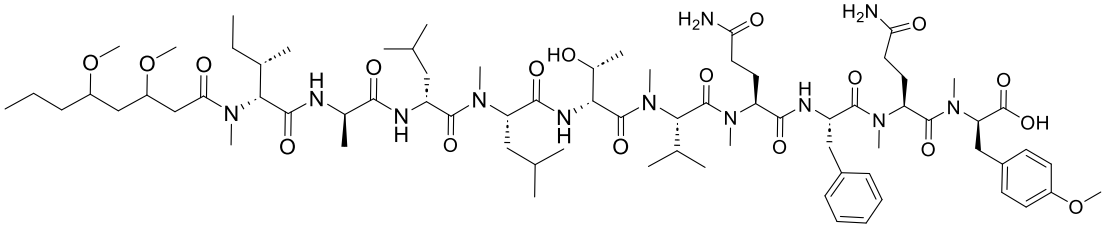
海洋シアノバクテリア由来新規リポペプチドの単離と構造決定

(慶大理工)○若井和樹・栗澤尚瑛・末永聖武

The structure and bioactivity of a new lipopeptide from marine cyanobacteria (*Faculty of Science and Technology. Keio University*) ○Kazuki Wakai, Naoaki Kurisawa, Kiyotake Suenaga

Marine cyanobacteria have attracted attention as a source of compounds with specific biological activity and structure. We isolated a new lipopeptide from an unidentified marine cyanobacterium collected at Kume Island, Okinawa. This lipopeptide is a new compound with five D-amino acids in peptide moiety and 3,5-dimethoxyoctanoic acid in polyketide moiety. The planar structure was determined by NMR and MS/MS analysis of the compound, as well as NMR and MS/MS analysis of its hydrolyzed fragments. The absolute stereostructure was determined by chiral columns for each amino acid hydrolyzed from the compound. We are currently attempting to determine the absolute stereostructure of polyketide moiety by synthesizing four possible stereoisomers and comparing NMR with its fragment.
Keywords: Lipopeptide; Marine cyanobacteria; A new ikoamide analog; Natural product chemistry

特異な生物活性や構造を持つ化合物の探索源として、海洋シアノバクテリアが注目されている。本研究では、沖縄県久米島で採集した未同定海洋シアノバクテリアより、新規リポペプチドを単離した。本物質は、ペプチド部位に D-アミノ酸を 5 つ持ち、ポリケチド部位として 3,5-ジメトシキオクタン酸を有する新規化合物である。その平面構造は NMR, MS/MS 解析に加え、本物質を加水分解して得たフラグメントについて NMR, MS/MS 解析を行うことにより決定した。また、絶対立体配置は本物質を加水分解して得た各アミノ酸についてキラル HPLC 分析等で決定した。ポリケチド部位の絶対立体配置については、可能な 4 つの立体異性体を合成し、本物質から得たフラグメントと NMR を比較することにより決定する。



Structure of the new lipopeptide

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海洋シアノバクテリア由来、抗マラリア活性ペプチド Hiyajyamine の単離構造決定および全合成研究

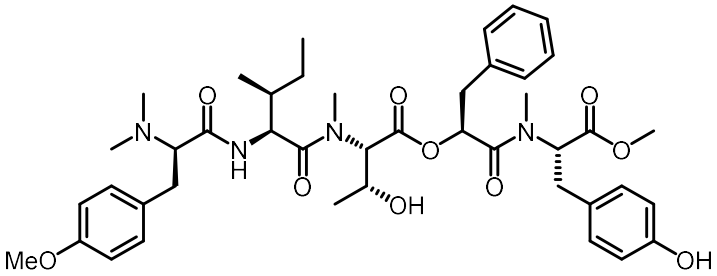
（慶応理工[1]）○梅田 海里[1]・栗澤 尚瑛[1]・末永 聖武[1]

Isolation, Structure Determination, and Total Synthesis of Antimalarial Peptide, Hiyajyamine, from Marine Cyanobacterium ([1]*Faculty of Science and Technology, Keio University*) ○Kairi Umeda, Naoaki Kurisawa, Kiyotake Suenaga

As a result of a series of investigations of secondary metabolites of marine cyanobacteria collected in Okinawa, an antimalarial peptide, hiyajyamine (**1**), was isolated. The planar structure of hiyajyamine (**1**) was determined by NMR analyses. The acid hydrolysis followed by the chiral HPLC analysis and Marfey's method[1)] determined the absolute configuration. Hiyajyamine (**1**) showed strong growth inhibitory activity against *Plasmodium falciparum* (IC_{50}: 0.5 μM). To confirm the biological activity of Hiyajyamine (**1**), the total synthesis of hiyajyamine has been carried out by solid-phase synthesis.

Keywords: marine natural products, cyanobacteria, solid-phase synthesis, Hiyajyamine, N,N-dimethylamino group

沖縄県産海洋シアノバクテリアから新規抗マラリア活性ペプチドである Hiyajyamine (**1**)を単離した。Hiyajyamine (**1**)の平面構造は NMR スペクトル解析により明らかにした。絶対立体配置は Hiyajyamine (**1**)の酸加水分解により得た各アミノ酸と標品をキラル HPLC 分析し、保持時間を比較して決定した。*N*-Me-Thr はキラルカラムに対して保持がなかったため Marfey 法[1)]によって決定した。Hiyajyamine (**1**)はマラリア原虫 *P. falciparum* に対して強い増殖阻害活性を示した(IC_{50}: 0.5 μM)。また、Hiyajyamine (**1**)の生物活性の確認のため、固相合成による全合成をおこなっている。



Hiyajyamine (**1**)

1) P. Marfey, *Carlsberg Res. Commun.* **1984**, *49*, 591-596.

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海洋シアノバクテリア由来新規鎖状ペプチド hedoamide の合成研究

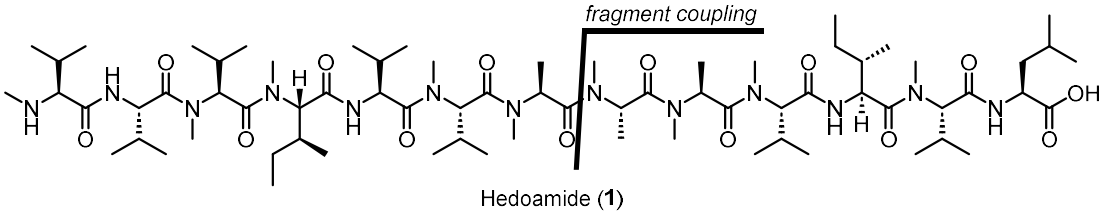
（慶大理工[1]・中央大理工[2]）○名倉 旭哉[1]・栗澤 尚瑛[1]・岩崎 有紘[2]・末永 聖武[1]
Synthetic study of hedoamide, a new linear peptide from marine cyanobacteria ([1]*Faculty of science and technology, Keio University,* [2]*Faculty of Science and Engineering, Chuo University*) ○Asaya Nakura,[1] Naoaki Kurisawa,[1] Arihiro Iwasaki,[2] Kiyotake Suenaga[1]

A novel antiparasitic drug is strongly desired due to the continuously appealed compounds with a novel pharmacophore and mode of action, we have investigated antiparasitic natural products from marine cyanobacteria collected in Okinawa. Hedoamide (**1**) is a novel antiparasitic compound isolated from an unidentified marine cyanobacterium in our group. Hedoamide (**1**) was an extremely *N*-methylated tridecapeptide composed entirely of aliphatic amino acids including *N*-Me-Val, *N*-Me-Ile and *N*-Me-Ala. To confirm the proposed structure and evaluate further biological activity, we have undertaken the synthetic study of hedoamide (**1**).

Toward total synthesis of **1**, we planned a model study with coupling reaction between *C*-terminus hexapeptide and *N*-terminus heptapeptide. These peptide chains are elongated with the reagent HATU. As a result, we synthesized *C*-terminus hexapeptide and *N*-terminus pentapeptide intermediates.

Keywords : marine natural products; cyanobacteria; peptide

抗寄生虫薬の開発のため、新規なファーマコフォアや作用機序を有する化合物の継続的な探索が続けられている。我々は南西諸島の海洋シアノバクテリアを標的にして探索研究を行い、その結果、沖縄本島で採集した未同定の海洋シアノバクテリアから単離された新規抗寄生虫化合物である hedoamide (**1**)を単離した。Hedoamide (**1**)は、*N*-Me-Val と *N*-Me-Ile と *N*-Me-Ala を含む脂肪族アミノ酸のみで構成される高度に *N*-メチル化されたトリデカペプチドである。我々は、hedoamide (**1**)の構造を確認し、更なる生物活性を評価するため、合成研究に着手した。Hedoamide (**1**)の全合成を目指し、*C* 末端ヘキサペプチドと *N* 末端ヘプタペプチドのフラグメントカップリングを行うこととし、各フラグメントは HATU で伸長することにした。その結果、*C* 末端ヘキサペプチドと *N* 末端ペンタペプチドの中間体を合成した。



Hedoamide (**1**)

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SERCA 結合部位同定を目的としたイエゾシド-アルキンプローブの合成研究

(慶大理工 [1])○能登 明佳理 [1]・寺沼 和哉 [1]・栗澤 尚瑛 [1]・末永 聖武 [1]
Synthetic study of iezoside-alkyne probe to identify the binding site on SERCA ([1]*Faculty of Science and Technology, Keio Univ.*) ○Akari Noto[1], Kazuya Teranuma[1], Naoaki Kurisawa[1], Kiyotake Suenaga[1]

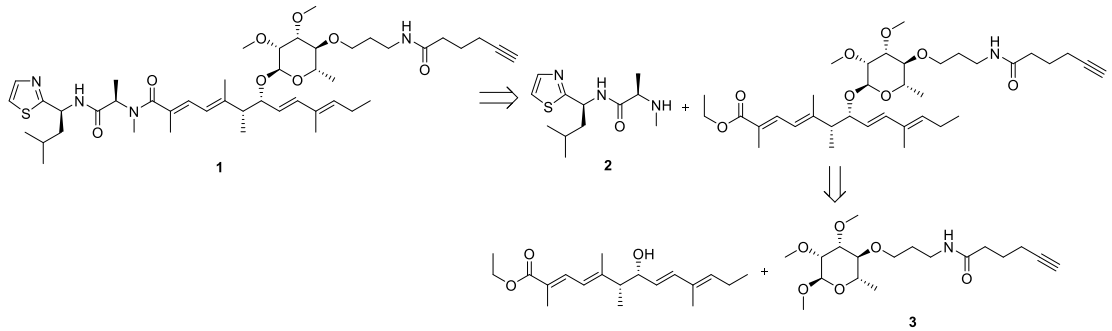
Iezoside is a peptide-polyketide hybrid glycoside, isolated from marine cyanobacterium *Leotochromothrix valpauliae* collected at Ie island, Okinawa in 2020 in our laboratory[1)]. It exhibits potent inhibitory activity against calcium pump (SERCA) (*Ki* 7.1 nM) and potent growth inhibitory activity against HeLa cells (IC_{50} 6.7 nM). However, the binding site of iezoside on SERCA and its interaction with biomolecules other than SERCA are unknown.

We have synthesized iezoside-alkyne probes that can be converted to various probes by click reaction to identify the binding site on SERCA. We have established a stereoselective synthetic route by improving the synthesis of the peptide unit, which required HPLC purification due to the racemization of the thiazole moiety in the previous study. We are also working on synthesizing a sugar unit containing a terminal alkyne.

Keywords : iezoside, SERCA inhibitor, iezoside-alkyne probes

イエゾシドは、2020 年に沖縄県伊江島で採取された海洋シアノバクテリア *Leptochromothrix valpauliae* より当研究室で単離された新規骨格を有するペプチド–ポリケチドハイブリッド配糖体である [1)]。強力なカルシウムポンプ（SERCA）阻害活性（*Ki* 7.1 nM）を示し、HeLa 細胞に対して強力な細胞増殖阻害活性（IC_{50} 6.7 nM）を示すことが明らかになっている。しかしながら、イエゾシドの SERCA への結合部位、SERCA 以外の生体分子に対する相互作用は不明である。

今回私たちは、イエゾシドの SERCA との結合部位を同定するため、クリック反応により各種目的のプローブに変換することが出来るイエゾシド–アルキンプローブ **1** の合成を行った。先行研究では、チアゾール合成時のラセミ化によりペプチドユニット **2** の HPLC 精製が必要であった。本研究ではその改良に取り組み、**2** の立体選択的な合成ルートを確立した。また、末端アルキンを含有する糖ユニット **3** の合成に取り組んだ。



1) Kurisawa, N.; Iwasaki, A.; Teranuma, K.; Dan, S.; Toyoshima, C.; Hashimoto, M.; Suenaga, K. *J. Am. Chem. Soc.* **2022**, 144, 24, 11019–11032

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沖縄県浦添市西洲産海洋シアノバクテリアに含まれる尿酸産生抑制物質の探索

（琉大院理工[1]・琉大教育[2]・（株）ナチュファルマ琉球[3]）○比嘉 星依夢[1]・八木澤 和正[1]・夏目 矩之[3]・照屋 俊明[1,2]

A novel uric acid production inhibitor from Okinawan marine cyanobacterium

([1]*Graduate School of Engineering and Science, University of the Ryukyus*, [2]*Faculty of Education, University of the Ryukyus,* [3]*NatuPharma Ryukyus Co., Ltd.*) ○Sein Higa,[1] Kazumasa Yagisawa,[1] Noriyuki Natsume,[3] Toshiaki Teruya[1,2]

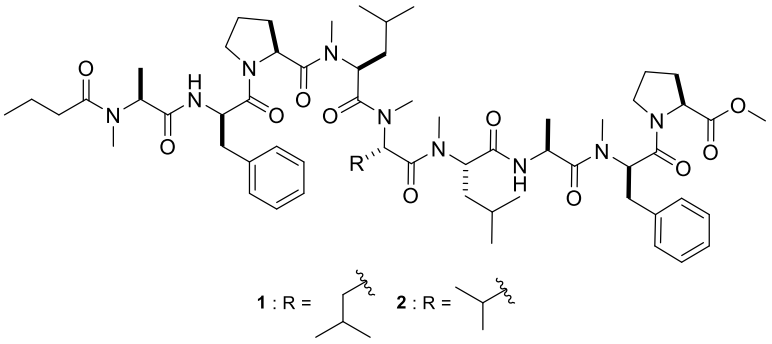
Many compounds have been isolated from marine organisms for pharmaceutical and other purposes. Among them, marine cyanobacteria are known to produce many compounds with various biological activities.

In this study, we collected an unidentified cyanobacterium from the coast of Irijima, Okinawa, Japan, and extracted it with MeOH. Compounds (**1**) and (**2**) were isolated from the extracts by reversed-phase HPLC. Their structures were elucidated by 1D and 2D NMR spectroscopy (COSY, HSQC, and HMBC) as well as HR-ESI-MS. Their absolute configurations of amino acid residues were determined using Marfey's analysis of the hydrolysates of **1** and **2**. In addition, we conducted inhibitory activity on uric acid formation in AML 12 cells and these compounds were shown to inhibit uric acid production.

Keywords : Marine Cyanobacteria

医薬品の開発などを目的として、海洋生物から多くの化合物が単離されており、特に探索が進められている海洋生物の一つとして、海洋シアノバクテリアが挙げられる。海洋シアノバクテリアが産生する二次代謝産物は新規化合物として多数報告され、これらの化合物は様々な生物活性を有することが確認されている。

本研究では、沖縄県浦添市西洲の海岸から未同定の海洋シアノバクテリアを採集し、MeOH で抽出を行った。得られた抽出物から逆相 HPLC を繰り返し行い compound (**1**)、(**2**)を単離した。**1**、**2** の平面構造は、各種 NMR スペクトル、MS の解析から、鎖状リポペプチドであることが判明した。**1**、**2** の絶対立体配置は、各種分解反応、Marfey 法を用いて決定した。その後、AML12 細胞を用いた尿酸産生抑制活性の評価を行ったところ、**1**、**2** は濃度依存的に尿酸産生を抑制することが明らかとなった。



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毒を持つ食虫哺乳類トガリネズミの顎下腺成分の種間比較

(名大農[1],名大院生命農[2], 北大低温研[3]) ○原望実[1]・矢野佑介[2]・福岡凌[2]・大舘智志[3]・北将樹[2]

Interspecies differences in submandibular gland components in shrews, venomous insectivorous mammals ([1]*School of Agricultural Sciences, Nagoya University*, [2]*Graduate School of Bioagricultural Sciences, Nagoya University*, [3]*Institute of Low Temperature Science, Hokkaido University*) ○Nozomi Hara,[1] Yusuke Yano,[2] Ryo Fukuoka,[2] Satoshi Ohdachi,[3] Masaki Kita[2]

Shrews are known to have neurotoxins in their saliva that paralyze preys to capture them efficiently. So far, *Blarina* Paralytic Peptides (BPPs) have been isolated from the submandibular gland of the short-tailed shrew *Blarina brevicauda*, but the presence of toxic components in other shrew species has been unknown. To elucidate the ecological and physiological significance of neurotoxins of mammalian origin, we performed chemical and molecular genetic analyses of submandibular gland components in Japanese shrews to establish interspecies differences.

Keywords : peptide; neurotoxins; calcium channel; venomous mammal

トガリネズミは唾液に神経毒を含み、獲物を麻痺させて効率的に捕獲するとされている。これまでに、北米に生息するブラリナトガリネズミの顎下腺から麻痺性ペプチド BPP 類が単離されているが、他の種では有毒成分の存在は不明である。そこで本研究では、哺乳類由来の神経毒の生態学・生理学的意義の解明を目指して、国内に生息するエゾトガリネズミとカラフトヒメトガリネズミの２種について顎下腺成分を化学分析し、種間比較を行った。その結果、国内種と北米種では成分が大きく異なり、BPP 類は国内種の顎下腺には含まれていないことが分かった。また、BPP2 のアミノ酸配列は、哺乳類で保存されているシンエンケファリン(SYN)の部分配列に類似している[1)]。そこで、分子遺伝学解析により国内種のゲノム DNA に含まれる SYN のコード領域配列を解読し、配列の比較を試みた。これまでの知見を報告する。

```
          1          11          21          31          41          51
BPP2      DCSQDCAACS I-LARPAELNT ETCILECEGK LSSLNTWGIC KEFLHPSKVD LP
hSYN      ECSQDCATCS YRLVRPADINF LACVMECEGK LPSLKIWETC KELLQLSKPE LP
rSYN      DCSQDCAKCS YRLVRPGDINF LACTLECEGQ LPSFKIWETC KDLLQVSKPE FP
          :****** **   *.**.::*   :* :****: * *:: *  * *::*: ** : :*
```

1) Yano Y, Fukuoka R, Maturana AD, Ohdachi SD, Kita M. *J Biol Chem*. **2023** Sep;299(9):105066.

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蛍光標識化が可能なポリアミン類縁体の効率合成

（横市大理）○大西 大河・入江 樂・及川 雅人

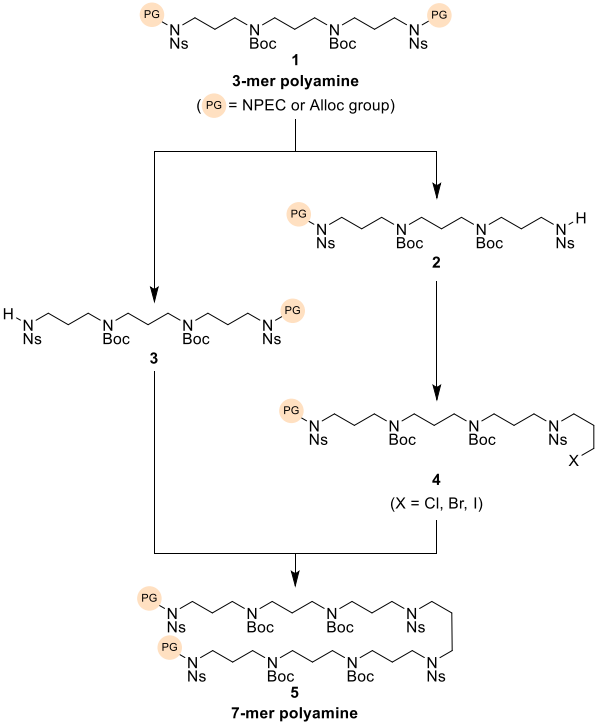
Concise synthesis of polyamine analogs for fluorescent labeling

(*Yokohama City University*) ○Taiga Ohnishi, Raku Irie, Masato Oikawa

Aculeines are polyamine-peptide-conjugated marine natural products that exhibit potent cytotoxicity by penetrating cell membranes and entering the nucleus.[1,2] We have previously synthesized a fluorescently labeled LCPA and observed that it also penetrates the plasma membrane and enters the nucleus. In this study, we attempted to construct a library of LCPAs with different chain lengths and evaluate their cell-penetrating activity. Through comprehensive investigation of reaction conditions, 7-mer polyamine **5** was successfully synthesized from 3-mer polyamine **1**. We furthermore synthesized the longer chain polyamines, and their fluorescent labelings are in progress.

Keywords : polyamine; cell-penetrating activity; fluorescent labeling; structure-activity relationships; N-alkylation

Aculeine A（ACU-A）は 2 本の長鎖ポリアミン（LCPA）と 44 残基からなるペプチド（AcuPep）を有する海洋天然物であり [1]、細胞膜の透過と核への侵入によって毒性を示す [2]。私たちはこれまでに、予備実験として合成した蛍光標識 LCPA が単独で細胞膜を透過し核へと侵入することを観察し、これにより ACU-A の膜透過性は LCPA によってもたらされている可能性が示唆された。この結果を踏まえ、演者らは LCPA の鎖長と細胞膜透過性の相関関係を明らかにするため、様々な鎖長の LCPA ライブラリーを構築し、それらを蛍光標識化して細胞に対する活性評価をおこなうこととした。



1,3-Diaminopropane から合成した 3 量体ポリアミン **1** を基本ユニットとし、末端保護基をそれぞれ選択的に除去した **2**、**3** を合成した。**2** をハロプロピル化して **4** とし、**3** とのカップリングによる 7 量体ポリアミン **5** の合成をおこなった。本研究ではハロゲン化物 **4** の組み合わせをはじめとする反応条件の系統的な検討を行い、**5** の合成経路を最適化した。ここで確立した手法を用いて、より長鎖のポリアミン合成もおこなった。現在は LCPA の蛍光標識化を試みている。

1) Matsunaga S. et al., *ChemBioChem* **2011**, *12*, 2191–2200.
2) Watari H. et al., *Chem. Lett.* **2023**, *52*, 185–189.

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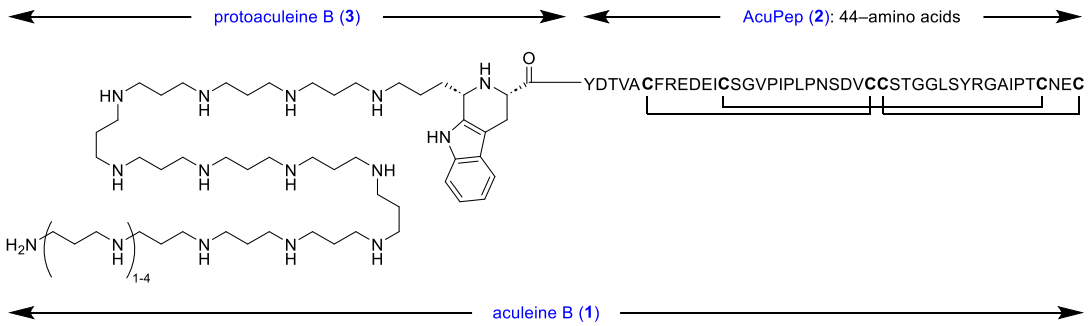
Aculeine 類のペプチド部分 AcuPep の構造解析

(横市大院生命ナノ[1]・京大院農[2]・函館高専[3]・北大院水[4])
○入江 樂[1]・入江 由美[2]・松永 智子[3]・酒井 隆一[4]・入江 一浩[2]・及川 雅人[1]
Structural analysis of AcuPep, a peptide moiety of aculeines ([1]*Yokohama City University*, [2]*Kyoto University*, [3]*National Institute of Technology, Hakodate College*, [4]*Hokkaido University*)
○Raku Irie[1], Yumi Irie[2], Satoko Matsunaga[3], Ryuichi Sakai[4], Kazuhiro Irie[2], Masato Oikawa[1]

Aculeine B (ACU-B), a polyamine-peptide conjugate isolated from a marine sponge, shows potent cytoxicity by disrupting cell membranes. The peptide moiety of ACU-B, AcuPep, consists of 44 amino acid residues and has three pairs of disulfide bonds formed by six cysteines. However, the folding pattern of AcuPep had yet to be determined. In this study, we successfully synthesized AcuPep whose behavior on HPLC matched that of an Edman degradation product derived from natural ACU-B. The structure of the synthetic AcuPep was then analyzed to determine the complete chemical structure of ACU-B.
Keywords : marine natural product; peptide; disulfide bond; structural analysis; solid-phase synthesis

Aculeine B（**1**）は細胞膜のかく乱により毒性を示す、ポリアミン–ペプチド複合型海洋天然物である[1]。44 アミノ酸残基からなるそのペプチド部分 AcuPep（**2**）には 3 組のジスルフィド結合が含まれるが、その組み合わせは未決定であった。演者らは AcuPep を固相合成し、リフォールディング条件に付すことによって、HPLC において天然物の Edman 分解物と保持時間の一致する異性体を主生成物として得た。この合成品を用いて各種構造解析（還元アルキル化、酵素消化、質量分析）をおこなった結果、ジスルフィド結合の組み合わせを Cys^{I}–Cys^{III}、Cys^{II}–Cys^{V}、Cys^{IV}–Cys^{VI} と決定した。以上により protoaculeine B（**3**）[2] の構造訂正[3] とあわせて aculeine B（**1**）の完全な構造を提案するに至った。



1) Matsunaga, S.; Jimbo, M.; Gill, M. B.; Lash-Van Wyhe, L. L.; Murata, M.; Nonomura, K.-i.; Swanson, G. T.; Sakai, R. *ChemBioChem* **2011**, *12*, 2191.
2) Matsunaga, S.; Kishi, R.; Otsuka, K.; Fujita, M. J.; Oikawa, M.; Sakai, R. *Org. Lett.* **2014**, *16*, 3090.
3) Irie, R.; Miyako, K.; Matsunaga, S.; Sakai, R.; Oikawa, M.; *J. Nat. Prod.* **2021**, *84*, 1203.

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ペプチド固相合成法に適用可能な新規セレノシステイン保護基の開発

（名大工[1]・名大院工[2]・名大ナノライフ研[3]）○吉富 文香[1]・中津 幸輝[2]・林 剛介[2]・村上 裕[2,3]

A Novel Protecting Group for Selenocysteine Applicable to Solid-phase Peptide Synthesis

([1]*School of Engineering, Nagoya University*, [2]*Graduate School of Engineering, Nagoya University* [3]*Institute of Nano-Life-Systems, Nagoya University*) ○Fumika Yoshitomi,[1] Koki Nakatsu,[2] Gosuke Hayashi,[2] Hiroshi Murakami[2,3]

Selenocysteine (Sec)-containing peptides are useful in site-specific modifications and peptide ligation reactions due to the high nucleophilicity of selenol. However, protecting groups for Sec available for solid-phase peptide synthesis (SPPS) are even fewer than those for other amino acids. And there exists only limited groups that can be efficiently deprotected under mild aqueous conditions, among the previously developed SPPS-compatible Sec protecting groups. In this study, we introduced a novel allylic protecting group, which we have developed as a protective group for cysteine, into Sec and examined its applicability in Fmoc SPPS and deprotection efficiency in aqueous solution. First, a Fmoc-Sec derivative with a novel allylic protecting group was synthesized in a three-step reaction using selenocystine as the starting material. We found that Fmoc SPPS using this compound successfully yielded the target peptide, which was revealed to be stable under the basic and acidic conditions used in Fmoc SPPS. We also observed that the novel allylic protecting group on Sec-containing peptide was deprotected rapidly and efficiently by treating a organometallic ruthenium complex[1)].
Keywords : Selenocysteine; Solid-phase Peptide Synthesis; Protecting Group

セレノシステイン含有ペプチドは、セレノールの高い求核性により、部位特異的修飾やペプチド連結反応において重宝される。しかし、ペプチド固相合成で利用可能なセレノシステインの保護基は他のアミノ酸に比べて少なく、またその中でも温和な条件下で効率よく脱保護可能な保護基は限られている。本研究では、システインの保護基として我々が開発してきた新規アリル系保護基をセレノシステインへ導入し、Fmoc ペプチド固相合成での適用可能性および脱保護能を検証することを目的とした。まず、設計したアリル系保護基を含む Fmoc 保護セレノシステイン誘導体を、セレノシスチンを出発原料として 3 段階の反応で合成した。この誘導体を用いて Fmoc ペプチド固相合成を行ったところ、目的ペプチドが得られ、Fmoc 固相合成で使用される塩基性および酸性条件で安定に存在することが明らかとなった。また、得られたペプチド中のアリル保護セレノシステインに対してルテニウム錯体 [1)]で処理することで、迅速かつ高効率に脱保護可能であることを明らかにした。

1) Organoruthenium-catalyzed chemical protein synthesis to elucidate the functions of epigenetic modifications on heterochromatin factors. Kamo N. et al., *Chem. Sci.*, **2021**,*12*, 5926.

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α-二置換アミノ酸を用いたペプチドチオエステル合成の効率化

（名大院工[1]・名大ナノライフ研[2]）○中村 元紀[1]・中津 幸輝[1]・林 剛介[1]・村上 裕[1.2]

Improved Synthesis of Peptide Thioester with α-Disubstituted Amino Acids ([1]*Graduate School of Engineering, Nagoya University*., [2]*Institute of Nano-Life-Systems, Institute of Innovation for Future Society, Nagoya University*) ○Genki Nakamura,[1] Koki Nakatsu,[1] Gosuke Hayashi,[1] Hiroshi Murakami[1.2]

Peptides thioester is an essential material for chemical protein synthesis employing Native Chemical Ligation[1]. We have previously developed thioester synthesis methods utilizing the N-S acyl shift at a cysteine residue and following diketopiperazine formation unique to the Cys-Pro sequence. In this study, we aimed to investigate the effect of replacing cysteine in the Cys-Pro sequence with α-methylcysteine (MeCys), an α-disubstituted amino acid, during the diketopiperazine formation. First, we attempted to synthesize a model peptide including MeCys-Pro sequence by Fmoc solid-phase peptide synthesis (SPPS). However, a truncated peptide lacking MeCys-Pro was generated to the same amount of the full-length peptide. Therefore, we optimized reaction conditions of SPPS such as temperature and coupling/deprotection reagents. Subsequently, the obtained peptide containing the MeCys-Pro sequence was used to test diketopiperazine formation. We observed a improved reaction rate of MeCys-Pro peptide compared to original Cys-Pro peptide.

Keywords :Peptide Thioester; Native Chemical Ligation; α-Methylcysteine; Diketopiperazine Formation; Solid-phase Peptide Synthesis

Native Chemical Ligation によるペプチド連結[1]には、C 末端にチオエステルを有するペプチドが必要不可欠である。これまでに我々は、システイン残基の N-S アシルシフトおよびCys-Pro配列特有のジケトピペラジン形成反応を利用したチオエステル合成法を開発してきた[2,3]。本研究では、Cys-Pro 配列中のシステインをα-二置換アミノ酸であるα-メチルシステイン（MeCys）に置き換えることで、ジケトピペラジン形成反応に及ぼす影響の検討を行うことを目的とした。まず MeCys-Pro 配列を有するモデルペプチドを Fmoc ペプチド固相合成によって合成を試みた。しかし、目的のペプチドに加えて MeCys-Pro が欠損したペプチドが同程度生成したため、合成条件の最適化を行った。その後、得られた MeCys-Pro 配列含有ペプチドを用いてジケトピペラジン形成反応を行ったところ、Cys-Pro 配列を含む従来のペプチドと比較して反応速度の向上が観測された。

1) P. E. Dawson, T. W. Muir, I. Clark-Lewis, S. B. Kent, *Science* 1994, **266**, 776–779.
2) K. Nakatsu, M. Yanase, G. Hayashi, A. Okamoto, *Org. Lett.* 2020, **22**, 4670-4674.
3) M. Yanase, K. Nakatsu, C. J. Cardos, Y. Konda, G. Hayashi, A. Okamoto, *Chem. Sci.* 2019, **10**, 5967-5975

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線維形成に関連する実測データと分子記述子を用いた細胞接着能を有するペプチド配列の探索

（甲南大学 FIRST[1]・甲南大学知能情報 [2]・神戸大院医 [3]）○寺尾泰晟 [1]・武川公 [3]・梅谷智弘 [2]・栢森史浩 [1]・臼井健二 [1]
Screening of peptide sequences with cell adhesion using molecular descriptors and measurement data related to fibril formation. ([1]*Graduate School of Frontiers of Innovative Research in Science and Technology, Konan University,* [2]*Faculty of Intelligence and Informatics, Konan University,* [3]*Graduate School of Medicine, Kobe University*)
○Taisei Terao[1], Akira Takekawa[3], Tomohiro Umetani[2], Fumihiro Kayamori[1], Kenji Usui[1]

The application of some peptide fibrils to biomaterials has been investigated. However, a method for the exhaustive design of peptides with properties required for biomaterials has not been achieved. In this study, we attempted to obtain a correlation between sequence and structure, and between structure and function. We demonstrated the design of peptides applicable to cell culture substrates. At first, 20 sequences were selected by adding one amino acid residue to the N-terminus of a short peptide that can form fibrils. Measurements were conducted to evaluate the potential for fibril formation. Next, principal component analysis was performed on various combinations of the obtained measurement values. The principal components (PC) in the selected PC1 and PC2 were interpreted based on the ca. 5000 molecular descriptors used in computational chemistry. Finally, several sequences applicable to cell culture substrates were designed using the interpreted molecular descriptors, tendency to fibril formation and tendency to cell adhesion, with the PCA 2D coordinates. The designed peptides showed higher potential for cell adhesion than gelatin, which is a typical cell adhesion substrate.
Keywords: Short peptide, β-sheet structure, Statistical analysis, Molecular descriptors, Cell adhesion.

近年、ペプチド線維を用いた生体材料の作製や応用研究は盛んに行われている1)。しかし、生体材料への応用に必要な特性を持つペプチド配列を、網羅的に探索し設計する手法は依然として少ない。本研究では、ペプチドの配列と構造、構造と特性の相関から、効率的に細胞接着基材へと適用可能なペプチド配列を探索・設計することを試みた。線維を形成する短鎖ペプチドをコア配列とし、コア配列の N 末端に標準アミノ酸を 1 残基ずつ付加した 20 種類の配列を作製した 2)。ペプチドの配列と線維形成の相関を解析するため、線維形成に関する実測データを得、それを用いて主成分分析を行った。3)。次に、各ペプチドの細胞接着に関する実測データを得、主成分分析より得られた二次元座標上に色で表記し、傾向を得た。二次元座標の第一主成分、第二主成分は、計算科学分野で使用される分子記述子と相関をとり、最も相関の高い分子記述子を用いて解釈を試みた。以上の二次元座標と分子記述子を用いて、線維を形成し細胞接着基材へ適用可能なペプチド配列の探索・設計を試みた。

1) P. C. Ke et al., *Chem. Soc. Rev.,***46**, *6492-6531* (2017). 2) K. Tenidis et al., *J. Mol. Biol.*, **295**, *1055-1071* **(**2000). 3) K. Usui et al., *Mol. BioSyst*., **2**, *417-420* (2006).

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ヒストンアシル化触媒の拡張を志向した新規ヌクレオソームリガンドの開発

（東大院薬 [1]）○竹内悠馬 [1]、野崎多実子 [1]、小野田真由 [1]、山次健三 [1]、川島茂裕 [1]、金井求 [1]

Developing novel nucleosome ligand for expansion of histone acylation catalyst ([1]*Graduate School of Pharmaceutical Sciences, The University of Tokyo*) ○Yuma Takeuchi[1], Tamiko Nozaki[1], Mayu Onoda[1], Kenzo Yamatsugu[1], Shigehiro Kawashima[1], Motomu Kanai[1]

Histones, which constitute nucleosomes, undergo various post-translational modifications by chromatin-modifying enzymes (Writers) to regulate gene expression. Abnormalities in this process are associated with various diseases, such as cancer. To understand the mechanisms of such diseases and to treat them, we aim to develop Artificial Chromatin Writers (ACWs) that can introduce various post-translational modifications to histones at will. ACWs not only work as chromatin-modifying enzymes but also introduce artificial post-translational modifications that are not possible with endogenous enzymes. We have developed a chemical catalyst that can regioselectively acylate catalyst-proximal lysine residues, directed by a nucleosome ligand.

To further expand the function and regioselectivity of the ACW, we designed a novel bivalent nucleosome ligand, called LANA-DBM, imitating the natural Writer's nucleosome-binding mode. LANA-DBM consists of a LANA peptide that binds to the histone acidic patch and a DNA-binding motif (DBM), polyarginine. LANA-DBM bound to nucleosomes more strongly than LANA alone. LANA-DBM-catalyst promoted the histone acylation reaction with a lower concentration than LANA-catalyst did. Furthermore, LANA-DBM-catalyst promoted regiodivergent histone acylation; various histone lysine residues were regioselectively acylated with LANA-DBM-catalyst.

In this presentation, we will discuss the design of LANA-DBM-catalyst and effects of histone acylation introduced by this catalyst on chromatin structure.

Keywords : Histone acylation; Epigenome manipulation; Ligand design; Regioselectivity

ヌクレオソームを構成するヒストンはクロマチン修飾酵素（Writer）により様々な翻訳後修飾を受けることで遺伝子発現を制御し、その異常はがんなどの多様な疾患に関わる。そのような疾患のメカニズム理解や治療を見据え、本研究では、多様なヒストン翻訳後修飾を自在に導入できる Artificial Chromatin Writer (ACW) の開発を目指している。ACW は化学触媒を活性中心に持ち、クロマチン修飾酵素の反応を模倣するだけでなく、酵素には不可能な非天然の翻訳後修飾の導入も可能である。我々は、近傍のリジン残基を位置選択的にアシル化する化学触媒を開発し、この化学触媒をヌクレオソームリガンドにつないだ分子が ACW として機能することを明らかにした。

今回、天然の Writer のヌクレオソーム結合様式を模倣し、ヒストン酸性領域に結合する LANA ペプチドと DNA 結合モチーフ (DBM) であるポリアルギニンを繋いだ 2 価性ヌクレオソームリガンド LANA-DBM を開発した。LANA-DBM は LANA 単独よりも強くヌクレオソームに結合し、必要触媒濃度の低減を実現した。さらに、LANA よりも LANA-DBM において触媒を導入可能な位置が拡張され、多様なヒストンリジン残基をそれぞれ位置選択的にアシル化することに成功した。

本発表では、開発したヒストンアシル化触媒のデザイン、および本触媒によって導入したヒストンアシル化がクロマチン構造に与える影響を議論したい。

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
H931(931, Bldg. 9 [3F])

[H931-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Yasuaki Kimura, Yoshiaki Masaki

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H931-3am-01]

Chemical synthesis of rare sugar-derived nucleosides

○Yutaka Narita[1], Natsuhisa Oka[1,2,3] (1. Fac. of Eng., Gifu Univ., 2. iGCORE, Gifu Univ., 3. COMIT, Gifu Univ.)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H931-3am-02]

Post-modification of nucleic acids with amino acids via a ciano group

○Takumi Yoshida[1], Natsuhisa Oka[1,2,3] (1. Fac. of Eng., Gifu Univ., 2. iGCORE, Gifu Univ., 3. COMIT, Gifu Univ.)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H931-3am-03]

Development of chemoselective condensation reaction of nucleoside 3'-*H*-phosphonothioate

○Harumi Okutsu[1], Yuhei Takahashi[1], Kazuki Sato[1], Takeshi Wada[1] (1. Tokyo University of Science)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H931-3am-04]

Development of purity assay method of boranophosphate DNAs by using PB/PO conversion reaction

○Kentaro matsumoto[1], Yuhei Takahashi[1], Kazuki Sato[1], Wada Takeshi[1] (1. Tokyo university of science)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H931-3am-05]

Photoreactivity of psoralens and trioxsalens for DNA duplexes

○Kazuhisa Fujimoto[1], Amin Md Al[2], Takanori Oyoshi[2] (1. Kyushu Sangyo University, 2. Shizuoka University)

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[H931-3am-06]

Interstrand Crosslinks using Oligonucleotides Containing 2’-Deoxythioguanosine

○Jamila Abbas Osman[1,2], Kazumitsu Onizuka[1,2], Yuuhei Yamano[1,2], Ahmed Mostafa Abdelhady[1,2], Fumi Nagatsugi[1,2] (1. Graduate school of science, Department of Chemistry, Tohoku University, 2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

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Japanese

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

[H931-3am-07]

Development and Comparison of 4-Thiouridine to Cytidine Chemical Base Conversion Reaction

○Sana Ohashi[1], Mayu Nakamura[1], Susit Archaryya[1], Masahito Inagaki[1], Naoko Abe[1], Yasuaki Kimura[1], Fumitaka Hashiya[2,3], Hiroshi Abe[1,2,3,4] (1. Graduate School of Science, Nagoya Univ., 2. Research Center for Material Science, Nagoya Univ., 3. CREST, Japan Science and Technology Agency, 4. Institute for Glyco-core Research (iGCORE), Nagoya Univ.)

English

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

[H931-3am-08]

Enzymatic incorporation and extension studies of the unnatural alkynylated purine-pyridazine base pair

○Wenjue Fan[1,2], Hidenori Okamura[1,2], Zhuoxin Dong[1,2], Giang Hoang Trinh[1,2], Fumi Nagatsugi[1,2] (1. IMRAM, Tohoku Univ., 2. Grad. Sch. Sci., Tohoku Univ.)

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

[H931-3am-09]

Synthesis and properties of antisense oligonucleotides containing 4'-*C*-(*N*-alkyl)aminoethyl thymidines.

○Kota Fujiki[1,5], Yoshihito Ueno[1,2,3,4] (1. The Graduate School of Natural Science and Technology, Gifu University, 2. Faculty of Applied Biological Science, Gifu University, 3. The United Graduate School of Agricultural Science, Gifu Univercity, 4. Center for One Medicine Innovative Translational Reseach(COMIT), Gifu university Institute for Advanced Study, Gifu University, 5. Convolution of Informatics and Biomedical Sciences on Glocal Alliances, CIBoG)

Japanese

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

[H931-3am-10]

Synthesis of 4'-*C*-aminoethoxy-2'-*O*-methyl-5-propynyluridine and its application for antisense oligonucleotide

○Yujun Zhou[1,4], Yoshihito Ueno[1,2,3,5] (1. The United Graduate School of Agriculture Science (UGSAS), Gifu University, 2. Faculty of Applied Biological Sciences, Gifu University, 3. Graduate School of Natural Sciences and Technology, Gifu Unviversity, 4. Convolution of Informatics and Biomedical Sciences on Glocal Alliances (CIBoG), Nagoya University, 5. Center for One Medicine Innovative Translational Research (COMIT), Tokai National Higher Education and Research System)

Japanese

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

[H931-3am-11]

Synthesis and evaluation of a thymidine dimer with an extended backbone at five prime position

○Shigetoshi Tachibana[1], Rie Ohnishi[1], Yoshiaki Masaki[1], Kohji Seio[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

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Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[H931-3am-12]
Synthesis of 5-methyluridine derivatives with sulfonamide or sulfonate modifications on the 2´ hydroxyl group and evaluation of their ability to form duplex chains

○Shuntaro Takigawa[1], Takahito Tomori[1], Koya Uekusa[1], Yoshiaki Masaki[1], Kohji Seio[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H931-3am-13]
Synthesis and properties of oligonucleotides having substituted 2´-*O*, 3´-*C*-bridged [3.2.0]bicycloarabinonucleoside

○Ayano P Tabira[1], Shunsuke Wakatsuki[1], Kohji Seio[1], Yoshiaki Masaki[1] (1. Sch. Life Sci. Tech., Tokyo Tech.)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[H931-3am-14]
Synthesis and Evaluation of Photolabile Selenium-Modified Nucleic Acid for Intracellular Gene Expression Switching

○Yuki Yoshida[1], Haruka Hiraoka[1], Hirotaka Murase[1,2], Naoko Abe[1], Fumitaka Hashiya[3], Hiroshi Abe[1,4,5] (1. Graduate School of Science, Nagoya University, 2. Department of Pharmacy, Sojo University, 3. Research Center for Materials Science, Nagoya University, 4. JST-CREST, 5. Institute for Glyco-core Research)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[H931-3am-15]
Construction of Chimeric Artificial Nucleic Acids (CANA) forward Inhibition of Pancreatic Cancer Transcription Factor BACH1 Ⅰ V: - Effects of Junction Position on Complex Stability and Cleavage Efficiency -

○Yuki Igarashi[1], Yuto Horiuchi[1], Mitsuyo Matsumoto[2], Yu Mikame[3], Masaki Nishijima[1], Yasuyuki Araki[1], Asako Yamayoshi[3], Kazuhiko Igarashi[2], Takehiko Wada[1] (1. Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2. Graduate School of Medicine, Tohoku University, 3. Graduate School of Biomedical Sciences, Nagasaki University)

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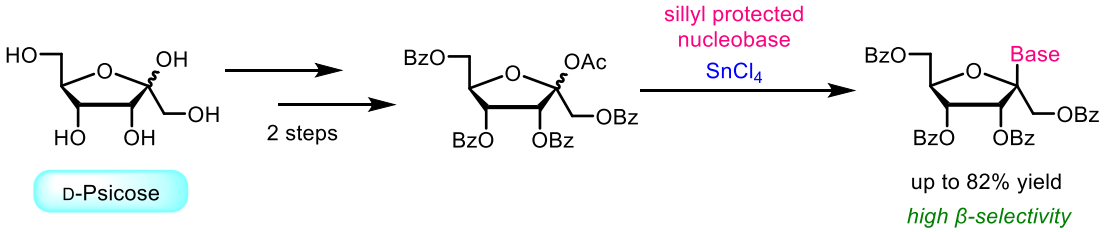
希少糖ヌクレオシドの化学合成法の開発

（岐大工[1]・岐大 iGCORE[2]・岐大 COMIT[3]）○成田 豊[1]・岡 夏央[1,2,3]
Chemical Synthesis of Rare Sugar-Derived Nucleosides ([1]*Faculty of Engineering, Gifu University*, [2]*iGORE, Gifu University,* [3]*COMIT, Gifu University*) ○Yutaka Narita,[1] Natsuhisa Oka[1,2,3]

Rare sugar is a general term for sugars with low abundance in nature, and their applications have been limited due to their rarity. In recent years, the mass production of some rare sugars has been industrialized, and much attention has been paid to their unique structures and properties. Nucleosides with a rare-sugar core are also attracting significant attention from researchers, and many examples of their synthesis have been reported.[1–3] However, there is still room for improvement, such as reaction efficiency, stereoselectivity, and the scope of substrates. In this study, we attempted to develop an efficient method for the synthesis of psicose-derived nucleosides. By screening the leaving groups of glycosyl donors, Lewis acids, and reaction conditions, we found that the reaction of 2-*O*-acetyl-1,3,4,6-tetra-*O*-benzoyl-D-psicofuranose with silylated nucleobases was promoted efficiently by tin(IV) chloride, and the corresponding nucleosides were obtained in good yield with high β-selectively.
Keywords : Rare sugar; *Nucleoside*; *Glycosylation*; *Nucleobase*; *β-Selective*

希少糖とは天然にわずかしか存在しない糖の総称であり、その希少性のためにこれまで応用が限られていたが、近年、その大量生産法が確立されたことで、その特異な構造や性質が注目を集めている。これまでに、D-psicose などの希少糖骨格をもつヌクレオシドの様々な合成法が報告されているが、収率や立体選択性、適用可能な核酸塩基などに改善の余地がある[1–3]。本研究では、D-psicose から種々の糖供与体を合成し、グリコシル化反応を経由する希少糖ヌクレオシドの効率的な合成法の開発を試みた。糖供与体の脱離基や Lewis 酸について検討した結果、D-psicose から 2 段階で合成可能な 1,3,4,6-tetra-*O*-benzoyl-D-psicofuranosyl acetate を糖供与体とし、塩化スズ(IV)を Lewis 酸として用いることで、様々な核酸塩基から希少糖ヌクレオシドがβ位選択的に収率良く得られることを見出した。



1) Grouiller, A.; Chattopadhyaya, J. *Acta Chem. Scand.* **1984**, *38b*, 367.
2) Roivainen, J.; Vepsäläinen, J.; Azhayev, A.; Mikhailopulo, I. A. *Tetrahedron Lett.* **2002**, *43*, 6553.
3) Ueda, A. *et al. Heterocycles,* **2018**, *97*, 729.

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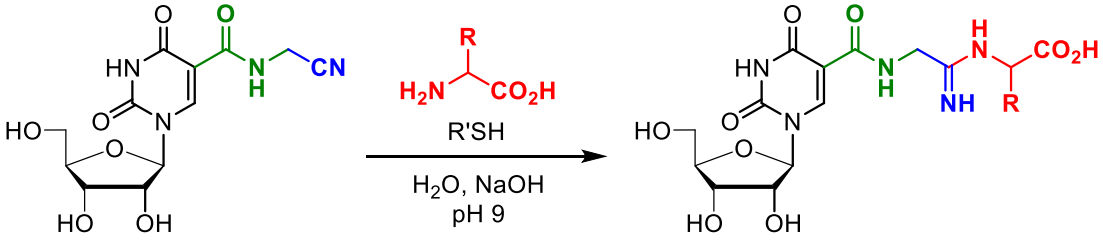
シアノ基を介したアミノ酸による核酸のポスト修飾法の開発

（岐大工[1]・岐大 iGCORE[2]・岐大 COMIT[3]）○吉田 拓未[1]・岡 夏央[1,2,3]
Post-modification of nucleic acids with amino acids via a cyano group ([1]*Faculty of Engineering, Gifu University*, [2]*iGCORE, Gifu University*, [3]*COMIT, Gifu University*)○Takumi Yoshida,[1] Natsuhisa Oka[1,2,3]

Cyano groups are chemically stable and can be introduced into various molecules, including nucleic acids. Chemoselective reaction of cyano groups would open a new route for the modifications of nucleic acids. We studied the addition reaction of nucleosides bearing a cyano group in aqueous media for application to the post-modification of nucleic acids. Inspired by the thiol-catalyzed addition of amino acids to nitriles[1)], we investigated the structure and reaction conditions that are applicable to the post-modification of nucleic acids. As a result, we found that an amide bond on the α position is necessary and that an N–H bond accelerates the reaction. Therefore, nucleosides bearing those requisite structures were synthesized and applied to the addition reaction with amino acids. The reaction proceeded efficiently to afford uridine derivatives bearing amino acids or peptides at the 5-positions in good yield. We are investigating its further applications to the addition of amino acids, peptides, and proteins to oligonucleotides.
Keywords : Cyano group; Nucleic acid; Post-modification; Amino acid

シアノ基は、核酸を始めとする様々な分子への導入が容易であり、化学的に安定である。シアノ基の低反応性を克服し、選択的に反応させることができれば、核酸などの複雑な分子の化学修飾法の幅は大きく広がる。本研究では、核酸のポスト修飾への応用を目指して、ヌクレオシドを基質とするシアノ基を介した水中での選択的付加反応の開発を試みた。まず、チオール触媒を用いるアミノ酸とニトリルの付加反応 [1)]を参考に、核酸のポスト修飾に適用可能な分子構造や反応条件を調査したところ、シアノ基の α 位にアミド結合が必要であり、N–H 結合があると効率良く反応が進行することを見出した。そこで、その分子構造をもつヌクレオシドを合成し、水溶液中でのアミノ酸の付加反応を試みたところ、反応は効率よく進行し、5 位にアミノ酸やペプチドが導入されたウリジン誘導体が良好な収率で得られた。今後は、オリゴヌクレオチドに対するアミノ酸やペプチド、タンパク質の付加反応を試みる予定である。



1) Singh, J.; Whitaker, D.; Thoma, B.; Islam, S.; Foden, C. S.; Aliev, A. E.; Sheppard, T. D.; Powner, M. W., *J. Am. Chem. Soc.* **2022**, *144*, 10151.

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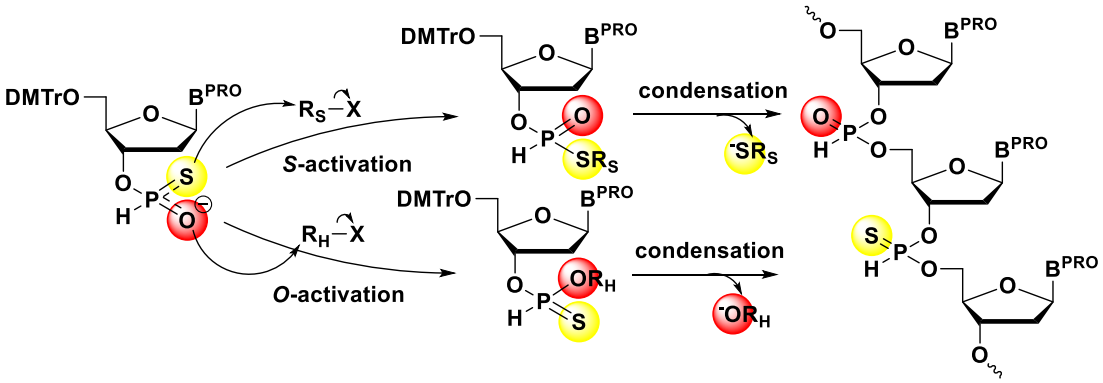
ヌクレオシド 3'-*H*-ホスホノチオエートの化学選択的縮合反応の開発

(東理大院薬 [1])○奥津 晴海 [1]・髙橋 裕平 [1]・佐藤 一樹 [1]・和田 猛 [1]
Development of chemoselective condensation reaction of nucleoside 3'-*H*-phosphonothioate ([1]*Graduate School of Pharmaceutical Science*) ○Harumi Okutsu,[1] Yuhei Takahashi,[1] Kazuki Sato,[1] Takeshi Wada[1]

A nucleoside 3'-*H*-Phosphonothioate is a useful monomer for the synthesis of *P*-modified oligonucleotides including a phosphorothioate. Since an *H*-phosphonothioate has sulfur and oxygen atoms as nucleophiles, it is necessary to control the chemoselectivity in the condensation reaction with a 5'-hydroxyl group. In our laboratory, we have already succeeded in the *O*-selective activation by using phosphonium type condensing reagents and obtain an *H*-phosphonothioate diester linkage. However, selective activation of a sulfur atom to obtain an *H*-phosphonate diester linkage has not yet been fully investigated. In this study, it was found that carbodiimide type condensing regents offered selective activation of sulfur atoms and afforded an internucleotidic *H*-phosphonate diester linkage. The details will be discussed in the presentation.

ヌクレオシド 3'-*H*-ホスホノチオエートはホスホロチオエート核酸などのリン原子修飾核酸の合成原料として有用な化合物として知られている。*H*-ホスホノチオエートは硫黄原子と酸素原子の 2 つの求核性原子を有するため、ヌクレオシド 5'-水酸基との縮合反応時に化学選択性を制御することで 2 種類のインターヌクレオチド結合を生成可能であると考えられる。当研究室ではすでにホスホニウム型縮合剤を用いることで酸素原子を選択的に活性化して *H*-ホスホノチオエートジエステル結合を生成することに成功している。しかしながら、硫黄原子を選択的に活性化して脱硫を伴って *H*-ホスホネートジエステル結合を生成する反応については未だ十分な検討がされていない。そこで本研究では、後者の条件について検討を行い、ソフトな求電子剤であるカルボジイミド型縮合剤を用いることで硫黄原子を選択的に活性化して、インターヌクレオチド *H*-ホスホネートジエステル結合を生成することに成功した。その詳細について報告する。



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日本化学会 第104春季年会 (2024)

PB/PO 化学変換を用いたボラノホスフェートＤＮＡの純度検定法の開発

○松本 健太郎[1]、髙橋 裕平[1]、佐藤 一樹[1]、和田 猛[1](1. 東京理科大学薬)

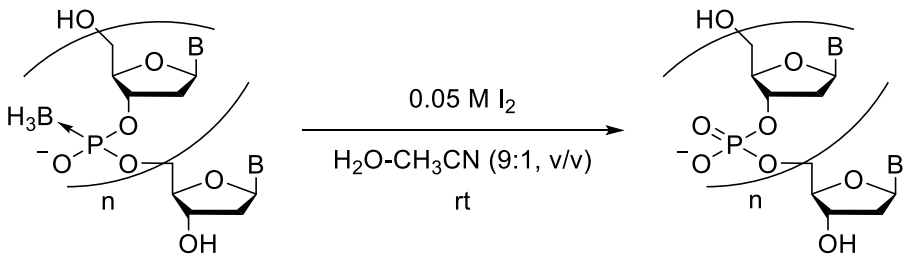
Development of purity assay method of boranophosphate DNAs by using PB/PO conversion reaction

○Kentaro Matsumoto[1], Yuhei Takahashi[1], Kazuki Sato[1], Wada Takeshi[1]
(1. *Graduate School of Pharmaceutical Sciences*, *Tokyo University of Science*)

Boranophosphate DNAs (PB-DNA), which have a borano group on a phosphorus atom, are attractive candidates for oligonucleotide therapeutics. However, they are eluted as multiple peaks during HPLC analysis due to the presence of diasteromers derived from a chirality of a phosphorus atom and the separation of a full length-product from shortmers is difficult. In this study, we develop a new method for the purity assay of PB-DNA by using transformation reaction of PB-DNAs into achiral PO-DNAs.
We have developed the conversion reaction of a PB-DNA 4 mer into the unmodified counterpart using I_2 in an aqueous solution and enabled the purity assay via LC-MS analysis.
Keywords : boranophosphate nucleic acid

リン原子にボラノ基を導入したボラノホスフェート DNA（PB-DNA）は、アンチセンス核酸として魅力的な性質を有している。しかし、PB-DNA はリン原子のキラリティーに起因する立体異性体が存在し、HPLC での分析の際に複数のピークを与え、目的物と副生成物との分離が困難になるという問題が生じる。本研究では、PB-DNA をリン原子にキラリティーがなく、立体異性体の存在しない天然型 DNA へ誘導することで、正確な純度検定を行う手法を検討した。

今回、水-アセトニトリル溶媒中ヨウ素を用いることで、4 量体レベルで PB-DNA の天然型 DNA への変換、及び LC-MS での分析による純度検定を行ったためこれを報告する。



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ソラレン、ならびにトリオキシサレンの DNA 二重鎖に対する光反応性

（九産大生命 [1]・静大院理 [2]・静大院創造 [3]・静大グリーン研 [4]）○藤本 和久 [1]・Amin Md Al[3]・大吉 崇文 [2, 3, 4]

Photoreactivity of psoralens and trioxsalens for DNA duplexes ([1]*Faculty of Life Science, Kyushu Sangyo University*, [2]*Graduate School of Science*, [3]*Graduate School of Integrated Science and Technology,* [4]*Research Institute of Green Science and Technology, Shizuoka University*) ○Kazuhisa Fujimoto,[1] Amin Md Ml,[3] Takanori Oyoshi[2, 3, 4]

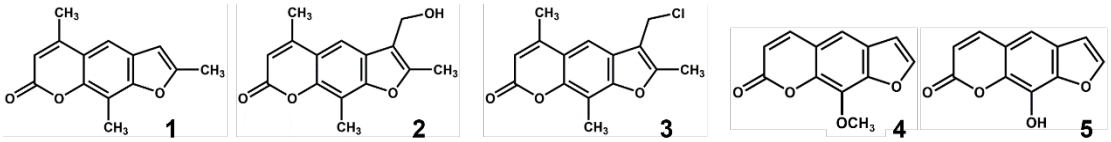
Psoralen and its derivatives photoreact with thymine residues in DNA duplexes. Although one of the derivatives, trioxsalen (4,5',8-trimethylpsoralen), has been reported to display a good photoreactivity for DNA duplexes more than psoralen itself, the photoreactivity has never been explored in detail. Here, we analyzed the photoreactivity of the various derivatives of psoralen and trioxysalen for DNA duplexes. Additionally, trioxsalen-modified peptides were prepared as a new class of cross-linking agent for DNAs.

The photoreactivities of psoralens and trioxsalens for DNAs were investigated by HPLC, so that **2** was found to show a good photoreactivity for DNA duplexes under a condition; yield: 24% and irradiation time: 60 s. This finding encourages us to develop a new class of DNA cross-linking agents using trioxsalen skeletons. In the molecular design of the cross-linking agents, short peptides were adopted as their basic skeleton because trioxasalens can be introduced into the side chains of peptides. We will also report the photoreactivities of trioxsalen-modified peptides for DNAs.

Keywords : Psoralen, Trioxsalen, Photoreaction, DNA, Cross-linking reaction

ソラレンやその誘導体は DNA 二重鎖中のチミンと光反応することが知られている。誘導体の一つであるトリオキシサレンも同様の光反応し、ソラレンよりも優れた光反応性を示すが、その DNA に対する光反応性は詳細に調べられていない。今回、幾つかのソラレン誘導体、ならびにトリオキシサレン誘導体を用いて、DNA との光反応性を検証した。さらに、DNA に対する光反応性クロスリンク剤としてトリオキシサレン修飾ペプチドを開発した。

ソラレン誘導体ならびにトリオキシサレン誘導体と DNA 二重鎖との光反応性を HPLC で解析したところ、365 nm の光を 60 秒照射下で **2** が比較的高収率（24%）で光反応生成物を与えることがわかった。この結果を踏まえて、トリオキシサレン修飾ペプチドを合成した。本講演において、トリオキシサレン修飾ペプチドの DNA に対する光反応性も併せて報告する。



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Interstrand crosslinks using oligonucleotides containing 2'-deoxythioguanosine

([1]*Graduate School of Science, Department of chemistry, Tohoku University*, [2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○Jamila Abbas Osman,[1,2] Kazumitsu Onizuka,[1,2] Yuuhei Yamano,[1,2] Ahmed Mostafa Abdelhady,[1,2] Fumi Nagatsugi[1,2]

Keywords: DNA, interstrand crosslinking, 2'-deoxythioguanosine, disulfide linkage, S-alkyl linkage

Interstrand crosslinking of nucleic acids is a strategy for creating thermally stable duplexes via covalent bond formation, with applications in therapeutics, chemical biology, and nanotechnology.[1] Within the context of oligonucleotide therapeutics, 2'-OMe-RNA featuring a crosslinked duplex at the terminal position demonstrated superior efficiency in inhibiting miRNA activity.[2] This study aims to establish crosslinking reactions using 2'-deoxythioguanine-containing oligonucleotides. By developing different crosslink products, valuable insights into the mechanism and structure-activity relationship toward miRNA targeting will be gained.

We designed oligo DNA duplexes that incorporated 2'-deoxythioguanosines at strategic proximal positions to promote interstrand crosslinking (Figure 1). Our results demonstrated efficient synthesis of disulfide cross-linked DNA duplexes through either chemical oxidation using an oxidizing agent or photo-irradiation employing 365 nm UV-light. Additionally, we synthesized S-alkyl crosslinked strands through thiolate-based dialkylation. In this presentation our molecular design, cross-linking reaction results and experiments verifying the crosslinked products formation will be reported.

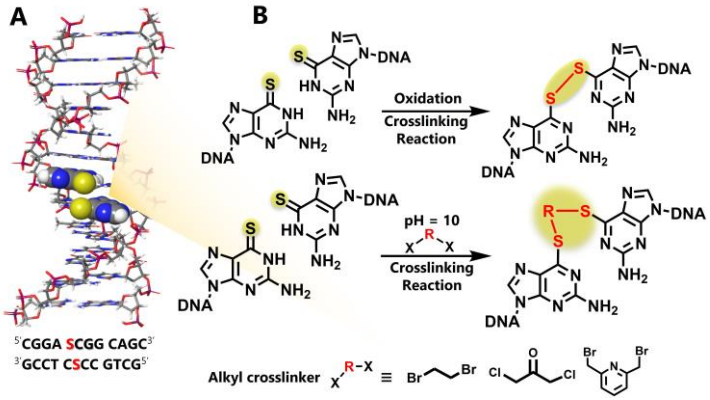

Figure 1. Interstrand crosslinking reaction using 2'-deoxythioguanosine bases. (A) Molecular modeling represents incorporation of 2'-deoxythioguanosine bases (S) in proximity position. CPK models indicate thioguanine bases. (B) Disulfide and S-alkyl crosslinking reactions utilizing 2'-deoxythioguanine bases.

1) K. Onizuka, Y. Yamano, A. M. Abdelhady, F. Nagatsugi, *Org. Biomol. Chem*. **2022**, *20*, 4699.
2) A. M. Abdelhady, Y. Hirano, K. Onizuka, H. Okamura, Y. Komatsu, F. Nagatsugi, *Bioorg. Med. Chem. Lett*. **2021**, *48*, 128257.

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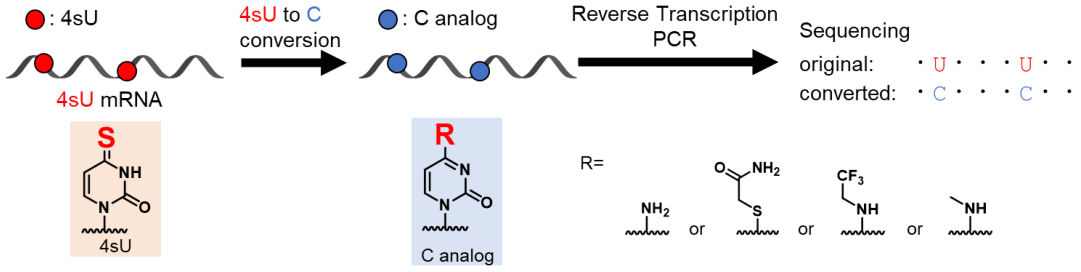
4-チオウリジンからシチジンへの新規化学的塩基変換反応の開発と比較

（名大院理[1]・名大物質科学国際研究センター[2]・CREST, 国立研究開発法人科学技術振興機構[3]・名大 iGCORE, 糖鎖生命コア研究拠点）○大橋 咲南[1]・中村真由[1]・Susit Acharyya[1]・稲垣雅仁[1]・阿部奈保子[1]・木村康明[1]・橋谷文貴[2,3]・阿部洋[1,3,4]
Development and Comparison of 4-Thiouridine to Cytidine Chemical Base Conversion Reaction ([1]*Graduate School of Science, Nagoya University*, [2]*Research Center for Material Science, Nagoya University,* [3]*CREST, Japan Science and Technology Agency,* [4]*Institute for Glyco-core Research (iGCORE), Nagoya University*) ○Sana Ohashi,[1] Mayu Nakamura,[1] Susit Acharyya,[1] Masahito Inagaki,[1] Naoko Abe,[1] Yasuaki Kimura,[1] Fumitaka Hashiya,[2,3] Hiroshi Abe[1,2,3,4]

Examining the RNA synthesis and degradation rate is essential for transcriptome analysis in the cells. For this purpose, 4-thiouridine (4sU), which contains thio-substitution on its 4 position, have been widely used. 4sU can be incorporated into the cells and metabolically labels newly synthesized RNA. While 4sU can be generally recognized as uridine by polymerases, it is known that some chemical base conversion reactions can convert the base recognition from uridine to cytidine. So far, there is no comparison of characteristics among each conversion method. In this research, we compared the three kinds of previously reported reactions: Osmium tetroxide treatment[1)], Iodoacetamide treatment[2)], Sodium periodate treatment[3)], and one newly developed reaction with 2,4-dinitrofluorobenzene.

Keywords : chemical base conversion; RNA modification; bioorganic chemistry; metabolic labeling; sequence analysis

RNA の生合成や分解速度を調べることは、細胞内のトランスクリプトームを解析するうえで重要である。ウリジンの 4 位が硫黄に置換された 4-チオウリジン (4sU) は、この目的でよく使用されている。細胞に取り込まれた 4sU は生合成中の RNA に取り込まれ、RNA を代謝標識する。4sU は通常、酵素によりウリジンと認識されるが、種々の化学的塩基変換反応を行うことにより、その塩基認識をウリジンからシチジンに変換できることが知られている。しかし、各変換反応における特徴の比較はいまだされていない。本研究では、既報の四酸化オスミウム[1)]、ヨードアセトアミド[2)]、過ヨウ素酸ナトリウム[3)]を使用した 3 手法に加え、新たに開発した 2,4-ジニトロフルオロベンゼンを用いた塩基変換法の計 4 種を用い、使用した試薬、変換反応時間、塩基変換効率、逆転写に与える影響を比較した。



1) R. Micura, et al., *Angew. Chem. Int. Ed.* **2017**, 56, 13479.
2) SL. Ameres, et al., *Nat. Methods* **2017**, 14(12), 1198.
3) MD. Simon, et al., *Nat. Methods* **2018**, 15, 221.

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Enzymatic incorporation and extension studies of the unnatural alkynylated purine-pyridazine base pair

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Department of Chemistry, Graduate School of Science, Tohoku University*) ○Wenjue Fan,[1,2] Hidenori Okamura,[1,2] Zhuoxin Dong,[1,2] Giang Hoang Trinh,[1,2] Fumi Nagatsugi,[1,2]

Keywords: Unnatural base pair, DNA, DNA polymerase, Enzymatic incorporation

Expansion of the genetic alphabet by unnatural base pair (UBPs) is considered as one of the most promising methods to enhance the functionality of DNA. Over the past decades, researchers have reported different types of UBPs which exhibit orthogonality in base pairing and enzymatic replication in the presence of canonical base pairs.[1] In our own effort to expand repertoire of UBPs, we have recently designed a novel type of UBPs, named alkynylated purine-pyridazine (**Pu-Pz**) pairs bearing additional hydrogen bonding modules (i.e., pseudo-nucleobases) in the major groove (**Fig. 1**).[2] These unnatural nucleosides formed stable base pairs based on complementarity of the pseudo-nucleobases as revealed by comprehensive T_m measurements, NMR studies and MD simulations. Furthermore, both alkynylated purines and pyridazines exhibited a good selectivity against the canonical nucleobases.

Toward the implementation for the DNA-based biotechnology, in this study, we further investigated the polymerase mediated incorporation of the **Pu-Pz** pairs. We envisioned that the presence of the hydrogen-bond acceptors in **Pu-Pz** pairs may provide the basis for polymerase recognition and that the pseudo-nucleobases would not interfere the formation of the complex with polymerase.[3] To test the hypothesis, the four different triphosphates of the unnatural nucleobases were first synthesized. A screening of DNA polymerases revealed that **Pu-Pz** pairs can be enzymatically incorporated into DNA by using KOD polymerase in full-length elongation (**Fig. 2**). To gain more insight about the selectivity of the base pairing properties of unnatural nucleobases, we also determined the kinetic parameters by single nucleotide insertion.

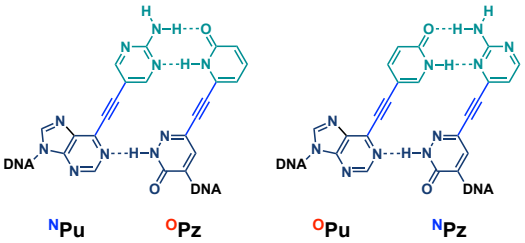

Figure 1 Structures of **Pu-Pz** base pairs.

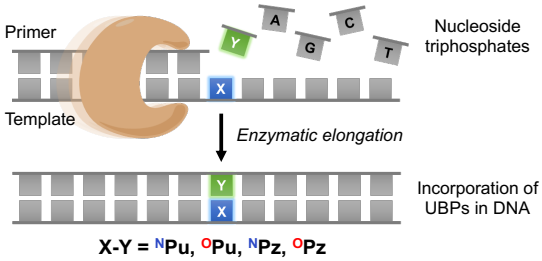

Figure 2 Schematic of full-length elongation.

1) M. Kimoto, I. Hirao, *Chem. Soc. Rev.* **2020**, *49*, 7602-7626. 2) H. Okamura, G. H. Trinh, Z. Dong, Y. Masaki, K. Seio, F. Nagatsugi, *Nucleic Acids Res.* **2022**, *50*, 3042-3055. 3) J. C. Morales, E. T. Kool, *J. Am. Chem. Soc.*, **1999**, *121*, 2323-2324.

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4'-*C*-(*N*-アルキル)アミノエチル修飾チミジンを含むアンチセンスオリゴヌクレオチドの合成及び性質評価

(岐大院自然[1]・岐大応用生物[2]・岐大院連農[3]・東海国立大学機構 COMIT[4]・名大 CIBoG[5]) ○藤木 皓大[1,5], 上野 義仁[1,2,3,4]

Synthesis and properties of antisense oligonucleotides containing 4'-*C*-(*N*-alkyl)aminoethyl thymidines (*[1]Graduate School of Natural Sciences and Technology, Gifu University, [2]Faculty of Applied Biological Sciences, Gifu University, [3]The United Graduate School of Agriculture Science (UGSAS), Gifu University, [4]Center for One Medicine Innovative Translational Research (COMIT), Tokai National Higher Education and Research System, [5]Convolution of Informatics and Biomedical Sciences on Glocal Alliances (CIBoG), Nagoya University*)

Keywords: Nucleic acid therapeutics, Antisense oligonucleotides, Chemical modification, Aminoalkyl-sidechain

Nucleic acid therapeutics are expected to be used for the treatment of some rare diseases. However, they have challenges to be solved, such as biological stability in vivo and cell membrane permeability. To overcome these challenges, chemically modified nucleic acids have been extensively studied. So far, in our group, we have synthesized nucleoside analogs with the aminoalkyl modifications at the 4' position of the sugar moiety[1) 2)]. Then, it was shown that oligonucleotides incorporating these nucleosides improve enzyme resistance properties of the in serum. In this study, we have examined the synthesis of nucleoside analogs with N-alkyl-aminoethyl sidechain, to expand the functions of oligonucleotides. Properties of oligonucleotides with these analogs were compared with those composed of natural nucleosides. It turned out that the modification improved enzyme resistance and altered thermodynamic properties of the oligonucleotides.

核酸医薬は低分子医薬では治癒が困難であった希少疾患に対しても創薬が可能であることから，次世代の治療として期待されている。しかし，核酸医薬は生体内での安定性の向上や細胞膜透過性の改善など，技術的に改善しなくてはいけない多くの課題を抱えている。これらの課題を解決するために化学修飾を施した人工核酸の開発研究が広く行なわれている。当研究室では，これまで糖部 4'位へのアミノアルキル修飾を行ったヌクレオシドを合成し，これを組み込んだオリゴヌクレオチドが生体内での酵素耐性を向上させることを見出している[1) 2)]。本研究で，オリゴヌクレオチドの更なる機能向上を目指し，アミノ基の先に更にアルキル鎖を伸長させたヌクレオシドアナログの合成を実施した。その結果，これらアナログを導入したオリゴヌクレオチドは，天然のヌクレオチドからなるオリゴヌクレオチドと比較し，酵素耐性の向上及び熱力学的な性質の変化することが明らかとなった。

1) Ueda, H.; Ueno, Y., *Bioorg. Med. Chem.,* **2022**, 60, 116690
2) Koizumi, K.; Ueno, Y. *et al*, *Bioorg. Med. Chem.*, **2018**, 26, 3521– 3534.

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4'-*C*-アミノエトキシ-2'-*O*-メチル-5-プロピニルウリジンの合成とアンチセンス核酸への応用

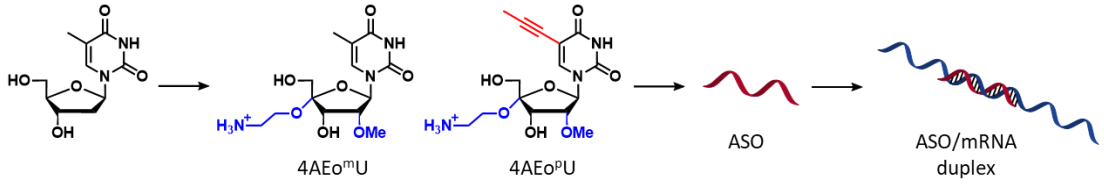
(岐大院連農[1]・岐大応用生物[2]・岐大院自然[3]・名大 CIBoG[4]・東海国立大学機構 COMIT[5]) ○ZHOU YUJUN[1,4]・上野 義仁[1,2,3,5]

Synthesis of 4′-*C*-aminoethoxy-2′-*O*-methyl-5-propynyluridine and its application for antisense oligonucleotide ([1]*The United Graduate School of Agriculture Science (UGSAS), Gifu University*, [2]*Faculty of Applied Biological Sciences, Gifu University*, [3]*Graduate School of Natural Sciences and Technology, Gifu University*, [4]*Convolution of Informatics and Biomedical Sciences on Glocal Alliances (CIBoG), Nagoya University*, [5]*Center for One Medicine Innovative Translational Research (COMIT), Tokai National Higher Education and Research System*) ○Yujun Zhou[1,4], Yoshihito Ueno[1,2,3,5]

4'-*C*-Aminoethoxy-2′-*O*-methyl (4AEo) modification, designed by our group, makes it feasible to improve nuclease resistance, while remaining almost the same gene repression ability as that of the natural type. In this study, in order to expand the application of 4AEo modification for antisense oligonucleotide (ASO), novel synthesis and evaluation of 5-propynyluridine analog (4AEo^{P}U) which was reported to further improve the thermal stability of ASO/RNA duplexes were completed. As a result, oligonucleotide containing 4AEo^{P}U showed superior physicochemical and biochemical properties compared to the native ASOs and might be a potential candidate for future ASO application.

Keywords : Oligonucleotide therapeutic; Antisense oligonucleotide; Chemical modification; Amino alkyl group; Propynyl group

これまでに我々の研究室では、糖部修飾ヌクレオシドアナログである 4′-*C*-アミノエトキシ-2′-*O*-メチルウリジン（4AEoU）を導入した siRNA が高い酵素耐性を有し、天然型と同程度に優れた遺伝子発現抑制能を示すことを見出している[1)]。しかし、当修飾ヌクレオシドの ASO における有用性はまだ明らかになっていない。本研究では、ASO への応用拡大および ASO/RNA 二本鎖の熱的安定性のさらなる向上を期待し、4AEo の塩基部 5-位にプロピニル基を導入した 4′-*C*-アミノエトキシ-2′-*O*-メチル-5-プロピニルウリジン（4AEo^{P}U）を新規に合成し、ASO における性質評価を行った。その結果、4AEo^{P}U は天然と比べて優れたヌクレアーゼ耐性を有し、*E. coli* 由来の RNase H 切断に影響を与えないことが明らかになった。さらに、50%融解温度測定により ASO/RNA 二本鎖形成能を評価したところ、4AEo^{m}U は天然と比べて二重鎖を不安定化したのに対し、4AEo^{P}U は著しく高い熱的安定化能を示した。



1) R. Tsukimura, R. Kajino, Y. Zhou, A. Chandela, Y. Ueno, *Results Chem.*, 3, **2021**, 100231.

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日本化学会 第104春季年会 (2024)

5′位を増炭したスルホンアミド骨格を有するチミジンダイマーの合成と物性評価

(東工大生命理工[1])○立花 茂載[1]、大西 里絵[1]、正木 慶昭[1]、清尾 康志[1]

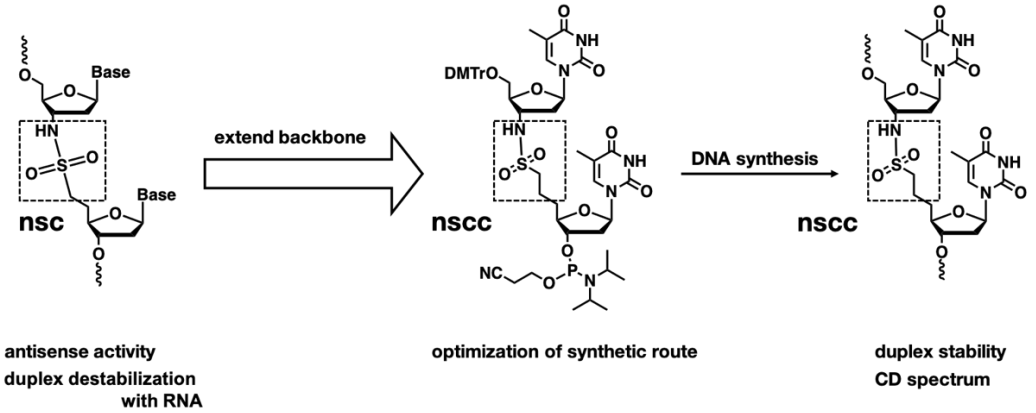
Synthesis and evaluation of a thymidine dimer with an extended backbone at five prime position ([1]*Graduate School of Life Science and Technology, Tokyo Institute of Technology*) ○ Shigetoshi Tachibana[1], Rie Ohnishi[1], Yoshiaki Masaki[1], Kohji Seio[1]

The widely used phosphorothioate backbone (PS backbone) in antisense nucleic acids has challenges such as toxicity from protein interactions and the presence of mixtures of diastereomers due to asymmetric centers. In order to overcome these drawbacks, we focused on nucleic acids with a sulfonamide backbone (nsc backbone). The nsc backbone, being uncharged and lacking asymmetric centers, has possibility to express good property. However, it is reported that nsc backbone destabilizes duplex formation with RNA. Drawing inspiration from studies on another backbone, we designed and synthesized nsc nucleic acids with a one-carbon increased backbone (nscc backbone). In this process, we established a mild synthetic pathway to avoid unstable intermediates. Including this optimization, we report the evaluation of duplex stability, CD spectra, and a comparison with nsc nucleic acids.

Keywords : nucleic acid therapeutics, antisense nucleic acid

アンチセンス核酸に広く使用されるホスホロチオエート骨格 (PS 骨格)は、タンパク質との相互作用による毒性の発現や、不斉中心由来の立体異性体の混在という課題が存在する。この欠点を克服するため、我々はスルホンアミド骨格 (nsc 骨格)を有する核酸に注目した。スルホンアミド骨格は無電荷かつ不斉中心が存在しないため、PS 骨格の問題を解決できる可能性がある。その一方で、nsc 骨格は RNA との二重鎖形成が不安定化するという課題が報告されている。

この課題は別の骨格でも研究されており、骨格を増炭することにより RNA との二重鎖形成を安定化させる効果が報告されている。この先行研究を基に、本研究では一炭素増炭した骨格 (nscc 骨格)を有する核酸を設計・合成した。その際、合成経路の検討を行い、不安定な中間体を経由しない穏和な合成経路の確立に成功した。そして、合成した化合物をオリゴ核酸に導入し、二重鎖安定性や CD スペクトル測定によって立体構造を評価、さらに従来の nsc 骨格を有する核酸と比較を行ったため報告する。



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日本化学会 第104春季年会 (2024)

2´水酸基にスルホンアミド修飾またはスルホネート修飾を有する5-メチルウリジン誘導体の合成および二重鎖形成能の評価

（東工大生命理工[1]）○瀧川 駿太朗[1]・友利　貴人[1]・植草 宏哉[1]・正木 慶昭[1]・清尾 康志[1]

Synthesis of 5-methyluridine derivatives with sulfonamide or sulfonate modifications on the 2′ hydroxyl group and evaluation of their ability to form duplex chains ([1]*Sch. Life Sci. Tech., Tokyo Tech.*) ○Shuntaro Takigawa[1], Takahito Tomori[1], Koya Uekusa[1], Yoshiaki Masaki[1], Kohji Seio[1]

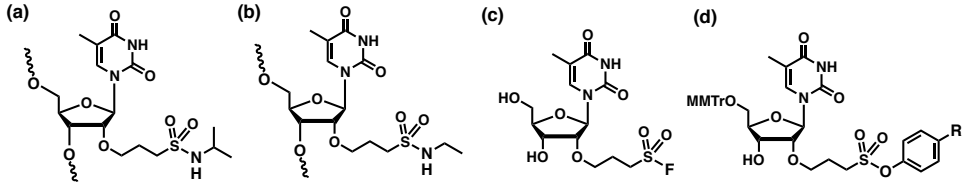
Antisense nucleic acids, a type of nucleic acid medicine, are used as therapeutic agents that target RNA. Antisense nucleic acids are designed to improve nuclease resistance and duplex stability by introducing a modified nucleic acid, so that they can more easily exert their medicinal effects. In this study, we focused on modified nucleic acids having a sulfonamide structure in the 2′ hydroxyl group as a modified nucleic acid to be introduced into antisense nucleic acids. Therefore, we synthesized two kinds (a, b) of 5-methyluridine derivatives having a sulfonamide structure at the 2′ hydroxyl group. The two synthesized modified nucleic acids were introduced into oligonucleotides, and their ability to form duplexes was evaluated by measuring the duplex melting temperature.

We also synthesized a 5-methyluridine derivative (c) with a sulfonyl fluoride modification at the 2′ hydroxyl group. Using the reactivity of sulfonyl fluoride, we succeeded in synthesizing a modified nucleic acid (d) with several sulfonate modifications by reacting it with phenol.

Keywords : Antisense oligonucleotides, Duplex melting temperature, Modified nucleic acid, Sulfonamide modification, Sulfonyl fluoride modification

核酸医薬品の一種のアンチセンス核酸は、RNA を標的とした治療薬として用いられる。アンチセンス核酸は修飾核酸の導入により核酸分解酵素耐性や二重鎖安定性などを向上させ、薬効をより発揮しやすいように工夫されている。本研究では、アンチセンス核酸に導入する修飾核酸として2´水酸基にスルホンアミド構造を有する修飾核酸に着目した。そこで、2´水酸基にスルホンアミド構造を持つ 5-メチルウリジン誘導体を２種類(a,b)合成した。合成した２種類の修飾核酸をオリゴヌクレオチドに導入し、二重鎖融解温度を測定することにより二重鎖形成能を評価した。

また、2´水酸基にスルホニルフルオリド修飾を有する 5-メチルウリジン誘導体(c)を合成した。スルホニルフルオリドの反応性を利用し、フェノールを反応させることで数種類のスルホネート修飾を持った修飾核酸(d)の合成に成功した。



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日本化学会 第104春季年会 (2024)

置換基導入した 2′-*O*, 3′-*C* 架橋アラビノフラノシルチミンを含むオリゴヌクレオチドの合成と性質

（東工大 生命理工 [1]）○田平 彩乃 [1]・若月 駿介 [1]・清尾 康志 [1]・正木 慶昭 [1]
Synthesis and properties of oligonucleotides having substituted 2′-*O*, 3′-*C*-bridged [3.2.0]bicycloarabinonucleoside ([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Ayano Tabira,[1] Shunsuke Wakatsuki,[1] Kohji Seio,[1] Yoshiaki Masaki[1]

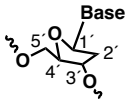
Sugar conformation of nucleotides is one of the key features that change the affinity to DNA or RNA and affinity of nucleic acid-protein interactions. Also, substitutions to a molecule are important to change properties of oligonucleotide therapeutics for development of efficient and safe therapeutic oligonucleotides.

In this study, we focused on 2′-*O*, 3′-*C*-bridged arabinofuranosyl thymine, which fixes the sugar to the O4′-*endo* conformation[1)], and we attempted to introduce a substitution to the 6′ position. We successfully synthesized 2′-*O*, 3′-*C*-bridged arabinofuranosyl thymine modified with a methoxy group as the substitution and incorporated it into oligonucleotides. The details will be reported.

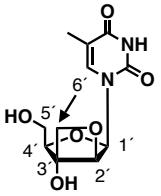
Keywords : Chemical modified nucleosides, sugar modification, fixed sugar conformation

核酸糖部の構造によって DNA や RNA への親和性や核酸-タンパク質の相互作用が変化することが知られている。また、核酸医薬の開発においては置換基を導入することで医薬品の性質を変化させ、安全性や効能向上などを志向した修飾が可能である。

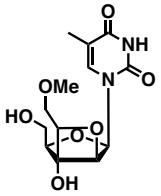
本研究では、核酸糖部を O4′-*endo* 構造に固定した 2′-*O*, 3′-*C* 架橋アラビノフラノシルチミン [1)]に着目し、その 6′位への置換基を導入することを検討した。ビシクロ環構築を鍵反応とし、置換基としてメトキシメチル基を導入した 2′-*O*, 3′-*C* 架橋アラビノフラノシルチミン誘導体の合成を達成した。また本誘導体を含むオリゴヌクレオチドの合成に成功した。その詳細について報告する。



O4′-*endo*構造



2′-*O*, 3′-*C*架橋アラビノフラノシルチミン
([3.2.0]bcT)



メトキシメチル化
2′-*O*, 3′-*C*架橋アラビノフラノシルチミン
(MOM[3.2.0]bcT)

1) Christensen, N. K.; Petersen, M.; Nielsen, P.; Jacobsen, J. P.; Olsen, C. E.; Wengel, J. *J. Am. Chem. Soc.* **1998**, *120*, 5458–5463.

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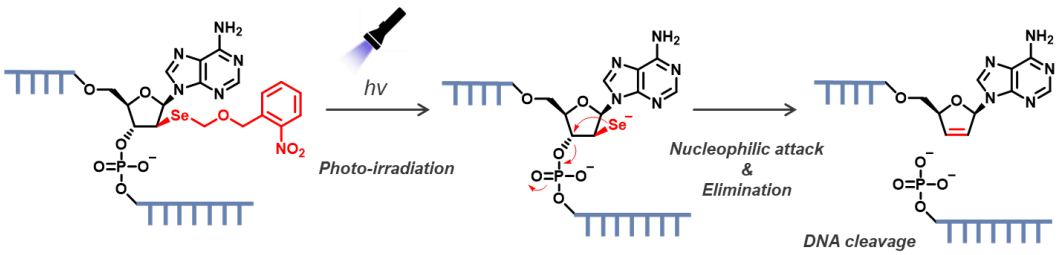
細胞内遺伝子発現スイッチングを志向した光分解性セレン修飾核酸の合成と評価

(名大院理[1]・崇城大薬[2]・名大物質科学国際センター[3]・JST-CREST[4]・iGCORE[5])
○吉田祐希[1]・平岡陽花[1]・村瀬裕貴[1,2]・阿部奈保子[1]・橋谷文貴[3]・阿部洋[1,4,5]
Synthesis and Evaluation of Photolabile Selenium-Modified Nucleic Acid for Intracellular Gene Expression Switching. (*[1]Graduate School of Science, Nagoya University, [2]Department of Pharmacy, Sojo University, [3]Research Center for Materials Science, Nagoya University, [4]JST-CREST, [5]Institute for Glyco-core Research*) ○ Yuki Yoshida[1], Haruka Hiraoka[1], Hirotaka Murase[2], Naoko Abe[1], Fumitaka Hashiya[3], Hiroshi Abe[1, 4, 5]

Synthesis of long-stranded DNA that encodes multiple genes for specific functions is an important technology in synthetic biology and can be applied to the development of gene therapy vectors that compensate for the loss of biological functions in diseases. Since the limit of elongation by PCR, a common method of double-stranded DNA synthesis, is several tens of thousands of base pairs, it is necessary to ligate multiple PCR products step by step to synthesize longer strands of DNA.[1)] However, in this method, the length and sequence of the sticky end are limited by the properties of the enzyme, making it difficult to control the reaction, such as the efficiency and specificity of the ligation. Therefore, we developed a technique to form sticky ends of arbitrary length and sequence for double-strand DNA products after PCR by using post-cleavage PCR primers containing photolabile selenium modification.
Keywords : modified nucleic acid; photolabile modification; DNA ligation

特定の機能を担う遺伝子群を複数コードするような長鎖 DNA の合成は合成生物学において重要な技術であると共に、疾患における生体機能の欠失を補う遺伝子治療ベクターの開発にも応用できる。一般的な二本鎖 DNA 合成法である PCR による伸長では数万塩基対程度が限界であるため、より長い長鎖 DNA の合成には、複数の PCR 産物を段階的に連結する必要がある。酵素反応により接着末端を形成させ連結させる方法が現在一般的に用いられているが、この方法では接着末端の長さや配列が酵素の性質により制限されており、連結効率や特異性など反応の制御が困難となっている[1)]。そこで我々の研究室では光分解性セレン修飾を含むポスト切断 PCR プライマーを用いることで、PCR 後の二本鎖 DNA 産物に対して任意の長さおよび配列の接着末端を形成する技術を開発した。



1). Carola Engler, Romy Kandzia, Sylvestre Marillonnet, *PLOS ONE*, **2008**, *3*, e3647.

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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 IV - ジャンクション配列の複合体安定性･切断効率への影響 -

（東北大多元研[1]・東北大院医[2]・長崎大院医歯薬[3]）○五十嵐 優希[1]・堀内 結翔[1]・松本 光代[1,2]・荒木 保幸[1]・西嶋 政樹[1]・三瓶 悠[3]・山吉 麻子[3]・五十嵐 和彦[2]・和田 健彦[1*]

A Construction of Chimeric Artificial Nucleic Acids (CANA) forward Inhibition of Pancreatic Cancer Transcription Factor BACH1 Ⅰ V: - Effects of Junction Position on Complex Stability and Cleavage Efficiency - ([1]*IMRAM, Tohoku Univ.*, [2]*Grad. Sch. Medicine., Tohoku Univ,* [3]*Grad. Sch. Biomed. Sci., Nagasaki Univ.*)○Yuki Igarashi,[1] Yuto Horiuti,[1] Mitsuyo Matsumoto,[1,2] Yasuyuki Araki,[1] Masaki Nishijima,[1] Yu Mikame,[3] Asako Yamayoshi,[3] Kazuhiko Igarashi,[2] Takehiko Wada[1*]

In order to apply oligonucleotide therapeutics as promising next-generation candidates of molecularly targeted pharmaceuticals, the following three issues should be improved: I) Off-target effects, II) Low cellular uptake capability, and Ⅲ) Low therapeutic efficacy mainly due to extremely low intracellular concentrations. We have proposed and demonstrated a novel design strategy to improve these issues by enhancing the RNase H-mediated target RNA cleavage efficiency by the chimeric artificial nucleic acids (CANAs), which consist of 5'-terminus modified DNA moiety conjugated with non-ionic peptide backbone artificial nucleic acid moiety such as PNA. In this study, the mRNA of BACH1, which was discovered by Prof. Igarashi and colleagues to play an important role in the malignant transformation and metastasis of pancreatic cancer, was set as the target RNA and the hybrid stabilities and RNase H-mediated cleavage efficiency of the target mRNA were investigated.

Keywords : Chimera Artificial Nucleic Acid; Oligonucleotide Therapeutics; Pancreatic Cancer; Bach1; Catalytic cleavage of target RNA

次世代分子標的薬モダリティーとして期待される核酸医薬の実用化には“オフターゲット効果”と“細胞内極低濃度に起因する低治療効果向上”が喫緊の解決課題である。我々は両課題解決を目指し、RNase H を活用した標的 RNA 触媒的切断戦略に焦点を当て、標的 RNA の位置選択的切断による触媒回転数の向上を実現し得る新規核酸医薬としてリン酸アニオン骨格 DNA/LNA(架橋型核酸)と PNA 等アミド骨格人工核酸を融合したキメラ人工核酸(CANA：図 1)を提案し、その有効性を報告してきた。

本研究では、五十嵐らが見出した膵臓癌転移や悪性化に関与する転写因子 BACH1 の mRNA 配列を標的として設定し、膵臓癌悪性化抑制に資する CANA の構造設計･合成と、複合体安定性や RNase H を活用した触媒的 RNA 切断機能に対するジャンクション部位の影響等、*in vitro* 特性ならびに機能について検討した結果を報告する。

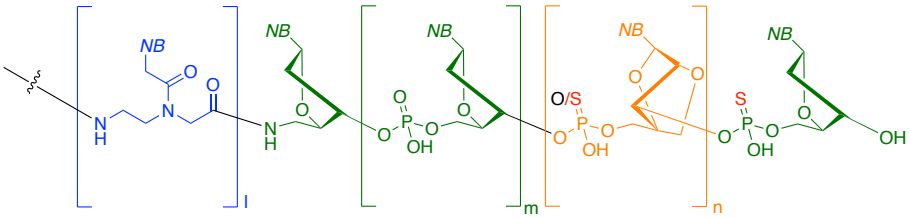

Fig.1 Structure of Chimeric Artificial Nucleic Acid (CANA).

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

Wed. Mar 20, 2024 9:00 AM - 11:40 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:40 AM UTC
H934(934, Bldg. 9 [3F])

[H934-3am] 17. Biofunctional Chemistry, Biotechnology

Chair: Takahiro Nakama, Tsuyoshi Takahashi

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[H934-3am-01]
Synthesis of amino acid from ammonia and pyruvate by visible-light irradiation using photo/biocatalyst

○Kyosuke Yamada[1], Yutaka Amao[2] (1. Osaka City University, 2. Osaka Metropolitan University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[H934-3am-02]
Effect of catalytic reactions resulting from the network formation of cascade enzymes

○Aoi Mameuda[1], Masahiro Takinoue[2], Koki Kamiya[1] (1. Graduate School of Science and Technology, Gunma University, 2. Department of Computer Science, School of Computing, Tokyo Institute of Technology)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[H934-3am-03]
NMR analysis of dimerization of amyloid β hydrophobic fragments by encapsulation in a giant spherical metallo-cage

○Yuta Onodera[1], Erina Takeuchi, Takahiro Nakama[1], Maho Yagi[2], Daishi Fujita[3], Koichi Kato[2], Makoto Fujita[1,2,4] (1. Graduate School of Engineering, The University of Tokyo , 2. Institute for Molecular Science, 3. iCeMS, Kyoto University, 4. Institutes for Advanced Study, The University of Tokyo)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[H934-3am-04]
NMR structural analysis of protein–lipid interactions by confinement in isolated space of spherical metallo-cages

○Miri Tadokoro[1], Takahiro Nakama[1], Hongkun Liu[1], Maho Yagi-Utsumi[2,3], Koichi Kato[2,3], Makoto Fujita[1,3,4] (1. Graduate School of Engineering, The University of Tokyo , 2. Graduate School of Pharmaceutical Sciences, Nagoya City University, 3. Institute for Molecular Science (IMS), 4. UTIAS, The University of Tokyo)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[H934-3am-05]
Protein Refolding by Releasing from Nanopores

○Ko Shinohara[1], Nobuhiko Hosono[1,2], Takashi Uemura[1,2] (1. Sch. of Eng., The Univ. of Tokyo, 2. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC

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[H934-3am-06]

Analysis of the hierarchical structure of the pH-responsive piston protein assembly

○Souta Masumura[1], Koki Date[1], Thuc Toan PHAM[1], Xin Li[1], Kosuke Kikuchi[1], Takafumi Ueno[1] (1. School of Life Science and Technology, Tokyo Institute of Technology)

Japanese

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

[H934-3am-07]

Investigation of Denaturation and Aggregation Behavior of Proteins under Microwave Irradiation

○Mizuki Yoshihara[1], Yuna Sakakibara[1], Ma Yunting[2], Yoshihiro Sasaki[2], Eito Fukushima[1], Haruya Yamaguchi[1], Hikaru Takaya[1] (1. Grad. Sch. of Teikyo Univ. of Sci., 2. Grad. Sch. of Eng., Kyoto Univ)

Japanese

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

[H934-3am-08]

Analysis of the Effect of Phosphorylation on HP1α Dynamics by ESR spectroscopy

○Toshiki Takei[1], Kohei Muraoka[1], Toru Kawakami[1], Toshiaki Arata[2], Isao Suetake[3], Hironobu Hojo[1] (1. Institute for Protein Research, Osaka University, 2. Osaka Metropolitan University, 3. Nakamura Gakuen Universtiy)

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

[H934-3am-09]

Evaluation of protein splicing activities of cysteine-less intein from hyperthermophiles

○Kanta Katagiri[1], Tsuyoshi Takahashi[1] (1. Gunma University)

Japanese

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

[H934-3am-10]

Selection of proteins that recognize a specific peptide sequence using engineered split intein

○Momoka Shimizu[1], Tsuyoshi Takahashi[1] (1. The Univ. of Gunma)

Japanese

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

[H934-3am-11]

Analysis of interactions between glycopeptides and sugar-recognizing F-box protein Fbs2

○Midori Aikyo[1], Haruka Inoue[1], Satoshi Takahashi[1], Nozomi Ishii[1], Ichiro Matsuo[1], Yukiko Yoshida[2], Tadashi Suzuki[3], Tsuyoshi Takahashi[1] (1. The Univ. of Gunma, 2. Tokyo Metropolitan Institute of Medical Science, 3. RIKEN)

Japanese

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

[H934-3am-12]

Selection of peptides that bind to Keap1 using split intein and reconstitution of kanamycin kinase

○Kana Nobusawa[1], Tsuyoshi Takahashi[1] (1. Gunma University)

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Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[H934-3am-13]
Construction of cyclized Renilla Luciferase using the Catcher/Tag system
○Makoto Ichikawa[1], Kei Nishida[1], Jun Yamaguchi[1], Eiry Kobatake[1], Masayasu Mie[1] (1. Tokyo Institute of Technology)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[H934-3am-14]
Modification of cholesterol-binding proteins by polymer grafting
○Tianjian Ma[1], Kei Nishida[1], Ikumi Sato[1], Masayasu Mie[1], Eiry Kobatake[1] (1. Tokyo Institute of Technology)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[H934-3am-15]
Construction of high-secretion expression system for albumin using Pichia pastoris
○Mizuki Komori[1], Nobutaka Fujieda[2,1], Yoshitsugu Morita[2] (1. Osaka Pref. Univ., 2. Osaka Metro. Univ.)

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生体触媒を用いた可視光照射によるアンモニアおよびピルビン酸からアミノ酸の合成

（大阪市大[1]・大阪公大[2]）○山田 恭佑[1]・天尾 豊[2]
Synthesis of amino acid from ammonia and pyruvate by visible-light irradiation using photo/biocatalyst ([1]*Osaka City University*, [2]*Osaka Metropolitan University*)
○Kyosuke Yamada,[1] Yutaka Amao[2]

Previous studies on the visible-light driven organic synthesis have mainly focused on building C-C bonds to synthesize organic compounds that are raw materials for biodegradable plastics. However, organic nitrogen compounds are necessary to synthesize nylon-based plastics. Amino acids are polymerized or copolymerized to produce biodegradable nylon. Therefore, this study aims to synthesize an amino acid, alanine, based on building C-N bonds from ammonia and pyruvate using visible light as driving force.

It has been reported that NAD^+ can be photoreduced by a system consisting of an electron donor, a photosensitizer, and an electron carrier[1]. By newly introducing a biocatalyst, L-alanine dehydrogenase (AlaDH) into this NADH regeneration system, we succeeded in developing a visible-light driven alanine production (Figure 1). We compared a visible-light irradiation condition and a dark condition and discussed a rate-determining step of this system.

Keywords : Enzyme; Visible-light irradiation; C-N bonds

これまでの可視光駆動による有機物合成は、生分解性プラスチックの原料となる化合物を合成するために、主に C-C 結合の形成に注目していた。しかしながら、ナイロン系のプラスチックを合成するためには有機窒素化合物が原料として必要不可欠である。有機窒素化合物であるアミノ酸は重合や共重合すると、生分解性ナイロンとなる。これらを背景に本研究では、アンモニアとピルビン酸から可視光をエネルギー源として、C-N 結合形成に基づく、アミノ酸であるアラニンの合成を試みた。

電子供与体、可視光増感剤および電子伝達体からなる系により NAD^+を NADH に光還元できることが報告されている [1)]。この NADH 再生系に新たに生体触媒である L-アラニン脱水素酵素 (AlaDH) を導入することにより、可視光駆動型アラニン合成系の構築に成功した (図 1) 。この合成系について、可視光照射条件と非照射条件の比較や律速段階について考察した。

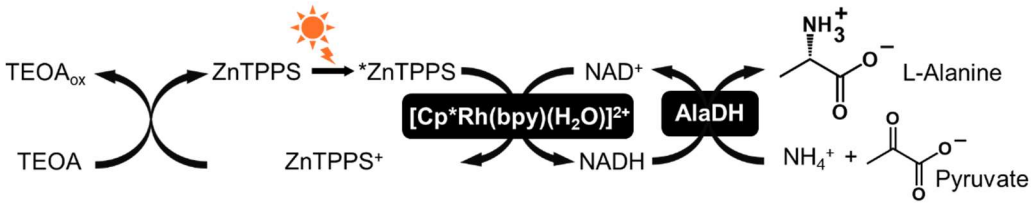

図 1. アンモニアとピルビン酸からの可視光駆動型アラニン合成系
TEOA: トリエタノールアミン、ZnTPPS: 亜鉛テトラフェニルポルフィリンテトラスルフォナート

1) E. Steckhan, *et al*., *Angew. Chem. Int. Ed.* **1990**, *29*, 388.

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酵素のネットワーク構造形成がもたらすカスケード反応への影響

（群馬大院理工 [1]・東工大情報理工学院 [2]）○豆生田 葵衣 [1]・瀧ノ上 正浩 [2]・神谷 厚輝 [1]

Effect of catalytic reactions resulting from the network formation of cascade enzymes

([1]*Graduate School of Science and Technology, Gunma University*, [2]*Department of Computer Science, School of Computing, Tokyo Institute of Technology*) ○Aoi Mameuda[1], Masahiro Takinoue[2], Koki Kamiya[1]

The proximity of enzymes in a cytoplasm causes efficient biocatalytic cascades. In our previous studies, we have controlled enzymatic reactions using reversible control of the network formation and dispersion of three enzymes (βGal, GOx, and HRP) via triple-branched DNAs. Here, the increase of the amylose degradation reaction catalyzed by β-amylase, maltase, and glucose oxidase was investigated by the network formation via triple-branched DNAs. Finally, the differences in the network formation of the enzymes and the reaction efficiency between the two different cascade reactions were discussed.

Keywords : Enzyme; ssDNA; Bioconjugation; DNA computing

細胞質内では酵素同士の近接に伴い，酵素が触媒する代謝反応は効率よく進む。細胞内環境の再現に向けて酵素同士を近接する様々な試みが行われているが，化学結合を介して高分子鎖によって物理的に近接させる方法[1]では，酵素同士の近接と分離における自由な制御は困難である。そこで，我々は高効率かつ制御可能なバイオリアクタの創成を目標とし，温度や pH，塩濃度変化を例とした外部刺激に応答して一本鎖への分離と二本鎖の形成を繰り返す三又構造を有する DNA を介して三種酵素(βGal, GOx，HRP)の可逆的な近接と分離を利用した酵素反応制御に成功した[2]。

今回は，β-アミラーゼ，マルターゼ，グルコースオキシダーゼの三種の酵素が触媒するアミロース分解反応を制御し，二つのカスケード反応から酵素の近接・分離と反応効率の関係や本システムの汎用性について議論する。まず，三種 miRNA 非存在下で三又構造を形成し，三種 miRNA 存在下で分離する DNA(DNA1, DNA2, DNA3)を介して，三種の酵素が近接した酵素-DNA 複合体ネットワークを作製した(Fig.1)。三種酵素が触媒するアミロース分解反応において，酵素-DNA 複合体ネットワークでは一定時間経過後の最終生成物の産生量が非修飾酵素と比較して増加した。

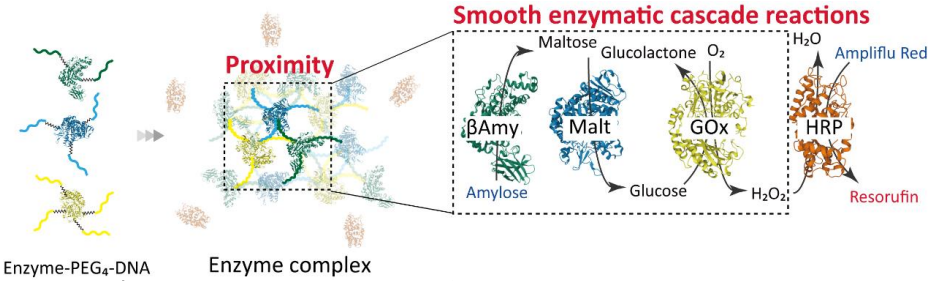

Fig.1 DNAを介したβAmy, Malt, GOxのネットワーク構造形成とカスケード反応

1. Grotzky, A., Nauser, T., Erdogan, H., Schlüter, A. D. & Walde, P. *J. Am. Chem. Soc.* **134**, 11392–11395 (2012).
2. Mameuda, A., Takinoue, M. & Kamiya, K. *Anal. Chem.* **95**, 9548–9554 (2023).

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巨大球状錯体への包接によるアミロイドβ疎水性断片の二量化の NMR 解析

（東大院工[1]・分子研[2]・京大 iCeMS[3]・東大国際高等研[4]）○小野寺悠太[1]・竹内絵里奈[1]・中間貴寛[1]・矢木真穂[2]・藤田大士[3]・加藤晃一[2]・藤田誠[1,2,4]

NMR analysis of dimerization of amyloid β hydrophobic fragments by encapsulation in a giant spherical metallo-cage ([1]*Graduate School of Engineering, the University of Tokyo*, [2]*Institute for Molecular Science,* [3]*iCeMS, Kyoto University,* [4]*UTIAS*) ○Yuta Onodera,[1] Erina Takeuchi,[1] Takahiro Nakama,[1] Maho Yagi-Utsumi,[2] Daishi Fujita,[3] Koichi Kato,[2] Fujita Makoto[1,2,4]

The analysis of initial aggregates of amyloid β (Aβ) proteins, which have been implicated in the neurotoxicity of Alzheimer's disease, is challenging due to their transient natures during the aggregation process. We have previously analyzed the monomeric structures of unstable, aggregating proteins by encapsulation in $M_{12}L_{24}$ giant spherical complexes formed by the self-assembly of bis(pyridine) ligands (L) and Pd^{2+} ions (M).[1,2] In this study, we conducted an NMR analysis of the dimerization of Aβ hydrophobic fragments by encapsulation in $M_{12}L_{24}$ metallo-cages (**Fig. 1**). Two ^{13}C, ^{15}N-labelled Aβ fragments $Aβ_{16-23}$ (KLVFFAED) were encapsulated in an $M_{12}L_{24}$ cage through the condensation with a ligand, thereby suppressing the random Aβ aggregation. Minor peaks appearing in the ^{1}H-^{15}N HSQC NMR spectra suggest the desymmetrization of two $Aβ_{16-23}$ peptides upon their association. The dimerized structure was analyzed in detail by three-dimensional and NOESY NMR measurements.

Keywords : Amyloid β; Protein encapsulation; Self-assembly; Alzheimer's disease; NMR structural analysis

アルツハイマー型認知症における神経毒性の要因とされるアミロイド β (Aβ)タンパク質の初期会合体は、凝集過程における過渡的な中間体であるためにその構造解析は困難である。当研究室では、ビスピリジン配位子(L)と Pd^{2+}イオン(M)の自己集合で形成される $M_{12}L_{24}$ 巨大球状錯体にタンパク質を包接し、凝集性の不安定な変性タンパク質の構造を解析してきた[1,2]。本研究では、$M_{12}L_{24}$ 錯体に Aβ 疎水性断片 2 分子を包接して錯体内での二量化を NMR で解析した(**Fig. 1**)。^{13}C, ^{15}N 標識 Aβ 疎水性断片 $Aβ_{16-23}$ (KLVFFAED)を 2 つ縮合させた配位子を合成し、$Aβ_{16-23}$ 2 分子を球状錯体へ包接することで Aβ 断片の無秩序な凝集を抑制した。^{1}H-^{15}N HSQC NMR スペクトルでは、$Aβ_{16-23}$ の会合に伴う非対称化を示唆するマイナーピークの出現が観測された。その Aβ 会合構造を三次元 NMR、NOESY 測定により詳細に解析した。

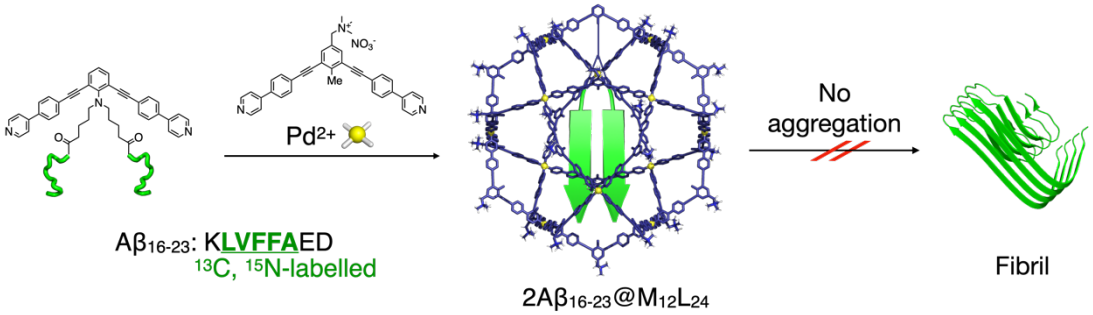

Fig. 1 NMR analysis of dimerization of Aβ fragment peptides ($Aβ_{16-23}$, KLVFFAED) by inhibition of Aβ aggregation via encapsulation in a self-assembled $M_{12}L_{24}$ spherical complex

1) D. Fujita, *et al., Chem* **2021**, *7*, 2672–2683. 2) T. Nakama, *et al., Chem. Sci.* **2023**, *14*, 2910–2914.

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球状錯体の孤立空間への閉じ込めによるタンパク質－脂質相互作用の NMR 構造解析

（東大院工 [1]・名市大院薬 [2]・分子研 [3]・東大国際高等研 [4]）○田所 美璃 [1]・中間 貴寛 [1]・劉 鴻琨 [1]・矢木 真穂 [2,3]・加藤 晃一 [2,3]・藤田 誠 [1,3,4]

NMR structural analysis of protein–lipid interactions by confinement within isolated space of metallo-cages ([1]*Graduate School of Engineering, The University of Tokyo,* [2]*Graduate School of Pharmaceutical Sciences, Nagoya City University,* [3]*Institute for Molecular Science (IMS),* [4]*UTIAS, The University of Tokyo*) ○Miri Tadokoro,[1] Takahiro Nakama,[1] Liu Hongkun,[1] Maho Yagi-Utsumi,[2,3] Koichi Kato,[2,3] Makoto Fujita[1,3,4]

We have previously demonstrated that weak protein–ligand interactions can be induced by the proximity effect of co-encapsulation in an isolated narrow space of a spherical metallo-cage formed by the self-assembly of bis(pyridine) and Pd(II) ions[1)]. In this study, we performed an NMR structural analysis of weak, dynamic protein–lipid interactions by confinement within the cage. A lipid-hydrolyzing enzyme and lipid molecules were co-encapsulated in the cage by condensation with bis(pyridine) (Fig. 1). ^{1}H–^{15}N HSQC NMR spectra of the caged protein showed an attenuation of the peak intensity when encapsulated with lipids. Peak assignment by 3D NMR revealed that the attenuation occurred at residues involved in the catalytic site to which a lipid is expected to bind. The results indicate that the encapsulation in the cage allows the analysis of weak protein–lipid interactions that cannot be observed in the free state.

Keywords : Protein encapsulation; Self-assembly; Protein–ligand interaction; Protein structural analysis; NMR

以前我々は、配位子と Pd(II)イオンの自己集合で形成する球状錯体の狭い孤立空間へ共包接することで、近接効果によりタンパク質―リガンド間の弱い相互作用を誘起できることを実証した [1)]。本研究では、この錯体孤立空間への閉じ込めを活用し、弱く動的なタンパク質―脂質相互作用の NMR 構造解析を行った。脂質を基質とする酵素と脂質分子をそれぞれ配位子に縮合することで球状錯体に共包接した(Fig. 1)。この包接タンパク質の ^{1}H–^{15}N HSQC NMR を測定したところ、脂質包接時にピーク強度の減衰が観測された。3 次元 NMR での帰属により、脂質が結合するとされる活性部位付近の残基でピークの減衰が生じたことが分かった。したがって、遊離の脂質との間には観測できない弱い相互作用を共包接により構造的に解析できることが示された。

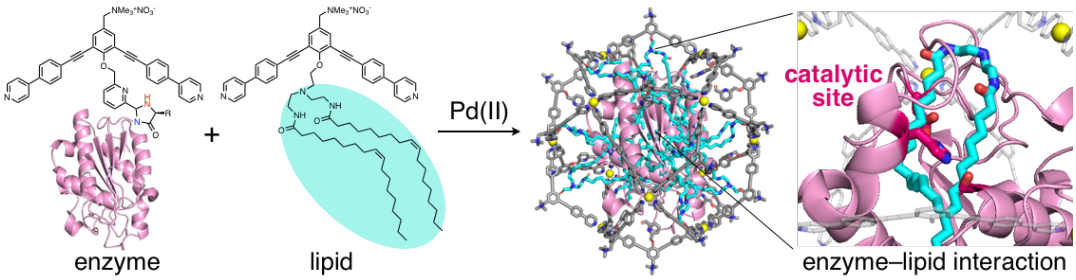

Figure 1. Structural analysis of protein–lipid interactions by co-encapsulation in a spherical metallo-cage

1) M. Tadokoro *et al.*, The 103rd CSJ Annual Meeting, 2023, D1411-3pm.

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ナノ細孔からの放出によるタンパク質のリフォールディング

（東大工[1]・東大院工[2]）○篠原 航[1]・細野 暢彦[1,2]・植村 卓史[1,2]
Protein Refolding by Releasing from Nanopores([1]*School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering, The University of Tokyo*) ○Ko Shinohara,[1] Nobuhiko Hosono,[1,2] Takashi Uemura[1,2]

Protein refolding technique is crucial in various fields, including medical sciences, protein engineering, and the development of biopharmaceuticals. However, conventional folding methods face challenges such as the aggregation of partially folded intermediates and the formation of insoluble and inactive inclusion bodies during the handling process.[1] This necessitates development of more efficient folding methods. In this study, we present a novel approach that utilizes a covalent organic framework (COFs) for protein refolding, offering higher efficiency and versatility（Figure 1）. Successful refolding was achieved through a cycle involving the introduction and release of denatured protein into the COF nanopores. In this process, the unfolded polypeptide chain is stretched and isolated within a one-dimensional pore of the COF. Releasing the polypeptide chain from the COF nanopores allowed us to efficiently fold it back into the native form without inducing aggregation.

Keywords：Protein, Folding, Covalent Organic Frameworks

タンパク質のリフォールディング技術はタンパク質工学やバイオ医薬品開発をはじめとした様々な生命工学・医療分野において不可欠な技術である。しかし、従来のフォールディング手法はその過程で部分的に折りたたまれた中間体の凝集や、不溶性で非活性な包含体の形成が起こるという課題を抱えており[1]、より効率の良いフォールディング手法が求められている。本研究では、より高い効率と汎用性が期待できるリフォールディング技術として新たに共有結合性有機構造体（COF）のナノ細孔を利用したアプローチを開発した（Figure 1）。まず、一本のポリペプチド鎖状態に変性したタンパク質を COF の一次元上ナノ細孔内へ導入し、孤立した伸長鎖状態で捕捉した。その後、伸長した状態のポリペプチド鎖を末端から順次 COF から放出させることで、タンパク質を凝集させることなくより高効率でリフォールディングさせることに成功した。

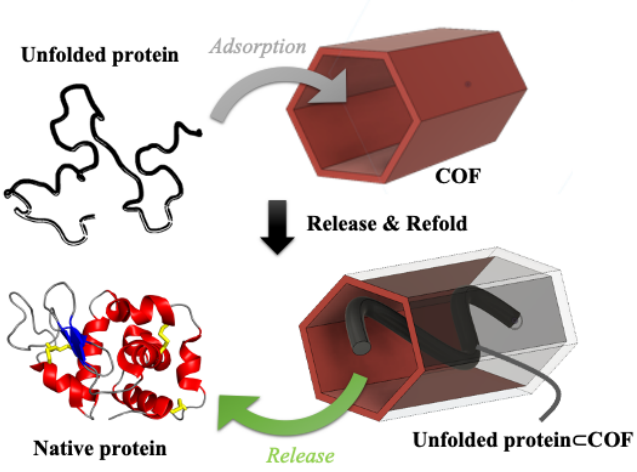

Figure 1. Schematic diagram of the refolding process using COF nanopores.

1) N. Kameta, M. Masuda, T. Shimizu, *ACS Nano* **2012**, *6*, 5249–5258.

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pH 応答性伸縮タンパク質集合体の階層構造解析

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Analysis of the hierarchical structure of the pH-responsive piston protein assembly ([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Souta Masumura,[1] Koki Date,[1] Thuc Toan Pham,[1] Xin Li,[1] Kosuke Kikuchi,[1] Takafumi Ueno[1]

Proteins can form hierarchical structures by self-assembly and exhibit emergent functions as supramolecules. We focused on type 51 refractile body (R-body) expressed by the intracellular symbiont of the paramecium. R-body is a protein complex that reversibly extends and contracts from a 400 nm rolled ribbon structure to a 20 μm spiral ribbon structure between pH 5 and pH 7 (Figure 1).[1,2] Previous studies have shown that the synthesis of the R-body requires the co-expression of four proteins. However, its hierarchical structure remains unclear.[2] In this study, we synthesized mutated R-bodies and characterized them by small-angle X-ray scattering (SAXS) measurements. We found that some of the mutants cannot show structural changes or characteristic lamellar structures, unlike the wild-type. The lamellar structure was observed in all those that were able to extend. The results provide insights into the formation mechanism of the hierarchical structure and the correlation to the extension and contraction.

Keywords : protein assembly; pH-responsivity; morphological change; small angle X-ray scattering (SAXS); scanning electron microscope (SEM)

タンパク質には自己集合によって階層構造を形成し、超分子構造体として特異な機能を発揮するものがある。我々は、ゾウリムシの細胞内共生体が発現するタンパク質超分子である 51 型 Refractile body (R-body) に着目した [1]。R-body は pH 5 と pH 7 の間で 400 nm のロール状リボン構造から 20 μm のらせん状リボン構造に可逆的に伸縮する (Figure 1)[2]。先行研究では 4 つのタンパク質の共発現が合成に必要とされているが、その階層構造は未だ不明である [2]。

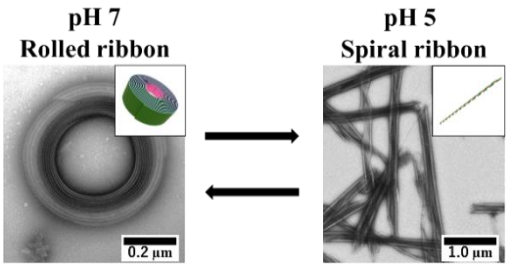

Figure 1. TEM image of R-body.[2]

そこで、本研究ではいくつかの変異体を作成し、X 線小角散乱法（SAXS）測定等による同定をおこなった。位相差顕微鏡によって伸縮機能の有無を確認し、SAXS によって WT に特徴的なラメラ構造の有無を確認した。伸縮機能やラメラ構造に変化を示す変異体を見出した一方で、伸縮が可能なものはいずれもラメラ構造を示すことを確認した。これらの結果をもとに、R-body の階層構造形成メカニズムと伸縮機能への寄与について考察した。

1) Pond, F. R. *et al*., *Microbiol. Rev.* 53, 25-67, **1989**.
2) Polka, J. K. *et al*., *ACS Synth. Biol*. 5, 303-311, **2016**.

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日本化学会 第104春季年会 (2024)

マイクロ波照射下における蛋白質の変性・凝集挙動

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Investigation of denaturation and Aggregation Behavior of Proteins under Microwave Irradiation ([1]*Grad. Sch. of Teikyo Univ. of Sci.*, [2]*Grad. Sch. of Eng., Kyoto Univ*, [3]*Institute for Molecular Science, National Institutes of Natural Science*) ○Mizuki Yoshihara,[1] Yuna Sakakibara,[1] Ma Yunting,[2] Yoshihiro Sasaki,[2] Eito Fukushima,[1] Haruya Yamaguchi,[1] Hikaru Takaya[1,3]

The denaturation and aggregation behaviors of various proteins, such as protease, carbonic anhydrase (CA2), cellulase, myoglobin, and bovine serum albumin (BSA), were evaluated under conventional heating (heat block (HB): 90°C) and microwave (MW) heating (100 W) by means of UV-visible absorption spectra. The denaturation and aggregation of CA2 were accelerated with increasing irradiation time. When 50 equivalents of trehalose was added to CA2 solution as a protein protecting agent, aggregation inhibition was clearly observed under both HB- and MW-heating conditions. In this presentation, the details of the denaturation/aggregation behavior of various proteins under MW irradiation conditions with/without protein protecting agents of trehalose and histidine will be reported.

Keywords : *microwave, protein, enzyme, denaturation, aggregation*

マイクロ波照射による蛋白質の変性・凝集挙動の機序を解明する目的で，様々なタンパク質にマイクロ波を照射して（100W，90 ℃），その変性・凝集挙動について，紫外－可視吸収スペクトル測定から算出した Aggregation Index（AI）値を用いて通常加熱を評価した。その結果，例えば炭酸脱水素酵素（CA2）では，照射時間が長くなると変性・凝集が促進されること，トレハロース 50 当量を CA2 溶液に添加すると，変性・凝集が抑制されること（Fig. 1），通常加熱（HB）条件では MW 照射下とは異なる変性・凝集挙動を示すことが明らかとなった（Fig. 2）。本発表では，アルカリプロテアーゼ，セルラーゼ，BSA 等の酵素/蛋白質の変性・凝集挙動およびトレハロース，ヒスチジンの抑制効果についても併せて報告する。

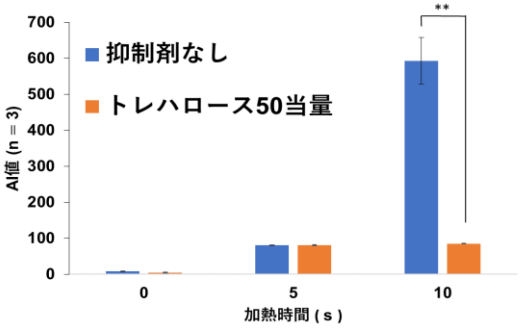

Fig.1 マイクロ波加熱における変性・凝集抑制効果

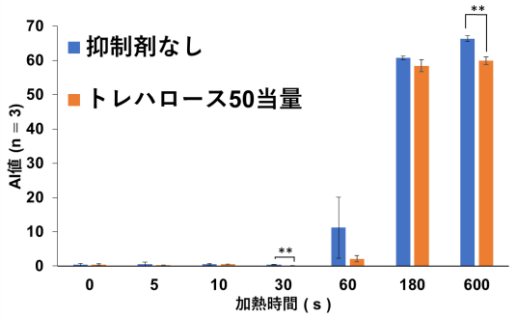

Fig.2 通常加熱（HB）における変性・凝集抑制効果

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HP1αの運動性にリン酸化が及ぼす影響のESRを用いた分析

（阪大蛋白研[1]・大阪公大理[2]・中村学園大[3]）○武居 俊樹[1]・村岡 浩平[1]・川上 徹[1]・荒田 敏明[2]・末武 勲[3]・北條 裕信[1]

Analysis of the Effect of Phosphorylation on HP1α Dynamics by ESR Spectroscopy ([1]*Institute for Protein Research, Osaka University,* [2]*Department of Biology, Graduate School of Science, Osaka Metropolitan University,* [3]*Department of Nutritional Sciences, Graduate School of Nutritional Sciences, Nakamura Gakuen University*) ○Toshiki Takei[1], Kohei Muraoka[1], Toru Kawakami[1], Toshiaki Arata[2], Isao Suetake[3], Hironobu Hojo[1]

Heterochromatin protein 1 (HP1) family has important functions in diverse biological processes to regulate the gene expression. HP1 has two well-known functionally distinct domains, chromo domain (CD) and chromo shadow domain (CSD). CD recognizes the trimethylation on Lys[9] of histone H3 (H3K9me3), and CSD contributes self-dimerization. To analyze the interaction between HP1α with DNA, we recently evaluated the dynamics of CD, CSD and the other unfolded regions: N tail, hinge region and C tail, using site-directed spin labeling on Cys side chain by ESR spectroscopy[1)]. The results indicated the possibility that HP1α regulates its own activity by loose intermolecular interaction through unfolded regions.

To obtain the further structural information of HP1α dynamics, we prepared phosphorylated HP1α by semi-synthetic strategy. The results of semi-synthesis of HP1α as well as ESR spectroscopy will be presented.

Keywords : HP1α; Semi-synthesis; Native chemical ligation; Electron spin resonance

Heterochromatin protein 1 (HP1) ファミリーは、ヒストン H3 の 9 番目の Lys におけるトリメチル化修飾を認識するタンパク質であり、ヘテロクロマチンの形成や遺伝子発現に重要な役割を担う。HP1 は chromo domain (CD) および chromo shadow domain (CSD) と呼ばれる 2 つのドメインを有しており、CD はトリメチル化修飾を認識し、CSD は自己の二量体形成に寄与する。近年我々は HP1α の構造を取らない領域の運動性と生理機能の関係に着目し、electron spin resonance (ESR) により HP1α の運動性を評価した。その結果、HP1α の構造を取らない領域同士が相互作用することにより、自身の活性を調節している可能性を示唆する結果を得ている[1)]。

本研究では、HP1α の構造を取らない N 末端領域に存在するリン酸化修飾と運動性の関係を検証するため、半合成戦略を用いてリン酸化修飾を有する HP1α を調製した。半合成および ESR の測定結果について報告する予定である。

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MGKKTKRTXD SSSSEDEEEY↓CVEKVLDRRV VKGQVEYLLK WKGFSEEHNT
WEPEKNLDAP ELISEFMKKY KKMKEGENNK PREKSESNKR KSNFSNSADD
IKSKKKREQS NDIARGFERG LEPEKIIGAT DSAGDLMFLM KWKDTDEADL
VLAKEANVKA PQIVIAFYEE RLTWHAYPED AENKEKETAK S
```

X: TOAC
S: Phophorylated Ser
↓: Ligation site

1) I. Suetake, K. Sato, T. Sugishita, Y. Mishima, T. Takei, T. Fujiwara, R. Mutoh, A. Shinohara, T. Takui, M. Miyata, H. Hojo, T. Arata, *Appl. Magn. Reson.*, **2023**, 54, 119-141.

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超好熱菌由来システインレスインテインのタンパク質スプライシング活性の評価

（群大理工[1]・群大院理工[2]）○片桐 栞太[1]・高橋 剛[2]

Evaluation of protein splicing activities of cysteine-less intein from hyperthermophiles

([1]*Department of Science and Technology, Gunma University,* [2]*Graduate School of Science and Technology, Gunma University*) ○Kanta Katagiri,[1] Tsuyoshi Takahashi[2]

Inteins are mobile genetic elements that are spliced out of proteins post-translationally. Inteins are classified into 3 classes based on sequence and the mechanism of splicing. Most inteins are members of class 1, and contain three conserved nucleophiles, serine, threonine, or cysteine. Inteins are widely used in the protein engineering field, and commonly used inteins contain cysteine at position 1 and/or +1. However, inteins containing cysteine can work only under reductive conditions. In the present study, we have attempted to construct the cysteine-less inteins capable of work under oxidative conditions. We have chosen two cysteine-less intein sequences derived from hyperthermophiles and the activities have been examined.

Keywords： protein trans-splicing; cysteine-less intein; hyperthermophile

タンパク質の部位特異的ラベル化は、タンパク質の機能解析において有用である。一方、インテインは、その両端に繋がっているポリペプチド鎖（N および C エクステイン）を連結させるタンパク質スプライシング活性をもつ酵素様のタンパク質である。インテイン部分が分割された分割型インテインを用いることで、2 つのポリペプチド鎖を連結させることができる。これまでに、天然型だけでなく、人工的に分割した分割インテインが多数開発され、タンパク質工学で広く利用されている。これら汎用的に使われているインテインは、主にクラス 1 に分類されるものであり、活性に必要なアミノ酸として、インテイン 1 残基目に Cys または Ser、C エクステイン 1 残基目に Cys、Ser、または Thr をもつ必要がある。高活性型インテインのほとんどは、インテイン内部や C エクステイン 1 残基目に Cys をもっているため、スプライシング反応は、還元的条件下で行う必要がある。そのため、抗体などのジスルフィド結合をもつタンパク質の部位特異的ラベル化などへの適用が困難となっている。しかし、Cys をもたない（cysteine-less; CL）インテインに関する報告例は少ない。本研究では、超好熱菌由来の 2 種類の CL インテインの大腸菌発現系を構築し、スプライシング活性について評価した。

CL インテインとして、超好熱菌 *Aeropyrum pernix* K1 由来 Ape0745 および *Thermococcus aggregans* 由来 Tag Pol-3 を採用した。スプライシング活性を簡便に評価するために、エクステインとして、TEM-1 βラクタマーゼ（BLA）を用いた。BLA 遺伝子の中央付近に、CL インテイン遺伝子を挿入し、タンパク質スプライシングの進行により、活性型 BLA が発現するよう設計した。大腸菌ペリプラズムでタンパク質を発現させ､酸化的条件下での CL インテインのスプライシング能について検討した。

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改変型分割インテインを用いた特定のペプチド配列を認識するタンパク質の探索

（群大理工[1]・群大院理工[2]）○清水 もも花[1]・高橋 剛[2]
Selection of proteins that recognize a specific peptide sequence using engineered split intein ([1]*Department of Science and Technology, Gunma University,* [2]*Graduate School of Science and Technology, Gunma University*) ○ Momoka Shimizu,[1] Tsuyoshi Takahashi[2]

Protein-protein interactions play important roles in many biological functions. Some proteins can recognize short peptide sequences in intrinsically disordered regions of proteins. These linear protein interaction sites are referred to as short linear motifs (SLiMs). On the other hand, we have engineered split inteins that have protein trans-splicing (PTS) activity based on Npu DnaE intein. We have successfully developed a system in which the peptide-protein interactions promote the PTS reaction using an engineered split intein. When β-lactamase and aminoglycoside 3'-phosphotransferase (APH) are used as PTS products, the peptide-protein interactions are able to be detected by antibiotic resistance of *Escherichia coli*. In the present study, we have attempted to construct a convenient method to discover proteins that bind to a specific peptide sequence using the split intein and reconstitution of APH.
Keywords： protein trans-splicing; split intein; peptide-protein interaction

タンパク質間相互作用は、生物機能の発現において重要な役割を担っている。タンパク質間相互作用では、タンパク質中の特定の立体構造をとらない天然変性領域（intrinsically disordered region; IDR）内にある、短鎖のペプチドモチーフ（short linear motif; SLiM）を介した相互作用が多く存在することが知られている。一方、当研究室では、タンパク質トンランススプライシング（protein trans-splicing; PTS）活性をもつ分割インテインを利用したペプチド–タンパク質間相互作用検出法の開発を行っている。この方法では、自発的な PTS 活性を示さないよう改変した分割インテインに、ペプチドと標的タンパク質をそれぞれ配置し、ペプチド–タンパク質間相互作用に依存して PTS 反応が進行する。PTS 反応の生成物として、βラクタマーゼ（BLA）や aminoglycoside 3'-phosphotransferase（APH）を用いることで、ペプチド–タンパク質間相互作用の有無を大腸菌の抗生物質耐性を指標として検出することができる。本研究では、分割インテインと分割 APH を利用したペプチド–タンパク質間相互作用検出法を用いて、特定のペプチド配列を認識するタンパク質の探索を試みた。

ペプチド–タンパク質間相互作用のモデルとして、p53 由来ペプチドや PMI（TSFAEYWNLLSP）などの MDM2 タンパク質に結合するペプチド配列を用いた。探索するタンパク質の遺伝子は、ヒト胎盤由来 cDNA ライブラリをもとにプラスミドを構築した。構築したプラスミドを用いて大腸菌を形質転換し、大腸菌のカナマイシン耐性を利用したスクリーニングを行った。

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糖鎖認識 F-box タンパク質 Fbs2 と糖ペプチドとの相互作用解析

（群大理工[1]・群馬大院理工[2]・東京都医学総合研究所[3]・理化学研究所[4]）○相京　碧[1]・井上　遥[2]・高橋　諭[2]・石井　希実[2]・松尾　一郎[2]・吉田　雪子[3]・鈴木　匡[4]・高橋　剛[2]

Analysis of interactions between glycopeptides and sugar-recognizing F-box protein Fbs2

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○Midori Aikyo,[1] Haruka Inoue,[2] Satoshi Takahashi,[2] Nozomi Ishii,[2] Ichiro Matsuo,[2] Yukiko Yoshida,[3] Tadashi Suzuki,[4] Tsuyoshi Takahashi[2]

Glycosylation of proteins is one of the most frequent types of protein post-translational modifications. Misfolded glycoproteins are degraded by endoplasmic reticulum-associated degradation (ERAD) pathway. During ERAD pathway, misfolded glycoproteins are ubiquitinated, deglycosylated, and degraded by proteasome. Skp1/Cullin/F-box (SCF) complexes are the largest family of E3 ubiquitin ligases. Fbs2 is a F-box protein that recognizes high-mannose type *N*-glycans. To investigate whether the recognition of Fbs2 is affected by the peptide sequence, we synthesized nine glycopeptides bearing the pentasaccharide unit ($Man_3GlcNAc_2$) and analyzed the interactions between the glycopeptides and Fbs2.

Keywords : Glycopeptide; Sugar-recognizing F-box protein; Skp1/Cullin/F-box complex; Fluorescence polarization

タンパク質の翻訳後修飾であるグリコシル化は、タンパク質の安定性や可溶性の向上などの物理学的特性だけでなく、様々な生物学的機能の発現に関与している。アスパラギンの側鎖に糖鎖が結合した *N* 結合型糖鎖をもつ糖タンパク質は、小胞体内で糖鎖付与とフォールディングが行われ、ゴルジ体へと輸送される。小胞体内でミスフォールドした糖タンパク質は、小胞体関連分解（ERAD）経路で、細胞質へと輸送された後ユビキチン化され、プロテアソームで分解される。Skp1/Cullin/F-box（SCF）複合体は、複数のタンパク質からなる E3 ユビキチンリガーゼである。F-box タンパク質である Fbs2 は、高マンノース型の *N* 結合型糖鎖を認識し、糖タンパク質のユビキチン化に関与していると考えられている。しかしながら、Fbs2 による糖タンパク質の認識において、糖鎖近傍のアミノ酸配列の影響についてはあまり分かっていない。本研究では、7 アミノ酸残基からなる糖ペプチドを合成し、Fbs2 との相互作用について検討した。

糖ペプチドは、Nrf1（nuclear factor erythroid-derived 2-related factor）のアミノ酸配列を元に設計した。Nrf1 には、*N* 結合型糖鎖付加に必要なコンセンサス配列が 9 箇所存在する。この 9 箇所のアミノ酸配列を元に、*N* 結合型糖鎖のコア 5 糖（$Man_3GlcNAc_2$）を中央に配置し、N 末端には、tetramethylrhodamine を導入した。Fbs2 は、大腸菌を用いて Skp1 との共発現により調製した。糖ペプチドと Fbs2 との相互作用について、蛍光偏光解消法により評価した。

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Keap1 タンパク質を標的とした分割インテインとカナマイシンキナーゼの再構成によるペプチドの探索

（群大院理工）○信澤　佳奈・高橋　剛

Selection of peptides that bind to Keap1 using split intein and reconstitution of kanamycin kinase (*Graduate School of Science and Technology, Gunma University*)
○Kana Nobusawa, Tsuyoshi Takahashi

Peptide molecules are expected as good candidates for pharmaceutical exploitation. Therefore, several methods to screen from a peptide library have been developed so far. We have attempted to develop a method to discover peptides that bind to target proteins based on split inteins. To do this, we have used an engineered split intein that has protein trans-splicing (PTS) activity on the basis of *Npu* DnaE intein. Moreover, using an aminoglycoside 3'-phosphotransferase (APH) as the splicing product, the peptide-protein interactions in *Escherichia coli* (*E. coli*) can be estimated by kanamycin resistance of *E. coli*. In this study, we attempted to select peptides that bind to Kelch-like ECH associating protein 1 (Keap1).

Keywords : split intein; protein trans-splicing; Kelch-like ECH associating protein 1

ペプチド分子は医薬品開発のための候補として期待されており、ペプチドライブラリから標的タンパク質と結合するペプチドの探索法が多数開発されている。当研究室では、タンパク質トランススプライシング（PTS）活性をもつ分割インテインを利用した、標的タンパク質結合ペプチド探索法の開発を行っている。これまでに、この分割インテインを通常とは異なる位置で分割することで、分割インテイン間の自発的な会合を抑制するようなインテインの開発を行い、ペプチド-タンパク質間の相互作用に依存して PTS 反応が進行する系を構築してきた。この改良型分割インテインの設計は、当研究室で開発した *Npu* DnaE インテイン改変体をもとに行った[1]。さらに、改良型分割インテインに、抗生物質カナマイシンを無毒化するカナマイシンキナーゼである aminoglycoside 3'-phosphotransferase（APH）の分割体を組み合わせた。これにより、PTS 反応の生成物として APH が生成することで、カナマイシン存在下での大腸菌の生育によってペプチド-タンパク質間の相互作用の有無を判別できる系を構築した。本研究では、分割インテインを用いた方法により、Kelch-like ECH associating protein 1 (Keap1)に結合するペプチドの探索を試みた。

ペプチドライブラリは、NNK（N = A, G, C, T; K = G, T）コドンを用いて 12 残基からなる遺伝子を構築した。構築したライブラリ遺伝子の下流側に、C インテインおよび APH の C 末端 7 アミノ酸配列に対応する遺伝子を配置した。標的タンパク質である Keap1 遺伝子は、APH の N 末端配列および N インテインの下流側に配置した。構築したプラスミドを大腸菌に導入し、カナマイシン含有培地でセレクションを行った。得られた大腸菌からプラスミド配列を解析し、得られたペプチドのアミノ酸配列を同定した。

1) M. Kawase *et al. ChemBioChem.* **22**, 577-584 (2021)

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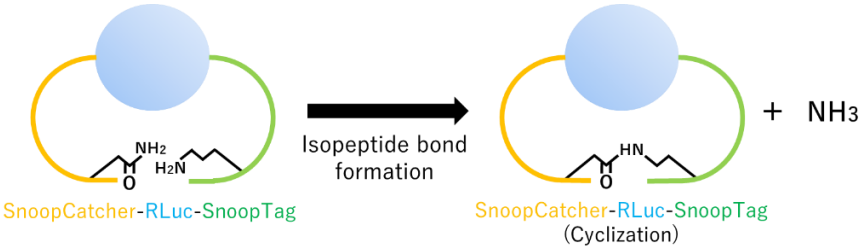
Catcher/Tag システムを利用した環状化 Renilla Luciferase の構築

（東工大生命理工[1]）○市川 真[1]・西田 慶[1]・山口 醇[1]・小畠 英理[1]・三重 正和[1]
Construction of cyclized Renilla Luciferase using the Catcher/Tag system ([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Makoto Ichikawa[1], Kei Nishida[1], Jun Yamaguchi[1], Eiry Kobatake[1], Masayasu Mie[1]

Head-to-tail cyclization of enzymes is an effective methodology to improve their stabilities including thermostability. Although the protein cyclization is performed via crosslinking between N- and C- terminal residues by using chemical or enzymatical reaction, there are some problems such as side reactions, lack of site specificity, and limited reaction conditions. The SnoopCatcher/SnoopTag system is one of methods for the formation of protein-protein conjugation. This system enables spontaneous and specific isopeptide bond formation between Catcher-Tag under mild conditions[1)]. In this study, we utilized SnoopCatcher/SnoopTag system for the protein cyclization to improve protein thermostability. Renilla Luciferase (RLuc), a luminescent enzyme from sea pansy, was selected as a model enzyme. SnoopCatcher and SnoopTag were fused with N- and C- terminal of RLuc, respectively, and cyclized by the isopeptide bond formation. The thermostability of cyclized RLuc was evaluated in terms of the aggregation, unfolding, and bioluminescence activity.
Keywords : Isopeptide bond; Cyclized protein; Luciferase

酵素の Head-to-Tail 型環状化は、熱安定性などの酵素の安定性を向上させるために有効な方法論である。タンパク質の環状化手法には、その N 末端と C 末端を化学反応や酵素反応により架橋する方法がある。しかしながら、これらの手法には副反応や部位特異性の欠如、反応条件の制限などの問題がある。そこで本研究では、タンパク質の環状化手法として、タンパク質間結合を形成する方法の一つである SnoopCatcher/SnoopTag システムに着目した。このシステムは、温和な条件下で Catcher-Tag 間における自発的かつ特異的なイソペプチド結合の形成を可能にする [1)]。ここでは、ウミシイタケ由来の発光酵素 Renilla Luciferase（RLuc）の熱安定性を向上させるために、SnoopCatcher/SnoopTag システムをタンパク質の環状化に利用した。SnoopCatcher と SnoopTag を RLuc の N 末端と C 末端にそれぞれ融合し、イソペプチド結合の形成により RLuc を環状化した。環状化した RLuc の熱安定性は、凝集、アンフォールディングおよび生物発光活性から評価した。



1) Programmable polyproteams built using twin peptide superglues. Veggiani G. *et al*., *Proc. Natl. Acad. Sci. USA* 2016, **113**, 1202–1207

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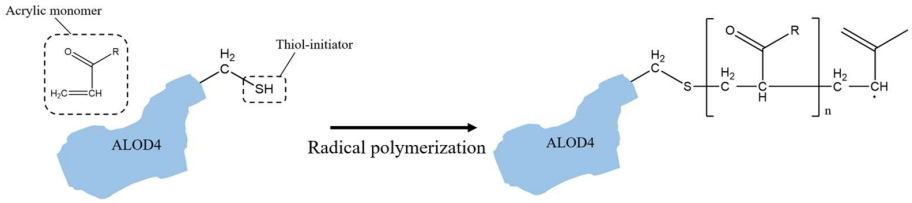
膜コレステロール結合性タンパク質の高分子修飾と機能評価

（東工大生命理工[1]）○馬 天健[1]・西田 慶[1]・佐藤 郁美[1]・三重 正和[1]・小畠 英理[1]
Modification of cholesterol-binding proteins by polymer grafting ([1]*School of Life Science and Technology, Tokyo Institute of Technology*) ○Tianjian Ma,[1] Kei Nishida,[1] Ikumi Sato,[1] Masayasu Mie,[1] Eiry Kobatake[1]

Interaction between membrane proteins and cholesterol in plasma membrane attracts much attention as an approach to control biological processes on cells. The domain 4 of anthrolysin O (ALOD4), derived from *Bacillus anthracis*, shows a cholesterol-binding activity on plasma membrane. It suggests that ALOD4 bound to membrane cholesterol could alter the membrane protein by suppressing the interaction between cholesterol and membrane protein. Although ALOD4 would be one of proteins to regulate the activity of membrane proteins, it is challenging to improve its physico-chemical properties such as solubility, aggregability, and degradability. In this study, we modified ALOD4 with synthetic polymers by grafting from polymerization for the improvement of physico-chemical properties. The ALOD4, containing one cysteine residue, were modified with hydrophilic acrylic polymers via thiol-initiated polymerization.
Keywords：Cholesterol-binding protein; Polymer grafting; Radical polymerization

細胞膜コレステロールと膜タンパク質間の相互作用は、細胞増殖や遊走、アルツハイマー病の原因であるアミロイド形成経路、Hedgehog シグナル伝達経路の活性化といった細胞機能に関わるシグナル伝達系と深く関わっている。ここで我々は、*Bacillus anthracis* 由来のタンパク質である anthrolysin O のドメイン 4 (ALOD4)に着目した。ALOD4 は細胞膜のコレステロールに対して結合活性を示す[1]だけでなく、コレステロールと膜タンパク質間の相互作用を抑制し、膜タンパク質の活性に影響を与えることが示唆されている。ALOD4 はコレステロール–膜タンパク質間の相互作用を制御するための有用な材料であると期待されるが、水溶解性や凝集性、分解性耐性といった物理化学的性質の改善が課題である。本研究では、ラジカル重合を用いた Grafting-from 法によって ALOD4 に合成高分子を修飾し、上記の物理化学的性質の改善を目指した。具体的には、ALOD4 を遺伝子工学的に改変することでシステインを一分子含む ALOD4 を構築し、チオールを連鎖移動剤とした親水性アクリレートモノマーのラジカル重合により高分子の修飾を実施した。



1) Switch-like responses of two cholesterol sensors do not require protein oligomerization in membranes. Gay, A. *et al*. *Biophys J.* **2015,** 108, 1459–1469.

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ピキア酵母を宿主とするアルブミンの高分泌発現系の構築

（阪府大生命[1]・大阪公大院農[2]）○小森 美月[1]・藤枝 伸宇[2]・森田 能次[2]
Construction of high-secretion expression system for albumin using Pichia pastoris
(*[1]Graduate School of Life and Environmental Sciences, Osaka Prefecture University, [2]Graduate School of Agriculture, Osaka Metropolitan University*) ○ Mizuki Komori,[1] Nobutaka Fujieda,[2] Yoshitsugu Morita.[2]

Pichia pastoris is a well-known host for powerful expressions of heterologous proteins and secretory signals allow secretion of target proteins into the medium. However, optimizing the secretory signal is necessary to achieve high expression levels[1]. On the other hand, human serum albumin (HSA) is a biomaterial in high demand in the medical field because of its long half-life in blood and its many biological roles. In this study, we constructed a secretory expression system of HSA based on the α-factor secretory signal using *Pichia pastoris* as a host and clarified the relationship between mutations in the signal and HSA expression levels.

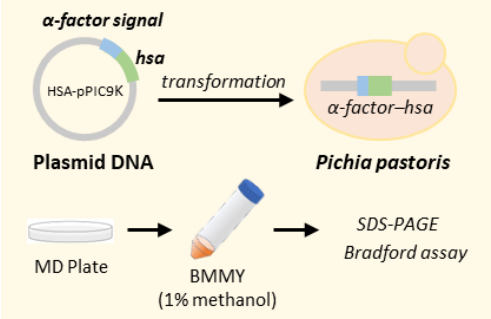

Fig 1. Construction of HSA expression system.

First, plasmid DNA encoding α-factor secretory signal and HSA was prepared and transformed *Pichia pastoris* (Fig. 1). The resulting *Pichia pastoris* was cultured in methanol-containing medium to induce the secretory expression. HSA expression into the medium was confirmed by SDS-PAGE, and the protein concentration of the supernatant was quantified by Bradford assay. In addition, HSA expression systems with the secretory signal mutants were constructed and the secretory expression levels were determined.

Keywords : Pichia pastoris; Human Serum Albumin; α-factor secretory signal

ピキア酵母は真核微生物の中でも強力な異種タンパク質発現系の宿主として知られている。また、分泌シグナルを利用することで目的タンパク質を細胞外に分泌発現することができる。しかし、高い発現量を得るには分泌シグナルの最適化が必要である[1]。一方、ヒト血清アルブミン（HSA）は血中半減期が長く、多くの生物学的役割を担うため、医療分野において需要が高い生体材料である。本研究では、ピキア酵母を宿主とした、α 因子分泌シグナルを用いた HSA の分泌発現系を構築し、分泌シグナルの変異と HSA 発現量の相関解析を目的とした。

まず、α 因子分泌シグナルと HSA をコードするプラスミド DNA を調製し、ピキア酵母を形質転換した（Fig. 1）。次に、メタノールを含む培地でピキア酵母を培養することで、HSA の分泌発現を誘導した。培養上清の SDS-PAGE から HSA の発現を確認し、Bradford 法により上清のタンパク濃度を定量した。さらに、分泌シグナルに変異導入した HSA 発現系も構築し、それぞれの分泌発現量を明らかにした。

1) J. Lin-Cereghino, *et al.*, *Gene*, **2013**, *519*, 311.

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

Wed. Mar 20, 2024 1:00 PM - 3:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:30 AM UTC H932(932, Bldg. 9 [3F])

[H932-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Eiji Nakata, Hiromu Kashida

English
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H932-3pm-01]

Artificial liposome compartment with DNA origami scaffold for size exclusion molecular transport

○shiwei zhang[1], Eiji Nakata[1], Peng Lin[1], Takashi Morii[1] (1. Kyoto university)

English
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H932-3pm-02]

In vitro model of RNA-Protein aggregates in myotonic dystrophy type 1

○Surachada Chuaychob[1,2], Wanqing Hou[2], Musashi Shimizu[2], Shun Nakano[2], Arivazhagan Rajendran[1,2], Eiji Nakata[1,2], Takashi Morii[1,2] (1. Integrated Research Center for Carbon Negative Science, Institute of Advanced Energy, Kyoto University, 2. Institute of Advanced Energy, Kyoto University)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H932-3pm-03]

Development of a method for simultaneous measurement of multiple factors in the intracellular local environment

○Mashal Asif[1], Eiji Nakata[1], Yuya Shibano[1], Peng Lin[1], Takashi Morii[1] (1. Institute of Advanced Energy, Kyoto University)

English
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H932-3pm-04]

Construction of an artificial CO_2 fixation compartment using DNA nanostructure as a scaffold

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

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H932-3pm-05]

Assembly of the functional proteins located on DNA nanostructures

○SHUHUI XIAN[1], Eiji Nakata[2], Peng Lin[2], Takashi Morii[2] (1. Kyoto University, 2. Institute of Advanced Energy, Kyoto University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H932-3pm-06]

Investigation of efficient amplification in ab initio DNA synthesis

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○Yuka Kataoka[1], Chihiro Kubo[1], Tomoko Wariishi[1], Hiroto Fujita[1], Masayasu Kuwahara[1] (1. Grad. Sch. Integrated Basic Sci., Nihon Univ.)

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

[H932-3pm-07]

Self-assembly of double-stranded DNA into micrometer-sized H-shaped structures

○Tetsunao Makino[1], Makiko Tanaka[1] (1. The University of Electro-Communications)

Japanese

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

[H932-3pm-08]

Exploration of Pt complex that induce DNA coacervate

○Ryu Tashiro[1], Takuma Yamada[1], Serika Yano[1], Ayane Araki[1], Hiroki Nishihara[1], Moe Nakagawa[1], Masako Uemura[1], Seiji Komeda[1] (1. Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science)

Japanese

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

[H932-3pm-09]

Design of template circular DNA for light-triggered activation of siRNA transcription utilizing gold nanoparticles

○Tomoki Ikemizu[1], Weijie Cheah[1], Yusuke Yonamine[2], Hideyuki Mitomo[2], Kuniharu Ijiro[2] (1. Hokkaido University Graduate School of Life Science, 2. Hokkaido University Research Institute for Electronic Science)

Japanese

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

[H932-3pm-10]

Imidazolium modified-silica support for facile DNA extraction from contaminants

○Yasuaki Kakikura[1] (1. Osaka Research Institute of Industrial Science and Technology)

Japanese

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

[H932-3pm-11]

Evaluation of helical amplification ability of using SNA tethering fluorescent dyes

○Itsumi Sugiyama[1], Hiromu Kashida[1], Hiroyuki Asanuma[1] (1. Grad. Sch. Eng., Nagoya Univ.)

Japanese

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

[H932-3pm-12]

Sequence analysis of SNA bearing artificial bases by duplex formation with DNA

○Nozomi Hibino[1], Hiroyuki Asanuma[1], Hiromu Kashida[1] (1. Grad. Sch. Eng., Nagoya Univ.)

Japanese

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

[H932-3pm-13]

Development of a novel method to analyze PNA sequences bearing artificial bases.

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○Kazuma Inagaki[1], Hiromu Kashida[1], Yuichiro Aiba[2], Osami Shoji[2], Hiroyuki Asanuma[1] (1. Grad. Sch. Eng., Nagoya Univ., 2. Grad. Sch. Sci., Nagoya Univ.)

Japanese

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

[H932-3pm-14]

Unique homopurine parallel-type triplex structure formed by XNA

○Lao Siyuan[1], Ariyoshi Jumpei[2], Sato Fuminori[1], Asanuma Hiroyuki[1], Kamiya Yukiko[1,2] (1. Nagoya University, 2. Kobe Pharmaceutical University)

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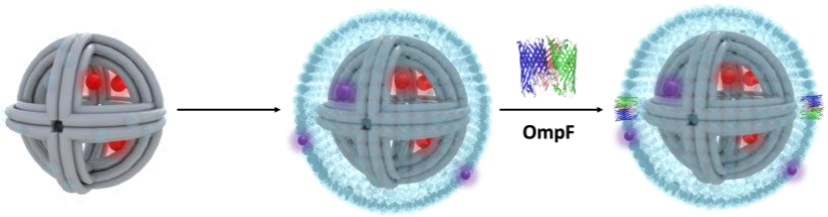
Artificial Liposome Compartment with DNA Origami Scaffold for Size Exclusion Molecular Transport

(*Institute of Advanced Energy, Kyoto University*) ○Shiwei Zhang, Eiji Nakata, Peng Lin, Takashi Morii

Keywords: DNA Origami; Membrane Protein; Liposome

Inside cells, complex metabolic reactions are highly organized and distributed in different organelles, allowing better control of biological processes.[1] Such organized systems have some advantages, because many cascade reactions suffer from incompatibilities such as cross-inhibition by components of the reaction system. In fact, spatially arranged enzymes are observed in organelles, which are thought to increase the efficiency of multistep processes. Understanding the characteristics of these reactions is key to the development of artificial metabolic systems and biosensors. Artificial compartments have the potential to mimic cellular organelles for applications such as drug delivery and biosensing.[2] These compartments can be constructed using a variety of materials, including liposomes, DNA origami, and inorganic nanoparticles. Isolation from the external environment and the organization of the molecules of interest on and/or within the compartment are key features. Membrane proteins, transporters, and channels are incorporated to control the transport of substances.[3] DNA nanotechnology provides ideal platforms of various sizes and shapes for the assembly of dyes, enzymes, proteins, and liposomes.[4] At the same time, rationally designed DNA nanostructures can serve as high-precision templates for the construction of confined membranes.

Here, an artificial compartment was constructed using a wireframe DNA origami skeleton (WS) that provided a platform for the introduction of molecules of interest encapsulated by liposomes. By incorporating the membrane protein OmpF into the liposome bilayer, the internal pH could be controlled and molecules <600 Da could be transported. This compartment can not only be isolated from the external environment, but can also control the transport of specific chemicals across the membrane. Ongoing research aims to develop a method to place a defined number of enzymes and membrane proteins on the DNA origami skeleton to construct a cascade reaction within the artificial compartment.



1) J. Yates, *Nat. Rev. Mol. Cell Biol.* **2005**, *6*, 702–714. 2) R. J. R. Peters, *Chem. Sci.* **2012**, *3*, 335-342. 3) G. Ghale, *Angew. Chem. Int. Ed.*, **2014**, *53*, 2762–2765. 4) P. Rothemund, *Nature*, **2006**, *440*, 297–302.

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In vitro model of RNA-Protein aggregates in myotonic dystrophy type 1

([1]*Integrated Research Center for Carbon Negative Science, Institute of Advanced Energy, Kyoto University,* [2]*Institue of Advanced Energy, Kyoto University*)
○Surachada Chuaychob,[1,2] Wanqing Hou,[1] Musashi Shimizu,[1] Shun Nakano,[1] Arivazhagan Rajendran,[1,2] Eiji Nakata,[1,2] Takashi Morii[1,2]
Keywords: CUG repeat RNA sequence; MBNL1 protein; RNP aggregate; DNA origami; AFM

Myotonic dystrophy type 1 (DM1) is a genetic disorder caused by CTG repeat expansions[1] that result in the aggregation of CUG repeat RNA sequences and MBNL1 protein (RNP)[2]. Although the causative genes for DM1 are known, researchers currently lack a suitable in vitro model that can reproduce the molecular and clinical phenotypes of this debilitating disease. To address this issue, we propose an in vitro system of RNP aggregates formed by RNA with over a thousand CUG repeats and MBNL1 proteins on DNA origami[3], which allows analysis by high-speed atomic force microscopy (AFM) measurements to study the aggregate formation. The in vitro model consists of two components: CUG repeat RNA with 28 repeats ($(CUG)_{28}$) and a rectangular DNA origami with 36 binding sites for the RNA (36-bs Rec-Ori) (Fig. 1). First, $(CUG)_{28}$ was transcribed outside of cells. The purified $(CUG)_{28}$ was then confirmed by denaturing PAGE before use. Second, the $(CUG)_{28}$ was assembled on 36-bs Rec-Ori, and the assembly was examined by AGE. Finally, MBNL1**Δ**105 protein, an MBNL1 mutant in which the C-terminal 111 amino acid residues were deleted, was first used to study the formation of the $(CUG)_{28}$-MBNL1**Δ**105 protein complex (RNP_m). MBNL1**Δ**105 protein was chosen because of the disruption of protein-protein interactions, resulting in the inhibition of aggregate formation. The RNP_m complex was directly observed by high-speed AFM. Analysis of AFM images showed an increase in height after RNP_m formation. This result emphasized that the in vitro model was successfully applied to evaluate the RNP_m complex. The formation of RNP aggregates by full-length MBNL1 will also be investigated to verify its aggregation mechanism in DM1 and to determine what the type of RNP aggregates are formed depending on the number of CUG repeats.

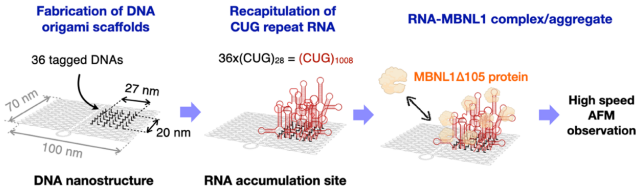

Fig. 1. In vitro model of CUG repeat RNA-MBNL1 protein aggregates on DNA origami.

1) G. Ho, *World J Clin Pediatr.* **2015,** *4, 66.* 2) O. Pettersson, *Nucleic Acids Res.* **2015,** *43, 2433.* 3) P.W.K. Rothemund, *Nature* **2006,** *440, 297.*

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Development of a method for simultaneous measurement of multiple factors in the intracellular local environment

([1]*Institute of Advanced Energy, Kyoto University*) ○ Mashal Asif,[1] Eiji Nakata,[1] Yuya Shibano,[1] Peng Lin,[1] Takashi Morii[1]

Keywords: biosensor; DNA origami; pH sensor; cathepsin sensor; macropinocytosis

Monitoring changes in the concentration and location of critical biological molecules as well as changes in the cellular environment, such as intracellular pH, enzymatic activity, or temperature, is a fundamental process for understanding cellular dynamics. Therefore, it is beneficial to track these factors simultaneously in a confined space.[1] DNA nanostructures are considered an ideal framework for assembling functional molecules at the nanoscale because of their programmability, which is controlled by genetic sequences. In particular, the DNA origami technique has facilitated the rapid fabrication of 2D and 3D nanostructures with precise geometries.[2] Compared to conventional single-molecule-based sensors, the assembly of multiple fluorescent sensors on a DNA scaffold offers distinct advantages.[3] DNA nanostructures serve as an ideal framework to spatially organize molecules with nanometer precision, taking advantage of their sequence-driven programmability.[4]

This study aims to understand the dynamics of macropinocytosis, an important cellular uptake process, by investigating pH changes[5] and cathepsin activity[6] (a key lysosomal enzyme) associated with macropinocytosis. A DNA scaffold was used to assemble a controlled number of pH and/or cathepsin sensors.[7,8] Two types of pH-sensitive fluorophores with different *pKa* values, i.e., fluorescein (CF) and Oregon Green (OG), together with the pH-insensitive fluorophore Alexa 750 (A750), were assembled on a DNA scaffold allowing ratiometric pH detection. Two cathepsin enzyme substrates, cathepsin B and cathepsin D substrates,[9] have also been assembled for independent activity detection. A multiple-target detectable sensor was successfully synthesized, which simultaneously detected both pH change and cathepsin (cathepsin B and D) activity in a test tube. This sensor will be utilized for intracellular application.

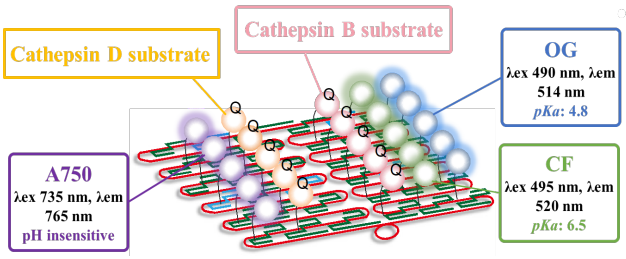

Fig. DNA scaffolded multiple-target detectable sensor for simultaneous detection of pH and cathepsin activity.

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Construction of an artificial CO_2 fixation compartment using DNA nanostructure as a scaffold

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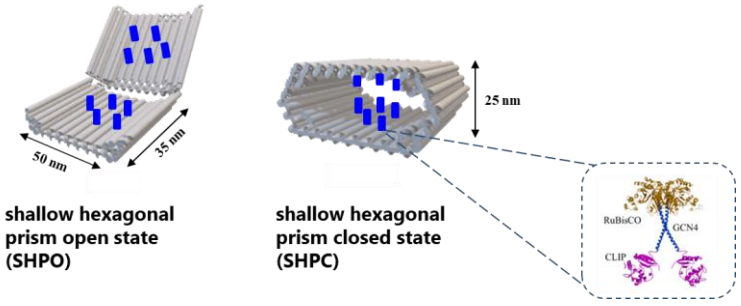
Keywords: CO_2 fixation; RuBisCO; DNA origami; Artificial compartment; Modular adaptor

Cellular systems tend to evolve intracellular organelles that persistently carry out biochemical reactions in small compartments. Substrate channeling is considered to be one of the most important factors to achieve highly efficient flow of successive enzymatic reactions in the compartments. Ribulose 1,5-bisphosphate carboxylase/oxygenase (RuBisCO), despite its low enzymatic activity, plays an important biological role in natural CO_2 fixation. In cyanobacteria, RuBisCO and carbonic anhydrase (CA) are encapsulated in carboxysomes with diameters of 100-200 nm.[1] These compact carboxysomes are thought to help RuBisCO overcome these shortcomings because of the packed RuBisCO conditions.

DNA nanostructures prepared by the DNA origami method can accurately assemble enzymes with precise limitation of the distance between the enzymes[2, 3]. Recent advances in reaction systems on DNA origami scaffolds show the potential for enhanced enzymatic activity.[4, 5] Here, we use dynamic DNA origami of the shallow hexagonal prism (SHP) to encapsulate RuBisCO in an artificial carboxysome. A modular adaptor (CLIP- GCN4) fused to RuBisCO (CG-RuBisCO) was constructed for assembly on SHP[3, 6]. The CO_2 fixation efficiency of CG-RuBisCO assembled on SHP will be investigated to understand the action of the natural carboxysome.



1) G. S, Espie, M. S, Kimber, *Photosynth Res*. **2011**, *109*, 7. 2) P. W. K, Rothemund, *Nature*. **2006**, *440*, 297. 3) T. M. Nguyen, E. Nakata, H. Dinh, T. Morii, *J. Am. Chem. Soc*. **2017**, *139*, 8487. 4) H. Dinh, E. Nakata, K. Mutsuda-Zapater, M. Saimura, M. Kinoshita, T. Morii, *Chem. Sci.* **2020**, *11*, 9088. 5) P. Lin, H. Dinh, Y. Morita, E. Nakata, T. Morii, *Adv. Func. Mater.* **2023**, *33*, 2215023. 6) H. Dinh, E. Nakata, P. Lin, M. Saimura, H. Ashida, T. Morii, *Bioorg. Med. Chem*. **2019**, *27*, 115.

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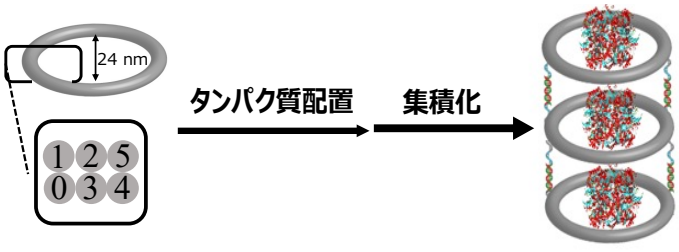
タンパク質を配置したDNAナノ構造体の集積化

(京大院エネ科[1]・京大エネ研[2]) ○鮮 樹輝[1]・中田 栄司[2]・Lin Peng[2]・森井 孝[2]
Assembly of the functional proteins located DNA nanostructures ([1]*Graduate School of Energy Science, Kyoto University,* [2]*Institute of Advanced Energy, Kyoto University*) ○Shuhui Xian[1], Eiji Nakata[2], Peng Lin[2], Takashi Morii[2]

In living organisms, various proteins and/or enzymes form complexes to efficiently convert and utilize energy. By mimicking the complex molecular systems observed in living organisms, diverse and highly efficient energy-utilizing systems can be realized that exceed the capabilities of a single enzyme alone. In our laboratory, we have focused on utilizing DNA nanostructures, such as DNA origami[1)], as a scaffold to construct energy-utilizing systems by locating enzymes, which is one of the functional biomolecules in living systems. Through our research, we have successfully developed the modular adaptor method, a simple and fast technique for locating enzymes on DNA nanostructures. By using this method, we have achieved high yields in integrating multiple types of proteins onto DNA nanostructures [2)]. In this study, we aim to further integrate protein-assembled DNA nanostructures to construct higher-order structures in which proteins are regularly and precisely arranged.
Keywords : DNA origami; Enzyme arrangement; Supramolecular structures and assemblies

生体内では、様々な物質が組織体を構築することで、多彩で高効率な機能を発揮している。このような高効率なシステムを試験管で構築するために、機能性タンパク質群を自在に配列して高次に集積させるための足場が必要となる。当研究室では、そのような構造ビルディングブロックとして、DNA origami 法[1)]に代表されるDNAナノ構造体に注目しており、DNAナノ構造体上に迅速かつ簡便にタンパク質を配置する方法「DNA結合性アダプター法」を開発し、DNAナノ構造体上に高収率に複数種類のタンパク質を配置することに成功している[2)]。本研究では、全長が数十ナノメートル程度のコンパクトなDNAナノ構造体を設計し、その構造体がさらに自己集積化することで、高次に集積化したタンパク質−DNAハイブリッド構造体の構築を目指す。本発表では、設計したDNAナノ構造体の設計と同定をおこない、その自己集積化についても評価をおこなった結果を報告する。



1) P. W. K. Rothemund, *Nature* **2006**, *440*, 297.
2) T. A. Ngo, H. Dinh, T. M. Nguyen, F. F. Liew, E. Nakata, T. Morii, *Chem. Commun*. **2019**, *55*, 12428.

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Ab initio DNA 合成における効率的増幅の検討

（日大院総合基）○片岡 由佳・久保 千尋・割石 智子・藤田 博仁・桒原 正靖
Investigation of efficient amplification in *ab initio* DNA synthesis (*Graduate School of Integrated Basic Science, Nihon University*) ○Yuka Kataoka, Chihiro Kubo, Tomoko Wariishi, Hiroto Fujita, Masayasu Kuwahara

Ab initio DNA synthesis with Prokaryotic DNA polymerases was found in the 1960's as a template/primer-independent DNA synthesis[1]. For example, *Thermococcus litoralis* (*Tli*) DNA polymerase can generate a pool of long linear oligonucleotide strands with random sequences in the presence of four deoxyribonucleoside triphosphates (dNTPs) and salts (*e.g.*, KCl, $(NH_4)_2SO_4$, and $MgCl_2$)[2,3]. Furthermore, it is known that the amplification efficiency can be accelerate by adding restriction endonucleases or nicking endonucleases[4]. It was revealed that sequences, which obtained by adding nicking endonuclease, generally contained repetitive sequences including its cleavage sites. However, the reaction mechanism has not yet been elucidated[5]. In this study, using evolutionary molecular engineering approaches, we enriched and identified sequences as amplifier element, which obtained by the isothermal nucleic acid amplification reaction in the presence of the nicking endonuclease. In this presentation, we will report on the correlation between the amplification efficiency and the primary and secondary structures of obtained sequences as well as their fragments.

Keywords : Ab initio DNA synthesis; Amplifier element; Isothermal nucleic acid amplification reaction; Sequencing

原核生物由来の DNA ポリメラーゼによる *ab initio* DNA 合成は、プライマーとテンプレートによらないヌクレオチド重合として 1960 年代に発見された [1]。例えば、*Thermococcus litoralis* (*Tli*) DNA ポリメラーゼは 4 つのデオキシリボヌクレオシド三リン酸 (dNTPs) と塩 (KCl, $(NH_4)_2SO_4$, $MgCl_2$ など) のみで長い直鎖状 DNA のランダムプールを生成する [2,3]。さらに、制限エンドヌクレアーゼやニッキングエンドヌクレアーゼなどを添加するとその増幅効率が高まることが知られている [4]。ニッキングエンドヌクレアーゼを添加して得られる配列はその認識部位を含む反復配列を多く含むことは明らかにされたが、その反応機構などは未だ解明されていない [5]。
本研究では、進化分子工学的手法により、ニッキングエンドヌクレアーゼを添加した等温核酸増幅反応で得られた増幅子を濃縮し、その配列を同定した。本発表では、得られた配列や断片化した配列の 1 次および 2 次構造等とその増幅効率との相関について報告する。

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二本鎖 DNA のマイクロメートルサイズの H 型構造体への自己集合

（電通大情報理工）○牧野　哲直・田仲　真紀子
Self-assembly of double-stranded DNA into micrometer-sized H-shaped structures (*Graduate School of Informatics and Engineering, The University of Electro-Communications*)
○Tetsunao Makino, Makiko Tanaka

The functions of biomolecules assembled in molecularly crowded environments have attracted attention in recent years. However, compared to the assemblies of proteins, which play significant roles in biochemical reactions within cells, knowledge regarding the assembly of DNA have been limited. Recently, we have revealed that short DNA with sticky ends self-assembles into hexagonal structures exceeding 10 μm in a crowded environment containing poly(ethylene glycol) and NaCl through heating and cooling processes.

In this study, we have newly discovered the formation of elongated H-shaped structures with a thickness of approximately 3 μm or less by the self-assembly of two kinds of double-stranded (ds) DNA with sticky ends (Fig. 1A). Furthermore, it was confirmed that the distribution within the H-shaped structures differs between two kinds of dsDNA with different lengths by Cy5-modified oligonucleotides (Fig. 1B). These results suggest that the formation of DNA assemblies in a crowded environment can be controlled by arbitrary DNA sequences.

Keywords：DNA, molecular crowding, self-assembly

細胞内はタンパク質や核酸、多糖類などの高分子で混み合う混雑環境であり、近年では分子混雑環境下で集合した生体分子の機能が注目を集めている。しかし、細胞内の生化学反応に大きく関与するタンパクの集合に比べ、DNA の集合に関する知見は多くない。我々はこれまでに、ポリエチレングリコールと NaCl を含む分子混雑環境下で、粘着末端を有する一種類の短鎖 DNA が 10 μm を超える大きさの六角形型構造体に自己集合することを発見している [1]。さらに本研究では、塩基長の異なる二種類の短鎖 DNA を用いることにより、太さが 3 μm 程度以下の細長い H 型の構造体が形成することを新たに発見した（Fig. 1A）。配列の末端に蛍光色素 Cy5 を修飾した結果、塩基長の違いにより H 型構造体内部の分布が異なることが明らかになった（Fig. 1B）。これらの結果により、分子混雑環境で形成される DNA 集合形態を塩基配列で制御できることが示唆された。

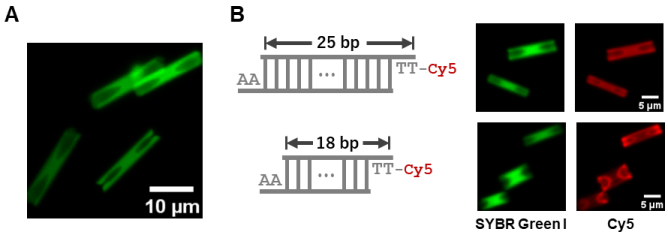

Fig.1 Fluorescence images of (A) H-shaped structures stained with SYBR Green I and (B) H- shaped structures containing Cy5-modified oligonucleotides.

1) T. Makino; D. Nakane; M. Tanaka, *ChemBioChem*, **2022**, *23*, e202200360.

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DNA のコアセルベートを誘導する白金錯体の探索

（鈴鹿医療科学大学薬）○田代 竜・山田　拓磨・矢野 芹佳・荒木 礼子・西原　大樹・中川 萌・植村 雅子・米田 誠治
Exploration of Pt complexes that induce DNA coacervate (Faculty of Pharmaceutical Sciences, Suzuka University of Medical Science) Ryu Tashiro, Takuma Yamada, Serika Yano, Ayane Araki, Moe Nakagawa, Hiroki Nishihara, Masako Uemura, Seiji Komeda

We explored platinum complexes that induce liquid-liquid phase separation of DNA and found that AMPZ, a pyrazolato-bridged platinum(II) dinuclear complex with antitumor activity, has a high ability to promote this phase separation. Furthermore, we observed that the AMPZ-mediated cross-linking reaction between DNA strands within the coacervate induces gelation. These results demonstrate the applicability of platinum complexes for phase separation and the ability to control the transformation from a coacervate to a gel by the reaction.
Keywords : DNA; platinum complex; liquid-liquid phase separation

液ー液相分離は、近年、細胞内での生命現象の制御と深い関わりがあることが明らかになっており、非常に注目されている物理現象である。コアセルベートとは、液ー液相分離によって物質が自発的に集合し形成する濃厚水溶液である。コアセルベートを金属錯体で制御する試みはこれまでほとんど行われておらず、コアセルベート形成を誘導する金属錯体の探索は、非常に興味深い試みである。我々は、7 種類の白金錯体から、生体分子である DNA の液-液相分離を誘導する白金錯体の探索を行った。1 本鎖 DNA とそれぞれの白金錯体を混合して顕微鏡観測を行ったところ、ピラゾラト架橋白金(II)二核錯体[{*cis*-Pt(NH_3)$_2$}$_2$(μ-OH)(μ-pyrazolato)](NO_3)$_2$ （AMPZ）が、DNA のコアセルベート形成を非常に高効率に誘導することを確認した。AMPZ はカチオン性錯体で、静電的な相互作用や、グアニン N7 位を介した共有結合によって DNA と結合する[1]。後者の反応の進行に伴って、AMPZ が異なる DNA 鎖のグアニンを架橋し、コアセルベートがゲル化することも明らかにした。今回の結果は、白金錯体の液-液相分離への応用性を示し、コアセルベートからゲルへの変換という状態の制御ができることを示している。

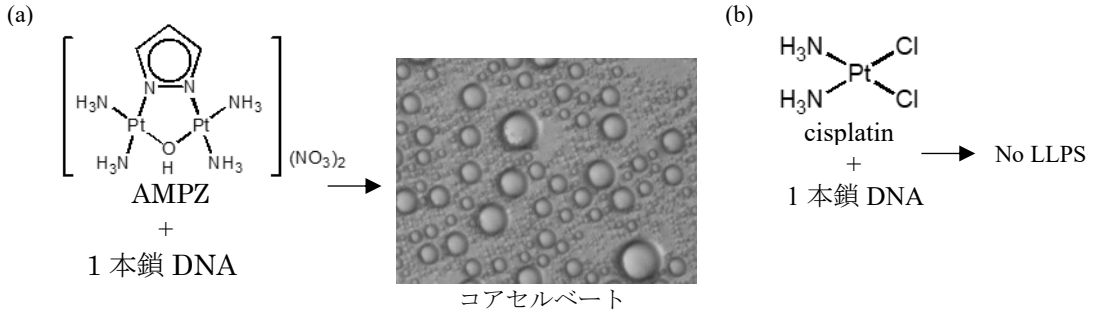

Figure 1. (a) AMPZ と 1 本鎖 DNA から形成されるコアセルベート(b) cisplatin と 1 本鎖 DNA からは液-液相分離がおこらない

1) Komeda et al., *Metallomics*, **2011**, 3, 650 655.

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金ナノ粒子を用いた光活性化 siRNA 転写のための鋳型環状 DNA の設計

（北大院生命 [1]・北大電子研 [2]）○池水友紀 [1]・Cheah Weijie[1]・与那嶺雄介 [2]・三友秀之 [2]・居城邦治 [2]

Design of Template Circular DNA for Light-triggered Activation of siRNA Transcription Utilizing Gold Nanoparticles ([1]*Graduate School of Life Science, Hokkaido University*, [2]*Research Institute for Electronic Science, Hokkaido University*) ○Tomoki Ikemizu,[1] Weijie Cheah,[1] Yusuke Yonamine,[2] Hideyuki Mitomo,[2] Kuniharu Ijiro[2]

RNA interference using siRNA suppresses expression of target proteins and holds promise as pharmaceuticals. However, its drug efficacy can be decreased due to biochemical degradation of siRNA and spatiotemporal control of RNA interference needs to be improved. We have previously investigated control of rolling circle transcription of siRNA using circular DNA as a template. Specifically, by combining circular DNA with gold nanoparticles (AuNP), transcription was suppressed by steric hindrance that prevents approach of RNA polymerase. In this study, we are developing a system in which circular DNA and AuNPs are linked through a double-stranded DNA linker and transcription is initiated by release of the circular DNA with heat generated by light irradiation (Figure 1a). In this presentation, we will report (1) introduction of a DNA linker into circular DNA at a position that does not interfere with transcription (Figure 1b), and (2) dissociation of the DNA linker by heating. We will also discuss dissociation of the DNA linker with green light irradiation.
Keywords : Transcription Control, Gold Nanoparticles, RNA Polymerase, Rolling Circle Transcription

siRNA を用いた RNA 干渉は、任意の標的タンパク質の発現を抑制できるため、医薬品への応用が期待されている。しかし、siRNA の生化学的な分解による薬効の低下や、RNA 干渉の時空間制御が課題である。我々はこれまでに、環状 DNA を鋳型とした siRNA のローリングサークル転写の制御を検討し、環状 DNA と金ナノ粒子（AuNP）を結合させることで、立体障害により RNA 合成酵素の接近を妨げ、転写を抑制することを見いだした。本研究では、抑制した転写を光照射で開始する系（Figure 1a）を構築するために、環状 DNA に対して転写を妨げない位置に DNA リンカーを導入し（Figure 1b）、加熱による DNA リンカーの解離を確認した。また緑色光の照射による DNA リンカーの解離も試みた。

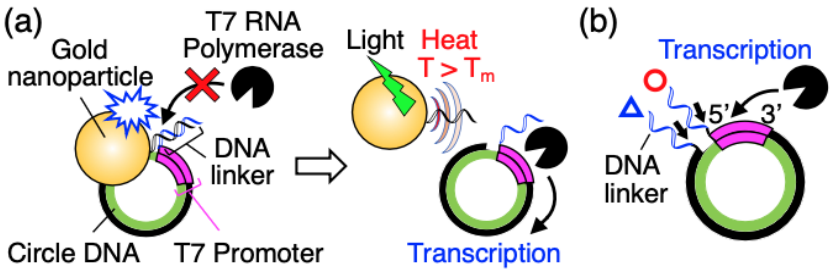

Fig. 1 (a) Suppression of siRNA transcription with a gold nanoparticle by blocking access of T7 RNA polymerase to the promoter. (b) Introduction of a DNA linker into a circle DNA template at a position which does not interfere with transcription.

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イミダゾリウム修飾シリカ担体を用いた夾雑物中からの簡便なDNA 抽出

（地方独立行政法人大阪産業技術研究所）○柿倉　泰明
Imidazolium modified-silica for facile DNA extraction from contaminants (*Osaka Research Institute of Industrial Science and Technology*)
○Yasuaki Kakikura

Imidazolium modified silica (IMS) was prepared toward facile DNA extraction from a series of complex sample matrices, such as milk and aqueous solutions with PCR inhibitors. The IMS was capable for specifically adsorbing DNA by electrostatic interactions with the imidazolium, followed by releasing the adsorbed DNA effectively by means of high concentration buffer. The results indicate that the developed method could be employ for nucleic acid testings.
Keywords : DNA Extraction; Imidazolium; Nucleic Acid Testing

核酸検査は、病原体などの標的に由来する核酸を増幅して検出する手法であり、微量の標的を高感度検出できる。そのため、医療や農畜産などの分野で広く活用されている。一方で、その前処理工程である核酸抽出に着目すると、遠心分離などの煩雑な操作を要する手法が標準的に用いられている。本発表では、シリカゲル表面にイミダゾリウムを修飾した核酸吸着体(Imidazolium modified silica, IMS)の作製、およびこれを用いた夾雑物を含む試料からの機器フリーDNA 抽出方法について検討した結果を報告する。

アルコキシシランを原料として、ゾル―ゲル法によりチオール基を有するシリカゲルを作製した。このシリカゲル表面に、ene-thiol 反応によってビニルイミダゾリウムを修飾して、IMS を得た。夾雑物を含む DNA 試料の一例として、市販の牛乳 1 mL 中に大腸菌(終濃度：10^3 CFU/mL)をスパイクし、90 ^{o}C で 10 分間加熱した液を用いた。IMS をピペットチップに装填し、DNA 試料を通液した。続いて、IMS を滅菌水で通液洗浄し、高濃度の緩衝液をピペッティングすることで溶出操作を行った。DNA の検出は、16S rRNA 遺伝子を検出対象としたリアルタイム PCR により行った。その結果、IMS への DNA の吸着、ピペッティング溶出操作による DNA の溶出、および溶出液を鋳型としたリアルタイム PCR 検出が可能であることを確認した。当日は、種々の PCR 阻害物質を含む試料からの DNA 抽出の検討結果についても併せて報告する。

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蛍光色素導入 SNA を利用したらせん増幅能評価

（名大院工）樫田 啓・○杉山 乙珠・浅沼 浩之
Evaluation of helical amplification ability of using SNA tethering fluorescent dyes (*Graduate School of Engineering, Nagoya University*) Hiromu Kashida, ○Itsumi Sugiyama, Hiroyuki Asanuma

Chiral amplification is a phenomenon where a small amount of chiral molecule induces and amplifies chirality of achiral supramolecular polymers. The amplified chiral information can be converted into CD and circularly polarized luminescence (CPL) signals. However, there are few reports of chiroptical amplification systems working in aqueous solution.

In previous study, we have reported a chiral amplification system using artificial nucleic acids. Serinol nucleic acid (SNA) oligomers having symmetrical sequences are achiral. The chirality of threoninol nucleic acids (*a*TNA) can be amplified by achiral SNA supramolecules. In addition, it can be converted into CPL signals when SNA was modified with pyrenyluracil (Up) tethering pyrene. In this study, we synthesized a new fluorescent base pyrenyladenine (Ap) and evaluate its chiroptical amplification ability.

Keywords: Serinol nucleic acid; Threoninol nucleic acid; Helical amplification; Circular dichroism

超分子キラル増幅（らせん増幅）とは、アキラル超分子に少量のキラル分子を添加した際に、そのキラリティが増幅する現象である。これを利用すれば、分子のキラル情報を CD や円偏光発光（CPL）の情報に変換できるため、非常に注目されている。しかしながら、これまでの大半の系は有機溶媒中で機能しており、水中で機能するキラル増幅系の報告は多くないのが現状であった。

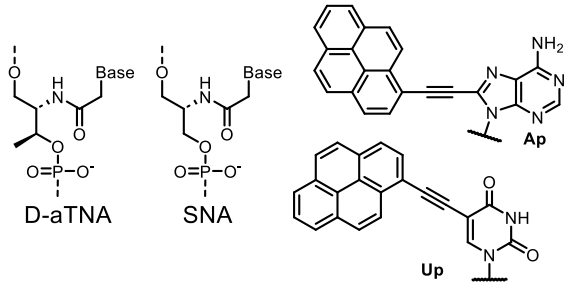

Fig. 1. Chemical structures of artificial nucleic acids.

それに対し、当研究室ではこれまでにセリノール核酸（SNA; Fig. 1）とトレオニノール核酸（*a*TNA）の二重鎖形成を用いたキラル増幅系を開発した [1]。対称な配列をもつ SNA オリゴマーはアキラルになるという極めてユニークな性質をもつ。このアキラル SNA 構造体に対し、少量の *a*TNA を添加した際に、そのキラリティが増幅することがわかった。また、SNA 中にピレニルウラシル（Up）を導入することで SNA のらせんの情報を CPL に変換することに成功している [2]。本研究では、新たにピレニルアデニン（Ap）を合成し、SNA に導入した。この Ap 導入 SNA オリゴマーのキラル増幅能について検討を行ったので報告する。

1) H. Kashida, K. Nishikawa, W. Shi, T. Miyagawa, H. Yamashita, M. Abe, H. Asanuma, *Chem. Sci.* **2021**, *12*, 1656-1660.
2) H. Kashida, K. Nishikawa, Y. Ito, K. Murayama, I. Hayashi, T. Kakuta, T. Ogoshi, H. Asanuma, *Chem. Eur. J.* **2021**, *27*, 14582-14585.

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DNA との二重鎖形成による人工塩基導入 SNA の配列解析

（名大院工 [1]）○日比野 希美 [1]・浅沼 浩之 [1]・樫田 啓 [1]
Sequence analysis of SNA bearing artificial bases by duplex formation with DNA ([1]*Graduate School of Engineering, Nagoya University*) ○Nozomi Hibino,[1] Hiroyuki Asanuma,[1] Hiromu Kashida[1]

Recently, enzymes and aptamers composed of xeno nucleic acids (XNAs) have attracted considerable attention owing to their high nuclease resistance and stability. However, there is no general method to analyze XNA sequences. We have developed a new sequence analysis method for XNAs by using duplex formation between XNA and DNA. Sequences of serinol nucleic acid (SNA) were successfully analyzed via this method. Since this method is based only on duplex formation, SNA oligomers bearing non-natural bases would also be analyzed.

In this study, we aimed to analyze longer SNA oligomers and 20mer SNA was successfully sequenced. We also tried to analyze SNA sequences containing non-natural bases.
Keywords : Xeno nucleic acid; Serinol nucleic acid; Sequencing; Cyanuric acid

高い酵素耐性や化学的安定性を持つことから人工核酸を用いた酵素やアプタマーが近年注目されている。しかしながら、従来の配列解析法は酵素による伸長反応を利用していたため、適用可能な人工核酸の化学構造に大幅な制限があった。それに対し、当研究室では、二重鎖形成を利用した人工核酸の新たな配列解析法を開発した。これまでにセリノール核酸 [1)]（SNA; Fig.1）10 量体の配列解析が可能であることを明らかにしている。本手法は二重鎖形成のみを利用しているため、従来法では困難であった様々な人工核酸の配列解析や修飾塩基導入核酸の配列解析も可能であるという特長がある。

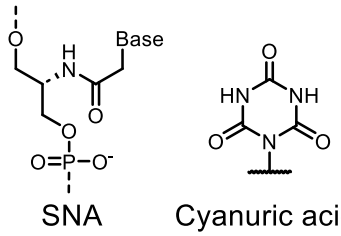

Fig. 1. Chemical structures of SNA and cyanuric acid.

そこで、本研究では本手法を更に発展させることでより長い SNA、及び人工塩基をもつ SNA の配列解析を目指した。具体的にはまず 20 量体 SNA の配列解析を目指した。末端をビオチン修飾した SNA に対し、10 量体のランダム配列を持つ DNA をそれぞれ二重鎖形成させ、ストレプトアビジン磁気ビーズ上に固定化した。その後、SNA と二重鎖形成した DNA 配列を溶出し、PCR で増幅して次世代シーケンサーによって配列解析を行った。その結果、元の SNA 配列に相補的な DNA 配列がそれぞれ得られた。すなわち、本手法を利用することでより長い鎖長をもつ SNA の配列解析が可能であることが明らかになった。本発表では更に、人工塩基であるシアヌル酸（Fig. 1）を導入した SNA の配列解析についても報告する予定である。

1) H. Kashida, K. Murayama, T. Toda, H. Asanuma, *Angew. Chem. Int. Ed.* **2011**, *50*, 1285-1288.

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人工塩基を導入した PNA 配列解析法の開発

(名大院工[1]・名大院理[2]) ○稲垣 和真[1]・樫田 啓[1]・愛場 雄一郎[2]・荘司 長三[2]・浅沼 浩之[1]
Development of a novel method to analyze PNA sequences bearing artificial bases ([1]*Graduate School of Engineering, Nagoya University*, [2]*Graduate School of Science, Nagoya University*)
○Inagaki Kazuma,[1] Hiromu Kashida,[1] Yuichiro Aiba,[2] Osami Shoji,[2] Hiroyuki Asanuma[1]

Sequencing methods are essential for the development of enzymes and aptamers composed of xeno nucleic acids (XNAs). However, there is no general method to analyze XNA sequences. In the previous study, we have developed a new method to sequence peptide nucleic acid (PNA). Since this method does not require enzymatic reactions, it can be used to analyze PNA bearing various non-natural bases. In this study, we analyzed PNA sequences containing artificial bases, pyrenyluracil and cyanuric acid. Effects of the number of these bases on the sequencing performances were investigated in detail.
Keywords : Xeno nucleic acid; Peptide nucleic acid; Pyrene; Cyanuric acid; Sequencing

人工核酸による酵素やアプタマーの開発を行うためには、配列解析が必須である。しかしながら、従来の配列解析法では適用可能な人工核酸の化学構造が大幅に制限されていた。それに対し、当研究室では二重鎖形成を利用することで人工核酸の配列を解析する新しい手法を開発した。この手法を利用することで、ペプチド核酸（PNA）[1)]の配列解析が可能であることを明らかにしている。本手法は酵素反応を利用しておらず、二重鎖形成のみを利用しているため、様々な人工塩基導入 PNA の配列解析が期待できる。

そこで本研究では、開発した配列解析法を利用することで様々な人工塩基導入PNAの配列解析を試みた。まず人工塩基シアヌル酸(Y ; Fig. 1)を導入した PNA 配列解析について検討を行った。Y モノマーを 3 個導入し、かつ末端をビオチン修飾した 10mer の PNA を、ランダム配列を持つ DNA を二重鎖形成させ磁気ビーズ上に固定化した。その後、二重鎖形成した DNA 配列を溶出し、PCR で増幅して次世代シーケンサーによる配列解析を行った。その結果、シアヌル酸導入 PNA の配列解析が可能であることが明らかとなった。本発表では、ピレニルウラシル(Up ; Fig. 1)導入の配列解析を行った結果や、人工塩基の数が配列解析結果に及ぼす効果についても併せて報告する予定である。

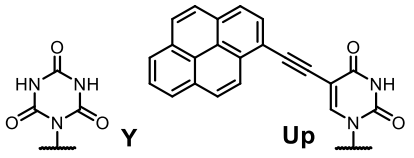

Fig. 1. Chemical structures of Y and Up.

1) P.E. Nielsen, M. Egholm, R.H. Berg, O. Buchardt, *Science*, **1991**, *254*, 1497-1500.

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パラレル型ホモプリン XNA が形成するユニークな三重鎖構造

(名古屋大学[1]・神戸薬科大学[2]) ○労 思源[1]・有吉 純平[2]・佐藤 史経[1]・神谷 由紀子[1,2]・浅沼 浩之[1]
Unique homopurine parallel-type triplex structure formed by XNA ([1]*Nagoya University*, [2] *Kobe Pharmaceutical University*) ○ Siyuan Lao,[1] Jumpei Ariyoshi,[2] Fuminori Sato,[1] Yukiko Kamiya,[1,2] Hiroyuki Asanuma[1]

Nucleic acids can form various multi-stranded structures through Watson-Crick base pair and Hoogsteen base pair. Acyclic artificial nucleic acid SNA (Serinol nucleic acid) and Threoninol Nucleic Acid (L-*a*TNA), developed by our lab., can hybridize with natural nucleic acid. Previous crystal structural data suggested that the RNA strand of SNA/RNA hybridize another SNA via Hoogsteen base pairing to form a unique parallel-type triplex structure C:G*G. This result prompted us to study XNA:RNA*XNA triplexes (XNA=SNA or L-*a*TNA) with the homopurine XNA-TFO in the parallel orientation. We found that the parallel XNA:RNA*XNA triplex was remarkably stable, even though A*A pair has a single hydrogen bond.
Keywords : Artificial nucleic acid, Triplex, homopurine parallel triplex

核酸はワトソン・クリック塩基対およびフーグスティーン塩基対を介して多重鎖構造を形成する超分子性を有している。一般的な三重鎖構造は、鎖の方向性に基づき平行型 Y:R*Y(：Watson-Crick 塩基対、*Hoogsteen 塩基対、R=プリン塩基、Y＝ピリミジン塩基)および逆平行型 Y:R*R に分類される。一方、我々は非環状型人工核酸である SNA と L-*a*TNA (Fig. 1)と RNA のヘテロ二重鎖の結晶構造解析において、SNA あるいは L-*a*TNA と RNA が C:G*G 平行型の三重鎖構造(Fig. 2 middle)が形成するという予期しない結果を得た[1]。そこで本研究では非環状型人工核酸が平行型 Y:R*R 三重鎖を形成可能か詳細に検討した。非環状型人工核酸同士の相互作用を避けるために、SNA と RNA からなるヘアピン型二重鎖(SNA:RNA)と、SNA-TFO を用いた。ゲルシフトアッセイと融解温度測定から、SNA:RNA*SNA は A*A 対が 1 本の水素結合にも関わらず(Fig.2 right)極めて安定な平行型三重鎖を形成することが明らかとなった[2]。L-*a*TNA では SNA より更に安定な三重鎖形成を形成した。

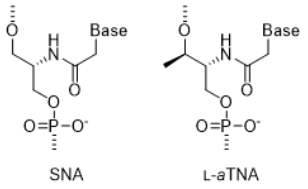

Fig. 1. Structures of SNA and L-*a*TNA

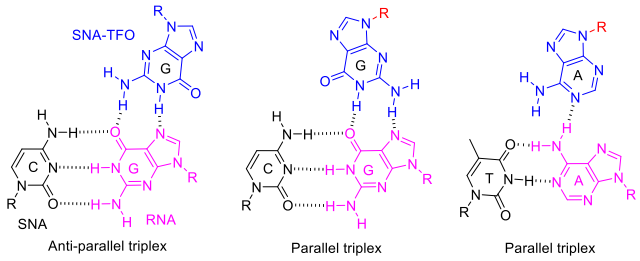

Fig. 2. C:G*G base pairs in antiparallel (left) and parallel (middle), and T:A*A (right) base pairs in parallel triplexes.

1) Y. Kamiya, *et al.*, *Commun. Chem.*, **2020**, *3*, 156.
2) Y. Kamiya, S. Lao, *et al.*, *Chem. Commun.* **2024**, DOI: 10.1039/d3cc05555h

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

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC H936(936, Bldg. 9 [3F])

[H936-3pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Akimitsu Okamoto, Takashi Sera

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[H936-3pm-01]
Inhibition of RNA replication of avian influenza virus using artificial RNA-cleaving enzymes

○Tomoaki Mori[1], Koichi Mori[1], Takashi Sera[1] (1. Okayama University)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[H936-3pm-02]
N-terminal Modification of Antibodies Using Triazolecarbaldehyde Derivatives Containing a Fluorescent Dye

○Yuya Maeda[1], Takanobu Yasuda[2], Akira Onoda[1,3] (1. Graduate School of Environmental Science, Hokkaido University, 2. Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, 3. Faculty of Environmental Earth Science, Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[H936-3pm-03]
Immobilization of green fluorescent protein with an N-terminally tagged alkyl chain onto the surface of liposome

○Lisa Tara Connolly[1], Akira Onoda[1,2] (1. Grad. School Env. Sci., Hokkaido Univ., 2. Faculty of Env. Earth Sci., Hokkaido Univ.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[H936-3pm-04]
Chemical protein synthesis via peptide ligation on PNA scaffold

○Sae Suzuki[1], Shingo Mizushima[1], Yukino Takeuchi[1], Gosuke Hayashi[1], Hiroshi Murakami[1,2] (1. Nagoya Univ., 2. Institute of nano-life-systems, Nagoya Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[H936-3pm-05]
Efficiency of protein translocation into HeLa cells depends on fusion sites of cell penetrating peptide sequence

○Akari Miwa[1], Koki Kamiya[1] (1. Grad. Sci. and Tech., Gunma Univ.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[H936-3pm-06]
Creation of enveloped viral replicas modified with nuclear-localized signal peptide

○Mizuki Wada[1], Kentarou Sakamoto[2], Hiroto Furukawa[2], Hiroshi Inaba[2], Kazunori Matsuura[2] (1. Faculty of Engineering, Tottori University, 2. Graduate School of Engineering, Tottori University)

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Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[H936-3pm-07]
Chemical diversification of C-terminal of proximal ubiquitin in the synthetic heterotypic polyubiquitin chain

○Takafumi Furuhata[1], Choi Bumkyu[1], Taiki Uno[1], Yusuke Sato[2], Kei Okatsu[3], Shuya Fukai[3], Akimitsu Okamoto[1] (1. The Univ. of Tokyo, 2. Tottori Univ., 3. Kyoto Univ.)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[H936-3pm-08]
Structure Controlled Synthesis of Heterotypic Ubiquitin Chain using Oxime Ligation

○Ryota Shinohara[1], Takafumi Furuhata[1], Seigo Yamada[1], Akimitu Okamoto[1] (1. The University of Tokyo)

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

English
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[H936-3pm-09]
GTP Responsiveness of Biomolecular Machine GroEL by Binding Pocket Engineering

○Ryotaro Toda[1], Kiyoshi Morishita[1], Takayuki Miki[1], Hideki Taguchi[2], Takuzo Aida[1,3] (1. The University of Tokyo, 2. Tokyo Institute of Technology, 3. RIKEN Center for Emergent Matter Science)

English
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[H936-3pm-10]
Development of Self-assembling Peptide Tags That Form Intracellular Droplets in Response to Hydrogen Peroxide

○Masatoshi Shimizu[1], Takuzo Aida[1], Takayuki Miki[1] (1. The Univ. of Tokyo)

English
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC
[H936-3pm-11]
Toward a near infrared (NIR) fluorescent chemigenetic indicator for Ca^{2+} based on photoactive yellow protein (PYP)-tag

○Takumi Yanagimachi[1], Takuya Terai[1], Robert E. Campbell[1] (1. Graduate School of Science, The University of Tokyo)

Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC
[H936-3pm-12]
Chemigenetic red calcium indicator: improvement through directed evolution and imaging applications

○Shosei Imai[1], Wenchao Zhu[1], Takuya Terai[1], Robert Earl Campbell[1] (1. The university of Tokyo)

Japanese
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC
[H936-3pm-13]

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Towards the development of chemigenetic Ca^{2+} indicators based on dihydrofolate reductase

○Kenryo Sakoi[1], Takuya Terai[2], Robert Earl Campbell[2] (1. School of Science, The University of Tokyo, 2. Graduate School of Science, The University of Tokyo)

Japanese
3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC
[H936-3pm-14]

Photoreaction of light-induced cluster forming protein TePixD and its downstream molecule

○Chihiro Aramoto[1], Yusuke Nakasone[1], Yusuke Masuda[1], Shunrou Tokonami[2], Masahide Terazima[1] (1. Kyoto University, 2. Gakushuin University)

Japanese
3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC
[H936-3pm-15]

Opto-control of protein activities utilizing dimerization of photosensor eBLUF

○Takafumi Kuno[1], Yusuke Nakasone[1], Kazuhiro Sakamaki[1], Masahide Terazima[1] (1. Kyoto Univ.)

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人工 RNA 切断酵素を用いた鳥インフルエンザウイルスの RNA 複製阻害

（岡大院ヘルス）○森 友明・森 光一・世良 貴史
Inhibition RNA replication of avian influenza virus using artificial RNA-cleaving enzymes (*Graduate School of Interdisciplinary Science and Engineering in Health Systems, Okayama University*) ○Tomoaki Mori, Koichi Mori, Takashi Sera

We previously developed an artificial DNA-cleaving enzyme that could specifically cleave a target DNA sequence in a DNA viral genome as novel antiviral drugs, and reported the DNA viral replication inhibition method in animal cells using this enzyme. To extend this replication inhibition method to RNA viruses, we also developed an artificial RNA-cleaving enzyme that targeted an RNA viral genome and reported that its enzyme could cleave the target RNA sequence in the RNA viral genome in vitro. In the present study, we examined whether our artificial RNA-cleaving enzyme could inhibit the replication of avian influenza virus in animal cells. Avian influenza viruses not only cause significant damage to the poultry industry, but are also concerned about causing a pandemic when the viruses acquire the ability to infect humans. During the viral replication process, a single-stranded negative-stranded RNA as the viral genome and its complementary single-stranded positive-RNA appear. We examined the inhibition of avian influenza viral RNA replication in animal cells using artificial RNA-cleaving enzymes targeting each of these two types of RNAs. We will present the details.
Keywords : Artificial RNA-cleaving enzyme; RNA virus; Avian influenza virus; Inhibition of viral replication

我々はこれまでに、新規の抗ウイルス剤として標的 DNA ウイルスのゲノムを特異的に切断できる人工 DNA 切断酵素を開発し、それを用いた動物細胞内での DNA ウイルス複製阻害法を報告している(1)。また、この複製阻害法を RNA ウイルスへ適用拡大するために RNA ウイルスのゲノムを標的とする人工 RNA 切断酵素を開発し、試験管内でその標的 RNA 配列を切断できることも報告している(2)。本研究では、動物細胞内において、我々の人工 RNA 切断酵素が RNA ウイルスの一種である鳥インフルエンザウイルスの複製を阻害できるかを検証した。鳥インフルエンザウイルスは養鶏業界に多大な被害を与えるだけでなく、ヒトへの感染能を獲得した場合のパンデミックが危惧されているウイルスである。ウイルスの複製過程では、ゲノムである一本鎖マイナス鎖 RNA とそれに相補的な一本鎖プラス RNA が現れる。今回、動物細胞内において、これら 2 種類の RNA をそれぞれ標的とした人工 RNA 切断酵素を用いて、鳥インフルエンザウイルスの RNA 複製阻害を検証したので、その詳細について報告する。

(1) Mino, T., Mori, T., Aoyama, Y. and Sera, T. (2013) *PLoS One* **8**, e856633.
(2) Mori, T., Nakamura, K., Masaoka, K., Fujita, Y., Morisada, R., Mori, K., Tobimatsu, Y. and Sera, T. (2016) *Biochem. Biophys. Res. Commun.* **479**, 736-740.

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トリアゾールカルボアルデヒド基により蛍光色素を N 末端に修飾した抗体の調製

(北大院環境科学[1]・東工大化生研[2]・北大院地球環境科学[3])
○前田 侑也[1]・安田 貴信[2]・小野田 晃[1,3]

N-terminal Modification of Antibodies Using Triazolecarbaldehyde Derivatives Containing a Fluorescent Dye ([1]*Grad. Sch. of Env. Sci., Hokkaido Univ.*, [2]*CLS, Tokyo Tech.*, [3]*Faculty of Env. Earth Sci., Hokkaido Univ.*) ○Yuya Maeda[1], Takanobu Yasuda[2], Akira Onoda[1,3]

Fluorescent labeling of proteins is widely used in the preparation of biosensors and other devices that visualize the dynamic behavior of biomolecules. Immunoassay enables selective and sensitive detection of the target by specific and robust antigen–antibody interaction. A site-specific and simple fluorescent labeling method for antibodies is important to obtain quality immunosensors. Previously, our group reported that 1*H*-1,2,3-triazole-4-carbaldehyde (TA4C) derivatives specifically react with the N-terminal amino group through the formation of a 4-imidazolidinone ring.[1] In this presentation, we will report the fluorescent labeling of antibodies with TA4C derivatives and characterization of the conjugate (Figure 1).
Keywords: Antibody; N-terminus; Chemical Modification; Site-specificity; Fluorescent Probes

タンパク質の蛍光標識は、生体内物質の動的挙動を可視化するバイオセンサーなどの調製に広く利用されている。バイオセンサーの中でもイムノアッセイは抗原抗体反応を利用した分析法であり、その特異性と親和性から検出感度や選択性に優れている。品質の高い免疫センサーを得るには、抗体に対して位置特異的かつ簡便に蛍光標識する手法が重要である。当研究室は、1*H*-1,2,3-トリアゾール-4-カルボアルデヒド (TA4C) 誘導体が N 末端のα-アミノ基に対して特異的に反応し、化学修飾できることを報告している [1)]。本研究は、TA4C 誘導体を用いて位置特異的に蛍光標識した抗体の調製を目的とした。蛍光色素を有する TA4C 誘導体を用いて N 末端に蛍光色素を連結した抗体を調製し、ESI-TOF MS および SDS-PAGE で評価した (Figure 1)。

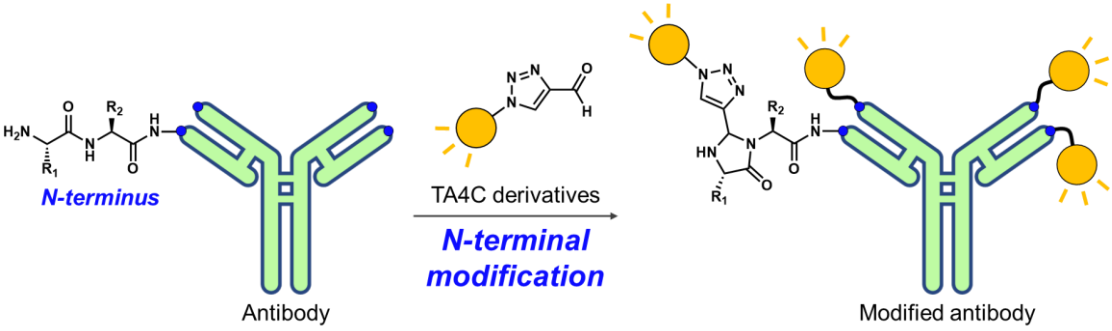

Figure 1. N-terminal modification of antibodies using TA4C derivatives containing a fluorescent dye.

1) A. Onoda, N. Inoue, E. Sumiyoshi, T. Hayashi, *ChemBioChem*, **2020**, 21, 1274.

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N 末端に長鎖アルキル基を修飾した緑色蛍光タンパク質のリポソーム表面への固定化

（北大院環境科学[1]・北大院地球環境科学[2]）○コノリー　里沙[1]・小野田　晃[2]

Immobilization of Green Fluorescent Protein with an N-terminally Tagged Alkyl Chain Onto The Surface of Liposome ([1]*Grad. Sch. Env. Sci., Hokkaido Univ.*, [2]*Grad. Sch. Env. Earth Sci., Hokkaido Univ.*) ○Lisa Connolly,[1] Akira Onoda[1,2]

Liposome is used as a carrier in DDS due to their excellent feature in reduced side effects and allergy. Modification of the liposome surface with peptides or proteins has been shown to improve in-vivo cell targeting in blood and inhibits uptake into the reticuloendothelial system. In this study, we aim to prepare targeting liposomes, in which proteins modified with alkyl chain at the N-terminus were immobilized onto the surface. Alkyl groups were linked on N-terminus of GFP using a triazolecarbaldehyde precursor developed in our group. We investigated methods for immobilization of modified GFP onto the surface of liposomes.

Keywords : Chemical Modification of Proteins; Site-specific-Modification; Liposme; Drug Delivery System; Fluorescent Probes

リポソームはリン脂質からなる小胞であり、生体適合性や生分解性を有するため副作用やアレルギーの軽減の点で優れた DDS のキャリアとして利用されている。より精度の高い薬物送達の実現に向けて組織や細胞への標的能を付与するために、リポソーム表層に化学修飾を施す研究が精力的になされている。本研究では、長鎖アルキル基を N 末端に位置特異的に連結した修飾タンパク質を、リポソーム表層に固定化することで、組織標的能の高いリポソームの調製を目指した。まずアルキル鎖 (C_n) を N 末端に特異的に修飾した緑色蛍光タンパク質 (C_n-GFP) を調製した。タンパク質修飾剤には、当研究室が開発した 1*H*-1,2,3-トリアゾール-4-カルボアルデヒド (TA4C) 誘導体を用いた[1]。ジムロート転移反応により骨格にアルキル鎖をもつ TA4C 誘導体 (C_n-TA4C) を合成した。TA4C 誘導体はイミダゾリジノン環を形成することにより、タンパク質の N 末端を特異的に修飾することが可能である。本発表では、TA4C 誘導体によって長鎖アルキル基を N 末端に修飾した GFP を、疎水性相互作用によってリポソーム表面へ固定化し、蛍光顕微鏡で評価した（Figure 1）。

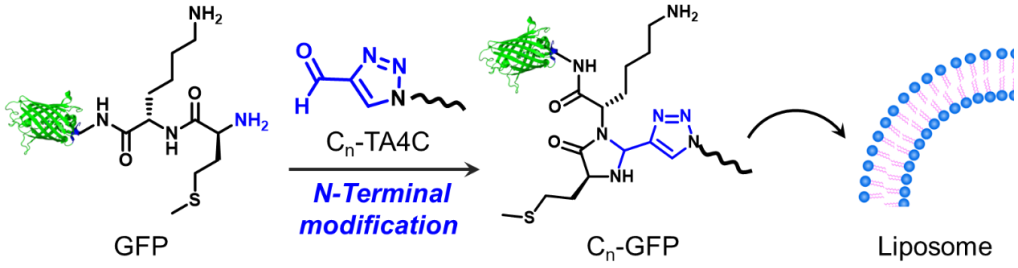

Figure 1. Embedding green fluorescent protein with N-terminal modification using TA4C derivative onto the surface of liposomes

1) A. Onoda, N. Inoue, E. Sumiyoshi, T. Hayashi, ChemBioChem, **2020**, 21, 1274.

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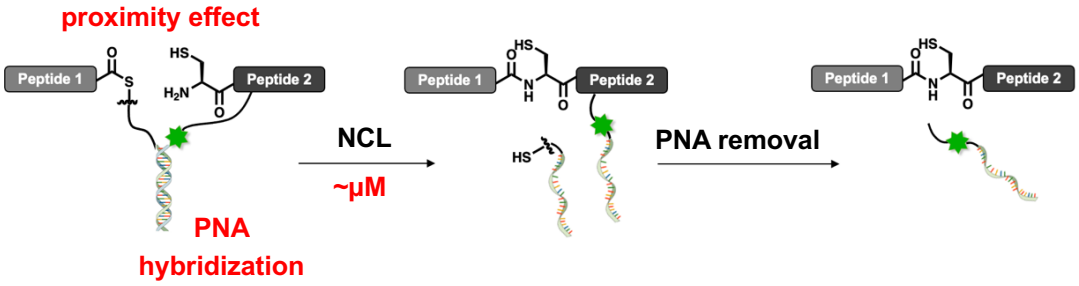
PNA 足場ペプチド連結反応によるタンパク質化学合成

(名大院工[1]・名大ナノライフ研[2]) ○鈴木 沙依[1]・水嶋 真吾[1]・竹内 優紀乃[1]・林 剛介[1]・村上 裕[1,2]
Chemical Protein Synthesis via Peptide Ligation on PNA Scaffold ([1]*Graduate School of Engineering, Nagoya University*, [2]*Institute of nano-life-systems, Nagoya University*) ○Sae Suzuki,[1] Shingo Mizushima,[1] Yukino Takeuchi,[1] Gosuke Hayashi,[1] Hiroshi Murakami[1,2]

In chemical protein synthesis, peptide ligation is a key reaction to assemble peptide segments. The most popular ligation reaction is native chemical ligation (NCL)[1], in which a peptide bearing thioester at the C-terminus reacts with a peptide bearing cysteine at the N-terminus. However, hydrophobic and aggregative peptides often can not be ligated under conventional NCL reaction conditions because of the difficulty in handling. To overcome this problem, we attempted to develop a proximity effect-assisted NCL reaction system using PNA hybridization to accelerate peptide ligation in a highly diluted condition. We demonstrated that the NCL on PNA scaffold proceeds at concentrations as low as single digit μM. Furthermore, we succeeded in the chemical protein synthesis by applying this PNA scaffold-mediated NCL system.
Keywords : Chemical Protein Synthesis; Native Chemical Ligation; PNA

タンパク質を有機化学的に作製する「タンパク質化学合成法」では、ペプチド同士を繋ぎ合わせるペプチド連結反応が鍵となる。最も頻用されているのは、チオエステル-システイン間の反応であるネイティブケミカルライゲーション（NCL）である[1)]。しかし疎水性の高いペプチドは、通常の NCL 反応条件で凝集・沈殿してしまうため、連結が困難である。そこで本研究では、ペプチド合成と相性の良いペプチド核酸、PNA をペプチドに導入し、PNA の二本鎖形成がもたらすペプチド断片の近接効果を利用することで、連結反応を加速させる手法の確立を目指した。ペプチド-PNA コンジュゲートを合成し、PNA を足場とした連結反応を行った結果、従来法と比べて 1000 倍程度の低濃度の条件（~μM）で NCL 反応が進行することを明らかにした。また、この PNA 足場 NCL 反応系を応用して、タンパク質の化学合成にも成功した。



1) Synthesis of protein by native chemical ligation. P. E. Dawson, et al. Science. 1994, 266, 776.

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膜透過性ペプチド配列の融合位置によるタンパク質の細胞内輸送効率の変化

（群馬大院理工[1]）○三輪 明星[1]・神谷 厚輝[1]
Efficiency of protein translocation into HeLa cells depends on fusion sites of cell penetrating peptide sequence (*Graduate School of Science and Technology, Gunma University*) ○Akari Miwa, Koki Kamiya

Cell penetrating peptides (CPPs)-mixing water-soluble proteins are translocated into live cells[1]. However, the low efficiency of endosomal escapes of biomolecules translocated by CPPs has a problem. In previous study, over tetrameric LK-1 peptides occurred a rapid protein internalization through endocytosis or direct translocation[2]. In this study, we investigate the efficiency of cytoplasm transportations of water-soluble proteins by changing the position and combination of two types of CPP sequences conjugated to proteins (Fig. 1a). Different types of CPP sequences-conjugated EGFP were expressed and purified to observe cytoplasm translocations into the HeLa cell. As a result, single peptide sequence-conjugated EGFP (N-terminal or C-terminal conjugate) was slightly uptaken into the Hela cell through endocytosis. In contrast, some combinations of two CPP sequences have the high efficiency cytoplasmic transport (Fig.1b). We identified the high efficiency transportation of proteins by differences of CPP-protein fusion site for highly transporting proteins into the living cell.
Keywords : Membrane; transportation; Cell Penetrating Peptide; HeLa cell

膜透過性ペプチド(CPP)は、タンパク質等を細胞内に輸送する能力を持つ[1]。しかし、CPP を介した生体高分子の輸送は、そのエンドソーム脱出効率の低さが問題とされている。先行研究で、LK-1 配列を連続して EGFP に導入するとエンドソーム脱出効率が変化することが報告されている[2]。そこで本研究では、タンパク質に付加する二種類の CPP 配列の位置・組み合わせを変更し、タンパク質の細胞質への輸送変化を検討した(Fig.1a)。モデルタンパク質として EGFP に CPP 配列を付与し、HeLa 細胞内の EGFP 由来の蛍光を観察した。その結果、N 末端または C 末端に 1 種類の CPP 配列を融合した EGFP はエンドソームに取り込まれる量が少なく、細胞質への移行は観察されなかった。一方、二つ以上の CPP 配列を付加した幾つかの EGFP 組み換え体はエンドソーム内への取り込みが上がり、細胞質への移行も確認された(Fig.1b)。本手法は既存の CPP 配列を活用することから、他の CPP 配列にも適応可能であり、CPP の輸送効率を改善することが期待される。当日は、配列の融合位置と輸送量の関係から導入した各 CPP 配列の役割についても報告する予定である。

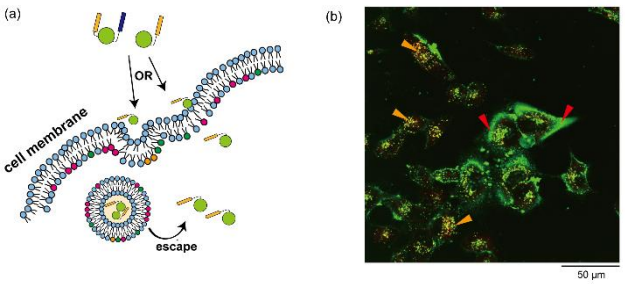

Fig.1 1 HeLa 細胞輸送実験の概略 (a)細胞内への輸送経路の模式図 (b)代表的な共焦点画像
橙:エンドソーム 赤:細胞質

1) Gallo, M., Defaus, S., and Andreu, D. Arch. Biochem. Biophys. 661, 74–86,2019
2) Jae Hoon Oh et al., *Adv. Sci.*, 2018, 1800240

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核局在シグナルペプチドを修飾したエンベロープ型ウイルスレプリカの創製

(鳥取大工[1]・鳥取大院工[2]) ○和田 瑞生[1]・坂本 健太郎[2]・古川 寛人[2]・稲葉 央[2]・松浦 和則[2]

Creation of enveloped viral replicas modified with nuclear-localized signal peptide

([1]*Faculty of Engineering, Tottori University*, [2]*Graduate School of Engineering, Tottori University*) ○ Mizuki Wada,[1] Kentarou Sakamoto,[2] Hiroto Furukawa,[2] Hiroshi Inaba,[2] Kazunori Matsuura[2]

Natural enveloped viruses are controlled the trafficking in cell by the infection, multiplication, and even budding. We have previously created enveloped viral replicas by complexing lipid bilayer with artificial viral capsids self-assembled from *β*-annulus peptide derived from tomato bushy stunt virus[1]. In this study, we created an enveloped viral replica modified with nuclear-localized signal (NLS) peptide (Fig. 1). DLS and TEM of the aqueous solution of enveloped viral replica modified with NLS revealed the formation of spherical assemblies covered with an envelope membrane with the size of about 114 nm. The enveloped viral replica modified with NLS was added to HeLa cell, and evaluated the intracellular trafficking behavior and nuclear localization.

Keywords : β-Annulus peptide; Enveloped viral replica; trafficking; Nuclear-localized signal peptide

天然のエンベロープ型ウイルスは、感染や増殖、出芽により細胞内でのトラフィッキングが制御されている。我々はこれまでに、TBSV 由来の*β*-Annulus ペプチドから自己集合した人工ウイルスキャプシドに脂質二分子膜を複合化することにより、エンベロープ型ウイルスレプリカを創製してきた [1]。しかし、細胞内の特定のオルガネラへトラフィッキングするウイルスレプリカの創製は未達成である。そこで本研究では、表面に核局在ペプチド(NLS)を提示したエンベロープ型ウイルスレプリカを創製した(Fig.1)。動的光散乱(DLS)測定により 114 nm 程度の集合体形成が確認され、透過型電子顕微鏡(TEM)観察では球状のキャプシドがエンベロープ膜に覆われていることが観察された。この NLS 修飾ウイルスレプリカを HeLa 細胞に添加することで、細胞内トラフィッキング挙動及び核局在を共焦点レーザー顕微鏡観察により評価した。

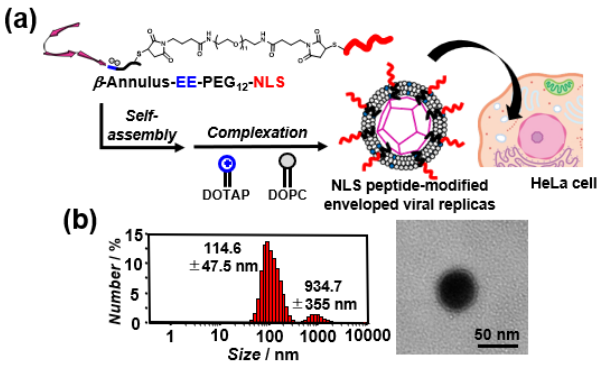

Fig.1 (a) construction of NLS peptide-modified enveloped viral replica and (b) the size distribution obtained from DLS and TEM image.

1) H. Furukawa et al., *Chem. Commun*., **56**, 7092 (2020)

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不均一鎖の近位ユビキチン C 末端への多様な化学修飾の導入

（東大院工[1]・鳥取大院工[2]・鳥取大 GSC センター[3]・京大院理[4]）○古畑 隆史[1]・崔 汎圭[1]・宇野 大輝[1]・佐藤 裕介[2,3]・尾勝 圭[4]・深井 周也[4]・岡本 晃充[1]
Chemical diversification of C-terminal of proximal ubiquitin in the synthetic heterotypic polyubiquitin chain ([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering, Tottori University*, [3]*Center for Research on Green Sustainable Chemistry, Tottori University*, [4]*Graduate School of Science, Kyoto University*) ○Takafumi Furuhata[1], Choi Bumkyu[1], Taiki Uno[1], Yusuke Sato[2,3], Kei Okatsu[4], Shuya Fukai[4], Akimitsu Okamoto[1]

Heterotypic polyubiquitin chains multimerized via multiple sites of lysine residues on ubiquitin have attracted much attention as post-translational modifications that potentially exhibit diverse structures and functions.[1)] To understand the relationship between functions and structures, a method to introduce appropriate chemical modifications that enables multifaceted evaluation is highly demanded. However, there has been no report of the method that is widely applicable to chemical engineering at the C-terminus of the proximal ubiquitin of the heterotypic chains using a variety of molecules including small molecules and biopolymers.[2)] In this study, we attempt to establish a method to efficiently introduce various chemical tags at the C-terminal of proximal ubiquitin including small molecules, nucleic acids, and proteins for the facile chemical diversification of heterotypic polyubiquitin chains in a post-synthetic manner. We will discuss the enzymatic construction and modification of structure-defined heterotypic polyubiquitin chains and the applications for understanding of their functions.
Keywords : Ubiquitin; Heterotypic chain; Chemical diversification

不均一ポリユビキチン鎖は、潜在的に多様な構造と機能を発揮しうる翻訳後修飾として注目を集めている[1)]。その機能と構造の結びつきの理解には、多面的な評価に向けて、実験系に応じて適切な化学修飾を導入する方法論が求められる。しかし、小分子から生体高分子に至るまで、ポリユビキチン鎖の基質修飾部位である近位 C 末端に化学修飾するために幅広く適応可能な化学修飾法は報告されていない[2)]。以上から、本研究ではユビキチン鎖の近位 C 末端への多様な化学修飾を可能とする方法論の確立を試みた。具体的には、C 末端ヒドラジド化ユビキチンを近位ユビキチンとして用いることで、特定の構造を持つ不均一ユビキチン鎖を酵素的に構築するとともに、小分子、核酸、タンパク質など多様なタグを導入した修飾体へと派生できることを実証した。本発表では、不均一ポリユビキチン鎖の構築と修飾に加え、その機能の理解に向けた応用展開について議論する予定である。

1) I. Dikic, B. A. Schylman *Nat. Rev. Mol. Cell Biol.* **2023**, *24*, 273–287. 2) X. Sui *et. al. Chem. Sci.* 2020, *11*, 12633–12646.

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オキシム連結反応を用いた不均一ポリユビキチン鎖の構造制御合成

(東大工[1] ・東大院工[2]) ○篠原　陵大[1]・古畑　隆史[2]・山田　征吾[2]・岡本　晃充[2]

Structure Controlled Synthesis of Heterotypic Ubiquitin Chain using Oxime Ligation

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○Ryota Shinohara,[1] Takafumi Furuhata, [2] Seigo Yamada,[2] Akimitsu Okamoto[2]

The heterotypic polyubiquitin chain is a post-translational protein modification with potential diversity of structures characterized by length, linkage types, and branching positions. Although it has been reported that K48/K63 branched chains potentially acquire different opposing functions, including enhancing the intracellular signaling mediated by ubiquitinated substrates and inducing substrate degradation, through branching *via* Lys48 (K48) on K63 chains,[1,2)] how the structural factors control the balance of these opposing functions is still elusive. For systematic study on the structure-function relationships of the K63/K48 heterotypic chain, enzymatic constructions of structure- defined heterotypic chains have been established recently.[3,4)] However, the synthetic ubiquitin chains linked with native isopeptide bonds are easily degraded by deubiquitinating enzymes (DUBs), making it difficult to assess their functions in the cellular environment. In the present study, we propose a chemical method for the structure-defined synthesis of DUB-resistant heterotypic chains. To this aim, we designed chemically engineered ubiquitin with a protected reactive group at its C-terminus as a building block, envisioning the stepwise elongation of ubiquitin chains with defined length, linkage types, and branching positions by repetitive cycles of deprotection and elongation *via* non-native isopeptide bonds.

Keywords：Polyubiquitin; Branched chain; Oxime ligation; Photodecaging

不均一ポリユビキチン鎖は長さ、結合様式、分岐位置に特徴づけられる多様な構造を持つタンパク質翻訳後修飾である。K63/K48 分岐鎖は K48 分岐によりシグナルの増強と基質の分解の一見相反する機能を獲得しうることが報告されている一方[1),2)]、この機能のバランスが長さと分岐位置によりいかに調節されるかは未だ明らかでない。そこで不均一鎖の構造機能相関の系統的評価に向け、構造を厳密に制御した不均一鎖を酵素的構築する手法の開発が進められてきた[3),4)]。しかし、酵素により合成されるユビキチン鎖は天然のイソペプチド結合を持ち、脱ユビキチン化酵素 (DUB) により容易に分解されるため、細胞内環境での機能評価が困難である。以上の背景から、本研究では DUB 耐性を持つ不均一鎖の構造制御合成法の確立を目指す。具体的には、C 末端の反応点を保護したユビキチンを反応ユニットとして用いることで、脱保護と伸長反応を繰り返してユビキチン鎖を段階的に伸長し、長さ・結合様式・分岐位置を規定した不均一鎖の非天然結合による効率的な構築を試みた。

1) *F. Ohtake et al., Mol. Cell* **2016***, 64,* 251-266; 2) *F. Ohtake et al., Proc. Natl. Acad. Sci. USA.* **2018**, *115*,E1401-E1408; 3) *J. Bode et al., ACS Cent. Sci.,* **2023***,* 9*, 8,* 1633-1641; 4) *A. Okamoto et al., J. Am. Chem. Soc*, **2023**, 145, *21*, 11690-11700

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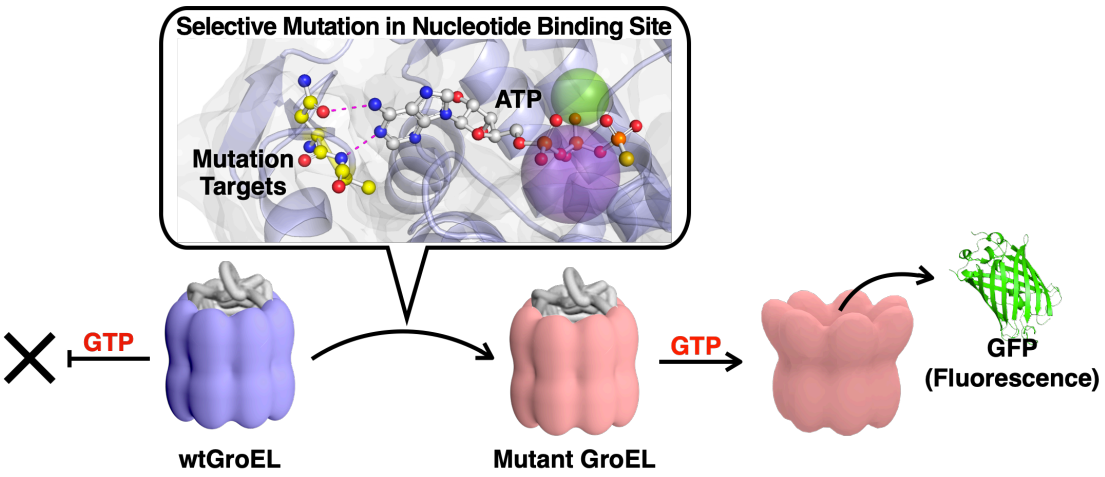
GTP Responsiveness of Biomolecular Machine GroEL by Binding Pocket Engineering

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Institute of Innovative Research, Tokyo Institute of Technology,* [3] *Center for Emergent Matter Science, RIKEN*)
○Ryotaro Toda,[1] Kiyoshi Morishita,[1] Hideki Taguchi,[2] Takuzo Aida[1,3]
Keywords: GroEL, Biomolecular Machines, Nanomaterials, GTP

Biomolecular machines play critical roles in biological processes such as cell division, material transport, and signal transduction by converting energy from the selective binding and hydrolysis of nucleotides into mechanical motions (e.g., F1 motor protein recognizes ATP and tubulin recognizes GTP). We reason that altering the nucleotide selectivity of biomolecular machines can lead to biotechnological tools with functions beyond those found in nature.

Chaperonin GroEL is an ATP-responsive biomolecular machine that can bind and release cargo via ATP-driven conformational changes, a feature that was exploited in the demonstration of a novel drug delivery system (DDS).[1] However, the abundance of ATP in both cancerous and healthy cells poses an inherent challenge to ATP-responsive DDS.

Here, we report GroEL mutants that respond to GTP, which is present at high concentrations only in cancer cells, by modifying residues around the base recognition part of the ATP binding site. GroEL mutants have been developed that hydrolyze GTP, as well ATP, with various activities, while wild-type GroEL (wtGroEL) exhibits no hydrolysis activity in the presence of GTP. Similarly, several of the developed mutants can bind denatured green fluorescence protein (GFP)[2] and release it in response to GTP, as well ATP, while wtGroEL exhibits no release in the presence of GTP. The further development of mutants with increased selectivity towards GTP over ATP is ongoing and is expected to lead to the development of tumor-selective DDS.



1) S. Biswas et al., *Nat. Chem.* **2013**, *5*, 613. 2) M. Yoshihide et al., *JBC.* **1997**, *19*, 272.

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Development of self-assembling peptide tags that form intracellular droplets in response to hydrogen peroxide

(*Graduate School of Engineering, The University of Tokyo*) ○Masatoshi Shimizu, Takuzo Aida, Takayuki Miki

Keywords: Liquid-liquid Phase Separation; Self-assembling peptide; Hydrogen peroxide; Intracellular supramolecular

Inside cells, proteins and nucleic acids undergo concentration, forming phase-separated liquid droplets. Various types of droplets have been reported and are deeply involved in diverse physiological events such as gene expression, metabolic reactions, and immune responses. To elucidate the mechanism of droplet formation and apply it for cell engineering, we have been developing a technique to artificially create droplets within cells using designed peptides. We have discovered that a 13-residue peptide with alternating tyrosine (Y) and lysine (K) residues (YK13) assists in droplet formation. Specifically, when NES (nuclear export signal)-YK13 fused super folder Green Fluorescent Protein (NES-YK13-sfGFP) was expressed in COS-7 cells, NES-YK13-sfGFP was found to generate droplets within the cells. To expand the scope of artificial droplets in cell engineering, controllable droplet formation in response to suitable environmental changes is required.

Here, we report the development of a peptide tag that responds to hydrogen peroxide (H_2O_2), a molecule involved in various biological events, to induce droplet formation. Using YK13 as a base sequence, we expressed sfGFP fused with various peptide sequences in cells and evaluated their responsiveness to H_2O_2. sfGFP fused with YK15(K6A/K10A), with two lysine residues replaced with alanine, dispersed uniformly. However, when H_2O_2 was added to the culture medium, NES-YK15(K6A/K10A)-sfGFP formed droplets within 5–10 minutes (Fig. 1). Further, droplet fusion and growth events were captured by time-lapse imaging. Efforts to reveal the mechanism of this process are ongoing.

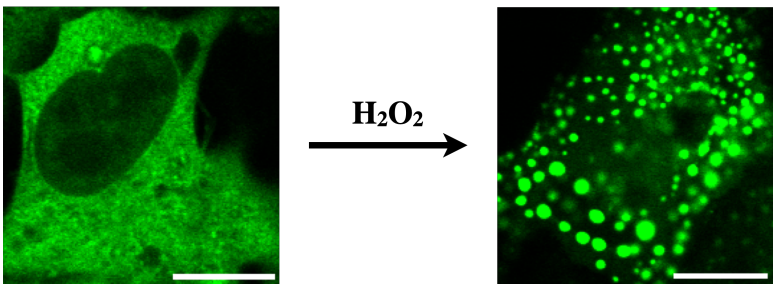

Fig. 1: COS-7 cells expressing NES-YK15(K6A/K10A)-sfGFP, before and after the addition of 25 mM of H_2O_2, observed by confocal microscopy (CLSM). Scale bars: 10 μm.

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Toward a near infrared (NIR) fluorescent chemigenetic indicator for Ca^{2+} based on photoactive yellow protein (PYP)-tag

([1]*Graduate School of Science, The University of Tokyo*) ○Takumi Yanagimachi,[1] Takuya Terai,[1] Robert E. Campbell[1]

Keywords: Chemigenetic indicator, Fluorescence, Near infrared (NIR), Calcium, Photoactive yellow protein (PYP)-tag

Calcium ion (Ca^{2+}) is a second messenger that regulates important bioactivities, such as muscle motions, neural activities, and fertilization. To study bioactivities of Ca^{2+} in model organisms *in vivo*, deep tissue imaging with near infrared (NIR) light is preferred due to its higher tissue penetration and lower phototoxicity. Recently, a new type of chemigenetic indicator, HaloCaMP, has been developed from a Ca^{2+}-binding protein calmodulin (CaM) and the HaloTag self-labeling protein, which was covalently linked to the synthetic NIR fluorescent dye Janelia Fluor 635 (JF_{635}).[1] This indicator possesses the benefits of both synthetic fluorophores and protein-based Ca^{2+} binding domains. Inspired by HaloCaMP, we propose that expanding the variety of chemigenetic indicators based on biorthogonal self-labeling proteins is important for enabling multiplex imaging. To address this issue, our lab has developed a new green fluorescent chemigenetic indicator, PYCaMP, which consists of CaM, photoactive yellow protein (PYP)-tag,[2] and its coumarin-based ligand, DMAC- CMK.[3] In this work, we aimed to develop NIR fluorescent chemigenetic Ca^{2+} indicators incorporating this CaM-PYP-tag fusion protein and NIR fluorophores (**Fig. 1**).

Kamikawa *et al.* developed a styryl pyridinium (SP)-based fluorescent ligand PCAF-SP with enhanced fluorescence intensity after being attached to PYP-tag.[4] Based on their research, we redesigned and synthesized a ligand designated 'PCAF-SP-Small' with a shortened PEG linker. We then performed optimization of the protein by many rounds of random and rational mutagenesis to achieve a Ca^{2+}-dependent $\Delta F/F_0 = 4.0$. We also observed the excitation and emission ratiometric fluorescent responses of this indicator by choosing the appropriate emission or excitation wavelengths (ex: $\Delta R/R_0 = 2.9$, em: $\Delta R/R_0 = 1.6$). Further efforts will be devoted to constructing robust NIR imaging tools applicable not only for multiplex imaging but also for quantitative measurement of Ca^{2+} concentration in tissues using ratiometry.

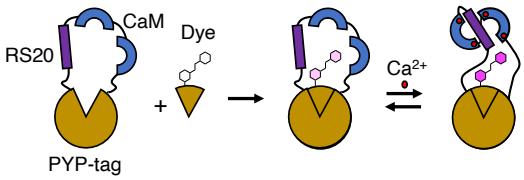

Figure 1 Schematic of a NIR fluorescent chemigenetic Ca^{2+} indicator based on PYP-tag.

1) Deo, C. *et al*. *Nat Chem Biol* **2021**, *17*, 718–723. 2) Hori, Y. *et al*. *J Am Chem Soc* **2009**, *131*, 16610–16611. 3) Terai, T. *et al*. *The 16th Symposium of Biorelevant Chemistry* **2022**, P141. 4) Kamikawa T. *et al*. *The 17th Annual Meeting of Japanese Society for Chemical Biology* **2023**.

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化学遺伝学赤色カルシウム指示薬の指向性進化法による改良とイメージング応用

（東大院理）○今井　渉世・朱　文超・寺井　琢也・Robert Earl Campbell
Chemigenetic red calcium indicator: improvement through directed evolution and imaging applications (*Graduate School of Science, The University of Tokyo*) ○Shosei Imai, Wenchao Zhu, Takuya Terai, Robert Earl Campbell

Fluorescent indicators, crucial for detecting ions or specific small molecules, are generally divided into two categories: small molecule-based indicators[1] and genetically encoded indicators using fluorescent proteins (FPs)[2]. Recently, we introduced a new type of chemigenetic calcium ion (Ca^{2+}) indicator that combined a green FP, a HaloTag self-labeling protein, and a synthetic Ca^{2+} chelator[3]. We expect that this design will address the shortcomings of conventional indicators. In this study, a similar Ca^{2+} indicator based on a red FP (RFP) was developed to facilitate multicolor imaging and *in vivo* applications. Initially, a prototype was identified by inserting a red FP into HaloTag, followed by labeling with a synthetic chelator derivative. Subsequently, site-saturation mutagenesis was performed targeting mainly at residues expected to be involved in interdomain hydrogen bonds. As a result, the fluorescence change was enhanced from 80% to 1370%. In the presentation, the developmental process and the imaging application using HeLa cells will be discussed.
Keywords : Fluorescent Protein; Chemigenetic Indicator; Fluorescent Biosensor; HaloTag

生体内におけるイオンや分子を検出する蛍光指示薬は、主に合成低分子を用いるもの[1]と遺伝的にコードされた蛍光タンパク質を用いるもの[2]二つに分けられる。それらの欠点を克服するため、我々は緑色蛍光タンパク質と合成キレーター、タンパク質タグ（HaloTag）から構成される化学遺伝学指示薬を最近報告した[3]。本研究では、既存の緑色センサーとの併用や *in vivo* での応用を可能にすべく、同様の設計で赤色化学遺伝学カルシウム指示薬を開発した。指示薬の原型は、赤色蛍光タンパク質を HaloTag に挿入し、合成キレーターでラベルすることで作成した。その後、ドメイン間に位置する残基を中心に部位飽和変異を導入することによって *in vitro* で蛍光変化を 80%から 1370 %へと改良させた。ここでは、その開発の過程と HeLa 細胞でのイメージング応用について報告する。



1) *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 13734. 2) *Chem. Rev.* **2018**, *118*, 11707. 3) *Nat. Chem. Biol.* **2023**, *19*, 38.

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ジヒドロ葉酸還元酵素を基本骨格とする化学遺伝学カルシウムセンサーの開発研究

（東大理[1]・東大院理[2]）○迫井 謙良[1]・寺井 琢也[2]・Robert Campbell[2]

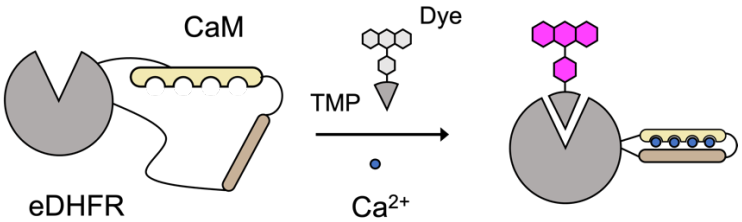
Towards the development of chemigenetic Ca^{2+} indicators based on dihydrofolate reductase

([1]*School of Science, the University of Tokyo*, [2]*Graduate School of Science, the University of Tokyo*) ○Kenryo Sakoi,[1] Takuya Terai,[2] Robert Campbell,[2]

Fluorescent indicators which can detect specific molecules and ions are important tools in biology because they enable us to visualize dynamic behaviors of analytes in cells. Such sensors are generally classified into small molecule-based indicators[1)] and genetically encoded indicators using fluorescent proteins[2)]. Recently, by combining synthetic ligand and protein tag, chemigenetic indicators have been developed to utilize advantages and overcome drawbacks of both types of sensors. Conventional sensors, however, use irreversible covalent bonds between dyes and protein tags that may led to photobleaching of the fluorophore and toxicity. Here, we focused on *E. coli* dihydrofolate reductase (eDHFR) and its noncovalent ligand (TMP) that was attached to a fluorescent molecule, as a new scaffold of reversible chemigenetic indicators. We first inserted a Ca^{2+} binding domain (CaM) into various sites of DHFR and made a prototype of chemigenetic Ca^{2+} indicator. Then, we improved the prototype sensor by randomizing the lengths and amino acid sequences of the linker parts.

Keywords : Fluorescent Indicator; Calcium Imaging; Protein Chemistry

蛍光センサーは、細胞内で特定の分子やイオンの動態を可視化できるため生物学における重要なツールである。蛍光センサーは合成低分子を用いるもの [1)]と遺伝的にコードされた蛍光タンパク質 [2)]を用いるものに大別されるが、近年、合成リガンドとタグタンパク質を用いることでこれらの利点を組み合わせた化学遺伝学蛍光センサーも開発されている [3)]。しかしその殆どは共有結合型であるため蛍光団の光退色や毒性が懸念される。そこで本研究では大腸菌ジヒドロ葉酸還元酵素（eDHFR）に着目し、その非共有結合リガンド（TMP）に蛍光色素を修飾した上で Ca^{2+}認識ドメイン（CaM）をタンパク質の様々な箇所に挿入し、新たな化学遺伝学 Ca^{2+}センサーの原型を作成した。その後リンカー残基の長さと種類をランダムに変化させて性能の向上を行った。



1) Gee *et al. Cell Calcium.*, **2000**, *27*, 97–106.
2) Dana *et al. Nat Methods.,* **2019**, *16*, 649–657.
3) Deo, C. *et al. Nat. Chem. Biol.* **2021**, *17*, 718–723.

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光誘起でクラスター化する光応答タンパク質 TePixD の反応と下流分子探索

（京都大学[1]・学習院大学[2]）○荒本 智大[1]・中曽根 祐介[1]・増田 悠祐[1]・床次 俊郎[2]・寺嶋 正秀[1]

Photoreaction of light-induced cluster forming protein TePixD and its downstream molecule

([1]*Kyoto University*, [2]*Gakushuin University*) ○Chihiro Aramoto,[1] Yusuke Nakasone,[1] Yusuke Masuda,[1] Shunro Tokonami,[2] Masahide Terazima[1]

TePixD is a protein derived from the thermophilic cyanobacterium Thermosynechococcus elongatus BP-1, forming a ring-shaped decamer.[1] TePixD is a light sensor protein that binds FAD as its chromophore, and it forms giant clusters in response to intense blue light in solution. To understand the physiological molecular mechanism of TePixD for light response, we purified the AAA (ATPases Associated with diverse cellular Activities) protein Tll0076, which is co-located in the same operon with TePixD in the genome, as a potential downstream molecule. SEC and SAXS analyses revealed that Tll0076 also forms ring-shaped multimers. Turbidity measurements and microscopic observations showed that Tll0076 forms giant clusters in solution. The molecular assembly is promoted by the presence of nucleotide such as ATP and by increasing salt concentrations and temperature. Currently, we are investigating the interactions between Tll0076 and TePixD using microscopy and various spectroscopic techniques.

Keywords : photoreaction, molecular assembly, cluster, light sensor protein

TePixD は好熱性シアノバクテリア Thermosynechococcus elongatus BP-1 由来の光センサータンパク質であり、リング状の十量体を形成する [1]。TePixD は発色団としてフラビン分子 FAD を持っており、溶液中で強い青色光を受けると集合反応が起こり巨大なクラスターを形成する。

TePixD の生理的な反応機構を調べるために、本研究ではゲノム上で TePixD とオペロンを組む AAA ファミリータンパク質 Tll0076 を下流分子の候補として精製し、その物性を調べた。サイズ排除クロマトグラフィーや X 線小角散乱法を用いた解析の結果、Tll0076 も溶液中でリング状の多量体を形成していることが判明した。さらに濁度解析や顕微鏡観察の結果、溶液中で液滴状の集合体を形成することがわかり、この分子集合は ATP などのヌクレオチドの存在、塩濃度の増加、溶液温度の増加によって促進された。現在は Tll0076 と TePixD の分子間相互作用について、顕微鏡や分光学的手法を用いた測定を行っている。

本会ではこれらの結果を基に、TePixD の光依存的なクラスター化反応や Tll0076 がその下流分子として機能する可能性について議論する。

1. Kita A, Okajima K, Morimoto Y, Ikeuchi M, Miki K. J Mol Biol. 2005. 349(1):1-9.

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光センサータンパク質 eBLUF の二量体化を利用したタンパク質活性の光制御

（京大院理[1]・京大院生命[2]）○久野 貴史[1]・中曽根 祐介[1]・酒巻 和弘[2]・寺嶋 正秀[1]
Opto-control of protein activities utilizing dimerization of photosensor eBLUF ([1]*Graduate School of Science, Kyoto University*, [2]*Graduate School of Biostudies, Kyoto University*)
○Takafumi Kuno,[1] Yusuke Nakasone,[1] Kazuhiro Sakamaki,[2] Masahide Terazima[1]

eBLUF is a light-sensing domain located at the C-terminus of the protein EB1, which is responsible for light-dependent intracellular signaling in bacteria. We previously investigated the photoreaction of eBLUF and observed that light illumination induces homo-dimerization of eBLUF. Interestingly, the dimer formed by a protomer in the light state and a protomer in the dark state is more stable than the dimer formed by two protomers in the light state[1)]. This unique property could be utilized for a tool of optogenetics. Toward this application, we generated several mutants and found some mutants exhibits higher dimerization efficiency. Additionally, we were able to observe the dimerization of eBLUF linked with soluble proteins such as maltose binding protein (MBP) at the termini of eBLUF. Furthermore, we successfully reconstituted split fluorescent proteins in a living cell using the dimerization of eBLUF.
Keywords : Photosensor Protein; Optogenetics; Protein-protein Interaction

eBLUF はバクテリアの細胞内シグナル伝達を担う光センサータンパク質 EB1 の C 末端に存在する光受容ドメイン（BLUF ドメイン）である。我々はこの eBLUF の光反応について、過渡回折格子法（TG 法）を主に用いた解析を行い、eBLUF が青色光照射により二量体化することを明らかにした。また興味深いことに、光状態同士や暗状態同士のペアより、暗状態と光状態のヘテロなペアが顕著に安定な二量体を形成することが分かった[1)]。こうした選択的な二量体化反応は、光遺伝学において有用であると考えられる。そこで本研究では、この eBLUF の二量体化反応を利用して、タンパク質の活性を光で操作することを目的とした研究を行った。まず、変異体を用いた解析により D137 が二量体化に重要であることが判明したため[2)]、D137 に変異を加えることにより、野生型と比較して顕著に二量体化を起こしやすい変異体を発見した。また、溶液中において、eBLUF に可溶性タンパク質を連結した状態での eBLUF の二量体化を観測することができた。さらに、eBLUF の C 末端に蛍光タンパク質 mCherry を 2 分割した断片をそれぞれ連結し、光照射による eBLUF の会合を介して mCherry が再構成される様子を蛍光検出により調べた。HeLa 細胞を用いた測定の結果、光照射による mCherry の再構成が蛍光発光として観測できた（図 1）。

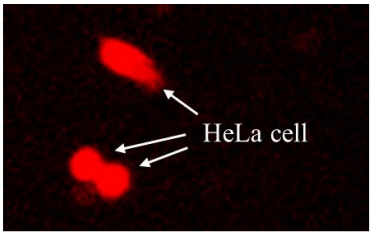

Figure 1. Fluorescent microscopy image of HeLa cells showing the reconstitution of mCherry.

1) K. Shibata, Y. Nakasone, M. Terazima, *J. Phys. Chem. B.* **2022**, 126, 1024.
2) K. Shibata, Y. Nakasone, M. Terazima, *J. Mol. Liq.* **2023**, 361, 119606.

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC H931(931, Bldg. 9 [3F])

[H931-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Masayasu Taki, Yutaro Saito

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[H931-3vn-01]

Synthesis of a Mg^{2+} Probe Consisting of a Phospha-Xanthone Dye and a Crown Ether-Type Ligand

○Yuichi Asada[1], Masayasu Taki[2], Shigehiro Yamaguchi[1,2,3] (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University, 3. Integrated Research Consortium on Chemical Science, Nagoya University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[H931-3vn-02]

Development of Aldehyde Dehydrogenase 1A1- and 1A3-responsive Turn-on Fluorescent Probes

○Yuki Nishida[1], Koki Miki[1], Huiying Mu[1], Koji Miki[1], Kouichi Ohe[1] (1. Kyoto University)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[H931-3vn-03]

Analysis of aminopeptidase using the amino acid-tethered oligodeoxynucleotide

○Reoto Mio[1], Tatsuya Nishihara[1], Kazuhito Tanabe[1] (1. Aoyama Gakuin University)

4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC

Break

English
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[H931-3vn-04]

Environment-sensitive and Super-photostable Probes for Monitoring Lipid Droplets through Fluorescence Lifetime Imaging

○junwei wang[1], Masayasu Taki[1], Shigehiro Yamaguchi[1,2,3] (1. ITbM, Nagoya University, 2. Department of Chemistry, Graduate School of Science, Nagoya University, 3. IRCCS, Nagoya University)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[H931-3vn-05]

Development of ^{19}F MRI Probe labeling β-lactamase

○Hiroto Fukuda[1], Masafumi Minoshima[1,2], Kazuya Kikuchi[1,3] (1. Graduate School of Engineering, Osaka Univ., 2. JST PRESTO, 3. Immunology Frontier Research Center, Osaka Univ.)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[H931-3vn-06]

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Development of ^{19}F MRI probe using gelled emulsion

○Shiho Sugiura[1], Tomoya Yamamoto[2,3], Kazuya Kikuchi[2,3] (1. Osaka University, School of Engineering, 2. Osaka University, Graduate School of Engineering, 3. Osaka University, Immunology Frontier Research Center)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[H931-3vn-07]

Evaluation of long-hyperpolarization-lifetime molecules for *in vivo* oximetry by hyperpolarized MRI

○Ruki Ashikaga[1], Yutaro Saito[2], Hiroyuki Yatabe[2], Yohei Kondo[2], Hiroshi Nonaka[2], Yoichi Takakusagi[3,4], Kazutoshi Yamamoto[5], Murali C. Krishna[5], Shinsuke Sando[2] (1. School of Engineering, The University of Tokyo, 2. Guraduate School of Engineering, The University of Tokyo, 3. National Institutes for Quantum Science and Technology, 4. Graduate School of Science, Chiba University, 5. National Institutes of Health, USA)

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ホスファキサントン色素を母骨格としたクラウンエーテル型 Mg^{2+} イオンプローブの合成

（名大院理[1]・名大 ITbM[2]・名大 IRCCS[3]）○浅田雄一[1]・多喜正泰[2]・山口茂弘[1,2,3]

Synthesis of a Mg^{2+} Probe Based on Phospha-xanthone Dye with a Crown Ether-type Ligand

([1]*Graduate School of Science, Nagoya University*, [2]*Institute of Transformative Bio-Molecules (ITbM), Nagoya University,* [3]*Integrated Research Consortium on Chemical Science (IRCCS), Nagoya University*) ○Yuichi Asada,[1] Masayasu Taki,[2] Shigehiro Yamaguchi,[1,2,3]

Mg^{2+} is the most abundant divalent metal ion in cells and plays important roles in various cellular functions, including neurotransmission and coenzyme activities. In this study, we developed a Mg^{2+} probe, **POXN-crown,** where a crown ether ligand was introduced into a phospha-xanthone dye (POXN). We envisioned that the interaction of Mg^{2+} with a carbonyl oxygen atom of the probe resulted in bathochromic shifts in the absorption and emission spectra. Upon addition of Mg^{2+} to **POXN-crown** in CH_3CN, a decrease in the absorption band at 412 nm and a concomitant increase of a new band at 480 nm were observed. Conversely, a significant enhancement in the fluorescence intensity was observed with increasing the concentration of Mg^{2+}. These fluorescence responses were selective to Mg^{2+} and no significant responses were observed in the presence of Na^+, K^+, and Ca^{2+}.

Keywords : fluorescent probe, phospha-xanthone dye, crown ether, magnesium ion

マグネシウムイオン (Mg^{2+}) は，細胞内で最も多い 2 価の金属イオンであり，神経伝達物質や補酵素など，多くの細胞内プロセスにおいて重要な役割を果たしている．これまで細胞内 Mg^{2+}を検出できる蛍光プローブがいくつか開発されてきたが，励起光による細胞毒性や蛍光変化の乏しさなどの問題があった．そこで本研究では，ホスファキサントン色素 (POXN) を母骨格とした Mg^{2+}蛍光プローブ **POXN-crown** を新たに合成した (Figure 1a)．POXN は，アミノ基をドナー，カルボニル基をアクセプターとする蛍光色素であり，クラウンエーテル型部位に Mg^{2+}が包摂されることで，カルボニル基の電子受容性が高まり，吸収および蛍光スペクトルが長波長シフトすることを期待した．実際，**POXN-crown** の CH_3CN 溶液に Mg^{2+}を添加したところ，吸収スペクトルにおいて，412 nm の吸収帯の減少とともに，480 nm の新たな吸収帯の増大が認められた (Figure 1b)．一方，371 nm の等吸収点で励起したところ，蛍光波長が変化しながら蛍光強度が大きく増大する様子が観察された (Figure 1c).

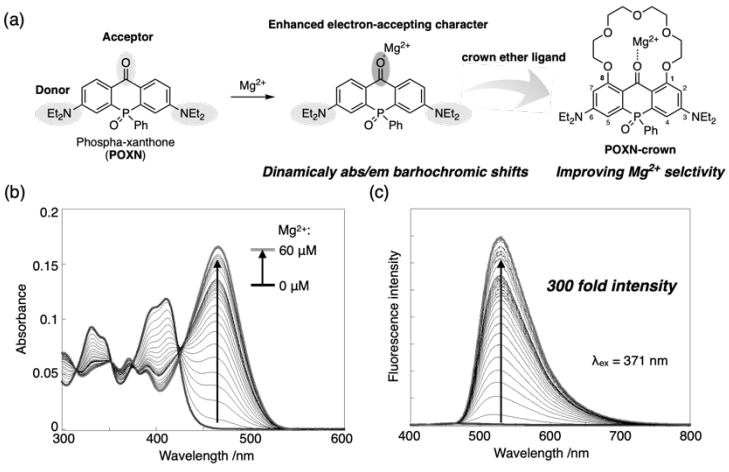

Figure 1. (a) The molecular design of POXN-based Mg^{2+} probe and (b) absorption and (c) fluorescence spectral changes of **POXN-crown** against Mg^{2+} in CH_3CN.

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アルデヒド脱水素酵素 1A1 および 1A3 に応答する turn-on 型蛍光プローブの開発

（京大院工）○西田　有輝・三木　康輝・Huiying Mu・三木　康嗣・大江　浩一
Development of Aldehyde Dehydrogenase 1A1- and 1A3-responsive Turn-on Fluorescent Probes (*Graduate School of Engineering, Kyoto University*) ○Yuki Nishida, Koki Miki, Huiying Mu, Koji Miki, Kouichi Ohe

Cancer stem cells (CSCs), which are subpopulation of cancer cells, are involved in tumor initiation, proliferation, and recurrence. Several aldehyde dehydrogenase (ALDH) isoforms are known to be overexpressed in CSCs and used as biomarkers for CSC detection. We have developed cyanine dyes bearing a formyl group which can act as turn-on fluorescent probes to detect ALDH1A1 and ALDH1A3 activity in CSCs.[1] However, the detection of ALDH1A3 activity is still difficult because of the low responsiveness of probe **Bn-A**. In this study, turn-on fluorescent probe **C5-A** with high responsiveness to ALDH1A3 was synthesized.[1c] Results of cell experiments with probe **C5-A** will be described in the presentation.

Keywords: Cancer Stem Cell; Fluorescence Probe; Aldehyde Dehydrogenase; Isoform

がんに小分布するがん幹細胞（CSC）はがんの発生や自己複製などに重要な役割を持つと言われている。CSC には、いくつかのアルデヒド脱水素酵素（ALDH）のアイソフォームが過剰発現していることが報告されており、それらはバイオマーカーとして用いられている。当研究室では、ホルミル基を持つシアニン色素が ALDH1A1 や 1A3 に応答し、発光する turn-on 型蛍光プローブとして機能することを明らかにした[1]。しかし、開発したプローブ **Bn-A** では ALDH1A3 に対する応答性が低いことが問題となっていた[1c]。本研究では、ALDH1A3 に対する応答性が高い turn-on 型赤色発光プローブ **C5-A** を開発した。プローブ **Bn-A** に対し ALDH1A3 を作用させたところ、1 時間後に発光量が約 1.5 倍の増大しか示さなかったが、開発したプローブ **C5-A** は約 12 倍の発光量を示した。プローブ **C5-A** を用いた細胞実験の結果についても発表する予定である。

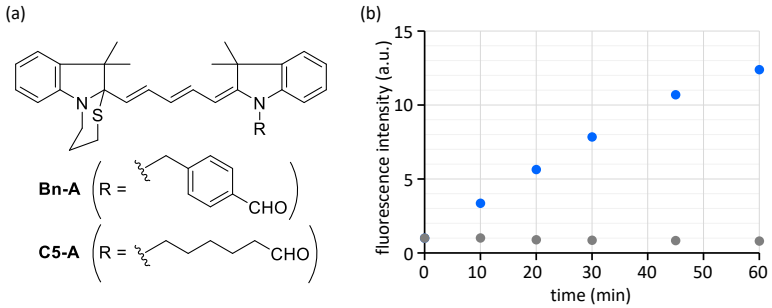

Figure1. (a) ALDH-responsive turn-on fluorescent probes **Bn-A** and **C5-A**. (b) Time-dependent fluorescence intensity change at 662 nm of probe **C5-A** with/without ALDH1A3 (50 nM).

[1] (a) M. Oe, K. Miki, Y. Ueda, Y. Mori, A. Okamoto, Y. Funakoshi, H. Minami, K. Ohe, *ACS Sens*. **2021**, *6,* 3320−3329. (b) M. Oe, K. Suzuki, K. Miki, H. Mu, K. Ohe, *ChemPlusChem* **2022**, *87,* e202200319. (c) K. Miki, D. Yamanaka, H. Mu, K. Miki, K. Ohe, The 103rd CSJ Annual Meeting, D1441-1am-07.

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アミノ酸標識人工核酸を用いたアミノペプチダーゼ活性評価手法の開発

（青山学院大理工）○三尾 玲緒斗・西原 達哉・田邉 一仁
Analysis of aminopeptidase using the amino acid-tethered oligodeoxynucleotide (*College of Science and Engineering, Aoyama Gakuin University*) ○Reoto Mio, Tatsuya Nishihara, Kazuhito Tanabe

In this study, we designed the amino acid-tethered oligodeoxynucleotide for the multiplex analysis of aminopeptidase activities. Aminopeptidase activities related to the several diseases such as tumor. Toward the analysis of alanine aminopeptidase N and leucine aminopeptidase activity, we synthesized the alanine and leucine tethered oligodeoxynucleotide (Ala-ODN and Leu-ODN) in this study. The combination of peptidase treatments and qPCR analysis led successfully to construct the molecular system to detect the activities of multiple peptidases simultaneously.
Keywords: Functional oligonucleotide; Enzymatic activity; Molecular probe

近年、血液をはじめとする生体サンプル中に含まれるアミノペプチダーゼの酵素活性と疾病との相関解析が盛んに行われている。疾病関連酵素の探索にあたり、蛍光プローブライブラリーを用いることにより、複数成分の酵素活性評価が実現している。しかし、蛍光波長の重なりから、酵素活性の同時評価には困難を伴うのが現状である。

以上を踏まえ、本研究では、複数成分のアミノペプチダーゼ活性の解析手法の構築を目指した。具体的には、各アミノペプチダーゼに対する基質部位と DNA 配列情報を対応付けた機能性核酸を設計した。Figure 1 に示したように、アミノペプチダーゼ N (APN)、及びロイシンアミノペプチダーゼ (LAP) に対する DNA プローブとして、アラニン、ロイシンを 5’末端に導入した機能性核酸の合成を進めた。この DNA プローブとアミノペプチターゼが反応して得られる酵素反応生成物 DNA を選択的に回収し定量することで、DNA 配列に対応した酵素の活性評価が可能となる。酵素反応生成物 DNA の選択的な回収にあたり、2-ピリジンカルボキシアルデヒド (PCA) を用いて、DNA プローブのアミノ基の選択的な保護を検討した。DNA プローブ、及び別途、化学合成した酵素反応生成物 DNA に対して、PCA 処理、続いてビオチン化を行った。その後、ストレプトアビジンによりビオチン化した酵素反応生成物 DNA を回収した。その結果、酵素反応生成物 DNA は回収量に影響を与えないのに対して、DNA プローブは回収量が抑制され、酵素反応生成物 DNA の選択的な回収が示唆された。現在、DNA プローブを用いたアミノペプチダーゼ活性評価を進めている。本発表では DNA プローブの設計、合成、機能評価について報告する。

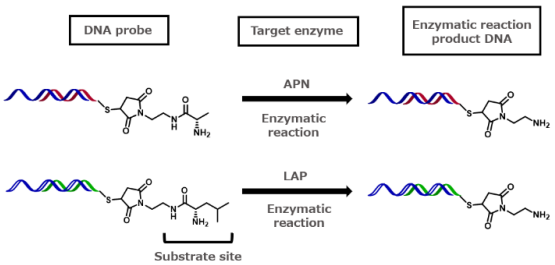

Figure 1. DNA probes for detection of APN and LAP activity

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Environment-sensitive and Super-photostable Probes for Monitoring Lipid Droplets through Fluorescence Lifetime Imaging

([1]*Institute of Transformative Bio-Molecules (WPI-ITbM)*, [2]*Graduate School of Science*, *Nagoya University*, [3]*Integrated Research Consortium on Chemical Sciences* (*IRCCS*), *Nagoya University* ○Junwei Wang,[1] Masayasu Taki,[1] Shigehiro Yamaguchi[1,2,3]

Keywords: Environment-sensitive probe; Fluorescence lifetime imaging; Lipid heterogeneity; Lipid catabolism; Super-resolution imaging

Lipids are essential biomolecules for constructing cellular membrane compartments, providing energy for cell survival under stress, and conveying physiological signals within the cell. As a hub of cellular lipid metabolism, lipid droplets (LDs) play central roles in maintaining lipid and energy homeostasis, and in mitigating the levels of hazardous lipid species. Disruption in lipid levels causes dysfunctions of lipid droplets, subsequently triggering abnormalities in LD-associated mechanisms.[1] Consequently, it is imperative to devise a precise and dependable strategy to visualize the dynamics of LD that delineates the lipid compositions and alterations. Herein, we have developed a red-emissive LD probe, LipiPB Red, based on a phosphole scaffold that exhibits exceptional photostability, remarkable polarity sensitivity, and robust retention within LDs (**Figure 1a**).

LipiPB Red was successfully employed not only for super resolution imaging of LDs using STED microscopy, but also for fluorescence lifetime imaging microscopy (FLIM), the latter of which allowed us to evaluate the diacylglycerol (DAG) and triacylglycerol (TAG) component ratios across LDs. LDs with higher DAG/TAG ratios, *i.e.*, those with more progressive TAG catabolism, exhibited a shorter fluorescence lifetime, suggesting that the probe was surrounded in a more polar environment. The FLIM analyses showcased that lipid characteristics is heterogeneous among individual LDs even in a single liver cancer cell and that adipose triglyceride lipase (ATGL) is a key player in LD catabolism. It was also found that the decrease in fluorescence lifetime caused by lipolysis occurred prior to LDs shrinkage (**Figure 1b**).

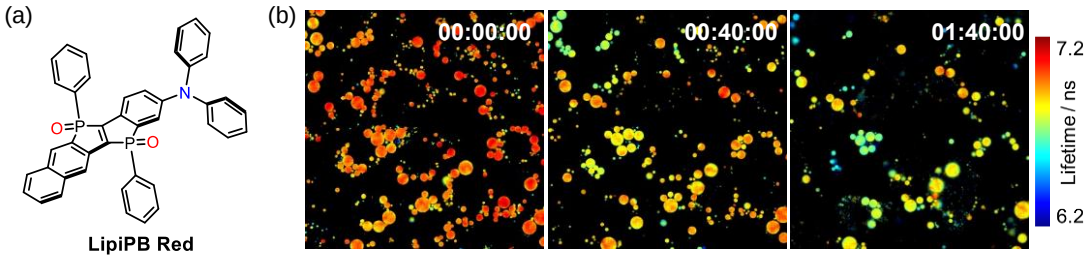

Figure 1. (a) Structure of LipiPB Red. (b) Time-lapse FLIM imaging during lipolysis of adipocytes upon treatment with forskolin.

1) M. Taki, K. Kajiwara, E. Yamaguchi, Y. Sato, S. Yamaguchi, *ACS Materials Lett.* **2021**, *3*, 42-49.

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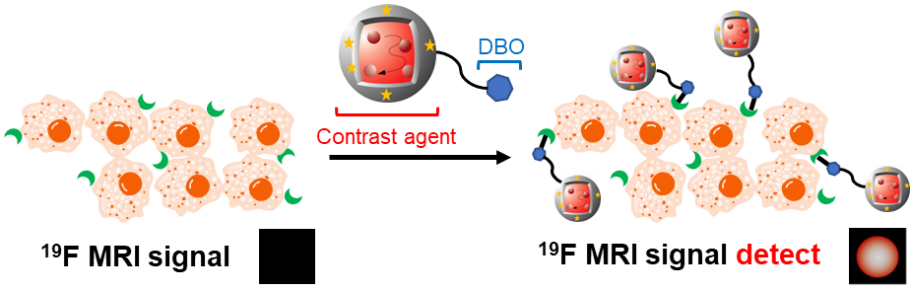
β-ラクタマーゼをラベル化する ^{19}F MRI プローブの開発

（阪大院工[1]・JST さきがけ[2]・阪大免フロ[3]）○福田寛人[1]・蓑島維文[1,2]・菊地和也[1,3]
Development of ^{19}F MRI Probe labeling β-lactamase ([1]*Graduate School of Engineering, Osaka Univ.*, [2]*JST PRESTO*, [3]*Immunology Frontier Research Center, Osaka Univ.*) ○Hiroto Fukuda,[1] Masafumi Minoshima,[1,2] Kazuya Kikuchi[1,3]

β-lactamase is a bacterial enzyme that hydrolyzes β-lactam antibiotics. This enzyme expresses in drug-resistance bacteria and is used as a reporter enzyme in mammalian cells. While fluorescent probes were developed for detecting β-lactamase, they are not able to detect it in deep tissue. To detect β-lactamase in vivo, we focus on ^{19}F magnetic resonance imaging (MRI) that can non-invasively visualize the probe localization in deep tissue without endogenous background signals. We have developed a nanoparticle comprised of perfluorocarbon core and a silica shell as a ^{19}F MRI nanoprobe.[1)] In addition, β-lactamase specifically binds to inhibitors containing diazabicyclooctane structure such as relebactam and avibactam.[2)] In this study, we designed and prepared a ^{19}F MRI nanoprobe for detection of β-lactamase by surface modification of the nanoparticles with β-lactamase inhibitors. We modified the nanoparticle surfaces with the diazabicyclooctane-based inhibitors and confirmed the increase of the number of the nanoparticles from β-lactamase expressing cells.
Keywords : MRI; β-lactamase

β-ラクタマーゼはβ-ラクタム系抗生物質を分解する細菌由来の酵素であり、薬剤耐性菌において発現しているだけでなく、レポーター遺伝子としても利用されている。従来の β-ラクタマーゼ検出を指向したプローブは、蛍光色素をベースにしているため、生体深部での検出はできない。そこで、^{19}F MRI に注目した。^{19}F MRI は生体深部を非侵襲的に画像化する手法であり、バックグラウンドシグナルなくプローブの局在をイメージングできる。我々は以前にパーフルオロカーボンをコアに有するシリカナノ粒子を開発し、^{19}F MRI による生体内局在の可視化に成功している [1)]。また、β-ラクタマーゼはジアザビシクロオクタン（DBO）構造を有する β-ラクタマーゼ阻害剤、レレバクタムやアビバクタムと特異的に結合することが知られている [2)]。

本研究では、生体深部における β ラクタマーゼの検出を目指し、β-ラクタマーゼをラベル化できる DBO リガンドをナノ粒子表面に修飾した ^{19}F MRI プローブを設計した。粒子表面にリガンドを修飾することで、β-ラクタマーゼを発現した細胞へのラベル化量が増加した。



1) H. Matsushita, *et al., Angew. Chem. Lnt. Ed.,* **2014**, *53*, 1008.
2) D. E. Ehmann, *et al., Proc. Natl. Acad. Sci.,* **2012**, *109*, 11663.

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^{19}F 化溶媒ゲルを内包した ^{19}F MRI プローブの開発

（阪大工学部 [1]・阪大院工 [2]・阪大免フロ [3]）○杉浦 志帆 [1]・山本 智也 [2,3]・菊地 和也 [2,3]

Development of ^{19}F MRI probe using gelled emulsion ([1]*School of Engineering, Osaka University*, [2]*Graduate School of Engineering, Osaka University,* [3]*Immunology Frontier Research Center, Osaka University*) ○ Shiho Sugiura,[1] Tomoya Yamamoto,[2,3] Kazuya Kikuchi,[2,3]

Magnetic Resonance Imaging (MRI) is a noninvasive imaging technique. ^{19}F MRI can trace localization of ^{19}F MRI contrast agent with high contrast because of 100% natural isotopic abundance and no biological background signal. We have developed fluorine-accumulated silica nanoparticle for ^{19}F MRI contrast agent[1)]. However, there are problems of persistence and toxicity *in vivo*.

In this study, we aim to develop the emulsion containing a ^{19}F solvent with internal gelation as novel lipid-nanoparticle-like ^{19}F MRI probes. We incorporated a low-molecular-weight organogelator, 12-hydroxystearic acid, into the ^{19}F solvent emulsion to improve its stability. The MR signals of this organogel had high intensity and long T_2 relaxation time, enough to be used for MRI experiments. We also investigated the conditions for introducing ^{19}F solvents and gelators into the emulsion. In this presentation, we will report the contribution of gelation to size stability and T_2 relaxation time.

Keywords : ^{19}F MRI; emulsion; organogel; supramolecular gel

磁気共鳴画像法 (MRI) は核磁気共鳴現象を利用した非侵襲的なイメージング手法である。生体内にほとんど存在しない ^{19}F を観測核種とした ^{19}F MRI は、^{19}F 核を有する造影剤の局在を高いコントラストで画像化することができる。これまでに、^{19}F 化溶媒を内包したナノ粒子の表面をシリカで被覆した ^{19}F MRI プローブが開発されてきた[1)]が、生体内への残存や毒性といった問題点があった。

本研究では ^{19}F 化溶媒を内包したエマルジョンの内部をゲル化することで、サイズ安定性を向上させた脂質ナノ粒子型 ^{19}F MRI プローブを設計した。^{19}F 化溶媒にゲル化剤である 12-ヒドロキシステアリン酸を加えて作製した有機ゲルは ^{19}F MRI 造影剤としての応用に充分な MR シグナル強度と長い T_2 緩和時間が確認された。また、エマルジョン内に ^{19}F 化溶媒とゲル化剤を導入する条件について検討を行った。本発表では、エマルジョン内部のゲル化によるサイズ安定性や T_2 緩和時間への寄与についても報告する予定である。

1) H. Matsushita, *et al*., *Angew. Chem. Lnt. Ed*., **2014**, 53, 1008.

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超偏極 MRI による *in vivo* 酸素濃度測定のための長寿命分子の評価

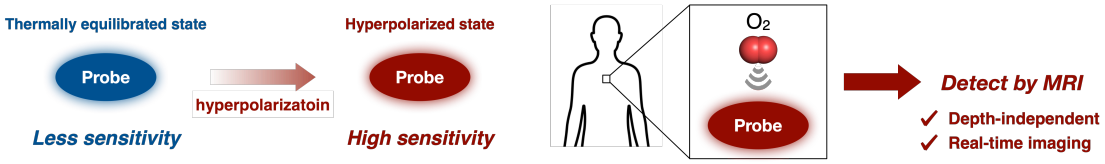
（東大工[1]・東大院工[2]・量子科学技術研究開発機構[3]・千葉大院融合理工[4]・米国国立衛生研究所[5]）○足利 留樹[1]・齋藤 雄太朗[2]・谷田部 浩行[2]・近藤 洋平[2]・野中 洋[2]・高草木 洋一[3,4]・山本 和俊[5]・Murali C. Krishna[5]・山東 信介[2]

Evaluation of long-hyperpolarization-lifetime molecules for *in vivo* oximetry by hyperpolarized MRI ([1]*School of Engineering, The University of Tokyo*, [2]*Guraduate School of Engineering, The University of Tokyo*, [3]*National Institutes for Quantum Science and Technology*, [4]*Graduate School of Science, Chiba University*, [5]*National Institutes of Health, USA*) ○Ruki Ashikaga[1], Yutaro Saito[2], Hiroyuki Yatabe[2], Yohei Kondo[2], Hiroshi Nonaka[2], Yoichi Takakusagi[3,4], Kazutoshi Yamamoto[5], Murali C. Krishna[5], Shinsuke Sando[2]

Oxygen plays an essential role in various biological phenomena, such as energy production, and the distribution and local concentration of oxygen *in vivo* are closely related to biological functions and diseases. Therefore, there is growing need for imaging technology to capture oxygen dynamics in the body. Although nuclear magnetic resonance imaging (MRI) is widely used for noninvasive and real-time observation of molecules in deep body regions, its sensitivity is often insufficient for detecting signals from molecular probes injected into the body. Dynamic nuclear polarization (DNP)[1)] can dramatically improve the sensitivity of MRI molecular probes, allowing the detection of signals *in vivo*. Oxygen imaging would be realized by the DNP technique and molecular probes designed to respond to oxygen. In this study, we designed, synthesized, and evaluated hyperpolarized MRI molecular probe candidates for biological oxygen imaging.

Keywords: nuclear magnetic resonance imaging; hyperpolarization; oxygen imaging

酸素分子はエネルギー産生などの様々な生命現象に必要不可欠な役割を担っており、生体内酸素の分布や局所濃度は生命機能や疾患と密接に関連する。そのため、このような生体内酸素の挙動をイメージングする技術が強く求められている。核磁気共鳴イメージング（MRI）は、生体深部を非侵襲的にリアルタイムで観測できる技術として、広く普及している。しかし、通常の MRI では感度が不十分であり、生体内に投与した分子プローブのシグナル観測は難しい。動的核偏極法（DNP）[1)]は分子プローブを高感度化し *in vivo* での検出を可能にする。酸素に応答する分子プローブのシグナルを設計し、DNP 法で高感度化して観測することで酸素イメージングが可能になると考えられる。本研究では、生体深部の酸素イメージングのための、超偏極 MRI 分子プローブの設計・合成および物性評価を行った。



1) J. H. Ardenkjær-Larsen *et al. Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 10158.

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC H934(934, Bldg. 9 [3F])

[H934-3vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Kohsuke Kuroda, Noriyuki Uchida

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[H934-3vn-01]

Development of Photo-Induced Electron Transfer Reversible Addition–Fragmentation Chain Transfer Polymerization Mediated by Calcein Acetoxymethyl as an Esterase Responsive Photocatalyst

○Kanta Ogura[1], Masahiko Nakamoto[2], Michiya Matsusaki[2] (1. Osaka University, 2. Graduate School of Engineering Osaka University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[H934-3vn-02]

Kinetics-Controlled Gel-Sol Transition and Cargo Release of Methionine-Containing peptides

○Yoshika Hara[1], Atsuya Yaguchi[1], Hirotsugu Hiramatsu[2], Takahiro Muraoka[1,3] (1. Tokyo University of Agriculture and Technology, 2. National Yang Ming Chiao Tung University, 3. KISTEC)

Japanese
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[H934-3vn-03]

Development of self-adjuvanting protein vaccines using gold nanoparticles as carriers

○Koki Murata[1], Naohiro Hayakawa[1], Masahiro Wakao[1], Yasuo Suda[1], Hiroyuki Shinchi[1] (1. Grad. Sch. Sci. and Eng., Kagoshima Univ.)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[H934-3vn-04]

Development of a Ratiometric Fluorescent Probe for Visualizing Lipid Peroxidation in Plasma Membrane

○Rina Tokunaga[1], Kosei Shioji[1], Hidefumi Iwashita[1] (1. Fukuoka University)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[H934-3vn-05]

Thermostability of a thermotolerant yeast by zwitterions

○Souta Uemori[1], Ayumi Hachisu[1], Kazuaki Ninomiya[2], Kosuke Kuroda[1] (1. Faculty of Biological Science and Technology, Institute of Science and Engineering, Kanazawa University, 2. Institute for Frontier Science Initiative, Kanazawa University)

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[H934-3vn-06]

Synthesis of fluorescence-derivative of DHA-containing phospholipids and its behavior in lipid bilayers.

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○Kotaro Shimizu[1], Masanao Kinoshita[1], Nobuaki Matsumori[1] (1. Kyushu University)

Japanese

4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[H934-3vn-07]

Synthesis and Evaluation of β-Glucan Mimicking Polymers Assembled with β-Glucan Oligosaccharides

○Atsushi Miyagawa[1], Nami Yamamoto[1], Ayane Ohno[1], Hatsuo Yammaura[1] (1. Nagoya Inst. Tech.)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[H934-3vn-08]

Controlling the spatial arrangement of the gold nanoparticles conjugated with the peptide on the self-assembling DNA nanostructure

○Yosuke Ochi[1], Yuki Gomibuchi[1], Takuo Yasunaga[1], Junichi Taira[1] (1. Kyushu Inst. of Tech.)

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カルセインアセトキシメチルをエステラーゼ応答性光触媒とした光誘起電子移動型−可逆的付加開裂連鎖移動重合法の確立

(阪大[1]・阪大院工[2]) ○小倉 勘汰[1]・仲本 正彦[2]・松崎 典弥[2]

Development of Photo-Induced Electron Transfer Reversible Addition–Fragmentation Chain Transfer Polymerization Mediated by Calcein Acetoxymethyl as an Esterase Responsive Photocatalyst ([1]*Osaka University,* [2]*Graduate School of Engineering, Osaka University*)

○Kanta Ogura,[1] Masahiko Nakamoto,[2] Michiya Matsusaki[2]

Photo-induced polymerization is of great interest in tissue engineering and/or cell imaging[1]. However, there is no report on a biomolecule-responsive photo-induced polymerization. Employing intra-cellular esterase responsive calcein acetoxymethyl as a photocatalyst, we report for the first time an esterase-responsive photo-induced electron transfer reversible addition-fragmentation chain transfer polymerization (PET-RAFT). Using HPMA, CPADB, and ascorbic acid as monomer, chain transfer agent and reductant, respectively, PET-RAFT was conducted in the presence of photocatalyst. The conversion rate after 24 hours reached 70% in the presence of esterase pre-treated photocatalyst, whereas no reaction was observed without esterase treatment. The result indicates enzyme-responsive PET-RAFT. This study would form the basis of polymer synthesis inside cells for tissue engineering/cell imaging.

Keywords: Cell imaging; Photo-induced electron transfer reversible addition–fragmentation chain transfer polymerization; Enzyme-responsive photocatalyst

組織工学や細胞イメージングにおいて、細胞存在下での光誘起高分子重合が注目されている[1]。しかし従来法では光照射された部分で一様に反応が進行するため、特定のタンパク質に応答した反応は実現できない。我々は細胞内エステラーゼ応答性光触媒としてカルセインアセトキシメチルを用いた光誘起電子移動型の可逆的付加開裂連鎖移動(PET-RAFT)重合を報告する(Figure 1A)。*N*-(2-ヒドロキシプロピル)メタクリルアミド(HPMA)、4-シアノ-4-(フェニルカルボノチオイルチオ)ペンタン酸(CPADB)およびアスコルビン酸をそれぞれモノマー、連鎖移動剤および還元剤として光触媒存在下で青色光を照射した(Figure 1B)。その結果エステラーゼ処理なしでは重合反応が全く進行しなかったのに対して、事前にエステラーゼ処理を施した光触媒存在下では 24 時間後の反応率が約 70%となった(Figure 1C)。以上のことよりエステラーゼに応答した PET-RAFT 重合が示唆された。本研究は蛍光性高分子の細胞内合成による細胞イメージング技術などへの応用が期待される。

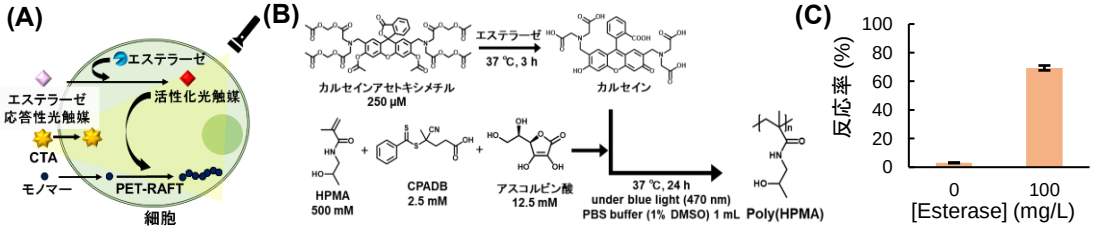

Figure 1. (A) Conceptual illustration of this study**. (B)** Reaction scheme of esterase-responsive PET-RAFT. **(C)** Conversion rate of PET-RAFT with or without esterase treatment.

1) J. Geng *et al*., *Nat. Chem.* **2019**, *11*, 579.

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メチオニン含有ペプチドでのゲルゾル転移と物質放出速度制御

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Kinetics-Controlled Gel-Sol Transition and Cargo Release of Methionine-Containing peptides

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For applications of gel-sol transition, kinetics control of the responses is important for matching the cargo-releasing velocity to the target biological events, so we aimed to developed that the material design can control cargo release rate based on molecular structure. We demonstrated a chemical control of redox-triggered gel-sol transition kinetics of self-assembling peptides. We utilized redox-active gel-forming peptides containing methionine (Met) residues at different positions. The hydrogels formed by these peptides had similar spectroscopic and rheological properties. Upon oxidation with H_2O_2, the peptides showed gel-to-sol macroscopic morphological changes and cargo release through β-sheet to α-helix conformational changes at the molecular scale. The peptides responded to the oxidation at different rate depending on the Met-position.

Keywords : Peptide Amphiphile; Hydrogel; Methionine Oxidation; Gel-Sol Transition; Cargo Release

刺激応答性ゲルは、ゾル化に伴い内包物質を放出できるため、物質輸送媒体としての利用が可能である。安定なゲル形成や多様な刺激でのゾル化は開発が進められている一方、分解特性を合理的に制御する指針は未だ十分に確立されていない。そこで、刺激に応答してゾル化する超分子ペプチドを用い、集合体分解速度を制御する分子設計指針の構築を目的とした。本研究では、生体内分子から着想を得て、酸化に応答するメチオニン残基を異なる位置に含む、両親媒性ゲル形成ペプチドを開発し[1)]、メチオニン残基の配置に応じた分解速度制御について検討した。

開発したペプチドが形成するゲルは、いずれも類似の分光学的、および物理的性質を有することが確認された。一方で、開発ペプチドの酸化体ではファイバー形成やゲル化が見られず、ゾル化のトリガーとなりうることが示唆された。これらのペプチドは、メチオニン残基の酸化によって、ゲルからゾルへの転移が生じ、内包物質を放出した。また、メチオニン残基の配置の違いにより、酸化に対する応答速度を変えることができた。これにより、ゲルからの物質放出速度の合理的制御を実現した。

1) Y. Hara, *et al*., *ChemBioChem.*, **2023**, e202200798 (VIP).

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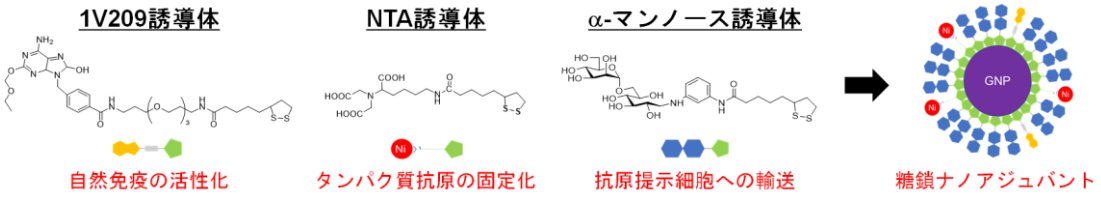
金ナノ粒子をキャリアに用いたセルフ・アジュバント機能を有する組換えタンパクワクチンの開発

（鹿大院理工）○村田 光紀・早川尚宏・若尾雅広・隅田泰生・新地 浩之
Development of self-adjuvanting protein vaccines using gold nanoparticles as carriers (*Graduate School of Science and Engineering, Kagoshima University*) ○Koki Murata, Naohiro Hayakawa, Masahiro Wakao, Yasuo Suda, Hiroyuki Shinchi

Recombinant protein vaccines are safe vaccines in which recombinant proteins are administrated as antigens. However, an adjuvant is needed to enhance the induction of antigen-specific immune responses due to the poor immunogenicity of protein antigens. In the previous study, we developed “Glyco-nanoadjuvants” consisting of gold nanoparticles co-immobilized with a synthetic small molecule ligand of toll-like receptor 7 and a sugar chain.[1)] In this study, we prepared a vaccine conjugated with Glyco-nanoadjuvant and recombinant protein. A recombinant spike protein (S1) of SARS-CoV-2 was used as a protein antigen. The protein was conjugated on the Glyco-nanoadjuvants through the interaction of poly-histidine and Ni-nitrilotriacetic acid. In vivo immunization study suggested that the self-adjuvanting protein vaccine enhanced the production of antibodies that inhibit binding S1 and human ACE2.
Keywords : Vaccine; Gold nanoparticle; Toll-like receptor ligand; Adjuvant

組換えタンパクワクチンは、遺伝子組み換えタンパク質を抗原とする安全性の高いワクチンである。一方、タンパク質抗原単独では免疫誘導活性に乏しく、免疫原性を高めるアジュバントの添加が必須である。我々はこれまでに、金ナノ粒子（GNPs）にToll 様受容体 7（TLR7）の合成低分子リガンド（1V209）と糖鎖を共固定化した糖鎖ナノアジュバントを開発し、この糖鎖ナノアジュバントが液性免疫と細胞性免疫の両方を強力に誘導することを見出した [1)]。本研究では、糖鎖ナノアジュバントと組換えタンパク質抗原を一体化した新規ワクチンを開発し、その免疫誘導活性を評価した。

既報 [1)]を参考に、1V209、ニトリロ三酢酸（NTA）、α-マンノースの 3 分子を、チオクト酸を介して GNP 表面に共固定化した糖鎖ナノアジュバントを調製した（下図参照）。タンパク質抗原には、新型コロナウイルス（SARS-CoV-2）のスパイクタンパク質 S1 を用いた。S1 は、C 末端に導入されたヒスチジン 8 量体と NTA に配位させたNi イオンとの相互作用を介して、GNP 表面に固定化した。効率良く S1 を固定化するために、NTA 誘導体の最適な固定化比率を検討したところ、1V209 誘導体、NTA 誘導体、α-マンノース誘導体の混合モル比が 1:2.5:6.5 の時に、より効率的に S1 を固定化できた。また、マウス骨髄由来樹状細胞における免疫賦活活性は、NTA を固定化してない糖鎖ナノアジュバントと同等であった。得られたワクチンのマウス体内での免疫誘導活性は、S1 特異的抗体の誘導活性および S1 が結合する受容体であるヒト ACE2 への結合阻害効果で評価した。その結果、糖鎖ナノアジュバントと 1 分子の S1 を一体化した場合に、S1-ヒト ACE2 結合の高い阻害活性が認められた。



1) Shinchi, H., Yamaguchi, T., *et al*., *Bioconjugate Chem*. **2019**, *30*(*11*), 2811-2821.

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細胞形質膜中の脂質過酸化を可視化するレシオ型蛍光プローブの開発

（福大院理）○徳永 里奈・塩路 幸生・岩下 秀文

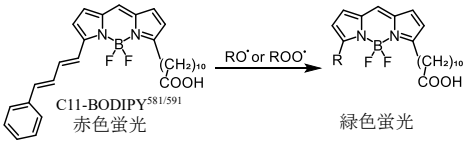
Development of a Ratiometric Fluorescent Probe for Visualizing Lipid Peroxidation in Plasma Membrane

(*Graduate School of Science, Fukuoka University*) ○Rina Tokunaga, Kosei Shioji, Hidefumi Iwashita

Ferroptosis, an iron-dependent cell death, is caused by lipid peroxidation of biomembrane by reactive oxygen species(1). However, it has not been shown which biomembrane is related to cell death. C11-BODIPY$^{581/591}$ has been used to visualize oxidation in unsaturated fatty acids. When the diene bond of C11-BODIPY$^{581/591}$ is oxidized by a radical reaction, the π-electron conjugation is cleaved, and the fluorescence changes from red to green color(2). Since C11-BODIPY$^{581/591}$ easily permeates the cell membrane and is introduced into the cell, it is unclear which biomembrane-derived lipid peroxidation is involved in ferroptosis. To elucidate that, lipid peroxidation should be detected in each biomembrane. We focused on a plasma membrane in biomembranes to identify biomembrane-associated with ferroptosis. A plasma membrane-targeted fluorescent probe for visualization of lipid peroxidation was synthesized and evaluated with ferroptosis-induced cells.

Keywords : ferroptosis; reactive oxygen species; lipid peroxidation; plasma membrane; fluorescent probe

フェロトーシスは細胞内鉄依存性細胞死であり、活性酸素が生体膜中の脂質を酸化することで引き起こされる(1)。しかし、どの生体膜で起こる脂質過酸化が細胞死に関係しているか明らかにされていない。不飽和脂肪酸中の酸化現象の可視化には、蛍光プローブ C11-BODIPY$^{581/591}$ が用いられている(2)。C11-BODIPY$^{581/591}$ は、酸化されるとπ電子共役系がラジカル反応により切断され、蛍光波長が赤から緑へと変化する特徴を持つ。



しかしながら、C11-BODIPY$^{581/591}$ は容易に細胞膜を透過し細胞内に導入されるため、どの生体膜由来の脂質過酸化を可視化しているか判別することはできない。フェロトーシスに関連する脂質過酸化がどの生体膜で起こっているのか解明するためには、蛍光プローブが特定の膜に局在し区別して検出する必要がある。そこで本研究ではフェロトーシスに関連する生体膜を同定するため、細胞形質膜に限定して膜の酸化を可視化する蛍光プローブを合成し、フェロトーシスを誘導した細胞を用いて評価した。

(1) R. Tian *et al*., *Nat Neurosci*, **2021**, *24*, 1020-1034.
(2) Drummen, G. P. C. *et al*., *Free Radic. Biol. Med*., **2002**, *33*, 473-490.

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双性イオンによる耐熱性酵母の耐熱化

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Thermostability of a thermotolerant yeast by zwitterions

([1]*Faculty of Biological Science and Technology, Institute of Science and Engineering, Kanazawa University*, [2] *Institute for Frontier Science Initiative, Kanazawa University*)
○Souta Uemori,[1] Ayumi Hachisu,[1] Kazuaki Ninomiya,[2] Kosuke Kuroda[1]

Microorganisms need to maintain a temperature for fermentation. However, microorganisms emit fermentation heat. Therefore, cooling is necessary due to fermentation heat. Therefore, energy costs for cooling can be reduced by making the microorganisms heat resistant. In this study, we investigated the thermostabilization of a thermotolerant yeast, *Kluyveromyces marxianus* (*K. marxianus*) using an artificial biocompatible zwitterion.

As a result, the OD_{600} of *K. marxianus* at 50 °C for 24 h was 2.0 and 1.2 with and without 0.1 M zwitterion. Thermostabilization was also observed with natural zwitterions at 0.1 – 1.0 M.

Keywords: Microorganism; Ionic Liquid; Zwitterion; Heat Resistance; Bioethanol

微生物が発酵を行うためには温度を一定に保つ必要がある。しかし、微生物は発酵時に発酵熱を排出する。そのため、発酵熱による温度上昇を抑制するために冷却する必要がある。そこで、微生物を耐熱化することで冷却のためのエネルギーコストを削減できる[1]。本研究では、生体適合性を持つ双性イオン[2](Fig. 1)を用いて耐熱性酵母である *Kluyveromyces marxianus*(*K. marxianus*)の耐熱化を検討した。

その結果、50 °C において *K. marxianus* を YPD 培地で 24 h 培養した場合、菌濃度を示す OD_{600} は 1.2 であった。一方で、OE_2imC_3C を 0.1 M 添加した場合、OD_{600} は 2.0 を示した。また、天然由来の双性イオンである TMG、L-carnitine では 0.5 M、1.0 M でも耐熱化が見られた (Fig. 2)。

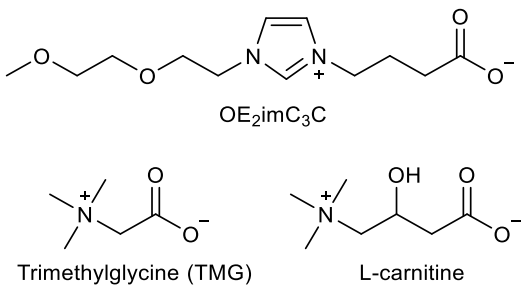

Fig. 1 Structures of zwitterions used in this study

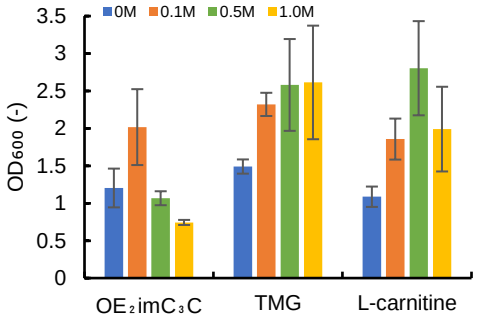

Fig. 2 OD_{600} of *K. marxianus* in the zwitterion solutions after 24 h cultivation at 50 °C

1) Abdel-Banat B. M. *et al*., *Appl. Microbiol. Biotechnol.,* **2010**, 85, 861-867
2) K. Kuroda *et al*., *J. Am. Chem. Soc*., **2017**, 139, 16052-16055

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ドコサヘキサエン酸含有リン脂質蛍光標識体の合成と脂質膜における挙動分析

（九大院理[1]）○清水 浩太郎[1]・木下 祥尚[1]・松森 信明[1]
Synthesis of fluorescence-derivative of DHA-containing phospholipids and its behavior in lipid bilayers. ([1]*Graduate School of Science, Kyushu University*) ○Kotaro Shimizu,[1] Masanao Kinoshita,[1] Nobuaki Matsumori[1]

Docosahexaenoic acid (DHA; C22:6) is a polyunsaturated fatty acid present in the brain nerve cells. In cell membranes, DHA exists not as a free acid but as an acyl chain of phospholipids. These DHA-containing phospholipids (DHA-PLs) are speculated to control several neural membrane proteins through changes in physicochemical properties of lipid membranes. However, their membrane behaviors and the mode of actions are not fully understood. PDPC (C16:0 / C22:6, Figure 1), one of DHA-PLs, is thought to show unique behaviors in phase separated membranes, because this lipid has both saturated chain and polyunsaturated chain.[1] Hence in this study, to evaluated PDPC's physical behaviors in lipid bilayers, we synthesized two-type of fluorescent PDPCs (Figure 1) and measured inter-lipid FRET in raft-like membrane. Based on the results, we will discuss the cluster formation of PDPC.
Keywords : fluorescence probe, polyunsaturated fatty acid, lipid bilayer, FRET

ドコサヘキサエン酸(DHA; C22:6ω−3)は脳神経細胞に存在する多価不飽和脂肪酸で、生体膜中で遊離の脂肪酸ではなく、主にリン脂質中のアシル鎖として存在する 。このような DHA 含有リン脂質（DHA-PL）は、細胞膜の構造や物性変化を介して脳機能に関連するタンパク質の活性を制御することが示唆されているが、その膜挙動や生理活性発現機構の詳細は明らかにされていない。DHA-PL の一つである PDPC (C16:0 / C22:6, Figure 1) は、分子内に飽和鎖と多価不飽和鎖が共存するハイブリッド脂質であることから、ラフト―非ラフト相分離膜において他のリン脂質とは異なる挙動を示すと考えられている[1]。そこで本研究では、PDPC の挙動を高精度で再現する蛍光プローブを合成し (Figure 1)、脂質膜中における物性を評価した。合成した二色の蛍光 PDPC を用いてラフト様膜における脂質間 FRET を測定し、PDPC のクラスター形成を検討した。

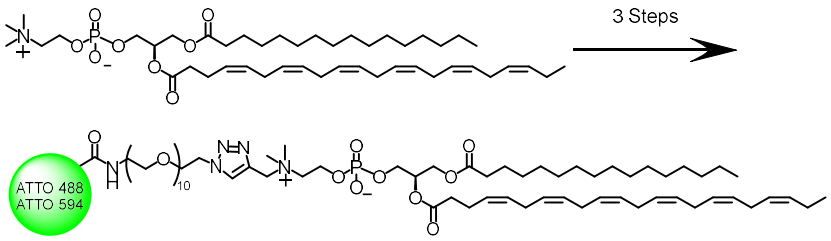

Figure 1. PDPC と蛍光 PDPC の構造式

1. Tetsuya Y; Samuel A. S. Line tension between domains in multicomponent membranes is sensitive to degree of unsaturation of hybrid lipids, *Soft Matter*, **2011**, *7*, 7021 – 7033.

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β-グルカンオリゴ糖を集積化したβ-グルカン模倣高分子の合成とその活性評価

（名工大院工）○宮川淳、山本菜未、大野綾音、山村初雄

Synthesis and Evaluation of β-Glucan Mimicking Polymers Assembled with β-Glucan Oligosaccharides (*Graduate School of Engineering, Nagoya Institute of Technology*)

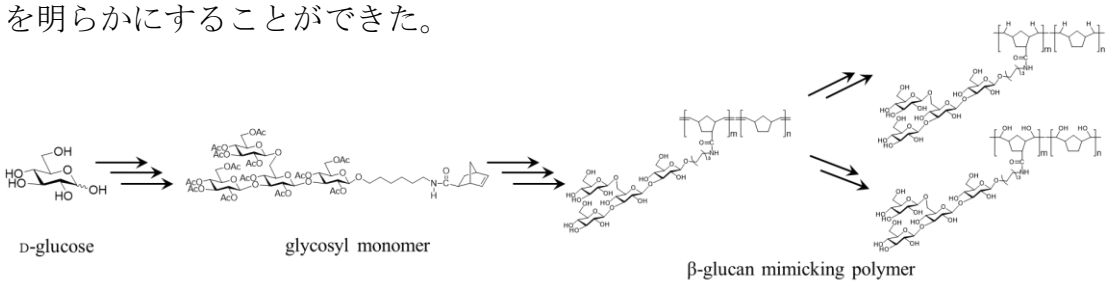
○Atsushi Miyagawa, Nami Yamamoto, Ayane Ohno, Hatsuo Yamamura

The β-1,3-glucans are recognized by dectin-1, a membrane protein, on cell surfaces and then induce immunological responses. To clarify the activation mechanism, β-1,3-glucan oligosaccharides were synthesized via glycosylation and were converted to glycosyl monomers. The glycosyl monomers were polymerized with norbornene using the Hoveyda-Grubbs 2nd generation catalyst. The β-1,3-glucan mimicking polymers were modified via hydrogenation and hydroxylation to introduce hydrogen and hydroxy groups to the polymer main chains. The binding affinities to dectin-1 of the polymers were investigated using the QCM system. Moreover, their effects on cytokine production in RAW264 cells were evaluated using ELISA. As a result, efficacious structural factors of β-1,3-glucan mimicking polymers that induce immunological responses, such as natural β-1,3-glucans, were found.

Keywords : β-1,3-glucan; polymer; dectin-1; macrophage; cytokine

多糖β-1,3-グルカンは、細胞膜上に存在する認識タンパク質 Dectin-1 と結合し、集積化することで免疫反応を活性化する。本研究では、免疫細胞を活性化するβ-グルカンの高分子構造を解明するため、β-グルカン模倣高分子を合成し、Dectin-1 との親和性評価およびサイトカイン産生誘導能を評価した。

始めにβグルカンオリゴ糖の合成のためにβ-1,3-グリコシル化によって、直鎖３糖およびその中央に分岐鎖をもつ分岐４糖を合成した。合成したオリゴ糖のアグリコンにノルボルネン基を導入し、開環重合を行って、β-グルカン模倣高分子を合成した。さらに、この高分子主鎖の二重結合に対し、水素添加反応およびジヒドロキシ化反応により修飾を行うことで、高分子主鎖構造の異なる高分子を得た。その後、QCM を用いて、これらの模倣高分子と Dectin-1 との親和性評価を行い、続いてマクロファージ RAW264 細胞を用いて、模倣高分子によるサイトカイン産生誘導を評価した。その結果、有効な高分子構造を明らかにすることができた。



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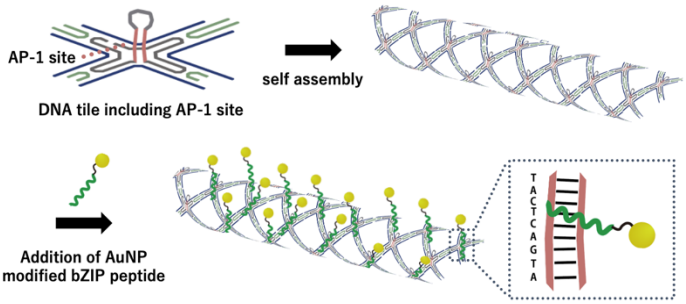
自発的に形成される DNA ナノ構造体上での金ナノ粒子修飾ペプチドの空間配置制御

（九工大院情報工）○越智 耀亮・五味渕 由貴・安永 卓生・平 順一
Controlling the spatial arrangement of the gold nanoparticles conjugated with the peptide on the self-assembling DNA nanostructure (*Graduate School of Computer Science and Systems Engineering, Kyushu Institute of Technology*) ○ Yosuke Ochi, Yuki Gomibuchi, Takuo Yasunaga, Junichi Taira

Technologies based on structural DNA nanotechnology, such as DNA origami and DNA tile, have been considered for the construction of precise and complex structures at the nanoscale [1]. The organization of metal nanoparticles on DNA nanostructures is expected to expand the usefulness of DNA nanostructures, since metal nanoparticles with controlled assembly state exhibit physical properties that are not found in individual particles [2]. In this study, we aimed to control the spatial arrangement of gold nanoparticles (AuNPs) covalently bound to the yeast transcription factor-derived peptide GCN4 bZIP peptide on DNA tile forming a tube-like structure [3]. In addition, the activator protein 1 (AP-1) binding sequence (TGACTCA) [4] was used as the peptide binding sequence. We obtained electron microscopy images suggesting the formation of tube-like structures of DNA tile and the partial binding of the gold nanoparticle-modified peptides to the tube-like structures.
Keywords : AP-1; DNA nanostructure; GCN4 bZIP; Gold nanoparticles; Transmission electron microscope

DNA origami や DNA tile 等に代表される構造 DNA ナノテクノロジーをベースとした技術は，ナノスケールでの精密かつ複雑な構造体構築への展開が検討されてきた [1]．集合状態が制御された金属ナノ粒子が粒子単体では見られない物性を示す [2] ことと併せ，これら DNA ナノ構造体上における金属ナノ粒子の組織化は DNA ナノ構造体の有用性拡大につながると期待される．本研究では，酵母転写因子由来ペプチド GCN4 bZIP ペプチドと共有結合させた金ナノ粒子（AuNPs）の空間配置を，チューブ様構造を形成する DNA tile 上 [3] で制御する検討を行った．なお，ペプチド結合配列として activator protein 1（AP-1）結合配列（TGACTCA）[4] を使用した．DNA tile のチューブ様構造の形成と，これに対する金ナノ粒子修飾ペプチドの部分的結合が示唆される電顕像が得られた．



1) Andre V. Pinheiro et al., *Nat. Nanotech.*, **6**, 763–772 (2011)
2) E. Roduner, *Chem. Soc. Rev.*, **35**, 583 (2006)
3) H. Yan et al., *Science*, **301**, 1882–1884 (2003)
4) IS. Chan et al., *Biochemistry*, **46**, 1663–1671 (2007)

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Academic Program [Oral A] | 18. Polymer：Oral A

Wed. Mar 20, 2024 9:00 AM - 11:00 AM JST | Wed. Mar 20, 2024 12:00 AM - 2:00 AM UTC
D341(341, Bldg. 3 [4F])

[D341-3am] 18. Polymer

Chair: Ryo Sekiya, Tatsuya Nishimura

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[D341-3am-01]

Synthesis and water retention properties under the low humidity of proton-conducting covalent organic frameworks bearing with alkyl functional groups

○Takashi Sato[1], Kouji Inagaki[1], Koki Fujiu[1], Masane Kin[1], Hiroyasu Tabe[2], Ryota Shinozaki[1], Aiko Fukazawa[2], Satoshi Horike[2], Takumi Okamoto[1] (1. DENSO CORPORATION, 2. Kyoto University)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[D341-3am-02]

Synthesis of sulfur-containing polymers with oligo (ethylene oxide) side chains and their properties as solid polymer electrolytes

○Takuya YOKOO[1], Akinari CHIBA[1], Kenichi OYAIZU[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[D341-3am-03]

Synthesis of Copolymers Containing TEMPO-disubstituted Fumarate and Their Electrochemical Properties

○Ryo Shirakawa[1], Kohei Ishigami[1], Kenichi Oyaizu[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[D341-3am-04]

Optical properties of nanographene materials with different kinds of photoemissive organic functional groups

○Saki Arimura[1], Ryo Sekiya[1], Takeharu Haino[1,2] (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM2, Hiroshima University)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[D341-3am-05]

Side-Chain Engineering of Thienothiophene-containing Polymer as Hole transporting Materials toward a Perovskite Solar Cell.

○Yu SAKAI[1], Masaki MINAI[1], Kenichi OYAIZU[1], Hiroyuki NISHIDA[1], Takeo SUGA[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[D341-3am-06]

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Development of semiconducting polymers consisting of novel π-extended building unit based on benzo[1,2-*d*:4,3-*d*']bisthiazole for organic photovoltaics

○Mayu Tomita[1], Hiroto Iwasaki[1], Kodai Yamanaka[1], Tubasa Mikie[1], Itaru Osaka[1] (1. The Univ. of Hiroshima)

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

[D341-3am-07]

Synthetic studies of human influenza virus inhibitors (II)
~Synthetic construction of key intermediates~

○Kaito Takanezawa[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Natsuoka[1,2,3] (1. Grad. Sch. & Sci. & Engin., Saitama University, 2. Adv. Inst. Innov. Tech., Saitama University, 3. Strategic Res. Ctr., Saitama University)

English

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

[D341-3am-08]

Synthetic studies of *N*-linked glycopolymers (Ⅶ): Preparation of a glycosyl monomer with different linker lengths

○Mio Sunaga[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)

Japanese

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

[D341-3am-09]

Development of a Highly Enantioselective Chiral Adsorbent Using a One-Handed Helical Poly(diphenylacetylene) Derivative

○Shota Sona[1], Hirose Daisuke[2], Maeda Katsuhiro[2,3] (1. Grad. Sch. of Frontier Sci. Initiative, Kanazawa Univ., 2. Grad. Sch. of Nat. Sci. and Tech., Kanazawa Univ., 3. WPI-NanoLSI, Kanazawa Univ.)

Japanese

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

[D341-3am-10]

Synthesis of alkynyl spacer-containing chiral polyguanidines and their noncovalent modification for organocatalyst design

○Daiki Mori[1], Keiji Minagawa[1,2], Yukihiro Arakawa[1] (1. Department of Applied Chemistry, Tokushima University, 2. Institute of Liberal Arts and Sciences, Tokushima University)

Japanese

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

[D341-3am-11]

Synthesis and Photo-Plasticization of Polyurethanes Containing
Azobenzene Moieties

○MARIN TAKEUCHI[1], Takenori Ikegaya[2], Shogo nobukawa[2], Yasuhiro Kohsaka[1,3,4] (1. Fac. of Textile Sci. and Tech., Shinshu Univ, 2. Grad. Sch. of Eng., NITech, 3. RISM, Shinshu Univ.,, 4. JST PRESTO)

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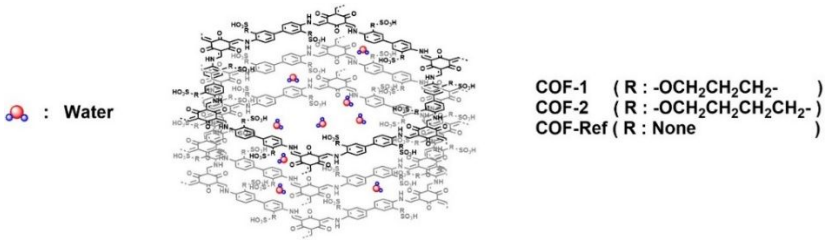
側鎖官能基を持つプロトン伝導性共有結合性有機構造体(COF)の合成と低湿下での水保持特性

（株式会社デンソー[1]・京大 WPI-iCeMS[2]・京大院理[3]）○佐藤　敬[1]・稲垣　孝治[1]・藤生　浩綺[1]・金　甫根[1]・田部　博康[2]・篠崎　良太[1]・深澤　愛子[2]・堀毛　悟史[2,3]・岡本　拓巳[1]
Synthesis and water retention properties under the low humidity of proton-conducting covalent organic frameworks bearing with alkyl functional groups (*[1]DENSO CORPORATION, [2] WPI-iCeMS, Kyoto University, [3] Graduate School of Science, Kyoto University*) ○Takashi Sato[1], Kouji Inagaki[1], Koki Fujiu[1], Masane Kin[1], Hiroyasu Tabe[2], Ryota Shinozaki[1], Aiko Fukazawa[2], Satoshi Horike[2,3], Takumi Okamoto[1]

Water is known as a key factor of proton carrier in polymer electrolyte fuel cell, but there is a problem which decreases water retention under the low humidity and the medium temperature. On the other hand, there are reports that the boiling point of water is increased in the micropores. Microporous covalent organic frameworks (COFs) are expected to increase the water retention property, but the relationship between water retention and proton conductivity is unexplored. Here we demonstrated the synthesis of COFs with different pore sizes by introducing alkyl chains, and evaluated water retention properties by humidity controlled thermal-analysis and proton conductivity.
Keywords：Covalent organic framework; proton conductivity; water retention; nano pore size; low humidity

プロトン伝導性高分子材料では、高分子内にトラップされた水がプロトンキャリアとして重要な役割を果たす。通常高分子内の水分量が減少する低湿中温環境では、プロトン伝導の低下が顕著である。本研究ではこの問題の解決を指向し、ナノ細孔を有する共有結合性有機構造体（COF）に着目した。これまでに、多孔質材料がナノ細孔への包摂に伴う水の沸点上昇により、低湿環境でも高い水保持性をもつことが報告されている[1)]。本研究では、細孔径が水保持性やプロトン伝導性に及ぼす効果を明らかにするために、鎖長の異なるアルキルスルホン酸部位をもつ COF を合成し、それぞれ XRD, 加湿-熱重量分析(HUM-TG)を利用して評価した。その結果、低湿（RH 20 %）下での水保持性が、アルキル鎖の長さの違いに由来する細孔構造に強く依存していることが分かった。



1) Boiling-point elevation of water confined in mesoporous MCM-41 materials probed by ^{1}H NMR. E. W. Hansen, R. Schmidt. M. Stöcker, *Stud. Surf. Sxi. Catal.* **1997**, *105*, 543.

謝辞：この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構（NEDO）の委託業務（JPNP20003）の結果得られたものです。

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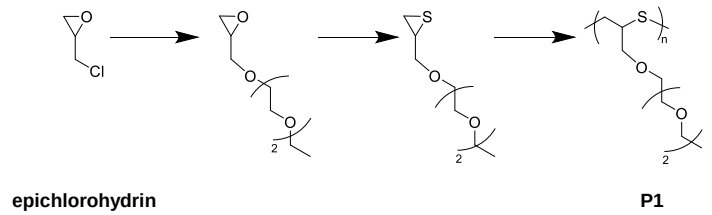
オリゴ(エチレンオキシド)側鎖を有する硫黄含有ポリマーの合成と高分子固体電解質としての特性

（早大理工）○横尾 拓哉・千葉 秋宣・小柳津 研一
Synthesis of sulfur-containing polymers with oligo(ethylene oxide) side chain and their properties as solid polymer electrolytes (*Dept. of Applied Chem., Waseda Univ.*)
○Takuya Yokoo, Akinari Chiba, Kenichi Oyaizu

Solid polymer electrolytes with lower flammability are intensively studied to improve safety and energy density of lithium-ion batteries. In PEO/LiTFSI composite, which is widely studied, oxygen atoms in the polymer interact excessively with lithium ions and disturb lithium-ion transportation. Based on the HSAB rule, sulfur-containing polymers seem to interact moderately with lithium-ion as a soft Lewis base, so they possibly have high ionic transportability. However, in most cases, sulfur-containing polymers are insoluble and difficult to process as a thin film with lithium salt. In this research, we synthesized a sulfur-containing polymer with oligo(ethylene oxide) side chain (**P1**) aiming at high solubility and processability (**Scheme 1**) and evaluated its ionic transportability. Composite of **P1** and lithium salt showed ionic conductivity above 10^{-6} S/cm, indicating its function as a solid polymer electrolyte.

Keywords: Solid polymer electrolyte; Sulfur-containing polymer; Lithium ion-conducting polymer

Li イオン電池の安全性向上およびエネルギー密度向上を目的として難燃性の高分子固体電解質の研究が精力的に行われている。高分子固体電解質において広く研究されているポリエチレンオキシド(PEO)/Li 塩系においては酸素原子と Li イオンの過度な相互作用が原因となりイオンの伝導が妨げられることが知られている[1]。ここで、HSAB則に基づくと酸素よりも柔らかいルイス塩基である硫黄を含むポリマーはLiイオンと適度に相互作用し、高いLiイオン伝導能を示す可能性がある。しかし、硫黄含有ポリマーの多くは溶媒に不溶であり、Li 塩との均一な混合が困難であるという課題があった。本報では溶解性と成形性の向上を目的として側鎖にオリゴ(エチレンオキシド)鎖を導入した硫黄含有ポリマー**P1** を合成し(**Scheme 1**)、そのイオン伝導能を評価した。**P1** と Li 塩からなる複合体は室温で 10^{-6} S/cm を超えるイオン伝導度を示し、高分子固体電解質として機能し得ることが分かった。



Scheme 1

1) Y. Zhao, Y. Wang, *Nanoscale Res. Lett.* **2019**, *14*, 366-342.

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TEMPO 二置換フマレート共重合体の合成とその電気化学特性

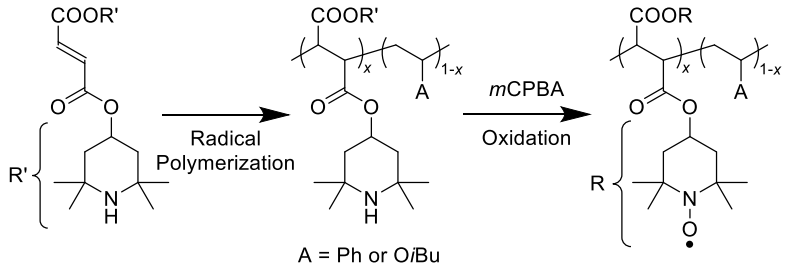
（早大理工 [1]）○白川 稜 [1]・石神 航平 [1]・小柳津 研一 [1]

Synthesis of Copolymers Containing TEMPO Disubstituted Fumarate and Their Electrochemical Properties ([1]*School of Advanced Science and Engineering, Waseda University*)
○Ryo Shirakawa,[1] Kohei Ishigami,[1] Kenichi Oyaizu[1]

TEMPO-substituted polymers can be used as organic cathode-active materials. TEMPO-monosubstituted polymethacrylate and polyacrylamide are synthesized through free radical polymerization. It has also been reported that TEMPO-multisubstituted monomers polymerize using transition metal catalysts. In this study, new-type TEMPO-substituted polymers were synthesized from piperidine-disubstituted fumarate as a radical-polymerizable monomer. The monomer was copolymerized with styrene and isopropyl vinyl ether. The copolymerization behavior is quite similar to those of normal fumarates. Upon oxidation using *m*CPBA, the polymers exhibited a reversible redox response at 0.34 V vs. Fc/Fc^+. Charge-discharge properties of the organic battery with the carbon composite cathodes containing the polymers will be presented.

Keywords : Organic Radical Battery; Polyfumarate; TEMPO; Cathode-active Material; Copolymerization

TEMPO 置換ポリマーは有機正極活物質として適用可能である。繰り返し単位当たり TEMPO が一置換されたポリメタクリレートやポリアクリルアミドは、前駆体ピペリジン置換モノマーのラジカル重合と続く酸化反応により簡便に合成可能である [1]。一方、複数の TEMPO が置換されたモノマーについては遷移金属触媒による重合例が報告されている [2), 3)]。本研究では、ラジカル重合可能な二置換モノマーであるピペリジン二置換フマレートを用いて TEMPO 置換ポリマーを合成した。スチレン及びイソプロピルビニルエーテルとの共重合では、一般的なフマル酸エステルと同様の共重合特性を示した。また、*m*CPBA 酸化により得られたポリマーはコモノマーに依らず 0.34 V vs. Fc/Fc^+で可逆的に酸化還元した。当該ポリマーを含有する炭素複合電極を用いたリチウム二次電池の充放電特性に関しても報告する。



1) K, Zhang; M. J. Monteiro; Z, Zia. *Polym. Chem.* **2016**, *7*, 5589-5614.
2) T. M. Pehl; F. Adams; M. Kränzlein; B. Rieger. *Macromolecules*. **2021**, *54*, 4089-4100.
3) K. Hatakeyama-Sato; S. Matsumoto; H. Takami; T. Nagatsuka; K. Oyaizu. *Macromol. Rapid Commun.* **2021**, *42*, 2100374.

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発光色の異なる複数の有機置換基を導入した新規ナノグラフェン材料の光物性

（広大院先進理工[1]・WPI-SKCM[2]）○有村咲紀[1]・関谷亮[1]・灰野岳晴[1,2]
Optical properties of nanographene materials with different kinds of photoemissive organic functional groups ([1] *Graduate School of Advanced Science and Engineering, Hiroshima University*, [2] *WPI-SKCM², Hiroshima University*) ○Saki Arimura,[1] Ryo Sekiya,[1] Takehru Haino,[1, 2]

Nanographenes, obtained from graphite, have a lot of carboxy groups on the edge. Using these carboxy groups, the nanographenes can be modified by distinct kinds of functional groups and are expected to show multiple functions. In this study, we developed light-emitting nanographene materials that reproduced intermediate colors depending on the variation of installed benzothiadiazole-triphenylamine unit (BTD-TPA, red-emitting) and phenyl-triphenylamine unit (Ph-TPA, blue-emitting) and benzothiadiazole-tetraphenylethylene unit (BTD-TPE, yellow-emitting) (Fig.1a). The photoluminescence spectra of NG-**2a** and NG-**2b** depended on the excitation wavelength, with NG-**2a** showing a purple emission color at 360 nm, and NG-**2b** showing white emission color at 380 nm. We will report the optical properties of NG-**2a** and NG-**2b**.

Keywords : Nanographene, Graphene, intermediate color

本研究では，それぞれ赤色，青色に発光する二種類のトリフェニルアミン誘導体(BTD-TPA, Ph-TPA)と黄色に発光するテトラフェニルエチレン(BTD-TPE)を発光団としてナノグラフェンに同時に導入することで，中間色の再現を目指した(Fig.1a)。ナノグラフェンはグラファイトの酸化分解により得られ，外周部に多数のカルボキシ基を有し，複数の置換基を導入することが可能である。この性質を利用して，BTD-TPA と Ph-TPA を導入した NG-**2a** と Ph-TPA と BTD-TPE を導入した NG-**2b** を合成した。この NG-**2a** と NG-**2b** は励起波長に依存した発光スペクトルを与え，NG-**2a** について，励起波長 360nm の光をあてると紫の発光色を示した。NG-**2b** について，励起波長 380nm の光をあてると白色を示した(Fig. 1b)。本発表では，それらの光物性について詳しく報告する。[1]

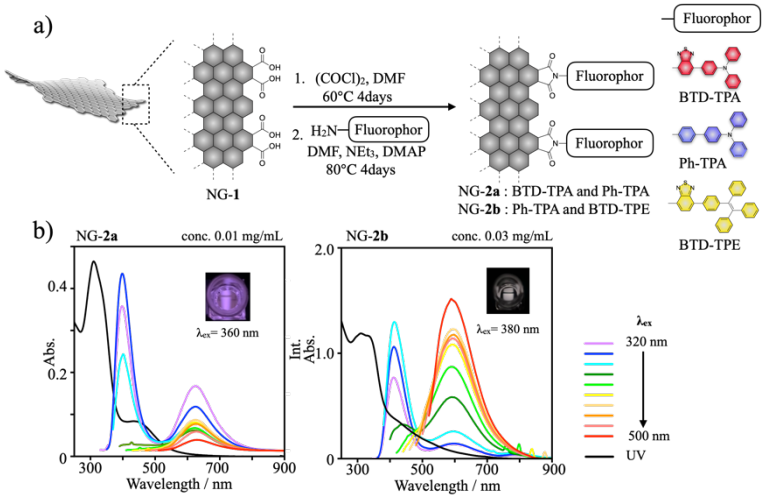

Figure 1. a) NG-**2a**, NG-**2b** の合成 b)発光の様子と励起波長を変化させたときの発光スペクトル

[1] Arimra S.; Matsumoto I.; Sekiya R.; Haino T., *Angew. Chem. Int. Ed.*,**2024**, *63*, e202315508

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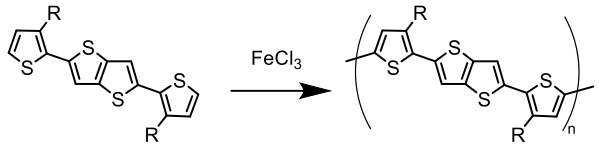
ホール輸送性チエノチオフェン含有共役ポリマーの側鎖設計とペロブスカイト太陽電池への適用

（早大理工）○酒井 悠・南井 正樹・小柳津 研一・西出 宏之・須賀 健雄
Side Chain Engineering of Thienothiophene-containing Polymer as Hole Transporting Materials toward a Perovskite Solar Cell. (*Dept of Applied Chem., Waseda Univ.*) ○Yu Sakai, Masaki Minai, Kenichi Oyaizu, Hiroyuki Nishide, Takeo Suga

Poly(3-hexylthiophene) (P3HT) has been reported as a dopant-free, hole-transporting layer for inorganic perovskite solar cells. For further improvement of the cell performance, the energy discrepancy between the valence band of the perovskite layer and the HOMO level of P3HT is one of concerns. Here we focused on the side chain lengths of thienothiophene-containing conjugated polymers with high co-planarity to improve crystallinity and HOMO levels, more suitable for all-inorganic perovskite layer. Chemical oxidative polymerization was performed to obtain P1-P4, respectively, and utilized to a passivation layer at the interface of perovskite and P3HT. The correlation between the side chain modification and cell performance will be discussed.
Keywords : hole-transporting material; conjugated polymer; perovskite solar cell; thienothiophene

ポリ(3-ヘキシルチオフェン)(P3HT)は、溶解性に優れており、有機トランジスタや有機薄膜太陽電池など広く用いられ、全無機ペロブスカイト太陽電池においてもドーパントフリーで高い効率を示すことが報告されているが、[1] さらなるセル効率の向上にはペロブスカイト層の価電子帯準位と HOMO 準位の乖離や界面での配向性の改良が求められている。[2] 本研究では、ホール輸送ポリマーの結晶性の向上と HOMO 準位の調節を目的として、高い共平面性をもつチエノチオフェン含有共役ポリマーに着目し、側鎖アルキル鎖長やヘテロ原子の導入による改良を試みた。

化学酸化重合により各種側鎖を有するチエノチオフェン含有ポリマー**P1-P4** を合成した。同様に Suzuki coupling により得られたポリマーを比較して、酸化重合により得られたオリゴマーで高いセル特性を示した。また、チエノチオフェン含有共役ポリマーを準位マッチング層として P3HT をさらに積層させた素子において、P3HT 単層よりも高い光電変換効率を示した(PCE = 13.1 %)。チエノチオフェン含有共役ポリマーの側鎖構造、結晶性と光電変換効率について相関づける。



R:Butyl, Octyl, Hexyl, OC_5H_{11}
P1 **P2** **P3** **P4**

Figure 1 Scheme of **P1-P4**

1) Zeng, Q. et. al., *Adv. Mater.* **2018**, 30, 1705393
2) Ming-Hua, L. et. al., *Adv. Mater.* **2020**, 10, 2000501

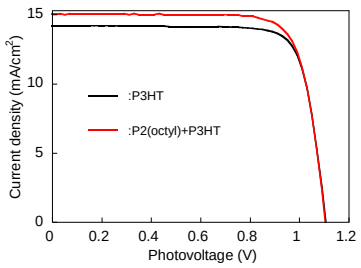


Figure 2 *J-V* curves of the perovskite solar cells using **P2** stacked on P3HT as HTL

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ベンゾビスチアゾールを基盤とした新規拡張π骨格とそれを有する半導体ポリマーの開発

（広大工[1]・広大院先進理工[2]）○冨田 真由[1]・岩崎 洋斗[2]・山中 滉大[2]・三木江 翼[1,2]・尾坂 格[1,2]

Development of semiconducting polymers incorporating novel π-extended building units based on benzo[1,2-*d*:4,3-*d*']bisthiazole for organic photovoltaics ([1]*School of Engineering,* [2]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Mayu Tomita,[1] Hiroto Iwasaki,[2] Kodai Yamanaka,[2] Tsubasa Mikie,[1,2] Itaru Osaka[1,2]

Development of new semiconducting polymers is crucial for improving the power conversion efficiency (PCE) of organic photovoltaic cells (OPVs). Recently, we have reported the synthesis of a number of polymers incorporating thiazole and/or thiazole-containing fused rings such as benzo[1,2-*d*:4,3-*d*']bisthiazole (iBBTz) and TBTz in their backbone, which exhibited relatively high PCE (Figure 1a and 1b). In this study, we designed and synthesized novel thiazole-containing fused rings having further π-extended structure and asymmetric structure, TNTz and TTBTz (Figure 1c and 1d), and semiconducting polymers based on these building units. We will discuss the optical properties, structures, and the performance of OPV devices using a nonfullerene acceptor.

Keywords : Thiazole, π -Conjugated polymers, Semiconducting polymers, Organic photovoltaics, Nonfullerene acceptors

有機薄膜太陽電池（OPV）のエネルギー変換効率（PCE）向上に向けて、半導体ポリマーの開発は重要である。これまでに当研究室では、チアゾールの電子欠損性や隣接するチオフェンとの非結合性相互作用などに着目し、含チアゾール縮環骨格を有する半導体ポリマーを開発してきた。最近では、ベンゾ［1,2-*d*:4,3-*d*'］ビスチアゾール（iBBTz）（Figure 1a）や、それにチオフェンが縮環された TBTz（Figure 1b）を有する半導体ポリマーが 13～15%と高い PCE を示すことを報告した [1]。本研究では、新たな含チアゾール縮環骨格として、さらにπ電子系が拡張され、非対称性な構造を有する TNTz および TTBTz（Figure 1c, d）と、これらの骨格を主鎖に有するポリマーを合成した。これにより、ポリマーが強い主鎖間相互作用とともに高い溶解性を有することを期待した。本講演では、ポリマーの諸物性や非フラーレンアクセプターを用いた OPV 素子の光電変換特性について議論する。

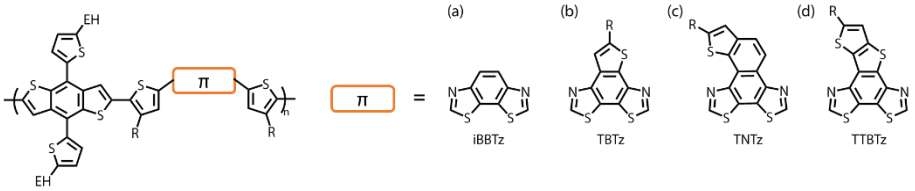

Figure 1.縮合多環骨格の化学構造 (a) iBBTz, (b) TBTz, (c) TNTz, (d) TTBTz

1) N. Nakao, *et al.*, *Adv. Sci*. **2023**, *10*, 2205682.

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ヒトインフルエンザ阻害剤に関するオリゴ糖鎖の合成 （Ⅱ）～鍵中間体の構築～

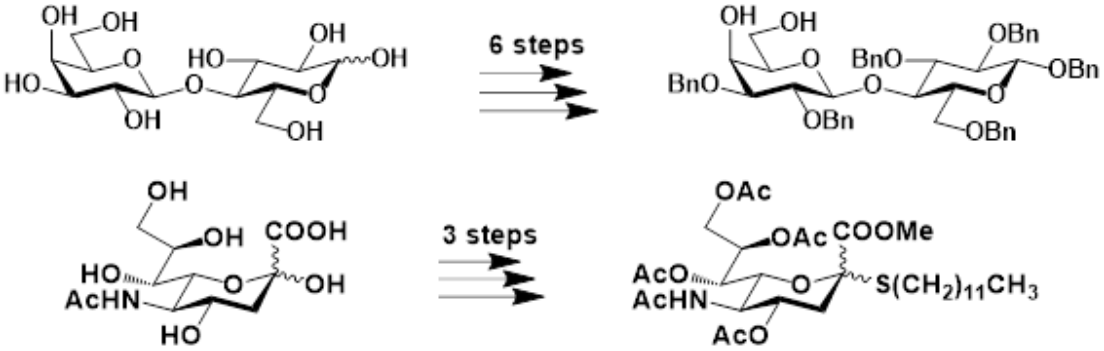
(埼大院理工[1]、埼大先端ラボ[2]、埼大戦略研究[3]) ○高根沢 開登[1]・松下 隆彦[1,2,3]・小山 哲夫[1]・幡野 健[1,2,3]・松岡 浩司[1,2,3]

Synthetic studies of human influenza virus inhibitors (II) ~Synthetic construction of key intermediates~ ([1]*Graduate School of Science and Engineering, Saitama University,* [2]*Advanced Institute of Innovative Technology ,* [3]*Strategic Research Center, Saitama University*) ○Kaito Takanezawa,[1] Takahiko Matsushita,[1,2,3] Tetsuo Koyama,[1] Ken Hatano,[1,2,3] Koji Matsuoka[1,2,3]

The surface of human influenza viruses contains a protein called hemagglutinin (HA), which is involved in human influenza virus infection. Human influenza viruses specifically recognize and bind to sialyl-lacto-terminal sugar chains (Neu5Acα2-6Galβ1-4GlcNAc) on the plasma membrane. Sialyl-α(2-6)-lactose (Neu5Acα2-6Galβ1-4Glc), which is structurally similar to this sugar chain, is inexpensive and has been used in inhibitor research [(1)]. Multivalent sialyl-α(2,6)-lactose is used as a decoy molecule to inhibit the function of hyaluronan through the multivalency effect. In this study, we synthesized derivatives of D-lactose and N-acetylneuraminic acid as starting materials. Subsequently, sialyl-α(2,6)-lactose is synthesized by glycosylation of each derivative. In this study, the synthesis of a lactose derivative and a sialic acid derivative was achieved.

Keywords: Human influenza virus; Hemagglutinin; Sialyl-α(2,6)-lactose

ヒトインフルエンザウイルス表面にはヘマグルチニン(HA)と呼ばれるタンパク質が存在し，HA はヒトインフルエンザウイルスの感染に関与する．ヒトインフルエンザウイルスは細胞膜上のシアリルラクト系構造(Neu5Acα2−6Galβ1−4GlcNAc)を末端に持つ糖鎖を特異的に認識し結合する．この糖鎖と構造がよく似たシアリルα(2,6)ラクトース(Neu5Acα2−6Galβ1−4Glc)は安価であり阻害剤研究に利用されてきた[(1)]．多価化したシアリルα(2,6)ラクトースをおとり分子として利用することで多価効果により，HA の働きを阻害する．本研究では，D-ラクトースと N-アセチルノイラミン酸を出発物として，それぞれの誘導体を合成する．その後，各誘導体をグリコシル化することでシアリルα(2,6)ラクトースを合成する．今回は，ラクトース誘導体とシアル酸誘導体の合成を達成した．



1). M. Nagao *et al.*, Design of Glycopolymers Carrying Sialyl Oligosaccharides for Controlling the Interaction with the Influenza Virus. *Biomacromolecules* **18**, 4385-4392 (2017).

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N-結合型糖鎖高分子の合成研究 (Ⅶ): 異なるリンカー長を持つ糖モノマーの合成

(埼大院理工[1]・埼大先端ラボ[2]・埼大戦略研究[3]) ○須永澪[1]・松下隆彦[1,2,3]・小山哲夫[1]・幡野健[1,2,3]・松岡浩司[1,2,3]

Synthetic studies of *N*-linked glycopolymers (Ⅶ): Preparation of a glycosyl monomer with different linker lengths ([1]Grad. Sci. & Engin. Saitama University, [2]Adv. Inst. Innov. Tech. Saitama University, [3] Strategic Res. Ctr. Saitama University) ○Mio Sunaga[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3]

The glycan cluster effect is a phenomenon that the sugar-protein interaction is enhanced by the aggregation of sugar chains. One of the methods to express this effect is the use of glycopolymers with appropriate molecular weight. In our previous study, several glycopolymers as a mimic of glycoproteins, which play important biological roles, have been synthesized (Figure 1). On the other hand, *N*-linked glycopolymers without linkers have been synthesized, but they do not exhibit the glycan clustering effects. In this study, *N*-linked glycopolymers with different linker lengths in order to elucidate the relationship between the linker length of *N*-linked glycopolymers and the glycan clustering effect were synthesized. Prior to the polymer preparation, we synthesized an *N*-acetyl-D-glucosamine (GlcNAc) monomer with a one-carbon spacer using GlcNAc, that was the pivotal key monomer of *N*-linked glycopolymers (Figure 2).

Keywords : Carbohydrate; Glycoprotein; glycopolymers; Radical Polymerizations

糖鎖クラスター効果とは、糖鎖が集合することにより、糖のタンパク質への相互作用が強くなる現象である[1)]。この効果を発現させる方法の 1 つとして、糖を高分子化させた糖ポリマーを利用する手法がある。この手法を用いて、重要な生物学的機能を担っている糖タンパク質の構造を模倣した糖ポリマーが、これまでにいくつか合成されてきた(**図 1**)。*O*-結合型糖ポリマーはリンカーの長さによって糖鎖クラスター効果の強さに違いがあることが分かっている。一方、*N*-結合型糖ポリマーはリンカーを持たないものが合成されているが、糖鎖クラスター効果を発現しないことを見出した。そこで本研究では、*N*-結合型糖ポリマーのリンカーの長さと糖鎖クラスター効果の詳細な関係を解明するために、リンカーの長さの異なる *N*-結合型糖ポリマーを合成することとした。

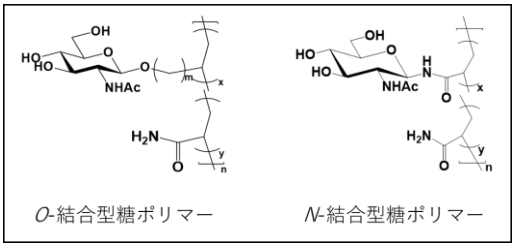

図 1　先行研究で合成された糖ポリマー

ポリマー調製に先立ち、*N*-結合型糖鎖の礎となる *N*-アセチル D-グルコサミンを出発物質とし、炭素数 1 のスペーサーを持つ GlcNAc 誘導体モノマーの合成を行った(**図 2**)。

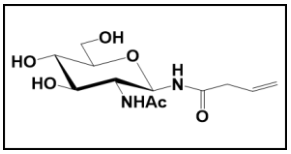

図 2　GlcNAc 誘導体モノマー

1) Lee, Y. C., *et al., J. Biol. Chem.* **1983**, 258,199-202

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一方向巻きらせん状ポリ(ジフェニルアセチレン)誘導体を用いた高選択性不斉吸着材料の開発

(金沢大院新学術[1]・金沢大院自然[2]・金沢大 WPI-NanoLSI[3]) ○惣名 翔大[1]・廣瀬 大祐[2]・前田 勝浩[2,3]

Development of a Highly Enantioselective Chiral Adsorbent Using a One-Handed Helical Poly(diphenylacetylene) Derivative ([1]*Grad. Sch. of Frontier Sci. Initiative, Kanazawa Univ.,* [2]*Grad. Sch. of Nat. Sci. and Tech., Kanazawa Univ.,* [3]*WPI-NanoLSI, Kanazawa Univ.*) ○Shota Sona,[1] Daisuke Hirose,[2] Katsuhiro Maeda,[2,3]

Many biologically and pharmacologically active compounds are chiral, and their physiological properties are often different between enantiomers. Enantioseparation by high-performance liquid chromatography (HPLC) using chiral stationary phases (CSPs) is one of the most useful methods for both analytical and preparative purposes in pharmaceutical and agrochemical fields. However, it usually requires a large amount of solvents for preparative purposes. In this study, we synthesized a one-handed helical poly(diphenylacetylene) derivative (poly-**1**) bearing chiral amide groups in the side chains and evaluated its chiral recognition ability as a chiral adsorbent (Figure 1). Adsorption and desorption experiments of chiral metal acetylacetonate complexes $M(acac)_3$ (M = Co, Cr and Ru) using poly-**1** as an adsorbent afforded almost enantiopure isomers (up to >99% ee) by a single adsorption/desorption operation. Furthermore, we also prepared a poly-**1**-coated chiral belt and tested if the chiral belt system can actually work for optical resolution of $M(acac)_3$ by continuous adsorption/desorption processes.

Keywords : Helix, Chiral, Poly(diphenylacetylene), Optical resolution, Chiral adsorption

医薬、農薬などの生物活性物質にはエナンチオマー間で異なる薬効を示すものが多く存在するため、これらの効率的な分離手法の開発が求められている。現在、最も利用されている分離手法として、キラル固定相を用いた高速液体クロマトグラフィー(HPLC)法による光学分割が知られている。しかし、この手法は、分取を目的する際には、一般に多量の溶媒を必要とする。本研究では、側鎖にキラルなアミド基を有する一方向巻きらせん状ポリ(ジフェニルアセチレン)誘導体(poly-**1**)を合成し、不斉吸着剤としてのキラル認識能力を評価した(Figure 1)。Poly-**1** を吸着剤として、ラセミの金属アセチルアセトナート錯体 $M(acac)_3$ (M = Co, Cr and Ru) の不斉吸着実験を行った。その結果、一回の吸着・脱着の操作によって、片方のエナンチオマーが極めて高い選択性で得られた(>99% ee)。さらに、poly-**1** を塗布したベルトを、連続的な吸脱着によって光学分割を行うキラルベルトシステムに適用した。

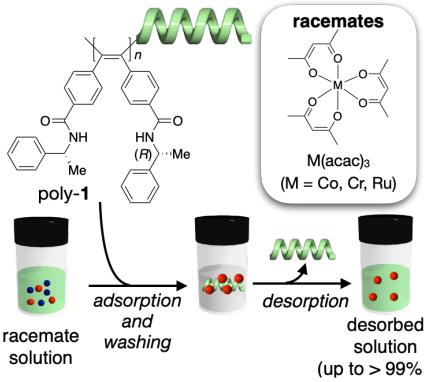

Figure 1. Schematic illustration of chiral adsorption experiment using poly-**1**.

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アルキニルスペーサー含有キラルポリグアニジンの合成とその非共有結合修飾による有機触媒設計

(徳島大院理工[1]・徳島大教養[2]) ○森 大騎[1]・南川 慶二[1,2]・荒川 幸弘[1]

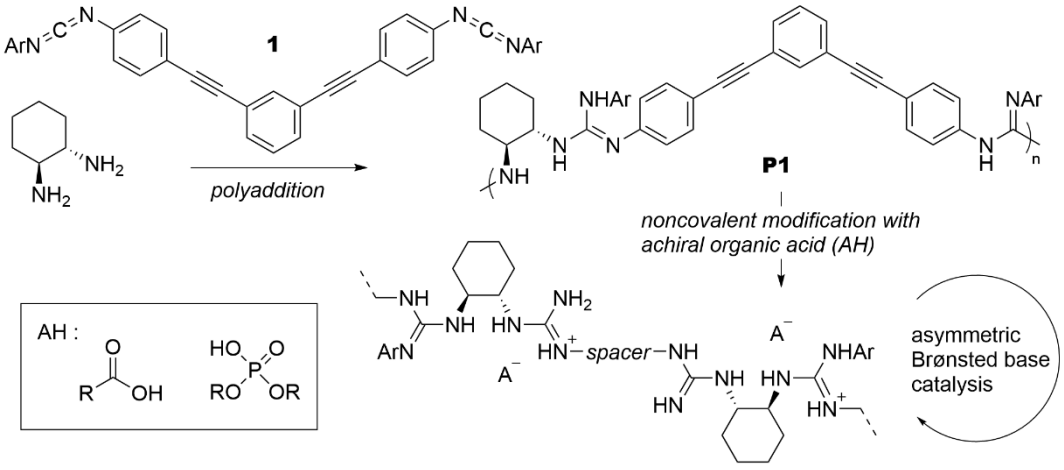
Synthesis of Alkynyl Spacer-containing Chiral Polyguanidines and Their Noncovalent Modification for Organocatalyst Design

([1]*Department of Applied Chemistry*, [2]*Institute of Liberal Arts and Sciences*, *Tokushima University*) ○Daiki Mori,[1] Keiji Minagawa,[1,2] Yukihiro Arakawa[1]

We have synthesized a novel biscarbodiimide compound containing alkynyl spacers and demonstrated that this biscarbodiimide can be used as a comonomer for polyaddition with chiral secondary and primary diamines. The resulting chiral polyguanidines exhibited asymmetric Brønsted base catalytic activity, and the stereoselectivity was significantly enhanced through noncovalent modification with achiral Brønsted acids, such as phosphoric acid diesters and carboxylic acids.

Keywords : Guanidine; Carbodiimide; Polyaddition; Polymeric Catalyst; Asymmetric Reaction

当研究室では、キラルなジアミンとビスカルボジイミドの重付加反応による光学活性ポリグアニジンの合成とその機能開拓について研究を進めている[1)]。本研究では、アルキニルスペーサーを有する新規ビスカルボジイミド **1** を設計・合成し、これが従来系では適用困難であった *trans*-1,2-シクロヘキサンジアミンを含むキラル第一級ジアミンと速やかに重付加反応を起こすことを明らかにした。また、生成した光学活性ポリグアニジン **P1** が不斉 Brønsted 塩基触媒として作用すること、さらにその立体選択性がリン酸ジエステルやカルボン酸などのアキラルなブレンステッド酸による非共有結合修飾によって大きく向上することを見出した（Scheme 1）。



Scheme 1. 本研究の概要（Ar = 1-naphthyl）

1) Hara, M.; Minagawa, K.; Imada, Y.; Arakawa, Y. *ACS Omega* **2021**, *6*, 33215–33223.

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アゾベンゼン骨格を主鎖に有するポリウレタンエラストマーの合成と光可塑化

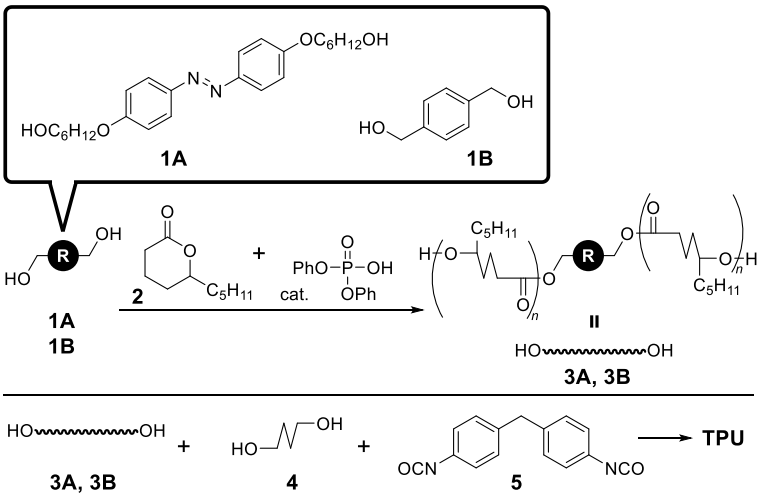
(信州大繊維[1]・名工大院工[2]・信州大先端材料研[3]・JST さきがけ[4]) ○竹内 真凜[1]・池谷 岳紀[2]・信川 省吾[3]・髙坂 泰弘[1,3,4]

Synthesis and Photo-Plasticization of Polyurethanes Containing Azobenzene Moieties

([1] *Fac. of Textile Sci. and Tech., Shinshu Uni,* [2] *Grad. Sch. of Eng., NITech*, *Fac. of Textile Sci. and Tech., Shinshu Univ., JST PRESTO*) Marin Takeuchi,[1] Takenori Ikegaya,[2] Shogo Nobukawa,[2] Yasuhiro Kohsaka[1,3,4]

Cis-trans photoisomerization of azobenzene (AB) in a resin matrix induces an increase in a local temperature[1)] and a decrease in a glass transition temperature of the resin.[2)] Herein, thermoplastic polyurethanes (TPUs) were synthesized from polymer diol **2**, prepared by ring-opening polymerization of **2**, chain-extension agent **4**, and diisocyanate **5**. In all TPUs, photoisomerization of the AB skeleton underwent under UV light irradiation, regardless of the position of the incorporated AB. The TPU containing AB skeletons in the soft segment exhibited a 74% decrease in the storage modulus after UV irradiation. Although the adhesion of this TPU onto a glass plate required heating to 190 °C, the adhesion after UV light irradiation was achieved at 140 °C.

Keywords : Thermoplastic polyurethane elastomer; Azobenzene ; photo-responsive materials; photo-isomerization; photo-plasticization



アゾベンゼン（AB）の *cis-trans* 光異性化を樹脂マトリックス中で行うと，AB 近傍の局所温度上昇[1)]や，ガラス転移温度の低下[2)]が誘起されることが報告されている．本研究では，**2** の開環重合で得られる高分子ジオール **3** と，鎖延長剤 **4**，ジイソシアナート **5** から熱可塑性ポリウレタンエラストマー (TPU) を合成し，アゾベンゼンの挿入位置が光可塑化現象に与える影響を調査した．TPU の主鎖に組み込まれたアゾベンゼンは挿入位置によらず，UV 光を照射すると光異性化することが確認された．このとき，ソフトセグメントに AB 骨格を挿入した試料では，UV 光照射に伴い貯蔵弾性率が 74%減少するとともに，ガラス基板に対する光接着温度が 190 °C から 140 °C に低下した．

1) J. Vapaavuori, A. Laventure, C. G. Bazuin, O. Lebel, C. Pellerin, *J. Am. Chem. Soc.* **2015**, *137*, 13510.
2) M. Maeda, S. Nobukawa, K. Inomata, *Polym. J.* **2022**, *54*, 269.

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Academic Program [Oral A] | 18. Polymer：Oral A

Wed. Mar 20, 2024 1:00 PM - 2:50 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:50 AM UTC D341(341, Bldg. 3 [4F])

[D341-3pm] 18. Polymer

Chair: Kazuko Nakazono, Jin Hotoyanagi

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[D341-3pm-01]
Synthesis and mechanical properties of hydrogels with rotaxane cross-linked structures

○Reo Onda[1], Haruka Minato[2], Daisuke Suzuki[2], Kazuko Nakazono[1] (1. Sch. of Mat and Eng., Tokyo Tech, 2. Grad. Sch. of Text Sci and Tech, Shinshu Univ.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[D341-3pm-02]
Synthesis of hydrogen-bonded crosslinked network polymers and their decross-linking using chemical stimuli

○Keita Aoki[1], Kiyoshi Masuda[1], Haruka Minato[2], Daisuke Suzuki[2], Kazuko Nakazono[1] (1. Sch. of Mat and Eng., Tokyo Tech, 2. Grad. Sch. of Text Sci and Tech, Sinshu Univ)

English
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[D341-3pm-03]
Synthetic studies of Glycopolymers having Porphyrin(VI) : Biological evaluation of glycopolymers having porphyrin against Hela cells

○Yuta Komano[1], Miho Suzuki[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3] (1. Saitama University, 2. Advanced Institute of Innovative Technology, Saitama University, 3. Health Sciences and Technology Research Area, Strategic Research Center, Saitama University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[D341-3pm-04]
LCST-type thermo-responsiveness of *N*,*N*′-dimethylpolyurea in water

○Keitaro Matsuoka[1,2], Mio Sasaki[2], Masanori Miyoshi[2], Akari Sugano[2], Takuro Tsutsumi[1,2], Kazuki Sada[1,2] (1. Fac. of Sci., Hokkaido Univ., 2. Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[D341-3pm-05]
Thermo-responsiveness of polyphenylacetylenes with hydrogen bond substituent

○Koki Takasu[1], Natsuki Inaba[2], Keitaro Matsuoka[2,3], Takuro Tsutsumi[2,3], Kazuki Sada[2,3] (1. Sch. of Sci., Hokkaido Univ., 2. Grad. Sch. of Chem. Si. and Eng., Hokkaido Univ.c, 3. Fac. of Sci., Hokkaido Univ.)

1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
Break

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Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[D341-3pm-06]
Thermally-cured Anionic Polymer Coatings for Responsive Hydrophilic Surface

○Homare KUWAHARA[1], Natsumi FUJI[1], Kenichi OYAIDU[1], Takeo SUGA[1] (1. Waseda University, School of Advanced Science and Engineering)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[D341-3pm-07]
Synthesis of Lipid Bilayer Adhesion Polymers Containing Zwitterions (II)
-Synthesis of Fluorescent-labeled Acrylamide Monomers-

○Hiroki Kato[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
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC
[D341-3pm-08]
Development of adhesive materials based on the synergy effect of the surface structure having vertically oriented pillars and electrostatic interactions

○Kaito Kishimoto[1], Jin Motoyanagi[1], Masahiko Minoda[1] (1. Grad. Sch. of Sci. and Tech., Kyoto Inst. of Tech.)

Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC
[D341-3pm-09]
Creation of a composite hydrogel composed of activated carbon and hydrogelator for a spreadable adsorbent material

○Mai HIRUKAWA[1], Yutaka OHSEDO[2] (1. Faculty of Human Life and Environment, NWU, 2. Fac. Eng., NWU)

Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC
[D341-3pm-10]
Reversible Hydrogenation and Dehydrogenation of Cyclopentanone-containing Polymer

○Tomoki Oura[1], Hiroyuki Odaki[1], Yusuke Kaiwa[1], Kenichi Oyaizu[1] (1. Waseda University, School of Advanced Science and Engineering)

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ロタキサン架橋構造を有するヒドロゲルの合成と力学特性

（東工大院物質[1]・信州大繊維[2]）○恩田 玲央[1]・湊 遥香[2]・鈴木 大介[2]・中薗 和子[1]

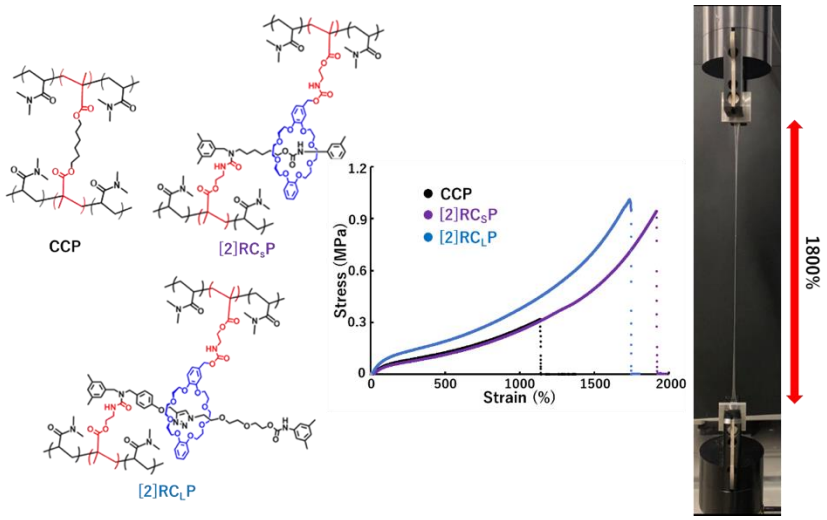
Synthesis and mechanical properties of hydrogels with rotaxane cross-linked structures

(*Department of Chemical Science and Engineering, Tokyo Institute of Technology*[1], *Graduate School of Textaile Science and Technology, Shinshu University*[2]) ○Reo Onda[1], Haruka Minato[2], Daisuke Suzuki[2], Kazuko Nakazono[1]

Rotaxane crosslinked hydrogels have attracted much attention due to their unique swelling and mechanical properties. While crosslinked polymers containing cyclodextrin-based polyrotaxane crosslinked structures have been well studied, we recently found structurally well-defined rotaxane crosslinking structures with a crown ether ring component also toughened the mechanical properties of crosslinked polymers. In this study, we report on hydrogels containing crown ether-based rotaxane crosslinked structures that exhibit high elongation properties.

Keywords : Hydrogel; Crosslinked polymer; Rotaxane; Crown ether

シクロデキストリンを輪成分にもつポリロタキサンを架橋したヒドロゲルは、ユニークな膨潤特性や力学特性を示すことから注目を集めている。最近、構造明確なクラウンエーテル型ロタキサンを架橋構造に有するエラストマーが強靭性を示すことが報告されているが[1]、ヒドロゲルについては未解明である[2]。本研究では、ヒドロゲルの力学特性におけるロタキサン架橋剤の効果を明らかにするため、クラウンエーテル型ロタキサン架橋剤を新たに設計・合成し、それらを用いてヒドロゲルを合成した。得られたゲルは、疎水的なロタキサン架橋構造を有しているにもかかわらず水を含んでよく膨潤し、高伸長性を示すことを見出した。



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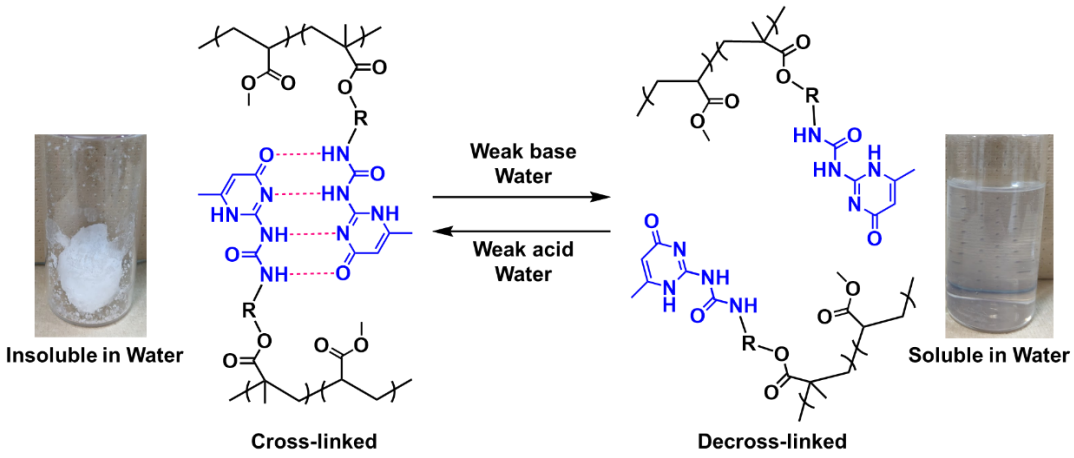
水素結合架橋ネットワークポリマーの合成と化学刺激による解架橋

（東工大物質理工[1]・信州大繊維[2]）○青木 渓汰[1]・増田 清司[1]・湊 遥香[2]・鈴木 大介[2]・中薗 和子[1]
Synthesis of hydrogen-bonded crosslinked network polymers and their decross-linking using chemical stimuli ([1]*Department of Chemical Science and Engineering, Tokyo Institute of Technology*, [2]*Graduate School of Faculty of Textile Science and Technology, Shinshu University*) ○Keita Aoki,[1] Kiyoshi Masuda,[1] Haruka Minato,[2] Daisuke Suzuki,[2] Kazuko Nakazono[1]

Ureidopyrimidinone (UPy) can crosslink polymers with stable hydrogen bonds and has attracted attention for its application in self-healing materials. On the other hand, complete decrosslinking of the UPy crosslinked polymers usually requires high temperature and a large amount of solvent due to the extremely stable hydrogen bonds. Recently, we have found efficient additives for the dissociation and decrosslinking of UPy hydrogen bonds under mild aqueous conditions and achieved quantitative material recycling of vinyl polymers with UPy pendants.
Keywords : Hydrogen bond crosslinking; Ureidopyrimidinone (UPy); Stimuli responsive decrosslinking property; Network polymer

架橋構造にウレイドピリミジノン(UPy)の水素結合を有する架橋高分子の自己修復特性に注目が集まっているが、UPy 間の水素結合は非常に安定であり、完全に解架橋するためには高温や多量の高極性溶媒を要する。最近、我々は新規メタクリレート型 UPy モノマーを開発し、アクリル酸メチルとの共重合体を合成し、キャスト法によりフィルムを作成した。得られた自立膜は弱塩基を含む水溶液に浸漬すると完全に溶解し、さらに弱酸で中和すると沈殿を生じた。これを回収・洗浄したところ、定量的に共重合体が回収され、UPy 架橋高分子の温和な条件での架橋制御およびマテリアルリサイクルを達成した。



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Synthetic Studies of Glycopolymers having Porphyrin (VI): Biological Evaluation of Glycopolymers having Porphyrin against Hela Cells

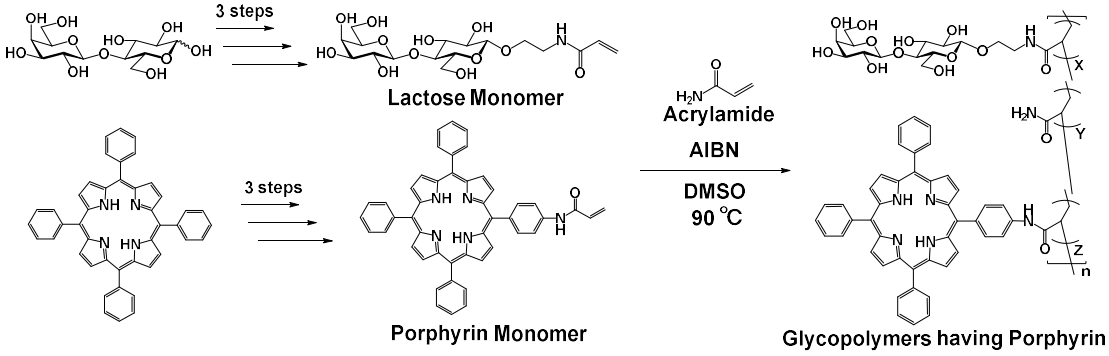
(*[1]Graduate School of Science and Engineering, [2]Advanced Institute of Innovative Technology, and [3]Health Sciences and Technology Research Area, Strategic Research Center, Saitama University,*) ○Yuta Komano[1], Miho Suzuki[1], Takahiko Matsushita[1,2], Tetsuo Koyama[1], Ken Hatano[1,2,3], and Koji Matsuoka[1,2,3]

Keywords: Photodynamic Therapy, Porphyrin, Glycopolymers, Hela Cells

Photodynamic therapy (PDT) is gaining attention as a treatment for cancer. In PDT, a photosensitizing agent is administered to a cancer patient, and the photosensitizing agent is selectively accumulated in the cancer cells that a patient has.[1)] The photosensitizer (PS) is then excited by laser light, and the excited energy is used to convert the oxygen present in the cells into singlet oxygen. The singlet oxygen is assumed to kill cancer cells.[2)] The selection of PSs in PDT is significantly important. Porphyrin derivatives are expected to be used as the candidates of PSs. However, their high hydrophobicity poses a problem for their use as PSs. In this study, we investigated the improvement of water solubility of porphyrins by introducing polymerizable substituents into porphyrins and copolymerizing them with highly hydrophilic lactose.

Lactose monomer and porphyrin monomer were synthesized in three steps, respectively. The glycopolymers having porphyrin skeletons were prepared by means of radical polymerization of each monomer with acrylamide. Furthermore, the optical properties of the synthesized glycopolymers having porphyrin were evaluated, and the same optical properties as those of the porphyrin derivatives were also confirmed. Subsequently, the ability of the glycopolymers having porphyrin skeletons to produce singlet oxygen was also confirmed.

The cellular accumulation and cytotoxicity of the synthesized glycopolymers having porphyrin skeletons were then evaluated using Hela cells. Cellular accumulation and phototoxicity of the polymers were confirmed.



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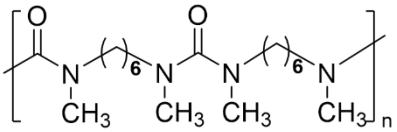
水中で LCST 型温度応答性を示す *N,N'*-ジメチルポリウレア

（北大院理[1]・北大院総化[2]）○松岡 慶太郎[1,2]・佐々木 美緒[1]・三好 正範[1]・菅野 明梨[1]・堤 拓朗[1,2]・佐田 和己[1,2]
LCST-type thermo-responsiveness of *N,N'*-dimethylpolyurea in water ([1]*Fac. of Sci., Hokkaido Univ.*, [2]*Grad. Sch. of Chem. Sci. and Eng., Hokkaido Univ.*) ○Keitaro Matsuoka[1,2], Mio Sasaki[1], Masanori Miyoshi[1], Akari Sugano[2], Takuro Tsutsumi[1,2], Kazuki Sada[1,2]

Thermo-responsive polymers exhibit a drastic change in solubility by changing the temperature. We have previously reported the development of N-alkylated nylon and its LCST-type thermo-responsiveness in water. As a result of inhibiting the construction of intermolecular hydrogen bonds between polymer main chains by *N*-alkylation of N-H bonds in nylon, *N*-alkylated nylon was dissolved in water by the construction of a hydrogen bond between H_2O and the tertiary amide group as a hydrogen bond acceptor. In this study, we focused on the ureido group as a hydrophilic group equivalent to an amide group and investigated the LCST-type thermo-responsiveness of *N,N'*-dimethylpolyurea.
Keywords : polyurea; nylon; thermo-responsive polymer; LCST; thermo-responsiveness

温度応答性高分子は周囲の温度変化に応じてその溶解性が劇的に変化する高分子である。水中における高分子鎖の下限臨界共溶温度（LCST）型温度応答性は、両親媒性側鎖を有する高分子の脱水和により生じると考えられており、盛んに研究されている。当研究室ではこれまでに、水中で LCST 型温度応答性を示す *N*-アルキル化ナイロンを開発している [1]。ナイロンの N-H 結合をアルキル化することで分子間水素結合の形成が阻害された結果、第三級アミド結合が親水基として機能し水と水素結合を形成することで溶解する。このことはユニット構造中において、両親媒性官能基の位置は側鎖に限らず主鎖に導入しても問題ないことを意味する。そこで今回は、アミド結合と同等の親水基であるウレイド結合を主鎖に有する *N,N'*-ジメチルポリウレアの LCST 型温度応答性を着想した。

N-四置換型のポリウレアは合成例がほとんどなかったことから [2]、重合法の開発を行った。その結果、ジカルボニルイミダゾリウム塩モノマーとジアミンモノマーを用いた重縮合を行うことで、*N,N'*-ジメチルポリウレアが得られた。温度変化透過度測定を行ったところ、*N,N'*-ジメチルポリウレア-6,6 が水中で LCST 型温度応答性を発現することを見出した。



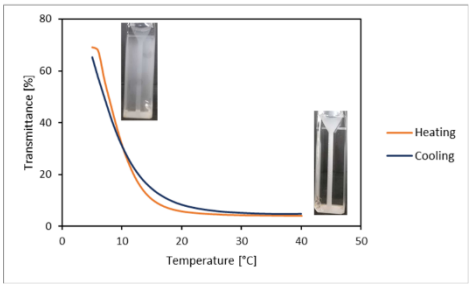


Figure. Transmittance change at 800 nm of *N,N'*-dimethyl polyurea-6,6 in water (scan rate1.5 °C/min).

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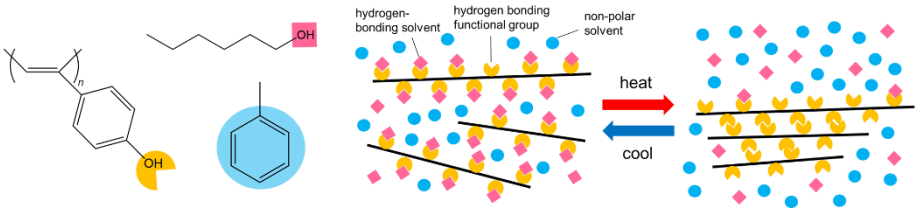
水素結合能を有する置換ポリフェニルアセチレンの温度応答性評価

（北大理[1]・北大院総化[2]・北大院理[3]）○鷹栖 光希[1]、稲葉 奈月[2]、松岡 慶太郎[2,3]、堤 拓朗[2,3]、佐田 和己[2,3]
Thermo-responsiveness of polyphenylacetylenes with hydrogen bond substituent ([1]*School of Sciences, Hokkaido University,* [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [3]*Faculty of Sciences, Hokkaido University*) ○Koki Takasu[1], Natsuki Inaba[2], Keitaro Matsuoka[2,3], Takuro Tsutsumi[2,3], Kazuki Sada[2,3]

Thermo-responsive polymers exhibit a drastic change in solubility by changing the temperature. As a versatile molecular design, we have established LCST-type thermo-responsiveness of the polymers with hydrogen bond group in binary solvents of hydrogen bonding solvents and non-polar solvents based on solvation and desolvation. Since we have applied this method to flexible vinyl polymer with hydroxy group such as poly(2-hydroxyethyl methacrylate) and poly(4-hydroxystyrene), the influence of flexibility in the main chain remained unclear. In this study, we demonstrated LCST-type thermo-responsiveness of substituted polyphenylacetylenes with rigid main chains. As one example, poly(4-hydroxyphenylacetylene) exhibited LCST-type phase separation in 1-hexanol/toluene. Thus, in our molecular design, thermo-responsiveness is not affected by the flexibility of main chains.
Keywords : Thermo-responsive Polymer, Polyphenylacetylene, Lower Critical Solution Temperature, LCST, Hydrogen Bond

温度応答性高分子は周囲の温度変化に応じ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 LCST 型温度応答性の分子設計として水素結合性溶媒と非極性溶媒の混合有機溶媒中における温度応答性を着想した[1)]。高分子の水素結合性官能基と水素結合性溶媒の水素結合を介した溶媒和により溶解した状態に対して、加熱により水素結合が切断されることで脱溶媒和が生じ、高分子が凝集することで不溶となる。この分子設計に基づき、汎用高分子であるポリ(2-ヒドロキシエチルメタクリレート)とポリ(4-ビニルフェノール)が混合溶媒中で LCST 型温度応答性を発現することを見出している。

本研究では LCST 型温度応答性に対する主鎖の柔軟性の影響を探索すべく、炭素-炭素二重結合を有する剛直な置換ポリフェニルアセチレンの混合有機溶媒中における温度応答性を評価した。ポリ(4-ビニルフェノール)の主鎖を二重結合に置き換えたポリ(4-ヒドロキシフェニルアセチレン)は 1-ヘキサノール/トルエンの混合溶媒中で LCST 型温度応答性を発現したことから、温度応答性は主鎖の柔軟性に影響されないことが示唆された。



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アニオン性ポリマー含有熱硬化膜の作成と親水応答性

（早大理工）○桒原 誉・藤井 捺未・小柳津 研一・須賀 健雄
Thermally-cured Anionic Polymer Coatings for Responsive Hydrophilic Surface
(*Dept. of Applied Chem., Waseda Univ.*)
○Homare Kuwahara, Natsumi Fujii, Kenichi Oyaizu, Takeo Suga

Hydrophilic polymer coatings have attracted much attention in self-cleaning, anti-fogging, and biocompatible surface. Here we design anionic polymers containing acrylic pendant groups, and synthesized, and added into hydrophobic or hydrophilic multifunctional acrylates. Thermal curing was performed to give hydrophilic coatings that combine superhydrophilicity of the surface with high mechanical strength.
Keywords : Anionic; Hydrophilicity; Crosslinking; Self-cleaning

水中・大気下で超親水性を示すアニオン性イオン含有ポリマーは、防汚・防曇コーティングとして期待される。当研究室では、ポスト機能化した側鎖を持つ親水性のポリマーを多官能アクリレートとともに熱硬化することで、簡便な親水性コーティングの作成を見出してきた。本研究では、アニオン性ポリマーに疎水性/親水性多官能アクリレートを添加し、表面の超親水性と高い機械強度を両立させた熱硬化膜を作成した。

ラジカル重合によりスルホン酸基を有するランダム共重合体(M_n ~ 50,000)を合成し、共重合モノマーのグリシジル基を有機酸で開環することで側鎖アクリル基を導入し **P1** を得た。スルホン酸及び側鎖アクリル基の組成により、溶剤溶解性は大きく異なり、x = 0.25 で疎水性・親水性多官能アクリレート(M313, M926 など)と親和性良く溶解性の良いポリマーが得られた。PET 基材または表面にシランカップリングで予めメタクリル基を導入した Al 基板上に成膜し、熱硬化膜を作成した。作成したコーティングは水中で親水性を発現した一方、空気中では親水性が低く留まり、外部環境により親疎水基が容易に Flip する応答性を示した。親水基の組成 x、各種多官能アクリレートの当量による親水応答性、防汚性について議論する。

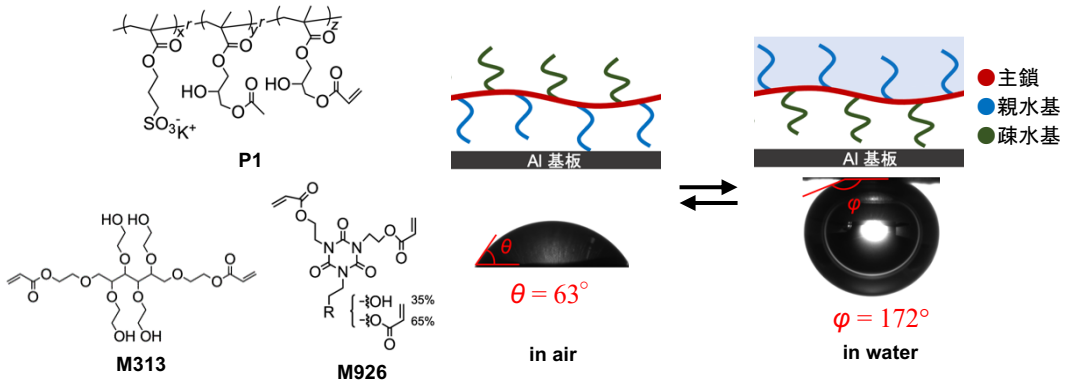

Fig. Structure of polymer (**P1**), crosslinker (M313, M926) and the Flip behavior of the coating.

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双性イオン含有脂質二重膜接着ポリマーの合成研究（Ⅱ） ～蛍光標識アクリルアミドモノマーの合成～

（埼大院理工[1]・埼大先端ラボ[2]・埼大戦略研究[3]）○加藤 裕規[1]・松下 隆彦[1,2,3]・小山 哲夫[1]・幡野 健[1,2,3]・松岡 浩司[1,2,3]

Synthesis of Lipid Bilayer Adhesion Polymers Containing Zwitterions (Ⅱ) -Synthesis of Fluorescent-labeled Acrylamide Monomers-

([1]*Graduate School of Science & Engineering, Saitama University*, [2]*Advanced Institute of Innovative Technology, Saitama University,* [3]*Strategic Research Center, Saitama University*) ○Hiroki Kato[1], Takahiko Matsushita[1,2,3], Tetsuo Koyama[1], Ken Hatano[1,2,3], Koji Matsuoka[1,2,3]

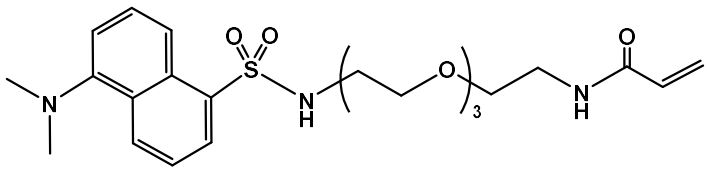
Cell membranes are composed mainly of phosphatidyl choline (PC), a zwitterion. When spherical polymers modified with 'PC-inverse' choline phosphate (CP) were added in the presence of cells, it was reported that the polymer adhered to the cell membrane due to the electrostatic interaction between PC and CP. We have synthesized zwitterionic polymers that adhere to lipid bilayers and are aiming to functionalize membrane surfaces through observing the behavior of the polymers toward cell membranes and liposomes, as well as the state of the membrane surface.

We firstly considered introducing dansyl which shows fluorescence into the polymer to confirm that the polymer would adhere to the membrane surface and began to synthesize dansyl monomers. The synthesis of the monomers was accomplished using tetraethylene glycol as starting material.

Keywords : Zwitterion; Polymer; Lipid Bilayer Adhesion

細胞膜は正と負の電荷をもつ双性イオンであるホスファチジルコリン(PC)を主として構成されていて、正・負の電荷の順序が PC と反対であるコリンホスフェイト(CP)で修飾された球状ポリマーを細胞存在下に加えたところ、細胞膜にポリマーが接着したことが報告されている[1)]。これは PC と CP に静電的な相互作用がはたらいたことによるものである。我々は、その仕組みを用いて脂質二重膜に接着するような双性イオン含有ポリマーを合成し、ポリマーの細胞膜やリポソームに対する挙動および膜表面の状態を観察することを通じて、膜表面の機能化を目指している。

まず、ポリマーが膜表面に接着したことを確認するために蛍光を示すダンシルをポリマーに導入することを考え、ダンシルモノマーの合成から取り組み始めた。テトラエチレングリコールを出発物質としてダンシルモノマーの合成を達成した。



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鉛直配向ピラー構造と静電相互作用とのシナジー効果に基づく表面接着性材料の創製

(京工繊大院工芸科学) ○岸本 海翔，本柳 仁，箕田 雅彦

Development of adhesive materials based on the synergy effect of the surface structure having vertically oriented pillars and electrostatic interactions

○Kaito Kishimoto, Jin Motoyanagi and Masahiko Minoda

The development of new adhesive materials that utilize weak molecular interactions such as hydrogen bonds, π-π interactions, and electrostatic interactions is attracting increasing attention. For example, it has been reported that the electrostatic interaction between two substrates grafted with positively and negatively charged polymer chains allows them to adhere to each other. Furthermore, synthetic polymer thin films with hierarchically ordered surface structure are expected to afford promising surface-functionalized materials usable in various fields. In this study, we focused on the synergy effect of the surface structure having vertically oriented pillars and electrostatic interactions. We prepared two types of pillar film bearing cationic and anionic polyelectrolyte brushes by using nanoimprinting using an AAO template, and subsequent surface-initiated ATRP of **MTAC** and **SPMK** (**Fig.1** and **2**). Furthermore, we also examined their adhesive properties by shear strength measurement.

Keywords: Nanoimprint, Surface-initiated **ATRP**, Adhesion materials, Electrostatic interactions, Surface structure modified with oriented polymer pillars

これ迄に様々な接着性材料が開発されているが、化学接着剤における 3 次元架橋形成による機構とは異なり、水素結合、π-π 相互作用、静電相互作用などが多点で働くことにより接着性を発現する表面機能材料に関心が持たれている。一例として、正と負の電荷をもつポリマー鎖をそれぞれグラフト修飾した 2 枚の基板間に働く静電相互作用により、基板どうしが接着できることが報告されている。他方、高密度で鉛直配向したサブミクロンスケールのピラー構造を表面に有する薄膜は、新たな表面機能材料として注目されている。本研究では、表面に **ATRP** 重合開始点を有する鉛直配向ピラーに、正と負の電荷を有するモノマー (**MTAC** と **SPMK**; **Fig. 1**) をグラフト修飾した階層的表面構造からなる薄膜を各々作製し、鉛直配向ピラー構造と静電相互作用とのシナジー効果に基づく表面接着性材料の創製を目指す。具体的には、ナノインプリント法と精密グラフト重合を併用して、グラフト修飾ピラーを持つ表面機能薄膜材料を作製した (**Fig. 2**)。両者の接着特性は、2 種の薄膜を水で濡れた状態で圧着し、乾燥させた後、剪断強度測定により評価した。

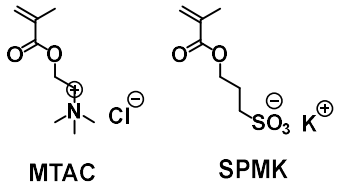

Fig. 1 Functional monomers in this study.

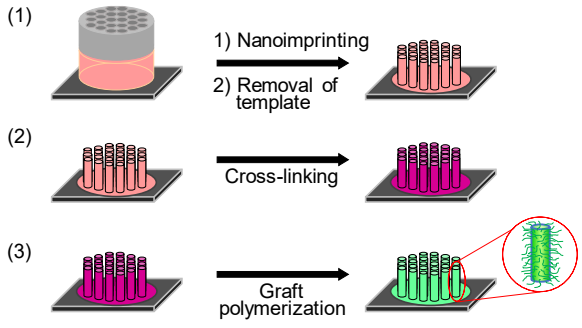

Fig. 2 Preparation of a polymer thin film with precisely-designed hierarchically ordered surface pillar structure by a combination of nanoimprinting and controlled graft polymerization.

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活性炭とゲル化剤を複合化した展延性ゲル状吸着材料の創製

（奈良女大生環[1]・奈良女大院工[2]）○比留川 舞[1]・大背戸 豊[2]
Creation of a composite hydrogel composed of activated carbon and hydrogelator for a spreadable adsorbent material ([1]*Faculty of Human Life and Environment, Nara Women's University*, [2]*Faculty of Engineering, Nara Women's University*) ○Mai Hirukawa,[1] Yutaka Ohsedo[2]

The problem of environmental pollution by hazardous substances is becoming more serious, and the creation of new adsorbent materials to maintain a suitable living environment is being actively pursued. We have attempted to create a new adsorbent composite hydrogel material by mixing NaPPDT and activated carbon powder. The composite hydrogel materials had sufficient mechanical properties for spreading. It was also found that placing the gel in an aqueous NaCl solution to make the gel insoluble in water could adsorb water-soluble dyes in the aqueous phase while maintaining the gel state. These results indicate that this material has become a potential candidate as a new adsorbent material applicable in the liquid phase.
Keywords : Activated Carbon, Composite hydrogel, Molecular gel, Thixotropic property

有害物質による環境汚染問題の拡がりを受けて、良好な生活環境の維持のための、新規吸着材料の創製が活発に行われている。なかでも活性炭は安価かつ有害物質除去に実績のある吸着材料ではあるが、新規吸着材料の原料としても注目されている。一方、水溶性芳香族ポリアミド系高分子ゲル化剤 (NaPPDT、Figure 1)[1)]は、単独では吸着能を有しないものの、水素結合にて三次元網目構造を形成し、有機あるいは無機材料を分散することが可能なゲル材料であることから[2-4)]、既存の吸着材料との複合化に興味が持たれる。本研究では、活性炭粉末と NaPPDT を適切に複合化した新たなゲル状吸着材料の創製を試みた。その結果、得られた複合ヒドロゲルは、ゲル化剤 (1 wt%でヒドロゲルを形成)に対して 10 倍の重量の活性炭を含むものの NaPPDT ゲル由来のチキソトロピー性（展延性）を維持していることが分かった。また塩水中では複合ヒドロゲルが水に不溶化するため、ゲル状態を保持しつつ、水相中の水溶性色素を吸着できることが分かった。これらの結果から、本研究の活性炭/NaPPDT 複合ヒドロゲルが水相で使用可能な新しい形態のゲル状吸着材料となる可能性が示された。

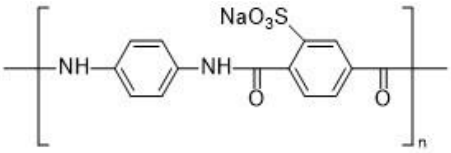

Figure 1 Chemical structure of NaPPDT.

1) Y. Ohsedo et al., *RSC Advances*, **2015**, *5*, 82772−82776. 2) Y. Ohsedo et al., *R. Soc. Open Sci.*, **2017**, *4*, 171117. 3) Y. Ohsedo, W. Ueno, *Gels*, **2023**, *9*, 679. 4) Y. Ohsedo, M. Sasaki, *New J. Chem.*, **2023**, *47*, 17817–17823.

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シクロペンタノンを骨格に含むポリマーの可逆的な水素化・水素発生

（早大理工）○大浦 智輝・小瀧 寛之・海和 雄亮・小柳津 研一
Reversible Hydrogenation and Dehydrogenation of Cyclopentanone-containing Polymer (*Dept. of Applied Chem., Waseda Univ.*) ○Tomoki Oura, Hiroyuki Odaki, Yusuke Kaiwa, Kenichi Oyaizu

Poly(2-cyclopenten-1-one) was obtained via anionic polymerization, and poly(5-norbornene-2-one) was synthesized via ring-opening metathesis polymerization of the corresponding monomers. These polymers were converted to the hydrogenated form under flowing hydrogen in the presence of iridium complex catalysts. The hydrogenated forms released hydrogen rapidly at 150°C in the presence of the iridium complex catalysts, regenerating the original polymers. Their capabilities of reversible hydrogen storage were demonstrated.
Keywords : Hydrogen Storage; Redox Polymer; Hydrogen Carrier Polymer

フルオレノンポリマーは、イリジウム(Ir)錯体触媒 [1]存在下において可逆的な水素化・水素発生が可能であると報告されている [2]。本研究では、さらなる質量水素密度の向上を目指し、シクロペンタノンに着目した(**Figure 1**)。シクロペンタノン骨格を含むポリマーでの可逆的水素貯蔵を目的として、ポリ(2-シクロペンテン-1-オン)をアニオン重合、ポリ(5-ノルボルネン 2-オン)を開環メタセシス重合により合成した。これらのポリマーは、Ir 錯体触媒存在下、常圧での水素フローにより水素付加体を形成した。また、これらのポリマーの水素付加体であるポリ(2-シクロペンテン-1-オール)、ポリ(5-ノルボルネン-2-オール)は、150°C の加熱により迅速に水素を放出し、再びポリ(2-シクロペンテン-1-オン)、ポリ(5-ノルボルネン 2-オン)を生成したことから、本報で合成したポリマーは可逆的な水素化・水素発生が可能であることが明らかとなった(**Figure 2**)。当日は、水素化・脱水素化の詳細について報告する。

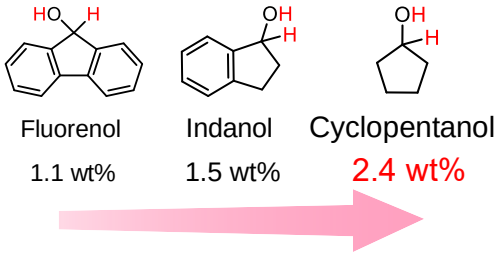

Figure 1 Mass hydrogen density of each compound.

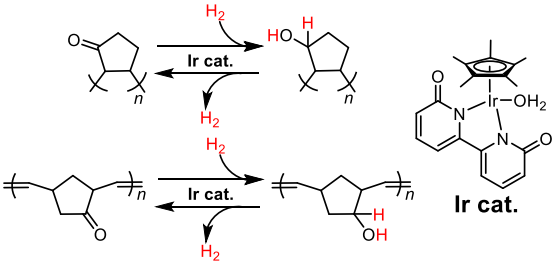

Figure 2 Scheme of the hydrogenation and dehydrogenation of poly(2-cyclopentene-1-one) and poly(5-norbornene-2-one).

1) R. Yamaguchi, *et al*., *Angew. Chem. Int. Ed.*, **2012**, 51, 12790.
2) K. Oka *et al*., *J. Org. Chem*. **2020**, 36, 5876-5879.

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Academic Program [Oral A] | 19. Colloid and Interface Chemistry : Oral A

Wed. Mar 20, 2024 1:00 PM - 3:40 PM JST | Wed. Mar 20, 2024 4:00 AM - 6:40 AM UTC
A1443(1443, Bldg. 14 [4F])

[A1443-3pm] 19. Colloid and Interface Chemistry

Chair: Motohiro Kasuya, Tomonori Ohba

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1443-3pm-01]

High-speed camera observation of the hydrogen evolution reaction

○Wacaco Tao[1], Daiki Sato[2], Tomohiro Fukushima[3], Kei Murakoshi[3] (1. School of Science, Hokkaido University, 2. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 3. Faculty of Science, Hokkaido University)

English
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1443-3pm-02]

Effects of surface nanostructures on the oxygen evolution reaction

○Andrew Harrison Propper[1], Daiki Sato[1], Ryoji Suzuki[1], Tomohiro Fukushima[1], Kei Murakoshi[1] (1. Hokkaido University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1443-3pm-03]

Control of oxygen evolution reaction using structured electrodes

○Kazuma Kobashigawa[1], Daiki Ashizawa[1], Tomohiro Fukushima[2], Kei Murakoshi[2] (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1443-3pm-04]

Observation and analysis of metal complex-immobilized ionic liquid-modified electrodes by surface-enhanced infrared spectroscopy

○Hiroto Wada[1], Tatsuya Kitagawa[1], Tomohiko Inomata[1], Tomohiro Ozawa[1], Hideki Masuda[2] (1. Graduate School of Engineering, Nagoya Institute of Technology, 2. Aichi Institute of Technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[A1443-3pm-05]

Catalyzation of Gold Surfaces by Modification with L-Proline Molecules, a naturally occurring homogeneous catalyst

○Tomoki Watanabe[1], Hidenori Noguchi[2], Mikio Ito[1,2] (1. National Institute of Technology, Tokyo College., 2. National Institute for Materials Science)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1443-3pm-06]

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Temperature-dependence of CO_2 Adsorption/Reaction
on $BaTiO_3$ Nano-catalyst

○Masatoshi Miyamoto[1], Smita Takawane[1], Takumi Watanabe[1], Tomonori Ohba[1] (1. Chiba 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

[A1443-3pm-07]

Development of a New Synthesis Method for Nanoporous Carbons Using Ionic Liquids with π-Conjugated Frameworks.

○Toshinori Seki[1], Kento Nakamura[1], Ryuta Sekiguchi[3], Taku Iiyama[2], Ryusuke Futamura[2] (1. Graduate School of Science and Technology, Shinshu University, 2. Faculty of Science, Shinshu University, 3. Faculty of Science and Technology, Hirosaki University)

Japanese

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

[A1443-3pm-08]

Synthesis and characterization of novel porous materials with temperature-responsive gels

○Tamao Sawada[1], Ryusuke Futamura[2], Taku Iiyama[2] (1. Graduate School of Science and Technology Department of Science , 2. Department of Chemistry, Faculty of Science, Shinshu University)

Japanese

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

[A1443-3pm-09]

Pore structure evaluation of carbon-based nanoporous materials using positron annihilation lifetime method

○Kei Kubo[1], Hayato Otsuka[1], Daisuke Saeki[1], Toshio Sakai[1], Katsumi Kaneko[1] (1. Shinshu univ.)

Japanese

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

[A1443-3pm-10]

Elucidation of the molecular mixing state in pore in liquid phase adsorption on activated carbon using X-ray scattering measurements

○Itsuki Tsubakihara[1], Kiri Sato[1], Ryusuke Futamura[1], Taku Iiyama[1] (1. Shinshu University)

Japanese

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

[A1443-3pm-11]

Water adsorption mechanism on activated carbon from the viewpoint of precise isothermal adsorption heat measurement

○Rin Iwatsuki[1], Ryusuke Futamura[2], Taku Iiyama[2] (1. Graduate School of Science and Technology, Shinshu University, 2. Faculty of Science, Shinshu University)

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

Break

Japanese

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

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[A1443-3pm-12]

Molecular Interactions and Adsorption Selectivity of Six-Membered Ring Alicyclic Hydrocarbons on ZIF-8 during Physisorption Process

○Takahiro Ueda[2], Yuta Yamada[1], Kota Fujii[1], Ryota Mihara[3], Taku Iiyama[3], Yasutaka Hamada[2], Mitsutaka Okumura[2] (1. Faculty of Science, Osaka University, 2. Graduate school of science, Osaka University, 3. Graduate school of science, Shinshu University)

Japanese

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

[A1443-3pm-13]

Formation of micro-solution and figure out opposite dissolution/precipitation phenomena induced by water physisorption

○Takeru Yokoyama[1], Yuka Matsuda[1], Takahiro Ueda[2], Ryusuke Futamura[3], Taku Iiyama[3] (1. Graduate School of Science and Technology, Shinshu University, 2. Dep. of Chem., Graduate School of Science, Osaka University, 3. Faculty of Scienece, Shinshu University)

Japanese

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

[A1443-3pm-14]

Adsorption behavior of several adsorbate under light irradiation on ZnS introduced FAU

○Saho Baba[1], Yukino Muramatsu[1], Satoshi Yamazaki[1] (1. Shizuoka Inst. of Sci. and Tech.)

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高速動画気泡生成計測による水素発生反応解析

(北大理[1]・北大院総化[2]・北大院理[3])
○田尾和花子[1]・佐藤大樹[2]・福島知宏[3]・村越敬[3]
High-speed camera observation of the hydrogen evolution reaction (*Department of Chemistry, Faculty of Science, Hokkaido University*)
○Wakako Tao, Daiki Sato, Tomohiro Fukushima, Kei Murakoshi

Hydrogen evolution reaction (HER) is the important reaction for the water electrolysis. The HER mechanisms have been analyzed from the Tafel plots in the electrochemical experiments. However, in the real electrolysis system, it is important to analyze the HER behavior in high current density region accompanying with the bubble formation. Here, we developed the use of the high-speed camera for the evaluation of the hydrogen evolution reaction from the metal nanostructure. Ag nanostructure was prepared from the electron beam lithography. Ag plate was also used as a control to evaluate the bubble formation process depending on the conditions.
Keywords : Hydrogen evolution reaction; High-speed camera observation; Bubble analysis

【序論】 水素発生反応(HER)においては、3 つの反応素過程が知られているが、高電流密度領域においては液抵抗や発生水素気泡による電極面積低下の観点から電子移動反応の解析が難しくなる。本研究では高速カメラを用いて、高電流密度領域における HER 気泡観察を行い、動画計測から反応素過程の解明を試みたので報告する。
【実験】 電子線ビームリソグラフィにより、グラッシーカーボン上にパターンを描画した。電子線蒸着により Ag を 100 nm 蒸着して Ag ナノ構造を表面に有する基板を作製した。作用極を Ag ナノ構造、対極と疑似参照電極を Au 線とした 3 極式セルを構築し、0.25 M Na_2SO_4 水溶液を電解質として、パルス定電位印加時における動画観測を行った。正立配置とした高速カメラを用いて、1 秒あたり 1000 フレームのフレームレートにて動画観測を行った。動画解析ソフトを利用して、気泡解析を行うことにより各電位における HER 気泡形成-成長の挙動を取得した。
【結果と考察】Fig. に高速カメラによる水素気泡発生挙動を示す。パルス電位印加後、HER に由来する還元電流が観測され、電流値から遅れて水素の気泡が観測され、その後徐々に気泡が成長するようするが観測された。気泡サイズの経時変化から水素の分子数、電流密度に関して検討を行ったところ、HER 電流密度 −0.1 A cm^{-2} を超える電流密度に相当する気泡成長が観測された。電極―電解質界面においては水素分子の物質量変化は電子移動反応、物質輸送、泡成長によって支配されており、気泡成長から水素発生反応を解析可能であるであることが明らかとなった。

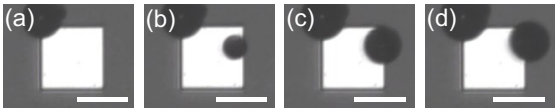

Fig. High-speed camera observation of the hydrogen evolution reaction at −1.15 V versus RHE. t = (a) 0.835 s, (b) 0.845 s, (c) 0.855 s, and (d) 0.865 s. Scale bar = 50 μm.

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Effects of surface nanostructures on the oxygen evolution reaction

(*Department of Chemistry, Faculty of Science, Hokkaido University*) ○Andrew Harrison Propper, Daiki Sato, Ryoji Suzuki, Tomohiro Fukushima, Kei Murakoshi

Keywords: Oxygen evolution, strong coupling, Nanostructure Electrodes, Interfacial Chemistry

Electrocatalytic water splitting represents a carbon-free method for hydrogen production. For widespread use, higher catalytic efficiency will be required, for which the half-cell reactions must be better understood. Utilization of the nanostructure for the electrocatalytic reactions are useful in terms of the increase in the electrode surface area and electric field localization. In this study, we explore the oxygen evolution reaction using Au nanostructures of various geometries. This will allow us to further understand the reaction by observing which energy states are involved in the OER. It may also offer a parameter that can be manipulated to modify chemical kinetics and reactivity.

Au nanostructures are fabricated by electron beam lithography. A 100 nm gold (Au) layer is deposited on FTO. The diameter of the nanodisks is 800 nm. Electrochemical experiments are conducted by using a three-electrode setup, with Au nanostructures on FTO as the working electrode, Ag/AgCl as a reference electrode, and Pt used as a counter electrode. NaOH + 1 M H_3PO_4 with a pH of 11 was utilized as an electrolyte solution. OER activity was monitored using a camera to observe the bubble growth rates from the nanostructures. The bubble growth was analyzed by the binarization of the images, followed by using software for the evaluation of the bubble area, size, and current density from the bubble growth.

The OER behavior of the Au nanostructure was first evaluated from electrochemical experiments. It was confirmed that applying an oxidating potential to the Au surface leads to the formation of the O_2. In figure 1, three images are shown in timesteps of about 0.1 seconds from left to right during a linear sweep voltammetry experiment. The growth of a single bubble is demonstrated in these pictures. Beneath each picture is the binarization of the images done with software to analyze the bubble growth. The growth rate of the bubbles can be utilized as the descriptor for the local OER current density. The observation of the bubble growth rate from the nanostructure was compared to the flat Au electrode. We observed faster growth rate on the nanostructured electrodes, indicating the enhanced OER activity on nanostructured electrodes.

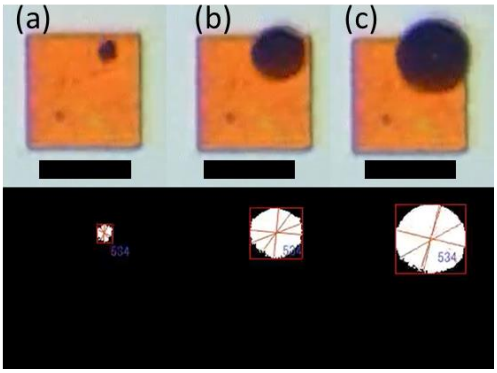

Figure 1: Images showing the oxygen bubble growth on a nanostructure, as well as the binarization of the images for analysis. The applied potential vs RHE is (a) 2.310 V at t = 0 (b) 2.313 V at t = 0.08 s (c) 2.313 V at 0.19 s. The scale bar under each nanostructure is 50 μm in length.

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酸素発生反応構造電極における活性制御

(北大院総化[1]・北大院理[2]) ○小橋川 和磨[1]・芦澤 大輝[1]・福島 知宏[2]・村越 敬[2]
Control of oxygen evolution reaction using structured electrodes (*Department of Chemistry, Faculty of Science, Hokkaido University*) ○Kazuma Kobashigawa, Daiki Ashizawa, Tomohiro Fukushima, Kei Murakoshi

In this study, we prepared micro-structured electrodes and evaluated the oxygen evolution activity. The structures of micro-structured electrodes were evaluated form SEM. The effect was evaluated by linear sweep voltammetry (LSV).

Keywords : electrocatalysis, oxygen evolution reaction, water electrolysis

【序論】 水素は最も注目されているエネルギー資源の一つであるが、水素製造においては、酸素発生反応(OER)の過電圧が高いことが課題となっている。分子の振動エネルギーと同程度のエネルギーを有する共振器においては、真空場のエネルギーと分子のエネルギーが量子相関を持つことによって、振動強結合状態が生じることが知られ、イオン溶媒和環境の制御が提案されている。[1] 本研究においては、振動強結合を発現しうる構造電極を作製し、OER の反応プロセスの変調を目的として研究を行った。
【実験】共振器が電極界面に配列されたマイクロ構造をガラス基板上に作製した後、Ni を 200 nm 蒸着させて構造電極とした(Fig.)。構造電極を作用極、Ag/AgCl を参照極、白金黒電極を対極とした三極式電気化学セルを構築し、1 M $NaClO_4$ + 3 mM NaOH (pH = 11) を弱塩基性電解質とした。−0.3 V vs. RHE で前処理を行った上で、酸素発生反応を行った。ポンプ式フロー装置により電解質を対流させながら、電気化学実験を行った。
【結果】 Fig.に示すように共振器となり得る溝の幅がサブマイクロメートルの精度で制御された構造電極の作製手法を確立した。ガラス基板上に作製しているために、種々の触媒金属を蒸着することによって構造電極として利用可能である。本系では、酸素発生挙動を 1.6 V 程度での立ち上がりの後に、電流値が一定値となり、2.2 V 付近にて再び OER に由来する電流値の増大が観測されたこれらは、それぞれ 1.6 – 2.2 V では弱塩基性条件に特徴的な OH^-の酸化拡散限界電流と 2.2 V より正電位領域では水の酸化反応に由来する。[2] 共振器構造電極では、振動強結合による水分子の解離促進により、この拡散限界電流の向上が期待される。

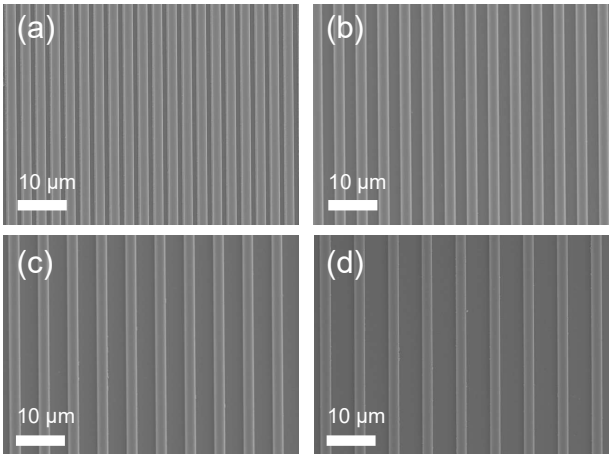

Fig. SEM image of the Ni-deposited cavity array structure. Cavity length = (a) 1.1 μm, (b) 2.2 μm, (c) 3.8 μm and (d) 4.8 μm.

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日本化学会 第104春季年会 (2024)

増強赤外分光法による金属錯体固定化イオン液体修飾電極の挙動解析

（名工大院工[1]、愛工大工[2]）○和田 寛大[1]・北川 竜也[1]・猪股 智彦[1]・小澤 智宏[1]・増田 秀樹[2]

Observation and analysis of metal complex-immobilized ionic liquid-modified electrodes by surface-enhanced infrared spectroscopy ([1]Graduate School of Engineering, Nagoya Institute of Technology, [2]Faculty of Engineering, Aichi Institute of Technology) ○Hiroto Wada,[1] Tatsuya Kitagawa,[1] Tomohiko Inomata,[1] Tomohiro Ozawa,[1] Hideki Masuda[2]

We have been using ionic liquid-modified electrodes to immobilize functional molecules on electrodes to develop electrode materials that can be used as catalysts and sensors[1]. This study investigated the potential-dependent behavior and interaction among the ionic liquid moieties modified on the electrode, the immobilized metal complexes, and the unmodified electrode surface by surface-enhanced infrared spectroscopy (SEIRAS) using the ionic liquid-modified electrode encapsulated with metal complexes. SEIRAS measurements using the negatively charged $[Fe(CN)_6]^{4-/3-}$complex showed enhanced and attenuated CN-derived peaks (2084 cm^{-1}, 2037 cm^{-1}) at potentials corresponding to $Fe^{II/III}$ of the complex at the unmodified gold electrode (Figure 1a). On the other hand, similar behavior was observed when the complex was encapsulated in the ionic liquid-modified electrode. However, the peaks (2180 cm^{-1}, 2130 cm^{-1}) shifted (Fig. 1b). This may be due to the interaction of the complexes encapsulated between the ionic liquids on the electrode with the cationic moieties of the ionic liquids. A similar study was conducted for the positively charged $[Ru(NH_3)_6]^{2+/3+}$ complex.

Keywords：　ionic liquid, surface-enhanced infrared spectroscopy, metal complex

我々はイオン液体を修飾した電極を用いて機能性分子を電極に固定化し、触媒やセンサーなどに利用可能な電極材料の開発を行ってきた[1)]。本研究では、金属錯体を固定化したイオン液体修飾電極を用い、電極上に修飾されたイオン液体部位と内包された金属錯体、および未修飾の電極表面間の電位に応じた挙動や相互作用について表面増強赤外分光法（SEIRAS）により検討した。負電荷を有する$[Fe(CN)_6]^{4-/3-}$錯体を用いた SEIRAS 測定では、未修飾の金電極では錯体の $Fe^{II/III}$ に該当する電位で CN に由来するピーク（2084 および 2037 cm^{-1}）の増強、減衰が確認された（Fig.1a）。一方、イオン液体修飾電極に錯体を内包した場合でも同様の挙動が観測されたが、各ピーク（2180 および 2130 cm^{-1}）がシフトした（Fig.1b）。これは電極上のイオン液体間に内包された錯体がイオン液体のカチオン部位と相互作用しているためと考えられる。同様に正電荷を有する$[Ru(NH_3)_6]^{2+/3+}$錯体についても検討した。

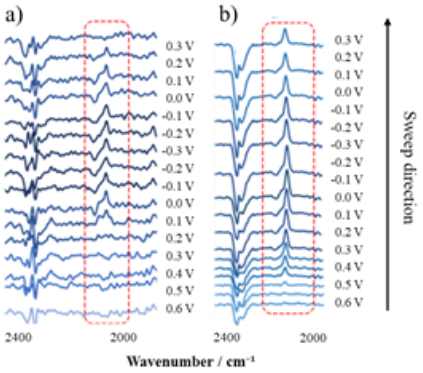

Fig. 1. Surface-enhanced infrared spectroscopy of [Fe(CN)6]4-/3- using a) bare Au electrode and b) ionic liquid-modified Au electrode

1) T. Kitagawa et al., *Chem. Commun.*, **2013**, *49*, 10184.; T. Kitagawa et al., *Chem. Commun.*, **2016**, *52*, 4780.; G. Iijima et al., *ACS Catalysis* **2018**, 8, 3, 1990-2000

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天然由来均一触媒である L-プロリンの表面修飾による金表面への触媒作用の付与

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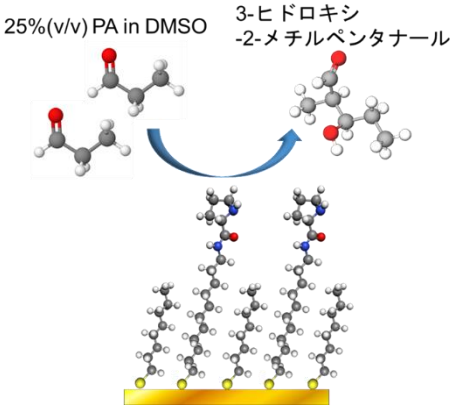
○渡邉 知樹[1]、野口 秀典[2]、伊藤 未希雄[1,2]
Catalyzation of Gold Surfaces by Modification with L-Proline Molecules, a naturally occurring homogeneous catalyst (1. National Institute of Technology, Tokyo College., 2. National Institute for Materials Science) ○Tomoki Watanabe[1], Hidenori Noguchi[2], Mikio Ito[1,2]

L-Proline is a naturally abundant molecule which has the unique property that it catalyzes direct intermolecular asymmetric aldol reactions and other reactions. Solid substrates modified with the catalyst molecules have two advantages. First, compared with conventional homogeneous catalysts, it is easy to remove the catalysts from the crude product. Second, compared with conventional heterogeneous catalysts, highly functional naturally or artificially synthesized catalysts can be realized. In this study, to prove the advantages of this strategy, L-proline was immobilized on a gold substrate surface and catalysis of the substrate was examined. L-proline was immobilized via a mixed self-assembled monolayer (SAM) on the gold surface. L-proline was linked to the mixed SAM with an amide bond. XPS measurements were carried out to evaluate the yield of the reaction between L-proline and the mixed SAM. The XPS measurements revealed that L-proline was effectively introduced on the mixed SAM surfaces. The catalysis of the L-proline modified substrate was confirmed by probing the surface in a solution containing propionaldehyde with an infrared reflection-absorption spectroscopy technique.
Key words: L-proline, self-assembled monolayer, surface, immobilization

L-プロリン(pro)は天然に豊富に存在する分子で、分子間不斉アルドール反応などに対して分子触媒として作用する。固体表面に分子触媒分を固定化することは、反応系からの触媒の分離が容易であること、触媒の選択により任意の機能を持つ表面を創成できるという利点を有する。本研究では、pro を金基板表面に固定化し、その触媒作用の発現と性能を調査した。pro は金基板表面にアミノ基を末端にもつ分子を含む混合自己組織化単分子膜（SAM）を作製し、SAM のアミノ基とのアミド結合により固定化した。Pro を固定した混合 SAM の XPS 測定の結果、pro が混合 SAM 表面に効果的に導入されていることがわかった。pro 修飾分子膜とプロピオンアルデヒド(PA)を含む溶液の界面の赤外反射吸収測定により、溶液中に PA 2 分子によるアルドール反応の生成物が検出された。この結果より表面修飾した pro が Scheme 1 に示す触媒作用を示し、固体表面に分子触媒由来の触媒作用を付与できることが分かった。



Scheme 1 PA のアルドール反応

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チタン酸バリウムナノ触媒を用いた二酸化炭素吸着反応の温度依存性

（千葉大学）○宮本 優俊・Smita Takawane・渡邊 拓実・大場 友則

Temperature-dependence of CO_2 Adsorption/Reaction on $BaTiO_3$ Nano-catalyst

([1]*Chiba University*)○Masatoshi Miyamoto,[1] Smita Takawane,[1] Takumi Watanabe,[1] Tomonori Ohba[1]

Effective CO_2 adsorption and reduction are inevitable requirement in carbon capture and utilization processes. In this work, nano-$BaTiO_3$ crystal was utilized for CO_2 adsorption at low temperature. The amounts of CO_2 adsorptions on the nanocrystal at 300, 500, and 700 K were reached to 420, 200 and 400 μmol g^{-1}, respectively. Despite small adsorption amount at high temperature the adsorption amount at 700 K was increased again, indicating that the nanocrystals preferentially chemisorbed/reduced CO_2 at 700 K.

K*eywords : Nano Ceramics, Thermal Catalyst, Adsorption, Interface, Carbon Capture and Utilization*

温室効果ガス排出量削減は環境科学において喫緊の課題となっており、特に排出量の多い温室効果ガスである CO_2 の低コスト吸収除去システムの構築が必要不可欠である。強誘電体であるチタン酸バリウムは四重極子モーメントを持つ CO_2 と強く相互作用すること、ナノサイズ化することで表面積を増加させ吸着量が増加することが期待されることから、本研究では、ナノサイズのチタン酸バリウムを合成し、300－700 K における CO_2 の吸収能を調べた。

熱重量分析により、300、500、700 K の各温度に対し、Ar 雰囲気で 4 時間加熱処理した後に、CO_2 を 4 時間流入した。CO_2 を 4 時間流入した後の重量増加量はそれぞれ 450、200、400 μmol g^{-1} となり、これをナノサイズのチタン酸バリウムの吸着量として評価した(図)。300 K の CO_2 吸着量と比較して、500 K では CO_2 吸着量が半分以下になるのに対し、700 K では CO_2 吸着量が再び増加し、300 K と同程度となった。一般的に物理吸着では温度の上昇に伴い吸着量が減少するが、700 K で吸着量が増加したことから、ナノサイズのチタン酸バリウムが CO_2 を化学吸着したことが示唆された。今後、CO_2 化学吸着のメカニズムについて解析すると同時に CO_2 反応性についても検討していく。

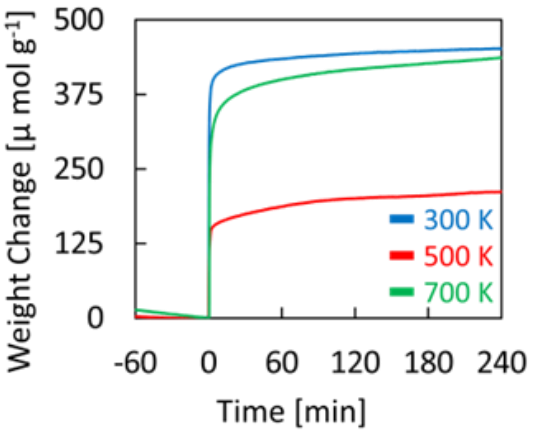

図 300－700 K における ナノサイズのチタン酸バリウムの CO_2 吸着量

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π共役系骨格を有するイオン液体を前駆体とした新規多孔性炭素合成法の開発

(信大院理[1]・信大理[2]・弘前大理工[3]) ○関 俊典[1]・中村 健人[1]・関口 龍太[3]・飯山 拓[2]・二村 竜祐[2]

Development of a New Synthesis Method for Nanoporous Carbons Using Ionic Liquids with π-Conjugated Frameworks.

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Ionic liquids (ILs) are room temperature molten salts that exist in liquid states without any solvent molecules. One of the most important features of ILs is that their chemical and physical properties can be controlled by introducing substituents in a framework of organic ions or by changing ion species. Previously we have reported the unique properties of ionic liquids with π-conjugated molecular nanocarbon moieties (π-conjugated ILs).

In this presentation, we show the novel synthesis of nanoporous carbons by heat treatment of π-conjugated ILs at a relatively low temperature without any template materials. Here, we call the obtained nanoporous carbon π-ILDC (*i.e.* π-conjugated Ionic Liquids Derived Carbon). Our results suggest that it is possible to precisely control the structure of porous carbon frameworks by using various π-conjugated ILs as precursors.

Keywords : Ionic Liquids; π-conjugated molecules; Porous carbons; Molecular Nanocarbons

イオン液体(IL)とは、溶媒分子に溶解せずとも、室温で液体として存在する溶融塩を指す。イオン液体の重要な特徴は、有機イオン骨格中への置換基の導入やイオン種の変更により、融点などの物性を制御できる点にある。我々は、π共役系分子のイオン液体骨格への導入により、π共役系分子の特徴を有するイオン液体が合成できると考え、これまでにベンゼン、ナフタレン及びアントラセンをカチオン骨格に導入したπ共役系 IL を合成してきた。合成したπ共役系 IL は、π共役系分子由来の蛍光発光や、嵩高いπ共役系置換基のための特異な融解挙動を示すことを明らかにした。

本研究ではπ共役系 IL を前駆体とする新規多孔性炭素の合成について報告する。π共役系 IL を 550℃ という比較的低温で熱処理することで、メソ孔性とミクロ孔性を併せ持つ新規多孔性炭素 (π-ILDC:π-conjugated Ionic Liquids Derived Carbon)の合成に成功した。これまでに、ベンゼン環やナフタレン環を有する IL からπ-ILDC の合成に成功しており、発表では細孔構造や表面組成、さらに前駆体の IL の液体構造と細孔特性の関係についても議論する。本手法により、種々のπ共役系 IL を前駆体とする多孔性炭素が得られ、多様な炭素骨格構造の制御へとつながる。

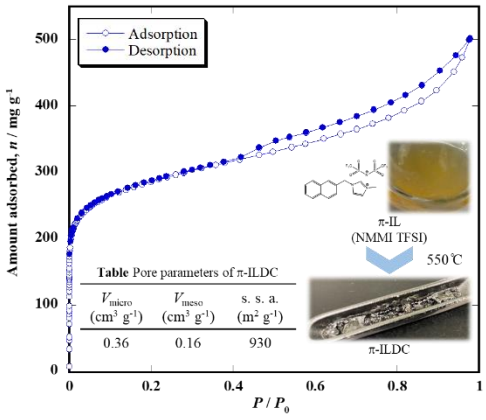

Fig. N_2 adsorption isotherm of π-ILDC at 77 K

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温度応答性ゲルを導入した新規多孔体の合成と物性解明

(信大院理[1]・信大理[2]) ○澤田 珠緒[1]・二村 竜祐[2]・飯山 拓[2]
Synthesis and characterization of novel porous materials with temperature-responsive gels ([1]*Graduate School of Science and Technology Department of Science*, *Shinshu University*, [2]*Department of Chemistry, Faculty of Science, Shinshu University*) ○Tamao Sawada,[1] Ryusuke Futamura,[2] Taku Iiyama[2]

Poly(*N*-isopropylacrylamide) (PNIPA) is a temperature-responsive polymer, which has a lower critical solution temperature (LCST) of about 33 °C. In this study, we have modified the pores of activated carbon fiber (ACF, AD'ALL Co.,LTD) with NIPA gel, obtained by cross-linking of PNIPA, and succeeded in the synthesis of a novel porous material with temperature responsiveness.

We measured the Nitrogen adsorption isotherms (77 K) and water adsorption isotherms (25 °C, 40 °C) for the composite NIPA gel /ACF. At 25 ℃, the saturated adsorption capacity of water was about 1.4 times larger than that measured with nitrogen. In contrast, at 40 ℃, the saturated adsorption capacity decreased to the same level as that of nitrogen. This is because at 25 °C, which is lower than the LCST, water molecules were taken up by the hydrophilic NIPA gel, while at 40 °C, which is higher than the LCST, the adsorption of water molecules was inhibited by the hydrophobic NIPA gel. From these results, we can say that we have succeeded in synthesizing a porous material with temperature responsiveness.

Keywords : Physisorption; Temperature-responsive gel; Hydrophilicity and Hydrophobicity

ポリ(*N*-イソプロピルアクリルアミド) (PNIPA) は約 33 ℃の下限臨界溶液温度 (LCST) を持つ温度応答性高分子であり、この温度を境にして低温では親水性、高温では疎水性となる相転移を起こす。本研究では PNIPA を架橋して得られる NIPA ゲルで活性炭素繊維(ACF, (株)アドール)の細孔を修飾し、温度応答性を持った新規多孔体の合成に成功した。

この複合材料 NIPA gel/ACF に対して窒素吸着等温線(77 K)と水吸着等温線(25 ℃, 40 ℃)を測定し比較した。水吸着等温線において 25 ℃での測定では飽和吸着容量は窒素の飽和吸着容量の約 1.4 倍の値を示した。対して 40 ℃の測定では、窒素の飽和吸着量程度に減少した。これは LCST より低い 25 ℃では親水的な NIPA ゲルに水分子が取り込まれ、対して LCST より高い 40 ℃の測定では疎水的な NIPA ゲルによって水分子の吸着が阻害されたためだと考えられる。この結果より、温度応答性を示す多孔体の合成に成功したと言える。

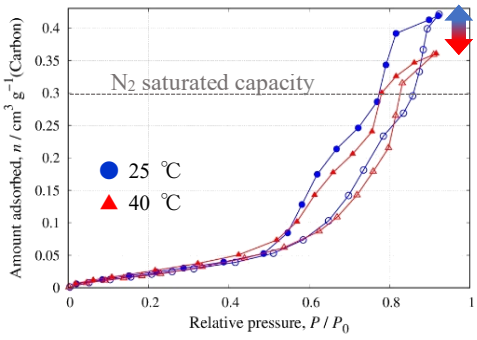

Fig. Water adsorption isotherms of NIPA gel/ACF (●: 25 ℃, ▲: 40 ℃)

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陽電子消滅寿命法によるカーボン系ナノ細孔体の細孔構造評価

（信州大 先鋭材料研究所[1]、信州大工[2]）○久保 圭[1]・大塚 隼人[1]・佐伯 大輔[1,2]・酒井 俊郎[2]・金子 克美[1]
Pore structure evaluation of carbon-based nanoporous materials using positron annihilation lifetime method ([1]*Research Initiative for Supra-Materials(RISM), Shinshu university*, [2] *Faculty of Engineering, Shinshu university*)○Kei Kubo[1], Hayato Otsuka[1], Daisuke Saeki[1,2], Toshio Sakai[2], Katsumi Kaneko[1]

Positron annihilation lifetime spectroscopy(PALS) has contributed to analyze pore structures of membranes[1]. However, it has not been well established for determination of the pore structure of nanoporous materials. This study compares the PALS method and other method for evaluation of pore structures of MFI zeolite and single wall carbon nanotube (SWCNT). The pore sizes of MFI by PALS method and Ar adsorption were 0. 5 nm, agreeing with that from the crystal structure[2]. On the other hand, the pore size of SWCNT by PALS method was 1.1 nm, being smaller than that from transmission microscopic observation by 0.2 nm.
Keywords : positron annihilation lifetime spectroscopy, ultramicropore, argon adsorption, amorphous porous materials

陽電子消滅寿命分光（Positron annihilation lifetime spectroscopy :PALS）法[1]は、分離膜などのサブナノスケールの細孔構造の解析に用いられるが、多孔質材料の細孔構造の決定法として用いられる気体吸着法や透過電子顕微鏡(TEM)観察法との比較が十分には検討されていない。本研究では結晶構造から細孔構造が分かる MFI ゼオライトおよびチューブ構造が TEM から既知の単層カーボンナノチューブ(SWCNT : 名城カーボン製 EC1.5)について、Ar 吸着法と TEM 観察を参照して、PALS 法の細孔構造決定の有効性を検討した。

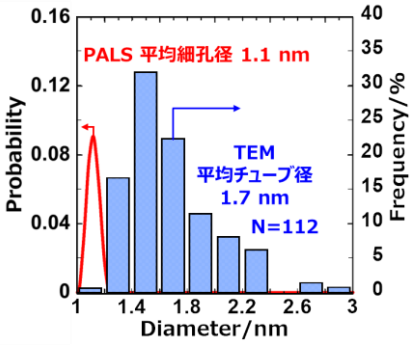

Fig. 1 Pore size distributions of SWCNT EC1.5 from PALS and TEM[3].

MFI ゼオライト（東ソー製)について、PALS 法および 87 K での Ar 吸着から細孔径分布を調べた。両方法からの細孔径分布はともに平均細孔径が 0.5 nm であった。この実測細孔径は結晶構造[2]からの実効的な細孔径に一致した。これを参照に、円筒状細孔を持つ SWCNT について、PALS 法から平均細孔径と TEM から平均チューブ径[3]を求めた。Fig.1 には TEM で求めたチューブ径分布を青色の棒グラフで示す。PALS 法からの平均細孔径（赤色）は 1.1 nm であった。炭素原子核間距離を示す TEM の、平均チューブ径は 1.7 nm [3]であり、炭素原子半径 0.34 nm を差し引くと細孔径は 1.3 nm となった。PALS と TEM 法による細孔径の差の要因については検討中である。

1) Ito K., Nakanishi H., Ujihira Y., *J. Phys. Chem. B*, **103**, *21*, 4555-4558, (1999).
2) R.Szostak, 'HANDBOOK OF Molecular Sieves', p.519, Van Nostrand Reinhold, New York, (1992).
3) S. Utsumi, A. Furuse, K. Kaneko et al, *Nature Nanotech*. in the third revision.

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活性炭への液相吸着における X 線散乱測定を用いた細孔内分子混合状態の解明

(1 信州大) ○椿原　樹 1・佐藤　きり 1・二村　竜祐 1・飯山　拓 1

Elucidation of the molecular mixing state in pore in liquid phase adsorption on activated carbon using X-ray scattering measurements ([1]*Shinshu University*)○Itsuki Tsubakihara[1], Kiri Sato[1], Ryusuke Futamura[1], Taku Iiyama[1]

Adsorption Phenomena at solid/liquid interface are widely used for purification and separation of substances and removal of toxic substances. However, the adsorption mechanism and the adsorption state in the liquid phase have not been well understood. This is because the liquid-adsorption system is a three-component system and the measurement inside the pore is prevented by the surrounding bulk solution. We used small-angle X-ray scattering (SAXS) measurements for liquid-phase adsorption systems, which can obtain the information only in the pores. In this study, liquid-phase adsorption isotherms using a refractometer of activated carbon/alcohol/water system were measured. SAXS profiles were measured of adsorbed samples to investigate the relationship between the amount of adsorption and the mixing state in the pore. In the 1-PrOH/water system, as shown in the figure, the SAXS intensity changes drastically with 1-PrOH concentration, These results directly demonstrate the mesoscopic state of liquid adsorption system.

Keywords : Liquid-phase adsorption, X-ray scattering, Density fluctuation

固液界面における液相吸着現象は物質の分離、精製や有害物質の除去などに広く用いられている。一方でその吸着のメカニズム及び吸着状態の理解は十分ではない。これは系が吸着質-溶媒-溶質の三成分系で複雑であることや、吸着媒の外部に存在する Bulk 溶液のために細孔内部の測定が困難であることが要因である。そこで我々は液相吸着試料に対して細孔内の情報のみを捉える小角 X 線散乱(SAXS)測定を用いた。

本研究では、任意に混和するアルコール/水系に対して、屈折率計を用いた活性炭の液相吸着等温線の測定と吸着試料に対する SAXS 測定を行い、吸着量と吸着媒細孔中での混合状態の関係について検討した。1-PrOH/水系の吸着等温線は 500 mg g-1 にも及ぶアルコールの正吸着を示した。溶液の混合比を変えた SAXS 強度も図のように大きく変化し、これまでにないメソスコピックなオーダーの吸着状態が明らかになった。

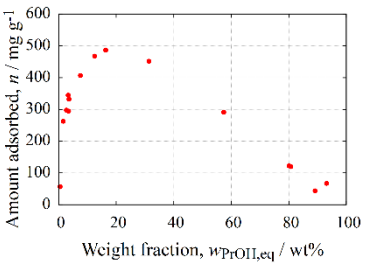

Fig.1 1-PrOH/水系に対する活性炭の液相吸着等温線(25 ℃)

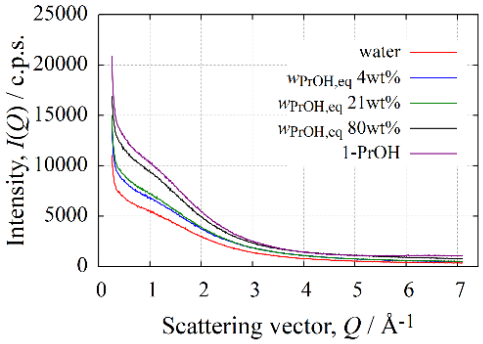

Fig.2 1-PrOH/水混合液中の活性炭の小角X線散乱測定結果

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精密等量吸着熱測定から見た活性炭への水吸着機構

（信大総理工[1]・信大理[2]）○岩月 倫[1]・二村 竜祐[2]・飯山 拓[2]

Water adsorption mechanism on activated carbon from the viewpoint of precise isothermal adsorption heat measurement ([1]*Graduate School of Science and Technology, Shinshu University,* [2]*Faculty of Science, Shinshu University*) ○Rin Iwatsuki,[1] Ryusuke Futamura,[2] Taku Iiyama[2]

Adsorbed water in the micropores shows unique properties different from the bulk water due to spatial confinement by the pore walls. We investigated the adsorption state of water in activated carbon pores by determine the isosteric heat of adsorption from water adsorption isotherms and water adsorption rate. As a result, isosteric heat of adsorption of activated carbon with 1.4 nm is similar to the heat of condensation in the bulk phase, but 0.6 nm pore showed a higher heat of adsorption than the heat of condensation. The activated carbon with pore width 1.4 nm showed a slower adsorption rate than 0.6 nm pore, and a different adsorption amount dependence. These results suggest that slight difference in pore size result in completely different adsorption mechanisms.

Keywords : Isosteric heat of adsorption, Water adsorption, Activated carbon

細孔内に吸着された水分子は細孔壁による空間制約によってバルク相では見られない特異な性質を示すことから注目を集めている。本研究では平均細孔径 0.6 nm と 1.4 nm の活性炭((株)アドール)の水吸着等温線を 10℃～25℃の範囲で合計 11 本測定し、Clausius-Clapeyron 式を適用して等量吸着熱を算出した。また、それぞれの活性炭の水吸着速度を測定し、吸着量に対する等量吸着熱と吸着速度の変化から細孔内に吸着した水分子の吸着状態を検討した。平均細孔径 1.4 nm の活性炭の等量吸着熱はバルク水の凝縮熱に近い値を示したが、0.6 nm の活性炭では凝縮熱より高い値を示し、吸着量の増加と共に減少した。一方、吸着速度は平均細孔径 1.4 nm の活性炭では吸着量変化に対して一定であったのに対して、0.6 nm の活性炭では速く、吸着量の増加と共に増加した。バルクの凝縮に近い 1.4 nm の細孔中と比べ、細孔壁によるポテンシャルエネルギーの安定化を受けた特異な現象が起きていると考えられる。

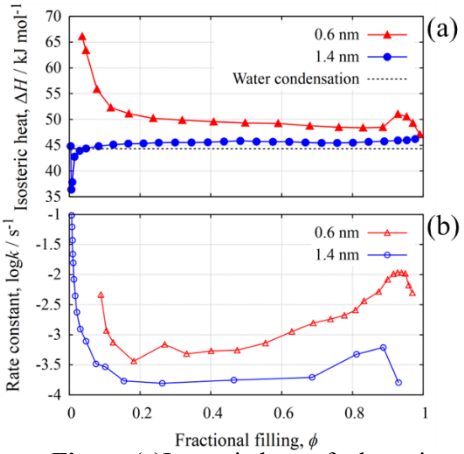

Figure (a)Isosteric heat of adsorption, (b)Adsorption rate

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ZIF-8 への 6 員環脂環式炭化水素の物理吸着過程における分子間相互作用と吸着選択性

（阪大院理[1]・阪大理[2]・信州大院理[3]）上田貴洋[1]・山田雄太[2]・藤井皓太[2]・三原龍太[3]・飯山　拓[3]・濱田諭敬[1]・奥村光隆[1]

Molecular Interactions and Adsorption Selectivity of Six-Membered Ring Alicyclic Hydrocarbons on ZIF-8 during Physisorption Process ([1]*Graduate School of Science, Osaka University*, [2]*School of Science, Osaka University*, [3]*Graduate School of Science and Technology, Shinshu University*) ○ Takahiro Ueda,[1] Yuta Yamada,[2] Kota Fujii,[2] Ryota Mihara,[3] Taku Iiyama,[3] Yasutaka Hamada,[1] Mitsutaka Okumura[1]

The adsorption rate of six-membered alicyclic hydrocarbons, including benzene, on ZIF-8, depends on the number and arrangement of π-electrons of the adsorbed molecule as well as the molecular cross-section. In this study, we examined the intermolecular interactions between the 2-methylimidazolate moiety and the adsorbate molecule by DFT calculations. It was found that the intermolecular interactions between the 2-methylimidazolate moiety and the adsorbate molecule are dominated by C-H/π interaction and the van der Waals interaction between the aliphatic groups. Furthermore, these interaction energies correlated well with activation energies for diffusion of adsorbed molecule, suggesting the one of the important factors to control the adsorption selectivity kinetically.

Keyword : Physisorption; Adsorption rate; Adsorption selectivity; Intermolecular interactions; ZIF-8

多孔性配位高分子の一種である ZIF-8 に対する 6 員環脂環式炭化水素類の物理吸着速度は、分子サイズだけでなく、π電子数やその配置に依存する[1]。しかし、これらの分子論的な理解は十分とはいえない。特に、吸着質分子と ZIF-8 の 6 員環開口部を形成する 2-メチルイミダゾール部位との詳細な分子間相互作用に関する知見は、ZIF-8 の 6 員環脂環式炭化水素類に対する速度論的吸着選択性を理解する上で非常に重要である。本研究では、2-メチルイミダゾール部位と吸着分子との分子間相互作用を DFT 計算により評価した。その結果、6 員環脂環式炭化水素類と 2-メチルイミダゾールとの相互作用エネルギーと吸着速度から得た活性化エネルギーとの間に良い相関がみられた（Fig. 1）。これは、吸着質-架橋配位子間の分子間相互作用が、6 員環脂環式炭化水素類に対する ZIF-8 の吸着選択性を支配する主たる要因であることを示唆している。

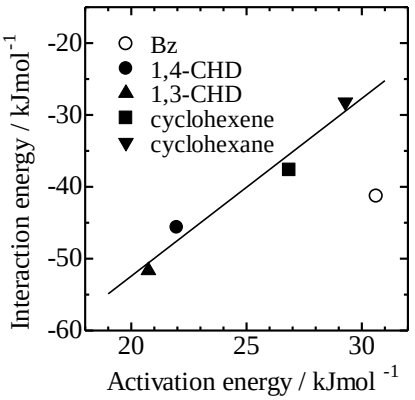

Fig.1 Plot of the adsorbate-linker interaction energy against the activation energy for diffusion of adsorbate molecule.

[1] 上田貴洋，山田雄太，日本化学会第 103 春季年会（2023.3.22-25）.

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日本化学会 第104春季年会 (2024)

水の物理吸着によるミクロ溶液の形成と逆析出・溶解現象の解明

(信大院総理工[1]・阪大院理[2]・信大理[3])
○横山 赳[1]・松田 優花[1]・上田 貴洋[2]・二村 竜祐[3]・飯山 拓[3]
Formation of micro-solution and figure out opposite dissolution/precipitation phenomena induced by water physisorption ([1]*Graduate School of Science and Technology, Shinshu University*, [2]*Graduate School of Science, Osaka University*, [3]*Faculty of Science, Shinshu University*) ○Takeru Yokoyama,[1] Yuka Matsuda,[1] Takahiro Ueda,[2] Ryusuke Futamura[3], Taku Iiyama[3]

Molecules in the nanospace show different behavior from bulk due to the interaction with the pore wall and spatial confinement. Among them, we focused on the micro-solution formed in the pore. We formed a “micro-solution” using MCM-41 as the vessel, dibenzyl as the solute and water as the solvent. In this study, we elucidate the dissolution/precipitation phenomena of the micro-solution and the rotational motion of the solute by water adsorption and NMR measurements.

Fig. 1 shows the adsorption isotherms for water of different fractional filling of dibenzyl (ϕ_{Dib}). The raw MCM ($\phi_{\mathrm{Dib}} = 0$) shows a general type V adsorption isotherm. However, $\phi_{\mathrm{Dib}} = 0.28, 0.64$ samples show a new type of adsorption isotherm that is not in the IUPAC classification. The saturated adsorption amount is constant, coincide with that of raw MCM-41, but independent ϕ_{Dib}. DSC and X-ray scattering measurements show that the second rise in the water adsorption isotherm is due to the dissolution/precipitation of the micro-solution. NMR results are also discussed.

Keywords : Micro-solution; Phase separation; Water Physisorption; NMR measurement

細孔内では空間的制限や細孔壁との相互作用のためにバルクとは異なる現象が起こる。我々は細孔内の「微小な溶液」に注目した。本研究ではジベンジルを導入したメソポーラスシリカ MCM-41 に水を物理吸着させ、ジベンジルを溶質、水を溶媒としたミクロ溶液を MCM-41 の細孔内に形成させた。この系に対し吸着等温線と NMR を用いて、ミクロ溶液の析出・溶解現象と溶質の運動について解明した。

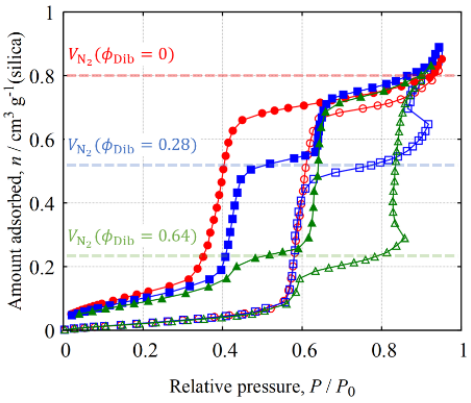

Fig. 1 ジベンジル導入体の水吸着等温線

Fig. 1 にジベンジルの充填率 (ϕ_{Dib}) を変えた MCM-41 の水吸着等温線を示す。ジベンジルの導入されていない試料 ($\phi_{\mathrm{Dib}} = 0$) が疎水性表面を持つ多孔体への水吸着で一般的な V 型の等温線形状を示したのに対し、$\phi_{\mathrm{Dib}} = 0.28, 0.64$の試料では IUPAC の分類にない 2 段階の立ち上がりを持つ等温線形状を示し、飽和吸着量はジベンジルが細孔内に存在しているにも関わらず$\phi_{\mathrm{Dib}} = 0$と一致した。DSC 測定、X 線散乱からこの特異的な 2 段階目の立ち上がりでは細孔内のジベンジルと吸着質の水の交換が生じていることが分かった。一般的な溶液では溶媒が増えると溶質の溶解量は増加するが、本系では溶媒に相当する水吸着量を増やすと溶質が析出している点が注目される。さらに ^{1}H 液体 NMR 測定から溶質のスピン-格子間緩和時間を測定し、水吸着量と細孔内溶液の溶解状態の関係を明らかにした。

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ZnS を導入した FAU への光照射下における種々の吸着質の吸着挙動

（静岡理工科大 [1]）○馬場 早穂 [1]・村松 雪乃 [1]・山﨑 誠志 [1]
Adsorption behavior of several adsorbate under light irradiation on ZnS introduced FAU([1]*Shizuoka Institute of Science and Technology*) ○Saho Baba[1], Yukino Muramatsu[1], Satoshi Yamazaki[1]

Adsorption measurements were carried out using CO_2, C_2H_6, Ar, N_2, and O_2 as adsorbents on ZnS introduced FAU in the dark and under 405 nm light irradiation. Figures 1 and 2 show the adsorption isotherms at adsorption temperatures of 30°C and -70°C, respectively. It was observed that for all adsorbates, the amount of adsorption was lower under 405 nm light irradiation than in the dark. Moreover, this tendency was more obvious when the adsorption temperature was lower. Since a decrease in the amount of adsorption was confirmed even for Ar, which is an inert molecule, it is thought that the decrease in the amount of adsorption under light irradiation is due to a repulsive force other than electrostatic repulsion.
Keywords : Faujasite, ZnS, ZnS introduced FAU, Adsorption measurement under light irradiation, several adsorbates

ZnS 導入 FAU への、暗状態と 405 nm の光照射下での CO_2、C_2H_6、Ar、N_2、O_2 吸着測定を行った。図 1 と 2 は、それぞれ吸着温度 30℃と－70℃で測定した吸着等温線である。吸着温度 30℃の CO_2 と C_2H_6 では、暗状態に比べて 405 nm の光照射下での吸着量が大きく減少している。一方、Ar、N_2、O_2 は吸着量の差が小さいが、わずかに光照射下の吸着量が少なくなっている。吸着温度－70℃で測定すると、温度を下げたことによる吸着量の増加が見られる。そのため、図 1 ではわずかな差であった Ar、N_2、O_2 でも光照射下での吸着量の減少が認められる。これらのことから、すべての吸着質で 405 nm の光照射下では、吸着量が減少することがわかった。不活性分子である Ar でも吸着量の減少が確認されたことから、静電反発以外の反発力が働いていると考えられる。

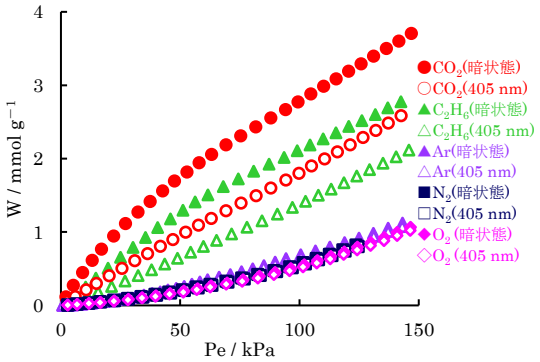

図 1　ZnS 導入 FAU の 30℃における光照射下(405 nm)と暗状態での CO_2、C_2H_6、Ar、N_2、O_2 吸着等温線

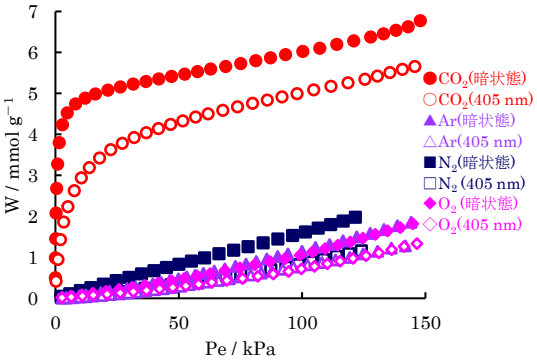

図 2　ZnS 導入 FAU の－70℃における光照射下(405 nm)と暗状態での CO_2、Ar、N_2、O_2 吸着等温線

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

Wed. Mar 20, 2024 10:30 AM - 11:30 AM JST | Wed. Mar 20, 2024 1:30 AM - 2:30 AM UTC
C442(442, Bldg. 4 [4F])

[C442-3am] 20. Materials Chemistry -Basic and Application-

Chair: Miho Aizawa, Tuyoshi Fukaminato

English
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[C442-3am-01]
Synthesis of Electrochromic Supramolecular Polymers Driven by Data Science

○Aiwei Zhao[1,2], Masayoshi Higuchi[1,2] (1. National Institute for Materials Science, 2. Osaka University)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[C442-3am-02]
Formation behavior of topographical surfaces on liquid-crystalline polymers by patterned cationic photopolymerization

○Yasuto Sasaki[1], Sayuri Hashimoto[1], Miho Aizawa[1,2], Kyohei Hisano[1], Shoichi Kubo[1], Atsushi Shishido[1] (1. Lab. for Chem. & Life Sci., Tokyo Tech, 2. PRESTO, JST)

Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[C442-3am-03]
Design of anisotropically mechanical polymer films by patterned photopolymerization of isotropic monomers

○Kyosuke Misaki[1], Yusho Kishimoto[1], Kyohei Hisano[1], Atsushi Shishido[1] (1. Tokyo Institute of Technology)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[C442-3am-04]
Development of Dithienonaphthobistriadiazole-Based π-Conjugated Polymers and Their Charge Transport Property

○Yuki Okazaki[1], Tsubasa Mikie[1,2], Itaru Osaka[1,2] (1. The Univ. of Hiroshima, 2. Graduate School of Advanced Science and Engineering, Hiroshima)

Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[C442-3am-05]
Synthesis of Hyper-branched Phthalocyanines Polymers for Photodynamic Therapy

○Chihiro Hashimoto[1], Sunnam Kim[1], Tsuyoshi Fukaminato[1] (1. Kumamoto Univ.)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[C442-3am-06]
Synthesis and properties of donor-acceptor polymers incorporating benzodichalcogenophenediones

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○Shohei Wada[1], Kohsuke Kawabata[1,2], Kazuo Takimiya[1,2,3] (1. Graduate School of Science, Tohoku University, 2. Riken Center for Emergent Matter Science (CEMS), 3. Advanced Institute for Materials Research (WPI-AIMR), Thohoku University)

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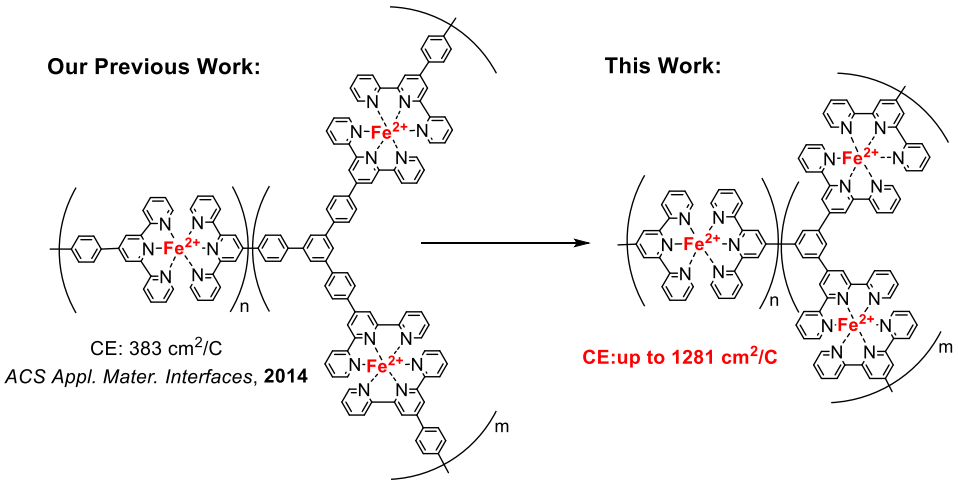
Synthesis of Electrochromic Supramolecular Polymers Driven by Data Science

([1]*National Institute for Materials Science*, [2]*Graduate School of Information Science and Technology, Osaka University*) ○Aiwei Zhao,[1,2] Masayoshi Higuchi[1,2]

Keywords: *electrochromic, coloration efficiency, data-science*

Materials informatics has recently garnered significant attention as a potent tool for the development of a wide array of functional materials. The successful integration of materials informatics into polymer design holds the promise of streamlining the synthesis of polymers with tailored properties, thereby enhancing efficiency and specificity in material engineering. Machine learning is a subset of artificial intelligence (AI), which involves algorithms learning from data to make predictions or decisions.[1] Bayesian optimization is a strategy used in machine learning for optimizing objective functions, which is useful in hyperparameter tuning for machine learning models.[2] The machine learning, especially Bayesian optimization method is widely used in materials science.

In this presentation, we report our recent approach on the search of electrochromic (EC) metallo-supramolecular polymers (MSPs) with the help of materials informatics. Four components were selected among many components of MSPs. Including the central metal, the ligand structures, the branch unit, and the degree of branching. Among all the combination of the variations, the selected number of the corresponding MSPs according to an orthogonal table were synthesized. A coloration efficiency (CE) of 1281 cm^2/C was obtained compared to our previous work.[3] We found that this method with statistics was useful to find the polymers with better EC properties quickly.



1) Jordan, M. I.; Mitchell, T. M. *Science,* **2015**, *349*, 255. 2) Snoek, J.; Larochelle, H.; Adams, R. P. *Adv. Neural Inf. Process. Syst.*, **2012**, *25*, 2951. 3) Hu, C.; Sato, T.; Zhang, J.; Moriyama, S.; Higuchi, M. *ACS Appl. Mater. Interfaces*, **2014**, *6*, 9118.

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パターン光カチオン重合による液晶高分子表面の凹凸構造形成挙動

（東工大化生研[1]・JST さきがけ[2]）○佐々木 康人[1]・橋本 彩有里[1]・相沢 美帆[1,2]・久野 恭平[1]・久保 祥一[1]・宍戸 厚[1]

Formation behavior of topographical surfaces on liquid-crystalline polymers by patterned cationic photopolymerization ([1]*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*, [2]*PRESTO, JST*) ○Yasuto Sasaki,[1] Sayuri Hashimoto,[1] Miho Aizawa,[1,2] Kyohei Hisano,[1] Shoichi Kubo,[1] Atsushi Shishido[1]

Surface topographies formed on liquid-crystalline (LC) polymer films exhibit various functionalities such as adhesiveness and optical diffraction. Photoinduced reactions have attracted great attention to induce various surface structures in a non-contact manner. Recently, we demonstrated that patterned radical photopolymerization of LCs induces microscale surface topographies driven by anisotropic molecular diffusion. However, photopolymerization in previous studies was carried out in a glass cell to avoid oxygen inhibition. In this study, we performed patterned photopolymerization of cationic LC monomers under ambient conditions. Molecular alignment in the obtained films was evaluated in detail to investigate the formation mechanism of surface structures.

Keywords: Liquid Crystal; Photopolymerization; Surface Topography; Molecular Alignment

液晶高分子フィルムにおける表面凹凸構造は，異種物質の表面接着変化や光回折の発現など様々な機能を付与できる [1,2]。非接触に多彩な表面凹凸を実現する方法として，光誘起物質移動が注目されている。われわれは，パターン光照射によるラジカル重合過程で生じる分子拡散を駆動力とした，マイクロメートルスケールの特異な表面構造形成を見出している [3,4]。しかしながら，ラジカル重合の酸素阻害を防ぐため，ガラスセル内での検討に留まっていた。本研究では，大気下で重合可能な光カチオン重合性液晶を用いた表面凹凸構造形成について検討した。

カチオン重合性の液晶性モノマー（OXT-1）および架橋剤（OXT-2）の混合物をレベリング剤とともに溶媒に溶解させ，光重合開始剤 CPI-210S を添加することで，重合用試料溶液とした。配向処理したガラス基板上に重合用試料をスピンコートし，アニール処理を施した後，様々な光照射幅を有するパターン光を用いて光重合を行った。最後に後重合を施すことで高分子フィルムを得た（**Figure 1**）。作製したフィルムの偏光顕微鏡およびレーザー顕微鏡観察を行い，分子配向性と表面凹凸形状を評価した。その結果，光照射パターン幅が凹凸構造形成挙動に大きく影響することを明らかにした。

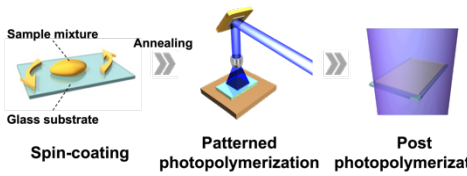

Figure 1. Schematics of photopolymerization process.

1) K. Mehta, D. Broer, *et al*., *Appl*. *Phys*. *Rev*. **2020**, *7*, 041306. 2) P. Zhang, A. P. H. J. Schenning, *et al*., *Small* **2023**, *19*, 2302051. 3) K. Hisano, A. Shishido, *et al*., *Appl. Phys. Express* **2016**, *9,* 072601. 4) S. Hashimoto, A. Shishido, *et al*., *ACS Appl. Mater. Interfaces* **2023**, *15*, 14760.

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等方性モノマーのパターン光重合による力学異方性フィルムの設計

（東工大化生研）○三崎 響介・岸本 勇勝・久野 恭平・宍戸 厚

Design of Anisotropically Mechanical Polymer Films by Patterned Photopolymerization of Isotropic Monomers (*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○Kyosuke Misaki, Yusyo Kishimoto, Kyohei Hisano, Atsushi Shishido

In recent years, high-performance polymer films that intrinsically possess excellent flexibility and processability have attracted much attention. Uniform, isotropic polymeric materials typically exhibit isotropic mechanical properties; however, structurally controlled materials demonstrate fascinating properties such as anisotropic mechanical functions[1)]. Recent developments in three-dimensional processing and composite materials technologies enabled the control of various mechanical properties by designing the spatial structure of polymeric materials[1-3)]. Among various advanced approaches, photo-based structural control methods offer the advantage of remote influence and the design of spatially patterned structures with a high resolution. Our group utilized spatially selective photopolymerization to achieve arbitrary molecular orientation and surface topographies[4)]. In this study, we fabricated mechanically anisotropic polymer films with spatially patterned hardness from isotropic monomers. We conducted a tensile test to understand the relationship between the irradiated optical pattern and the resulting mechanical properties of the films.

Keywords: Photopolymerization; Flexible device; Film; Tensile test; Mechanical function

フレキシブルデバイスの発展において，柔軟性かつ成形加工性に優れた高分子材料が注目されている。一般的な均質等方材料は等方的な力学物性を示すのに対して，空間構造が制御された材料は均質等方材料とは異なる物性・機能を示すことが知られている [1)]。最近では，三次元造形技術や複合化技術の発展を皮切りに，高分子材料の空間構造を制御することで力学特性を制御する手法が数多く報告されている [1–3)]。これまでにわれわれは，空間選択的な光重合を用いることで，分子配向や表面凹凸構造を制御できることを見出している [4)]。光刺激を用いるため非接触かつパターン化が容易であり，物質移動を利用して局所構造を自在に設計できる利点を備えている。本研究では，この光重合技術を展開することで，等方性モノマーを用いて，組成・硬さ分布がパターニングされた高分子フィルムを作製した（**Fig. 1**）。微細な組成パターンが制御されたフィルムの力学特性を解析し，幾何構造と物性の関係について検討した。

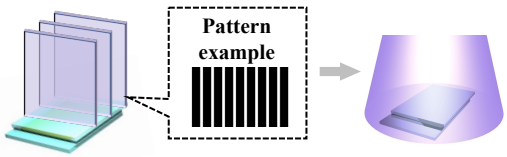

Figure 1. Schematic illustration of patterned photopolymerization for inscribing geometric structures into polymer thin films.

1) R. Lakes, *Nature* **1993**, *361*, 511. 2) X. Fang *et al.*, *Nat. Mater.* **2022**, *21*, 869. 3) D. R. King *et al.*, *ACS Appl. Mater. Interfaces* **2019**, *11*, 35343. 4) A. Shishido *et al.*, *Sci. Adv.* **2017**, *3*, e1701610.

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ジチエノナフトビストリアゾール骨格を基調とした半導体ポリマーの合成と物性

（広大工[1]・広大院先進理工[2]）○岡﨑 優季[1]・三木江 翼[1,2]・尾坂 格[1,2]

Synthesis and Properties of A Dithienonaphthobistriazole-Based Semiconducting Polymer

([1]*School of Engineering,* [2]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Yuki Okazaki,[1] Tsubasa Mikie,[1,2] Itaru Osaka[1,2]

Recently, we have reported that dithienonaphthobisthiadiazole (TNT)-based semiconducting polymers such as **PTNT2T** showed high charge carrier mobilities due to the strong intermolecular interaction between the TNT moieties in the π-stacked polymer chains. In this work, we synthesized a novel electron-deficient building unit, dithienonaphthobistriazole (TNA), in which the thiadiazole moiety of the TNT unit is replaced with triazole. In addition, we synthesized a TNA-based polymer **PTNA2T** and studied its electrochemical and optical properties. **PTNA2T** had higher HOMO energy level and shorter absorption wavelength region than **PTNT2T**.

Keywords : Semiconducting polymer; Conjugated polymer; Electron-deficient building unit; Thiadiazole; Triazole

チアジアゾールなどのアゾール部位を有する拡張π電子系骨格は優れた電子物性を有することから、半導体ポリマーのビルディングユニットとして有用である。当グループでは、最近、新規に開発したジチエノナフトビスチアジアゾール（TNT）が、非常に強い分子間相互作用を示し、これをビルディングユニットとするポリマー群（**PTNT2T** など）が高い電荷輸送性や光電変換特性を示すことを報告した（Figure 1）。本研究では、TNT のチアジアゾール部位をトリアゾールに変換した新規骨格であるジチエノナフトビストリアゾール（TNA）とそれを有する半導体ポリマー**PTNA2T** を合成した（Figure 1）。TNA に置換基が導入可能であることから、**PTNA2T** は **PTNT2T** よりも高い溶解性を示した。また、**PTNA2T** は **PTNT2T** よりも高い HOMO 準位と、短波長領域の吸収帯を有することがわかった。これは、アミン窒素の電子供与性により、TNA 骨格の電子欠損性が低下したことに起因すると考えられる。

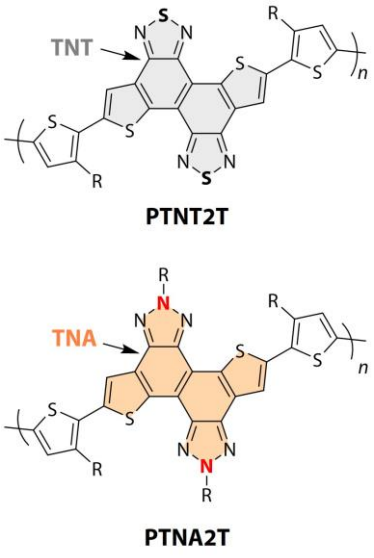

Figure 1. Chemical structures of **PTNT2T** and **PTNA2T**.

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光線力学療法に向けたフタロシアニンのハイパーブランチポリマーの合成

（熊大工）○橋本 千優・深港 豪・金 善南
Synthesis of Hyper-branched Phthalocyanine Polymers for Photodynamic Therapy (*Department of Applied Chemistry & Biochemistry, Kumamoto University*) ○ Chihiro Hashimoto, Tsuyoshi Fukaminato, Sunnam Kim

Phototherapy, which is a non-invasive treatment with excellent spatiotemporal control, is expected to be applied to cancer treatments for physically weak patients. For postoperative adjuvant chemotherapy including photodynamic therapy (PDT) is required a novel photosensitizer that can be activated by irradiation with near-infrared light. Although phthalocyanine derivatives have a large absorption coefficient in near-infrared wavelength region compared with other photosensitizers, the solubility in aqueous solution is quite poor. In this study, we tried to synthesize a water-soluble phthalocyanine hyperbranched polymer in which a hydrophilic polymer chain was introduced into the axial ligand of a phthalocyanine with silicon as the central element. We also investigated the generation of singlet oxygen and cytotoxicity in an aqueous solution under near-infrared light irradiation.
Keywords : Phthalocyanine; Hyperbranched polymer; Photosensitizer; Near-infrared light; Singlet oxygen

近赤外光増感剤を用いた光線力学療法が、時空間制御性のある光がん治療法として注目されている。この際、用いられる光増感剤として、近赤外領域に強い吸収を有するフタロシアニン (Pc) 誘導体が有望視されているものの、その水溶液に対する溶解性の低さが一つの課題となっている。本研究では、シリコンを中心元素とする Pc 誘導体の軸配位子として親水性高分子鎖を導入した水溶性のシリコンフタロシアニンハイパーブランチポリマー(SiPc-HBP)(Fig. 1)を合成し、水溶液中における活性酸素発生能について検討した。合成した SiPc-HBP は水溶液に可溶であったものの、吸収スペクトルにおいてフタロシアニン由来の 670 nm 付近のピークに加えて、850 nm 付近に凝集体に起因するピークが観測された。この結果に基づき、活性酸素発生のプローブ分子である 1,3-ジフェニルイソベンゾフラン(DPBF)を含む水溶液中の SiPc-HBP に、凝集体のみが吸収する 790 nm の近赤外光を照射すると、DPBF に由来する吸収バンドが著しく減少したことから、通常の Pc よりもより長波長側の近赤外光で効率よく活性酸素を発生できることが確認された。当日は、凝集体の形状や近赤外光照射による細胞毒性の結果を含め、得られた結果の詳細について発表する。

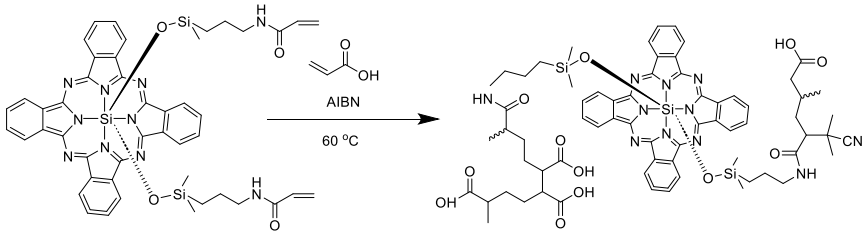

Fig. 1 Synthesis of a silicon-phthalocyanine hyper-brunched polymer (SiPc-HBP).

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キノイド型ベンゾジカルコゲノフェンジオン骨格をもつドナー-アクセプターポリマーの合成と評価

（東北大院理[1]・理研 CEMS[2]・東北大 WPI-AIMR[3]）○和田 将平[1]・川畑 公輔[1,2]・瀧宮 和男[1,2,3]

Synthesis and properties of donor-acceptor polymers incorporating benzodichalcogenophenediones ([1]*Graduate School of Science, Tohoku University*, [2]*Riken Center for Emergent Matter Science (CEMS),* [3]*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University*) ○Shohei Wada,[1] Kohsuke Kawabata,[1,2] Kazuo Takimiya[1,2,3]

Recently, we reported that a D-A-D oligomer based on an electron-deficient quinoidal benzodifurandione (Fig. 1, X = O) exhibited higher carrier transport properties than that of the benzodithiophenedione-based counterpart (Fig. 1, X = S).[1] In this study, we synthesized a series of D-A polymers incorporating these quinoidal moieties (PO-Rs and PS-Rs) to investigate the impact of chalcogen atoms on the semiconducting properties of the polymers. PO-Rs and PS-Rs had similar HOMO energy levels (−5.3 eV), whereas PO-Rs had slightly higher LUMO energy levels (−3.9 eV) than those of PS-Rs (−4.0 eV), resulting in larger optical bandgaps of PO-Rs (1.0 eV) than those of PS-Rs (0.8 eV). These results suggest that the oxygen-containing quinoidal moiety has weaker electron-accepting nature than the sulfur-containing counterpart. Field-effect transistors based on PO-Rs exhibited higher hole and electron mobilities than those based on PS-Rs regardless of the side chains.

Keywords : Organic semiconductor, Donor-acceptor polymer, Quinoidal structure

最近我々は、電子受容性のキノイド型ベンゾジカルコゲノフェンジオン骨格（Fig. 1 点線部 X = O, S）を基盤とする D-A-D 型のオリゴマー半導体において、含酸素類縁体が含硫黄類縁体より優れた電荷輸送特性を示すことを報告した。[1] 本研究では、これらのキノイド骨格を組み込んだD-Aポリマー PO-R および PS-R を合成し（Fig. 1）、カルコゲン原子置換がポリマーの半導体物性に与える影響を調査した。PO-R と PS-R の HOMO 準位は約−5.3 eV と同程度であったのに対し、PO-R の LUMO 準位（−3.9 eV）は PS-R（−4.0 eV）よりもわずかに高かった。また、PO-R の光学バンドギャップ（1.0 eV）は PS（0.8 eV) よりも大きく、以上の結果から含酸素キノイド骨格の電子受容性が含硫黄骨格よりも低いことが示唆された。PO-R と PS-R を用いた電界効果トランジスタは何れも両極性のトランジスタ特性を示し、可溶性側鎖に関わらず PS-R よりも PO-R を用いた素子の方が高い電荷移動度を示した。

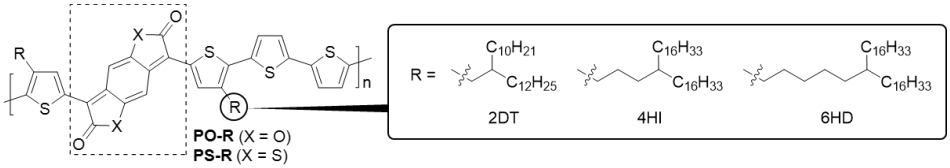

Fig. 1. Chemical structures of benzodichalcogenophenedione-based D-A polymers.

1) K. Kawabata and K. Takimiya, *Chem. Mater.*, **2023**, *35* (18), 7628.

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

Wed. Mar 20, 2024 1:30 PM - 3:20 PM JST | Wed. Mar 20, 2024 4:30 AM - 6:20 AM UTC C443(443, Bldg. 4 [4F])

[C443-3pm] 20. Materials Chemistry -Basic and Application-

Chair: Kenji Okada, Taichi Ikeda

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[C443-3pm-01]
Effect of electrode structure on morphology of deposition layer in Ag deposition-based electrochromic device

○Haruka Shimanuki[1], Syun Uji[2], Kazuki Nakamura[2], Norihisa Kobayashi[2] (1. Fac.Eng.,Chiba Univ., 2. Grad.Sch.Eng.,Chiba Univ.)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[C443-3pm-02]
Research on adhesion strength of fiber reinforced resin

○Tomoya Oikawa[1], Hidetoshi Hirahara[1], Jing Sang[1], Sumio Aisawa[1], Naoyuki Sekine[2], Shiori Masuda[2], Shinobu Komiyama[3] (1. Iwate Univ., 2. SUBARU Corporation, 3. Nihon Parkerizing CO.,Ltd.)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[C443-3pm-03]
Luminescence properties of imidazolium acetate-based ionic liquids containing chiral Eu(III) complexes

○Arata Suzuki[1], Ziying Li[2], Norihisa Kobayashi[2], Kazuki Nakamura[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
[C443-3pm-04]
Oriented growth of metal-organic framework on single crystals of copper-based mineral

○Yuka Koseki[1], Kenji Okada[1], Arisa Fukatsu[1], Masahide Takahashi[1] (1. Osaka Metropolitan University)

Japanese
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC
[C443-3pm-05]
Electrochemical control of emission color of europium ion in electrolytic solution containing crown ether.

○Genta Yoshida[1], Ryoto Yabuta[2], Norihisa Kobayashi[2], Kazuki Nakamura[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

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

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[C443-3pm-06]

Ionic Polymer-Metal Composite Actuators Consisting of Nafion and Gold Nanowire Electrodes

○Taichi Ikeda[1] (1. National Institute for Materials Science)

Japanese

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

[C443-3pm-07]

Chiroptical properties of hybrid material composed of chiral nematic liquid crystals and luminescent Eu(III) complexes

○Yusuke Sagawa[1], Takuro Kawahata[2], Norihisa Kobayashi[2], Kazuki Nakamura[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese

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

[C443-3pm-08]

Hybridization of β-detonate Eu(III) complexes and synthetic clay minerals and their luminescent properties.

○Ryota Nishiyama[1], RONG CAO[2], Kazuki Nakamura[2], Norihisa Kobayashi[2] (1. Fac. Eng., Chiba Univ., 2. Grad. Sch. Eng., Chiba Univ.)

Japanese

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

[C443-3pm-09]

Synthesis of mesostructured organosiloxane-based thin films using alkoxysilanes with an alkylammonium group

○Kazutomo Ido[1], Yuki Saito[1], Yoshiaki Miyamoto[1], Takamichi Matsuno[1,2], Atsushi Shimojima[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Kagami Memorial Research Institute for Materials Science and Technology, Waseda University)

Japanese

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

[C443-3pm-10]

Synthesis and characterization of ionic plastic crystals with perovskite-type structure

○Hiroaki Mine[1], Hirokazu Shimooka[1], Tatsuo Okauchi[1], Mitsuru Kitamura[1] (1. Kyushu Institute of Technology)

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銀析出型エレクトロクロミック素子における電極形状が析出銀形態に与える影響

○島貫 遥[1]、宇治 駿[2]、中村 一希[2]、小林 範久[2]（1. 千葉大工、2. 千葉大院工）

Effect of Electrode Structure on Morphology of Deposition Layer in Ag Deposition-based Electrochromic Device ○Haruka Shimanuki[1], Syun Uji[2], Kazuki Nakamura[2], Norihisa Kobayashi[2] ([1] *Fac.Eng.,Chiba Univ.*, [2]*Grad.Sch.Eng., Chiba Univ.*)

Electrochromism is defined as reversible color change induced by electrochemical reactions. We have reported electrochromic (EC) devices which showed transparent, mirror, black and various color states. The fusion of Ag nanoparticles on the electrode causes a decrease in color purerity. In this study, we used inverse opal electrode as working electrode of the device. The Ag deposion was observed and its electro-optics properties were investigated.
Keywords: Electrochromism; Silver; Localized surface plasmon resonance (LSPR); Inverse opal structure

エレクトロクロミズムとは電気化学的な酸化還元反応により物質の色が変化する現象である。我々の研究室では、単一素子で透明状態から鏡や黒、様々な有彩色を発現可能なエレクトロクロミック（EC）素子を報告してきた[1)]。同素子では、析出銀ナノ粒子同士の融着は色純度の低下を招く原因となる。本研究では、銀析出型EC素子の電極に逆オパール構造を導入し、析出銀の観察および電気光学特性の測定を行った。

$AgNO_3$を10 mmol/L、LiBrを50 mmol/Lの濃度でDMSOに溶解させた電解液を調製した。作用極としてFTO電極上に逆オパール構造を導入した電極を用い、3電極型電気化学セルを作製した。定電位V = −2.5 V(vs. Ag/Ag^+)（印加時間t = 300 s）を印加することにより銀ナノ粒子を析出させた際の電極表面のSEM画像をFig.1に示す。 FTO電極表面に析出した銀が逆オパール構造の表面まで成長し、凹凸の多い形状の銀粒子を形成している様子が確認された。Fig.2に析出銀の暗視野顕微観察画像を示す。銀ナノ粒子は赤色や青色など多様な色の散乱光を示すことが明らかとなった。析出面は黒色を呈しており、粒径の異なる金属粒子の混在によって多重散乱が発生したと考えられる。

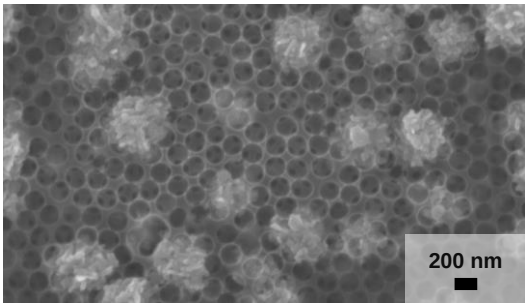

Fig.1 SEM image of the inverse opal electrode after the potential application of −2.5 V for 300 s.

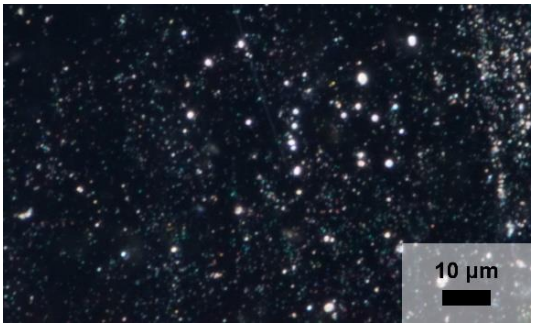

Fig.2 Dark-field microscopy image of the Ag nanoparticles after the potential application of −2.5 V for 300 s.

1) A. Tsuboi et al., *Chem. Mater*, **2014**, 26, 6477.

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繊維強化樹脂の表面改質に関する研究

(岩手大院[1]・SUBARU[2]・日本パーカライジング[3]) 平原 英俊[1]・○及川 智也[1]・桑静[1]・會澤 純雄[1]・関根 尚之[2]・増田 汐里[2]・小見山 忍[3]
Surface modification of fiber reinforced resin ([1]Iwate Univ, [2]SUBARU Corporation, [3]Nihon Parkerizing Co.,Ltd.) Hidetoshi Hirahara[1], ○ Tomoya Oikawa[1], Jing Sang[1], Sumio Aisawa[1], Naoyuki Sekine[2], Masuda Shiori[2], Shinobu Komiyama[3]
Keywords: fiber-reinforced resin, release agent, adhesive strength

Reducing the weight of aircraft and automobiles is important because it leads to improved mileage and fuel efficiency. Currently, metal materials such as aluminum and titanium are sometimes used in aircraft and automobile components, but there are high expectations for the application of fiber-reinforced resin, which is a lightweight and strong material. However, it is considered that contaminants remain on the surface of fiber-reinforced resin during the molding process, which may affect the adhesive strength with other substances. Therefore, the purpose of this research is to investigate cleaning methods for fiber-reinforced resin surfaces. XPS analysis revealed that the surface of the fiber-reinforced resin before cleaning contained 13.9 at% silicon. This is thought to be because the mold release agent during molding was transferred to the surface of the fiber-reinforced resin. In addition, the elemental concentration ratio of silicon decreased to 7.9 at% by ultrasonic cleaning with ethanol, which suggests that the mold release agent on the surface of the fiber-reinforced resin was removed, but the cleaning was not sufficient.

In addition, after various washings, the reinforcing fiber resin and epoxy were composited by hot pressing, and then the shear strength was measured. The untreated shear strength was 4.18×10^6 Pa, and after washing with distilled water it was 3.36×10^6 Pa, but after washing with ethanol it was 4.74×10^6 Pa, which improved the shear strength.

航空機や自動車の軽量化は走行距離や燃費の向上につながるため重要視されている。現在、航空機や自動車の部材にはアルミニウムやチタンなどの金属材料が使われる場合があるが、軽量で強い材料である繊維強化樹脂の応用が期待されている。しかし、繊維強化樹脂は成形過程で表面に汚染物質が残存し、他の物質との密着強度に影響を及ぼす可能性が考えられる。そのため本研究では繊維強化樹脂表面の洗浄方法の検討を目的とする。XPS 分析から洗浄前の繊維強化樹脂表面にはケイ素が 13.9 at.%含まれていることが明らかになった。これは金型成形時の離型剤が繊維強化樹脂表面に転写されたためと考えられる。また、エタノールで超音波洗浄することによりケイ素の元素濃度比が 7.9 at%に減少していることから、繊維強化樹脂表面の金型離型剤が除去されたが洗浄が十分でないことが考えられた。

さらに、各種洗浄後の強化繊維樹脂とエポキシを熱プレスにより複合化後、せん断強度を測定した。未処理のせん断強度が 4.18×10^6 Pa、蒸留水洗浄後が 3.36×10^6 Pa なのに対してエタノール洗浄後が 4.74×10^6 Pa となり、エタノール洗浄によりせん断強度が向上することが明らかになった。

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キラル Eu(Ⅲ)錯体を含む酢酸イミダゾリウム系イオン液体の発光特性

(1. 千葉大工、2. 千葉大院工)○鈴木 嵐太[1]・子瑩 李[2]・小林 範久[2]・中村 一希[2]

Luminescence Properties of Imidazolium Acetate-based Ionic Liquids Containing Chiral Eu(III) Complexes. ([1]*Fac. Eng., Chiba Univ.*, [2]*Grad. Sch. Eng., Chiba Univ.*) ○Arata Suzuki[1], Ziying Li[2], Norihisa Kobayashi[2], Kazuki Nakamura[2]

Ionic liquids exhibit characteristic properties such as non-volatility and non-flammability, and are expected to be low environmental impact matrix. In addition, Eu(Ⅲ) complexes are luminescent materials with excellent characteristics such as long luminescence lifetime and high color purity. Previously, we have demonstrated that the luminescence properties of chiral Eu(Ⅲ) complexes are significantly enhanced by the hybridization with alkylammonium salts. In this report, we aim to demonstrate these luminescence-enhancing effects in ionic liquids by measuring the luminescence performance of a hybrid system consisting of an imidazolium acetate-based ionic liquid and a chiral Eu(Ⅲ) complex.

Mixed solutions of Eu(*D*-facam)$_3$ and EMImOAc were prepared at a concentration ratio of 1:0~1:50 in 1-butanol, with Eu(*D*-facam)$_3$ at a concentration of 0.02 mmol/L. Emission spectra were measured for each solution (Fig. 1), and it was found that the addition of EMImOAc enhanced the emission intensity of the Eu(Ⅲ) complex. In particular, the luminescence intensity from $^5D_0 \rightarrow {}^7F_2$ transition was 74 times higher with 50 equivalents of EMImOAc compared to Eu(*D*-facam)$_3$ alone. The luminescence spectral shape and luminescence lifetime analysis suggest that the coordination environment and symmetry of the Eu(Ⅲ) complexes were affected by the addition of EMImOAc, resulting in improved luminescence properties.

イオン液体は、不揮発性、不燃性など特徴的な性質を有し、環境負荷の低いマトリクスとして期待されている。また、Eu(Ⅲ)錯体は、発光寿命が長く、色純度の高い優れた特徴を有する発光材料である。これまで我々は、キラル Eu(Ⅲ)錯体にアルキルアンモニウム塩を作用させることで発光特性が著しく向上することを明らかとした[1-3]。本報ではこれらの発光増強効果のイオン液体中における発揮を目指し、酢酸イミダゾリウム系イオン液体とキラル Eu(Ⅲ)錯体のハイブリッド系の発光特性の測定を行った。

1-butanol を溶媒とし、Eu(*D*-facam)$_3$ 濃度（0.02 mmol/L）に対して酢酸イミダゾリウム(EMImOAc)を [Eu(*D*-facam)$_3$]:[EMImOAc] =1:0~1:50 となるように混合した。各溶液について、配位子励起(350 nm)にて蛍光スペクトル測定を行った（Fig. 1)。その結果、Eu(*D*-facam)$_3$ に対し EMImOAc の添加により発光強度が増強し、EMImOAc を 50 当量添加した際は$^5D_0 \rightarrow {}^7F_2$の遷移において Eu(*D*-facam)$_3$ 単体の 74 倍の発光強度を示した。発光スペクトル形状および発光寿命の解析から EMImOAc の添加によって Eu(Ⅲ)錯体の配位環境や対称性が影響を受けた結果、発光性が向上したものと考えられる。

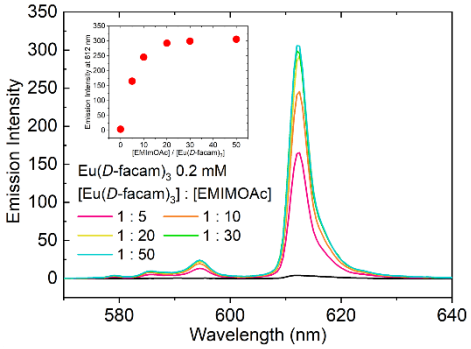

Fig.1 Emission spectra of Eu(*D*-facam)$_3$ and EMImOAc / Eu(*D*-facam)$_3$ solution at various concentration ratio of in 1-butanol.
Insert:Changes in the emission intensity of Eu(*D*-facam)$_3$ 613 nm with increasing concentrations of EMimOAc.

1) H. Minami et al, *Chem. Commun.* 2020, 56, 13532-13535
2) Ziying Li et al., *Chem. PhysChem.* 2021, 22, 2511-2516
3) Ziying Li et al., *J, Mater, Chem. C,* 2023, 11, 118-126

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銅系鉱物単結晶上における金属有機構造体(MOF)の配向成長

（大阪公立大学[1]）○小関 友香[1]・岡田 健司[1]・深津 亜里紗[1]・高橋 雅英[1]
Oriented growth of metal-organic framework on single crystals of copper-based mineral ([1]*Osaka Metropolitan University*) ○Yuka Koseki,[1] Kenji Okada,[1] Arisa Fukatsu,[1] Masahide Takahashi[1]

Metal-organic framework (MOF) composed of metal ions and organic linkers is expected for various application owing to its chemical and structural diversity. Highly oriented MOF thin films are required to integrate MOF into separation membrane or optical/electronic devices. We have previously reported the epitaxial growth of MOF crystals on nanobelt assembly films of metal hydroxides[1),2)] Finding single crystal substrate for the MOF epitaxial growth remains challenge. In this work, we found that Cu-based mineral (botallackite: $Cu_2(OH)_3Cl$) could be a potential substrate for the oriented growth of Cu paddle-wheel type MOF. Crystals of botallackite were immersed into methanol solution of organic linkers and acetic acid. Then, rod shaped crystals were grown on surface of botallackite crystals. The longitudinal axis, that corresponds to the 1D pore direction, of rod shaped crystals were oriented in same direction. Crystallographic relationship between the mineral and the MOF was investigated by X-ray diffraction.
Keywords : Metal-organic framework; mineral; oriented growth; epitaxial growth

金属有機構造体(MOF)は金属イオンと有機配位子から構成される骨格を持つ多孔質材料であり、その化学的・構造的設計性の高さからさまざまな分野での応用が期待されている。特に分離膜や光学・電子デバイスなど MOF を薄膜として使用する分野では高い配向性を有する MOF 薄膜が求められており、当研究グループでは金属水酸化物ナノ構造体上での MOF のエピタキシャル成長による面外/面内配向 MOF 薄膜の作製を報告してきた [1),2)]。大きな実用的なサイズの単結晶基板を足場として MOF のエピタキシャル成長を実現することでさらに高い配向性と実用性を有する MOF 配向薄膜の作製が期待できる。本研究では銅系鉱物ボタラカイト($Cu_2(OH)_3Cl$)単結晶を基板として用いて Cu paddle-wheel 系 MOF ($Cu_2(bdc)_2dabco$ (bdc=1,4-benzenedicarboxylate, dabco=1,4-diazabicyclo[2.2.2]octane))のエピタキシャル成長を試みた。Bdc、dabco、酢酸のメタノール溶液にボタラカイト(Fig. (a))を浸漬することで表面上にロッド形状の結晶が向きを揃えて形成された(Fig. (b))。ロッド形状結晶の長軸が同じ方向に向いており、長軸方向に存在する MOF の 1 次元細孔が配向していることが示唆された。鉱物と MOF の結晶方位関係は X 線回折法により調査した。

1) P. Falcaro et al., Nature. Mater., 2017, 16, 342-348
2) K. Okada et al., Chem. Sci., 2020, 11, 8005-8012

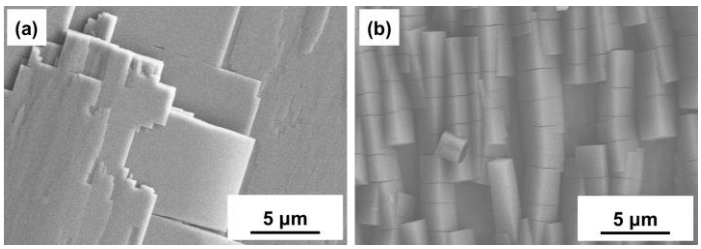

Figure. SEM images of (a) a botallackite crystal and (b) rod shaped crystals on a botallackite crystal

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クラウンエーテルを含む電解液中におけるユーロピウムイオンの電気化学的発光特性制御

(千葉大工[1]・千葉大院工[2]) ○吉田 紘汰[1]・藪田 龍人[2]・小林 範久[2]・中村 一希[2]

Electrochemical Control of Emission Color of Europium Ion in Electrolytic Solution Containing Crown Ether.

(*[1]Fac. Eng., Chiba Univ., [2]Grad. Sch. Eng., Chiba Univ.*) ○Genta Yoshida,[1] Ryoto Yabuta,[2] Norihisa Kobayashi,[2] Kazuki Nakamura [2]

Lanthanide complexes show unique luminescence properties such as high color-purity emission spectra and long luminescence lifetime. The luminescence color of Eu ion differ depending on their valence. Trivalent Eu ions (Eu^{3+}) show red luminescence, and divalent Eu ions (Eu^{2+}) show blue luminescence. In this study, we aimed to improve stabilization of Eu^{2+} in electrolytic solution by introducing crown ether. In this paper, we controlled the emission color by electrochemical redox reaction of Eu ion in electrolytic solution containing crown ether.

Keywords : Eu ion; Photoluminescence; Redox reaction; Electrofluorochromism; Red emission

希土類イオンの一種である Eu イオンは、その価数によって発光色が異なり、Eu^{3+}は f-f 遷移による赤色発光、Eu^{2+}は d-f 遷移による青色発光を示す。安定な Eu^{3+}に比べて、空気中や溶液中で不安定な Eu^{2+}発光の有機溶媒中での研究や、Eu^{2+}↔Eu^{3+}の発光制御に関する研究は非常に少ない[1)2)]。本研究では、Eu^{2+}を溶液中で安定化させることが知られているクラウンエーテルを共存させることで Eu イオンの電気化学的な発光色の制御を目指した。

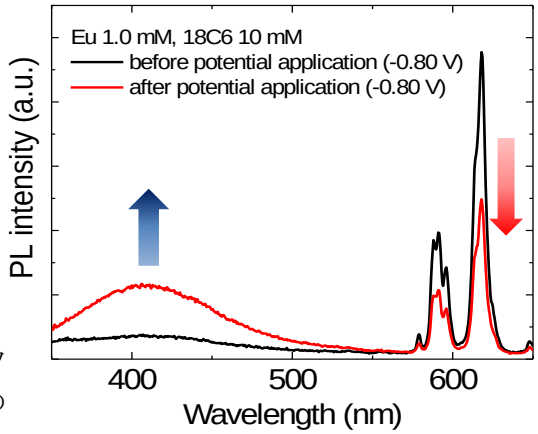

Fig.1 Emission spectra of Eu $(NO_3)_3 \cdot 6H_2O$ solution containing crown ether with application of reduction potential (−0.80 V vs. Ag/Ag^+, 300 s).

Acetonitrile に、支持電解質として Tetra-n-butylammonium perchlorate を 100 mmol/L、$Eu(NO_3)_3 \cdot 6H_2O$ を 1.0 mmol/L、18-Crown 6-Ether （18C6）を 10 mmol/L となるように溶解させた。この溶液を用いて 3 電極型電気化学セルを構築し、Eu^{3+}の還元電位である−0.80 V を印加した際の発光スペクトルを測定した（Fig.1）。電位印加前に比べ、還元電位の印加後は Eu^{3+}の発光である 615 nm の発光強度が減少した一方、410 nm の青色発光ピークが新たに確認できた。また、18C6 を含まない溶液では電位印加後もこの青色発光ピークは出現しなかった。以上の結果から、18C6 を含む電解液中では Eu^{3+}/Eu^{2+}の電気化学的な酸化還元反応が可能となり、発光色の制御が実現したことが示唆された。

1) Hiroyuki Ohno, Hideyuki Yoshihara, ***Solid State Ionics***, 1995, **80**, 251-259.
2) Ryoto Yabuta, Norihisa Kobayashi, Kazuki Nakamura, ***Phys. Chem. Chem. Phys***., 2023, **25**, 25979-25984.

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ナフィオンと金ナノワイヤ電極からなるイオン性高分子-金属複合体アクチュエータ

（物材機構）○池田 太一
Ionic Polymer-Metal Composite Actuators Consisting of Nafion and Gold Nanowire Electrodes (*Research Center for Macromolecules and Biomaterials, National Institute for Materials Science*) ○Taichi Ikeda

Ionic polymer-metal composite (IPMC) actuator consisting of Nafion and gold nanowire (Au-NW) electrodes was prepared using hot pressing.[1)] As a reference device, IPMC actuator consisting of Nafion and gold thin films was also prepared. It was confirmed that the shape of Au-NW was transformed by heat and pressure in hot-pressing process. The best temperature for hot pressing was 90 ºC. Au-NW film can be an electrode with thinner (about 150 nm) and lower surface resistivity (about 0.5 Ω sq^{-1}) than the conventional electrode prepared by electroless plating. Since the gold nanowire electrode has larger contact area with Nafion than the gold film, the former exhibited larger capacitance and larger displacement in actuation (**Fig**.1b, 1c).
Keywords : Ionic polymer-metal composite; Actuator; Gold nanowire; Nafion; Capacitor

ナフィオンと金ナノワイヤ(Au-NW)電極からなるイオン性高分子-金属複合体(IPMC)アクチュエータをホットプレス法により作成した[1)]。参照デバイスとしてナフィオンと金薄膜からなる IPMC アクチュエータも作成した。ホットプレスの過程で金ナノワイヤは熱と圧力のために形態変化を起こすことを確認した。ホットプレスの際の最適な温度は 90ºC であった。Au-NW 膜は無電解メッキ法により作成された従来の電極よりも薄くて(約 150 nm)、低表面抵抗(約 0.5 Ω sq^{-1})の電極となりうる。金ナノワイヤ電極の方が金薄膜よりもナフィオンとの接触面積が大きいため、大きな静電容量と大きなアクチュエーション変位を示すことを確認した(**Fig**.1b, 1c)。

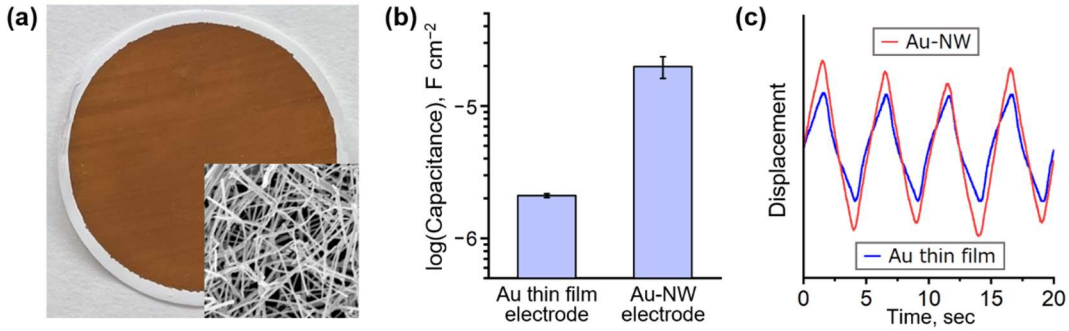

Fig. 1 (a) Au-NW film (inset: SEM image), (b) Capacitance data, (c) Actuation behavior.

1) Taichi Ikeda “Gold nanowire mesh electrode for electromechanical device” *Scientific Reports* **2023**, *13*, 16669.

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キラルネマティック液晶と発光性 Eu(III)錯体の複合体におけるキロプティカル特性

（千葉大工[1]・千葉大院工[2]）○佐川 祐介[1]・川畑 琢郎[2]・小林 範久[2]・中村 一希[2]

Chiroptical Properties of Hybrid Material Composed of Chiral Nematic Liquid Crystals and Luminescent Eu(III) complexes ([1]*Faculty of Engineering, Chiba University*, [2]*Graduate School of Engineering, Chiba University*) ○ Yusuke Sagawa,[1] Takuro Kawahata,[2] Norihisa Kobayashi,[2] Kazuki Nakamura[2]

Lanthanide complexes are known to show superior luminescence properties such as high color purity, long-lived excited state, and excellent luminescence efficiency. On the other hand, chiral nematic liquid crystals consisted of helically twisted layer structure reflect circularly polarized light at specific wavelengths depending on helical layer structures.

In this study, we aimed to prepare hybrid system containing Eu(III) complexes and chiral nematic liquid crystals for creation of novel circularly polarized luminescence medium.

Transmittance and circular dichroic (CD) spectra of chiral nematic liquid crystal of hydroxypropyl cellulose aqueous solution were measured (Fig. 1). The transmittances of cells with various HPC concentrations showed light reflection and resulted decrease of transmittance at specific wavelength. And in the CD measurement, large negative CD signal was observed at the wavelength corresponding to light reflection.

Keywords : Chiral nematic liquid crystal; Eu(III) complexes; Selective reflection; Circular polarized luminescence

希土類錯体は高い色純度や優れた発光効率といった特徴的な発光特性を持つ材料である。また、液晶は様々な配向状態をとるが、特にらせん状にねじれた層構造を作る液晶をキラルネマティック液晶は、らせん構造において特定の波長および方向性の円偏光を選択的に反射する。本研究ではこの液晶の特性を活かした新規円偏光発光媒体の構築を目指し、Eu(III)錯体とキラルネマティック液晶の複合媒体の作製を行った。

キラルネマティック層を示すヒドロキシプロピルセルロース（HPC）水溶液を、カバーガラス 2 枚で挟んだ液晶セルにおいて、透過・CD スペクトルの測定を行った（Fig.1）。HPC 濃度が 65, 66, 70 wt%のセルは、それぞれのブラッグ反射に対応した波長で透過率が減少した（>600, 560, 470 nm）。また、CD スペクトルでは、それらの選択反射波長において大きな負のシグナルが観測された。液晶セルの円偏光フィルムを通した観察から、これらの液晶セルは入射光の右円偏光成分のみ選択的に反射することで、CD スペクトルでは負のシグナル（左円偏光成分）が観測されたものと推察される。

発表では、同 HPC と Eu(III)錯体の複合化とその発光性に関しても報告する。

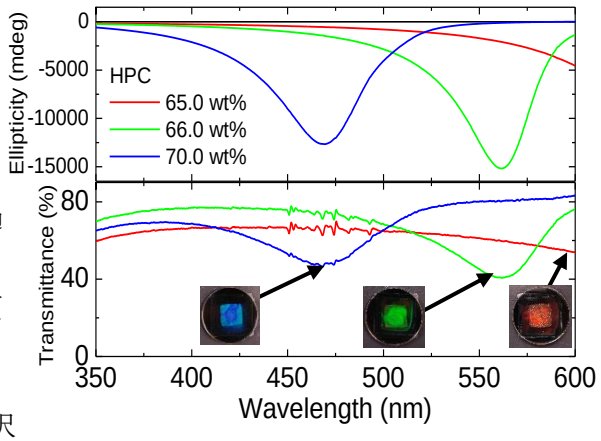

Fig. 1 CD (top) and transmission (bottom) spectra of HPC solutions at the various concentrations. Inset: Photographs of liquid crystal cells at the various concentrations of HPC using left circular polarization filter.

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β-ジケトナート Eu(III)錯体と合成粘土鉱物の複合化およびその発光特性

(千葉大工[1]、千葉大院工[2]) ○西山　亮太[1]・曹　栄[2]・中村　一希[2]・小林　範久[2]

Hybridization of β-diketonate Eu(III) Complexes and Synthetic Clay Minerals and Properties

([1]*Fac. Eng., Chiba Univ.*, [2]*Grad. Sch. Eng., Chiba Univ.*)
○Ryota Nishiyama,[1] Rong Cao,[2] Kazuki Nakamara,[2] Norihisa Kobayashi[2]

Clay can easily exchange its exchangeable cations in the interlayers with external cations. On the other hand, Eu(III) complexes have superior luminescence properties, such as high color purity, long emission lifetime and so on. In this research, we aim to create novel photo-functional materials by hybridizing clay compound with Eu(III) complexes. In this study, we prepared composite material with clay and $Eu(TTA)_3phen$. And we analyzed their luminescence properties. With the addition and increasing concentration of clay compound, the luminescence intensity of Eu(III) complex at 612 nm was enhanced. This suggests that the incorporation of Eu(III) ions into the interlayers of clay contributes to the enhancement of luminescence property.

Keywords: Clay; Europium; Lanthanide(III) complexes; Red luminescence

層状粘土鉱物(clay)は層間に存在している交換性陽イオンと外部の陽イオンを交換し、原子レベルで平滑な表面に化学種を固定化することが可能である。また、Eu(III)錯体は、色純度が高い長寿命な赤色発光を示すなど、発光材料として優れた特徴を有する。我々は clay と Eu(III)錯体を複合化させた、新たな光機能性材料の創成を目指している。本研究では、膨潤性粘土鉱物の一種である有機化スメクタイトに赤色発光を示す Eu(III)錯体を吸着させ、粘土複合膜における発光特性を評価した。

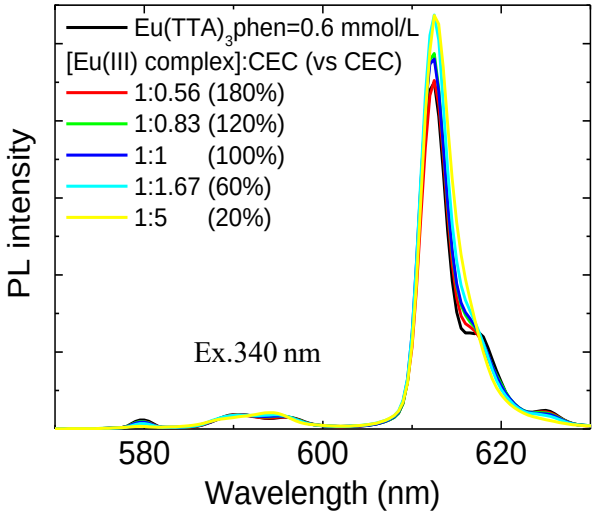

Fig. 1 Emission spectra of $Eu(TTA)_3phen$ and $Eu(TTA)_3phen$/STN solution at various concentration ratio of [Eu(III) complex]/CEC in acetonitrile. Excitation wavelength was 340 nm.

アセトニトリルを溶媒とし、$Eu(TTA)_3phen$ 濃度を 0.6 mmol/L に固定し、[Eu(III) complex]:CEC=1:0、1:0.56、1:0.83、1:1、1:1.67、1:5 となるように $Eu(TTA)_3phen$/スメクタイト混合溶液を調整した。各溶液について配位子励起による発光スペクトルを測定した(Fig. 1)。有機化スメクタイトの添加量の増加に伴って、612 nm の Eu(III)錯体由来の赤色発光の発光強度が増加し、[Eu(III) complex]:CEC=1:5 のときの 612 nm における発光強度はスメクタイトを添加していない溶液と比較すると 19.3%増加した。発表では、より詳細な発光特性解析や膜状態との比較についても報告する。

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アルキルアンモニウム基を有するアルコキシシランを用いた有機シロキサン系メソ構造体薄膜の作製

(早大先進理工[1]・早大材研[2]) ○井戸 一智[1]・齊藤 優希[1]・宮本 佳明[1]・松野 敬成[1,2]・下嶋 敦[1,2]

Synthesis of Mesostructured Organosiloxane-based Thin Films Using Alkoxysilanes with an Alkylammonium Group

([1]*School of Advanced Science and Engineering, Waseda University,* [2]*Kagami Memorial Research Institute for Materials Science and Technology, Waseda University*) ○Kazutomo Ido[1], Yuki Saito[1], Yoshiaki Miyamoto[1], Takamichi Matsuno[1,2], Atsushi Shimojima[1,2]

Organosiloxane-based materials have high stability derived from inorganic frameworks and the properties of organic groups. Emergence of new functions is expected by controlling mesoscale structures. In this study, organosiloxane thin films with a two-dimensional (2D) hexagonal mesostructure were prepared through co-hydrolysis and polycondensation of alkylammonium-modified alkoxysilane and ethylene-bridged alkoxysilane. Swelling and crack healing behaviors upon water vapor exposure were investigated.

Keywords : Organosiloxane; Mesostructured thin film; Sol–gel method; Self-healing

【緒言】有機シロキサン系材料は無機骨格由来の高い熱的・化学的安定性を有し、有機基の選択や分子～メソスケールの構造制御によって様々な機能の発現が期待できる [1)]。最近我々は、ラメラ構造の有機シロキサン–界面活性剤メソ複合体薄膜が高湿度下で膨潤し、クラックの修復性を発現することを報告した [2)]。このような自己修復挙動とメソ構造の相関を理解することは基礎化学的に重要である。本研究では、長鎖アルキルアンモニウム基を有するアルコキシシランを利用して、界面活性剤が有機シロキサン骨格にグラフト化された二次元(2D)ヘキサゴナル構造を有する薄膜を作製した(Fig. 1)。作製した薄膜へ水蒸気を暴露した際のメソ構造の膨潤性やクラック修復挙動を調査した。

【実験方法】アルキルアンモニウム基を有するオルガノトリアルコキシシランとエチレン架橋型トリアルコキシシランの共加水分解・重縮合過程で、反応溶液を Si 基板上にスピンコートすることで薄膜を作製した(Fig. 1)。ヌープ圧子を押し込むことで薄膜表面にクラックを付与した。薄膜表面に水蒸気(> 90%RH)を数十秒間暴露した際の膨潤挙動、さらにクラックの修復挙動を調査した。

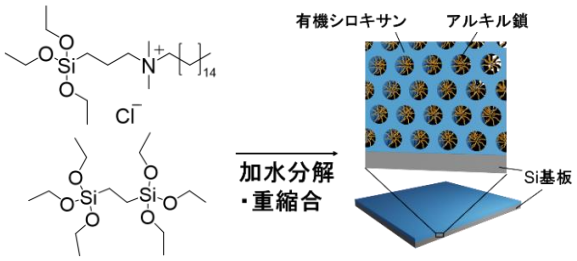

Fig. 1 2D ヘキサゴナル構造を有する薄膜の作製スキーム

【実験結果】作製した薄膜の GI-SAXS パターンより、2D ヘキサゴナル構造由来の回折パターンが確認された。さらに、湿度変化に伴ってメソ構造が可逆的に膨潤(> 90%RH)・収縮(50%RH)することが分かった。また、光学顕微鏡像および SEM 像より、水蒸気暴露によってクラックが部分的に閉じる様子が観察された。水蒸気暴露の停止後もクラックの再開裂が確認されなかったことから、クラックの修復が示唆された。

1) K. Kuroda *et al*., *Chem. Mater.* **2014**, *26*, 211. 2) S. Kodama *et al*., *ACS Appl. Polym. Mater.* **2021**, *3*, 4118.

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ペロブスカイト型構造を有する柔粘性イオン結晶の合成と物性評価

（九州工大院工）○三根 裕朗・下岡 弘和・岡内 辰夫・北村 充
Synthesis and characterization of ionic plastic crystals with perovskite-type structure (*Graduate School of Engineering, Kyushu Institute of Technology*) ○Hiroaki Mine, Hirokazu Shimooka, Tatsuo Okauchi, Mitsuru Kitamura

[MDABCO]K[I_x (PF_6)$_{1-x}$]$_3$ (MDABCO = N-methyl-N'-diazabicyclo[2.2.2]octonium) crystals with ABX_3-type perovskite structure were successfully synthesized from an aqueous solution. A trigonal to cubic phase transition was observed around room temperature, resulting in significant changes in volume and entropy. This is thought to be due to the transition to the plastic crystal phase. Here, we report on the influence of the motion of MDABCO cation and PF_6 anion on the phase transition behavior of [MDABCO]K[I_x (PF_6)$_{1-x}$]$_3$ crystals.
Keywords：*Organic-inorganic perovskite*

ABX_3 型有機-無機ペロブスカイト化合物[MDABCO](NH_4)I_3(MDABCO: N-メチル-N'-ジアザビシクロ[2.2.2]オクトニウム)は $BaTiO_3$ に匹敵する大きな自発分極を持ち、強誘電体材料などとして注目されている [1]。本研究では、B サイトと X サイトを K^+ イオンと PF_6^-イオンで置換した[MDABCO]K[I_x (PF_6)$_{1-x}$]$_3$（$x = 0, 0.01$）を作製し、その相転移挙動について調べた。図 1 の示差走査熱量測定(DSC)の結果が示すように、どちらの試料も相転移に伴う大小 2 つのピークが室温付近に観察された。この 2 段階の相転移でのエントロピー変化は約 $\Delta S \approx 40$ J·mol^{-1}·K^{-1} と大きいことから、高温では柔粘性結晶相と考えられる。本講演では、この二段階の相転移について考察するために行った誘電性の評価結果について述べ、[MDABCO]K[I_x (PF_6)$_{1-x}$]$_3$ 結晶内おける MDABCO イオンと PF_6 イオンの運動について考察する。

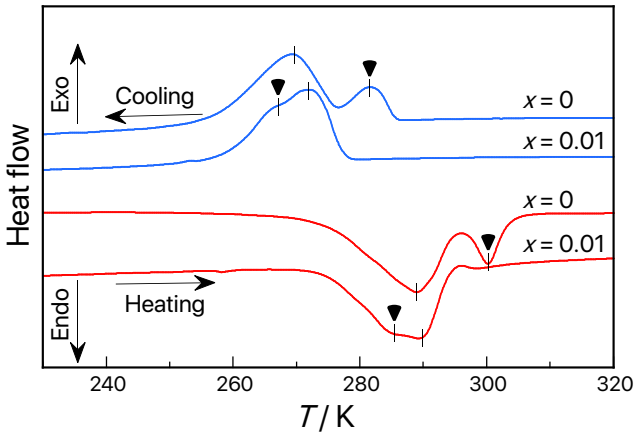

Fig. 1. DSC curves of [MDABCO]K[I_x (PF_6)$_{1-x}$]$_3$.

1) H.-Y. Ye *et al*., *Science* **2018**, *361*, 151.

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

Wed. Mar 20, 2024 3:55 PM - 5:15 PM JST | Wed. Mar 20, 2024 6:55 AM - 8:15 AM UTC C442(442, Bldg. 4 [4F])

[C442-3vn] 20. Materials Chemistry -Basic and Application-

Chair: Sachio Yoshihara, Yuta Nishina

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[C442-3vn-01]
Analysis of organic additives in metal-plating bath forby use of boron-doped diamond electrode

○Sachio Yoshihara[1] (1. Utsunomiya University)

Japanese
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[C442-3vn-02]
Characterization of Surface of Diamond Electrodes Treated by Various Methods

○Yuki Tsuda[1], Takashi Yamamoto[1], Yasuaki Einaga[1] (1. Keio Univ.)

English
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[C442-3vn-03]
Microstructural analysis and performance evaluation of carbon hybrid electrode materials.

○HAONAN ZHANG[1], WENLIANG ZHU[1] (1. Kyoto Institute of Technology)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[C442-3vn-04]
Preparation and characterization of precisely pore-size-controlled boron-doped carbon

○Kentaro Ohkura[1], Yuta Nishina[1] (1. The Univ. of Okayama)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[C442-3vn-05]
Preparing liquid crystalline dispersion of high aspect ratio carbon nanotubes

○Nodoka Kosugi[1,2], Keiko Kojima[2], Hirokuni Jintoku[2], Kazufumi Kobashi[2], Toshiya Okazaki[2,1] (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

Japanese
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[C442-3vn-06]
Synthesis of cationic polymer-graphene oxide composites and application for adsorbents

○Ryota Kimura[1], Yuta Nishina[1,2] (1. Okayama University, 2. RCIS)

Japanese
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC
[C442-3vn-07]
Synthesis of redox-active plastic crystal containing tetrachloroferrate ion and its application to solid refrigerant

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○Takuya Ono[1], Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[C442-3vn-08]

Characterization of biomass adsorbed L-ascorbic acid and reducing ability for Fe(III)

○Ryuki Ikeda[1], Yui Igaki[1], Takumi Akinaga[1], Yuko Shikami[2], Toshiyuki Miyauchi[2] (1. Graduate of Chubu University, 2. Chubu University)

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ボロンドープダイヤモンド電極を用いた金属めっき浴中の有機添加剤の分析

（宇都宮大）○吉原 佐知雄

Analysis of organic additives in metal-plating bath for by use of boron-doped diamond electrode (Utsunomiya University)

Boron-doped diamond (BDD) is originally an insulator. Electrical conductivity is implemented by adding boron to diarmonds. BDD has chemical and physical stability, also shows wide potential window, low background current, etc. as its own electrochemical properties. Therefore, BDD is highly sensitive and quite stable as the electrode. In this study, such a BDD has been tested for the analysis of organic additives in metal plating baths, e.g. quantitative analysis of quadrol additives in copper plating bath, and of polyethylene imine in the silver plating bath. Finally we have elucidated their oxidation mehcanism.

Keywords : Boron-doped diamond electrode, Metal, plating bath, Quadrol , Polyethylene Imine

ダイヤモンドにホウ素を添加することで導電性が付与された電極材料である。BDDはダイヤモンド本来の物理的安定性はそのままに、広い電位窓、低いバックグラウンド電流など固有の電気化学特性も有している。そのため、高感度で長期的な電気化学測定が可能な材料である。この BDD を用い、金属めっき浴中の添加剤の分析を試みた。具体的には銅めっき液中の添加剤クアドロール(Fig. 1)、銀めっき液中のポリエチレンイミン PEI の定量(Fig. 2)やその反応メカニズム [1]について検討した。[2]

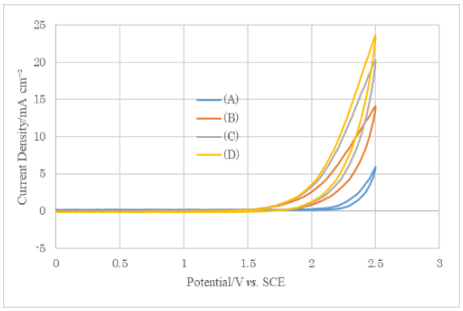

Fig 1 BDD による CV 測定結果
(A) 0 mol dm⁻³ (B) 0.05 mol dm⁻³
(C) 0.10 mol dm⁻³ (D) 0.15 mol dm⁻³.

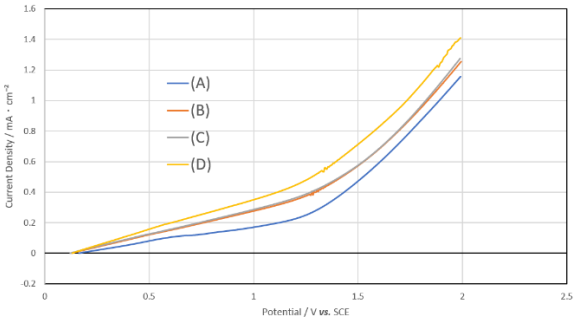

Fig.2 PEI の分子量別測定
(A) Blank (B) PEI 600 (C) PEI 1800 (D) 10000

1) Decomposition reaction using OH radical has been reported. A. V. Karim, P. V. Nidheesh, and M. A. Oturan, *Curr Opin Electrochem,* **30**, 100855 (2021)
2) 佐伯泰我,大貫孝浩,吉原佐知雄,石川祥久,元井 健一郎,及川 哲史, ボロンドープダイヤモンド電極を用いたピロリン酸銅めっき浴中の有機添加剤クアドロールの分析, 表面技術, **74**(7), 367（2023）

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さまざまな処理により終端変化させたダイヤモンド電極表面の評価

（慶大理工）○津田 裕紀[1]・山本 崇史[1]・栄長 泰明[1]

Characterization of Surface of Diamond Electrodes Treated by Various Methods ([1]*Keio University*) ○Yuki Tsuda,[1] Takashi Yamamoto,[1] Yasuaki Einaga[1]

Boron-doped diamond (BDD) has excellent electrochemical properties, and the surface termination can be changed by various treatments. However, the knowledge of surface functional groups of BDD, especially their ratios and distribution, has not been fully elucidated, which is necessary to fabricate electrode surfaces suitable for various applications. This study aims at determining the composition of surface functional groups of BDD treated by different methods. BDD treated by hydrogen plasma (HP) were used as a starting point. Anodic oxidation (AO) or UV/ozone (UV) was applied as an oxidation treatment and cathodic reduction (CR) or HP was applied as a reduction treatment. Surface of each BDD was characterized by cyclic voltammetry (CV) measurements in an aqueous solution of $K_4[Fe(CN)_6]$, and by X-ray photoelectron spectroscopy (XPS) measurements. A series of CV and XPS measurements revealed that (i) BDD is more easily oxidized by UV than AO, (ii) BDD after AO is more easily reduced by CR than BDD after UV, and (iii) BDD can be converted into hydrogen-terminated state by HP, regardless of the preceding oxygen-terminated state. Overall, the degree of oxidation/reduction is dependent on the treatment methods, which is probably attributed to the coexistence of highly reactive and less reactive sites at the BDD surface.

Keywords: Boron-Doped Diamond; Surface Treatment; Electrochemistry; X-Ray Photoelectron Spectroscopy

優れた電気化学特性をもつホウ素ドープダイヤモンド (BDD) はさまざまな処理で表面終端を変えることができる[1,2]。しかしながら、BDD 表面に存在する官能基の比率や分布などの理解は十分に進んでおらず、用途に見合う電極表面の作製にはその知見が必要である。そこで本研究では、処理方法と BDD 表面の官能基情報を対応づけることを目的とした。

水素プラズマ処理 (HP) を行った BDD を基準となる表面状態とし、酸化処理として陽極酸化 (AO) または UV オゾン (UV) を、還元処理として陰極還元 (CR) または HP を行った。BDD のそれぞれの表面は $K_4[Fe(CN)_6]$水溶液中でのサイクリックボルタンメトリー (CV) 測定、および X 線光電子分光 (XPS) 測定により評価した。一連の CV 測定ならびに XPS 測定の結果から、(i) 酸素終端化は UV の方が促進されること、(ii) CR による水素終端化は AO 後の方が促進されること、(iii) HP による水素終端化は AO 後と UV 後で大きな差が見られないことがわかった。このように、処理方法によって酸化／還元のされやすさに差が生じる要因は、BDD 表面に反応性が高い部位と低い部位が混在しているためであると考えられる。

1) J. V. Macpherson, *Phys. Chem. Chem. Phys.* **2015**, *17*, 2935.
2) N. Yang, J. V. Macpherson, Y. Einaga, G. M. Swain et al., *Chem. Soc. Rev.* **2019**, *48*, 157.

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Microstructural Analysis and Performance Evaluation of Carbon Hybrid Electrode Materials

([1]*Ceramic Physics Laboratory, Kyoto Institute of Technology*, [2]*Molecular Chemistry and Engineering, Kyoto Institute of Technology*) ○Haonan Zhang[1], Yumi Yoshida[2], Elia Marin[1], Giuseppe Pezzotti[1], Wenliang Zhu[1]

Keywords : Electrode Materials; PKC; Activated carbon; Microstructure

Currently, due to the rapid industrial development, the depletion of energy resources continuously challenges researchers to explore new low-cost energy storage materials with superior performance and simple device fabrication process. Carbon hybrid compound electrode materials, comprised of polyvinylidene fluoride/potassium carbonate (PKC), show superior performance at the percolation threshold due to the formation of interfacial activated carbon (AC), besides the advantages of low cost, easy production, light weight, and high flexibility in structure, making them promising for carbon-based supercapacitors.[1] However, owing to the complex reactions involved in the thermal treatment and easy alteration of the structure of generated AC,[2,3] how to efficiently control PVDF dehydrofluorination for the formation of AC, as well as to optimize material performance remains yet to be solved.

In this study, the microstructure and electrochemical properties of carbon hybrid compounds PKC prepared under various conditions, particularly by changing thermal treatment temperature (200ºC, 220ºC, 240ºC), and adding different additives (H_2O, $KHCO_3$, cobalt oxide/hydroxide, etc) in the systems, during the material production process were evaluated by Raman spectroscopy, X-ray photoelectron spectroscopy, and electrochemical impedance spectroscopy. The effects of microstructure changes of generated ACs induced by the change in the fabrication conditions on material properties were clarified, thus to optimize the production process and to achieve the highest level of material performance.

Significant alterations of the Raman *D* and *G* bands for generated activated carbon, and of the C-C / C=C related peaks in high-resolution C1s XPS spectra for the PKC samples could be observed, exhibiting distinct variations of I_D/I_G and sp^2/sp^3 ratios among the samples. The results revealed a significant dependence of the AC microstructure on both temperature and additives in the carbon hybrid materials, and water plays an important role in the reactions due to the combination of dehydroxylation and decomposition of $KHCO_3$.

According to the results, the existence of optimal temperature, and optimal amounts of additives for the systems was confirmed: The most significant performance was demonstrated for the case of heat treatment at 220ºC. Adding a certain amount of $KHCO_3$ or extrinsic H_2O to PKC could increase the content of carbon ring structures and reduce the electrical resistance, resulting in a better performance, as the optimized performance of the PKC systems was found by adding 5% $KHCO_3$ and 5% H_2O to PKC due to the competition of dehydroxylation and $KHCO_3$ decomposition during thermal treatment. Addition of cobalt oxide/hydroxide showed a decrease in the electrical conductivity, but could improve the EC performance owing to the Faradaic redox reactions upon charging/discharging processes.

The clarification of the influence of thermal treatment temperature and additives on microstructures of activated carbon, and the control in the PVDF dehydrofluorination process could provide the foundation for applications for flexible energy storage.

1) M. Wang, et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 9123. 2) W. Zhu, et al., *Phys. Chem. Chem. Phys.* **2019**, *21*, 2382. 3) W. Zhu, et al., *Materials Today Communications* 2022, *32*, 103884.

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細孔径を精密に制御したホウ素ドープカーボンの作製とその物性評価

（岡大院自然[1]・岡山大 RCIS[2]）○大倉健太郎[1]・仁科勇太[1,2]

Preparation and characterization of precisely pore-size-controlled boron-doped carbon

([1]*Graduate School of Environmental, Life, Natural Science and Technology, Okayama University*, [2]*RCIS, Okayama University*) ○Kentaro Ohkura,[1] Yuta Nishina[1,2]

Boron-doped carbon has garnered attention for its applications as multifunctional catalysts and electrode materials. However, conventional methods for synthesizing boron-doped carbon involve the use of precursors with oxygen-boron bonds, such as boric acid or phenylboronic acid. The formation of carbon-boron bonds from these raw materials requires high temperatures to cleave the stable oxygen-boron bonds. In this study, we focused on the ethynyl group, allowing low-temperature carbonization. We employed triethynylborane as a boron compound containing the ethynyl group in this research. Remarkably, using this compound, we successfully confirmed the characteristic D and G bands of carbon through Raman spectroscopy at an extremely low temperature of 200 °C. Furthermore, elemental analysis using XPS provided conclusive evidence of boron doping.

Keywords : Carbon material; Lewis acid; Porous material; Boron-doped carbon

ホウ素をドープしたカーボンは多機能触媒や電極材料として注目を集めている。しかしながら、従来のホウ素ドープカーボンの合成では、ホウ酸やフェニルボロン酸のような酸素ーホウ素結合を有する原料を使用している。このようなホウ素源をカーボン中にドープするには結合エネルギーが高い酸素ーホウ素結合を切断する必要があるため、高い温度を要する。そこで、低温で炭素化が可能な官能基としてエチニル基に着目した（図 1）。本研究では、エチニル基含有ホウ素化合物としてトリエチニルボランを使用した。この化合物は 200 °C という低い温度でカーボン特有の D, G バンドをラマン分光法により確認することができた（図 2）。また、ホウ素がドープされていることも XPS による元素分析により確認することができた。

その他の構造解析および得られたホウ素ドープカーボンの応用例については当日報告する。

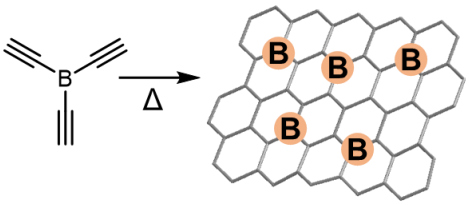

図 1. トリエチニルボランを用いるホウ素ドープカーボンの合成

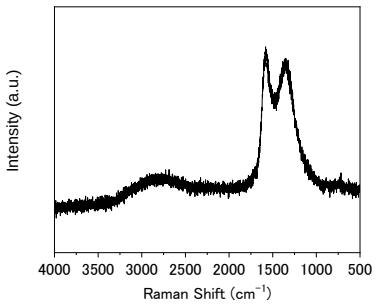

図 2. 200 ℃で処理して得られた生成物の Raman スペクトル

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アスペクト比が大きいカーボンナノチューブ分散液の作製とその液晶の観察

(筑波大学[1]・産業技術総合研究所[2]) ○小杉のどか[1,2]・児島敬子[2]・神徳啓邦[2]・小橋和文[2]・岡崎俊也[2,1]

Preparing liquid crystalline dispersion of high aspect ratio carbon nanotubes ([1]*University of Tsukuba,* [2]*National Institute of Advanced Industrial Science and Technology*) ○Nodoka Kosugi[1,2],Keiko Kojima[2], Hirokuni Jintoku[2], Kazufumi Kobashi[2], Toshiya Okazaki[2,1]

Carbon nanotubes (CNTs) are nanomaterials with excellent properties such as high mechanical strength and high electrical conductivity. To control the orientation of CNTs is important for the fiber and film applications, and one of the effective methods is to use liquid crystalline dispersions. We successfully prepare CNT dispersion with larger aspect ratio (*L*/*D*) (~1378) by dispersing high crystallinity double-walled CNTs with a surfactant. The prepared dispersion shows the lower transition concentrations from isotropic phase to biphasic state and from biphasic state to nematic phase than those with smaller *L*/*D*[1)]. This is in agreement with the Onsager theory. On the other hand, the orientation of the prepared CNT film was as low as that of the smaller *L*/*D*.

Keywords : Carbon nanotube; Liquid Crystal; Surfactant

カーボンナノチューブ（以下 CNT）は多くの場合その優れた特性をチューブ軸方向に発現する。したがって、CNT の応用には配向を制御することが重要であり、その方法の一つとして液晶性分散液の作製がある。先行研究から、分散液中の CNT のアスペクト比が大きいほど液晶相の相転移濃度が低くなることが分かっている[1)]。

そこで、本研究では高品質 2 層 CNT に界面活性剤を加えて分散することで、アスペクト比の大きな棒状 CNT 分散液の作製に成功した。作製した分散液は濃度が高くなるにしたがって等方相～二相共存状態～ネマティック相と液晶相転移し、その相転移濃度は既報のアスペクト比が小さい CNT 分散液と比較して低濃度であり、Onsager 理論に矛盾しない結果となった。一方で、同分散液から作製した CNT 膜の配向度は既報のアスペクト比の小さい CNT 分散液と同程度の値に留まった。

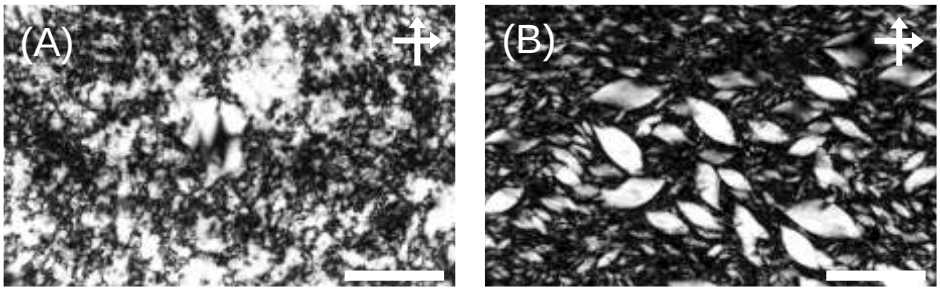

図.（A)ネマティック相および(B)二相共存状態の偏光顕微鏡像. スケールバーは 200 μm.

(1) Liquid-crystalline behaviors of single-walled carbon nanotube aqueous dispersions with different nanotube aspect ratios and surfactants. K. Kojima, *et al* ., *Appl. Phys. Exp.*, **2022**, 15, 125003.

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酸化グラフェン-カチオン性ポリマー複合体の合成と吸着特性の評価

（岡山大工[1]，岡山大 RCIS[2]）○木村 亮太[1]・仁科 勇太[2]
Synthesis of cationic polymer-graphene oxide composites and application for adsorbents
([1]*Faculty of Engineering, Okayama University,* [2] *RCIS, Okayama University*)
○Ryota Kimura[1], Yuta Nishina[2]

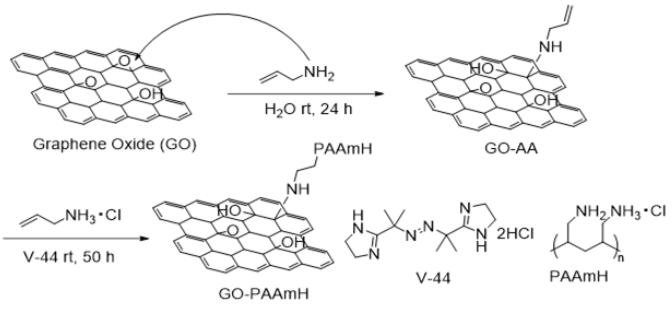
Graphene oxide (GO) is a sheet-like carbon material with a thickness of approximately 1 nm and a high specific surface area. It has abundant oxygen functional groups such as hydroxy, carboxy, and epoxy groups on its surface. Amines react with epoxy groups, enabling covalent surface modification. The oxygen functional groups give GO a strong negative charge, causing it to quickly aggregate when mixed with cationic polymers. In this study, we synthesized cationic polymer-GO composites by the grafting-from method and evaluated their properties as adsorbents.

Keywords: Graphene oxide, virus, adsorption, polymer composite

酸化グラフェン（GO）は，厚みが約 1 nm のシート状炭素材料であり，高い比表面積，良好な水分散性を有していることから，色素・重金属・ウイルスなど様々な物質に対する吸着剤としての応用が検討されている [1,2]．GO は表面に豊富な酸素官能基（ヒドロキシ基，エポキシ基，カルボキシ基など）を有している．特にエポキシ基は，アミンと温和な条件でも反応し，共有結合形成による GO の表面修飾が可能である [1]．

一方，表面の酸素官能基は，GO に強い負電荷を与えるため，ポリエチレンイミンやポリアリルアミン等のカチオン性ポリマーを加えると速やかに凝集する．

本研究では，アリルアミンにより GO の表面にアルケン部位を形成した後，ラジカル重合を用いてポリマーを成長させる“grafting-form”法を用いることで，GO の急激な凝集を防ぎつつ，GO とアミノ基を有するカチオン性ポリマーの複合体（GO-PAAmH）の合成に成功した．次に，合成した複合体の吸着性能の評価を行った．カチオン性およびアニオン性色素を用いて，GO と今回合成した GO-PAAmH を比較すると，アニオン性色素に対してのみ GO-PAAmH の吸着性能の大幅な向上が確認された．また，この性能向上は PAAmH と GO を物理的に混ぜ合わせたものよりも顕著であった．さらに，表面に負電荷を有するウイルスへの吸着特性を検討したところ，GO に比べて GO-PAAmH は大幅な性能の向上が確認された．



1) Shibahara R., Kamiya K., Nishina Y., *Nanoscale Adv.,* 3, (2021), 5823-5829.
2） Pramanik A., Kolawole O., Ray P., *et al. ACS Omega,* 8, (2023), 44942-4495.

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四塩化鉄イオンを含むレドックス活性な柔粘性結晶の合成と固体冷媒への応用

（東大理[1]）○大野 拓哉[1]・周 泓遥[1]・山田 鉄兵[1]

Synthesis of redox-active plastic crystal containing tetrachloroferrate ion and its application to solid refrigerant ([1]*School of Science, Department of Chemistry, the University of Tokyo*)
○Takuya Ono,[1] Hongyao Zhou,[1] Teppei Yamada[1]

Plastic crystals (PCs) are a class of materials where the consisting molecules are isotropically rotating while maintaining an ordered lattice system. PCs show unique physical properties. For example, the phase transition from the solid to the PC phase is accompanied by a large entropy change (~20 J/g) due to the molecular rotations. In this study, we aim to control the phase transition by electrochemical redox reaction and apply plastic crystals as a solid refrigerant.

Choline tetrachloroferrate(III) [1)] ($ChlFeCl_4$) was synthesized by mixing choline chloride and ferrous (III) chloride. Differential scanning calorimetry revealed that this crystal transforms to the plastic phase at 6 °C. The redox activity of $ChlFeCl_4$ was evaluated by preparing its electrode. The electrochemical cell was fabricated with the electrode, which is paired with a Prussian blue analog electrode, and the two electrodes were separated by a solid polymer electrolyte (Figure 1a). Reversible charge–discharge curves (Figure 1b) show that $ChlFeCl_4$ is electrochemically active. The results of solid-state electrochemical refrigeration will be reported in the presentation.

Keywords :　Plastic Crystals; Redox-active Materials; Solid Refrigerants

柔粘性結晶ではその構成分子が規則的配列を保ちつつも等方性回転をしており、通常の結晶では見られない物性を示す。 例えば、固相から柔粘性結晶相への相転移時には、分子回転に由来する大きなエントロピー変化 (~20 J/g) を伴う。本研究では、電気化学的に相転移を制御し、柔粘性結晶の固体冷媒としての可能性を探索した。

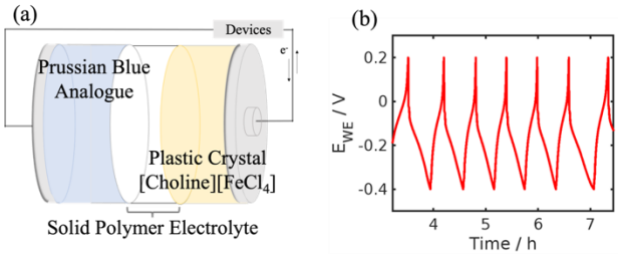

Figure 1. a) An electrochemical cell of $ChlFeCl_4$ paired with PBA as the counter electrode b) The charge and discharge curves measured at 5 μA cm^{-2}.

コリンとテトラクロロ鉄(III)酸 [1)] からなるイオン対 ($ChlFeCl_4$)を、塩化コリンと塩化鉄(III)を混ぜる事で合成した。示差走査熱量測定により 6 ℃で柔粘性結晶相への相転移が示された。また、プルシアンブルー類縁体を対極に組み二電極間に固体電解質を挟む事で、$ChlFeCl_4$ のレドックス活性を測定した (Figure 1a) 。可逆な充放電曲線 (Figure 1b) が得られ、$ChlFeCl_4$ がレドックス活性である事が示された。本発表では固体電気化学的冷却についての予備実験の結果も紹介する予定である。

1)　I. de Pedro et al., *Phys.Chem.Chem.Phys.*, **2013**, *15*, 12724

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L-アスコルビン酸固定化バイオマスの特性と Fe(III)に対する還元能

（中部大院工[1]・中部大工[2]）○池田 琉稀[1]・井垣 侑生[1]・秋永 拓未[1]・爾見 優子[2]・宮内 俊幸[2]
Characterization of Biomass adsorbed L-ascorbic acid and reducing ability for Fe(III)
([1]*Graduate of Chubu University*, [2]*Chubu University*) ○ Ryuki Ikeda,[1] Yui Igaki,[1] Takumi Akinaga,[1] Yuko Shikami,[2] Toshiyuki Miyauchi[2]

The solid reductant was prepared by adsorbing L-ascorbic acid on chemical treated biomass, such as Cedar, Beech and Kenaf. Its surface observed by XPS. As a result, polyamine was introduced by observation of nitrogen. Fe(III) was reduced by solid reductant. In the batch method, reducing Fe(III) in hydrochloric acid solution at 95 °C was 558 mg g^{-1} for based on Cedar. In the column method, when reducing 100 mg L^{-1} Fe(III) in hydrochloric acid solution at 100 °C, the reducing ability was 687 mg g^{-1} for based on Cedar. Adsorbing of L-ascorbic acid on biomass could to prepared a solid reductant with potential for industrial application.
Keywords : Solid reductant; Biomass; Ferric reduction; Chelate resin; L-ascorbic acid

【背景】L-アスコルビン酸は安価で還元作用に優れており、酸化を受けるとデヒドロアスコルビン酸に変化するが、他の化学反応へ影響を及ぼすことはない。しかし、水に溶けやすく還元後に分離が困難であり単一的な反応しか起こせない欠点がある。そこで、水に不溶な植物由来バイオマスへ L-アスコルビン酸を固定化することによりその欠点を克服し、連続的な反応を可能とする固体還元剤の合成を目指した。
【実験】植物由来バイオマスであるスギ、ブナおよびケナフへ塩酸を用いて前処理を行い不純物除去し、セルロースの末端アルデヒド基を活性化した。その後、トリエチレンテトラミンを用いてポリアミンの導入を行い、ポリアミン型キレート樹脂を得た。そのキレート樹脂へ、L-アスコルビン酸を吸着させ固体還元剤を合成した。この固体還元剤の物性評価と Fe(III)に対する還元能評価を行った。
【結果および考察】XPS での表面分析では、400 eV 付近に窒素由来のピークが検出され、ポリアミンの導入が確認できた。また、スギを基体とする固体還元剤を用いてバッチ法で還元操作を行ったところ 95 °C で最も高い還元能を示し、1 g あたり 558 mg の Fe(III)を還元した。さらに、カラム法では 100 mg L^{-1} の Fe(III)溶液を展開したところ、4000 mL まで溶出液中に Fe(III)は確認されず、還元量は 687 mg g^{-1} であった(Fig.1)。水に可溶である L-アスコルビン酸を植物由来バイオマスに固定化することで、水に不溶で連続反応に使用可能な固体還元剤の合成が可能であった。

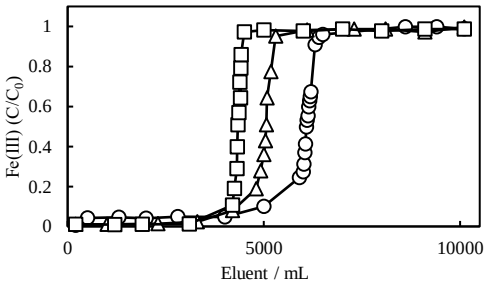

Fig. 1 Breakthrough curves for Fe(III) on biomass
Resin, 1.0 g; Column, 8φ × 400 mm; Flow rate, 2.5 mL min^{-1}; Temperature, 100 °C; Developing solution, 100 mg L^{-1} Fe(III) containing 0.3 mol L^{-1} HCl; ○, Based on Cedar; △, Based on Beech; □, Based on Kenaf.

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Academic Program [Oral A] | 21. Energy and Related Chemistry, Geo and Space Chemistry：Oral A

Wed. Mar 20, 2024 1:00 PM - 2:30 PM JST | Wed. Mar 20, 2024 4:00 AM - 5:30 AM UTC
A1455(1455, Bldg. 14 [5F])

[A1455-3pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Kenya Kubo, Masahiro Goto

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1455-3pm-01]
Thermoelectric property of nanosuructured MgSiSn thin films

○Masahiro Goto[1], Michiko Sasaki[1,2] (1. NIMS, 2. The Univ. of Tokyo)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1455-3pm-02]
Dependence of thermoelectric performance of PEDOT:PSS/Graphene multilayer thin films on the amounts of Graphene

○Keito Uchida[1], Yuma Watanabe[2], Syunya Sakane[2,3], Hideki Tanaka[2] (1. Chuo University Graduate School, 2. Chuo University, 3. Ibaraki University)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1455-3pm-03]
Characterization of Graphene/Copper Nanoparticle Composite Materials for Thermoelectric Conversion Application

○LIAO WEILI[1], Saitou Kouki[1], Sakane Shunya[1,2], Tanaka Hideki[1] (1. Chuo University Graduate School, 2. Ibaraki University)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1455-3pm-04]
Thermoelectric properties of Ag_2Se nanowires /BBL:PEI composite films and their composition dependence

○Haruna Kasugai[1], Shunichiro Miwa, Shunya Sakane[2,3], Hideki Tanaka[2] (1. Chuo University Graduate School, 2. Chuo University, 3. Ibaraki 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
[A1455-3pm-05]
Improvement of thermoelectric properties of α-Cu_2Se nanowires by annealing

○Yusuke Morikawa[1], Kazuki Munakata[1], Insoo Kang[2], Shunya Sakane[2,3], Hideki Tanaka[2] (1. Chuo University Graduate School, 2. Chuo University, 3. Ibaraki University)

Japanese
2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

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[A1455-3pm-06]

Study on amine solutions used for direct air capture using solar heat

○Ryo Murai[1], Yukio Furukawa[1], Dongmin Seo[1] (1. Waseda University)

Japanese

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

[A1455-3pm-07]

DFT-based Prediction of Half-Lives and Internal Conversion Spectra of ^{235m}U halide

○So Hashiba[1], Masashi Kaneko[1], Ryotaro Masuda[1], Yudai Shigekawa[2], Yoshitaka Kasamatsu[1] (1. Osaka University, 2. RIKEN)

Japanese

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

[A1455-3pm-08]

Noise Reduction in Neutron In-beam Mössbauer Spectroscopy

○Kenya Kubo[1], Mio Yoshida[2], Yasuo Watanabe[2], Yoshio Kobayashi[2], Wataru Sato[3], Jun Miyazaki[4], Mototsugu Mihara[5], Takashi Nagatomo[7], I-Huan Chiu[6], Takahito Osawa[6] (1. ICU, 2. University of Electro-communications, 3. Kanazawa Univ., 4. Dendai, 5. Osaka Univ., 6. JAEA, 7. RIKEN)

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MgSiSn 系薄膜熱電材料のナノ構造化と熱電特性

（物材機構[1]・東大工[2]）○後藤 真宏[1]・佐々木道子[1,2]

Thermoelectric properties of nanostructured MgSiSn-based thin films ([1] *Research Center for Materials Nanoarchitectonics(MANA), National Institute for Materials Science(NIMS)*, [2]*School of Engineering, The University of Tokyo*)○Masahiro Goto,[1] Michiko Sasaki[1,2]

In the field of materials development, attention is increasingly focused on the development of new materials that actively utilize not only the composition of elemental species but also the unique physical properties manifested by differences in their nanostructures. In order to do this efficiently, it is necessary to have a material fabrication method that can precisely, systematically, and efficiently change these properties. We have developed a combinatorial sputter coating system (COSCOS) to achieve the requirements. Thermoelectric thin films have much attention as a stand-alone power source for IoT devices; however, thermoelectric materials made of less toxic and inexpensive materials have problems with their low conversion efficiency. MgSiSn-based thermoelectric materials have excellent features such as low cost, non-toxicity, low density, and light weight. However, the performance is still not enough, and higher performance is desired. One way to achieve this is nanostructuring.

In this study, multilayer films of Mg_2Si and Sn with different thicknesses were fabricated using the sputtering method, and thin-film thermoelectric materials with different nanostructures were fabricated. The thermoelectric properties of these materials were significantly changed, and a guideline for improving thermoelectric properties by nanostructuring was obtained.

Keywords : Thermoelectric; Sputter; Thin film; Combinatorial; Nanostructure

材料開発分野において、元素種の組成だけではなく、そのナノ構造の違いによる特異な物性発現を積極的に活用した新規材料開発が注目されつつある。これを効率良く実行するためには、これを精確にかつ系統的に効率良く変化させられる材料作製手法が必要である。我々は、これを実現するためにコンビナトリアルスパッタコーティングシステム（COSCOS）を開発した。今回は、熱電薄膜への応用を行った。IoT デバイスの自立電源として熱電材料が注目されているが、毒性が少なく、安価な材料を用いた熱電材料は、その変換効率が低い問題を抱えている。そこで、その代表的な材料の一つである MgSiSn 系薄膜のナノ構造制御が可能かどうかを検証すると共に、熱電性能向上の可能性を検討した。今回、膜厚の異なる Mg_2Si と Sn の多層膜を作製し、ナノ構造の異なる薄膜熱電材料を作製した。それらの熱電特性は大きく変化し、ナノ構造化による熱電特性向上の指針が得られた。

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PEDOT:PSS/グラフェン積層薄膜における熱電特性向上の熱電特性におけるグラフェン積層量依存性

（中央院理工 [1]・中央理工 [2]・茨大院理工 [3]）○内田 京杜 [1]・渡邊 勇真 [2]・坂根 駿也 [3]・田中 秀樹 [2]

Dependence of thermoelectric performance of PEDOT:PSS/Graphene multilayer thin films on the amounts of Graphene

([1] *Faculty of Science and Engineering, Chuo University Graduate School*, [2]*Faculty of Science and Engineering, Chuo University,* [3]*Faculty of Science and Engineering, Ibaraki University Graduate School*) ○Keito Uchida,[1] Yuma Watanabe,[2] Shunya Sakane,[3] Hideki Tanaka[2]

Thermoelectric materials can directly convert heat into electricity. Among them, PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid)) is expected to improve performance for π-π interaction with graphene. In this study, PEDOT:PSS/graphene multilayer thin films were prepared by spin-coating method to measure the dependence of performance on the amount of graphene and elucidate the mechanism. Graphene and PEDOT:PSS solution were stacked on a glass substrate and finally annealed (300 °C) to prepare the sample. The structure was evaluated by Raman spectroscopy, and the thermoelectric performance was evaluated by measuring the electrical conductivity σ by van der Pauw method and the Seebeck coefficient S by a self-made device. From the Raman spectrum, a band of C=C symmetric stretching of PEDOT was observed. The π-π interaction was confirmed by the shift of this to the higher wavenumber compared to PEDOT:PSS alone. σ increased compared to graphene alone as the amount of graphene increased, and then began to decrease. This may be due to a fluctuation in the effect of interfacial π-π interactions on the sample.S increased compared to graphene alone, but remained constant regardless of the amount of graphene. The above shows that the enhancement of thermoelectric performance due to the π-π interaction is mainly observed at σ and is maximized at the amount of graphene where the interaction is maximized.

Keywords：*Thermoelectric materials; Graphene; PEDOT:PSS; Electrical conductivity; Spin coating*

熱電材料は熱を電気に直接変換出来る。その中でも PEDOT:PSS(ポリ(3,4-エチレンジオキシチオフェン):ポリスチレンスルホン酸)は、グラフェンとの π-π 相互作用による性能向上が期待されている[1]。本研究は、スピンコート法で PEDOT:PSS/グラフェン積層薄膜を作成し、熱電性能のグラフェン積層量依存性の測定及び機構解明を目的とした。

ガラス基板上に、グラフェン及び PEDOT:PSS 溶液を積層し、最後にアニール(300 ℃)を行い試料を作成した。ラマン分光法で構造評価を行い、van der Pauw 法で電気伝導率σを、自作装置でゼーベック係数 S をそれぞれ測定する事で熱電性能評価を行った。

ラマンスペクトルより、PEDOT の C=C 対称伸縮のバンドが観測された。このバンドが PEDOT:PSS 単体に比べて高波数側にシフトしていたことから π-π 相互作用の形成を確認した。σは、グラフェン積層量の増加に伴いグラフェン単体に比べ一旦増加した後、減少に転じた。これは試料に与える界面の π-π 相互作用の影響の増減に由来すると考えられる。また S は、グラフェン単体に比べ増加したが、グラフェン積層量に関係せず一定であった。以上より、π-π 相互作用による熱電性能の向上は主としてσで見られ、相互作用が最大化されたグラフェン積層量において最大化される事が分かった。

1) K. Xu, G. Chen, and D. Qiu, *J. Mater. Chem. A,* **2013**, *1*, 12395‐12399.

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熱電変換応用に向けたグラフェン/銅ナノ粒子複合材料のアニール効果

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Annealing Effect on Graphene/Copper Nanoparticle Composite Materials for Thermoelectric Conversion Application ([1] *Faculty of Science and Engineering, Chuo University Graduate School*, [2]*Faculty of Science and Engineering, Ibaraki University Graduate School*) 〇Weili Liao,[1] Kouki Saito,[1] Shunya Sakane,[2] Hideki Tanaka[1]

Thermoelectric materials can directly convert thermal energy to electric energy. Previously, we have reported an enhancement in conductivity (σ) by combining graphene and copper nanoparticles, forming a conductive bridge. In this study, we synthesized graphene and copper nanoparticles via the photoreduction method, investigating the optimal annealing conditions by varying parameters such as annealing duration and temperature. I used Photoreduction first, I made a solution comprises 3% of copper acetate, 2% of graphene dispersion, 95% of ethanol. They were irradiated by ultraviolet rays at 24hours.I dropped the solution which was after irradiation on the glass substrate, then spin coated it, finally annealed it in an electric stove (300,350,400℃) to prepare the sample. The structure was evaluated by X-RAY diffraction and scanning electron microscopy, and the thermoelectric performance was evaluated by measuring the electrical conductivity σ by van der Pauw method and the Seebeck coefficient S by a self-made device. From X-RAY diffraction, I can get the peak of copper nanoparticles and identify the presence of different phases such as copper oxide crystal surface (200) peak in 36 degrees and copper crystal surface (111) peak in 42 degrees. From scanning electron microscopy, I got the size and distribution of copper nanoparticles and copper nanoparticles were observed.
Keywords：*Thermoelectric materials, Copper nanoparticle, Graphene, Seebeck coefficient*

熱電材料は、熱を直接電気エネルギーに変換可能材料である。これまで我々は、グラフェンと銅ナノ粒子を組み合わせることで導電ブリッジが形成され、ゼーベック係数 S を向上することを報告してきた。本研究では、光還元法によりグラフェンと銅ナノ粒子を合成し、アニール処理時間や処理温度などを変え、最適なアニール条件を調査した。光還元法を最初に使用し、酢酸銅 3%、グラフェン分散液 2%、エタノール 95%からなる溶液を作製し、紫外線に 24 時間照射された。照射後の溶液をガラス基板に滴下し、スピンコートし、電気炉で(300,350,400℃)アニールし、試料を作製した。試料の構造は X 線回折と走査型電子顕微鏡によって評価され、van der Pauw法による電気伝導率σと自作の装置によるSeebeck係数Sの測定で評価された。X 線回折から、銅のピークを得ることができ、酸化銅結晶表面(200)のピークが 36 度に、銅結晶表面(111)のピークが 42 度にあることが確認された。走査型電子顕微鏡から、銅ナノ粒子のサイズと分布を得ることができ、銅ナノ粒子が観察された。

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Ag_2Se ナノワイヤ/BBL:PEI 複合膜の熱電特性およびそのナノワイヤ含有量依存性

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Thermoelectric properties of Ag_2Se nanowires /BBL:PEI composite films and their composition dependence ([1]*Graduate School of Science and Engineering, Chuo University*, [2]*Faculty of Science and Engineering, Chuo University*, [3] *Faculty of Science and Engineering, Ibaraki University Graduate School*) ○Haruna Kasugai[1], Syunichiro Miwa[1], Shunya Sakane[3], Hideki Tanaka[2]

Thermoelectric (TE) materials can directly convert heat into electricity, evaluated by the power factor ($S^2\sigma$) using the Seebeck coefficient (S) and electrical conductivity (σ). Organic materials are promising for utilizing waste heat near room temperature. BBL:PEI (Poly(benzobisimidazobenzophenanthroline):Polyethyleneimine) is an n-type organic TE material with more than an order of magnitude lower σ compared to p-type materials[1], presenting a challenge for improving its performance. In this study, Ag_2Se nanowires (NWs) were introduced into BBL:PEI to enhance its TE properties. BBL:PEI and Ag_2Se NWs were alternately filtered to create a stacked thin film. Varying the amount of Ag_2Se, its effect on TE properties was measured. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) were used for structural characterization. TE properties were evaluated by measuring S and σ using a homemade device and the van der Pauw method, respectively. Increasing the amount of Ag_2Se NWs led to an increase in σ. This can be attributed to the formation of conductive paths through the NWs' structure. While σ increased, S remained constant, resulting in $S^2\sigma$.

Keywords : Thermoelectric materials; Silver selenide; Nanowires; Conductive polymer; Photoreduction

熱電材料は、熱を電気に直接変換することが出来、その性能はゼーベック係数 S、電気伝導率 σ を用いて出力因子($S^2\sigma$)で評価することが出来る。室温近傍の廃熱を利用する熱電材料として有機材料が注目されている。BBL:PEI(ポリ(ベンゾビスイミダゾベンゾフェナントロリン:ポリエチレンイミン)は n 型の有機熱電材料であり、p 型よりも σ が二桁低いことから[1]、より性能の向上が課題となっている。本研究では、BBL:PEI に Ag_2Se ナノワイヤ(NWs)を導入し、BBL:PEI の熱電性能の向上を目指した。BBL:PEI と Ag_2Se NWs を交互に吸引ろ過し、積層薄膜を作製した。このとき Ag_2Se の含有量を変化させ、その物性変化を測定した。構造評価は、X 線回折法(XRD)、走査型電子顕微鏡(SEM)、エネルギー分散型 X 線分析(EDX)を行った。物性評価は、自作装置による S の測定と、van der Pauw 法にて σ の測定を行った。

Ag_2Se NWs の含有量が大きくなるほど σ は増加した。これは、Ag_2Se を加えたことで、NWs 構造による伝導パスが形成されたためであると考えられる。σ が増加した一方で S は維持されたため、出力因子は向上した。

1) Yang, L, *et al. Chem. Mater*. **2019**, 31, 6412−6423.

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α-Cu_2Se ナノワイヤにおけるアニールによる熱電特性向上

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Improvement of thermoelectric properties of α-Cu_2Se nanowires by annealing([1]*Graduate School of Science and Engineering, Chuo University*, [2]*Faculty of Science and Engineering, Chuo University*, [3] *Graduate School of Science and Engineering, Ibaraki University*) ○ Yusuke Morikawa,[1] Kazuki Munakata,[1] Insoo Kang,[2] Shunya Sakane,[3] Hideki Tanaka[2]

Thermoelectric materials can directly convert thermal energy into electrical energy, and their performance can be evaluated by the power factor ($S^2\sigma$), where S is Seebeck coefficient and σ is electrical conductivity. Copper selenide is a low-cost and low-toxicity thermoelectric material, among which α-Cu_2Se exhibits high $S^2\sigma$ at room temperature. In our previous work, we have successfully synthesized single-phase α-Cu_2Se nanowires (NWs) using photoreduction method[1)]. In this study, we aimed to improve $S^2\sigma$ by synthesizing single-phase α-Cu_2Se NWs using a photoreduction method and improving the crystallinity by annealing. Se NWs were synthesized according to a previous report, mixed with an aqueous copper acetate solution and ethanol, and then α-Cu_2Se NWs were synthesized by irradiation with ultraviolet light. A thin film was prepared by cold pressing α-Cu_2Se NWs, and then annealed in vacuum to evaluate the thermoelectric properties. Scanning electron microscopy (SEM) revealed that the α-Cu_2Se NWs thin film maintained its wire structure even after annealing. Furthermore, X-ray crystal structure analysis (XRD) revealed that α-Cu_2Se was retained. Regarding thermoelectric properties, S decreased, but σ improved, resulting in an improvement in $S^2\sigma$. The significant increase in σ is thought to be due to improved crystallinity.
Keywords : Thermoelectric materials; Cu_2Se; Nanowires; Vacuum annealing; Photoreduction

熱電材料は熱を直接電気エネルギーに変換可能であり、その性能はゼーベック係数 S と電気伝導率σを用いて出力因子 ($S^2\sigma$)で評価できる。セレン化銅は低コストで低毒性の熱電材料であり、中でもα-Cu_2Se は室温で高い $S^2\sigma$を示す。これまで、我々は光還元法を用いて単相α-Cu_2Se ナノワイヤ (NWs)の合成に成功してきた[1)]。本研究では光還元法を用いて単相α-Cu_2Se NWs を合成し、アニールによりα-Cu_2Se NWs の結晶性を向上させることで$S^2\sigma$を向上させることを目的とした。

既報に従って Se NWs を合成し、酢酸銅水溶液、エタノールと混合した後、紫外光照射によりα-Cu2Se NWs を合成した。α-Cu_2Se NWs をコールドプレスして薄膜を作製し、その後真空でアニールをして熱電特性評価を行った。

走査型電子顕微鏡 (SEM)より、アニール後もα-Cu_2Se NWs 薄膜はワイヤ構造を保っていることが分かった。また X 線結晶構造解析 (XRD)により、α-Cu_2Se を保持していることがわかった。さらに熱電特性に関しては、S は低下したがσは向上し結果として $S^2\sigma$が向上した。σが大幅に増加したことから、結晶性が向上したことが考えられる。

1) Sakane, S. *et al*. *ACS Omega* **2022**, *7*, 32101-32107.

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太陽熱を利用する大気 CO_2 回収に使用するアミン回収液に関する研究

（早大院・理工）○村井稜・徐東民・古川行夫

Study on amine solutions used for direct air capture using solar heat

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○Ryo Murai, Dongmin Seo, Yukio Furukawa

A method for capture of CO_2 from the atmosphere is called direct air capture (DAC). DAC is necessary for negative CO_2 emission. However, high cost of DAC is a problem to be solved. In this paper, we have performed a feasibility study on a new low-cost DAC method with an amine solution absorbent and solar heat CO_2 desorption. The amine solution requires large CO_2 absorption at a low CO_2 concentration (about 400 ppm) of the atmosphere. A DMSO solution of MEA (30 wt%, 5.28 mol/L) and a DMSO solution of benzylamine (BZA) (30 wt%, 2.97 mol/L) were used as absorbents. A 50 mL amine solution in a flat container was placed in a room for 24 h. The reaction products and the absorbed CO_2 contents in the absorbents were determined using ^{13}C-NMR. The carbamate and carbamic acid were formed from the reaction between CO_2 and amine. These species cannot be separately observed by ^{13}C-NMR. ^{13}C-NMR results indicated that the adsorbed CO_2 contents of the MEA and BZA solutions were 1.74 mol/L (amount of absorbed CO_2/amount of amine L = 0.33, near the equilibrium value) and 0.78 mol/L (L = 0.26), respectively. We regenerated CO_2 from the absorbents using a solar cooker (heater power in sunny weather, about 400 W/m^2). The CO_2 desorption efficiencies of the MEA and BZA solutions were 100 and 94 %, respectively. The temperatures of the absorbents probably were in the range from 100 to 140 °C. As a result, a DAC method based on the amine solution absorbent and solar heating is promising.

Keywords: CO_2 capture; direct air capture; ^{13}C-NMR; amine absorbent; solar heat

CO_2 を大気から直接回収する方法は direct air capture (DAC）と呼ばれている．CO_2 ネガティブエミッションを実現するためには DAC が必要であるが，コストが高いことが問題となっている．本研究では，CO_2 回収剤としてアミン溶液を用い，太陽熱により CO_2 を放散する低コスト DAC の実現性を検討した．アミン溶液としては，大気中の低い CO_2 濃度（約 400 ppm）でも吸収量が大きいことが必要である．MEA の DMSO 溶液（30 wt%, 5.28 mol/L）と benzylamine (BZA)の DMSO 溶液（30 wt%, 2.97 mol/L）などに関して，50 mL の溶液を静置して大気中 CO_2 を 24 h 吸収させた．^{13}C-NMR を用いて CO_2 とアミンの反応生成物を明らかにして吸収された CO_2 量を測定した．CO_2 はアミンと反応してカルバメートまたはカルバミン酸（これらの化合物は ^{13}C-NMR で区別できない）として溶液中に蓄えられた．MEA と BZA 溶液の CO_2 吸収量はそれぞれ 1.74 mol/L（吸収 CO_2 物質量/アミン物質量 L = 0.33，ほぼ平衡時の値）と 0.78 mol/L（L = 0.26）となった．ソーラークッカー（晴れの天気でヒーター出力約 400 W/m^2）を用いて太陽熱による CO_2 放散を行った．MEA と BZA 溶液の放散率はそれぞれ 100 と 94 %であり，溶液の温度は 100～140 °C 程度になっていると推測される．以上の結果は，太陽熱を利用した DAC は有望であることを示している．

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DFT 計算による ^{235m}U ハロゲン化物の半減期・内部転換電子スペクトルの予測

(阪大理[1]・阪大院理[2]・理研[3]) ○橋場 奏[1]・金子 政志[2]・益田 遼太郎[2,3]・重河 優大[3]・笠松 良崇[2,3]

DFT-based Prediction of Half-Lives and Internal Conversion Spectra of ^{235m}U halides ([1]*School of Science, Osaka University,* [2]*Graduate School of Science, Osaka University*, [3]*RIKEN*) ○So Hashiba,[1] Masashi Kaneko,[2] Ryotaro Masuda,[2,3] Yudai Shigekawa,[3] Yoshitaka Kasamatsu[2,3]

^{235m}U is an excited state of the ^{235}U nucleus and decays through the internal conversion (IC) process by emitting the orbital electrons. The excitation energy of ^{235m}U with 76.8 eV is extremely low. This situation enables the interaction between the ^{235m}U nucleus and the outer-shell electrons, leading to the variation of the half-life depending on its chemical environment.[1)] We previously investigated the change of the half-life and the IC electron spectrum of ^{235m}U collected on Cu and reacted with hydrogen halide gas. However, the chemical states of ^{235m}U were unclear and the mechanism of the variety of half-life has not been fully elucidated.
In this study, relativistic DFT calculations were performed for uranyl (VI) halide complexes comprehensively as well as population analysis. The possible chemical species were predicted by comparing the density of states (DOS) with the experimental IC electron spectra. The calculation of the half-life of the estimated chemical species was also demonstrated.
Keywords : DFT calculation, Half-life, ^{235m}U, Nuclear isomer, Internal conversion

^{235m}U は ^{235}U 原子核の励起状態であり、軌道殻電子にエネルギーを与える内部転換過程により脱励起する。励起エネルギーが 76.8 eV と非常に小さいため、外殻電子のみ放出され、半減期は化学状態により変化することが知られている[1)]。これまで、本研究グループにより、銅板上に捕集した U に対しハロゲン化水素ガスと反応させ、半減期及び内部転換電子スペクトルの測定が行われた。しかし、^{235m}U の化学状態は不明であり、半減期変化の詳細なメカニズムは解明されていない。

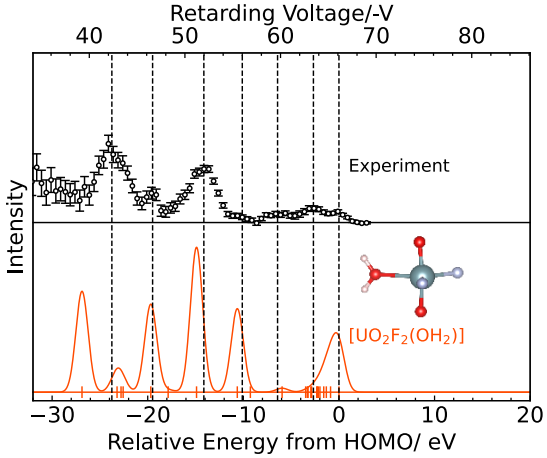

Fig. 1 Experimental Spectrum of ^{235m}U reacted with HF and calculated partial density of states (PDOS) of uranium 6p orbital.

本研究では、六価ウラニル(UO_2^{2+})に対しハロゲンを配位させた化合物に対し、網羅的に相対論的 DFT 計算を行った。密度解析による結果と内部転換電子スペクトルの比較から、^{235m}U がどのような化学状態を取っているのかの推定を行った。さらに、実験と最も近い化学種に対し半減期の計算を行い、実験値との比較、半減期変化の考察を行った。

1) M. Neve de Mevergnies, *et.al.*, Phys. Lett., **49B**, 428 (1974).

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中性子インビームメスバウアー分光法のノイズ低減

(国際基督教大[1]・電通大[2]・金沢大[3]・東京電機大[4]・大阪大[5]・理研[6]・原研[7]) ○久保謙哉[1]・吉田実生[2]・渡辺裕夫[2]・小林義男[2]・佐藤渉[3]・宮﨑淳[4]・三原基嗣[5]・長友傑[6]・邱奕寰[7]・大澤崇人[7]

Noise Reduction in Neutron In-beam Mössbauer Spectroscopy ([1]*ICU,* [2]*University of Electro-Communications,* [3]*Kanazawa University,* [4]*Tokyo Denki University,* [5]*Osaka University,* [6]*RIKEN,* [7]*JAEA*)○M. Kenya Kubo,[1] Mio Yoshida,[2] Yasuo Watanabe,[2] Yoshio Kobayashi,[2] Wataru Sato,[3] Jun Miyazaki,[4] Mototsugu Mihara,[5] Takashi Nagatomo,[6] I-Huan Chiu,[7] Takahito Osawa[7]

Neutron in-beam Mössbauer spectroscopy using the ^{56}Fe(n, γ)^{57}Fe reaction provides information about the chemical and physical states of the ^{57}Fe atoms after the nuclear reaction with a MeV order of energy. We constructed an in-beam Mössbauer spectroscopy system at the PGA port of the JRR-3 nuclear reactor at JAEA before the Great East Japan Earthquake. During the ten-year-long shutdown of the JRR-3 facility after the quake, we developed a very effective noise reduction method for the in-beam Mössbauer spectroscopy of ^{57}Fe originating from the β-decay of ^{57}Mn using an anti-coincidence detection of β-rays and γ-rays at the Heavy Ion Medical Accelerator in Chiba (HIMAC). We try to apply a similar noise reduction method to improve the quality of the in-beam Mössbauer spectra after the resumption of JRR-3. The configuration change at the PGA port did not allow a replication of the previous experiments. Several adaptations to the new configuration were carried out. A Mössbauer spectrum of a stainless-steel foil was obtained as a first step.

Keyword: In-beam Mössbauer spectroscopy, ^{56}Fe(n, γ)^{57}Fe reaction, noise reduction

中性子捕獲反応 ^{56}Fe(n, γ)^{57}Fe を利用した ^{57}Fe のインビームメスバウアー分光法は、中性子捕獲反応という非常に高い核反応エネルギーを経験した ^{57}Fe 原子の生成後約 1 μs 以内の ^{57}Fe 原子の化学的および物理的状態に関する情報を与える．我々は原子力研究所(JAEA)東海キャンパスにある 3 号炉の即発 γ 線分析(PGA)ポートで ^{57}Fe のインビームメスバウアー分光実験を行っていたが，東日本大震災によって 3 号炉は 10 年あまり閉鎖となった．その間に重イオン加速器施設 HIMAC で ^{57}Mn を線源とする ^{57}Fe のインビームメスバウアー分光法のためにβ線とγ線の反同時計数という新たなノイズ低減法を開発し，SN 比を 10 倍改善することに成功した．3 号炉の運転再開とともに，新しいノイズ低減法を中性子インビームメスバウアー分光法へ適用すべく実験を再開した．PGA ポート周辺の装置配置変更により震災前と全く同様の装置配置はできなくなり SN 比が低下した．種々装置の再配置等の試行錯誤を繰返し，過去と同程度の SN 比でステンレス箔のメスバウアースペクトルの取得に成功した．今後さらにβ-γ反同時計数による SN 比の改善を実施し，種々の鉄化合物に対してインビームメスバウアー分光測定を行う予定である．

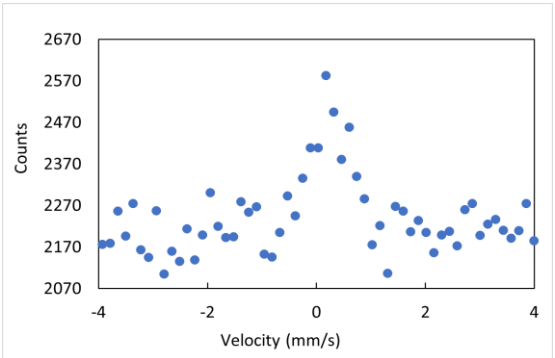

Figure 1. Neutron in-beam Mössbauer spectrum of a stainless-steel foil.

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