

Sat. Mar 26, 2022

A204

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

[A204-4pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational ChemistryChair: Takeshi Yoshikawa, Hirotoshi Mori
1:30 PM - 2:50 PM A204 (Online Meeting)**[A204-4pm-01] Development of a highly accurate docking scoring function using machine learning**○Shota Minami¹, Kazuhiro Fujimoto¹, Takeshi Yanai¹ (1. Nagoya University)

1:30 PM - 1:50 PM

[A204-4pm-02] Chemical-Data-Driven Validation of Physical Theories of Liquid Crystals○Yoshiaki Uchida¹, Shizuo Kaji², Naoto Nakano³ (1. Osaka University, 2. Kyushu University, 3. Kyoto University)

1:50 PM - 2:10 PM

[A204-4pm-03] Atomic-Number-Correlated Molecular Model for Deciphering Transmission Electron Microscopic Images○Koji Harano¹, Junfei Xing¹, Keishi Takeuchi¹, Ko Kamei¹, Takayuki Nakamuro¹, Eiichi Nakamura¹ (1. The University of Tokyo)

2:10 PM - 2:30 PM

[A204-4pm-04] Electronic Structure Informatics of Singlet Fission in Indigoids○Fabian Weber¹, Hirotoshi Mori^{1,2} (1. Chuo University, Tokyo, 2. Institute for Molecular Science (IMS), Okazaki)

2:30 PM - 2:50 PM

F302

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

[F302-4am] 03. Physical Chemistry -Structure-Chair: Hirosuke Matsui, Hiro Minamimoto
9:00 AM - 10:40 AM F302 (Online Meeting)**[F302-4am-01] *In situ* HERFD-XANES/RIXS measurements of adsorbed oxygen species on Pt/C electrocatalysts in polymer electrolyte fuel cells under operating conditions**○Hiroko Miwa¹, Takefumi Yoshida¹, Tomoya Uruga², Takehiko Sasaki³, Takuma Kaneko²,Tomohiro Sakata², Kotaro Higashi², Oki Sekizawa², Yasuhiro Iwasawa¹ (1. The University of Electro-Communications, 2. Japan Synchrotron Radiation Research Institute, 3. The University of Tokyo)

9:00 AM - 9:20 AM

[F302-4am-02] 3D imaging of degradation process at the interface of rubber and metal by CT-XAFS○Hirosuke Matsui¹, Yuta Muramoto¹, Tomoya Uruga², Takashi Kakubo³, Naoya Amino³, Duy Tai Dinh⁴, Hieu Chi Dam⁴, Mizuki Tada¹ (1. Nagoya University, 2. JASRI/SPRING-8, 3. The Yokohama Rubber Co. Ltd., 4. JAIST)

9:20 AM - 9:40 AM

[F302-4am-03] Adsorption structure of water on Pt(533)Naoki Nagatsuka¹, Toya Muratani¹, Noboru Shibata¹, Ichihiko Tsuchiya¹, ○Kazuya Watanabe¹ (1. Graduate School of Science, Kyoto Univ.)

9:40 AM - 10:00 AM

[F302-4am-04] Adsorption and surface reaction of formic acid on Cu(977) surface with a (100) microfacet○Wataru Osada¹, Shunsuke Tanaka¹, Young Hung Choi¹, Kozo Mukai¹, Jun Yoshinobu¹ (1. The Institute for Solid State Physics, University of Tokyo)

10:00 AM - 10:20 AM

[F302-4am-05] Spectroscopic Investigation of High Pressure Hydrogen Evolution Reaction○Nobuaki Oyamada¹, Hiro Minamimoto², Kei Murakoshi² (1. Hokkaido University Graduate School of Chemical Sciences and Engineering, 2. Hokkaido University Faculty of Science)

10:20 AM - 10:40 AM

F203

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

[F203-4am] 04. Physical Chemistry -Properties-Chair: Tomoyuki Mochida, Takashi Takeda
9:00 AM - 10:40 AM F203 (Online Meeting)**[F203-4am-01] Effects of Formamides on Intermolecular Vibrations of 1- Methyl-3-**

Octylimidazolium Tetrafluoroborate

○Masatoshi Ando¹, Yue Peng¹, Atsuya Tashiro²,

Masahiro Kawano², Toshiyuki Takamuku²,
Hideaki Shirota¹ (1. Chiba University, 2. Saga
University)

9:00 AM - 9:20 AM

[F203-4am-02] Alkyl chain length dependence of
conformational distribution in ionic
liquids.

○Hiroki Sumida¹, Yoshifumi Kimura^{1,2},
Takatsugu Endo² (1. Graduate School of
Science and Engineering, Doshisha University,
2. Faculty of Science and Engineering,
Doshisha University)

9:20 AM - 9:40 AM

[F203-4am-03] Effect of Substrate Surface on Photo-
induced Crawling Motion of Azobenzene
Crystals and its Application

○Yasuo Norikane^{1,2}, Masaru Hayashino^{2,1}, Mio
Ohnuma¹, Kouji Abe¹, Yoshihiro Kikkawa¹,
Koichiro Saito¹, Kengo Manabe¹, Kouji Miyake¹,
Miki Nakano¹, Naoki Takada¹ (1. National
Institute of Advanced Industrial Science and
Technology (AIST), 2. University of Tsukuba)

9:40 AM - 10:00 AM

[F203-4am-04] Mass transport of nano/micro materials
driven by photo-induced crawling motion
of crystals

○Koichiro Saito¹, Yasuo Norikane^{1,2} (1.
National Institute of Advanced Industrial
Science and Technology (AIST), 2. University of
Tsukuba)

10:00 AM - 10:20 AM

[F203-4am-05] Study on the Mechanism of Bending in the
Crystals of Benzene Derivatives with
Halogen and Methyl Groups

○Hayato Anetai¹, Yoshitaka Matsushita²,
Takahito Ohmura², Masayuki Takeuchi² (1.
NIMS ICYS, 2. NIMS)

10:20 AM - 10:40 AM

J401

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

[J401-4am] 07. Inorganic Chemistry

Chair: Minoru Osada, Yuichi Shimakawa

9:00 AM - 11:40 AM J401 (Online Meeting)

[J401-4am-01] Electron doping into La doped Sr_2IrO_4 by

hydrogen ion beam irradiation

○Yuta Yamashita¹, Mitsuhiro Maesato¹,
GyeongCheol Lim¹, Akira Chikamatsu^{2,4}, Tetsuya
Hasegawa², Takahiro Ozawa³, Markus Wilde³,
Katsuyuki Fukutani^{3,5}, Hiroshi Kitagawa¹ (1.
Fac. of Science, Kyoto Univ., 2. Dept. of
Chemistry, The Univ. of Tokyo, 3. Inst. of
Industrial Science, The Univ. of Tokyo, 4. Fac. of
Science, Ochanomizu Univ., 5. NSEC, JAEA)

9:00 AM - 9:20 AM

[J401-4am-02] Highly electron doped TaON single crystal
-growth and properties-

○Kohdai Ishida¹, Daichi Kato¹, Hiroshi
Kageyama¹ (1. Department of Energy and
Hydrocarbon Chemistry, Graduate School of
Engineering, Kyoto University)

9:20 AM - 9:40 AM

[J401-4am-03] Structure-property relationships in
geometrically frustrated magnets
 $\text{Ln}_2\text{LiFeO}_6$ with unusually high valence
 Fe^{5+} ion

○Masato Goto¹, Sean Injac¹, Takashi Saito²,
Akira Matsuo³, Koichi Kindo³, Tamio Oguchi⁴,
Yuichi Shimakawa¹ (1. Kyoto University, 2.
KEK, 3. The University of Tokyo, 4. Osaka
University)

9:40 AM - 10:00 AM

[J401-4am-04] Conduction mechanism Analysis of Mixed
Anion Compounds $\text{La}_2\text{SrF}_4\text{S}_2$

○Shintaro Tachibana¹, Kazuto Ide², Hisatsugu
Yamasaki², Takeshi Tojigamori², Hidenori Miki²,
Takashi Saito³, Takashi Kamiyama³, Yuki
Orikasa¹ (1. Ritsumeikan University, 2. Toyota
Motor Corporation, 3. High Energy Accelerator
Research Organization)

10:00 AM - 10:20 AM

[J401-4am-05] Dynamics, Geometry, and Electronic State
of Single Ag(I) Site in MFI Zeolite Efficient
for Xe Adsorption/Separation

○Akira Oda^{1,2}, Hiroe Kozai³, Kyoichi Sawabe^{1,2},
Atsushi Satsuma^{1,2}, Takahiro Ohkubo³,
Yasushige Kuroda³ (1. Nagoya University, 2.
Elements Strategy Initiative for Catalysts and
Batteries (ESICB), 3. Okayama University)

10:20 AM - 10:40 AM

[J401-4am-06] Synthesis and Evaluation of Hyper-

multinary Compound by Utilizing Quasi-sub-nanoparticle

○Takamasa Tsukamoto^{1,2,3}, Nozomi Yoshida¹, Tatsuya Moriai¹, Tetsuya Kambe^{1,3}, Kimihisa Yamamoto^{1,3} (1. Tokyo Institute of Technology, 2. PRESTO, JST, 3. ERATO, JST)
10:40 AM - 11:00 AM

[J401-4am-07] Successive phase transitions caused by unusually high valence Fe^{3.5+} ions in A-site layer-ordered double-perovskites $RBaFe_2O_6$ (R =rare earth metals)
○Makoto Iihoshi¹, Sean Dusan Injac¹, Midori Patino Amano¹, Masato Goto¹, Yuichi Shimakawa¹ (1. Kyoto Univ.)
11:00 AM - 11:20 AM

[J401-4am-08] VT-VH-MCD Spectroscopic Study of the Magnetic Interaction in the Excited States of Lanthanide-Porphyrin Complexes with Different Hetero-Cyclododecane Ligands
○Langit Cahya Adi¹, Anas Santria¹, Naoto Ishikawa¹ (1. Chemistry Department, Graduate School of Science, Osaka University)
11:20 AM - 11:40 AM

B304

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

[B304-4am] 08. Catalysts and Catalysis

Chair: Yosuke Kageshima, Hideki Kato

9:00 AM - 11:20 AM B304 (Online Meeting)

[B304-4am-01] Photoelectrochemical Water Oxidation in visible light over a Lead-Titanium Oxyfluoride Photoanode Prepared by a Particle Transfer Method
○Ryusuke Mizuochi¹, Kengo Oka², Kazuhiko Maeda¹ (1. Tokyo Institute of Technology, 2. Kindai University)
9:00 AM - 9:20 AM

[B304-4am-02] Measurement of the pseudo overpotential for water oxidation by nano-sized heterogeneous metal oxide catalyst
○Megumi Okazaki¹, Yasuomi Yamazaki², Shunsuke Nozawa³, Osamu Ishitani¹, Kazuhiko Maeda¹ (1. Tokyo Institute of Technology, 2. Seikei University, 3. High Energy Accelerator Research Organization)

9:20 AM - 9:40 AM

[B304-4am-03] Synthesis and Photocatalytic Hydrogen Peroxide Production on Zr-MOF with Missing-Linker Defects
○Yoshifumi Kondo¹, Yasutaka Kuwahara^{1,2,3}, Kohsuke Mori^{1,2}, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. PRESTO, JST)
9:40 AM - 10:00 AM

[B304-4am-04] Investigation of Photocatalytic CO₂ Reduction using Photoconductive Coordination Polymer with Metal–Sulfur Bonds
○Yoshinobu Kamakura¹, Disuke Tanaka², Kazuhiko Maeda¹ (1. Tokyo Institute of Technology, 2. Kwansei Gakuin University)
10:00 AM - 10:20 AM

[B304-4am-05] Plasma surface modification of C₃N₄ improves durability of photocatalytic CO₂ reduction with RuRu supramolecular photocatalyst
○Noritaka Sakakibara¹, Mitsuhiro Shizuno¹, Tomoki Kanazawa², Akira Yamakata³, Shunsuke Nozawa², Tsuyohito Ito⁴, Kazuo Terashima⁴, Kazuhiko Maeda¹, Osamu Ishitani¹ (1. Tokyo Tech., 2. KEK, 3. TTI, 4. The Univ. of Tokyo)
10:20 AM - 10:40 AM

[B304-4am-06] Development of PtRu alloy nanoparticle cocatalysts for water splitting photocatalysts
Christian Mark Pelicano¹, ○Masaki Saruyama¹, Toshiharu Teranishi¹ (1. Kyoto Univ.)
10:40 AM - 11:00 AM

[B304-4am-07] Noble metal-based nanostructured catalysts for hydrogenation and dehydrogenation reactions via plasmon-assisted catalysis
○Priyanka Verma¹, Yasutaka Kuwahara^{1,2,3}, Kohsuke Mori^{1,2}, Hiromi Yamashita^{1,2} (1. Osaka University, 2. ESICB, Kyoto University, 3. JST PRESTO)
11:00 AM - 11:20 AM

J403

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

[J403-4am] 09. Coordination Chemistry,
Organometallic Chemistry

Chair: Hirotohi Sakamoto, Junpei Yuasa
9:00 AM - 11:40 AM J403 (Online Meeting)

[J403-4am-01] Luminescence properties of silver(I) and copper(I) coordination polymers bridged by dimethylpyrazine

Taiki Kuwahara¹, Hideki Ohtsu¹, [○]Kiyoshi Tsuge¹ (1. University of Toyama)
9:00 AM - 9:20 AM

[J403-4am-02] Semiconductive Nature of Two-Dimensional Coordination Polymers Containing Ag-S Network

[○]Ryohei Akiyoshi¹, Daisuke Tanaka¹ (1. Kwansei Gakuin University)
9:20 AM - 9:40 AM

[J403-4am-03] *N*-Methylation of Amines via CO₂ Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes Supported by a

N,N''-Diarylethylenetriamine Ligand
[○]Koichi Shinohara¹, Hayato Tsurugi¹, Kazushi Mashima¹ (1. Osaka Univ.)
9:40 AM - 10:00 AM

[J403-4am-04] Solvent induced structural change and optical properties of nona-coordinated Eu(III) complexes having unsymmetric tridentate ligand

[○]Yoshinori Okayasu¹, Junpei Yuasa¹ (1. Grad. Sch. Sci., TUS)
10:00 AM - 10:20 AM

[J403-4am-05] CPL and CD spectra of achiral Eu(III) complex in solution containing amino acids

[○]Munetaka Iwamura¹, Koichi Nozaki¹, Miho Sakai¹, Yuzuki Nakauchi¹ (1. University of Toyama)
10:20 AM - 10:40 AM

[J403-4am-06] Syntheses and magnetic properties of lanthanide(III) complexes ligated by bis(nitronyl nitroxide-2-ide)gold(I) anion
[○]Ryu Tanimoto¹, Shuichi Suzuki², Daisuke Shiomi¹, Rika Tanaka³, Takeshi Naota², Masatoshi Kozaki¹, Keiji Okada¹ (1. Grad. Sch. of Sci., Osaka City Univ., 2. Grad. Sch. of Eng. Sci., Osaka Univ., 3. Grad. Sch. of Eng., Osaka

City Univ.)

10:40 AM - 11:00 AM

[J403-4am-07] Surface Attachment and Circularly Polarized Luminescence of Luminous Terbium Complex on Silica Surface with Chiral Ligands

[○]Sora Shirai¹, Kensuke Ikeda², Satoshi Muratsugu¹, Hidetaka Nakai², Mizuki Tada^{1,3} (1. Dept. Chem. Nagoya Univ., 2. Dept. Appl. Chem. Kindai Univ., 3. RCMS, Nagoya Univ.)
11:00 AM - 11:20 AM

[J403-4am-08] Excitation pathway of near-infrared luminescence in Yb³⁺ complex with tripodal Schiff base

[○]Atsuko Masuya-Suzuki¹, Rika Nakamura¹, Satoshi Goto¹, Ryunosuke Karashimada¹, Nobuhiko Iki¹ (1. Tohoku University)
11:20 AM - 11:40 AM

J202

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

[J202-4am] 09. Coordination Chemistry,
Organometallic Chemistry

Chair: Yoshinori Yamanoi, Takanori Shima
9:00 AM - 11:40 AM J202 (Online Meeting)

[J202-4am-01] Synthesis and Catalytic Activity of Atrane-type Group 14 Cations with Hard and Soft Lewis Superacidity

[○]Daiki Tanaka¹, Akihito Konishi¹, Makoto Yasuda¹ (1. Osaka University)
9:00 AM - 9:20 AM

[J202-4am-02] Synthesis and Reactivity of Early Transition Metal Methylene Complexes via Transmetalation of Dinuclear Zinc Methylene Species

[○]Takashi Kurogi^{1,2}, Kazuhiko Takai¹ (1. Okayama Univ., 2. Kyoto Univ.)
9:20 AM - 9:40 AM

[J202-4am-03] Dinitrogen Cleavage and Functionalization by Carbon Dioxide at a Ditungsten Dihydride Framework

[○]Qingde ZHUO¹, Zhaomin HOU¹, Shima Takanori¹ (1. RIKEN)
9:40 AM - 10:00 AM

[J202-4am-04] The Syntheses and Structures of

Dinitrogen Chromium Complexes

Supported with Triamidoamine Ligands

○Yoshiaki Kokubo¹, Yuji Kajita¹, Hideki Masuda¹

(1. Aichi Institute of Technology)

10:00 AM - 10:20 AM

[J202-4am-05] Properties of Dimetallene Dianions

Bearing Triptycyl Framework

○Ryohei Nishino¹, Mao Minoura¹ (1. College of

Science, Rikkyo University)

10:20 AM - 10:40 AM

[J202-4am-06] Computational Design and Evaluation of

Substituted PCP-Type Ligands for Mo-

Catalyzed Nitrogen Fixation

○Akihito Egi¹, Hiromasa Tanaka², YoshiakiNishibayashi³, Kazunari Yoshizawa¹ (1.

Institute for Materials Chemistry and

Engineering, Kyushu University, 2. School of

Liberal Arts and Science, Daido University, 3.

School of Engineering, The University of

Tokyo)

10:40 AM - 11:00 AM

[J202-4am-07] High ionic conductivity in 2D-layered Ti-

MOF by Li salts mechanical insertion

○Marvin Kevin Sarango Ramirez¹, YukihiroYoshida¹, Dae-Woon Lim², Hiroshi Kitagawa¹

(1. Kyoto University, 2. Yonsei University)

11:00 AM - 11:20 AM

[J202-4am-08] Synthesis a Zr-mellitate MOF and its ion-

exchange property

○Genki Hatakeyama¹, Masaki Nishio, KoukiOka², Teppei Yamada¹ (1. The University of

Tokyo, 2. Osaka University)

11:20 AM - 11:40 AM

J402

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

[J402-4am] 09. Coordination Chemistry,
Organometallic Chemistry

Chair: Yutaka Hitomi, Kyoko Nozaki

9:00 AM - 11:40 AM J402 (Online Meeting)

[J402-4am-01] The Synthesis and reactivity of PBP-Pincer

Perfluororhodacyclopentanes

○Shinya Hayashi¹, Toshiki Murayama¹, ShuheiKusumoto¹, Kyoko Nozaki¹ (1. The University

of Tokyo)

9:00 AM - 9:20 AM

[J402-4am-02] Dynamics of Transmetalation of the

Binuclear Au(I) Diaryl Complexes and Their
Synthetic Application to Macrocyclization○Yusuke Yoshigoe¹, Yoshitaka Tsuchido¹,Hidetoshi Kawai¹, Kohtarō Osakada², ShinichiSaito¹ (1. Tokyo Univ. of Science, 2. Tokyo

Institute of Tech.)

9:20 AM - 9:40 AM

[J402-4am-03] Conversion from Phosphinine Pincer Metal

Complexes to Metallabenzenes Triggered
by O₂ Oxidation○Koichiro Masada¹, Shuhei Kusumoto¹, KyokoNozaki¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[J402-4am-04] Synthesis and structural analysis of a gold

cluster Au₁₈S₂(SR)₁₂ (R = 2,4,6-
C₆H₂ⁱPr₃CH₂) protected by bulky thiolate
ligands○Taro Shigeta¹, Shinjiro Takano¹, TatsuyaTsukuda^{1,2} (1. Graduate School of Science,

The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)

10:00 AM - 10:20 AM

[J402-4am-05] Benzimidazolines as New Acyl Donors for

Photocatalytic Transformations of

Unactivated Alkenes: Intermolecular

Hydroacylation and 3-Component

Acylcarboxylation *via* CO₂ Insertion○Yutaka Saga¹, Taito Watanabe¹, YusukeNakayama¹, Mio Kondo^{1,2}, Shigeyuki Masaoka¹

(1. Department of Applied Chemistry Graduate

School of Engineering Osaka University, 2. JST

PRESTO)

10:20 AM - 10:40 AM

[J402-4am-06] Synthesis of Deuterated Alcohols via

Hydrogen Transfer Process Catalyzed by

Iridium Complexes

Moeko Itoga¹, Masako Yamanishi¹, YoshijiTakemoto¹, ○Hiroshi Naka¹ (1. Grad. Sch. of

Pham. Sci., Kyoto Univ.)

10:40 AM - 11:00 AM

[J402-4am-07] Rapid Alkane Functionalization with H₂O₂

Catalyzed by Monocopper Complexes with

Medpa Tridentate Ligand and its

Derivatives

○kyosuke Fujikawa¹, momoe Kawahashi¹,

yutaka Hitomi¹, masahito Kodera¹ (1. Doshisha University)

11:00 AM - 11:20 AM

[J402-4am-08] Photochromism in polymorphic crystals of a rhodium dithionite complex

○Yuu Kajiwar¹, Seiya Miyata¹, Hidetaka Nakai¹ (1. Dept. Appl. Chem. Kindai Univ.)

11:20 AM - 11:40 AM

K1

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

[K1-4am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Yasujiro Murata, Hidehiro Sakurai

9:00 AM - 11:00 AM K1 (Online Meeting)

[K1-4am-01] Design and Synthesis of Oxygen-Embedded TriQuinoline and its Strategic Applications

○Toi Kobayashi¹, Naoya kumagai¹ (1. Keio university)

9:00 AM - 9:20 AM

[K1-4am-02] Molecular Motion Restriction of Tetraphenylethylene Enabled by a Linked Rotaxane Structure to Enhance the Robustness of Fluorescent Properties

○Hiromichi V. Miyagishi¹, Hiroshi Masai¹, Jun Terao¹ (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

9:20 AM - 9:40 AM

[K1-4am-03] Synthesis and Properties of Perfluorocubane

○Masafumi Sugiyama¹, Midori Akiyama¹, Yuki Yonezawa¹, Kyoko Nozaki¹, Takashi Okazoe^{1,2} (1. The University of Tokyo, 2. AGC Inc.)

9:40 AM - 10:00 AM

[K1-4am-04] Syntheses and Properties of BAR_2 -Bridged Azafulvene Compounds Base on Five-Membered Chelate Rings

○TIANCHENG TAN¹, SHUAIFENG HU¹, MINH ANH TRUONG¹, RICHARD MURDEY¹, TOMOYA NAKAMURA¹, ATSUSHI WAKAMIYA¹ (1. Kyoto University Institute for Chemical Research)

10:00 AM - 10:20 AM

[K1-4am-05] Spirofluorene Based Novel [2]rotaxanes: Synthesis and NMR Studies

○Showkat Rashid¹, Takashi Murakami¹, Yusuke Yoshigoe¹, Shinichi Saito¹ (1. Tokyo University of

Science)

10:20 AM - 10:40 AM

[K1-4am-06] Development of Boron and Nitrogen-Doped Polycyclic Heteroaromatics Exhibiting Full-Color Narrowband Emissions

○Minlang Yang^{1,2}, In Seob Park², Takuma Yasuda^{1,2} (1. Grad. Sch. of Eng., Kyushu Univ., 2. IFRC, Kyushu Univ.)

10:40 AM - 11:00 AM

K3

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

[K3-4am] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Takuji Hatakeyama, Itaru Osaka

9:00 AM - 11:20 AM K3 (Online Meeting)

[K3-4am-01] Synthesis, Properties, and π -Extension of B_4N_4 -Heteropentalene Derivatives

○Junki Kashida^{1,2}, Yoshiaki Shoji^{1,2}, Takanori Fukushima^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech., 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

9:00 AM - 9:20 AM

[K3-4am-02] Synthesis of Boron-Containing Oligoacenes by the Cyclocondensation of *o*-Diborylarene Derivatives

○Tetsuyoshi Tsukada^{1,2}, Yoshiaki Shoji^{1,2}, Takanori Fukushima^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech., 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

9:20 AM - 9:40 AM

[K3-4am-03] Generation of homosumanene *ortho*-quinone under photo-irradiation and its synthetic application to azaacene-fused homosumanenes

○Maiki Nishimoto¹, Yuta Uetake^{1,2}, Yumi Yakiyama^{1,2}, Uwe H. F Bunz³, Hidehiro Sakurai^{1,2} (1. Graduate School of Engineering, Osaka Univ., 2. ICS-OTRI, Osaka Univ., 3. Ruprecht-Karls-Universität Heidelberg)

9:40 AM - 10:00 AM

[K3-4am-04] Dielectric Response of Difluorinated Sumanene Caused by the In-plane Motion

○Minghong Li¹, Kohei Sambe², Tomoyuki Akutagawa², Kazunari Matsuda³, Takashi Kajitani⁴,

Takanori Fukushima⁴, Yumi Yakiyama^{1,5}, Hidehiro Sakurai^{*1,5} (1. Osaka University, 2. Tohoku University, 3. Kyoto University, 4. Tokyo Institute of Technology, 5. Osaka University ICS-OTRI)
10:00 AM - 10:20 AM

[K3-4am-05] Functionalization of Benzene-Fused Pentafulvalenes and Its Application to Extended π -Electronic Systems

○Masahiro Hayakawa^{1,2}, Naoyuki Sunayama², Yu Matsuo², Aiko Fukazawa² (1. Nagoya University, 2. Kyoto University)
10:20 AM - 10:40 AM

[K3-4am-06] Development of Corannulene-based Covalent Cages

○Haruka Kano¹, Hiroko Yamada¹, Naoki Aratani¹ (1. NAIST)
10:40 AM - 11:00 AM

[K3-4am-07] Synthesis and Properties of a Triply Fused N-Confused Porphyrin Dimer

○Osamu Iwanaga¹, Masatoshi Ishida¹, Hiroyuki Furuta¹ (1. Kyushu University)
11:00 AM - 11:20 AM

H201

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

[H201-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Ryo Sekiya, Koichi Kodama
9:00 AM - 11:20 AM H201 (Online Meeting)

[H201-4am-01] Synthesis and Chiral Optical Property of Resorcinarene-based Metal-Coordination Capsule Possessing Chiral Internal Space

○Kentaro Harada¹, Ryo Sekiya¹, Takeharu Haino¹ (1. Hiroshima University)
9:00 AM - 9:20 AM

[H201-4am-02] “Solvent-Induced Chirality Switching” in the Enantioseparation of Chlorine-Substituted Tropic Acids via Diastereomeric Salt Formation

○Srinivas Chandrasekaran¹, Takuji Hirose¹, Koichi Kodama¹ (1. Saitama University)
9:20 AM - 9:40 AM

[H201-4am-03] Dynamic Triple-helical Metallocryptand: Time-Programmable Helicity Inversion Triggered by Alkali Metal Ions

○Sk Asif Ikbal¹, Masahiro Ehara², Yoko Sakata^{1,3}, Shigehisa Akine^{1,3} (1. WPI-Nano Life Science Institute, Kanazawa University, 2. Institute for Molecular Science, Research Center for Computational Science, 3. Graduate School of Natural Science and Technology, Kanazawa University)
9:40 AM - 10:00 AM

[H201-4am-04] Chemometrics-coupled chiral recognition using D- π -A typed cyanostilbenes

○Kaede Kawaguchi¹, Ayana Moro¹, Yuji Kubo¹ (1. Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University)
10:00 AM - 10:20 AM

[H201-4am-05] Poly(quinoxaline-2,3-diyl) as a Traceless Nonbonding-Interaction-Based Chiral Shift Reagent

○Takaya Fujie¹, Takeshi Yamamoto¹, Michinori Sugimoto¹ (1. Kyoto Univ.)
10:20 AM - 10:40 AM

[H201-4am-06] Cyclic Bifluorenylidene Trimer: Relationship between Dynamic Behaviors and Structural Characteristics

○Akira Nagai^{1,2}, Tomoya Ishizuka², Takahiko Kojima², Masayuki Takeuchi^{1,2} (1. NIMS, 2. Univ. of Tsukuba)
10:40 AM - 11:00 AM

[H201-4am-07] Photo-induced Reversal of Supramolecular Chirality

○Takuho Saito¹, Daisuke Inoue¹, Yuichi Kitamoto³, Shiki Yagai² (1. Grad. Sch. of Sci. & Eng., Chiba Univ., 2. IGPR, Chiba Univ., 3. Grad. Sch. of Eng., Tohoku Univ.)
11:00 AM - 11:20 AM

K6

Academic Program [Oral B] | 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry- | Oral B

[K6-4am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Toshiki Nokami, Nobuhiro Yanai
9:00 AM - 11:20 AM K6 (Online Meeting)

[K6-4am-01] Long-Range Intramolecular Singlet Fission in Polyyne-Linked Pentacene Dimers

○Hayato Sakai¹, Masaaki Fuki², Nikolai

Tkachenko³, Yasuhiro Kobori², Taku Hasobe¹ (1. Department of Chemistry, Faculty of Science and Technology, Keio University, 2. Kobe University, Molecular Photoscience Research Center, 3. Tampere University, Faculty of Engineering and Natural Sciences)

9:00 AM - 9:20 AM

[K6-4am-02] Development of photoreaction through halogen-bonding

○Eiji Yamaguchi¹, Akichika Itoh¹ (1. Gifu Pharmaceutical University)

9:20 AM - 9:40 AM

[K6-4am-03] Development of Mononuclear Aluminum Complexes Core Carbazole Dendrimer

○Kohei NAKAO¹, Minori FURUKORI³, Takuya HOSOKAI³, Ken ALBRECHT^{1,2,4} (1. IMCE, Kyushu Univ., 2. Grad. Sci. Eng. Sci., Kyushu Univ., 3. AIST, 4. JST-PRESTO)

9:40 AM - 10:00 AM

[K6-4am-04] Development of transition metal-free photochemical CO₂ reduction enabled by photosensitized regeneration of organohydride

○Wei Bin Xie¹, Jia Sheng Xu¹, Ubaidah Md Idros¹, Jouji Katsuhira¹, Masaaki Fuki¹, Masahiko Hayashi¹, Yasuhiro Kobori¹, Ryosuke Matsubara¹ (1. Kobe university)

10:00 AM - 10:20 AM

[K6-4am-05] *Regio*-specific cross-dehydrogenative coupling reaction of simple polycyclic aromatic hydrocarbons with polyfluoroarenes

○Ryota Sato¹, Junpei Kuwabara², Takaki Kanabara² (1. TREMS, Univ. of Tsukuba, 2. TREMS, Univ. of Tsukuba)

10:20 AM - 10:40 AM

[K6-4am-06] Observation of Negative Activation Enthalpy in Amine Conjugate Addition to π -Conjugated Molecules

○Haruki Sanematsu^{1,2}, Masayuki Takeuchi^{1,2}, Atsuro Takai² (1. Univ. of Tsukuba, 2. NIMS)

10:40 AM - 11:00 AM

[K6-4am-07] Substituent effects on gas-phase stabilities of benzenes having positive point charges in the vicinity

○Kazuhide Nakata¹ (1. Sci. Res. Ctr., Hosei

Univ.)

11:00 AM - 11:20 AM

K307

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

[K307-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Akira Matsumoto, Takeru Torigoe

9:00 AM - 11:20 AM K307 (Online Meeting)

[K307-4am-01] Acceptorless Dehydrogenative Cross-coupling Reactions Enabled by Photoredox/Hydrogen-Atom Transfer Cooperative Catalysis

○Kodai Minami¹, Kohsuke Ohmatsu^{1,2}, Takashi Ooi^{1,2} (1. Graduate School of Engineering, Nagoya University, 2. WPI-ITbM, Nagoya University)

9:00 AM - 9:20 AM

[K307-4am-02] Site-selective α -C(sp³)-H Alkylation of Alcohols and Primary Amines Promoted by Photoredox, HAT, and Bond-Weakening Hybrid Catalysis

○Kentaro Sakai¹, Kounosuke Oisaki¹, Motomu Kanai¹ (1. Grad. Sch. Pharm. Sci., the Univ. of Tokyo)

9:20 AM - 9:40 AM

[K307-4am-03] Photo-induced C-H bond thiocyanation and one-pot isomerization to isothiocyanates

○Bumpei Maeda¹, Yusuke Aihara², Ayato Sato², Toshinori Kinoshita², Kei Murakami¹ (1. Kwansei Gakuin University, 2. Nagoya University)

9:40 AM - 10:00 AM

[K307-4am-04] Selective C(sp³)-H Functionalization of Valine Residues via Interactions between Ammonium Group at the N-terminus and the Decatungstate Photocatalyst

○Jizhou Song², Takeru Torigoe^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

10:00 AM - 10:20 AM

- [K307-4am-05] Decatungstate-catalyzed Site-selective C(sp³)-H Alkylation of 2-Methylanilinium Salts Controlled by Noncovalent Interactions
 ○Jialin Zeng², Takeru Torigoe^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)
 10:20 AM - 10:40 AM
- [K307-4am-06] Cationic DABCO-based Catalyst for Site-Selective C–H Alkylation via Photoinduced Hydrogen-Atom Transfer
 ○Akira Matsumoto¹, Keiji Maruoka^{1,2} (1. Kyoto University, 2. Guangdong University of Technology)
 10:40 AM - 11:00 AM
- [K307-4am-07] 1,2-Bis-perfluoroalkylations of Alkenes and Alkynes with Perfluorocarboxylic Anhydrides
 ○Takuma Tagami¹, Yuma Aoki¹, Shintaro Kawamura¹, Mikiko Sodeoka¹ (1. RIKEN)
 11:00 AM - 11:20 AM

B104

Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B

[B104-4am] 16. Natural Products Chemistry, Chemical Biology

Chair: Makoto Yoritake, Takayuki Ohyoshi
 9:00 AM - 11:20 AM B104 (Online Meeting)

- [B104-4am-01] Synthetic Studies on Enigmazole B
 ○Yoshihiro Goda¹, Haruhiko Fuwa¹ (1. Chuo University)
 9:00 AM - 9:20 AM
- [B104-4am-02] Synthetic Studies toward C-linked Hyaluronan Oligomer Analogues
 ○Noriaki Kiya¹, Makoto Yoritake¹, Go Hirai¹ (1. Grad. Sch. Pharm. Sci., Kyushu Univ.)
 9:20 AM - 9:40 AM
- [B104-4am-03] Synthesis and functional analysis of gut-associated lymphoid-tissue-resident bacterial lipooligosaccharide partial structure
 ○Tomoya Uto¹, Atsushi Shimoyama^{1,2}, Haruki Yamaura¹, Koji Hosomi³, Jun Kunisawa³, Koichi

Fukase^{1,2} (1. Graduate School of Science, Osaka University, 2. PRC, Graduate School of Science, Osaka University, 3. National Institutes of Biomedical Innovation, Health, and Nutrition)

9:40 AM - 10:00 AM

- [B104-4am-04] Synthesis of sialyl glycopeptide utilizing TFA-labile Bn-type protected sialic acid optimized for sialylation and solid-phase peptide synthesis
 ○Shun Ito^{1,2}, Yuya Asahina^{1,2}, Yasuhiro Kajihara¹, Hironobu Hojo^{1,2} (1. Graduate School of Science and, 2. Institute for Protein Research, Osaka univ.)
 10:00 AM - 10:20 AM

- [B104-4am-05] Semisynthetic Study of Glycoprotein Interleukin-6 (IL-6)
 ○Yanbo Liu¹, Yuta Maki^{1,2}, Ryo Okamoto^{1,2}, Yasuhiro Kajihara^{1,2} (1. Dept. Chem., Grad. Sch. Sci., Osaka Univ., 2. PRC, Grad. Sch. Sci., Osaka Univ.)
 10:20 AM - 10:40 AM

- [B104-4am-06] Synthetic Study of Antibiotic Cyclopeptide Pargamicin A
 ○Tetsuya Inaba¹, Masahito Yoshida¹, Hideo Kigoshi¹ (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)
 10:40 AM - 11:00 AM

- [B104-4am-07] Synthetic study of nemorosonol and hyperuralone A having a tricyclo[4.3.1.0]decane skeleton
 ○Keisuke Mitsugi¹, Toru Takabayashi¹, Takayuki Ohyoshi¹, Hideo Kigoshi¹ (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)
 11:00 AM - 11:20 AM

G202

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[G202-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Hitoshi Kasai, Yuki Goto
 9:00 AM - 11:40 AM G202 (Online Meeting)

- [G202-4am-01] Fabrication of novel nano-prodrugs that release drugs with high efficiency in

cancer cells

○Keita Tanita¹, Yoshitaka Koseki¹, Ryuju Suzuki¹, Anh T. N. Dao¹, Hitoshi Kasai¹ (1. IMRAM, Tohoku university)

9:00 AM - 9:20 AM

[G202-4am-02] Parametrization of Karplus Equation for N-Methylated Peptides

○Yota Shiratori¹, Takumi Ueda², Koh Takeuchi², Jumpei Morimoto¹, Shinsuke Sando¹ (1. The Univ. of Tokyo, 2. The Univ. of Tokyo)

9:20 AM - 9:40 AM

[G202-4am-03] Development of designer thiopeptides with grafted noncanonical sequences inhibiting a target protein of interest

○Kakeru Narumi¹, Kyohei Miyairi, Yuki Goto¹, Hiroaki Suga¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[G202-4am-04] Directed Evolution of Cytochrome P450BM3 for Responding Natural Products as Decoy Molecules for Direct Benzene Hydroxylation without Chemical Synthesis

○Yuya Yokoyama¹, Masayuki Karasawa¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1. Nagoya University, 2. RIKEN Spring-8)

10:00 AM - 10:20 AM

[G202-4am-05] The creation of rigid hemoprotein multimers triggered by metal coordination

○Hiroaki Inaba¹, Yuma Shisaka¹, Garyo Ueda¹, Erika Sakakibara¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1. Nagoya university, 2. RIKEN SPring-8)

10:20 AM - 10:40 AM

[G202-4am-06] Visible light driven NADH regeneration using a system of water-soluble zinc porphyrin and homogeneously polymer-dispersed rhodium nanoparticles and application to CO₂ fixation with enzyme

○Takayuki Katagiri¹, Masanobu Higashi¹, Yutaka Amao¹ (1. Osaka City University)

10:40 AM - 11:00 AM

[G202-4am-07] Efficient production of value-added chemicals in cyanobacteria by metabolic regulation using light sensor proteins

○Shunichi Kobayashi¹, Shota Atsumi², Kazunori Ikebukuro¹, Ryutaro Asano¹ (1. Tokyo Univ. of Agric. and Technol., 2. Univ. of California Davis)

11:00 AM - 11:20 AM

[G202-4am-08] Functionalization of cycloparaphenylene by biocatalysts

○Atsushi Usami¹, Kazuma Amaike¹, Katsutoshi Hori¹, Kenichiro Itami¹ (1. Nagoya Univ.)

11:20 AM - 11:40 AM

G201

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B

[G201-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Eiji Nakata, Noriko tarashima

9:00 AM - 11:20 AM G201 (Online Meeting)

[G201-4am-01] Cosolvent improves the enzymatic ligation of DNA origami

○Arivazhagan Rajendran¹, Kirankumar Krishnamurthy¹, Eiji Nakata¹, Takashi Morii¹ (1. Institute of Advanced Energy, Kyoto University)

9:00 AM - 9:20 AM

[G201-4am-02] Construction of a CO₂ fixing enzyme assembly on 3D DNA nanostructure

○Hiroaki Konishi¹, Huyen Dinh², Eiji Nakata^{1,2}, Takashi Morii^{1,2}, Haruyuki Atomi³ (1. Graduate School of Energy Science, Kyoto University, 2. Institute of Advanced Energy, Kyoto University, 3. Graduate School of Engineering, Kyoto University)

9:20 AM - 9:40 AM

[G201-4am-03] Photoreactive molecular glue for enhancing the efficacy of DNA aptamers

○Ai Kohata¹, Kou Okuro², Takuzo Aida¹ (1. The University of Tokyo, 2. The University of Hong Kong)

9:40 AM - 10:00 AM

[G201-4am-04] Effect of neuronal RNA G-quadruplex structures on cellular phase separation

○Sefan Asamitsu¹, Moe Kawasaki², Yuki Hirose³, Yasushi Yabuki², Gengo Kashiwazaki⁴, Anandhakumar Anandhakumar⁵, Toshikazu Bando³, Hiroshi Sugiyama^{3,6}, Norifumi Shioda²

(1. RIKEN Center for Biosystems Dynamics Research, 2. Institute of Molecular Embryology and Genetics, Kumamoto University, 3. Graduate School of Science, Kyoto University, 4. Graduate School of Agriculture, Kindai University, 5. Ludwig Cancer Research Oxford, University of Oxford, 6. Institute for Integrated Cell-Material Sciences, Kyoto University)
10:00 AM - 10:20 AM

[G201-4am-05] Replacement of oxygen with sulfur on the furanose ring of cyclic dinucleotide enhances the immunostimulatory effect by STING activation.

○Noriko Saito tarashima¹, Mao Kinoshita¹, Aki kondo¹, Noriaki Minakawa¹ (1. Tokushima Univ.)

10:20 AM - 10:40 AM

[G201-4am-06] Cancer-cell-selective cytotoxicity of a dicopper complex having 1,8-naphthalimide as a targeting unit

○Machi Hata¹, Yutaka Hitomi¹, Masahito Koda¹ (1. Doshisha University)

10:40 AM - 11:00 AM

[G201-4am-07] Development of a peptide forming a hydrogel with higher-order structural transition and application to tissue regeneration

○Atsuya Yaguchi¹, Hirotsugu Hiramatsu², Itsuki Ajioka^{3,4}, Takahiro Muraoka^{1,4} (1. Tokyo University of Agriculture and Technology, 2. National Yang Ming Chiao Tung University, 3. Tokyo Medical and Dental University, 4. KISTEC)

11:00 AM - 11:20 AM

A202

Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B

[A202-4am] 19. Colloid and Interface Chemistry

Chair: Katsuaki Konishi, Hideya Kawasaki

9:00 AM - 10:40 AM A202 (Online Meeting)

[A202-4am-01] Self-assembly properties of polyvinylpyrrolidone-protected anisotropic silver plates at air/water interface

○Kosuke Sugawa¹, Yutaro Hayakawa¹, Masato

Furuya¹, Joe Otsuki¹, Kaoru Tamada² (1. Nihon University, 2. Kyushu University)

9:00 AM - 9:20 AM

[A202-4am-02] Formation and Structural Characterization of Supramolecular Copolymers in Liquid Crystalline Phase

○Daiki Morishita¹, Xujie Zhang, Yoshimitsu Itoh¹, Takuzo Aida^{1,2} (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. RIKEN CEMS)

9:20 AM - 9:40 AM

[A202-4am-03] Fluorous Synthetic Channels Enabling both Ultrafast Water Permeation and High Salt Reflection

○Shuo CHEN¹, Yoshimitsu ITOH^{1,2}, Ryota HIRAHARA¹, Takeshi KONDA¹, Tsubasa AOKI¹, Kohei SATO¹, Takuzo AIDA^{1,3} (1. The Univ. of Tokyo, 2. PRESTO JST, 3. RIKEN CEMS)

9:40 AM - 10:00 AM

[A202-4am-04] Incorporation of Basic α -Hydroxy Acid Residues into Primitive Polyester Microdroplets for RNA Segregation

○Tony Z Jia^{1,2}, Niraja Bapat^{1,3}, Ajay Verma³, Irena Mamajanov¹, H. James Cleaves^{1,2,4}, Kuhan Chandru^{5,6} (1. Earth-Life Science Institute, Tokyo Institute of Technology, 2. Blue Marble Space Institute of Science, 3. Department of Biology, Indian Institute of Science Education and Research, 4. Institute for Advanced Study, 5. Department of Physical Chemistry, University of Chemistry and Technology, Prague, 6. Space Science Centre (ANGKASA), Institute of Climate Change, National University of Malaysia)

10:00 AM - 10:20 AM

[A202-4am-05] Self-Healable and Humidity-Resistant Polymer Glasses: New Strategies Based on Nano-Phase Separation

○Yuta Fujisawa¹, Yiling Nan¹, Atsushi Asano², Yu Yanagisawa¹, Keiichi Yano¹, Yoshimitsu Itoh¹, Takuzo Aida^{1,3} (1. The University of Tokyo, 2. National Defense Academy, 3. RIKEN Center for Emergent Matter of Science)

10:20 AM - 10:40 AM

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

[A204-4pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Takeshi Yoshikawa, Hirotooshi Mori

Sat. Mar 26, 2022 1:30 PM - 2:50 PM A204 (Online Meeting)

[A204-4pm-01] Development of a highly accurate docking scoring function using machine learning

○Shota Minami¹, Kazuhiro Fujimoto¹, Takeshi Yanai¹ (1. Nagoya University)

1:30 PM - 1:50 PM

[A204-4pm-02] Chemical-Data-Driven Validation of Physical Theories of Liquid Crystals

○Yoshiaki Uchida¹, Shizuo Kaji², Naoto Nakano³ (1. Osaka University, 2. Kyushu University, 3. Kyoto University)

1:50 PM - 2:10 PM

[A204-4pm-03] Atomic-Number-Correlated Molecular Model for Deciphering Transmission Electron Microscopic Images

○Koji Harano¹, Junfei Xing¹, Keishi Takeuchi¹, Ko Kamei¹, Takayuki Nakamuro¹, Eiichi Nakamura¹ (1. The University of Tokyo)

2:10 PM - 2:30 PM

[A204-4pm-04] Electronic Structure Informatics of Singlet Fission in Indigoids

○Fabian Weber¹, Hirotooshi Mori^{1,2} (1. Chuo University, Tokyo, 2. Institute for Molecular Science (IMS), Okazaki)

2:30 PM - 2:50 PM

機械学習を用いた高精度なドッキングスコアの開発

(名大院理¹・名大 ITbM²) ○南 翔太¹・藤本 和宏^{1,2}・柳井 毅^{1,2}

Development of a highly accurate docking scoring function using machine learning (¹Graduate School of Science, Nagoya University, ²WPI-ITbM, Nagoya University) ○Shota Minami,¹ Kazuhiro J. Fujimoto,^{1,2} Takeshi Yanai^{1,2}

Structure based drug design (SBDD) is expected to greatly contribute to reducing the enormous cost of new drug development, and indeed many drugs have been developed using SBDD. Among several SBDD methods, docking simulation is a powerful tool for predicting protein-ligand binding conformations and ligand binding affinities based on computer simulations. While currently available methods are able to predict the ligand binding conformations with high accuracy, they remain incapable of accurately predicting the ligand binding affinity. In this study, we add fingerprints that describe the structure of the ligand and the surrounding protein information as new descriptors to the scoring function, and perform regression analysis using machine learning models such as Lasso and LightGBM. As a result, we succeeded in developing a scoring function to achieve highly accurate binding affinity prediction.

Keywords : Docking Simulation; Machine Learning; Fingerprint **【最大 5 words】**

標的タンパク質の立体構造情報に基づく化合物設計(SBDD : Structure based drug design) は新薬開発にかかる莫大なコスト削減に大いに貢献できるものとして期待されており、SBDD を用いた多くの薬剤が開発されている。SBDD にはいくつかの手法があるが、タンパク質-リガンド間の結合様式やリガンドの結合親和性を、コンピューターシミュレーションを用いて予測する手法はドッキングシミュレーションと呼ばれる。現在提案されている手法はリガンド結合様式を高い精度で予測可能となっているが、リガンドの結合親和性を精度よく予測できないという問題を抱えている。そこで、本研究では、PMFScore と呼ばれるスコア関数に新しい記述子としてリガンドの構造やリガンド周辺タンパク質の情報を記述するフィンガープリントを加え、Lasso 回帰や LightGBM といった機械学習の手法を用いて回帰分析を行うことで高精度な結合親和性予測を実現するためのスコア関数を開発した。

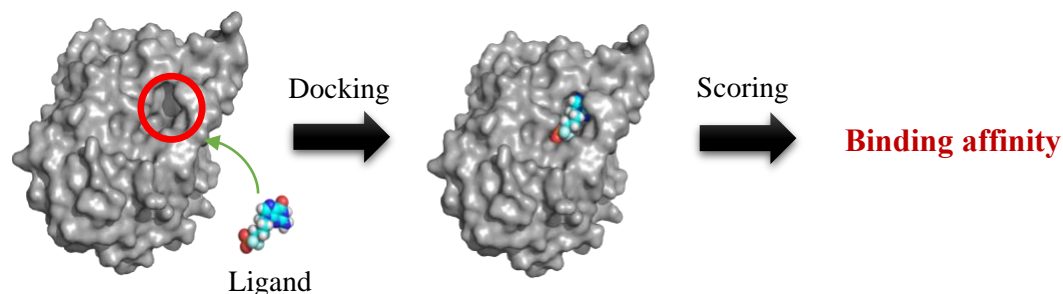


Fig 1 ドッキング計算の流れ

化学的データを用いた液晶の物性理論の検証

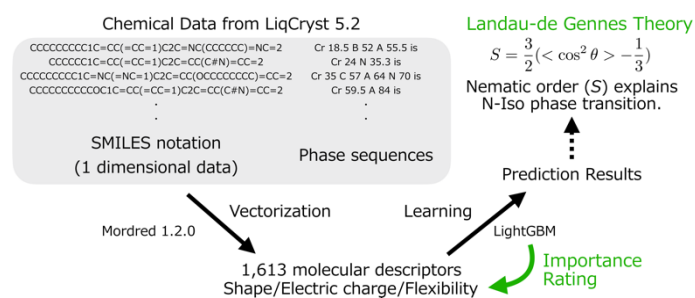
(阪大院基礎工¹・九大IMI²・京大国際高等教育院³) ○内田 幸明¹・鍛冶 静雄²・中野 直人³

Chemical-Data-Driven Validation of Physical Theories of Liquid Crystals (¹*Graduate School of Engineering Science, Osaka University*, ²*Institute of Mathematics for Industry, Kyushu University*, ³*Institute for Liberal Arts and Sciences, Kyoto University*) ○Yoshiaki Uchida,¹ Shizuo Kaji,² Naoto Nakano³

Liquid crystalline phases are states that molecules with anisotropic shapes exhibit, but physicists explain their properties not based on molecular fine structures but based on intuitive assumptions. The phase transition behaviors have been explained with order parameters in phenomenological theories. Order parameters are generally accounted for by single molecular properties in microscopic mean-field theories. In contrast, we will introduce a chemical data-driven method to test and develop physical theories which are useful for the materials chemistry. As examples, we tested the assumptions of the phenomenological Landau theory of liquid crystals, and confirmed the importance of molecular flexibility in addition to the molecular shape and intermolecular electrostatic interactions commonly accounted for in mean-field theories of liquid crystals.

Keywords: *Liquid Crystals; Machine Learning; Phenomenological Theory; Mean Field Theory*

液晶相は異方的な形状を持つ分子が示す状態であるが、物理学者は分子構造ではなく、物理的直感に基づいてその特性を説明する。例えば、相転移挙動は、現象論的な理論で秩序変数を使って説明されてきた¹⁾。また、この秩序変数は、一般に単分子の性質を粗視化した平均場理論によって説明される²⁾。本講演では、化学データを用いて、物理的な仮定から独立して物理理論を検証し、これを材料化学に適用できる形に発展させる手法を紹介する。この手法により液晶の現象論的ランダウ理論の仮定を検証できたほか、液晶の平均場理論を構築するために一般的に行われている分子形状や分子間静電相互作用に加えて、分子の柔軟性を仮定する必要性が示唆された。このような洞察は、全く新しい材料特性を持つ化合物を創製するための、定量的なメソスケール理論につながる可能性がある。



- 1) P. G. de Gennes, J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1993).
- 2) M. Osipov, Molecular Theories of Liquid Crystals. *Handbook of Liquid Crystals*, 1–54 (John Wiley & Sons, 2nd Edition, Vol. 1, Chap. 5, 2014).

透過電子顕微鏡像と分子構造をつなぐ原子番号相関分子模型の提案

(東大院理) ○原野 幸治・Junfei Xing・竹内 啓志・亀井 恒・中室 貴幸・中村 栄一
Atomic-Number-Correlated Molecular Model for Deciphering Transmission Electron Microscopic Images (*Department of Chemistry, The University of Tokyo*) ○Koji Harano, Junfei Xing, Keishi Takeuchi, Ko Kamei, Takayuki Nakamuro, Eiichi Nakamura

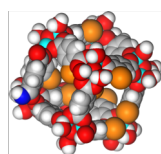
We propose a new molecular model that correctly reflects the characteristics of molecular images taken with an atomic-resolution transmission electron microscope. The "atomic-number-correlated molecular model" (ZC model), which uses the atomic number-dependent image radius determined by electron microscope image simulation as the display radius, enables us to reproduce electron microscopic images of various materials, from individual organic molecules to inorganic solids such as zeolite and sodium chloride.

Keywords : *Single Molecule Imaging; Transmission Electron Microscopy; Molecular Model; Structural Analysis; Atomic Radius*

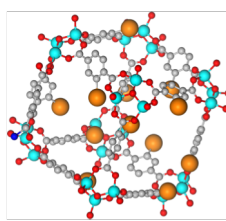
近年の電子顕微鏡（電顕）技術の発展により，原子や分子，さらにはその集合体の動きや反応をあたかも分子模型をみるがごとくに観察することが可能となった．しかし，実際に実験で得られた電顕像を模型で描き出そうとすると，化学者が慣れ親しんだ球棒あるいは空間充填模型から予想されるものとは大きく異なる．これは，空間充填模型は原子の電子雲の広がりを反映した模型であるのに対し，電子顕微鏡像にあらわれる原子像の濃さはその原子の原子番号(Z)に依存したものになるからである．この不一致が分子科学における原子分解能電顕の普及を妨げていた．本研究では我々は，電顕像シミュレーションを用いた検討により、電子線量に応じた画像ノイズを考慮すると，電顕像において視認される原子サイズが原子番号に強い相関を示すことを発見した．これに基づき，原子分解能透過電子顕微鏡で撮影した分子像の特徴を正しく反映する新しい分子模型として，電顕像シミュレーションを用いて決定した原子番号に依存した原子像半径を表示半径に用いた「原子番号相関模型(ZC model)」を新たに提唱した.¹⁾この模型を用いる事で，ひとつひとつの有機分子像から，ゼオライトや塩化ナトリウムのような無機物の固体まで，様々な物質の電顕像を模型で再現することが可能となった．

Z-correlated atomic radii

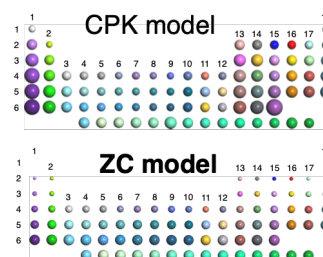
New molecular model reflecting nuclear charge



CPK model



ZC model



1) J. Xing, K. Takeuchi, K. Kamei, T. Nakamuro, K. Harano, E. Nakamura, Atomic-Number (Z)-Correlated Atomic Sizes for Deciphering Electron Microscopic Molecular Images, *arXiv*, 2107.01490.

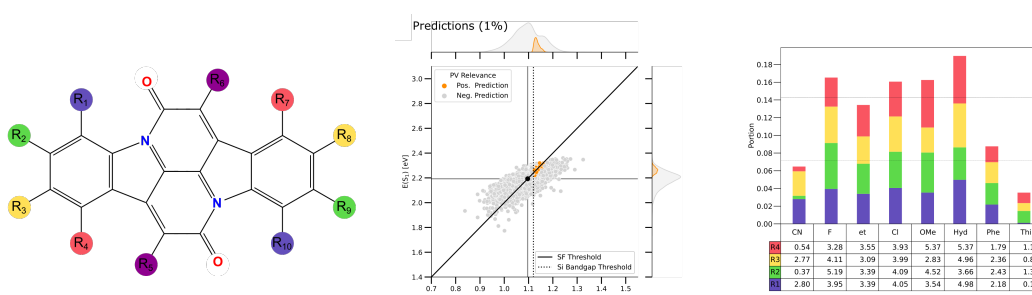
Electronic Structure Informatics of Singlet Fission in Indigoids

(¹Department of Applied Chemistry, Chuo University, ²Institute for Molecular Science, Okazaki) ○Fabian Weber,¹ Hirotoshi Mori^{1,2}

Keywords: Electronic Structure Informatics, Singlet Fission, Molecular Design, Machine Learning

To design photovoltaic cells that may go beyond the Shockley-Queisser limit, singlet fission (SF) has been identified as a potential upgrade to existing photovoltaic cell technology.¹ In SF, a singlet excited state located on one monomer can transition into a dimeric state of coupled triplets, which eventually decouples to yield two excited triplet states of lower energy from one photon. When the SF material's first triplet energy lies above the photovoltaic semiconductor's band gap this opens the possibility to exceed 100% internal quantum efficiency.² Even though several organic compounds have been identified as SF materials already, designing long-lived and efficient SF materials poses a large challenge: While it is widely agreed that there must exist an energetic requirement with respect to the excited states, the molecular design principles that promote SF are not yet fully understood.

To discover such common rules in SF molecules, in this work a chemical subspace of cibalackrot³ with over 4 million molecules was studied, combining techniques of high throughput screening with predictions of excitation energies from machine learning. Choosing specific energy requirements, we first identify a number of potential SF molecules with triplet excitation energies above the silicon band gap and then proceed to extract common design rules using machine learning classification techniques. It is found that in cibalackrot-type molecules, there are direct correlations between the energetic condition and the atomic charges, as well as spin density in specific aromatic rings of the molecule.



1) M.C. Hanna, A.J. Nozik, *J. Appl. Phys.* **2006**, 100, 074510. 2) M.C. Beard, J.C. Johnson, J.M. Luther, A.J. Nozik, *Phil. Trans. R. Soc. A* **2015**, 373, 20140412. 3) W. Zeng, O. El Bakouri, D.W. Szczepanik, H. Bronstein, H. Ottosson, *Chem. Sci.* **2021**, 12, 6159.

[F302-4am] 03. Physical Chemistry -Structure-

Chair: Hirosuke Matsui, Hiro Minamimoto

Sat. Mar 26, 2022 9:00 AM - 10:40 AM F302 (Online Meeting)

[F302-4am-01] *In situ* HERFD-XANES/RIXS measurements of adsorbed oxygen species on Pt/C electrocatalysts in polymer electrolyte fuel cells under operating conditions

[○]Hiroko Miwa¹, Takefumi Yoshida¹, Tomoya Uruga², Takehiko Sasaki³, Takuma Kaneko², Tomohiro Sakata², Kotaro Higashi², Oki Sekizawa², Yasuhiro Iwasawa¹ (1. The University of Electro-Communications, 2. Japan Synchrotron Radiation Research Institute, 3. The University of Tokyo)

9:00 AM - 9:20 AM

[F302-4am-02] 3D imaging of degradation process at the interface of rubber and metal by CT-XAFS

[○]Hirosuke Matsui¹, Yuta Muramoto¹, Tomoya Uruga², Takashi Kakubo³, Naoya Amino³, Duy Tai Dinh⁴, Hieu Chi Dam⁴, Mizuki Tada¹ (1. Nagoya University, 2. JASRI/SPRING-8, 3. The Yokohama Rubber Co. Ltd., 4. JAIST)

9:20 AM - 9:40 AM

[F302-4am-03] Adsorption structure of water on Pt(533)

Naoki Nagatsuka¹, Toya Muratani¹, Noboru Shibata¹, Ichihiko Tsuchiya¹, [○]Kazuya Watanabe¹ (1. Graduate School of Science, Kyoto Univ.)

9:40 AM - 10:00 AM

[F302-4am-04] Adsorption and surface reaction of formic acid on Cu(977) surface with a (100) microfacet

[○]Wataru Osada¹, Shunsuke Tanaka¹, Young Hung Choi¹, Kozo Mukai¹, Jun Yoshinobu¹ (1. The Institute for Solid State Physics, University of Tokyo)

10:00 AM - 10:20 AM

[F302-4am-05] Spectroscopic Investigation of High Pressure Hydrogen Evolution Reaction

[○]Nobuaki Oyamada¹, Hiro Minamimoto², Kei Murakoshi² (1. Hokkaido University Graduate School of Chemical Sciences and Engineering, 2. Hokkaido University Faculty of Science)

10:20 AM - 10:40 AM

In situ HERFD-XANES/RIXS measurements of adsorbed oxygen species on Pt/C electrocatalysts in polymer electrolyte fuel cells under operating conditions

(¹*Innovation Research Center for Fuel Cells, The University of Electro-Communications,*
²*Japan Synchrotron Radiation Research Institute,* ³*Graduate School of Frontier Sciences,*
The University of Tokyo) ○Hiroko Ariga-Miwa,¹ Takefumi Yoshida,¹ Tomoya Uruga,^{1,2}
 Takehiko Sasaki,³ Takuma Kaneko,² Tomohiro Sakata,² Kotaro Higashi,² Oki Sekizawa,²
 Yasuhiro Iwasawa,¹

Keywords: *In situ* HERFD-XANES; *in situ* RIXS; DFT calculations; Pt nanoparticles; Polymer Electrolyte Fuel cell (PEFC)

Polymer Electrolyte Fuel cell (PEFC) is one of the most promising power sources, which has great potential to realize low or even zero emissions. Performance and long-term durability of electrocatalysts especially on cathode, usually composed of Pt or Pt based nanoparticles as active components are critical problems to be solved for next-generation PEFC systems. Thus, obtaining atomistic insights of Pt nanoparticle catalysts under PEFC operation conditions are strongly required. Researches utilizing well-defined single crystal surfaces have been proceeded in the fundamental aspect to provide useful information about adsorbates and Pt surface structures. However, the adsorption and catalysis properties of the Pt nanoparticle electrocatalysts under PEFC operating conditions are still not clear, due to the lack of methodology.

We have applied an *in situ* High Energy Resolution Fluorescence Detected X-ray Absorption Near-Edge Structure (HERFD-XANES) spectroscopy for *operando* observations of Pt/C cathode catalysts in PEFCs under operating conditions at BL36XU beamline in SPring-8. Applying potential from 0.4 to 1.0 V (Figure 1), Pt L_{III}-edge HERFD-XANES difference spectra were well fitted with three characteristic absorption peaks. Moreover, another peak appeared by applying more than 1.1 V. FDMNES simulations of the spectra for DFT optimized structure models showed that three peaks observed at low potentials could be assigned to two adsorbed oxygen species (O, OH) and edge oxidation states, and the other peak observed at high potentials could be assigned to (111) facet oxidation states of Pt nanoparticles at the cathode.

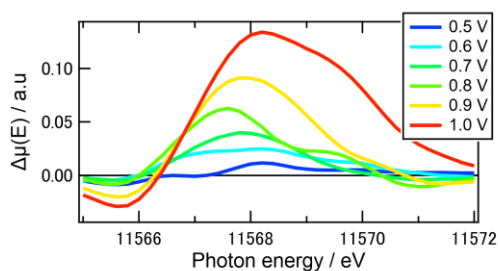


Figure 1. Pt L_{III}-edge HERFD-XANES difference spectra referred to the spectrum at 0.4 V.

3D imaging of degradation process at the interface of rubber and metal by CT-XAFS

(¹Nagoya University, ²JASRI/SPring-8, ³The Yokohama Rubber Co. Ltd., ⁴JAIST)

○Hirosuke Matsui,¹ Yuta Muramoto,¹ Tomoya Uruga,² Takashi Kakubo,³ Naoya Amino,³ Duy Tai Dinh,⁴ Hieu Chi Dam,⁴ Mizuki Tada¹

Keywords: 3D X-ray imaging; rubber degradation; Cu K-edge CT-XAFS

Brass (Cu-Zn alloy)-coated steel cords, which are the structural reinforcements of rubber tires, react with sulfur in rubber to form complex multilayers of metal sulfides. During practical use under high-temperature and humidified conditions, the structure and chemical composition of the multilayer gradually change by sulfurization, leading to decrease in adhesion strength, but the structure and spatial distribution of metal sulfides have not been clarified well. In this study, we investigated the nondestructive visualization of the degradation process of the rubber-brass interface by Cu-K-edge CT-XAFS imaging for the first time.

A rubber sample containing 1 wt% of brass particles (Cu/Zn ratio = 75/25, $\phi 0.3 \times 0.2 \mu\text{m}$) was processed for initial vulcanization. After the first Cu K-edge CT-XAFS measurement, typical hydrothermal degradation for 3 days was performed for the sample. The CT-XAFS measurements and the hydrothermal degradation processes (+11 days and +(11+14) days) were repeated for the sample. The CT-XAFS measurements were performed for the same field of view of the sample and the set of CT-XAFS imaging data was subjected to linear combination fitting analysis ($E = 8.850\text{--}9.200 \text{ keV}$) for the three components of brass (Cu^{0+}), Cu_2S (Cu^{1+}), and CuS (Cu^{2+}). The reconstruction of the parameters of the amounts of the three species was conducted and the three-dimensional images of the distribution of the species were obtained.

Fig. 1 shows the reconstructed 3D images of brass, Cu_2S , and CuS distribution in the rubber sample visualized by the CT-XAFS. The brass particles originally existed in the rubber sample and Cu_2S , which was key for the adhesion of rubber and brass, was formed around the brass particles. After the hydrothermal treatment, the formation of Cu_2S and CuS was clearly observed in the three-dimensionally reconstructed images obtained by the CT-XAFS imaging. Accompanied with the increase in the reaction time of the hydrothermal treatment, the distribution of Cu_2S and CuS were widely changed in the rubber sample. The CT-XAFS imaging and the spatial distribution of the sulfide species will be discussed.

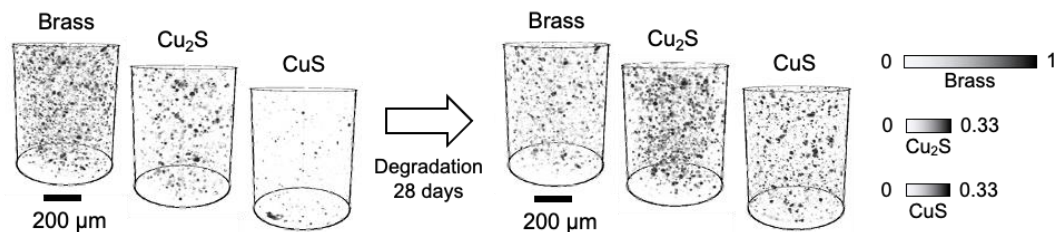


Fig. 1 3D images of brass, Cu_2S , and CuS distributions in rubber visualized by CT-XAFS.

Pt(533)面における水分子の吸着構造

(京大院理) 長塚直樹・村谷統哉・柴田昂・土屋維智彦・○渡邊一也

Adsorption structure of water on Pt(533) (*Graduate School of Science, Kyoto University*) Naoki Nagatsuka, Toya Muratani, Noboru Shibata, Ichihiko Tsuchiya, ○Kazuya Watanabe

In this work, we study the structure of water layer at Pt step site on Pt(533) by using heterodyne-detected sum-frequency generation spectroscopy under an ultrahigh vacuum. Figure 1 shows $\text{Im } \chi^{(2)}$ spectra in the OH stretching region obtained from H_2O covered Pt(533) at 140 K. A negative band grows with coverage indicating that water forms a hydrogen bond network in which proton is pointing toward the Pt substrate. At less than 0.33 ML, water predominantly forms a one-dimensional chain along the Pt step. While both of zig-zag and L-wire structures have been predicted as the water chain structure in the previous theoretical studies,¹⁾ the dominance of the negative band supports the latter structure. We further studied HD-isotope dependence of the signals and found that the water chain structure depends on the isotope concentration.

Keywords : water; Platinum; sum-frequency generation; vibrational spectroscopy

白金／水界面での水の構造を明らかにすることは水溶液の電極反応機構を考えるうえで重要である．本研究では，超高真空下での Pt(533)表面上の水分子吸着構造をヘテロダイン検出和周波発生振動分光を用いて調べた．Fig. 1 に H_2O を吸着した Pt(533)面の OH 伸縮振動領域の $\text{Im } \chi^{(2)}$ スペクトルを示す．被覆率とともに振幅が増大する負の信号が観測され，プロトンが Pt 基板側に向けた水素結合ネットワークが成長していることを示唆する．0.33 ML 以下において吸着水は，Pt ステップ上に 1 次元鎖を形成することが知られている．これまでこの一次元鎖構造として zig-zag 構造と L-wire 構造が理論的に予測されているが¹⁾，観測された負のバンドは後者の構造を支持する．我々はさらに，信号の HD 同位体依存性も調べ，1 次元鎖の構造が同位体比に依存して変化することを見出した．

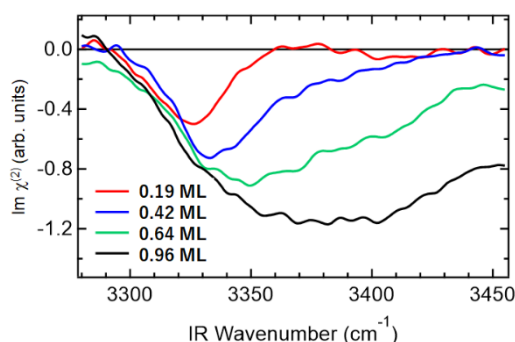


Fig. 1: $\text{Im } \chi^{(2)}$ spectra of H_2O adsorbed on Pt(533) at 138 K.

The water coverage is indicated in the figure.

1) Y. Litman *et al.*, *J. Chem. Phys.* **2018**, 148, 102320.

Adsorption and surface reaction of formic acid on the Cu(977) surface with a (100) microfacet

(¹The Institute for Solid State Physics, University of Tokyo) ○ Wataru Osada,¹ Shunsuke Tanaka,¹ YoungHun Choi,¹ Kozo Mukai,¹ Jun Yoshinobu¹

Keywords: Formic acid; Copper; Step sites; Hydrogen-bonding; Adsorption

Chemical recycling of CO₂ is an attractive approach to mitigate the CO₂ emission originating from human activity. Formic acid (HCOOH) is one of the hydrogenated products of CO₂ and catalytically decompose into H₂ and CO₂. Therefore, it has been expected to be one of the hydrogen carrier/storage materials.¹ In addition, formate species, which are formed on the catalyst surface in the HCOOH decomposition process, is a candidate of the stable intermediate in methanol synthesis on the Cu-based catalyst. Thus, the surface chemistry of HCOOH and formate on the Cu surface is an important issue for chemical CO₂ recycling.

We have investigated the surface chemistry of HCOOH including adsorption, decomposition, and desorption on the Cu(977) surface. Using high-resolution X-ray photoelectron spectroscopy we found that the Cu(977) surface has a higher activity for HCOOH dissociation; the conversion ratio of HCOOH to formate was 29% on Cu(977), while that on Cu(997) is reported to be 17%.² We systematically conducted temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) to reveal the detailed process of HCOOH on Cu(977). Two molecular desorption peaks of HCOOH were observed at ~170 K (α desorption from the terrace) and ~250 K (β desorption from the step). Bidentate formate species were decomposed and desorbed as CO₂ and H₂ at 458 K, which is higher than the decomposition temperature of 450 K on Cu(997).² Thus, on Cu(977), both HCOOH and formate at the step sites were more stably adsorbed than on Cu(997). IRAS spectra show hydrogen-bonding network of HCOOH molecules was developed on Cu(977) unlike Cu(997), which is evidenced by the observation of the out-of-plane bending mode of the O-H bond at ~980 cm⁻¹. In addition, the carbonyl stretching mode of monodentate formate (1650 cm⁻¹) was very broadened at 140-220 K, indicating that the hydrogen-bonded complex was formed between HCOOH and monodentate formate.³ The vibrational peaks related to the complex disappeared at 220-240 K. That temperature region is well consistent with the β desorption, indicating the complex decomposed into HCOOH and formate above 220 K. We conclude the high activity on the Cu(977) surface is due to the stabilization of bidentate formate and the formation of the hydrogen-bonded complex at the step site. A (100) microfacet at the step would produce these factors.

1) J. Eppinger *et al.*, *ACS Energy Lett.* **2017**, 2, 188. 2) Y. Shiozawa *et al.*, *J. Chem. Phys.* **2020**, 152, 044703. 3) B. W. J. Chen *et al.*, *ACS Catal.* **2020**, 10, 10812.

Spectroscopic Investigation of High Pressure Hydrogen Evolution Reaction

(¹Graduate School of Chemical Sciences and Engineering, and ²Department of Chemistry, Faculty of Science, Hokkaido University) ○Nobuaki Oyamada,¹ Hiro Minamimoto,² Kei Murakoshi²

Keywords: Surface-Enhanced Raman Scattering (SERS); Static Pressure; Interfacial Water Structure; Isotopic Effects; Hydrogen Evolution Reaction (HER)

The water molecules at the electrode interface play a crucial role in the electrochemical reactions. However, the relationship between the interfacial structure and the reaction efficiency is still under discussion.¹ Surface-enhanced Raman scattering (SERS) observations could be the powerful tool to get insight of interfacial water structure.^{2,3} Recently, at the nanostructured surface, we have reported that the unique isotopic selectivity on the hydrogen evolution reactions (HER) could be observed.⁴ In this study, we have conducted electrochemical SERS measurements at the nanostructure interface in the mixture solution of D₂O and H₂O to probe the HER process under static pressure control, enabling to reduce the bubble effects. Through attempts, we have obtained detail information about the electrode interface during HER.

SERS spectra were obtained at roughed Ag electrode in the three-electrode cell under static pressure at 50 MPa (Fig. a). Fig. b shows SERS spectra of the mixture solution of D₂O and H₂O with different mixed ratio at HER potential region. The vibrational modes of H₂, HD, D₂ modes were observed at 4149, 3618, and 2964 cm⁻¹, respectively. Each band intensity ratio indicates the relative amounts of evolved gases at interface. The OH and OD stretching modes of interfacial molecules were also observed at 2500 and 3400 cm⁻¹, respectively. Interestingly, although the band intensity ratio of the stretching mode reflects the bulk components, each production ratio shows distinct values. This difference reflects the kinetic information about the isotopic selectivity of HER at the nanostructured interface. As the result, we have evaluated correlation between water and HER by static pressured electrochemical SERS.

1) Z. Q. Tian, *et al.*, *Nat. Mater.* **2019**, 18, 697. 2) N. Oyamada, *et al.*, *Chem. Lett.* **2019**, 48, 820.
3) N. Oyamada, *et al.*, *J. Phys. Chem. C* **2019**, 123, 24740. 4) H. Minamimoto, *et al.*, *Electrochim. Acta* **2019**, 304, 87.

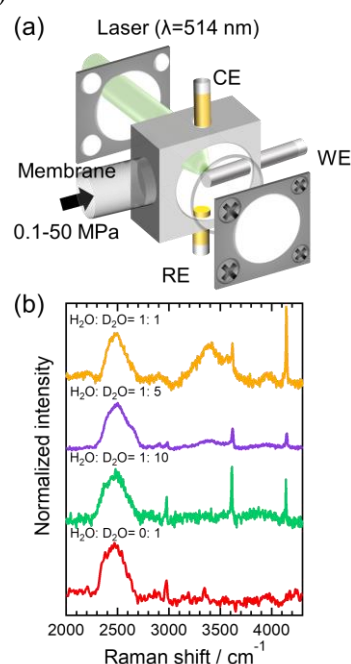


Fig. (a) Schematic picture for electrochemical SERS measurements under static pressure control. (b) Electrochemical SERS spectra of H₂, HD, and D₂ obtained in 0.5 M NaClO₄ aq. at 50 MPa. Each mixed ratio of H₂O and D₂O is indicated in the figure. The electrochemical potentials for each spectrum were (orange, green) -1.11 and (purple, red) -1.31 V vs. RHE.

Academic Program [Oral B] | 04. Physical Chemistry -Properties- | Oral B**[F203-4am] 04. Physical Chemistry -Properties-**

Chair: Tomoyuki Mochida, Takashi Takeda

Sat. Mar 26, 2022 9:00 AM - 10:40 AM F203 (Online Meeting)

[F203-4am-01] Effects of Formamides on Intermolecular Vibrations of 1- Methyl-3-Octylimidazolium Tetrafluoroborate○Masatoshi Ando¹, Yue Peng¹, Atsuya Tashiro², Masahiro Kawano², Toshiyuki Takamuku², Hideaki Shirota¹ (1. Chiba University, 2. Saga University)

9:00 AM - 9:20 AM

[F203-4am-02] Alkyl chain length dependence of conformational distribution in ionic liquids.○Hiroki Sumida¹, Yoshifumi Kimura^{1,2}, Takatsugu Endo² (1. Graduate School of Science and Engineering, Doshisha University, 2. Faculty of Science and Engineering, Doshisha University)

9:20 AM - 9:40 AM

[F203-4am-03] Effect of Substrate Surface on Photo-induced Crawling Motion of Azobenzene Crystals and its Application○Yasuo Norikane^{1,2}, Masaru Hayashino^{2,1}, Mio Ohnuma¹, Kouji Abe¹, Yoshihiro Kikkawa¹, Koichiro Saito¹, Kengo Manabe¹, Kouji Miyake¹, Miki Nakano¹, Naoki Takada¹ (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. University of Tsukuba)

9:40 AM - 10:00 AM

[F203-4am-04] Mass transport of nano/micro materials driven by photo-induced crawling motion of crystals○Koichiro Saito¹, Yasuo Norikane^{1,2} (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. University of Tsukuba)

10:00 AM - 10:20 AM

[F203-4am-05] Study on the Mechanism of Bending in the Crystals of Benzene Derivatives with Halogen and Methyl Groups○Hayato Anetai¹, Yoshitaka Matsushita², Takahito Ohmura², Masayuki Takeuchi² (1. NIMS ICYS, 2. NIMS)

10:20 AM - 10:40 AM

Effects of Formamides on Intermolecular Vibrations of 1-Methyl-3-octylimidazolium Tetrafluoroborate

(¹Department of Chemistry, Chiba University, ²Graduate School of Science and Engineering, Saga University, ³Faculty of Science and Engineering, Saga University) ○Masatoshi Ando,¹ Yue Peng,¹ Atsuya Tashiro,² Masahiro Kawano,² Toshiyuki Takamuku,³ Hideaki Shirota¹

Keywords: Ionic liquid; Molecular liquid; Mixture; fs-RIKES; Low-frequency spectrum

In this study, we have investigated the low-frequency spectra of 1-methyl-3-octylimidazolium tetrafluoroborate ([MOIm][BF₄]) mixtures with formamide (FA), *N*-methylformamide (NMF), and *N,N*-dimethylformamide (DMF) using femtosecond Raman induced Kerr effect spectroscopy (fs-RIKES).^{1,2} Because these formamides have different hydrogen-bonding (HB) abilities, we can examine the effects of the hydrogen bonds between formamides and [MOIm][BF₄] on the intermolecular vibrations in detail.

Figure 1 shows the low-frequency spectra of [MOIm][BF₄] mixtures with FA, NMF, and DMF. As increasing the molecular liquid (ML) mole fraction X_{ML} , the spectral intensity for the [MOIm][BF₄] mixtures gradually increased. In neat liquids, FA has a peak at 100 cm⁻¹ and a shoulder at 200 cm⁻¹ and NMF also has a shoulder at 130 cm⁻¹. Quantum chemical calculations for clusters of FA and NMF have reported that FA and NMF have the vibrational bands of linear HB network at 100 cm⁻¹ and FA also has those of two-dimensional HB network at 200 cm⁻¹.³ Thus, the peak and shoulder of FA at 100 and 200 cm⁻¹ and the shoulder of NMF at 130 cm⁻¹ observed in this study can be attributed to the HB vibrations. The spectral shapes of the mixtures gradually changed from neat [MOIm][BF₄] to each formamide liquid with increasing X_{ML} .

To characterize the X_{ML} dependence of the low-frequency spectra, the plots of the first moment M_1 , which is the center frequency of the spectrum, vs. X_{ML} for the mixtures are shown in Figure 2. As increasing X_{ML} , the M_1 of the low-frequency spectra for the [MOIm][BF₄]/FA increased and that for the [MOIm][BF₄]/DMF decreased. FA has the vibrational bands of the two-dimensional HB network even at low X_{ML} , so the M_1 has shifted to the higher frequency side. DMF may invade to the polar region in [MOIm][BF₄] and make the interionic interaction weaken. On the other hand, the [MOIm][BF₄]/NMF showed almost no concentration dependence of the M_1 in $X_{ML} \leq 0.7$ but the M_1 increased in $X_{ML} \geq 0.8$. This X_{ML} dependence is similar to those of [MOIm][BF₄] mixtures with methanol, acetonitrile, and dimethyl sulfoxide.⁴ It implies that NMF does not much influence on the ionic network of [MOIm][BF₄] in $X_{ML} \leq 0.7$ but break it in $X_{ML} \geq 0.8$.

References

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- 2) H. Shirota, *J. Chem. Phys.* **2005**, *122*, 044514.
- 3) H. Torii and M. Tasumi, *Int. J. Quant. Chem.* **1998**, *70*, 241.
- 4) M. Ando, et. al., *J. Phys. Chem. B* **2020**, *124*, 7857.

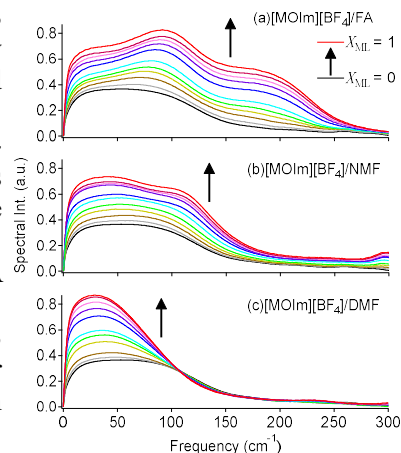


Figure 1. Low-frequency spectra of [MOIm][BF₄] mixtures with (a) FA, (b) NMF, and (c) DMF.

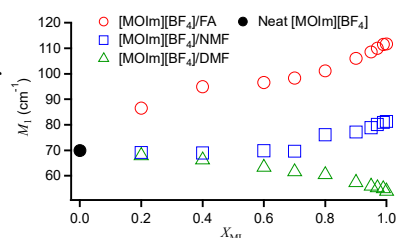


Figure 2. Plots of M_1 vs. X_{ML} for [MOIm][BF₄] mixtures with FA, NMF, and DMF.

Alkyl chain length dependence of conformational distribution in ionic liquids.

(¹Graduate School of Science and Engineering, Doshisha University, ²Faculty of Science and Engineering, Doshisha University) ○Hiroki Sumida,¹ Yoshifumi Kimura,^{1,2} Takatsugu Endo²

Keywords: Ionic liquids; Melting point; Conformation; Molecular Dynamics; Nuclear magnetic resonance

Ionic liquids (ILs) are defined as salts with melting point below 100 °C. Since the melting point is the crucial physical property for ILs, numerous investigations have been made to answer why ionic liquids have such a low melting point as salts. Thermodynamically, melting point (T_m) is expressed by $T_m = \Delta_{\text{fus}}H/\Delta_{\text{fus}}S$ where $\Delta_{\text{fus}}H$ is the fusion enthalpy and $\Delta_{\text{fus}}S$ is the fusion entropy. Contrary to the conventional discussion¹⁾, we have found that $\Delta_{\text{fus}}S$ plays a more important role than $\Delta_{\text{fus}}H$ in lowering melting point of ILs²⁾, i.e., large $\Delta_{\text{fus}}S$ of ILs drastically lowers their T_m . Since most ILs have flexible alkyl chains, the conformational entropy (S_{conf}) in the liquid state may contribute to the large $\Delta_{\text{fus}}S$ of ILs. In this research, conformations of the alkyl chain, e.g., trans, gauche, gauche', were analyzed by molecular dynamics (MD) simulations and NMR spectroscopy to estimate S_{conf} of ILs in the liquid state. 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nmim][NTf₂]) were used for both simulations and experiments.

First, S_{conf} of the ILs with different alkyl chain lengths in the liquid states were estimated from *NPT* MD trajectories (Fig. 1. (a)). The black line in the figure represents maximum S_{conf} where the population of all conformations of the alkyl chain exists equally. Estimated S_{conf} in the ILs (red circles) was always lower than the maximum S_{conf} and the gap was widened when the alkyl chain was lengthened. It was found that the small S_{conf} originated from the large population of the trans conformation (e.g., Fig. 1. (b)). A similar result was also obtained from J-coupling constants of NMR experiments. NMR measurement suggested that strong interactions among the alkyl chains were feasible in the trans conformation.

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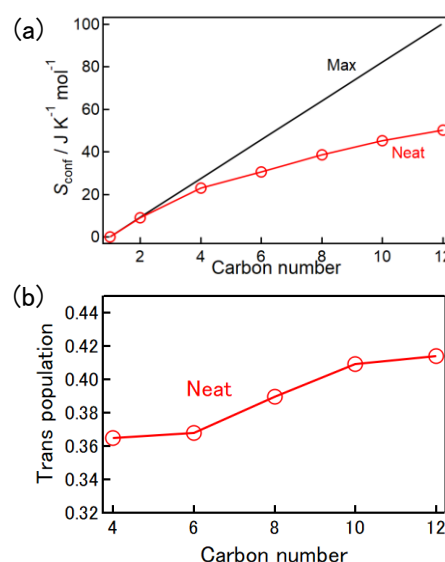


Fig. 1. (a) S_{conf} versus the carbon number of the alkyl chain in the IL cation. (b) Population of the trans conformation of N-C-C-C versus the carbon number of the alkyl chain in the IL cation.

アゾベンゼン結晶における光誘起結晶移動現象の基板表面の効果とその利用

(産総研¹・筑波大院²) ○則包 恭央^{1,2}・林野 優^{1,2}・大沼 未央¹・安部 浩司¹
 ・吉川 佳広¹・齋藤 滉一郎¹・真部 研吾¹・三宅 晃司¹・中野 美紀¹・高田 尚樹¹
 Effect of Substrate Surface on Photo-induced Crawling Motion of Azobenzene Crystals and its Application (¹AIST, ²Graduate School of Science and Technology, University of Tsukuba)
 ○Yasuo Norikane,^{1,2} Masaru Hayashino,^{1,2} Mio Ohnuma,¹ Koji Abe,¹ Yoshihiro Kikkawa,¹
 Koichiro Saito,¹ Kengo Manabe,¹ Koji Miyake,¹ Miki Nakano,¹ Naoki Takada¹

Crystals of azobenzenes show crawling motion when crystals on a glass surface are irradiated by light.^{1,2} Crystals of 3,3'-dimethylazobenzene (DMAB) crawl by irradiation of two light sources (365 and 465 nm) from different directions.¹ To control the velocity and morphology of crystal, and to apply to carry another substance, understanding the mechanism of the crawling motion is required. In this study, we investigated the effect of substrate surfaces on the crawling motion of DMAB. We found that the velocity and morphology were drastically dependent on the wettability of the surface.^{3,4} In addition, we have fabricated patterned surfaces and proved that the crystal motion can be differentiated by the pattern.⁴

Keywords : Azobenzene; Organic crystal; Photoisomerization; Solid-liquid phase transition

ガラス基板上に乗せたアゾベンゼン誘導体の結晶は光照射により基板上を移動する^{1,2)}。例えば、3,3'-ジメチルアゾベンゼン(DMAB)の結晶に紫外光と可視光を異なる方向から同時に照射すると、結晶が紫外光から遠ざかる方向に移動する¹⁾。結晶の移動速度や形態を制御し、さらに他の物質を運搬するシステムに発展させるためには、移動現象の理解が必須である。本研究では、種々の基板上での DMAB の結晶移動挙動を観察し、移動速度と形態は基板表面の濡れ性に大きく依存することを見出した^{3,4)}。また、表面パターンニングを施した基板上での結晶移動の制御を行った⁴⁾。

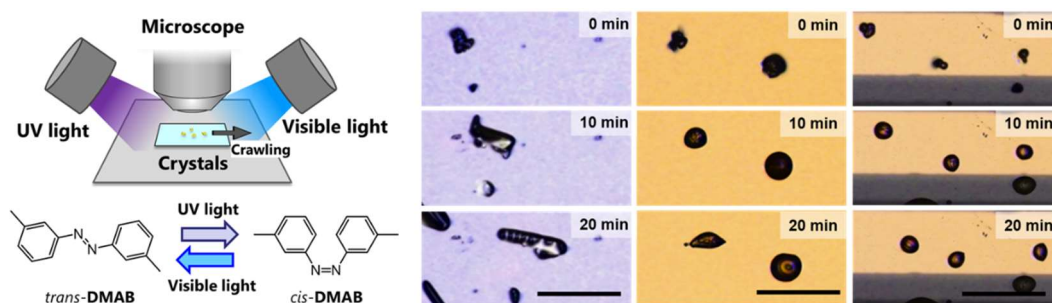


Figure 1. Schematic diagram of the experimental setup (left). Examples of microscopy images of DMAB crystals during the irradiation on various surfaces (right). Scale bar: 100 μm .

1) E. Uchida, R. Azumi, Y. Norikane, *Nat. Commun.* **2015**, 6, 7310. 2) K. Saito, M. Ohnuma, Y. Norikane, *Chem. Commun.* **2019**, 55, 9303-9306. 3) Y. Norikane, M. Hayashino, M. Ohnuma, K. Abe, Y. Kikkawa, K. Saito, K. Manabe, K. Miyake, M. Nakano, N. Takada, *Front. Chem.* **2021**, 9, 684767. 4) Y. Norikane, M. Hayashino, M. Ohnuma, K. Abe, Y. Kikkawa, K. Saito, K. Manabe, K. Miyake, M. Nakano, N. Takada, *Langmuir* **2021**, 37, 14177-14185.

光誘起結晶移動を利用したナノ・マイクロ材料運搬

(産総研¹・筑波大院²) ○齋藤 滉一郎¹・則包 恭央^{1,2}

Mass transport of nano/micro materials driven by photo-induced crawling motion of crystals (¹AIST, ²Graduate School of Science and Technology, University of Tsukuba) ○Koichiro Saito,¹ Yasuo Norikane^{1,2}

Crystals of azobenzene derivatives that show crawling motion on a glass substrate by light irradiation have been reported.¹ In the case of 4-(methylamino)azobenzene (4-MAAB), when the crystals are irradiated with blue visible light from the back side of the glass substrate, the crystals move away from the light source.² Since the crawling direction can be controlled according to the irradiation direction, it is expected to be applied to the mass transportation method that does not require a flow channel. However, there have been no reports that demonstrate the transportation of nano/micro materials. In this study, we succeeded in transporting fluorescent nanoparticles or microparticles on a glass substrate by mixing them with 4-MAAB crystals. It was also found that the change in the brightness of the fluorescence was repeated during the transportation process. This result suggests that the fluorescent nanoparticles are flowing along with the crystal movement.

Keywords : Azobenzene; Organic crystal; Photoisomerization; Solid-to-liquid phase transition

光照射によってガラス基板上を移動するアゾベンゼン誘導体の結晶が報告されている¹⁾。4-メチルアミノアゾベンゼン(4-MAAB)の場合、ガラス基板裏側から青色の可視光を結晶に照射すると、結晶が光源から遠ざかる方向に移動する²⁾。光の照射方向に応じて移動方向を変化させられるため、流路を必要としない微量物質運搬技術への応用が期待される。一方で、実際にナノ・マイクロ材料を運搬した例は報告されていない。本研究では、蛍光性のナノ粒子またはマイクロ粒子を 4-MAAB の結晶と混合し、ガラス基板上での運搬を達成した。また、運搬の過程で蛍光の明暗が繰り返されることを見出した。結晶移動によって蛍光性ナノ粒子が流動していることが示唆され、移動機構の解明につながる知見が得られた。

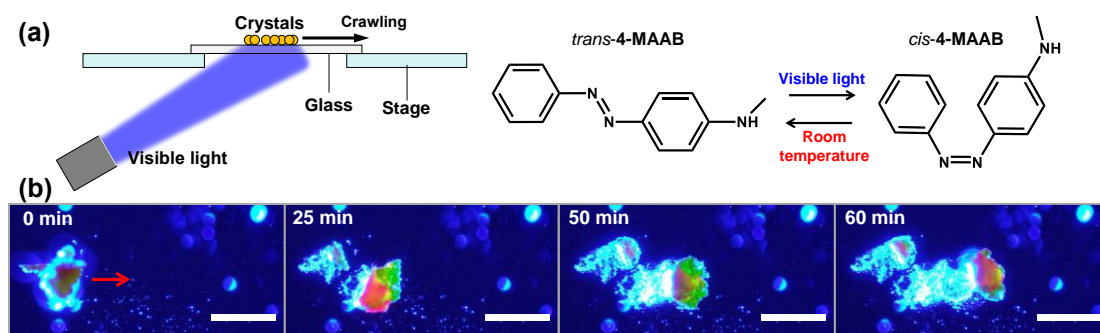


Figure 1. (a) Schematic diagram of the experimental setup. (b) Microscopy images of 4-MAAB crystals that transport red fluorescent nanoparticles. Scale bar: 200 μm .

1) E. Uchida, R. Azumi, Y. Norikane, *Nat. Commun.* **2015**, 6, 7310. 2) K. Saito, M. Ohnuma, Y. Norikane, *Chem. Commun.* **2019**, 55, 9303-9306.

ハロゲンとメチル基を有するベンゼン誘導体結晶の曲がるメカニズムの解明

(¹ICYS, ²NIMS) 〇 姉帯 勇人¹・松下 能孝²・大村 孝仁²・竹内 正之²
 Study on the Mechanism of Bending in the Crystals of Benzene Derivatives with Halogen and Methyl Groups (¹ICYS, ²NIMS) 〇 Hayato Anetai,¹ Yoshitaka Matsushita,² Takahito Ohmura,² Masayuki Takeuchi²

Organic crystals are attractive class of materials with high designability of their physical properties; in recent years, some organic crystals that bend like a wire in response to external stress have been reported. In order to form an unbreakable flexible organic crystal with desired functions, one should investigate the effect of the substituents in the π -electron compounds. In this research, we prepared single crystals of benzene derivatives with halogen or methyl groups as the model compounds and their flexibilities and mechanical properties were examined.

Keywords : Organic Crystals, Plastic Deformation, Halogen-halogen Interaction, π - π Stacking Interaction

有機結晶は物性の設計自由度が高いことから注目を集める材料であるが、有機結晶の多くは壊れやすく、その材料応用は困難である。近年、外部応力に対して針金の様に曲がる有機結晶が数多く報告されている。例えば、ヘキサクロロベンゼン結晶では、塑性変形時にヘキサクロロベンゼン分子間の Cl-Cl 相互作用が再配向することで、優れた塑性変形を示す。¹そこで本研究では、モデル分子としてハロゲンまたはメチル基を有するベンゼン誘導体 (**Br0-Br6, I2**)の単結晶を作製し、柔軟性と機械的性質におよぼす π 電子化合物の置換基の効果を調べたので報告する。

Br0, Br1, Br2, Br3 結晶は室温で、**Br4, Br6, I2** 結晶は加熱時に、塑性変形した(Fig.1)。またこれらの結晶は、2方向に曲がる結晶(**Br0, Br1, Br3** :Group A)と1方向にしか曲がらない結晶(**Br2, Br4, Br6, I2** :Group B)に分類された。単結晶 X 線構造解析と Hirshfeld 表面解析より、この違いは分子間の π - π 相互作用の有無と関連していた。以上より、ハロゲンとメチル基を導入したベンゼン誘導体結晶は塑性変形を示し、かつその置換基の種類と数を変える事で、結晶の曲がり方を制御する事が可能となった。

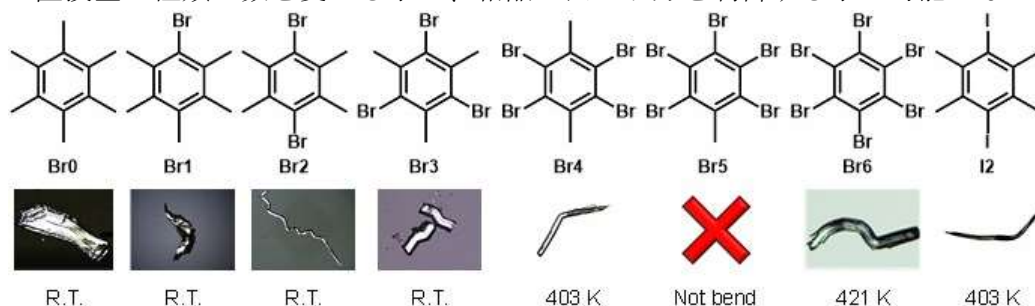


Fig.1 ハロゲンまたはメチル基置換ベンゼン誘導体の分子構造と結晶の曲げ試験

1) K. Panda, S. Ghosh, N. Yasuda, T. Moriwaki, G. D. Mukherjee, C. M. Reddy, P. Naumov, *Nat. Chem.* **2015**, *7*, 65–72.

[J401-4am] 07. Inorganic Chemistry

Chair: Minoru Osada, Yuichi Shimakawa

Sat. Mar 26, 2022 9:00 AM - 11:40 AM J401 (Online Meeting)

[J401-4am-01] Electron doping into La doped Sr_2IrO_4 by hydrogen ion beam irradiation

○Yuta Yamashita¹, Mitsuhiko Maesato¹, GyeongCheol Lim¹, Akira Chikamatsu^{2,4}, Tetsuya Hasegawa², Takahiro Ozawa³, Markus Wilde³, Katsuyuki Fukutani^{3,5}, Hiroshi Kitagawa¹
 (1. Fac. of Science, Kyoto Univ., 2. Dept. of Chemistry, The Univ. of Tokyo, 3. Inst. of Industrial Science, The Univ. of Tokyo, 4. Fac. of Science, Ochanomizu Univ., 5. NSEC, JAEA)

9:00 AM - 9:20 AM

[J401-4am-02] Highly electron doped TaON single crystal -growth and properties-

○Kohdai Ishida¹, Daichi Kato¹, Hiroshi Kageyama¹ (1. Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University)

9:20 AM - 9:40 AM

[J401-4am-03] Structure-property relationships in geometrically frustrated magnets $\text{Ln}_2\text{LiFeO}_6$ with unusually high valence Fe^{5+} ion

○Masato Goto¹, Sean Injac¹, Takashi Saito², Akira Matsuo³, Koichi Kindo³, Tamio Oguchi⁴, Yuichi Shimakawa¹ (1. Kyoto University, 2. KEK, 3. The University of Tokyo, 4. Osaka University)

9:40 AM - 10:00 AM

[J401-4am-04] Conduction mechanism Analysis of Mixed Anion Compounds $\text{La}_2\text{SrF}_{4-x}\text{S}_x$

○Shintaro Tachibana¹, Kazuto Ide², Hisatsugu Yamasaki², Takeshi Tojigamori², Hidenori Miki², Takashi Saito³, Takashi Kamiyama³, Yuki Orikasa¹ (1. Ritsumeikan University, 2. Toyota Motor Corporation, 3. High Energy Accelerator Research Organization)

10:00 AM - 10:20 AM

[J401-4am-05] Dynamics, Geometry, and Electronic State of Single Ag(I) Site in MFI Zeolite Efficient for Xe Adsorption/Separation

○Akira Oda^{1,2}, Hiroe Kozai³, Kyoichi Sawabe^{1,2}, Atsushi Satsuma^{1,2}, Takahiro Ohkubo³, Yasushige Kuroda³ (1. Nagoya University, 2. Elements Strategy Initiative for Catalysts and Batteries (ESICB), 3. Okayama University)

10:20 AM - 10:40 AM

[J401-4am-06] Synthesis and Evaluation of Hyper-multinary Compound by Utilizing Quasi-sub-nanoparticle

○Takamasa Tsukamoto^{1,2,3}, Nozomi Yoshida¹, Tatsuya Moriai¹, Tetsuya Kambe^{1,3}, Kimihisa Yamamoto^{1,3} (1. Tokyo Institute of Technology, 2. PRESTO, JST, 3. ERATO, JST)

10:40 AM - 11:00 AM

[J401-4am-07] Successive phase transitions caused by unusually high valence $\text{Fe}^{3.5+}$ ions in A-site layer-ordered double-perovskites RBaFe_2O_6 (R =rare earth metals)

○Makoto Iihoshi¹, Sean Dusan Injac¹, Midori Patino Amano¹, Masato Goto¹, Yuichi

Shimakawa¹ (1. Kyoto Univ.)

11:00 AM - 11:20 AM

[J401-4am-08] VT-VH-MCD Spectroscopic Study of the Magnetic Interaction in the
Excited States of Lanthanide-Porphyrin Complexes with Different
Hetero-Cyclododecane Ligands

[○]Langit Cahya Adi¹, Anas Santria¹, Naoto Ishikawa¹ (1. Chemistry Department, Graduate
School of Science, Osaka University)

11:20 AM - 11:40 AM

Electron Doping into La doped Sr_2IrO_4 by Hydrogen Ion Beam Irradiation

(¹*Fac. of Sci. Kyoto Univ.*, ²*Dept. of Chemistry The Univ. of Tokyo*, ³*Inst. of Industrial Science The Univ. of Tokyo*, ⁴*Fac. of Sci. Ochanomizu Univ.*, ⁵*NSEC JAEA*) ○Y. Yamashita,¹ M. Maesato,¹ G. Lim,¹ A. Chikamatsu,^{2,4} T. Hasegawa,² T. Ozawa,³ M. Wilde,³ K. Fukutani,^{3,5} H. Kitagawa¹

Keywords: Hydrogen ion beam, Iridate, Transport property

Iridates have the potential to exhibit unique electronic properties because of the relatively large spin-orbit coupling with same energy scale of the electron correlations. As a typical example, Sr_2IrO_4 is considered to be an exotic $J_{\text{eff}} = 1/2$ Mott insulator¹ and has some similarities to the parent compound of high-temperature superconducting cuprates. Theoretical studies on the possible unconventional superconductivity of carrier-doped Sr_2IrO_4 have encouraged experimental researches.² However, the superconductivity has not yet been observed experimentally in the layered iridates. Recently, we performed hydrogen ion beam irradiation into Sr_2IrO_4 thin film and observed a large decrease in electrical resistivity due to high-density electron doping, but neither a metallic behavior nor a superconducting transition was observed.³ Here we report on the effects of the La substitution in Sr_2IrO_4 on hydrogen implantation.

Thin films of $\text{Sr}_{2-x}\text{La}_x\text{IrO}_4$ ($x = 0.01, 0.03, 0.05, 0.10$) were deposited on $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$ (LSAT) (001) substrates by pulsed laser deposition (PLD) under the partial oxygen pressure (P_{O_2}) of 1 mTorr at the substrate temperature of 800 °C. Hydrogen was implanted into the $\text{Sr}_{2-x}\text{La}_x\text{IrO}_4$ films at 100 K with an acceleration voltage of 2.0 kV. The dose of hydrogen was estimated by the ion current. We performed *in situ* electrical transport measurements and observed a large decrease in resistivity after the irradiation. In addition, the resistivity further decreased irreversibly when the sample was heated to room temperature and cooled again. The ex-situ Hall effect measurement revealed an increase in n-type carrier of $\text{Sr}_{2-x}\text{La}_x\text{IrO}_4$. The carrier density was found to be nearly constant regardless of the La concentration. Furthermore, in order to investigate the correlation between the concentration of hydrogens and the La concentration, we carried out nuclear reaction analysis. It revealed the less concentration of hydrogen in the La-substituted Sr_2IrO_4 than that in non-substituted Sr_2IrO_4 .

1) B. J. Kim, *et al.*, *Phys. Rev. Lett* **101**, 076402 (2008). 2) H. Watanabe, *et al.*, *Phys. Rev. Lett* **110**, 027002 (2013). 3) Y. Yamashita, *et al.*, *Phys. Rev. B* **104**, L041111 (2021).

Highly electron doped TaON single crystal -growth and properties-

(¹ Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan)○

Kohdai Ishida,¹ Daichi Kato,¹ Hiroshi Kageyama^{1*}

Keywords: Single crystal; TaON; flux growth; electron doping; oxygen vacancy

Transition metal oxynitrides have attractive properties such as visible-light responsive catalysts, nontoxic pigments, ferroelectricity and magnetic properties. Recently In the double perovskite $\text{La}_2\text{MnTaO}_5\text{N}$, partial anion order enhances spin frustration despite a small tolerance factor.^[1] In order to reach a deeper understanding of the observed properties of transition metal oxynitrides, measurements using single crystals are of crucial importance. For BaTaO_2N by using BaCN_2 flux cubic transparent single crystals were grown to a size of approximately 3.1 μm and ferroelectricity with complete phase inversion was observed on an oxynitride perovskite crystal for the first time.^[2] However, single crystals were limited to relatively small ones (less than 10 μm), because transition metal oxynitrides are easily decomposed into oxides or reduced at high temperature.

Using a flux method, we have succeeded in growing platelet single crystals of TaON, with a typical size of $50 \times 100 \times 10 \mu\text{m}^3$. In contrast to the reported yellow powder samples, the obtained crystals contain a large amount of oxygen vacancy ($x = 0.06$ in TaO_{1-x}N) and exhibit a metallic behavior with a large anisotropy of $\rho/\rho_{ab} \sim 10^3$, in contrast to the previously reported Ta-based oxynitride powder specimens, which are insulators. Moreover, we could grow different crystal morphologies by changing the flux choice. In this presentation, we will present the detailed studies of highly doped TaON single crystal and its physical properties.

References

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- [2] A. Hosono, Y. Masubuchi, S. Yasui, M. Takesada, T. Endo, M. Higuchi, M. Itoh, S. Kikkawa, *Inorg. Chem.* **2019**, 58 (24), 16752–16760.

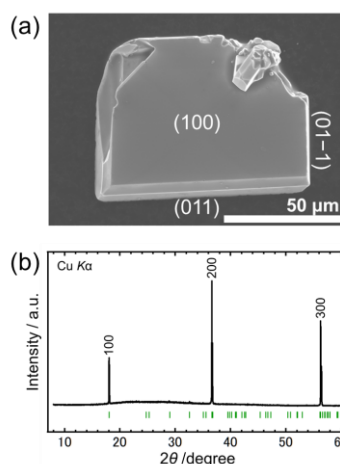


Figure 1. (a) SEM image of TaON single crystal. (b) XRD patterns of TaON crystal.

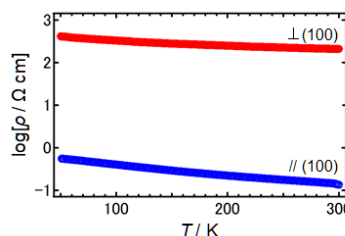


Figure 2. Temperature dependence of electrical resistivity ρ in TaON black crystal, demonstrating high anisotropy.

異常高原子価 Fe^{5+} を含む幾何学的フラストレート磁性体 $\text{Ln}_2\text{LiFeO}_6$ の構造物性相関

(京大化研¹・高エネルギー加速器研究機構²・東大物性研³・阪大スピセンター⁴)
 ○後藤 真人¹・Sean Injac¹・齊藤 高志²・松尾 晶³・金道 浩一³・小口 多美夫⁴・島川 祐一¹

Structure-property relationships in geometrically frustrated magnets $\text{Ln}_2\text{LiFeO}_6$ with unusually high valence Fe^{5+} ion (¹ ICR, Kyoto university, ² KEK, ³ ISSP, the University of Tokyo, ⁴ CSRN, Osaka University) ○Masato Goto,¹ Sean Injac,¹ Takashi Saito,² Akira Matsuo,³ Koichi Kindo,³ Tamio Oguchi,⁴ Yuichi Shimakawa,¹

Geometrically frustrated magnets have attracted attention owing to their magnetic physical properties. We succeeded in synthesizing *B*-site-ordered double perovskites $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$) with a frustrated f.c.c. lattice of unusually high valence Fe^{5+} ions. Despite large antiferromagnetic interactions between Fe^{5+} spins, the magnetic ordering is strongly suppressed. In addition, canted magnetic structures are stabilized only for $\text{Ln} = \text{Sm}$ and Eu . We will show the structure-property relationships in the geometrically frustrated magnets.

Keywords : *B-Site-Ordered Double Perovskite; Geometrically Frustrated Magnet; Unusually High Valence Ion; High Pressure Synthesis*

幾何学的フラストレート磁性体は反強磁性秩序の抑制に起因した新奇物性の発現の舞台として注目を集めている。磁性イオンが面心立方格子を形成する *B* サイト岩塩秩序型ダブルペロブスカイト $\text{A}_2\text{BB}'\text{O}_6$ は、その代表的な物質系の一つであり、bond valence glass などの興味深い磁性が多く報告されている^[1]。本研究では、異常高原子価の Fe^{5+} を含む $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$) の合成に成功し、それらの構造物性相関を解明した^[2,3]。

$\text{Ln} = \text{La}$ は菱面体晶の結晶構造をもつ一方で、 $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$ はいずれも単斜晶構造をもつことが分かった (図 1)。また、鉄の価数については、 ^{57}Fe メスバウアー分光測定や DFT 計算結果から +5 価であることが確かめられた。磁化率の温度依存性から、 $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$ はいずれもワイス温度の絶対値よりも非常に低い温度で磁気相転移を示すことが判明した。一方で、 $\text{Ln} = \text{Sm}, \text{Eu}$ では磁気転移温度以下で自発磁化が生じること (図 2)、 $\text{Ln} = \text{Nd}$ のみ強磁場磁化過程において異常が見られることから、磁氣的基底状態がランタノイドに強く依存することも示唆された。講演では、詳細を示すとともに、それらのランタノイド依存性について議論する予定である。

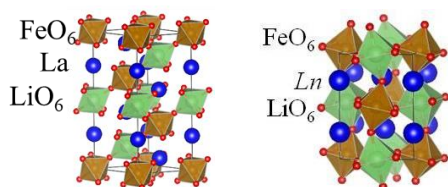


図 1. $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$) の結晶構造。

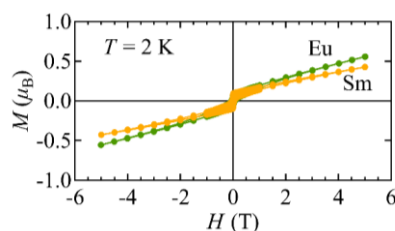


図 2. $\text{Ln}_2\text{LiFeO}_6$ の 2 K での磁化過程。

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複合アニオン化合物 $\text{La}_2\text{SrF}_4\text{S}_2$ における導電メカニズム解析

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Conduction Mechanism Analysis of Mixed Anion Compounds $\text{La}_2\text{SrF}_4\text{S}_2$ (¹*Graduate School of Life Sciences, Ritsumeikan University*, ²*Advanced Material Engineering Div., Toyota Motor Corporation*, ³*High Energy Accelerator Research Organization (KEK)*) ○ Shintaro Tachibana,¹ Kazuto Ide,² Hisatsugu Yamasaki,² Takeshi Tojigamori,² Hidenori Miki,² Takashi Saito,³ Takashi Kamiyama,³ Yuki Oriksa¹

All solid state fluoride-ion batteries(FIBs) are highly attracted attention due to high theoretical energy density and high safety compared with those of conventional lithium-ion batteries(LIBs). However, it is far from practical use because there is no solid electrolyte which exhibits high ionic conductivity and offers wide electrochemical potential window like lithium-ion conductor. To our best knowledge, there is few reports on the fluoride ion conductor materials containing mixed-anion compounds. Mixed-anion compounds have recently attracted attention, and unique structures with mixed anions have been reported. Therefore, using mixed-anion compounds could realize much higher physical properties than ever before. In this study, we prepared La-Sr-F-S compounds by solid-state reaction under vacuum. The crystal structure of the synthesized compounds were characterized by X-ray diffraction, neutron diffraction, and ¹⁹F MAS NMR. We visualized fluoride-ion conduction pathway among La-Sr-F-S compounds. **Keywords :** Fluoride Ion Batteries; Mixed Anion Compounds; Solid Electrolytes;

全固体フッ化物イオン二次電池は次世代蓄電池の候補である¹。実用化へ向けた最大の課題は、高いイオン伝導率と広い電位窓を両立した固体電解質が無いことである²。既報のフッ化物イオン伝導体は、単一アニオンの化合物であり、材料探索の領域を拡張する必要がある。我々は、フッ化硫化物群に着目し、 $\text{Yb}_3\text{F}_4\text{S}_2$ の合成および導電特性評価を行った。しかしながら、Yb の混合価数による電子伝導性が確認され、固体電解質としての適用は不可であった³。そこで、本研究では、 $\text{Yb}_3\text{F}_4\text{S}_2$ の Yb サイトを元素置換したフッ化硫化物 $\text{La}_2\text{SrF}_4\text{S}_2$ 化合物を合成し、フッ化物イオン伝導体を見出した。粉末 X 線回折(XRD)、中性子回折(ND)および ¹⁹F MAS NMR 測定を用いて、平均構造および局所構造の観点から $\text{La}_2\text{SrF}_4\text{S}_2$ の導電メカニズムを明らかにした。フッ化硫化物 $\text{La}_2\text{SrF}_4\text{S}_2$ は、格子欠陥の制御なしにフッ化物イオン伝導経路を既に確保しており、 $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ 等で見られる F⁻空孔を起点とする既報のフッ化物イオン伝導体と異なる機構を有することが判明した。

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- 3) S. Tachibana, K. Ide, T. Tojigamori, Y. Yamamoto, H. Miki, H. Yamasaki, Y. Kotani, Y. Oriksa, *Chem. Lett.*, **2021**, *50(1)*, 120-123

Dynamics, Geometry, and Electronic State of Single Ag(I) Site in MFI Zeolite Efficient for Xe Adsorption/Separation

(¹Graduate School of Engineering, Nagoya University, ²Elements Strategy Initiative for Catalysts and Batteries (ESICB), ³Graduate School of Natural Science and Technology, Okayama University) ○Akira Oda,^{1,2} Hiroe Kozai,³ Kyoichi Sawabe,^{1,2} Atsushi Satsuma,^{1,2} Takahiro Ohkubo,³ Yasushige Kuroda³

Keywords: Keywords : Xe adsorption/separation, Ag(I) zeolite, reactive center dynamics

Xe adsorption/separation technology is needed for expanding the application of Xe existing in the air with only 0.087 ppm.^{1, 2} Here, we report MFI zeolite containing a high concentration of single Ag(I) sites capable of Xe separation with 100% selectivity from Kr and O₂ under the near practical condition (**Figure 1**). We designed this material through the environmentally benign ion-exchange procedure. Only the evacuation at around 473 K allowed us to activate this material and use it for Xe adsorption/separation applications. The adsorption site was identified as the single Ag(I) site by a combination of FTIR spectroscopy using CO as a probe molecule, wavelet transform EXAFS, differential adsorption heat of Xe, ¹²⁹Xe NMR spectroscopy, energy calculation with DLPNO-CCSD(T) method, ¹²⁹Xe chemical shift calculation at DLPNO-MP2 method, ab initio molecular dynamics simulation, and Kohn-Sham molecular orbital analysis. It was shown that the single Ag(I) site captures the Xe atom via Xe-5p→Ag(I)-5s donation interaction. This driving force originates from the superior acidic property of the Ag(I) ion, endowed by the coordination with the framework AlO₄ tetrahedra in the zeolite. Since the valence orbital energies of Kr are lower than those of Xe, the Kr-4p→Ag(I)-5s donation interaction is not so strong. Thus, the single Ag(I) zeolite formed in zeolite selectively interacts with Xe even under the co-presence of Kr and enables the selective Xe capture. The present work provides atomic-level insights into how we can create the Xe adsorption/separation functionality using the local geometry of the porous materials.

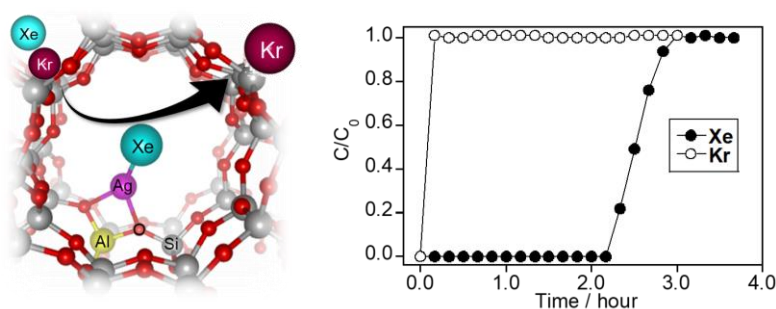


Figure 1. (left) Schematic view of the Xe/Kr separation over the single Ag(I) site in MFI zeolite via the formation of the stable Ag(I)–Xe complex. (right) Breakthrough curves of Xe and Kr observed on Ag(I)/MFI at 298 K under the 50 ppm Xe/ 500 ppm Kr/ 200 kPa O₂ gas mixture.

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準サブナノ領域を活用した超多元素混合微粒子の合成と評価

(東工大化生研¹・JST-さがけ²・JST-ERATO³) ○塚本 孝政^{1,2,3}・吉田 希生¹・森合 達也¹・神戸 徹也^{1,3}・山元 公寿^{1,3}

Synthesis and Evaluation of Hyper-multinary Compound by Utilizing Quasi-sub-nanoparticle (¹Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, ²PRESTO, JST, ³ERATO, JST) ○Takamasa Tsukamoto,^{1,2,3} Nozomi Yoshida,¹ Tatsuya Moriai,¹ Tetsuya Kambe,^{1,3} Kimihisa Yamamoto^{1,3}

Multinary compounds composed of multiple elements have attracted worldwide attention due to their unique properties not found in conventional alloys or compounds. However, the synthesis of such materials has been extremely difficult because of the thermodynamic limitation. In this study, we newly investigated the synthesis of hyper-multinary compounds by utilizing spontaneous amorphization behavior of ultrasmall structures in quasi-sub-nanometer range (2-3 nm). By applying the template synthetic method of alloy clusters using macromolecular capsules¹⁻⁴⁾, a hyper-multinary quasi-sub-nanomaterial composed of 56 elements was successfully synthesized (Fig.1). This material had an amorphous structure with 2-3 nm particle size and exhibited properties unique to hyper-multinary systems such as liquid-like fluidity under STEM observation and an unusual air-oxidation behavior.

Keywords : Hyper-multinary Compound; Quasi-sub-nano Region; Amorphous; Nanoparticle; Cluster

多数の元素から構成された多元化合物は、従来の合金や化合物には見られない特異な性質を示すことから世界的に注目されている。しかしながら、元素混合における熱力学的な制限により、このような物質の合成はこれまで困難とされていた。本研究では、準サブナノメートル (2~3 nm) の極小構造が示す自発的なアモルファス化挙動を利用することで、この制限を克服した超多元素混合物質の合成を目指した。高分子カプセルを利用した多元合金クラスターの鋳型合成法¹⁻⁴⁾の応用し、56種類の元素から構成される多元素混合微粒子の合成に初めて成功した (Fig.1)。この超多元微粒子は粒径 2~3 nm のアモルファス構造を持ち、電子顕微鏡観察下において液体のような流動性を示した。加えて、通常の単体のバルクやナノ粒子には見られない特殊な空気酸化挙動など、多元素混合微粒子に特有の物性が明らかになった。

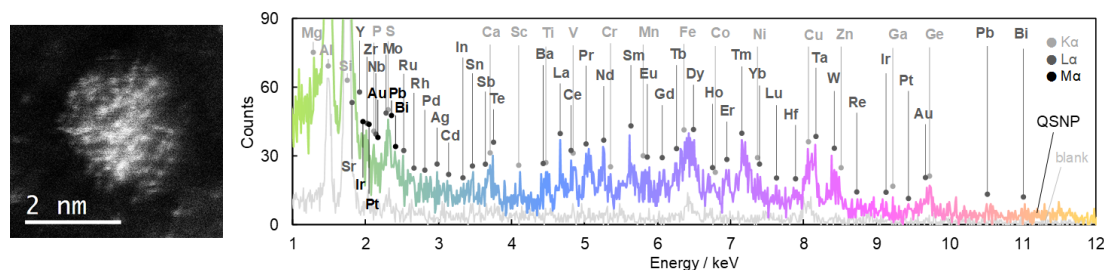


Fig. 1 STEM image and EDS spectra of the hyper-multinary quasi-sub-nanomaterial.

[1] T. Tsukamoto et al., *Nat. Commun.* **2018**, 9, 3873. [2] T. Tsukamoto et al., *Nat. Rev. Chem.* **2021**, 5, 338. [3] T. Tsukamoto et al., *Acc. Chem. Res.* **2021**, 54, 4486. [4] T. Tsukamoto et al., *Angew. Chem. Int. Ed.* **2022**, in press.

A サイト層状ダブルペロブスカイト酸化物 $RBaFe_2O_6$ (R : 希土類金属)における異常高原子価 $Fe^{3.5+}$ イオンに起因する逐次相転移

(京大化研¹) ○飯星 真¹・Sean Injac¹・Midori Amano¹・後藤 真人¹・島川 祐一¹
 Successive phase transitions caused by unusually high valence $Fe^{3.5+}$ ions in A -site layer-ordered double-perovskites $RBaFe_2O_6$ (R = rare-earth metals) (¹ICR, Kyoto University) ○Makoto Iihoshi,¹ Sean Injac,¹ Midori Amano,¹ Masato Goto,¹ Yuichi Shimakawa¹

We synthesized A -site layer-ordered double-perovskites $RBaFe_2O_6$ (R = rare-earth metals) with unusually high valence $Fe^{3.5+}$ ions. $RBaFe_2O_6$ was found to show a structural, charge, and magnetic transition near room temperature followed by additional magnetic transitions at low temperatures. We will discuss possible phase transition mechanisms and also the effects of the ionic radius and magnetic moment of rare-earth metals to the transition behaviors.

Keywords : Unusually high valence; Perovskite; Phase transition

我々は、異常高原子価状態 $Fe^{3.5+}$ をもつ A サイト層状ダブルペロブスカイト $RBaFe_2O_6$ (R^{3+} : 希土類金属) に注目し (Fig.1)、価数状態の不安定性に起因した相転移について研究している。前回の発表では、 $R = Nd, Sm$ についての合成と構造・物性変化を報告し、構造相転移を伴う多段階の磁気転移を起こすことを明らかにした。今回の講演ではさらに詳細な物性評価の結果に加えて、新たに合成に成功した $R = Gd, Tb, Y$ についての物性も報告する。

合成した試料はいずれも室温より高温で構造相転移を伴う磁気転移を示し、低温領域でさらなる磁気転移を示したが、新たに合成した $R = Gd, Tb, Y$ の試料は低温での磁化率の温度依存性において $R = Nd, Sm$ の試料とは異なる挙動を示した (Fig.2)。講演では、 ^{57}Fe メスバウアー分光測定の結果から推測される逐次相転移のメカニズムを考察するとともに、希土類金属 R のサイズ効果や希土類磁気モーメントの大きさが相転移に及ぼす影響についても議論する。

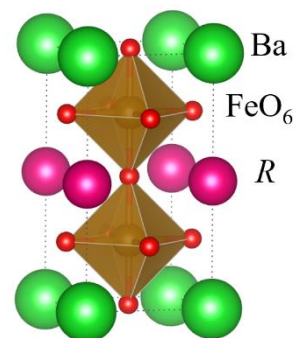


Fig.1 : A サイト層状ダブルペロブスカイト $RBaFe_2O_6$

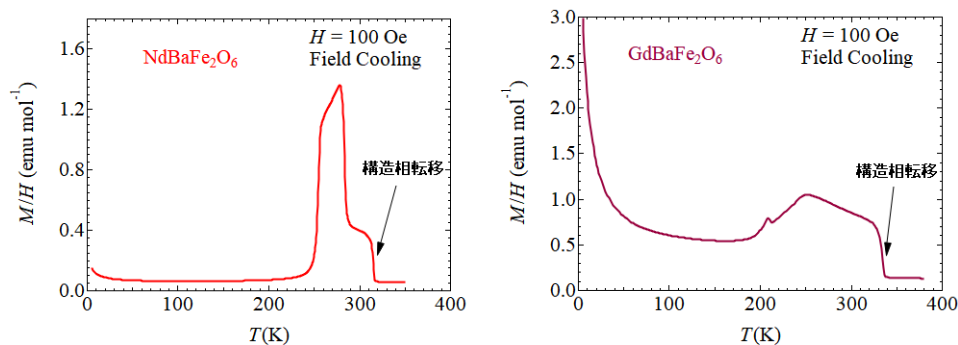


Fig.2 : $RBaFe_2O_6$ ($R = Nd, Gd$)の磁化率の温度依存性

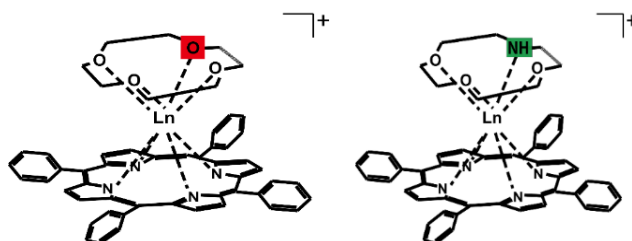
VT-VH-MCD Spectroscopic Study of the Magnetic Interaction in the Excited States of Lanthanide-Porphyrin Complexes with Different Hetero-Cyclododecane Ligands

(¹Department of Chemistry, School of Science, Osaka University) ○Langit Cahya Adi,¹
Anas Santria,¹ Naoto Ishikawa,¹

Keywords: Magnetic circular dichroism, lanthanides, porphyrin

The electronic interactions between orbital angular momentum of porphyrin denoted as **L** and the total angular momentum of lanthanides (III) **J** in lanthanide (Ln)-porphyrinoid molecular systems were investigated with variable-temperature and variable-magnetic field magnetic circular dichroism (VT-VH-MCD) spectroscopy where lanthanide(III) are Tb(III) and Dy(III). Here, investigations were carried out on [Ln(TPP)Crown]Cl and [Ln(TPP)Azacrown]Cl (TPP: 5,10,15,20-tetraphenylporphyrinato; Crown: 12-crown-4 ether or 1,4,7,10-tetraoxacyclododecane; Azacrown: 1-aza-12-crown-4 ether or 1,4,7-Trioxa-10-azacyclododecane). The aim of this research was to investigate how **J–L** interaction (Δ_{JL}) is tuned by symmetric non-aromatic ligand (12-crown-4 ether) and asymmetric ligand (1-aza-12-crown-4 ether). Furthermore, *ab-initio* RASSCF calculation was performed to investigate the electronic energy states at ground state, the angular momentum at excited states, and magnitude of **J–L** interaction.

The interaction was determined by simulation-based fitting to experimental A_1/D_0 ratios (A_1 : the A-term intensity, D_0 : the oscillator strength of the band) for Q(0,0) and Q(1,0) bands, detected in visible wavelength region, and B(0,0) band, appearing near UV region, all of which correspond to the $\pi-\pi^*$ transition within porphyrin. By treating **J** to be constant and **L** as a variable, it was found that different symmetries of the non-aromatic ligands did not alter orbital angular momentum of the complexes. However, the interaction was observed to increase in all bands when the symmetric ligand was replaced with the symmetric one.



[B304-4am] 08. Catalysts and Catalysis

Chair: Yosuke Kageshima, Hideki Kato

Sat. Mar 26, 2022 9:00 AM - 11:20 AM B304 (Online Meeting)

[B304-4am-01] Photoelectrochemical Water Oxidation in visible light over a Lead-Titanium Oxyfluoride Photoanode Prepared by a Particle Transfer Method○Ryusuke Mizuochi¹, Kengo Oka², Kazuhiko Maeda¹ (1. Tokyo Institute of Technology, 2. Kindai University)

9:00 AM - 9:20 AM

[B304-4am-02] Measurement of the pseudo overpotential for water oxidation by nano-sized heterogeneous metal oxide catalyst○Megumi Okazaki¹, Yasuomi Yamazaki², Shunsuke Nozawa³, Osamu Ishitani¹, Kazuhiko Maeda¹ (1. Tokyo Institute of Technology, 2. Seikei University, 3. High Energy Accelerator Research Organization)

9:20 AM - 9:40 AM

[B304-4am-03] Synthesis and Photocatalytic Hydrogen Peroxide Production on Zr-MOF with Missing-Linker Defects○Yoshifumi Kondo¹, Yasutaka Kuwahara^{1,2,3}, Kohsuke Mori^{1,2}, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. PRESTO, JST)

9:40 AM - 10:00 AM

[B304-4am-04] Investigation of Photocatalytic CO₂ Reduction using Photoconductive Coordination Polymer with Metal–Sulfur Bonds○Yoshinobu Kamakura¹, Disuke Tanaka², Kazuhiko Maeda¹ (1. Tokyo Institute of Technology, 2. Kwansei Gakuin University)

10:00 AM - 10:20 AM

[B304-4am-05] Plasma surface modification of C₃N₄ improves durability of photocatalytic CO₂ reduction with RuRu supramolecular photocatalyst○Noritaka Sakakibara¹, Mitsuhiko Shizuno¹, Tomoki Kanazawa², Akira Yamakata³, Shunsuke Nozawa², Tsuyohito Ito⁴, Kazuo Terashima⁴, Kazuhiko Maeda¹, Osamu Ishitani¹ (1. Tokyo Tech., 2. KEK, 3. TTI, 4. The Univ. of Tokyo)

10:20 AM - 10:40 AM

[B304-4am-06] Development of PtRu alloy nanoparticle cocatalysts for water splitting photocatalystsChristian Mark Pelicano¹, ○Masaki Saruyama¹, Toshiharu Teranishi¹ (1. Kyoto Univ.)

10:40 AM - 11:00 AM

[B304-4am-07] Noble metal-based nanostructured catalysts for hydrogenation and dehydrogenation reactions via plasmon-assisted catalysis○Priyanka Verma¹, Yasutaka Kuwahara^{1,2,3}, Kohsuke Mori^{1,2}, Hiromi Yamashita^{1,2} (1. Osaka University, 2. ESICB, Kyoto University, 3. JST PRESTO)

11:00 AM - 11:20 AM

Photoelectrochemical Water Oxidation in Visible Light over a Lead-Titanium Oxyfluoride Photoanode Prepared by a Particle Transfer Method

(¹*School of Science, Tokyo Institute of Technology*, ²*Faculty of Science and Engineering, Kindai University*) ○Ryusuke Mizuochi¹, Kengo Oka², Kazuhiko Maeda¹

Keywords: Artificial photosynthesis; Solar fuel; Photoelectrochemistry; Water oxidation; Mixed anion compound

Photoelectrochemical water splitting has attracted much attention as a method to generate hydrogen, a promising clean energy source. For the photoanodes used in this method, there is a need for materials that possess a narrow band gap responsive to visible light, suitable band-edge potentials for water splitting, and stability against photogenerated holes. We have previously reported a lead-titanium oxyfluoride, $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$, as a material that satisfies these requirements.¹ However, the oxyfluoride photoanode has not showed the satisfactory photocurrent value compared to other competitive one such as BiVO_4 . One of the reasons for this is that the conductivity of the oxyfluoride electrode is poor due to the relatively large size of the oxyfluoride particles synthesized through solid-state reaction. In the present work, we have investigated the $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ photoanode prepared by a particle transfer method, where the electrode with low intergranular resistance has the good conductivity.² Its method intends to enhance the activity of water oxidation.

$\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ powder was synthesized according to our previous report¹ and then deposited tightly onto a titanium substrate through the particle transfer method.² Subsequently, the as-deposited electrode was loaded with cobalt phosphate (Co-Pi) by an electrodeposition method, which is known to a water oxidation promoter.

The as-prepared Co-Pi/ $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ /Ti electrode showed a clear anodic photocurrent under visible light of longer wavelengths than ~ 400 nm. In our previous report,¹ surface modification with TiO_2 was necessary to improve conductivity of the $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ photoanode in order to obtain a significant anodic-photocurrent. By contrast, conductivity of that is already sufficient in using the particle transfer method. Besides, the Ti electrode without $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ powder showed almost no photocurrent, indicating that the obtained photocurrent was caused by the photoabsorption of $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ itself. Furthermore, the photocurrent was enhanced by loading Co-Pi. In this presentation, the effect of the deposition conditions and substrate metals on the water oxidation activity in the particle transfer method will be discussed.

1) N. Hirayama, H. Nakata, H. Wakayama, S. Nishioka, T. Kanazawa, R. Kamata, Y. Ebato, K. Kato, H. Kumagai, A. Yamakata, K. Oka, K. Maeda, *J. Am. Chem. Soc.*, **2019**, *141*, 17158.

2) T. Minegishi, N. Nishimura, J. Kubota, K. Domen, *Chem. Sci.*, **2013**, *4*, 1120.

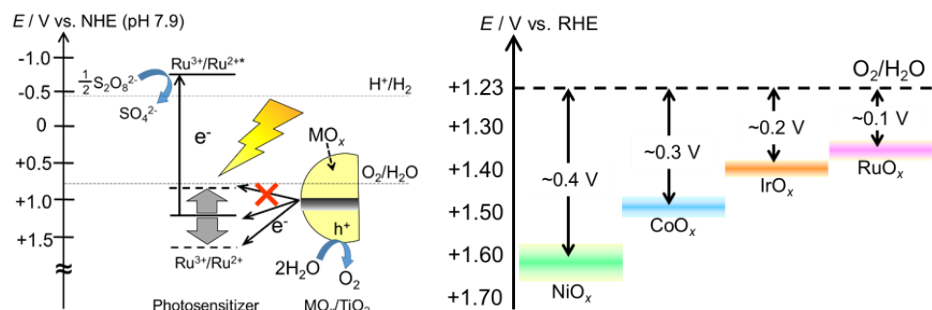
Measurement of the pseudo overpotential for water oxidation by nano-sized heterogeneous metal oxide catalyst

(¹*School of Science, Tokyo Institute of Technology*, ²*Graduate School of Science and Technology, Seikei University*, ³*Institute of Materials Structure Science, High Energy Accelerator Research Organization*) ○Megumi Okazaki,¹ Yasuomi Yamazaki,² Shunsuke Nozawa,³ Osamu Ishitani,¹ Kazuhiko Maeda¹

Keywords: Metal Oxide Nanoparticle; Water Oxidation; Semiconductor Photocatalyst; Ruthenium complex

Metal oxide (MO_x) nanoparticles loaded onto a semiconductor photocatalyst are known as water oxidation cocatalysts, which improve charge separation ability to enhance the photocatalytic activity.¹ It is considered that the water oxidation ability of MO_x – that is, pseudo-overpotential for water oxidation – is strongly related to electrochemical potential of electrons in the MO_x. However, the quantitative discussion of those potentials in heterogeneous MO_x nanoparticles has hardly been done due to the difficulty in directly estimating those potentials for highly dispersed nanoparticle catalysts on the semiconductor surface.

In this work, we have established the estimation method of electrochemical potentials of electron by applying a photochemical water oxidation system to measure the pseudo-overpotentials for nano-sized water oxidation catalyst.² The potentials of electrons in MO_x nanoparticle (M = Co, Ni, Ru and Ir) were quantitatively estimated using Ru(II) tris-diimine type photosensitizers. In this reaction system, the photochemical water oxidation proceeds or not reflects whether the electron transition from MO_x to Ru^{3+/2+}. The potentials of MO_x and Ru^{3+/2+} were adjusted by changing pH conditions in reactant solution and substituent in their ligands, respectively. As a result, we succeeded in estimating not only the potentials of MO_x but also the pseudo-overpotentials from the calculation of energy gaps between O₂/H₂O and MO_x potentials. The order of estimated pseudo-overpotentials were almost same with the results originally obtained from electrochemical catalysts.³



1) K. Maeda, *J. Photochem. Photobiol.* **2011**, 12, 237. 2) D. Hong, S. Fukuzumi, *et al.*, *J. Am. Chem. Soc.* **2012**, 134, 19572. 3) M. Okazaki, Y. Yamazaki, O. Ishitani, K. Maeda, *et al.*, *submitted*.

Synthesis and Photocatalytic Hydrogen Peroxide Production on Zr-MOF with Missing-Linker Defects

(¹Graduate School of Engineering, Osaka University, ²Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, ³JST PRESTO)

○Yoshifumi Kondo,¹ Yasutaka Kuwahara,^{1,2,3} Kohsuke Mori,^{1,2} Hiromi Yamashita^{1,2}

Keywords: Metal-Organic Framework; Hydrogen Peroxide; Structural Defect

Metal-organic frameworks (MOFs) are a class of coordination compounds composed of metal clusters and organic linkers. Their porosity, high surface area, and modularity have a great potential for catalyst materials. Some amine-functionalized MOFs were reported to be active toward photocatalytic hydrogen peroxide (H_2O_2) production via O_2 reduction.¹ An amine-functionalized Zr-based MOF (UiO-66- NH_2) is expected to be effective for photocatalytic H_2O_2 production due to high stability and large surface area. However, it shows limited photocatalytic activity despite the visible-light absorption property. Previous theoretical and experimental studies have showed the introduction of missing-linker sites in UiO-66- NH_2 is an effective approach to enhance the photocatalytic activity due to increasing charge transfer capability.^{2,3} In this work, we synthesized defective UiO-66- NH_2 and applied it to photocatalytic H_2O_2 production.⁴

Defective UiO-66- NH_2 (UiO-66- NH_2 -X; X is the amount of the acetic acid added during the synthesis) was synthesized via solvothermal method with acetic acid. Based on ^1H -NMR and TG-DTA analysis, the amount of missing-linker defects in UiO-66- NH_2 -X increased by increasing concentration of acetic acid added. UiO-66- NH_2 -X was dispersed in an O_2 -saturated acetonitrile solution containing benzyl alcohol as an electron donor. H_2O_2 was produced over all samples with light ($\lambda > 350 \text{ nm}$) irradiation. The produced amount of H_2O_2 utilizing defective UiO-66- NH_2 -X was higher than that of the pristine UiO-66- NH_2 (Fig. 1). The improved amount of H_2O_2 obtained by UiO-66- NH_2 -X was attributed to not only the promotion of reaction rate but also the suppression of H_2O_2 decomposition by introducing missing-linker defects.

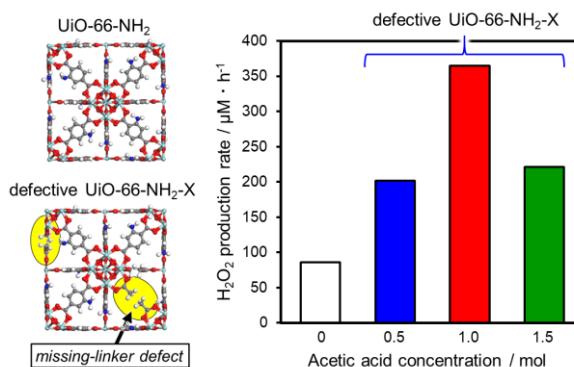


Fig. 1 Photocatalytic H_2O_2 production under light irradiation using UiO-66- NH_2 and defective UiO-66- NH_2 -X (X = 0.5, 1.0, 1.5).

- 1) Y. Isaka, Y. Kondo, Y. Kawase, Y. Kuwahara, K. Mori, H. Yamashita, *Chem. Commun.* **2018**, 54, 9270.
- 2) A. D. Vos, K. Hendrickx, P. V. D. Voort, V. V. Speybroeck, K. Lejaeghere, *Chem. Mater.* **2017**, 29, 3006.
- 3) X. Ma, L. Wang, Q. Zhang, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2019**, 58, 12175.
- 4) Y. Kondo, Y. Kuwahara, K. Mori, H. Yamashita, *J. Phys. Chem. C* **2021**, 125, 27909.

Investigation of Photocatalytic CO₂ Reduction using Photoconductive Coordination Polymer with Metal–Sulfur Bonds

(¹*School of Science, Tokyo Institute of Technology*, ²*School of Science, Kwansei Gakuin University*) ○Yoshinobu Kamakura,¹ Daisuke Tanaka,¹ Kazuhiko Maeda¹

Keywords: Coordination polymer, Photocatalyst, CO₂ reduction, Photoconductivity

CO₂ reduction by visible light has attracted much attention because of an increasing apply to sustain our society. Most photocatalytic systems for CO₂ reduction into HCOOH rely on precious and rare metal components such as Ru complexes for building block of photocatalytic system as catalytic and/or light-absorbing centers. Coordination polymers (CPs) are potential candidates because of their high structural designability. CPs containing the (–M–S–)_n infinite sheet structure absorb visible light and appear high photoconductivity under irradiation. While CPs containing the (–M–S–)_n structure are potential candidates for visible-light driven CO₂ reduction, however, there have been no investigation on their use as photocatalysts for CO₂ reduction.

We demonstrated that Pb-based photoconductive CPs containing the (–Pb–S–)_n infinite sheet structure with semiconducting band structure.¹⁾ This CP photocatalyze CO₂ reduction upon visible-light to give HCOOH in the presence of electron donor (Figure 1). The photocatalytic activity showed high apparent quantum yields (2.6% at 400 nm; 12.4% at 365 nm) and selectivity (>99%). This is the first example of photocatalytic CO₂ reduction using CPs containing the (–Pb–S–)_n infinite sheet structure, confirmed by isotope tracer experiment with ¹³CO₂.

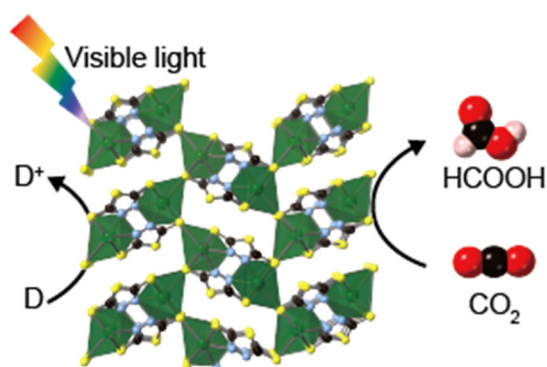


Figure 1. The schematic CO₂ photoreduction using Pb-based CPs containing the (–Pb–S–)_n infinite sheet structure.

1) Y. Kamakura, S. Fujisawa, K. Takahashi, H. Toshima, Y. Nakatani, H. Yoshikawa, A. Saeki, K. Ogasawara, D. Tanaka, *Inorg. Chem.* **2021**, *60*, 12691–12695.

Plasma surface modification of C₃N₄ improves durability of photocatalytic CO₂ reduction with RuRu supramolecular photocatalyst

(¹Tokyo Institute of Technology, ²High Energy Accelerator Research Organization, ³Toyota Technological Institute, ⁴The University of Tokyo) ○Noritaka Sakakibara,¹ Mitsuhiro Shizuno,¹ Tomoki Kanazawa,² , Kosaku Kato,³ Akira Yamakata,³ Shunsuke Nozawa,² Tsuyohito Ito,⁴ Kazuo Terashima,⁴ Kazuhiko Maeda,¹ Osamu Ishitani¹

Keywords: *supramolecular photocatalyst; carbon nitride, plasma surface modification*

For realizing sustainable energy management, hybrid photocatalyst combined with a supramolecular photocatalyst and a semiconductor is one of the promising concepts.¹ In the design of hybrid photocatalyst, the control of interface should be essential for the photocatalytic activity. Here, we performed surface modification of C₃N₄ nanosheet by using plasma in hydroquinone-containing aqueous solution² to gain better interfacial affinity between C₃N₄ and a supramolecular photocatalyst. Plasma in aqueous solution is a promising technique that can modify surface properties of inorganic particles such as carbon nanotube and boron nitride, without changing the original bulk properties.

By the plasma surface modification of C₃N₄ nanosheet, uniform deposition of oxygen-rich carbon layer based on sp² bonding structure was tentatively identified with a TEM observation and an XPS measurement, while bulk properties of C₃N₄ was maintained after the plasma surface modification. In the photocatalytic CO₂ reduction under visible light irradiation with C₃N₄ on which a Ru(II)-Ru(II) supramolecular photocatalyst was fixed via phosphonic anchoring groups³ (Fig. 1), the plasma surface modification improved the durability of formic acid production by three times. Turnover number of HCOOH production recorded ~50000 in an optimal condition. This result demonstrates positive effect of the plasma surface modification on the photocatalytic activity in the hybrid system.

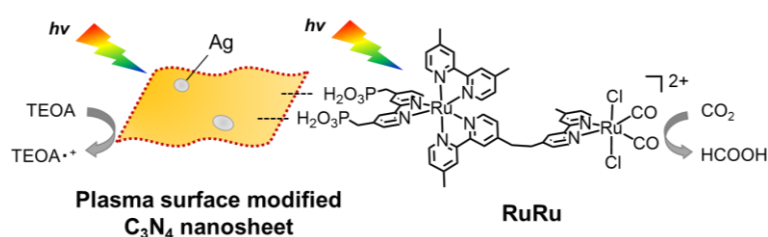


Figure 1 Illustration of the hybrid photocatalyst composed of plasma surface modified C₃N₄ nanosheet and RuRu.

- 1) A. Nakada, H. Kumagai, M. Robert, O. Ishitani, K. Maeda, *Acc. Mater. Res.* **2021**, 2, 458.
- 2) N. Sakakibara, K. Inoue, S. Takahashi, T. Goto, T. Ito, K. Akada, J. Miyawaki, Y. Hakuta, K. Terashima, Y. Harada, *Phys. Chem. Chem. Phys.* **2021**, 23, 10468.
- 3) R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani, K. Maeda, *J. Am. Chem. Soc.* **2016**, 138, 5159.

水分解光触媒用 PtRu 合金ナノ粒子助触媒の開発

(京大化研¹) Christian Mark Peilcano¹・○猿山 雅亮¹・寺西 利治¹

Development of PtRu Alloy Nanoparticle Cocatalysts for Water Splitting Photocatalysts
(¹*Institute for Chemical Research, Kyoto University*) Christian Mark Pelicano,¹ ○Masaki Saruyama,¹ Toshiharu Teranishi¹

PtRu alloy nanoparticles (NPs) were synthesized as cocatalysts of photocatalyst for water splitting. PtRu alloy NPs loaded Al-doped SrTiO₃ (STOA) with CrO_x and CoOOH showed higher photocatalytic water splitting activity than Pt counterpart. Electrochemical measurements exhibited PtRu NPs have intrinsically higher catalytic activity of hydrogen evolution reaction than Pt NPs. In addition, alloying with Ru decreases the work function of Pt to lower the Schottky barrier height between NP/STOA interface, promoting photo-excited electron transfer from STOA to NP as confirmed by transient absorption measurements.

Keywords : Cocatalyst; Photocatalyst; Alloy; Nanoparticle

助触媒は光触媒に担持することで、電荷分離を促進するとともに水分解反応の活性化エネルギーを下げる重要な役割をもつ。助触媒には水分解反応に高い触媒活性をもつ貴金属が汎用的に用いられるが、合金についてはほとんど試されていない。本研究では、水分解光触媒用の水素生成側の助触媒として PtRu 合金ナノ粒子を合成し、光触媒活性における合金化の効果を検証した。Polyvinylpyrrolidone を配位子としたポリオール還元法によって 1.4 nm の PtRu 合金ナノ粒子を合成した (図 a)。PtRu 合金ナノ粒子を Al ドープ SrTiO₃ (STOA) 光触媒上に CrO_x、CoOOH とともに担持すると (図 b)、Pt ナノ粒子を用いたときよりも高い水分解光触媒活性を示した (図 c)。中性条件での電気化学測定で助触媒自体の触媒活性を評価すると、PtRu ナノ粒子は Pt や Ru のナノ粒子よりも高い水素生成触媒活性をもつことが分かった。また過渡吸収測定により、PtRu 担持 STOA では光励起後の STOA からの電子移動が Pt 担持の場合よりも速いことが分かった。これは Ru との合金化が Pt の仕事関数を小さくし、光触媒とのショットキー障壁が下がったことによる効果と考えられる。

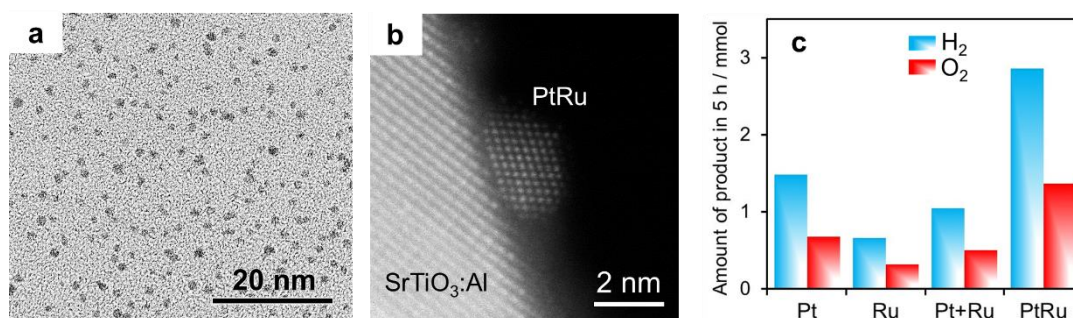


図 (a) PVP 保護 PtRu 合金ナノ粒子の STEM 像、(b) PtRu 担持 SrTiO₃:Al の HAADF-STEM 像、(c) 0.1 wt% ナノ粒子 + 0.1wt% CrO_x + 0.6wt% CoOOH 担持 SrTiO₃:Al の光触媒的ガス発生量比較 (触媒: 10 mg、水: 10 mL、300 W Xe ランプ)。

Noble Metal-based Nanostructured Catalysts for Hydrogenation and Dehydrogenation Reactions via Plasmon-assisted Catalysis

(¹Graduate School of Engineering, Osaka University, ²ESICB, Kyoto University, ³JST PRESTO) ○Priyanka Verma,¹ Yasutaka Kuwahara,^{1,2,3} Kohsuke Mori,^{1,2} Hiromi Yamashita^{1,2}

Keywords: Plasmonic catalysis; Porous Materials; Chemoselective hydrogenation

The plasmonic metal nanoparticles (NPs) interact with the incoming photons to create significant absorption and scattering cross-sections leading to unique chemical and physical properties. The interaction and oscillation of electrons creates a strong electromagnetic field around the metal NP when irradiated at the resonant frequency of light. In the last decade, plasmonic catalysts have been widely researched for their characterization and application in diverse chemical reactions under visible light irradiation conditions.¹

In our recent research report, a combination of Ag NPs with single site Ti-oxide moiety (Ag/Ti-SBA-15) was developed to link together Vis-active plasmonic and UV-active single site photocatalysts for the enhanced hydrogen production activity from ammonia borane (AB) under UV-vis light irradiation.¹ The X-ray absorption near edge structure spectroscopy confirmed the existence of Ti-oxide single-site species in a highly dispersed manner. A reaction rate of 3.3 $\mu\text{mol min}^{-1}$ was obtained under UV-vis light irradiation which was twice to the Ag/SBA-15 catalyst. Furthermore, plasmonic Ag NPs prepared by following a similar synthesis strategy on metal oxide support materials, for example, CeO₂/SBA-15 and bare commercial metal oxide supports (TiO₂, Al₂O₃ and ZrO₂) displayed active performance in the chemoselective reduction of *p*-nitrostyrene (*p*-NS) to *p*-aminostyrene (*p*-AS) utilizing AB as an *in-situ* source of hydrogen.² The superior chemoselective performance in the formation of *p*-AS was obtained when green LED light was irradiated during the reaction (**Figure 1**).

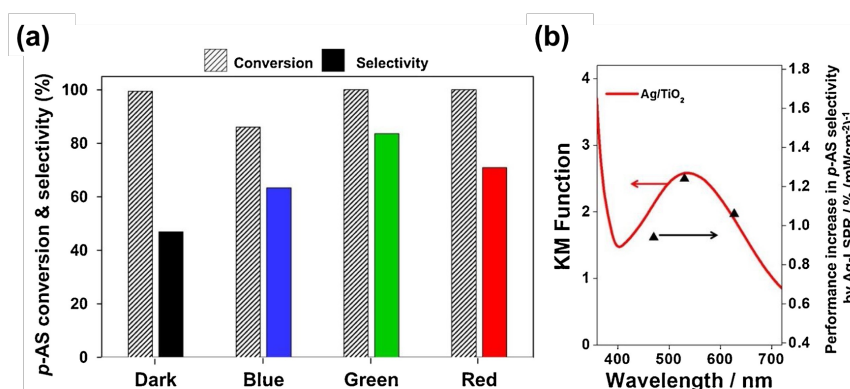


Figure 1. (a) Effect of different wavelengths of LED over Ag/TiO₂; (b) Action spectrum of Ag/TiO₂.

1) P. Verma, K. Mori, Y. Kuwahara, R. Raja, H. Yamashita, *Mater. Adv.*, **2021**, 2, 880-906. 2) P. Verma, Y. Kuwahara, K. Mori, H. Yamashita, *Catal. Today*, **2019**, 324, 83-89.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[J403-4am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Hirotohi Sakamoto, Junpei Yuasa

Sat. Mar 26, 2022 9:00 AM - 11:40 AM J403 (Online Meeting)

[J403-4am-01] Luminescence properties of silver(I) and copper(I) coordination polymers bridged by dimethylpyrazineTaiki Kuwahara¹, Hideki Ohtsu¹, [○]Kiyoshi Tsuge¹ (1. University of Toyama)

9:00 AM - 9:20 AM

[J403-4am-02] Semiconductive Nature of Two-Dimensional Coordination Polymers Containing Ag-S Network[○]Ryohei Akiyoshi¹, Daisuke Tanaka¹ (1. Kwansei Gakuin University)

9:20 AM - 9:40 AM

[J403-4am-03] *N*-Methylation of Amines *via* CO₂ Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes Supported by a *N,N''*-Diarylethylenetriamine Ligand[○]Koichi Shinohara¹, Hayato Tsurugi¹, Kazushi Mashima¹ (1. Osaka Univ.)

9:40 AM - 10:00 AM

[J403-4am-04] Solvent induced structural change and optical properties of nona-coordinated Eu(III) complexes having unsymmetric tridentate ligand[○]Yoshinori Okayasu¹, Junpei Yuasa¹ (1. Grad. Sch. Sci., TUS)

10:00 AM - 10:20 AM

[J403-4am-05] CPL and CD spectra of achiral Eu(III) complex in solution containing amino acids[○]Munetaka Iwamura¹, Koichi Nozaki¹, Miho Sakai¹, Yuzuki Nakauchi¹ (1. University of Toyama)

10:20 AM - 10:40 AM

[J403-4am-06] Syntheses and magnetic properties of lanthanide(III) complexes ligated by bis(nitronyl nitroxide-2-ide)gold(I) anion[○]Ryu Tanimoto¹, Shuichi Suzuki², Daisuke Shiomi¹, Rika Tanaka³, Takeshi Naota², Masatoshi Kozaki¹, Keiji Okada¹ (1. Grad. Sch. of Sci., Osaka City Univ., 2. Grad. Sch. of Eng. Sci., Osaka Univ., 3. Grad. Sch. of Eng., Osaka City Univ.)

10:40 AM - 11:00 AM

[J403-4am-07] Surface Attachment and Circularly Polarized Luminescence of Luminous Terbium Complex on Silica Surface with Chiral Ligands[○]Sora Shirai¹, Kensuke Ikeda², Satoshi Muratsugu¹, Hidetaka Nakai², Mizuki Tada^{1,3} (1. Dept. Chem. Nagoya Univ., 2. Dept. Appl. Chem. Kindai Univ., 3. RCMS, Nagoya Univ.)

11:00 AM - 11:20 AM

[J403-4am-08] Excitation pathway of near-infrared luminescence in Yb³⁺ complex with tripodal Schiff base[○]Atsuko Masuya-Suzuki¹, Rika Nakamura¹, Satoshi Goto¹, Ryunosuke Karashimada¹, Nobuhiko Iki¹ (1. Tohoku University)

11:20 AM - 11:40 AM

Luminescence Properties of Silver(I) and Copper(I) Coordination Polymers Bridged by Dimethylpyrazine

(Graduate School of Science and Engineering, University of Toyama) Taiki Kuwahara, Hideki Ohtsu, ○Kiyoshi Tsuge

Keywords: Silver Complex; Copper Complex; Luminescence; Charge-transfer Excited State

We have been studying about luminescent copper(I) and silver(I) complexes with the $\{M_2X_2\}$ unit coordinated by PPh_3 and N-heteroaromatic ligands. Though the copper complexes with this unit have been widely studied,¹ examples of silver congeners are still limited. Recently, we have prepared the silver coordination polymers having the $\{M_2X_2\}$ unit, $[Ag_2X_2(PPh_3)_2(\mu-L)]_n$ (X: I, Br; L: pyrazine (pyz), aminopyrazine (ampyz), methylpyrazine (Mepyz)) by using excess amount of bridging ligands, revealing their efficient luminescence from charge-transfer (CT) excited state (ES).² Here, we report the synthesis and luminescence properties of 2,4-dimethylpyrazine (Me_2pyz) complexes $[Ag_2X_2(PPh_3)_2(\mu-Me_2pyz)]_n$ (X: I, Br, Cl; **AgX-Me₂pyz**) together with the corresponding copper complexes $[Cu_2X_2(PPh_3)_2(\mu-Me_2pyz)]_n$ (X: I, Br; **CuX-Me₂pyz**).

The silver and copper complexes **MX-Me₂pyz** were prepared by the reaction of MX, PPh_3 , and Me_2pyz in appropriate reaction ratios in organic solvents. Single crystal X-ray structure analysis showed that they are one dimensional coordination polymers composed of $\{M_2X_2(PPh_3)_2\}$ unit and bridging Me_2pyz and that they form isomorphous crystals. Both the silver and the copper complexes are strongly emissive at room temperature in the solid state as shown in Fig. 1. Their emission maxima and quantum yields are listed in Table 1, together with their averaged emission lifetime. By comparison with the pyz, ampyz, and Mepyz complexes,² their emissive ES were ascribed to the CT transition from $\{M_2X_2\}$ core to the π^* orbital of Me_2pyz . Because 4d orbitals of the silver ion are more stable than the 3d orbitals of the copper ion, the silver complexes showed the emission bands at higher energy than the copper complexes. Comparison of the excitation and emission spectra implied that the silver complexes undergo larger relaxation at ES than the copper complexes reflecting more flexible nature of the coordination geometry of a silver ion.

1) K. Tsuge, *et al.*, *Coord. Chem. Rev.* **2016**, 306, 636. 2) T. Kuwahara, *et al.*, *Inorg. Chem.* **2021**, 60, 1299.

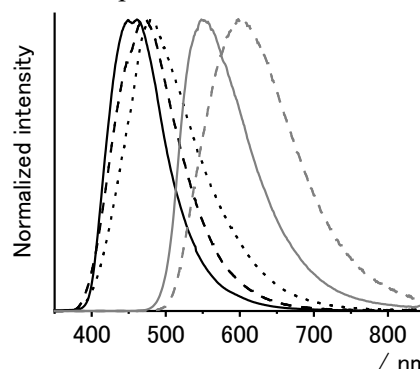


Fig.1 Emission spectra of **MX-Me₂pyz** (λ_{ex} : 330 nm). M: Ag (black), Cu (grey); X: I (solid), Br (broken), Cl (dotted).

Table 1. Photophysical properties of **MX-Me₂pyz**.

X	M = Ag			M = Cu		
	λ_{max}/nm	Φ	$\tau_{av}/\mu s$	λ_{max}/nm	Φ	$\tau_{av}/\mu s$
I	455	0.80	1.3	548	0.90	4.1
Br	470	0.65	5.9	600	0.65	8.0
Cl	480	0.90	11.7	--	--	--

Semiconductive Nature of Two-Dimensional Coordination Polymers Containing Ag-S Network

(School of Science, Kwansei Gakuin University) ○Ryohei Akiyoshi, Daisuke Tanaka

Keywords: Coordination Polymer; Ag(I) Complex; Semiconductive Property

Two-dimensional (2D) materials that include graphene and transition metal dichalcogenides are of significant interest due to their unique properties resulting from 2D nature. Of these, 2D coordination polymers (2D CPs) have attracted considerable attention over recent years because they show various interesting properties associated not only with 2D nature but also arising from both inorganic and organic blocks. Until now, our group focuses on sulfur-coordinated CPs (S-CPs) that exhibit semiconductive property and excellent photoconductivity and reports photocatalytic property for water splitting.¹ However, the reports about 2D S-CPs are quite limited in spite of their potential application.

Herein, we succeeded in synthesizing two 2D S-CPs of type $[\text{Ag}(\text{tzdt})]_n$ (KGF-24) and $[\text{Ag}_2(\text{tzdt})(\text{TFA})]_n$ (KGF-25) (Htzdt = 1,3-thiazolidine-2-thione, TFA = trifluoroacetic acid), and their crystal structure, band structure, and photoconductive property were discussed in detail. The S-CPs were obtained by solvothermal synthesis using CF_3COOAg and Htzdt at metal ion/ligand ratio of 1:1 for KGF-24 and at 2:1 for KGF-25, respectively (Figure 1). Single crystal X-ray structural analysis indicated that both KGF-24 and KGF-25 formed 2D layer structure comprising Ag-S network. The photoconductive properties were investigated by time-resolved microwave conductivity (TRMC) experiments, in which the maximum values of $\phi\Sigma\mu_{\text{max}}$ (ϕ = quantum yield of charge-carrier generation; $\Sigma\mu$ = sum of the hole and electron mobilities) were determined to be $3.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for KGF-24 and $2.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for KGF-25, which were comparable to those of other photoconductive S-CPs.¹ As a result of the first-principle calculations using CASTEP, it is likely that the Ag-S layer network contributes to the observed photoconductive property.

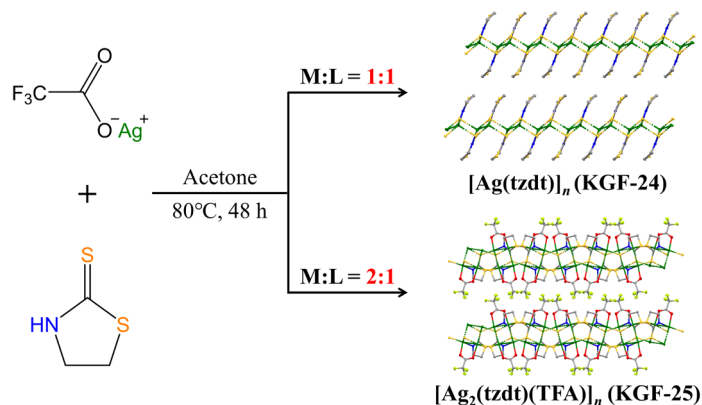


Figure 1. Synthesis of $[\text{Ag}(\text{tzdt})]_n$ (KGF-24) and $[\text{Ag}_2(\text{tzdt})(\text{TFA})]_n$ (KGF-25).

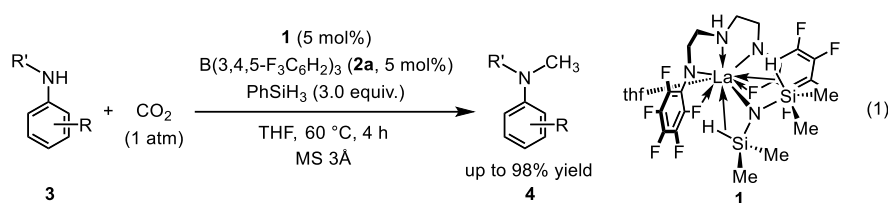
1. Y. Kamakura, P. Chinapang, S. Masaoka, A. Saeiki, K. Ogasawara, S. R. Nishitani, H. Yoshikawa, T. Katayama, N. Tamai, K. Sugimoto, D. Tanaka, *J. Am. Chem. Soc.*, **2020**, *142*, 27.

N-Methylation of Amines *via* CO₂ Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes Supported by a *N,N'*-Diarylethylenetriamine Ligand

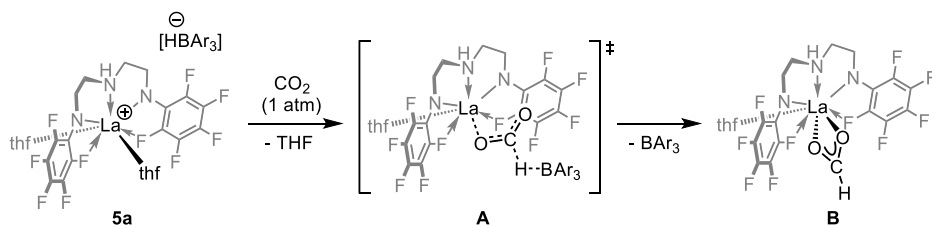
(Graduate School of Engineering Science, Osaka University) ○Koichi Shinohara, Hayato Tsurugi, Kazushi Mashima

Keywords: Carbon Dioxide; N-Methylation; Lanthanum Complex; DFT Study; Non-covalent Interaction

Carbon dioxide (CO₂) is an inexpensive and renewable C1 feedstock for producing various chemical compounds, although its thermodynamic stability makes it difficult to directly fix into organic compounds.^{1,2} Transition metal-catalyzed hydrosilylation of CO₂ using hydrosilanes as reductants is one of synthetically effective methods to produce silylformates (HCO₂SiR₃) and bis(silyl)acetals (CH₂(OSiR₃)₂), both of which are useful C1 sources. Herein, we report *N*-methylation of anilines *via* the reduction of CO₂ by PhSiH₃, which was catalyzed by a lanthanum complex, La(L)[N(SiHMe₂)₂](thf) (L = a dianionic *N,N'*-bis(pentafluorophenyl)diethylenetriamine ligand), upon treated with B(3,4,5-F₃C₆H₂)₃ (eq. 1). Lanthanum hydridoborate complex, [La(L)(thf)₂][HB(3,4,5-F₃C₆H₂)₃] (**5a**), was characterized by NMR measurements as a key intermediate. DFT calculations revealed that the transition state species **A** involves the coordination of CO₂ to the lanthanum center through an interaction of the electrophilic carbon of CO₂ with hydride on the borate anion, and subsequent elimination of B(3,4,5-F₃C₆H₂)₃ generates lanthanum formate species **B** (Scheme 1). Details of substrate scope and reaction mechanism are discussed in this presentation.



Scheme 1. CO₂ Reduction Step Clarified by the DFT Calculations (Ar = 3,4,5-F₃C₆H₂)



- 1) K. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365. 2) Y. Li, X. Fang, K. Junge, M. Beller, *Angew. Chem., Int. Ed.* **2013**, *52*, 9568.

非対称三座配位子を有する 9 配位 Eu(III)錯体の溶媒による構造変化と光学特性評価

(東理大院理) ○岡安 祥徳・湯浅 順平

Solvent induced structural change and optical properties of nona-coordinated Eu(III) complexes having unsymmetric tridentate ligand

(Grad. Sch. Sci., TUS) ○Yoshinori Okayasu, Junpei Yuasa

The nona-coordinated chiral Eu(III) complexes ((*R*)-iPr, (*R*)-iBu, and (*R*)-Ph) have been synthesized. Comparing the emission spectra in the crystal and in solution, the emission spectrum of (*R*)-iPr and (*R*)-iBu in acetonitrile shows the same spectrum shape as that in the crystal. However, the emission spectrum of (*R*)-Ph in toluene shows the same spectrum shape as that in the crystal. Slight differences in the substituents result in different coordination structures of the nona-coordinated Eu(III) complex in solution.

Keywords : Lanthanide complex; β -diketonate ligand; Circularly polarized luminescence; Circular dichroism; unsymmetry

金属錯体の構造や光学特性は中心金属の性質によって決定される。希土類イオンは適切な配位子設計を施すことで、色純度の高い鮮やかな発光を示し魅力的な光学特性を示す。一方で、高次の配位数をとり、置換活性であることから希土類イオンの種類や配位子のわずかな違いで異性体構造を生成することが知られている。これに関連し

て、当研究室では三座補助配位子と非対称な β -ジケトナート配位子によって構成される非対称 9 配位 Eu(III)錯体の溶液中での構造決定方法論に関して報告している¹⁾。

本研究では、側鎖に異なる置換基を有する非対称な三座補助配位子を 1 分子、 β -ジケトナート配位子を 3 分子もつ 9 配位 Eu(III)錯体の溶液中での構造と光学特性を評価した。

これらの 9 配位 Eu(III)錯体の溶液中での構造を推定するために、結晶の発光スペクトルと低極性および高極性溶媒での発光スペクトルを測定した(Figure 1)。興味深いことに側鎖に Ph をもつ錯体ではトルエン溶液中と結晶中での発光スペクトル形状が一致し、側鎖に iPr, iBu をもつ錯体はアセトニトリル溶液中と結晶中での発光スペクトル形状が一致した。このことから、側鎖のわずかな違いによって溶液中での 9 配位 Eu(III)錯体の構造が異なることがわかった。

1) Okayasu, Y.; Yuasa, J. *J. Phys. Chem. Lett.* **2021**, *12*, 6867–6874.

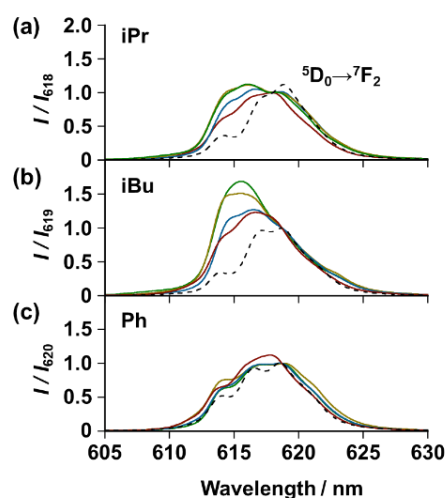


Figure 1. (a)–(c) Emission spectra of (*R*)-iPr, (*R*)-iBu, and (*R*)-Ph in toluene (yellow line), CHCl₃ (green line), CH₂Cl₂ (blue line) and CH₃CN (black line) (concentration: 1.0×10^{-5} M), where the emission intensity is normalized at the 620 nm.

CPL and CD spectra of achiral Eu(III) complex in solution containing amino acids

(¹Graduate School of Science and Engineering, Toyama University) ○Munetaka Iwamura, Miho Sakai, Yuzuki Nakauchi, Koichi Nozaki,

Keywords: Circular dichroism; Circularly polarized luminescence; Chiral sensing; Amino acid, Allosteric effect

[Eu(pda)₂][−] (pda: 1,10-phenanthroline-2,9-dicarboxylic acid) exhibits emission assignable to the f-f transition in the metal center. The Eu complex does not exhibit circularly polarized luminescence (CPL) in an aqueous solution as expected from its achiral structure. However, it exhibits circularly polarized luminescence (CPL) in aqueous solutions containing chiral amino acids such as arginine and histidine.¹ This indicates that interactions between the [Eu(pda)₂][−] and amino acids induce the structural change of [Eu(pda)₂][−] from achiral- to a chiral structure. However, the detail of the chiral structure is still unclear. In this study, we investigated CD spectra of [Eu(pda)₂][−] in aqueous solutions to elucidate the structure of the complex in the solutions containing amino acids.

Figure 1a shows CD spectra of [Eu(pda)₂][−] in aqueous solutions containing arginine at the concentrations of 0.51-101 mM. It has an intense CD peak at 340 nm, which is assigned to $\pi\pi^*$ transition in the phenanthroline moiety. The aspect of the concentration dependence of $\Delta\epsilon$ for the CD at 340 nm is very close to the concentration dependence of g_{lum} values of the CPL (Figure 1b)¹. This indicates that the species exhibiting CD spectra are identical to those exhibiting the CPL signals. The CD spectra are well in accord with that expected from TDDFT calculation for [Eu(pda)₂][−] with *D*₂ structure (Figure 1c). CD spectra of solutions containing L-histidine show opposite signs of that for the solution of arginine. This indicates that the structure of [Eu(pda)₂][−] in the histidine solution is different from that in the arginine solution although their CPL spectra are close to each other.

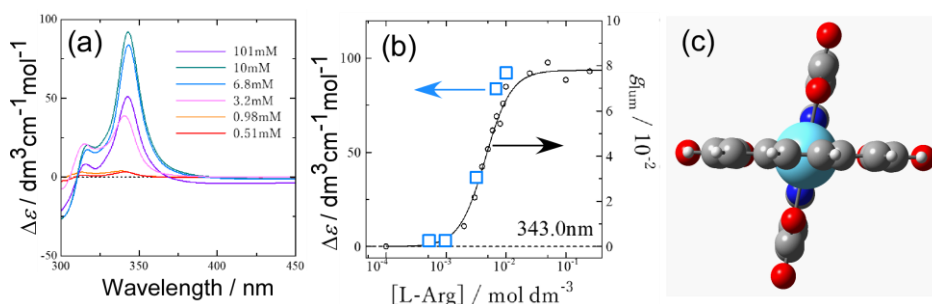


Figure 1 (a) CD spectra of [Eu(pda)₂][−] in aqueous solutions containing L-arg at various concentrations. ([Eu] = 0.1 mM, [Arg] = 0.51 mM - 10 mM) (b) Concentration dependence of $\Delta\epsilon$ and g_{lum} (c) Expected structure of [Eu(pda)₂][−] in solution containing L-arg.

Ref. 1) K. Okutani, K. Nozaki, M. Iwamura, *Inorganic Chemistry* **2014**, 53, 5527.

ビス(ニトロニルニトロキシド)金(I)錯体が配位した希土類(III)錯体の合成と磁気的性質

(阪市大院理¹・阪大院基礎工²・阪市大院工³) ○谷本 理勇¹・鈴木修一²、塩見大輔¹、田中里佳³、直田 健²、小寄正敏¹、岡田恵次¹

Syntheses and magnetic properties of lanthanide(III) complexes ligated by bis(nitronyl nitroxide-2-ide)gold(I) anion (¹Graduate School of Science, Osaka City University, ²Graduate School of Engineering Science, Osaka University, ³Graduate School of Engineering, Osaka City University) ○Ryu Tanimoto¹, Shuichi Suzuki², Daisuke Shiomi¹, Rika Tanaka³, Takeshi Naota², Masatoshi Kozaki¹ and Keiji Okada¹

Nitronyl nitroxide (NN) has been widely used as a stable spin source. Recently we found that radical metalloids, which are consisted of NN-2 ide radical anion(s) and metal ion (Pt, Ag, Au, Cu), showed unique redox properties and reactivities. In this study, we have newly synthesized Ln(III) complexes (Ln = Sm, Eu, Gd, Tb, Dy) ligated with NN-Au-NN anions ($S = 1/2 \times 2$) as new multi-spin molecular systems and found unique magnetic properties based on the intramolecular exchange interactions.

Keywords : Lanthanide; Gadolinium; Nitronyl Nitroxide; Gold; Radical

ニトロニルニトロキシドラジカル (NN) は、その電子スピンや酸化還元特性が注目されて広く研究されている。最近我々は、NN ラジカルが C2 位で金属元素に直結した各種金属錯体に注目し、それらの酸化還元特性や反応性を明らかにしてきた^{1,2}。さらに最近では NN 部が直結した金(I)イオンを複数有する錯体の合成にも成功し、特異な分子内スピン間相互作用を明らかにしつつある³。今回、金(I) イオンに二つの NN が直接配位したアニオン性金属錯体 **1**⁻ を配位子とする希土類(III)錯体 **Ln-1₃** (Ln = Sm, Eu, Gd, Tb, Dy) の合成に成功し、それらの磁気物性の解明を検討したので報告する。

希土類錯体 **Ln-1₃** は 3 当量の **1**⁻ と対応する硝酸塩を混合することで合成した。得られた錯体はいずれも空気下溶液中でも高い安定性を有していた。X 線構造解析の結果、**Ln-1₃** は希土類イオンに対して三つの **1**⁻ がキレート配位しており、磁性をもつ希土類イオンと 1 個と 6 個の NN ($S = 1/2$) から構成されていることがわかった (Figure 1)。SQUID を用いて **Ln-1₃** の磁気特性を調査したところ、**Gd-1₃** では分子内スピン間相互作用のために、磁化率の複雑な温度依存性が観測された。

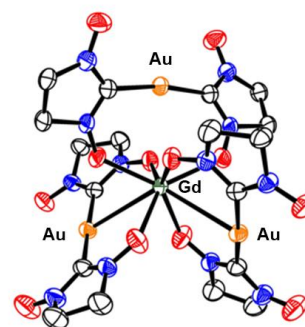


Figure 1. ORTEP figures of **Gd-1₃**. CH₃ groups were omitted for clarity.

1) Tanimoto, R.; Okada, K. et al. *Eur. J. Inorg. Chem.* **2018**, 1198. 2) Tanimoto, R.; Okada, K. et al. *Chem. Lett.* **2014**, 43, 678. 3) Suzuki, S.; Kozaki, M.; Okada, K. et al. *Chem. Eur. J.* **2021**, 27, 11450.

Surface Attachment and Circularly Polarized Luminescence of Luminous Terbium Complex on Silica Surface with Chiral Ligands

(¹Dept. Chem. Nagoya Univ., ²Dept. Appl. Chem. Kindai Univ. ³RCMS, Nagoya Univ.)

○Sora Shirai,¹ Kensuke Ikeda,² Satoshi Muratsugu,¹ Hidetaka Nakai,² Mizuki Tada^{1,3}

Keywords: Chirality; Silica Surface; Chiral Ligand; Terbium Complex; Circularly Polarized Luminescence

Chiral metal complexes immobilized on solid surfaces are investigated for applications to solid chiral sensors, heterogeneous asymmetric catalysts etc. We investigated a new preparation method of surface-attached chiral metal complexes via chirality induction of metal complexes on a solid surface modified with chiral ligands. The induction of the chirality of an achiral terbium (Tb) complex (**1**_{Tb})¹ was investigated on a silica (SiO₂) modified with chiral benzyl alcohol ligands (Figure 1).

SiO₂ surface was modified with newly-prepared chiral benzyl alcohol ligands (**L(R/S)**) and SiO₂ attaching the chiral ligands (**L(R/S)/SiO₂**) was prepared. UV-vis and FT-IR suggested that the structure of **L(R/S)** was maintained on the SiO₂ surface. The solid-state CD of **L(R/S)/SiO₂** showed inversed peaks at 230 nm (Figure 2(A)), which was similar to the solution-state CD of **L(R/S)**, suggesting that the chirality of **L(R/S)** was retained on the SiO₂ surface.

1_{Tb} was attached to **L(R/S)/SiO₂** by the impregnation method (**1**_{Tb}/**L(R/S)/SiO₂**). The DR UV-vis of **1**_{Tb}/**L(R/S)/SiO₂** showed absorption peak at around 301 nm (Figure 2(B)), which was similar to the solution-state UV-vis of **1**_{Tb}, suggesting that the structure of **1**_{Tb} was kept on the SiO₂ surface. The solid-state CPL of **1**_{Tb}/**L(R/S)/SiO₂** showed inversed CPL peaks around 550 nm, which suggested that the chirality of **1**_{Tb} was actually induced by the coordination of **1**_{Tb} to **L(R/S)/SiO₂**. The CPL peak intensities of **1**_{Tb}/**L(R/S)/SiO₂** were obviously larger than that of **1**_{Tb}/(*R/S*)-1-phenylethanol in acetonitrile solution. These results strongly indicated that the unique CPL property of **1**_{Tb} was induced at the SiO₂ surface by the coordination to the surface-functionalized chiral ligands.

1) H. Nakai, *et al.*, *Chem. Commun.*, **2014**, 50, 15737-15739.

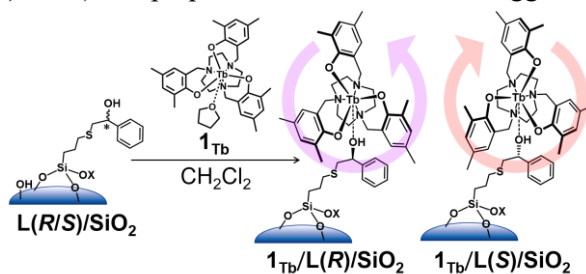


Figure 1. Chirality induction of **1**_{Tb} with **L(R/S)/SiO₂**.

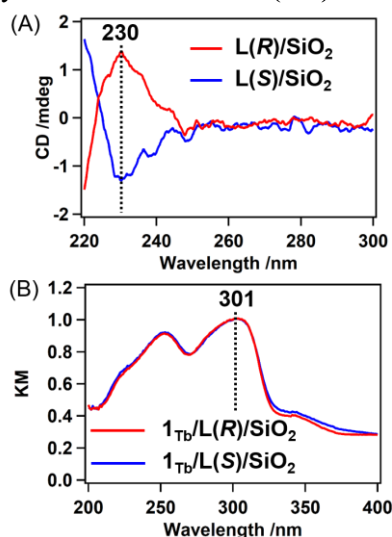


Figure 2. (A) Solid-state CD spectra of **L(R/S)/SiO₂**. (B) DR UV-vis spectra of **1**_{Tb}/**L(R/S)/SiO₂**.

Excitation pathway of near-infrared luminescence in Yb³⁺ complex with tripodal Schiff base

(¹Graduate School of Environmental Studies, Tohoku University) ○ Atsuko Masuya-Suzuki,¹ Rika Nakamura,¹ Satoshi Goto,¹ Ryunosuke Karashimada,¹ Nobuhiko Iki¹

Keywords: Near-infrared luminescence; Schiff base; Redox

Trivalent lanthanide (Ln³⁺) ions show luminescence with attractive features originating from the 4f electrons. So far, a sensitization of the Ln³⁺ luminescence through a light absorption by a ligand and a subsequent energy transfer to the Ln³⁺ center has been extensively studied. Among the Ln³⁺ ions, a unique sensitization path with Ln³⁺/Ln²⁺ redox has been proposed for the ytterbium (Yb³⁺) ion, which has only one excited level (²F_{5/2}: ~10350 cm⁻¹).¹ There are relatively few studies on this redox-mediated sensitization for the near-infrared Yb³⁺ luminescence. Recently, we studied luminescence property of the Yb³⁺ complex with a tripodal Schiff base (YbL^{CH₃}, Figure (a)) and proposed the sensitization path with the ligand-to-metal charge transfer (LMCT) state, which acts as the intermediate state of the redox-mediated sensitization (Figure (b)).² In this work, to obtain further insight into this sensitization, we prepared Yb³⁺ complexes with ligand having Cl or Br at 5-position (YbL^{Cl}, YbL^{Br}, Figure (a)) and (YbL^R)_x(LuL^R)_{1-x} co-crystals (R = CH₃, Cl), and studied their photophysical properties.

Upon the ligand excitation, YbL^{Cl} and YbL^{Br} showed the Yb³⁺ luminescence in DMF, respectively. The values of the sensitization efficiency (η) for YbL^{Cl} and YbL^{Br} were found to be 20 and 19%, respectively. These values were significantly smaller than that of YbL^{CH₃} (35%). This observation indicates that the electron-withdrawing group may increase the LMCT energy level and result in the decrease in η . The Yb³⁺ luminescence intensity of the co-crystals (YbL^R)_x(LuL^R)_{1-x} increased as x was decreased. Time-resolved profile of the Yb³⁺ luminescence ($x = 0.01$) showed growth and decay components (Figure (c)). The growth component was not observed for $x > 0.2$. From these results, we infer that the close packing of YbL^R and LuL^R in the crystal induced an excited state with long lifetime.

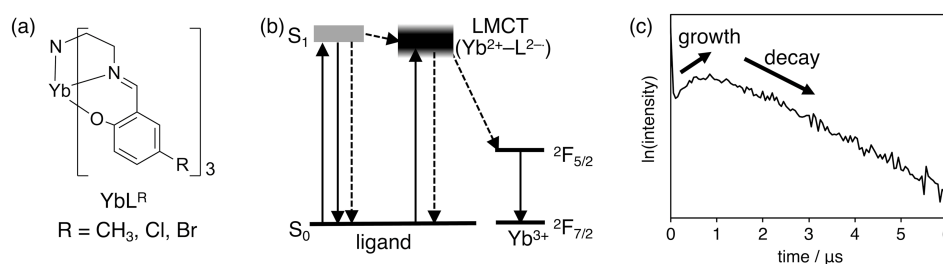


Figure (a) Structure of YbL^R, (b) proposed sensitization path for YbL^R, and (c) time-resolved profile of Yb³⁺ luminescence of (YbL^{CH₃})_{0.01}(LuL^{CH₃})_{0.99} co-crystal.

- 1) W. D. Horrocks, P. J. Bolender, W. D. Smith, R. M. Supkowski, *J. Am. Chem. Soc.*, **119**, 5972 (1997).
- 2) A. Masuya-Suzuki, S. Goto, T. Kambe, R. Karashimada, Y. Kubota, N. Iki, *ChemistryOpen*, **10**, 46 (2021).

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[J202-4am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Yoshinori Yamanoi, Takanori Shima

Sat. Mar 26, 2022 9:00 AM - 11:40 AM J202 (Online Meeting)

[J202-4am-01] Synthesis and Catalytic Activity of Atrane-type Group 14 Cations with Hard and Soft Lewis Superacidity○Daiki Tanaka¹, Akihito Konishi¹, Makoto Yasuda¹ (1. Osaka University)

9:00 AM - 9:20 AM

[J202-4am-02] Synthesis and Reactivity of Early Transition Metal Methylene Complexes via Transmetallation of Dinuclear Zinc Methylene Species○Takashi Kurogi^{1,2}, Kazuhiko Takai¹ (1. Okayama Univ., 2. Kyoto Univ.)

9:20 AM - 9:40 AM

[J202-4am-03] Dinitrogen Cleavage and Functionalization by Carbon Dioxide at a Ditanium Dihydride Framework○Qingde ZHUO¹, Zhaomin HOU¹, Shima Takanori¹ (1. RIKEN)

9:40 AM - 10:00 AM

[J202-4am-04] The Syntheses and Structures of Dinitrogen Chromium Complexes Supported with Triamidoamine Ligands○Yoshiaki Kokubo¹, Yuji Kajita¹, Hideki Masuda¹ (1. Aichi Institute of Technology)

10:00 AM - 10:20 AM

[J202-4am-05] Properties of Dimetallene Dianions Bearing Triptycyl Framework○Ryohei Nishino¹, Mao Minoura¹ (1. College of Science, Rikkyo University)

10:20 AM - 10:40 AM

[J202-4am-06] Computational Design and Evaluation of Substituted PCP-Type Ligands for Mo-Catalyzed Nitrogen Fixation○Akihito Egi¹, Hiromasa Tanaka², Yoshiaki Nishibayashi³, Kazunari Yoshizawa¹ (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. School of Liberal Arts and Science, Daido University, 3. School of Engineering, The University of Tokyo)

10:40 AM - 11:00 AM

[J202-4am-07] High ionic conductivity in 2D-layered Ti-MOF by Li salts mechanical insertion○Marvin Kevin Sarango Ramirez¹, Yukihiro Yoshida¹, Dae-Woon Lim², Hiroshi Kitagawa¹ (1. Kyoto University, 2. Yonsei University)

11:00 AM - 11:20 AM

[J202-4am-08] Synthesis a Zr-mellitate MOF and its ion-exchange property○Genki Hatakeyama¹, Masaki Nishio, Kouki Oka², Teppei Yamada¹ (1. The University of Tokyo, 2. Osaka University)

11:20 AM - 11:40 AM

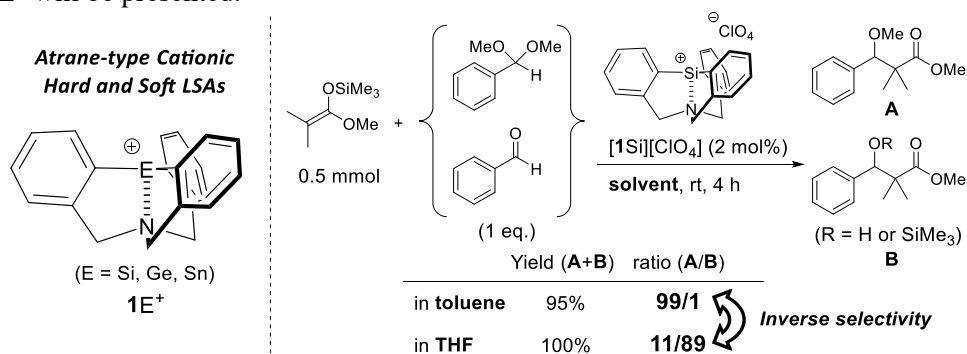
Synthesis and Catalytic Activity of Atrane-type Group 14 Cations with Hard and Soft Lewis Superacidity

(Graduate School of Engineering, Osaka University) ○ Daiki Tanaka, Akihito Konishi, Makoto Yasuda

Keywords: Group 14 Elements, Atrane, Cationic Species, Hard and Soft Lewis Superacid, Lewis Acid Catalyst

Lewis acid is one of the most vital reagents utilized for many chemical transformations. Recently, hard and soft Lewis superacids (LSAs) with a neutral heavier group 14 element center have attracted attention in terms of their broad range of affinity for various substrates from hard to soft Lewis basic substrates.^{1,2} Heavier group 14 cations (R_3E^+ : E = Si, Ge, Sn) also have the potential to work as hard and soft LSAs because they have a high electron affinity and Lewis acidity enough to cleave various bonds such as a C–F and Si–H bond. However, the application of these species as a catalyst remains a challenging issue mainly due to the high affinity of substrates. The introductions of various substituents stabilize the cationic center but inhibit the employment as catalysts. For silyl cation species, there are some reports that describe the utilizations of them to catalytic reactions. In the case of germyl and stannyl cation species, only a few stoichiometric reactions have been reported and their reactivities remain unclear.

The synthesis and isolation of atrane-type molecules $1E^+$ (E = Si, Ge, and Sn) having a cationic group 14 metal center will be reported.³ The cations $1E^+$ act as hard and soft LSAs, which readily interact with various hard and soft Lewis basic substrates. The rigid atrane-framework stabilizes the localized positive charge on the metal center and assists the formation of the well-defined highly coordinated states of $1E^+$. The cations were applicable to the hydrodefluorination, Friedel-Crafts reaction, alkyne cyclization, and carbonyl reduction as Lewis acid catalysts. Most notably, $[1Si][ClO_4]$ exhibited an unique chemoselectivity that depends on a solvent in the competitive reaction of silyl enol ether with a mixture of benzaldehyde dimethyl acetal and benzaldehyde. The structures, Lewis acidity, and reactivity of $1E^+$ will be presented.



1) L. Greb *et al.* *Angew. Chem. Int. Ed.* **2020**, 59, 20930. 2) M. Driess *et al.* *Angew. Chem. Int. Ed.* **2021**, 60, 13656. 3) D. Tanaka, A. Konishi, M. Yasuda, *Chem. Asian J.* **2021**, 16, 3118.

二核亜鉛メチレン種からのトランスメタル化による前周期遷移金属メチレン錯体の合成と反応

(岡山大院自然¹・京大院理²) ○黒木 堯^{1,2}・高井 和彦¹

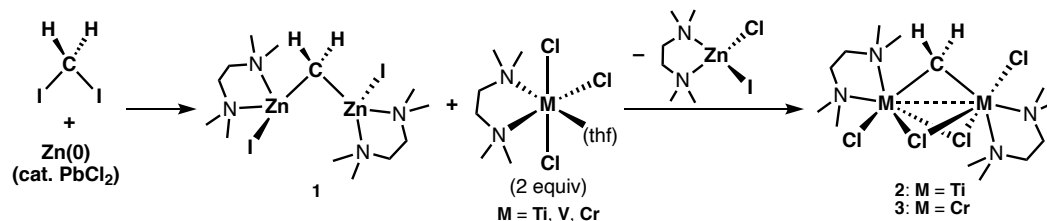
Synthesis and Reactivity of Early Transition Metal Methylene Complexes via Transmetallation of Dinuclear Zinc Methylene Species

(¹Graduate School of Natural Science and Technology, Okayama University, ²Graduate School of Science, Kyoto University) ○Takashi Kurogi,^{1,2} Kazuhiko Takai¹

Transmetallation of organozinc species to transition metals has been widely utilized for generation of various organometallic species and catalysts, e.g. Negishi coupling. Zinc μ -methylene species can be generated by reduction of CH_2X_2 with $\text{Zn}(0)$ in the presence of a catalytic amount of PbCl_2 .¹ We have recently reported synthesis and characterization of dinuclear zinc μ -methylene complexes.² Here, we report synthesis of dinuclear early transition metal μ -methylene complexes via transmetallation of zinc μ -methylene **1** to early transition metal chlorides. Treatment of zinc methylene **1** with two equivalents of titanium and chromium trichlorides resulted in formation of dinuclear methylene complexes of titanium (**2**) and chromium (**3**), respectively. Transmetallation of zinc μ -methylene **1** to vanadium(III) chlorides also proceeded to generate vanadium methylene species. Reactivity of μ -methylene complexes **2** and **3** will also be reported in this presentation.

Keywords : Zinc Methylene; Early Transition Metal; Transmetallation; Chromium; Titanium

有機亜鉛反応剤から遷移金属中心へのトランスメタル化は、根岸カップリングに代表されるような様々な有機金属活性種の発生や有機金属触媒系の構築に幅広く利用されてきた。触媒量の PbCl_2 存在下、 CH_2X_2 を $\text{Zn}(0)$ で還元することで二つの亜鉛間をメチレン配位子が架橋する亜鉛メチレン種が生成する¹⁾。最近、我々は二核構造を有する亜鉛の架橋メチレン種の合成、単離と結晶構造を報告した²⁾。今回、二核亜鉛メチレン種 **1** と前周期遷移金属塩化物のトランスメタル化により、種々の前周期遷移金属メチレン錯体を合成し、その反応性を検討した。亜鉛メチレン種 **1** にチタンおよびクロムの三塩化物を 2 当量作用させたところ、架橋メチレン配位子を有する二核チタン錯体 **2** と二核クロム錯体 **3** が得られた。また、III 価のバナジウム塩化物を用いた場合にもバナジウムのメチレン種が発生することも見いだした。合成したチタンおよびクロムのメチレン錯体 **2** と **3** の反応性についても併せて報告する。



1) K. Takai, T. Kakiuchi, K. Kataoka, K. Utimoto, *J. Org. Chem.* **1994**, 59, 2668.

2) Y. Nishida, H. Hosokawa, M. Murai, K. Takai, *J. Am. Chem. Soc.* **2015**, 137, 114.

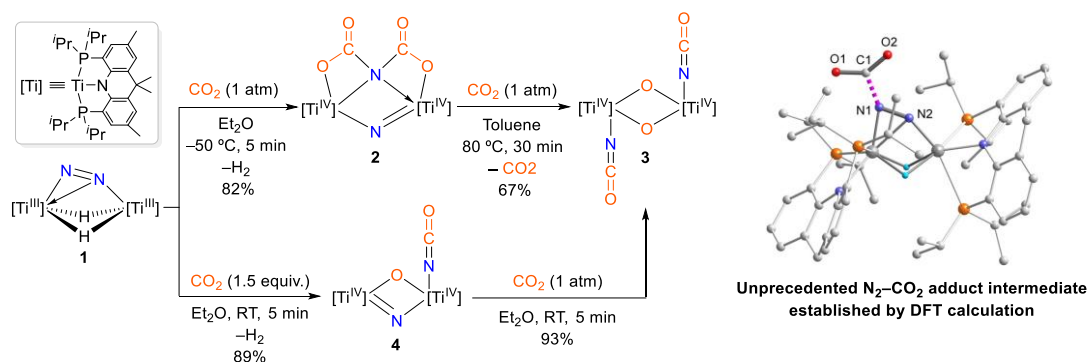
Dinitrogen Cleavage and Functionalization by Carbon Dioxide at a Ditungsten Dihydride Framework

(¹Organometallic Chemistry Laboratory, RIKEN, ²Advanced Catalysis Research Group, RIKEN, ³School of Chemical Engineering, Dalian University of Technology, ⁴PetroChina Petrochemical Research Institute) ○Qingde Zhuo¹, Jimin Yang³, Zhenbo Mo¹, Xiaoxi Zhou¹, Takanori Shima^{1,2}, Yi Luo^{3,4}, and Zhaomin Hou^{1,2}

Keywords: Dinitrogen Functionalization; Carbon Dioxide; Ditungsten Dihydride Framework

Dinitrogen (N₂) and carbon dioxide (CO₂) are among the most inert molecules. The coupling of these two molecules through N–C bond formation and N–N and C–O bond cleavage is highly challenging and has not been reported previously.¹ We report here the reaction of a well-defined dinitrogen ditungsten hydride complex (**1**)² with CO₂, which involved not only N–C bond formation but also N–N and C–O bond cleavage (Scheme 1). Exposure of the dinitrogen ditungsten hydride complex **1** with CO₂ (1 atm) at –50 °C selectively yielded a nitrido/*N,N*-dicarboxylated-amido complex **2** through N₂ cleavage and dicarboxylation at one nitrogen atom. When **1** was mixed with 1.5 equiv of CO₂ at room temperature, a nitrido/oxo/isocyanate complex **4** was formed through N₂ cleavage, CO₂ partial deoxygenation and N=C double bond formation. The reaction of **4** with CO₂ (1 atm) at room temperature yielded the diisocyanate complex **3**. While **2** did not react with CO₂ at room temperature, it was converted to **3** under 1 atm CO₂ at 80 °C. Computational studies revealed that the reaction was initiated by the nucleophilic attack of the N₂ unit in **1** to CO₂.

Scheme 1



1) Previous studies on the reaction of N₂ with CO₂ without N–N and C–O bond cleavage: a) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Angew. Chem., Int. Ed.* **2007**, *46*, 2858. b) D. J. Knobloch, H. E. Toomey, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, *130*, 4248. c) Y. Nakanishi, Y. Ishida, H. Kawaguchi, *Angew. Chem., Int. Ed.* **2017**, *56*, 9193.

2) Z. Mo, T. Shima, Z. Hou, *Angew. Chem., Int. Ed.* **2020**, *59*, 8635.

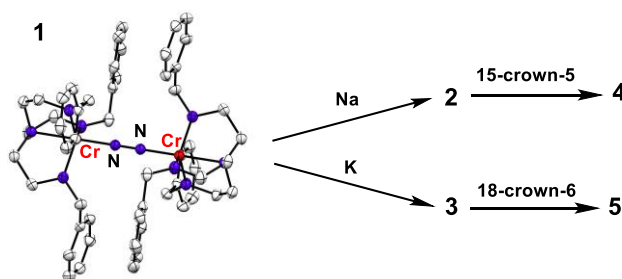
The syntheses and Structures of Dinitrogen Chromium Complexes Supported with Triamidoamine Ligands

(Graduate School of Engineering, Aichi Institute of Technology) ○Yoshiaki Kokubo, Yuji Kajita, and Hideki Masuda

Keywords: Chromium Complex; Dinitrogen Complex; Dinitrogen Activation; Dinuclear Complex; Triamidoamine Ligand

Transition metal dinitrogen complexes are intensively studied for N₂ reduction. Catalytic reduction of N₂ to NH₃ was achieved by Schrock with a molybdenum dinitrogen complex supported with a triamidoamine ligand.¹ Nishibayashi group also reported a catalytic reduction of N₂ by using Mo complex and water as a proton source recently.² In contrast to the many variations of Mo and W complexes with dinitrogen, examples of chromium complex are rare.

In this study, we synthesized triamidoamine ligand with benzyl (L³⁻ = tris(2-amidoethyl)amine, R = Bn) and prepared a novel chromium complex by reacting CrCl₃ with L^R under N₂. The structure of chromium complex revealed a dichromium complex with a bridging N₂ ligand, [$\{\text{Cr}(\text{L}^{\text{R}})\}_2(\text{N}_2)$] (**1**) (Scheme 1), which is composed of two species, **1a** and **1b**, in a unit cell. The N—N bonds in **1a** and **1b** are 1.188(4) and 1.185(7) Å, respectively. The N—N stretching vibration ($\nu(^{14}\text{N}—^{14}\text{N})$) of **1** was observed at 1772 cm⁻¹. Complex **1** reacted with Na or K to give a dinitrogen-chromium(II) complex with an alkaline ion, [$\{\text{CrNa}(\text{L}^{\text{Bn}})(\text{N}_2)(\text{Et}_2\text{O})\}_2$] (**2**) or [$\{\text{CrK}(\text{L}^{\text{Bn}})(\text{N}_2)\}_4(\text{Et}_2\text{O})_2$] (**3**), respectively, and complexes **2** and **3** reacted with 15-crown-5 and 18-crown-6 to form their crown-ether adducts, [$\text{CrNa}(\text{L}^{\text{Bn}}(\text{N}_2)(15\text{-crown-5}))$] (**4**) and [$\text{CrK}(\text{L}^{\text{Bn}})(\text{N}_2)(18\text{-crown-6})$] (**5**), respectively (Scheme 1). Their structures were confirmed by X-ray analysis. The IR spectra gave the $\nu(^{14}\text{N}—^{14}\text{N})$ at 1813 cm⁻¹ for **2**, at 1804 and 1774 cm⁻¹ for **3**, at 1813 cm⁻¹ for **4**, and at 1807 cm⁻¹ for **5**, respectively. Additionally, all of complexes, **1**, **2**, **3**, **4**, and **5**, reacted with a reductant and a proton source to give NH₃ and/or N₂H₄, and **1** gave only N₂H₄ when using HCl. In this presentation, we will report crystal structures, characterization, and reactivities of these dichromium-dinitrogen complexes.



Scheme 1

1) R. R. Schrock et al., *Science* **2003**, 301, 76. 2) Y. Nishibayashi et al., *Nature*, **2019**, 568, 536.

Properties of Dimetallene Dianions Bearing Triptycyl Framework

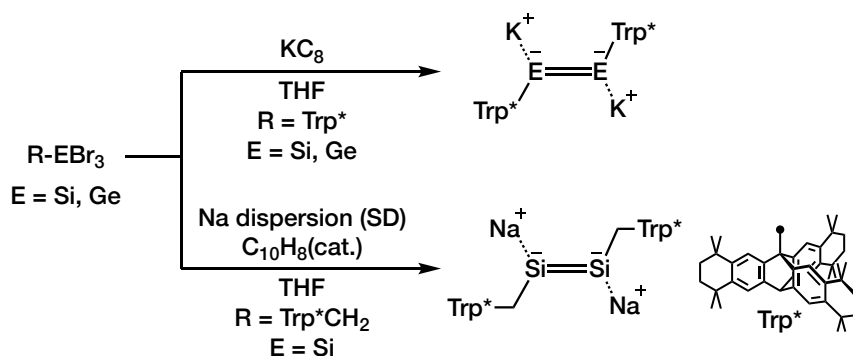
(College of Science, Rikkyo University) ○Ryohei Nishino, Mao Minoura

Keywords: Triptycene, Dimetallene, Disilene, Dianion, X-ray Crystallographic Analysis

Heavier analog of vinyl anion, dimetallenides¹⁾ (dimetallene monoanions) can be utilized as building blocks for double bonds between group 14 elements. Dimetallene dianions are assumed to have a potential role of introducing two functional groups into the E=E bond. However, synthetic examples²⁾ are so limited due to their high reactivity and lack of suitable synthetic routes.

We have developed the aliphatic steric protection group having triptycyl framework and extended its peripheral position (Trp*). Dipotassiodisilene and -digermene ($K_2[Trp^*_2E_2]$, E = Si, Ge) were synthesized by taking advantage of Trp* groups. In addition, we also have synthesized the disilene dianion bearing 9-triptycylmethyl framework $[Na_2(Trp^*CH_2Si)_2]$ which can provide the larger space on the Si=Si bond moiety than Trp*-substituted disilene dianions. In this presentation, we report the synthesis and properties of these compounds.

The reaction of Trp^*EBr_3 (E = Si, Ge) with KC_8 yielded the corresponding $K_2[Trp^*_2E_2]$ as the thermally stable red crystals, respectively. Each structure was determined by X-ray crystallographic analysis and revealed the effective steric protection of Trp* groups around E=E double bond moiety. Disiodidisilene bearing Trp*CH₂ groups was synthesized by the reduction of $Trp^*CH_2SiBr_3$ with sodium dispersion (SD) in the presence of naphthalene as a catalyst. X-ray crystallographic analysis revealed the larger reaction space around Si=Si bond moiety. The details of the structural properties of dimetallene dianions will be discussed.



1) D. Scheschkewitz, *Angew. Chem. Int. Ed.*, **2004**, 43, 2965-2967; M. Ichinohe, K. Sanuki, S. Inoue, A. Sekiguchi, *Organometallics*, **2004**, 23, 3088-3090. 2) K. Haga, M. Ichinohe, A. Sekiguchi, 93rd CSJ annual meeting, C. Cui, *J. Am. Chem. Soc.*, **2020**, 142, 4131-4135; M. Tian, J. Zhang, L. Guo, C. Cui, *Chem. Sci.* **2021**, 12, 14635; L. Pu, M. O. Senge, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.*, **1998**, 120, 12682-12683; A. Rit, J. Campos, H. Niu, S. Aldridge, *Nat. Chem.*, **2016**, 8, 1022-1026.

置換基導入 PCP 配位子を用いた触媒的アンモニア生成反応の理論的研究

(九州大先導研¹・大同大教養²・東大院工³) ○江木 晃人¹・田中 宏昌²・西林仁昭³・吉澤 一成¹

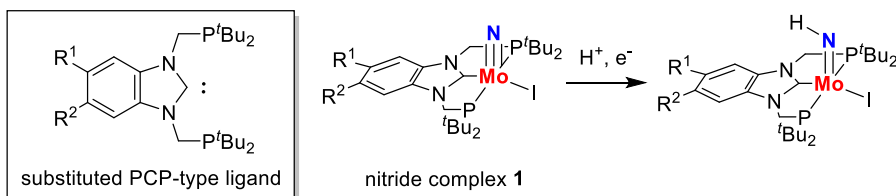
Computational Design and Evaluation of Substituted PCP-Type Ligands for Mo-Catalyzed Nitrogen Fixation (¹*Institute for Material Chemistry and Engineering, Kyushu University*, ²*School of Liberal Arts and Science, Daido University*, ³*Graduate School of Engineering, The University of Tokyo*) ○Akihito Egi,¹ Hiromasa Tanaka,² Yoshiaki Nishibayashi,³ Kazunari Yoshizawa¹

Nishibayashi's group prepared molybdenum-iodine complex bearing phosphine- and *N*-heterocyclic carbene-based PCP-type pincer ligand (1,3-bis((di-*tert*-butylphosphino)methyl)benzimidazol-2-ylidene) and demonstrated the catalytic dinitrogen-ammonia transformation under ambient conditions in presence of proton and electron sources. ($\text{N}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_3$) [1] To enhance the catalytic activity furthermore, the electronic properties of the molybdenum-iodine complex should be controlled. In this study, we introduce substitutes into 5- and 6-position of the benzimidazole skeleton in the PCP-type ligand and perform density-functional theory (DFT) calculations to evaluate substituent effects focusing on the N-H bond formation reaction of nitride complex **1**.

Keywords : Nitrogen fixation, Molybdenum complex, Density functional theory calculations, Substituent effect, Ammonia

西林らは、*N*-ヘテロ環状カルベン構造を含む PCP 型ピンサー配位子を有するモリブデン-ヨウ素錯体を合成したのち、プロトン付加剤と還元剤を用いることでこれを触媒とした触媒的な窒素固定反応を達成した。¹ 配位子への置換基導入によるモリブデン-ヨウ素錯体の電子状態の制御は触媒活性のさらなる向上に対して有効だと考えられる。しかし、この PCP 型ピンサー配位子の置換基効果はこれまで検討されたことがなかった。本研究では、置換基導入 PCP 型ピンサー配位子及びモリブデン-ヨウ素錯体をモデリングするとともに、DFT 計算を用いて触媒活性への影響を予測する。

触媒活性は中間体として考えられるニトリド錯体 **1** の N-H 結合形成過程に対する DFT 計算によって評価した。



1) A. Eizawa, K. Arashiba, A. Egi, H. Tanaka, K. Nakajima, K. Yoshizawa and Y. Nishibayashi *Chem. Asian J.* **2019**, *14*, 2091-2096.

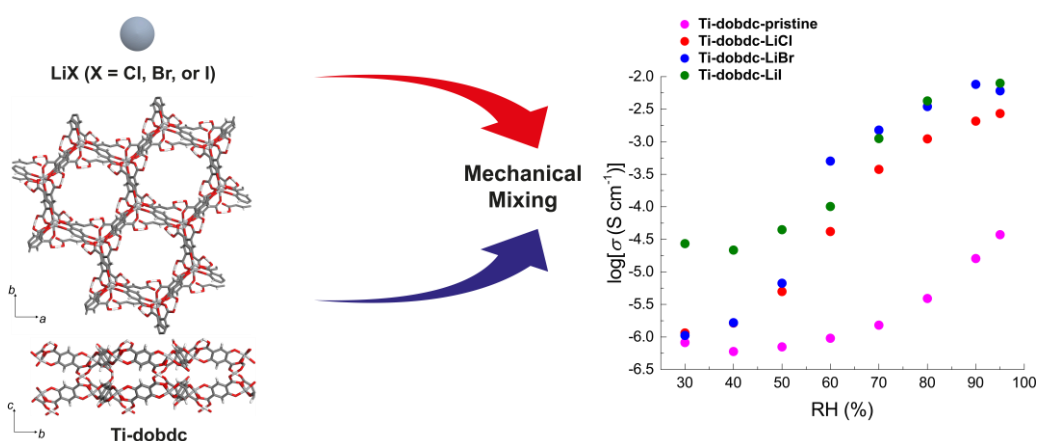
High Ionic Conductivity in 2D-layered Ti-MOF by Li Salts Mechanical Insertion

(¹Graduate School of Science, Kyoto University, ²College of Science and Technology, Yonsei University) ○Marvin Kevin Sarango Ramirez,¹ Yukihiro Yoshida,¹ Dae-Woon Lim,^{1,2} Hiroshi Kitagawa¹

Keywords: MOF; Ionic conductivity; Li salt intercalation; Layered structure

Solid-state electrolyte is a key element for safety and high performance in fuel cell and battery systems. Recently, porous metal–organic frameworks (MOFs) have emerged as a platform of solid-state ionic conductors due to their designability and structural stability.¹ Typically, ionically conductive MOFs are achieved through the insertion of charge carriers by post-synthetic methods such as the dipping in charge carrier solution or the mechanical mixing. In particular, the mechanical mixing with charge carriers allows for precise *solvent-free* insertion of charge carriers.

Herein, we demonstrate the high ionic conductivity ($\sigma > 10^{-2} \text{ S cm}^{-1}$) in the 2D-layered Ti-dobdc framework ($\text{Ti}_2[(\text{Hdobdc})_2(\text{H}_2\text{dobdc})]$, H_4dobdc : 2,5-dihydroxyterephthalic acid) through the LiX salt (X = Cl, Br, or I) mechanical intercalation. The incorporation of LiX salts in the layered MOF (Ti-dobdc-LiX, X = Cl, Br, or I) improved the structural stability and boosted the H_2O adsorption property. At low humidity (RH = 30%), the Ti-dobdc-LiI shows a two-order of magnitude higher conductivity ($\sigma = 2.73 \times 10^{-5} \text{ S cm}^{-1}$) than the other samples, indicating that hydrophilicity and ionic/covalent character of LiX favor high ionic conductivity. Furthermore, at higher humidity (RH = 95%) all Ti-dobdc-LiX samples show superior ionic conductivity than the pristine sample by two-order magnitude. Further details are presented and discussed.



1) Thakur, A.K.; Majumder, M.; Patole, S.P.; Zaghib, K.; Reddy, M.V. *Mater. Adv.* **2021**, 2, 2457-2482.

Synthesis of a Zr-mellitate MOF and Its Ion-Exchange Property

(¹Graduate School of Science, The University of Tokyo) ○Genki Hatakeyama,¹

Masaki Nishio,¹ Kouki Oka,¹ Teppei Yamada¹

Keywords: Metal-Organic Frameworks; UiO-66; Ion-Exchange; Ammonium ion

Metal-organic frameworks (MOFs) are microporous materials containing metal ions and organic linkers, and are applicable toward catalysis, gas storage/separation, molecular sensing, drug delivery, etc. MOFs are also attracting attention as ion-exchange materials, and the adsorption of heavy atoms ions such as mercury or cadmium ions has been vigorously studied^{1,2}. However, due to the low stability of MOFs against water, reversible ion-exchange by MOFs has not yet been realized. In this study, we report a novel MOF composed of zirconium and mellitic acid, which is resistant to acid or ammonium ion aqueous solution. The ion-exchange properties of this MOF were evaluated.

The hydrothermal reaction of zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and mellitic acid in an aqueous solution containing acetic acid and ammonium chloride to give microcrystalline powder (hereafter Zr-mellitate). The powder X-ray diffraction (PXRD) pattern indicated that the structure is isostructural to a previous MOF consisting of sulfoterephthalate and zirconium³, and four carboxyl groups were present without coordination in the framework. According to the elemental analysis, pristine Zr-mellitate contains one ammonium cation per ligand. With the treatment of 12 mM hydrochloric acid, 77% of the ammonium ions were released into the solution. From the result, one carboxy group per ligand can act as the ion-exchange site (Figure 1). The protonated Zr-mellitate can adsorb ammonium and potassium cations by the further ion-exchange reaction. The PXRD pattern showed that the structure of Zr-mellitate was maintained during these ion-exchange processes (Figure 2).

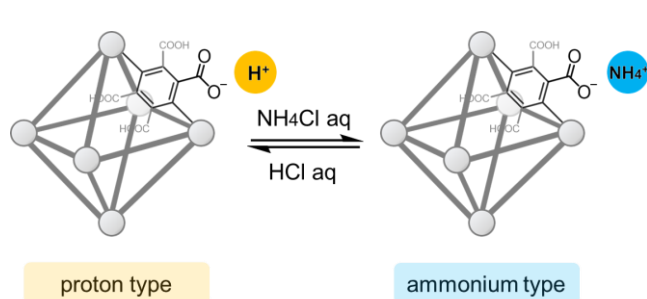


Figure 1. Reversible ion-exchange in Zr-mellitate

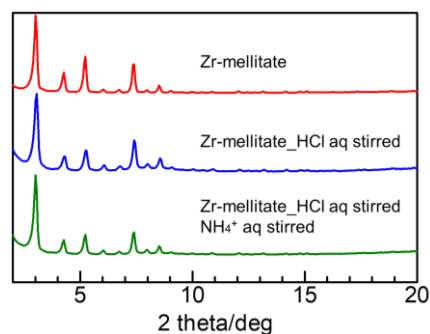


Figure 2. PXRD of Zr-mellitate

- 1) S. Gao et al., *Coord. Chem. Rev.* **2021**, 443, 214034. 2) J. Kaushal et al., *Environ. Sci. Pollut. Res.* **2020**, 27, 44771. 3) H. Kitagawa et al., *J. Am. Chem. Soc.* **2015**, 137, 11498.

[J402-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Yutaka Hitomi, Kyoko Nozaki

Sat. Mar 26, 2022 9:00 AM - 11:40 AM J402 (Online Meeting)

[J402-4am-01] The Synthesis and reactivity of PBP-Pincer**Perfluororhodacyclopentanes**○Shinya Hayashi¹, Toshiki Murayama¹, Shuhei Kusumoto¹, Kyoko Nozaki¹ (1. The University of Tokyo)

9:00 AM - 9:20 AM

[J402-4am-02] Dynamics of Transmetalation of the Binuclear Au(I) Diaryl Complexes and Their Synthetic Application to Macrocyclization○Yusuke Yoshigoe¹, Yoshitaka Tsuchido¹, Hidetoshi Kawai¹, Kohtaro Osakada², Shinichi Saito¹ (1. Tokyo Univ. of Science, 2. Tokyo Institute of Tech.)

9:20 AM - 9:40 AM

[J402-4am-03] Conversion from Phosphinine Pincer Metal Complexes to Metallabenzenes Triggered by O₂ Oxidation○Koichiro Masada¹, Shuhei Kusumoto¹, Kyoko Nozaki¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[J402-4am-04] Synthesis and structural analysis of a gold cluster Au₁₈S₂(SR)₁₂ (R = 2,4,6-C₆H₂ⁱPr₃CH₂) protected by bulky thiolate ligands○Taro Shigeta¹, Shinjiro Takano¹, Tatsuya Tsukuda^{1,2} (1. Graduate School of Science, The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)

10:00 AM - 10:20 AM

[J402-4am-05] Benzimidazolines as New Acyl Donors for Photocatalytic Transformations of Unactivated Alkenes: Intermolecular Hydroacylation and 3-Component Acylcarboxylation *via* CO₂ Insertion○Yutaka Saga¹, Taito Watanabe¹, Yusuke Nakayama¹, Mio Kondo^{1,2}, Shigeyuki Masaoka¹ (1. Department of Applied Chemistry Graduate School of Engineering Osaka University, 2. JST PRESTO)

10:20 AM - 10:40 AM

[J402-4am-06] Synthesis of Deuterated Alcohols via Hydrogen Transfer Process Catalyzed by Iridium ComplexesMoeko Itoga¹, Masako Yamanishi¹, Yoshiji Takemoto¹, ○Hiroshi Naka¹ (1. Grad. Sch. of Pharm. Sci., Kyoto Univ.)

10:40 AM - 11:00 AM

[J402-4am-07] Rapid Alkane Functionalization with H₂O₂ Catalyzed by Monocopper Complexes with Medpa Tridentate Ligand and its Derivatives○kyosuke Fujikawa¹, momoe Kawahashi¹, yutaka Hitomi¹, masahito Kodera¹ (1. Doshisha University)

11:00 AM - 11:20 AM

[J402-4am-08] Photochromism in polymorphic crystals of a rhodium dithionite complex○Yuu Kajiwar¹, Seiya Miyata¹, Hidetaka Nakai¹ (1. Dept. Appl. Chem. Kindai Univ.)

11:20 AM - 11:40 AM

The Synthesis and Reactivity of PBP-Pincer Perfluororhodacyclopentanes

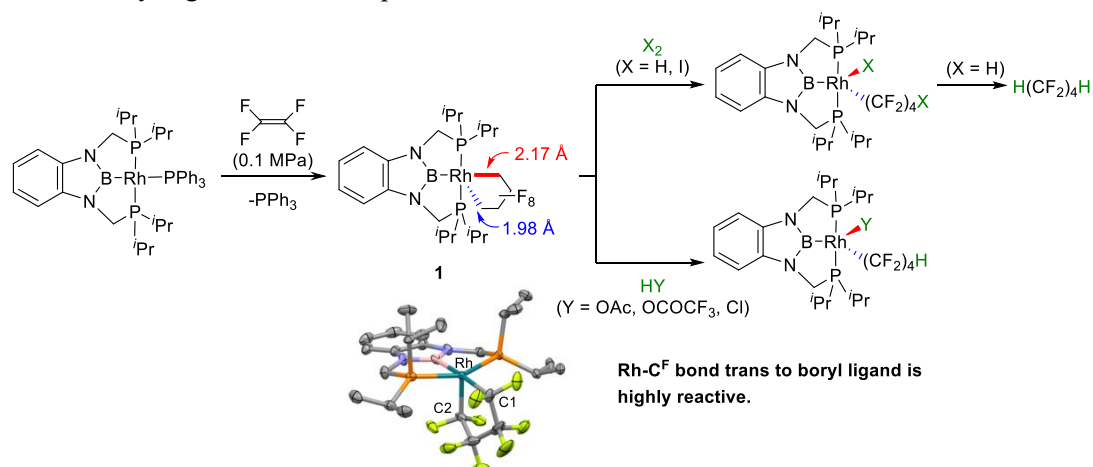
(Graduate School of Engineering, The University of Tokyo) ○ Shinya Hayashi, Toshiki Murayama, Shuhei Kusumoto, Kyoko Nozaki

Keywords: Rh; PBP-pincer; rhodacycle; tetrafluoroethylene; perfluorometallacyclopentane

Oligomerization of tetrafluoroethylene (TFE) has been attracting great attention because of the industrial importance of polyfluoroalkyl building blocks. Although the oxidative cyclization of TFE and low-valent transition metals has been studied for more than half a century, selective oligomerization of TFE is still challenging due to the extraordinary stability of octafluorometallacyclopentane.¹

We employed rhodium complex bearing PBP pincer ligand expecting enhancement of nucleophilicity of the fluoroalkyl group by strong electron-donation from the anionic boryl ligand. The complex $\text{PBPRh}^{\text{III}}(\text{CF}_2)_4$ (**1**) was formed by the oxidative cyclization of the $\text{PBPRh}^{\text{I}}-\text{PPh}_3$ complex with two TFE molecules in 65% yield. Single-crystal X-ray crystallographic analysis revealed that **1** has a square pyramidal geometry, and the Rh–C bond trans to boryl ligand (2.17 Å) is largely elongated compared to the Rh–C bond at the apical position (1.98 Å).

The hydrogenolysis of **1** proceeded under mild conditions (room temperature, 1 atm of H_2) affording 1,1,2,2,3,3,4,4-octafluorobutane in 89% yield, which demonstrated high reactivity of **1** compared to the precedented example with Ni complexes (at 100 °C, under H_2 pressure of 68 atm).² The iodinolysis and the protonolysis of **1** also proceeded selectively at ambient temperature. The high nucleophilicity of Rh–C^F bond can be attributed to the strong effect of boryl ligand in the PBP pincer skelton.³



1) T. A. Manuel, S. L. Stafford, F. G. A. Stone, *J. Am. Chem. Soc.* **1961**, 83, 249. 2) K. A. Giffin, L. A. Pua, I. Korobkov, R. T. Baker, *Polyhedron* **2019**, 157, 458. 3) Y. Masuda, M. Hasegawa, M. Yamashita, K. Nozaki, N. Ishida, M. Murakami, *J. Am. Chem. Soc.* **2013**, 135, 7142.

二核金 (I) ジアリール錯体間で起こるトランスメタル化の動的挙動と環化反応への応用展開

(東理大理¹・東工大²) ○吉越 裕介¹、土戸 良高¹、河合 英敏¹、小坂田 耕太郎²、斎藤 慎一¹

Dynamics of Transmetalation of the Binuclear Au(I) Diaryl Complexes and Their Synthetic Application to Macrocyclization (¹*Faculty of Science, Tokyo University of Science*, ²*Laboratory for Chemistry and Life Science Institute of Innovative Research, Tokyo Institute of Technology*.)

We have uncovered the dynamics of transmetalation of Au complex, which can be applied into the macrocyclization reaction. The CDCl₃ solution of a mixture of two kinds of symmetrical binuclear Au(I) diaryl complexes (**1-HH** and **1-FF**) gave the equilibrated mixture of symmetrical and unsymmetrical Au(I) complexes (**1-HF**) which is the exchanged product of aryl ligands on Au complexes (Figure 1). The kinetics study and theoretical consideration suggested the mechanism of the above reaction. The above dynamic behavior of the Au(I) diaryl complex has been combined into the macrocyclization process to yield the cyclic oligonuclear Au complexes effectively. Detail will be discussed in this presentation.

Keywords : Au(I) complex, Transmetalation, Dynamics, Kinetics, Macrocyclization

本研究では、二核ジアリール金(I)錯体間のアリール配位子交換について、その反応機構の推定と環状錯体化反応への応用をおこなった。まず Au₂Ph₂(dcpm) (**1-HH**) と Au₂(C₆H₄-4-F)₂(dcpm) (**1-FF**) を CDCl₃ に溶解 ([**1-HH**]₀ = [**1-FF**]₀ = 1.0 mM) させ、室温下 (~30 °C) にて NMR を測定した (Figure 1) 。アリール配位子交換反応は~30 分以内に平衡に達し、**1-HH**, **1-FF** および **1-HF** の混合溶液を与えた。低温下 (0 °C) で反応を追跡し、その反応速度定数を $k(k_{-1}) = 0.30 \pm 0.039 ((8.6 \pm 0.80) \times 10^{-2}) \text{ M}^{-1} \cdot \text{s}^{-1}$ と決定した。支持配位子の異なる金錯体 **2-HH** と **2-FF** では、所望の反応はほとんど進行しない。すなわち、この反応は配位子特異的である。発表では反応の速度論的解析の詳細と、その動的性質を利用した環状分子合成への応用を紹介する¹⁾。

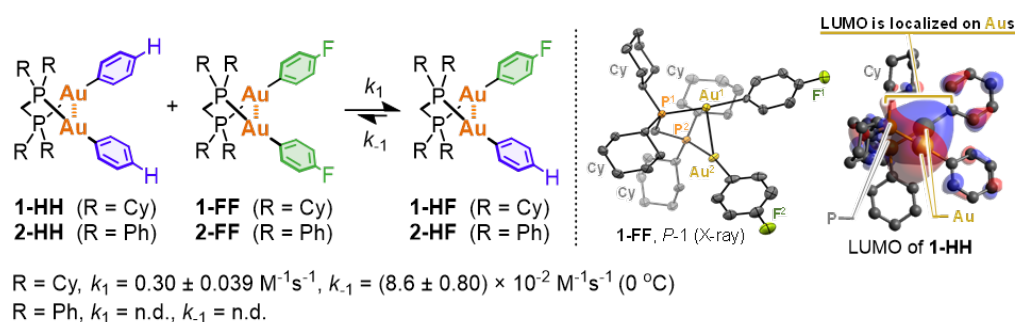


Figure 1. Reactions of Au(I) complexes (**1-HH** and **1-HF**) and their kinetic rates (k and k_{-1}); the solid state structure of **1-FF**; the optimized structure of **1-HH** with its LUMO.

(1) Yoshigoe, Y.; Tanji, Y.; Saito, S.; Osakada, K.; Tsuchido, Y.; Kawai, H. DOI: 10.33774/chemrxiv-2021-v89w1.

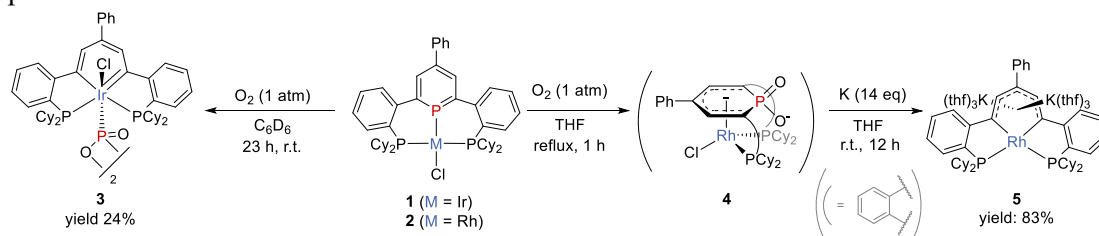
Conversion from Phosphinine Pincer Metal Complexes to Metallabenzenes Triggered by O₂ Oxidation

(Graduate School of Engineering, The University of Tokyo) ○Koichiro Masada, Shuhei Kusumoto, Kyoko Nozaki

Keywords: Phosphinine; Metallabenzene; Rhodium Complex; Iridium Complex; Pincer Complex

Since Kekulé proposed the correct structure of benzene in 1865, tremendous progress has been made in the chemistry of aromatic compounds. In this context, transition-metal-based metallabenzenes, where a CH group on a benzene ring is replaced by a transition metal fragment, have attracted great interest¹ for the participation of metal d orbital in π conjugation of an aromatic system. After Thorn and Hoffman predicted the aromatic character of mangano- and rhoda-benzenes,² metallabenzenes have been synthesized with some late transition metals, such as Mo, Re, Fe, Ru, Os, Ir, Ni, and Pt.¹ Although various methods for the synthesis of metallabenzene have been developed, the scope of each methodology is confined by the character of transition metal centers, and thus, metallabenzenes lack of general synthetic methodology.³ Herein, we report the new route to metallabenzenes from phosphinine (phosphabenzene), directly swapping the phosphorous atom for a transition metal fragment.

Novel phosphine-phosphinine-phosphine pincer iridium (I) complex **1** and rhodium (I) complex **2** were first synthesized. The reaction of complex **1** with an atmospheric pressure of oxygen gas resulted in a spontaneous crystallization of iridabenzene **3** in 24% yield. This method, the transformation of phosphinine to metallabenzene was further applied to the synthesis of rhodabenzene, which has never been addressed in any method.⁴ Complex **2** was treated with an atmospheric pressure of oxygen gas to afford pentadienyl rhodium (III) complex **4**. Notably, further reduction of complex **4** by an excess amount of potassium metal afforded rhodabenzene **5**. The structure of rhodabenzene **5** was unambiguously determined by single-crystal X-ray diffraction analysis. The mechanism of the formation of metallabenzenes and the aromaticity of them will be discussed in this presentation as well.



1) Chen, D.; Hua, Y.; Xia, H. *Chem. Rev.* **2020**, *120* (23), 12994–13086. 2) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39–45. 3) Chen, J.; Jia, G. *Coord. Chem. Rev.* **2013**, *257* (17–18), 2491–2521. 4) Wu, H. P.; Lanza, S.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21* (14), 2824–2826.

Synthesis and Structural Analysis of a Gold Cluster $\text{Au}_{18}\text{S}_2(\text{SR})_{12}$ ($\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Pr}_3\text{CH}_2$) Protected by Bulky Thiolate Ligands

(¹Graduate School of Science, The University of Tokyo, ²ESICB, Kyoto University)

○Taro Shigeta,¹ Shinjiro Takano,¹ Tatsuya Tsukuda^{1,2}

Keywords: Ligand-Protected Gold Cluster; Superatom; Interlocked Cage Structure; Single-Crystal X-Ray Diffraction; Density Functional Theory Calculation

The structure of the organic ligands and their binding interactions with the gold clusters have a significant impact on the geometric structure and physicochemical properties of the gold clusters.¹⁾ For example, associative interaction between the adjacent ligands enhances the photoluminescence quantum yields by rigidification of the Au cores,²⁾ whereas repulsive interaction between the adjacent ligands results in direct coordination of thiolates to the Au core^{3,4)} and formation of S^{2-} ligands on the Au core.⁵⁾ In this study, a new gold cluster, $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$, was obtained using a bulky thiol, interaction between the adjacent ligands 2,4,6-triisopropylbenzyl mercaptan (TipbSH, Fig. 1).

$\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ was isolated via the following steps: (i) reduction of $\text{AuClS}(\text{CH}_3)_2$ with NaBH_4 in the presence of TipbSH; (ii) incubation at 80°C in the presence of an excess amount of TipbSH; (iii) purification by gel permeation chromatography; (iv) fractional precipitation. Single-crystal X-ray diffraction analysis revealed that $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ has a deformed octahedral Au_6 core clutched by two tridentate $\text{S}[\text{Au}_2(\text{STipb})_2]_3$ units in an interlocked manner (Fig. 2). The electronic structures of $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ and a simplified model $\text{Au}_{18}\text{S}_2(\text{SCH}_3)_{12}$ were investigated by density functional theory calculations. Comparison of the HOMO-1 in Fig. 3 indicates that the electron density in the region between the two Au_3 units in $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ is much smaller than that in $\text{Au}_{18}\text{S}_2(\text{SCH}_3)_{12}$. Therefore, we propose that the Au_6 core is better viewed as a face-to-face dimer of Au_3 superatoms rather than a Au_6 superatom and that the interaction between the two Au_3 superatoms is weakened by the steric repulsion owing to the bulky TipbS ligands.

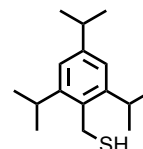


Fig. 1. Structure of TipbSH

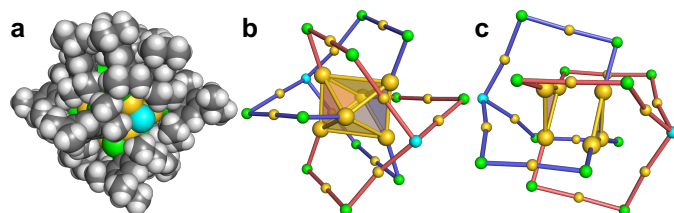


Fig. 2. X-ray structure of $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$. (yellow: Au, green: S of STipb, cyan: S, gray: C, white: H)

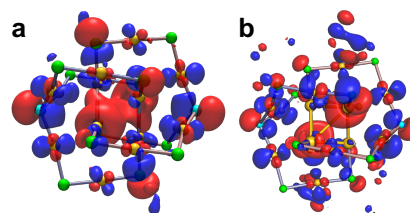


Fig. 3. Shape of Kohn-Sham orbital of HOMO-1 of (a) $\text{Au}_{18}\text{S}_2(\text{SCH}_3)_{12}$ and (b) $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$.

1) S. Takano *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 1683. 2) K. Pyo *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 8244. 3) J. Nishigaki *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 14295. 4) J. Nishigaki *et al.*, *Chem. Commun.* **2014**, *50*, 839. 5) R. Jin *et al.*, *Chem. Rev.* **2016**, *116*, 10346.

Benzimidazolines as New Acyl Donors for Photocatalytic Transformations of Unactivated Alkenes: Intermolecular Hydroacylation and 3-Component Acylcarboxylation *via* CO₂ Insertion

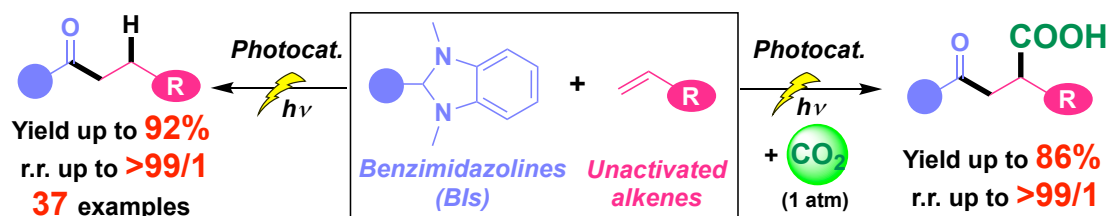
(¹Graduate School of Engineering, Osaka University, JST PRESTO) ○Yutaka Saga¹, Taito Watanabe¹, Yusuke Nakayama¹, Mio Kondo^{1,2}, Shigeyuki Masaoka¹

Keywords: *Benzimidazolines; Photoredox Catalyst; CO₂ Gas; 3-Component Reaction; Hydroacylation*

Ketones are versatile and ubiquitous structural motifs found in many biologically active natural products and pharmaceuticals. In recent years, photocatalytic hydroacylation of alkenes received considerable attentions as an attractive method for accessing ketones from abundant and cheap feedstocks under mild conditions¹⁾. However, there have been only few examples to accomplish the reaction with unactivated alkenes, and the substrates in previous reports were strictly limited to activated alkenes, such as Michael radical acceptors (e.g. acrylates, malonitriles and so on) or 1,1'-disubstituted ethylene derivatives. In this regard, the versatile synthetic methodology enabling hydroacylation of unactivated alkenes is strongly demanded.

Herein, we achieve the first photocatalytic hydroacylation of unactivated alkenes without using acyl radical species, which is the conventional and dominant acyl donors for this kind of reaction²⁾. A key to our success was to employ benzimidazolines (BIs) as new acyl donor precursors. We demonstrated that BI radicals, formed by one-electron oxidation of BIs, can function as unprecedented acyl donors for photocatalytic hydroacylation of unactivated alkenes. Moreover, our mild, general and simple system enabled the excellent compatibility with highly sensitive functional groups (i.e. carboxylic acid, boronic acid, phosphine etc.) as well as the broad substrate scopes (37 examples).

Furthermore, we also achieved the first 3-component acylcarboxylation of alkenes with BIs as acyl donors *via* CO₂ insertion. Detailed reaction development, investigations on substrate generalities as well as mechanistic studies will be given in the presentation.



1) M. Zhang, J. Xie, C. Zhu, *Nat. Commun.*, **2018**, 9, 3517. 2) Y. Saga, Y. Nakayama, M. Kondo, S. Masaoka, *manuscript in preparation*.

Synthesis of Deuterated Alcohols via Hydrogen Transfer Process Catalyzed by Iridium Complexes

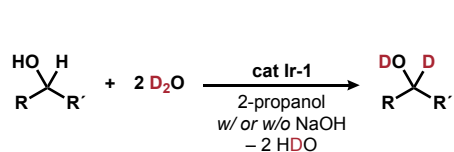
(Graduate School of Pharmaceutical Sciences, Kyoto University)

Moeko Itoga, Masako Yamanishi, Yoshiji Takemoto, and ○Hiroshi Naka

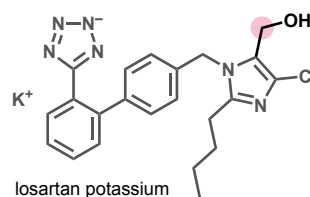
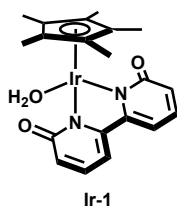
Keywords: Iridium, Deuteration, Alcohol, Deuterium, Deuterated Drug

Deuterium incorporation at the α -position of hydroxyl groups is an attractive strategy to improve the stability of drugs, as the alcohol moiety in pharmaceuticals is often susceptible to metabolism. While several transition-metal catalysts for the deuteration of alcohols have been reported,¹ many of these catalysts tend to be deactivated by nucleophilic functional groups such as imidazole and tetrazole. Thus, chemoselective α -deuteration of highly functionalized alcohols remains a significant challenge.

We herein report the α -selective, iridium(III)-bipyridonate-catalyzed deuteration of alcohols using deuterium oxide (D_2O) as the primary deuterium source. We chose an iridium–bipyridonate complex (**Ir-1**) for the direct deuteration of alcohols through hydrogen transfer process because **Ir-1** is known as a structurally robust, excellent catalyst for reversible dehydrogenation of alcohols, as demonstrated by Fujita and coworkers.² Unlike known catalytic systems, the present deuteration method enabled the direct, chemoselective deuteration of primary and secondary alcohols under basic or neutral conditions without being affected by coordinative functional groups. Successful substrates for deuterium labelling include the pharmaceuticals losartan potassium, rapidosept, guaifenesin, and diprophylline.



+ Compatible with nucleophilic functional groups
+ Excellent α selectivity under neutral conditions



References

- [1] (a) Klei, S. R.; Golden, J. T.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 2092. (b) Maegawa, T.; Fujiwara, Y.; Inagaki, Y.; Monguchi, Y.; Sajiki, H. *Adv. Synth. Catal.* **2008**, *350*, 2215. (c) Fujiwara, Y.; Iwata, H.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Chem. Commun.* **2010**, *46*, 4977. (d) Khaskin, E.; Milstein, D. *ACS Catal.* **2013**, *3*, 448. (e) Chatterjee, B.; Gunanathan, C. *Org. Lett.* **2015**, *17*, 4794. (f) Bai, W.; Lee, K. -H.; Tse, S. K. S.; Chan, K. W.; Lin, Z.; Jia, G. *Organometallics*, **2015**, *34*, 3686. (g) Price, N. P. J.; Hartman, T. M.; Vermillion, K. E. *Anal. Chem.* **2015**, *87*, 7282. (h) Kar, S.; Goeppert, A.; Sen, R.; Kothandaraman, J.; Prakash, G. K. S. *Green Chem.* **2018**, *20*, 2706.
- [2] Kawahara, R.; Fujita, K.; Yamaguchi, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 12790.

Medpa 三座配位子およびその誘導体の単核銅錯体が触媒する H₂O₂ による高速アルカン酸化

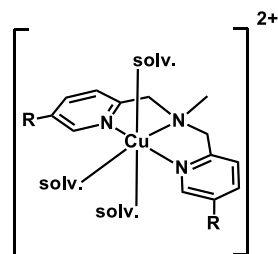
(同志社大理工、同志社大院理工¹⁾) ○藤川 恭祐¹・川橋 桃瑛²・人見 穰^{1,2}・小寺 政人^{1,2}

Rapid Alkane Functionalization With H₂O₂ Catalyzed by Monocopper Complexes With Medpa Tridentate Ligand and its Derivatives (¹*Undergraduate School of Science and Engineering, Doshisha University,* ²*Graduate School of Science and Engineering, Doshisha University*) ○Kyosuke Fujikawa,¹ Momoe Kawahashi,² Yutaka Hitomi,^{1,2} Masahito Kodera^{1,2}

Cu-enzyme particulate methane monooxygenases (pMMO) catalyze conversion of methane to methanol via O₂-activation at ambient conditions. It is proposed that pMMO has one or two Cu(II) ions at the active center, but the reaction mechanism and reactive species have not been clarified yet. We have developed various copper complexes to mimic the active site and function of pMMO. In this work, we found that monocopper complexes with Medpa and its 5-substituted derivatives [Cu(II)(Medpa^{5-R})(MeCN)]²⁺ (R = H (**1**), CH₃ (**2**), CF₃ (**3**)) catalyze rapid oxidation of cyclohexane with H₂O₂. Stopped-flow technique showed the formation of a highly reactive peroxodicopper intermediate in the initial stage of reaction. Here, we report the spectroscopic and kinetic studies for the cyclohexane oxidation catalyzed by **1-3**.

Keywords : monocopper(II) complex; cyclohexane oxidation

自然界では、メタン酸化細菌に存在する膜結合型の銅酵素である pMMO が酸素分子を活性化してメタンからメタノールへの変換を触媒している。pMMO の活性中心には単核または二核銅が存在するとされているが^[1,2]、その詳細な反応機構や酸化活性種は不明のままである。我々は、三核銅(II)錯体が H₂O₂ によるアルカン酸化を高速で触媒することを見出した。今回は、この三核錯体に含まれる三座配位構造に着目した。本研究では、三座配位子 Medpa、このピリジン 5 位にメチル基、またはトリフルオロ基を導入した Medpa^{5-R} を用いた単核銅(II)錯体[Cu(Medpa^{5-R})(MeCN)]²⁺ (R = H (**1**), CH₃ (**2**), CF₃ (**3**))が、H₂O₂ によるシクロヘキサン酸化を高速で触媒することを見出した。速度論解析、並びに電子スペクトルの結果より反応初期に酸化活性種として非常に高活性な二核銅ペルオキシド錯体が生成することを見出したので報告する。



1) W.-H. Chang, H.-H. Lin, I.-K. Tsai, S.-H. Huang, S.-C. Chung, I.-P. Tu, S.S.-F. Yu, S. I. Chan, *J. Am. Chem. Soc.* **2021**, *143*, 9922-9932

2) M. O. Ross, F. MacMillan, J. Wang, A. Nisthal, T. J. Lawton, B. D. Olafson, S. L. Mayo, A. C. Rosenzweig, B. M. Hoffman, *Science*, **2019**, *364*, 566-570

Fig. 1 The chemical structures of **1-3**

R = H (**1**), CH₃ (**2**), CF₃ (**3**)

Photochromism in Polymorphic Crystals of a Rhodium Dithionite Complexes

(Dept. Appl. Chem. Kindai Univ.) ○Yuu Kajiwar, Seiya Miyata, Hidetaka Nakai

Keywords: Crystalline-State Reaction, Photochromism, Polymorphism, Rhodium Complex, Dithionite Complex.

In polymorph crystal, a certain compound exists in different crystallographic structures. Studies on the polymorphic crystals of photochromic compounds with reversible switching functions are very useful for constructing new switching devices and materials. However, there are limited examples of photochromic compounds that show not only crystalline-state photochromism but also polymorphism.

In this context, we have recently demonstrated that rhodium dinuclear complexes with a photo-responsive dithionite ligand $[(Cp^R Rh)_2(\mu-CH_2)_2(\mu-O_2SSO_2)]$ (1^R) (Me: CH₃, Pro: *n*-C₃H₇, Pen: *n*-C₅H₁₁ etc.) show crystalline-state photochromism with 100% interconversion ratio; 1^R shows type-*T* photochromism in which the $\mu-O_2SSO_2$ complex (1^R) isomerizes to the corresponding $\mu-O_2SOSO$ complex (2^R) by photoreaction and 2^R returns to 1^R by thermal reaction (Figure 1a).¹ Intriguingly, a newly prepared rhodium dithionite complex with *n*-methoxypropyl moieties (1^{MPro} , R = MPro; *n*-C₃H₆OCH₃) forms two polymorphic crystals (α - and β -crystals, Figure 1b). The difference between the α - and β -crystals is ascribed to the different arrangement of the Cp^{MPro} ligand in 1^{MPro} (Figure 1c). Herein, we report photochromism in the α - and β -crystals of 1^{MPro} .

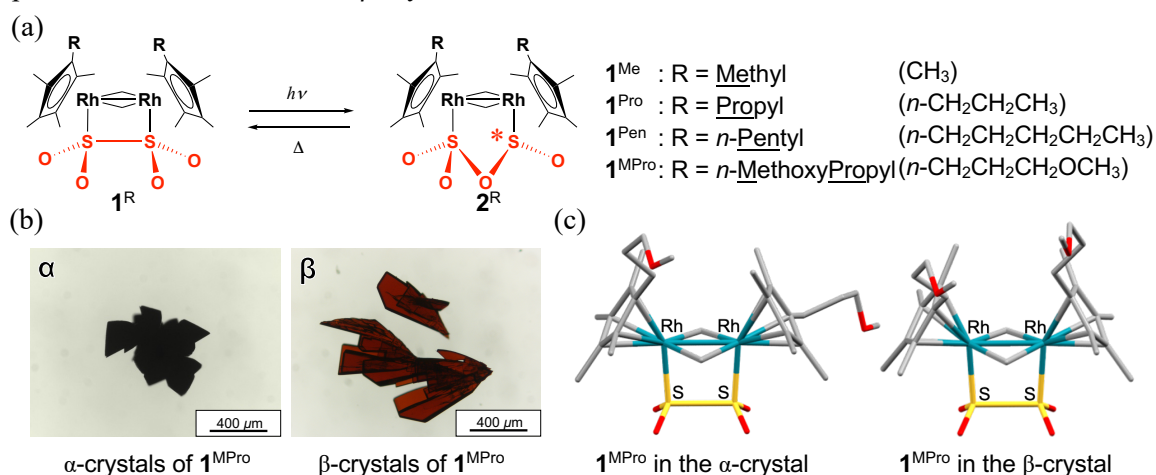


Figure 1. (a) Photochromism of rhodium dithionite complexes, 1^R (R = Me, Pro, Pen, MPro etc.). (b) photographs of the α - (left) and β - (right) crystals of 1^{MPro} . (c) Capped stick drawings of 1^{MPro} in the α - (left) and β - (right) crystals.

1) (a) H. Nakai et al., *J. Am. Chem. Soc.* **2008**, *130*, 17836. (b) H. Nakai et al., *Chem. Commun.* **2016**, 52, 4349. (c) H. Nakai et al., *Dalton Trans.* **2020**, 49, 1721.

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[K1-4am] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Yasujiro Murata, Hidehiro Sakurai

Sat. Mar 26, 2022 9:00 AM - 11:00 AM K1 (Online Meeting)

[K1-4am-01] Design and Synthesis of Oxygen-Embedded TriQuinoline and its Strategic Applications○Toi Kobayashi¹, Naoya kumagai¹ (1. Keio university)

9:00 AM - 9:20 AM

[K1-4am-02] Molecular Motion Restriction of Tetraphenylethylene Enabled by a Linked Rotaxane Structure to Enhance the Robustness of Fluorescent Properties○Hiromichi V. Miyagishi¹, Hiroshi Masai¹, Jun Terao¹ (1. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

9:20 AM - 9:40 AM

[K1-4am-03] Synthesis and Properties of Perfluorocubane○Masafumi Sugiyama¹, Midori Akiyama¹, Yuki Yonezawa¹, Kyoko Nozaki¹, Takashi Okazoe^{1,2} (1. The University of Tokyo, 2. AGC Inc.)

9:40 AM - 10:00 AM

[K1-4am-04] Syntheses and Properties of BAr₂-Bridged Azafulvene Compounds Base on Five-Membered Chelate Rings○TIANCHENG TAN¹, SHUAIFENG HU¹, MINH ANH TRUONG¹, RICHARD MURDEY¹, TOMOYA NAKAMURA¹, ATSUSHI WAKAMIYA¹ (1. Kyoto University Institute for Chemical Research)

10:00 AM - 10:20 AM

[K1-4am-05] Spirofluorene Based Novel [2]rotaxanes: Synthesis and NMR Studies○Showkat Rashid¹, Takashi Murakami¹, Yusuke Yoshigoe¹, Shinichi Saito¹ (1. Tokyo University of Science)

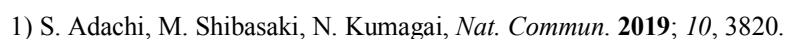
10:20 AM - 10:40 AM

[K1-4am-06] Development of Boron and Nitrogen-Doped Polycyclic Heteroaromatics Exhibiting Full-Color Narrowband Emissions○Minlang Yang^{1,2}, In Seob Park², Takuma Yasuda^{1,2} (1. Grad. Sch. of Eng., Kyushu Univ., 2. IFRC, Kyushu Univ.)

10:40 AM - 11:00 AM

(*Graduate School of Pharmaceutical Sciences, Keio University*) ○ Toi Kobayashi¹, Naoya Kumagai¹

Recently, a head-to-tail type quinoline trimer featuring an atomic size void space, TriQuinoline (TQ), was uncovered as a pseudo-planar material exhibiting unusual physicochemical properties.¹ We designed a new non-flat quinoline trimer oxa-TriQuinoline (o-TQ) comprising of three quinoline units concatenated at 2,8-positions with three oxygen atoms. o-TQ was synthesized from a known compound, 2-fluoroquinolin-8-ol, by conventional S_NAr reaction in a single step. While X-ray crystallography and DFT calculation revealed that o-TQ preferred a bended structure, complexation with Cu(I) cation in a tridentate fashion furnished a conformationally fixed bowl-shape o-TQ/Cu(I) complex. This complex exhibited aggregation-induced emission (AIE) properties and strongly emissive ($\lambda_{\text{max}} = 592 \text{ nm}$, $\Phi = 0.21$) in the solid state. Conformational restriction endowed the complex with chirality and the thus obtained π -bowl displayed supramolecular complexation with non-flat aromatics of specific curvature *via* both π - π and CH- π interactions. ¹H/¹³C NMR and CSI-MS provided experimental evidence for the complexation of o-TQ/Cu(I) with corannulene, sumanene, a fullerene derivative as well as [12]CPP, which were also supported by DFT calculations.



Molecular Motion Restriction of Tetraphenylethylene Enabled by a Linked Rotaxane Structure to Enhance the Robustness of Fluorescent Properties

(Graduate School of Arts and Sciences, The University of Tokyo)

○Hiromichi V. Miyagishi, Hiroshi Masai, Jun Terao

Keywords: Linked Rotaxane Structure; Cyclodextrins; Fluorescent Materials; Tetraphenylethylene; Aggregation-Induced Emission Enhancement

The restriction of local molecular motions is critical for improving the fluorescence quantum yields (FQYs) and the photostability of fluorescent dyes. Herein, we report a supramolecular approach to enhance the performance of fluorescent dyes by incorporating a linked rotaxane structure with permethylated α -cyclodextrins (Figure 1A). Tetraphenylethylene (TPE) derivatives generally exhibit low FQYs in solution due to the molecular motions in the excited state. We show that TPE with linked rotaxane structures on two sides displayed up to 15-fold higher FQYs (Figure 1B). Detailed investigations with variable temperature ^1H NMR, UV-Vis, and photoluminescence spectroscopy revealed that the linked rotaxane structure rigidifies the TPE moiety and thus suppresses the local molecular motions and non-radiative decay. Moreover, the linked rotaxane structure enhanced the FQY of the dye in various solvents and improved the photostability through the inhibition of local molecular motions in the excited TPE (Figure 1C).¹

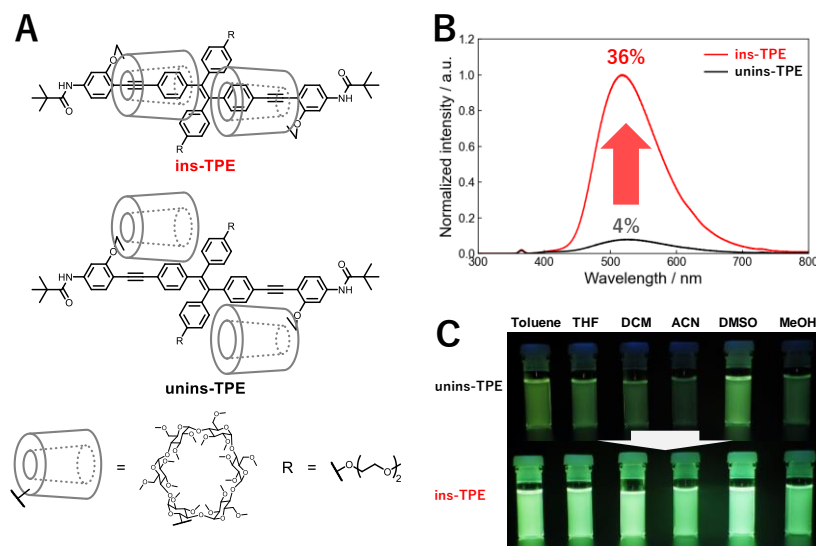


Figure 1. (A) Chemical Structures of an insulated TPE derivative with linked rotaxane structure (**ins-TPE**) and its uninsulated counterpart (**unins-TPE**). (B) Photoluminescence (PL) spectra of **ins-TPE** and **unins-TPE** ($1.0 \times 10^{-5} \text{ mol L}^{-1}$ in 1,2-dichloroethane, excited at 365 nm). The PL spectra were normalized to the same number of absorbed photons. (C) Photographs of **ins-TPE** and **unins-TPE** in various solvents ($1.0 \times 10^{-5} \text{ mol L}^{-1}$, excited at 365 nm).

1) Miyagishi, H. V.; Masai, H.; Terao, J. *Chem. Eur. J. in press*, doi: 10.1002/chem.202103175.

Synthesis and Properties of Perfluorocubane

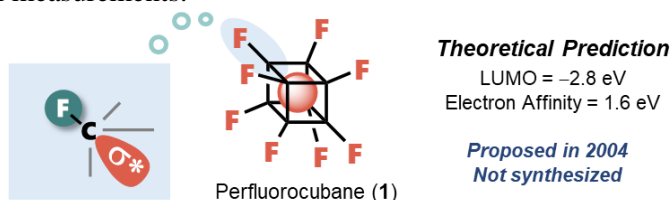
(¹Graduate School of Engineering, The University of Tokyo, ²AGC Inc.) ○Masafumi Sugiyama,¹ Midori Akiyama,¹ Yuki Yonezawa,¹ Kyoko Nozaki,¹ Takashi Okazoe^{1,2}

Keywords: Cubane; Fluorine; Electron acceptor; Single crystal x-ray diffraction analysis

The electronic and optical properties of organic molecules are dominated by their frontier orbitals and the orbitals which possess close energy levels to frontier orbitals. For π -conjugated molecules, the energy levels of the orbitals can be modulated by extension of π -conjugation and/or introduction of heteroatoms. Therefore, most of functional organic molecules have consisted of π -conjugated scaffolds, namely, they mostly possess carbon-carbon or carbon-hetero atom multiple bonds. Contrary to this trend, there is a possibility to utilize σ^* orbitals to form a stabilized vacant orbital and modulate properties of molecules. Fluorine makes the antibonding σ^* orbitals of C-F single bonds polarizing to the carbon, because fluorine is the most electron negative atom.¹ Thus, appropriate molecular designs to gather multiple σ^* orbitals of C-F bonds inside a cyclic or cage-shaped molecule would give a novel type of stabilized vacant orbital, which will accept an electron. One of the most ideal molecules to prove this hypothesis is perfluorocubane (**1**), predicted to possess high electron affinity of 1.6 eV and an unprecedentedly lower lying vacant orbital ($E_{\text{LUMO}} = -2.8$ eV).² Accordingly, **1** will possibly work as a novel class of electron acceptor without any π -conjugation. Consequently, synthesis of **1** would disclose the novel science field utilizing σ orbitals.

We achieved the first synthesis and structure determination of perfluorocubane (**1**), which has not been synthesized even after 17 years from the first proposal of its structure.³ The key step was liquid-phase direct fluorination of cubane derivatives with fluorine gas, which allowed efficient introduction of multiple fluorine atoms. Its structure was determined by the single crystal X-ray diffraction analysis, NMR spectroscopy and Raman spectroscopy. Physical properties of neutral perfluorocubane were investigated by photochemical and electrochemical measurements.

Furthermore, the radical anion of **1** was observed using a matrix-isolation ESR technique, which suggested that an electron was accepted inside the cage of **1**.



(1) O'hagan, D. *Chem. Soc. Rev.* **2008**, 37, 308–319. (2) Irikura, K. K. *J. Phys. Chem. A* **2008**, 112, 983–988. (3) Kato, T.; Yamabe, T. *J. Chem. Phys.* **2004**, 120, 1006–1016.

Acknowledgement

We thank Prof. Dr. Komaguchi (Hiroshima University) for matrix-isolation ESR measurement.

Syntheses and Properties of BAR_2 -Bridged Azafulvene Compounds Base on Five-Membered Chelate Rings

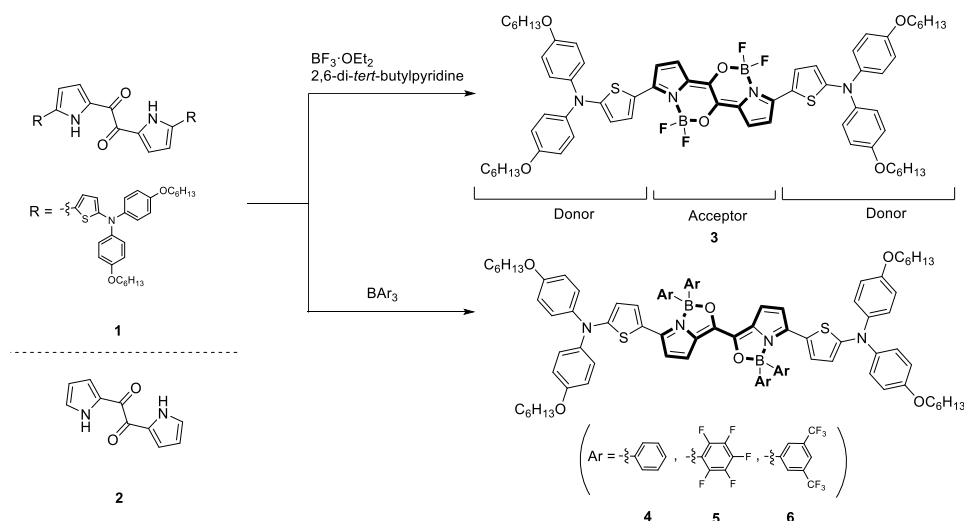
(Institute for Chemical Research, Kyoto University) ○Tiancheng Tan, Shuaifeng Hu, Minh Anh Truong, Richard Murdey, Tomoya Nakamura, Atsushi Wakamiya

Keywords: Donor-Acceptor Molecule, Boron, Near-Infrared Absorption, Azafulvene

In a previous study, we developed a strong electron acceptor based on BF_2 -bridged azafulvene dimer with six-membered chelate rings. Featuring this acceptor, the donor-acceptor-donor molecule **3** functions as a near-infrared (NIR) absorbing dye with high photostability.¹

In the present study, the fluorines on boron atom are substituted with aryl groups in order to further tune the energy gap. BAR_2 -bridged azafulvene with six-membered chelate rings was readily synthesized by refluxing **2** with BAR_3 in toluene. Interestingly, the reaction of **1** with BAR_3 gave products **4–6**, all featuring BAR_2 five-membered chelate rings. The structures of **5** and **6** were confirmed by single crystal X-ray analysis.

The substituent effect was investigated using cyclic voltammetry. The first reduction potential of **4** in CH_2Cl_2 shows at $E_{1/2} = -1.01$ V (vs. Fc/Fc^+), whereas that of compound **5** and **6** were observed at more positive potentials of $E_{1/2} = -0.87$ V and -0.82 V, respectively. The introduction of electron withdrawing groups on the boron atoms led onto the enhancement of electron-accepting ability. In this presentation, we will discuss the synthesis of these compounds, as well as their electronic and optical properties.



1) H. Shimogawa, Y. Murata, A. Wakamiya, *Org. Lett.* **2018**, 20, 5135.

Spirofluorene Based Novel [2]Rotaxanes: Synthesis and NMR Studies

(Department of Chemistry, Faculty of Science, Tokyo University of Science.) ○Showkat Rashid,¹ Takashi Murakami,¹ Yusuke Yoshigoe,¹ Shinichi Saito¹

Key words: Spirofluorene, phenanthroline-Cu complex, [2]rotaxanes, NMR studies.

Synthesis of a series of spirofluorene based [2]rotaxanes has been accomplished in an efficient manner, using the coupling ability of the corresponding phenanthroline-Cu macrocyclic complexes.¹ These novel molecular entities, which are entitled to application oriented structural manipulations, have differences in both the axle as well as macrocyclic components. ¹⁹F as well as ¹H NMR studies brought many interesting facts to surface, wherein it was observed that size/structure of the macrocyclic component is very important to give rise to the spatial interactions between the individual components of these rotaxanes. Smaller macrocycles were found to interact substantially with the axle moiety which eventually leads to desymmetization of the whole system. Size of the axle component in terms of the length of alkyl chain was found to have far less to no effect. Photophysical properties of these rotaxanes were also examined.

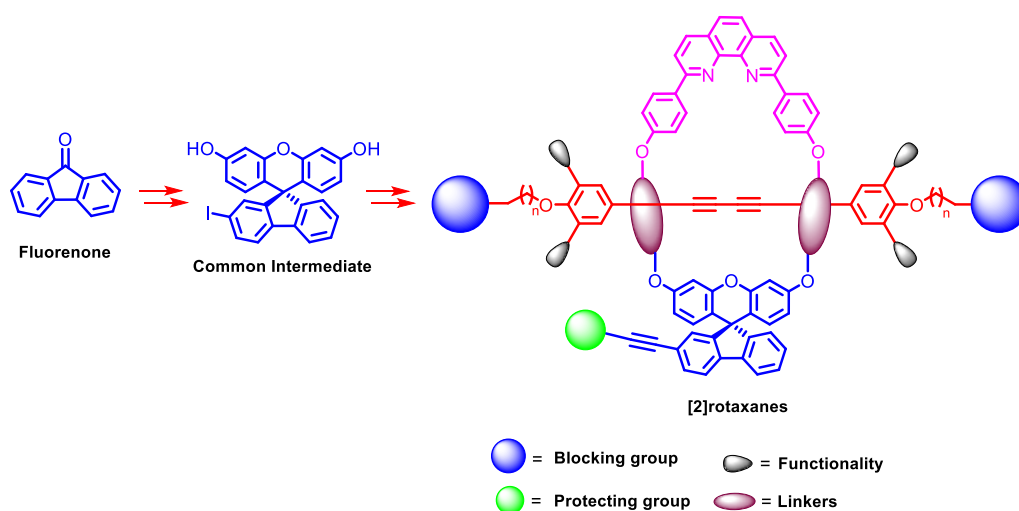


Fig. 1: Synthesis of fluorene based [2]rotaxanes

References:

1. (a) Saito, S., Takahashi, E., Nakazono, K. *Org. Lett.* **2006**, 8, 5133. (b) Saito, S., Takahashi, E., Wakatsuki, K., Inoue, K., Orikasa, T., Sakai, K., Yamasaki, R., Mutoh, Y., Kasama, T. *J. Org. Chem.* **2013**, 78, 3553

Development of Boron and Nitrogen-Doped Polycyclic Heteroaromatics Exhibiting Full-Color Narrowband Emissions

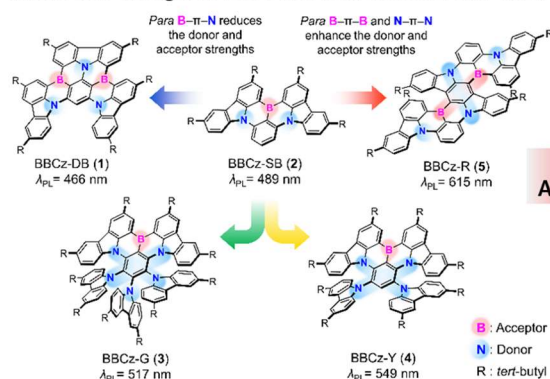
(¹Grad. Sch. Eng., Kyushu Univ. ²IFRC, Kyushu Univ.) ○Minlang Yang,^{1,2} In Seob Park,² Takuma Yasuda^{1,2}

Keywords: Thermally Activated Delayed Fluorescence; Organic Light-Emitting Diodes; Multi-Resonance; Narrowband Emission; Organoboron

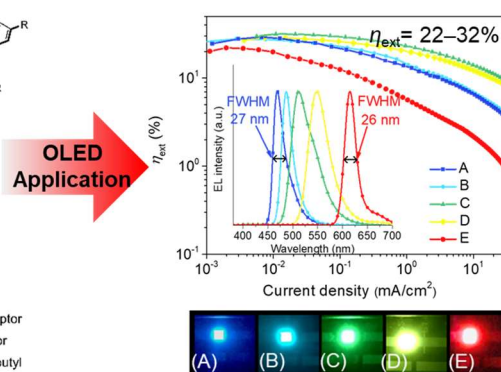
Polycyclic aromatic hydrocarbons (PAHs) have attracted immense interest because of their attractive optoelectronic properties associated with the rigid and planar π -conjugated frameworks. Incorporating main group elements into PAHs is an effective strategy to modulate the key properties of the parent π -conjugated systems.

Herein, we demonstrate that the strategic implementation of electron-accepting tricoordinate boron and electron-donating carbazole subunits into PAHs produces a family of attractive full-color luminophores that can emit narrowband thermally activated delayed fluorescence (TADF). These five compounds were synthesized through nucleophilic aromatic substitution reactions, followed by electrophilic borylations. In dilute solutions, these compounds exhibited full-color photoluminescence (PL) from deep blue to deep red ($\lambda_{\text{PL}} = 466\text{--}615\text{ nm}$) with full-width at half maxima as small as $<40\text{ nm}$ and absolute PL quantum yields as high as 85%–98%. The transient PL decay measurements revealed the TADF characteristics. Owing to their ideal emission properties, we achieved, for the first time, full-color and narrowband organic light-emitting diodes based on this family of emitters. Notably, all devices showed impressively high maximum external electroluminescence quantum efficiencies of 22%–32%.¹

Molecular design of full-color narrowband MR-TADF



Efficient and high color purity RGB OLEDs



1) M. Yang, I. S. Park, T. Yasuda, *J. Am. Chem. Soc.* **2020**, *142*, 19468–19472.

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[K3-4am] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Takuji Hatakeyama, Itaru Osaka

Sat. Mar 26, 2022 9:00 AM - 11:20 AM K3 (Online Meeting)

[K3-4am-01] Synthesis, Properties, and π -Extension of B₄N₄-Heteropentalene Derivatives○Junki Kashida^{1,2}, Yoshiaki Shoji^{1,2}, Takanori Fukushima^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech., 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

9:00 AM - 9:20 AM

[K3-4am-02] Synthesis of Boron-Containing Oligoacenes by the Cyclocondensation of *o*-Diborylarene Derivatives○Tetsuyoshi Tsukada^{1,2}, Yoshiaki Shoji^{1,2}, Takanori Fukushima^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech., 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

9:20 AM - 9:40 AM

[K3-4am-03] Generation of homosumanene *ortho*-quinone under photo-irradiation and its synthetic application to azaacene-fused homosumanenes○Maiki Nishimoto¹, Yuta Uetake^{1,2}, Yumi Yakiyama^{1,2}, Uwe H. F Bunz³, Hidehiro Sakurai^{1,2} (1. Graduate School of Engineering, Osaka Univ., 2. ICS-OTRI, Osaka Univ., 3. Ruprecht-Karls-Universität Heidelberg)

9:40 AM - 10:00 AM

[K3-4am-04] Dielectric Response of Difluorinated Sumanene Caused by the In-plane Motion○Minghong Li¹, Kohei Sambe², Tomoyuki Akutagawa², Kazunari Matsuda³, Takashi Kajitani⁴, Takanori Fukushima⁴, Yumi Yakiyama^{1,5}, Hidehiro Sakurai^{*1,5} (1. Osaka University, 2. Tohoku University, 3. Kyoto University, 4. Tokyo Institute of Technology, 5. Osaka University ICS-OTRI)

10:00 AM - 10:20 AM

[K3-4am-05] Functionalization of Benzene-Fused Pentafulvalenes and Its Application to Extended π -Electronic Systems○Masahiro Hayakawa^{1,2}, Naoyuki Sunayama², Yu Matsuo², Aiko Fukazawa² (1. Nagoya University, 2. Kyoto University)

10:20 AM - 10:40 AM

[K3-4am-06] Development of Corannulene-based Covalent Cages○Haruka Kano¹, Hiroko Yamada¹, Naoki Aratani¹ (1. NAIST)

10:40 AM - 11:00 AM

[K3-4am-07] Synthesis and Properties of a Triply Fused N-Confused Porphyrin Dimer○Osamu Iwanaga¹, Masatoshi Ishida¹, Hiroyuki Furuta¹ (1. Kyushu University)

11:00 AM - 11:20 AM

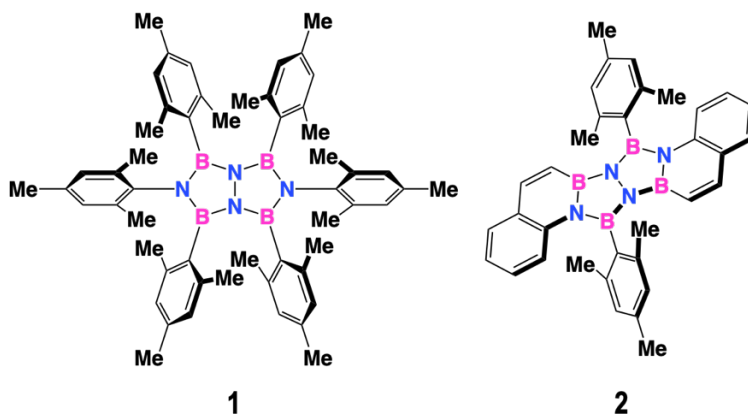
Synthesis, Properties, and π -Extension of B₄N₄-Heteropentalene Derivatives

(¹Lab. Chem. Life Sci., Tokyo Tech., ²Sch. Mater. and Chem. Tech., Tokyo Tech.)

○Junki Kashida^{1,2}, Yoshiaki Shoji^{1,2}, Takanori Fukushima^{1,2}

Keywords: BN-Containing π -Conjugated Molecule; Element Substitution; Pentalene; Phosphorescence; Host Material

The replacement of C–C bonds of π -conjugated molecules with isoelectronic but polar B–N bonds can endow π -conjugated molecules with new electronic and optoelectronic properties. We recently showed that a 1,3,2,4-diazadiboretidine derivative, featuring a cyclic B₂N₂ four-membered ring with an isoelectronic structure of cyclobutadiene, displays blue phosphorescence in solution at room temperature.^[1] Here we report the synthesis and properties of a B₄N₄-heteropentalene derivative (**1**).^[2] Due to the steric protection by six mesityl groups, **1** showed remarkable stability toward air and even water. Single-crystal X-ray analysis of **1** revealed bonding characters of the B₄N₄-heteropentalene moiety. Compound **1** emits short-wavelength blue phosphorescence in a glassy matrix at 77 K, indicating that **1** has a high triplet energy. Motivated by this finding, we fabricated an OLED device using **1** and Ir(ppy)₃ as a host material and green phosphorescence emitter, respectively, where a relatively high external quantum efficiency (~15%) was achieved. In this presentation, we also report the synthesis and properties of a new π -extended B₄N₄-heteropentalene (**2**).



- [1] Y. Shoji, Y. Ikabata, I. Ryzhii, R. Ayub, O. El Bakouri, T. Sato, Q. Wang, T. Miura, B. S. B. Karunathilaka, Y. Tsuchiya, C. Adachi, H. Ottosson, H. Nakai, T. Ikoma, T. Fukushima, *Angew. Chem. Int. Ed.*, **2021**, 60, 21817–21823.
- [2] J. Kashida, Y. Shoji, Y. Ikabata, H. Taka, H. Sakai, T. Hasobe, H. Nakai, T. Fukushima, *Angew. Chem. Int. Ed.*, **2021**, 60, 23812–23818.

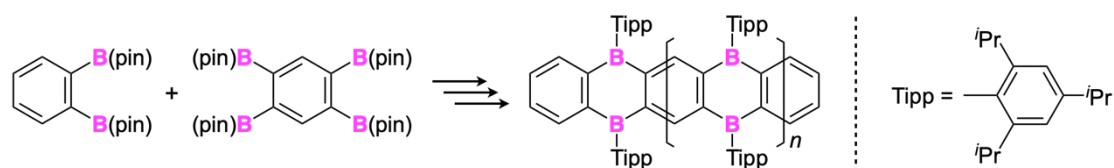
o -ジボリルアレーン誘導体の環化縮合によるホウ素含有オリゴアセンの合成

(東工大化生研¹・東工大物質理工²) ○塚田 哲義^{1,2}・庄子 良晃^{1,2}・福島 孝典^{1,2}
 Synthesis of Boron-Containing Oligoacenes by the Cyclocondensation of o -Diborylarene Derivatives (¹*Lab. Chem. Life Sci., Tokyo Tech.*, ²*Sch. Mater. and Chem. Tech., Tokyo Tech.*)
 ○Tetsuyoshi Tsukada,^{1,2} Yoshiaki Shoji,^{1,2} Takanori Fukushima^{1,2}

When linking π -conjugated units by a tri-coordinated boron atom, $p_{\pi}-\pi^*$ interaction operates to extend the LUMO of the π -conjugated units. Based on this notion, we focused on a 9,10-diboraanthracene unit as a new building block to develop electron-accepting π -conjugated oligomers and polymers. o -Bis(dihydroboryl)benzene derivatives have been reported to undergo a spontaneous cyclocondensation to form a 9,10-diboraanthracene skeleton. We found that the cyclocondensation reactions of multi-borylated arenes afford π -conjugated oligomers and polymers that contains boron atoms periodically. In this presentation, we will report the synthesis, structure, and properties of new boron-containing oligoacene derivatives.

Keywords: Boron-containing π -conjugated molecule; Cyclocondensation; Oligoacene

π 共役骨格に三配位のホウ素原子を導入すると、ホウ素の空の 2p 軌道と π 電子系との $p_{\pi}-\pi^*$ 相互作用により LUMO が拡張し、その準位が低下する。これを踏まえると、アントラセンの 9,10 位に二つのホウ素原子が導入された 9,10-ジボラアントラセンは、高い電子受容性を示す π 電子系化合物のビルディングブロックとして興味深い。Wagner らは、 o -ジボリルベンゼン誘導体の環化縮合により 9,10-ジボラアントラセン骨格が得られることを報告している^[1]。我々は、この反応をホウ素多置換化合物に適用することで、ホウ素が高密度かつ周期的に組み込まれたネットワーク構造が構築できると考えた。今回我々は、 o -ジボリルベンゼンおよび 1,2,4,5-テトラボリルベンゼン誘導体を用いた環化縮合により、共役長の異なる複数のボラアセンオリゴマーを合成することに成功した。本発表では、得られたボラアセンオリゴマーの構造および電子物性について報告する。



[1] Ö. Seven, Z.-W. Qu, H. Zhu, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Chem. Eur. J.* **2012**, *18*, 11284.

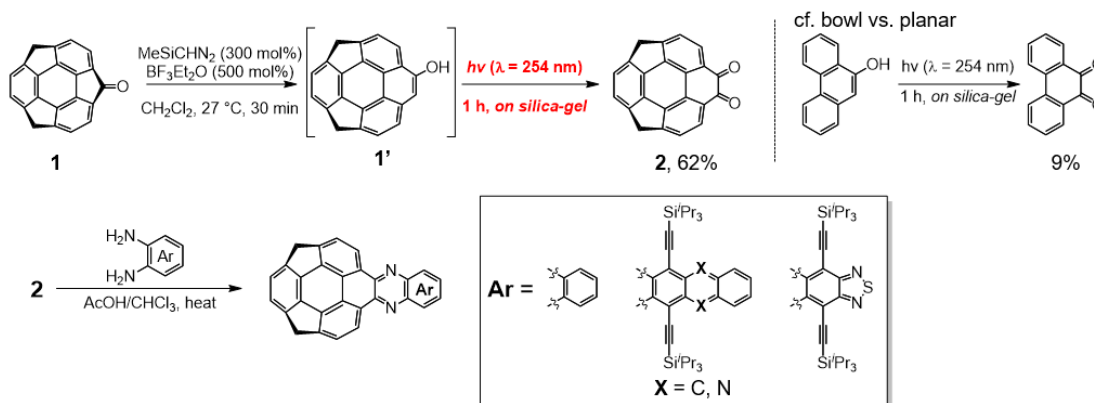
Generation of homosumanene *ortho*-quinone under photo-irradiation and its synthetic application to azaacene-fused homosumanenes

(¹Grad. Sch. Eng., Osaka Univ., ²ICS-OTRI, Osaka Univ., ³Ruprecht-Karls-Universität Heidelberg) ○ Maiki Nishimoto,¹ Yuta Uetake,^{1,2} Yumi Yakiyama,^{1,2} Uwe. H. F. Bunz,³ Hidehiro Sakurai^{1,2}

Keywords: Curved π -conjugated system; Sumanene; Ring-expansion; Homosumanene; Azaacene.

Highly strained buckybowls, such as sumanene, are suitable as a starting material to synthesize less distorted buckybowls through a series of ring-expansion reactions.¹ Recently, we have reported synthesis of C70 fragment, homosumanene via Büchner–Curtius–Schlotterbeck reaction from sumanenone (**1**).² In the course of our previous work, we noticed that hydroxyhomosumanene (**1'**) generated by treating **1** with Me₃SiCHN₂ was oxidized during the purification to give *o*-quinone (**2**) as a byproduct. In this study, we investigated the synthesis of **2** and its azaacene-fused derivatives.

Aerobic oxidation of **1'** proceeded efficiently on silica gel to give **2** in 62% yield under the irradiation of UV light (254 nm). The reaction of planar analogue having a substructure of **1'** proceeded much slower than **1'**, which was attributed to the structural difference between planar and curved π -system. The condensation reaction between **2** and aromatic diamines took place to afford azaacene-fused homosumanenes (**3–6**). Single crystal X-ray diffraction analyses of azaacenes showed stacked structures due to the interactions between each bowl. Cyclic voltammetry measurements suggested that they have high electron affinity due to the combination of curved buckybowl and electron-deficient azaacene structures.



- 1) S. Hishikawa, Y. Okabe, R. Tsuruoka, S. Higashibayashi, H. Ohtsu, M. Kawano, Y. Yakiyama, H. Sakurai, *Chem. Lett.* **2017**, 46, 1556.
- 2) M. Nishimoto, Y. Uetake, Y. Yakiyama, H. Sakurai, *J. Org. Chem.* accepted.

Dielectric Response of Difluorinated Sumanene Caused by the In-plane Motion

(¹Grad. Sch. Eng., Osaka Univ., ²Grad. Sch. Eng., Tohoku Univ., ³Inst. Adv. Ener., Kyoto Univ., ⁴Inst. Innov. Res., Tokyo Inst. Tech., ⁵ICS-OTRI, Osaka Univ.)

○Minghong Li¹, Kohei Sambe², Tomoyuki Akutagawa², Kazunari Matsuda³, Takashi Kajitani⁴, Takanori Fukushima⁴, Yumi Yakiyama^{1,5}, Hidehiro Sakurai^{1,5}

Keywords: Sumanene; Dielectric response; In-plane motion

Organic molecule-based crystalline dielectric materials have attracted broad attention from chemists in recent years to develop new organic electronic devices. In their designing strategy, the molecular motion induced by the external dielectric field is required to maximize the polarization effect in the materials to realize a large dielectric constant. When we pay attention to the molecular motion in curved- π aromatics and their supramolecular complexes, especially to them containing C₆₀, it is found that they often show characteristic smoothness as exemplified by the molecular peapod.¹⁾ Such examples indicate that the “curve-to-curve” contact in the curved- π aromatics will afford the smooth molecular motion in the solid state. Sumanene (**1**) is one of the representative buckybowls and is known to show unique properties such as bowl inversion behaviour derived from its unique bowl shape.²⁾ Especially **1** affords unidirectionally arranged π -stacking columns in the solid state.³⁾ However, this nature also makes the bowl inversion behaviour of **1** useless for the induction of dielectric response in the solid state. In this context, we instead focused on the in-plane motion of **2** in its columnar structure and attempted to utilize this motion to bring out the dielectric response (Fig. 1). In this work, we designed and synthesized a new curved π -conjugated molecule difluorosumanene (**2**), which possesses two fluorine atoms on the same benzylic carbon on pristine sumanene to possess a large dipole moment along the in-plane direction. Thermal analyses, variable temperature X-ray diffraction and IR measurements indicated the presence of in-plane motion of **1** although no clear phase transition was involved. Indeed, the dielectric measurement using its both powder and single crystal clearly showed that both real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant were enhanced above ~360 K at 1 MHz with a Debye-type dielectric relaxation, confirming the in-plane motion of **1** induced by the external electric field.

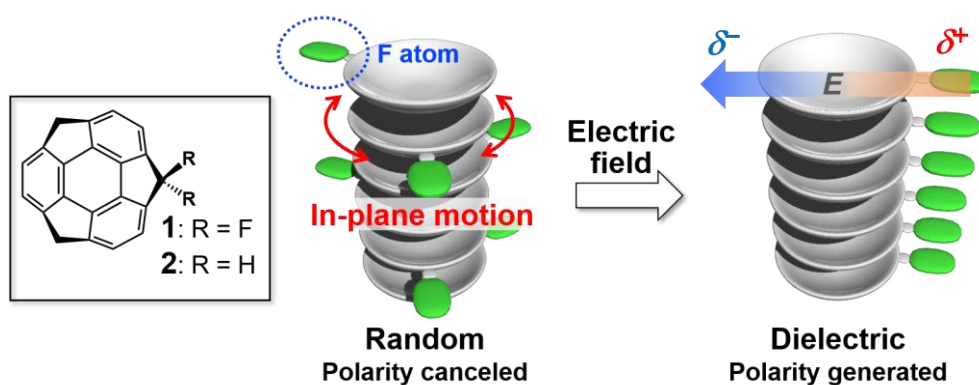


Fig. 1. Molecular structure of **1** and **2**, and Conceptual figure for this work.

References

- 1) S. Sato, T. Yamasaki, H. Isobe, *Proc. Natl. Acad. Sci.* **2014**, *111*, 8374. 2) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878. 3) a) H. Sakurai, T. Daiko, H. Sakane, T. Amaya, T. Hirao, *J. Am. Chem. Soc.* **2005**, *127*, 11580; b) S. Mebs, M. Weber, P. Luger, B. M. Schmidt, H. Sakurai, S. Higashibayashi, S. Onogi and D. Lentz, *Org. Biomol. Chem.* **2012**, *10*, 2218.

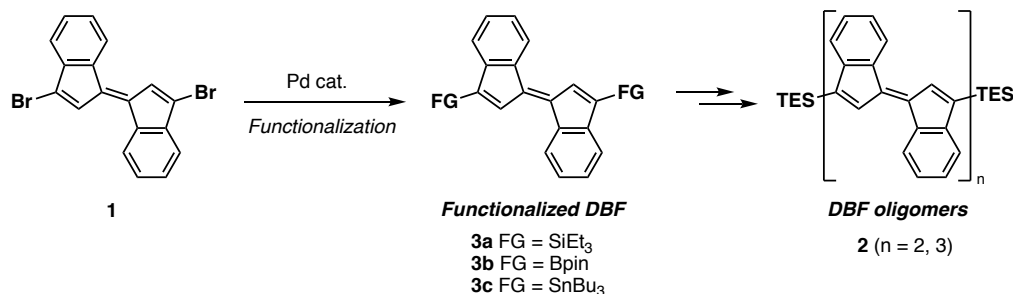
ベンゼン縮環ペンタフルバレンの官能基化と拡張 π 電子系への展開

(名大院理¹・京大 iCeMS²) ○早川 雅大^{1,2}・砂山 尚之²・松尾 優²・深澤 愛子²
 Functionalization of Benzene-Fused Pentafulvalenes and Its Application to Extended π -Electronic Systems (¹Graduate School of Science, Nagoya University, ²WPI-iCeMS, Kyoto University) ○Masahiro Hayakawa,^{1,2} Naoyuki Sunayama,² Yu Matsuo,² Aiko Fukazawa²

The poly(pentafulvalene), an one-dimensional conjugated polymer of pentafulvalene, is of interest not only due to its characteristic structure which composes of a C₆₀ fragment, but also to its potential as narrow-bandgap materials as predicted by computational studies.¹ Although we have recently succeeded in isolation of the dibenzopentafulvalene (DBF) oligomers **2**, the synthesis of these oligomers remains challenging as they were obtained only in low yields as an unexpected byproducts in the Negishi coupling reaction using dibrominated DBF **1**.² In this study, we thoroughly investigated the functional group transformations of **1** and succeeded in the synthesis of functionalized DBFs **3a–c**. By using **1** and **3** as key precursors, π -extended DBFs and well-defined DBF oligomers **2** could be obtained in reasonable yields. These structures and properties of π -extended DBFs thus obtained will also be discussed.

Keywords : Pentafulvalene; π -conjugation; Nonbenzenoid hydrocarbon; Conjugated oligomer; Electrochemical properties

ペンタフルバレンは 2 電子還元で安定な非ベンゼン系炭化水素の一種であり、これを直接連結した共役ポリマーはフラーレン C₆₀ の部分構造を一次元鎖に展開した構造をもつ。このポリマーは、きわめて狭いバンドギャップをもつ材料の候補として理論的に予測されている¹。最近我々は、ベンゼン縮環ペンタフルバレンオリゴマー **2** の合成を初めて報告したが²、このオリゴマーはジブロモペンタフルバレン **1** を用いた根岸カップリング反応の副生成物としてわずかに得られるのみであり、その合成には依然として問題を抱えていた。今回、**1** の反応性を精査し、ケイ素やホウ素、スズ官能基をもつ **3a–c** の合成法を確立した。これらを鍵中間体とすることで、オリゴマー **2** の収率を改善すると共に、さまざまな π 拡張型ジベンゾペンタフルバレンの合成を達成した。得られた化合物の構造や基礎物性についても議論する。



1) (a) Wennerstroem, O. *Macromolecules* **1985**, 18, 1977. (b) Hong, S. Y. *Chem. Mater.* **2000**, 12, 495. (c) Hong, S. Y.; Lee, K. W. *Chem. Mater.* **2000**, 12, 155. 2) 砂山, 早川, 田巻, 山口, 深澤, 日本化学会第 101 春季年会, A17-1am-04 (2020).

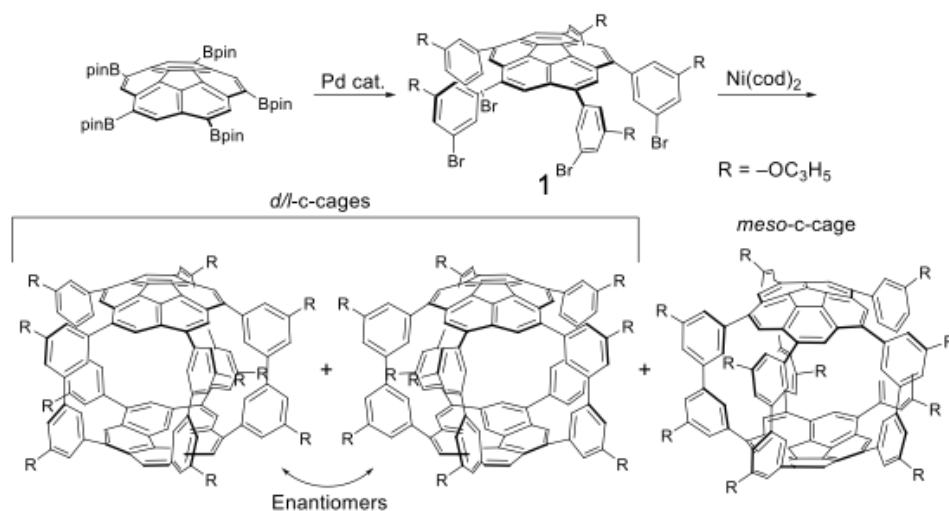
Development of Corannulene-based Covalent Cages

(Graduate School of Science and Technology, Nara Institute of Science and Technology)

○Haruka Kano, Hiroko Yamada, Naoki Aratani

Keywords: Corannulene, Caged compound, Chirality

Synthetic covalent cages having a well-defined inside cavity have received great interest, since those molecules can stably encapsulate guest molecules inside and are more rigid than supramolecules. In this study, we succeeded in the synthesis of five-fold biphenylene-bridged corannulene dimers (**c-cages**) by the nickel-mediated homo-coupling of a pentakis-bromophenyl corannulene **1** (Scheme 1).



Scheme 1. Synthesis of *d/l* and *meso*-**c-cages**.

The products were mixture of *d/l* and *meso* **c-cages**, and their separation was achieved by HPLC. Each **c-cage** incorporates a single molecule of DMF used as co-solvent which was confirmed by ^1H NMR and single-crystal X-ray analysis (Figure 1). The enantiomers of the *d/l* **c-cage** were optically separated by chiral HPLC, which gave the mirror-image circular dichroism (CD) spectra.

Encapsulation of other guest molecules was investigated to check the guest-dependent physical properties of **c-cages**.

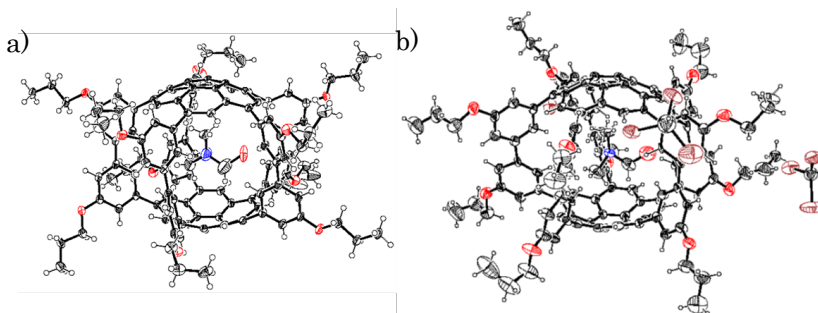


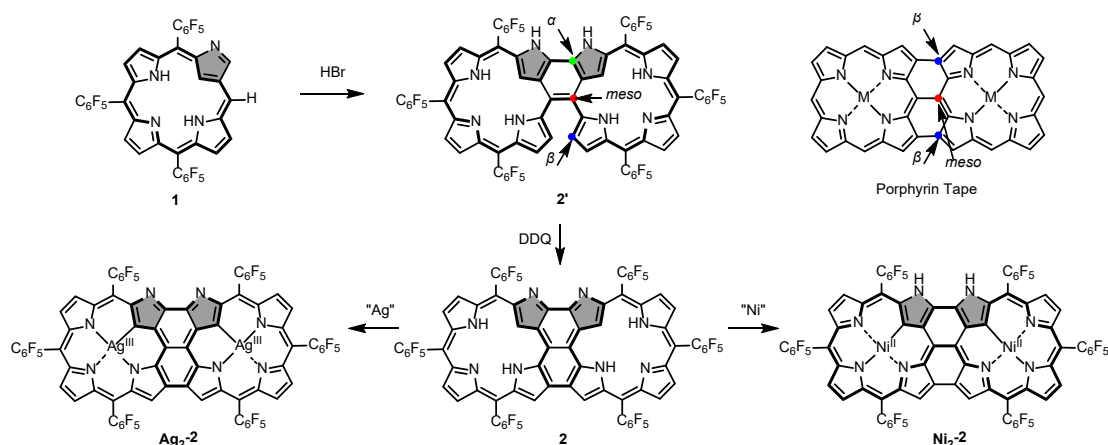
Figure 1. Single crystal X-ray structures of a) *d/l* and b) *meso* **c-cages**.

Synthesis and Properties of Triply Fused N-Confused Porphyrin Dimer

(Graduate School of Engineering, Kyushu University) ○Osamu Iwanaga, Masatoshi Ishida, Hiroyuki Furuta

Keywords: *N*-confused porphyrin, porphyrin tape, aromaticity/antiaromaticity

meso-meso, β - β , β '- β ' Triply linked porphyrin arrays, namely porphyrin tapes, have been extensively investigated on their remarkable electron-transporting capabilities and the nonlinear optical properties caused by the unique laterally π -conjugated structure.^{1,2} To gain further insight into the aromaticity effect of the porphyrin tapes, we have synthesized a novel α - α' , *meso-meso*, β - β ' triply linked dimeric porphyrin isomer (**2**) via the stepwise oxidative dimerization of 5-unsubstituted *N*-confused porphyrin (**1**) in this work.



Treatment of **1** with hydrogen bromide in toluene under reflux afforded α - α' , *meso-meso* doubly linked porphyrin dimer (**2'**) with global Hückel 38π aromaticity. Subsequently, the doubly fused **2'** was oxidized with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to furnish the triply linked porphyrin dimer **2**. Consistent with the NH tautomeric feature (2H vs. 3H forms in the core) of the *N*-confused porphyrins, coordination of silver(III) and nickel(II) ions yielded the bis-metal complexes, **Ag₂-2** and **Ni₂-2**, respectively, with distinct electronic features. Exclusively, a local paratropic ring-current was realized on the benzo[*e*]pyrrolo[3,2-*g*]indole moiety in **Ag₂-2**. In contrast, a strong paratropic ring current was emerged in **Ni₂-2** along with the distinct global Hückel antiaromaticity as inferred from the study on the NMR spectroscopy and the DFT calculations. The unique complexation-induced aromaticity switching is characteristic for the isomeric *N*-confused porphyrin tape **2**. The optical and electrochemical properties of these complexes will be presented in detail.

1) T. Tanaka, A. Osuka, *Chem. Eur. J.* **2018**, *24*, 17188.

2) A. Nakai, J. Kim, T. Tanaka, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2021**, *60*, 26540.

[H201-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Ryo Sekiya, Koichi Kodama

Sat. Mar 26, 2022 9:00 AM - 11:20 AM H201 (Online Meeting)

[H201-4am-01] Synthesis and Chiral Optical Property of Resorcinarene-based Metal-Coordination Capsule Possessing Chiral Internal Space

○Kentarō Harada¹, Ryo Sekiya¹, Takeharu Haino¹ (1. Hiroshima University)

9:00 AM - 9:20 AM

[H201-4am-02] “*Solvent-Induced Chirality Switching*” in the Enantioseparation of Chlorine-Substituted Tropic Acids via Diastereomeric Salt Formation

○Srinivas Chandrasekaran¹, Takuji Hirose¹, Koichi Kodama¹ (1. Saitama University)

9:20 AM - 9:40 AM

[H201-4am-03] Dynamic Triple-helical Metallocryptand: Time-Programmable Helicity Inversion Triggered by Alkali Metal Ions

○Sk Asif Ikbal¹, Masahiro Ehara², Yoko Sakata^{1,3}, Shigehisa Akine^{1,3} (1. WPI-Nano Life Science Institute, Kanazawa University, 2. Institute for Molecular Science, Research Center for Computational Science, 3. Graduate School of Natural Science and Technology, Kanazawa University)

9:40 AM - 10:00 AM

[H201-4am-04] Chemometrics-coupled chiral recognition using D- π -A typed cyanostilbenes

○Kaede Kawaguchi¹, Ayana Moro¹, Yuji Kubo¹ (1. Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University)

10:00 AM - 10:20 AM

[H201-4am-05] Poly(quinoxaline-2,3-diyl) as a Traceless Nonbonding-Interaction-Based Chiral Shift Reagent

○Takaya Fujie¹, Takeshi Yamamoto¹, Michinori Sugimoto¹ (1. Kyoto Univ.)

10:20 AM - 10:40 AM

[H201-4am-06] Cyclic Bifluorenylidene Trimer: Relationship between Dynamic Behaviors and Structural Characteristics

○Akira Nagai^{1,2}, Tomoya Ishizuka², Takahiko Kojima², Masayuki Takeuchi^{1,2} (1. NIMS, 2. Univ. of Tsukuba)

10:40 AM - 11:00 AM

[H201-4am-07] Photo-induced Reversal of Supramolecular Chirality

○Takuho Saito¹, Daisuke Inoue¹, Yuichi Kitamoto³, Shiki Yagai² (1. Grad. Sch. of Sci. & Eng., Chiba Univ., 2. IGPR, Chiba Univ., 3. Grad. Sch. of Eng., Tohoku Univ.)

11:00 AM - 11:20 AM

キラルな包接空間を有する金属配位型レゾルシンアレーンカプセルの合成とキラル光学特性

(広大院先進理工¹) ○原田 健太郎¹・関谷 亮¹・灰野 岳晴¹

Synthesis and Chiral Optical Property of Resorcinarene-based Metal-Coordination Capsule
(¹Graduate School of Advanced Science and Engineering, Hiroshima University) ○Kentaro Harada,¹ Ryo Sekiya,¹ Takeharu Haino¹

Our group has reported that the two resorcinarene-based cavitands are self-assembled with copper cations to form dissymmetric capsule **1** (Fig. 1a). In this study, encapsulation of (AcOH)₂•(2*S*,3*S*)-**G1a-f** fulfilling the size of the cavity realized the formation of diastereomeric host-guest complex (AcOH)₂•(2*S*,3*S*)-**G1d**•(*M*)-**1** with 91% *de*. (Fig. 1b, 1c). After the removal of the chiral guests, enantiomerically enriched chiral capsule (*M*)-**1** was obtained. Achiral biphenyl guest **G2** was synthesized possessing two fluorescent benzothiadiazole moieties (Fig. 1d). ¹H NMR and ESI-MS suggested the 1:1 host-guest complexation of **G2**•(*M*)-**1**. CD spectra and DFT calculation demonstrated that the dynamic axial chirality of **G2** within (*M*)-**1** was biased to (*R*)-helicity, giving rise to the CPL emission at 645 nm assigned to the emission of benzothiadiazole moieties (Fig. 1d).

Keywords : Supramolecular Capsule; Molecular Recognition; Chirality; Host-Guest Systems

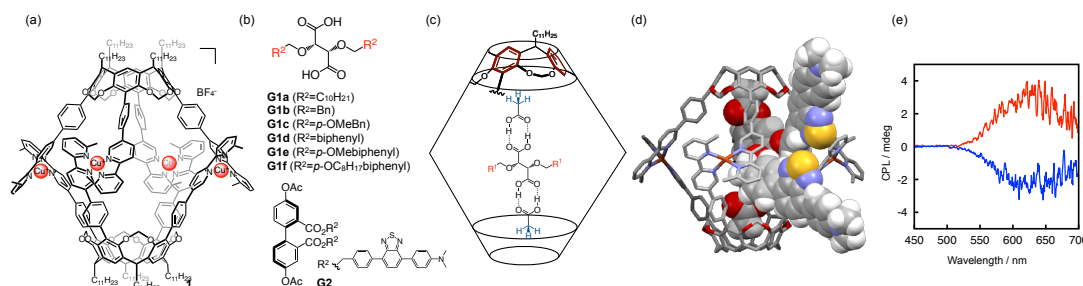


Fig. 1 (a) Molecular structure of **1** (b) Molecular structure of **G1a-f** and **G2** (c) Host-guest complex of **1** and chiral hydrogen bonded trimeric complex consisting of two acetic acid and (2*S*,3*S*)-**G1**, (d) Energy-minimized structure of host-guest complex of (*P*)-**1** and **G2**, (e) CPL spectra of host-guest complex of **1** and **G2**, (red line) **G2**•(*P*)-**1**, (blue line) **G2**•(*M*)-**1**.

当研究室は、四つのピリジン部位を有するレゾルシンアレーンキャビタンドが一価の銅イオンと自己集合し、*D*₄ 対称性の **1** を形成することを報告した(Fig. 1a)¹⁾。今回、包接空孔の要求する分子長をもつ水素結合三量体(AcOH)₂•(2*S*,3*S*)-**G1d** が選択的に包接されることで、(AcOH)₂•(2*S*,3*S*)-**G1d**•(*M*)-**1** が高いジアステレオ過剰率(91% *de*)で形成されたことが明らかになった(Fig. 1b, 1c)。さらに、ゲストの除去により光学純度の高いキラルカプセル(*M*)-**1** が得られた。次に、長波長領域で発光するベンゾチアジアゾール骨格を二つ有するアキラルゲスト **G2** を設計した(Fig. 1d)。**G2** と(*M*)-**1** との会合挙動を調査したところ、1:1 ホスト-ゲスト錯体 **G2**•(*M*)-**1** が形成されることがわかった。また、CD および DFT 計算より、包接された **G2** の動的軸性キラルが片側に誘導され、(*R*)-**G2**•(*M*)-**1** の形成が示唆された。さらに、(*R*)-**G2**•(*M*)-**1** のベンゾチアジアゾールの発光に帰属される 645 nm で CPL が観測された(Fig. 1d)。

1) Imamura, T.; Maehara, T.; Sekiya, R.; Haino, T. *Chem. Eur. J.* **2016**, 22, 3250-3254.

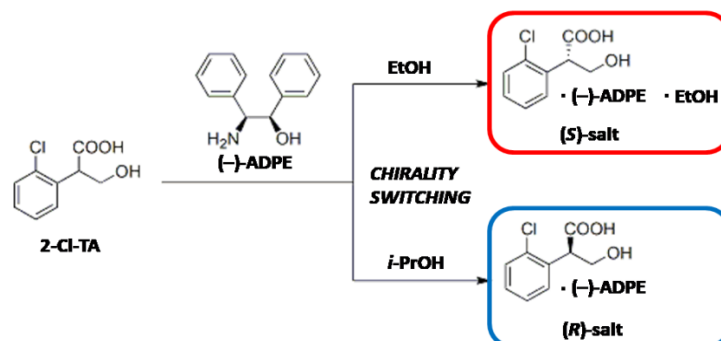
2) Harada, K.; Sekiya, R.; Maehara, T.; Haino, T. *Org. Biomol. Chem.* **2019**, 17, 4729-4735.

“Solvent-Induced Chirality Switching” in the Enantioseparation of Chlorine-Substituted Tropic Acids via Diastereomeric Salt Formation

(¹Graduate School of Science and Engineering, Saitama University) ○ Srinivas Chandrasekaran,¹ Takuji Hirose,¹ Koichi Kodama¹

Keywords: Optical Resolution; Diastereomeric Salt; Chirality Switching; Tropic Acid; Crystal Structures

The optical resolution via diastereomeric salt formation is a widely employed method for obtaining optically pure acidic and basic compounds on an industrial scale. In this method, a target racemate is combined with an optically active resolving agent and enantioseparation is enabled by crystallization. ‘*Solvent-induced chirality switching resolution*’ is a phenomenon in which the stereochemistry of a less-soluble diastereomeric salt changes depending on the solvent used for crystallization in optical resolution by diastereomeric salt formation. Optically pure tropic acid (TA) and its derivatives are important compounds for the production of pharmaceuticals. Among the TA derivatives reported to date, enantiopure chlorine-substituted TA is an important chiral building block of hyoscyamine derivatives. Previously, we reported solvent-induced chirality switching during the optical resolution of racemic TA using (–)-ADPE.¹ To expand the scope of solvent-induced chirality switching resolution, herein we demonstrate an efficient solvent-induced chirality switching resolution of racemic 2-chlorotropic acid (*rac*-2-Cl-TA) with (–)-ADPE via diastereomeric salt formation. The recrystallization of the diastereomeric salts of *rac*-2-Cl-TA from branched alcohols such as *i*-PrOH and *s*-BuOH afforded (*R*)-2-Cl-TA, whereas (*S*)-2-Cl-TA was obtained from linear alcohols such as MeOH, EtOH, and *n*-PrOH. The chirality switching mechanism was elucidated from the crystal structures of the diastereomeric salts, which revealed that the incorporation of the solvent in the (*S*)-2-Cl-TA salt crystals played a key role in chirality switching by reinforcing the supramolecular structure of the salt. However, no chirality switching was achieved for racemic 3-chlorotropic acid and 4-chlorotropic acid. The position of the chlorine substituent plays an important role in the solvent-induced chirality switching effect.



1) K. Kodama, N. Kurozumi, H. Shitara, T. Hirose, *Tetrahedron*, **2014**, 70, 7923.

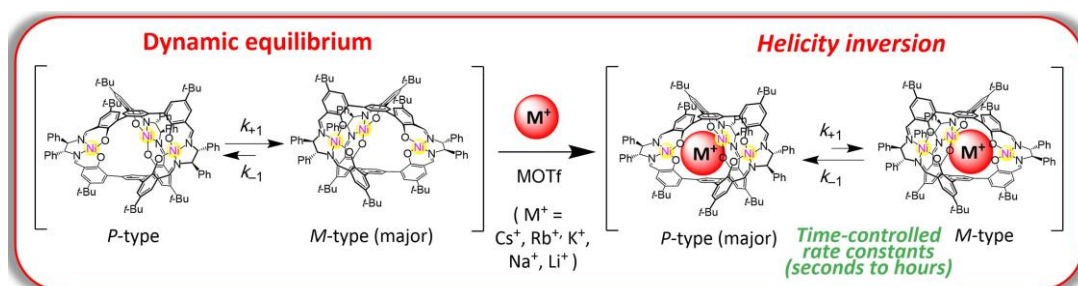
Dynamic Triple-helical Metallocryptand: Time-Programmable Helicity Inversion Triggered by Alkali Metal Ions

(¹Nano Life Science Institute, Kanazawa University, ²Institute for Molecular Science, Research Center for Computational Science, ³Graduate School of Natural Science and Technology, Kanazawa University) ○Sk Asif Ikbal,¹ Masahiro Ehara,² Yoko Sakata,^{1,3} Shigehisa Akine^{1,3}

Keywords: Helicity inversion; Selective encapsulation; Chirality switch; Alkali metal ions; Metallocryptand

‘Helicity inversion’ is one of the most sophisticated processes in biological and artificial systems.¹ Biological DNA and proteins often alter their helix sense in response to particular external stimuli and switch biologically important events in controlled time scale. Dynamic helical molecules, which are capable of undergoing reversible helicity inversion, are useful as a basic framework for chiral switching systems. There have been several examples of dynamic helical molecules whose helix inversion rates can be tuned by changing solvent polarity, constituent metal ions of helicates, etc.¹⁻³ However, in order to efficiently control the helix inversion rate, combination of such a dynamic helix inversion with host-guest complexation would be effective.

A novel chiral tris(salen)-type trinickel(II) cryptand was designed and synthesized. This complex was characterized by various spectroscopic techniques such as ¹H NMR, ESI-MS, UV-vis, CD spectroscopy, and X-ray crystallography, as well as the theoretical calculations. The nickel(II) cryptand underwent a dynamic interconversion between the *P* and *M* isomers in solution, preferring *M*-isomer, with a half-life of $t_{1/2} = 5.0$ min. Guest encapsulation studies on a series of alkali metal ions were performed with this metallocryptand. The present metallocryptand offers time-tunable helicity inversion on the time scales from seconds to hours ($t_{1/2} = 12$ sec for K^+ complex; $t_{1/2} = 1.05$ h for Cs^+ complex).



Scheme 1. Dynamic Triple-helical Metallocryptand for recognition of alkali metal ions and helicity inversion.

1) H. Miyake, H. Tsukube, *Chem. Soc. Rev.*, **2012**, *41*, 6977-6991. 2) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front.*, **2014**, *1*, 53-57. 3) S. Akine, M. Miyashita, T. Nabeshima, *Inorg. Chem.*, **2021**, *60*, 12961-12971.

Chemometrics-coupled chiral recognition using D- π -A typed cyanostilbenes

(¹Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University)

○Kaede Kawaguchi,¹ Ayana Moro,¹ Yuji Kubo,¹

Keywords: Chemometrics; Chiral Recognition; Aggregation-Induced Emission; Boronic acid; Cyanostilbenes

Detection of chirality is analytically significant because the enantio-purity of products is essential for various applications in the pharmaceutical, agrochemical, and food industry. Fluorescence sensing for chirality is a highly sensitive, facile, and cost-effective method for determining enantiomer purity. However, the synthesis of well-designed host molecules is often tedious. We focused on the boronate ensembles with aggregation-induced emission (AIE) units because enantio-dependent aggregation modes endow the systems with chiral sensing capability.

Two types of boronic acid-appended D- π -A cyanostilbenes were synthesized to produce chiral boronate ensembles *via* dehydration with tartaric acid (Fig. 1a). The aggregation-induced high sensitivity and positional effect of the CN group on the emission properties resulted in fingerprint-like emission responses for several chiral diamines. These responses were suitable for chiral recognition and calibration using linear discriminant analysis (LDA) or artificial neural network (ANN). Remarkably, the enantiomer pairs of chiral diamines were discriminated in 100% of accuracy by LDA. Furthermore, data processing with an ANN allowed for the accurate determination and prediction of enantiomer excess (% ee) for *trans*-1,2-cyclohexanediamines (**CHDAs**) with a mean absolute error of 0.86 % (Fig. 1b).¹⁾

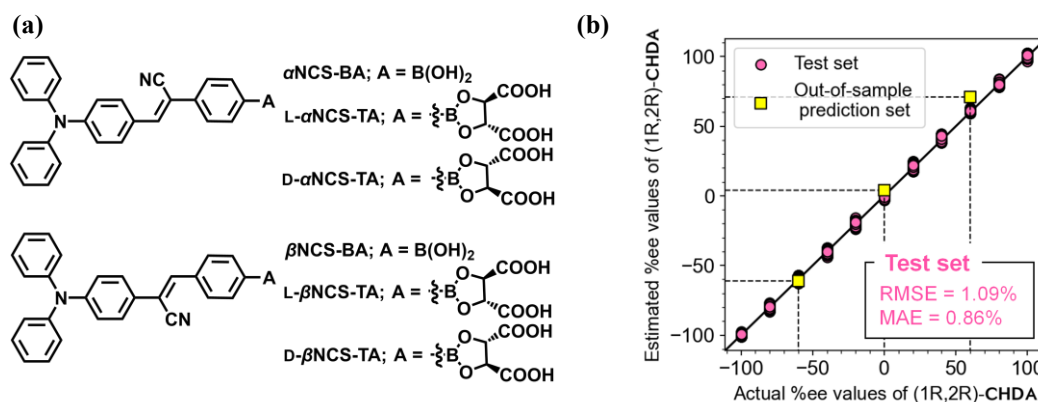


Fig. 1 (a) Chemical structures of boronic acid-appended cyanostilbenes and analogs. (b) Parity plots of ANN predicted and experimental % ee values of (1R, 2R)-CHDA.

1) K. Kawaguchi, A. Moro, S. Kojima, Y. Kubo, *Chem. Commun.*, **2021**, 57, 12952–12955.

Poly(quinoxaline-2,3-diyl) as a Traceless Nonbonding-Interaction-Based Chiral Shift Reagent

(Graduate School of Engineering, Kyoto University) ○Takaya Fujie, Takeshi Yamamoto, Michinori Suginome

Keywords: Chiral recognition; Relaxation filter; Helical polymer; Haloalkane; Chirality

Chiral shift reagents in NMR analysis have attracted wide attention as a method for the facile determination of an enantiomeric ratio of chiral organic compounds.¹ The method has potential advantages of availability of a wide array of chiral shift reagents suitable for various different chiral analytes. However, the analysis is mostly limited to the analytes that have specific bonding interaction such as coordination, hydrogen bonding, and acid-base interaction. Moreover, because of the need for high loading of chiral shift reagents, overlapping of their signals with those of analytes has been general problem in the quantification of enantiomeric ratios. We show here the use of helically chiral poly(quinoxaline-2,3-diyl) (PQX) bearing chiral ether side chains as a “traceless” NMR chiral shift reagent for various racemic compounds including styrene oxide (SO) (Figure 1a). The differentiation of the signals of two enantiomers was based on nonbonding interaction containing dispersion and electrostatic forces between the analytes and PQX, leading to differentiable up-field shifts of the ¹H NMR signals without broadening (Figure 1b and c). Selective suppression of polymer NMR signals using the *T*₂ filter (CPMG-PROJECT² pulse sequence) enabled the PQX to serve as a traceless chiral shift reagent, with which only ¹H-NMR signals of the analytes were observable (Figure 1d). This nonbonding interaction based enantiodifferentiation method could be applied to various chiral compounds such as haloalkanes, ethers, and carbonyl compounds.

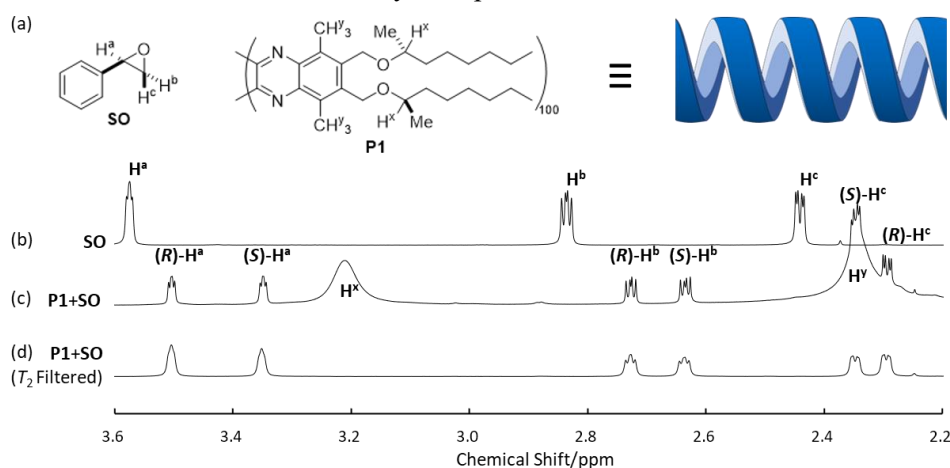


Figure 1. (a) Structure of helically chiral (*R*)-P1 and (*R*)-styrene oxide (SO) (b) ¹H-NMR of *rac*-SO in cyclohexane-*d*₁₂. (c) ¹H-NMR spectrum of *rac*-SO and P1 in cyclohexane-*d*₁₂. (d) *T*₂-filtered spectrum of (c).

1) T. Wenzel *Differentiation of Chiral Compounds Using NMR Spectroscopy*. Wiley, **2018**.

2) A. Aguilar, M. Nilsson, G. Bodenhausen, G. Morris *Chem. Commun.* **2011**, 48, 811.

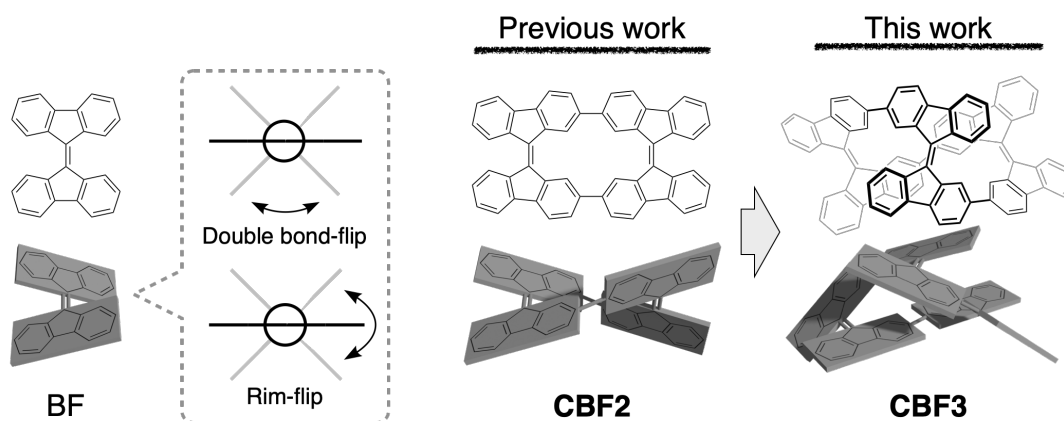
Cyclic Bifluorenylidene Trimer: Relationship between Dynamic Behaviors and Structural Characteristics

(¹ National Institute for Materials Science, ² Graduate School of Science and Technology, University of Tsukuba) ○Akira Nagai,^{1,2} Tomoya Ishizuka,² Takahiko Kojima,² Masayuki Takeuchi^{1,2}

Keywords: polycyclic aromatic hydrocarbon; chirality; dynamic behavior; macrocycle; spiral

Many molecules mimicking macroscopic machines, such as rotors, gears, and so forth, have been synthesized.¹ However, they occasionally cannot transfer the motion due to an unexpected motion.² Exploiting molecular units enabling infallible motion transmission is an important issue in constructing molecular machines. As a dynamic unit of molecular machine, we chose 9,9'-bifluorenylidene (BF), one of the polyaromatic hydrocarbons having a thermally isomerizable C=C double bond via rim-flip and double bond-flip mechanism.³ In our previous research, we synthesized the cyclic dimer of BF (**CBF2**) that only showed the rim-flipping motion.⁴

In this research, we synthesized a cyclic trimer (**CBF3**) which is supposed to isomerize both via rim-flip and double bond-flip mechanism. Since **CBF3** has a chirality derived from its twisted structure, the optical resolution of **CBF3** was performed; the chiroptical property of **CBF3** indicates that the racemization of **CBF3** occurs thermally at room temperature. The racemization mechanism was proposed through the ¹H EXSY measurement and DFT calculation. The characteristic of this mechanism is that three double bonds in **CBF3** are isomerized in a continuous fashion. This result, the interlocking motion of several movable points, is of importance in the field relating to molecular machines.



1) a) M. Schmittel, et al, *Chem. Rev.* **2020**, 120, 125. b) D. A. Leigh, et al, *Chem. Rev.* **2015**, 115, 10081. 2) M. A. Van Hove, et al, *J. Phys. Chem. C* **2018**, 122, 25067. 3) O. Kikuchi, et al, *Bull. Chem. Soc. Jpn.* **1986**, 59, 3043. 4) M. Takeuchi, et al, *Org. Chem. Front.* **2017**, 4, 650.

Photo-induced Reversal of Supramolecular Chirality

(¹Graduate School of Science and Engineering, Chiba University, ²Institute for Global Prominent Research, Chiba University, ³Graduate School of Engineering, Tohoku University) ○Takuho Saito,¹ Daisuke Inoue,¹ Yuichi Kitamoto,³ Shiki Yagai²

Keywords: Supramolecular Chirality; Photoresponsivity; Azobenzene; Nucleation; Self-assembly

Transcription of molecular chirality to supramolecular chirality in molecular self-assembly is of great importance not only for elucidating the origin of homochirality in nature but also for developing functional materials with chiroptical properties.¹ Supramolecular chirality is generally regulated by the chiral information of the monomers via thermodynamically favorable packing. Recent studies, however, revealed that metastable assemblies formed by kinetic self-assembly conditions exhibit opposite supramolecular chirality. Several examples of such reversal of supramolecular chirality have been reported for kinetically controlled self-assembly of π -conjugated molecules,² but strict control of such kinetic conditions by light-irradiation remains challenging.^{2b}

Herein we report the photo-induced reversal of supramolecular chirality using a scissor-shaped azobenzene dyad **1** possessing chiral side chains via amide groups (Fig. 1a).³ Upon cooling a nonpolar solution of **1**, the formation of left-handed helical fibers was suggested from negatively bisignate Cotton effect (Fig. 1b, blue spectrum). By UV-irradiation, left-handed fibers were converted to monomeric *cis*-isomers due to *trans*→*cis* photoisomerization of azobenzene chromophores with a tiny amount of “survived aggregates” (Fig. 1b, pink spectra). Remarkably, subsequent visible-light irradiation led to the sufficient *cis*→*trans* back isomerization of azobenzene units, which results in the formation of right-handed helical fibers as suggested by the reversal of CD signals (Fig. 1b, red spectrum). Detailed investigation indicates that nucleation mechanism plays an important role on the reversal of supramolecular chirality.

[1] E. Yashima et al., *Chem. Rev.* **2016**, *116*, 13752. [2] a) E. W. Meijer et al., *Nature* **2012**, *481*, 492.; b) M. Yamauchi, S. Yagai et al., *Nat. Commun.* **2015**, *6*, 8936. [3] a) S. Yagai, M. Yamauchi et al., *J. Am. Chem. Soc.* **2012**, *134*, 18205.; b) T. Saito, S. Yagai, *Eur. J. Org. Chem.* **2020**, 2475.; c) K. Tashiro, T. Saito, S. Yagai et al., *Chem. Rec.* **2022**, 10.1002/tcr.202100252.

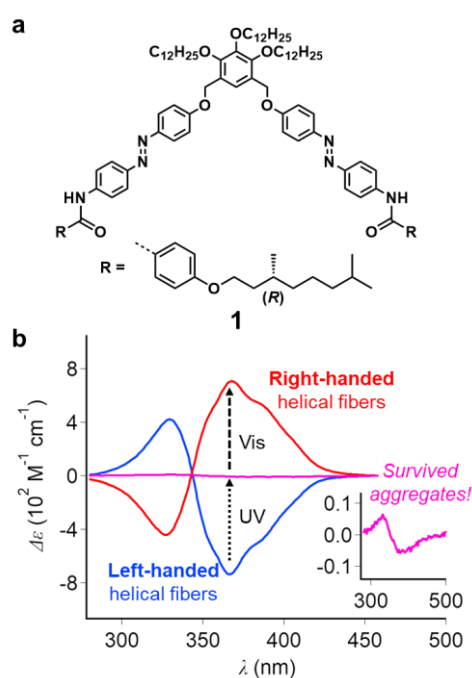


Figure 1. a) Molecular structure of **1**. b) CD spectra of **1** obtained after cooling (blue spectrum), after subsequent UV-irradiation (pink spectra) and further after visible-irradiation (red spectrum).

[K6-4am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Toshiki Nokami, Nobuhiro Yanai

Sat. Mar 26, 2022 9:00 AM - 11:20 AM K6 (Online Meeting)

[K6-4am-01] Long-Range Intramolecular Singlet Fission in Polyyne-Linked Pentacene Dimers

○Hayato Sakai¹, Masaaki Fuki², Nikolai Tkachenko³, Yasuhiro Kobori², Taku Hasobe¹ (1. Department of Chemistry, Faculty of Science and Technology, Keio University, 2. Kobe University, Molecular Photoscience Research Center, 3. Tampere University, Faculty of Engineering and Natural Sciences)

9:00 AM - 9:20 AM

[K6-4am-02] Development of photoreaction through halogen-bonding

○Eiji Yamaguchi¹, Akichika Itoh¹ (1. Gifu Pharmaceutical University)

9:20 AM - 9:40 AM

[K6-4am-03] Development of Mononuclear Aluminum Complexes Core Carbazole Dendrimer

○Kohei NAKAO¹, Minoru FURUKORI³, Takuya HOSOKAI³, Ken ALBRECHT^{1,2,4} (1. IMCE, Kyushu Univ., 2. Grad. Sci. Eng. Sci., Kyushu Univ., 3. AIST, 4. JST-PRESTO)

9:40 AM - 10:00 AM

[K6-4am-04] Development of transition metal-free photochemical CO₂ reduction enabled by photosensitized regeneration of organohydride

○Wei Bin Xie¹, Jia Sheng Xu¹, Ubaidah Md Idros¹, Jouji Katsuhira¹, Masaaki Fuki¹, Masahiko Hayashi¹, Yasuhiro Kobori¹, Ryosuke Matsubara¹ (1. Kobe university)

10:00 AM - 10:20 AM

[K6-4am-05] *Regio*-specific cross-dehydrogenative coupling reaction of simple polycyclic aromatic hydrocarbons with polyfluoroarenes

○Ryota Sato¹, Junpei Kuwabara², Takaki Kanabara² (1. TREMS, Univ. of Tsukuba, 2. TREMS, Univ. of Tsukuba)

10:20 AM - 10:40 AM

[K6-4am-06] Observation of Negative Activation Enthalpy in Amine Conjugate Addition to π -Conjugated Molecules

○Haruki Sanematsu^{1,2}, Masayuki Takeuchi^{1,2}, Atsuro Takai² (1. Univ. of Tsukuba, 2. NIMS)

10:40 AM - 11:00 AM

[K6-4am-07] Substituent effects on gas-phase stabilities of benzenes having positive point charges in the vicinity

○Kazuhide Nakata¹ (1. Sci. Res. Ctr., Hosei Univ.)

11:00 AM - 11:20 AM

長距離分子内一重項分裂を示すポリイン架橋ペンタセン二量体

(慶大理工¹・神戸大分子フォト²・タンペレ大学³) ○酒井 隼人¹・婦木 正明²・Tkachenko Nikolai³・小堀 康博²・羽曾部 卓¹

Long-Range Intramolecular Singlet Fission in Polyene-Linked Pentacene Dimers (¹Department of Chemistry, Faculty of Science and Technology, Keio University, ²Kobe University, Molecular Photoscience Research Center, ³Faculty of Engineering and Natural Sciences, Tampere University) ○ Hayato Sakai,¹ Masaaki Fuki,² Nikolai Tkachenko,³ Yasuhiro Kobori,² Taku Hasobe¹

Singlet Fission (SF) is a multi-exciton generation process that generates two individual triplet excitons from one-photon absorption. Many examples have been reported for covalently-linked molecular dimers because the close interaction between two chromophore units are required for occurrence of SF. In contrast, there is no observation of long-range intramolecular SF (ISF) at a spacer length of ca. 30 Å. Considering the previous reports of long-range photoinduced electron transfer, polyene is a good candidate for the useful spacer for long-range ISF. In this study, we newly synthesized a series of pentacene (Pc) dimers linked by polyene units with different spacer lengths and examined the detail photophysical processes such as the spacer length and solvent polarity-dependent rate constants.

Keywords : Pentacene; Dimer; Polyene; Singlet Fission

一重項分裂 (SF) は、近隣する二分子間で一光子の吸収過程から二つの三重項励起子を生成する光物理過程であり、量子収率が最大 200%まで達するため高効率な光エネルギー変換系の構築が期待できる。SF の発現には、励起一重項状態のエネルギーが励起三重項状態のエネルギーの 2 倍以上のエネルギー条件を満たす必要がある。ペンタセン(Pc)を代表とするアセンは、このエネルギー条件を満たすため SF 発現可能な分子群で、アセンを様々な架橋部位で連結した二量体で数多くの SF が観測されている。一般に、SF 発現には、色素間の強い相互作用が必要なので、2 つの色素の近接的な配置が必須である。したがって、分子内 SF はこれまでに色素間距離が 10 Å 以内もしくは同程度での二量体で数多く観測されており、色素間距離が 30 Å 程度におよぶ長距離で観測した例はない。一方、ポリインは、優れた分極性のπ-共役分子で長距離での色素間カップリングが可能なリンカーである。したがって、ポリインを介した共有結合で Pc 二分子を連結すると、従来にはない長距離での SF 発現が期待できる。本研究ではペンタセンを一連の鎖長が異なるポリインで架橋した二量体 (Fig. 1) を合成し、長距離分子内 SF の初観測に成功した。ポリインの鎖長依存性や溶媒効果についても報告する。

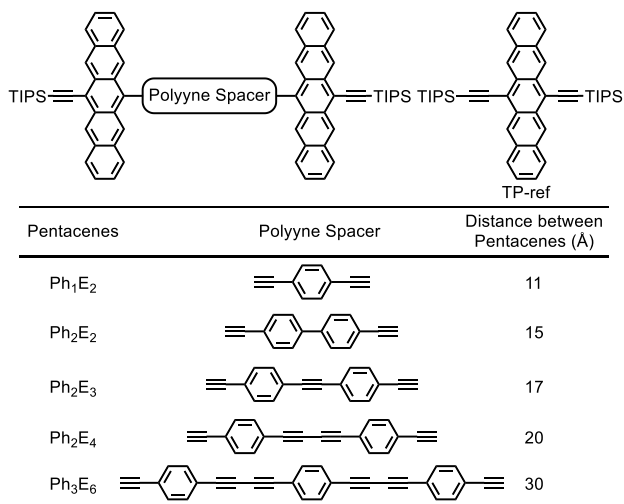


Fig. 1 Chemical structures of Pc dimers and the distances between two Pc units optimized by the B3LYP/6-31G level.

ハロゲン結合を介した光反応の開発研究

(岐阜薬大¹) ○山口 英士¹・伊藤 彰近¹

Development of photoreaction through halogen-bonding

(¹Gifu Pharmaceutical University) ○Eiji Yamaguchi,¹ Akichika Itoh¹

Recently, photoreactions using charge-transfer complexes have been studied in recent years due to provide a new pathway for the activation mode of small molecules. We have focused on the formation of C-T complexes *via* non-covalent interactions such as halogen-bonding interaction, and have been developing reactions based on their photochemical activation system.

For example, we have found that the formation of a halogen-bonding complex of CBr₄ with pyridine as a Lewis base, followed by light irradiation, results in the cleavage of the C–Br bond to produce carbon radical species.

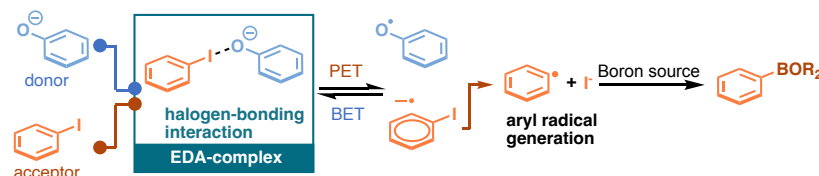
It was also found that halogen-bonding complexes of aryl halides with phenols can give aryl radicals under visible light irradiation, and it was found that the C–B bond formation reaction proceeds. In this reaction, the phenoxide present in the system under basic conditions is the key to the reaction progress, and the aryl halide forms a 1:1 complex with the phenoxide, giving more than 50 boronic acid ester derivatives in good yields. In this presentation, we will report on our recent results using these recent halogen-bonding interaction.

Keywords : Photo-reaction; C–X activation; Carbon radical; Halogen-bonding interaction

電荷移動錯体を利用した光反応は、新たな分子の活性化経路を供給するため、近年活発に研究がされている。我々は、ハロゲン結合を介した、電荷移動錯体の形成に着目し、その光化学的活性化による分子変換反応の開発を行っている。

例えば、CBr₄に対し、ピリジン類などのルイス塩基を作用させることでハロゲン結合を介した錯体の形成、その後の光照射により C–Br 結合の開裂により炭素ラジカル種が生成することを見出している。この現象を利用することで、様々な炭素ラジカル種を発生可能であることや、多様な反応様式で生成物を与えることを明らかにした。¹⁻³ また、アリールハライドとフェノール類とのハロゲン結合錯体が可視光照射下、アリールラジカルを与えることも同様に見出し、これを利用することで C–B 結合形成反応が進行することが明らかになった。この反応は、塩基性条件下で系中に存在するフェノキシドが反応進行の鍵であること、フェノキシドとはアリールハライドは 1:1 の錯体を形成していることなどがわかっており、50 種類以上のボロン酸エステル誘導体を良好な収率で与えた。

本発表では、最近のハロゲン結合を利用した最近の研究成果について報告する。



1) K. Matsuo, T. Yoshitake, E. Yamaguchi, A. Itoh, *Molecules* **2021**, 26, 6781. 2) K. Matsuo, T. Kondo, E. Yamaguchi, A. Itoh, *Chemical & Pharmaceutical Bulletin* **2021**, 69, 796-801. 3) K. Matsuo, E. Yamaguchi, A. Itoh, *J. Org. Chem.* **2020**, 85, 10574.

単核アルミニウム錯体をコアとするカルバゾール dendrimer の創製

(九大先導研¹・九大院総理工²・産総研 物質計測標準³・JST-さがけ⁴) ○中尾 晃平¹・古郡 美紀³・細貝 拓也³・アルブレヒト 建^{1,2,4}

Development of Mononuclear Aluminum Complexes Core Carbazole Dendrimer (¹IMCE, Kyushu Univ., ²Grad. Sci. Eng. Sci., Kyushu Univ., ³AIST, ⁴JST-PRESTO) ○Kohei Nakao,¹ Minori Furukori,³ Takuya Hosokai,³ Ken Albrecht^{1,2,4}

Thermally activated delayed fluorescence (TADF) materials for pure organic compounds have been considered as an attractive technology to obtain 100% internal quantum efficiency (IQE) without using rare metals. Very recently, light-metal-based TADF materials have been reported and achieved high-performance organic light-emitting devices (OLEDs). In this study, we have developed a novel series of mononuclear aluminum complexes with carbazole dendrimer-type ligands. We successfully synthesized the derivatives with different molecular skeleton and evaluated material properties. From results, the photoluminescence quantum yield (PLQY) is up to 87% and changed emission color from blue to green.

Keywords : Aluminum complex; Organic light-emitting diode; Thermally activated delayed fluorescence; Dendrimer; Carbazole

レアメタルを用いずに内部量子効率 (IQE) 100% を実現する純有機化合物から成る熱活性化遅延蛍光 (TADF) 材料が注目されている。最近では軽金属を用いた TADF 材料も報告され始めており、有機 EL 素子の高性能化を実現している。本研究では、TADF 材料を示す単核アルミニウム錯体をコアとするカルバゾール dendrimer の開発を目的とした。実際に、対称性の異なる誘導体を合成し、物性評価を行った。分子骨格を対称とすることで発光量子収率 (PLQY) が 87% にまで向上し、発光色は青色から緑色へ変化した。当日は材料物性と分子構造の関係を議論する。

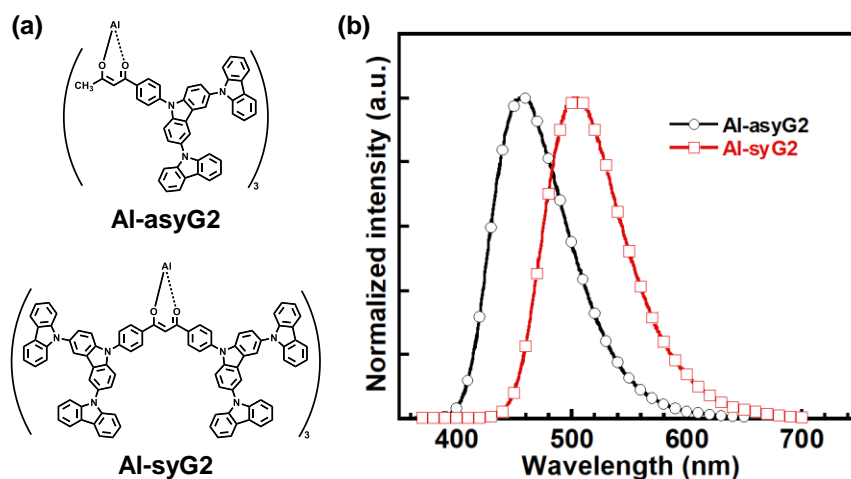


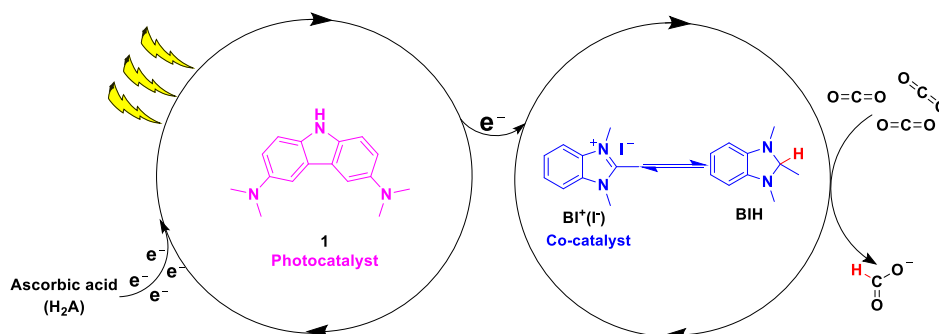
Figure 1 (a) chemical structure of the materials and (b) PL spectra in toluene solution

Development of transition metal-free photochemical CO₂ reduction enabled by photosensitized regeneration of organohydride

(Graduate School of Science, Kobe University) ○ Weibin Xie, Jiasheng Xu, Ubaidah Md Idros, Jouji Katsuhira, Masaaki Fuki, Masahiko Hayashi, Yasuhiro Kobori, Ryosuke Matsubara

Keywords: carbon dioxide reduction; photochemical catalytic; organohydride

The ever-increasing demand for fossil fuels has exacerbated dramatic energy shortages and massive greenhouse gas emissions, particularly carbon dioxide.¹ Using renewable solar light as an energy source to convert carbon dioxide into value-added chemical fuels is an ideal approach to address the current predicament.² As a thermodynamically stable gas CO₂, its reduction requires high-energy as inputs. Besides, the selectivity of the formed products deserves consideration.³ Thus, developing an efficient photocatalyst system is an indispensable key to achieving photocatalytic reduction of carbon dioxide and practical solar energy storage. Herein, we utilized organic photocatalytic cycle to provide electrons for regeneration of **BIH** from **BI⁺(I⁻)** as a strategy and successfully designed and demonstrated an ideal approach that photocatalytic conversion of CO₂ to value-added formate comprising carbazole moiety as a visible light-driven photosensitizer, benzimidazoline-based organohydride as co-catalyst, and ascorbic acid as a sacrificial reductant using visible light irradiation at 400 nm. In this case, photocatalyst and co-catalyst show strong durability and fast rate: based on photocatalyst (TON_{HCOO⁻} = 8820 and TOF_{HCOO⁻} = 2205/h) and based on co-catalyst (TON_{HCOO⁻} = 6070 and TOF_{HCOO⁻} = 1520/h). Besides, current reaction system for photocatalytic CO₂ reduction reaction showed exclusive selectivity to yield formate as a sole product, while formaldehyde, oxalate, CO, and H₂ as potential evolved products were not detected by ¹³C-labeling experiment and GC-based quantitative analysis of evolved gases experiment. Finally, using dehydroascorbic acid instead of ascorbic acid as sacrificial reductant in the photocatalytic reduction of CO₂ to fully corroborate that a two-time oxidation of ascorbic acid (four electrons provided per molecule) via intermediate dehydroascorbic acid was involved, which was consistent with more than 100% yield.⁴



- 1) S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.* **2013**, 52, 7372.
- 2) H. Shen, T. Peppel, J. Strunk, Z. Sun, *Sol. RRL.* **2020**, 4, 1900546.
- 3) K. Li, B. Peng, T. Peng, *ACS Catal.* **2016**, 6, 7485.
- 4) W. Xie, J. Xu, U. Md Idros, J. Katsuhira, M. Fuki, M. Hayashi, Y. Kobori, R. Matsubara, posted in *ChemRxiv*, doi:10.26434/chemrxiv-2021-ch3ts.

単純な多環芳香族炭化水素とポリフルオロアレーンの位置特異的脱水素型クロスカップリング反応

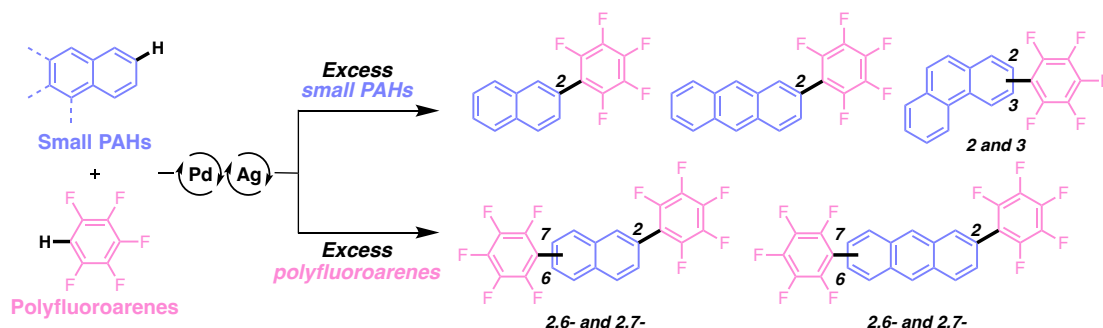
(筑波大院数理物質 TREMS¹) ○佐藤 亮太¹・桑原 純平¹・神原 貴樹¹

Regio-specific cross-dehydrogenative coupling reaction of simple polycyclic aromatic hydrocarbons with polyfluoroarenes (¹*TREMS, Univ. of Tsukuba*) ○Ryota Sato,¹ Junpei Kuwabara,¹ Takaki Kanbara¹

Cross-dehydrogenative coupling (CDC) reaction, which uses C-H bonds as reactive sites, is a powerful tool for step and atom economical synthesis. In general, the CDC reaction occurs at electrophilically favored sites. For example, Pd-catalyzed C-H bond activation of naphthalene generally occurs at the 1-position of naphthalene. To the best of our knowledge, there is only one report of Pd-catalyzed 2-position selective C-H bond activation.^[1] In this research, we discovered 2-position selective CDC reaction of naphthalene and other polycyclic aromatic hydrocarbons with polyfluoroarenes. The study on the reaction mechanism revealed that the *regio*-specificity of this reaction is involved at the reductive elimination step, not at the C-H bond cleavage step. The *regio*-specific CDC reaction can access to conjugated molecules, which are expected to act as *n*-type semiconductor materials, by only one step reaction without complicated introductions of reactive functional groups.

Keywords : Cross-dehydrogenative coupling reaction; Palladium catalyst; C-H bond activation reaction; Reductive elimination; Polyfluoroarene.

脱水素型クロスカップリング (CDC) 反応は基質の C-H 結合を反応点とするため、短段階合成の有力な反応である。一般的に、Pd 触媒による C-H 結合切断は求電子的に有利な箇所でも優先的に進行し、ナフタレンにおいては通常 1 位で進行する。ナフタレンの 2 位選択的な C-H 結合切断を経たクロスカップリング反応は我々の知る限り 1 例のみである。^[1] 本研究では、ナフタレン等の多環芳香族炭化水素とポリフルオロアレーンの CDC 反応において、2 位選択的に反応が進行することを見出した。本反応の位置選択性は、C-H 結合切断反応ではなく、還元的脱離の段階で決まることが反応機構に関する調査から明らかになった。本反応により、*n* 型有機半導体材料としての応用が期待できる化合物を、事前官能基化を回避して 1 段階で合成できる。



[1] J. Q. Yu et al., *Nature* **2017**, 551, 489.

Observation of Negative Activation Enthalpy in Amine Conjugate Addition to π -Conjugated Molecules

(¹Faculty of Pure and Applied Sciences, University of Tsukuba, ²Molecular Design and Function Group, National Institute for Materials Science: NIMS)

○Haruki Sanematsu,^{1,2} Masayuki Takeuchi,^{1,2} Atsuro Takai²

Keywords: Conjugate Addition; Negative Activation Enthalpy; π -Conjugated Molecule; Amine; Click Reaction

Amine conjugate addition to alkenes activated by an electron-withdrawing group has been widely used to prepare N-atom containing functional molecules. Recently, we have found novel amine conjugate addition of electron-withdrawing π -conjugated molecules such as naphthalenediimide (NDI) that proceeds rapidly in quantitative yields to afford amino-functionalized π -systems.¹⁾ However, the reaction mechanism of why such reactions of π -conjugated molecules proceed so efficiently is not fully scrutinized.

In this work, we systematically investigated the reaction mechanism of amine conjugate addition using several vinyl-group appended π -conjugated molecules. We found that the reaction of large π -conjugated molecules like a vinyl-substituted NDI (**vNDI1**) with dibutylamine exhibited unusual negative temperature dependence in polar solvents: the lower the temperature, the faster the rate. Eyring plot afforded the negative activation enthalpy ($-15.0 \text{ kJ mol}^{-1}$) in 1,2-dimethoxyethane (**Fig. 1a**), indicating the existence of pre-equilibrium reaction that forms a stable complex.²⁾ The detail spectroscopic and theoretical analyses of the reaction mechanism revealed that two amine molecules are involved in the reaction, one of which acts as an internal catalyst, as shown in **Fig. 1b**. We infer that the stabilization of the intermediate complex by the resonance structure of the π -system is the key to the efficient amine conjugate addition.

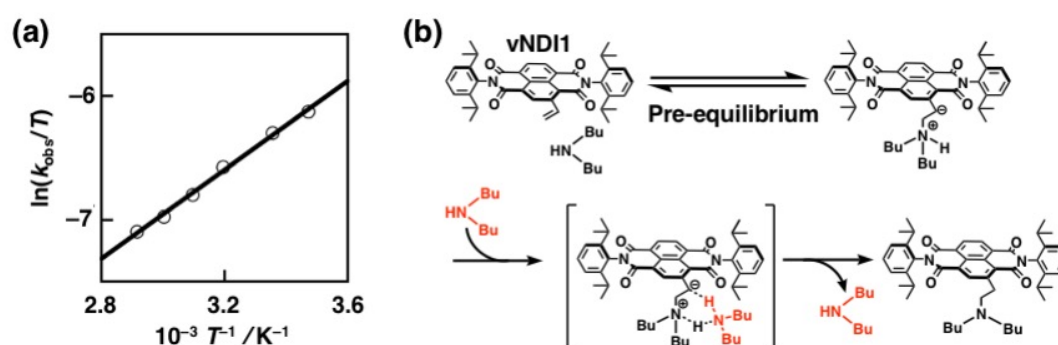


Fig. 1 (a) Eyring plot of the reaction of **vNDI1** with dibutylamine in 1,2-dimethoxyethane. (b) Plausible reaction mechanism of amine conjugate addition to **vNDI1**.

1) H. Sanematsu, *et al. Chem. Eur. J.* **2021**, 27, 934. 2) J. G. Miller, *et al. J. Am. Chem. Soc.* **1975**, 97, 4036.

近傍に正の点電荷を持つベンゼンの気相安定性に及ぼす置換基効果

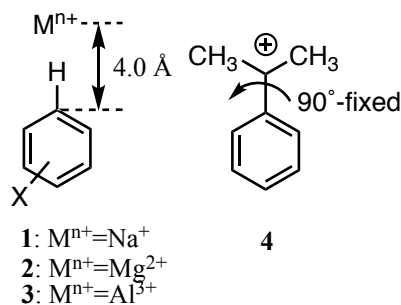
(法大自然科学セ) ○中田 和秀

Substituent effects on gas-phase stabilities of benzenes having positive charges in the vicinity
(*Science Research Center, Hosei University*) ○Kazuhide Nakata

In the previous work, we computationally determined substituent effects on stabilities of dications and compared them one another. It was shown that substituent effects of highly electron-deficient dications can be correlated by an extended Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+ \Delta \sigma_R^+ + s^+ \Delta \sigma_s^+)$) (1) implementing the third term. In this research, substituent effects on the stabilities of benzenes (**1–3**) having various amount of point charge in the vicinity were computationally determined. Obtained substituent effects were compared with those of α, α -dimethylbenzyl cations (**4**) having 90°-fixed dihedral-angle between the cationic side chain and the benzene ring that have been used as a reference system of σ^0 . In the comparison, plots of *meta*-EDGs gave an excellent linear correlations in **1–3**. While plots of *para*-EDGs are on the correlation line, those of EWGs significantly deviated from the correlation line depending the degree of the positive charge. These facts reveal that unique degrees of the saturation effect are operating on the stabilities of **1–3** although the through-resonance effects are always negligible. Statistical analyses conclude that Eq (1) well works in the substituent-effect analyses of electron deficient species regardless of their electron deficiency.

Keywords : *Electron Deficient Species; Gas-Phase Stability; Substituent Effect; DFT calculation; Extended Yukawa-Tsuno Equation*

以前、種々のジカチオンについて、気相安定性に及ぼす置換基効果を計算化学によって決定し、互いに比較した。その結果、高度に電子不足のジカチオンの置換基効果は、新たな電子効果を相関する第三項を導入した拡張湯川-都野式 ($-\Delta E_X = \rho(\sigma^0 + r^+ \Delta \sigma_R^+ + s^+ \Delta \sigma_s^+)$) (1)によって精度良く相関されることが示唆された。本研究では、近傍に点電荷を配置したベンゼン(**1–3**)を選択し、気相安定性に及ぼす置換基効果を計算化学によって検討した。得られたの置換基効果を、 σ^0 基準系である 90°-固定 α, α -ジメチルベンジルカチオン(**4**)の置換基効果と比較した。電子不足化学種 **1–3** に関して、全置換体のプロットでは劣った直線相関を示す一方で、*meta*-EDG のプロットは優れた直線相関を与えた。また、*para*-R 基のプロットは、この相関線上に位置する一方、EWG のプロットは正電荷の量に応じてそれぞれの系で相関線から顕著な片寄りを示した。この事実は、**1–3** の安定性に直接共鳴効果は寄与しない一方で、各系に固有のサチュレーション効果が寄与していることを示す。統計解析の結果、モノカチオンからトリカチオンに至るまで電子不足の度合いによらず、置換基効果が式(1)によって精度よく解析されることが明らかになった。



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

[K307-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Akira Matsumoto, Takeru Torigoe

Sat. Mar 26, 2022 9:00 AM - 11:20 AM K307 (Online Meeting)

[K307-4am-01] Acceptorless Dehydrogenative Cross-coupling Reactions Enabled by Photoredox/Hydrogen-Atom Transfer Cooperative Catalysis

[○]Kodai Minami¹, Kohsuke Ohmatsu^{1,2}, Takashi Ooi^{1,2} (1. Graduate School of Engineering, Nagoya University, 2. WPI-ITbM, Nagoya University)

9:00 AM - 9:20 AM

[K307-4am-02] Site-selective α -C(sp³)-H Alkylation of Alcohols and Primary Amines Promoted by Photoredox, HAT, and Bond-Weakening Hybrid Catalysis

[○]Kentaro Sakai¹, Kounosuke Oisaki¹, Motomu Kanai¹ (1. Grad. Sch. Pharm. Sci., the Univ. of Tokyo)

9:20 AM - 9:40 AM

[K307-4am-03] Photo-induced C-H bond thiocyanation and one-pot isomerization to isothiocyanates

[○]Bumpei Maeda¹, Yusuke Aihara², Ayato Sato², Toshinori Kinoshita², Kei Murakami¹ (1. Kwansei Gakuin University, 2. Nagoya University)

9:40 AM - 10:00 AM

[K307-4am-04] Selective C(sp³)-H Functionalization of Valine Residues via Interactions between Ammonium Group at the N-terminus and the Decatungstate Photocatalyst

[○]Jizhou Song², Takeru Torigoe^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

10:00 AM - 10:20 AM

[K307-4am-05] Decatungstate-catalyzed Site-selective C(sp³)-H Alkylation of 2-Methylanilinium Salts Controlled by Noncovalent Interactions

[○]Jialin Zeng², Takeru Torigoe^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

10:20 AM - 10:40 AM

[K307-4am-06] Cationic DABCO-based Catalyst for Site-Selective C-H Alkylation via Photoinduced Hydrogen-Atom Transfer

[○]Akira Matsumoto¹, Keiji Maruoka^{1,2} (1. Kyoto University, 2. Guangdong University of Technology)

10:40 AM - 11:00 AM

[K307-4am-07] 1,2-Bis-perfluoroalkylations of Alkenes and Alkynes with Perfluorocarboxylic Anhydrides

[○]Takuma Tagami¹, Yuma Aoki¹, Shintaro Kawamura¹, Mikiko Sodeoka¹ (1. RIKEN)

11:00 AM - 11:20 AM

Acceptorless Dehydrogenative Cross-coupling Reactions Enabled by Photoredox/Hydrogen-Atom Transfer Cooperative Catalysis

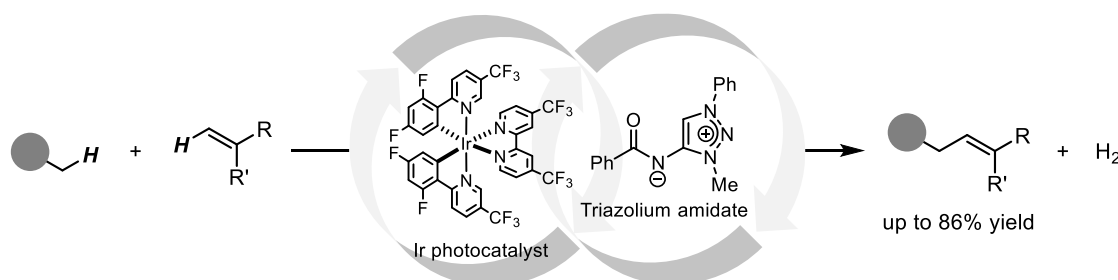
(Graduate School of Engineering, Nagoya University, WPI-ITbM, Nagoya University)

○Kodai Minami, Kohsuke Ohmatsu, Takashi Ooi

Keywords: Photoredox catalyst; Hydrogen-atom transfer catalyst; Acceptorless dehydrogenative coupling; Ionic organic molecular catalyst

Development of efficient and sustainable transformations is of central importance in the field of synthetic chemistry. Acceptorless dehydrogenative cross-coupling (ADC) between two different C–H bonds represents one of the most powerful methodologies to address this issue. Compared to conventional oxidative dehydrogenative coupling, ADC proceeds without any external oxidants, releasing molecular hydrogen as a sole byproduct. However, harsh reaction conditions are generally required, owing to the thermodynamically unfavorable nature of hydrogen evolution. Recently, electro- and photochemistry have made notable contributions to this field by taking advantage of facile dehydrogenation via cathodic proton reduction or the merger of transition-metal hydrogen evolution catalysis with photoredox catalysis.¹ Despite these significant advances, the catalyses available for ADC reactions are still very limited; hence, the potential of this mode of transformations is yet to be fully explored.²

Here, we have discovered an unconventional cooperative catalytic platform for the development of ADC reactions. The combined use of iridium-based photosensitizer and zwitterionic triazolium amidate³ enabled the C–H/C–H cross-coupling between various heteroatom-containing C–H donors and terminal alkenes without the need for any oxidants, hydrogen evolution catalysts, or electrodes. A key to establishing this catalysis is the susceptibility of the conjugate acid of the triazolium amidate, amide triazolium, toward single-electron reduction to complete the catalytic cycle.



- 1) Lei, A. *et al. Chem. Rev.* **2019**, *119*, 6769.
- 2) Wu, J. *et al. Nat. Commun.* **2020**, *11*, 1956. (b) Murakami, M. *et al. J. Am. Chem. Soc.* **2020**, *142*, 3366. (c) Li, C.-J. *et al. Nat. Commun.* **2021**, *12*, 4010.
- 3) Ooi, T. *et al. ACS Catal.* **2020**, *10*, 2627.

Site-selective α -C(sp^3)-H Alkylation of Alcohols and Primary Amines Promoted by Photoredox, HAT, and Bond-Weakening Hybrid Catalysis

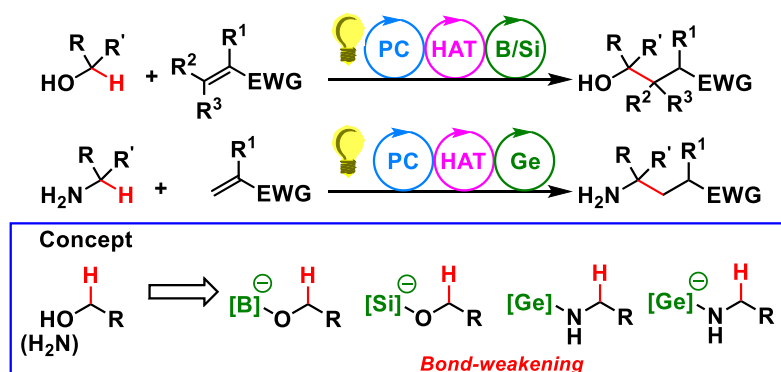
(Graduate School of Pharmaceutical Sciences, The University of Tokyo) ○Kentaro Sakai, Kounosuke Oisaki, Motomu Kanai

Keywords: C-H functionalization; Hydrogen atom transfer catalysis; Photoredox catalysis; Bond-weakening catalysis; Hybrid catalysis

The development of catalytic C(sp^3)-H functionalization reactions can explore various applications, such as the discovery of functional materials and drugs. To realize functionalization of unreactive C(sp^3)-H bonds, hydrogen atom transfer (HAT) catalysts have been attracting much attention because of their mild reaction conditions.¹ However, most of reported HAT catalysis have limited substrate scopes, which can only target the weakest or highly hydridic C(sp^3)-H bonds in the substrate. Targeting other C(sp^3)-H bonds in high regioselectivity under catalyst-control remains challenging.

We would like to report ternary hybrid catalyst systems consisting of photoredox (PC), HAT, and bond-weakening catalysts.² The bond-weakening catalyst design is based on DFT calculations uncovering that α -C(sp^3)-H bonds of alcohol^{3a,3b} and primary amine^{3c} substrates were effectively weakened by complexation as silicates, borates, and germane/germate species. These bond-weakening phenomena accelerates the HAT process of specific C(sp^3)-H bonds, leading to catalyst-controlled site-selectivity of C(sp^3)-H functionalization.

In this talk, we would like to focus mainly on the α -C(sp^3)-H alkylation of primary amines promoted by the PC-HAT-Ge hybrid system.



1) Capaldo, L.; Quadri, L. L.; Ravelli, D., *Green Chem.*, **2020**, 22, 3376. 2) Precedents of the hybrid system: a) MacMillan, D. W. C. and co-workers, *Science* **2015**, 349, 1532. b) Taylor, M. S. and co-workers, *J. Am. Chem. Soc.*, **2019**, 141, 5149. 3) a) **Sakai, K.**; Oisaki, K.; Kanai, M., *Adv. Synth. Catal.*, **2020**, 362, 337. b) **Sakai, K.**; Oisaki, K.; Kanai, M., *Synthesis*, **2020**, 52, 2171. c) **Sakai, K.**; Oisaki, K.; Kanai, M., *manuscript in preparation*

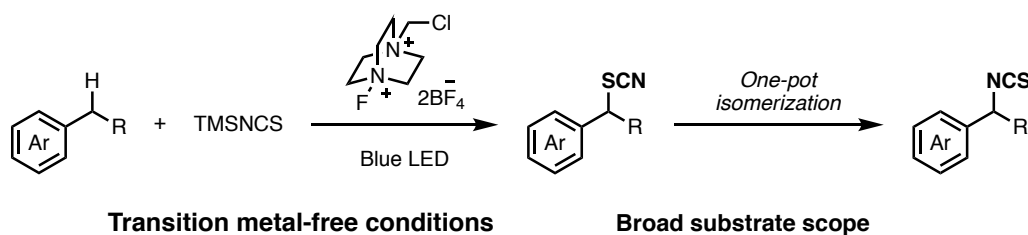
Photo-induced C–H bond thiocyanation and one-pot isomerization to isothiocyanates

○Maeda Bumpei,¹ Yusuke Aihara,² Ayato Sato,² Toshinori Kinoshita,² Kei Murakami¹
 (¹*Graduate School of Science and Engineering, Kwansei Gakuin University,* ²*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*)

Keywords: radical, thiocyanate, isothiocyanate, C–H bond activation, photo-irradiation

Thiocyanates and isothiocyanates are widely present in natural products and pharmaceuticals. They act not only as bioactive compounds but are also utilized as an organic synthetic toolbox. They are easily transformed into various functional groups such as heterocycles, sulfur-based, or nitrogen-based functional groups. Despite the various synthetic methods of thiocyanates have been developed such as substitution reactions or cyanations of thiols or disulfides, thiocyanations of unactivated aliphatic C–H bonds have been still challenging. Recently, two C–H thiocyanation reactions were reported: one is a copper-catalyzed reaction¹ and the other is AIBN-initiated reaction². Because the isomerization of thiocyanates into isothiocyanates can occur due to Lewis acid or heat, the substrate scopes of the reported methods were relatively limited. Thus, a novel C–H thiocyanation without transition metal in mild reaction conditions is required. The recent development of photo-induced reactions motivated us to develop a new C–H thiocyanation reaction with visible light irradiation³.

Herein, we describe a C–H thiocyanation using Selectfluor as a HAT reagent under visible light irradiation. We envisioned that the transition metal-free thiocyanation under mild conditions would be feasible with light irradiation. This reaction was applied to various substrates without isomerization. Additionally, we developed the one-pot synthesis of isothiocyanates following the corresponding C–H thiocyanation.



- 1) Cu-catalyzed reaction: Jiang, C.; Chen, P.; Liu, G. *CCS Chem.* **2020**, 2, 1884–1893.
- 2) AIBN-initiated reaction with excess amount of substrate: Wu, D.; Duan, Y.; Liang, K.; Yin, H.; Chen, F.-C. *Chem. Commun.* **2021**, 57, 9938–9941.
- 3) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, 81, 6898–6926.

ペプチド主鎖の末端アンモニウム基とデカタングステン酸塩光触媒との相互作用を利用した選択的なバリン残基の C(sp³)-H 官能基化

(九大先導研¹・九大院総理工²) ○宋 濟舟²・鳥越 尊^{1,2}・國信 洋一郎^{1,2}

Selective C(sp³)-H Functionalization of Valine Residues via Interactions between Ammonium Group at the N-terminus and the Decatungstate Photocatalyst (¹*Institute for Materials Chemistry and Engineering, Kyushu University*, ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○ Jizhou Song,¹ Takeru Torigoe,^{1,2} Yoichiro Kuninobu^{1,2}

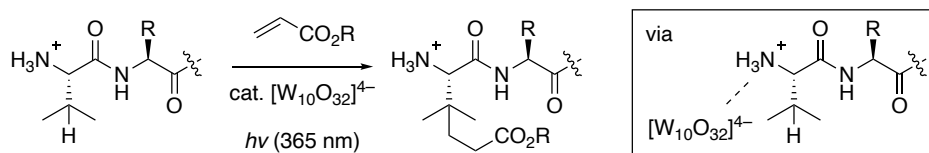
Functionalization of aliphatic residues in peptides is one of the most challenging issues in synthetic organic chemistry. We have developed a new method for regioselective C(sp³)-H functionalization using a decatungstate photocatalyst controlled by noncovalent interactions.¹ Based on this method, we envisioned that selective C(sp³)-H functionalization of aliphatic amino acid residues in peptides would be realized.

The TFA salt of valine methyl ester reacted with ethyl acrylate in the presence of the decatungstate photocatalyst under UV irradiation. On the other hand, the reaction of *N*-acetylvaline methyl ester did not give the C(sp³)-H alkylated product, indicating the ammonium group of the substrate is important for the reaction. Selective functionalization of a valine residue in a peptide containing two valine residues was also successful.

Keywords : C(sp³)-H Functionalization, Site-selectivity, Noncovalent Interaction, Aliphatic Residue, Peptide

ペプチドの脂肪族残基への官能基導入は従来の官能基変換に基づく手法では困難な位置への官能基導入を達成するものであり、その実現が切望されている。我々は最近、アニオン性を有するデカタングステン酸塩光触媒と基質のアンモニウム基との相互作用を利用する位置選択的な C(sp³)-H 結合の官能基化反応を報告した¹。本手法に基づき、ペプチド中のバリン残基選択的な C(sp³)-H 結合の変換に取り組んだ。

デカタングステン酸塩光触媒を用い、紫外光照射下バリンメチルエステルのトリフルオロ酢酸塩のアルキル化反応を検討したところ、目的生成物が得られた。一方で、*N*-アセチルバリンメチルエステルでは目的の反応は進行しなかったことから、基質中のアンモニウム基が重要であることが示唆された。また、二つのバリン残基を含むペプチドのアルキル化反応を検討したところ、選択的な変換に成功した。



1) 曾 嘉林, 鳥越 尊, 國信 洋一郎 日本化学会第 100 春季年会 3H8-04

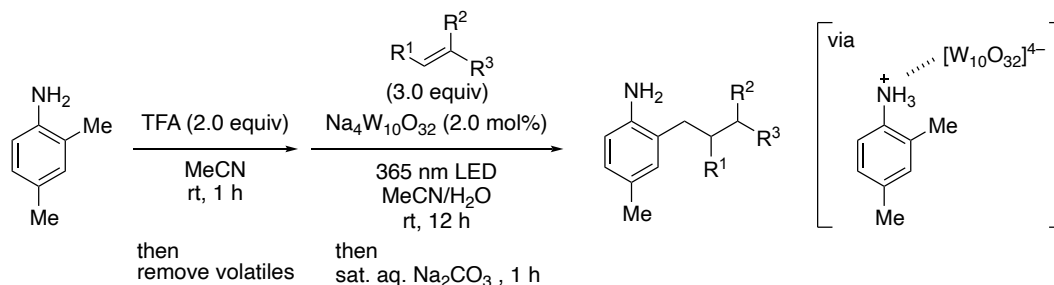
Decatungstate-catalyzed Site-selective C(sp³)-H Alkylation of 2-Methylanilinium Salts Controlled by Noncovalent Interactions

(¹*Institute for Materials Chemistry and Engineering, Kyushu University,* ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Jialin Zeng,² Takeru Torigoe,^{1,2} Yoichiro Kuninobu^{1,2}

Keywords: C(sp³)-H Transformation; Site-selectivity; Noncovalent Interaction; Decatungstate Photocatalyst; Radical

Regioselective C(sp³)-H functionalization is one of the most significant issues in organic synthesis. Although radical chemistry is a powerful tool for the activation of C(sp³)-H bonds, it is still difficult to convert C(sp³)-H bonds in a similar environment with high selectivity because the selectivity of hydrogen atom abstraction is generally determined by the steric and the electronic properties of the C(sp³)-H bonds. We have reported iridium-catalyzed *meta*-selective C(sp²)-H borylation, which was controlled by hydrogen bonds between the designed ligand and the functional group of substrates.¹ To develop regioselective C(sp³)-H functionalization through radical pathway, we focused on the noncovalent interactions between the substrate and the catalyst. We envisioned the anionic decatungstate photocatalyst, which is known as an efficient catalyst for C(sp³)-H functionalization, should interact with the cationic functional group of substrates.² Herein, we report a site-selective C(sp³)-H alkylation of 2-methylanilinium salts via radical intermediates.

The TFA salt of 2,4-dimethylaniline was reacted with electron-deficient alkenes in the presence of the decatungstate photocatalyst under UV irradiation. The C(sp³)-H alkylation proceeded at the proximal methyl group with high selectivity. A variety of 2-methylanilines could be applied to this reaction, and the synthetic conversion of the product was also successful. Mechanistic studies indicated the existence of the interaction between the ammonium group of substrates and the decatungstate photocatalyst.



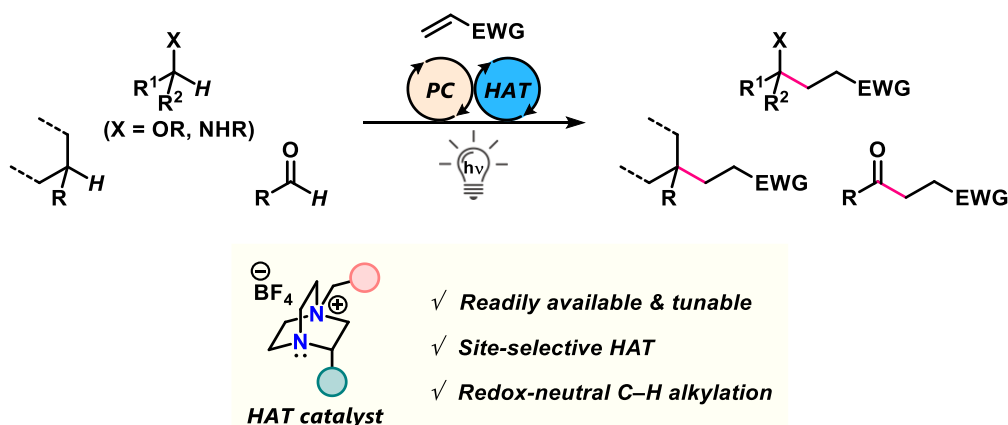
1) Y. Kuninobu, H. Ida, M. Nishi, M. Kanai, *Nature Chem.* **2015**, 7, 712. 2) J. Zeng, T. Torigoe, Y. Kuninobu, The 100th CSJ Annual Meeting, 3H8-04.

Cationic DABCO-based Catalyst for Site-Selective C–H Alkylation via Photoinduced Hydrogen-Atom Transfer

(¹Graduate School of Pharmaceutical Sciences, Kyoto University, ²School of Chemical Engineering and Light Industry, Guangdong University of Technology) ○ Akira Matsumoto,¹ Keiji Maruoka^{1,2}

Keywords: Hydrogen-atom Transfer; Photoredox Catalyst; Aminium Radical; C–H Functionalization; Redox Mediator

Hydrogen-atom transfer (HAT) provides powerful synthetic methods to directly functionalize C–H bonds in atom- and step-economical manners. The recent progress by merging HAT catalysis with photochemistry has enabled diverse functionalizations of various C–H bonds that are difficult by classical methods.¹ Since the reactivity and selectivity of the HAT process are highly dependent on the structure of HAT mediator, the development of HAT catalysts with different structural characteristics is important to expand the potential of HAT chemistry. Here, we have designed a novel class of cationic HAT catalysts based on the readily available and tunable 1,4-diazabicyclo[2.2.2]octane (DABCO) structure. A cooperative use of the HAT catalyst with an organophotoredox catalyst under visible-light irradiation enables efficient C–H alkylation of substrates ranging from unactivated hydrocarbons to complex molecules. Notably, a HAT catalyst with an additional substituent adjacent to nitrogen atom as the catalytic center has improved the site-selectivity. Mechanistic studies suggested that the *N*-substituent of the catalyst plays a crucial role, assisting in the generation of a dicationic aminium radical as an active species for the HAT process.



1) For recent reviews, see: a) Cao, H.; Tang, X.; Tang, H.; Yuan, Y.; Wu, J. *Chem Catalysis* **2021**, *1*, 523–598. b) Capaldo, L.; Ravelli, D.; Fagnoni, M. *Chem. Rev.* doi: 10.1021/acs.chemrev.1c00263.

1,2-Bis-perfluoroalkylations of Alkenes and Alkynes with Perfluorocarboxylic Anhydrides

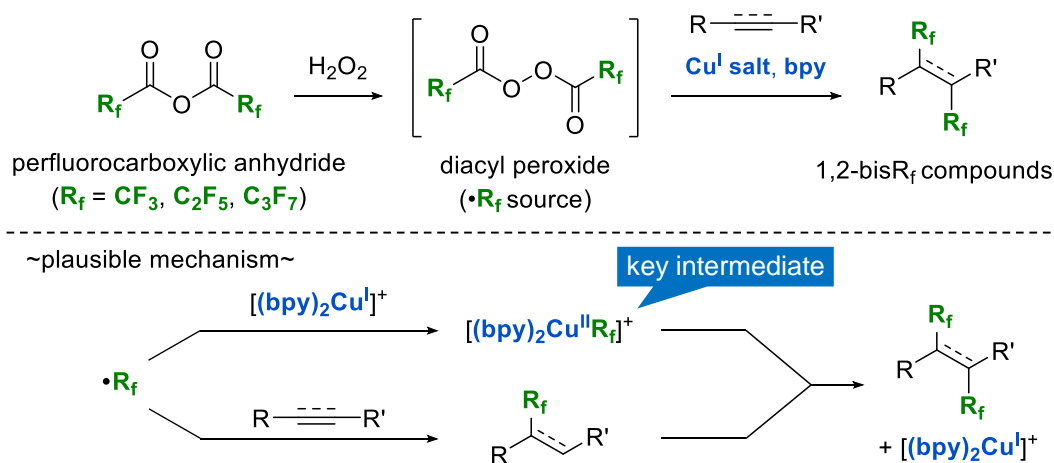
(¹Center for Sustainable Resource Science, RIKEN, ²Cluster for Pioneering Research, RIKEN)

○Takuma Tagami,¹ Yuma Aoki,¹ Shintaro Kawamura,^{1,2} Mikiko Sodeoka^{1,2}

Keywords: Perfluoroalkylation; Perfluorocarboxylic anhydrides; Diacyl peroxides; Perfluoroalkyl radicals; Organocopper intermediates

Perfluoroalkyl-containing organic molecules are of interest as pharmaceuticals and organic functional materials because of their improved physical, chemical, and biological properties derived from their fluorine atoms. Among perfluoroalkyl molecules, alkanes and alkenes bearing two perfluoroalkyl groups on their vicinal carbons are expected to exhibit unique functions; thus methods toward the 1,2-bis-perfluoroalkylation of alkenes and alkynes have been actively studied for nearly 50 years. Whereas various 1,2-bis-trifluoromethylations have been well established by using sophisticated trifluoromethylating reagents in the last decade, 1,2-bis-perfluoroalkylations that can introduce long perfluoroalkyl chains still have room for improvement due to the limitation of perfluoroalkylating reagents.

We developed the Cu-mediated 1,2-bis-perfluoroalkylation of alkenes and alkynes by using inexpensive and readily available perfluorocarboxylic anhydrides.¹ Diacyl peroxides were generated in situ from the carboxylic anhydride and hydrogen peroxide, which are served as a perfluoroalkyl radical source ($\bullet R_f$). The reaction allowed us to obtain various 1,2-bis-perfluoroalkylated compounds including unique tetrasubstituted alkenes. Addition of bipyridyl ligand was found to improve the product yield. Our mechanistic studies suggested that the key step in this reaction should be the formation of a stable perfluoroalkylcopper intermediate $[(bpy)_2Cu^{II}R_f]^+$ with the aid of a bipyridyl ligand; the intermediate plays the role in introducing the second perfluoroalkyl group to the alkyl- or vinyl-radical generated by the reaction of the substrate alkene or alkyne with perfluoroalkyl radical.



1) T. Tagami, Y. Aoki, S. Kawamura, M. Sodeoka, *Org. Biomol. Chem.* **2021**, *19*, 9148.

Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B**[B104-4am] 16. Natural Products Chemistry, Chemical Biology**

Chair: Makoto Yoritake, Takayuki Ohyoshi

Sat. Mar 26, 2022 9:00 AM - 11:20 AM B104 (Online Meeting)

[B104-4am-01] Synthetic Studies on Enigmazole B○Yoshihiro Goda¹, Haruhiko Fuwa¹ (1. Chuo University)

9:00 AM - 9:20 AM

[B104-4am-02] Synthetic Studies toward C-linked Hyaluronan Oligomer Analogues○Noriaki Kiya¹, Makoto Yoritake¹, Go Hirai¹ (1. Grad. Sch. Pharm. Sci., Kyushu Univ.)

9:20 AM - 9:40 AM

[B104-4am-03] Synthesis and functional analysis of gut-associated lymphoid-tissue-resident bacterial lipooligosaccharide partial structure○Tomoya Uto¹, Atsushi Shimoyama^{1,2}, Haruki Yamaura¹, Koji Hosomi³, Jun Kunisawa³, Koichi Fukase^{1,2} (1. Graduate School of Science, Osaka University, 2. PRC, Graduate School of Science, Osaka University, 3. National Institutes of Biomedical Innovation, Health, and Nutrition)

9:40 AM - 10:00 AM

[B104-4am-04] Synthesis of sialyl glycopeptide utilizing TFA-labile Bn-type protected sialic acid optimized for sialylation and solid-phase peptide synthesis○Shun Ito^{1,2}, Yuya Asahina^{1,2}, Yasuhiro Kajihara¹, Hironobu Hojo^{1,2} (1. Graduate School of Science and, 2. Institute for Protein Research, Osaka Univ.)

10:00 AM - 10:20 AM

[B104-4am-05] Semisynthetic Study of Glycoprotein Interleukin-6 (IL-6)○Yanbo Liu¹, Yuta Maki^{1,2}, Ryo Okamoto^{1,2}, Yasuhiro Kajihara^{1,2} (1. Dept. Chem., Grad. Sch. Sci., Osaka Univ., 2. PRC, Grad. Sch. Sci., Osaka Univ.)

10:20 AM - 10:40 AM

[B104-4am-06] Synthetic Study of Antibiotic Cyclopeptide Pargamicin A○Tetsuya Inaba¹, Masahito Yoshida¹, Hideo Kigoshi¹ (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

10:40 AM - 11:00 AM

[B104-4am-07] Synthetic study of nemorosonol and hyperuralone A having a tricyclo[4.3.1.0]decane skeleton○Keisuke Mitsugi¹, Toru Takabayashi¹, Takayuki Ohyoshi¹, Hideo Kigoshi¹ (1. Degree Programs in Pure and Applied Sciences, University of Tsukuba)

11:00 AM - 11:20 AM

エニグマゾール B の全合成研究

(中大理工) ○合田 佳弘・不破 春彦

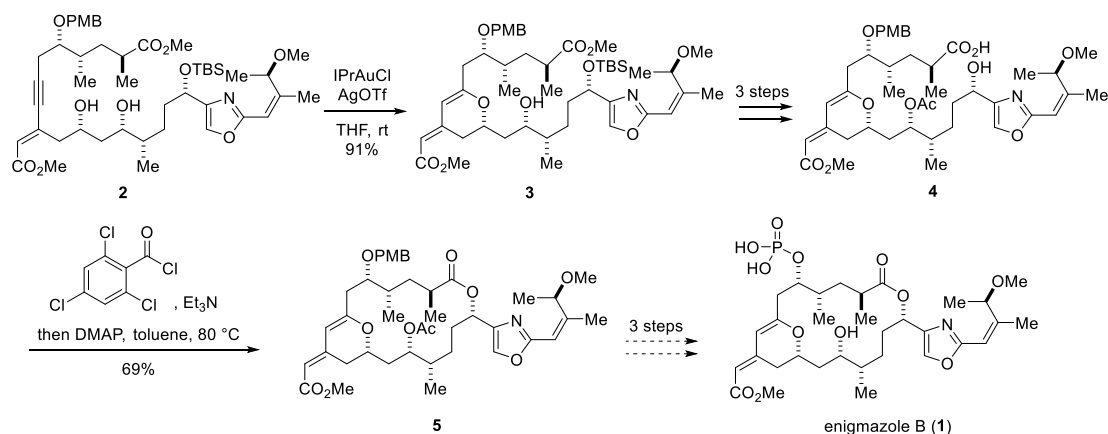
Synthetic Studies on Enigmazole B (*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○Yoshihiro Goda, Haruhiko Fuwa

Enigmazole B (**1**) was isolated from a Papua New Guinean marine sponge *Cinachyrella enigmatica*. This natural product selectively inhibits the proliferation of cancer cells expressing mutant c-Kit. Accordingly, enigmazole B represents an intriguing starting point for the development of new chemotherapeutics for the treatment of acute myelogenous leukemia and gastrointestinal stromal tumors. In this presentation, we will report on our progress toward the total synthesis of enigmazole B. Intramolecular hydroalkoxylation of **2** under IPrAuCl/AgOTf catalysis afforded dihydropyran **3**. Yamaguchi macrolactonization of seco-acid **4**, which was obtained in three steps from **3**, delivered 18-membered macrolactone **5**.

Keywords : Macrolide; Marine natural products; Total Synthesis; Dihydropyran; Antitumor activity

Enigmazole B (**1**)はパプアニューギニア諸島沿岸で採集された海綿 *Cinachyrella enigmatica* から単離された海洋マクロリドである^{1,2)}。本天然物は、変異型 c-kit 発現細胞に対して選択的な毒性を示すことから、急性骨髄性白血病や消化管間質腫瘍の治療薬シーズとして期待される。今回我々は、本天然物のマクロラクトン骨格の構築を達成したので、その詳細を報告する。

アルキンジオール **2** を IPrAuCl/AgOTf で処理すると分子内ヒドロアルコキシ化が進行し、ジヒドロピラン **3** を高収率で与えた。化合物 **3** から 3 工程の保護基の変換で得たセコ酸 **4** に対し、山口マクロラクトン化を行い、マクロラクトン **5** を中程度の収率ながら得ることに成功した。現在、化合物 **5** から **1** への変換を検討中である。



1) Gustafson, K. R. et al. *J. Am. Chem. Soc.* **2010**, *132*, 10278. 2) Smith, A. B. et al. *J. Org. Chem.* **2018**, *83*, 6110.

代謝耐性型ヒアルロナンオリゴマーの合成研究

(九大院薬) ○木谷 憲昭・寄立 麻琴・平井 剛

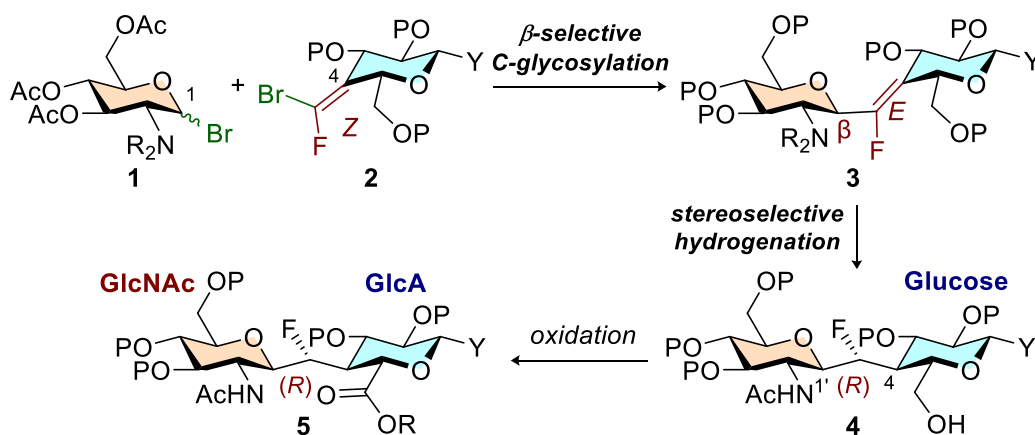
Synthetic Studies toward C-linked Hyaluronan Oligomer Analogues (*Graduate School of Pharmaceutical Sciences, Kyushu University*) ○Noriaki Kiya, Makoto Yoritake, Go Hirai

Hyaluronan (Hyaluronic acid, HA) is a mucopolysaccharide of extracellular matrix composed of repeated glucuronic acid (GlcA) and *N*-acetylglucosamine (GlcNAc): $[-\beta(1,4)\text{-GlcA}-\beta(1,3)\text{-GlcNAc-}]_n$, which exhibits various biological functions depending on their molecular size. However, the function of HA oligomer has yet to be clarified due to their enzymatic degradation by hyaluronidases. Thus, we designed the CHF-linked HA analogues containing metabolically stable and structurally similar C-glycoside moiety between C1 of GlcNAc and C4 of GlcA, which would be useful for the analysis of the function of HA oligomers. In this meeting, we will disclose the synthesis of CHF-linked HA analogues.

Keywords : Hyaluronan; C-glycoside; Glycan

ヒアルロナン (HA) のオリゴマー (4–20 糖) は、“糖鎖長” により炎症応答や細胞分化など多様な生理活性を発揮することが知られている¹⁾。しかし、HA は酵素により代謝されるため、それらの活性の真偽は明確でない。本研究では、代謝される $\beta(1,4)$ -O グリコシド結合の酸素原子をすべて炭素原子に置換した代謝耐性型 HA オリゴマーの合成を目指した。今回我々は、O グリコシドの安定配座を模倣できる(R)-CHF 連結型、O グリコシドがとり得ない配座を優先する(S)-CHF 連結型、柔軟な配座をとり得る CH_2 連結型の 3 種のアナログ合成に取り組んだ。

ブロモ糖 **1** と Z 体のブロモフルオロオレフィン **2** の β 選択的な C グリコシル化及び水素添加により(R)-CHF グリコシド **4** を構築後、酸化反応により HA オリゴマーの単量体 **5** を合成できた。さらに、E 体のブロモフルオロオレフィンを同様の工程で反応させることで(S)-CHF グリコシドを、フッ素を還元する水素添加反応で処理することで CH_2 グリコシドを調製した。本会ではその詳細に関して報告する。



1) Cowman, M. K. *Hyaluronan and Hyaluronan Fragments*, 1st ed.; Elsevier Inc., 2017; Vol. 74.

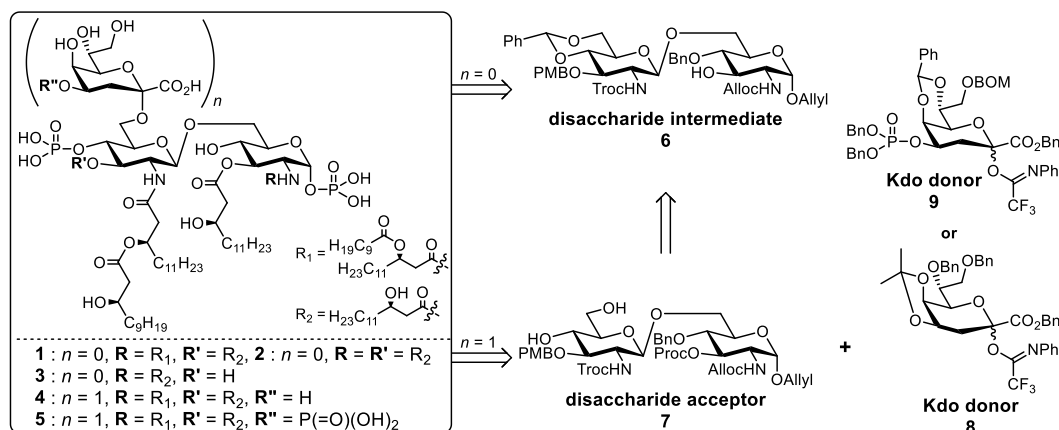
Synthesis and function of gut-associated lymphoid-tissue-resident *Alcaligenes faecalis* lipooligosaccharide partial structures

(¹Graduate School of Science, Osaka University, ²PRC, Graduate School of Science, Osaka University, ³National Institutes of Biomedical Innovation, Health, and Nutrition) ○Tomoya Uto¹, Atsushi Shimoyama^{1,2}, Haruki Yamaura¹, Koji Hosomi³, Jun Kunisawa³, Koichi Fukase^{1,2}
Keywords: symbiotic bacteria; lipid A; Kdo; lipooligosaccharide; innate immunity

Alcaligenes faecalis is a Gram-negative bacterium inhabiting the gut-associated lymphoid-tissue, such as Peyer's patches. We previously reported that lipooligosaccharide (LOS) extracted from *A. faecalis* showed efficient antibody production effect without triggering any harmful responses¹, thus *A. faecalis* LOS and its active center lipid A are expected to be applied as a vaccine adjuvant.

We recently characterized the chemical structure of *A. faecalis* LOS and synthesized its lipid A moiety **1-3** via disaccharide intermediate **6**². *A. faecalis* LOS and synthesized lipid A **1** showed the TLR4-dependent immunostimulating activities, while synthesized *A. faecalis* lipid A **2, 3**, which were the main components in *A. faecalis* LOS, worked as TLR4 antagonists. Thus, there was a functional divergence between the main component lipid As and LOS. On the other hand, we previously found that the Kdo linking lipid A and core oligosaccharide affect the immune function of lipid A³.

In this study, to investigate how Kdo impacts the immune function of *A. faecalis* lipid A, we synthesized *A. faecalis* Kdo-lipid A **4, 5**. After glycosylation of **7** with Kdo donor **8**⁴ whose sugar backbone was fixed in a boat-like conformation to enhance the α -selectivity of glycosylation, selective removal of protective groups and sequential introduction of fatty acids afforded *A. faecalis* Kdo-lipid A **4**. In a similar strategy to the synthesis of **4**, we also synthesized **5** from **7** and Kdo donor **9**. Bioassay using HEK-Blue™ hTLR4 indicated that Kdo-lipid A **4** showed slightly stronger immunostimulating activity than lipid A **1**.



(1) *Mucosal Immunology* **2018**, *11*, 693. (2) *Angew. Chem. Int. Ed.* **2021**, *60*, 10023. (3) *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 1475. (4) *SYNLETT* **2011**, *16*, 2359.

シアリル化と SPPS に最適化した TFA 感受性 Bn 型保護シアル酸によるシアリル糖ペプチド合成

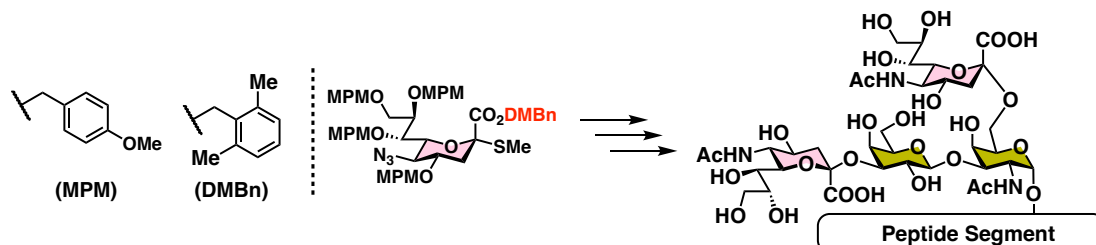
(阪大院理¹・蛋白質研究所²)○伊藤 駿^{1,2}・朝比奈 雄也^{1,2}・梶原 康宏¹・北條 裕信^{1,2}

Sialyl glycopeptide synthesis utilizing TFA-labile Bn-type protected sialic acid optimized for sialylation and SPPS (¹*Graduate School of Science and, ²Institute for Protein Research, Osaka University*) ○Shun Ito,^{1,2} Yuya Asahina,^{1,2} Yasuhiro Kajihara,¹ Hironobu Hojo^{1,2}

Recently, we have synthesized sialyl glycopeptides conveniently by a protecting group strategy combining 4-methoxybenzyl (MPM) and 4-methylbenzyl (MBn) groups. However, the yield and stereoselectivity of sialylation using protected sialic acid donor by these protecting groups were not satisfactory due to the acid instability of the MPM group. Therefore, we found a newer protecting group strategy by introducing a 2,6-dimethylbenzyl (DMBn) group into the sialic acid C-1 carboxy group. The improved sialyl donor was found to give the desired oligosaccharide in high yield and almost perfect stereoselectivity in sialylation. In addition, it was found that DMBn could be deprotected by trifluoroacetic acid (TFA). Namely, a novel sialic acid donor can be applied to both sialylation and peptide solid-phase synthesis¹⁾. Currently, we have successfully prepared glycoamino acids and glycopeptides with $\alpha(2,6)$ - and $\alpha(2,3)$ -linked sialic acids.

Keywords : Sialic acid; Glycopeptide; TFA-labile Protecting Group

近年我々は、TFA 感受性保護基 4-メトキシベンジル (MPM) 基と 4-メチルベンジル (MBn) 基を組み合わせた保護基戦略を見出した。これら保護基はペプチド固相合成後のトリフルオロ酢酸 (TFA) で脱保護可能であり、簡便なシアリル糖ペプチド調製を可能とした。しかし、MPM 基の酸不安定性により、シアリル化による糖鎖の構築は満足できるものではなかった。そこで我々は、シアル酸 C-1 カルボキシ基に 2,6-ジメチルベンジル (DMBn) 基を導入した、より新しい保護基戦略を見出した。改良されたシアル酸供与体は、シアリル化において高収率かつほぼ完全な立体選択性で目的のオリゴ糖を与え、加えて DMBn 基も TFA により脱保護できることがわかった。すなわち、新規シアル酸ドナーは、シアリル化とペプチド固相合成の双方に応用できることを示した¹⁾。現在、(2,6)-および(2,3)-結合のシアル酸を有する糖アミノ酸および糖ペプチドの調製に成功している。



1) S. Ito, Y. Asahina, H. Hojo *Tetrahedron* 2021, 97, 132423.

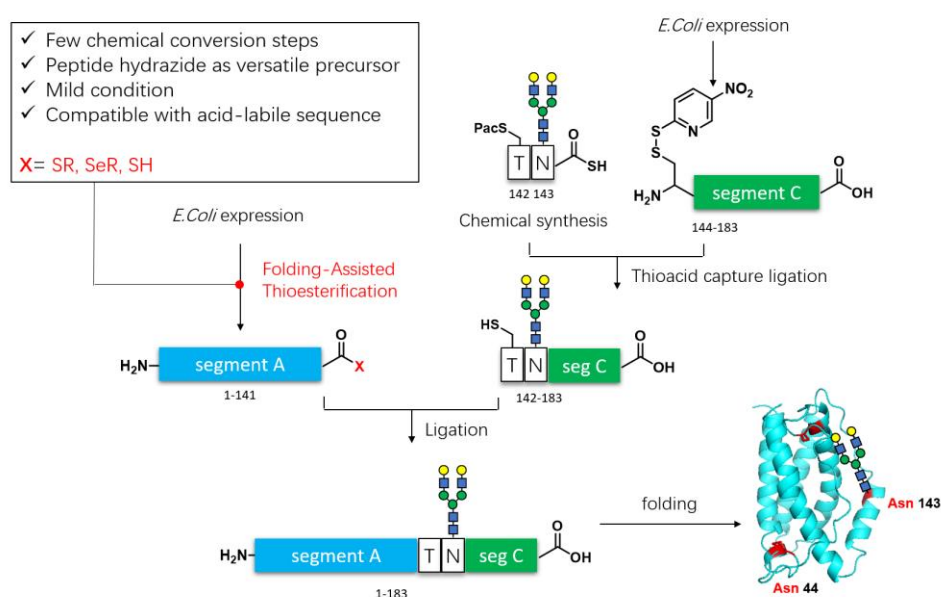
Semisynthetic Study of Glycoprotein Interleukin-6 (IL-6)

(¹Graduate School of Science and ²Project Research Center for Fundamental Science, Osaka University) ○Yanbo Liu¹, Ryo Okamoto^{1,2}, Yuta Maki^{1,2}, Yasuhiro Kajihara^{1,2}

Keywords: glycoprotein; semi-synthesis; interleukin-6; expressed-peptide thioesterification; thioacid capture ligation

Preparation of glycoproteins having homogeneous oligosaccharides is essential approach for understanding the glycan function at molecular level. However, current mammalian cell expression system is usually not able to yield such homogeneous form. Moreover, total chemical synthesis using solid phase peptide synthesis (SPPS) is time-consuming.

In this research project, we have been establishing a novel semisynthetic strategy without using SPPS in order to obtain homogeneous glycoprotein within a few chemical conversion steps. In this strategy, the challenging expressed-peptide thioesterification of N-terminal segment consist of 141 residues is achieved by a newly developed folding-assisted thioesterification method. In this method, peptide hydrazide derivative is obtained as a versatile precursor that can be utilized for various ligation method. The glycopeptide is prepared by thioacid capture ligation using chemically synthesized asialylglycodipeptide and an expressed peptide.¹ The final ligation step which afford full-length glycosylated IL-6 is examined using thioester, selenoester or thioacid derivative which are prepared via folding-assisted thioesterification.



- 1) Kota Nomura, Yuta Maki, Ryo Okamoto, Ayano Satoh, and Yasuhiro Kajihara, *J. Am. Chem. Soc.* **2021**, *143*, 10157-10167

抗菌活性環状ペプチド Pargamicin A の合成研究

(筑波大院数理物質¹) ○稲葉 哲也¹・吉田 将人¹・木越 英夫¹

Synthetic Study of Antibiotic Cyclopeptide Pargamicin A (¹*Degree Programs in Pure and Applied Sciences, University of Tsukuba*) ○Tetsuya Inaba,¹ Masahito Yoshida,¹ Hideo Kigoshi¹

Pargamicin A (**1**), isolated from *Amycolatopsis* sp. ML-1-hf4, is an 18-membered cyclopeptide consisting of unusual amino acids such as γ -hydroxy piperazic acid, *N*-methyl- β -hydroxy valine, and *N*-hydroxy isoleucine¹. Although the natural product exhibits potent antibacterial activity against vancomycin-resistant enterococci, the absolute configuration of *N*-hydroxy isoleucine has not been determined. Therefore, we planned the total synthesis of **1** for the determination of absolute configuration. The retrosynthetic analysis of pargamicin A (**1**) is shown below. After the solution-phase peptide synthesis of **2** from the sarcosine derivative, macrolactamization and removal of the Bn group would furnish the desired natural product. In this presentation, we will report the details of the synthetic study of pargamicin A (**1**).

Keywords : Natural product; Cyclopeptide; Piperazic acid; Antibacterial activity

Pargamicin A (**1**)は、放線菌 *Amycolatopsis* sp. ML-1-hf4 から単離・構造決定された 18 員環の抗菌活性環状ペプチドであり、 γ -ヒドロキシピペラジン酸や *N*-メチル- β -ヒドロキシバリン、*N*-ヒドロキシイソロイシンなど複数の異常アミノ酸を含む¹。 **1** は、バンコマイシンなどの抗生物質が効かない多剤耐性菌に対して強力な抗菌活性を示すが、*N*-ヒドロキシイソロイシン残基の絶対立体配置は決定されていない。そこで、天然物の不明の絶対立体配置の決定を目的として、**1** の全合成を検討した。以下に逆合成を示す (図 1)。すなわち、サルコシン誘導体から液相ペプチド合成により **2** を得た後、マクロラクタム化と続く脱保護により所望の天然物を得ることにした。本発表では、**1** の合成研究についてその詳細を報告する。

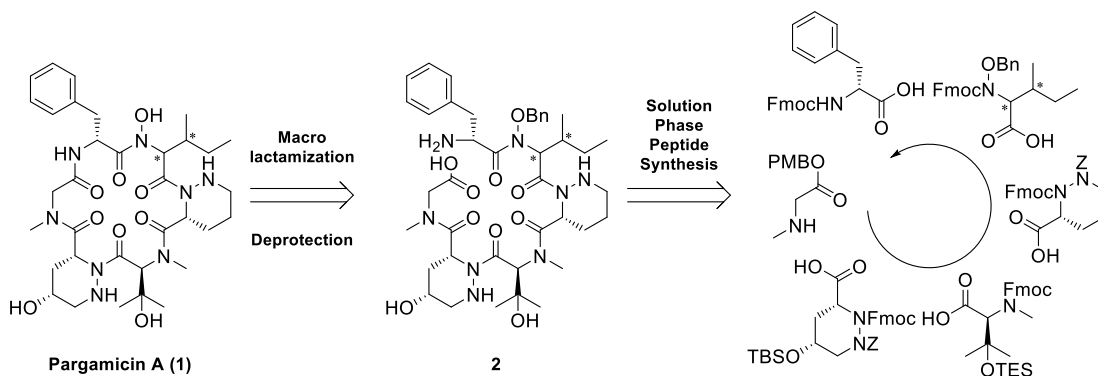


図 1 Pargamicin A (**1**)の逆合成

Reference: Igarashi, M.; Sawa, R.; Kinoshita, N.; Hashizume, H.; Nakagawa, N.; Homma, Y.; Nishimura, Y.; Akamatsu, Y. *J. Antibiot.* **2008**, *61*, 387–393.

Synthetic study of nemorosonol and hyperuralone A having a tricyclo[4.3.1.0]decane skeleton

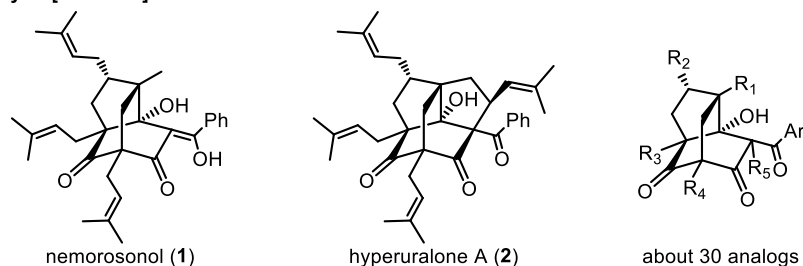
(Degree Programs in Pure and Applied Sciences, University of Tsukuba) ○Keisuke Mitsugi, Toru Takabayashi, Takayuki Ohyoshi, Hideo Kigoshi

Keywords: polycyclic polyprenylated acylphloroglucinol, tricyclo[4.3.1.0]decane skeleton, nemorosonol, hyperuralone A, unified total syntheses

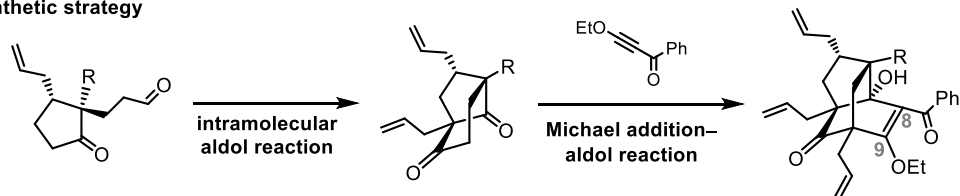
About 30 PPAPs having the tricyclo[4.3.1.0^{3,7}]decane skeleton are known, and these PPAPs show various biological activities. Examples include nemorosonol (**1**), which has the most basic structure, and hyperuralone A (**2**), which has one of the most complex structures. (+)-**1**¹⁾ has no reported biological activity, while its enantiomer²⁾ shows antimicrobial activities against various fungi. In addition, **2** has a tetracyclo[5.3.1.1^{4,9}.0^{4,11}]dodecane skeleton and exhibits cytotoxicity against human lung cancer cells A549³⁾. Despite these attractive structures and biological activities, there are few synthetic reports of these PPAPs. Therefore, we aimed to establish a unified synthetic strategy for these PPAPs.

First, we established a synthetic strategy through intramolecular aldol reaction, which give a bicyclic skeleton, and tandem Michael addition–intramolecular aldol reaction using 3-ethoxy-1-phenyl-2-propyn-1-one. Tandem Michael addition–intramolecular aldol reaction enabled introduction of a benzoyl group at the C8 position and control of the degree of oxidation at the C9 position at the same time. Based on this synthetic strategy, we achieved concise total synthesis of nemorosonol (**1**) and investigated the synthesis of hyperuralone A (**2**).

PPAPs having tricyclo[4.3.1.0^{3,7}]decane skeleton



unified synthetic strategy



- 1) Monache, F. D. Monache, G. D.; Pinheiro, R. M.; Radics, L. *Phytochemistry* **1988**, 27, 2305.
- 2) Oya, A.; Tanaka, N.; Kusama, T.; Kim, S. Y.; Hayashi, S.; Kojima, M.; Hishida, A.; Kawahara, N.; Sakai, K.; Gonoi, T.; Kobayashi, J. *J. Nat. Prod.* **2015**, 78, 258.
- 3) Zhang, J.-J.; Yang, J.; Liao, Y.; Yang, X.-W.; Ma, J.-Z.; Xiao, Q.-L.; Yang, L.-X.; Xu, G. *Org. Lett.* **2014**, 16, 4912.

[G202-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Hitoshi Kasai, Yuki Goto

Sat. Mar 26, 2022 9:00 AM - 11:40 AM G202 (Online Meeting)

- [G202-4am-01] Fabrication of novel nano-prodrugs that release drugs with high efficiency in cancer cells
○Keita Tanita¹, Yoshitaka Koseki¹, Ryuju Suzuki¹, Anh T. N. Dao¹, Hitoshi Kasai¹ (1. IMRAM, Tohoku university)
9:00 AM - 9:20 AM
- [G202-4am-02] Parametrization of Karplus Equation for N-Methylated Peptides
○Yota Shiratori¹, Takumi Ueda², Koh Takeuchi², Jumpei Morimoto¹, Shinsuke Sando¹ (1. The Univ. of Tokyo, 2. The Univ. of Tokyo)
9:20 AM - 9:40 AM
- [G202-4am-03] Development of designer thiopeptides with grafted noncanonical sequences inhibiting a target protein of interest
○Kakeru Narumi¹, Kyohei Miyairi, Yuki Goto¹, Hiroaki Suga¹ (1. The University of Tokyo)
9:40 AM - 10:00 AM
- [G202-4am-04] Directed Evolution of Cytochrome P450BM3 for Responding Natural Products as Decoy Molecules for Direct Benzene Hydroxylation without Chemical Synthesis
○Yuya Yokoyama¹, Masayuki Karasawa¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1. Nagoya University, 2. RIKEN Spring-8)
10:00 AM - 10:20 AM
- [G202-4am-05] The creation of rigid hemoprotein multimers triggered by metal coordination
○Hiroaki Inaba¹, Yuma Shisaka¹, Garyo Ueda¹, Erika Sakakibara¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1. Nagoya university, 2. RIKEN Spring-8)
10:20 AM - 10:40 AM
- [G202-4am-06] Visible light driven NADH regeneration using a system of water-soluble zinc porphyrin and homogeneously polymer-dispersed rhodium nanoparticles and application to CO₂ fixation with enzyme
○Takayuki Katagiri¹, Masanobu Higashi¹, Yutaka Amao¹ (1. Osaka City University)
10:40 AM - 11:00 AM
- [G202-4am-07] Efficient production of value-added chemicals in cyanobacteria by metabolic regulation using light sensor proteins
○Shunichi Kobayashi¹, Shota Atsumi², Kazunori Ikebukuro¹, Ryutaro Asano¹ (1. Tokyo Univ. of Agric. and Technol., 2. Univ. of California Davis)
11:00 AM - 11:20 AM
- [G202-4am-08] Functionalization of cycloparaphenylene by biocatalysts
○Atsushi Usami¹, Kazuma Amaike¹, Katsutoshi Hori¹, Kenichiro Itami¹ (1. Nagoya Univ.)
11:20 AM - 11:40 AM

Fabrication of Novel Nano-Prodrugs that Release Drugs with High Efficiency in Cancer Cells

(¹*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*)

○Keita Tanita,¹ Yoshitaka Koseki,¹ Ryuju Suzuki,¹ Anh. T. N. Dao,¹ Hitoshi Kasai¹

Keywords: Drug Delivery System; Reprecipitation Method; Anticancer Drug

In recent years, drug nanoparticles called nano-prodrugs (NPDs), which are composed only prodrug molecules, have been proposed and fabricated. The NPDs have a higher drug loading ratio than conventional nanodrugs using carrier, and there are many reports on various NPDs, which composed of substituents-conjugated SN-38.^{1,2} Most of these SN-38 derivative NPDs exhibits relatively higher pharmacological activity *in vitro* compared to irinotecan, a clinically used water-soluble prodrug of SN-38. However, it was concerned that those SN-38 derivative NPDs would be partially dissociated in blood through esterase-induced metabolism of the ester bond that connects SN-38 to the substituents. Therefore, it is necessary to develop novel NPDs that release SN-38 only after accumulated in tumor tissues. In this study, we focused on glutathione (GSH) as a cancer cell-specific trigger. GSH is a tripeptide that reduce disulfide (S-S) bond and presents at high concentration in cancer cells (ca. 10 mM). It was hypothesized that the prodrugs with S-S bond in their molecular design were able to release a drug only inside cancer cells.

SN-38 prodrugs with S-S bond (SNC4DC) were synthesized (Fig. 1 (a)). Subsequently, the obtained SN-38 prodrugs were fabricated into novel NPDs and followed by evaluation of their drug release behavior and *in vivo* anticancer activities. It was showed that SNC4DC was released SN-38 monomer under S-S bond reducing conditions by intramolecular cyclization. As shown in Figure 1 (b), the SNC4DC NPDs- administered group showed the higher activity compared to the irinotecan-administered groups.

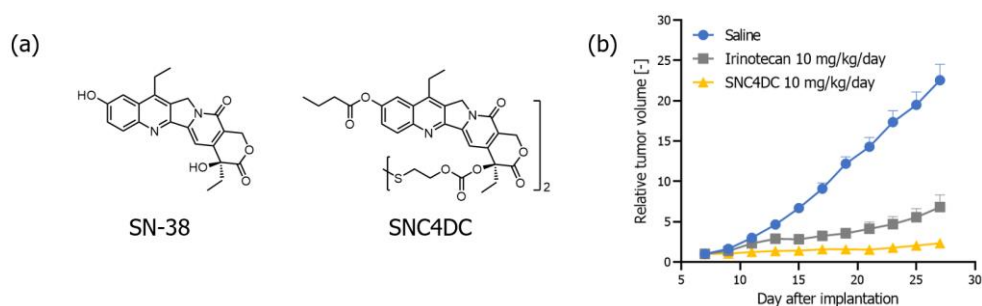


Figure 1. (a) Chemical structure of SN-38 and SN-38 prodrug, (b) *In vivo* experiment of SNC4DC NPDs. The relative tumor volume was determined as V/V_0 (V_0 was the initial tumor volume before treatment).

1) Y. Koseki *et al.*, *Bull. Chem. Soc. Jpn.* **2019**, 92, 1305–1313.

2) K. Tanita *et al.*, *Chem. Lett.* **2020**, 49, 222–224.

N メチルペプチドに適用可能なカープラス式の導出

(東大院工¹・東大院薬²) ○白鳥 陽太¹・上田 卓見²・竹内 恒²・森本 淳平¹・山東 信介¹

Parameterization of Karplus Equation for *N*-Methylated Peptides (¹*Graduate School of Engineering, The University of Tokyo*, ²*Graduate School of Pharmaceutical Sciences, The University of Tokyo*) ○Yota Shiratori,¹ Takumi Ueda,² Koh Takeuchi,² Jumpei Morimoto,¹ Shinsuke Sando¹

For structure determination of peptides, the NOE intensity which depends on the internuclear distance, and the spin-spin coupling constant $^3J_{\text{HN-CH}}$ which depends on dihedral angle ϕ , are used. In contrast, for structure determination of *N*-methylated peptides, only NOE has been used. Thus, the available information that can be utilized for structure determination is less for *N*-methylated peptides than standard peptides, and the accuracy of structure determination is lower. A method to estimate ϕ angle of *N*-methylated peptides has been desired to improve the accuracy of structure determination.

For peptides, the correlation between dihedral angle ϕ and spin-spin coupling constant $^3J_{\text{HN-CH}}$ is described by a Karplus equation. Therefore, ϕ angle of peptides in solution can be estimated from experimental 3J values and the Karplus equation. However, because amide protons are missing due to *N*-methylations, this Karplus equation cannot be applied to *N*-methylated peptides, making it difficult to estimate the ϕ angle of *N*-methylated peptides. In this study, we clarified the relationship between the backbone ϕ angle and spin-spin coupling constant $^3J_{\text{CN-CH}}$ through NMR measurements of cyclic peptides containing *N*-methylalanine residues¹⁾ and derived a Karplus equation which can be applied to *N*-methylated peptides.

Keywords : *N*-Methylated Peptides; Karplus Equation; Nuclear Magnetic Resonance (NMR); Structure Analysis

通常、ペプチドの立体構造推定には、核間距離に依存する NOE 強度と二面角 ϕ に依存するスピン-スピンカップリング定数($^3J_{\text{HN-CH}}$)を用いる。これに対して、*N* メチルペプチドの立体構造推定には NOE のみが用いられてきた。そのため、ペプチドと比較して、立体構造推定に利用できる実験値が少なく、立体構造推定の精度が低い。従って、立体構造推定の精度を上げるために、*N* メチルペプチドの二面角を推定する手法が望まれる。

ペプチドの二面角 ϕ と $^3J_{\text{HN-CH}}$ 値の相関はカープラス式によって記述され、 3J 値の測定によりペプチドの二面角 ϕ が推定できる。*N* メチルペプチドについては、*N* メチル化によってアミドプロトンが失われており、既存のペプチドのカープラス式が適用できないため、二面角 ϕ の推定が困難である。そこで本研究では、*N* メチルアラニン残基を含む環状ペプチド¹⁾の NMR 測定を通じて二面角 ϕ と $^3J_{\text{CN-CH}}$ 値との関係を明らかにし、*N* メチルペプチドに適用可能なカープラス式を導出した。

- 1) J. Chatterjee, D. Mierke, H. Kessler, *J. Am. Chem. Soc.* **2006**, 128, 15164.

標的タンパク質阻害する非天然アミノ酸配列を移植した人工チオペプチドの開発

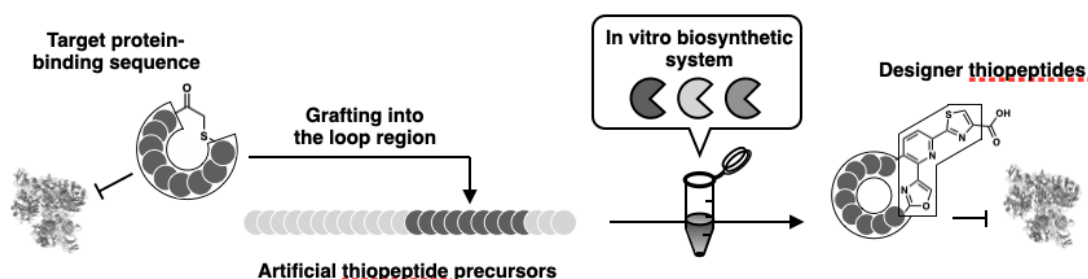
(東京大学¹) ○成見 翔¹、宮入 恭平¹、後藤 佑樹¹、菅 裕明¹

Development of designer thiopeptides with grafted noncanonical sequences inhibiting a target protein of interest (¹*Graduate School of Science, The University of Tokyo*) ○Kakeru Narumi¹, Kyohei Miyairi¹, Yuki Goto¹, Hiroaki Suga¹

Thiopeptides, a class of natural product peptides, commonly have characteristic backbone heterocycles such as azoles and ring-closing pyridine moiety. Because of their enhanced hydrophobicity compared to backbone amides, thiopeptides often show cell membrane permeability and inhibit intracellular targets. Therefore, thiopeptides have been utilized as promising candidates for drug discovery. However, the sources of bioactive thiopeptides have been limited to native natural products and their derivatives, and thus the development of thiopeptide drugs with the desired activity has required extensive screening and serendipity. Towards the on-demand design of de novo thiopeptides inhibiting proteins of interest, we aim to establish a system for the development of designer thiopeptides with artificial loop sequences targeting a specific protein.

Our group has previously reconstituted the biosynthetic pathway of a thiopeptide lactazole *in vitro* and demonstrated the production of various thiopeptide analogs containing artificial sequence compositions²⁾. In this study, several artificial thiopeptide precursors, in which β -galactosidase- or SIRT2-binding sequences characterized by *in vitro* selection inhibitory cyclic peptides³⁾ are grafted into the loop region, were designed. One-pot expression and posttranslational modification of these chimeric precursors in the *in vitro* biosynthetic system led to the objective designer of thiopeptides. The resulting thiopeptides retained the designed inhibitory activity against the targets. This result opens a way to develop de novo thiopeptides with the desired bioactivity.

Keywords: Peptidic natural products; Peptide drugs; Posttranslational modification



1) The transcription factor FOXM1 is a cellular target of the natural product thiostrepton. Hegde, N., Sanders, D., Rodriguez, R. et al. *Nat. Chem.* **2011**, 3, 725–731.

2) Minimal lactazole scaffold for *in vitro* thiopeptide bioengineering, Alexander A. Vinogradov, et al. *Nat. Commun.* **2020**, 11, 2272.

3) Discovery of Macrocyclic Peptides Armed with a Mechanism-Based Warhead: Isoform-Selective Inhibition of Human Deacetylase SIRT2, J. Morimoto et al. *Angew. Chem. Int. Ed.* **2012**, 51, 14.

化学合成を必要としない酵素的ベンゼン水酸化反応を指向した、天然物デコイ分子応答シトクロム P450BM3 変異体の指向性進化法による開発

(名大院理¹・理研 Spring-8²) ○横山 侑弥¹・唐澤 昌之¹・有安 真也¹・愛場 雄一郎¹・杉本 宏²・荘司 長三¹

Directed Evolution of Cytochrome P450BM3 for Responding Natural Products as Decoy Molecules for Direct Benzene Hydroxylation without Chemical Synthesis (¹*Graduate School of Science, Nagoya University*, ²*RIKEN, Spring-8*) ○Yuya Yokoyama,¹ Masayuki Karasawa,¹ Shinya Ariyasu,¹ Yuichiro Aiba,¹ Hiroshi Sugimoto,² Osami Shoji¹

Cytochrome P450BM3 (P450BM3) catalyzes efficient hydroxylation of long-chain fatty acids. Our research group has reported that synthetic dummy substrates “Decoy Molecules” enable hydroxylation of non-native substrates such as benzene by P450BM3.¹⁾ In this research, we aim at developing the reaction system without synthesis and addition of decoy molecules. Therefore, we applied directed evolution in order to engineer P450BM3 mutants recognizing C10-acyl homoserine lactone (C10-AHL), produced by a kind of bacteria, as a decoy molecule. After four rounds of evolution through screening of 5472 mutants by whole-cell benzene hydroxylation in the presence of C10-AHL, the evolved P450BM3 mutant shows about 70-fold higher activity than WT with C10-AHL. We will discuss the evolutionary trajectory and the detail of mutants including X-ray crystal structures and binding affinities against C10-AHL. **Keywords :** *Cytochrome P450; Decoy Molecules; Directed Evolution; N-Acyl Homoserine Lactone; Direct Benzene Hydroxylation*

当研究室では、長鎖脂肪酸を高効率に水酸化するシトクロム P450BM3 に対して、天然基質を模倣して化学合成したデコイ分子の添加によるベンゼンなどの非天然基質の水酸化を報告している¹⁾。本研究では、既存のデコイ分子と似た骨格を有し、一部の細菌が分泌する C10-アシルホモセリンラクトン (C10-AHL) に着目し、C10-AHL に応答して高い活性を示す P450BM3 変異体を開発し、C10-AHL 分泌菌と P450BM3 変異体発現大腸菌の共培養によるデコイ分子の合成と添加が不要な反応系開発を目的とした (図 1)。

計 5472 変異体を C10-AHL 存在下での菌体内ベンゼン水酸化反応によってスクリーニングし、四世代に渡る指向性進化を実施したところ、図 2 のような各世代の変異体が得られ、最終的に開発した第四世代変異体は C10-AHL 存在下で野生型の約 70 倍の活性を示した。現在、開発した変異体の結晶構造解析や C10-AHL との結合親和性などを調査しており、進化の過程と併せて報告する。

1) O. Shoji, *et. al.*, *Angew. Chem. Int. Ed.* **2017**, 56, 10324-10329.

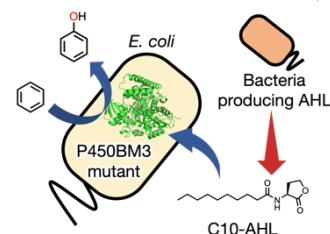


図 1 C10-AHL 分泌菌を用いた菌体内ベンゼン水酸化反応。

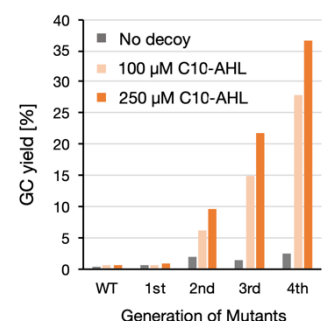


図 2 開発した変異体による菌体内ベンゼン水酸化活性。

金属配位によって構築される剛直なヘムタンパク質多量体

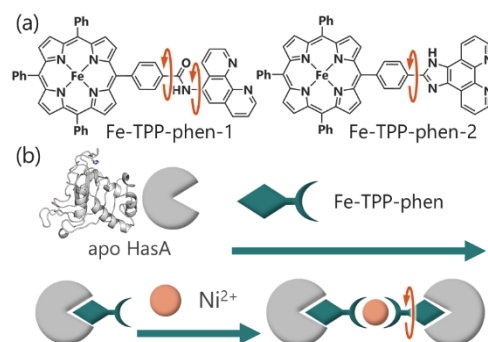
(名大院理¹・理研 SPring-8²) ○稲葉 大晃¹・四坂 勇磨¹・上田 我竜¹・榊原 えりか¹・有安 真也¹・愛場 雄一郎¹・杉本 宏²・荘司 長三¹

The creation of rigid hemoprotein multimers triggered by metal coordination (¹*Graduate School of Science, Nagoya University*, ²*RIKEN SPring-8*) ○Hiroaki Inaba¹, Yuma Shisaka¹, Garyo Ueda¹, Erika Sakakibara¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹

Heme acquisition system protein A (HasA) can capture various synthetic complexes other than heme such as Fe-tetraphenylporphyrin (Fe-TPP)^{[1][2]}. In this study, we have attempted to construct HasA multimers using a metal coordination site rigidly linked with the phenyl group of Fe-TPP (Fig.). Because this rigid structure can restrict the motion of multimers to rotary motion along a limited number of axes of the porphyrin derivatives, the multimer can be applied to recognition of biomolecules using interface between HasAs. We designed two porphyrin complexes linked with a phenanthroline moiety by two different linkers and successfully incorporated Fe-TPP-phen-1 into HasA. After adding Ni²⁺ ion to the solution of Fe-TPP-phen-1 HasA, the results of size-exclusion chromatography and UV/Vis spectroscopy suggest formation of HasA dimer. Moreover, structural prediction using a molecular mechanics method suggests the HasA dimer can be constructed without steric hindrance between HasAs.

Keywords : Hemoprotein; Porphyrin; Supramolecular chemistry

緑膿菌などのグラム陰性菌が分泌するヘム獲得タンパク質 (HasA) は、一般的にヘムタンパク質への複合化が困難な、鉄テトラフェニルポルフィリン (Fe-TPP) などの人工金属錯体を捕捉できる^{[1][2]}。そこで、TPP のフェニル基から配位子を連結することで、金属配位による HasA 多量体の構築が可能であると考えた。また、リンカー部分を剛直に設計することで、HasA 多量体の運動を金属錯体の回転運動に制限し、界面を利用して生体分子を認識できると予想している。剛直な HasA 多量体の構築を目指し、剛直な金属錯体として、Fe-TPP とフェナントロリン (phen) を剛直に連結した錯体 (Fe-TPP-phen) をリンカーの異なる 2 種類を設計した (図 a)。合成した Fe-TPP-phen-1 と HasA を混合することで複合化を行った。カラムクロマトグラフィーによる精製を行い、UV/Vis スペクトルと ESI-TOF-MS の結果から複合体形成を確認した。精製した複合体に Ni²⁺ を添加したところ、サイズ排除クロマトグラフィーと UV/Vis スペクトルの結果から 2 量体の形成が示唆された (図 b)。さらに、MM 法による 2 量体構造の予測を行ったところ、立体障害なく構築可能であることが示唆された。現在は、Fe-TPP-phen-2 についても同様の検討を行うとともに、得られた HasA 多量体の同定を行っている。



[1] H. Uehara, *et al.*, *Angew. Chem. Int. Ed.* **2017**, 56, 15279. [2] Y. Shisaka, *et al.*, *Manuscript in preparation*.

Visible light driven NADH regeneration using a system of water-soluble zinc porphyrin and homogeneously polymer-dispersed rhodium nanoparticles and application to CO₂ fixation with enzyme

(¹Graduate School of Science, Osaka City University, Research Center for Artificial Photosynthesis, Osaka City University) ○Takayuki Katagiri,¹ Masanobu Higashi,² Yutaka Amao^{1,2}

Keywords: Coenzyme; Visible light; Carbon-carbon bond formation; Metal nano particles; Homogeneous catalyst

Enzymes have high catalytic activity and selectivity in ambient conditions. NADH is widely used as a cofactor with the function of electron donor in enzymatic redox reactions. In general, the supply of NADH is a major challenging factor due to its high cost and low stability, which have stimulated the development of NADH regeneration systems.¹ Recently, photochemical NADH regeneration has attracted much attention because solar energy is clean, inexpensive, abundant, and renewable. However, in the direct NAD⁺ photoreduction, it has been frequently reported that enzymatically inactive byproducts (1,2- or 1,6-NADH isomers, and NAD dimer) can be formed.² In this study, we devoted to constructing the novel and simple visible light driven regioselective NADH regeneration system. As far as we have surveyed, we discovered the catalytic activity of Rh nanoparticles dispersed by polyvinylpyrrolidone (Rh-PVP) in the visible light driven selective NADH regeneration for the first time. This system consists of triethanolamine (TEOA) as an electron donor, zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) as a photosensitizer, and Rh-PVP (Fig. 1). Only 1,4-NADH was produced as the reduction product of NAD⁺, which was validated by HPLC analysis and an enzymatic assay. It was also proposed an NADH regeneration mechanism. First, NAD⁺ was adsorbed to the surface of Rh-PVP with the carbonyl of amide. A hydride species at the surface of Rh-PVP could attack the C4 position of nicotinamide and form 1,4-NADH directly. The hydride transfer is the key to avoiding the radical intermediate and NAD dimer formation. In addition, we constructed the photochemical conversion system combined NADH regeneration system and NAD⁺-dependent malate dehydrogenase. By using this system, we have successfully achieved the L-malate synthesis based on the CO₂ fixation to pyruvate with visible light energy.

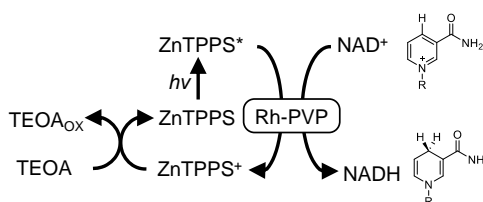


Fig. 1. Scheme of visible light driven NADH regeneration with the system consisted of TEOA, ZnTPPS, Rh-PVP, and NAD⁺.

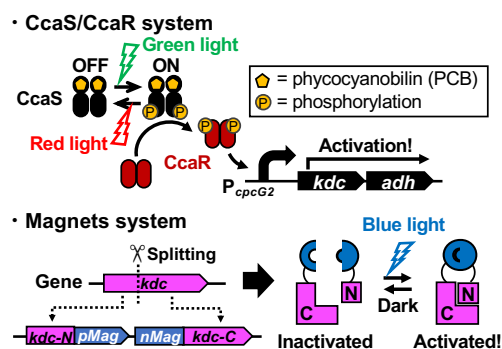
- 1) X. Wang, T. Saba, H. H. P. Yiu, R. F. Howe, J. A. Anderson, J. Shi, *Chem*, **2017**, 2, 621.
- 2) T. Saba, J. Li, J. W. H. Burnett, R. F. Howe, P. N. Kechagiopoulos, X. Wang, *ACS Catal.*, **2021**, 11, 283.

Efficient Production of Value-added Chemicals in Cyanobacteria by Metabolic Regulation Using Light Sensor Proteins

(¹Graduate School of Engineering, Tokyo University of Agriculture and Technology, ²University of California Davis) ○ Shunichi Kobayashi,¹ Shota Atsumi,² Kazunori Ikebukuro,¹ Ryutaro Asano¹

Keywords: Cyanobacteria; Light Sensor Protein; Light-regulated Gene Expression; Metabolic Engineering; Synthetic Biology

Cyanobacteria have been engineered by integrating heterologous biosynthetic pathways to produce value-added chemicals from CO₂. As the timings of gene expression and/or enzyme activation are critical factors for efficient production, the chemical inducer-dependent production has been demonstrated. However, the use of the chemical inducers is not ideal for scale-up production because of its high operation costs. In this study, to avoid the use of chemical inducers, we attempted the light-induced production of valuable alcohols in *Synechocystis* sp. PCC 6803 (PCC 6803) using two light sensor proteins, CcaS and Magnets (Fig.). The green light sensor protein CcaS regulates the ON/OFF of gene expression by green/red light, coworking with transcription factor CcaR¹. Whereas the Magnets consisting of pMag and nMag forms heterodimer by blue light².



Isobutanol and 3-methyl-1-butanol (3MB) are valuable alcohols as alternatives to gasoline and can be produced by integrating two enzymes, keto-acid decarboxylase (KDC) and alcohol dehydrogenase (ADH), into the amino acid biosynthesis pathway³. When the *kdc* and *adh* were expressed under the control of CcaS/CcaR system, we found that the production of alcohols was induced under red and green light illumination and repressed under red light illumination alone. Production titers of isobutanol and 3MB reached 238 mg L⁻¹ and 75 mg L⁻¹, respectively, and these values are comparable to those reported in previous studies using chemical inducers. Then, after splitting KDC into two fragments, we designed a blue light responsive KDC (OptoKDC) by fusing pMag and nMag to the N- and C-terminal fragment of the split KDC, respectively (Fig.). When the OptoKDC was expressed in *E. coli*, we found that isobutanol production was induced by blue light and repressed by dark or red light, suggesting that the OptoKDC has a potential for application in PCC 6803. This study demonstrates the potential use of the light sensor proteins for production of valuable chemicals in cyanobacteria.

1) Y. Hirose, T. Shimada, R. Narikawa, M. Katayama, M. Ikeuchi, *Proc. Natl. Acad. Sci. USA*. **2008**, 105, 9528-33, 2) F. Kawano, H. Suzuki, A. Furuya, M. Sato, *Nat. Commun.* **2015**, 6, 6256, 3) S. Atsumi, W. Higashide, J. C. Liao, *Nat. Biotechnol.* **2009**, 27, 1177-80

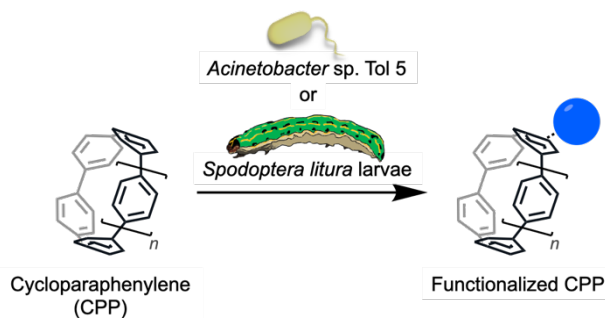
Functionalization of cycloparaphenylene by biocatalysts

(¹Research Center for Materials Science, Nagoya University, ²Graduate School of Engineering, Nagoya University, ³Graduate School of Science, Nagoya University, ⁴Institute of Transformative Bio-Molecules (WPI-ITbM)) ○ Atsushi Usami¹, Kazuma Amaike¹, Katsutoshi Hori², Kenichiro Itami^{3,4}

Keywords: Molecular Nanocarbons, Cycloparaphenylene, Biotransformation, Biocatalysts

Molecular nanocarbons, nanometer-sized carbon materials composed of polycyclic aromatic hydrocarbons, have various physical properties and are applicable to materials chemistry.¹ Recently, some molecular nanocarbons have been revealed to have new properties and applicability through functionalization-based structural modifications.² However, because the molecular nanocarbon that can be regioselective functionalized is limited, there is still a requirement for a universal method to break the status quo.

We have recently focused on a biotransformation reaction, known as a highly regioselective transformation reaction, as a new way to functionalize molecular nanocarbon derivatives. This represents a green process that can be used to realize the production of chemicals that are inaccessible by traditional organic synthesis. Biocatalysts we chosen are two organisms that are resistant to various organic compounds. One is a toluene-degrading Gram-negative bacterium *Acinetobacter* sp. Tol 5, and the other is a polyphagous insect, *Spodoptera litura* larvae (Lepidoptera, Noctuidae).^{3,4} In this study, the C-H bond functionalization of cycloparaphenylene and its derivatives, the shortest sidewall segment of carbon nanotubes, were investigated by biocatalysts.



1) a) Cheung, Y. K.; Watanabe, K.; Segawa, Y.; Itami, K. *Nat. Chem.* **2021**, *13*, 255. b) Matsuoka, W.; Ito, H.; Sarlah, D.; Itami, K. *Nat. Commun.* **2021**, *12*, 3940. c) Segawa, Y.; Kuwayama, M.; Hijikata, Y.; Fushimi, M.; Nishihara, T.; Pirillo, J.; Shirasaki, J.; Kubota, N.; Itami, K. *Science* **2019**, *365*, 272. d) Povie, G.; Segawa, Y.; Nishihara, T.; Miyauchi, Y.; Itami, K. *Science* **2017**, *356*, 172.

2) a) Nagase, M.; Kato, K.; Yagi, A.; Segawa, Y.; Itami, K. *Beilstein J. Org. Chem.* **2020**, *16*, 391. b) Kubota, N.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 1356.

3) a) Hori, K.; Yamashita, S.; Ishii, S.; Kitagawa, M.; Tanji, Y.; Unno, H. *J. Chem. Engineer. Jpn.* **2001**, *34*, 1120. b) Usami, A.; Ishikawa, M.; Hori, K. *Biosci. Biotechnol. Biochem.* **2018**, *82*, 2012.

4) Marumoto, S.; Okuno, Y.; Miyamoto, Y.; Miyazawa, M. *J. Mol. Catal., B Enzym.* **2015**, *115*, 160.

[G201-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Eiji Nakata, Noriko tarashima

Sat. Mar 26, 2022 9:00 AM - 11:20 AM G201 (Online Meeting)

[G201-4am-01] Cosolvent improves the enzymatic ligation of DNA origami○Arivazhagan Rajendran¹, Kirankumar Krishnamurthy¹, Eiji Nakata¹, Takashi Morii¹ (1. Institute of Advanced Energy, Kyoto University)

9:00 AM - 9:20 AM

[G201-4am-02] Construction of a CO₂ fixing enzyme assembly on 3D DNA nanostructure○Hiroaki Konishi¹, Huyen Dinh², Eiji Nakata^{1,2}, Takashi Morii^{1,2}, Haruyuki Atomi³ (1. Graduate School of Energy Science, Kyoto University, 2. Institute of Advanced Energy, Kyoto University, 3. Graduate School of Engineering, Kyoto University)

9:20 AM - 9:40 AM

[G201-4am-03] Photoreactive molecular glue for enhancing the efficacy of DNA aptamers○Ai Kohata¹, Kou Okuro², Takuzo Aida¹ (1. The University of Tokyo, 2. The University of Hong Kong)

9:40 AM - 10:00 AM

[G201-4am-04] Effect of neuronal RNA G-quadruplex structures on cellular phase separation○Sefan Asamitsu¹, Moe Kawasaki², Yuki Hirose³, Yasushi Yabuki², Gengo Kashiwazaki⁴, Anandhakumar Anandhakumar⁵, Toshikazu Bando³, Hiroshi Sugiyama^{3,6}, Norifumi Shioda² (1. RIKEN Center for Biosystems Dynamics Research, 2. Institute of Molecular Embryology and Genetics, Kumamoto University, 3. Graduate School of Science, Kyoto University, 4. Graduate School of Agriculture, Kindai University, 5. Ludwig Cancer Research Oxford, University of Oxford, 6. Institute for Integrated Cell-Material Sciences, Kyoto University)

10:00 AM - 10:20 AM

[G201-4am-05] Replacement of oxygen with sulfur on the furanose ring of cyclic dinucleotide enhances the immunostimulatory effect by STING activation.○Noriko Saito tarashima¹, Mao Kinoshita¹, Aki kondo¹, Noriaki Minakawa¹ (1. Tokushima Univ.)

10:20 AM - 10:40 AM

[G201-4am-06] Cancer-cell-selective cytotoxicity of a dicopper complex having 1,8-naphthalimide as a targeting unit○Machi Hata¹, Yutaka Hitomi¹, Masahito Kodera¹ (1. Doshisha University)

10:40 AM - 11:00 AM

[G201-4am-07] Development of a peptide forming a hydrogel with higher-order structural transition and application to tissue regeneration○Atsuya Yaguchi¹, Hirotsugu Hiramatsu², Itsuki Ajioka^{3,4}, Takahiro Muraoka^{1,4} (1. Tokyo University of Agriculture and Technology, 2. National Yang Ming Chiao Tung University, 3. Tokyo Medical and Dental University, 4. KISTEC)

11:00 AM - 11:20 AM

Cosolvent Improves the Enzymatic Ligation of DNA Origami

(¹*Institute of Advanced Energy, Kyoto University*) ○Arivazhagan Rajendran, Kirankumar Krishnamurthy, Eiji Nakata, Takashi Morii

Keywords: Enzymatic Ligation; Cosolvent; DNA Ligase; DNA Origami; DNA Nanotechnology

The invention of structural DNA nanotechnology has led to the creation of various two- (2D) and three-dimensional (3D) structures in the size range of ~10-20 nm. During the past one and a half decades, the field has seen enormous growth due to the addition of the scaffolded DNA origami method¹ which enabled the synthesis of nanostructures with ~100 nm in diameter. Since then various structures have been synthesized with sub-nanometer addressability, and also self-assembled to create even larger structures in micrometer scale.² These structures have been used for the nanopatterning of various nanoparticles and quantum dots, attachment of carbon nanotubes, immobilization of biomolecules, carriers of drugs, and for the analysis of single molecular reactions and processes.³⁻⁴

Despite the proof-of-concept demonstrations on the applications, the real-life utilization of the origami materials is limited due to their insufficient stability. There have been limited efforts to stabilize the DNA origami against thermal, mechanical, and chemical modifications. These limited strategies relied either on the enzymatic ligation of staple strand nicks or by photo-chemically cross-linking the two strands of duplex DNA in the origami. We have recently performed a detailed characterization on the enzymatic ligation of 2D DNA origami to establish the optimized conditions.⁵ Under the optimized conditions, up to 10 staples ligation with a maximum ligation efficiency of 55% was achieved. Also, the ligation is found to increase the thermal stability of the origami as low as 5°C to as high as 20°C, depending on the structure. Besides our initial demonstration, due to the tightly packed anti-parallelly oriented arrangement of multiple duplexes in the origami and the difficulties in the accessibility of the nicks by ligase, enzymatic ligation was only partly successful. To further enhance the enzymatic ligation of origami, we have carried out the effect of cosolvent, and identified the best performing cosolvent. Our results indicated that the cosolvent enhances the enzymatic ligation.

1) P. W. K. Rothmund, *Nature* **2006**, *440*, 297. 2) A. Rajendran, M. Endo, Y. Katsuda, K. Hidaka, H. Sugiyama, *ACS Nano* **2011**, *5*, 665. 3) A. Rajendran, M. Endo, H. Sugiyama, *Angew. Chem. Int. Ed.* **2012**, *51*, 874. 4) A. Rajendran, E. Nakata, S. Nakano, T. Morii, *ChemBioChem* **2017**, *18*, 696. 5) A. Rajendran, K. Krishnamurthy, A. Giridasappa, E. Nakata, T. Morii, *Nucleic Acids Res.* **2021**, *49*, 7884.

3次元 DNA ナノ構造体を用いた CO₂ 固定化酵素の集積化

(京大院エネ¹・京大エネ研²・京大院工³) ○小西 宏明¹・Dinh Huyen²・中田 栄司^{1,2}・跡見 晴幸³・森井 孝^{1,2}

Construction of a CO₂ fixing enzyme assembly on 3D DNA nanostructure (¹*Graduate School of Energy Science, Kyoto University*, ²*Institute of Advanced Energy, Kyoto University*, ³*Graduate School of Engineering, Kyoto University*) ○Hiroaki Konishi¹, Dinh Huyen², Eiji Nakata^{1,2}, Haruyuki Atomi³, Takashi Morii^{1,2}

Enzymes in living cells are known to be spatially restricted in a specific manner, such as the oligomeric states of enzymes and the arrangement of sequential enzymes in compartments. It is thought that metabolic enzymes are also organized in such a way to control the concentration of intermediates and the efficiency of cascade reactions. Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO), which is involved in carbon fixation reactions in many autotrophic organisms, forms multimers and fills up the protein compartment carboxysome with carbonic anhydrase¹⁾, but the effect of enzyme cluster is not clear. By construction of a packed condition of RuBisCO complexes in vitro, we can analyze the mechanism of efficient metabolic reactions in vivo. In this study, we investigated the method of assembling RuBisCO derived from the thermophilic archaeon *Thermococcus kodakarensis* (*Tk*-RuBisCO)²⁾ on DNA nanostructures constructed by DNA origami method³⁾ via DNA-binding proteins⁴⁾.

Keywords : DNA nanostructure, RuBisCO, protein adaptor

生体細胞内での酵素は、単一の酵素が多量体を構築したり、複数の酵素が区画内で連続して配置され組織を形成することで、反応物や中間体の濃度を制御して反応の効率化を実現していると考えられる。独立栄養生物内に存在する酵素 RuBisCO は二酸化炭素固定化反応を担う酵素であり、区画の中で多量体が集合して高効率な反応を進める系が存在する¹⁾が、集積化による影響は不明である。このような酵素複合体を試験管内で再現することで、生体内での高効率な代謝反応の機構を解析できる。本研究では、ホモ十量体からなる好熱性古細菌由来の RuBisCO (*Tk*-RuBisCO)²⁾ に着目し、DNA オリガミ法³⁾で構築した DNA ナノ構造体上に、DNA 結合性タンパク質由来のタンパク質アダプター⁴⁾を介して集積させる方法を検討した。



1) Bonacci, W. *Proc. Natl. Acad. Sci. U.S.A.* 2012, **109**, 478-483. 2) Kitano K.; Maeda N.; Fukui T.; Atomi H.; Imanaka T.; Miki, K.; *Structure* 2001, **9**, 473-481. 3) P. W. K. Rothmund, *Nature* 2006, **440**, 297-302. 4) Ngo, T. A.; Nakata, E.; Saimura, M.; Kodaki, T.; Morii, T. *Methods* 2014, **67**, 142-150.

Photoreactive Molecular Glue for Enhancing the Efficacy of DNA Aptamers

(¹Graduate School of Engineering, The University of Tokyo, ²Faculty of Science, The University of Hong Kong) ○Ai Kohata,¹ Kou Okuro,² Takuzo Aida¹

Keywords: Molecular Glue; Photo-Immobilization; DNA Aptamer; Protein

DNA aptamers are attractive synthetic analogues of antibodies because of their high target selectivity and physicochemical stability. However, for practical utilization under physiological conditions, their binding affinities to target proteins are not sufficiently high. To overcome this problem, DNA aptamers with photoreactive motifs have been developed for covalent conjugation with target proteins. However, chemically modified aptamers are not guaranteed to maintain their intrinsic affinities to target proteins.

In the present study, we developed “photoreactive molecular glue (^{BP}Glue-N₃)” that can provide a universal strategy for enhancing the efficacy of DNA aptamers.¹ ^{BP}Glue-N₃ noncovalently adheres to a DNA aptamer/target protein conjugate, and then covalently stabilizes it upon UV exposure. By means of ^{BP}Glue-N₃-mediated photocrosslinking, we successfully enhanced the inhibitory effect of DNA aptamer SL1, which selectively binds to a receptor protein c-Met,² against its interaction with hepatocyte growth factor (HGF; Figure 1). Without the UV exposure, ^{BP}Glue-N₃ readily comes off the aptamer, resulting in the negligibly weak inhibition of the HGF/c-Met interaction.

1) A. Kohata, *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 13937. 2) R. Ueki, *et al.*, *Chem. Commun.* **2014**, *50*, 13131.

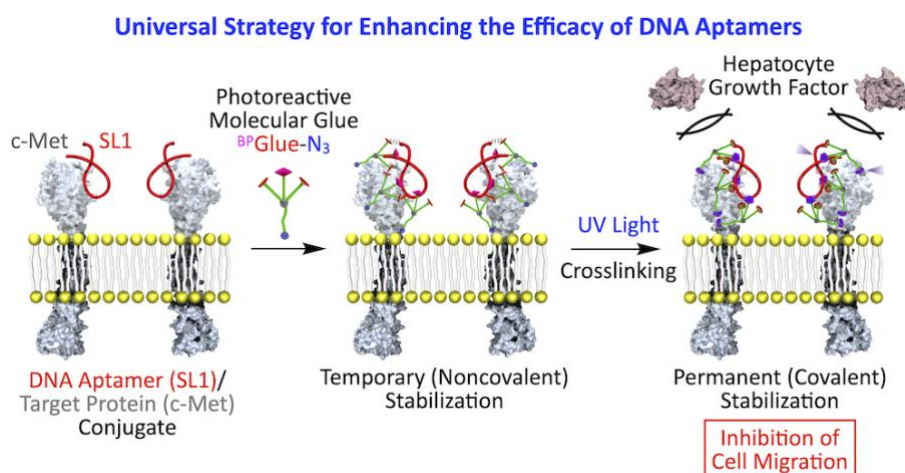


Fig. 1 Schematic illustration of how the efficacy of DNA aptamer (SL1) can be enhanced by photoreactive molecular glue (^{BP}Glue-N₃).

神経細胞におけるグアニン四重鎖 RNA 構造の相分離現象に与える影響

(理化学研究所 生命機能科学研究センター¹、熊本大学発生医学研究所²、京都大学大学院理学研究科³、近畿大学農学部⁴、Ludwig Cancer Research Oxford, University of Oxford⁵、京都大学物質-細胞統合システム拠点⁶) ○朝光 世煌¹、川嵯 萌²、廣瀬 優希³、矢吹 悌²、柏崎 玄伍⁴、Anandhakumar Chandran⁵、板東 俊和³、杉山 弘^{3,6}、塩田 倫史²

Effect of neuronal RNA G-quadruplex structures on cellular phase separation (¹RIKEN Center for Biosystems Dynamics Research, ²Institute of Molecular Embryology and Genetics, Kumamoto University, ³Graduate School of Science, Kyoto University, ⁴Graduate School of Agriculture, Kindai University, ⁵Ludwig Cancer Research Oxford, University of Oxford, ⁶Institute for Integrated Cell-Material Sciences, Kyoto University) ○Sefan Asamitsu¹, Moe Kawasaki², Yuki Hirose³, Yasushi Yabuki², Gengo Kashiwazaki⁴, Anandhakumar Anandhakumar⁵, Toshikazu Bando³, Hiroshi Sugiyama^{3,6}, Norifumi Shioda²

It is known that a continuous guanine-rich RNA sequence forms a quadruple-stranded structure, termed a G-quadruplex. It has been suggested that there are about 4,000 G4RNAs in the human transcriptome, but most of their physiological functions are still unknown. In this presentation, we will report the results of our study on the effect of G4RNA structures on cellular phase separation in neurons.

Keywords : RNA secondary structure; G-quadruplex; Phase separation; Neuron

連続したグアニンを豊富に含む RNA 配列では、4 本の鎖からなる四重鎖構造 (RNA グアニン四重鎖: G4RNA) が形成されることが知られている。G4RNA は、ヒトのトランスクリプトームにおいて約 4,000 個存在することが示唆されているが、そのほとんどの生理機能は未だ不明である。本発表では、神経細胞における G4RNA 構造の相分離現象に与える影響に関する研究結果を報告する。

環状ジヌクレオチド糖部 4'位への硫黄原子の導入は STING アゴニスト活性を増強させる

(徳大院薬) ○田良島 典子・木下 真緒・近藤 明希・南川 典昭

Replacement of oxygen with sulfur on the furanose ring of cyclic dinucleotide enhances the immunostimulatory effect by STING activation (*Graduate School of Pharmaceutical Science, Tokushima University*) ○Noriko Saito-Tarashima, Mao Kinoshita, Aki Kondo, Noriaki Minakawa

In this study, we designed and synthesized CDN analogs that have sulfur atoms instead of oxygen atoms in the furanose rings. Evaluation of STING agonist activity in cellular systems has revealed that the 4'-thio modified CDN analogs have greatly enhanced the STING agonist activity. In this presentation, we will report these details.

Keywords : *Cyclic dinucleotides; stimulator of interferon genes; 4'-thionucleic acids*

ヌクレオチド 2 分子から構成される環状化合物である環状ジヌクレオチド類 (cyclic dinucleotides, CDNs) は、哺乳動物細胞において stimulator of interferon genes (STING) のリガンドとして機能し、自然免疫を強く賦活化する。この機構に基づく新たな医薬品の創出へ向け、安定性に優れた CDNs 等価体の創製が求められている。

我々のグループはこれまでにヌクレオチド糖部フラノース環 4'位の酸素原子を硫黄原子へと置換した 4'-チオ核酸類を開発し、このものが高い PDE 抵抗性を発揮することを報告した¹⁾。そこで本研究では、4'-チオヌクレオチドにより構成される CDNs の網羅的合成を計画した。まずはじめに、アデノシン型の CDN である c-di-4'-thioAMP (**1**) および **2** (Figure 1) を合成し、STING を介した自然免疫誘導能を評価した結果、両者は天然型の c-di-AMP と比較して高い自然免疫誘導能を示すことが明らかとなった²⁾。さらに、**1** は c-di-AMP 選択的分解酵素である YybT に対して優れた分解抵抗性を発揮することが示された³⁾。以上の結果を踏まえ、その他複数の 4'-チオ CDNs の合成ならびに活性評価も行ったので、本発表ではそれらの詳細について報告する。

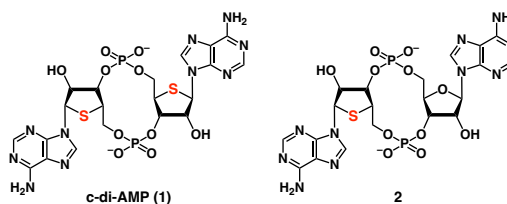


Figure 1 c-Di-4'-thioAMP (**1**) および **2** の構造

1) Synthesis and physical and physiological properties of 4'-thioRNA: application to post-modification of RNA aptamer toward NF- κ B, S. Hoshika, N. Minakawa, A. Matsuda, *Nucleic Acids Res.* **2004**, *32*, 3815.

2) Replacement of oxygen with sulfur on the furanose ring of cyclic dinucleotides enhances the immunostimulatory effect via STING activation, N. Saito-Tarashima, M. Kinoshita, Y. Igata, Y. Kashiwabara, N. Minakawa, *RSC Med. Chem.* **2021**, *12*, 1519.

3) Synthesis and evaluation of c-di-4'-thioAMP as an artificial ligand for c-di-AMP riboswitch, K. Shiraishi, N. Saito-Tarashima, Y. Igata, K. Murakami, Y. Okamoto, Y. Miyake, K. Furukawa, N. Minakawa, *Bioorg. Med. Chem.* **2017**, *25*, 3883.

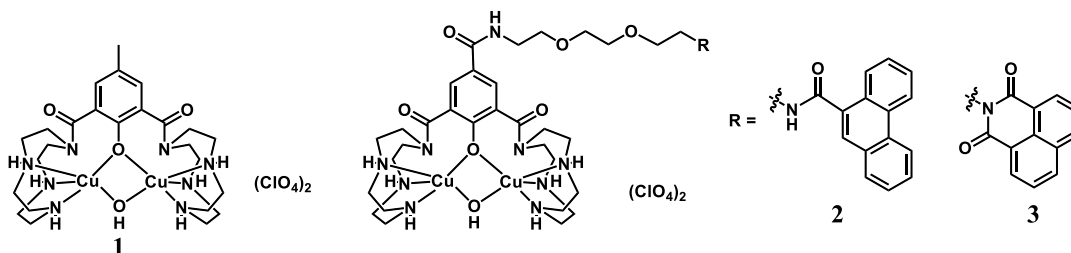
Cancer-cell-selective cytotoxicity of a dicopper complex having 1,8-naphthalimide as a targeting unit

(Graduate School of Science and Engineering, Doshisha University) ○Machi Hata, Yutaka Hitomi, Masahito Kodera

Keywords: Dicopper Complex; DNA Cleavage Activity; Cytotoxicity; Mitochondria

Bleomycin is an antibiotic anticancer agent that shows high catalytic activity in cleavage of double-strand DNA. However, it exerts heavy side effects to lungs in the long-term use.^[1] The reason is that it acts on both cancer and normal cells non-selectively. So, metal complexes exerting cancer-cell-selective cytotoxicity may be useful to develop a new type of anticancer agent that suppresses the side effects. So, we focus on specific environments of cancer cells. The mitochondrial dysfunction in cancer cells increases H₂O₂ concentration. Metal complexes capable of targeting mitochondrial DNA (mtDNA) and activating H₂O₂ may induce mitochondrial apoptosis by cutting mtDNA. This may lead to the development of new anticancer agents that enable the cancer-cell-selective cytotoxicity.

Recently, we reported that a dicopper(II) complex with a *p*-cresol-derived ligand having two amide-tether connected 1,4,7,10-tetraazacyclododecane groups at 2,6-positions (Hbcamide), [Cu₂(μ-OH)(bcamide)](ClO₄)₂ (**1**). This complex shows oxidative DNA cleavage activity in the presence of H₂O₂, but **1** showed relatively low cytotoxicity.^[2] In this study, to enhance the DNA cleavage activity and cytotoxicity by mimicking role of a DNA-targeting site of bleomycin, we synthesized new dicopper complexes having a phenanthrene and 1,8-naphthalimide conjugates as a DNA-targeting, [Cu₂(μ-OH)(bcamide-P3-phen)](ClO₄)₂ (**2**) and [Cu₂(μ-OH)(bcamide-P3-naph)](ClO₄)₂ (**3**). The DNA targeting effects of **2** and **3** were 9-fold higher in DNA cleavage activity, and about 20-fold higher in cytotoxicity than **1**, and **1–3** show cancer-cell-selective cytotoxicity. The intracellular visualization and caspase activity assays revealed that **2** and **3** exerts cytotoxicity via mitochondrial apoptosis. Therefore, the mitochondrial apoptosis may explain the relatively high cancer-cell-selective toxicity of **1–3**. These results may shed light on the development of new anticancer drugs to reduce the heavy side-effects.



[1] S.-X. Huang, Z. Feng, L. Wang, U. Galm, E. Wendt-Pienkowski, D. Yang, M. Tao, J. M. Coughlin, Y. Duan and B. Shen, *J. Am. Chem. Soc.* **2012**, *134*, 13501–13509.

[2] Y. Kadoya, K. Fukui, M. Hata, R. Miyano, Y. Hitomi, S. Yanagisawa, M. Kubo, M. Kodera, *Inorg. Chem.* **2019**, *58*, 14294–14298.

Development of a peptide forming a hydrogel with higher-order structural transition and application to tissue regeneration

(¹Tokyo University of Agriculture and Technology, ²National Yang Ming Chiao Tung University, ³Tokyo Medical and Dental University, ⁴KISTEC) ○Atsuya Yaguchi,¹ Hirotugu Hiramatsu,² Itsuki Ajioka,^{3,4} Takahiro Muraoka^{1,4}

Keywords: Peptides; Self-Assembly; Hydrogel; Higher-Order Structure; Tissue Regeneration

The extracellular matrices (ECMs) provide a biological niche for regulating cellular responses by regulating not only cell adhesion but also the binding and release of secreted proteins. In regenerative medicine, as artificial ECMs, self-assembling peptide hydrogels can be widely used because of their cell-adhesive properties and degradability into chemically-defined molecules. However, incorporating and releasing secreted proteins are generally incompatible, and development of peptidic materials capable of incorporating and releasing secreted proteins remains mostly unexplored.

Here, we developed a novel cell-adhesive fiber-forming peptide allowing efficient incorporation and sustained release of vascular endothelial growth factor (VEGF), and the peptide gel showed cell transplantation-free regenerative therapeutic effects on a subacute-chronic phase mouse stroke model.¹ We focused on dynamic higher-order structural transition as a new approach to achieving efficient protein binding and sustained release functions. The AxxxA and GxxxG motif, amino acid sequences in which two alanines or glycines are present across three residues, found in membrane proteins that transform the structure from α -helix² to β -strand in response to the external environment to form nanofibers.³ Inspired by this dynamic property, we have developed the alternating amphiphilic peptide JigSAP (Ac-RIDARMRADIR-NH₂) with the AxxxA motif. JigSAP formed supramolecular nanofibers and a hydrogel (Fig. 1a) through a helix-to-strand transition (Fig. 1b) under physiological conditions. The fibers were dispersed homogeneously in the hydrogel. The supramolecular properties of JigSAP hydrogel allowed efficient incorporation and sustained release of VEGF-JigSAP (Fig. 1c). JigSAP incorporating VEGF-JigSAP showed enhanced angiogenesis *in vitro* (Fig. 1d) and demonstrated regenerative therapeutic effects in a subacute-chronic phase mouse stroke model.

- 1) A. Yaguchi *et al.*, *Nat. Commun.* **2021**, 12, 6623.
- 2) D. Eisenberg *et al.*, *Biochemistry* **2002**, 41, 5990-5997.
- 3) S. O. Smith *et al.*, *Biochemistry* **2005**, 44, 3591-3597.

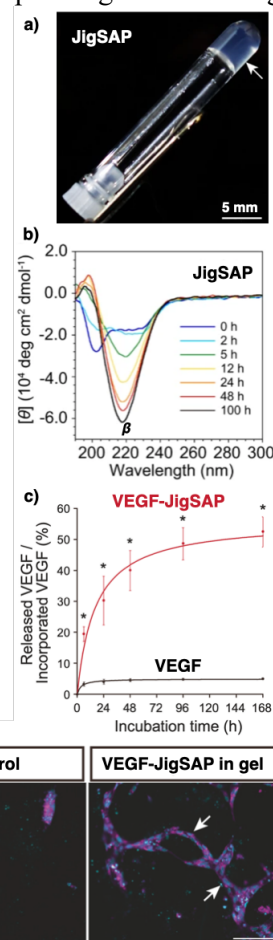


Fig. 1 a) Photograph of JigSAP hydrogel. b) Time-course CD spectral change of JigSAP after dissolved in a buffer. c) Time-course releasing profile of VEGF from JigSAP hydrogel. d) LEL (magenta) and DAPI (cyan) fluorescence images of HUVECs.

Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B**[A202-4am] 19. Colloid and Interface Chemistry**

Chair: Katsuaki Konishi, Hideya Kawasaki

Sat. Mar 26, 2022 9:00 AM - 10:40 AM A202 (Online Meeting)

[A202-4am-01] Self-assembly properties of polyvinylpyrrolidone-protected anisotropic silver plates at air/water interface○Kosuke Sugawa¹, Yutaro Hayakawa¹, Masato Furuya¹, Joe Otsuki¹, Kaoru Tamada² (1. Nihon University, 2. Kyushu University)

9:00 AM - 9:20 AM

[A202-4am-02] Formation and Structural Characterization of Supramolecular Copolymers in Liquid Crystalline Phase○Daiki Morishita¹, Xujie Zhang, Yoshimitsu Itoh¹, Takuzo Aida^{1,2} (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. RIKEN CEMS)

9:20 AM - 9:40 AM

[A202-4am-03] Fluorous Synthetic Channels Enabling both Ultrafast Water Permeation and High Salt Reflection○Shuo CHEN¹, Yoshimitsu ITOH^{1,2}, Ryota HIRAHARA¹, Takeshi KONDA¹, Tsubasa AOKI¹, Kohei SATO¹, Takuzo AIDA^{1,3} (1. The Univ. of Tokyo, 2. PRESTO JST, 3. RIKEN CEMS)

9:40 AM - 10:00 AM

[A202-4am-04] Incorporation of Basic α -Hydroxy Acid Residues into Primitive Polyester Microdroplets for RNA Segregation○Tony Z Jia^{1,2}, Niraja Bapat^{1,3}, Ajay Verma³, Irena Mamajanov¹, H. James Cleaves^{1,2,4}, Kuhan Chandru^{5,6} (1. Earth-Life Science Institute, Tokyo Institute of Technology, 2. Blue Marble Space Institute of Science, 3. Department of Biology, Indian Institute of Science Education and Research, 4. Institute for Advanced Study, 5. Department of Physical Chemistry, University of Chemistry and Technology, Prague, 6. Space Science Centre (ANGKASA), Institute of Climate Change, National University of Malaysia)

10:00 AM - 10:20 AM

[A202-4am-05] Self-Healable and Humidity-Resistant Polymer Glasses: New Strategies Based on Nano-Phase Separation○Yuta Fujisawa¹, Yiling Nan¹, Atsushi Asano², Yu Yanagisawa¹, Keiichi Yano¹, Yoshimitsu Itoh¹, Takuzo Aida^{1,3} (1. The University of Tokyo, 2. National Defense Academy, 3. RIKEN Center for Emergent Matter of Science)

10:20 AM - 10:40 AM

ポリビニルピロリドン保護異方性銀ナノプレートの気／水界面自己集積特性

(日大理工¹・九大先導研²) ○須川 晃資¹・早川祐太郎¹・古谷雅人¹・大月 穰¹・玉田 薫²

Self-assembly properties of polyvinylpyrrolidone-protected anisotropic silver plates at air/water interface (¹College of Science & Technology, Nihon University, ²Institute for Materials Chemistry and Engineering, Kyushu University) ○ Kosuke Sugawa,¹ Yutaro Hayakawa,¹ Masato Furuya,¹ Joe Otsuki,¹ Kaoru Tamada²

Two-dimensional assemblies of metal nanoparticles can be a platform for creating strong bonds with photofunctional molecules. In this study, we report a novel assembly technique that can be applied to nanoparticles with various shapes and sizes through the control of surface properties of metal nanoparticles. Polyvinylpyrrolidone was modified with citrate-protected silver nanoprisms (AgPRs) *via* modification with polyethyleneimine. When the butanol colloidal solution was dropped into water in a petri dish, the solution was once completely miscible with water. However, AgPRs spontaneously accumulated at the air/water interface at high density over about 2 hours. In the presentation, in addition to elucidating the assembling mechanism, the application example of the assemblies will be discussed.

Keywords : Metal nanoparticles; Silver Nanoprisms; Localized Surface Plasmon Resonance; Self-Assembly; Polyvinylpyrrolidone

金属ナノ粒子の2次元集積・アレイ構造は、光機能性分子との強い結合を生み出すプラットフォームになりうる。これまでに様々な構築手法が開発されてきたが、¹⁾本研究では、金属ナノ粒子の表面性状制御を通じた、種々の形状・サイズのナノ粒子に適用できる、新規な集積法の開発を報告する。

モデル粒子としてクエン酸で保護された異方性の銀ナノプリズム (AgPRs) にポリエチレンイミンの修飾を介してポリビニルピロリドンを修飾した。このブタノール分散液をシャーレ上に張った水にゆっくりと滴下すると、コロイド溶液は、一度は水に完全に混和するが、2時間ほどの時間を掛けて、自発的に気／水界面に高密度に集積した。諸条件を検討することにより、①混和時、AgPRsは安定に分散すること、②集積には開放系が要されること、③気／水界面への集積は、他のアルコール分散溶媒でも誘起されうることなどが確認された。発表では機構の解明の他、応用例についても言及する。

【謝辞】本研究はJSPS 科研費 19H05627 (分担) の助成を受けたものです。

【参考文献】1) A. Yoshida et al., *Langmuir*, **2012**, 28, 17153. など。

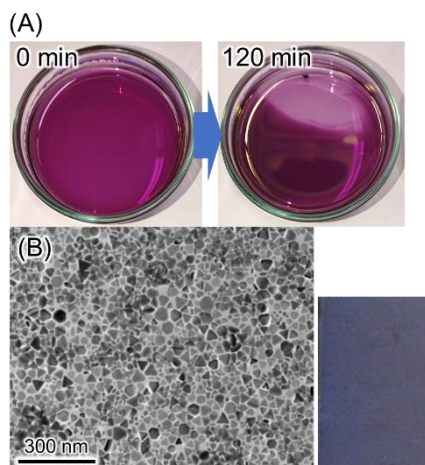


図 1. (A) 気／水界面への AgPRs の集積の写真, (B) 集積体の TEM 像および写真。

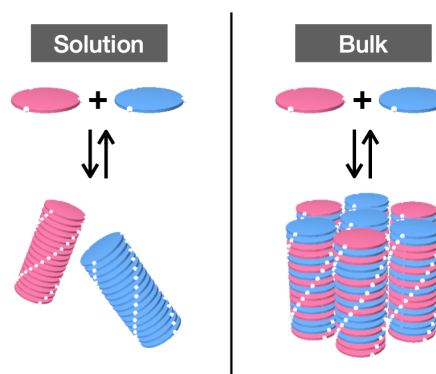
Formation and Structural Characterization of Supramolecular Copolymers in Liquid Crystalline Phase

(¹Graduate School of Engineering, The University of Tokyo, ²RIKEN Center for Emergent Matter Science) ○Daiki Morishita,¹ Xujie Zhang, Yoshimitsu Itoh,¹ Takuzo Aida^{1,2}

Keywords: Supramolecular Polymerization; Supramolecular Copolymerization; Columnar Liquid Crystal; One-Dimensional Supramolecular Assembly

Supramolecular copolymerization is a powerful tool to design supramolecular materials for emergent functions. To date, supramolecular copolymerization has been mainly studied in dilute solution, and has not been well investigated in bulk, which is more important for material applications.¹ In supramolecular polymerization in bulk, it is necessary to consider the interaction between polymer chains and spatial packing, which was unnecessary to consider in solution. Therefore, supramolecular copolymerization has been achieved only by utilizing a strong complimentary hydrogen bonding unit which enables different monomers to assemble in an alternating fashion even in bulk.²

In this study, based on our previous work on supramolecular polymerization in liquid crystalline phase,^{3,4} we report the first supramolecular copolymerization in liquid crystalline phase without utilizing complimentary hydrogen bonding units. We prepared two types of monomers having a porphyrin core, one with alkyl chains via amide groups as side chains, and the other with ethylene glycol chains instead of alkyl chains. Alkyl chains and ethylene glycol chains are incompatible with each other, but a common unit was introduced at the end of each chain to promote monomer compatibility. Each monomer alone formed supramolecular polymer both in dilute solution and in columnar liquid crystalline state. When these monomers were copolymerized, they formed self-sorted supramolecular polymers in solution, while blocky supramolecular copolymers were formed in liquid crystals. In this presentation, we will report the structural identification based on optical properties and liquid crystal phase behavior, and the difference in polymerization behavior between dilute solution and liquid crystalline state.



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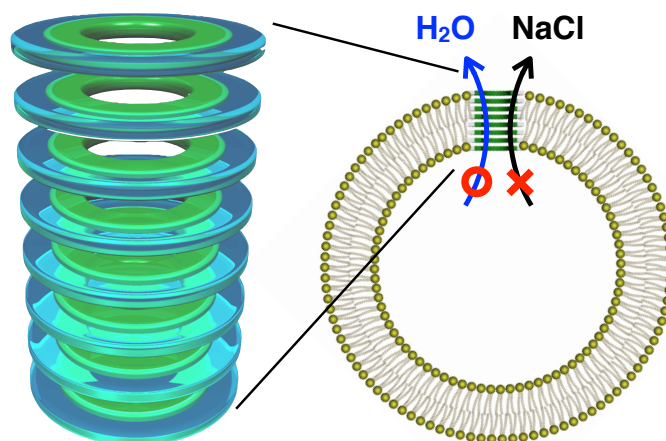
Fluorous Synthetic Channels Enabling Both Ultrafast Water Permeation and High Salt Reflection

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Keywords: Supramolecular Polymerization; Synthetic Water Channel; Teflon-like Interior Surface

The Teflon[®] surface, densely covered with fluorine atoms, is superhydrophobic. Although the hydrophobic interior surface is recognized to play an essential role in the ultrafast water permeation in aquaporins,¹ no fluorous nanochannel with a Teflon-like superhydrophobic interior surface has been explored for water permeation. Recent reports showed that water clusters in the vicinity of fluorous compounds break to yield many hydroxy dangling bonds, whereas considerably fewer dangling bonds are generated with the hydrocarbon analogs.² This observation indicates that a nanochannel with a Teflon[®]-like superhydrophobic interior surface can suppress the formation of water clusters that likely diffuse more sluggishly than nonclustered water molecules. Therefore, this study was aimed at investigating water permeation through such fluorous nanochannels.

In this presentation, we show a series of fluorous oligoamide macrocycles with different interior diameters which can undergo supramolecular polymerization in phospholipid bilayer membranes to form fluorous nanochannels. The smallest-diameter nanochannel can permeate water with a flux two orders of magnitude greater than those of aquaporins or carbon nanotubes, the best reported water channels. Furthermore, it furnished a nearly perfect salt reflectance for desalination.³



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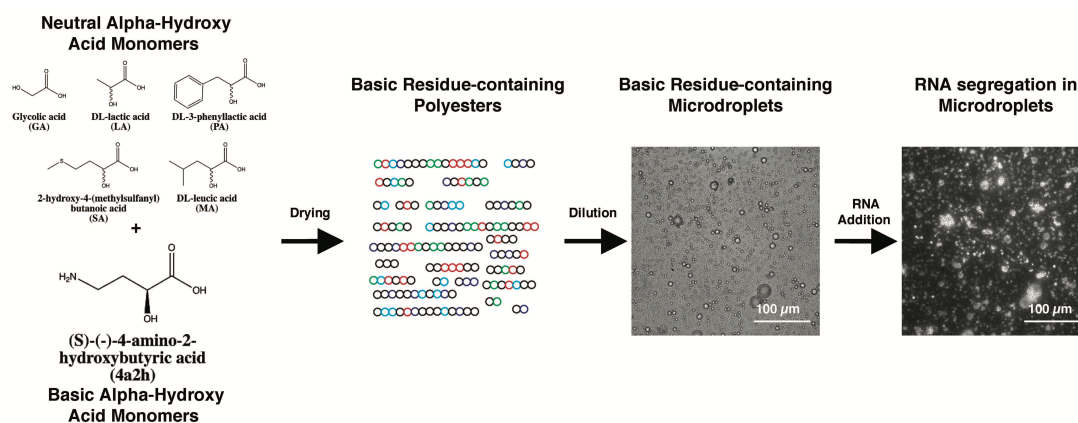
Incorporation of Basic α -Hydroxy Acid Residues into Primitive Polyester Microdroplets for RNA Segregation

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Keywords: Origins of Life, Prebiotic Chemistry, Chemical Evolution, Protocells, Liquid-Liquid Phase Separation

Nucleic acid segregation and compartmentalization were likely essential functions that primitive compartment systems resolved during evolution. Recently, polyester microdroplets generated from dehydration synthesis of various α -hydroxy acids (α HA) were suggested as potential primitive compartments. Some of these droplets can differentially segregate and compartmentalize organic dyes, proteins, and nucleic acids. However, the previously studied polyester microdroplets included limited α HA chemical diversity, which may not reflect the chemical diversity available in the primitive Earth environment. Here, we increased the chemical diversity of polyester microdroplet systems by combinatorially adding an α HA monomer with a basic side chain, 4-amino-2-hydroxybutyric acid (4a2h), which was incorporated with different ratios of other α HAs containing uncharged side chains to form combinatorial heteropolyesters via dehydration synthesis. Incorporation of 4a2h in the polymers resulted in the assembly of some polyester microdroplets able to segregate fluorescent RNA or potentially acquire intrinsic fluorescent character, suggesting that minor modifications of polyester composition can significantly impact the functional properties of primitive compartments. This study suggests one process by which primitive chemical systems can increase diversity of compartment “phenotype” through simple modifications in their chemical composition.



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Self-Healable and Humidity-Resistant Polymer Glasses: New Strategies Based on Nano-Phase Separation

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Keywords: Self-Healing Material; Polymer Blend; Nano-Phase Separation

Self-healable polymers are expected to be game-changing materials that can solve environmental problems caused by plastic waste. In 2018, we reported poly(ether thiourea) that is mechanically robust yet readily repairable without heating and melting.¹ Later, other groups reported several related studies.² We recently reported a humidity-tolerant version of self-healable polymer glass using dicyclohexylmethane units.³ Our next step is to confer a self-healing property on non-healable polymers by simple blending. If such a strategy is possible, the development of self-healing polymers should be much more accelerated.

Here we report that a non-healable polymer turned to be self-healable at ambient temperatures by blending only a small amount of self-healable poly(ether thiourea). Interestingly, the resultant polymer blend nearly maintained the intrinsic properties of the non-healable polymer such as mechanical and hydrophobic natures. Detailed investigations using solid-state NMR spectroscopy revealed that a nano-phase separated structure was crucial to provide the non-healable polymer with the self-healing properties.⁴



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