

Wed. Mar 22, 2023

K202

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

[K202-1am] 02. Theoretical Chemistry,
Chemoinformatics, and Computational
Chemistry

Chair: Gergely Juhasz, Satoshi Takahashi

9:00 AM - 11:10 AM K202 (K202, Lecture Hall Bldg. [2F])

[K202-1am-01] Study on Calculation of Electron Density
Distribution of Centrosymmetric Mg₃BN₃
High Pressure Phase via Maximum
Entropy Method Incorporating Discrete
Cosine Transform

○Hideo Hiraguchi¹ (1. The Institution of
Professional Engineers, Japan)

9:00 AM - 9:20 AM

[K202-1am-02] Theoretical Study on Adhesion Interaction
of Epoxy Resin with Graphene and
Graphene oxide

○Amit Shrestha¹, Yosuke Sumiya, Kazunari
Yoshizawa (1. Kyushu University)

9:20 AM - 9:40 AM

[K202-1am-03] Differences of molecular absorption on
titanium-dioxide surface - a
computational study

○Gergely Juhasz¹ (1. Tokyo Institute of
Technology)

9:40 AM - 10:00 AM

[K202-1am-04] Exploration of stable structures of host
guest materials: A comparison with
density functional theory calculations and
particle swarm optimization

○Shuta Fukuura¹, Takashi Yumura¹, Yohei
Nishidate² (1. Kyoto Institute of Technology,
2. University of Aizu)

10:10 AM - 10:30 AM

[K202-1am-05] Switching of self-assembly pathway for
Pd₆L₄ square-based pyramid by NO₃⁻

○Satoshi Takahashi¹, Tsukasa Abe¹, Tomoki
Tateishi², Hirofumi Sato^{3,4}, Shuichi Hiraoka¹
(1. Graduate School of Arts and Sciences, The
Univ. of Tokyo, 2. iCeMS, Kyoto University, 3.
Department of Molecular Engineering, Kyoto
University, 4. 5 Fukui Institute for Fundamental

Chemistry, Kyoto University)

10:30 AM - 10:50 AM

[K202-1am-06] A DMRG/CASPT2 Investigation of
Metalloporphyrins: Quantifying Ligand
Noninnocence in Archetypal 3d and 4d
Element Derivatives

QUAN MANH PHUNG¹, ○YASINMUCHAMMAD¹, TAKESHI YANAI¹, ABHIKGHOSH² (1. Nagoya University, 2. UiT-The
Arctic University of Norway)

10:50 AM - 11:10 AM

K502

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

[K502-1am] 07. Inorganic Chemistry

Chair: Eisuke Yamamoto, Nobuyoshi Miyamoto

9:00 AM - 10:50 AM K502 (K502, Lecture Hall Bldg. [5F])

[K502-1am-01] Mechanism for neat monolayer tiling of
2D nanosheets by a spin-coating method

○Nobuyuki Sakai¹, Takayoshi Sasaki¹ (1.
National Institute for Materials Science)

9:00 AM - 9:20 AM

[K502-1am-02] A Novel Synthesis Method of Palladium
Nanosheets with Thickness Control

○Sumiya Ando¹, Eisuke Yamamoto², Makoto
Kobayashi², Minoru Osada^{2,3} (1. Nagoya Univ.,
2. IMaSS, Nagoya Univ., 3. WPI-MANA, NIMS)

9:20 AM - 9:40 AM

[K502-1am-03] Synthesis of amorphous silica nanosheets
using solid-state surfactant and
investigation of the exfoliation behavior

○Eisuke Yamamoto¹, Yuma Takezaki¹, Makoto
Kobayashi¹, Minoru Osada^{1,2} (1. Nagoya
University, 2. International Center for Materials
Nanoarchitectonics, National Institute for
Materials Science)

9:40 AM - 10:00 AM

[K502-1am-04] Molecular simulation and thermodynamic
analysis of saturated water content in
organomontmorillonite

○Masaya Miyagawa¹, Keigo Tozaki¹, Fumiya
Hirosawa¹, Hiromitsu Takaba¹ (1. Kogakuin
university)

10:10 AM - 10:30 AM

[K502-1am-05] Structural analyses of monodisperse

nanosheet assemblies by small-angle X-ray scattering

○Nobuyoshi Miyamoto¹ (1. Fukuoka Inst. Technol.)

10:30 AM - 10:50 AM

K305

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

[K305-1pm] 08. Catalysts and Catalysis

Chair: Kohsuke Mori, Seiji Yamazoe

1:10 PM - 3:40 PM K305 (K305, Lecture Hall Bldg. [3F])

[K305-1pm-01] Revealing Hydrogen Spillover Pathways in Reducible Metal Oxide Supports

○Kazuki Shun¹, Kohsuke Mori¹, Hiromi Yamashita¹ (1. Graduate School of Engineering, Osaka University)

1:10 PM - 1:30 PM

[K305-1pm-02] Reaction mechanism of CO/CO₂ photo-conversion into ethylene and propylene using cobalt metal nanoparticle-supported ZrO₂.

○Keisuke Hara¹, Rumiko Hirayama¹, Rento Ishii¹, Kaori Niki¹, Yasuo Izumi¹ (1. Chiba University)

1:30 PM - 1:50 PM

[K305-1pm-03] Electrocatalytic reduction of carbon monoxide to multicarbon products on a copper-single atom catalysts

○Keitaro Ohashi¹, Takashi harada¹, Shuji Nakanishi¹, Kazuhide Kamiya¹ (1. Osaka Univ.)

1:50 PM - 2:10 PM

[K305-1pm-04] Chemoselective hydrogenation of nitro compounds over Ir-based hybrid clustering catalysts

○Shun Hayashi¹, Tetsuya Shishido^{2,3} (1. Natl. Mus. Nat. Sci., 2. Tokyo Metrop. Univ., 3. ESICB, Kyoto Univ.)

2:10 PM - 2:30 PM

[K305-1pm-05] Elucidation of molecular adsorption states of strong base metal oxide cluster by X-ray absorption spectroscopy

○Tomoki Matsuyama¹, Hiroki Nagakari¹, Soichi Kikkawa¹, Naomi Kawamura², Kotaro Higashi², Naoki Nakatani¹, Seiji Yamazoe^{1,3} (1. Tokyo

Metropolitan University, 2. JASRI, 3. JST-PRESTO)

2:40 PM - 3:00 PM

[K305-1pm-06] Acid-Base Bifunctionality of Ti-based Perovskite Nanoparticles for Cyanosilylation

○Takeshi Aihara¹, Wataru Aoki¹, Keigo Kamata¹, Michikazu Hara¹ (1. Tokyo Institute of Technology)

3:00 PM - 3:20 PM

[K305-1pm-07] Homogeneous Investigation of N-Heterocyclic Carbene Stabilized Au-Nanoclusters for Electrocatalysis

○Samuel Jacob^{1,2}, Joey DeJesus¹, Emily Albright², Yasuyo Tezuka¹, Masakazu Nambo¹, Cathleen Crudden^{2,1} (1. Nagoya University, 2. Queens University)

3:20 PM - 3:40 PM

K505

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

[K505-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Naoki Ishida, Yoshiaki Tanabe

1:10 PM - 3:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-1pm-01] Construction of Molecular Gears Based on Lanthanoid Double-decker Complexes with Phthalocyanine and Naphthalocyanine Functionalized with Four Planar Peripheral Substituents

○Jeevithra Dewi Subramaniam¹, Toshio Nishino¹, Gwénaél Rapenne^{1,2} (1. Nara Institute of Science and Technology, 2. University of Toulouse, France)

1:10 PM - 1:30 PM

[K505-1pm-02] Photoluminescence Properties of Mononuclear Europium(III) and Gadolinium(III) Complexes with Tetradentate Schiff Base Ligands in the Solid State

○Masanobu Tsuchimoto¹, Toshiki Sakata¹, Naoki Takeda¹, Shuhei Itoh¹, Tomoaki Sugaya¹, Hyuma Masu², Masayuki Watabnabe³ (1. Chiba Institute of Technology, 2. Chiba University, 3. Japan Atomic Energy Agency)

1:30 PM - 1:50 PM

[K505-1pm-03] Synthesis of Dinuclear Titanium Oxalate Complexes Supported by a Tris(phenolato)amine Ligand

○Akira Okumura¹, Florentine Mohr¹, Thomas Paul Spaniol¹, Jun Okuda¹ (1. RWTH Aachen Univ.)

1:50 PM - 2:10 PM

[K505-1pm-04] Transformation of dinitrogen and alkenes to alkyl amines at a trititanium polyhydride framework

○Takanori Shima¹, Ping Wu², Ryota Owada¹, Gen Luo², Zhaomin Hou¹ (1. RIKEN, 2. Anhui University)

2:10 PM - 2:30 PM

[K505-1pm-05] Transformation of Pyridines to Cyclopentadienyl Units by Denitrogenation in a PNP-Ligated Ditungsten Hydride Framework

○Xiaoxi ZHOU¹, Qingde ZHUO¹, Takanori SHIMA¹, Xiaohui KANG², Zhaomin HOU¹ (1. RIKEN, 2. Dalian Medical University)

2:40 PM - 3:00 PM

[K505-1pm-06] Reaction of a Titanium Dinitrogen Complex Bearing an (ONO)-Ligand with CO₂ and CS₂

○Yutaka Ishida¹, Sui Hasegawa¹, Hiroyuki Kawaguchi¹ (1. Tokyo Institute of Technology)

3:00 PM - 3:20 PM

[K505-1pm-07] Precise control of metal-centered chirality of pentacoordinate chiral-at-vanadium(V) complexes using chiral auxiliaries

○Ayako Hino¹, Koichi Nagata¹, Hitoshi Ube¹, Mitsuhiko Shionoya¹ (1. The Univ. of Tokyo)

3:20 PM - 3:40 PM

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

[K505-1vn] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Daisuke Tanaka, Satoshi Horike

4:10 PM - 6:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-1vn-01] Liquid-liquid transition in coordination polymer melt studied by dynamic mechanical analysis

○Taichi Nishiguchi¹, Yuki Ohara², Kentaro

Kadota³, Satoshi Horike^{2,3} (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. iCeMS, KUIAS, Kyoto University)

4:10 PM - 4:30 PM

[K505-1vn-02] Glass formation of coordination polymers driven by dehydration treatment

○Zeyu FAN¹, Yong-Sheng Wei², Satoshi Horike^{2,1} (1. Graduate School of Engineering, Kyoto University, 2. Institute for Advanced Study, Kyoto University)

4:30 PM - 4:50 PM

[K505-1vn-03] Photo-generated extremely long-lived spin-polarized radicals in metal-organic frameworks

○Kana Orihashi¹, Akio Yamauchi¹, Saiya Fujiwara⁴, Kenichiro Tateishi⁴, Tomohiro Uesaka⁴, Asada Mizue⁵, Toshikazu Nakamura⁵, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,3} (1. Kyushu Univ., 2. CMS, Kyushu Univ., 3. FOREST, JST, 4. RIKEN, 5. Institute for Molecular Science)

4:50 PM - 5:10 PM

[K505-1vn-04] Semiconductive Nature of Lead(II) Coordination Polymers with Benzenethiol Derivatives

○Ryohei Akiyoshi¹, Akinori Saeki², Daisuke Tanaka¹ (1. Kwansei Gakuin University, 2. Osaka University)

5:10 PM - 5:30 PM

[K505-1vn-06] Inverse Guest Adsorption and Luminescent Response in an Au(I)-based Metal–Organic Framework

○Haruka Yoshino¹, Masaki Saigo², Kiyoshi Miyata², Ken Onda², Hitoshi Miyasaka¹ (1. Institute for Materials Research, Tohoku University, 2. Graduate School of Science, Kyushu University)

6:00 PM - 6:20 PM

[K505-1vn-07] Charge-driven Assembly of Water-soluble Ionic Metal–Organic Polyhedra with Enzymes

○Benjamin Le Ouay¹, Ryosuke Minami¹, Purna Kanta Boruah¹, Masaaki Ohba¹ (1. Kyushu University)

6:20 PM - 6:40 PM

K506

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

**[K506-1vn] 09. Coordination Chemistry,
Organometallic Chemistry**

Chair: Shin Takemoto, Takanori Shima

4:10 PM - 6:40 PM K506 (K506, Lecture Hall Bldg. [5F])

[K506-1vn-01] Synthesis of tris(dinitrogen) iron(0)

complexes stabilized by organosilicon ligands

○Reon Ishii¹, Yusuke Sunada^{1,2} (1. Graduate School of Engineering, The University of Tokyo, 2. Institute of Industrial Science, The University of Tokyo)

4:10 PM - 4:30 PM

[K506-1vn-02] Synthesis and Reactivity of Doubly Oxido-Bridged Diruthenium Complex with Terminal Hydroxido Ligands

○Tomoyo Misawa-Suzuki¹, Nanako Asai¹, Hirotaka Nagao¹ (1. Fac. of Sci. and Tech., Sophia Univ.)

4:30 PM - 4:50 PM

[K506-1vn-03] Anion-Exchange-Induced Modulation of Electric Field Response in a Two-Dimensional Bis(terpyridine)metal(II) complex polymer

○Kenji Takada¹, Hiroshi Nishihara¹ (1. Tokyo University of Science, Research Institute for Science & Technology)

4:50 PM - 5:10 PM

[K506-1vn-04] Intramolecular C-H Bond Activation and Functionalization by Low-Valent Cobalt Complexes with Diamide Ligands

○Suiho Kobayashi¹, Tsubasa Hatanaka¹, Yasuhiro Funahashi¹ (1. Osaka Univ.)

5:10 PM - 5:30 PM

[K506-1vn-05] Heterobimetallic Pt/Main Group Metal Complexes in Metal-Metal Cooperative Bond Activation

○GOVINDARAJAN RAMADOSS¹, Shubham Deolka¹, Eugene Khaskin¹, Serhii Vasylevskyi¹, Robert R. Fayzullin², Shrinwantu Pal¹, Julia R. Khusnutdinova¹ (1. Okinawa Institute of Science and Technology Graduate University, 2. Arbuzov Institute of Organic and Physical

Chemistry FRC Kazan Scientific Center, Russian Academy of Sciences 8

Arbuzov Street, Kazan, 420088 (Russian Federation))

5:40 PM - 6:00 PM

[K506-1vn-06] Fabrication of oriented conductive metal-organic framework thin film by dry process.

○Seoungmin Chon¹, Ryo Nakayama², Shunta Iwamoto¹, Shigeru Kobayashi¹, Ryota Shimizu¹, Taro Hitosugi^{2,1} (1. Tokyo Institute of Technology, 2. the University of Tokyo)

6:00 PM - 6:20 PM

[K506-1vn-07] Selective CuAAC Transformation of Cu(I) Complex Surrounded by Multiple Reactive Points

○Takuya SHIBUE¹, Shang RONG¹, Kazuyuki KUBO¹, Shoko KUME¹, Tsutomu MIZUTA¹ (1. Hioshima Univ.)

6:20 PM - 6:40 PM

K404

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

[K404-1am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Hiroshi Naka, Mamoru Ito

9:00 AM - 11:40 AM K404 (K404, Lecture Hall Bldg. [4F])

[K404-1am-01] Regioselective Distal C-C Bond

Formations via Ir-Catalyzed C-H Activation along with Chain-Walking

○King Hung Nigel Tang¹, Tokutake Ryo¹, Uchida Kanako¹, Nishihara Kazuki¹, Ito Mamoru¹, Shibata Takanori¹ (1. Waseda University)

9:00 AM - 9:20 AM

[K404-1am-02] Synthesis of 3,4-Fused-2-Quinolone Derivatives via Site-Selective C-H Functionalization by Cp* Rh(III) Catalysis.

○naohiro hirako¹, takeshi yasui¹, yasihiko yamamoto¹ (1. The Univ. of Nagoya)

9:20 AM - 9:40 AM

[K404-1am-03] Cationic Rhodium(I) Tetrafluoroborate-Catalyzed Intramolecular Carbofluorination of Alkenes via C-F

Bond Cleavage of Acyl Fluorides

○Tomoki Yoshida¹, Masaya Ohta¹, Takuya Kodama^{1,2}, Mamoru Tobisu^{1,2} (1. Osaka University, 2. ICS-OTRI, Osaka University)
9:40 AM - 10:00 AM

[K404-1am-04] Cobalt/Photoredox Dual Catalysis-Enabled Cycloisomerization of Eneidyne via C–H Bond Activation

○Keiji Yamada¹, Takeshi Yasui¹, Yoshihiko Yamamoto¹, Nobuaki Koga² (1. Grad. Sch. Pharm. Sci., Nagoya Univ., 2. Grad. Sch. Informatics., Nagoya Univ.)
10:00 AM - 10:20 AM

[K404-1am-05] An Iridium Precatalyst for Transfer Dehydration of Amides to Nitriles
Marie Ono¹, Toshiaki Asai², Asuka Naraoka¹, Yasuhiro Ohki³, Yoshiji Takemoto¹, ○Hiroshi Naka¹ (1. Grad. Sch. of Pharm. Sci., Kyoto Univ., 2. Grad. Sch. of Sci., Nagoya Univ., 3. Inst. Chem. Res., Kyoto Univ.)
10:40 AM - 11:00 AM

[K404-1am-06] Rhodium-Catalyzed Selective Synthesis of Silicon-containing Cyclic Compounds by Intramolecular and Intermolecular Hydrofunctionalization of Alkynes
○Kazuto Fuji², Kohei Sekine^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)
11:00 AM - 11:20 AM

[K404-1am-07] Magnesium of C–F and C–O Bonds Catalyzed by Rhodium–Aluminum Bimetallic Complexes
○Ikuya Fujii¹, Haruka Kido¹, Ryota Higo¹, Kazuhiko Semba¹, Yoshiaki Nakao¹ (1. Grad. Sch. Eng., Kyoto Univ.)
11:20 AM - 11:40 AM

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

[K404-1vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kazuhiko Semba, Kei Muto
4:10 PM - 5:30 PM K404 (K404, Lecture Hall Bldg. [4F])

[K404-1vn-01] Palladium-Catalyzed Synthesis of 4-Sila-4H-benzo[d][1,3]oxazines by

Intramolecular Hiyama Coupling

○Donghyeon Lee¹, Ryo Shintani¹ (1. Osaka University)
4:10 PM - 4:30 PM

[K404-1vn-02] Palladium–catalyzed unimolecular fragment coupling of amides via elimination and translocation of isocyanate
○Ryoma Shimazumi¹, Riku Tanimoto¹, Takuya Koama^{1,2}, Mamoru Tobisu^{1,2} (1. Osaka univ., 2. ICS-OTRI)
4:30 PM - 4:50 PM

[K404-1vn-03] Mechanoredox/Nickel Dual Catalytic System for Force-Induced Cross-Coupling Reactions
○Tamae Seo¹, Koji Kubota^{1,2}, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)
4:50 PM - 5:10 PM

[K404-1vn-04] Dehydrogenative Three-Component Coupling of Alkylarenes, CO and Phenols
○Naoki Ishida¹, Hiroki Shinoya¹, Tairin Kawasaki¹, Masahiro Murakami¹ (1. Kyoto University)
5:10 PM - 5:30 PM

K603

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

[K603-1pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Suguru Ito, Takashi Hirose
1:50 PM - 3:40 PM K603 (K603, Lecture Hall Bldg. [6F])

[K603-1pm-01] Synthesis of the longest aza[n]helicene
○Yusuke Matsuo¹, Takayuki Tanaka¹, Shu Seki¹ (1. Kyoto University)
1:50 PM - 2:10 PM

[K603-1pm-02] Synthesis and photophysical properties of chiral 1,7-7',1'-cyclopyrenylene oligomers
○Ryo Kurosaki¹, Rémi Métivier², Hiroko Yamada¹, Naoki Aratani¹ (1. NAIST, 2. ENS Paris-Saclay)
2:10 PM - 2:30 PM

[K603-1pm-03] Solvent dependency of the charge separation and the near-infrared emission

of sumanenetrone-based dyes

○Junyi Han¹, Youhei Takeda¹, Hayato Sakai²,
Taku Hasobe², Yuta Uetake^{1,3}, Yumi
Yakiyama^{1,3}, Hidehiro Sakurai^{1,3} (1. Graduate
School of Engineering, Osaka Univ., 2. Fac. Sci.
Tech., Keio Univ., 3. ICS-OTRI, Osaka Univ.)

2:30 PM - 2:50 PM

[K603-1pm-04] Theoretical analysis and device
application of C₃-chiral truxenes showing
an excellent circularly polarized
luminescence property on fluorescence
and phosphorescence

○Fumitaka Ishiwari¹, Takuya Omine¹, Takashi
Hirose², Tadashi Mori¹, Naoya Aizawa¹, Akinori
Saeki¹ (1. Osaka University, 2. Kyoto
University)

3:00 PM - 3:20 PM

[K603-1pm-05] Organic Triboluminescence Polar Crystals
Composed of a Host– Dopant System

○Takuya Ogaki^{1,2}, Yasunori Matsui^{1,2}, Hiroshi
Ikeda^{1,2} (1. Grad. Sch. Eng., Osaka Metro.
Univ., 2. RIMED, Osaka Metro. Univ.)

3:20 PM - 3:40 PM

K606

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

[K606-1pm] 12. Organic Chemistry -Organic
Crystals, Supramolecular Chemistry-

Chair: Takashi Nakamura, Yumi Yakiyama

1:00 PM - 3:40 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-1pm-01] Anthracene-based molecular tweezers:

Construction of a giant spherical
assembly based on hierarchical self-
complementarity

○Masahiro Yamashina¹, Yuta Sawanaka¹, Shinji
Toyota¹ (1. School of Science, Tokyo Inst. of
Tech.)

1:00 PM - 1:20 PM

[K606-1pm-02] Molecular Dynamics Study on the
Structure– Property Relationship of Self-
Assembled Gear-Shaped Amphiphile
Molecules with/without Methyl Groups

○Moe Murata¹, Osamu Kobayashi¹, Shuichi
Hiraoka², Tomomi Shimazaki¹, Masanori
Tachikawa¹ (1. Yokohama City University, 2.

The University of Tokyo)

1:20 PM - 1:40 PM

[K606-1pm-03] A twisted chiral cavitand with five-fold
symmetry and its length-selective binding
properties

○Tanhao Shi¹, Yuuya Nagata², Shigehisa
Akine³, Shunsuke Ohtani¹, Kenichi Kato¹,
Tomoki Ogoshi^{1,3} (1. Kyoto University, 2.
Hokkaido University, 3. Kanazawa University)

1:40 PM - 2:00 PM

[K606-1pm-04] Two-dimensional living supramolecular
polymerization improved by using a
comonomer and a dummy monomer

○ZHEHUI JIN^{1,2}, Norihiko Sasaki⁵, Masayuki
Takeuchi^{4,2}, Yutaka Wakayama^{1,2}, Kazunori
Sugiyasu³ (1. Kyushu University, 2. National
Institute for Materials Science, 3. Kyoto

University, 4. University of Tsukuba, 5. Tottori
University)

2:00 PM - 2:20 PM

[K606-1pm-05] Facet-selective Block Co-crystallization of
Two-different Spin-crossover Metal
Complexes

○Tomoya Fukui^{1,2}, Masahiro Tsuchiya^{1,2},
Takanori Fukushima^{1,2} (1. CLS, Tokyo Tech.,
2. Sch. Mater. and Chem. Tech., Tokyo Tech.)

2:30 PM - 2:50 PM

[K606-1pm-06] Self-assembling behaviors and properties
of platinum(II) complexes possessing
chiral hydrophilic bis(phenylisoxazolyl)
benzene moieties

○Masaya YOSHIDA¹, Takehiro HIRAO¹,
Takeharu HAINO^{1,2} (1. Graduate School of
Advanced Science and Engineering, Hiroshima
University, 2. WPI-SKCM², Hiroshima
University)

2:50 PM - 3:10 PM

[K606-1pm-07] Supramolecular Polymerization of
Photofunctional Thiophene-Fused
[4*n*]Annulenes: Chiral Superstructures
and Chiroptical Properties

○Tsubasa Aoki¹, Takayoshi Akiyama¹, Takuzo
Aida^{1,2}, Yoshimitsu Itoh^{1,3} (1. Grad. Sch. of
Eng., The Univ. of Tokyo, 2. RIKEN CEMS, 3.
PRESTO, JST)

3:10 PM - 3:30 PM

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

[K606-1vn] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kenichi Kato, Yoshimitsu Itoh

4:10 PM - 6:40 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-1vn-01] Signal-amplification Sensing via

Sumanene-based Supramolecular Polymerization

○Hiroaki Mizuno¹, Hironobu Nakazawa², Akihisa Miyagawa³, Yumi Yakiyama², Susumu Kawauchi⁴, Hidehiro Sakurai², Gaku Fukuhara¹

(1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Applied Chemistry, Osaka University, 3. Department of Chemistry, University of Tsukuba, 4. Tokyo Tech Academy for Convergence of Materials and Informatics, Tokyo Institute of Technology)

4:10 PM - 4:30 PM

[K606-1vn-02] Anion- π Interaction in the Polyanionic {Mo₁₃₂} Cage

○Chinatsu MURATA¹, Jaesob SHIN¹, Yukatsu SHICHIBU^{1,2}, Katsuaki KONISHI^{1,2} (1. Grad. Sch. Env. Sci., Hokkaido Univ., 2. Fac. Env. Earth Sci., Hokkaido Univ.)

4:30 PM - 4:50 PM

[K606-1vn-03] Synthesis and Dynamic Properties of Stapled α -Helical Peptides

○Naoki Ousaka¹, Mark MacLachlan^{1,2}, Shigehisa Akine^{1,3} (1. Kanazawa Univ. NanoLSI, 2. The Univ. of British Columbia, 3. Kanazawa Univ. Grad. Sch. of Nat. Sci. &Tech.)

4:50 PM - 5:10 PM

[K606-1vn-04] Acceleration and deacceleration of helicity inversion speeds in a dynamic helical trinickel(II) metallocryptand by alkali metal ion binding

○Sk Asif Ikbal¹, Pei Zhao², Masahiro Ehara², 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)

5:10 PM - 5:30 PM

[K606-1vn-05] Colorimetric Chiral Sensing Using

Supramolecular Organogels Formed by Carbamoylated Riboflavin and Melamine Derivative

○Marina Oka¹, Ryo Kozako¹, Hiroki Iida¹ (1. Graduate School of Natural Science and Technology, Shimane University)

5:40 PM - 6:00 PM

[K606-1vn-06] Formation of a metastable Pd₄L₈

interlocked cage complex based on the energy ratchet mechanism

○Tsukasa Abe¹, Shuichi Hiraoka¹ (1. The Univ. of Tokyo)

6:00 PM - 6:20 PM

[K606-1vn-07] Supramolecular reactions in a dynamic solution

○Munenori Numata¹, Takemori Haruna, Kanzaki Chisako (1. Kyoto Prefectural University)

6:20 PM - 6:40 PM

K602

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

[K602-1am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Shohei Saito, Shuzo Hirata

9:00 AM - 11:40 AM K602 (K602, Lecture Hall Bldg. [6F])

[K602-1am-01] Intramolecular Singlet Fission and Chiroptical Properties of Chiral Acene Dimers

○Hayato Sakai¹, Yasuyuki Araki², Takehiko Wada², Nikolai Tkachenko³, Taku Hasobe¹ (1. Keio University, 2. Tohoku University, 3. Tampere University)

10:20 AM - 10:40 AM

[K602-1am-02] Transient Absorption Spectroscopic Analysis of Energy Transfer Process in the Solid-state Upconversion System

○Yasunori Matsui^{1,2}, Takumi Takahashi¹, Masaya Kanoh¹, Takuya Ogaki^{1,2}, Hiroshi Ikeda^{1,2} (1. Grad. Sch. Eng., Osaka Metro. Univ., 2. RIMED, Osaka Metro. Univ.)

10:40 AM - 11:00 AM

[K602-1am-03] Photo-Induced Triplet Depletion Allowing Higher-Resolution Afterglow

○Kikuya Hayashi¹, Keiki Fukumoto², Shuzo

Hirata¹ (1. The Univ. of Electro-Commun., 2. KEK)

11:00 AM - 11:20 AM

[K602-1am-04] Vibronic Couplings and Spin-Orbit Couplings in Intersystem Crossing Processes

○Wataru Ota^{1,2}, Motoyuki Uejima³, Tohru Sato^{1,2} (1. Fukui Institute for Fundamental Chemistry, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. MOLFEX, Inc.)

11:20 AM - 11:40 AM

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

[K602-1pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Nobuhiro Yanai, Taku Hasobe

1:30 PM - 3:40 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-1pm-01] Controlling Molecular Orientation to Improve Photon Upconversion Efficiency

○Catherine Helenna Mulyadi^{1,2}, Masanori Uji^{1,2}, Nobuhiro Yanai^{1,2} (1. Kyushu University, 2. FOREST, JST)

1:30 PM - 1:50 PM

[K602-1pm-02] Efficient Photon Upconversion System using Porous Film to Generate UV Light from Visible Light

○Naoyuki Harada¹, Masanori Uji¹, Baljeet Singh¹, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,2,3} (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. FOREST, JST)

1:50 PM - 2:10 PM

[K602-1pm-03] Near-Infrared Light Absorbing Organic Molecules towards Photothermal Cancer Therapy

○Kazuya Yoshida¹, Vasudevan Pillai Biju^{1,2}, Yuta Takano^{1,2} (1. Grad. Sch. Env. Sci., Hokkaido Univ., 2. RIES)

2:10 PM - 2:30 PM

[K602-1pm-04] What is the reason why the ring-opening quantum yield is smaller than the ring-closure one and their sum is smaller than unity in many 6 π -electron photochemical electrocyclic reactions?

○Takao Kobayashi¹, Shinichiro Nakamura²,

Motoyuki Shiga³ (1. Mitsubishi Chemical Corporation, 2. Kumamoto University, 3. Japan Atomic Energy Agency)

2:40 PM - 3:00 PM

[K602-1pm-05] Effect of *para*-substituents of PyBTM radical derivatives on high-efficiency solution fluorescence properties

○Yohei Hattori¹, Ryota Kitajima¹, Ryota Matsuoka², Tetsuro Kusamoto², Kingo Uchida¹ (1. Ryukoku University, 2. Institute for Molecular Science)

3:00 PM - 3:20 PM

[K602-1pm-06] Fluorescent Force Probe for Real-time Imaging of Hydrodynamic Stress Field

○Sachika Akitomo¹, Takuya Yamakado¹, Hidetsugu Kitakado¹, Ryo Kimura¹, Reiko Kuriyama², Kazuya Tatsumi², Kazuyoshi Nakabe², Shohei Saito¹ (1. Graduate School of Science, Kyoto University, 2. Graduate School of Engineering, Kyoto University)

3:20 PM - 3:40 PM

K703

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

[K703-1am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Jumpei Taguchi, Yoshiaki Shoji

9:00 AM - 11:10 AM K703 (K703, Lecture Hall Bldg. [7F])

[K703-1am-01] Facile synthesis and evaluation of polyfluoroarylated anthracene derivatives via *regio*-selective cross-dehydrogenative C-H/C-H coupling reaction

○Ryota Sato¹, Junpei Kuwabara¹, Takeshi Yasuda², Takaki Kanbara¹ (1. Tsukuba Research Center for Energy Materials Science (TREMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 2. National Institute for Materials Science)

9:00 AM - 9:20 AM

[K703-1am-02] Synthesis of a NHC-Coordinated Germylene with a Biphenylene Unit

○Shogo Morisako¹, Takahiro Sasamori¹ (1. Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials

Sciences (TREMS), Univ. of Tsukuba)

9:20 AM - 9:40 AM

[K703-1am-03] Comparison of structures, optical properties, and reactivity between linear and cyclic disilane-bridged trimeric framework

○Yoshinori Yamanoi¹, Teppei Yamada¹ (1. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[K703-1am-04] Iron-Catalyzed C–O Activation/Tandem Tetra-annulation for Synthesis of Carbon-bridged Oligo-(p-arylenevinylene)

○MENGQING CHEN¹, Rui Shang¹, Eiichi Nakamura¹ (1. The Univ. of Tokyo)

10:10 AM - 10:30 AM

[K703-1am-05] Spiro-conjugated 1,4-Dihydropentalenes: Short-step Synthesis by Iron-catalysis and Materials Properties.

○Aziz Khan¹, Mengqing Chen¹, Rui Shang¹, Eiichi Nakamura¹ (1. The University of Tokyo)

10:30 AM - 10:50 AM

[K703-1am-06] Cationic Indium Catalyzed C-O Bond Formation Reaction

○Mitsuhiro Yoshimatsu¹, Manoka Kikuchi¹, Rintaro Saito¹, Hiroki Goto¹ (1. Department of Chemistry, Faculty of Education, Gifu University)

10:50 AM - 11:10 AM

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

[K703-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Shogo Morisako, Yoshinori Yamanoi

1:50 PM - 3:40 PM K703 (K703, Lecture Hall Bldg. [7F])

[K703-1pm-01] Development of synthetic methodology for AB₂-type arsines and investigation of catalytic activity utilizing arsa-Buchwald ligands.

○Akifumi Sumida¹, Kenta Ogawa¹, Hiroaki Imoto¹, Kensuke Naka¹ (1. Kyoto Institute of Technology)

1:50 PM - 2:10 PM

[K703-1pm-02] Emission properties of Eu(III) nitrate complexes bearing arsine oxides

○Toshiki Fujii¹, Yuichi Kitagawa², Yasuchika Hasegawa², Hiroaki Imoto¹, Kensuke Naka¹ (1. Grad. Sch. of Sci. and Tec., Kyoto Inst. of Tech., 2. WPI-ICReDD and Fac. of Eng., Hokkaido Univ.)

2:10 PM - 2:30 PM

[K703-1pm-03] Development of Catalytic Arsa-Wittig Reaction and Design Strategy of Arsenic Catalysts

○Ryoto Inaba¹, Junya Yukiyasu¹, Takashi Yumura¹, Hiroaki Imoto¹, Kensuke Naka¹ (1. Kyoto Institute of Technology)

2:30 PM - 2:50 PM

[K703-1pm-04] Development of Iridium-Catalyzed C(sp³)-C(sp²) [1,5]-Silyl Rearrangement Reaction

○Jiawei Qiu¹, Tsuyoshi Matsuzaki¹, Makoto Sako¹, Kenichi Murai¹, Junichi Uenishi¹, Kazushi Mashima¹, Takeyuki Suzuki¹, Mitsuhiro Arisawa¹ (1. Osaka University)

3:00 PM - 3:20 PM

[K703-1pm-05] Design and Synthesis of Spliceostatin A Derivatives: Structure-Activity Relationship Study related to Enone moiety of Spliceostatin A

○Satoru Hirabayashi¹, Noriko Ohta¹, Yuko Tsuyuguchi¹, Yue Li¹, Yusuke Yoshikawa¹, Banzhong Lin¹, Megumi Fumimoto¹, Junichi Haruta¹, Makoto Sako¹, Kenichi Murai¹, Keisuke Nimura¹, Mitsuhiro Arisawa¹ (1. The Univ. of Osaka)

3:20 PM - 3:40 PM

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

[K703-1vn] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Akihito Konishi, Kento Iwai

4:10 PM - 5:30 PM K703 (K703, Lecture Hall Bldg. [7F])

[K703-1vn-01] Thermal Cyclization of Linear Arylalkynes Facilitated by Folding inside a Molecular Cage

○Georgi Rosenov Genov¹, Hiroki Takezawa¹, Harumi Hayakawa¹, Makoto Fujita^{1,2} (1. University of Tokyo, 2. Institute for Molecular Science)

4:10 PM - 4:30 PM

[K703-1vn-02] TEtraQuinoline (TEQ) and Other Cyclic Quinoline Oligomers, a New Family of Macrocycles

○Wei Xu¹, Haru Nonaka¹, Ryota Yagami¹, Mizuki Nishiwaki¹, Ayami Takeda¹, Naoya Kumagai^{1,2}
(1. Keio University, 2. Institute of Microbial Chemistry)

4:30 PM - 4:50 PM

[K703-1vn-03] Novel synthesis of multi-substituted quinoline derivatives using alkylidenemalononitriles and unsaturated aldehydes by organocatalyst

○Xiaolei Han¹, Naoki Mori¹, Yujiro Hayashi¹ (1. Tohoku Univ.)

4:50 PM - 5:10 PM

[K703-1vn-04] Intramolecular Cyclization Reactions of Arylpropargyl Amides of Electron-deficient α, β -Alkenyl Carboxylates

○Zhichao Wang¹, Shoko Yamazaki², Tsumoru Morimoto³, Akiya Ogawa¹ (1. Osaka Metropolitan University, 2. Nara University of Education, 3. NARA Institute of Science and Technology)

5:10 PM - 5:30 PM

K705

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

[K705-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Ryo Yazaki, Yoshihiro Nishimoto

1:00 PM - 3:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-1pm-01] Highly Stereoselective Synthesis of γ, δ -Unsaturated Quaternary α -Amino Esters via the Tandem *N*-Alkylation/Claisen Rearrangement of α -Imino Allylesters

○Isao Mizota¹, Toshikazu Fukaya¹, Yumi Miwa¹, Yoshinari Kobayashi¹, Tomoki Ejima¹, Mizuki Yamaguchi¹, Makoto Shimizu¹ (1. Mie University)

1:50 PM - 2:10 PM

[K705-1pm-02] Selective Defluoroaminoxylation of perfluoroalkylarenes by organic photoredox catalysis

○Naoki Sugihara¹, Yoshihiro Nishimoto¹, Makoto Yasuda¹ (1. Graduate School of Engineering, Osaka University)

2:10 PM - 2:30 PM

[K705-1pm-03] 1,4-Addition Reaction of 2H-Heptafluoropropane to Unsaturated C-C bond

○Yusuke Higashi¹, Kotono Shima¹, Mikiya Suzuki¹, Moe Hosokawa², Kiyomi Kakiuchi¹, Tsuyoshi Kawai¹, Tsumoru Morimoto¹ (1. Nara Institute of Science and Technology, 2. Daikin Industries, Ltd.)

2:30 PM - 2:50 PM

[K705-1pm-04] α -Amino acid and peptide synthesis using catalytic cross-dehydrogenative coupling

○Taro Tsuji¹, Kayoko Hashiguchi¹, Mana Yoshida¹, Tetsu Ikeda¹, Yunosuke Koga¹, Yusaku Honda¹, Tsukushi Tanaka¹, Suyong Re², Kenji Mizuguchi^{2,3}, Daisuke Takahashi¹, Ryo Yazaki¹, Takashi Ohshima¹ (1. The Univ. of Kyushu, 2. NIBIOHN, 3. The Univ. of Osaka)

3:00 PM - 3:20 PM

[K705-1pm-05] Oxidative Dearomative Coupling Reaction of Arenols Using Hypohalite Catalysis

○Takehiro Kato¹, Muhammet Uyanik¹, Kazuaki Ishihara¹ (1. Nagoya University)

3:20 PM - 3:40 PM

E1662

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

[E1662-1am] 16. Natural Products Chemistry, Chemical Biology

Chair: Takuya Kaji, Toyonobu Usuki

9:00 AM - 11:30 AM E1662 (1612, Bldg. 16 [1F])

[E1662-1am-01] Total synthesis of pigments with azulene skeleton in an edible blue mushroom

○Kiyotaka Maruoka¹, Ryuju Suzuki¹, Takaaki Kamishima², Yoshitaka Koseki¹, Toshihiro Murafuji³, Hitoshi Kasai¹ (1. IMRM, the Univ. of Tohoku, 2. Genesis Research Institute, Inc., 3. Graduate School of Science and Technology for Innovation, the Univ. of Yamaguchi)

9:00 AM - 9:20 AM

- [E1662-1am-02] Δ^4 -dinor-OPDAs, novel ancestral jasmonates of *Marchantia polymorpha*
 ○Takuya Kaji¹, Hidenori Yoshimatsu¹, Nobuki Kato¹, Haruka Sakurai¹, Yang Gangqiang², Guillermo H. Jimenez-Aleman³, Roberto Solano³, Minoru Ueda^{1,4} (1. Sciences, Tohoku Univ., 2. Pharmacy, Yantai University, 3. CNB-CSIC, 4. Life Sciences, Tohoku Univ.)
 9:20 AM - 9:40 AM
- [E1662-1am-03] JA-Ile-lactone enhanced accumulation of alkaloid in tomato
 ○Rina Saito¹, Takuya Kaji², Taichi Okumura², Toshiya Muto¹, Hiroshi Abe³, Sohei Yamagami¹, Yousuke Takaoka², Minoru Ueda^{1,2} (1. Grad. Sch. Lifesci., Tohoku Univ., 2. Grad. Sch. Sci., Tohoku Univ., 3. RIKEN BRC)
 9:40 AM - 10:00 AM
- [E1662-1am-04] Chemical regulation of crosstalk between jasmonate and ethylene by peptide-based chemical tools
 ○Yousuke Takaoka¹, Ruiqi Liu¹, Qi Li¹, Minoru Ueda^{1,2} (1. Grad. Sci., Tohoku Univ., 2. Grad. Life Sciences, Tohoku Univ.)
 10:10 AM - 10:30 AM
- [E1662-1am-05] Glycolipids as ligands and molecular probes for C-type lectin receptor Mincle; synthesis and biological functional analysis
 ○Takanori Matsumaru¹, Kana Okubo¹, Kasumi Sakuratani¹, Kodai Sueyoshi¹, Shusuke Fujii¹, Juri Takayama¹, Yamasaki Sho^{2,3}, Yukari Fujimoto¹ (1. Fac. Sci. Tech., Keio Univ., 2. Research Institute for Microbial Diseases, Osaka Univ., 3. Immunology Frontier Research Center (IFReC), Osaka Univ.)
 10:30 AM - 10:50 AM
- [E1662-1am-06] Development of tyrosinase-based proximity protein labeling in living cells
 ○Yuna Matsuda¹, Hao Zhu¹, Jae Hoon Oh², Hideki Nakamura^{1,2}, Muneo Tsujikawa², Tomonori Tamura¹, Itaru Hamachi^{1,2} (1. Graduate School of Engineering, Kyoto University, 2. JST ERATO)
 10:50 AM - 11:10 AM
- [E1662-1am-07] Relationships between catalyst-

promoted oxygenation level of amyloid β and cytotoxicity
 ○Ryota Matsukawa¹, Masahiro Furuta¹, Harunobu Mitsunuma^{1,2}, Shigehiro Kawashima¹, Youhei Sohma³, Motomu Kanai¹
 (1. Grad. Sch. Pharm. Sci., Tokyo Univ., 2. JST PRESTO, 3. Sch. Pharm. Sci., Wakayama Med. Univ.)
 11:10 AM - 11:30 AM

D1443

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

[D1443-1pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Shuhei Higashibayashi, Toshitaka Okamura
 2:00 PM - 3:40 PM D1443 (1443, Bldg. 14 [4F])

- [D1443-1pm-01] Stereochemical assignment of macrolide natural products by GIAO NMR calculation and DP4+ analysis
 ○Keisuke Murata¹, Hiroto Mori¹, Haruhiko Fuwa¹ (1. Chuo University)
 2:00 PM - 2:20 PM
- [D1443-1pm-02] Total Synthesis of Lobatamides
 ○Soichiro Yasui¹, Shona Banjo¹, Yoshiyuki Nagashima¹, Yuto Okada¹, Eiko Nakasuji¹, Keisuke Nakata¹, Noritaka Chida¹, Toshitaka Okamura¹, Takaaki Sato¹ (1. Keio University)
 2:20 PM - 2:40 PM
- [D1443-1pm-03] Isolation and Structure Elucidation of Cytotoxic Substances from Marine Mollusk *Aplysia kurodai* and Elucidation of their Origins
 ○Yusuke Hioki¹, Eri Anshita², Tatsuya Sato³, Toyoki Iwao⁴, Atsushi Kawamura^{1,5}, Tsunematsu Yuta^{1,6}, Masaki Kita¹ (1. Graduate School of Bioagricultural Sciences, Nagoya University, 2. School of Agricultural Sciences, Nagoya University, 3. Zakko Club, 4. Toba Fisheries Science Center, 5. Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 6. Institute for Advanced Research, Nagoya University)
 2:40 PM - 3:00 PM
- [D1443-1pm-04] Development and mechanistic studies

of photo-mediated [4+2] cycloaddition for rapid assembly of *iboga*-type scaffold
 ○Gavin Tay¹, Soushi Nishimura¹, Hiroki Kubota¹, Hiroki Oguri¹ (1. The University of Tokyo)

3:00 PM - 3:20 PM

[D1443-1pm-05] Syntheses of tricyclic diterpenes based on site-selective iodination and selective 6-*endo* radical cyclization
 ○Riichi Hashimoto¹, Kengo Hanaya¹, Shuhei Higashibayashi¹, Takeshi Sugai¹ (1. Keio university)

3:20 PM - 3:40 PM

E1662

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

[E1662-1pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Daisuke Takahashi, Gosuke Hayashi
 2:20 PM - 3:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-1pm-01] Efficient Synthesis of Tag-Modified Peptide Thioester Facilitated by γ -Substituted Proline

○Koki Nakatsu¹, Gosuke Hayashi¹, Hiroshi Murakami^{1,2} (1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.)
 2:20 PM - 2:40 PM

[E1662-1pm-02] Stereospecific syntheses of aryl C-glycosides with glycosyl trifluoroborate
 ○Kazuki Kurahayashi¹, Kengo Hanaya¹, Takeshi Sugai¹, Go Hirai², Shuhei Higashibayashi¹ (1. Fac. Pharm., Keio Univ., 2. Grad. Sch. Pharm. Sci., Kyushu Univ.)
 2:40 PM - 3:00 PM

[E1662-1pm-03] Regio- and Stereoselective β -Arabinofuranosylation Using a Boron-Mediated Aglycon Delivery Method
 ○Kazuki Inaba¹, Yuna Naito¹, Mina Tachibana¹, Kazunobu Toshima¹, Daisuke Takahashi¹ (1. Keio University)
 3:00 PM - 3:20 PM

[E1662-1pm-04] Chemical synthesis of ganglioside TACAs and their conjugation to alpha-galactosyl

ceramide for cancer vaccine constructs
 ○Mads Hartvig Clausen¹ (1. Technical University of Denmark)
 3:20 PM - 3:40 PM

E1661

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

[E1661-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Hiromu Kashida, Tamaki Endoh
 9:00 AM - 11:10 AM E1661 (1611, Bldg. 16 [1F])

[E1661-1am-01] Development of Cu(II)-responsive DNAzymes by chemoenzymatic incorporation of picolinic acid ligands
 ○Kohei Sakurai¹, Yusuke Takezawa¹, Mitsuhiko Shionoya¹ (1. Grad. School of Science, The Univ. of Tokyo)
 9:00 AM - 9:20 AM

[E1661-1am-02] Metal-dependent Regulation of Hybridization Behaviors of DNA Strands Containing Iminodiacetic Acid-modified Uracil Bases
 ○Keita Mori¹, Yusuke Takezawa¹, Mitsuhiko Shionoya¹ (1. Grad. School of Science, The Univ. of Tokyo)
 9:20 AM - 9:40 AM

[E1661-1am-03] Development of a sequencing method for XNA by using duplex formation
 ○Hiromu Kashida¹, Emiri Kagawa¹, Yuka Shimizu¹, Keisuke Toya¹, Yuichiro Aiba², Osami Shoji², Hiroyuki Asanuma¹ (1. Grad. Sch. Eng., Nagoya Univ., 2. Grad. Sch. Sci., Nagoya Univ.)
 9:40 AM - 10:00 AM

[E1661-1am-04] Development of *PureCap* Analogs for Co-transcriptional Capping Enable Synthesis of Fully Capped Messenger RNA
 ○Masahito Inagaki¹, Naoko Abe¹, Zhenmin Li¹, Yuko Nakashima^{1,2}, Susit Acharyya¹, Kazuya Ogawa¹, Daisuke Kawaguchi¹, Haruka Hiraoka¹, Bannno Ayaka¹, Zheyu Meng¹, Mizuki Tada¹, Tatsuma Ishida¹, Pingxue Lyu¹, Kengo Kokubo¹, Hirotaka Murase¹, Fumitaka Hashiya², Yasuaki Kimura¹, Satoshi Uchida^{4,3}

Abe Hiroshi^{1,5,6,2} (1. Nagoya University, 2. Research Center for Materials Science, Nagoya University, 3. Kyoto Prefectural University of Medicine, 4. iCONM, 5. JST-CREST, 6. iGCORE)
10:10 AM - 10:30 AM

[E1661-1am-05] NMR analysis of mismatch base pair recognition mechanism by naphthyridine derivatives

○Shuhei Sakurabayashi^{1,2}, Kyoko Furuita¹, Noriaki Sugiura², Takeshi Yamada², Toshimichi Fujiwara¹, Kazuhiko Nakatani², Chojiro Kojima^{1,3} (1. Institute for Protein Research, Osaka University, 2. SANKEN, Osaka University, 3. Yokohama National University)

10:30 AM - 10:50 AM

[E1661-1am-06] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (86): Intracellular multicolor detection of multiple chemicals using signaling light-up aptamers

○Tamaki Endoh¹, Jia-Heng Tan², Shuo-Bin Chen², Naoki Sugimoto^{1,3} (1. FIBER, Konan University, 2. Sun Yat-sen University, 3. FIRST, Konan University)

10:50 AM - 11:10 AM

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

[E1661-1vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Koji Oohora, Nobutaka Fujieda

4:10 PM - 6:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-1vn-01] Proposed BciC enzymatic hydrolysis and decarboxylation mechanism

○Mitsuaki Hirose¹, Jiro Harada², Yuichiro Kashiwama³, Hitoshi Tamiaki¹ (1. Ritsumeikan Univ., 2. Kurume Univ., 3. Fukui Univ. of Technol.)

4:10 PM - 4:30 PM

[E1661-1vn-02] Fabrication of Oil-in-Water (O/W) emulsions using enzyme reactive self-assembling peptides

○Ayato Higuchi¹, Rie Wakabayashi¹, Masahiro Goto^{1,2}, Norihiro Kamiya^{1,2} (1. The Univ. of Kyushu, 2. Center for Future Chemistry, The

Univ. of Kyushu)

4:30 PM - 4:50 PM

[E1661-1vn-03] Dispersion of protein nanoparticle in water/DMSO mixed solvent

○Maika Yamashita¹, Norifumi Kawakami¹, Kenji Miyamoto¹ (1. Keio University)

4:50 PM - 5:10 PM

[E1661-1vn-04] Studies on the association character and structural analysis of antibody light chain that tetramerizes by domain swapping

○Takahiro Sakai¹, Shohei Yamaguchi¹, Tsuyoshi Mashima¹, Naoya Kobayashi¹, Hideaki Ogata⁴, Emi Hifumi², Taizo Uda³, Shun Hirota¹ (1. Nara Inst. Sci. Tech., 2. Oita Univ., 3. ISIT, 4. University of Hyogo)

5:10 PM - 5:30 PM

[E1661-1vn-05] Development of Artificial Metalloenzymes with 2-His-1-Carboxylate Facial Triad toward Stereoselective Michael Addition Reaction

○Ryusei Matsumoto¹, Saho Yoshioka², Yoshitsugu Morita¹, Nobutaka Fujieda^{1,2} (1. Osaka Metropolitan University, 2. Osaka Prefecture University)

5:40 PM - 6:00 PM

[E1661-1vn-06] Catalytic C-H bond amination by engineered hemoproteins containing iron porphycene as an artificial cofactor

○Yoshiyuki Yoshiyuki¹, Koji Oohora¹, Takashi Hayashi¹ (1. Osaka University)

6:00 PM - 6:20 PM

[E1661-1vn-07] Directed Evolution of Myoglobin Reconstituted with an Iron Corrole Complex: Development of Artificial Peroxidase with Enhanced Catalytic Activity

○Koki Takeuchi¹, Shunsuke Kato¹, Takashi Hayashi¹ (1. Graduate School of Engineering, Osaka University)

6:20 PM - 6:40 PM

E1662

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

[E1662-1vn] 17. Biofunctional Chemistry, Biotechnology

Chair: Masayasu Taki, Yoshitaka Koseki
4:10 PM - 6:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-1vn-01] Design and application of functional oligonucleotides encoding the information of intracellular target metabolite

○Yuto Motohashi¹, Shuhei Moritani¹, Tatsuya Nishihara¹, Kazuhito Tanabe¹ (1. Aoyama Gakuin University)

4:10 PM - 4:30 PM

[E1662-1vn-02] Functional Thin-Layer Chromatography for Tissue Glutathione Imaging

○Tatsuya Nishihara¹, Koki Nishida¹, Rika Tsukame¹, Kazuhito Tanabe¹ (1. Aoyama Gakuin University)

4:30 PM - 4:50 PM

[E1662-1vn-03] Development of prodrug nanoparticles with highly selective drug release in cancer cells

○Aki Shibata¹, Yoshitaka Koseki¹, Keita Tanita¹, Ryuju Suzuki¹, Anh T.N. Dao^{1,2}, Hitoshi Kasai¹ (1. IMRAM, Tohoku University, 2. Nagasaki University)

4:50 PM - 5:10 PM

[E1662-1vn-04] Synthesis of β -lactamase-mediated activation of an SN-38-cephalosporin conjugate and their anticancer properties

○Yoshitaka Koseki¹, Mitsuki Uehara¹, Ryuju Suzuki¹, Anh Thi Ngoc Dao², Hitoshi Kasai¹ (1. Tohoku Univ., 2. Nagasaki Univ.)

5:10 PM - 5:30 PM

[E1662-1vn-05] Viscosity-Responsiveness and Melanosomal Visualization in Living Cells using Water-Soluble Fluorescent Probe

○Junya Adachi¹, Haruka Oda¹, Toshiaki Fukushima¹, Hiroka Sugai², Kohei Sato¹, Hiroshi Kimura¹, Kazushi Kinbara¹ (1. Tokyo Inst. Tech., 2. Univ. of Tsukuba)

5:40 PM - 6:00 PM

[E1662-1vn-06] Structure-property relationships of NIR-emissive phospho-rhodamine dyes and their utilization in cell imaging

○Yoshiki Tanaka¹, Masayasu Taki², Shigehiro Yamaguchi^{1,2} (1. Graduate school of science, Nagoya University, 2. ITbM, Nagoya University)

6:00 PM - 6:20 PM

[E1662-1vn-07] Design, synthesis, and chiroptical properties of figure-eight shaped macrocycles composed of bispyrrolidinoindoline alkaloidal scaffold
○Tasuku Honda¹, Daiji Ogata², Makoto Tsurui³, Takahiro Muraoka⁴, Yuichi Kitagawa³, Yasuchika Hasegawa³, Junpei Yuasa², Hiroki Oguri¹ (1. The University of Tokyo, 2. Tokyo University of Science, 3. Hokkaido University, 4. Tokyo University of Agriculture and Technology)

6:20 PM - 6:40 PM

K301

Academic Program [Oral B] | 18. Polymer | Oral B

[K301-1pm] 18. Polymer

Chair: Hiroharu Ajiro, Takeshi Yamamoto

1:20 PM - 3:40 PM K301 (K301, Lecture Hall Bldg. [3F])

[K301-1pm-01] Extrapolation performance Improvement

by quantum chemical calculations for machine learning-based predictions of flow-synthesized binary copolymers.

○Shogo Takasuka¹, Shunto Oikawa¹, Takayoshi Yoshimura², Sho Ito¹, Yosuke Harashima¹, Tomoaki Takayama¹, Shigehito Asano³, Akira Kurosawa³, Tetsunori Sugawara³, Miho Hatanaka², Tomoyuki Miyao¹, Takamitsu Matsubara¹, Yuya Ohnishi³, Hiroharu Ajiro¹, Mikiya Fujii¹ (1. Nara Institute of Science and Technology, 2. Keio University, 3. JSR Corporation)

1:20 PM - 1:40 PM

[K301-1pm-02] Synthesis of heat-resistant polymer particles by dispersion polymerization and RAFT precipitation polymerization of styrene with maleimide derivatives

○Shun Yamazaki¹, Daisuke Aoki¹, Tatsuo Taniguchi¹, Takashi Karatsu¹, Takeshi Wakiya², Koki Okura² (1. Chiba university, 2. Sekisui Chemical Company)

1:40 PM - 2:00 PM

[K301-1pm-03] Monomer Sorting and Parallel Polymerization in Bichannel MOFs

○Keat Beamsley¹, Nobuhiko Hosono¹, Takashi

Uemura¹ (1. Grad. Sch. of Eng., The Univ. of Tokyo)

2:00 PM - 2:20 PM

[K301-1pm-04] Synthesis of double-stranded polymers via controlled crosslinking in coordination nanospaces

○Masahiro Abe¹, Tomohito Mori², Yuki Kametani³, Takashi Uemura³ (1. Graduate School of Frontier Sciences, The University of Tokyo, 2. School of Engineering, The University of Tokyo, 3. Graduate School of Engineering, The University of Tokyo)

2:20 PM - 2:40 PM

[K301-1pm-05] Highly efficient polymerization behavior using molecular flow field induced by scanning wave photopolymerization

○Takuto Ishiyama¹, Hirona Nakamura¹, Miho Aizawa^{1,2}, Kyohei Hisano¹, Shoichi Kubo¹, Atsushi Shishido¹ (1. Tokyo Institute of Technology, 2. PRESTO, JST)

2:40 PM - 3:00 PM

[K301-1pm-06] Development of Alternating Copolymerization by Ring-Opening Metathesis Polymerization of Fluoroalkenes

○Kaoru Tashiro¹, Midori Akiyama¹, Kimiaki Kashiwagi², Takashi Okazoe^{1,2} (1. The Univ. of Tokyo, 2. AGC Inc.)

3:00 PM - 3:20 PM

[K301-1pm-07] Screw-Sense Induction to Poly(quinoxaline-2,3-diyl) Bearing Achiral Amino Groups by Addition of Chiral Acids in Water

○Tomonori Yamawaki¹, Ren Hirano¹, Takeshi Yamamoto¹, Michinori Sugimoto¹ (1. Kyoto university)

3:20 PM - 3:40 PM

B445

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

[B445-1am] 19. Colloid and Interface Chemistry

Chair: Masaki Saruyama, Yosuke Okamura

9:00 AM - 11:30 AM B445 (445, Bldg. 4 [4F])

[B445-1am-01] Reversible control of dispersibility of cubic gold nanoparticles induced by

visible light irradiation

○Koichiro Saito¹, Keegan McGehee^{1,2}, Yasuo Norikane^{1,2} (1. AIST, 2. Univ. of Tsukuba)

9:00 AM - 9:20 AM

[B445-1am-02] Sonication-induced nanocrystallization of a gold cluster enabled by encapsulation in micelles

○Yuki Saito¹, Ayano Suda², Maki Sakai², Yukatsu Shichibu^{1,2}, Katsuaki Konishi^{1,2} (1. Fac. of Env. Earth Sci., Hokkaido Univ., 2. Grad. Sch. of Env. Sci., Hokkaido Univ.)

9:20 AM - 9:40 AM

[B445-1am-03] Fabrication and Unique Characterization of Polymeric Nanofiber Suspension as Novel Anisotropic Nanomaterials.

○Hayato Yokose¹, Naoya Ichihara¹, Yosuke Okamura^{1,2} (1. Grad. Sch. of Eng., Tokai Univ., 2. Micro/Nano Tech. Center, Tokai Univ.)

9:40 AM - 10:00 AM

[B445-1am-04] Structure– Function Relationship Studies of Hydrophobic Ligands for Stable Colloidal Nanoparticles

○Tatsuya Sudo¹, Shohei Yamashita¹, Hidehiro Kamiya¹, Yohei Okada (1. Tokyo University of Agriculture and Technology)

10:00 AM - 10:20 AM

[B445-1am-05] Dispersibility Study of Surface-modified TiO₂ Nanoparticles: Thermodynamics of Dispersion and Agglomeration in Less-polar Solvents

○Shohei Yamashita¹, Yukina Ito¹, Tatsuya Sudo¹, Hidehiro Kamiya¹, Yohei Okada¹ (1. Tokyo University of Agriculture and Technology)

10:30 AM - 10:50 AM

[B445-1am-06] Anisotropic control of three-dimensional nanoparticle superlattices

○Masaki Saruyama¹, Toshiharu Teranishi¹ (1. Kyoto Univ.)

10:50 AM - 11:10 AM

[B445-1am-07] Colloidal synthesis of coherent InP/ZnS core/shell nanocrystals and their optoelectronic applications

○Kazuhiro Nemoto¹, Naoto Shirahata^{1,2,3} (1. National Institute for Materials Science, 2. Hokkaido University, 3. Chuo University)

11:10 AM - 11:30 AM

[K202-1am] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Gergely Juhasz, Satoshi Takahashi

Wed. Mar 22, 2023 9:00 AM - 11:10 AM K202 (K202, Lecture Hall Bldg. [2F])

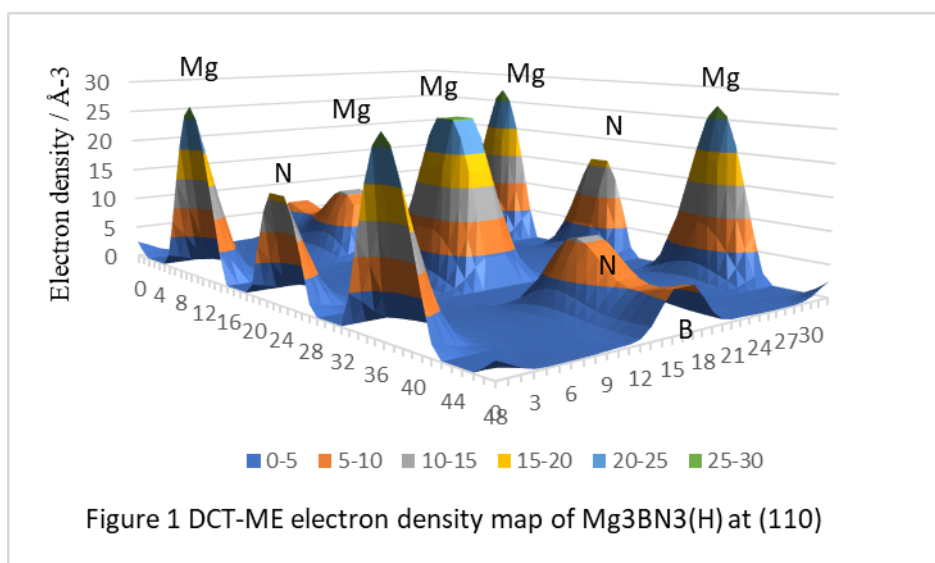
- [K202-1am-01] Study on Calculation of Electron Density Distribution of Centrosymmetric Mg₃BN₃ High Pressure Phase via Maximum Entropy Method Incorporating Discrete Cosine Transform
○Hideo Hiraguchi¹ (1. The Institution of Professional Engineers, Japan)
9:00 AM - 9:20 AM
- [K202-1am-02] Theoretical Study on Adhesion Interaction of Epoxy Resin with Graphene and Graphene oxide
○Amit Shrestha¹, Yosuke Sumiya, Kazunari Yoshizawa (1. Kyushu University)
9:20 AM - 9:40 AM
- [K202-1am-03] Differences of molecular absorption on titanium-dioxide surface - a computational study
○Gergely Juhasz¹ (1. Tokyo Institute of Technology)
9:40 AM - 10:00 AM
- [K202-1am-04] Exploration of stable structures of host guest materials: A comparison with density functional theory calculations and particle swarm optimization
○Shuta Fukuura¹, Takashi Yumura¹, Yohei Nishidate² (1. Kyoto Institute of Technology, 2. University of Aizu)
10:10 AM - 10:30 AM
- [K202-1am-05] Switching of self-assembly pathway for Pd₆L₄ square-based pyramid by NO₃⁻
○Satoshi Takahashi¹, Tsukasa Abe¹, Tomoki Tateishi², Hirofumi Sato^{3,4}, Shuichi Hiraoka¹
(1. Graduate School of Arts and Sciences, The Univ. of Tokyo, 2. iCeMS, Kyoto University, 3. Department of Molecular Engineering, Kyoto University, 4. 5 Fukui Institute for Fundamental Chemistry, Kyoto University)
10:30 AM - 10:50 AM
- [K202-1am-06] A DMRG/CASPT2 Investigation of Metalloporphyrins: Quantifying Ligand Noninnocence in Archetypal 3d and 4d Element Derivatives
QUAN MANH PHUNG¹, ○YASIN MUCHAMMAD¹, TAKESHI YANAI¹, ABHIJ GHOSH² (1. Nagoya University, 2. UiT-The Arctic University of Norway)
10:50 AM - 11:10 AM

Study on Calculation of Electron Density Distribution of Centrosymmetric Mg_3BN_3 High Pressure Phase via Maximum Entropy Method Incorporating Discrete Cosine Transform

(¹Professional Engineer, Japan belonging to the Institution of Professional Engineers, Japan) ○Hideo Hiraguchi ¹

Keywords: 3-dimensional DCT; Electron Density Distribution Maps; Maximum Entropy Method; Mg_3BN_3 high pressure phase

The electron density distribution map of $\text{Mg}_3\text{BN}_3(\text{H})^{1)-3)}$ via the Maximum Entropy Method^{5), 6)} incorporating the 3-dimensional discrete cosine transform (3D-DCT)⁴⁾ has been obtained in Fig. 1. For these calculations, $Fhkl(h=0\sim4, k=0\sim4, l=0\sim4)$ and $33\times33\times49$ voxels in the unit cell were used. The 3D-DCT electron density map whose negative electron densities were replaced for $0.1/\text{\AA}$ was used for a starting electron density map for the Maximum Entropy calculation incorporating into the 3D-DCT. As shown in Fig.1, a top of each electron density peak is more rounded than the normal Maximum Entropy maps. However, the value of constraint function C is 180, when each σ is set as 5%. Further convergence is a challenge for the near future.



1) H.HIRAGUCHI, O.SAKATA, H.HASHIZUME, A.TAKENAKA, O.FUKUNAGA.(1990). J. Cryst. Soc.Jp. OB-11, 32. 2) H. HIRAGUCHI, H. HASHIZUME, O. FUKUNAGA, A. TAKENAKA, M. SAKATA.(1991). J. Appl. Cryst. 24. 3) H. HIRAGUCHI, H. HASHIZUME, S. SASAKI, S. NAKANO, O. FUKUNAGA. (1993). Acta Cryst. B49. 4)H. HIRAGUCHI.(2021).J.Appl.Cryst. 5) M. Sakata & M. Sato, Acta Cryst. A46, 263-270, 1990. 6) M. Sakata, R. Mori, S. Kumazawa, M. Takata & H. Toraya, J. Appl. Cryst. 23, 526-534, 1990.

Theoretical Study on the Adhesion Interaction of Epoxy Resin with Graphene and Graphene Oxide

(Institute for Material Chemistry and Engineering and IRCCS, Kyushu University 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan) ○Amit Shrestha, Yosuke Sumiya, Kazuki Okazawa, Takahiro Uwabe, and Kazunari Yoshizawa

Keywords: Graphene oxide, Density functional theory, Adhesion, Epoxy resin

Carbon fiber-reinforced plastic (CFRP) composites are used in many applications due to their various properties, such as lightweight and high strength. To enhance the performance of such composites, the interfacial adhesion strength between reinforcing fillers and polymer matrices needs to be improved. Graphene possesses great potential as an excellent filler for polymer matrices such as epoxy resin (ER). However, the graphene surface is hydrophobic and exhibits poor adhesive behavior with ER, limiting its application in nanocomposites. The adhesion strength can be improved by using graphene oxide (GO), which is obtained by functionalizing the graphene surface with oxygen-containing groups (epoxides and hydroxyls). To investigate their difference, we analyzed the adhesion interfaces of ER to graphene and GO based on density functional theory (DFT) with dispersion correction.¹

The ER was modeled by the structure (**3**) formed by the curing reactions of diglycidyl ether of bisphenol A (**1**) and the curing agent (**2**) in Figure 1. The adhesion force for each interface was estimated from the maximum value of the force curve obtained by differentiating the energy curve when **3** pulls off the surface. The adhesion force for graphene was 335 MPa and for GO was 558 MPa. Decomposition of the adhesion forces into DFT and dispersion components revealed that the dispersion contribution did not change much at both interfaces, but the DFT contribution to the adhesion force at the ER/GO interface was significant.

Applying the crystal orbital Hamiltonian population (COHP) analysis to the interactions at each interface, it was found that the bonding-type interactions of the hydrogen bonds and OH- π interactions between the functional groups of **3** and the GO surface contribute to the adhesive strength. Here, the epoxide on the GO surface was not involved in these interactions, only the hydroxy groups. Also, these bonding-type interactions were absent at the ER/graphene interface. Therefore, it was found that ER adhered to the graphene surface only through dispersion interaction, while for the GO surface, interactions involving charge transfer as well as dispersion interaction contributed to the adhesive strength.

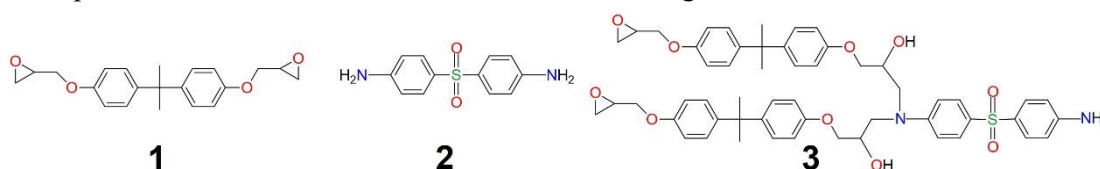


Fig.1 The structures of **1-3**.

1) Shrestha, A.; Sumiya, Y. Okazawa, K.; Uwabe, T.; Yoshizawa, K. submitted.

Differences of molecular absorption on titanium-dioxide surfaces - a computational study

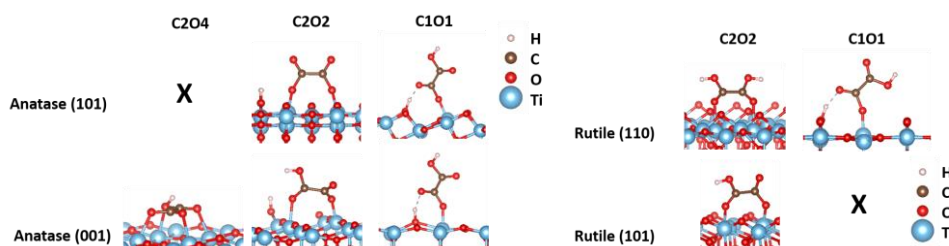
(School of Science, Tokyo Institute of Technology) ○Gergely JUHASZ

Keywords: Bayesian optimization, DFTB, TiO₂, anatase, rutile

Titanium dioxide is a common electrochemical and catalytic component. Such an electrode or catalyst surface can be covered with the two most common phase of TiO₂, anatase and rutile phases, and different facets of them. The ration of these phases as well that the surfaces can be controlled by different synthetic approaches. We have studied the absorption of mono- and dicarboxylic acid molecules on anatase (001), (101) and rutile (110) and (101) surfaces. In this talk we focus on the absorption oxalic acid, as it shows a fascinating variety of binding modes.

We performed our calculations of slab models of titanium dioxide phases in vacuum (without considering the solvent effect) and a single isolate oxalic acid per unit. The calculations were performed using DFTB method (DFTB+ software) and matsci parameters as they have been proved to produce comparable results to DFT calculation at the fraction of the cost.

Oxalic acid has a wide variety of options to connect to oxide surfaces depending on the geometry of its two carboxylic groups and the protonation state of these groups. We have found that on anatase (001), and rutile (110) surfaces both carboxylic group tend to connect to the surface, while on anatase (101) and rutile(101) single group attachment is a competitive alternative (see in Figure bellow). These differences are mostly coming form the O – O distance on the given TiO₂ surfaces. The binging between the surface and acid is strong (binding energies between 90-300 kJ /mol), however the competitive binding of several oxalic acid molecules may favor other isomers that allow more dense packing.



Exploration of stable structures of host guest materials: A comparison with density functional theory calculations and particle swarm optimization

(¹Graduate School of Engineering, Kyoto Institute of Technology, ²University of Aizu)

○Shuta Fukuura,¹ Takashi Yumura,¹ Yohei Nishidate²

Keywords: Density functional theory (DFT) calculations; Geometry optimization; Machine learning; Particle swarm optimization; Carbon nanotubes

In recent years, quantum chemical calculations can be applied to design nanometer-sized host-guest materials. In particular, geometry optimization is necessary to obtain energetically stable nano-structures. It is well known that widely used algorithms in geometry optimization, such as the conjugate gradient (CG) method, is time-consuming and requires us proper set of the initial structure for the fast termination of optimization. In addition, the algorithms frequently find local minima instead of the global minima. To solve these problems, the current study utilizes the particle swarm optimization (PSO), a kind of artificial intelligence algorithm, for the optimization of host-guest structures consisting of an iodobenzene monomer inside carbon nanotubes, where host-guest interactions are important to determine molecular orientations.

To evaluate the PSO algorithm, we explored stable orientations of an iodobenzene inside a carbon nanotube using PSO. In exploring stable structures, we ignored the distortion of iodobenzenes and nanotubes, treating interactions between them with Lennard-Jones (LJ) potential. The results were compared with stable structures obtained from density functional theory (DFT) optimizations¹⁾ in terms of internuclear separations between host and guest as shown in Figure 1. In fact, from Figure 1, we found that the LJ-combined PSO calculations, costing less computational resources, can yield inner iodobenzene orientation comparable to those obtained from accurate and costly DFT optimizations, although there are applicability limitations.

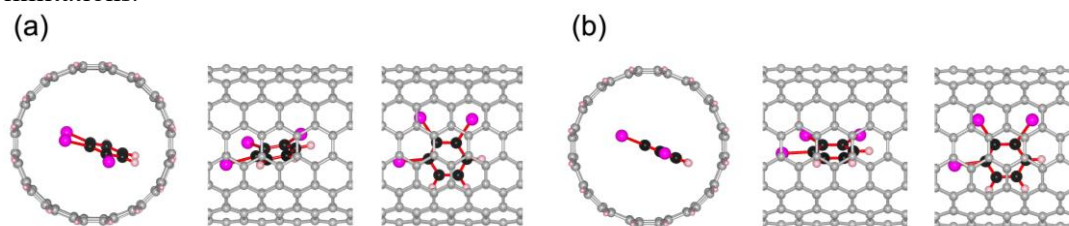


Figure 1. Stable structures of 1,2,3-triiodobenzene inside an (8,8) carbon nanotube obtained by (a) DFT optimizations and (b) LJ-combined PSO calculations.

1) T. Yumura, S. Fukuura, R. Miki, *J. Phys. Chem. C* **2022**, *126*, 365-377.

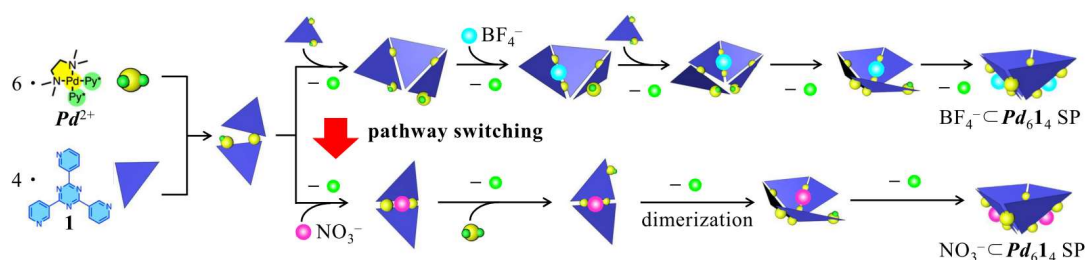
Switching of self-assembly pathway for Pd₆L₄ square-based pyramid by NO₃⁻

(¹Graduate School of Arts and Sciences, The University of Tokyo, ²iCeMS, Kyoto University, ³Department of Molecular Engineering, Kyoto University, ⁴Fukui Institute for Fundamental Chemistry, Kyoto University) ○Satoshi Takahashi,¹ Tsukasa Abe,¹ Tomoki Tateishi,² Hirofumi Sato,^{3,4} Shuichi Hiraoka¹

Keywords: Molecular Self-Assembly; Chemical Master Equation; Kinetic Control

Molecular self-assembly proceeds under both thermodynamic and kinetic controls, the former of which has long been the major strategy to obtain the objective products. On the other hand, in kinetically controlled self-assembly, the final assemblies can be produced with the yields higher the Boltzmann distribution by pathway selection. Although a proper approach that can modulate energy landscape of molecular self-assembly is needed to realize such a situation, so far this phenomenon has not been investigated from that point of view.

In this study¹, based on the complementary experimental results, we have revealed from numerical simulations (NASAP, numerical analysis of self-assembly process) that the reaction pathway switching can be realized for the self-assembly of a Pd₆L₄ square-based pyramid (SP) complex due to the catalytic and kinetic template effects of NO₃⁻. A reaction network model was prepared with 592 elementary reactions among 112 chemical species expected to be formed in the course of the global self-assembly reaction. From the fitting to the corresponding experimental results obtained by QASAP (quantitative analysis of self-assembly process)², rate constants of the elementary reactions for seven classes were obtained. Reaction frequencies derived from the time evolution of the elementary reactions led to the dominant reaction pathway and the rate-determining step for forming the Pd₆L₄ SP. How the pathway switching is achieved is discussed based on the comparison of the rate constant parameters in the present NASAP results and those given in the absence of NO₃⁻.³



1) T. Abe et al., submitted. 2) S. Hiraoka, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 957; S. Hiraoka, *Israel J. Chem.* **2018**, *59*, 151; S. Hiraoka et al., *Chem. Rec.* **2021**, *21*, 443. 3) T. Tateishi et al., *Inorg. Chem.* **2021**, *60*, 16678.

A DMRG/CASPT2 Investigation of Metalloporphyrins: Quantifying Ligand Noninnocence in Archetypal 3d and 4d Element Derivatives

(¹Graduate School of Science, Nagoya University, ²UiT-The Arctic University of Norway)

Quan Manh Phung,¹ OYasin Muchammad,¹ Takeshi Yanai,¹ Abhik Ghosh²

Keywords: DFT; DMRG; CASPT2; porphyrin; ligand noninnocence **[5 words at most]**

We reported a quantitative study of seven archetypal metalloporphyrins to elucidate their degree of ligand noninnocence (porphyrin radical character) using hybrid density functional theory (B3LYP) and density matrix renormalization group (DMRG). In decreasing order of non-innocent character, we identified them to be Mn[Cor]Cl > Fe[Cor]Cl > Fe[Cor](NO) > Mo[Cor]Cl₂ > Ru[Cor](NO) \approx Mn[Cor]Ph \approx Fe[Cor]Ph \approx 0 ([Cor] refers to unsubstituted porphyrin ligand).

DMRG-CASSCF/CASPT2 also yielded detailed excited state energetics, explicating periodic patterns of the transition elements involved. In this study, we further confirmed the previously studied ground state of Fe[Cor](NO) system ($S = 0$) to be best described as a non-innocent structure, where the locally $S = \frac{1}{2}$ {FeNO}⁷ unit is antiferromagnetically coupled to a porphyrin radical. Whereas the Ru[Co](NO) system was found to be non-innocent, as it conforms {RuNO}⁶-Cor³⁻, having a locally closed-shell porphyrin.

In addition, the closest excited state of Fe[Cor](NO) that conforms a ferromagnetically coupling $S = 1$ {FeNO}⁷-Cor²⁻ state is only about ~17.5 kcal/mol higher than the $S = 0$ ground state. Comparatively, the triplet first excited state of Ru[Cor](NO) has a much larger gap with its ground state at 37.4 kcal/mol. The same way that Mo[Cor]Cl₂ exhibits an adiabatic doublet-quartet gap of 36.1 kcal/mol. These large gaps associated with metal-ligand spin coupling in Ru[Cor](NO) and Mo[Cor]Cl₂ indicate the much greater covalent character of the 4d- π interactions compared to that of involving 3d orbitals.

[229 words]

1) Q.M. Phung, Y. Muchammad, T. Yanai, and A. Ghosh, *JACS Au* **2021**, 1, 12, 2303–2314

Academic Program [Oral B] | 07. Inorganic Chemistry | Oral B**[K502-1am] 07. Inorganic Chemistry**

Chair: Eisuke Yamamoto, Nobuyoshi Miyamoto

Wed. Mar 22, 2023 9:00 AM - 10:50 AM K502 (K502, Lecture Hall Bldg. [5F])

[K502-1am-01] Mechanism for neat monolayer tiling of 2D nanosheets by a spin-coating method○Nobuyuki Sakai¹, Takayoshi Sasaki¹ (1. National Institute for Materials Science)

9:00 AM - 9:20 AM

[K502-1am-02] A Novel Synthesis Method of Palladium Nanosheets with Thickness Control○Sumiya Ando¹, Eisuke Yamamoto², Makoto Kobayashi², Minoru Osada^{2,3} (1. Nagoya Univ., 2. IMaSS, Nagoya Univ., 3. WPI-MANA, NIMS)

9:20 AM - 9:40 AM

[K502-1am-03] Synthesis of amorphous silica nanosheets using solid-state surfactant and investigation of the exfoliation behavior○Eisuke Yamamoto¹, Yuma Takezaki¹, Makoto Kobayashi¹, Minoru Osada^{1,2} (1. Nagoya University, 2. International Center for Materials Nanoarchitectonics, National Institute for Materials Science)

9:40 AM - 10:00 AM

[K502-1am-04] Molecular simulation and thermodynamic analysis of saturated water content in organomontmorillonite○Masaya Miyagawa¹, Keigo Tozaki¹, Fumiya Hirose¹, Hiromitsu Takaba¹ (1. Kogakuin university)

10:10 AM - 10:30 AM

[K502-1am-05] Structural analyses of monodisperse nanosheet assemblies by small-angle X-ray scattering○Nobuyoshi Miyamoto¹ (1. Fukuoka Inst. Technol.)

10:30 AM - 10:50 AM

スピncコート法によるナノシートの単層稠密配列メカニズム

(物質・材料研究機構) ○坂井 伸行・佐々木 高義

Mechanism for Neat Monolayer Tiling of 2D Nanosheets by a Spin-Coating Method (*National Institute for Materials Science*) ○Nobuyuki Sakai, Takayoshi Sasaki

Although a spin-coating technique realizes the neat monolayer tiling of 2D nanosheets,¹⁾ the mechanism of how the nanosheets are tiled has not been clarified yet. In the present study,²⁾ we have systematically examined by microscopic observations how the nanosheets are deposited on a substrate surface at various rotation speeds. As a result, we have found that the neat monolayer tiling of nanosheets is attained on the solvent surface, and then the monolayer film is transferred onto the substrate surface upon evaporation of the solvent (Figure 1). We have also clarified how the rotation speed governs the deposition behaviors, which can predict the optimum conditions for the neat monolayer tiling over an entire surface of the substrate.

Keywords : 2D Nanosheet; Spin-Coating; Monolayer Film; Neat Tiling

スピncコート法によりナノシートを単層で稠密配列できることが報告されているが¹⁾、そのメカニズムは明らかにされていない。既報ではスピncコートの際に発生する遠心力によりナノシートが基板の端から中心に向けてパッキングされていき単層稠密配列が実現すると述べられている¹⁾。しかし、スピncコートの際にナノシートにかかる遠心力は小さく、スピncコートを行う数分間ではナノシートはほとんど動かないことが確かめられた。本研究では²⁾、さまざまな回転速度のもと、ナノシートが基板表面にどのように堆積するかを顕微鏡観察により体系的に調べ、ナノシートの単層稠密配列メカニズムを検討した。その結果、スピncコート中にナノシートが溶媒表面で単層稠密配列し、溶媒の蒸発に伴って基板表面に転写されることがわかった(図 1)。また、回転速度と堆積挙動の関係から、基板表面全体で単層稠密配列が達成されるための条件を予測する方法を見出した。

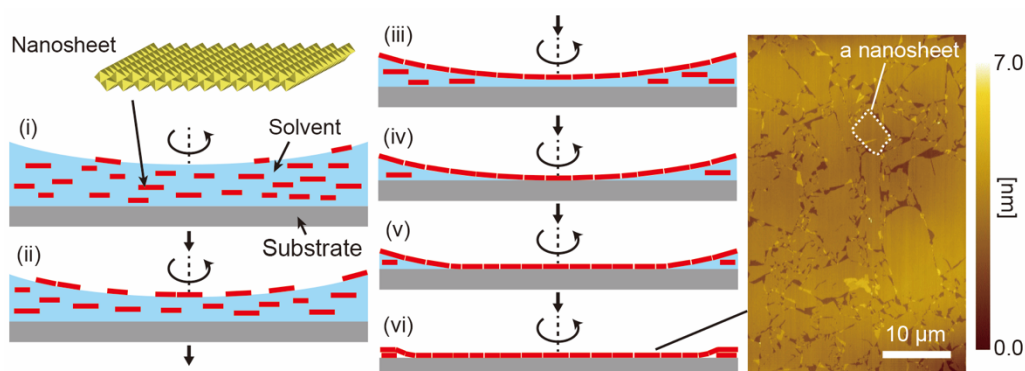


Figure 1. Schematic illustration of the formation process of a monolayer film of neatly tiled nanosheets on a substrate surface during the spin-coating, and an AFM image of the resulting film.

1) K. Matsuba, C. Wang, K. Saruwatari, Y. Uesasaki, K. Akatsuka, M. Osada, Y. Ebina, R. Ma, T. Sasaki, *Sci. Adv.* **2017**, 3, e1700414.; 2) N. Sakai, T. Sasaki, *Langmuir* **2022**, 38, 12399.

A Novel Synthesis Method of Palladium Nanosheets with Thickness Control

(¹Graduate School of Engineering, Nagoya University, ²IMaSS, Nagoya University, ³WPI-MANA, National Institute for Materials Science) ○ Sumiya Ando,¹ Eisuke Yamamoto,² Makoto Kobayashi,² Minoru Osada^{2,3}

Keywords: Nanosheets; Palladium; Carbon Monoxide

Two-dimensional (2D) nanosheets with a few atomic thicknesses show unique properties different from 3D bulk counterparts. In the field of catalysis, noble metal nanosheets are expected to be an efficient way to decrease the usage of noble metals because of its high specific surface area and extraordinary high catalytic activity. Among such rare metal nanosheets, palladium (Pd) nanosheets have been synthesized using carbon monoxide (CO) as both reductants of Pd ions and adsorbents on 111 facets making Pd grown into 2D shape. However, conventional methods using a compressed CO gas cylinder or metal carbonyls as a CO source have serious drawbacks, such as the difficulty of large-scale synthesis and impurities contamination.¹ Moreover, designed synthesis of molecularly thin Pd nanosheets still remains a challenge.

Here, we report a novel synthesis method of Pd nanosheets using 2, 4, 6-Trichlorophenyl Formate (TCPF) as a CO source.² This organic material decomposes and emits CO gas when it reacts with weak base. Therefore, there are no problems with handling compressed CO gas and contamination with hetero metal atoms. In addition, introduction speed of weak base, such as ammonia (NH₃), is controlled by hydrolysis speed of urea. This makes it possible to control introduction speed of CO gas, that is, thickness of Pd nanosheet.

In our presentation, we also address the thickness dependent properties of Pd nanosheets.

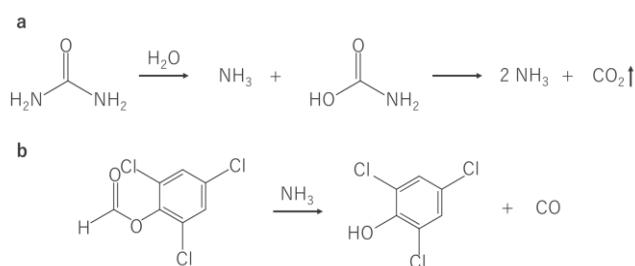


Figure 1 | Reaction Scheme of CO gas generation for synthesis of thickness controlled Pd nanosheets. a, NH₃ evolution from hydrolysis of urea. b, Decomposition of TCPF caused by reaction with NH₃.

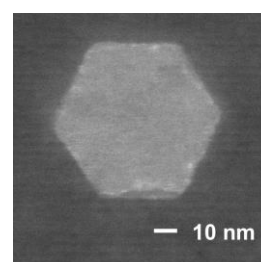


Figure 2 | Synthesized Pd nanosheets.

1. M. Luo, *et. al.*, *Nature*, 2019, **574**, 81-85.
2. H. Konishi, *et. al.*, *Chem. Pharm. Bull.*, 2018, **66**, 562-567.

固体界面活性剤を利用したアモルファスシリカナノシートの合成条件および剥離挙動の調査

(名大¹・NIMS²) ○山本 瑛祐¹・竹崎 佑麻¹・小林 亮¹・長田 実^{1,2}

Synthesis of amorphous silica nanosheets using solid-state surfactant and investigation of the exfoliation behavior (¹Nagoya University, ²International Center for Materials Nanoarchitectonics, National Institute for Materials Science) Eisuke Yamamoto,¹ ○Yuma Takezaki,¹ Makoto Kobayashi,¹ Minoru Osada^{1,2}

Silica constitutes the most abundant part of the Earth's crust, and the effective utilization of silica with precisely controlled morphology has been well studied. In particular, amorphous silica nanosheets have attracted great attentions because of their unique properties different from bulk amorphous silica. Recently, we found a new approach for synthesizing the colloidal amorphous silica nanosheets with molecularly thin thickness; exfoliation of nonionic surfactant amorphous silica lamellar hybrids. Here, we investigated the formation mechanism and critical factors for synthesizing lamellar hybrids. The lamellar hybrids were formed by adding tetraethoxysilane into the dispersion of solid-state surfactant formed below Krafft point. It was found that surfactant with solid phase was the suitable for the formation of layered hybrids suitable for exfoliating monolayer amorphous silica nanosheets.

Keywords : Amorphous silica; Nanosheets; Solid State Surfactants;

シリカは地殻上で最もありふれた化合物であり、その構造や形態制御を通じた有効活用は元素戦略上重要である。中でも、分子レベルの薄さを有するアモルファスシリカナノシートは、バルクと異なる構造や機械的特性を有するため注目を集めている。

¹⁾ 最近、我々は非イオン性界面活性剤-アモルファスシリカ層状複合体を剥離することで、厚み 1nm のアモルファスシリカナノシートの合成を達成した。本研究では、この前駆物質となる層状複合体の合成条件を明らかにした。層状複合体は、非イオン性界面活性剤を塩酸中に分散させたのちにテトラエトキシシラン(TEOS)を添加することで合成される。この TEOS 添加時の温度を 3℃ から 80℃ まで変化させて攪拌したところ、得られた粉末 XRD パターンから、40℃ 以下で合成した場合のみ層状複合体が得られることが明らかになった (Fig.1 (a))。この温度は界面活性剤のアルキル鎖が規則的に配列した固体相からミセル相に変化する温度(クラフト点)であった (Fig.1 (a))。クラフト点以下で合成した層状複合体はいずれも 1 層のナノシートとして剥離可能であり (Fig. 1(b))、アモルファスシリカナノシートの合成におけるキーファクターが明らかとなった。

1) E.Gao, *et al.*, *J. Appl. Phys.*, **2016** 119, 014301.

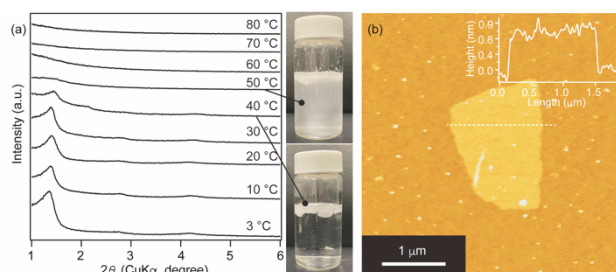


Fig. 1 (a) XRD patterns of the lamellar hybrids synthesized at various temperatures, (b) AFM image of the amorphous silica nanosheets synthesized at 3 °C.

分子シミュレーションと熱力学的解析による有機モンモリロナイトの飽和含水量の決定

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Molecular simulation and thermodynamic analysis of saturated water content in organomontmorillonite (¹Kogakuin University) ○Masaya Miyagawa,¹ Keigo Tozaki,¹ Fumiya Hirosawa,¹ Hiromitsu Takaba¹

Despite numerous studies on adsorption of aromatic compounds in organoclay, the adsorption mechanism has yet to be understood comprehensively. The presence of water molecule in the interlayer is one of the biggest factors to make it difficult to investigate the interlayer morphology. In the present study, we investigated the saturated water content in organoclay modeled by molecular dynamics (MD) and Grand canonical Monte Carlo methods. Analyzing the non-bond energy of H₂O in the organoclay is lower than that in the bulk model when the water content is small, indicating H₂O is more stable in the organoclay. The consistency is observed when the water content is 13.2wt%, which is suggested experimentally by thermogravimetry. Thus, it is found that the saturated water content is estimated theoretically. *Keywords: Molecular dynamics; Organoclay; Montmorillonite; Grand canonical Monte Carlo; Adsorption*

有機粘土が水溶液系で示す芳香族化合物の吸着については、半世紀以上の研究の蓄積がすでにあるにもかかわらず、吸着メカニズムだけでなく層間構造すらわかっていないことが非常に多い。近年では放射光を用いた X 線回折法で層間隔を直接測定することが可能になっているが¹⁾、層間は水分子を大量に含むため実験による構造の探究は容易ではない。我々はこれまでに分子動力学 (MD) 法を用いて有機モンモリロナイト層間の構造を明らかにしてきた^{2,3)}。本研究では、C₁₆H₃₃N(CH₃)₃⁺で修飾されたモンモリロナイト複合体 (Mont-C₁₆) についてさまざまな含水率のモデルを作製し、熱力学的に解析することで飽和含水率を決定すること、およびフェノール類で見られる選択的な吸着をシミュレーションで再現することを目的とした。

既報²⁾と同様の手法で Mont-C₁₆ のモデルを作製した。含水モデルは Grand canonical Monte Carlo 法で水分子を層間に配置し、NPT アンサンブルで MD 計算を実行することで作製した。層間の水分子の非結合性エネルギー E_{Clay} をバルク水のそれ E_{Bulk} と比べると含水率が < 13.2wt% では $E_{\text{Clay}} < E_{\text{Bulk}}$ であり、水分子は層間でより安定であることがわかる。13.2wt% のモデルでは $E_{\text{Clay}} = E_{\text{Bulk}}$ であることから、層間の水は飽和状態であると考えられる。実際、この値は Mont-C₁₆ の熱重量分析から推察される含水率とよく一致している⁴⁾。つまり、Mont-C₁₆ の飽和含水率は実験をせずとも分子シミュレーションでさまざまな構造のモデルを作製し、そのエネルギーを解析することで決定できることがわかった。発表では、溶媒和自由エネルギーに基づいたフェノールの吸着選択性についても議論する。

1) T. Okada et al., *Langmuir* **2021**, 37, 10469. 2) M. Miyagawa et al., *ACS Omega* **2021**, 6, 19314.

3) M. Miyagawa et al., *Langmuir*, **2022**, 38, 3514. 4) A. Abbas et al., *Appl. Clay Sci.* **2017**, 142, 21.

小角 X 線散乱による単分散ナノシート集合体の構造解析

(福岡工大工) 宮元展義

Structural Analyses of Monodisperse Nanosheet Assemblies by Small-Angle X-ray Scattering
(Department of Life, Environment, and Applied Chemistry, Fukuoka Institute of Technology) ○
Nobuyoshi Miyamoto

We have been investigating self-assembled superstructures and liquid crystal phases that are consist of inorganic nanosheets dispersed in a solvent¹⁾²⁾. For the structural analyses of such systems, in-situ techniques such as small angle scattering (SAS) and optical microscopy are important. In SAS analyses, generally, experimental data are fitted to theoretical scattering curves such as disk form factor and lamellar structural factor. However, experimental systems usually consist of complicated hierarchical structures, partial orientation, and random aggregation so that precise structural analyses are not straightforward. Here we report structural analyses of monodisperse nanosheet assemblies by comparing the experimental data with the numerically calculated scattering curves of the nanosheets with any arbitrary shape and superstructures. The numerical SAS curves of uniform isotropic dispersion of nanosheets coincided with analytical and experimental data. The experimental SAS data of various nanosheet superstructures were finely reproduced by the numerical calculations.

Keywords : Numerical Calculation, Small Angle Scattering, Monodisperse Nanosheets; Self-assembly

我々はこれまで、溶媒に分散した無機ナノシートが自発的に形成するさまざまな超構造や液晶状態についての研究を進めてきた¹⁾²⁾。このような系の構造解析では、その場観察できる小角散乱法や光学顕微鏡が有力な手段となる。小角散乱法では、一般的に、円板形状因子やラメラ構造因子などの解析的に得られる理論散乱曲線にフィッティングして構造解析を行うことが多い。しかし実際の実験系では、複雑な階層構造や、配向、凝集体などが混在しており、正確な構造同定が難しい場合も多い。そこで本研究では、任意形状のナノシートが形成した、任意の集合構造からの散乱パターンを数値計算し、実験データとの比較を行うことにより、単分散ナノシート集合体の構造解析を試みた。無配向で均一分散状態のナノシートの散乱曲線の数値計算結果は、解析解や実験データとよく一致した。さらに、さまざまな超構造を形成したナノシート分散系の散乱データは、数値計算によってよく再現された。]

1) N. Miyamoto et al. "Chapter 5: Inorganic Nanosheets as Soft Materials." In "*Functionalization of Molecular Architectures – Advances and Applications on Low-Dimensional Compounds*," Shikanaka, K., Ed. Pan Stanford Publishing: Singapore, 2019; pp 123-157.

2) N. Miyamoto et al., "Chapter 8: Colloidal nanosheets." In "*Inorganic Nanosheets and Nanosheet-Based Materials*", Nakato, T. et al., Eds. Springer Japan: Tokyo, 2017; pp 201-260.

[K305-1pm] 08. Catalysts and Catalysis

Chair: Kohsuke Mori, Seiji Yamazoe

Wed. Mar 22, 2023 1:10 PM - 3:40 PM K305 (K305, Lecture Hall Bldg. [3F])

- [K305-1pm-01] Revealing Hydrogen Spillover Pathways in Reducible Metal Oxide Supports**
○Kazuki Shun¹, Kohsuke Mori¹, Hiromi Yamashita¹ (1. Graduate School of Engineering, Osaka University)
1:10 PM - 1:30 PM
- [K305-1pm-02] Reaction mechanism of CO/CO₂ photo-conversion into ethylene and propylene using cobalt metal nanoparticle-supported ZrO₂.**
○Keisuke Hara¹, Rumiko Hirayama¹, Rento Ishii¹, Kaori Niki¹, Yasuo Izumi¹ (1. Chiba University)
1:30 PM - 1:50 PM
- [K305-1pm-03] Electrocatalytic reduction of carbon monoxide to multicarbon products on a copper-single atom catalysts**
○Keitaro Ohashi¹, Takashi harada¹, Shuji Nakanishi¹, Kazuhide Kamiya¹ (1. Osaka Univ.)
1:50 PM - 2:10 PM
- [K305-1pm-04] Chemoselective hydrogenation of nitro compounds over Ir-based hybrid clustering catalysts**
○Shun Hayashi¹, Tetsuya Shishido^{2,3} (1. Natl. Mus. Nat. Sci., 2. Tokyo Metrop. Univ., 3. ESICB, Kyoto Univ.)
2:10 PM - 2:30 PM
- [K305-1pm-05] Elucidation of molecular adsorption states of strong base metal oxide cluster by X-ray absorption spectroscopy**
○Tomoki Matsuyama¹, Hiroki Nagakari¹, Soichi Kikkawa¹, Naomi Kawamura², Kotaro Higashi², Naoki Nakatani¹, Seiji Yamazoe^{1,3} (1. Tokyo Metropolitan University, 2. JASRI, 3. JST-PRESTO)
2:40 PM - 3:00 PM
- [K305-1pm-06] Acid-Base Bifunctionality of Ti-based Perovskite Nanoparticles for Cyanosilylation**
○Takeshi Aihara¹, Wataru Aoki¹, Keigo Kamata¹, Michikazu Hara¹ (1. Tokyo Institute of Technology)
3:00 PM - 3:20 PM
- [K305-1pm-07] Homogeneous Investigation of N-Heterocyclic Carbene Stabilized Au-Nanoclusters for Electrocatalysis**
○Samuel Jacob^{1,2}, Joey DeJesus¹, Emily Albright², Yasuyo Tezuka¹, Masakazu Nambo¹, Cathleen Crudden^{2,1} (1. Nagoya University, 2. Queens University)
3:20 PM - 3:40 PM

Revealing Hydrogen Spillover Pathways in Reducible Metal Oxide Supports

(¹Graduate School of Engineering, Osaka University)

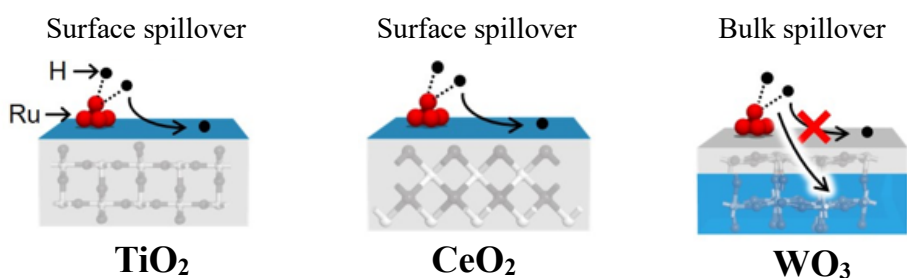
○Kazuki Shun,¹ Kohsuke Mori,¹ Hiromi Yamashita¹

Keywords: Hydrogen Spillover; Reducible Metal Oxides; Non-equilibrium Alloy Nanoparticle

Hydrogen spillover is a dynamic phenomenon which is initiated by the dissociation of hydrogen molecules followed by the migration onto the reducible metal oxide supports.¹ Spilled hydrogen atom shows specific behavior compared with gaseous hydrogen, thus it dramatically promotes the reduction of metal ions and the catalytic performance. However, in-depth understanding of its dynamic behavior, such as at what temperature it can take place, what pathway it follows, and the region to where hydrogen migrates, is still poorly understood because the observation method is not well established.

Our group has succeeded in the synthesis of binary alloy NPs catalysts with essentially immiscible metal combinations (Ru-Ni and Rh-Cu) on a TiO₂ support by utilizing spilled hydrogen atoms as a strong reductant. On the other hand, non-reducible γ -Al₂O₃ and MgO supports, whose hydrogen spillover abilities are inferior to that of TiO₂, afforded segregated NPs under the identical synthetic conditions.²⁻³ This means that the formation of non-equilibrium alloys strongly reflects the hydrogen spillover ability of the support surface.

In this work, we evaluated hydrogen spillover pathways in typical reducible metal oxide supports such as TiO₂, CeO₂ and WO₃ by combining the specific formation of non-equilibrium Ru-Ni alloy nanoparticle, *in-situ* techniques, kinetic analysis, and density functional theory calculation. The combined experiments revealed that TiO₂ and CeO₂ allowed the preferential migration of dissociated hydrogen atoms over their surfaces, whereas hydrogen atoms preferably migrated within the bulk over WO₃.⁴



1) W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinici, J. Bokhoven, *Nature*, **2017**, 541, 68. 2) S. Masuda, K. Shun, K. Mori, Y. Kuwahara, H. Yamashita, *Chem. Sci.*, **2020**, 16, 4194. 3) K. Mori, K. Miyawaki, and H. Yamashita, *ACS Catal.*, **2016**, 6, 3128. 4) K. Shun, K. Mori, S. Masuda, N. Hashimoto, Y. Hinuma, H. Kobayashi and H. Yamashita, *Chem. Sci.*, **2022**, 13, 8137.

コバルト金属ナノ粒子担持 ZrO₂ を用いたエチレン/プロピレンへの CO/CO₂ 光変換反応機構

(千葉大学¹) ○原 慶輔¹・平山 瑠海子¹・石井 蓮音¹・二木 かおり¹・泉 康雄¹
 Reaction mechanism of CO/CO₂ photo-conversion into ethylene and propylene using cobalt metal nanoparticles supported on ZrO₂ (¹*Graduate School of Science, Chiba University*)
 Keisuke Hara¹, Rumiko Hirayama¹, Rento Ishii¹, Kaori Niki¹, Yasuo Izumi¹.

Cobalt nanoparticles were supported on monoclinic ZrO₂ and the photocatalyst was reduced under H₂ at various temperatures. Using the combination of ¹³CO₂, ¹³CO, H₂, and/or D₂O and UV-visible light irradiation, ethylene and propylene were major products (Table 1b–d). The reaction mechanism was investigated by in-situ FTIR measurements and DFT calculations using VASP. The results demonstrated that both CO₂ and CO were adsorbed on the ZrO₂ surface, then the H-added COH species transferred onto the metallic Co nanoparticle surface via the interface between them. The CHOH, CH₂, and CH₃ species were favorable on the metallic Co surface. Furthermore, the CHOH and CH₂ species tend to C–C couple resulting in ethylene and propylene as one of the most favorable reaction pathway. On the other hand, non-adiabatic molecular dynamics calculations revealed that the excited electrons transfer owing to light irradiation transferred from ZrO₂ to CO₂ and/or CO on the femtosecond scale.

Keywords : Photocatalytic conversion, CO₂ Conversion, DFT calculation, Non-adiabatic molecular dynamics calculation

Monoclinic-ZrO₂ にコバルトナノ粒子を担持し、H₂ 雰囲気下での還元温度を変えながら、¹³CO₂ 及び ¹³CO、H₂ 及び D₂O を反応ガスとして用いて、紫外可視光照射したところ、エチレン、プロピレンを主生成物として得た(表 1b–d)。さらに in-situ FTIR 測定、および VASP を用いた DFT 計算により反応機構を調べた。その結果 CO₂ 及び CO いずれも ZrO₂ 表面に吸着し、次に H 付加された COH 種が界面を経由してコバルト金属ナノ粒子表面に移行し、CHOH・CH₂・CH₃ 種が有利に存在することがわかった。さらに CHOH 種と CH₂ 種とが C–C 結合しやすく、エチレン、プロピレンに至る経路が有力と認められた。また非断熱分子動力学計算により ZrO₂ からの光励起電子は CO₂ や CO へ fs スケールで移行することも明らかとなった。

Table 1. Kinetic Data on Photoconversion of CO₂ Using the Co (7.5 wt %)-ZrO₂ Photocatalyst

entry	catalyst	reactants	<i>T</i> _{reduction} (K)	formation rate (μmol h ⁻¹ g _{cat} ⁻¹)					
				¹³ CO	¹³ CH ₄	¹³ C ₂ H ₄	¹³ C ₂ H ₆	¹³ C ₃ H ₆	¹³ C ₃ H ₈
a	Co–ZrO ₂	¹³ CO ₂ (2.3 kPa) + H ₂ (21.7 kPa)	–	0.016	<0.002	<0.002	<0.002	<0.002	<0.002
b				11	190	<0.002	3.4	<0.002	0.25
c		¹³ CO ₂ (2.3 kPa) + H ₂ (2.3 kPa)	973	40	52	<0.002	1.1	<0.002	0.082
d		¹³ CO (2.3 kPa) + H ₂ (21.7 kPa)		–	5.2	0.17	0.58	0.72	0.96
e		¹³ CO (2.3 kPa) + H ₂ (2.3 kPa)		–	2.2	5.2	0.17	0.23	0.024

Electrocatalytic reduction of carbon monoxide to multicarbon products on copper-single atom catalysts

(¹Graduate School of Engineering Science, Osaka University) ○Keitaro Ohashi,¹ Takashi Harada,¹ Shuji Nakanishi,¹ Kazuhide Kamiya¹

Keywords: CO₂/CO Electroreduction; Single Atom Catalysts; First-Principles Calculation

The electrochemical CO₂ reduction reaction (CO₂RR) is an attractive strategy for closing the carbon cycle by converting CO₂ to value-added multicarbon products (C₂₊), using renewable electricity. Considering that C₂₊ products are formed via carbon monoxide (CO) dimerization,¹ the development of efficient electrocatalysts for CO reduction reaction (CORR) to C₂₊ products is highly required. Single-atom electrocatalysts (SAECs), which are composed of singly isolated metal sites supported on heterogeneous substrates, have attracted considerable recent attention as next-generation electrocatalysts for various key reactions from the viewpoint of the environment and energy. Our group has recently demonstrated that SAECs composed of metal-modified covalent triazine frameworks (M-CTFs) exhibit various unique electrocatalytic functions depending on the metal species.^{2,3} Herein, we attempted to apply copper-modified CTF (Cu-CTF) as the electrocatalyst to reduce gaseous CO to C₂₊.

Cu-CTF was synthesized based on the reported method,⁴ and the catalyst ink was drop-coated on gas diffusion electrodes (GDEs) (Fig. 1). The faradaic efficiency (FE) for acetate and ethylene in 1 M KOH at -1.0 V (vs. reversible hydrogen electrode) reached up to 27.2% and 16.2%, respectively. To elucidate the reaction mechanism of the selectively produced acetate, CORR was performed by changing the electrolyte to 5 M NH₃ and 1 M KCl. In this electrolyte, the formation of acetamide was observed with the FE of 4.7%, which is produced via nucleophilic attack of ammonia on ketene (C=C=O) intermediate. The density functional theory (DFT) calculation indicated that in the process of C₂₊ formation on Cu-CTF, C-C bond reaction proceeds by the insertion of a CO molecule into adsorbed *CHO intermediate, which is a one-electron reduction reaction intermediate of CO.

1) Kortlever, R. *et al. J. Phys. Chem. Lett.* **2015**, 6 (20), 4073–4082. 2) Kamiya, K. *Chem. Sci.* **2020**, 11 (32), 8339–8349. 3) **Ohashi, K.** *et al. J. Phys. Chem. C.* **2021**, 125 (20) 4) Kamiya, K. *et al. Nat. Commun.* **2014**, 5.

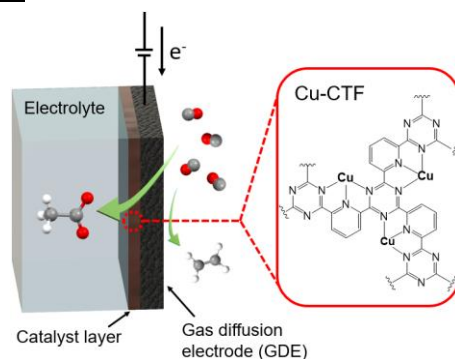


Figure 1. Schematic illustration of CORR on Cu-CTF/GDE.

Chemoselective hydrogenation of nitro compounds over Ir-based hybrid clustering catalysts

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³ESICB, Kyoto University) ○Shun Hayashi,¹ Tetsuya Shishido^{2,3}

Keywords: Iridium; Hybrid Cluster; Chemoselective Hydrogenation; Nitro Group

Chemoselective hydrogenation of nitroaromatics to form anilines especially in the presence of other reducible groups such as C=C is one of the important reactions in the production of fine chemicals. Since the catalytic activities of heterogeneous nanoparticle catalysts varies with the adjacent oxide species, forming a high density of metal/oxide interfaces is important to improve the selectivity.^{1,2} We had previously reported a catalyst preparation method, namely hybrid clustering, for the efficient formation of metal/oxide interfacial active sites.³ In this study, supported Ir-based catalysts were prepared by using hybrid clusters as precursors. The effect of the preparation method on the activity for 4-nitrostyrene hydrogenation is discussed in comparison with typical Ir based catalysts.

The hybrid clustering catalyst, Ir₄Mo₄/Al₂O₃, was prepared by using a hybrid cluster, [(IrCp*)₄Mo₄O₁₆] (Cp* = η^5 -C₅Me₅), as a precursor.⁴ In the 4-nitrostyrene hydrogenation, Ir₄Mo₄/Al₂O₃ selectively reduced the nitro group to produce 4-aminostyrene (Figure 1a). In contrast, the coimpregnated catalyst, Ir-Mo/Al₂O₃, prepared from H₂IrCl₆ and (NH₄)₆Mo₇O₂₄·4H₂O, reduced both nitro and vinyl groups nonselectively (Figure 1b). This suggests that the formation of the Ir/MoO_x interfaces is essential for the selective hydrogenation of nitro groups and that hybrid clustering is an efficient way to form a high density of such interfaces. The local structures and the formation mechanism of the Ir/MoO_x interfaces will be discussed based on X-ray absorption spectroscopy.

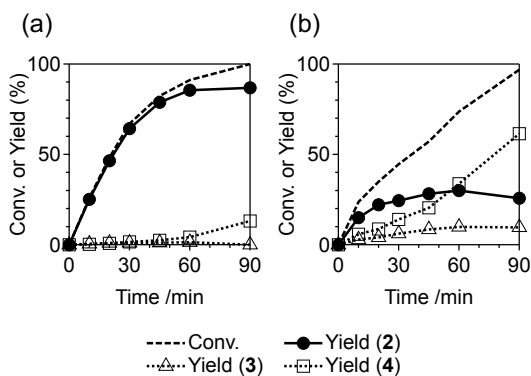
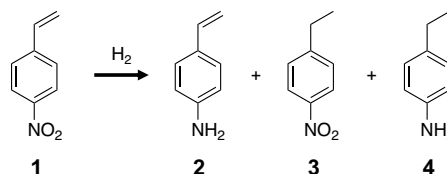


Figure 1. Time course of hydrogenation of 4-nitrostyrene (**1**) over (a) Ir₄Mo₄/Al₂O₃ and (b) Ir-Mo/Al₂O₃. Reaction conditions: **1** (0.1 mmol), H₂ (0.3 MPa), toluene (1 mL), catalyst (10 mg, Ir: 0.52 mol%), 303 K.

1) Corma, A. *et al. J. Am. Chem. Soc.* **2008**, *130*, 8748. 2) Wang, Y. *et al. Angew. Chem. Int. Ed.* **2020**, *59*, 12736. 3) Hayashi, S.; Shishido, T. *ACS Appl. Mater. Interfaces.* **2021**, *13*, 22332. 4) Hayashi, Y. *et al. J. Am. Chem. Soc.* **1988**, *110*, 3666.

Elucidation of molecular adsorption states of strong base metal oxide cluster by X-ray absorption spectroscopy

(¹Graduate School of Science, Tokyo Metropolitan University, ²Japan Synchrotron Radiation Research Institute (JASRI), ³JST PRESTO) ○Tomoki Matsuyama,^{1,2} Hiroki Nagakari,¹ Soichi Kikkawa,¹ Naomi Kawamura,² Kotaro Higashi,² Naoki Nakatani,¹ Seiji Yamazoe^{1,3}

Keywords: Metal Oxide Cluster; Base Catalyst; Homogeneous Catalyst; HERFD-XAS

Metal oxide clusters consisting of group-V transition metals such as $[\text{M}^{\text{V}}_6\text{O}_{19}]^{8-}$ ($\text{M}^{\text{V}}=\text{Nb}$, Ta) have a strong basicity that is comparable to MgO. Nevertheless, they are not deactivated by molecular adsorption and catalyze Knoevenagel condensation reactions and CO_2 fixation reactions.¹ In this study, we investigated unique molecular adsorption states on $[\text{M}^{\text{V}}_6\text{O}_{19}]^{8-}$ by high-energy-resolved fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) which enables direct observation of the crystal field correlated with structural change.² We have acquired XANES spectra of Nb K- and Ta L_3 -edges in the HERFD mode and successfully observed changes in the crystal field attributed to molecular adsorption for the first time.

Tetrabutylammonium salts of $[\text{M}^{\text{V}}_6\text{O}_{19}]^{8-}$ were synthesized by a microwave-assisted hydrothermal method in reference to the literature³ and characterized by infrared spectra and electrospray ionization mass spectra. Molecular adsorption states of $[\text{Nb}_6\text{O}_{19}]^{8-}$ (Nb6) were studied by pre-edge peaks in Nb K-edge HERFD-XANES spectra (Fig.a). When 1% CO_2 gas with N_2 balance and acid-base indicators as adsorbents were added to Nb6 DMF solution, the intensity of pre-edge peaks in both XANES spectra decreased compared to the pristine Nb6. These results indicate that CO_2 and protons adsorbed to the same base sites with an increase in their octahedral symmetry. Ta L_3 -edge HERFD-XANES spectra (Fig.b) also reflected d -orbital splitting affected by molecular adsorption to $[\text{Ta}_6\text{O}_{19}]^{8-}$ (Ta6). From the increasement of splitting width by CO_2 adsorption, we conclude that Ta6 activated CO_2 accompanied with the increase of the octahedral symmetry near the active site of Ta6 (Fig.c).

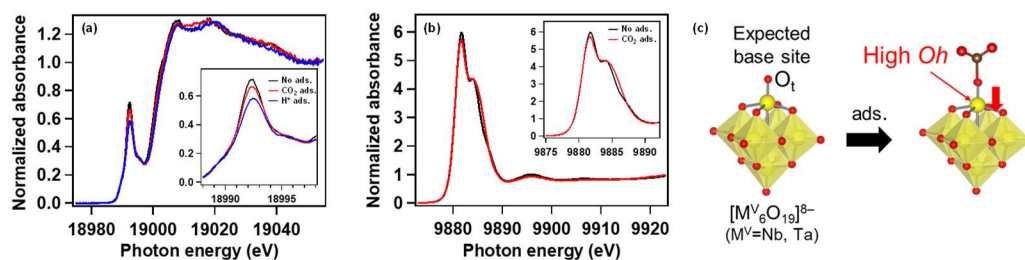


Figure (a) HERFD-XANES spectra at Nb K-edge and (b) those at Ta L_3 -edge. (c) Expected molecular adsorption states.

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Ti 含有ペロブスカイトナノ粒子の酸・塩基協奏作用によるシアノシリル化反応

(¹東京工業大学 フロンティア材料研究所) ○相原 健司¹・青木 航流¹・鎌田 慶吾¹・原 亨和¹

Acid–Base Bifunctionality of Ti-based Perovskite Nanoparticles for Cyanosilylation (¹Tokyo Institute of Technology) ○Takeshi Aihara¹, Wataru Aoki¹, Keigo Kamata¹, Michikazu Hara¹

Catalytic activities of perovskite oxides for oxidation, electrochemical, and photocatalytic reactions have been widely investigated. However, acid–base catalysis of perovskite oxides has not been sufficiently explored. In this study, synthesis for Ti-based perovskites and catalytic activity for cyanosilylation were investigated. Highly pure Ti-based perovskite nanoparticles were successfully synthesized by sol–gel method using malic acid, and the specific surface area of SrTiO₃ was 46 m²g^{−1} which was about 10 times larger than that of commercially available SrTiO₃. SrTiO₃ showed the highest cyanosilylation activity among the tested catalysts. Poisoning effect of acetic acid and pyridine for cyanosilylation over SrTiO₃ revealed that acid and base sites on SrTiO₃ cooperatively activate carbonyl compounds and trimethyl cyanide (TMSCN), respectively, which results in high catalytic performance.

Keywords : Perovskite nanoparticles; Acid–base; Cyanosilylation

ペロブスカイト酸化物は、酸化触媒や光触媒としてよく利用されるが、酸・塩基性質に関する知見は未だ少ない^{1),2)}。本研究では、高純度・高比表面積な Ti 含有ペロブスカイトナノ粒子の合成、ならびにシアノシリル化反応に対する触媒活性を検討した。

リンゴ酸を用いたゾル–ゲル法にて合成したチタン酸塩は、いずれも高純度・高比表面積なナノ粒子であった。中でも SrTiO₃ の比表面積は 46 m² g^{−1} であり、市販品(4 m²g^{−1})より 10 倍以上の大きな値を示した。得られた種々のペロブスカイトナノ粒子を用いて、シアノシリル化反応を検討した。TiO₂ や Mg(OH)₂ がほとんど活性を示さなかった一方、いずれのペロブスカイトでも反応は進行し、中でも SrTiO₃ は最も高い活性を示した (Figure 1)。SrTiO₃ を用いた本反応について、酢酸とピリジン添加剤として被毒実験を行ったところ、いずれの分子を添加した場合でも活性の低下が確認されたことから、本反応は酸・塩基点の両点で促進されていることが示唆された。

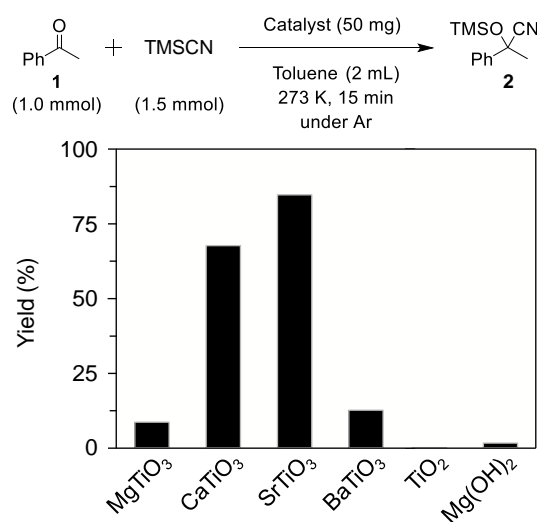


Figure 1. Cyanosilylation of acetophenone with TMSCN over various catalysts.

1) K. Kamata, *Bull. Chem. Soc. Jpn.* **2019**, 92, 133

2) F. Polo-Garzon, Z. Wu, *J. Mater. Chem. A* **2018**, 6, 2877

Homogeneous Investigation of N-Heterocyclic Carbene Stabilized Au-Nanoclusters for Electrocatalysis

(¹*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*, ²*Department of Chemistry, Queen's University*) ○ Samuel Jacob,¹ Joey DeJesus,¹ Emily Albright,² Yasuyo Tezuka,¹ Masakazu Nambo,¹ Cathleen Crudden^{1,2}

Keywords: Gold Nanocluster, Electrocatalyst, Carbon Dioxide Reduction, Hydrogen Evolution

Gold nanoclusters (AuNC) are among the most well studied type of NCs and are reputable for their ability to catalyze several reactions of energy importance electrochemically, such as hydrogen evolution reaction (HER) and CO₂ reduction reaction (CO₂RR). Typically, AuNCs are stabilized by either phosphine or thiol-based ligands, however, our lab has recently spearheaded the synthesis and characterization of several new AuNCs stabilized by N-heterocyclic carbenes (NHC).¹⁻⁵ Interestingly, regardless of ligand identity, the electrochemical nature of AuNCs remains surprisingly understudied. Despite the molecular nature of AuNCs, examples of electrochemical homogeneous characterization are scarce and most electrocatalytic experiments are performed heterogeneously.^{1,6,7} The evaluation of the heterogeneous performance of molecular catalysts is valuable, however, homogeneous electrochemical studies of molecular catalysts provide a wealth of information important for benchmarking catalytic performance, understanding reaction mechanisms, and structural optimization.

As such, our group is interested in expanding the current AuNC catalytic field through the implementation of in-depth homogeneous studies for various reactions of energy importance. Herein, we report the investigation of a family of atomically precise Au₁₃NCs supported by Bis-NHC ligands for electrocatalytic homogeneous HER. From our investigation, we have determined that the mechanism for HER is influenced by the NHC ligand functionality, acid p_Ka, and applied potential. As such, various stepwise catalytic EC reaction mechanisms can be accessed by the manipulation of these parameters. Utilizing this knowledge, we have extended our study towards CO₂RR to optimize reaction conditions for selective CO production and H₂ evolution suppression, a deleterious side reaction for CO₂RR. To the best of our knowledge, this is the first in-depth homogeneous study for HER utilizing AuNCs.

1) Kawawaki, T.; Negishi, Y. *Nanomaterials* **2020**, *10* (2). 2) Yi, H.; Osten, K. M.; Levchenko, T. I.; et al. *Chem Sci* **2021**, *12* (31), 10436-10440. 3) Man, R. W. Y.; Yi, H.; Malola, S.; et al. *J. Am. Chem. Soc.* **2022**, *144* (5), 2056-2061. 4) Lummis, P. A.; Osten, K. M.; Levchenko, T. I.; et al. *JACS Au* **2022**, *2* (4), 875-885. 5) Kulkarni, V. K.; Khirak, B. N.; Takano, S.; et al. *J. Am. Chem. Soc.* **2022**. 6) Kwak, K.; Lee, D. *Acc Chem Res* **2019**, *52* (1), 12-22. 7) Yang, D.; Wang, J.; Wang, Q.; et al. *ACS Nano* **2022**, *16* (10), 15681-15704.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[K505-1pm] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Naoki Ishida, Yoshiaki Tanabe

Wed. Mar 22, 2023 1:10 PM - 3:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-1pm-01] Construction of Molecular Gears Based on Lanthanoid Double-decker Complexes with Phthalocyanine and Naphthalocyanine Functionalized with Four Planar Peripheral Substituents○Jeevithra Dewi Subramaniam¹, Toshio Nishino¹, Gwénaél Rapenne^{1,2} (1. Nara Institute of Science and Technology, 2. University of Toulouse, France)

1:10 PM - 1:30 PM

[K505-1pm-02] Photoluminescence Properties of Mononuclear Europium(III) and Gadolinium(III) Complexes with Tetradentate Schiff Base Ligands in the Solid State○Masanobu Tsuchimoto¹, Toshiki Sakata¹, Naoki Takeda¹, Shuhei Itoh¹, Tomoaki Sugaya¹, Hyuma Masu², Masayuki Watabnabe³ (1. Chiba Institute of Technology, 2. Chiba University, 3. Japan Atomic Energy Agency)

1:30 PM - 1:50 PM

[K505-1pm-03] Synthesis of Dinuclear Titanium Oxalate Complexes Supported by a Tris(phenolato)amine Ligand○Akira Okumura¹, Florentine Mohr¹, Thomas Paul Spaniol¹, Jun Okuda¹ (1. RWTH Aachen Univ.)

1:50 PM - 2:10 PM

[K505-1pm-04] Transformation of dinitrogen and alkenes to alkyl amines at a trititanium polyhydride framework○Takanori Shima¹, Ping Wu², Ryota Owada¹, Gen Luo², Zhaomin Hou¹ (1. RIKEN, 2. Anhui University)

2:10 PM - 2:30 PM

[K505-1pm-05] Transformation of Pyridines to Cyclopentadienyl Units by Denitrogenation in a PNP-Ligated Dititanium Hydride Framework○Xiaoxi ZHOU¹, Qingde ZHUO¹, Takanori SHIMA¹, Xiaohui KANG², Zhaomin HOU¹ (1. RIKEN, 2. Dalian Medical University)

2:40 PM - 3:00 PM

[K505-1pm-06] Reaction of a Titanium Dinitrogen Complex Bearing an (ONO)-Ligand with CO₂ and CS₂○Yutaka Ishida¹, Sui Hasegawa¹, Hiroyuki Kawaguchi¹ (1. Tokyo Institute of Technology)

3:00 PM - 3:20 PM

[K505-1pm-07] Precise control of metal-centered chirality of pentacoordinate chiral-at-vanadium(V) complexes using chiral auxiliaries○Ayako Hino¹, Koichi Nagata¹, Hitoshi Ube¹, Mitsuhiko Shionoya¹ (1. The Univ. of Tokyo)

3:20 PM - 3:40 PM

Construction of Molecular Gears based on Lanthanoid Double-decker Complexes for Intermolecular Gearing Motion Study

(¹Division of Material Science, Nara Institute of Science and Technology, ²University of Toulouse) ○Subramaniam Jeevithra Dewi,¹ Nishino Toshio,¹ Rapenne Gwénaél^{1,2}

Keywords: Molecular Gear; Double-decker Complex; Lanthanoid; Porphyrinoid; Helicity

Artificial molecular machines are molecules capable to execute mechanical-like movements as an outcome of an appropriate external stimuli. There are now many examples like motors, shuttles, tweezers, nanocars and gears.¹ Various kinds of molecular gears have been proposed,² among them, double-decker complexes, in which lanthanoid ion is sandwiched between two porphyrinoid ligands such as porphyrin, phthalocyanine or naphthalocyanine, are attractive structural motifs for molecular gears since the ligands can rotate around metal ions.³

In this study, we report the construction of double-decker complexes of cerium(IV) as new prototypes of molecular gears. Phthalocyanines substituted at the α -position with π -planar bulky substituents were used to synthesize two homoleptic and one heteroleptic double-decker complexes. It is expected that the upper and lower ligands tightly engage and work as gear due to these bulky and rigid substituents. A C_{4h} symmetric phthalocyanine **H₂Pc1** having 3,6-di-*tert*-butyl-carbazole at the α -position was employed and synthesized as a sub-unit of the gearing system.⁴ Ce(**Pc1**)₂ was obtained in 40% yield through the complexation of **H₂Pc1** with Ce(acac)₃·nH₂O under microwave irradiation. The structure of Ce^{IV}(**Pc1**)₂ was confirmed by single crystal X-ray structure analysis (Fig. 1). Desymmetrised A3B-type phthalocyanine **H₂Pc2** bearing one phenothiazine and three 3,6-di-*tert*-butyl-carbazole at the α -position was also synthesized as the same manner as Ce(**Pc1**)₂. The formation of the complexes was confirmed with ¹H-NMR, 2D-NMR, and MALDI-TOF-MS. To study molecular gearing on surface with STM, our final target is constituted of a thioether-functionalized porphyrin as the anchoring ligand and a carbazole-functionalized naphthalocyanine as the cogwheel (Fig. 2). Thanks to the helical chirality of this double-decker complex, we hope to build a train of gears with consecutive molecules of opposite chirality.

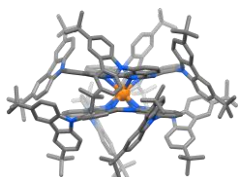


Fig. 1: X-ray structure of Ce^{IV}(**Pc1**)₂ (side view)

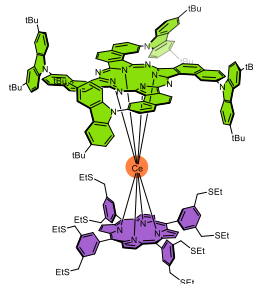


Fig. 2: Gear to study on surface with STM

1) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines: A Journey into the Nano World*, Wiley-VCH, Weinheim, **2003**. 2) G. Rapenne et al., *Chem. Eur. J.* **2021**, 27, 12019. 3) M. Takeuchi et al., *Chem. Eur. J.* **2010**, 16, 8285. 4) M. Kimura et al., *Chem. Eur. J.* **2017**, 23, 15446.

四座のシッフ塩基を配位子とするユウロピウム(III)単核錯体と ガドリニウム(III)単核錯体の固体の発光特性

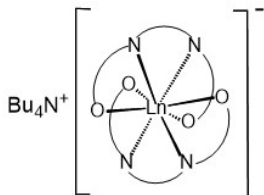
(千葉工大¹・千葉大²・原子力機構³) ○槌本昌信¹・坂田俊樹¹・武田直樹¹・
伊藤晋平¹・菅谷知明¹・榊 飛雄真²・渡邊雅之³

Photoluminescence Properties of Mononuclear Europium(III) and Gadolinium(III) Complexes with Tetradentate Schiff Base Ligands in the Solid State (¹Faculty of Engineering, Chiba Institute of Technology, ²Center for Analytical Instrumentation, Chiba University, ³Nuclear Science and Engineering Center, Japan Atomic Energy Agency) ○Masanobu Tsuchimoto,¹ Toshiki Sakata,¹ Naoki Takeda,¹ Shuhei Itoh,¹ Tomoaki Sugaya,¹ Hyuma Masu,² Masayuki Watabnabe³

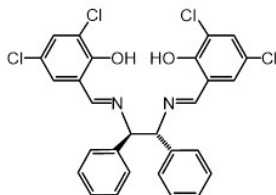
Mononuclear Schiff base-europium(III) complexes $X[Eu(L)_2]$ (X: counter cation; L: Schiff base ligand) have a mononuclear structure with two Schiff base ligands in a meridional form. The mononuclear europium(III) complexes display red photoluminescence based on the f-f transitions by excitation with UV light. However, the emission intensities of the mononuclear europium(III) complexes in the solid state at 298 K are drastically different among the complexes with different counter cations. Recently, we found that the mononuclear europium(III) complex with the Schiff base ligands derived from stilbenediamine $Bu_4N[Eu(L)_2]$ has two types of crystals: high luminescent white crystals and weakly luminescent yellow crystals. In this study, we report the structures and luminescence properties of the two types of crystals of the europium(III) and gadolinium(III) complexes.

Keywords : Europium Complex; Gadolinium Complex; Photoluminescence; Schiff Base; Structure

四座のシッフ塩基を配位子とする Eu(III)単核錯体 $X[Eu(L)_2]$ (X: 対イオン、L: シッフ塩基配位子)は、2 個のシッフ塩基配位子が meridional 型に配位した 8 配位の単核構造をとる。この Eu(III)単核錯体は、紫外線を照射すると f-f 遷移に由来する赤色発光を示すが、298 K における固体の発光では、対イオンの違いにより発光強度が大きく異なる特徴がある。近年、スチルベンジアミンから誘導したシッフ塩基を配位子とする Eu(III)単核錯体 $Bu_4N[Eu(L)_2]$ には、強発光する白色の結晶と、弱く発光する黄色結晶の 2 種の結晶があることが明らかになった。本研究では、Eu(III)錯体と Gd(III)錯体について、これらの 2 種の結晶の構造と発光特性について報告する。



$Bu_4N[Ln(3,5-Cl_2sal-stien)_2]$
(Ln=Eu, Gd)



$H_2\{3,5-Cl_2sal-(R,R)-stien\}$

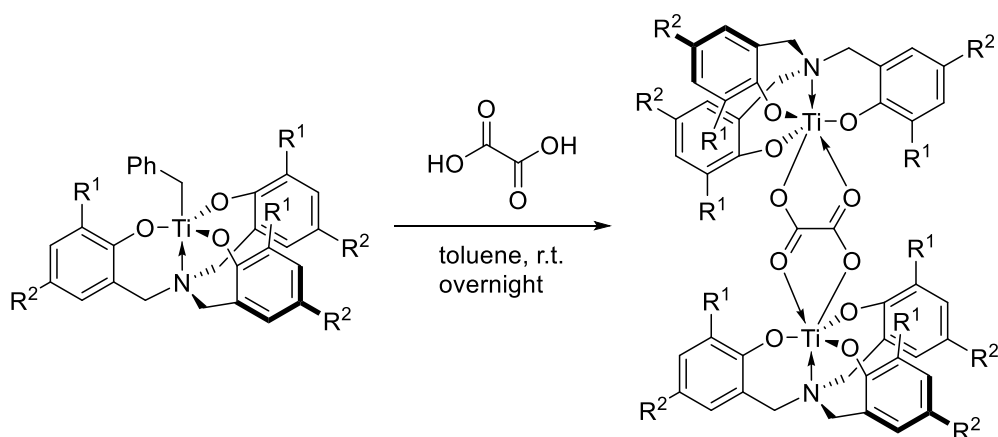
Synthesis of Dinuclear Titanium Oxalate Complexes Supported by a Tris(phenolato)amine Ligand

(RWTH Aachen Univ.) ○Akira Okumura, Florentine Mohr, Thomas Paul Spaniol, Jun Okuda

Keywords: Titanium Complex, Oxalate, Reduction, Carbon Dioxide, Phenolate Ligand

Carbon dioxide (CO_2) could become an attractive C1 building block for synthetic chemistry to produce sustainable chemicals and polymers.¹ However, because of the high thermodynamically stability and inertness of CO_2 , catalytic transformation of CO_2 remains challenging. It is known that CO_2 can be catalytically transformed by organometallic complexes, heterogeneous catalysts, and electrocatalysts. Especially, the electrochemical reduction of CO_2 to formate and oxalate can offer C1 and C2 key intermediates.² As model compounds, metal formate and oxalate complexes are important to understand the coordination and reaction mode of CO_2 at metal centers. We have recently reported that titanium(IV) chlorido complex, which bears a sterically bulky tris(phenolato)amine(O_3N) ligand, can be transformed to titanium(IV) formate complexes.³ Here, we report that dinuclear titanium(IV) oxalate complex can be synthesized by protonolysis of the titanium(IV) benzyl precursor.

When titanium(IV) benzyl complex ($[(\text{O}_3\text{N})\text{TiBn}]$) was treated with 0.5 equiv. of oxalic acid in toluene at room temperature overnight, dinuclear titanium(IV) oxalate complex ($[(\text{O}_3\text{N})\text{Ti}(\text{C}_2\text{O}_4)\text{Ti}(\text{O}_3\text{N})]$) was obtained as dark orange powder in 75% yield. Single-crystal X-ray diffraction analysis revealed that two titanium(IV) centers are bridged by an oxalate dianion with $\mu, \kappa\text{O}$ -coordination mode. This dinuclear titanium(IV) oxalate complex was reduced by potassium metal to give a yellow complex, whose two titanium(IV) atoms are reduced to titanium(III).



1) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.*, **2014**, *114*, 1709. 2) a) E. Schuler, M. Demetriou, N. R. Shiju, G.-J. M. Gruter, *ChemSusChem*, **2021**, *14*, 3636. b) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem. Soc. Rev.*, **2009**, *38*, 89. 3) A. Okumura, P. Ghana, F. Fink, R. Schmidt, A. Hoffmann, T. P. Spaniol, S. Herres-Pawlis, J. Okuda, *Dalton Trans.*, **2022**, *51*, 14345.

チタンヒドリドを用いた窒素分子とアルケンからのアルキルアミン合成

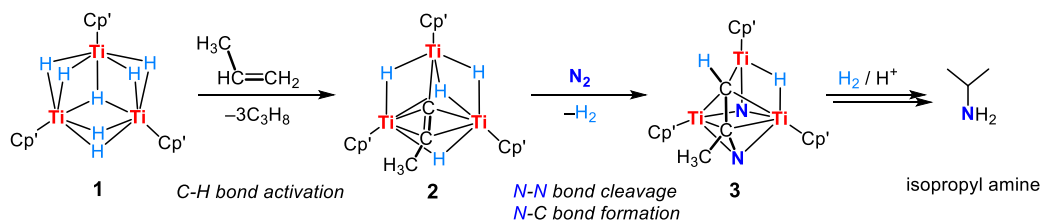
(理研¹・Anhui Univ.²) 〇島 隆則¹・Ping Wu²・大和田 凌太¹・Gen Luo²・侯 召民¹
Transformation of dinitrogen and alkenes to alkyl amines at a trititanium polyhydride framework (¹RIKEN, ²Anhui University) 〇Takanori Shima,¹ Ping Wu,² Ryota Owada,¹ Gen Luo,² Zhaomin Hou¹

Direct synthesis of nitrogen-containing organic compounds from dinitrogen (N₂) and commodity chemicals is of great interest but remains a challenge. N₂ functionalization by transition metal complexes generally requires electrophilic carbon sources to form N–C bond. To develop simpler and more straightforward methods for synthesis of a variety of nitrogen-containing organic compounds, studies of transformation of N₂ with readily available abundant carbon sources is of highly importance. Here we present a trititanium polyhydride mediated transformation of N₂ with non-activated alkenes to alkyl amines. C(sp²)-H and N≡N bond activation, and reductive N–C bond coupling reactions sequentially take place under mild conditions. Computational studies reveal that the split nitride species is readily bonded to the alkenyl carbon rather than the bridging hydride or the other protons.

Keywords : N₂ Functionalization; Hydride; Alkenes; Alkylamines

含窒素有機化合物は、生命体、医薬分野などに欠かせない重要化合物である。これらの化合物は、通常、エネルギー多消費プロセスであるハーバー・ボッシュ法で得られるアンモニアを窒素源として合成される。近年、省エネ・省資源、短工程化の観点から、窒素分子を利用した含窒素有機化合物の合成研究に注目が集まっている。遷移金属錯体による窒素分子の官能基化においては、窒素分子を還元するための還元剤とともに、通常、求電子的な炭素源が必要である。一方で、より容易に入手しやすい単純炭化水素類を炭素源として用いることは難しかった。本研究では、チタンヒドリド錯体 **1**¹⁾によって窒素分子と汎用的な不飽和炭化水素であるアルケンから、アルキルアミンを直接合成することに成功した。

錯体 **1** とプロピレンとの反応で、C(sp²)-H 結合切断を経て錯体 **2** が得られた。錯体 **2** はさらに窒素分子と反応し、N-N 結合の切断、N-C 結合形成を経て、錯体 **3** を与えた。計算化学の結果、切断された窒素種は、活性化された炭素原子と選択的に結合するプロセスがエネルギー的に最も有利であることが明らかになった。得られた錯体 **3** を水素化・水分解することでイソプロピルアミンを得た。同様にして、他の脂肪族、芳香族アルケンと窒素分子から、対応するアルキルアミンを良好な収率で得た。



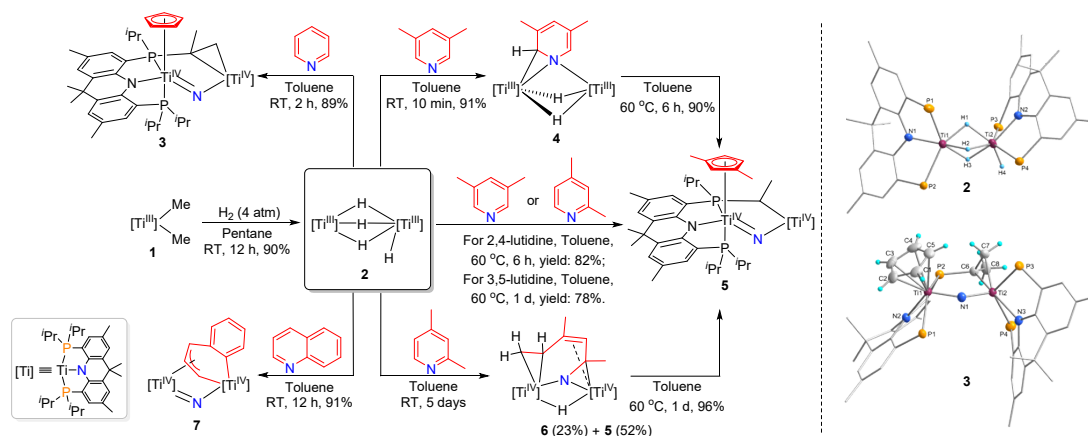
1) T. Shima, S. Hu, G. Luo, X. Kang, Y. Luo, Z. Hou, *Science* **2013**, 340, 1549.

Transformation of Pyridines to Cyclopentadienyl Units by Denitrogenation in a PNP-Ligated Ditunganium Hydride Framework

(¹Organometallic Chemistry Laboratory, RIKEN CPR, ²Advanced Catalysis Research Group, RIKEN CSRS, ³College of Pharmacy, Dalian Medical University) ○Xiaoxi Zhou,¹ Qingde Zhuo,¹ Takanori Shima,^{1,2} Xiaohui Kang,³ Zhaomin Hou^{1,2}

Keywords: Titanium Hydrides; Pyridine; C–N bond cleavage; Hydrodenitrogenation

Investigating the reactions of aromatic N-heterocycles with transition metal hydrides is of fundamental interest and practical importance, given its relevance to important industrial processes such as hydrodenitrogenation (HDN).¹ Here, we report the synthesis of a novel PNP-ligated dititanium tetrahydride complex **2** and its unique reactivity towards pyridines. The hydrogenolysis of titanium dimethyl complex **1** [(*acri*PNP)TiMe₂]² with H₂ afforded complex **2** in high yield. Reaction of **2** with pyridine led to the formation of the cyclopentadienyl (Cp) complex **3**, in which pyridine was directly denitrogenated to a Cp unit by the cleavage of the two N–C bonds and formation of a new C–C bond. When 3,5-lutidine or 2,4-lutidine was subjected to the reaction with complex **2**, the 1,3-dimethyl-substituted Cp product **5** was obtained. In these reactions, two key intermediates, i.e., an intermediate **4** derived from pyridine unit coordination and an intermediate **6** derived from the cleavage of one C–N bond, were isolated successfully. Reaction of **2** with quinoline gave a metalacyclic complex **7** through the cleavage of both C–N bonds of quinoline. The mechanistic details of these pyridine skeletal editing reactions were clarified by DFT calculations. This work may provide insights for designing new catalysts for the HDN of aromatic N-heterocycles under milder conditions as well as for other useful chemical transformations.



1) a) M. Bachrach, T. J. Marks, J. M. Notestein, *ACS Catal.* **2016**, *6*, 1455. b) S. Hu, G. Luo, T. Shima, Y. Luo, Z. Hou, *Nature Commun.* **2017**, *8*, 1866.

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

(ONO) 型配位子を持つチタン窒素錯体と二酸化炭素及び二硫化炭素との反応

(東工大理) ○石田 豊・長谷川 慧・川口 博之

Reaction of a Titanium Dinitrogen Complex Bearing an (ONO)-Ligand with CO₂ and CS₂
(School of Science, Tokyo Institute of Technology) ○Yutaka Ishida, Sui Hasegawa, Hiroyuki Kawaguchi

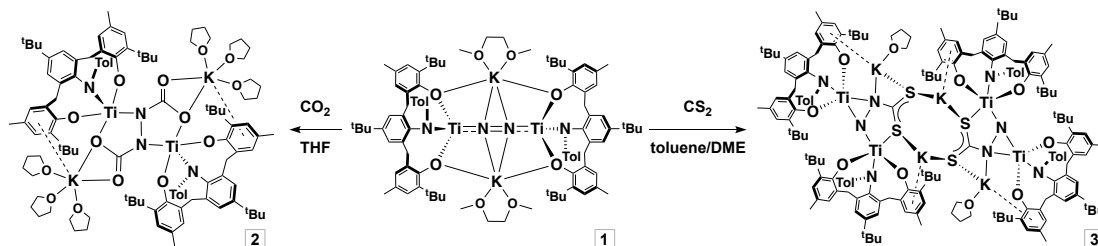
We report N–C bond formation reaction of a titanium dinitrogen complex [$\{K(dme)\}_2\{(ONO)Ti\}_2(\mu-N_2)$] (**1**) with CO₂ or CS₂. Exposure of the dinitrogen complex **1** in THF to a CO₂ atmosphere produced a dinuclear complex bridged by the $\mu-N,N'$ -[N₂(CO₂)₂] ligand (**2**), which each N atom of the N₂ unit is carboxylated. In contrast, addition of excess CS₂ to a toluene/DME solution of **1** yielded [$\{K(dme)\}_2\{(ONO)Ti\}_2\{\mu-N_2(CS_2)\}$] (**3**), incorporating one CS₂ molecule via N–C bond formation

Keywords : Functionalization of Dinitrogen; Titanium Complex; Carbon Dioxide; Carbon Disulfide

N–C 結合形成反応による N₂ の直截的な分子変換に興味を持たれる中、窒素錯体と二酸化炭素の反応による N–C 結合形成の例が報告されている¹⁻⁴。今回、(ONO)型配位子を持つ二核チタン窒素錯体 **1** と二酸化炭素及び二硫化炭素⁵ との反応による N–C 結合生成反応を検討した。

窒素錯体 **1** と二酸化炭素は THF 中で瞬時に反応し、異なる窒素原子上で二酸化炭素が反応した $\mu-N,N'$ -[N₂(CO₂)₂] 二核錯体 **2** が収率 83% で得られた。X 線結晶構造解析により構造を決定し、二つの TiN₂CO 五員環は平面構造を持つことが分かった。

窒素錯体 **1** のトルエン/DME 溶液に小過剰の二硫化炭素を加えると反応はゆっくりと進行した。THF/ヘキサンからの再結晶により、 $\mu-(N_2CS_2)$ フラグメントが二つのチタン間に架橋した錯体 **3** が収率 44% で得られた。X 線結晶構造解析の結果、カリウム原子を介した四核錯体であることが分かった。¹⁵N 同位体ラベルした錯体 **3** の THF 中での ¹⁵N NMR では、 δ 322 ppm と 533 ppm に結合定数 $J_{NN} = 15.0$ Hz を伴ったシグナルが観測され、結晶構造で見られた分子構造を保持していることが示唆された。



- 1) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Angew. Chem. Int. Ed.* **2007**, 46, 2858.
- 2) D. J. Knobloch, H. E. Toomey, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, 130, 4248.
- 3) Y. Nakanishi, Y. Ishida, H. Kawaguchi, *Angew. Chem. Int. Ed.* **2017**, 56, 9193
- 4) Q. Zhou, J. Yang, Z. Mo, X. Zhou, T. Shima, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **2022**, 144, 6972.
- 5) R. J. Burford, L. Castro, L. Maron, J. E. Hein, M. D. Fryzuk, *Dalton Trans.* **2018**, 47, 7983.

Precise control of metal-centered chirality of pentacoordinate chiral-at-vanadium(V) complexes using chiral auxiliaries

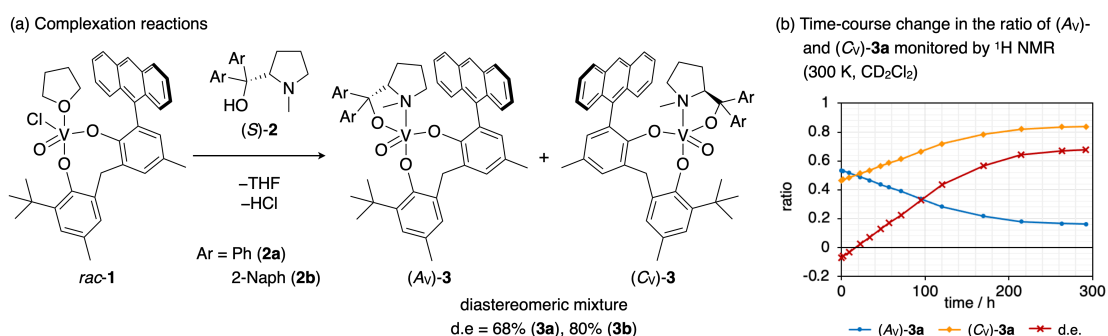
(Graduate School of Science, The University of Tokyo) ○Ayako Hino, Koichi Nagata, Hitoshi Ube, Mitsuhiko Shionoya

Keywords: Chirality, Chiral-at-metal complex, Asymmetric induction, Oxovanadium(V) complex

Chiral-at-metal complexes are metal complexes with metal-centered chirality and are attracting much attention as asymmetric catalysts.¹ Compared to relatively substitution-inert metals,^{1,2} controlling and stabilizing the absolute configuration at the substitutionally labile metal centers are challenging due to rapid racemization, and to date there have been limited examples of pentacoordinate chiral-at-metal complexes with high configurational stability.³

Oxovanadium(V) complexes have drawn attention for their biological activity and catalytic applications.⁴ However, isomerization occurs quickly at the metal center due to low coordination stability in solution.⁵ In this study, by using a chiral bidentate ligand, we have succeeded in controlling the metal-centered chirality of generally labile, pentacoordinate chiral-at-vanadium(V) complexes in solution, and in achieving high diastereoselectivity and suppression of stereoinversion at the metal center.

The reaction of *rac*-**1** with an enantiopure chiral aminoalcohol, (*S*)-**2**, yielded a diastereomeric mixture of pentacoordinate chiral-at-vanadium(V) complexes (*A_V*)- and (*C_V*)-**3** (Figure (a)). The structures of (*A_V*^{*}, *S_N*^{*}, *S_C*^{*})- and (*C_V*^{*}, *S_N*^{*}, *S_C*^{*})-**3a** were determined by single crystal XRD analyses using racemic **2a** to confirm the inversed absolute configurations at the metal center. The slow stereoinversion process of **3** was monitored by NMR (Figure (b)) and CD spectroscopy. The difference in their thermodynamic stability resulted in asymmetric induction at the labile metal center, causing the equilibrium state between the two to be put away. Finally, (*C_V*, *S_N*, *S_C*)-**3** was preferentially formed with 68% (**3a**) and 80% (**3b**) diastereomeric excess, respectively, after 300 h.



1) T. Cruchter, V. A. Larionov, *Coord. Chem. Rev.* **2018**, 376, 95. 2) H. Brunner, *Angew. Chem. Int. Ed.* **1999**, 38, 1194. 3) J. Pérez-Prieto *et al.* *Organometallics* **2010**, 29, 703. 4) M. Delferro *et al.* *Chem. Rev.* **2019**, 119, 2128. 5) D. Rehder *et al.* *Inorg. Chem.* **1993**, 32, 1844.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[K505-1vn] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Daisuke Tanaka, Satoshi Horike

Wed. Mar 22, 2023 4:10 PM - 6:40 PM K505 (K505, Lecture Hall Bldg. [5F])

[K505-1vn-01] Liquid– liquid transition in coordination polymer melt studied by dynamic mechanical analysis○Taichi Nishiguchi¹, Yuki Ohara², Kentaro Kadota³, Satoshi Horike^{2,3} (1. Faculty of Engineering, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. iCeMS, KUIAS, Kyoto University)

4:10 PM - 4:30 PM

[K505-1vn-02] Glass formation of coordination polymers driven by dehydration treatment○Zeyu FAN¹, Yong-Sheng Wei², Satoshi Horike^{2,1} (1. Graduate School of Engineering, Kyoto University, 2. Institute for Advanced Study, Kyoto University)

4:30 PM - 4:50 PM

[K505-1vn-03] Photo-generated extremely long-lived spin-polarized radicals in metal-organic frameworks○Kana Orihashi¹, Akio Yamauchi¹, Saiya Fujiwara⁴, Kenichiro Tateishi⁴, Tomohiro Uesaka⁴, Asada Mizue⁵, Toshikazu Nakamura⁵, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,3} (1. Kyushu Univ., 2. CMS, Kyushu Univ., 3. FOREST, JST, 4. RIKEN, 5. Institute for Molecular Science)

4:50 PM - 5:10 PM

[K505-1vn-04] Semiconductive Nature of Lead(II) Coordination Polymers with Benzenethiol Derivatives○Ryohei Akiyoshi¹, Akinori Saeki², Daisuke Tanaka¹ (1. Kwansei Gakuin University, 2. Osaka University)

5:10 PM - 5:30 PM

[K505-1vn-06] Inverse Guest Adsorption and Luminescent Response in an Au(I)-based Metal– Organic Framework○Haruka Yoshino¹, Masaki Saigo², Kiyoshi Miyata², Ken Onda², Hitoshi Miyasaka¹ (1. Institute for Materials Research, Tohoku University, 2. Graduate School of Science, Kyushu University)

6:00 PM - 6:20 PM

[K505-1vn-07] Charge-driven Assembly of Water-soluble Ionic Metal-Organic Polyhedra with Enzymes○Benjamin Le Ouay¹, Ryosuke Minami¹, Purna Kanta Boruah¹, Masaaki Ohba¹ (1. Kyushu University)

6:20 PM - 6:40 PM

Liquid–Liquid Transition in Coordination Polymer Melt Studied by Dynamic Mechanical Analysis

(¹Graduate School of Engineering, Kyoto University, ²Institute for Advanced Study, Kyoto University) ○Taichi Nishiguchi,¹ Yuki Ohara,¹ Kentaro Kadota,² Satoshi Horike^{1,2}

Keywords: Coordination polymer; Melting; Glass transition; Dynamic mechanical analysis

Melting and glassy coordination polymers (CPs) have been attracting attention as novel functional materials due to their optical properties, moldability, and mechanical durability.¹ The network and coordination structures in the melt states were analyzed in detail for some melting CP systems.² However, mechanical properties or dynamics of the melt are still remaining to be elucidated, and a comprehensive understanding of transition behavior in CPs did not progress. The melting and glass transition behaviors of CPs have been discussed assuming a single melt phase.

We studied the properties of supercooled melt states of Cu(TFSI)₂(bip)₂ (**1**, TFSI[−] = Bis(trifluoromethanesulfonyl)imide, bip = 1,3-Bis(1*H*-imidazol-1-yl)propane, Fig. a). Dynamic mechanical analysis (DMA) observed a reversible rheological transition depending on temperature, and suggested a liquid–liquid transition (Fig. b). The application of mechanical stimuli in DMA formed a different melt state with the same components. Two melt states underwent a glass transition at different temperatures. X-ray scattering analysis revealed their structural dissimilarities and different crystallization behavior. The variety of nanometer-scale network structures in melt states explains these differences.

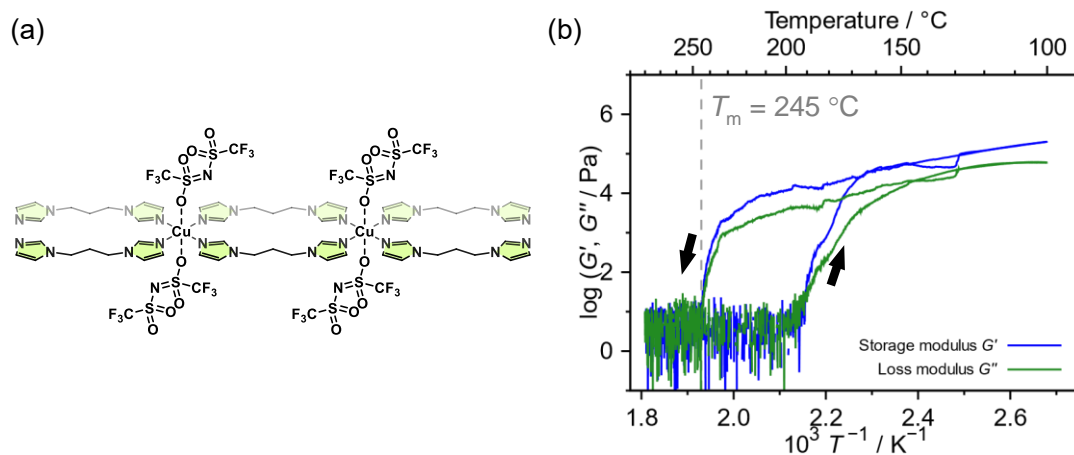


Fig. (a) Schematic representation of crystal structure of **1** (b) Temperature-ramp DMA profile of **1** melt. The dashed line represents the melting temperature of **1** crystal.

1) S. Horike, *et al.*, *Chem. Rev.* **2022**, 122, 4163.

2) T. D. Bennett, F.-X. Coudert, *et al.*, *Nat. Mater.* **2017**, 16, 1149.

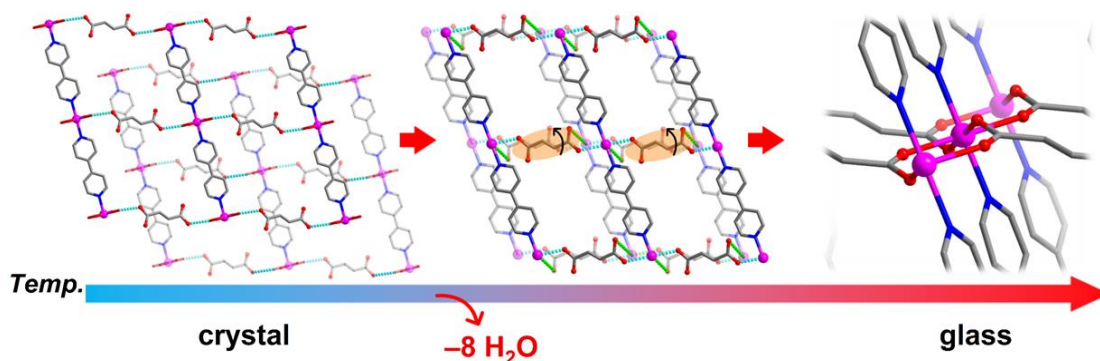
Glass formation of coordination polymers driven by dehydration treatment

(¹Graduate School of Engineering, Kyoto University, ²Institute for Advanced Study, Kyoto University) ○Zeyu Fan,¹ Yong-Sheng Wei,² Satoshi Horike^{1,2}

Keywords: coordination polymers, metal-organic frameworks, glass, phase transition

Coordination polymer (CP) and metal-organic framework (MOF) glasses have been emerged as new class of glass materials. Their structures and functionalities can be adjusted by changing the inorganic and organic building blocks. The high processability, structural dynamics and grain boundary free character enable them to form monoliths and membranes for ion conductivity, gas separation and optical applications.¹ Similar with conventional inorganic glasses, CP/MOF glasses are usually obtained by melt-quenching process. However, most CP/MOFs did not melt and directly decompose irreversibly upon heating.² It is essential to develop new method to fabricate CP/MOF glasses.

One of the most used ligands for constructing CP/MOFs are carboxylate ligands. Nevertheless, there is no carboxylate-based CP/MOF glasses until now, which is due to the alternative coordination environment and strong coordination bond between metal and carboxylates. Here we develop the direct glass-formation process through thermal dehydration of a series of carboxylate (fumarate, fum and terephthalate, bdc) and pyridine (4,4'-bipyridine, bpy and 1,2-di(pyridin-4-yl)ethene, bpee) based Co^{2+} one-dimensional (1D) CPs which contain water molecules as ligands. Loss of coordination water through heat treatment causes local structural rearrangement of the 1D coordination networks, which is monitored by *in-situ* variable-temperature (VT) PXRD, FT-IR and synchrotron X-ray. Glass transition is confirmed by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA). These glasses form bulk monoliths through hot-press technique and their grain-boundary free character is examined by cross-section SEM.



1) S. Horike et al., *Chem. Rev.* **2022**, 122, 4163. 2) J. A. Mason et al., *J. Am. Chem. Soc.* **2021**, 143, 2801.

Photo-generated extremely long-lived spin-polarized radicals in Metal-Organic Frameworks

(¹Grad. Sci. Eng., Kyushu Univ., ²CMS, Kyushu Univ., ³FOREST, JST, ⁴RIKEN, ⁵Institute for Molecular Science.) ○Kana Orihashi,¹ Akio Yamauchi,¹ Saiya Fujiwara,⁴ Kenichiro Tateishi,⁴ Tomohiro Uesaka,⁴ Mizue Asada,⁵ Toshikazu Nakamura,⁵ Nobuo Kimizuka,^{1,2} Nobuhiro Yanai^{1,2,3}

Keywords: Polarized radical; Metal-organic framework; EPR; Photoexcited triplet

The generation and control of the electron spin polarization (ESP) is a crucial foundation not only for a wide range of quantum technologies but also for dynamic nuclear polarization (DNP), which is a technique to enhance the signal intensity of NMR and MRI. In addition to the generation of ESP, elongated spin-lattice relaxation times of the electron spin (T_{1e}) is desired for expanding the scope of future quantum technology and DNP. However, in conventional systems, T_{1e} has been limited to less than a few μ s at room temperature. In this work, we have discovered photo-generated spin-polarized radicals with extremely long lifetime in acene-based metal-organic frameworks (MOFs).

To obtain large ESP at room temperature, we employed 5,12-diazatetracene (DAT) which can produce polarized triplets by photo-irradiation. We synthesized new ligand DPyDAT by modifying DAT with pyridine as a coordination site to the metal. Pillared-layer type of the MOF was synthesized with DPyDAT, Zn ion and carboxylic ligand. DAT moieties are aligned one-dimensionally with relatively close distance in the skeleton of the MOF. ESP formation in the MOF was evaluated by time-resolved ESR measurements at room temperature. The ESR spectrum of the MOF showed, in addition to the DAT triplet-derived pattern, a relatively sharp emissive peak of radical origin around 342 mT. Significantly, spin-lattice relaxation time T_{1e} was found to be as long as 275 μ s by pulsed ESR inversion recovery sequence at 342 mT at room temperature. We will also show the relationship between assembly structure of acenes and the T_{1e} value by comparing different MOF structures.

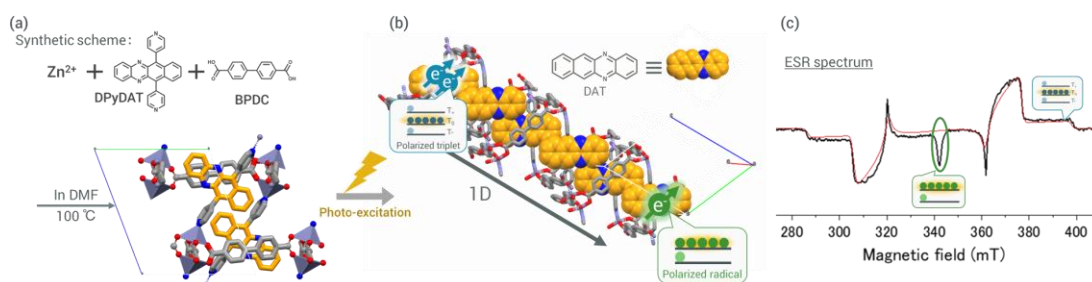


Fig. 1 (a) Synthetic scheme and structure of the MOF. (b) Schematic image of this work. (c) Tr-ESR spectrum of the MOF.

1) S. Fujiwara, N. Matsumoto, K. Nishimura, N. Kimizuka, K. Tateishi, T. Uesaka, N. Yanai, *Angew. Chem. Int. Ed.* **2022**, 61, e2021157.

Semiconductive Nature of Lead(II) Coordination Polymers with Benzenethiol Derivatives

(¹*School of Science, Kwansei Gakuin University*, ²*Graduate School of Engineering, Osaka University*) ○Ryohei Akiyoshi,¹ Akinori Saeki,² Daisuke Tanaka¹

Keywords: Coordination Polymer; Lead; Semiconductive Nature; Charge Transport

Conductive metal-organic frameworks (MOFs) and coordination polymers (CPs) have attracted increasing attention in recent years for diverse applications in electrocatalysis and chemiresistive sensing.¹ Among them, sulfur-coordinated CPs (S-CPs) containing $(-M-S-)_n$ network have been extensively investigated because they often exhibit small band gap as well as excellent band-like transport.² However, to the best of our knowledge, there is a general lack of reports concerned with the crystal structures of S-CPs due to their low crystallinity.

Herein, we reported the synthesis of Pb(II) S-CPs, $[Pb(X-SPhOMe)_2]_n$ ($X = ortho$ (**KGF-32**), *meta* (**KGF-33**), and *para* (**KGF-34**)) and discussed their crystal structures and semiconductive properties. Single crystals of **KGF-32**, **KGF-33**, and **KGF-34** were obtained as pale-yellow needle crystals, light-yellow needle crystals, and dark-brown plate crystals, respectively. Single crystal X-ray structural analyses revealed that **KGF-32** and **KGF-33** incorporating methoxy group on *ortho* or *meta* positions formed an 1D structure composed of one-dimensionally extended $(-Pb-S-)_n$ chain, whereas **KGF-34** which had methoxy substituent on *para* position shows the formation of 2D structure with $(-Pb-S-)_n$ layer (**Figure 1**). Time-resolved microwave conductivity (TRMC) experiments demonstrated that **KGF-34** exhibits highest TRMC signal intensity ($\phi\Sigma\mu_{\max} = 1.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) among all MOFs and CPs to date. First-principles calculations showed that a 2D layer comprising a $(-Pb-S-)_n$ network plays a crucial role in the high photoconductivity. In this presentation, we will discuss the detail of crystal structure and semiconductive nature for **KGF-32**, **KGF-33**, and **KGF-34**.

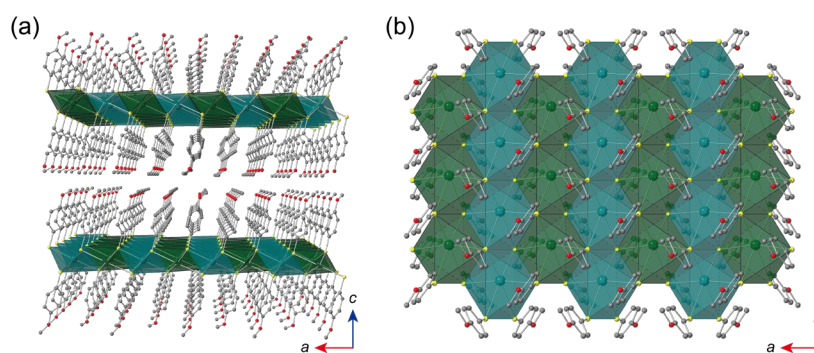


Figure 1. Crystal structure of **KGF-34**.

1) L. S. Xie, G. Skorupskii, M. Dinca, *Chem. Rev.* **2020**, *50*, 8536. 2) Y. Kamakura, D. Tanaka, *Chem. Lett.* **2021**, *50*, 523.

Inverse Guest Adsorption and Luminescent Response in an Au(I)-based Metal–Organic Framework

(¹*Institute for Materials Research, Tohoku University*, ²*Graduate School of Science, Kyushu University*) ○Haruka Yoshino,¹ Masaki Saigo,² Kiyoshi Miyata,² Ken Onda,² Hitoshi Miyasaka,¹

Keywords: Coordination polymer/Metal–Organic Framework, Luminescent property, Metallophilic interactions, Inverse Guest Adsorption

Stimuli-responsive luminescent coordination polymers (CPs) and metal-organic frameworks (MOFs) composed of metal ions and organic ligands have attracted considerable attention for the development of novel photofunctional materials such as chemical sensors owing to their highly regular, flexible, and designable frameworks.

Here, we prepared a novel CP $\{\text{Zn}^{\text{II}}(\text{pz})[\text{Au}^{\text{I}}(\text{CN})_2]_2\}$ (pz = pyrazine; **1**) with an interpenetrated 3-D structure based on cyanide-bridged Au–Zn–Au linkages and bidentate pz ligands (**Fig. (a)**). **1** showed a light-blue phosphorescence ($\lambda_{\text{em}} = 462 \text{ nm}$, $\lambda_{\text{ex}} = 365 \text{ nm}$) originating from aurophilic interactions in the framework. In addition, Guest adsorption properties were investigated to explore the guest-sensing ability of **1**. Despite no adsorption for nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), and carbon monoxide (CO) and solvent guests, **1** displayed size-inverse and selective adsorption behavior for carbon disulfide (CS_2) at the room temperature with efficient host-guest interactions, in which the emission intensity of the framework drastically and reversibly changed along with CS_2 adsorption/desorption process (**Fig. (b), (c)**). Therefore, we focus on the details of the CS_2 -responsivity of **1** because this harmful guest is one of the important chemicals in the field of industrial society; however, it is also known the detrimental effects on human health and the environment.

The correlation between the luminescent property and the structural change was investigated by *ex situ* single-crystal X-ray diffraction and photoluminescent measurements under CS_2 vapor. The CS_2 -adsorbed state of **1** possessed an interpenetrated 3-D structure with two types of Au–Au distances induced by CS_2 adsorption. The resultant size-inverse and guest-selective luminescent change of **1** might be due to the CS_2 -driven changes in structure and emission decay process.

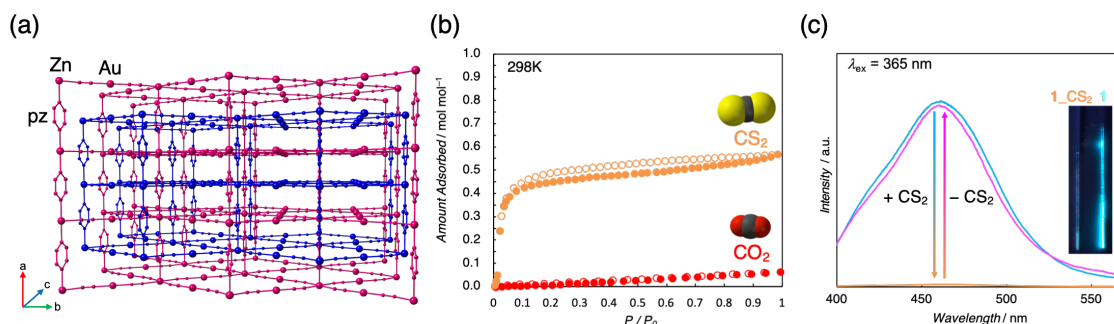


Fig.(a) Crystal structure of **1**, **(b)** size-inverse guest adsorption at 298 K, **(c)** CS_2 -induced luminescent variations at room temperature.

Charge-driven assembly of Water-soluble Ionic Metal-Organic Polyhedra with Enzymes

(¹*Graduate School of Science, Kyushu University*) ○Benjamin Le Ouay,¹ Ryosuke Minami,¹ Purna K. Boruah,¹ Masaaki Ohba¹

Keywords: *Metal-organic polyhedral, Enzyme immobilization, self-assembly*

Metal-organic polyhedra (MOPs) are a fascinating class of compounds, that can be used as elementary bricks for the realization of complex organized materials. MOPs are zero-dimensional analogues of MOFs, with a high intrinsic porosity, but also the capability to be dispersed as molecularly defined single entities in selected solvents and recombined in a controlled manner. However, their typically low solubilities and stabilities in water preclude most application in association with biological systems. This calls for the design of new MOPs, that would enable the design bio-hybrid MOP-based systems. One promising application is for the immobilization of catalytically active enzymes. Recently, this domain saw a strong interest in the use of MOFs as immobilization matrix, combining high activity enabled by the MOF microporosity as well as good stabilization performances. In this context, establishing a novel strategy that provides a general way to build microporous networks able to integrate a wide variety of enzymes in mild conditions (i.e. aqueous medium, room temperature, neutral pH with minimal salts or additive,...) is extremely relevant for a wide range of applications.

Hereby, we describe for the first time how MOPs can act as an efficient immobilization matrix for enzyme [1]. The targeted design of MOPs with Rh-centers and pending arms bearing either cationic or anionic groups offered both a good solubility in water, as well as a high affinity for enzymes with an isoelectric point (pI) below or above 7, respectively.

Using BSA, we demonstrate the formation of assemblies with cationic MOPs, that were obtained either in a colloidal state or as precipitated powder, depending on the initial MOP-to-protein ratio. Assemblies were obtained by simple mixing of BSA and MOP aqueous solutions, without additive nor chemical modification required. The method was then transposed to Catalase, that has also a pI below 7. In this case, immobilization resulted in a significant maintenance of catalytic activity with a reduction by only one Log, on par with that of other MOF immobilization systems. Furthermore, the immobilization in a solid material enabled recyclability for the enzyme. Meanwhile, Cytochrome C, with a peroxidase activity and a pI above 7, we used anionic MOPs to prepare assemblies. In this case, the activity was not only maintained, but was even significantly improved for the immobilized enzyme, by a factor 44. This effect was attributed to interaction between Cytochrome C and the highly ionic network of MOPs surrounding it.

As such, MOPs offer a powerful and versatile way to immobilize proteins and notably catalytically active enzymes. The very mild assembly conditions, as well as MOP intrinsic porosity, contribute to the high activity of the enzymes after immobilization.

[1] Submitted

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[K506-1vn] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Shin Takemoto, Takanori Shima

Wed. Mar 22, 2023 4:10 PM - 6:40 PM K506 (K506, Lecture Hall Bldg. [5F])

[K506-1vn-01] Synthesis of tris(dinitrogen) iron(0) complexes stabilized by organosilicon ligands○Reon Ishii¹, Yusuke Sunada^{1,2} (1. Graduate School of Engineering, The University of Tokyo, 2. Institute of Industrial Science, The University of Tokyo)

4:10 PM - 4:30 PM

[K506-1vn-02] Synthesis and Reactivity of Doubly Oxido-Bridged Diruthenium Complex with Terminal Hydroxido Ligands○Tomoyo Misawa-Suzuki¹, Nanako Asai¹, Hirotaka Nagao¹ (1. Fac. of Sci. and Tech., Sophia Univ.)

4:30 PM - 4:50 PM

[K506-1vn-03] Anion-Exchange-Induced Modulation of Electric Field Response in a Two-Dimensional Bis(terpyridine)metal(II) complex polymer○Kenji Takada¹, Hiroshi Nishihara¹ (1. Tokyo University of Science, Research Institute for Science & Technology)

4:50 PM - 5:10 PM

[K506-1vn-04] Intramolecular C-H Bond Activation and Functionalization by Low-Valent Cobalt Complexes with Diamide Ligands○Suiho Kobayashi¹, Tsubasa Hatanaka¹, Yasuhiro Funahashi¹ (1. Osaka Univ.)

5:10 PM - 5:30 PM

[K506-1vn-05] Heterobimetallic Pt/Main Group Metal Complexes in Metal-Metal Cooperative Bond Activation○GOVINDARAJAN RAMADOSS¹, Shubham Deolka¹, Eugene Khaskin¹, Serhii Vasylevskyi¹, Robert R. Fayzullin², Shrinwantu Pal¹, Julia R. Khusnutdinova¹ (1. Okinawa Institute of Science and Technology Graduate University, 2. Arbuzov Institute of Organic and Physical Chemistry FRC Kazan Scientific Center, Russian Academy of Sciences 8 Arbuzov Street, Kazan, 420088 (Russian Federation))

5:40 PM - 6:00 PM

[K506-1vn-06] Fabrication of oriented conductive metal-organic framework thin film by dry process.○Seoungmin Chon¹, Ryo Nakayama², Shunta Iwamoto¹, Shigeru Kobayashi¹, Ryota Shimizu¹, Taro Hitosugi^{2,1} (1. Tokyo Institute of Technology, 2. the University of Tokyo)

6:00 PM - 6:20 PM

[K506-1vn-07] Selective CuAAC Transformation of Cu(I) Complex Surrounded by Multiple Reactive Points○Takuya SHIBUE¹, Shang RONG¹, Kazuyuki KUBO¹, Shoko KUME¹, Tsutomu MIZUTA¹ (1. Hiroshima Univ.)

6:20 PM - 6:40 PM

有機ケイ素配位子によって安定化されたトリス(二窒素)鉄(0)錯体の合成

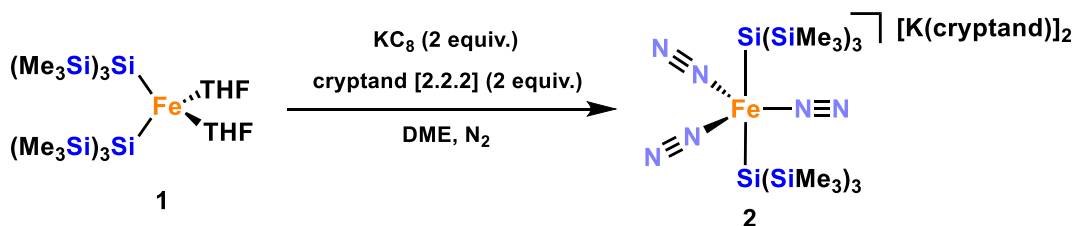
(東大院工¹・東大生研²) ○石井 玲音¹・砂田祐輔^{1,2}

Synthesis of tris(dinitrogen) iron(0) complexes stabilized by organosilicon ligands (¹*Graduate School of Engineering*, ²*Institute of Industrial Science, The University of Tokyo*) ○Reon Ishii¹, Yusuke Sunada^{1,2}

It is known that iron dinitrogen complexes can function as highly active catalysts and often be used as an alternative of noble metal catalysts. Furthermore, conversion reactions of coordinated dinitrogen molecules have also attracted much attentions^{1),2)}. Construction of low-valent and electron-rich iron centers could be considered as an efficient way to improve the reactivity of iron dinitrogen complexes. In this study, novel iron(0) dinitrogen complex **2** was synthesized by two-electron reduction of iron(II) disilyl complex **1** under a dinitrogen atmosphere. Dinitrogen molecules in complex **2** was suggested to be activated by various spectroscopic analyses as well as a single crystal X-ray diffraction analysis, and reactivity of complex **2** was also investigated.

Keywords : Dinitrogen complex; Low valent iron complex; Organosilicon ligand

鉄二窒素錯体は窒素分子の変換反応の観点や、貴金属触媒を代替する高活性な触媒としての機能の観点など、多方面から興味を集めている^{1),2)}。ここで、鉄二窒素錯体の反応性を高めるためには、低原子価で電子豊富な鉄中心の構築が重要である。そこで本研究では、有機ケイ素配位子の強いσ供与性に着目し、シリル配位子を2つ有する鉄(0)二窒素錯体の合成を行った。まず、我々が最近開発した鉄(II)ジシリル錯体 **1** を窒素雰囲気下で KC₈ を用いて 2 電子還元したところ、3 つの二窒素配位子を有する鉄(0)錯体の合成に成功した。単結晶 X 線構造解析および赤外分光法により鉄(0)錯体における窒素分子の活性化の程度について評価するとともに、本錯体の反応性も検討したので併せて報告する。



- 1) S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2016**, 7, 12181.
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Synthesis and Reactivity of Doubly Oxido-Bridged Diruthenium Complex with Terminal Aqua/Hydroxido Ligands

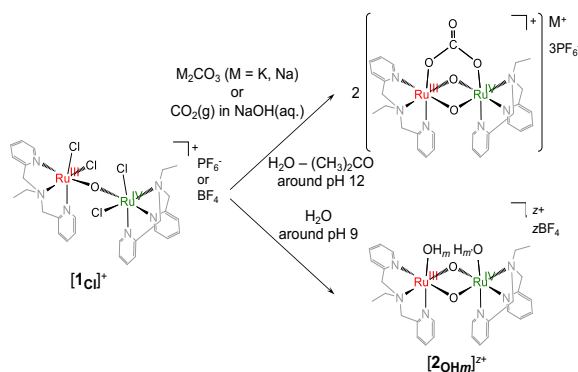
(¹*Fac. of Sci. and Tech., Sophia University*) ○Tomoyo Misawa-Suzuki,¹ Nanako Asai,¹ Hirotaka Nagao¹

Keywords: Dinuclear Complex; Doubly Oxido-Bridged; Redox Behaviors; Spectroscopic Behaviors

We have been studying syntheses, structures, electrochemical and spectroscopic properties of a series of diruthenium complexes having the $\{\text{Ru}_2(\mu\text{-O}(\text{H}))_n\}$ ($n = 1, 2$) core bearing ethylbis(2-pyridylmethyl)amine (ebpma),¹⁾ which could be the structural model compounds of metalloenzymes in nature. We have reported a carbonato-bridged complex having the $\{\text{Ru}_2(\mu\text{-O})_2\}$ core, $\text{M}[\{\text{Ru}^{\text{III,IV}}(\text{ebpma})\}_2(\mu\text{-O})_2(\mu\text{-O}_2\text{CO})_2](\text{PF}_6)_3$, which was prepared through reactions of the singly oxido-bridged diruthenium complex with chlorido ligands, $[\{\text{Ru}^{\text{III,IV}}\text{Cl}_2(\text{ebpma})\}_2(\mu\text{-O})]\text{PF}_6$ ($[\mathbf{1Cl}]\text{PF}_6$),^{1d)} with carbonate sources in aqueous solution of around pH 12^{1a)} (Scheme 1 upper).

In aqueous solutions containing NaOH or KOH around pH 9 without any possible bidentate donor ligands, in this work, a doubly oxido-bridged Ru(III)-Ru(IV) complex with terminal aqua/hydroxido ligands, $[\{\text{Ru}^{\text{III,IV}}(\text{OH}_m)(\text{ebpma})\}_2(\mu\text{-O})_2](\text{BF}_4)_z$ ($[\mathbf{2OH}_m](\text{BF}_4)_z$; $m = 1$ or 2), was synthesized from $[\mathbf{1Cl}]^+$ (Scheme 1 lower). The reactivity of $[\mathbf{2OH}_m]^{z+}$ in acetone and acetonitrile, and properties in aqueous solutions were investigated by electrochemical and spectroscopic methods. In a pH 9 aqueous solution at 60 °C within around 15 min., all the four chlorido ligands of $[\mathbf{1Cl}]^+$ were dissociated, resulting in the framework conversion from $\{\text{Ru}_2(\mu\text{-O})\}$ to $\{\text{Ru}_2(\mu\text{-O})_2\}$ and the coordination of terminal OH_m ligands. The ESI MS supported the doubly bridged structure ($m/z = 725.8$).

$[\mathbf{2OH}_m]^{z+}$ showed an MLCT band at 337 nm and an IVCT-like band at 1028 nm in a pH 9.2 water, which was attributed to the transitions on the $\{\text{Ru}_2(\mu\text{-O})_2\}$ core and similar to those of our series of the Ru(III)-Ru(IV) system having the $\{\text{Ru}_2(\mu\text{-O})_2\}$ core.^{1a,c)} Upon dissolution of $[\mathbf{2OH}_m]^{z+}$ into acetone or acetonitrile, the X-ray crystallography of the obtained crystalline samples revealed that two OH_m ligands were substituted or reacted with the solvent used. We will discuss the electrochemical and spectroscopic behaviors and reactivity of $[\mathbf{2OH}_m]^{z+}$ in solution.



Scheme 1. Synthesis of $[\mathbf{2OH}_m]^{z+}$.

1) a) T. Misawa-Suzuki, H. Nagao *et al.*, *Inorg. Chem.* **2021**, 60, 9996; b) *Inorg. Chem.* **2020**, 59, 612; c) *Inorg. Chem.* **2016**, 55, 6830; d) T. Suzuki, H. Nagao *et al.*, *Eur. J. Inorg. Chem.* **2014**, 4040.

Anion-Exchange-Induced Modulation of Electric Field Response in a Two-Dimensional Bis(terpyridine)metal(II) Complex Polymer

(¹Research Institute for Science & Technology, Tokyo University of Science)

○Kenji Takada¹, Hiroshi Nishihara¹

Keywords: Coordination Polymer; Thin Films; Terpyridine; Anion-Exchange

Coordination nanosheets (CONASHs) are emerging two-dimensional materials prepared in bottom-up ways via coordination bonds. The high degree in freedom for the choice in ligands and metals results in a rich variety of functionality of the CONASHs.¹ When a framework of CONASHs is ionic, counter ions should be included in the CONASHs. Therefore, in ionic coordination nanosheets, the choice of counter ions gives another degree of freedom in the composition and functions.

Bis(terpyridine)metal(II) complex nanosheets, M-tpy (M = Fe, Co, and Zn), are cationic CONASHs, whose framework features electrochemical and photophysical functions such as electrochromism, redox conductivity, and photoluminescence.²⁻⁴ We previously reported anion-exchange for Zn-tpy with luminescent dye anions and their photofunctions.⁴ This result motivated us to investigate new electronic functions of redox-active M-tpy via anion-exchange reaction.

In this research, post-synthetic anion-exchange reaction of chloride-containing Co-tpy was examined. The chloride anions were efficiently replaced by other anions such as BF_4^- and $[\text{Ni}(\text{mnt})_2]^{n-}$ ($n = 1$ or 2). In addition, the response to electric field of Co-tpy on interdigitated array electrodes (IDAs) was modulated by anion-exchange (**Fig. 1**). The mechanism of these phenomena will be discussed based on the electronic states of the CONASH and the anions.

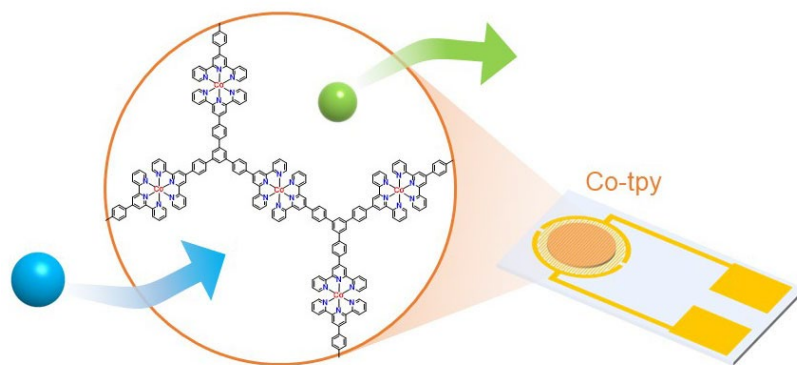


Fig. 1. Electronic field response modulation of Co-tpy via anion-exchange

- 1) H. Maeda, K. Takada, N. Fukui, S. Nagashima, H. Nishihara, *Coord. Chem. Rev.* **2022**, 470, 214693.
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Intramolecular C-H Bond Activation and Functionalization by Low-Valent Cobalt Complexes with Diamide Ligands

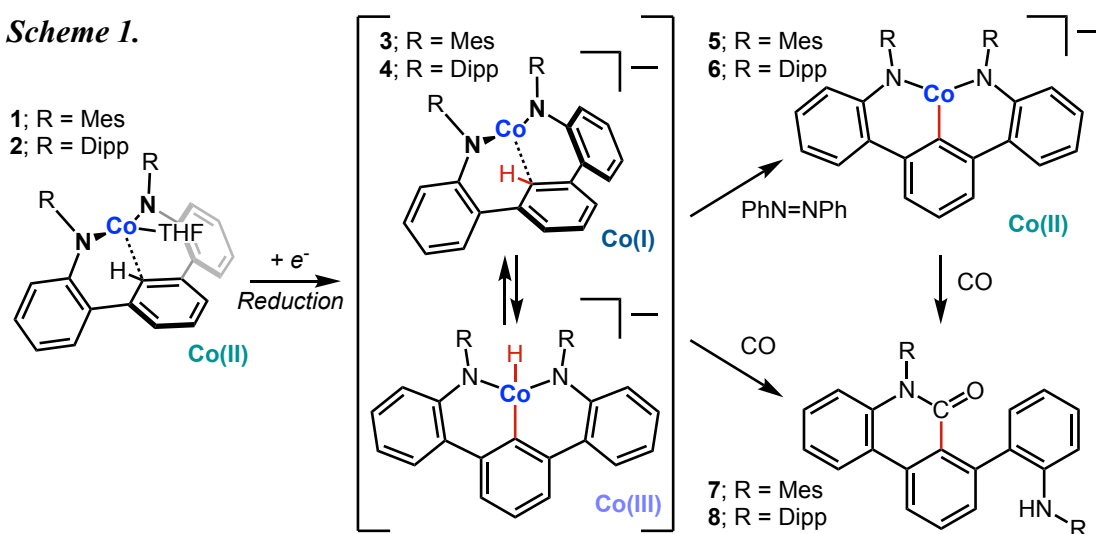
(Osaka Univ.) ○Suiho Kobayashi, Tsubasa Hatanaka, Yasuhiro Funahashi

Keywords: C-H Activation; Coordinatively Unsaturated Complexes; Electron-Donating Ligands; Low-Valent Cobalt; Oxidative Addition

Cobalt has attracted much attention as one of the most promising elements in the first-row transition metals to catalyze C-H bond functionalization, and many examples have been thus far reported. To achieve oxidative addition of C-H bond by low-valent cobalt, we performed synthesis and reduction of cobalt complexes with highly electron-donating terphenyl diamide ligands, TDA^R (R = Mes, Dipp).

The Co(II) complexes **1** and **2** were synthesized by reactions of cobalt chlorides with potassium salts of the ligands. And then reduction of the Co(II) complexes **1** and **2** were found to provide Co(I) complexes **3** and **4** (*Scheme 1*). X-ray analysis revealed that the cobalt centers in all complexes are interacted with the central aromatic ring of the terphenyl ligand, and also the interaction becomes stronger by reduction of the cobalt centers. With these reduced cobalt complexes in hand, we explored reactivities of low-valent cobalt complexes, and found several unique reactions. For instance, addition of azobenzene to the complexes **3** and **4** resulted in C-H bond activation of the central aromatic ring involving hydrogen atom transfer to azobenzene to form Co(II) complexes **5** and **6**. We also achieved C-C bond formation reaction between organic substrates and the TDA^R ligands. In particular, reactions of the complexes **3-6** with CO were found to afford generation of organic products **7** or **8**. The formation of **7** and **8** is probably accomplished by C-H activation of the phenyl ring, CO insertion into the Co-C bond, and reductive elimination from the cobalt center.

Scheme 1.

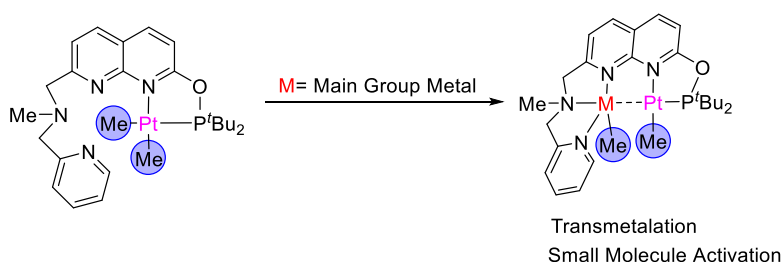


Heterobimetallic Pt/Main Group Metal Complexes in Metal-Metal Cooperative Bond Activation

(¹Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University; ²Arbuzov Institute of Organic and Physical Chemistry, FCR Kazan Scientific Center, Russian Academy of Sciences) ○ Govindarajan Ramadoss,¹ Shubham Deolka,¹ Eugene Khaskin,¹ Serhii Vasylevskyi,¹ Robert R. Fayzullin,² Shrinwantu Pal,¹ Julia R. Khusnutdinova*¹

Keywords: Heterobimetallic, Transmetalation, Metal-Metal cooperation, Small-molecule activation.

Heterobimetallic complexes which hold two metals in close proximity have been the subject of current interest due to their vital role in small molecule activation and catalysis via metal–metal cooperativity. However, the selective synthesis of heterobimetallic complexes still presents a significant challenge, many research groups rely on the thorough optimization of the ligand design to overcome this issue.¹ Our group focused on the synthesis of unsymmetrical naphthyridine-based binucleating ligands containing distinct binding environments. Such ligand design allowed us to form selective heterobimetallic complexes via stepwise synthesis. As a result, recently we reported the selective formation of Pt/Cu and Pt/Zn heterobimetallic complexes showing close metal-metal interaction and promoting cooperative small molecule activation (H₂, Si-H, B-H, and C-H).² In this work, we report Pt/main group heterobimetallic complexes and their metal-metal cooperative reactivity in the activation of silanes and boranes. We demonstrate how the synergistic interaction plays an important role in metal-metal cooperative small molecule activation, transmetalation, and retrotransmetalation relevant to Stille and Negishi coupling reactions. Metal-Metal interactions were analyzed by QTAIM studies.



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- 2) a). S. Deolka, O. Rivada, S. L. Aristizábal, R. R. Fayzullin, S. Pal, K. Nozaki, E. Khaskin, J. R. Khusnutdinova, *Chem.Sci.* **2020**, *11*,5494. b) R. Govindarajan, S. Deolka, E. Khaskin, R. R. Fayzullin, S. Pal, S. Vasylevskyi, J. R. Khusnutdinova, *Chem. Eur. J.* **2022**, e202201639.

Fabrication of oriented conductive metal-organic framework thin film by dry process

(¹Department of Materials and Chemical Technology, Tokyo Institute of Technology, ²Department of Chemistry, the University of Tokyo) ○Seungmin Chon,¹ Ryo Nakayama,² Shunta Iwamoto,¹ Shigeru Kobayashi,¹ Ryota Shimizu,¹ and Taro Hitosugi²

Keywords: Metal–organic framework; vapor phase deposition; thin film; orientation control;

Metal–organic frameworks (MOFs) consist of metal ions and ligands that show crystalline porous structure. Recently, electrically conductive two-dimensional (2D) MOF, Cu₃(HHTP)₂ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), attracts attention in device applications such as electronics and chemiresistive sensors [1,2]. For such applications, the oriented thin film is desired due to its anisotropic property and structure, and has been fabricated by the wet process [3]. Compared to the wet process, the dry process shows the advantage of device fabrication because of reduced damage at the interface caused by solvent. However, no report is available for the synthesis of orientated Cu₃(HHTP)₂ thin film by dry process. In this study, we show a novel two-step dry process combining vapor phase deposition and pyridine vapor annealing to fabricate oriented Cu₃(HHTP)₂ thin film.

As a first step, Cu₃(HHTP)₂ thin films were deposited on Al₂O₃ (0001) using infrared-pulsed-laser deposition (IR-PLD) [4,5]. Cu(OAc)₂ (copper acetate anhydrous) and HHTP were mixed with infrared absorbers (Si), followed by pelletization to make metal and ligand targets, respectively. The thin films were deposited at 100 °C in a multilayer form: alternate deposition of HHTP layer (10 nm) and Cu(OAc)₂ (8 nm) was repeated 5 times. As a second step, the fabricated multilayer films were annealed under pyridine vapor; the deposited film and a 3 μL of pyridine were separately set in a gasket-sealed cell (7 ml) under air. The cell was annealed at 60 °C for 24h. The structural characterization was performed by X-ray diffraction (XRD).

XRD patterns indicate the formation of oriented Cu₃(HHTP)₂ thin film (Figure). The out-of-plane pattern only shows a broad peak near 28°, originating from the interlayer spacing of Cu₃(HHTP)₂ 002 (red star). In the in-plane pattern, sharp peaks corresponding to the 100, 200, and 210 Miller indices were observed. Thus, in-plane orientation may be at random, confirming the successful fabrication of (001)-oriented Cu₃(HHTP)₂ film.

1. Song *et al.*, *Mater. Chem. Front.*, **2021**, 5, 3422.
2. Rubio-Gimenez *et al.*, *Angew. Chem. Int. ed.*, **2018**, 57, 15086.
3. Ma *et al.*, *Nat. Commun.*, **2022**, 13, 6347
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5. Oguchi, Hitosugi *et al.*, *ACS Appl. Electron. Mater.* **2019**, 1, 1792.
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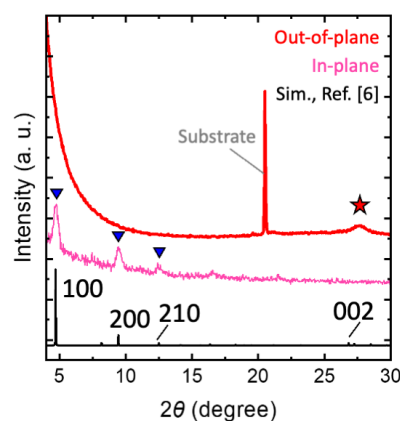


Figure : X-ray diffraction patterns of the film.

周辺にエチニル基を集積した Cu(I) 錯体の選択的 CuAAC 変換

(広島大院先進理工¹⁾) ○澁江 拓哉¹・Shang Rong¹・久保 和幸¹・久米 晶子¹・水田勉¹
 Selective CuAAC Transformation of Cu(I) Complex Surrounded by Multiple Reactive Points
 (¹Hiroshima Univ.) ○Takuya SHIBUE,¹ Rong SHANG,¹ Kazuyuki KUBO,¹ Shoko KUME,¹
 Tsutomu MIZUTA¹

Cu(I)-catalyzed azide-alkyne cycloadditions (CuAAC) have enabled active template synthesis by linking coordination and catalytic activity, while selective conversion among multiple reaction points is still a challenge due to its intricate multinuclear intermediate formation. We aimed to develop a regulated CuAAC system by confining a Cu center in a rigid coordination surrounded by four equivalent ethynyl moieties. By monitoring CuAAC of this complex, we found that CuAAC proceeds in a regulated stepwise manner, which was analyzed as self-accelerated second-order reactions for Cu. Moreover, the competition of internal and external ethynyl moieties resulted in an unprecedented regulations of CuAAC, that proceeded with a sequence of two autocatalyses.

Keywords : CuAAC Reaction; Asymmetry Transformation; Autocatalysis; Selectivity

Cu(I)を触媒としたアジドアルキン環化付加(CuAAC)は高い官能基選択性、温和な条件下で進行し、活性テンプレートによる超分子合成を可能にしてきた。一方で中間体として Cu(I)の複核構造形成などが関わり、反応を精密かつ積極的に制御するには未知の部分が多いため、複数の反応点での選択的な CuAAC には、保護・脱保護¹やキラル中心の導入²などを要する。我々は Cu(I)に対し強固な配位を取る[Cu(phen)₂]⁺錯体の周辺に4つの等価なエチニル基を集積することで、Cu(I)の配位構造と CuAAC の進行を強く相関させ、①錯体内部の4つのアルキンの変換に対する選択性②錯体内部のアルキンと外部のアルキンの逐次的な自触媒反応について見出した。

[Cu(diethynylphen)₂]⁺と 4-methylbenzylazide(Az)との反応を ¹H NMR で追跡したところ、4つのアルキンの反応はランダムではなく、異性体のうち1つだけを選択的に經由して進行することが分かった。また、[Cu(diethynylphen)₂]⁺と外部アルキンである 4-ethynyltoluene を競争させ Az との反応を行ったところ、錯体分子内の反応の完結後に外部分子の反応が自触媒的に起こるという興味深い結果が得られた(図)。これらの反応性を速度論解析およびトリアゾール形成が誘起する配位構造の変化から考察した。

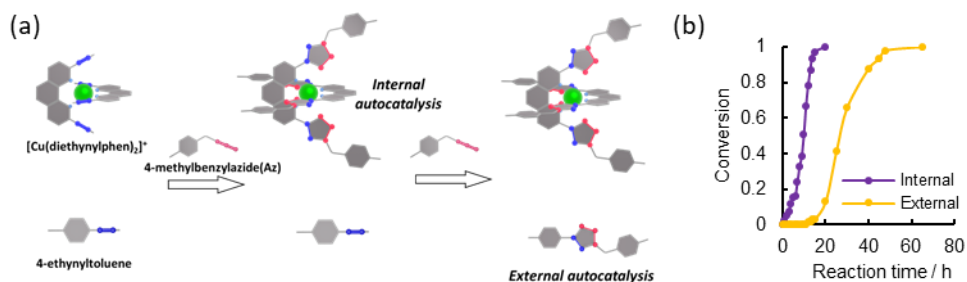


図 (a) [Cu(diethynylphen)₂]⁺と 4-ethynyltoluene の競争的 CuAAC 進行 (b) Ethynyl 基の 1,2,3-triazole への変換に見られる逐次的自触媒効果(acetone-d₆)

1) Allan et al., *J. Org. Chem.*, **2017**, 82, 5461-5468. 2) He et al., *J. Am. Chem. Soc.*, **2021**, 143, 16302-16310.

[K404-1am] 10. Organic Chemistry -Organometallic Compounds-

Chair: Hiroshi Naka, Mamoru Ito

Wed. Mar 22, 2023 9:00 AM - 11:40 AM K404 (K404, Lecture Hall Bldg. [4F])

[K404-1am-01] Regioselective Distal C-C Bond Formations via Ir-Catalyzed C-H Activation along with Chain-Walking○King Hung Nigel Tang¹, Tokutake Ryo¹, Uchida Kanako¹, Nishihara Kazuki¹, Ito Mamoru¹, Shibata Takanori¹ (1. Waseda University)

9:00 AM - 9:20 AM

[K404-1am-02] Synthesis of 3,4-Fused-2-Quinolone Derivatives via Site-Selective C-H Functionalization by Cp* Rh(III) Catalysis.○naohiro hirako¹, takeshi yasui¹, yasihiko yamamoto¹ (1. The Univ. of Nagoya)

9:20 AM - 9:40 AM

[K404-1am-03] Cationic Rhodium(I) Tetrafluoroborate-Catalyzed Intramolecular Carbofluorination of Alkenes via C-F Bond Cleavage of Acyl Fluorides○Tomoki Yoshida¹, Masaya Ohta¹, Takuya Kodama^{1,2}, Mamoru Tobisu^{1,2} (1. Osaka University, 2. ICS-OTRI, Osaka University)

9:40 AM - 10:00 AM

[K404-1am-04] Cobalt/Photoredox Dual Catalysis-Enabled Cycloisomerization of Eneidyne via C-H Bond Activation○Keiji Yamada¹, Takeshi Yasui¹, Yoshihiko Yamamoto¹, Nobuaki Koga² (1. Grad. Sch. Pharm. Sci., Nagoya Univ., 2. Grad. Sch. Informatics., Nagoya Univ.)

10:00 AM - 10:20 AM

[K404-1am-05] An Iridium Precatalyst for Transfer Dehydration of Amides to NitrilesMarie Ono¹, Toshiki Asai², Asuka Naraoka¹, Yasuhiro Ohki³, Yoshiji Takemoto¹, ○Hiroshi Naka¹ (1. Grad. Sch. of Pharm. Sci., Kyoto Univ., 2. Grad. Sch. of Sci., Nagoya Univ., 3. Inst. Chem. Res., Kyoto Univ.)

10:40 AM - 11:00 AM

[K404-1am-06] Rhodium-Catalyzed Selective Synthesis of Silicon-containing Cyclic Compounds by Intramolecular and Intermolecular Hydrofunctionalization of Alkynes○Kazuto Fuji², Kohei Sekine^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

11:00 AM - 11:20 AM

[K404-1am-07] Magnesiation of C-F and C-O Bonds Catalyzed by Rhodium-Aluminum Bimetallic Complexes○Ikuya Fujii¹, Haruka Kido¹, Ryota Higo¹, Kazuhiko Semba¹, Yoshiaki Nakao¹ (1. Grad. Sch. Eng., Kyoto Univ.)

11:20 AM - 11:40 AM

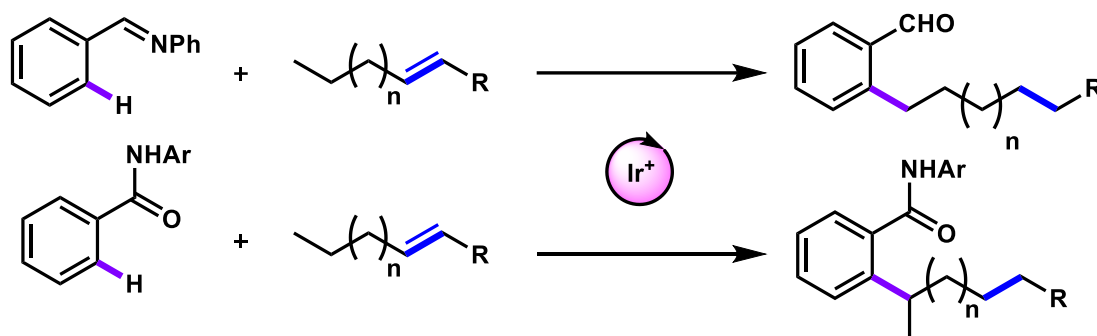
Regioselective Distal C–C Bond Formations via Ir-Catalyzed C–H Activation along with Chain-Walking

(School of Advanced Science and Engineering, Waseda University) ○King Hung Nigel Tang, Tokutake Ryo, Uchida Kanako, Nishihara Kazuki, Ito Mamoru, Shibata Takanori

Keywords: C–H Activation, Chain-Walking, Cationic Iridium Catalyst, Regioselective, C–C Bond Formation

Chain walking strategy is a powerful tool to move alkene to a new position away from the original position. Consecutive isomerization of double bonds along a hydrocarbon chain allows the introduction of a remote functional group which is generally difficult to achieve. Since the pioneering work of the palladium-catalyzed cycloisomerization of 1,*n*-dienes published by Kochi and Kakiuchi,¹ many groups have utilized chain-walking strategy in organic synthesis.^{2,3} On the other hand, one of the most widely studied methods to connect two molecule is C–H activation. In 1993, Murai *et al.* published the insertion of alkene to a sp^2 C–H bond using a ruthenium catalyst.⁴ Yet, these two strategies did not meet until 2017.⁵ To the best of our knowledge, there are only two reports on the cooperative strategy of C–H bond activation and chain-walking.^{5,6}

We herein report a regioselective remote C–C bond formation via sp^2 C–H activation along with chain-walking enabled by a cationic iridium catalyst. The choice of the directing group can greatly determine the mode of addition of the alkene to the product. When an imino group was used as a directing group, linear products can be exclusively obtained.⁷ On the other hand, when a carbamoyl group was used, high branched/linear ratio, i.e., >20:1, was realized. The fine-tuning of ligand for iridium catalyst can control the presented regioselectivity.



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2) Kochi, T.; Kanno, S.; Kakiuchi, F. *Tetrahedron Lett.* **2019**, *60*, 150938.

3) Ghosh, S.; Patel, S.; Chatterjee, I. *Chem. Commun.* **2021**, *57*, 11110-11130.

4) Kamatani, A.; Sonoda, M.; Sekine, S.; Kakiuchi, F.; Chatani, N.; Tanaka, Y.; Murai, S. *Nature* **1993**, *366*, 529-531.

5) Ebe, Y.; Onoda, M.; Nishimura, T.; Yorimitsu, H. *Angew. Chem. Int. Ed.* **2017**, *56*, 5607-5611.

6) Borah, A. J.; Shi, Z. *J. Am. Chem. Soc.* **2018**, *140*, 6062-6066.

7) Tang, K. H. N.; Uchida, K.; Nishihara, K.; Ito, M.; Shibata, T. *Org. Lett.* **2022**, *24*, 1313-1317.

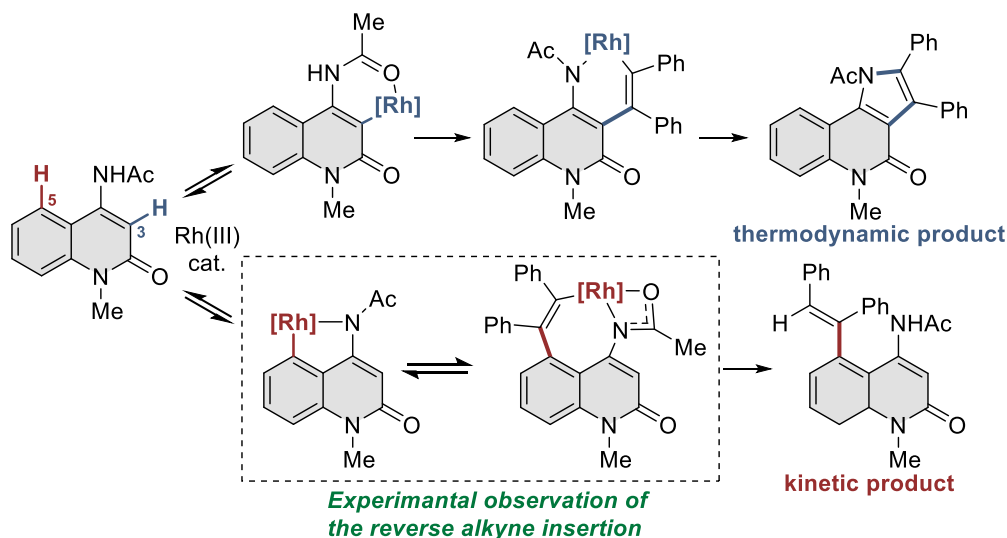
Synthesis of 3,4-Fused-2-Quinolone Derivatives via Site-Selective C–H Functionalization by Cp* Rh(III) Catalysis

(¹Graduate School of Pharmaceutical Sciences, Nagoya University) ○ Naohiro Hirako,¹ Takeshi Yasui,¹ Yoshihiko Yamamoto¹

Keywords: 2-Quinolone; C–H functionalization; Rhodium; Oxidative annulation

2-Quinolone derivatives fused at the C3- and C4-positions are important motifs found in natural products, biologically active substances, and approved drugs. Therefore, the development of efficient methods for the synthesis of 3,4-fused-2-quinolones from readily available substrates is an important mission for drug discovery. Oxidative annulation of 2-quinolones with alkynes involving the C–H activation is one of the most efficient methods for the preparation of 3,4-fused 2-quinolones. However, there are no reports involving the C3-selective intermolecular C–H functionalization of 2-quinolones although the C5-selective C–H functionalization to obtain 4,5-fused 2-quinolones have been reported.¹⁾

Herein, we report the oxidative annulation of 2-quinolones with alkynes to provide 3,4-fused 2-quinolones via Cp* Rh(III) catalyzed C3-selective C–H functionalization. The mechanistic study elucidated that the alkyne insertion is reversible, and the site-selectivity is thermodynamically controlled, although the alkyne insertion is generally recognized as an irreversible process because of the high activation barrier of its reverse process, β -carbon elimination, in most cases.



- 1) a) S. Mochida, M. Shimizu, K. Hirano, T. Satoh, M. Miura, *Chem. Asian J.* **2010**, *5*, 847. V. S. Thirunavukkarasu, M. Donati, L. Ackermann, *Org. Lett.* **2012**, *14*, 3416. c) P. K. Dutta, M. K. Ravva, S. Sen, *J. Org. Chem.* **2019**, *84*, 1176.

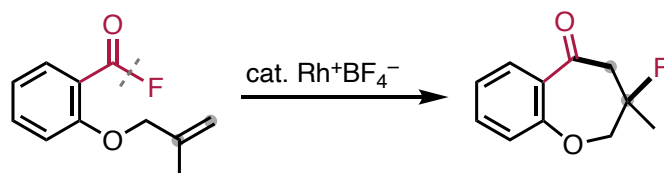
Cationic Rhodium(I) Tetrafluoroborate-Catalyzed Intramolecular Carbofluorination of Alkenes via C–F Bond Cleavage of Acyl Fluorides

(¹Graduate School of Engineering, Osaka University, ²ICS-OTRI, Osaka University)

○Tomoki Yoshida,¹ Masaya Ohta,¹ Takuya Kodama,^{1,2} Mamoru Tobisu^{1,2}

Keywords: Rhodium Catalyst; Carbofluorination; Organic Fluorine Compounds; Acyl Fluorides; Carbon–Fluorine Bond Cleavage

Organic fluorine compounds play an important role in diverse fields including materials, agrochemical, and pharmaceutical sciences.¹ The development of catalytic reactions that allow for the synthesis of complex fluorinated compounds in an efficient manner is the key to further advancement in these areas of research. If a carbon–fluorine bond in fluorinated molecules is cleaved and an alkene or alkyne can be inserted in a catalytic manner, it would offer a powerful tool for the synthesis of complicated organic fluorine compounds from simpler organofluorine building blocks with a 100% atom economy. Such an insertion reaction requires a catalyst that can mediate both cleavage and formation of a C–F bond, which represents a daunting challenge. In fact, only two examples of catalytic carbofluorination of unsaturated compounds via the activation of a C–F bond have been reported to date.^{2,3} Herein, we report on intramolecular carbofluorination of alkenes using acyl fluorides via C–F bond cleavage, which is catalyzed by a rhodium tetrafluoroborate salt.⁴



References

- 1) Selected reviews: (a) Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 214–231; (b) Müller, K.; Faeh, C.; Diederich, F. *Science*, **2007**, *317*, 1881–1886; (c) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320–330.
- 2) (a) Fujimoto, H.; Kodama, T.; Yamanaka, M.; Tobisu, M. *J. Am. Chem. Soc.* **2020**, *142*, 17323–17328; (b) Yu, X.; Meng, Q.-Y.; Daniliuc, C. G.; Studer, A. *J. Am. Chem. Soc.* **2022**, *144*, 7072–7079.
- 3) Catalytic insertion of carbenes into a C–F bond of benzyl fluorides was recently reported: Wang, F.; Nishimoto, Y.; Yasuda, M. *J. Am. Chem. Soc.* **2021**, *143*, 20616–20621.
- 4) Yoshida, T.; Ohta, M.; Kodama, T.; Tobisu, M. *ChemRxiv*, **2022**, preprint. DOI: 10.26434/chemrxiv-2022-2rrsc

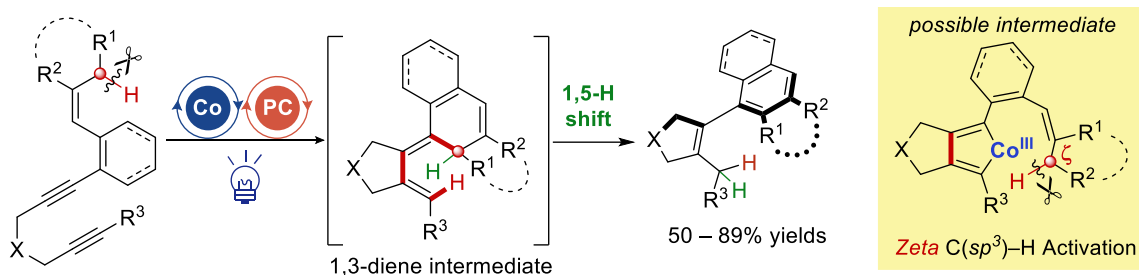
Cobalt/Organophotoredox Dual Catalysis-Enabled Cycloisomerization of 1,5,10-Enediynes via C(sp³)-H Activation

(¹Graduate School of Pharmaceutical Sciences, Nagoya University, ²Graduate School of Information Science, Nagoya University) ○Keiji Yamada,¹ Nobuaki Koga,² Takeshi Yasui,¹ Yoshihiko Yamamoto¹

Keywords : Photoredox catalysis, Cobalt, Cycloisomerization, C-H activation

C-H functionalization reactions using high-valent group 9 metal catalysts such as Rh^{III} and Co^{III} species have been recognized as a powerful method allowing access to various complex molecules from non-preactivated substrates. In particular, Rh^{III} and Co^{III} complexes generated in situ from the corresponding low-valent metal species by the oxidative cyclization of 1,6-diynes or 1,6-enynes have also been employed for such fascinating transformations.¹⁾ This type of transformation includes the cyclization process in addition to the C-H functionalization, which potentially leads to efficient construction of complex polycyclic frameworks. However, reports on such redox-neutral and highly atom-economic transformations have been significantly limited.

Herein, we report a novel cobalt/photoredox dual-catalysis-enabled cycloisomerization of 1,5,10-enediynes via C(sp³)-H bond activation at *zeta*-position to the metal center of cobaltacyclopentadiene intermediates. We performed several control experiments and theoretical calculations to elucidate the mechanism of this intriguing transformation, indicating that the C(sp³)-H bond cleavage proceeds through σ -bond metathesis in the cobaltacyclopentadiene intermediate. To the best of our knowledge, the site-selective C-H bond functionalization at *zeta*-position to the metal center of metallacycle species has not been reported to date although the cyclization reactions involving γ -, δ -, and ϵ -C-H activation have been developed²⁾.



1) (a) K. Tanaka, Y. Otake, A. Wada, K. Noguchi, M. Hirano, *Org. Lett.* **2007**, *9*, 2203. (b) E. Santhoshkumar, S. Mannathan, C-H. Cheng, *Org. Lett.* **2014**, *16*, 4208.

2) (a) Y. Oonishi, Y. Kitano, Y. Sato, *Angew. Chem. Int. Ed.* **2012**, *51*, 7305–7308. (b) Y. Kawaguchi, S. Yasuda, C. Mukai, *Angew. Chem. Int. Ed.* **2016**, *55*, 10473–10477. (c) Y. Oonishi, S. Sakamoto, Y. Sato, *Synthesis* **2021**, *53*, 2976–2983.

An Iridium Precatalyst for Transfer Dehydration of Amides to Nitriles

(¹Graduate School of Pharmaceutical Sciences, Kyoto University, ²Graduate School of Science, Nagoya University, ³Institute for Chemical Research, Kyoto University)

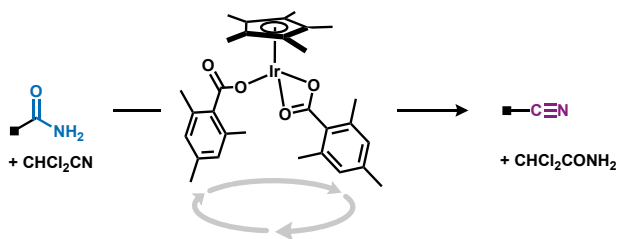
Marie Ono,¹ Toshiki Asai,² Asuka Naraoka,¹ Yasuhiro Ohki,³ Yoshiji Takemoto,¹ Hiroshi Naka¹

Keywords: Iridium; Nitriles; Amides; Dehydration; Transfer Dehydration

Metal-catalyzed, homodesmotic transfer reaction is a valuable synthetic tool for converting a specific functional group to other ones with a minimal loss of chemical energy. A remarkable example is the ruthenium-catalyzed asymmetric transfer hydrogenation of carbonyl compounds developed by Noyori using alcohols as H₂ donors. Homodesmotic transfer catalysis has been recently recognized as a new strategy for reaction development.

The palladium-catalyzed transfer dehydration of primary amides with nitriles is a characteristic homodesmotic transfer reaction.^[1] This reaction can be typically carried out under aqueous conditions in the presence of palladium(II) catalysts (typically PdCl₂) and acetonitrile (H₂O acceptor) at room temperature and is frequently used for producing functionalized nitriles. During our previous studies on the synthetic applications of the palladium-catalyzed transfer dehydration catalysis,^[2] we wondered if the transfer dehydration of amides with nitriles could be catalyzed by other metals, which should offer multiple options for synthetic uses. However, to the best of our knowledge, there has been no metallic species other than palladium known to catalyze homodesmotic transfer dehydration of amides to nitriles using nitriles as water acceptors.^[3]

Herein, we report a structurally well-defined iridium complex, IrCp*(MesCO₂)₂ [Mes = 2,4,6-trimethylphenyl], as an active precatalyst for the transfer dehydration of amides to nitriles. This precatalyst promoted the dehydration of amides using dichloroacetonitrile as a water acceptor with comparable functional group compatibility to previously reported palladium catalysts.^[1,2]



- [1] S. I. Maffioli, E. Marzorati, A. Marazzi, *Org. Lett.* **2005**, 7, 5237-5239.
- [2] H. Okabe, A. Naraoka, T. Isogawa, S. Oishi, H. Naka, *Org. Lett.* **2019**, 21, 4767-4770.
- [3] Our preliminary results were communicated in the CSJ annual meeting 2021 [A16-1am-05].

ロジウム触媒を用いたアルキンの分子内および分子間ヒドロ官能基化による含ケイ素環状化合物の選択的な合成

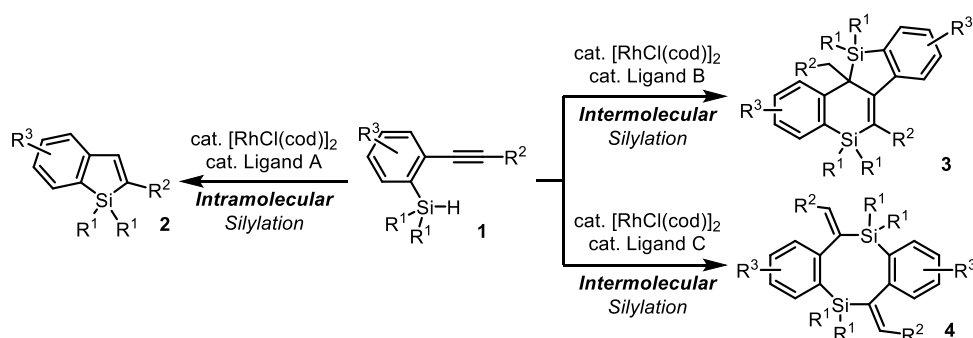
(九大先導研¹・九大院総理工²) ○藤 和人²・関根 康平^{1,2}・國信 洋一郎^{1,2}

Rhodium-Catalyzed Selective Synthesis of Silicon-containing Cyclic Compounds by Intramolecular and Intermolecular Hydrofunctionalization of Alkynes (¹*Institute for Materials Chemistry and Engineering, Kyushu University*, ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Kazuto Fuji,² Kohei Sekine,^{1,2} Yoichiro Kuninobu^{1,2}

In the case of molecules with two reaction sites, the selectivity for intramolecular and intermolecular reactions is sometimes a problem. For instance, platinum-catalyzed hydrosilylation of (2-hydrosilylaryl)alkynes **1** with an alkyne moiety and a hydrosilyl group afforded a mixture of benzosiloles and polymeric products by intramolecular and intermolecular hydrosilylation. In this research, we investigated the rhodium-catalyzed hydrosilylation of **1** to control the selectivity of intramolecular and intermolecular reactions. We revealed that intramolecular and intermolecular reactions could be controlled by changing the phosphine ligands of the rhodium complex to afford three types of silicon-containing cyclic compounds **2–4** with high selectivity.

Keywords : Rhodium Catalyst; Silylation; Alkyne; Cyclization; Silicon-containing Cyclic Compound

分子内に2か所の反応点をもつ分子では、分子内および分子間反応の競合が問題となる。分子内にアルキン部位とヒドロシリル基を有する(2-ヒドロシリルアリアル)アルキン **1** の白金触媒によるヒドロシリル化では、分子内および分子間反応の進行により、ベンゾシロールおよびポリマーの混合物が得られる¹⁾。本研究では、分子内および分子間反応の制御を目的として、ロジウム触媒を用いる化合物 **1** のヒドロシリル化を検討した。その結果、ロジウム触媒におけるホスフィン配位子を変えることにより、分子内および分子間反応を制御することに成功した。分子内反応では高選択的にベンゾシロール **2** が得られ、分子間反応では異なる構造を有する2種類の含ケイ素環状分子 **3** および **4** がそれぞれ高選択的に得られた。



✓Ligand control ✓High selectivity ✓Novel silacyclic compounds

1) Märkl, G.; Berr, K.-P. *Tetrahedron Lett.* **1992**, 33, 1601.

ロジウム-アルミニウム複核金属錯体を触媒とする C-F および C-O 結合のマグネシウム化反応

(京大院工) ○藤井 郁哉・城戸 春香・肥後 諒大・仙波 一彦・中尾 佳亮

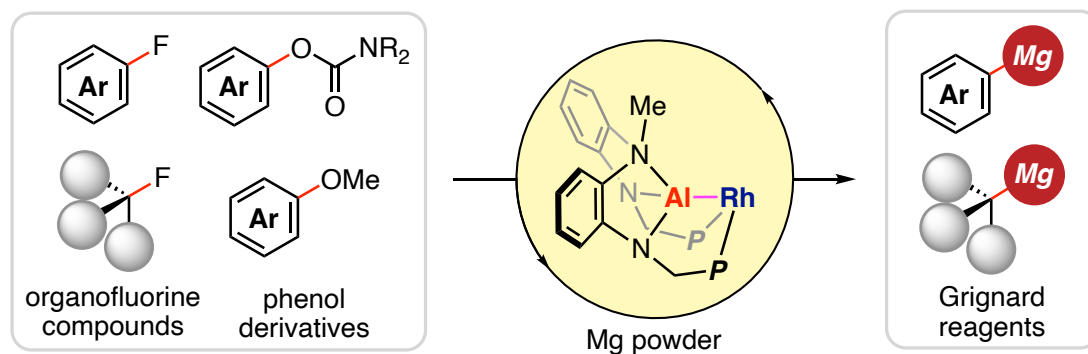
Magnesiation of C-F and C-O Bonds Catalyzed by Rhodium-Aluminum Bimetallic Complexes (Graduate School of Engineering, Kyoto University) ○Ikuya Fujii, Haruka Kido, Ryota Higo, Kazuhiko Semba, Yoshiaki Nakao

Since the innovative discovery by Grignard, organomagnesium reagents have played many important roles in organic synthesis due to their high reactivity in various transformations. Conventionally, they have been prepared from the corresponding organobromides and easy-to-handle magnesium turnings or powder. On the other hand, it has been difficult to prepare organomagnesium reagents from organofluorine compounds or phenol derivatives. Herein, we report the magnesiation of organofluorine compounds and phenol derivatives such as aryl ethers and aryl carbamates with magnesium powder catalyzed by rhodium-aluminum bimetallic complexes.

Keywords : Rhodium; Aluminum; C-F activation; C-O activation; Grignard Reagents

グリニャール反応剤は、多様に変換できるため有機合成化学において有用である。通常、それらは反応性の高い有機臭化物とマグネシウムから調製される。一方、安定な有機フッ化物やフェノール誘導体からグリニャール反応剤を調製することは困難である。例えば、有機フッ化物の炭素-フッ素結合のマグネシウム化には、Rieke マグネシウムなどの高活性マグネシウム反応剤を必要とする¹⁾。また、コバルト触媒によるフェノール誘導体の炭素-酸素結合マグネシウム化反応が報告されているが、ビフェニルやナフタレンなどの多環式フェノール誘導体の反応に制限される²⁾。

今回我々は、ロジウム-アルミニウム複核金属錯体が有機フッ化物³⁾およびアリールエーテルやアリールカーバメートなどのフェノール誘導体のマグネシウム化反応を触媒することを明らかにしたので報告する。



1) R. D. Rieke, S. E. Bales *J. Chem. Soc., Chem. Commun.* **1973**, 879.

2) E. Pietrasiak, S. Ha, S. Jeon, J. Jeong, J. Lee, J. Seo, E. Lee *J. Org. Chem.* **2022**, 87, 8380.

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

[K404-1vn] 10. Organic Chemistry -Organometallic Compounds-

Chair: Kazuhiko Semba, Kei Muto

Wed. Mar 22, 2023 4:10 PM - 5:30 PM K404 (K404, Lecture Hall Bldg. [4F])

[K404-1vn-01] Palladium-Catalyzed Synthesis of 4-Sila-4*H*-benzo[*d*][1,3]oxazines by Intramolecular Hiyama Coupling

○Donghyeon Lee¹, Ryo Shintani¹ (1. Osaka University)

4:10 PM - 4:30 PM

[K404-1vn-02] Palladium- catalyzed unimolecular fragment coupling of amides via elimination and translocation of isocyanate

○Ryoma Shimazumi¹, Riku Tanimoto¹, Takuya Koama^{1,2}, Mamoru Tobisu^{1,2} (1. Osaka univ., 2. ICS-OTRI)

4:30 PM - 4:50 PM

[K404-1vn-03] Mechanoredox/Nickel Dual Catalytic System for Force-Induced Cross-Coupling Reactions

○Tamae Seo¹, Koji Kubota^{1,2}, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

4:50 PM - 5:10 PM

[K404-1vn-04] Dehydrogenative Three-Component Coupling of Alkylarenes, CO and Phenols

○Naoki Ishida¹, Hiroki Shinoya¹, Tairin Kawasaki¹, Masahiro Murakami¹ (1. Kyoto University)

5:10 PM - 5:30 PM

パラジウム触媒を用いた分子内檜山カップリングによる 4-シラ-4*H*-ベンゾ[*d*][1,3]オキサジンの合成

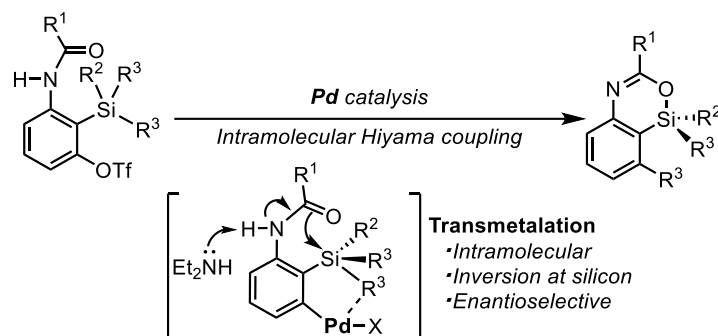
(阪大院基礎工) ○Lee Donghyeon・新谷 亮

Palladium-Catalyzed Synthesis of 4-Sila-4*H*-benzo[*d*][1,3]oxazines by Intramolecular Hiyama Coupling (*Graduate School of Engineering Science, Osaka University*) ○Donghyeon Lee, Ryo Shintani

A palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines, silicon-switched analogs^[1] of biologically relevant 4*H*-benzo[*d*][1,3]oxazines,^[2] was developed by the intramolecular Hiyama coupling of 3-amido-2-(arylsilyl)aryl triflates. The present reaction is an unusual way of utilizing the Hiyama coupling, enabling the synthesis of value-added organosilanes as the main products. The intramolecular nature of transmetalation with inversion of the stereochemistry at the silicon center was revealed by the mechanistic investigation, and an asymmetric variant of this process was also demonstrated to give silicon-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines with high enantioselectivity.

Keywords : *Palladium catalyst; Organosilicon compounds; Asymmetric synthesis; Hiyama coupling*

含ケイ素環状有機化合物は生理活性物質や有機材料に見られる有用な化合物群である^[1]。本研究では、3-アミド-2-(アリアルシリル)アリアルトリフラートを基質として用いた分子内檜山カップリングによって、4-シラ-4*H*-ベンゾ[*d*][1,3]オキサジンを効率よく合成する方法を開発した。これらは、生理活性物質としてよく知られる 4*H*-ベンゾ[*d*][1,3]オキサジン^[2]の炭素一つをケイ素に置き換えた新規化合物群である。また、本反応は檜山カップリングを有機ケイ素化合物の変換反応に応用した数少ない例の一つでもある。交差実験及び反応前後でのケイ素上の立体化学を調べることによって、本反応が分子内のトランスメタル化で進行し、その際にケイ素上の立体が反転することを明らかにした。さらに、適切なキラル配位子を用いることでエナンチオ選択的なトランスメタル化による不斉合成への展開にも成功した。



[1] R. Ramesh, D. S. Reddy, *J. Med. Chem.* **2018**, *61*, 3779. [2] D. S. Zinad, A. Mahal, R. K. Mohapatra, A. K. Sarangi, M. R. F. Pratama, *Chem. Biol. Drug Des.* **2020**, *95*, 16.

Palladium-Catalyzed Unimolecular Fragment Coupling of Amides via Elimination and Translocation of Isocyanate

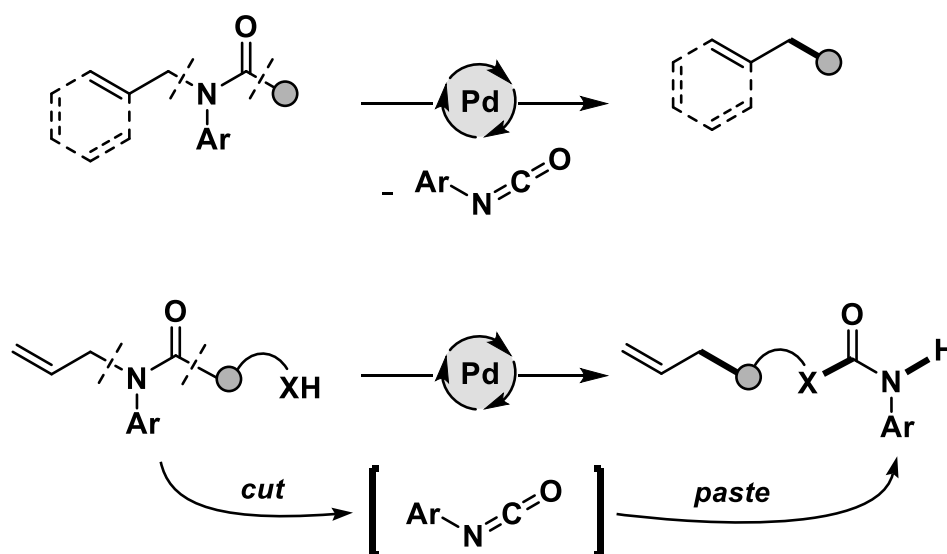
(¹Graduate School of Engineering, Osaka University, ²ICS-OTRI)

○ Ryoma Shimazumi,¹ Takuya Kodama^{1,2} Mamoru Tobisu^{1,2}

Keywords: *deisocyanation; migration; intramolecular coupling reaction; amide; palladium catalyst*

Unimolecular fragment coupling (UFC) is a useful method for forming new bonds from readily available starting materials via elimination of small molecules. A catalytic decarboxylation reaction of esters¹⁾ is a typical example of UFC. If amides, instead of esters, can be used in a catalytic UFC, it would serve as powerful bond-forming methods using abundant amine and carboxylic acid building blocks. However, such a UFC of amides have not been reported to date.

We have developed palladium-catalyzed UFC reactions of amides for forging new carbon–carbon and carbon–heteroatom bonds via the elimination of isocyanate. In addition, we have also developed an amide group migration reaction in which the eliminated isocyanate is trapped by a pendant nucleophile.²⁾



1) Weaver, J. D.; Recio, A.; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846.

2) Shimazumi, R.; Tanimoto, R.; Kodama, T.; Tobisu, M. *J. Am. Chem. Soc.* **2022**, *144*, 11033.

メカノレドックス/ニッケル協働触媒による機械的な力を駆動力としたクロスカップリング反応の開発

(北海道大学大学院工学研究院¹・北海道大学 WPI-ICReDD²)

○瀬尾 珠恵¹・久保田 浩司^{1,2}・伊藤 肇^{1,2}

Mechanoredox/Nickel Dual Catalytic System for Force-Induced Cross-Coupling Reactions
(¹Graduate School of Engineering, Hokkaido University, ²WPI-ICReDD, Hokkaido University)

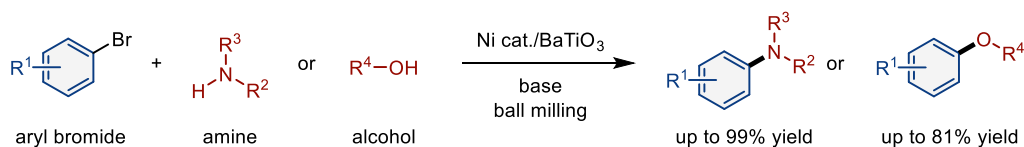
○Tamae Seo,¹ Koji Kubota,^{1,2} Hajime Ito^{1,2}

Recently, we have developed mechanoredox reactions using piezoelectric materials and ball milling.^{1,2} In these reactions, distorted piezoelectric materials in response to mechanical impact provided by ball milling can act as charge transfer catalysis that promotes single electron oxidation and reduction. Here we report the development of a metallamechanoredox catalysis that combines piezoelectric catalysis and nickel-based catalysis to realize force-induced C–N and C–O cross-coupling reactions.³ These reactions were characterized by broad substrate scope, inexpensive catalysts combination, no requirement of bulk solvents, short reaction time and ease of multi-gram scale synthesis. These features suggest that the present force-induced platform provides a more attractive alternative to conventional solution-based metallaphotoredox catalysis.

Keywords : Mechanochemistry; Redox Reaction; Ball Mill; Nickel; Piezoelectric Material

最近我々は、圧電材料とボールミルを用いたメカノレドックス反応を報告した^{1,2}。この反応では、ボールミルの機械的な力により歪んだ圧電材料が、一電子酸化還元を制御する触媒として機能する。本研究では、このメカノレドックス触媒とニッケル触媒が協働して作用するメタラメカノレドックス触媒を開発し、機械的な力により駆動する C–N および C–O クロスカップリング反応の開発に成功した³。本手法は短時間かつ有機溶媒をほとんど必要とせず、安価な触媒系で反応を行うことが可能である。さらに幅広い基質適用範囲を示し、マルチグラムスケール合成にも成功している。本手法は、従来のメタラフォトレドックス触媒反応の代替手法になることが期待される。

Mechanoredox/Nickel Dual Catalytic System for Force-Induced Cross-Coupling Reactions



- Merging mechanoredox with transition-metal catalysis ■ Inexpensive catalytic combination
- No need for bulk solvents ■ Short reaction time ■ Broad scope ■ Multi-gram scale synthesis

- 1) Kubota, K.; Pang, Y.; Miura, A.; Ito, H. *Science*, **2019**, 366, 1500.
- 2) Pang, Y.; Lee, J. W.; Kubota, K.; Ito, H. *Angew. Chem. Int. Ed.* **2020**, 59, 22570.
- 3) Corcoran, E. B.; Pirnot, M. T.; Lin, S.; Dreher, S. D.; DiRocco, D. A.; Davies, I. W.; Buchwald, S. L.; MacMillan, D. W. C. *Science*, **2016**, 353, 279.

アルキルアレーンと一酸化炭素、フェノールの脱水素三成分カップリング反応

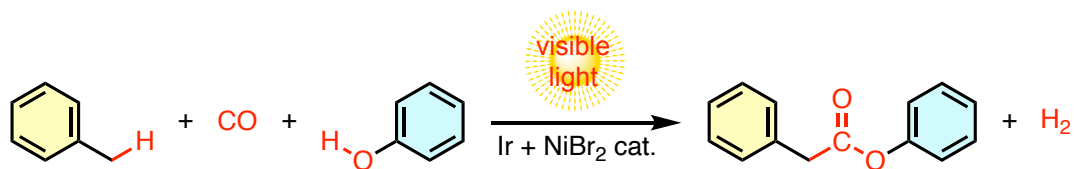
(京大院工) ○石田 直樹・篠矢 裕貴・河崎 泰林・村上 正浩

Dehydrogenative Three-Component Coupling of Alkylarenes, CO and Phenols (*Graduate School of Engineering, Kyoto University*) ○Naoki Ishida, Hiroki Shinoya, Tairin Kawasaki, Masahiro Murakami

Dehydrogenative coupling liberating gaseous hydrogen is one of the ideal methods of connecting organic molecules since it offers a straightforward and atom-economical pathway from readily available materials. However, it is generally difficult to realize, and the examples remain significantly limited. Herein we report the dehydrogenative three-component coupling reaction of alkylarenes with carbon monoxide and phenols. It proceeds upon irradiation with visible light in the presence of iridium and nickel bromide complexes. The benzylic C–H and phenolic O–H bonds are cleaved to combine with carbon monoxide to give esters and release gaseous hydrogen. The C(Ar)–Br and C(Ar)–B bonds, which often participate in transition metal-catalyzed thermal cross-couplings, remain unreacted under the present reaction conditions. The N–H bonds in amides and O–H bonds in aliphatic alcohols also survive.

Keywords : *Dehydrogenative Coupling; Carbonylation; Photoredox*

水素ガスの放出を伴う脱水素カップリング反応は最も直接的で原子効率に優れた理想的な有機骨格構築手法の一つである。しかし、この形式の反応は一般に実現が難しく、報告例は少ない。本発表では新たに見出したアルキルアレーンと一酸化炭素、フェノールの脱水素三成分カップリング反応を報告する。この反応は、可視光の照射下、イリジウム錯体の臭化ニッケル錯体の作用で進行する。ベンジル位の炭素–水素結合とフェノールの酸素–水素結合が切断されて一酸化炭素と結合し、エステルを与えると同時に水素ガスを放出する。遷移金属触媒を用いた熱的なクロスカップリングでは反応することが多い sp^2 炭素–臭素結合や sp^2 炭素–ホウ素結合は反応しない。また、アミドの窒素–水素結合やアルコールの酸素–水素結合も反応せず、フェノールの酸素–水素結合が選択的にエステル結合を形成する。



Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[K603-1pm] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Suguru Ito, Takashi Hirose

Wed. Mar 22, 2023 1:50 PM - 3:40 PM K603 (K603, Lecture Hall Bldg. [6F])

[K603-1pm-01] Synthesis of the longest aza[n]helicene○Yusuke Matsuo¹, Takayuki Tanaka¹, Shu Seki¹ (1. Kyoto University)

1:50 PM - 2:10 PM

[K603-1pm-02] Synthesis and photophysical properties of chiral 1,7-7',1' - cyclopyrenylene oligomers○Ryo Kurosaki¹, Rémi Métivier², Hiroko Yamada¹, Naoki Aratani¹ (1. NAIST, 2. ENS Paris-Saclay)

2:10 PM - 2:30 PM

[K603-1pm-03] Solvent dependency of the charge separation and the near-infrared emission of sumanetrione-based dyes○Junyi Han¹, Youhei Takeda¹, Hayato Sakai², Taku Hasobe², Yuta Uetake^{1,3}, Yumi Yakiyama^{1,3}, Hidehiro Sakurai^{1,3} (1. Graduate School of Engineering, Osaka Univ., 2. Fac. Sci. Tech., Keio Univ., 3. ICS-OTRI, Osaka Univ.)

2:30 PM - 2:50 PM

[K603-1pm-04] Theoretical analysis and device application of C₃-chiral truxenes showing an excellent circularly polarized luminescence property on fluorescence and phosphorescence○Fumitaka Ishiwari¹, Takuya Omine¹, Takashi Hirose², Tadashi Mori¹, Naoya Aizawa¹, Akinori Saeki¹ (1. Osaka University, 2. Kyoto University)

3:00 PM - 3:20 PM

[K603-1pm-05] Organic Triboluminescence Polar Crystals Composed of a Host-Dopant System○Takuya Ogaki^{1,2}, Yasunori Matsui^{1,2}, Hiroshi Ikeda^{1,2} (1. Grad. Sch. Eng., Osaka Metro. Univ., 2. RIMED, Osaka Metro. Univ.)

3:20 PM - 3:40 PM

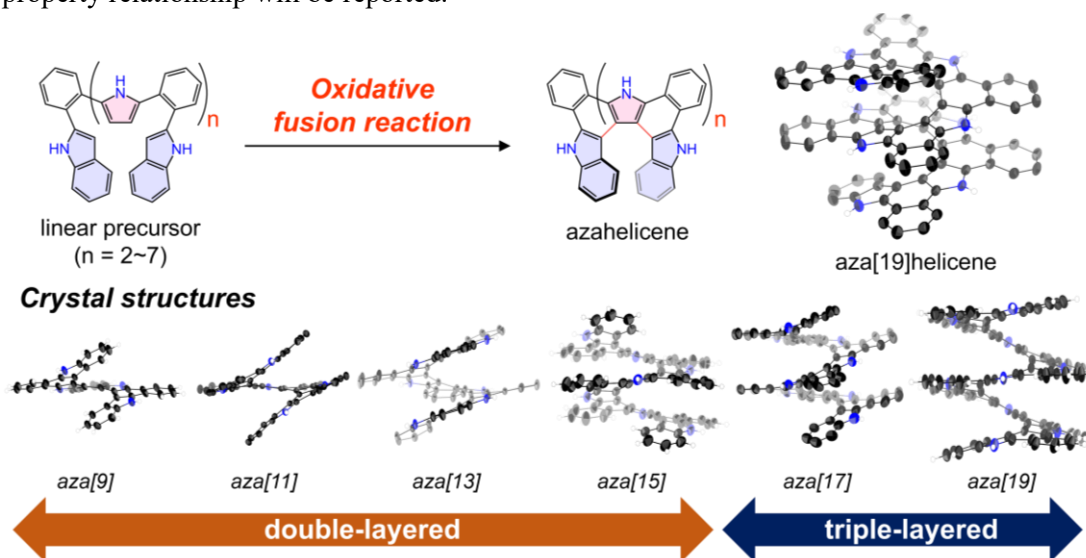
Synthesis of the longest aza[n]helicene

(¹Graduate School of Science, Kyoto University, ²Graduate School of Engineering, Kyoto University) ○Yusuke Matsuo,¹ Takayuki Tanaka,² Shu Seki²

Keywords: helicene, azahelicene, oxidative fusion reaction, π -conjugated system

In recent years, helicenes have been attracting attention as excellent chiral materials. To improve their chiroptical properties, π -extension is a reliable method while the synthesis of longer helicenes, especially those consisting of a triple-layered structure, is difficult because of the large strain in the central layer and poor solubility in common organic solvents.¹⁾ Further, systematic characterizations of their properties depending on the helical pitches have not been performed satisfactorily.²⁾

Heteroatom-incorporation has been adopted to change the helical diameters and to install functional sites, and recently, we have reported the synthesis of aza[7]helicenes via oxidation of the linear precursor consisting of pyrroles and indoles with *ortho*-phenylene bridges.³⁾ Such azahelicenes were found to be soluble in THF with the aid of hydrogen bonding interaction. Therefore, we attempted the synthesis of longer azahelicenes of different helical pitches systematically utilizing one-shot oxidative fusion reactions. This approach enabled us to obtain six new aza[n]helicenes ($n = 9, 11, 13, 15, 17, 19$). We confirmed all the crystal structures, in which aza[17]helicene and aza[19]helicene were found to be triple-layered. All aza[n]helicenes show high solubility in THF and their absorption and fluorescence spectra are red-shifted with increasing the helical pitches. In this presentation, all these results as well as their structure-property relationship will be reported.



- 1) K. Mori, T. Murase, M. Fujita, *Angew. Chem. Int. Ed.* **2015**, 54, 6847. 2) Y. Nakakuki, T. Hirose, H. Sotome, M. Gao, D. Shimizu, R. Li, J. Hasegawa, H. Miyasaka, K. Matsuda, *Nat. Commun.* **2022**, 13, 1475. 3) F. Chen, T. Tanaka, T. Mori, A. Osuka, *Chem. Eur. J.* **2018**, 24, 7489.

Synthesis and photophysical properties of chiral 1,7-7',1'-cyclopyrenylene oligomers

(¹Graduate School of Science and Technology, Nara Institute of Science and Technology,

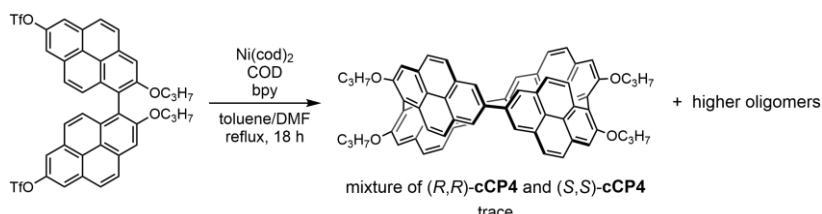
²Supramolecular and Macromolecular Photophysics and Photochemistry, ENS Paris-Saclay)

○Ryo Kurosaki,¹ Rémi Métivier,² Hiroko Yamada,¹ Naoki Aratani,¹

Keywords: Pyrene; Cyclic Oligomers; Chirality; Emission

Arylene macrocycles constitute one of the most important shape-persistent oligomers. Pyrene is a unique polycyclic aromatic hydrocarbon among those building units for larger cycloarylenes because of its highly emissive property and large π -surface. Previously, we have reported a series of directly linked 1,8- or 4,10-cyclic pyrene oligomers with intriguing properties, such as ring-strain-driven reaction,¹ the incorporation of guest molecules,² macrocyclic chirality with an odd number of pyrene unit,³ and structural conversion upon heating.⁴

In order to make a rigid chiral framework based on cyclopyrenylene, Ni-mediated coupling reaction of a 1,1'-bipyrenyl with trifluoromethanesulfonyloxy groups at 7 and 7' positions was performed and gave a series of chiral 1,7-7',1'-cyclic pyrene oligomers **cCP_n** (Scheme 1). Cyclic tetramer **cCP4** is a chiral molecule and is expected to produce CPL-CT emission through host-guest interaction with an achiral acceptor molecule. Actually, the fluorescence spectrum of the complex of **cCP4** with 1,2,4,5-tetracyanobenzene (TCNB) in the solid state showed a large redshift, confirming the formation of the CT complex (Figure 1). The interaction between **cCP_n** and various electron-deficient guest molecules has been evaluated for their photophysical properties.



Scheme 1. Synthesis of **cCP_n** with Ni(cod)₂.

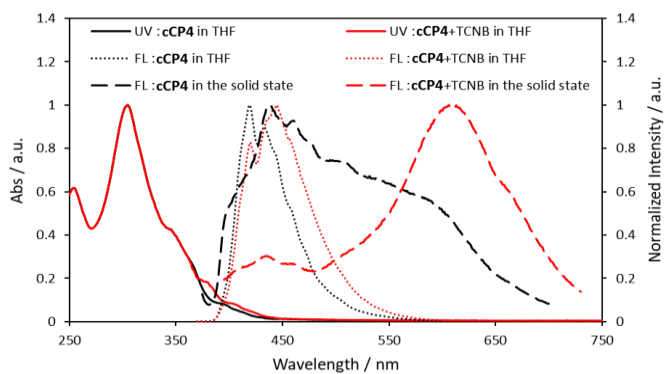


Figure 1. UV-vis and fluorescence spectra of **cCP4** with and without TCNB.

1) R. Kurosaki, et al. *Chem. Sci.* **2019**, *10*, 6785. 2) R. Kurosaki, et al. *Chem. Commun.* **2019**, *55*, 9618.

3) R. Kurosaki, et al. *Chem. Lett.* **2020**, *49*, 892. 4) R. Kurosaki, et al. *Chem. Eur. J.* in revision.

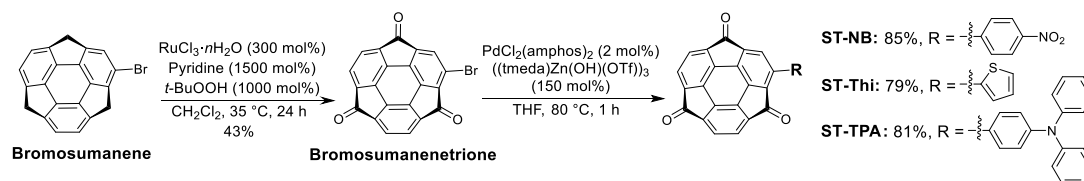
Solvent Dependency of the Charge Separation and the Near-Infrared Emission of Sumanenetrione-based Dyes

(¹Graduate School of Engineering, Osaka University, ²Faculty of Science and Technology, Keio University, ³ICS-OTRI, Osaka University) ○Han Junyi,¹ Youhei Takeda,¹ Hayato Sakai,² Taku Hasobe,² Yuta Uetake,^{1,3} Yumi Yakiyama,^{1,3} Hidehiro Sakurai^{1,3}

Keywords: Sumanenetrione; Donor-Acceptor Type Molecule; Curved- π Conjugated Molecule; Optoelectronic Property

Sumanenetrione (ST) is a triketone derivative of curved- π conjugated sumanene. It is known to show a strong electron-accepting ability close to C_{60} .¹ However, due to the low reactivity of the peripheral aromatic carbons and limited sequential approach to its functionalization, the derivatization of ST was not well investigated. We recently found an effective functionalization method to prepare various Donor-Acceptor (D-A) type ST derivatives that show unique emission properties. In this work, we report the synthesis of ST-based new D-A type molecules and their optoelectronic properties with a particular focus on the luminescence property of ST-TPA.

Synthesis of functionalized STs was achieved by recently reported Lewis acid-mediated Suzuki-Miyaura coupling reaction² using bromosumanenetrione, which can be prepared from previously reported bromosumanene³ through Ru-mediated oxygenation (Scheme 1).



Scheme 1. Synthesis of ST-based D-A type molecules.

All the derivatives showed two main absorption bands at both the UV range (250 nm to 500 nm) and the visible region reaching 800 nm, indicating their charge-transferring nature from the substituent to ST moiety. In the case of ST-NB and ST-Thi emission spectra, clear emission was observed in CH_2Cl_2 at 600 nm and 680 nm, respectively (Figure 1a).

Meanwhile, ST-TPA did not show emission in CH_2Cl_2 but showed strong NIR emission at 703 nm in Hexane (Figure 1b).

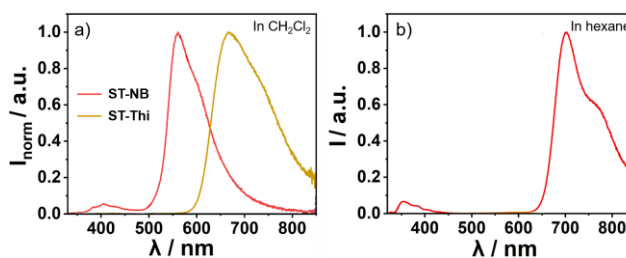


Figure 1. Emission spectra of a) ST-NB and ST-Thi (λ_{ex} = 320 nm), b) ST-TPA (λ_{ex} = 300 nm).

1) a) T. Amaya, M. Hifumi, M. Okada, Y. Shimizu, T. Moriuchi, K. Segawa, Y. Ando, T. Hirao, *J. Org. Chem.*, **2011**, 76, 8049. b) S. Higashibayashi, B. B. Shrestha, Y. Morita, M. Ehara, K. Ohkubo, S. Fukuzumi, H. Sakurai, *Chem. Lett.*, **2014**, 43, 1297. 2) T. Niwa, Y. Uetake, M. Isoda, T. Takimoto, M. Nakaoka, D. Hashizume, H. Sakurai, T. Hosoya, *Nat. Catal.*, **2021**, 4, 1080. 3) T. Amaya, S. Seki, T. Moriuchi, K. Nakamoto, T. Nakata, H. Sakane, A. Saeki, S. Tagawa, T. Hirao, *J. Am. Chem. Soc.*, **2009**, 131, 408.

C₃キラルなトルキセン類の蛍光およびリン光における優れた円偏光発光特性の理論解析とデバイス応用

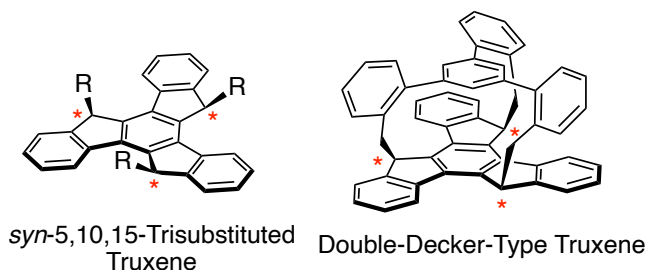
(阪大院工¹・京大化研²) ○石割 文崇¹、大峰 拓也¹、廣瀬 崇至²、森 直¹、相澤 直矢¹、佐伯 昭紀¹

Theoretical Analysis and Device Application of C₃-Chiral Truxenes Showing an Excellent Circularly Polarized Luminescence Property on Fluorescence and Phosphorescence (¹Graduate School of Engineering, Osaka University, ²Institute for Chemical Research, Kyoto University) ○Fumitaka Ishiwari¹, Takuya Omine¹, Takashi Hirose², Tadashi Mori¹, Naoya Aizawa¹, Akinori Saeki¹

We show that C₃-chiral truxenes exhibit excellent CPL with dissymmetric factor (*g* value) of the order of 10⁻². Vibrational calculations and variable-temperature CPL measurements suggested that molecular vibrations dramatically lower the *g* value of CPL. Furthermore, at low temperature, C₃-chiral trimethyltruxene exhibits long-lifetime and strong phosphorescent CPL. A conformationally rigid double-decker-type truxene with thermally robust CPL properties at high temperature was applied as an emitter of electroluminescence devices exhibiting circularly polarized electroluminescence with a high *g* value. In the presentation, we will show the theoretical analysis on the CPL properties of C₃-chiral truxenes and device application.

Keywords : Circularly Polarized Luminescence, Truxenes, Molecular Vibration, Phosphorescence, OLED

5,10,15 位に *syn* の立体配置で置換基を有するトルキセン類は、 π 電子系に直結した三つの不斉炭素原子を有する C₃ キラル分子である (図)。この種のトルキセン類は簡便な合成方法が確立されており多くの合成の報告例があるものの^{1,2}、意外にもこれまでにその不斉に関しては一切注目されておらず、光学分割の例もなかった。最近我々は、その光学活性体を初めて単離し、C₃ キラルトルキセン類が高い異方性因子 (*g* 値 = 1.6×10^{-2}) を示す優れた円偏光発光 (CPL) 特性を示すことを発見した。理論計算と極低温領域の温度可変 CPL 測定から、分子振動が *g* 値を大幅に低下させる可能性が示唆され、5,10,15 位の置換基を連結したより剛直なダブルデッカー型トルキセン²は、室温下でさらに高い *g* 値 (2.2×10^{-2}) を示すことを見出した。加えて、トルキセン類は 77 K 程度の低温状態において長波長側にリン光を示すが、ある誘導体はこのリン光に由来する CPL を示した。発表では、前述の実験と理論計算の詳細に加え、このリン光 CPL に対する理論的解釈、およびデバイス応用について述べる予定である。



- 1) M. Echavarren *et al.*, *Acc. Chem. Res.*, **2019**, 52, 1812.
- 2) M. Echavarren *et al.*, *Chem. Eur. J.*, **2002**, 8, 2879.

ホストドーパント系で構成される有機トリボルミネッセンス極性結晶

(阪公大院工¹・阪公大 RIMED²) ○大垣 拓也^{1,2}・松井 康哲^{1,2}・池田 浩^{1,2}

Organic Triboluminescence Polar Crystals Composed of a Host–Dopant System

(¹Grad. Sch. Eng., Osaka Metro. Univ., ²RIMED, Osaka Metro. Univ.) ○Takuya Ogaki,^{1,2} Yasunori Matsui,^{1,2} Hiroshi Ikeda^{1,2}

Triboluminescence (TL) is a luminescence phenomenon induced by mechanical stimuli, which is expected to be utilized as stimuli-responsive luminescence materials without any photoexcitation. To achieve organic TL, luminescent organic polar crystals are required to mechanically induce charge separation and recombination by piezoelectric effect. However, it is difficult to rationally design organic polar crystals. To overcome the difficulty, in this work, we propose a new concept, “organic TL polar crystal”, which is composed of a host–dopant system (Fig. 1a). In the system, a highly-luminescent material such as thermally activated delayed fluorescence molecule is doped into a polar crystal host. In the “organic TL polar crystals”, energy transfer occurs from the excited state of host generated by mechanical stimuli to the luminescent dopant (Fig. 1b). Thus, color-tunable TL is possible regardless of the luminescence properties of the host materials.

Keywords : Triboluminescence; Mechanoluminescence; Polar Crystals; Energy Transfer; Thermally Activated Delayed Fluorescence

機械的刺激による発光現象であるトリボルミネッセンス (TL) は、光励起を必要としない刺激応答性発光材料としての利用が期待されている。有機 TL では圧電効果によって機械的に電荷分離および再結合を誘起するために、その実現には発光性の有機極性結晶が必要となるが、合理的設計は困難である。そこで本研究では、熱活性化遅延蛍光分子などの高発光性材料を極性結晶ホストにドーピングしたホストドーパント系で構成される「有機 TL 極性結晶」を開発した (Fig. 1a)。この「有機 TL 極性結晶」では、機械的刺激によって生成したホストの励起状態から発光性ドーパントへのエネルギー移動が起こる (Fig. 1b)。そのため、ホスト材料の発光性に関わらず、発光色が制御可能な TL を達成できる。

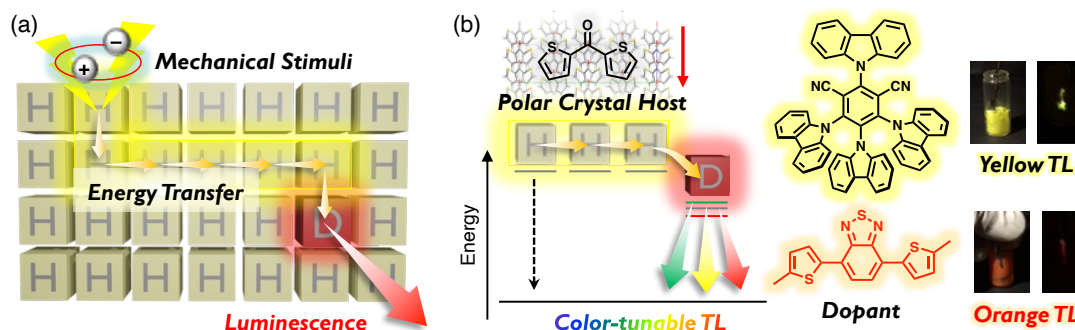


Fig. 1. (a) A schematic illustration of “organic TL polar crystals” composed of a host–dopant system. (b) Energy diagram of a host and a dopant. Photographs show TL from the polar crystals.

[K606-1pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Takashi Nakamura, Yumi Yakiyama

Wed. Mar 22, 2023 1:00 PM - 3:40 PM K606 (K606, Lecture Hall Bldg. [6F])

- [K606-1pm-01] Anthracene-based molecular tweezers: Construction of a giant spherical assembly based on hierarchical self-complementarity
○Masahiro Yamashina¹, Yuta Sawanaka¹, Shinji Toyota¹ (1. School of Science, Tokyo Inst. of Tech.)
1:00 PM - 1:20 PM
- [K606-1pm-02] Molecular Dynamics Study on the Structure– Property Relationship of Self-Assembled Gear-Shaped Amphiphile Molecules with/without Methyl Groups
○Moe Murata¹, Osamu Kobayashi¹, Shuichi Hiraoka², Tomomi Shimazaki¹, Masanori Tachikawa¹ (1. Yokohama City University, 2. The University of Tokyo)
1:20 PM - 1:40 PM
- [K606-1pm-03] A twisted chiral cavitand with five-fold symmetry and its length-selective binding properties
○Tanhao Shi¹, Yuuya Nagata², Shigehisa Akine³, Shunsuke Ohtani¹, Kenichi Kato¹, Tomoki Ogoshi^{1,3} (1. Kyoto University, 2. Hokkaido University, 3. Kanazawa University)
1:40 PM - 2:00 PM
- [K606-1pm-04] Two-dimensional living supramolecular polymerization improved by using a comonomer and a dummy monomer
○ZHEHUI JIN^{1,2}, Norihiko Sasaki⁵, Masayuki Takeuchi^{4,2}, Yutaka Wakayama^{1,2}, Kazunori Sugiyasu³ (1. Kyushu University, 2. National Institute for Materials Science, 3. Kyoto University, 4. University of Tsukuba, 5. Tottori University)
2:00 PM - 2:20 PM
- [K606-1pm-05] Facet-selective Block Co-crystallization of Two-different Spin-crossover Metal Complexes
○Tomoya Fukui^{1,2}, Masahiro Tsuchiya^{1,2}, Takanori Fukushima^{1,2} (1. CLS, Tokyo Tech., 2. Sch. Mater. and Chem. Tech., Tokyo Tech.)
2:30 PM - 2:50 PM
- [K606-1pm-06] Self-assembling behaviors and properties of platinum(II) complexes possessing chiral hydrophilic bis(phenylisoxazolyl) benzene moieties
○Masaya YOSHIDA¹, Takehiro HIRAO¹, Takeharu HAINO^{1,2} (1. Graduate School of Advanced Science and Engineering, Hiroshima University, 2. WPI-SKCM², Hiroshima University)
2:50 PM - 3:10 PM
- [K606-1pm-07] Supramolecular Polymerization of Photofunctional Thiophene-Fused [4*n*]Annulenes: Chiral Superstructures and Chiroptical Properties
○Tsubasa Aoki¹, Takayoshi Akiyama¹, Takuzo Aida^{1,2}, Yoshimitsu Itoh^{1,3} (1. Grad. Sch.

of Eng., The Univ. of Tokyo, 2. RIKEN CEMS, 3. PRESTO, JST)

3:10 PM - 3:30 PM

アントラセンを有する分子ピンセット：階層的な自己相補性に基づく巨大球状集合体の構築

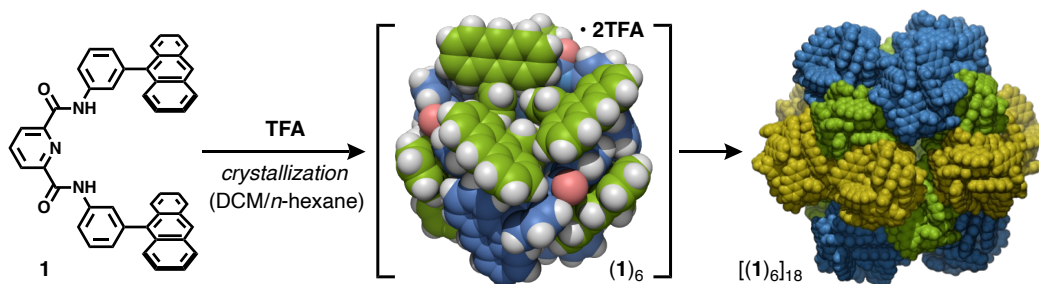
(東工大理) ○山科 雅裕・澤中 祐太・豊田 真司

Anthracene-based molecular tweezers: Construction of a giant spherical assembly based on hierarchical self-complementarity (*School of Science, Tokyo Institute of Technology*) ○Masahiro Yamashina, Yuta Sawanaka, Shinji Toyota

HIV capsid is composed of self-complementary and hierarchical assembly of multiple identical protein subunits. Here we report anthracene-based molecular tweezers which formed a self-complementary cyclic hexamer in the crystalline state. The hexamer exhibited blue fluorescence and high mechanical and thermal stability. Furthermore, the hexamers assembled into a giant cuboctahedron and rhombohedral assemblies through hierarchical assembling behavior in the presence of TFA.

Keywords: self-complementarity; molecular tweezers; anthracene; hierarchical assembly

ヒト免疫不全ウイルス (HIV) のキャプシドは、複数の同一タンパク質が自己相補的かつ段階的に集合することで構築される^[1]。本研究では、アントラセンを有する分子ピンセット **1** が環状集合体を経て巨大な球状集合体を構築することを見出したので報告する。**1** は自己相補的な水素結合と π 相互作用が協働することで、結晶中で6分子が噛み合った環状6量体(**1**)₆を形成した。(b>1)₆は32種類の異性体の中から高選択的に形成し、結晶中で水色蛍光を発すると共に (ϕ = 21%)、高い機械的・熱的安定性を有していた。一方で、トリフルオロ酢酸 (TFA) を添加して再結晶を行うと、18個の(**1**)₆がさらに球状集積した[(**1**)₆]₁₈を形成することが、X線結晶構造解析により明らかとなった。[(**1**)₆]₁₈は直径約7 nm、分子量70 kDa、立方八面体の幾何学構造を有し、内部には約10⁴ Å³の空間が存在していた。さらに、(**1**)₆は結晶中で菱面体状の格子空間[(**1**)₆]_nも形成しており、[(**1**)₆]₁₈はその格子内部に取り込まれていた^[2]。本講演ではこれらの集合体の構造や物性を詳細に議論する。



References

- [1] G. Zhao, J. R. Perilla, E. L. Yufenyuy, X. Meng, B. Chen, J. Ning, J. Ahn, A. M. Gronenborn, K. Schulten, C. Aiken, P. Zhang, *Nature* **2013**, 497, 643.
- [2] Y. Sawanaka, M. Yamashina, H. Ohtsu, S. Toyota, *Nature Commun.* **2022**, 13, 5648.

歯車状両親媒性分子の自己集合体におけるメチル基の効果の理論的解析

(横浜市大院生命ナノ¹・東大院総合文化²) ○村田 萌¹・小林 理¹・平岡 秀一²・島崎 智実¹・立川 仁典¹

Molecular Dynamics Study on the Structure-Property Relationship of Self-Assembled Gear-Shaped Amphiphile Molecules with/without Methyl Groups (¹Graduate School of Nanobioscience, Yokohama City University, ²Graduate School of Arts and Sciences, University of Tokyo) ○Moe Murata,¹ Osamu Kobayashi,¹ Shuichi Hiraoka,² Tomomi Shimazaki,¹ Masanori Tachikawa¹

The nanocube is the hexamer of six gear-shaped amphiphile molecules (GSA) self-assembled in water and can encapsulate guest molecules *via* a gap formed on the pole region. To elucidate the effect of methyl groups (Me) on the equator and poles in the nanocube on the encapsulation rate, we conducted molecular dynamics simulations for five different nanocubes. The nanocube without Me on the poles easily formed a gap on the pole region without significant deformation of its cubic structure. We believe our study shows the strategy to design the self-assembled nanocubes with encapsulation efficiency.

Keywords : Molecular Dynamics; Self-assembly; Amphiphile

平岡らは歯車状両親媒性分子(GSA) 6 分子が水溶媒中で自己集合し、箱型構造の「ナノキューブ」(Fig 1)を形成することを報告した^{1,2}。ナノキューブは極部分からゲスト分子を内包し³、内包の速さはナノキューブ内のメチル基の有無によって異なる⁴が、その詳細な機構は不明である。そこで本研究では、この機構解明のため、Fig. 1 に示した極および赤道におけるメチル基の数が異なる 5 種類のナノキューブについて、分子動力学シミュレーションを実行した。

Fig. 2 に、構造変化の程度を示す平均二乗偏差(RMSD)と極の孔の面積(S_{pole})に関する二次元ヒストグラムを示す。極にメチル基をもつナノキューブ(Fig. 2(a))と比べて、同メチル基をもたないナノキューブ(Fig. 2(b))では、RMSD の値が小さくても極の孔が大きく開きやすい傾向が見られ、それにより Fig. 2(b)では内包が起りやすいことが示唆された。以上より、極部分のメチル基を除くことで、内包が起りやすいナノキューブの実現が期待できる。

1) S. Hiraoka, *et al.*, *J. Am. Chem. Soc.* **130**, 14368-14369 (2008). 2) Y.-Y. Zhan, *et al.*, *Commun. Chem.* **1**, 14 (2018). 3) M. Murata, *et al.*, *J. Phys. Chem. B*, (2023) in press. 4) Y.-Y. Zhan, *et al.*, *Nat. Commun.* **10**, 1440. (2019).

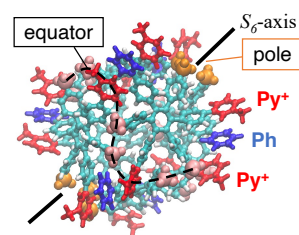


Fig 1. ナノキューブの構造

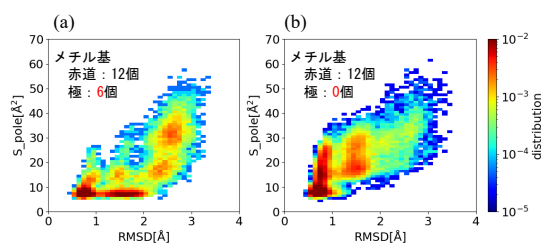


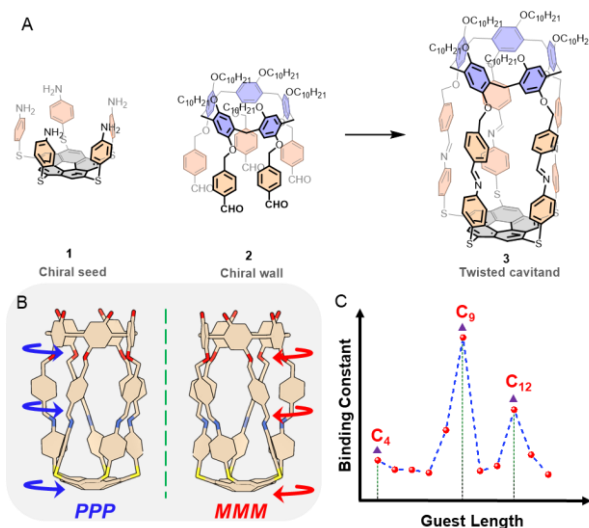
Fig 2. RMSD(横軸)と極の孔の大きさ(縦軸)に関する二次元ヒストグラム
赤道のメチル基はともに 12 個で、極のメチル基は(a) 6 個、(b) 0 個である。

A twisted chiral cavitand with five-fold symmetry and its length-selective binding properties

(¹Graduate School of Engineering, Kyoto University, ²WPI Institute for Chemical Reaction Design and Discovery, Hokkaido University, ³WPI Nano Life Science Institute, Kanazawa University, ⁴Graduate School of Natural Science and Technology, Kanazawa University) ○ Tanhao Shi¹, Yuuya Nagata², Shigehisa Akine^{3,4}, Shunsuke Ohtani¹, Kenichi Kato¹, Tomoki Ogoshi^{1,3}

Keywords: Pillar[n]arene; Corannulene; Dynamic covalent bond; Host-guest interaction

Controlling the chirality in bottom-up synthesis to construct architectures with specific chirality is a challenging target. Here, by using corannulene **1** as seed¹ and rim-differentiated pillar[5]arene **2** as chiral wall², the bottom-up synthesis towards twisted cavitand with five-fold symmetry was achieved. Because of the rigidity of the hedges, both the unit flip of pillar[5]arene and inversion of corannulene were inhibited after crosslinking, fixing the chirality. Moreover, the hedges tilt into two directions, endowing the cavitand with a twisted and chiral body. Through the dynamic covalent bonds, all the subcomponents tilted in the same direction and the thermodynamically stable cavitands with matching chirality (*PPP* and *MMM*) were generated selectively. The entrance, body, and bottom of the twisted cavitand all exhibited as binding sites, endowing the cavitand with length-selective binding property towards α,ω -dibromoalkanes. And three maxima in binding constants were observed³.



(A) Preparation of twisted cavitand **3**. (B) Self-sorting chirality of **3**. (C) Length-selective binding properties of **3**.

1) Ronson, T. K., et al. *J. Am. Chem. Soc.* **2020**, *142*, 10267. 2) Fa, S., et al. *Chem. Lett.* **2019**, *48*, 1278. 3) Shi, T. H., et al. *J. Am. Chem. Soc.* **2022**, *144*, 23677.

Two-Dimensional Living Supramolecular Polymerization Improved by Using a Comonomer and a Dummy Monomer

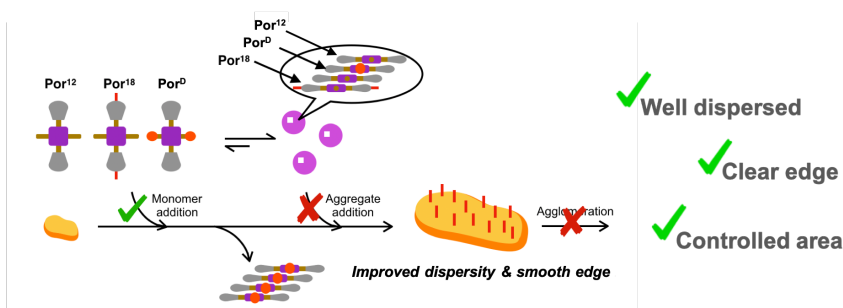
(¹Kyushu University, ²National Institute for Materials Science, ³University of Tottori, ⁴University of Tsukuba, ⁵Kyoto University) ○Zhehui Jin,^{1,2} Norihiko Sasaki,³ Masayuki Takeuchi,^{2,4} Yutaka Wakayama,^{1,2} Kazunori Sugiyasu⁵

Keywords: Supramolecular polymerization; Nanosheets; Porphyrins

Supramolecular polymerization under kinetic control has led to the development of living supramolecular polymerization (LSP), which has permitted the synthesis of supramolecular polymers with controlled length and narrow length distribution.¹ The general concept of LSP has been established; however, interrelated synthetic methodology has yet to be developed. In this study, we focused on improving LSP by using a comonomer and a dummy monomer to solve problems which we encountered in our previous study.

In our previous work,²⁻⁴ we succeeded in two-dimensional LSP to obtain supramolecular nanosheets with controlled area and aspect ratio. LSP basically worked well; however, (1) supramolecular nanosheets are prone to agglomerate through stacking, thus resulting in precipitation, and (2) the supramolecular nanosheets are rough round the edges.

To solve the problem (1), we designed a new porphyrin monomer, **Por¹⁸**, which possesses solubilizing alkyl chains which are longer than those in the previous monomer, **Por¹²**. We found that copolymerization of **Por¹⁸** and **Por¹²** resulted in dispersible supramolecular nanosheets. As for the problem (2), we revisited the formation mechanism of the supramolecular nanosheets. We found that a dummy monomer (**Por^D**) could affect the pathways of supramolecular polymerization, and consequently, the edge of supramolecular nanosheets became smooth. We believe that the present study paves the way for the further development of precision supramolecular polymerization.



1) S. Ogi., et al., *Nat. chem.* **2014**, 6, 188-195. 2) T. Fukui, et al., *Nat. Chem.* **2017**, 9, 493-499. 3) N. Sasaki, et al., *Chem. Eur. J.* **2020**, 26, 7840-7846. 4) N. Sasaki et al., *Nat. Commun.* **2020**, 11, 3578.

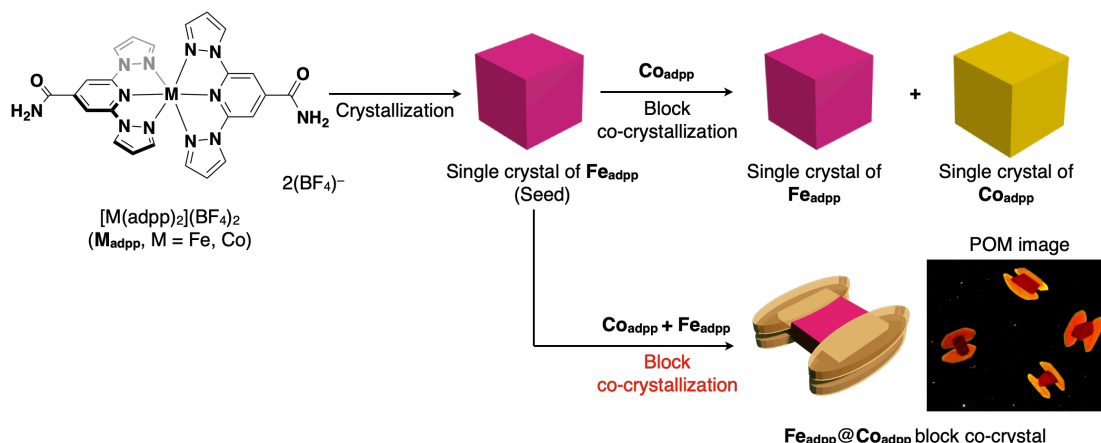
異種スピנקロスオーバー錯体を用いた面選択的シード結晶化によるブロック共結晶の構築

(東工大化生研¹・東工大物質理工²) ○福井 智也^{1,2}・土屋 雅弘^{1,2}・福島 孝典^{1,2}
 Facet-selective Block Co-Crystallization of Two-Different Spin-Crossover Metal Complexes
 (¹Lab. Chem. Life Sci., Tokyo Tech., ²Sch. Mater. and Chem. Tech., Tokyo Tech.) ○Tomoya Fukui,^{1,2} Masahiro Tsuchiya,^{1,2} Takanori Fukushima^{1,2}

As exemplified by block-co-polymers, block structures composed of different materials are expected to emerge functions, which are not achieved by single-component systems. We are working on the preparation of block co-crystals with two different compartments of spin-crossover metal complexes. For this purpose, here we chose spin crossover Fe(II) and Co(II) complexes with 2,6-dipyrazolylpyridine ligands for constructing block co-crystals. After many trials, we found a system that shows facet-selective crystal growth of cobalt complex from seed crystals of iron complex, resulting in block co-crystals with complex morphology. In this presentation, we will discuss the detail of facet-selective block co-crystallization based on single-crystal X-ray diffraction, SEM-EDX, and micro-Raman spectroscopy.

Keywords : Block structure; Block co-crystal; Block co-crystallization; Spin crossover; Hydrogen bond

ブロックコポリマーに代表されるように、異種物質が連結されたブロック構造体は、単成分系では得られない機能を発現することが期待されている。我々は、異種結晶をコンパートメントとして接合したブロック共結晶を創製し、各ブロック固有の性質がシナジーした新機能創出を目指す研究を展開している。今回、ジピラゾリルピリジン誘導体を配位子とするスピנקロスオーバー錯体の結晶を構成要素とするブロック共結晶の作製について検討した。数多くの検討の結果、鉄錯体結晶をシードとしてコバルト錯体に鉄錯体がドーピングされた固溶体を結晶化させた際に面選択的な結晶成長を示す系を見いだしたので報告する。



Self-assembling behaviors and properties of platinum(II) complexes possessing chiral hydrophilic bis(phenylisoxazolyl) benzene moieties

(¹Graduate School of Advanced Science and Engineering, Hiroshima University, ²WPI-SKCM², Hiroshima University) ○ Masaya Yoshida,¹ Takehiro Hirao,¹ Takeharu Haino^{1,2}

Keywords: Supramolecular chemistry; Self-assembly; Circular dichroism; Nano structure; micelle

Our group reported that AIE-active micelles were formed through the self-assembly of a platinum(II) complex possessing achiral triethylene glycol (TEG) side chains.^[1] The hydrophobic effect and the intermolecular Pt-Pt interaction of the platinum center drove the formation of the micelles. In this study, we will discuss the self-assembling behaviors of (*R*)- and (*S*)-**1** possessing the stereogenic centers on the TEG chains (Figure 1a). The self-assembling behaviors were studied in THF/water mixed solvent. THF/water (40/60, v/v) mixed solvent induced the self-assembly of (*R*)- and (*S*)-**1**, which formed the micelle-like nanostructures that exhibited CD signals (Figure 1b, c).^[2]

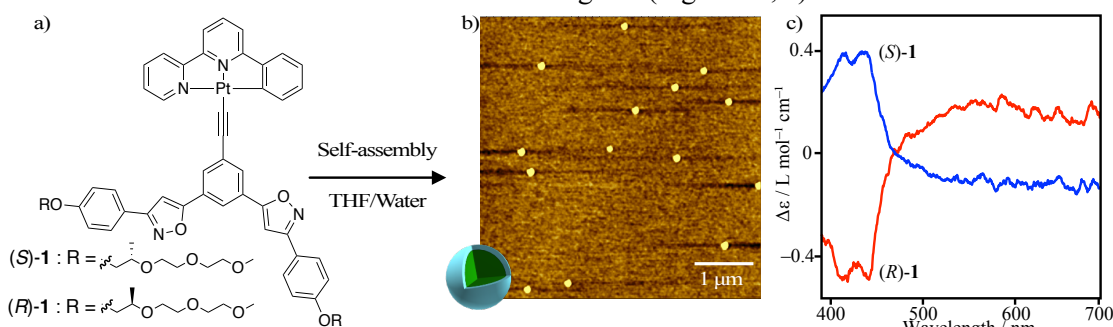


Figure 1. a) Molecular structures of chiral platinum complexes (*S*)-**1** and (*R*)-**1**. b) AFM image ($5 \mu\text{m} \times 5 \mu\text{m}$) of (*S*)-**1** ($5 \times 10^{-4} \text{ M}$) on mica used THF/water (40/60, v/v). c) CD spectra of (*S*)-**1** (blue) and (*R*)-**1** (red) ($5 \times 10^{-4} \text{ M}$) in THF/water (40/60, v/v) at 5 °C.

An achiral perylene bisimide **2** was encapsulated within the micelle-like nanostructures of (*R*)- or (*S*)-**1** in THF/water (40/60, v/v) mixed solvent, resulting in the intense CD signals observed at the absorption band of **2**. Accordingly, the micelle-like nanostructures provide the chiral binding environments where the induced CD of **2** was generated.

[1] Hirao, T.; Tsukamoto, H.; Ikeda, T.; Haino, T. *Chem. Commun.*, **2020**, 56, 1137–1140.

[2] Yoshida, M.; Hirao, T.; Haino, T. *Org. Biomol. Chem.*, **2021**, 19, 5303–5311.

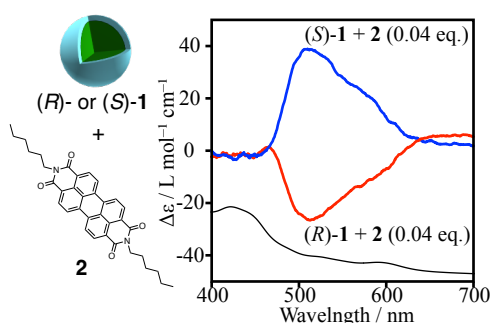


Figure 2. CD and UV-Vis (black line) spectra of coassemble micelles of (*S*)-**1** and **2** (blue), (*R*)-**1** and **2** (red) ($5 \times 10^{-4} \text{ M}$) in THF/water(40/60, v/v).

Supramolecular Polymerization of Photofunctional Thiophene-Fused $[4n]$ Annulenes: Chiral Superstructures and Chiroptical Properties

(¹*Grad. Sch. of Eng., The Univ. of Tokyo*, ²*RIKEN CEMS*, ³*PRESTO, JST*) ○Tsubasa Aoki,¹ Takayoshi Akiyama,¹ Takuzo Aida,^{1,2} Yoshimitsu Itoh^{1,3}

Keywords: Chirality; Supramolecular Polymer; $[4n]$ Annulene; Thiophene; CPL

Non-planar π -motifs are potential monomers to obtain new functional supramolecular polymers due to their chiral core and dynamic ring-inversion behavior. However, less research has been done because of difficulties in synthesizing a suitable monomer and structural characterization of the polymer. Recently, we have developed supramolecular polymers of chiral thiophene-fused $[4n]$ annulene (**COT**) derivatives, which brought the first example of an alternating heterochiral sequence of the polymer and photo-suspendable chain growth by photochemically fluttering monomers.^{[1],[2]} Both phenomena were never seen in the previous supramolecular polymers. Notably, the **COT** monomers exhibit the excited-state aromaticity (Baird aromaticity) as we reported in the previous work.^[3] In this presentation, we report our recent studies on **COT**-based supramolecular polymers focusing on (i) an optically active racemic supramolecular polymer,^[4] (ii) enhancement of circularly polarized luminescence (CPL) upon supramolecular polymerization (Figure).^[5]

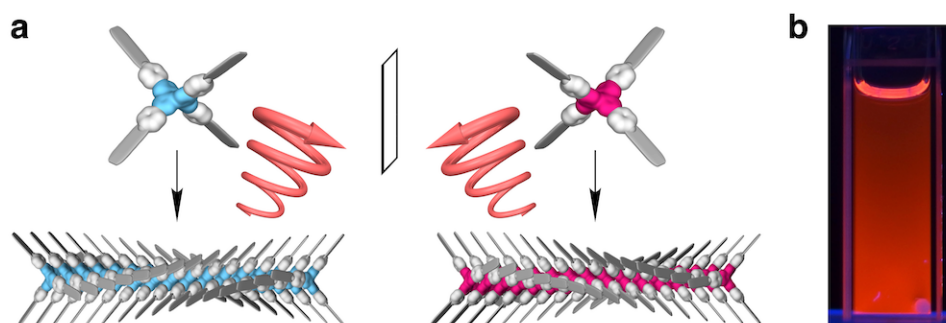


Figure (a) Schematic Representation of a **COT**-Based Supramolecular Polymer and (b) Photograph of Emissive Polymer Solution upon UV irradiation.

[1] M. Ueda, T. Aoki *et al.*, *JACS* **2021**, *143*, 5121. [2] T. Aoki *et al.*, *JACS* **2022**, *144*, 7080. [3] M. Ueda *et al.*, *Nat. Commun.* **2017**, *8*, 346. [4] T. Aoki *et al.*, *submitted*. [5] T. Aoki *et al.*, *submitted*.

[K606-1vn] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kenichi Kato, Yoshimitsu Itoh

Wed. Mar 22, 2023 4:10 PM - 6:40 PM K606 (K606, Lecture Hall Bldg. [6F])

[K606-1vn-01] Signal-amplification Sensing via Sumanene-based Supramolecular Polymerization

○Hiroaki Mizuno¹, Hironobu Nakazawa², Akihisa Miyagawa³, Yumi Yakiyama², Susumu Kawauchi⁴, Hidehiro Sakurai², Gaku Fukuhara¹ (1. Department of Chemistry, Tokyo Institute of Technology, 2. Department of Applied Chemistry, Osaka University, 3. Department of Chemistry, University of Tsukuba, 4. Tokyo Tech Academy for Convergence of Materials and Informatics, Tokyo Institute of Technology)

4:10 PM - 4:30 PM

[K606-1vn-02] Anion- π Interaction in the Polyanionic {Mo₁₃₂} Cage

○Chinatsu MURATA¹, Jaesob SHIN¹, Yukatsu SHICHIBU^{1,2}, Katsuaki KONISHI^{1,2} (1. Grad. Sch. Env. Sci., Hokkaido Univ., 2. Fac. Env. Earth Sci., Hokkaido Univ.)

4:30 PM - 4:50 PM

[K606-1vn-03] Synthesis and Dynamic Properties of Stapled α -Helical Peptides

○Naoki Ousaka¹, Mark MacLachlan^{1,2}, Shigehisa Akine^{1,3} (1. Kanazawa Univ. NanoLSI, 2. The Univ. of British Columbia, 3. Kanazawa Univ. Grad. Sch. of Nat. Sci. &Tech.)

4:50 PM - 5:10 PM

[K606-1vn-04] Acceleration and deacceleration of helicity inversion speeds in a dynamic helical trinickel(II) metallocryptand by alkali metal ion binding

○Sk Asif Ikbal¹, Pei Zhao², Masahiro Ehara², 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)

5:10 PM - 5:30 PM

[K606-1vn-05] Colorimetric Chiral Sensing Using Supramolecular Organogels Formed by Carbamoylated Riboflavin and Melamine Derivative

○Marina Oka¹, Ryo Kozako¹, Hiroki Iida¹ (1. Graduate School of Natural Science and Technology, Shimane University)

5:40 PM - 6:00 PM

[K606-1vn-06] Formation of a metastable Pd₄L₈ interlocked cage complex based on the energy ratchet mechanism

○Tsukasa Abe¹, Shuichi Hiraoka¹ (1. The Univ. of Tokyo)

6:00 PM - 6:20 PM

[K606-1vn-07] Supramolecular reactions in a dynamic solution

○Munenori Numata¹, Takemori Haruna, Kanzaki Chisako (1. Kyoto Prefectural University)

6:20 PM - 6:40 PM

スマネン超分子ポリマーによるシグナル増幅センシング

(東工大理¹・阪大院工²・筑波大数理物質³・東工大 TAC-MI⁴) ○水野 裕彬¹・中澤 廣宣²・宮川 晃尚³・焼山 佑美²・川内 進⁴・櫻井 英博²・福原 学¹

Signal-amplification Sensing via Sumanene-based Supramolecular Polymerization
(¹Department of Chemistry, Tokyo Institute of Technology, ²Department of Applied Chemistry, Osaka University, ³Department of Chemistry, University of Tsukuba, ⁴Tokyo Tech Academy for Convergence of Materials and Informatics, Tokyo Institute of Technology,) ○ Hiroaki Mizuno,¹ Hironobu Nakazawa,² Akihisa Miyagawa,³ Yumi Yakiyama,² Susumu Kawauchi,⁴ Hidehiro Sakurai,² Gaku Fukuhara¹

In this study, we synthesized indole-modified sumanene as a chemosensor, which was then mixed with unmodified sumanene to afford a sumanene-based hetero supramolecular polymer. Surprisingly, a binding constant of the supramolecular polymer upon the complexation of methyl benzoate was enhanced by a factor of up to 11, comparing to that obtained from the sumanene chemosensor.

Keywords : Sumanene; Supramolecular Polymer; Molecular Recognition

我々はこれまでに高分子主鎖をシグナル増幅リポーターとしたシグナル増幅センシング (SASS) を提唱し、実践してきた¹⁾。本研究では、結晶中でカラム状の超分子ポリマーを形成するスマネン (**1**, Figure 1a)²⁾に着目し、超分子ポリマーによりシグナルを増幅させる系へと展開した。インドールを **1** に修飾したスマネン化学センサー (**2**, Figure 1b) を合成し、モデルゲスト分子としてメチルベンゾエート (**MB**) をセンシングした結果、**1** と **2** の共存下では $K = 79 \text{ M}^{-1}$ となり、**2** のみの場合 ($K = 7 \text{ M}^{-1}$) と比較して平衡定数が 11 倍増幅した (Figure 1b)。本発表では、スマネン超分子ポリマーによるシグナル増幅機構ならびにステロイド類をセンシングした結果について報告する。

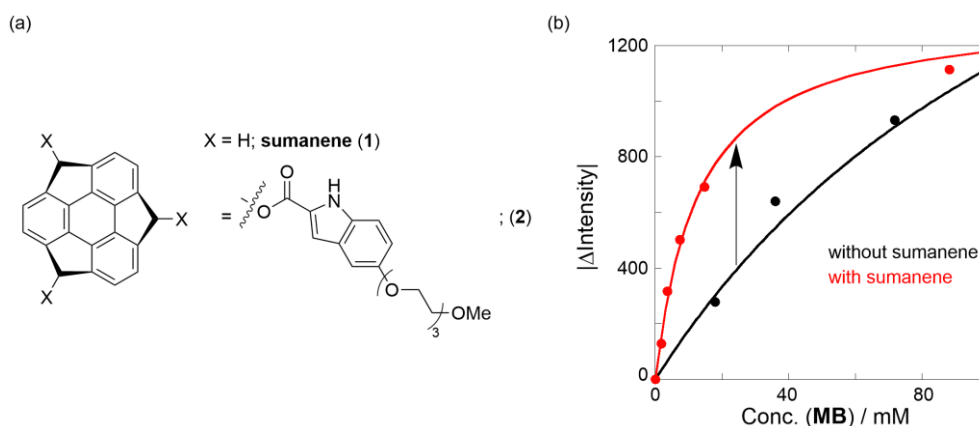


Figure 1. (a) Chemical structures of sumanene (**1**) and its chemosensor (**2**). (b) Result of non-linear least-squares fitting, assuming the 1 : 1 stoichiometry, to determine the binding constant of **2** (black) or the supramolecular polymer (red) upon the complexation of **MB**.

1) Fukuhara, G. *J. Photochem. Photobiol. C* **2020**, 42, 100340.

2) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, 301, 1878.

ポリアニオン性の $\{\text{Mo}_{132}\}$ ケージにおけるアニオン- π 相互作用

(北大院環境¹・北大地球環境²) ○村田千夏¹・申裁燮¹・七分勇勝^{1,2}・小西克明^{1,2}
 Anion- π Interaction in the Polyanionic $\{\text{Mo}_{132}\}$ Cage (¹*Grad. Sch. Env. Sci., Hokkaido Univ.*,
²*Fac. Env. Earth Sci., Hokkaido Univ.*) ○Chinatsu Murata,¹ Jaesob Shin,¹ Yukatsu Shichibu,^{1,2}
 Katsuaki Konishi^{1,2}

Anion- π interaction is usually found with highly electron-deficient aromatic rings. Herein we report that such π -interactions can occur, even with mono-substituted benzenes whose electron deficiency is not so high, inside the polyanionic cage of $[\text{Mo}_{132}\text{O}_{372}]^{42-}$ (denoted by $\{\text{Mo}_{132}\}$). Systematic studies on the guest preference in the inclusion into the inner space reveal that the polar guests with a strongly electron-withdrawing group show enhanced affinities when compared with less polar guests. Coupled with control experiments using related araliphatic and aliphatic guests, it is implied that the polyanionic nature of the host facilitates to interact with the aromatic ring with a slight $\delta+$ character arising from the π -conjugated electron-withdrawing substituents, boosting the anion- π interactions.

Keywords : Polyoxometalate; π -interaction; Host-guest

【緒言】 アニオン- π 相互作用は、電子求引基に誘起された芳香環上の $\delta+$ な π 平面とアニオン種の間でみられる相互作用である。^[1] 一方で、巨大な金属酸化物クラスターの一種である $[\text{Mo}_{132}\text{O}_{372}(\text{L})_{30}]^{42-}$ (以下: $\{\text{Mo}_{132}\}$) は、ポリアニオン性を有するホスト化合物として報告されている (Fig.1)。^[2] 表面にはナノサイズの空孔が存在し、内部に十分な空間をもつことから、水中における疎水効果を駆動力としたゲスト内包が報告されてきたが、それ以外の要素について詳細な研究が行われていなかった。そこで本研究ではアニオン性 $\{\text{Mo}_{132}\}$ ホストと π 平面を有する一置換ベンゼンをゲストとした水中での内包挙動を追跡し、アニオン- π 相互作用の影響について調べた。

【結果・考察】 $\{\text{Mo}_{132}\}$ の D_2O 溶液に、種々の一置換ベンゼンを加え水中でのゲスト内包を行った。定量は添加 96 h 後における $\{\text{Mo}_{132}\}$ 1 分子あたりの内包数を内部標準法から算出した。その結果、シアノ基をはじめとする電子求引基をもつゲストの著しい内包増大がみられることが明らかとなった (Fig 2)。内包に寄与しているのが官能基だけの働きか、 π 共役面の効果かどうかを調べるために、共役が途中で分断されているシアン化ベンジルによる内包挙動を調べた。定量の結果、顕著な内包はみられなかったことから $\{\text{Mo}_{132}\}$ ホストの内包には、電子求引基によって引き起こされた電子不足な π 表面によるアニオン- π 相互作用が作用している可能性を示した。

[1] K. R. Dunbar *et al.*, *Chem. Soc. Rev.*, **2008**, 37, 68.

[2] A. Müller *et al.*, *Chem. Soc. Rev.*, **2012**, 41, 7431.

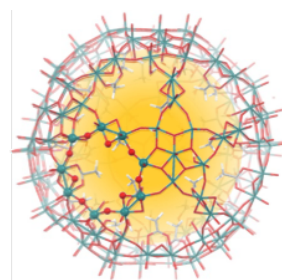


Fig.1 Structure of $\{\text{Mo}_{132}\}$.

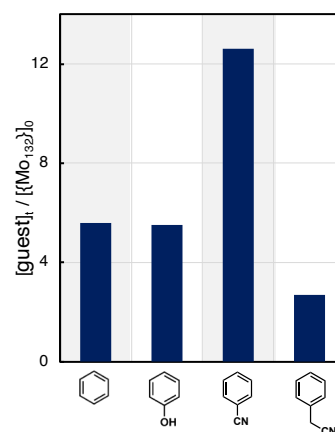


Fig.2 Amounts of mono-substituted guests included within the $\{\text{Mo}_{132}\}$.

ステープル化した α -ヘリカルペプチドの合成と動的性質

(金沢大 NanoLSI¹・ブリティッシュコロンビア大^{1,2}・金沢大院自然^{1,3}) ○逢坂 直樹¹・Mark J. MacLachlan^{1,2}・秋根 茂久^{1,3}

Synthesis and Dynamic Properties of Stapled α -Helical Peptides (¹WPI Nano Life Science Institute, Kanazawa University, ²Department of Chemistry, University of British Columbia, ³Graduate School of Natural Science and Technology, Kanazawa University) ○Naoki Ousaka¹・Mark J. MacLachlan^{1,2}・Shigehisa Akine^{1,3}

We have successfully designed and synthesized stapled dynamic α -helical peptides exhibiting a slow interconversion between the right- and left-handed helices, whose preferred handedness can be reversibly switched by alternative addition of an appropriate base and acid.

Keywords : Helical Structure; α -Helix; Peptide; Helix Inversion

1951年にPaulingらにより α -ヘリックス構造が発見されて以来¹、多種多様な人工らせん分子・高分子・超分子が合成されてきた^{2,3}。中でも、外部刺激に応答して右巻きと左巻きのらせんの優先性がゆっくりと反転する興味深い動的性質を示すらせんが見出されており、メモリー材料などへの応用が期待される^{2,3}。しかし、生物学的に最も重要な構造モチーフの1つである α -ヘリックスにおいて、このような動的な性質を示す例は皆無であり、その実現は α -ヘリックス構造の本質を理解する一助になるだけでなく、これまでに見出された α -ヘリックス構造の安定性を凌駕する極めて剛直な構造を与えることが予想される。

本研究では、らせん形成性の高いアキラルなアミノ酸残基 (Aib, Ac₆C, Api) のみからなるペプチドの側鎖間を分子内架橋 (ステープル化) するとともに C 末端にカルボキシ基を有する光学活性なアミノ酸残基を導入することで、酸・塩基の刺激に応答してらせんの巻き方向の優先性が可逆的かつ著しく遅く反転する α -ヘリカルペプチドの合成に成功した (Figure 1)。

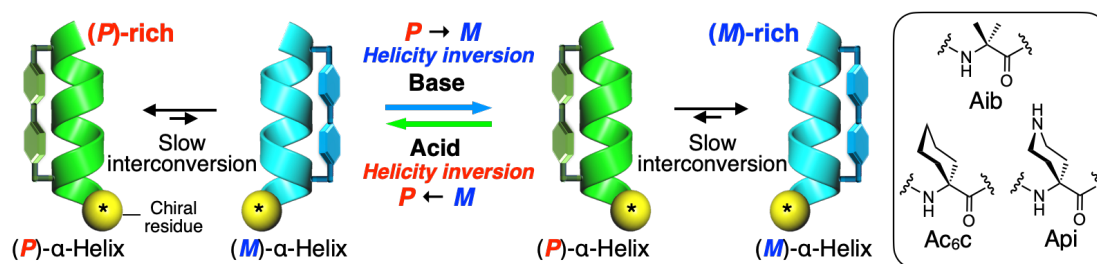


Figure 1. Schematic representation of acid/base-triggered reversible helicity inversion of a stapled α -helical peptide. Chemical structures of helicity-inverting achiral amino acid residues are also shown.

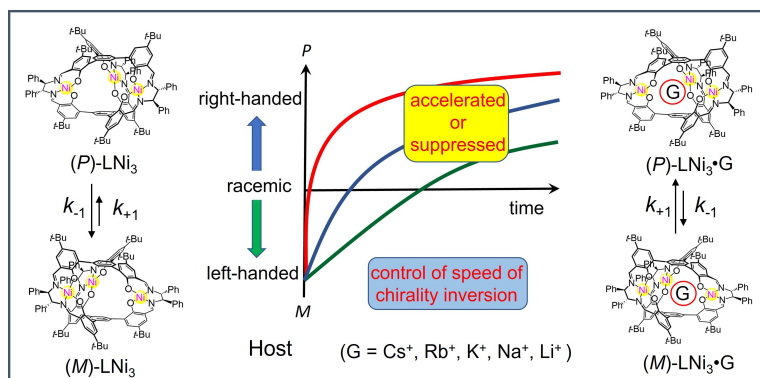
- 1) Pauling, L.; Corey, R. B.; Branson, H. R. *Proc. Natl. Acad. Sci. USA*, **1951**, 37, 205.
- 2) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, 109, 6102.
- 3) Yashima, E.; Ousaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. *Chem. Rev.* **2016**, 116, 13752.

Acceleration and deacceleration of helicity inversion speeds in a dynamic helical trinickel(II) metallocryptand by alkali metal ion binding

(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 Pei Zhao,² Masahiro Ehara,² Shigehisa Akine^{1,3}

Keywords: Helicity inversion; Dynamic structural conversion; Alkali metal ions; Ion recognition; Nickel complex

Development of artificial dynamic helical molecules with controllable helix inversion rate can be useful to make chiral memory materials.¹ Most of the previous reports of stimuli-responsive chiral molecules have been focused only on the equilibrium states before and after stimulation but not on controlling the kinetics.¹ We have already demonstrated that the helicity inversion kinetics of trinickel(II) cryptands can be controlled by guest recognition in the cryptand cavity.^{2,3} Here we present the detailed kinetic and thermodynamic studies of the trinickel(II) cryptand in the presence of the guests. The trinickel(II) complex is in slow dynamic equilibrium between *P* and *M* isomers in solution, preferring one isomer in major concentration. The guest binding with a series of alkali metal ions caused significant changes in the *P*/*M* ratios, which were analyzed in terms of binding constants, isomerization constants, and rate constants. We will focus on the determination of energy diagrams of the helicity inversion (isomerization) and ion recognition. The apparent binding affinity at the transition state for each guest will be discussed.



Scheme 1. Concept of regulating the speed of helicity inversion by non-covalent binding with alkali metal ions.

1) S. Akine, H. Miyake, *Coord. Chem. Rev.* **2022**, 486, 214582. 2) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front.*, **2014**, 1, 53. 3) S. A. Ikbal, M. Ehara, Y. Sakata, S. Akine, The 102nd CSJ annual meeting, **2022**.

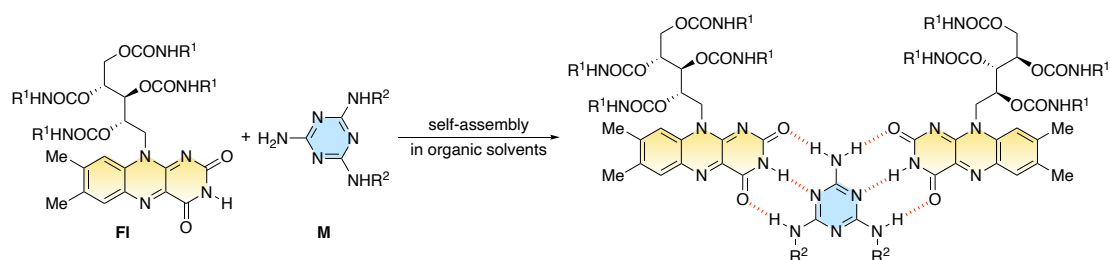
Colorimetric Chiral Sensing Using Supramolecular Organogels Formed by Carbamoylated Riboflavin and Melamine Derivative

(Graduate School of Natural Science and Technology, Shimane University) ○Marina Oka, Ryo Kozako, Hiroki Iida

Keywords: Supramolecular Gel; Flavin; Melamine; Chirality; Chiral Sensing

Riboflavin, a naturally occurring π -conjugated organic molecule, has an optical activity derived from the ribityl group and exhibits attractive functions such as organocatalysis and redox activity. Therefore, polymers and supramolecules containing riboflavin would act as attractive functional materials. Among them, supramolecular gels containing riboflavin derivatives are expected to exhibit unique functions that are originated from combining the high stimulus-responsive characteristic of supramolecular gels and the diverse properties of riboflavin. However, only a few examples of the riboflavin-derived supramolecular gels have been reported, and there have been no examples of functional gels utilizing the chirality of riboflavin.¹ Recently, our group found that a riboflavin derivative bearing an optically active carbamate-protected ribityl group (**FI**) and a melamine derivative possessing two monoalkylated amino groups (**M**) are self-assembled to form chiral supramolecular gels in organic solvents.

Flavin compounds have absorption in the visible light region caused by their π -conjugated structure and have attracted an increasing attention as photocatalysts for the aerobic oxidation of alcohols and thiols under visible light irradiation.² The flavins also display the redox activity, thus their colors are significantly changed in each redox state. Taking advantage of the photo- and redox-catalysis, in this work, we attempted colorimetric sensing of chiral alcohols using the asymmetric catalysis of the chiral supramolecular gel consisting of **FI** and **M**. As a result, the color of the supramolecular gel was changed enantioselectively upon the addition of optically active alcohols.



- 1) a) S. Manna, A. Saha, A. K. Nandi, *Chem. Commun.*, **2006**, 4285. b) S. Kawamorita, M. Fujiki, Z. Li, T. Kitagawa, Y. Imada, T. Naota, *ChemCatChem*, **2019**, *11*, 878. c) M. Cariello, B. Dietrich, L. Thomson, V. Gauci, A. Boyer, S. Sproules, G. Cooke, A. Seddon, D. J. Adams, *Chem. Eur. J.*, **2022**, *28*, 1725.
- 2) a) H. Schmaderer, P. Hilgers, R. Lechner, B. König, *Adv. Synth. Catal.*, **2009**, *351*, 163. b) M. Oka, D. Katsube, T. Tsuji, H. Iida, *Org. Lett.*, **2020**, *22*, 9244.

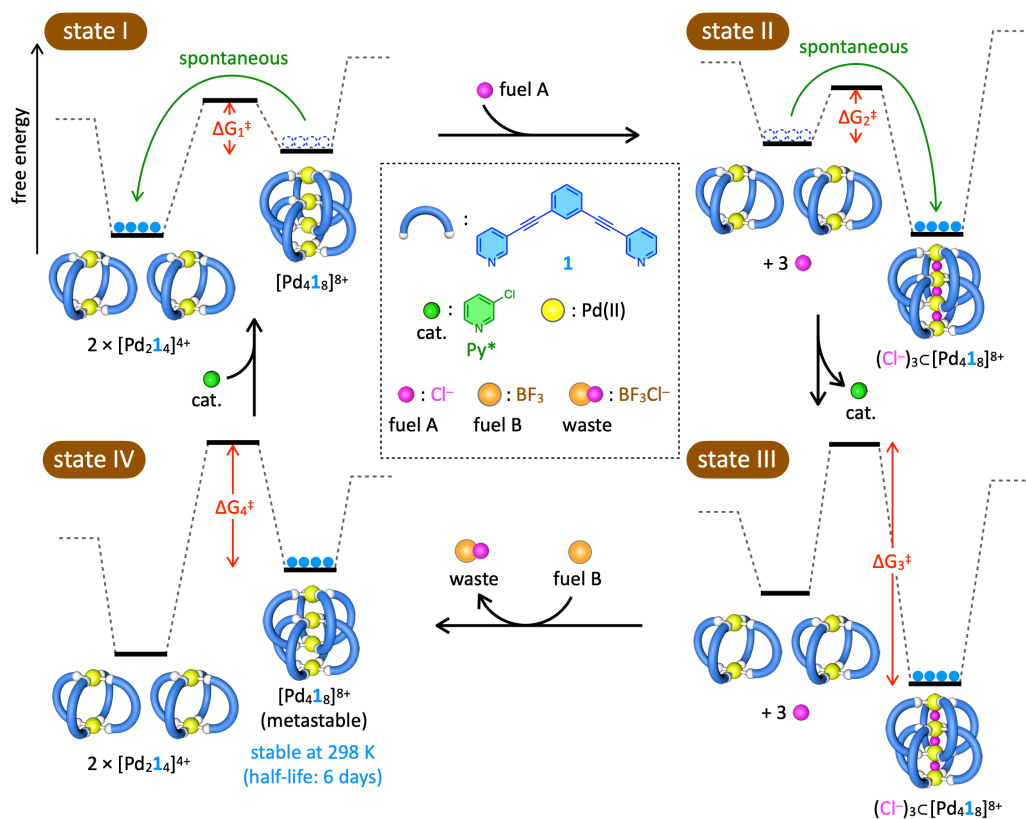
Formation of a metastable Pd_4L_8 interlocked cage complex based on the energy ratchet mechanism

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

○Tsukasa Abe, Shuichi Hiraoka

Keywords: Interlocked cage, Kinetic control, Energy ratchet mechanism, Metastable

Although $(\text{X}^-)_3\text{C}[\text{Pd}_4\text{L}_8]$ interlocked cages (IC) have been reported so far,¹ no attempt to produce a metastable IC without X^- was made, because reversible $\text{Pd(II)}-\text{L}$ coordination bonds cause the conversion of the metastable IC into two Pd_2L_4 cages under thermodynamic control. Here, we report a metastable Pd_4L_8 IC by removing Cl^- from the $(\text{X}^-)_3\text{C}[\text{Pd}_4\text{L}_8]^{8+}$ IC under the condition where ligand exchanges are prevented (without cat.). Addition of Py^* as a cat. to the metastable IC caused the conversion of the metastable IC into two $[\text{Pd}_2\text{L}_4]^{4+}$ cages. As the $(\text{Cl}^-)_3\text{C}[\text{Pd}_4\text{L}_8]^{8+}$ IC was produced by addition of Cl^- to the $[\text{Pd}_2\text{L}_4]^{4+}$ cage in the presence of cat., a directional cycle of transition was realized with two kinds of fuels (A and B) and the catalyst that modulates the energy landscape by energy ratchet mechanism.



1) a) M. Fukuda, R. Sekiya, R. Kuroda, *Angew. Chem., Int. Ed.* **2008**, 47, 706, b) S. Freye, J. Hey, A. Torras-Galán, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem., Int. Ed.* **2012**, 51, 2191.

溶液の運動性に基づく新しい超分子形成反応

(京都府大院 生命環境) ○沼田 宗典・竹森 はるな・神崎 千沙子

Supramolecular reactions in a dynamic solution (*Graduate School of Life and Environmental Sciences, Kyoto Prefectural University*) ○Munenori Numata, Haruna Takemori, Chisako Kanzaki

One of the fundamental issues in supramolecular chemistry is to incorporate multi-functional molecules into a single supramolecular structure. In the recent advance of this area, the emergency of molecular complexity along the polymer chain has been accomplished through precise controlling over kinetic self-assembly processes. On the other hand, folding of the created polymer chains as well as their further hierarchical assemblies toward two- or three-dimensional architectures, which are ubiquitous in Nature, has remained a challenging task in supramolecular chemistry. Porphyrins are fascinating molecules not only from its unique photonic properties but also from scaffold for placing a functional moiety at their peripheral position. Here, we report the supramolecular co-polymerization of two types of water-soluble porphyrins. We found that electrostatic interpolymer interactions caused their hierarchical assembly, finally affording a double stranded helix structure at micrometer range.

Keywords : *Supramolecular structures; Kinetic control; Supramolecular polymerization; Microflow; Non-equilibrium*

複雑性と階層性を内在した超分子構造を創製するためには、分子間力の数と位置の精密制御が必要である。これまでプロトン (H^+) 化を鍵として超分子会合を引き起こす Tetrakis(4-sulfonatophenyl)porphyrin (TPPS) を用い、マイクロフロー空間内における定常的な溶液の流れが、能動的な分子会合を引き起こす駆動力となることを報告している (図 1a)¹⁾。本研究では、TPPS の4つのスルホン酸基のうち、対角 (trans) に位置する2つをアミノ基で置換した $H_2TPPS_2-NH_2$ 及びエチレングリコール (EG) 部位で置換した $H_2TPPS_2-NH-EG$ の設計・合成を行い、これら新規 TPPS 誘導体のマイクロフロー空間における会合挙動を精査した (図 1b)。その結果、マイクロフロー空間内における H^+ 化と疎水相互作用の著しい促進効果により、2種類のモノマー分子からランダム共重合体やブロック共重合体の創製が可能になることが解った。さらに、創製した共重合体は表面電荷の解消を駆動力として自発的に μm サイズの二重らせん構造へと組織化することも明らかとなった (図 1c)。分子配列に基づく高度な階層性を持つ超分子の創製について詳細に報告する。

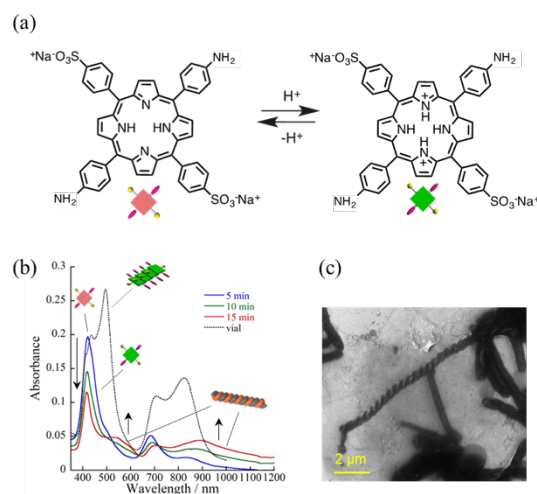


図1 : (a) TPPS₂-NH₂の構造 ; (b) 時間依存UV-Vis スペクトル (1 mm cell, r.t.); (c)マイクロフロー空間を用いて創製した二重らせん構造 (走査型電子顕微鏡像)

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

[K602-1am] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Shohei Saito, Shuzo Hirata

Wed. Mar 22, 2023 9:00 AM - 11:40 AM K602 (K602, Lecture Hall Bldg. [6F])

[K602-1am-01] Intramolecular Singlet Fission and Chiroptical Properties of Chiral Acene Dimers

[○]Hayato Sakai¹, Yasuyuki Araki², Takehiko Wada², Nikolai Tkachenko³, Taku Hasobe¹
(1. Keio University, 2. Tohoku University, 3. Tampere University)

10:20 AM - 10:40 AM

[K602-1am-02] Transient Absorption Spectroscopic Analysis of Energy Transfer Process in the Solid-state Upconversion System

[○]Yasunori Matsui^{1,2}, Takumi Takahashi¹, Masaya Kanoh¹, Takuya Ogaki^{1,2}, Hiroshi Ikeda^{1,2}
(1. Grad. Sch. Eng., Osaka Metro. Univ., 2. RIMED, Osaka Metro. Univ.)

10:40 AM - 11:00 AM

[K602-1am-03] Photo-Induced Triplet Depletion Allowing Higher-Resolution Afterglow

[○]Kikuya Hayashi¹, Keiki Fukumoto², Shuzo Hirata¹ (1. The Univ. of Electro-Commun., 2. KEK)

11:00 AM - 11:20 AM

[K602-1am-04] Vibronic Couplings and Spin-Orbit Couplings in Intersystem Crossing Processes

[○]Wataru Ota^{1,2}, Motoyuki Uejima³, Tohru Sato^{1,2} (1. Fukui Institute for Fundamental Chemistry, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. MOLFEX, Inc.)

11:20 AM - 11:40 AM

キラルアセン二量体の分子内一重項分裂およびキロプティカル特性

(慶大理工¹・東北大多元研²・タンペレ大学³) ○酒井 隼人¹・荒木 保幸²・和田 健彦²・Nikolai V. Tkachenko³・羽曾部 卓¹

Intramolecular Singlet Fission and Chiroptical Properties of Chiral Acene Dimers (¹Department of Chemistry, Faculty of Science and Technology, Keio University, ²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, ³Faculty of Engineering and Natural Sciences, Tampere University) ○Hayato Sakai,¹ Yasuyuki Araki,² Takehiko Wada,² Nikolai V. Tkachenko,³ Taku Hasobe¹

Singlet fission (SF) is able to generate two triplet excitons from one photon absorption between two neighboring chromophore units. Acene is one of the representative compounds for occurrence of efficient SF. Although various reports on the covalently-linked acene dimers with high-yield triplet excited states through SF are already published, the research number regarding the synthesis and observation of SF utilizing molecular dimers bridged by chiral linker units are quite limited. More importantly, no attention has been paid to the relationship between the chiroptic property and excited-state dynamics associated with SF, so far. In this study, we synthesized a series of acene (i.e., pentacene and tetracene) dimers bridged by chiral units. The details on the relationship between chiroptical and SF properties will be discussed in this presentation.

Keywords : Acene; Dimer; Chiroptical Property; 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) やテトラセン (Tc) 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。架橋部位にキラルユニットを用いた二量体に関して注目すると、SF に関する報告は二例あるが^{1,2}、SF の関与する励起状態とキロプティカル特性の関連は皆無である。

本発表では、キラル分子をリンカーとして用いた Pc および Tc の二量体を合成 (Fig. 1) し、キラル分光と過渡吸収分光を併用し、SF が関与するキロプティカル特性に関して評価した。

- 1) Lakhwani, G. et al., *J. Phys. Chem. A* **2021**, 125, 7226–7234
- 2) Guldi, D. M. et al., *ChemPhotoChem* **2020**, 4, 5168–5174

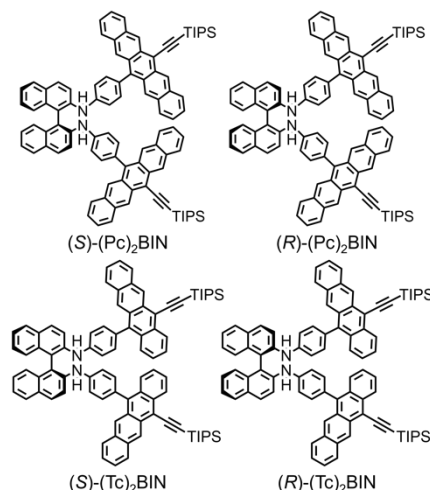


Fig. 1 Chemical structures of chiral acene dimers in this study.

Transient Absorption Spectroscopic Analysis of Energy Transfer Process in the Solid-state Upconversion System

(¹Grad. Sch. Eng., Osaka Metro. Univ., ²RIMED, Osaka Metro. Univ.)

○Yasunori Matsui,^{1,2} Takumi Takahashi,¹ Masaya Kanoh,¹ Takuya Ogaki,^{1,2} Hiroshi Ikeda^{1,2}

Keywords: Time-resolved Spectroscopy; Energy Transfer; Triplet–Triplet Annihilation; Dexter Mechanism

Photon upconversion (UC) is a molecular technology that converts a low-energy light to a higher-energy light by employing triplet energy transfer from an energy donor (D) and triplet–triplet annihilation (TTA) of energy acceptors (A). To realize UC in the solid state, efficient triplet energy harvesting and suppression of fluorescence resonance energy-transfer quenching are required. For this purpose, we employed solution-processed polyurethane (PU) composites containing D, an energy mediator (M), and a dyad DPA–Ad–DPA^{1,2} as A (Fig. 1). In this work, we analyzed the energy transfer behavior in the PU composites (Fig. 1 and 2) by using transient absorption analysis.

First, we prepared the PU composites containing platinum octaethylporphyrin (PtOEP) and various concentrations of anthracene (Ant) and 9,10-diphenylanthracene (DPA). The Stern–Volmer analysis obtained by phosphorescence quenching of ³PtOEP* by DPA provided quenching rate constant (k_Q) is $1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. This k_Q value is almost 1/10 of that in a CH₂Cl₂ solution, suggesting that slow molecular diffusion occurs in the PU composite.

Transient absorption analysis (Fig. 3) was conducted for the PU composite containing PtOEP (0.1 mM), Ant (10 mM), and DPA (1 mM). Photoexcitation of the PU composite provided T–T absorption bands of ³Ant* at 425 nm ($\varepsilon = 4.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) formed by energy transfer from ³PtOEP*. After 10 μs of excitation, broad absorption of ³DPA* was observed at 448 nm ($1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) but ³Ant* remained. These results suggest that partial energy harvesting occurred from ³DPA* to DPA to promote TTA.

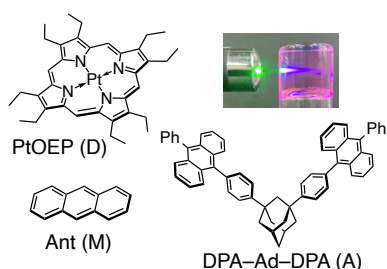


Fig. 1. Structures of PtOEP, Ant, and DPA–Ad–DPA, and a photograph of the PU composite.

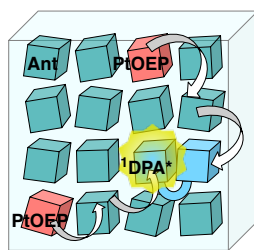


Fig. 2. A schematic representation of polymer composites containing PtOEP, Ant, and DPA–Ad–DPA.

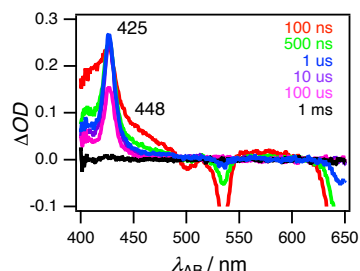


Fig. 3. Transient absorption spectra of the PU composite of PtOEP (0.1 mM), Ant (10 mM), and DPA (1 mM) ($\lambda_{\text{EX}} = 532 \text{ nm}$).

1) Kanoh, M.; Matsui, Y.; Ogaki, T.; Ikeda, H. *et al. J. Phys. Chem. B*, **2021**, 125, 4831–4837.

2) Matsui, Y.; Kanoh, M.; Ikeda, H. *et al. J. Photochem. Photobiol. A: Chem.*, **2020**, 387, 112107.

Photo-Induced Triplet Depletion Allowing Higher-Resolution Afterglow

(¹Graduate School of Informatics and Engineering, The Univ. of Electro-Commun., ²High Energy Accelerator Research Organization) ○Kikuya Hayashi,¹ Keiki Fukumoto,² Shuzo Hirata¹

Keywords: Triplet Exciton; Photoionization; Room-Temperature Phosphorescence; High-Resolution Microscopy

Stimulated emission depletion microscopy uses stimulated emission from the singlet excited state of a chromophore, which allows super-resolution fluorescence images.¹ However, fluorescence imaging is often interfered by emission from surrounding environment in the presence of fluorescent impurities. As an imaging technique independent of fluorescent impurity, afterglow imaging using persistent room-temperature phosphorescence (RTP) has been reported.² However, no possible stimulated emission from the lowest triplet excited state (T_1) precludes us to make higher resolution-afterglow emission images.

Here, we demonstrate photoinduced triplet depletion and improved resolution of afterglow emission using the depletion. After ceasing excitation, persistent RTP from an amorphous β -estradiol film doped with 1 wt% chromophore **1** (Figure 1a) was depleted by the strong photoirradiation with a longer wavelength than an absorption wavelength of **1** (depletion beam) (Figure 1b). Triplet depletion possibility depending on irradiance of different depletion beam-colors indicates that a photoionization from the lowest unoccupied molecular orbital (LUMO) in T_1 over vacuum level of **1** triggers the triplet depletion ((i) in Figure 1c). Analyses of charge generation and upconversion emission behavior by irradiation of the depletion beam indicate that triplet depletion mechanism includes a process in which electrons eventually return to the highest occupied molecular orbital (HOMO) of **1** ((ii) in Figure 1c). By simultaneously focusing excitation and specially modulated depletion beam onto the film, a higher resolution afterglow emission was observed due to the triplet depletion (right in Figure 2).

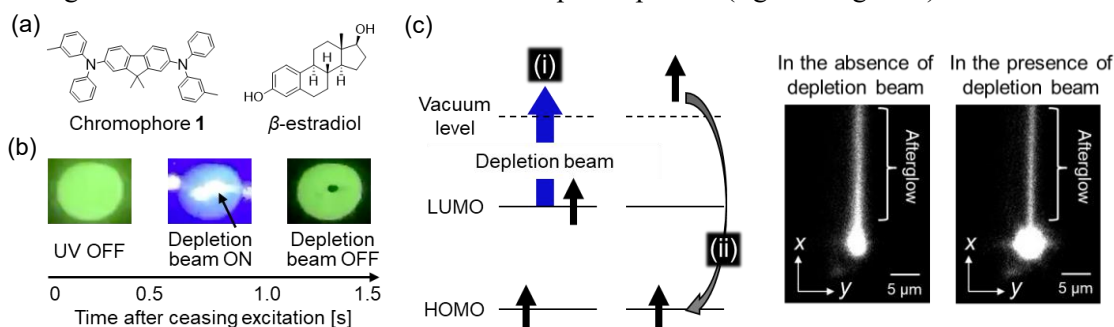


Figure 1. (a) Chemical structures. (b) Photographs showing RTP depletion. (c) Energy diagram illustrates RTP depletion mechanism.

1) S. W. Hell, J. Wichmann, *Opt. Lett.* **1994**, *19*, 780.

2) I. Battacharjee, S. Hirata, *Adv. Mater.* **2020**, *32*, 2001348.

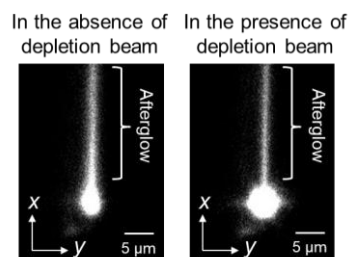


Figure 2. High-resolution afterglow imaging. Left and right show in the absence and presence of donut-shaped depletion beam, respectively.

系間交差過程における振電相互作用とスピン軌道相互作用

(京大福セ¹・京大院工²・MOLFEX³) ○大田 航^{1,2}・上島 基之³・佐藤 徹^{1,2}
Promoting and Accepting Modes in Internal Conversion Processes (¹*Fukui Institute for Fundamental Chemistry, Kyoto University*, ²*Graduate School of Engineering, Kyoto University*, ³*MOLFEX, Inc.*) Wataru Ota,^{1,2} Motoyuki Uejima,³ ○Tohru Sato^{1,2}

An analytical expression for the rate constant of the intersystem crossing (ISC) in a molecule was derived using the mixed-spin crude adiabatic (CA) representation. All vibrational modes were considered to be on an equal footing in the rate expression. In the mixed-spin CA representation, the ISC can be regarded as a transition accompanying one-phonon emission and absorption, thereby clarifying the dependence of the ISC rate constant on the vibronic couplings and spin-orbit couplings. One of the advantages of this representation is that the driving force for the ISC is the same vibronic couplings as for the internal conversion, allowing a unified treatment of the nonradiative transitions. Another advantage is that the origin of the vibronic couplings can be elucidated by their density forms, i.e., vibronic coupling densities (VCDs), which can be utilized for rational molecular design. Using the concept of VCD, the ISC processes can be understood and controlled in terms of electronic states and vibrational modes separately. Based on the obtained expression, we quantitatively calculated the ISC rate constant of 9-fluorenone and investigated the role of vibronic couplings and spin-orbit couplings on the ISC processes.

Keywords : *Intersystem Crossing; Nonradiative Transition; Vibronic Coupling; Spin-Orbit Coupling*

Mixed-spin crude adiabatic 表現を用いて、全ての振動モードを考慮した系間交差速度定数の解析解を導出した。この表現では、系間交差はフォノンを駆動力とし、異なるスピン多重度の状態がスピン軌道相互作用により混合した状態間の遷移だとみなすことができる。そのため、フォノンを駆動力として、同一のスピン多重度間を遷移する内部転換と統一的な枠組みを与える。さらに、crude adiabatic 表現を用いることで、振電相互作用の起源を振電相互作用密度(VCD)により明らかにし¹⁾、系間交差を制御した分子設計に応用することが可能である。なお、良く用いられる pure-spin 基底では、mixed-spin 基底と異なり、系間交差はスピン軌道相互作用を駆動力として進行するとみなされる²⁾。得られた解析解に基づき、9-フルオレノンの S₁ から T₂、および S₁ から T₁ への系間交差速度定数を定量的に計算し、系間交差過程における主要なプロモーションモードと、電子励起エネルギーを受け取るアクセプティングモードを決定した。それらの振動モードの VCD 解析から、9-フルオレノンにおける系間交差の起源を特定した。

- 1) T. Kato, N. Haruta, and T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation* (Springer, 2021).
- 2) B. R. Henry and W. Siebrand, *J. Chem. Phys.* **1971**, *54*, 1072.

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

[K602-1pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Nobuhiro Yanai, Taku Hasobe

Wed. Mar 22, 2023 1:30 PM - 3:40 PM K602 (K602, Lecture Hall Bldg. [6F])

[K602-1pm-01] Controlling Molecular Orientation to Improve Photon Upconversion Efficiency

○Catherine Helenna Mulyadi^{1,2}, Masanori Uji^{1,2}, Nobuhiro Yanai^{1,2} (1. Kyushu University, 2. FOREST, JST)

1:30 PM - 1:50 PM

[K602-1pm-02] Efficient Photon Upconversion System using Porous Film to Generate UV Light from Visible Light

○Naoyuki Harada¹, Masanori Uji¹, Baljeet Singh¹, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,2,3} (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. FOREST, JST)

1:50 PM - 2:10 PM

[K602-1pm-03] Near-Infrared Light Absorbing Organic Molecules towards Photothermal Cancer Therapy

○Kazuya Yoshida¹, Vasudevan Pillai Biju^{1,2}, Yuta Takano^{1,2} (1. Grad. Sch. Env. Sci., Hokkaido Univ., 2. RIES)

2:10 PM - 2:30 PM

[K602-1pm-04] What is the reason why the ring-opening quantum yield is smaller than the ring-closure one and their sum is smaller than unity in many 6 π -electron photochemical electrocyclic reactions?

○Takao Kobayashi¹, Shinichiro Nakamura², Motoyuki Shiga³ (1. Mitsubishi Chemical Corporation, 2. Kumamoto University, 3. Japan Atomic Energy Agency)

2:40 PM - 3:00 PM

[K602-1pm-05] Effect of *para*-substituents of PyBTM radical derivatives on high-efficiency solution fluorescence properties

○Yohei Hattori¹, Ryota Kitajima¹, Ryota Matsuoka², Tetsuro Kusamoto², Kingo Uchida¹ (1. Ryukoku University, 2. Institute for Molecular Science)

3:00 PM - 3:20 PM

[K602-1pm-06] Fluorescent Force Probe for Real-time Imaging of Hydrodynamic Stress Field

○Sachika Akitomo¹, Takuya Yamakado¹, Hidetsugu Kitakado¹, Ryo Kimura¹, Reiko Kuriyama², Kazuya Tatsumi², Kazuyoshi Nakabe², Shohei Saito¹ (1. Graduate School of Science, Kyoto University, 2. Graduate School of Engineering, Kyoto University)

3:20 PM - 3:40 PM

Controlling Molecular Orientation to Improve Photon Upconversion Efficiency

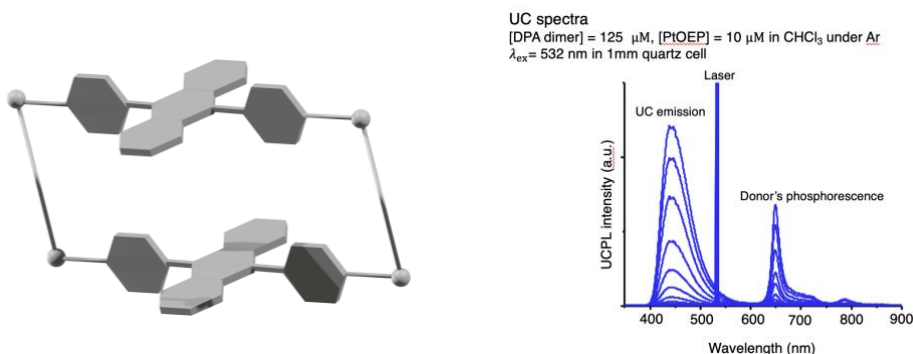
(¹Center of Molecular Systems, Kyushu University) ○Catherine Helenna Mulyadi,¹ Masanori Uji,¹ Nobuhiro Yanai,¹

Keywords: Photon upconversion, Triplet-triplet annihilation, Spin statistical factor, Dimer

Triplet-triplet annihilation photon upconversion (TTA-UC) is a promising research field for various photonic applications due to tunable spectral range and non-coherent light source utilization. Recent research has been aiming to enhance TTA-UC performance, such as the UC efficiency (η_{UC}), which is crucial especially in energy-harvesting related applications. The UC efficiency is comprised of spin statistical factor (f) and quantum yield of energy transfer processes (Φ_{ISC} , Φ_{TTET} , Φ_{TTA}) and fluorescence (Φ_{FL}), as described in the equation below:

$$\eta_{UC} = f \Phi_{ISC} \Phi_{TTET} \Phi_{TTA} \Phi_{FL}$$

According to the research by Bossanyi et al., the spin statistical factor, the probability of singlet state acceptor formation after TTA process, can be improved by fixating parallel orientation of the acceptor molecules.¹ With this molecular design, the f value can increase significantly from 40% to 66.7% in solution system. Therefore, this research tries to prove this theory by synthesizing a parallel-oriented dimer of a widely known acceptor molecule (9,10-diphenylanthracene, DPA) with Schiff-base linker then observing its optical properties. The DPA dimer is successfully synthesized, and its optical properties resemble those of the single DPA molecule. In addition, the upconverted fluorescence of DPA dimer was observed at 446 nm using PtOEP as the donor molecule. We'll report the detailed UC parameters in this presentation.



1) David G. Bossanyi, Yoichi Sasaki, Shuangqing Wang, Dimitri Chekulaev, Nobuo Kimizuka, Nobuhiro Yanai, and Jenny Clark, *JACS Au* **2021** 1 (12), 2188-2201.

ポーラスフィルムを用いた高効率な可視 - 紫外アップコンバージョン材料の開発

(九大院工¹・九大 CMS²・JST 創発³) ○原田 直幸¹・宇治 雅記¹・Baljeet Singh¹・君塚 信夫^{1,2}・楊井 伸浩^{1,2,3}

Efficient Photon Upconversion System using Porous Film to Generate UV Light from Visible Light (¹*Graduate School of Engineering, Kyushu University*, ²*CMS, Kyushu University*, ³*FOREST, JST*) ○Naoyuki Harada,¹ Masanori Uji,¹ Baljeet Singh,¹ Nobuo Kimizuka,^{1,2} Nobuhiro Yanai^{1,2,3}

Triplet-triplet annihilation-based photon upconversion (TTA-UC) converts lower-energy (longer-wavelength) light into higher-energy (shorter-wavelength) light, which can be applied in solar cells, photocatalysis, and biological imaging. Recently, TTA-UC materials that convert visible light to ultraviolet light (UV), which are useful for photocatalysis and photo-redox reactions, have attracted much attention. However, most conventional examples are solution systems, which use volatile organic solvents and are difficult to handle for applications. In this study, we developed a film material that shows efficient upconversion using a porous film. As an emitter, we used UV-emissive TIPS-Nph (Figure 1).^[1] This film sandwiched between quartz substrates exhibited upconversion performance comparable to conventional solution systems. Moreover, it is found to be possible to use weak light of about sunlight ($\sim \text{mW cm}^{-2}$).

Keywords : Photon upconversion; Triplet-triplet annihilation; Visible light; Ultraviolet light; Porous film

低いエネルギー（長波長）光をより高いエネルギー（短波長）光に変換するための三重項 - 三重項消滅に基づくフォトン・アップコンバージョン（TTA-UC）技術は、太陽電池や光触媒、生体イメージングへの応用が可能である。最近では、光触媒や光レドックス反応等に有用な可視光から紫外光へ変換する TTA-UC 材料が研究され始めている。しかしながら、従来材料の多くは光学セルを用いた溶液系であり、揮発性の有機溶媒を使用していること、応用化にあたり扱いにくいことなどの問題点があった。本研究では、ポーラスフィルムを用いることで取り扱いが容易なアップコンバージョンを示すフィルム材料の開発を行った。

発光体として高効率な TTA-UC が報告されている紫外発光性の TIPS-Nph を用いた (Figure 1)。^[1] 石英基板で挟んだ本フィルムは従来の溶液系と同等のアップコンバージョン性能を示すことが分かり、太陽光程度 ($\sim \text{mW cm}^{-2}$) の弱い励起光の利用が可能であることが明らかとなった。

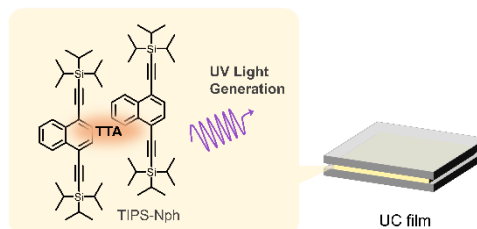


Figure 1 Schematic illustration of a TTA-UC film.

[1] N. Harada, Y. Sasaki, M. Hosoyamada, N. Kimizuka, N. Yanai, *Angew. Chem. Int. Ed.* **2021**, *60*, 142.

Near-Infrared Light-Absorbing Organic Molecules towards Photothermal Cancer Therapy

(¹Graduate School of Environmental Science, Hokkaido University, and ²Research Institute for Electronic Science, Hokkaido University.) ○Kazuya Yoshida,¹ Vasudevanpillai Biju,^{1,2} Yuta, Takano,^{1,2}

Keywords: Photothermal therapy; rosamine; cancer; electron transfer

Modern cancer treatment is mainly by surgery, radiation therapy, and chemotherapy. However, the invasion of normal tissues and drug-resistant cancers are often problems. Therefore, alternative and non-invasive treatments are desired. Phototherapy, including photodynamic therapy (PDT) and photothermal therapy (PTT), has attracted attention in cancer treatments because of its advantages, such as locally selective treatment, low invasiveness, minimal side effects, and effectiveness against resistant cancers. PDT is a technique that uses a photosensitizing agent with high tumor affinity and laser irradiation in the presence of oxygen to generate reactive oxygen species (ROS) to cause tumor cell death. However, the efficacy of PDT is greatly affected by tumor hypoxia. In contrast, PTT uses photothermal agents to damage cancer cells by generating thermal energy through light irradiation. The oxygen concentration does not limit its use. The development of organic materials that absorb near-infrared (NIR) light for PTT is preferable in terms of bio-permeability and biodegradability. In this study, we design and synthesize photo-functional molecules based on sulfone-rosamine (Fig. 1), which absorb and utilize NIR light efficiently. Their photothermal effects are verified, and their molecular dynamics in cancer cells and the photothermal killing effect are revealed.

The sulfone-rosamine derivative in Fig. 1 showed the main absorption peak at 704 nm in PBS, indicating its light harvesting ability in the NIR region. After 10 min of a xenon lamp irradiation, the temperature of the solution is increased by 16.2 °C, indicating that the sulfone-rosamine derivative possesses a sufficient photothermal effect. Since there is no change in the absorption spectrum before and after the xenon lamp irradiation (Fig. 2), the sulfone-rosamine derivative is highly photostable. Subcellular localization shows that the sulfone-rosamine derivative is taken up by living cells and is mainly localized in lysosomes. The cell-killing effect of the sulfone-rosamine derivative is also verified, and the results will be presented in the presentation.

1) L. Li et al. *Chem. Eng. J.* **417**, 128844 (2021).

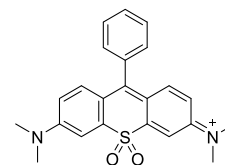


Fig. 1 The structure of sulfone-rosamine.

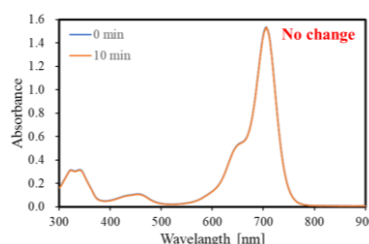


Fig. 2 Absorption spectra of a sulfone-rosamine dye before and after the Xe lamp irradiation (290 mW / spot).

何故、多くの 6π 電子系光化学的電子環状反応に於いて、開環量子収率は閉環量子収率よりも小さく、それらの和が1より小さいのか？

(三菱ケミカル株式会社¹・熊本大学²・日本原子力研究開発機構³) ○小林 高雄¹・
中村 振一郎²・志賀 基之³

What is the reason why the ring-opening quantum yield is smaller than the ring-closure one and their sum is smaller than unity in many 6π -electron photochemical electrocyclic reactions? (¹Mitsubishi Chemical Corporation, ²Kumamoto University, ³Japan Atomic Energy Agency)
○Takao Kobayashi¹, Shinichiro Nakamura², Motoyuki Shiga³

In many 6π -electron photochemical electrocyclic reaction systems such as photochromic molecules of diarylethenes, there is an empirical rule that the ring-opening quantum yield is smaller than the ring-closure one and their sum is smaller than unity, the reason for which has not been clarified experimentally or theoretically for a long time. In this study, we have successfully revealed the reason why this empirical rule is fulfilled through nonadiabatic molecular dynamics (NAMD) simulations of both photochemical ring-opening and ring-closure reactions of CHD/cZc-HT, which is a 6π -electron electrocyclic reaction model system, on highly accurate potential energy surfaces at the highly accurate level of XMS-CASPT2.

Keywords : Photochemical electrocyclic reaction; Cyclohexadiene/Hexatriene; Quantum Yield; Conical Intersection; Nonadiabatic Molecular Dynamics;

フォトクロミック分子であるジアリールエテンなどの多くの 6π 電子系光化学的電子環状反応系では、開環量子収率が閉環量子収率より小さく、それらの和が 1 より小さいという経験則があり、その理由は長い間実験的にも理論的にも明らかにされてこなかった。本研究では 6π 電子系電子環状反応モデル系である CHD/cZc-HT の光化学的開環及び閉環反応を対象に超高精度ポテンシャルエネルギー (XMS-CASPT2 レベル) 曲面上で非断熱分子動力学 (NAMD) シミュレーションを実行することにより、この経験則が成立する理由を明らかにした。

$$QY(P|R) = \sum_{DP=\{P6, C4, O4, C2\}} B(P|DP, R) * D(DP|R)$$

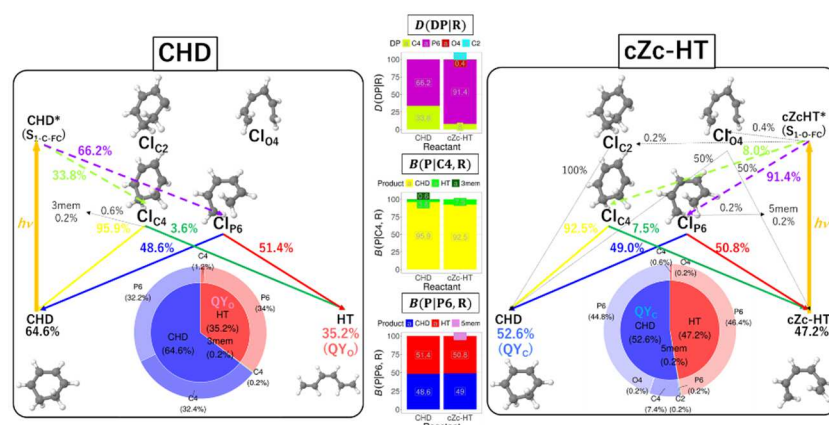


Figure 1: Schematic photochemical electrocyclic reaction pathways from S_1 Franck-Condon states of CHD(left) and cZc-HT(right) to products for each decay passway obtained by NAMD simulations.

PyBTM ラジカル誘導体のパラ置換基が高効率溶液蛍光特性に与える効果

(龍谷大学¹・分子科学研究所²) ○服部 陽平¹・北島 稜大¹・松岡 亮太²・草本 哲郎²・内田 欣吾¹

Effect of *para*-substituents of PyBTM radical derivatives on high-efficiency solution fluorescence properties (¹Ryukoku University, ²Institute for Molecular Science) ○Yohei Hattori,¹ Ryota Kitajima,¹ Ryota Matsuoka,² Tetsuro Kusamoto,² Kingo Uchida¹

Fluorescence of stable triarylmethyl radicals has attracted much attention for applications such as highly efficient OLED materials.¹⁾

We have found that diphenylpyridylmethyl radical derivatives, PyBTM²⁾ and F₂PyBTM³⁾ had high photostability. Substituting chlorine atoms at the *para*-position of the methyl group using micellar Suzuki-Miyaura coupling reaction,⁴⁾ we prepared Mes₂F₂PyBTM with high fluorescence quantum yields in solutions.⁵⁾

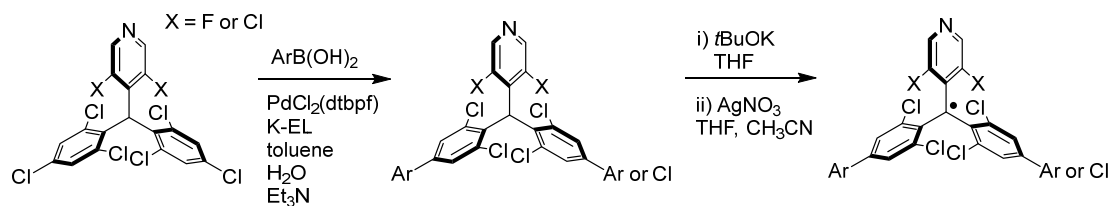
We have recently synthesized new radicals with other *para*-substituents. We will report on their fluorescent properties and discuss the role of the *para*-substituents.

Keywords : Radical, Fluorescence, Luminescence, Donor-Acceptor System, DFT Calculation

安定発光ラジカルは、高効率の有機 EL 材料となることから注目を集めている¹⁾。

我々は、安定なジフェニルピリジルメチルラジカル誘導体である PyBTM²⁾や F₂PyBTM³⁾が高い光安定性を示すことを見出した。メチル基に対するパラ位の塩素をミセル中の鈴木・宮浦カップリングで選択的にアリール基に置換する方法⁴⁾を用いることで、パラ位をメシチル基に付加した F₂PyBTM を合成したところ、クロロホルム中で 69%の高い蛍光量子収率を示した。ここでメシチル基のオルト位のメチル基はトリアリールメチル部位とメシチル基の共役を抑える役割を担っている⁵⁾。

新たにオルト位のメチル基を減らしたラジカルや、メチル基より嵩高いイソプロピル基に変更したラジカル等の新規ラジカル数点を合成したので、その蛍光特性について報告し、オルト位の置換基の役割について考察する。



1) X. Ai, E. W. Evans, S. Dong, A. J. Gillett, H. Guo, Y. Chen, T. J. H. Hele, R. H. Friend, F. Li, *Nature* **2018**, 563, 536.

2) Y. Hattori, T. Kusamoto, H. Nishihara, *Angew. Chem. Int. Ed.* **2014**, 53, 11845.

3) Y. Hattori, T. Kusamoto, H. Nishihara, *RSC Adv.* **2015**, 5, 64802.

4) S. Mattiello, F. Corsini, S. Mecca, M. Sassi, R. Ruffo, G. Mattioli, Y. Hattori, T. Kusamoto, G. Griffini, L. Beverina, *Mater. Adv.* **2021**, 2, 7369–7378.

5) Y. Hattori, R. Kitajima, W. Ota, R. Matsuoka, T. Kusamoto, T. Sato, K. Uchida, *Chem. Sci.* **2022**, 13, 13418–13425.

流体応力場のリアルタイムイメージングを志向した蛍光 Force Probe の分子設計と合成

(京大院理¹・京大院工²) ○秋友祥香¹・山角拓也¹・北鹿渡秀嗣¹・木村 僚¹・栗山 怜子²・巽 和也²・中部主敬²・齊藤尚平¹

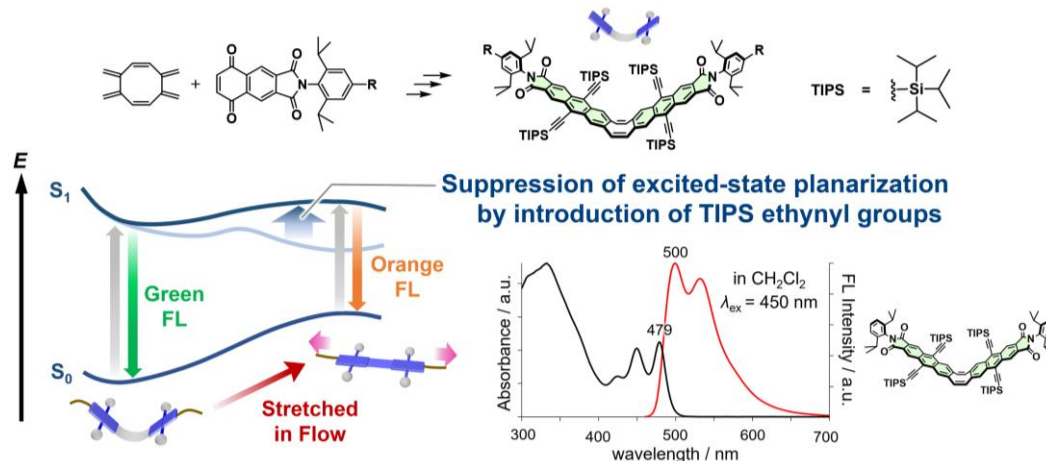
Fluorescent Force Probe for Real-time Imaging of Hydrodynamic Stress Field

(¹Graduate School of Science, Kyoto University, ²Graduate School of Engineering, Kyoto University) Sachika Akitomo,¹ Takuya Yamakado,¹ Hidetsugu Kitakado,¹ Ryo Kimura,¹ Reiko Kuriyama,² Kazuya Tatsumi,² Kazuyoshi Nakabe,² Shohei Saito¹

The conventional FLAP force probe requires the adjustment of solvent viscosity for visualizing hydrodynamic stress field, because the excited-state planarization occurs in the low-viscosity solvents even without stress. We designed a new FLAP molecule bearing TIPS ethynyl groups. The molecule is expected to suppress spontaneous planarization in the excited state, and therefore it will work as a force probe even in low-viscosity solvents. Here, we report synthesis and photophysical properties of this novel FLAP molecule.

Keywords : Fluorescent Force Probe; Excited State; Conformational Change; Polymer Solution; Hydrodynamic Stress Field

羽ばたく蛍光分子 FLAP は両翼の剛直な骨格と柔軟な 8π 系からなり、コンフォメーション変化に伴い、力に応答して二重蛍光を示す^{1,2}。この FLAP を高分子鎖に導入することで、高分子溶液の流れ場において伸長応力を可視化できる³。しかし従来の FLAP 骨格では、光励起状態における自発的な平面化のため、低粘度溶媒中では張力の有無によらず平面構造に起因する蛍光しか見られず、伸長応力評価のためには高粘度の溶媒を用いる必要があった。そこで、従来の FLAP のアントラセンイミド骨格に TIPS エチニル基を導入することで、励起状態平面化を抑制し⁴、低粘度の溶媒中でも伸長応力への応答が期待される新たな FLAP 骨格を設計・合成した。



[1] R. Kotani, S. Yokoyama, S. Nobusue, S. Yamaguchi, A. Osuka, H. Yabu, and S. Saito, *Nat. Commun.* **2022**, *13*, 303.

[2] T. Yamakado and S. Saito, *J. Am. Chem. Soc.* **2022**, *144*, 2804.

[3] 山本和佳, 栗山怜子, 北鹿渡秀嗣, 齊藤尚平, 巽 和也, 中部主敬, 流体力学会誌「ながれ」第40巻 (2021) 第6号 378 ページ.

[4] T. Yamakado, K. Otsubo, A. Osuka, and S. Saito, *J. Am. Chem. Soc.* **2018**, *140*, 6245.

[K703-1am] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Jumpei Taguchi, Yoshiaki Shoji

Wed. Mar 22, 2023 9:00 AM - 11:10 AM K703 (K703, Lecture Hall Bldg. [7F])

[K703-1am-01] Facile synthesis and evaluation of polyfluoroarylated anthracene derivatives via *regio*-selective cross-dehydrogenative C-H/C-H coupling reaction

○Ryota Sato¹, Junpei Kuwabara¹, Takeshi Yasuda², Takaki Kanbara¹ (1. Tsukuba Research Center for Energy Materials Science (TREMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 2. National Institute for Materials Science)

9:00 AM - 9:20 AM

[K703-1am-02] Synthesis of a NHC-Coordinated Germylene with a Biphenylene Unit

○Shogo Morisako¹, Takahiro Sasamori¹ (1. Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Sciences (TREMS), Univ. of Tsukuba)

9:20 AM - 9:40 AM

[K703-1am-03] Comparison of structures, optical properties, and reactivity between linear and cyclic disilane-bridged trimeric framework

○Yoshinori Yamanoi¹, Teppei Yamada¹ (1. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[K703-1am-04] Iron-Catalyzed C–O Activation/Tandem Tetra-annulation for Synthesis of Carbon-bridged Oligo-(p-arylenevinylene)

○MENGQING CHEN¹, Rui Shang¹, Eiichi Nakamura¹ (1. The Univ. of Tokyo)

10:10 AM - 10:30 AM

[K703-1am-05] Spiro-conjugated 1,4-Dihydropentalenes: Short-step Synthesis by Iron-catalysis and Materials Properties.

○Aziz Khan¹, Mengqing Chen¹, Rui Shang¹, Eiichi Nakamura¹ (1. The University of Tokyo)

10:30 AM - 10:50 AM

[K703-1am-06] Cationic Indium Catalyzed C-O Bond Formation Reaction

○Mitsuhiro Yoshimatsu¹, Manoka Kikuchi¹, Rintaro Saito¹, Hiroki Goto¹ (1. Department of Chemistry, Faculty of Education, Gifu University)

10:50 AM - 11:10 AM

位置選択的脱水素型 C-H/C-H クロスカップリング反応による polyfluoroarylated anthracene 誘導体の簡便合成と機能評価

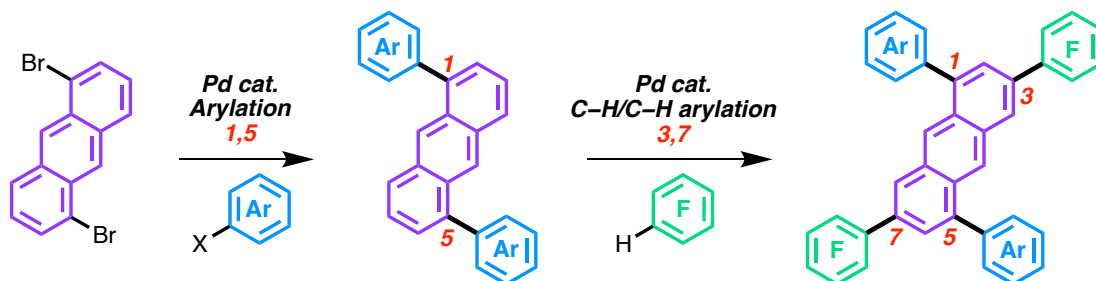
(筑波大院数理物質 TREMS¹・物質・材料研究機構 NIMS²) ○佐藤 亮太¹・桑原 純平¹・安田 剛²・神原 貴樹¹

Facile synthesis and evaluation of polyfluoroarylated anthracene derivatives via *regio*-selective dehydrogenative C-H/C-H cross-coupling reaction (¹TREMS, Univ. of Tsukuba, ²NIMS, National Institute for Materials Science) ○Ryota Sato,¹ Junpei Kuwabara,¹ Takeshi Yasuda,² 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. Recently, we developed a CDC reaction between polyfluoroarene and simple acene with unique regio-selectivity, which proceeded at sterically vacant positions. [1] We envisioned that multiple arylated acenes could be synthesized by combining this unique regio-selective CDC reaction with conventional cross-coupling reactions in a complementary manner. In this presentation, we show that this protocol can easily introduce different aryl groups into anthracene. Their basic properties and electroluminescent properties were evaluated. In addition, we will also show the semiconducting properties of the anthracene derivatives synthesized so far.

Keywords : Cross-dehydrogenative coupling reaction; Palladium catalyst; C-H bond activation reaction; Anthracene; 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、簡便合成の有力な反応である。最近我々は、polyfluoroarene と単純な acene の CDC 反応が一般的な Pd 触媒による C-H 結合切断とは異なり、立体的に空いた位置で選択的に反応することを見出した。[1] この特殊な位置選択的 CDC 反応を従来法のクロスカップリング反応と相補的に組み合わせることで、複雑な multiple arylated acene が合成できると考えた。本研究では、1,5-dibromoanthracene を出発原料に、従来法と CDC 反応により異なる aryl 基を簡便かつ精密に導入できることを明らかにした。さらに、それらの基礎特性や有機 EL 特性等を評価した。併せて、これまで合成した polyfluoroarylated anthracene 誘導体の半導体特性についても紹介する。



[1] R. Sato, T. Iida, T. Kanbara, and J. Kuwabara, *Chem. Commun.* **2022**, 58, 11511–11514.

NHCが配位したビフェニレン置換ゲルミレンの合成

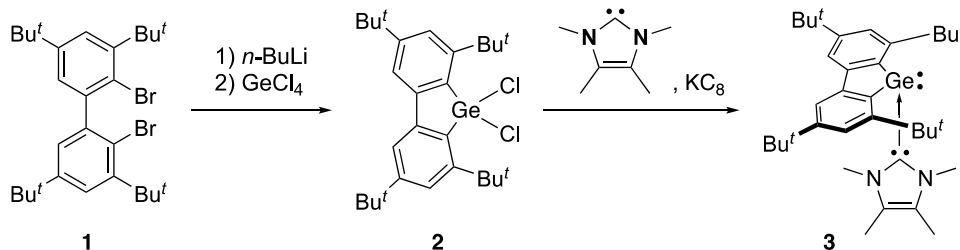
(筑波大数理物質¹・TREMS²) ○森迫 祥吾^{1,2}・笹森 貴裕^{1,2}

Synthesis of a NHC-Coordinated Germylene with a Biphenylene Unit (¹ Faculty of Pure and Applied Sciences, Univ. of Tsukuba, ²TREMS, Univ. of Tsukuba,) ○Shogo Morisako,^{1,2} Takahiro Sasamori^{1,2}

Carbenes, divalent two-coordinated carbon chemical species, have a wide variety of uses in organic chemistry field. A germylene, a heavier analogue of a carbene, should exhibit the singlet ground state with a lone-pair and an empty 4p orbital, which cause its nucleophilic and electrophilic characters. Especially, aryl-substituted germylenes are known to be highly reactive enough to cleave σ -bond of a hydrogen molecule and thus expected to be effective small molecule activator. We have previously reported the generation of a biphenylene-substituted germylene at low temperature, which underwent facile dimerization to give the spirogermabifluorene derivative as a final product. In this study, we aimed to isolate the biphenylene-substituted germylene as a *N*-heterocyclic carbene (NHC) coordinated complex. Dichlorogermene **2** was prepared by dilithiation of **1** followed by the reaction with GeCl_4 . The NHC-coordinated germylene **3** was generated by the reduction of **2** in the presence of NHC. Herein, we will report the details of the synthesis and reactivity of **3**

Keywords : Germylene; Germanium; Biphenylene; Metallylene

二価二配位炭素化学種であるカルベンの高周期類縁体であるゲルミレンは、一般的に基底一重項状態をとり、その孤立電子対と空の 4p 軌道に由来する求核性と求電子性を併せ持つことが知られている。アリール置換ゲルミレンは、水素分子の σ 結合を切断するほどの高い反応性を示し¹⁾、小分子変換反応への応用が期待されている。既に我々は、かさ高いビフェニレン置換ゲルミレンが低温条件下で発生することを報告しているが、室温では二量化を経て、対応するスピロゲルマビフルオレン誘導体を与える²⁾。本研究では、*N*-ヘテロサイクリックカルベン (NHC) の配位による熱力学的安定化を活用して、ゲルミレン-NHC 錯体の合成を検討した。まず、ジブロモビフェニル **1** のジリチオ体と GeCl_4 との反応により、ジクロロゲルマン **2** を合成した。NHC 存在下、化合物 **2** を還元することで目的の NHC 配位ゲルミレン **3** を単離した。現在、ゲルミレン **3** の反応性についても調査しており、合わせて報告する。



(1) Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fetting, S. Nagase, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 16272–16282. (2) S. Morisako, K. Noro, T. Sasamori, *Inorganics* **2021**, *9*, 75.

直鎖状および環状ジシラン架橋三量体の構造、光学特性、反応性の比較

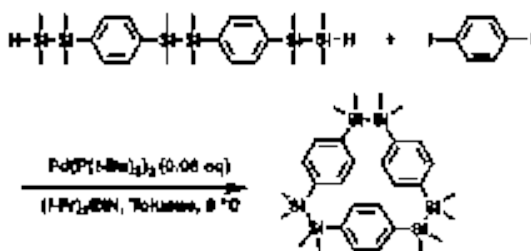
(東大院理) 山野井慶徳・山田鉄兵

Comparison of Structures, Optical Properties, and Reactivity of Linear and Cyclic Disilane-Bridged Trimers (*School of Science, The University of Tokyo*) Yoshinori Yamanoi, Teppei Yamada

Organosilicon compounds are widely used in light-emitting materials and pharmaceuticals. Compounds incorporating disilane bridges in their molecular structures are linked by conjugation between the overlapping π orbitals of the aromatic ring moiety and the σ orbitals of the disilane moiety (σ - π conjugation). The incorporation of σ - π conjugation results in a bulky and flexible backbone, which is expected to exhibit physical properties different from those of conventional compounds with a C=C backbone. Since the dimer and tetramer of the disilane-bridged cyclic dimer have already been reported, the trimer has not yet been reported. We synthesized a disilane-bridged cyclic trimer (c-Ph3) and a disilane-bridged linear trimer (l-Ph3) for comparison, and measured the optical properties of these compounds. AgSbF₆ was added to these compounds, and the complex formation was confirmed by NMR, UV-vis, and mass spectrometry.

Keywords : Organosilane; Complexation; Photoluminescence

有機ケイ素化合物は発光材料や医薬品などで幅広く用いられている。分子構造にジシラン架橋を導入した化合物は芳香環の π 軌道とジシランの σ 軌道の重なりによって共役を形成する (σ - π 共役)。 σ - π 共役は嵩高く柔軟な骨格を持つので、従来の C=C 骨格を持つ化合物とは異なった物性を示すことが期待されている。ジシラン架橋環状体のうち 2 量体と 4 量体は既に論文化しているが、3 量体はまだ報告されていない。今回はジシラン架橋環状 3 量体(c-Ph3)を下図のように合成した。また、比較対象としてジシラン架橋直鎖 3 量体(l-Ph3)を合成し、光学物性を測定した。さらに、AgSbF₆ を加え、錯体形成する様子を NMR、UV-vis、質量分析で確認した。



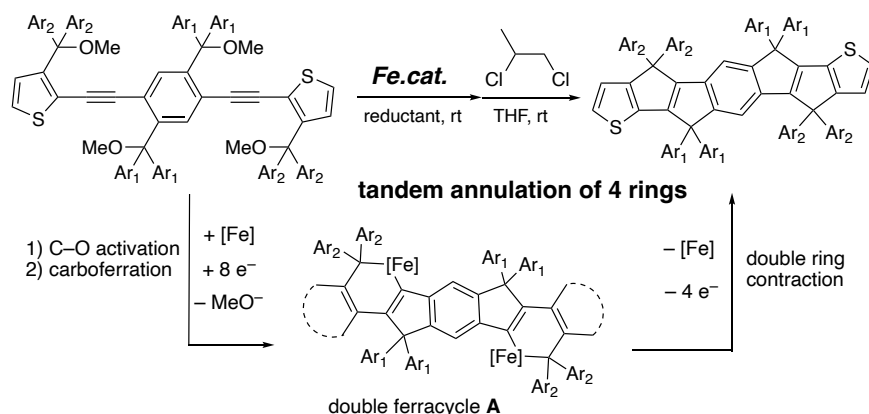
- 1) Omoto, K.; Nakae, T.; Nishio, M.; Yamanoi, Y.; Kasai, H.; Nishibori, E.; Mashimo, T.; Seki, T.; Ito, H.; Nakamura, K.; Kobayashi, N.; Nishihara, H. *J. Am. Chem. Soc.* **2020**, *142*, 12651–12657.
- 2) Shimada, M.; Yamanoi, Y.; Ohto, T.; Pham, S.-T.; Yamada, R.; Tada, H.; Omoto, K.; Tashiro, S.; Shionoya, M.; Hattori, M.; Jimura, K.; Hayashi, S.; Koike, H.; Iwamura, M.; Nozaki, K.; Nishihara, H. *J. Am. Chem. Soc.* **2017**, *139*, 11214–11221.

Iron-Catalyzed C–O Activation/Tandem Tetra-annulation for Synthesis of Carbon-bridged Oligo-(p-arylenevinylene)

(Department of Chemistry, Graduate School of Science, The University of Tokyo) ○Mengqing Chen, Rui Shang, Eiichi Nakamura

Keywords: Iron; Tetra-annulation; Carbon-bridged Oligo-(p-arylenevinylene)

Carbon bridging in the form of a strained 1,4-dihydropentalene framework, effectively flattening and stabilizing oligophenylenevinylene systems, is useful for the development of optoelectronic materials.¹ The typical rigid and planar 1,4-dihydropentalene framework was accessed using lithiation and Friedel-Crafts reaction, limiting the synthetic modularity.² due to the involving a strong carbon nucleophile and carbenium intermediate susceptible for cationic rearrangement. We reported an iron-catalyzed single-pot tandem cyclization of a diarylacetylene into 1,4-dihydropentalene in high yield using a catalytic amount of $\text{FeCl}_2/\text{PPh}_3$ as a catalyst, Mg/LiCl as a mild reductant after sequential addition of 1,2-dichloropropane as a mild oxidant.³ Herein, we report the design and synthesis of conjugated dithiophenes of the highest HOMO level among known conjugated dithiophenes using iron-catalyzed tandem tetra-cyclization strategy. These bithiophenes made are expected to be applied to construct donor-acceptor-type small molecule and conjugated polymeric materials of narrow optical gaps.



1) Tsuji, H.; Nakamura, E. *Acc. Chem. Res.* **2019**, *52*, 2939–2949. 2) a) Zhu, X.; Tsuji, H.; Navarrete, J. T. L.; Casado, J.; Nakamura, E. *J. Am. Chem. Soc.* **2012**, *134*, 10254–10259. b) Lu, H.; Nakamuro, T.; Yamashita, K.; Yanagisawa, H.; Nureki, O.; Kikkawa, M.; Gao, H.; Tian, J.; Shang, R.; Nakamura, E. *J. Am. Chem. Soc.* **2020**, *142*, 18990–18996. 3) M. Chen, W. Sato, R. Shang, E. Nakamura. *J. Am. Chem. Soc.* **2021**, *143*, 6823–6828.

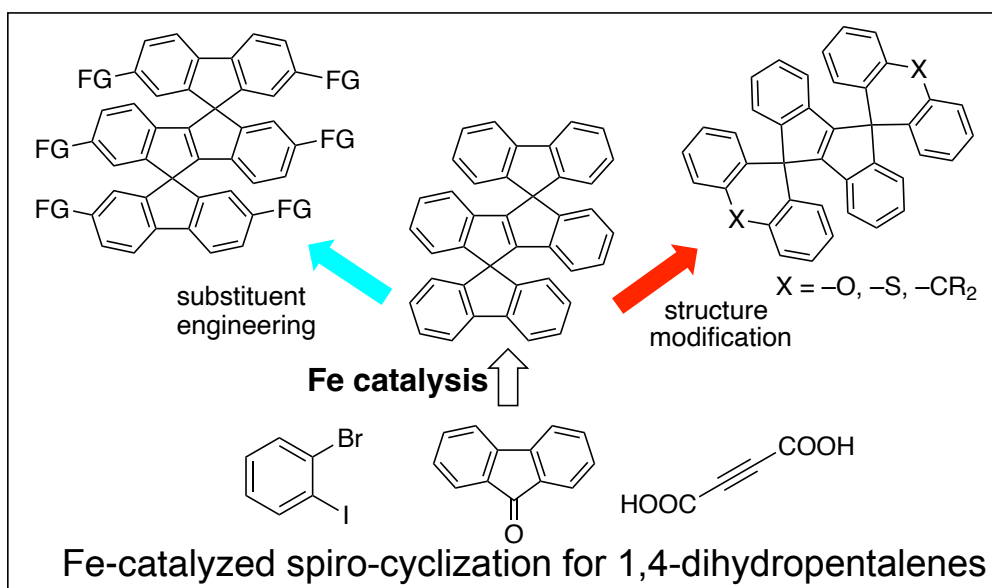
Spiro-conjugated 1,4-Dihydropentalenes: Short-step Synthesis by Iron-catalysis and Materials Properties

(¹Molecular Technology Innovation, Department of Chemistry, Graduate School of Science, The University of Tokyo)

○Aziz Khan,¹ Mengqing Chen,¹ Rui Shang,¹ and Eiichi Nakamura¹

Keywords: Iron-catalysis, spiro-conjugation, 1,4-dihydropentalenes, annulation, electronic materials

The spiro-conjugated systems attract considerable attention from both synthetic and material chemists for their structural novelty and desired properties as optoelectronic materials. However, the synthetic incorporation of stimuli-responsive vinylene moieties into spiro-conjugated systems is challenging due to cationic rearrangement in established synthetic routes. Herein, we designed and synthesized a series of pure hydrocarbon spiro-conjugated 1,4-dihydropentalene systems incorporating highly strained vinylene moiety by utilizing the iron-catalyzed tandem cyclization approach. The new spiro-conjugated 1,4-dihydropentalenes showed promising optoelectronic properties and high stability in both solution and their film states, indicating their promising application as host and charge transporting materials for organic electronic devices. Introducing donor and acceptor functionalities on the spiro-conjugated 1,4-dihydropentalene system, and synthetically doping them with heteroatoms are expected to facilitate the development of electronic materials for light-emitting and charge transport.



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- 1) M. Chen, W. Sato, R. Shang, E. Nakamura, *J. Am. Chem. Soc.*, **2021**, *143*, 6823.
- 2) H. Hamada, Y. Itabashi, R. Shang, E. Nakamura, *J. Am. Chem. Soc.*, **2020**, *142*, 2059.
- 3) H. Hamada, T. Nakamuro, K. Yamashita, H. Yanagisawa, O. Nureki, M. Kikkawa, K. Harano, R. Shang, E. Nakamura, *BCSJ*, **2020**, *93*, 776.

カチオン性インジウムを用いた炭素－酸素結合形成反応

(岐阜大教) ○吉松三博・菊地真歌・齋藤麟太郎・後藤弘樹

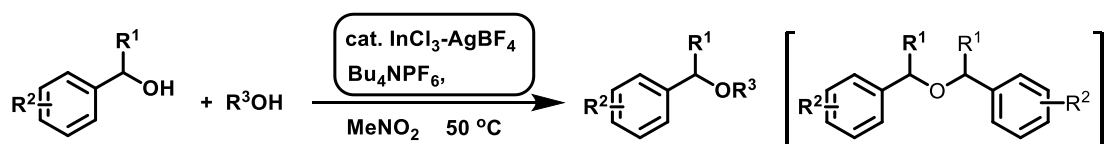
Cationic Indium Catalyzed C–O Bond Formation Reaction (¹*Department of Chemistry, Faculty of Education, Gifu University*) ○Mitsuhiro Yoshimatsu, Manoka Kikuchi,¹ Rintaro Saito, Hiroki Goto

Previously, we reported the cationic indium catalyzed C–C bond formation reaction of propargyl alcohols with some aromatics. In this presentation, we will report the C–O bond formation of some benzyl alcohols, not propargyl alcohols. The cationic indium catalyzed C–O bond formation of some alcohols proceeded via the bimolecular dehydration process to give the unsymmetrical ethers in good yields.

Keywords : Indium; C–O bond formation; Ether; Carbocation

アルコールの脱水過程は水のみが副生する最も環境にやさしい化学プロセスである。近年、アルコールの脱水過程を利用した C–C、C–O、C–N 結合形成反応の開発が積極的に進められている。特に、C–O 結合形成過程は天然物や医薬品などの合成において、極めて重要なプロセスである。しかし、強力な脱水剤となる触媒の開発と共に、異なるアルコール間から非対称エーテルの構築を如何に選択的に進めるかという課題¹がある。近年我々は、カチオン性インジウム触媒を利用したプロパルギルアルコールの C–C および C–O 結合形成反応を報告²⁾した。本反応は、強力なルイス酸であるカチオン性インジウムの働きと中間でエーテルを介することで、今まで不安定で発生が困難であった α 位にアルキル基が置換したプロパルギルカチオンの発生とその求核付加反応の開発に成功した。この発見によって、様々な α -アルキル置換プロパルギル化合物が良好に得られるようになった。今回我々は、この触媒系をアルキンのないより一般的なアルコールを用いた C–O 形成反応に利用することを計画した。

基質として 1 等量の 1-フェニルエタノールに対して 5 等量の 1-ヘキサノールを選択し、以前の触媒系である 0.2 等量のインジウムクロリドと 0.4 等量の過塩素酸銀をニトロメタン溶媒中にて反応を行ったところ、(1-(hexyloxy)ethyl)benzene が収率 69% で得られた。同一分子から成るエーテルの生成は認められなかった。条件を精査して、銀としてテトラフルオロボラート塩、反応温度は 50°C が適当であり、その収率は 84% まで上昇した。様々な基質を選択し、C–O 結合形成過程の一般性を確認した。



1) Aryl boronic acid catalyzed dehydrative substitution of benzylic alcohols. S. Estopina-Duan, L. J. Donnelly, E. B. Mclean, B. M. Hockin, A. M. Z. Slawin, J. E. Taylor, *Chem. Eur. J.* **2019**, 25, 3950; 2) M. Yoshimatsu et al., 有機典型元素化学討論会, 2022.

[K703-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Shogo Morisako, Yoshinori Yamanoi

Wed. Mar 22, 2023 1:50 PM - 3:40 PM K703 (K703, Lecture Hall Bldg. [7F])

- [K703-1pm-01] Development of synthetic methodology for AB₂-type arsines and investigation of catalytic activity utilizing arsa-Buchwald ligands.
○Akifumi Sumida¹, Kenta Ogawa¹, Hiroaki Imoto¹, Kensuke Naka¹ (1. Kyoto Institute of Technology)
1:50 PM - 2:10 PM
- [K703-1pm-02] Emission properties of Eu(III) nitrate complexes bearing arsine oxides
○Toshiki Fujii¹, Yuichi Kitagawa², Yasuchika Hasegawa², Hiroaki Imoto¹, Kensuke Naka¹ (1. Grad. Sch. of Sci. and Tec., Kyoto Inst. of Tech., 2. WPI-ICReDD and Fac. of Eng., Hokkaido Univ.)
2:10 PM - 2:30 PM
- [K703-1pm-03] Development of Catalytic Arsa-Wittig Reaction and Design Strategy of Arsenic Catalysts
○Ryoto Inaba¹, Junya Yukiyasu¹, Takashi Yumura¹, Hiroaki Imoto¹, Kensuke Naka¹ (1. Kyoto Institute of Technology)
2:30 PM - 2:50 PM
- [K703-1pm-04] Development of Iridium-Catalyzed C(sp³)-C(sp²) [1,5]-Silyl Rearrangement Reaction
○Jiawei Qiu¹, Tsuyoshi Matsuzaki¹, Makoto Sako¹, Kenichi Murai¹, Junichi Uenishi¹, Kazushi Mashima¹, Takeyuki Suzuki¹, Mitsuhiro Arisawa¹ (1. Osaka University)
3:00 PM - 3:20 PM
- [K703-1pm-05] Design and Synthesis of Spliceostatin A Derivatives: Structure-Activity Relationship Study related to Enone moiety of Spliceostatin A
○Satoru Hirabayashi¹, Noriko Ohta¹, Yuko Tsuyuguchi¹, Yue Li¹, Yusuke Yoshikawa¹, Banzhong Lin¹, Megumi Fumimoto¹, Junichi Haruta¹, Makoto Sako¹, Kenichi Murai¹, Keisuke Nimura¹, Mitsuhiro Arisawa¹ (1. The Univ. of Osaka)
3:20 PM - 3:40 PM

AB₂ 型ヒ素化合物の合成法の開拓及び arsa-Buchwald 配位子を用いた触媒活性の調査

(京工繊大院工芸) ○隅田 滉史・小川 健太・井本 裕顕・中 建介

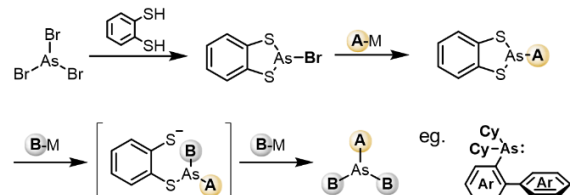
Development of synthetic methodology for AB₂-type arsines and investigation of catalytic activity utilizing arsa-Buchwald ligands. (Graduate School of Science and Technology, Kyoto Institute of Technology) ○Akifumi Sumida, Kenta Ogawa, Hiroaki Imoto, Kensuke Naka

The palladium catalyzed cross-coupling reactions are widely used in various fields, and ligands are one of the most important factors for activity and selectivity. Today, the mainstream of the ligands is organophosphorus. On the other hand, some organoarsenic ligands show higher activity and selectivity in some reactions compared with organophosphorus ones. However, there are few reports of arsine ligands, which are attributed to their synthetic methods. Herein, we have developed the efficient synthetic methodology for AB₂-type organoarsenic to construct the arsine ligand library. In addition, we synthesized novel arsa-Buchwald ligands with various alkyl substituents and screened arsa-Buchwald ligands by applying them for Suzuki-Miyaura coupling reaction. Finally, we investigated the substrate scope for various aryl halides and boronic acids and evaluated steric/electronic properties of some arsa-Buchwald ligands.

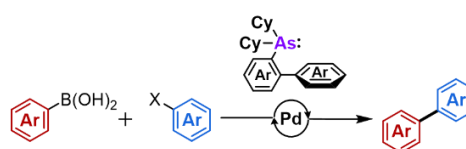
Keywords : Organoarsenic compound, AB₂-type ligand, palladium catalyst, Buchwald ligand, Suzuki-Miyaura cross-coupling

金属触媒によるカップリング反応は様々な分野において重要な反応であり、配位子は反応性や選択性を決定する重要な要素の一つである。現在の主流はリン配位子であり盛んに研究が行われている¹。一方でヒ素配位子はリン配位子よりも高活性²、高選択的な触媒能を示す例が報告されている。このように配位子としての可能性を秘めているのにも関わらず、優れたヒ素配位子の報告例は極めて少ない。これはヒ素化合物の合成を行う上で危険な前駆体を用いる必要があり、合成法が制限されていたからである。そこで本研究では AsBr₃ に対して benzenedithiol を導入することで得られる、bromo-benzodithiaarsole を用いることで高効率な AB₂ 型ヒ素配位子の合成法の開発を行った。この合成法を利用し種々の電子リッチな AB₂ 型ヒ素配位子ライブラリーの構築に成功した。またこの反応を利用して合成した Buchwald 配位子のヒ素類縁体を鈴木宮浦カップリングに適用しスクリーニングすることで、適したヒ素配位子を見出した。またこの配位子を用いて様々な基質での活性を調査した。さらに計算科学によって arsa-Buchwald 配位子の立体・電子的な特性について解明した。

Synthetic scheme



Suzuki-Miyaura cross-coupling



- 1) R. J. Lundgren, M. Stradiotto, *Chem. Eur. J.*, **2012**, 18, 9758. 2) V. Farina, B. Krishnan, *J. Am. Chem. Soc.*, **1991**, 113, 9585.

有機ヒ素化合物を有する硝酸ユウロピウム錯体の発光特性

(京工繊大院工芸¹・北大 WPI-ICReDD、北大院工²) ○藤井 俊樹¹・北川 裕一²・長谷川 靖哉²・井本 裕顕¹・中 建介¹

Emission properties of Eu(III) nitrate complexes bearing arsine oxides (¹*Grad. Sch. of Sci. and Tec., Kyoto Inst. of Tech*, ²*WPI-ICReDD and Fac. of Eng., Hokkaido Univ.*) ○Toshiki Fujii¹, Yuichi Kitagawa², Yasuchika Hasegawa², Hiroaki Imoto¹, Kensuke Naka¹

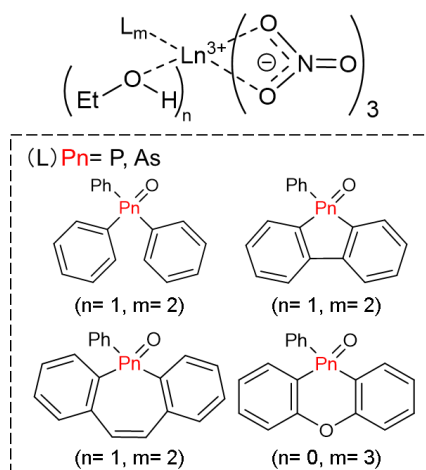
A europium (Eu³⁺) complex exhibits red luminescence with small FWHM through photosensitized energy transfer from antenna ligands. In the development of luminescent Eu³⁺ complex, the design of antenna ligand has an important role. Phosphine oxide is a typical motif of antenna ligand due to the wide selection of the aryl substitutes. On the other hand, the emission properties of Eu³⁺ complex with arsine oxides have not been studied in detail.

In this study, we synthesized Eu³⁺ complexes with arsine oxides. The Eu³⁺ complexes with arsine oxides exhibited higher photosensitization efficiency and emission intensity of the electric dipole moment than the phosphine analogues. According to experimental and theoretical investigations, the heavy atom effect and high atomic polarizability of arsenic enhanced emission properties of Eu³⁺ complexes. In addition, the annulation structures affected the emission properties of the Eu³⁺ complexes.

Keywords : *Organoarsenic compound; Europium; Photosensitization; Heavy atom effect; Phosphine*

ユウロピウム(Eu³⁺)錯体は、アンテナ配位子からの光増感エネルギー移動により半値幅が小さい赤色発光を示す。発光性 Eu³⁺錯体の開発においては、光増感エネルギー移動に関与するアンテナ配位子の設計は重要な役割を担う。配位子設計の中で、アリール置換基の幅広い設計による Eu³⁺錯体の高効率発光を実現できることから、ホスフィンオキシドは代表的なアンテナ配位子である。一方、アルシンオキシド含有 Eu³⁺錯体は、発光特性に関する詳細な研究例がない。

本研究では、アルシンオキシド含有 Eu(NO₃)₃ 錯体を合成し、ヒ素の特徴がもたらす Eu³⁺錯体の発光特性への影響について明らかにした。それぞれの Eu³⁺錯体の発光特性を評価した結果、ヒ素を用いた場合、リンに比べ高い光増感エネルギー移動効率および電気双極子の高い発光強度を示した。そして理論計算および各種光学測定機器より、ヒ素の重原子効果と高い分極率により発光特性が向上したことを解明した¹⁾。さらに、新たに合成した縮環型配位子の π 共役系骨格によって Eu³⁺錯体の発光特性が大きく変化した^{1b)}。



1) (a) T. Fujii, Y. Kitagawa, Y. Hasegawa, H. Imoto, K. Naka, *Inorg. Chem.* **2021**, *60*, 8605. (b) T. Fujii, Y. Kitagawa, Y. Hasegawa, H. Imoto, K. Naka, *Inorg. Chem.* **2022**, *61*, 17762.

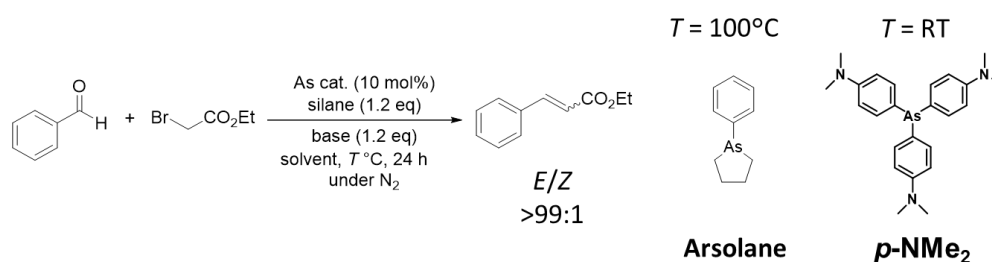
触媒的 arsa-Wittig 反応の開発とヒ素触媒の設計戦略

(京工繊大院工芸) ○稲葉 凌斗・行安 純哉・湯村 尚史・井本 裕顕・中 建介
 Development of Catalytic Arsa-Wittig Reaction and Design Strategy of Arsenic Catalyst
 (Grad. Sch. of Sci. and Tech., Kyoto Inst. of Tech.) ○Ryoto Inaba, Junya Yukiyasu, Takashi Yumura, Hiroaki Imoto, Kensuke Naka

Catalytic Wittig reaction is one of the most famous reactions for the formation of carbon-carbon double bonds. The concept of catalytic Wittig reaction is that the produced phosphine oxide is selectively reduced in situ by using silane as a reducing agent. This reaction has two problems. One is the limitation of skeleton of phosphine catalyst to react catalytically. The other is difficulty to control *E/Z* selectivity. On the other hand, arsa-Wittig reaction has excellent *E*-selectivity compared with catalytic Wittig reaction. In this work, we synthesized arsolane as a catalyst, and conducted DFT calculations to reveal the difference in *E/Z* selectivity between phosphorus and arsenic catalysts. Moreover, we designed arsenic catalyst (*p*-NMe₂) to achieve room temperature catalytic arsa-Wittig reaction with excellent *E*-selectivity.

Keywords : Wittig reaction; Organoarsenic chemistry

触媒的 Wittig 反応はカルボニル化合物と有機ハロゲン化物からアルケンを合成する非常に有用な反応として知られている。この反応は副生するホスフィンオキシドを効率的に還元することで触媒的に進行させることに成功した。しかし、そのためにはリン触媒を環骨格にする必要があるという骨格上の制限がある。それに加えこの反応は *E/Z* 選択性が温度に強く依存し制御が困難である。一方、ヒ素に変えた arsa-Wittig 反応はリンに比べ高い *E* 体選択性を示すことが知られている。本研究では、リン触媒にならって環骨格を有するヒ素触媒を合成し、リンとヒ素での選択性の違いを計算により明らかにした。更に、環状に縛られないヒ素触媒ならではの設計を行うことで室温で高効率・高選択的に反応を進行させることを達成した(Scheme 1)。



Scheme 1. Catalytic arsa-Wittig reaction

- 1) R. Inaba, I. Kawashima, T. Fujii, T. Yumura, H. Imoto, K. Naka *Chem. Eur. J.* **2020**, 26, 13400-13407.
- 2) J. Yukiyasu, R. Inaba, T. Yumura, H. Imoto, K. Naka *Org. Chem. Front.* **2022**, 9, 6786-6794.

イリジウム触媒を用いる C(sp³)-C(sp²)[1,5]-シリル転位反応の開発

(阪大院薬¹・阪大産研²) ○仇 稼イ¹・松崎 剛²・佐古 真¹・村井 健一¹・上西 潤一¹・真島 和志¹・鈴木 健之²・有澤 光弘¹

Development of Iridium-Catalyzed C(sp³)-C(sp²) [1,5]-Silyl Rearrangement Reaction (¹Graduate School of Pharmaceutical Sciences, Osaka University, ²SANKEN, Osaka University) ○Jiawei Qiu,¹ Tsuyoshi Matsuzaki,² Makoto Sako,¹ Kenichi Murai,¹ Junichi Uenishi,¹ Kazushi Mashima,¹ Takeyuki Suzuki,² Mitsuhiro Arisawa¹

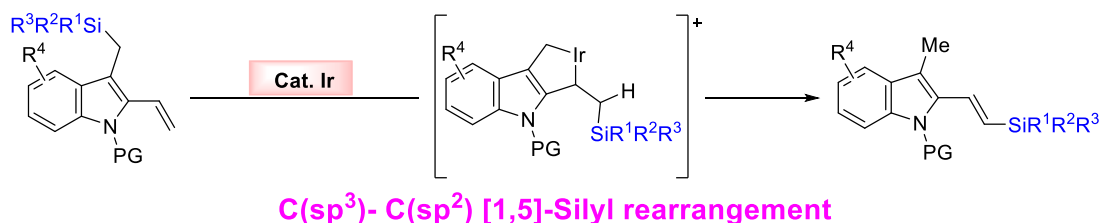
Silyl rearrangement reactions have attracted attention in recent years that easily construct new bonds (e.g., O-Si bonds and C-Si bonds). The most frequently reported example of silyl rearrangement reaction is Brook rearrangement. The driving force of this reaction is attributed to big difference between Si-O and Si-C bond energies (about 269 kJ/mol). On the other hand, more useful silyl rearrangement reaction to form new C-Si bond is still difficult and unexplored.

Here, we have developed Iridium-catalyzed C(sp³)-C(sp²) [1,5]-silyl rearrangement reaction using 2-vinyl-3-silylmehtyl heterocyclic compounds as substrates. This reaction shows high novelty due to its silyl rearrangement from C(sp³) to C(sp²) and long-range 1,5-migration, which is considered difficult. Also, it is worth noting that this reaction is a new example using an iridium catalyst [IrCl(cod)]₂.

Keywords : Silyl Rearrangement; Heterocyclic Aromatic Compound; 1,5-Migration

シリル基転位反応は、新しい結合（例えば、酸素—ケイ素結合と炭素—ケイ素結合など）形成反応として近年注目を集めている。シリル基転位反応における一番多い報告例は、ブルック転位を代表とする炭素から酸素へのシリル基転位である¹⁾。この反応の駆動力はケイ素—酸素結合とケイ素—炭素結合のエネルギー差(269kJ/mol)に起因しており、熱力学的支配の生成物が得られる。一方、シリル基転位反応による炭素—ケイ素の形成反応は、未開拓な状況である。

今回我々は、2-ビニル-3-シリルメチル芳香族ヘテロ環化合物とイリジウム触媒を用いるシリル基の C(sp³)-C(sp²)[1,5]-転位反応を見出した。本反応は sp³ 炭素から sp² 炭素へのシリル基転位であることと、困難とされている長距離[1,5]位のシリル基転位反応であることから、新規性の高い反応である。本反応がイリジウム触媒[IrCl(cod)]₂を用いる新しい反応例であることは特筆に値する。



PG = Ts, Ms, etc. R¹ or R² or R³ = Me, Ph, Bn, etc. R⁴ = H, Me, Cl, CF₃, F, etc.

1) For review, see: N. Lee, C. Tan, D. Leow, *Asian J. Org. Chem.* **2019**, 8, 25-31.

Spliceostatin A 誘導体の設計と合成： エノン部位に関する構造活性相関研究

(阪大院薬¹・阪大院医²) ○平林 怜¹・太田 徳子²・露口 結子¹・Yue Li²・吉川 祐介¹・Bangzhong Lin¹・文元 めぐみ¹・春田 純一¹・佐古 真¹・村井 健一¹・二村 圭祐²・有澤 光弘¹

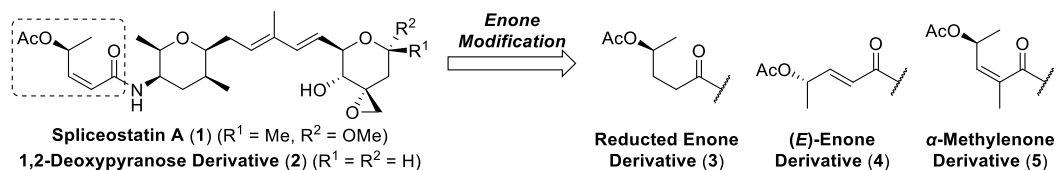
Design and Synthesis of Spliceostatin A Derivatives: Structure-Activity-Relationship Study related to Enone moiety of Spliceostatin A (¹Graduate School of Pharmaceutical Sciences, Osaka University, ²Graduate School of Medicine, Osaka University) ○Satoru Hirabayashi¹, Noriko Ohta², Yuko Tsuyuguchi¹, Yue Li², Yusuke Yoshikawa¹, Banzhong Lin¹, Megumi Fumimoto¹, Junichi Haruta¹, Makoto Sako¹, Kenichi Murai¹, Keisuke Nimura², Mitsuhiro Arisawa¹

Prostate cancer is one of the most frequently detected cancers in men. Especially, in case of developing into castration-resistant prostate cancer (CRPC), there are no effective therapy, so drug development for the treatment of CRPC is important. Recently, we found that Spliceostatin A (**1**) exhibits the CRPC proliferation inhibition activity. However, *in vivo* toxicity studies in normal mice showed that **1** caused mouth death within 12 h of administration. To reduce the toxicity of **1**, we successfully synthesized an acid-stable derivative (**2**) and succeeded in attenuating the toxicity compared to **1** based on *in vivo* toxicity studies using normal mice. In this study, to investigate the importance of enone moiety of **1** for the CRPC proliferation inhibitory activity, we designed and synthesized three novel derivatives (**3-5**). As a results of biological evaluation, the proliferation inhibitory activity of those derivatives (**3-5**) was lost. Furthermore, as a results of metabolic stability tests, it is found that the geometrical isomerism of enone moiety of **1** made the differential selectivity of human or mouse CYP.

Keywords : Castration-Resistant Prostate Cancer; Spliceostatin A; Structure-Activity Relationship Study

前立腺がんは、男性がんの中で最も罹患率が高い。特に、従来の薬剤が効果を示さない去勢抵抗性前立腺がん（CRPC）に進行した場合、有効な治療法はないため、新規薬剤開発が望まれる。最近、我々は Spliceostatin A (**1**) が CRPC 増殖抑制活性を示すことを見出している。しかしながら、*wild type* のマウスを用いた **1** の *in vivo* 毒性試験では、12 時間位以内にマウスが死亡する毒性が確認された¹⁾。この毒性を減弱化すべく、**1** の酸に安定な誘導体 **2** の合成に成功しており²⁾、**1** と比較して *in vivo* 毒性試験においてマウスが死亡する毒性は観測されなかった。

本研究では、CRPC 増殖抑制活性における **1** のエノン部位の重要性を調査すべく、3 つのエノン誘導体 (**3-5**) を設計・合成した。誘導体 (**3-5**) の活性評価試験の結果、CRPC 増殖抑制活性は消失した。さらに、代謝安定性試験の結果、**1** のエノン部位の幾何異性がヒトおよびマウス CYP の種差選択性を生み出すことが明らかとなった。



1) *Cancer Res.* **2019**, *79*, 5204-5217., 2) *ACS Med. Chem. Lett.* **2020**, *11*, 1310-1315.

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

[K703-1vn] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Akihito Konishi, Kento Iwai

Wed. Mar 22, 2023 4:10 PM - 5:30 PM K703 (K703, Lecture Hall Bldg. [7F])

[K703-1vn-01] Thermal Cyclization of Linear Arylalkynes Facilitated by Folding inside a Molecular Cage

[○]Georgi Rosenov Genov¹, Hiroki Takezawa¹, Harumi Hayakawa¹, Makoto Fujita^{1,2} (1. University of Tokyo, 2. Institute for Molecular Science)

4:10 PM - 4:30 PM

[K703-1vn-02] TEtraQuinoline (TEQ) and Other Cyclic Quinoline Oligomers, a New Family of Macrocycles

[○]Wei Xu¹, Haru Nonaka¹, Ryota Yagami¹, Mizuki Nishiwaki¹, Ayami Takeda¹, Naoya Kumagai^{1,2} (1. Keio University, 2. Institute of Microbial Chemistry)

4:30 PM - 4:50 PM

[K703-1vn-03] Novel synthesis of multi-substituted quinoline derivatives using alkylidenemalononitriles and unsaturated aldehydes by organocatalyst

[○]Xiaolei Han¹, Naoki Mori¹, Yujiro Hayashi¹ (1. Tohoku Univ.)

4:50 PM - 5:10 PM

[K703-1vn-04] Intramolecular Cyclization Reactions of Arylpropargyl Amides of Electron-deficient α, β -Alkenyl Carboxylates

[○]Zhichao Wang¹, Shoko Yamazaki², Tsumoru Morimoto³, Akiya Ogawa¹ (1. Osaka Metropolitan University, 2. Nara University of Education, 3. NARA Institute of Science and Technology)

5:10 PM - 5:30 PM

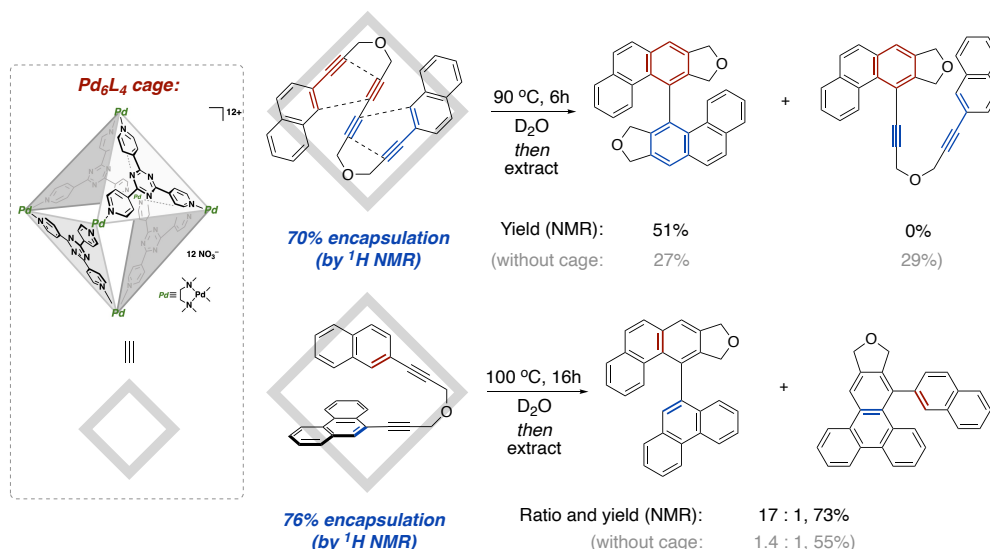
Thermal Cyclization of Linear Arylalkynes Facilitated by Folding inside a Molecular Cage

(¹Department of Applied Chemistry, School of Engineering, The University of Tokyo,
²Division of Advanced Molecular Science, Institute for Molecular Science (IMS)) ○Georgi
 Rosenov Genov,¹ Hiroki Takezawa,¹ Harumi Hayakawa,¹ Makoto Fujita^{1,2}

Keywords: Tetradehydro-Diels-Alder Reaction; Cyclisation Reaction; Host-Guest; Inclusion Compounds

The tetradehydro-Diels-Alder (TDDA) reaction is a useful transformation for the rapid assembly of polycyclic scaffolds from simple linear precursors in a single synthetic step. However, the reaction suffers from inefficient conversion and poor selectivity, requiring careful substrate design and harsh reaction conditions to overcome the inherent entropic cost for this transformation.¹

Herein we report an efficient site-selective TDDA transformation within a self-assembled supramolecular Pd₆L₄ cage.² Despite the large size, the flexibility of the employed substrates allows for the efficient encapsulation within the host cavity. The rate of thermal cyclisation of the encapsulated guest was found to be greatly enhanced, as well as product selectivity has been observed. The efficiency of this system relies on the precise conformational control of the substrate within the confined space of the host molecule. This effect was clearly demonstrated on two related substrate classes, one of which can undergo two subsequent cyclisation reactions, with the product shape dictating the selectivity of the process.



1) a) P. Wessig, G. Muller, *Chem. Rev.* **2008**, *108*, 2051. b) W. Li, L. Zhou, J. Zhang, *Chem. Eur. J.* **2016**, *22*, 1558. 2) G. R. Genov, H. Takezawa, H. Hayakawa, M. Fujita, *manuscript in preparation*

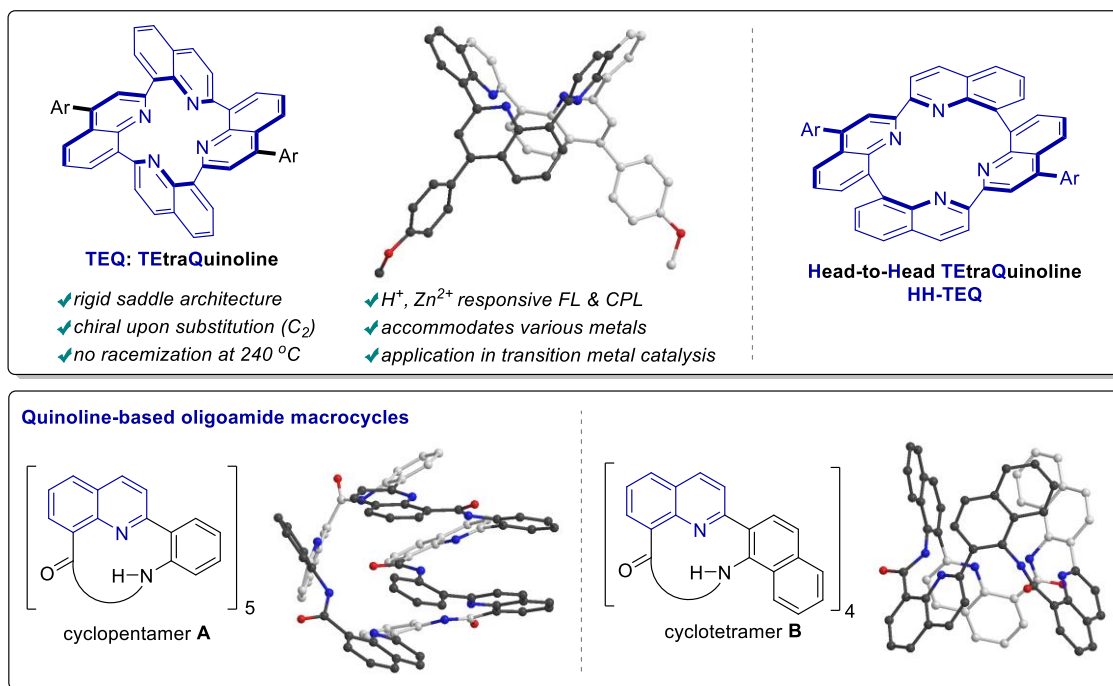
TEtraQuinoline (TEQ) and Other Quinoline oligomers, a New Family in Macrocyclic Compounds

(Graduate School of Pharmaceutical Sciences, Keio University) OWei Xu, Haru Nonaka, Ryota Yagami, Mizuki Nishiwaki, Ayami Takeda, Naoya Kumagai

Keywords: quinoline, macrocyclic compounds, heterocyclic compounds, catalysis, fluorescence

Macrocyclic chemistry has received sustained attention because of not only their fascinating structures linked with their specific functions, but also a large number of naturally occurring macrocycles featuring porphyrin frameworks. Based on our previous work of TriQuinoline (TQ),¹ a unique quasi-flat head-to-tail quinoline trimer exhibiting unusual physical and chemical properties, we endeavored to construct non-flat oligo-quinoline architectures.

TEtraQuinoline (TEQ), a head-to-tail quinoline tetramer, is an advanced form of TQ embedding additional quinoline unit and acquires a characteristic saddle-shape with inwardly oriented four sp^2 nitrogen atoms.² C_2 symmetric substituted TEQ entails considerably high energy barrier for flipping to secure its chirality, which was experimentally supported by no erosion of enantiomeric excess even at 240 °C. TEQ accommodates various kinds of transition metal cations, e.g. Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Pd^{2+} , to form corresponding metal complexes as confirmed by X-ray crystallography, exerting catalytic activity and cation-dependent fluorescence. A related TEQ congener with head-to-head connectivity, amide-linked helical quinoline cyclic pentamer **A** and tetramer **B** will be also comparatively discussed.



1) S. Adachi, M. Shibasaki, N. Kumagai, *Nat. Commun.* **2019**, *10*, 3820.

2) W. Xu, Y. Nagata, N. Kumagai, *J. Am. Chem. Soc.*, **2023**, in press.

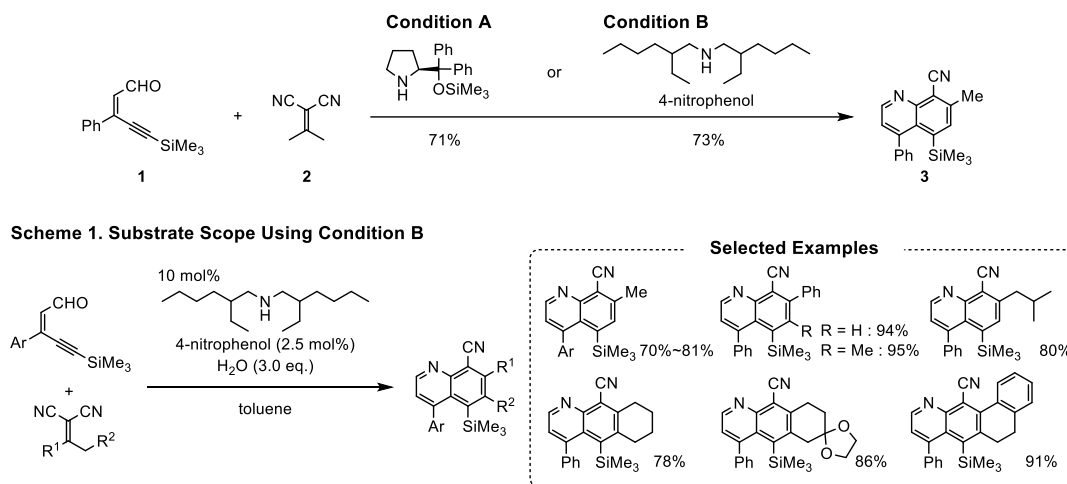
Novel synthesis of multi-substituted quinoline derivatives using alkylidenemalononitriles and unsaturated aldehydes by organocatalyst

(Graduate School of Science, Tohoku University) ○ Xiaolei Han, Naoki Mori, Yujiro Hayashi

Keywords: Quinoline; Organocatalyst; Domino reaction

Since there are many medicines possessing a multi-substituted quinoline moiety, it is important to develop an efficient method for their synthesis. Many conventional synthetic methods use aniline derivatives as starting materials. Herein, we will report a new one-pot method for the synthesis of multi-substituted quinoline derivatives from unsaturated aldehydes and alkylidenemalononitriles using an organocatalyst.

First, with the aim of developing a new asymmetric Michael reaction, a mixture of β -alkynyl- α,β -unsaturated aldehyde **1** and isopropylidenemalononitrile (**2**) was treated with diphenylprolinol silyl ether¹ developed in our laboratory. In this case, the tetrasubstituted quinoline derivative **3** was obtained unexpectedly. (Condition A). Since **3** has no chiral centers, we tried to find an inexpensive and easily available amine catalyst. After several trials, **3** was obtained in the similar yield when di(2-ethylhexyl)amine and 4-nitrophenol were used as catalysts (Condition B). This reaction has a wide substrate generality, and the quinoline derivatives were obtained in high yields (Scheme 1).



1) Y. Hayashi, *et al.*, *Angew. Chem. Int. Ed.* **2005**, 44, 4212.

電子欠乏性 α, β -アルケニルカルボン酸アリールプロパルギルアミドの分子内環化反応

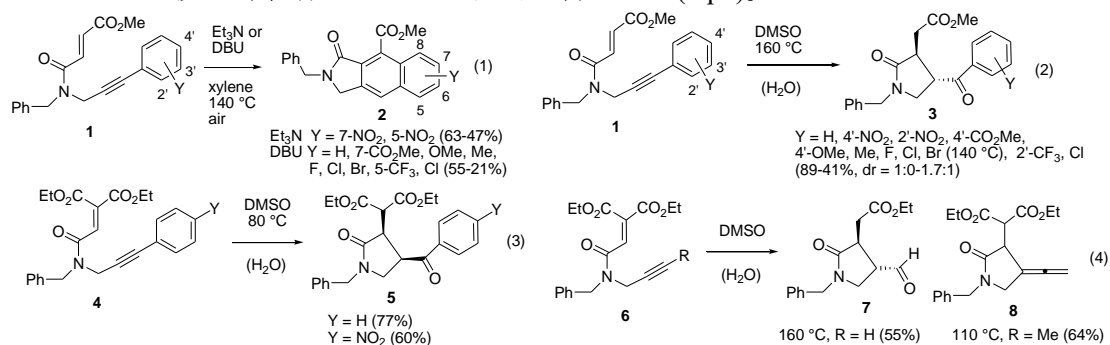
(大阪公立大院工¹・奈良教育大学²・奈良先端科学技術大学院大学³) ○王 智超¹・山崎 祥子² 森本積³・小川 昭弥¹

Intramolecular Cyclization Reactions of Arylpropargyl Amides of Electron-deficient α, β -Alkenyl Carboxylates (¹Osaka Metropolitan Univ., ²Nara University of Education, ³Nara Institute of Science and Technology) ○ Zhichao Wang,¹ Shoko Yamazaki,² Tsumoru Morimoto,³ Akiya Ogawa¹

Intramolecular cyclization reactions of arylpropargyl amides of electron-deficient α, β -alkenyl carboxylates such as fumarates and ethenetricarboxylates were investigated. The reaction of the fumaramides with base, Et₃N or DBU in xylenes at 140 °C under air gave benz[*f*]isoindoline derivatives in 63-21% yields. The benz[*f*]isoindolines may be produced via formation of an allenic intermediate, intramolecular Diels-Alder reaction, proton transfer, and dehydrogenation by oxygen. On the other hand, the reaction of fumaramide derivatives in DMSO at 160 °C gave aroyl-substituted pyrrolidine derivatives as major products in 89-41% yields, probably via addition of water. Furthermore, cyclization reactions of H and Me substituted alkyne derivatives were investigated. Selective synthesis of various types of products, such as formyl-substituted pyrrolidine derivatives and ene cyclized products was achieved.

Keywords : Intramolecular cyclization reaction; Arylalkyne; Fumaramide; Benz[*f*]isoindoline; Pyrrolidine derivatives

アリールプロパルギル fumarate アミド **1** をキシレン中 Et₃N または DBU 存在下 140 °C で加熱すると、分子内 Diels-Alder 反応を経て、ベンズ[*f*]イソインドリン骨格をもつ三環性化合物が 63-21%の収率で得られた(eq 1)。一方、**1** を DMSO 中で 160 °C で加熱するとアロイル基 trans 置換ピロリジン誘導体が主生成物として得られた。系内の水が関与した環化反応が起こったと考えられる(eq 2)。アリールプロパルギルエテントリカルボン酸アミド誘導体の反応では DMSO 中で 80 °C でアロイル基 cis 置換ピロリジン誘導体が 77-60%の収率で得られた(eq 3)。さらに H および Me 置換プロパルギルアミド **6** の DMSO 中の反応を検討したところ、同様の環化-水付加アルデヒド **7** またはエン反応環化体 **8** などが選択的に得られた(eq 4)。



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

[K705-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Ryo Yazaki, Yoshihiro Nishimoto

Wed. Mar 22, 2023 1:00 PM - 3:40 PM K705 (K705, Lecture Hall Bldg. [7F])

[K705-1pm-01] Highly Stereoselective Synthesis of γ, δ -Unsaturated Quaternary α -Amino Esters via the Tandem *N*-Alkylation/Claisen Rearrangement of α -Imino Allylesters

[○]Isao Mizota¹, Toshikazu Fukaya¹, Yumi Miwa¹, Yoshinari Kobayashi¹, Tomoki Ejima¹, Mizuki Yamaguchi¹, Makoto Shimizu¹ (1. Mie University)

1:50 PM - 2:10 PM

[K705-1pm-02] Selective Defluoroaminoxylation of perfluoroalkylarenes by organic photoredox catalysis

[○]Naoki Sugihara¹, Yoshihiro Nishimoto¹, Makoto Yasuda¹ (1. Graduate School of Engineering, Osaka University)

2:10 PM - 2:30 PM

[K705-1pm-03] 1,4-Addition Reaction of 2H-Heptafluoropropane to Unsaturated C-C bond

[○]Yusuke Higashi¹, Kotonno Shima¹, Mikiya Suzuki¹, Moe Hosokawa², Kiyomi Kakiuchi¹, Tsuyoshi Kawai¹, Tsumoru Morimoto¹ (1. Nara Institute of Science and Technology, 2. Daikin Industries, Ltd.)

2:30 PM - 2:50 PM

[K705-1pm-04] α -Amino acid and peptide synthesis using catalytic cross-dehydrogenative coupling

[○]Taro Tsuji¹, Kayoko Hashiguchi¹, Mana Yoshida¹, Tetsu Ikeda¹, Yunosuke Koga¹, Yusaku Honda¹, Tsukushi Tanaka¹, Suyong Re², Kenji Mizuguchi^{2,3}, Daisuke Takahashi¹, Ryo Yazaki¹, Takashi Ohshima¹ (1. The Univ. of Kyushu, 2. NIBIOHN, 3. The Univ. of Osaka)

3:00 PM - 3:20 PM

[K705-1pm-05] Oxidative Dearomative Coupling Reaction of Arenols Using Hypohalite Catalysis

[○]Takehiro Kato¹, Muhammet Uyanik¹, Kazuaki Ishihara¹ (1. Nagoya University)

3:20 PM - 3:40 PM

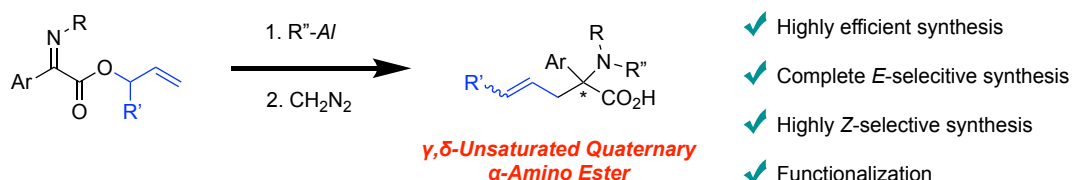
Highly Stereoselective Synthesis of γ,δ -Unsaturated Quaternary α -Amino Esters via the Tandem *N*-Alkylation/Claisen Rearrangement of α -Imino Allylesters

(Graduate School of Engineering, Mie University) ○Isao Mizota, Toshikazu Fukaya, Yumi Miwa, Yoshinari Kobayashi, Tomoki Ejima, Mizuki Yamaguchi, Makoto Shimizu

Keywords: α -Iminoallyl Esters; Umpolung Reaction; *N*-Alkylation; Quaternary Aminoesters; Claisen Rearrangement

γ,δ -Unsaturated α -amino acids are important molecular backbones present in many natural products and pharmaceuticals such as antithrombotic agents and antibacterial agents. γ,δ -Unsaturated α -amino esters are also important building blocks for the synthesis of α -methylene- γ -butyrolactone or pyrrolidine, which are the core units in many natural products. Therefore, much attention has been paid to the development of practical and efficient approaches to obtain γ,δ -unsaturated α -amino acid derivatives.

Previously, we have reported umpolung reactions for α -imino esters (*N*-alkylation) and integrated various reactions using *N*-alkylation.^{1,2} These methods allow the free introduction of various substituents on nitrogen and can yield α -amino acid derivatives in one-pot reactions. In addition, we have previously reported a tandem *N*-alkylation/Claisen rearrangement of α -iminoallyl esters to give γ,δ -unsaturated α -amino esters; however, there are some limitations to this reaction.³ Herein, we would like to report a more efficient synthetic method to achieve γ,δ -unsaturated quaternary α -amino esters using a broad range of substrates. In addition, a highly *E*- and *Z*-selective Claisen rearrangement was achieved by controlling the reaction conditions and substrates. Moreover, further transformations of the products was achieved.



- 1) I. Mizota, M. Shimizu, *Chem. Rev.* **2016**, *16*, 688.
- 2) I. Mizota, Y. Nakamura, S. Mizutani, N. Mizukoshi, S. Terasawa, M. Shimizu, *Org. Lett.* **2021**, *23*, 4168.
- 3) I. Mizota, K. Tanaka, M. Shimizu, *Tetrahedron Lett.* **2012**, *53*, 1847.

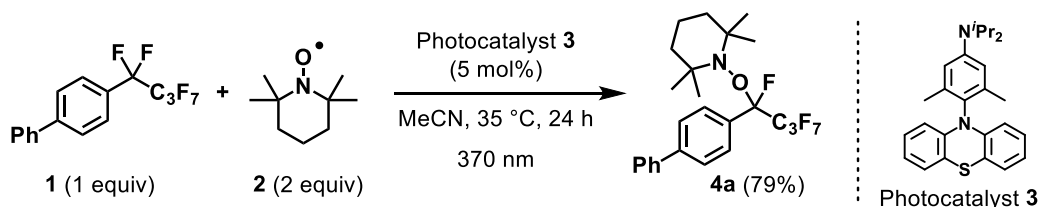
Selective Defluoroaminoxylation of Perfluoroalkylarenes by Organic Photoredox Catalysis

(Graduate School of Engineering, Osaka University) ○Naoki Sugihara, Yoshihiro Nishimoto, Makoto Yasuda

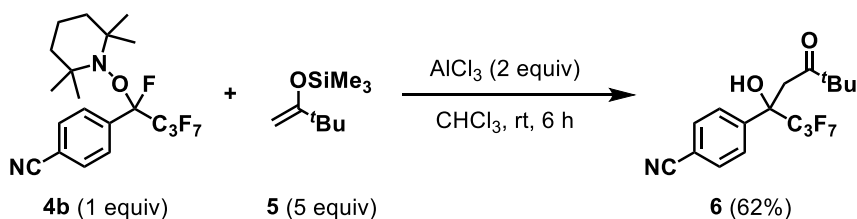
Keywords: C–F bond transformation; photoredox catalyst; fluorinated compound; radical

Fluoroalkyl groups are often utilized in various field such as medicines and agrochemicals because its incorporation can drastically change the properties of biologically active small molecules. A number of methods have been reported for the efficient construction of perfluoroalkylated compounds. A selective transformation of carbon–fluorine (C–F) bond is a straightforward strategy for the synthesis of complicated multi-fluorinated compounds from perfluoroalkyl compounds.¹ Although perfluoroalkyl units are inert and difficult to transform selectively, we recently reported selective defluoroallylation of perfluoroalkylarenes using allylic stannanes by photoredox catalysis.² We envisioned that other radical acceptors also works well. Herein, we report selective defluoroaminoxylation of perfluoroalkylarenes by organic photoredox catalysis.

In the investigation for the reaction of perfluoroalkylarene **1a** with TEMPO **2** in the presence of organic photoredox catalysts, photocatalyst **3** was found to be the most effective catalyst, which afforded aminoxylated product **4a**. Transient-absorption spectroscopy studies disclosed dimethyl substituent in **3** played an important role in prolongation of excited triplet life time and that enable the reaction to proceed efficiently.



Further C–F bond transformation of aminoxylated product **4** was successful. The reaction of **4b** with silyl enol ether **5** in the presence of AlCl_3 proceeded to afford fluorinated alcohol **6**. This result showed a potential of **4** for precursors of various fluorinated alcohols.



1) Y. Nishimoto, N. Sugihara, M. Yasuda, *Synthesis* **2022**, 2765.

2) N. Sugihara, K. Suzuki, Y. Nishimoto, M. Yasuda, *J. Am. Chem. Soc.* **2021**, 143, 9308.

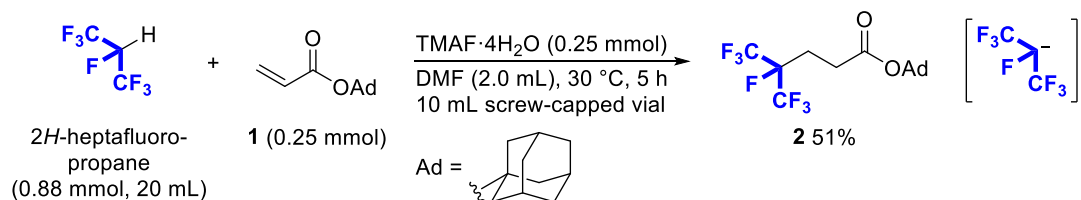
1,4-Addition of 2*H*-Heptafluoropropane to Unsaturated C-C Bond

(¹*Division of Materials Science, Nara Institute of Science and Technology (NAIST)*, ²*Daikin Industries, Ltd*) ○ Yusuke Higashi,¹ Kotono Shima,¹ Mikiya Suzuki,¹ Moe Hosokawa,² Kiyomi Kakiuchi,¹ Tsuyoshi Kawai,¹ and Tsumoru Morimoto¹

Keywords: 2*H*-Heptafluoropropane; 1,4-Addition Reaction; Heptafluoroisopropyl Group

Perfluoroalkyl-containing organic compounds are often found in a wide range of fields, including pharmaceuticals, pesticide, electronic materials and polymer materials.¹ Although many researchers have developed synthetic methods for such compounds, most of them involve the introduction of primary fluoroalkyl groups, such as CF₃ and C₂F₅, and few methods have been developed to introduce secondary or tertiary perfluoroalkyl groups. Even in the case of the introduction of the simplest secondary perfluoroalkyl group, only some reactions have been reported for the introduction of (CF₃)₂FC groups from hexafluoropropene, CF₃CF=CF₂, or 2-iodoheptafluoropropane, (CF₃)₂CFI. In all of these methods, the radical species, (CF₃)₂FC•, is involved in the reaction as an important intermediate, but considering the electronic properties of the (CF₃)₂FC group, synthetic transformation via the anion species, (CF₃)₂FC[−], also have potential to become an effective method for the introduction of the (CF₃)₂FC group. Herein, we report a new synthetic reaction which proceeds via the generation of anion species from 2*H*-heptafluoropropane, (CF₃)₂FCH.

The reaction of (CF₃)₂FC-H with 1-adamantyl acrylate (**1**) in the presence of Me₄N⁺F[−]·4H₂O (TMAF·4H₂O) in anhydrous DMF at 30 °C for 5 h afforded 1-adamantyl 3-heptafluoropropylpropanoate (**2**), in which (CF₃)₂FC group is introduced at the terminus of conjugated system, in 50% yield (Scheme).² In this reaction, the fluoride ion acts as a strong base under nonaqueous conditions, deprotonating from (CF₃)₂FC-H to generate the anionic species, (CF₃)₂FC[−], which forms a bond with the β-position carbon of the α,β-unsaturated ester in the manner of 1,4-addition. Also, it was found that DMF not only acts as a solvent, but also, contributes to the stabilization of (CF₃)₂FC[−] generated in situ, as in the other fluoroalkyl anion such as [−]CF₃ and [−]C₂F₅. This represents the first reaction in which (CF₃)₂FC group is introduced into an aliphatic chain using (CF₃)₂FC-H as the raw material. Furthermore, it was found that the present method is applicable to the 1,4-addition reaction into a wide variety of electron-deficient alkenes to yield the corresponding 1,4-adducts in moderate to high yields.



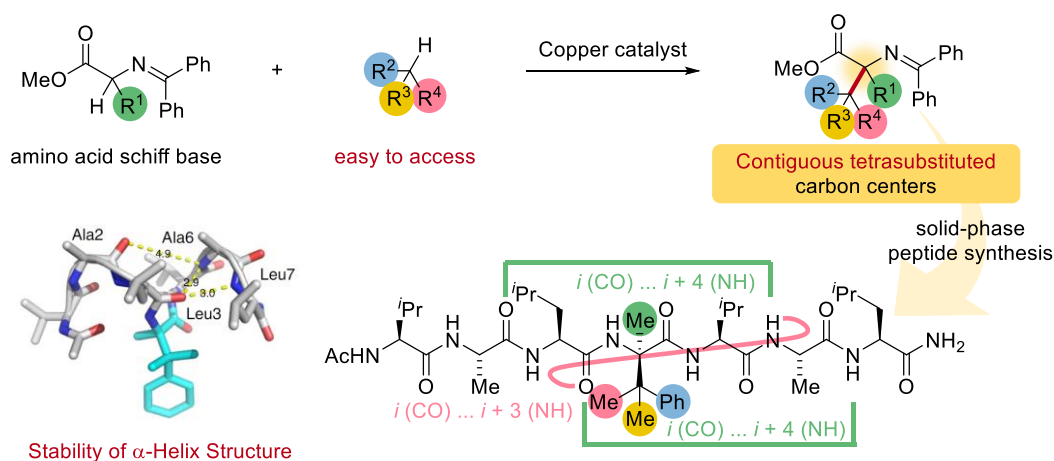
1) N. Shibata *et al.* *ASC Omega* **2020**, 5, 10633-10640. 2) T. Morimoto *et al.* JP2021-188866; PCT/JP2022-118114.

α -Amino acid and peptide synthesis using catalytic cross-dehydrogenative coupling

(¹ *The Univ. of Kyushu*, ² *NIBIOHN*, ³ *The Univ. of Osaka*) ○Taro Tsuji¹, Kayoko Hashiguchi¹, Mana Yoshida¹, Tetsu Ikeda¹, Yunosuke Koga¹, Yusaku Honda¹, Tsukushi Tanaka¹, Suyong Re², Kenji Mizuguchi^{2,3}, Daisuke Takahashi¹, Ryo Yazaki¹, Takashi Ohshima¹

Keywords: Amino Acid; Metal Catalyst

Ionic or radical α -amino Schiff base methods are well known for the synthesis of α,α -disubstituted α -amino acids.^{1,2} However, the incorporation of sterically demanding groups is challenging with ionic methods, and radical methods require prefunctionalization of the substrates. We have developed a dehydrogenative coupling process of α -amino acid Schiff bases with hydrocarbon feedstocks for the synthesis of α,α -disubstituted α -amino acid derivatives.³ These α -amino acid derivatives were transformed into C- and N-protected amino acids, which could be easily incorporated into peptide synthesis. A range of α -amino acid derivatives could be readily accessed, which includes, notably, those that bear contiguous quaternary centers. Circular dichroism measurements show that the helical peptide structure is stabilized by the highly sterically congested unnatural α -amino acid.



- 1) (a) Wang, J.; Liu, X.; Feng, X. *Chem. Rev.* **2011**, *111*, 6947. (b) Maruoka, K.; Ooi, T. *Chem. Rev.* **2003**, *103*, 3013. (c) Henning, V.; Stefan, B. *Org. Biomol. Chem.* **2007**, *5*, 406.
- 2) Brandhofer, T.; Mancheno, O. G. *Eur. J. Org. Chem.* **2018**, 6050.
- 3) Tsuji, T.; Hashiguchi, K.; Yoshida, M.; Ikeda, T.; Koga, Y.; Honda, Y.; Tanaka, T.; Re, S.; Mizuguchi, K.; Takahashi, D.; Yazaki, R.; Ohshima, T. *Nat. Synth.* **2022**, *1*, 304.

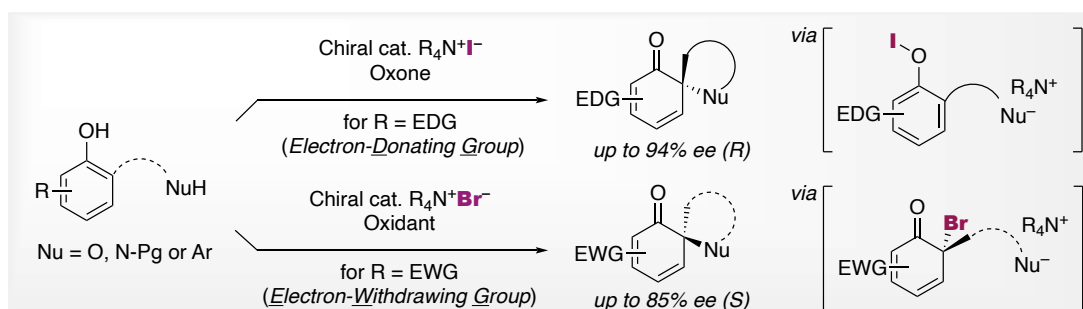
Oxidative Dearomative Coupling Reaction of Arenols Using Hypohalite Catalysis

(Graduate School of Engineering, Nagoya University) ○Takehiro Kato, Muhammet Uyanik, Kazuaki Ishihara

Keywords: Hypohalite catalysis; Oxidative dearomatization; Phenol; Enantioselective; Oxone

Enantioselective oxidative dearomatization of arenols is an important tool for the synthesis of several biologically important compounds. Many elegant strategies have been developed using transition metal or hypervalent iodine catalysts or reagents.¹ In this regard, we have developed chiral quaternary ammonium hypoiodite-catalyzed enantioselective oxidative dearomatization of 1-naphthols.² However, long times (~3 days) were required to complete the reactions, even for these highly reactive substrates. Notably, no reaction took place for the oxidation of phenols.

Here, we developed a high-performance ammonium hypohalite catalysis for the enantioselective oxidative dearomatization reactions. Hypohalite catalytic active species could be generated *in situ* from the corresponding chiral quaternary ammonium halides with environmentally benign oxidants such as oxone or potassium bromate. Only inorganic wastes were generated from the oxidant used. By using hypoiodite catalysis, the oxidation of a wide range of naphthols and electron-rich phenols could proceed under mild conditions to afford the corresponding spirolactones with high enantioselectivity.^{3,4} On the other hand, by using hypobromite catalysis, oxidative dearomatization of electron-deficient phenols, which were hardly reactive using the hypoiodite catalysis, readily proceeded to give the corresponding inter- and intramolecular dearomative C–O, C–N and C–C coupling adducts. We also achieved the first enantioselective hypobromite catalysis for oxidative dearomative coupling reactions. Notably, control experiments revealed that the reaction mechanism of hypobromite catalysis might be different from that of hypoiodite catalysis.



1) S.-L. You, *Asymmetric Dearomatization Reactions*, John Wiley & Sons, Hoboken, **2016**. 2) M. Uyanik, N. Sasakura, E. Kaneko, K. Ohori, K. Ishihara, *Chem. Lett.* **2015**, 44, 179. 3) M. Uyanik, T. Kato, N. Sahara, O. Katade, K. Ishihara, *ACS Catal.* **2019**, 9, 11619. 4) M. Uyanik, N. Sahara, O. Katade, K. Ishihara, *Org. Lett.* **2020**, 22, 560.

[E1662-1am] 16. Natural Products Chemistry, Chemical Biology

Chair: Takuya Kaji, Toyonobu Usuki

Wed. Mar 22, 2023 9:00 AM - 11:30 AM E1662 (1612, Bldg. 16 [1F])

[E1662-1am-01] Total synthesis of pigments with azulene skeleton in an edible blue mushroom

○Kiyotaka Maruoka¹, Ryuju Suzuki¹, Takaaki Kamishima², Yoshitaka Koseki¹, Toshihiro Murafuji³, Hitoshi Kasai¹ (1. IMRM, the Univ. of Tohoku, 2. Genesis Research Institute, Inc., 3. Graduate School of Science and Technology for Innovation, the Univ. of Yamaguchi)

9:00 AM - 9:20 AM

[E1662-1am-02] Δ^4 -dinor-OPDAs, novel ancestral jasmonates of *Marchantia polymorpha*

○Takuya Kaji¹, Hidenori Yoshimatsu¹, Nobuki Kato¹, Haruka Sakurai¹, Yang Gangqiang², Guillermo H. Jimenez-Aleman³, Roberto Solano³, Minoru Ueda^{1,4} (1. Sciences, Tohoku Univ., 2. Pharmacy, Yantai University, 3. CNB-CSIC, 4. Life Sciences, Tohoku Univ.)

9:20 AM - 9:40 AM

[E1662-1am-03] JA-Ile-lactone enhanced accumulation of alkaloid in tomato

○Rina Saito¹, Takuya Kaji², Taichi Okumura², Toshiya Muto¹, Hiroshi Abe³, Sohei Yamagami¹, Yousuke Takaoka², Minoru Ueda^{1,2} (1. Grad. Sch. Lifesci., Tohoku Univ., 2. Grad. Sch. Sci., Tohoku Univ., 3. RIKEN BRC)

9:40 AM - 10:00 AM

[E1662-1am-04] Chemical regulation of crosstalk between jasmonate and ethylene by peptide-based chemical tools

○Yousuke Takaoka¹, Ruiqi Liu¹, Qi Li¹, Minoru Ueda^{1,2} (1. Grad. Sci., Tohoku Univ, 2. Grad. Life Sciences, Tohoku Univ)

10:10 AM - 10:30 AM

[E1662-1am-05] Glycolipids as ligands and molecular probes for C-type lectin receptor Mincle; synthesis and biological functional analysis

○Takanori Matsumaru¹, Kana Okubo¹, Kasumi Sakuratani¹, Kodai Sueyoshi¹, Shusuke Fujii¹, Juri Takayama¹, Yamasaki Sho^{2,3}, Yukari Fujimoto¹ (1. Fac. Sci. Tech., Keio Univ., 2. Research Institute for Microbial Diseases, Osaka Univ., 3. Immunology Frontier Research Center (IFReC), Osaka Univ.)

10:30 AM - 10:50 AM

[E1662-1am-06] Development of tyrosinase-based proximity protein labeling in living cells

○Yuna Matsuda¹, Hao Zhu¹, Jae Hoon Oh², Hideki Nakamura^{1,2}, Muneo Tsujikawa², Tomonori Tamura¹, Itaru Hamachi^{1,2} (1. Graduate School of Engineering, Kyoto University, 2. JST ERATO)

10:50 AM - 11:10 AM

[E1662-1am-07] Relationships between catalyst-promoted oxygenation level of amyloid β and cytotoxicity

○Ryota Matsukawa¹, Masahiro Furuta¹, Harunobu Mitsunuma^{1,2}, Shigehiro Kawashima¹

, Youhei Sohma³, Motomu Kanai¹ (1. Grad. Sch. Pharm. Sci., Tokyo Univ., 2. JST PRESTO, 3. Sch. Pharm. Sci., Wakayama Med. Univ.)

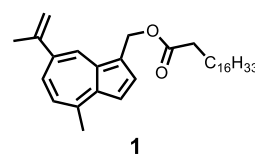
11:10 AM - 11:30 AM

Total synthesis of pigments with azulene skeleton in an edible blue mushroom

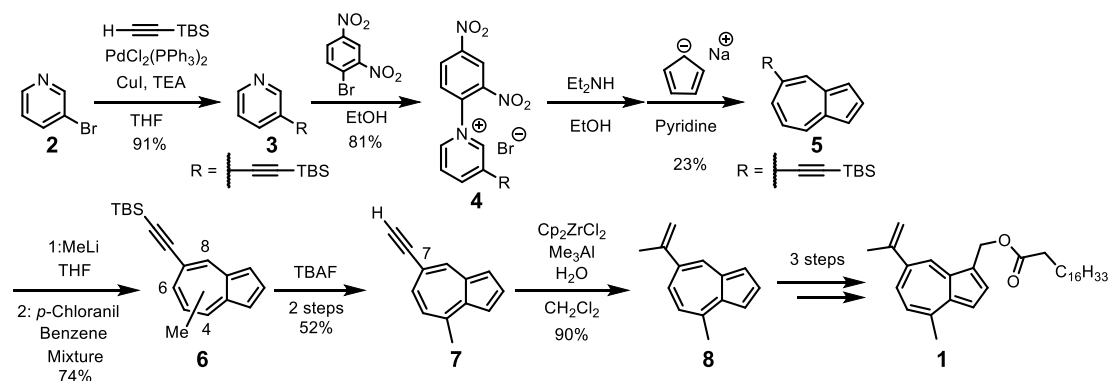
(¹*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,* ²*Genesis Research Institute, Inc.,* ³*Graduate School of Science and Technology for Innovation, Yamaguchi University.*) ○ Kiyotaka Maruoka,¹ Ryuju Suzuki,¹ Takaaki Kamishima,² Yoshitaka Koseki,¹ Toshihiro Murafuji,³ Hitoshi Kasai¹

Keywords: Azulene; Blue pigments; Total synthesis; Natural products; Nanoparticles

There has been a worldwide shift in food coloring from synthetic to natural pigments because of the increasing needs of our consumers for food safety. Currently, the major carotenoids used for magenta and yellow are fat-soluble. Fine particulation of carotenoid pigments makes it possible to color them also in aqueous systems.¹ For cyan, however, all natural pigments that are available are water-soluble. Fat-soluble blue pigments are needed to enable coloring of a wide range of foods.² To develop a natural blue organic pigment, we focused our attention on fat-soluble pigment **1** containing in the edible mushroom, *Lactarius Indigo*.³ Here, we presented the total synthesis and basic physical properties of **1**.



Compound **3** with an ethynyl group was obtained by Sonogashira coupling using **2**. To construct the azulene skeleton, the azulene derivative **5** was successfully synthesized by the Hafner method.⁴ (**3**→**5**) The regioisomer mixture **6** was obtained via nucleophilic addition reaction with methyl lithium to **5** and re-aromatization with an oxidant. The desilylation of this mixture **6** afforded **7** with C4 methyl group as a single compound by silica gel column chromatographic separation. The conversion of the ethynyl group at C-7 position to an isopropenyl group proceeded by carbometalation reaction (**7**→**8**). The side chain moiety was then constructed, and we achieved the first total synthesis of the desired **1** with a total yield of 3.7%.



1) S. Ghosh *et al.*, *Appl. Biochem. Biotechnol.*, **2021**, 193, 3787. 2) A. G. Newsome *et al.*, *J. Agric. Food Chem.*, **2014**, 62, 6498. 3) H. D. Harmon *et al.*, *Cell. Mol. Life Sci.*, **1980**, 36, 54. 4) K. Hafner, *Org. Synth.*, **1990**, 7, 15.

ゼニゴケの新規始原 jasmonate, Δ^4 -dinor-OPDA の合成・同定

(東北大院・理¹・煙台大・薬²・CNBC・植物分子遺伝³・東北大院・生命⁴)

○加治 拓哉¹、吉松 幸徳¹、加藤 信樹¹、櫻井 春香¹、楊 剛強²、Guillermo H. Jimenez-Aleman³、Roberto Solano³、上田 実^{1,4}

Δ^4 -dinor-OPDAs, novel ancestral jasmonates of *Marchantia polymorpha*

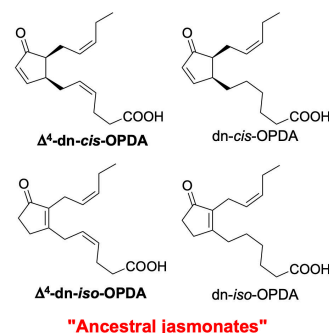
(¹Graduate School of Sciences, Tohoku University, ²School of Pharmacy, Yantai University, ³CNB-CSIC, ⁴Graduate School of Life Sciences, Tohoku University)

○Takuya Kaji¹, Hidenori Yoshimatsu¹, Nobuki Kato¹, Haruka Sakurai¹, Gangqiang Yang², Guillermo H. Jimenez-Aleman³, Roberto Solano³, Minoru Ueda^{1,4}

Recently, evolution of plant hormone signaling attracts attention and dn-OPDAs were previously identified as ancestral jasmonates in the model bryophyte *Marchantia polymorpha* which belongs to the basal land plant in the phylogenetic tree. Phytohormone jasmonates regulate myriad of bioactivities including plant defense responses. On the other hand, subsequent recent studies indicated the existence of other bioactive ligands than dn-OPDAs. In this situation, we identified the Δ^4 -dn-OPDAs as novel ancestral plant hormones of *M. polymorpha*, which are biosynthesized from EPA independent of hexadecanoid pathway of dn-OPDAs. Herein, we will report synthetic preparation of Δ^4 -dn-OPDAs and the *in-vitro* evaluation of binding activity against *Mp*COI1-*Mp*JAZ co-receptor. As a result of pull-down assay, Δ^4 -dn-iso-OPDA was suggested as the primary ancestral jasmonate in *M. polymorpha*.

Keywords: Plant hormone, Natural products chemistry, Chemical biology, Organic synthesis

植物ホルモニングナル伝達系の進化が近年注目されており、基部陸上植物の蘚苔類モデル植物であるゼニゴケにおいて dn-OPDA 類が始原ジャスモン酸として同定された¹。植物ホルモングラスモン酸は防御応答など様々な生物活性を制御する。一方で、続く研究によって dn-OPDA のほかに活性な始原ジャスモン酸が存在することが示唆された²。我々は dn-OPDA の生合成経路とは別に存在する EPA から生合成される Δ^4 -dn- cis/iso-OPDA が新規始原ジャスモン酸リガンドの候補分子であることを見出した³。 Δ^4 -dn- cis/iso-OPDA の同定や生物活性評価を目的とした化学合成および合成した化合物のゼニゴケの COI1-JAZ 共受容体への結合活性評価などを通して Δ^4 -dn-iso-OPDA がゼニゴケの主要な始原ジャスモン酸であることが強く示唆された。本発表ではそれらの詳細を報告する。



- 1) Monte, I., *et al.*, *Nat. Chem. Biol.*, **14**, 480-488 (2018).
- 2) Soriano, G. *et al.*, *New Phytol* **233**, 1401-1413 (2022).
- 3) Kneeshaw, S., *et al.*, *PNAS*, **119**, 36 (2022).

ジャスモン酸イソロイシンラクトンによる植物アルカロイド生産活性化

(東北大院生命科学¹・東北大院理²・理研 BRC³) ○齊藤 里菜¹・加治 拓哉²・奥村 太知²・武藤 俊哉¹・安部 洋³・山神 壮平¹・上田 実^{1,2}

JA-Ile-lactone Enhanced Accumulation of Alkaloid in Tomato (¹Graduate School of Life Sciences, Tohoku University, ²Graduate School of Science, Tohoku University, ³RIKEN BRC)
○ Rina Saito,¹ Takuya Kaji,² Taichi Okumura,² Toshiya Muto,¹ Hiroshi Abe,³ Sohei Yamagami,¹ Minoru Ueda^{1,2}

(+)-7-*iso*-Jasmonoyl-L-isoleucine (JA-Ile) is a plant hormone that functions as a protein-protein interaction (PPI) inducer between F-box protein COI1 and transcription repressors JAZ, leading to secondary metabolites production as well as plant growth inhibition. We found that a cyclized JA-Ile (JA-Ile-lactone, JILa) induced tomatine production without causing growth inhibition in *Solanum lycopersicum*. We also confirmed that JILa induced tomatine production in a COI1-dependent manner. However, JILa did not bind to COI1-JAZ co-receptor pairs. In contrast, 12OH-JA-Ile, a hydroxylated product of JILa could be a genuine bioactive form of JILa which was perceived by some COI1-JAZ co-receptor pairs. We also report the mode of action of JILa that revealed by gene expression analysis and metabolites analysis.

Keywords : Plant hormone; Jasmonic acid; Secondary metabolites; Mode-of-Action

植物ホルモン(+)-7-*iso*-Jasmonoyl-L-isoleucine (JA-Ile) は、植物体内で COI1-JAZ 共受容体と結合し、二次代謝産物生合成を活性化する。しかしこれに伴って、JA-Ile は植物に深刻な生長阻害を引き起こす。

我々は、JA-Ile 誘導体 JA-Ile-lactone (JILa)^{1,2} が、ナス科のモデル植物トマトに対して、生長阻害を引き起こすことなく、ステロイドアルカロイド配糖体であるトマチンの生合成を活性化することを見出した。さらに COI1 変異体植物を用いた検討により、JILa の活性が COI1 依存的であることを確認した。しかし、JILa はトマトの COI1-JAZ 共受容体に結合せず、その代わりに JILa の加水分解物 12OH-JA-Ile が共受容体に結合する活性本体であることが分かった。また、12OH-JA-Ile は 13 種の COI1-JAZ 共受容体ペアのうちの一部に選択的に結合することも明らかになった。遺伝子発現解析と代謝物解析から、JILa が成長阻害を引き起こすことなくトマチン生合成を活性化する分子機構を見出すことができた。本発表では、その詳細を報告する。

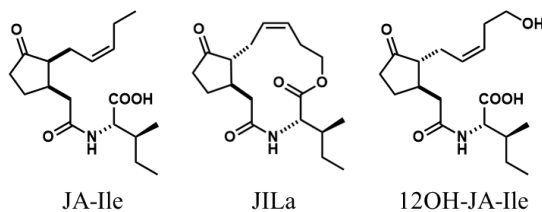


Figure1. JA-Ile, JILa 及び 12OH-JA-Ile の化学構造

- 1) G. H. Jimenez-Aleman., *et al.*, *Org. Biomol. Chem.* **2017**, *15*, 3391-3395.
- 2) G. H. Jimenez-Aleman., *et al.*, *Org. Biomol. Chem.* **2015**, *13*, 5885-5893.

ペプチド型ケミカルツールによるジャスモン酸とエチレン間クロストークの化学制御

(東北大院理¹・東北大院生命科学²) ○高岡 洋輔¹・劉 瑞琦¹・李 奇¹・上田 実^{1,2}
 Chemical regulation of crosstalk between jasmonate and ethylene by peptide-based chemical tools (¹Graduate School of Science, Tohoku University, ²Graduate School of Life Sciences, Tohoku University) ○Yousuke Takaoka,¹ Liu Ruiqi,¹ Li Qi,¹ Minoru Ueda^{1,2}

Jasmonate and ethylene are plant hormones that act synergistically or antagonistically regulate plant growth and defense through their master transcription factors (TFs) MYCs and EIN3/EIL1. Recently, JAZ10.4, a JAZ10 splice variant, which accumulates downstream of the jasmonate response, and has been reported to be involved in desensitization in the JA signaling. We herein designed and synthesized a JAZ10.4-based peptide chemical tool, that acts MYC-selective inhibitor *in vivo* as well as *in vitro*. Furthermore, this molecule showed uncoupling activity for MYCs-EIN3/EIL1 crosstalk regulatory system.

Keywords : Plant hormone; Protein-protein interaction; Peptide; Transcription factor

植物ホルモンであるジャスモン酸 (JA) とエチレン (ET) は、植物の生長と虫害・病原菌耐性において拮抗的に作用する。このクロストーク機構には、それぞれのシグナル伝達における主要転写因子 MYC2/3/4 と EIN3/EIL1 によるタンパク質間相互作用が関与することが示唆されているが、その制御メカニズムは不明点が多い (Fig. 1)¹⁻³。本研究では、JA 応答の下流で蓄積し、その脱感作に関わるスプライスバリエント JAZ10.4 に着目し、これに基づくペプチド型ケミカルツールを設計・合成した^{4,5}。この分子は興味深いことに、MYC 選択的に結合し EIN3 にはほとんど結合しないこと、シロイヌナズナにジャスモン酸と同時投与すると、MYC 下流の応答を抑制する一方で、EIN3/EIL1 下流の応答を亢進することが明らかとなった。すなわち本ペプチドは、JA/ET 間クロストークを化学制御可能であり、JA/ET クロストーク機構解明に有効なケミカルツールとなることが期待される。

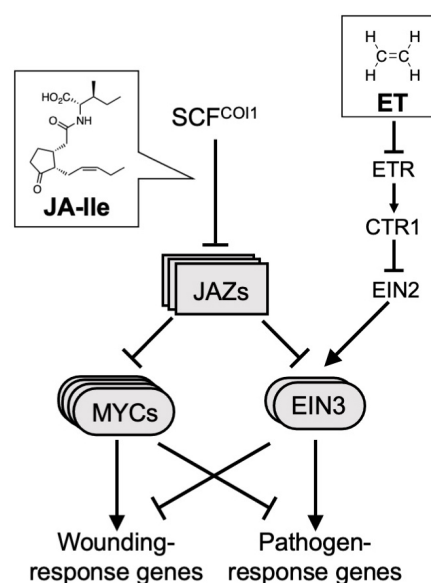


Fig. 1. JA/ET 間クロストークに関わる転写因子ネットワーク.

- 1) Howe, G.A. *et al. Annu. Rev. Plant Biol.* **69**, 20.1 (2018). 2) Takaoka, Y. *et al. J. Biol. Chem.*, **298**, 101504 (2022). 3) Liu, R. *et al. Biosci. Biotechnol. Biochem.*, **86**, 1405 (2022). 4) Moreno, J.E. *et al. Plant Physiol.* **162**, 1006 (2013). 5) Zhang, F. *et al. Proc. Natl. Acad. Sci.* **114**, 1720 (2017).

C 型レクチン受容体 Mincle リガンドおよび標識プローブとしての糖脂質：合成と機能解析

(慶大理工¹・阪大微研²・阪大 IFR³) ○松丸 尊紀¹・大久保 花菜¹・櫻谷 香澄¹・末吉 耕大¹・藤井 秀輔¹・高山 珠理¹・山崎 晶^{2,3}・藤本 ゆかり¹

Glycolipids as ligands and molecular probes for C-type lectin receptor Mincle; synthesis and biological functional analysis (¹*Faculty of Science and Technology, Keio University*, ²*Research Institute for Microbial Disease, Osaka University*, ³*Immunology Frontier Research Center (IFReC), Osaka University*) ○Takanori Matsumaru,¹ Kana Okubo,¹ Kasumi Sakuratani,¹ Kodai Sueyoshi,¹ Shusuke Fujii,¹ Juri Takayama,¹ Sho Yamasaki,^{2,3} Yukari Fujimoto¹

Mincle, a C-type lectin receptor (CLR), recognizes various glycolipids from microbes and dead host cells, leading to the activation of innate immune system. Recent studies revealed that the importance of lipid moieties of the glycolipid ligand for Mincle-mediated signaling activity, but the lipid structures–activity relationships are not fully understood. The intracellular behavior of Mincle and the ligands are also unexplored.

In order to understand these biological roles, we synthesized characteristic ligand structures, including fungal β -mannosyloxymannitol glycolipid “44-2”, trehalose diester with lipid-modification, and their analogues. The ligand structure–Mincle-mediated signaling activity relationships were then analyzed. Based on the established synthetic method, we also synthesized molecular probes and utilized them for observation of the intracellular behavior of Mincle and the ligand.

Keywords : Glycolipid; C-type lectin receptor; Mincle; Innate immunity

C 型レクチン受容体の一種である Mincle はマクロファージなど免疫細胞の表層に発現し、微生物由来の複合脂質や自己の損傷細胞由来の代謝物など、多様な構造を認識して自然免疫を制御する。これまでの研究から、活性発現においてリガンド脂質部位の重要性が明らかとなっているが、その構造活性相関の詳細は不明である。また Mincle の機能についても不明な点が多く、例えば、Mincle のリガンド認識における受容体やリガンド分子の細胞内挙動についての詳細は明らかになっていない。我々は特徴的な脂質構造を有し、強力な Mincle アゴニスト活性を示す天然物である β -mannosyloxymannitol glycolipid “44-2”¹⁾ およびその誘導体や、脂質部位に極性基を導入したトレハロースジエステル誘導体²⁾ を合成し活性評価に展開することで、各構造活性相関を明らかにした。さらに確立したリガンド合成法を用いて分子プローブを合成し、生細胞イメージング解析へ展開することで、Mincle 依存的な細胞内挙動を観測したので報告する。

1) Matsumaru, T.; Sakuratani, K.; Yanaka, S.; Kato, K.; Yamasaki, S.; Fujimoto, Y. *Eur. J. Org. Chem.* **2022**, 20, e202200109.

2) Matsumaru, T.; Sueyoshi, K.; Okubo, K.; Fujii, S.; Sakuratani, K.; Saito, R.; Ueki, K.; Yamasaki, S.; Fujimoto, Y. *Bioorg. Med. Chem.* **2022**, 75, 117045.

チロシナーゼを用いた生細胞での近傍タンパク質ラベル化法の開発

(京大院工¹・JST ERATO²) ○松田 侑奈¹、朱 浩¹、Jae Hoon Oh²、中村 秀樹^{1,2}、辻川 宗男²、田村 朋則¹、浜地 格^{1,2} (1. 京大院工、2. JST ERATO)

Development of tyrosinase-based proximity protein labeling in living cells (¹*Graduate School of Engineering, Kyoto University*, ²*JST ERATO*) ○Yuna Matsuda,¹ Hao Zhu,¹ Jae Hoon Oh,² Hideki Nakamura,^{1,2} Muneeo Tsujikawa,² Tomonori Tamura,¹ Itaru Hamachi^{1,2}

Enzyme-catalyzed proximity labeling (PL) is one appearing method to large-scale obtain protein localization and interaction information under a live condition. The current PL enzymes, however, have the limitations of requiring H₂O₂ (1 mM) for the activation (peroxidases), undergoing a slow labeling reaction (BioID: 18-24 h), and suffering from high background labeling (TurboID). In this context, we are developing a new PL strategy based on tyrosinase, which can address the above issues. This presentation will profile the tyrosinase-catalyzed protein labeling in testing tubes and demonstrate its use for organelle proteomics.

Keywords : Proximity labeling; Enzyme; Tyrosinase; Organelle proteomics

酵素触媒を利用した近傍ラベル化法 (PL) は、生細胞でのタンパク質の局在や相互作用の情報を大規模に得るための手法として近年注目されている。しかし、既存の PL 酵素には以下の課題が指摘されている。(1) 活性化に 1 mM の H₂O₂ を添加する必要がある (ペルオキシダーゼ)。(2) ラベル化反応が遅い (BioID: 18-24 時間)。(3) ラベル化のバックグラウンドが高い (TurboID)。これらの課題を克服するため、我々はチロシナーゼに基づいた新規の PL 戦略の開発を進めている。本発表では、試験管内でのチロシナーゼ触媒のタンパク質ラベル化の基本特性を述べ、本手法がオルガネラプロテオミクスに有用であることを示す。

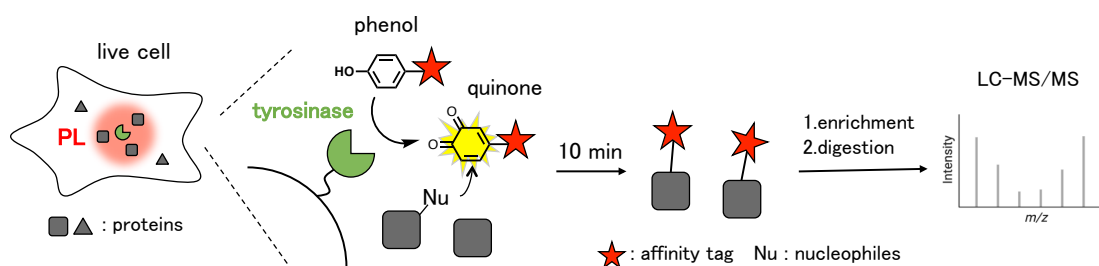


Figure 1. Tyrosinase-based proximity protein labeling

- 1) Hyun-Woo, R. *et al. Science* **339**, 1328–1331 (2013).
- 2) Roux, K. J., Kim, D. I., Raida, M. & Burke, B. J. *Cell Biol.* **196**, 801–810 (2012).
- 3) Branon, T. C. *et al. Nat. Biotechnol.* **36**, 880–887 (2018).

触媒によるアミロイド β の酸素化度と細胞毒性の相関

(東大院薬¹・JST さきがけ²・和医大薬³) ○松川 亮汰¹・古田 将大¹・三ツ沼 治信^{1,2}・川島 茂祐¹・相馬 洋平³・金井 求¹

Relationships between catalyst-promoted oxygenation level of amyloid β and cytotoxicity (¹*Graduate School of Pharmaceutical Science, University of Tokyo*, ²*JST PRESTO*, ³*School of Pharmaceutical Science, Wakayama Medical University*) ○Ryota Matsukawa,¹ Masahiro Furuta,¹ Harunobu Mitsunuma,^{1,2} Shigehiro A. Kawashima,¹ Yohei Sohma,³ Motomu Kanai¹

Amyloid β (A β), a peptide associated with Alzheimer's disease, exhibits neurotoxicity by aggregating through hydrophobic interactions and accumulating in extracellular spaces. Catalytic photooxygenation of A β improves the hydrophilicity of A β by introducing oxygen atoms into A β , which reduces its aggregative properties and cytotoxicity. On the other hand, no quantitative relationship between the oxygenation level of oxygenated A β and its cytotoxicity has been investigated. In the present study, we examined relationship between oxygenation level of A β and viability of PC12 cells.

A β was aggregated under physiological conditions for 1 hour and then irradiated with various concentrations of photooxygenation catalyst for 9 hours to oxygenate A β with different oxygenation yields. After these samples were added to cultured PC12 cells and the mixture was incubated for 3 days, the relationship between the oxygenation level of A β and cell viability was examined by counting the number of viable cells. The viability of PC12 cells treated with non-oxygenated A β was approximately 60%, whereas that treated with oxygenated A β with only 2% yield recovered to 100%. This suggests that oxygenated A β is highly effective in reducing cytotoxicity.

Keywords : Amyloid β ; Catalytic photooxygenation; Alzheimer's disease; Cell viability

アルツハイマー病関連ペプチドであるアミロイド β (A β) は疎水性相互作用によって凝集し、細胞外に蓄積することで神経毒性を発揮する。所属研究室では A β の触媒的光酸素化にて酸素原子を導入し、親水性を向上させることで、凝集能を低下させ、細胞毒性を低減することを見出している¹⁾。一方、どの程度 A β を酸素化することで細胞毒性の低減につながるかといった定量関係は明らかでない。そこで本研究では A β の酸素化率と PC12 細胞の生存率の関係を調べることにした。

A β を生理条件下で 1 時間凝集させた後、様々な濃度の光酸素化触媒と共に 9 時間光照射することで酸素化率の異なる酸素化 A β を作成した²⁾。これを PC12 細胞に加えて 3 日間培養した後、生細胞数を数えることで A β の酸素化率と細胞生存率の関係を調べた。その結果、未酸素化 A β を加えた場合の細胞生存率が 60%程度であったのに対し、わずか 2%酸素化された A β を加えた場合では細胞生存率は 100%まで回復した。これにより酸素化 A β が高い細胞毒性低減の効果を持つことが示唆された。

1) Y. Sohma, T. Sawazaki, M. Kanai, *Org. Biomol. Chem.*, **2021**, *19*, 10017-10029.

2) N. Nagashima, S. Ozawa, M. Furuta, M. Oi, Y. Hori, T. Tomita, Y. Sohma, M. Kanai, *Sci. Adv.* **2021**, *7*, eabc9750.

Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B**[D1443-1pm] 16. Natural Products Chemistry, Chemical Biology**

Chair: Shuhei Higashibayashi, Toshitaka Okamura

Wed. Mar 22, 2023 2:00 PM - 3:40 PM D1443 (1443, Bldg. 14 [4F])

[D1443-1pm-01] Stereochemical assignment of macrolide natural products by GIAO NMR calculation and DP4+ analysis○Keisuke Murata¹, Hirotohi Mori¹, Haruhiko Fuwa¹ (1. Chuo University)

2:00 PM - 2:20 PM

[D1443-1pm-02] Total Synthesis of Lobatamides○Soichiro Yasui¹, Shona Banjo¹, Yoshiyuki Nagashima¹, Yuto Okada¹, Eiko Nakasuji¹, Keisuke Nakata¹, Noritaka Chida¹, Toshitaka Okamura¹, Takaaki Sato¹ (1. Keio University)

2:20 PM - 2:40 PM

[D1443-1pm-03] Isolation and Structure Elucidation of Cytotoxic Substances from Marine Mollusk *Aplysia kurodai* and Elucidation of their Origins○Yusuke Hioki¹, Eri Anshita², Tatsuya Sato³, Toyoki Iwao⁴, Atsushi Kawamura^{1,5}, Tsunematsu Yuta^{1,6}, Masaki Kita¹ (1. Graduate School of Bioagricultural Sciences, Nagoya University, 2. School of Agricultural Sciences, Nagoya University, 3. Zakko Club, 4. Toba Fisheries Science Center, 5. Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 6. Institute for Advanced Research, Nagoya University)

2:40 PM - 3:00 PM

[D1443-1pm-04] Development and mechanistic studies of photo-mediated [4+2] cycloaddition for rapid assembly of *iboga*-type scaffold○Gavin Tay¹, Soushi Nishimura¹, Hiroki Kubota¹, Hiroki Oguri¹ (1. The University of Tokyo)

3:00 PM - 3:20 PM

[D1443-1pm-05] Syntheses of tricyclic diterpenes based on site-selective iodination and selective 6-*endo* radical cyclization○Riichi Hashimoto¹, Kengo Hanaya¹, Shuhei Higashibayashi¹, Takeshi Sugai¹ (1. Keio university)

3:20 PM - 3:40 PM

GIAO NMR 計算と DP4+解析によるマクロリドの立体配置の帰属

(中央大理工) ○村田 佳亮・森 寛敏・不破 春彦

Stereochemical assignment of macrolide natural products by GIAO NMR calculation and DP4+ analysis (*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University*) ○Keisuke Murata, Hiroto Mori, Haruhiko Fuwa

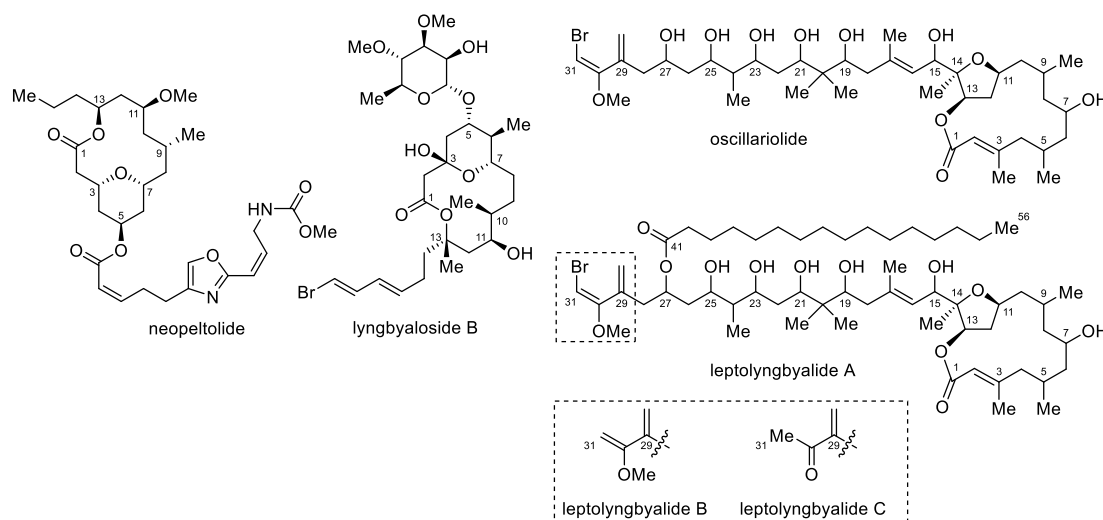
GIAO NMR calculation¹/DP4+ analysis² is now widely used for the structure assignment of natural products. However, there are not many applications of GIAO NMR calculation/DP4+ analysis to macrolides. This is at least in part because a huge number of conformers are usually generated in conformational searches of macrolides owing to the inherent conformational flexibility of the macrocyclic skeleton.

In this study, we evaluated the accuracy of DP4+ analysis by its application to two macrolide natural products, neopeltolide and lyngbyaloside B. Next, we applied NMR calculation/DP4+ analysis to the assignment of the relative configuration of the macrolactone domain of leptolyngbyalide A–C³/oscillariolide⁴.

Keywords : Macrolides; Stereochemical assignment; Quantum chemical calculation

GIAO NMR 計算¹と DP4+解析²は天然物の構造決定に最近よく利用される手法である。しかし、マクロリド化合物への適用例は少なく、大員環骨格の柔軟性に起因して生じる多数の配座異性体の計算にかかるコストが課題である。

本研究では、マクロリド天然物 neopeltolide と lyngbyaloside B を用いて DP4+解析の確度を検証した。さらに、GIAO NMR 計算と DP4+解析で、これまで立体配置が決定されていなかった leptolyngbyalide A–C³/oscillariolide⁴ マクロ環部の相対配置の帰属を行ったので、その詳細を報告する。



- 1) Pulay, P. *et al. J. Am. Chem. Soc.* **1990**, *112*, 8261. 2) Sarotti, M. *et al. J. Org. Chem.* **2015**, *80*, 12526.
- 3) Piel, J.; Moreno, P. *et al. Nat. Chem. Biol.* **2019**, *15*, 813. 4) Murakami, M. *et al. Tetrahedron Lett.* **1991**, *32*, 2391. 5) Murata, K.; Mori, H.; Fuwa, H. *Bull. Chem. Soc. Jpn.* DOI: 10.1246/bcsj.20220253.

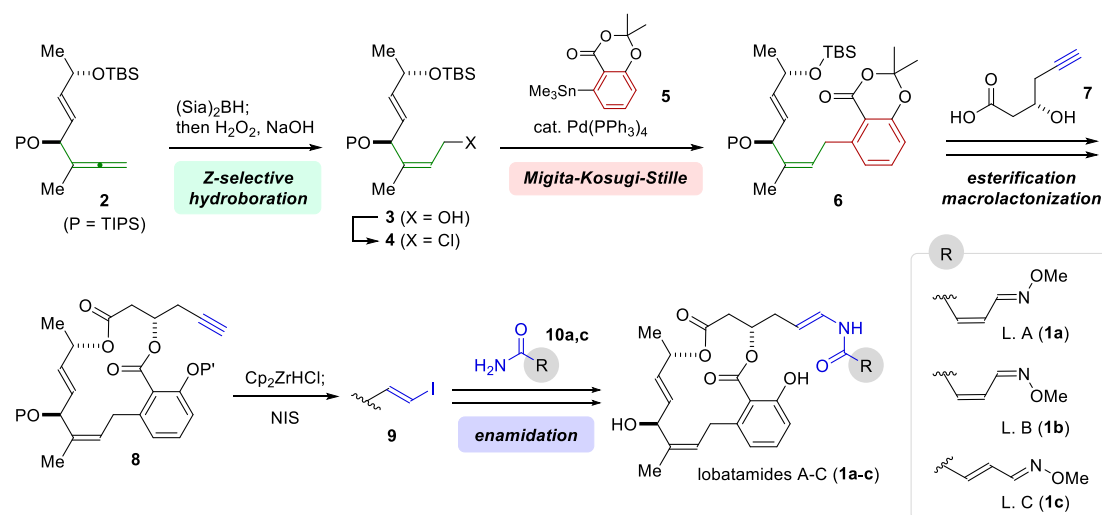
Total Synthesis of Lobatamides

(Keio University) ○Soichiro Yasui, Shona Banjo, Yoshiyuki Nagashima, Yuto Okada, Eiko Nakasuji, Keisuke Nakata, Noritaka Chida, Toshitaka Okamura, Takaaki Sato

Keywords: lobatamide; total synthesis; enamide

Lobatamides A-C (**1a-c**) were isolated from a southwestern Pacific tunicate, and are known to inhibit V-ATPases as potent antitumor macrolides.^{1a,b} Structurally, they share a common macrobisactone framework with various enamide side chains. These enamides would play an important role for their biological activity, although the systematic structure-activity relationship are not investigated.²⁾ In this presentation, we report the total synthesis of lobatamides based on the stereoselective construction of *Z*-allylic arene moiety, and the late-stage installation of the enamide side chains from the terminal alkyne.

The *Z*-selective hydroboration of 1,1-disubstituted allene **2** and subsequent Migita-Kosugi-Stille coupling provided (*Z*)-allylic arene moiety **6**.³⁾ The common macrobisactone framework **8** was then prepared through intermolecular esterification with **7** and ynamide-mediated macrolactonization. The salient feature of our synthetic strategy was the late-stage diversification from alkyne intermediate **8**. Treatment of **8** with the Schwartz reagent (Cp_2ZrHCl) and NIS provided (*E*)-vinyl iodide **9** without affecting the macrobisactone group.^{4a,b} Finally, the total synthesis of lobatamides A (**1a**) and C (**1c**) was achieved by the copper-mediated enamidation with **10a** and **10c**, and the global deprotection.



1) a) J. A. Porco *et al.*, *J. Org. Chem.* **1997**, 62, 8968. b) K. Suzumura *et al.*, *Tetrahedron Lett.* **1997**, 38, 7573. 2) J. A. Porco *et al.*, *J. Am. Chem. Soc.* **2002**, 124, 5650. 3) T. Sato; N. Chida *et al.*, *Chem. Asian. J.* **2018**, 13, 1024. 4) a) T. Kan *et al.*, The 142nd Annual Meeting of the Pharmaceutical Society of Japan (**2021**), b) S. L. Buchwald *et al.*, *Org. Lett.* **2003**, 5, 3667.

海洋軟体動物アメフラシ由来細胞毒性物質の単離・構造決定とその起源の解明

(¹名大院生命農・²名大農・³ざっこクラブ・⁴鳥羽市水産研・⁵信大バイオメディカル研・⁶名大高等研究院) ○日置 裕介¹・庵下 恵理²・佐藤 達也³・岩尾 豊紀⁴・河村 篤^{1,5}・恒松 雄太^{1,6}・北 将樹¹

Isolation and Structure Elucidation of Cytotoxic Substances from Marine Mollusk *Aplysia kurodai* and Elucidation of their Origins (¹Graduate School of Bioagricultural Sciences, Nagoya University, ²School of Agricultural Sciences, Nagoya University, ³Zakko Club, ⁴Toba Fisheries Science Center, ⁵Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, ⁶Institute for Advanced Research, Nagoya University) ○Yusuke Hioki,¹ Eri Anshita,² Tatsuya Sato,³ Toyoki Iwao,⁴ Atsushi Kawamura,⁵ Yuta Tsunematsu,⁶ Masaki Kita¹

The herbivorous sea hare, *Aplysia kurodai* is known to possess cytotoxic compounds such as aplaminones and aplyronines. These compounds have been thought to be derived from sea algae or their associated microorganisms, however, their origins and acquisition pathways are still unclear. To establish the origin of these cytotoxic compounds, we conducted a comprehensive LC-MS/MS analysis of the secondary metabolites of the sea algae collected at the habitat of sea hare and a genetic analysis of the associated microbes.

The investigation of the high polar fraction of *A. kurodai* led us to the isolation of new cytotoxic aplaminone analogs. The LC-MS/MS analysis of the extracts of sea algae collected at the habitat of *A. kurodai* revealed that the algae belonging to the *Laurencia* complex contained aplaminones and aplyronines, and the presence/absence of the compounds varied by the collection sites. These results indicate that the origins of aplaminones and aplyronines could be microbes associated with the *Laurencia* complex. The genomic investigation of the microbes is undergoing.

Keywords : Marine Natural Products; Structure Elucidation; LC-MS/MS; Cytotoxicity; Biosynthetic Gene

藻食性海洋軟体動物アメフラシ (*Aplysia kurodai*) には aplaminone 類や aplyronine 類等の様々な有毒物質が含まれ、これらは餌の海藻や海藻に付着する微生物が生産すると考えられている。しかしながら、その獲得経路や化合物の起源となる生物の多くは未解明である。今回我々は、アメフラシ由来細胞毒性物質の起源生物を解明するため、アメフラシが餌とする海藻の二次代謝成分の包括的 LC-MS/MS 解析と海藻に付着する微生物メタゲノムの解析を行った。

これまでのアメフラシ由来新規化合物探索により、アメフラシの高極性画分から新規 aplaminone 類縁体 5 種を単離・構造決定した。また、これら化合物はアメフラシが餌とする海藻に由来すると推測し、アメフラシが生息する三重県近海にて採取した海藻の抽出エキスについて、その二次代謝成分を LC-MS/MS により解析した。その結果、アメフラシが餌とする紅藻ソゾ類に aplaminone 類と aplyronine 類が含まれることが分かった。興味深いことに、これら化合物の有無は、同種の海藻であっても採取場所によって異なっていたことから、その起源生物はソゾ類に付着する微生物であることが示唆された。現在、ソゾ類に付着する微生物メタゲノムの解析を行っている。

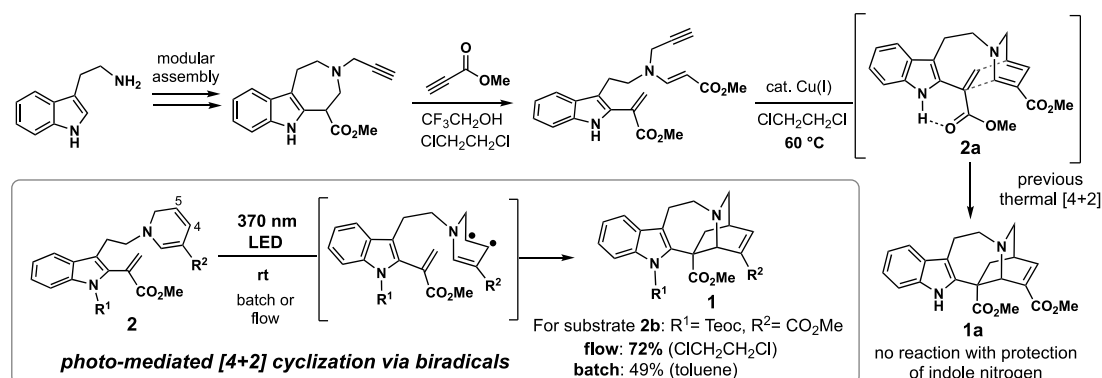
Development and mechanistic studies of photo-mediated [4+2] cycloaddition for rapid assembly of *iboga*-type scaffold

(¹Graduate School of Science, The University of Tokyo, ²Graduate School of Engineering, Tokyo University of Agriculture and Technology) ○Gavin Tay,¹ Soushi Nishimura,¹ Hiroki Kubota,² Hiroki Oguri¹

Keywords: Iboga alkaloids; Photocycloaddition; Dihydropyridine; Multipotent biomimetic intermediate; Photoflow reaction

Iboga-type indole alkaloids are a pharmaceutically significant class of natural products known for its psychoactive and anti-drug addiction properties. In our previous biomimetic synthesis, *iboga*-type scaffold **1a** was assembled via thermal-assisted intramolecular Diels–Alder cycloaddition between the dihydropyridine (DHP) ring and vinylindole methyl acrylate moiety of **2a** in 48% yield.¹ However, the attempted thermal [4+2] cycloaddition of substrates with protection of indole nitrogen resulted in no conversion to form *iboga*-type scaffold **1**. In this study, we achieved the photo-mediated [4+2] cyclization of various substrates with modifications of substituents R¹ and R² for efficient and flexible assembly of the *iboga*-type scaffold **1** at room temperature in the absence of any photocatalysts or sensitizers.

Modular assembly of building blocks to form ene-yne and subsequent Cu(I)-catalyzed 1,6-DHP ring formation² produced cyclization precursor **2** with protection of indole nitrogen.² A representative substrate **2b** (R¹ = Teoc, R² = CO₂Me) exhibits characteristic UV absorption at 365 nm. Photoirradiation at this wavelength region substantially improved the yield of the target *iboga*-type scaffold **1b** up to 72% (batch condition: 48%) with application of micro-flow system. Through computational, spectroscopic, and mechanistic studies, we hypothesize that the photo [4+2] cyclization would be triggered by site-selective activation of C4–C5 double-bond in the DHP unit, which then undergoes a stepwise pathway presumably via open-shelled biradical intermediates. Compared to the thermal cycloadditions, this approach featuring relatively unexplored photo-induced [4+2] cyclizations has been demonstrated to have both broader substrate scopes under milder reaction conditions and practical advantages using series of precursors stable enough to be isolated.



1) Mizoguchi, H.; Oikawa, H.; Oguri, H. *Nat. Chem.* **2014**, *6*, 57.

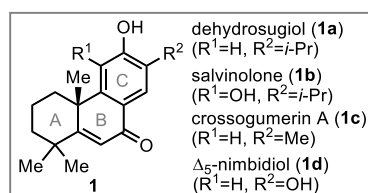
2) Mizoguchi, H.; Watanabe, R.; Minami, S.; Oikawa, H.; Oguri, H. *Org. Biomol. Chem.* **2015**, *13*, 5955.

Syntheses of tricyclic diterpenes based on site-selective iodination and selective 6-*endo* radical cyclization

(¹Faculty of Pharmacy, Keio University) ○ Riichi Hashimoto,¹ Kengo Hanaya,¹ Shuhei Higashibayashi,¹ Takeshi Sugai¹

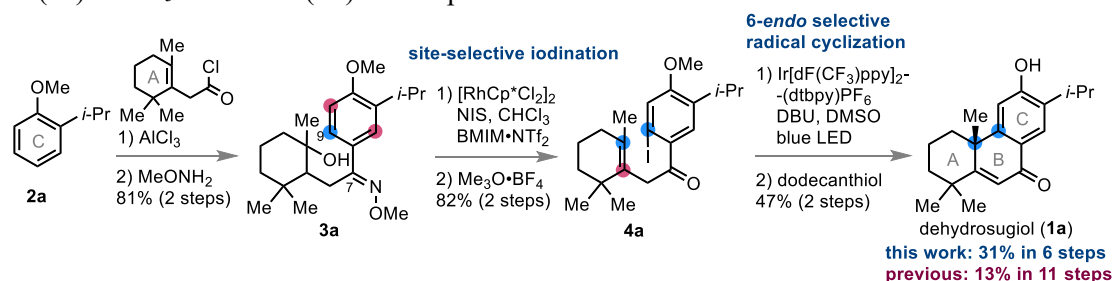
Keywords: Tricyclic Diterpenes; Short-step Synthesis; Site-selective Iodination; Radical Cyclization

【 Introduction 】 Tricyclic abietane and podocarpane diterpenes (**1a-d**) consist of different substitution patterns on C ring and show diverse biological activities.¹⁾ Reported syntheses required many steps to enhance the oxidation level of B ring as well as the introduction of substituents on C ring after cationic polyene cyclization.²⁾ Here we accomplished the short-step syntheses of highly oxidized tricyclic diterpenes (**1a-d**) featuring site-selective iodination and selective 6-*endo* radical cyclization as key steps.



【 Results 】 Friedel-Crafts acylation between substituted methoxybenzene **2a** and acid chloride **3a** followed by oxime formation gave oxime ether **3a** in 81% yield. Rh-catalyzed iodination in a mixture of ionic liquid and CHCl₃ proceeded site-selectively at C9 position. Oxime at C7 position promoted the iodination as the strong directing group. Dehydration of hydroxy group and deprotection of oxime ether were realized in one step with Meerwein reagent, giving cyclic precursor **4a** in 82% yield from oxime ether **3a**.

Radical cyclization of **4a** was investigated by photoredox catalysts under irradiation of blue light. Although 5-*exo* cyclization took place preferentially than 6-*endo* cyclization in most of investigated conditions, the combination of Ir[dF(CF₃)ppy]₂(dtbpy)PF₆ with DBU in DMSO realized preferential 6-*endo* cyclization. Finally, the synthesis of dehydrosugiol (**1a**) was accomplished by deprotection. Our synthetic route improved the total yield and the number of steps (31% in 6 steps) from so far reported synthesis (13% in 11 steps). In similar manner with synthesis route of **1a**, we also accomplished the syntheses of salvinolone (**1b**), crossogumerin A (**1c**) and Δ^5 -nimbiol (**1d**) in 6 steps.



1) M. A. González, *Nat. Prod. Rep.* **2015**, 32, 684.

2) M. Tada *et al.*, *Bioorg. Med. Chem.* **2001**, 9, 347.

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

[E1662-1pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Daisuke Takahashi, Gosuke Hayashi

Wed. Mar 22, 2023 2:20 PM - 3:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-1pm-01] Efficient Synthesis of Tag-Modified Peptide Thioester Facilitated by γ -Substituted Proline

○Koki Nakatsu¹, Gosuke Hayashi¹, Hiroshi Murakami^{1,2} (1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.)

2:20 PM - 2:40 PM

[E1662-1pm-02] Stereospecific syntheses of aryl C-glycosides with glycosyl trifluoroborate

○Kazuki Kurahayashi¹, Kengo Hanaya¹, Takeshi Sugai¹, Go Hirai², Shuhei Higashibayashi¹ (1. Fac. Pharm., Keio Univ., 2. Grad. Sch. Pharm. Sci., Kyushu Univ.)

2:40 PM - 3:00 PM

[E1662-1pm-03] Regio- and Stereoselective β -Arabinofuranosylation Using a Boron-Mediated Aglycon Delivery Method

○Kazuki Inaba¹, Yuna Naito¹, Mina Tachibana¹, Kazunobu Toshima¹, Daisuke Takahashi¹ (1. Keio University)

3:00 PM - 3:20 PM

[E1662-1pm-04] Chemical synthesis of ganglioside TACAs and their conjugation to alpha-galactosyl ceramide for cancer vaccine constructs

○Mads Hartvig Clausen¹ (1. Technical University of Denmark)

3:20 PM - 3:40 PM

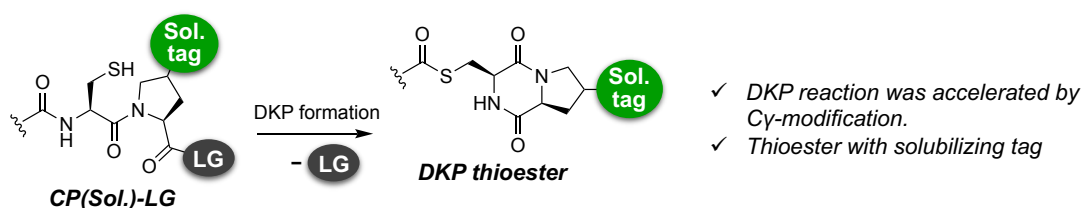
Efficient Synthesis of Tag-Modified Peptide Thioester Facilitated by γ -Substituted Proline

(1. Graduate School of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ.) ○Koki Nakatsu¹, Gosuke Hayashi¹, Hiroshi Murakami^{1,2}

Keywords: Proline derivatives; Thioester; Diketopiperazine; Peptide Ligation; Fmoc Solid-Phase Peptide Synthesis

Native chemical ligation (NCL) is an effective strategy to ligate side-chain unprotected peptide segments between an N-terminal cysteine peptide and a C-terminal peptide thioester in neutral aqueous conditions.¹ To introduce a base-labile thioester moiety through Fmoc solid-phase peptide synthesis (SPPS), many thioester surrogates have been designed and reported by peptide chemists. Cysteinyl-prolyl-leaving group (CP-LG) is easily introduced to a peptide in Fmoc Solid-Phase Peptide Synthesis and converts into thioester through diketopiperazine (DKP) formation. The effect of leaving group to reaction rate in DKP formation has been reported intensively.²⁻⁴ However, few studies have reported the effect of other substitutions to DKP formation. Proline substitutions at γ position greatly affect the cis-trans conversion of prolyl amide and puckering of pyrrolidine ring of proline.⁵ We hypothesized that γ -modified proline is an effective tool to investigate the nature of DKP formation.

Herein, we will discuss the effect of γ -substitution of proline of CP-LG on DKP formation using CP-pyrazole peptides. Some modifications indicated a great improvement in the rate of DKP reaction. In addition, we report peptide ligation using peptide thioester with solubilizing tag attached to the γ -position of the proline to ease the handling of peptides in ligation reaction and purification steps.



- (1) Dawson, P. E.; Muir, T. W.; Clark-Lewis, I.; Kent, S. B. *Science* **1994**, 266, 776.
- (2) Kawakami, T.; Kamauchi, A.; Harada, E.; Aimoto, S. *Tetrahedron Lett.* **2014**, 55, 79.
- (3) Yanase, M.; Nakatsu, K.; Cardoso, C. J.; Konda, Y.; Hayashi, G.; Okamoto, A. *Chem. Sci.* **2019**, 10, 5967.
- (4) Nakatsu, K.; Yanase, M.; Hayashi, G.; Okamoto, A. *Org. Lett.* **2020**, 22, 4670.
- (5) Newberry, R. W.; Raines, R. T. *Top. Heterocycl. Chem.* **2017**, 48, 1.

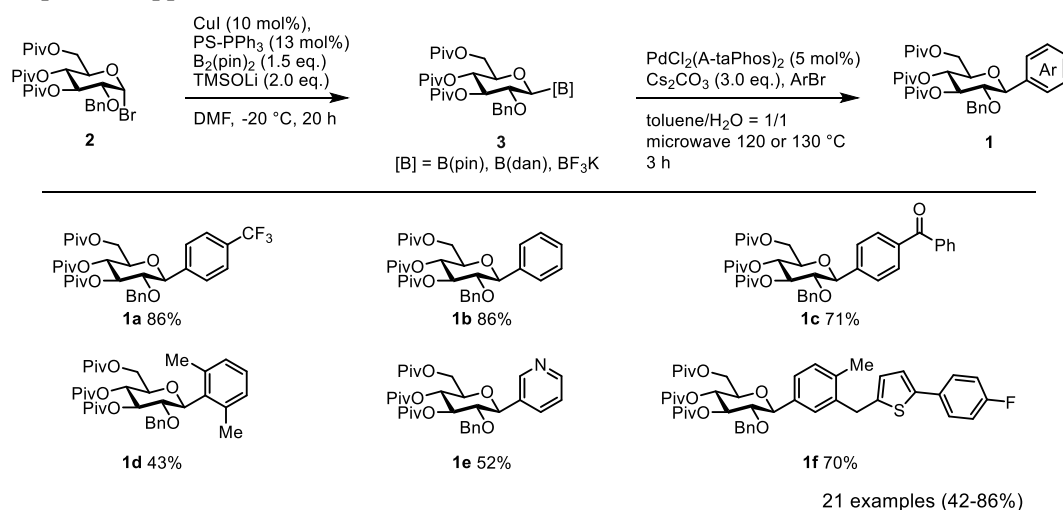
Stereospecific syntheses of aryl C-glycosides with glycosyl trifluoroborate

(¹Faculty of Pharmacy, Keio University, ²Graduate School of Pharmaceutical Sciences, Kyushu University) ○ Kazuki Kurahayashi,¹ Kengo Hanaya,¹ Takeshi Sugai,¹ Go Hirai,² Shuhei Higashibayashi²

Keywords: Aryl C-glycoside; Organoboron reagent; Cross-coupling; Stereospecific synthesis

Aryl C-glycosides, whose sugars are directly connected through C-C bond with aromatic rings, show various biological activities. In contrast to O-glycosides which are readily hydrolyzed under acidic conditions or by glycosidases, C-glycosides are highly stable and utilized as medicines. Since natural and pharmaceutical C-glycosides have a single stereochemistry of either α and β , the desired stereoisomer is desirable. Reported synthetic methods have several disadvantages such as a mixture of α and β products, highly toxic reagents, or many steps.¹⁻³⁾ To overcome these disadvantages in so-far reported methods, we developed Cu-catalyzed stereoselective synthesis of glycosyl borates and the subsequent Pd-catalyzed stereospecific cross-coupling between glycosyl borates and aryl bromides to produce aryl β -C-glycosides **1**.

Firstly, we investigated various conditions in the synthesis of glycosyl boronate from glycosyl bromide **2**, and succeeded in developing β -selective borylation with Cu catalyst. Using β -glycosyl trifluoroborate **3** and aryl bromides, aryl β -C-glycosides **1** were stereospecifically synthesized in high yield with Pd catalyst. The β -configuration of glycosyl trifluoroborates was stereoretentively transferred to that of C-glycosides, and aryl bromides with various functional groups were applicable.



1) M. A. Walczak, *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 12049. 2) G. Hirai, *et al.*, *Org. Lett.* **2021**, *23*, 1940. 3) M. A. Walczak, *et al.*, *Org. Lett.* **2021**, *23*, 4289.

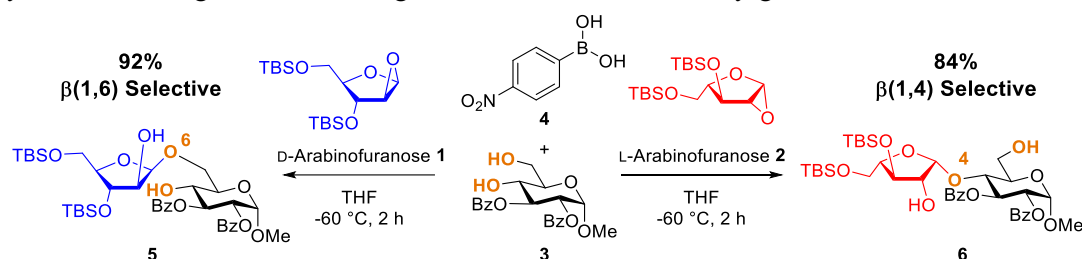
Regio- and Stereoselective β -Arabinofuranosylation Using a Boron-Mediated Aglycon Delivery Method

(Faculty of Science and Technology, Keio University) ○Kazuki Inaba, Yuna Naito, Mina Tachibana, Kazunobu Toshima, Daisuke Takahashi

Keywords: β -Arabinofuranosylation; Boron-Mediated Aglycon Delivery; Regioselective; Stereoselective; Boronic Acid

β -Arabinofuranoside (β -Arbf)-containing glycans have attracted much attention in many research fields due to their interesting biological activities. However, stereoselective construction of β -Arbf linkages has remained challenging owing to the non-availability of neighboring-group participation, the unfavorable anomeric effect, and steric hindrance of the substituent at the C2 position. In addition, furanose is favored by the S_N1 pathway due to its structural and electronic properties compared to pyranose, resulting in the blunted stereoselectivity.¹ In this context, we focused on our boron-mediated aglycon delivery (BMAD), which can construct 1,2-*cis* pyranosides with high regio- and stereoselectivities and we investigated the application of this method for regio- and stereoselective β -arabinofuranosylation.

Initially, the glycosylation of 4,6-diol acceptor **3** with 1,2-anhydro-D-arabinofuranose **1** using a boronic acid catalyst **4** was found to proceed smoothly to give $\beta(1,6)$ -D-Arbf **5** in high yield with high regio- and complete β -stereoselectivities. In addition, it was confirmed that when 1,2-anhydro-L-arabinofuranose **2** was used, the regioselectivity was reversed and $\beta(1,4)$ -L-Arbf **6** was obtained in high yield,² indicating the regioselectivity was completely reversed depending on the optical isomerism of the donor used and was predictable a priori.³ In addition, it was also successfully reversed the regioselectivity for the *cis*-3,4-diol acceptors in the glycosylations using donors **1** and **2**. Mechanistic studies using DFT calculations revealed that the present glycosylation undergoes via S_N1 -type mechanism. Furthermore, the usefulness of this present method was demonstrated by the chemical synthesis of a fragment of arabinogalactan derived from timothy grass.



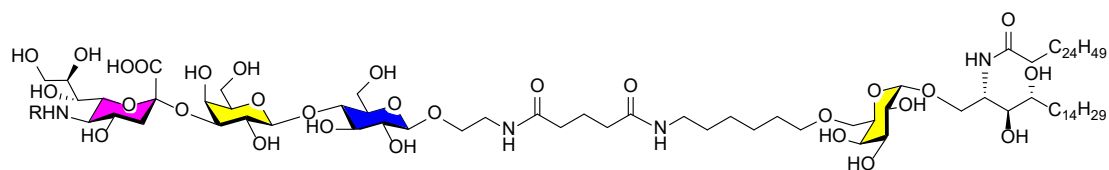
- 1) A. B. Mayfield, J. B. Mettemich, A. H. Trotta, E. N. Jacobsen, *J. Am. Chem. Soc.* **2020**, *142*, 4061. 2) M. Tanaka, A. Nakagawa, N. Nishi, K. Iijima, R. Sawa, D. Takahashi, K. Toshima, *J. Am. Chem. Soc.* **2018**, *140*, 3644. 3) M. Tanaka, K. Sato, R. Yoshida, N. Nishi, R. Oyamada, K. Inaba, D. Takahashi, K. Toshima, *Nat. Commun.* **2020**, *11*, 2431.

Chemical synthesis of ganglioside TACAs and their conjugation to alpha-galactosyl ceramide for cancer vaccine constructs

¹Center for Nanomedicine and Theranostics, Department of Chemistry, Technical University of Denmark ○Mads H. Clausen¹

Keywords: Gangliosides; Cancer; Vaccines; Oligosaccharides; Glycolipids

Immunotherapy is revolutionizing cancer therapy by harnessing the power of the innate and adaptive immune system against cancer cells and providing a more tumor-selective approach in assistance to traditional treatments.¹ The identification of tumor-associated carbohydrate antigens (TACAs), aberrant glycans decorating the surface of tumor cells, has paved the way for the development of TACA-based cancer vaccines.² TACA-based cancer vaccines have not yet reached the clinic and addressing some of the limitations that characterize classical approaches in carbohydrate cancer vaccine development can provide access to more effective candidates. In this context, iNKT cells have emerged as central players in cancer vaccine therapies. Indeed, recent reports have shown that iNKT cell-activating glycolipids, such as α -galactosylceramide (α GalCer), can enhance the immune response against co-delivered cancer antigens by stimulating iNKT cells to serve as universal T helpers.^{3–5} As this strategy appears to be well-suited to break the natural immunotolerance against TACAs,⁵ here we present our synthetic efforts towards the preparation of ganglioside TACAs- α GalCer conjugates, their formulation in liposomes, and their immunological evaluation *in vitro* and *in vivo*.⁶ The synthesis relies on the preparation of a suitably functionalized α GalCer moiety, the expeditious preparation of ganglioside TACAs via improved reactions in sialic acid chemistry, and the conjugation of the two components to obtain novel cancer vaccine candidates.



1) M. Dougan, G. Dranoff, *Annu. Rev. Immunol.* 2009, 27, 83–117; 2) D. H. Dube, C. R. Bertozzi, *Nat. Rev. Drug Discov.* 2005, 4, 477–488; 3) Y. Zhang, R. Springfield, S. Chen, X. Li, X. Feng, R. Moshirian, R. Yang, W. Yuan, *Front. Immunol.* 2019, 10, 11–15; 4) M. Speir, I. F. Hermans, R. Weinkove, *Drugs* 2017, 77, 1–15; F. Broecker, S. Götze, J. Hudon, D. C. K. Rathwell, C. L. Pereira, P. Stallforth, C. Anish, P. H. Seeberger, *J. Med. Chem.* 2018, 61, 4918–4927; C. Romanò, H. Jiang, S. Tahvili, P. Wei, U. B. Keiding, G. Clergeaud, J. R. Henriksen, T. L. Andresen, A. E. Hansen, D. Christensen, M. H. Clausen, *ChemRxiv* 2021, DOI 10.33774/CHEMRXIV-2021-L2SVH.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[E1661-1am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Hiromu Kashida, Tamaki Endoh

Wed. Mar 22, 2023 9:00 AM - 11:10 AM E1661 (1611, Bldg. 16 [1F])

[E1661-1am-01] Development of Cu(II)-responsive DNAzymes by chemoenzymatic incorporation of picolinic acid ligands○Kohei Sakurai¹, Yusuke Takezawa¹, Mitsuhiko Shionoya¹ (1. Grad. School of Science, The Univ. of Tokyo)

9:00 AM - 9:20 AM

[E1661-1am-02] Metal-dependent Regulation of Hybridization Behaviors of DNA Strands Containing Iminodiacetic Acid-modified Uracil Bases○Keita Mori¹, Yusuke Takezawa¹, Mitsuhiko Shionoya¹ (1. Grad. School of Science, The Univ. of Tokyo)

9:20 AM - 9:40 AM

[E1661-1am-03] Development of a sequencing method for XNA by using duplex formation○Hiromu Kashida¹, Emiri Kagawa¹, Yuka Shimizu¹, Keisuke Toya¹, Yuichiro Aiba², Osami Shoji², Hiroyuki Asanuma¹ (1. Grad. Sch. Eng., Nagoya Univ., 2. Grad. Sch. Sci., Nagoya Univ.)

9:40 AM - 10:00 AM

[E1661-1am-04] Development of *PureCap* Analogs for Co-transcriptional Capping Enable Synthesis of Fully Capped Messenger RNA○Masahito Inagaki¹, Naoko Abe¹, Zhenmin Li¹, Yuko Nakashima^{1,2}, Susit Acharyya¹, Kazuya Ogawa¹, Daisuke Kawaguchi¹, Haruka Hiraoka¹, Bannno Ayaka¹, Zheyu Meng¹, Mizuki Tada¹, Tatsuma Ishida¹, Pingxue Lyu¹, Kengo Kokubo¹, Hirotaka Murase¹, Fumitaka Hashiya², Yasuaki Kimura¹, Satoshi Uchida^{4,3}, Abe Hiroshi^{1,5,6,2} (1. Nagoya University, 2. Research Center for Materials Science, Nagoya University, 3. Kyoto Prefectural University of Medicine, 4. iCONM, 5. JST-CREST, 6. iGCORE)

10:10 AM - 10:30 AM

[E1661-1am-05] NMR analysis of mismatch base pair recognition mechanism by naphthyridine derivatives○Shuhei Sakurabayashi^{1,2}, Kyoko Furuita¹, Noriaki Sugiura², Takeshi Yamada², Toshimichi Fujiwara¹, Kazuhiko Nakatani², Chojiro Kojima^{1,3} (1. Institute for Protein Research, Osaka University, 2. SANKEN, Osaka University, 3. Yokohama National University)

10:30 AM - 10:50 AM

[E1661-1am-06] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (86): Intracellular multicolor detection of multiple chemicals using signaling light-up aptamers○Tamaki Endoh¹, Jia-Heng Tan², Shuo-Bin Chen², Naoki Sugimoto^{1,3} (1. FIBER, Konan University, 2. Sun Yat-sen University, 3. FIRST, Konan University)

10:50 AM - 11:10 AM

Development of Cu(II)-responsive DNAzymes by chemoenzymatic incorporation of picolinic acid ligands

(¹Graduate School of Science, The University of Tokyo) ○Kohei Sakurai,¹ Yusuke Takezawa,¹ Mitsuhiro Shionoya¹

Keywords: Artificial DNA; Chemoenzymatic synthesis; DNAzyme; Metal complex; DNA nanotechnology

DNA is one of the most versatile building blocks for constructing nanoscale structures due to its highly programmable sequence-dependent self-assembly. The regulation of DNA structure and function by external stimuli has also attracted increasing attention. Metal-mediated artificial base pairs^[1] are formed by metal coordination of ligand-modified nucleosides with a specific metal ion and have been used to develop metal-responsive DNA systems.^[2] To synthesize various ligand-modified DNA strands, we examined post-synthetic modifications that incorporate ligands chemoenzymatically after DNA synthesis.^[3]

In this study, a picolinic acid (pic) ligand was post-synthetically incorporated into DNA strands by DNA glycosylase reaction and reductive amination. A 15-mer DNA duplex with a pair of pic ligands in the middle was prepared. Melting analysis showed that the addition of 1 equiv. of Cu^{II} ions significantly stabilized the pic-modified duplex ($\Delta T_m = +31.0$ °C), probably due to the formation of an interstrand pic–Cu^{II}–pic complex.

The pic-modified DNA was then applied to the development of Cu^{II}-responsive DNAzymes. A known RNA-cleaving DNAzyme (E5) was divided into two and a pair of pic ligands were incorporated into the stem region (Fig. 1a). The addition of 1 equiv. of Cu^{II} ions resulted in an 8.3-fold increase in DNAzyme activity (Fig. 1b). This is due to the hybridization of the two strands by pic–Cu^{II}–pic complex formation, forming a catalytically active structure. These results suggest that the pic-modified DNA synthesized by chemoenzymatic reaction can be further applied to the construction of various metal-responsive DNA nanostructures.

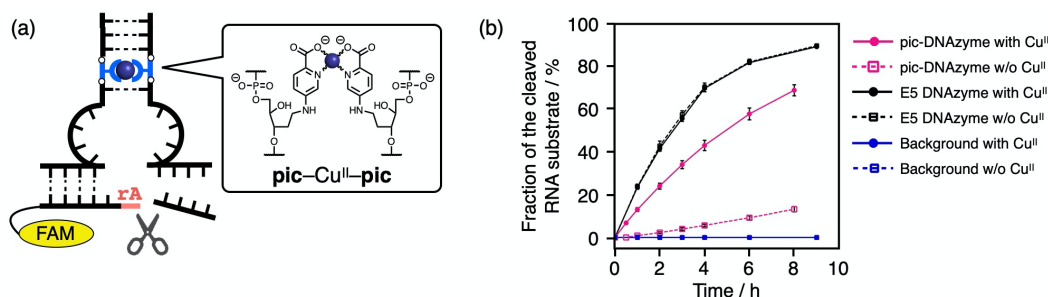


Fig. 1 (a) Design of Cu^{II}-responsive RNA-cleaving DNAzyme containing a pair of pic ligands. “rA” in the substrate represents an adenosine ribonucleotide at the cleaving site. (b) Time-course analysis of the RNA cleavage by pic-modified DNAzyme. [DNAzyme] = 1.0 μ M, [substrate] = 10 μ M, [Cu^{II}] = 0 or 1.0 μ M in 10 mM MOPS (pH 7.0), 1 M NaCl, 10 mM MgCl₂, 25 °C. Error bars: standard errors ($N = 3$).

[1] Y. Takezawa *et al.*, *Chem. Lett.* **2017**, 46, 622. [2] Y. Takezawa *et al.*, *Angew. Chem., Int. Ed.* **2020**, 59, 21488. [3] K. Sakurai *et al.*, the 101st CSJ annual meeting, **2021**, G101-2pm-03.

Metal-dependent Regulation of Hybridization Behaviors of DNA Strands Containing Iminodiacetic Acid-modified Uracil Bases

(¹Grad. School of Science, The Univ. of Tokyo) ○Keita Mori,¹ Yusuke Takezawa,¹ Mitsuhiro Shionoya¹

Keywords: Metal-mediated Base Pair; DNA Nanotechnology; Modified Nucleobase; Artificial DNA; Iminodiacetic Acid

Stimuli-responsive DNA assemblies have attracted increasing attention. In particular, metal ions are useful triggers due to the reversible and selective complexation with specific ligands. We previously developed metal-responsive DNA nanodevices driven by base pair switching of a "bifacial" 5-hydroxyuracil (U^{OH}) nucleobase between hydrogen-bonded $\text{U}^{\text{OH}}\text{--A}$ and metal-mediated $\text{U}^{\text{OH}}\text{--Gd}^{\text{III}}\text{--U}^{\text{OH}}$ base pairs.^{1,2} However, the $\text{U}^{\text{OH}}\text{--Gd}^{\text{III}}\text{--U}^{\text{OH}}$ pairing required sequential incorporation of U^{OH} , which limited the flexibility of sequence design. In this study, we have developed a novel bifacial uracil base that forms a single metal-mediated base pair, which was used to control DNA hybridization behaviors.³ An *N,N*-dicarboxymethyl-5-aminouracil (**dcaU**) base was designed by modifying the 5-position of the uracil with an iminodiacetic acid ligand. The **dcaU** base was expected to function as a tetradentate ligand to form a metal-mediated **dcaU**– Gd^{III} –**dcaU** pair and a hydrogen-bonded **dcaU**–A pair (Fig. 1a).

The **dcaU** nucleoside was newly synthesized from 5-bromo-2'-deoxyuridine and incorporated into DNA strands (**1** and **2**) by standard phosphoramidite chemistry. Melting analysis showed that duplex **1·2** with a **dcaU**–**dcaU** pair was stabilized by the addition of Gd^{III} ions ($\Delta T_{\text{m}} = +16.1\text{ }^{\circ}\text{C}$), indicating the formation of a single **dcaU**– Gd^{III} –**dcaU** pair. In contrast, duplex **1·3** with a **dcaU**–A pair was destabilized upon Gd^{III} addition ($\Delta T_{\text{m}} = -3.5\text{ }^{\circ}\text{C}$). While duplex **1·3** was more stable than duplex **1·2** under Gd^{III} -free conditions, duplex **1·2** showed higher stability in the presence of Gd^{III} .

These results indicate the Gd^{III} -dependent base pair switching between **dcaU**–A and **dcaU**– Gd^{III} –**dcaU**. The **dcaU** base was further applied to switch the DNA hybridization behaviors (Fig. 1b). Strand **1** (15 mer) was mixed with complementary strands **2** (15 mer) and **3'** (13 mer) containing **dcaU** and A, respectively. By the addition of Gd^{III} ions, the hybridization partner of strand **1** was exchanged from **3'** to **2**, forming duplex **1·2** with the **dcaU**– Gd^{III} –**dcaU** pair. Furthermore, the sequential addition of Gd^{III} ions and EDTA resulted in reversible strand exchange.

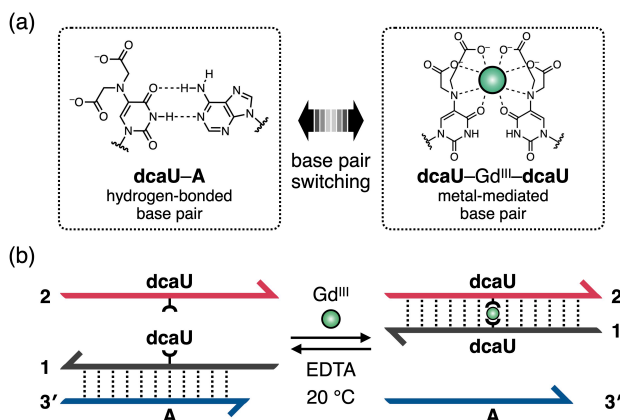


Fig. 1 (a) Gd^{III} -responsive base pair switching of an *N,N*-dicarboxymethyl-5-aminouracil (**dcaU**) base, (b) Gd^{III} -dependent exchange of the hybridization partner of **dcaU**-containing strand **1**.

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- 2) K. Mori, Y. Takezawa, M. Shionoya, the 101st CSJ annual meeting, **2021**, A25-1am-07.
- 3) K. Mori, Y. Takezawa, M. Shionoya, *Chem. Sci.* **2023**, in press. DOI: 10.1039/D2SC06534G

二重鎖形成を利用した人工核酸配列解析法の開発

(名大院工¹・名大院理²) ○樫田 啓¹・香川 恵未莉¹・清水 優香¹・戸谷 恵介¹・愛場 雄一郎²・荘司 長三²・浅沼 浩之¹

Development of a sequencing method for XNA by using duplex formation (¹Graduate School of Engineering, Nagoya University, ²Graduate School of Science, Nagoya University) ○ Hiromu Kashida,¹ Emiri Kagawa,¹ Yuka Shimizu,¹ Keisuke Toya,¹ Yuichiro Aiba,² Osami Shoji,² Hiroyuki Asanuma¹

Recently, enzymes and aptamers composed of xeno nucleic acids (XNAs) have attracted considerable attention owing to their high nuclease resistance and stability. However, there is no general method to analyze XNA sequences. In this study, we developed a new method to sequence XNA. Biotin-modified serinol nucleic acid (SNA) was hybridized with randomized DNA, and was immobilized onto magnetic beads. Then, DNA strands forming duplexes with SNA were eluted and amplified by PCR. As a result, a DNA sequence complementary to the original SNA sequence was obtained via next-generation sequencing (NGS). Moreover, this method can also be used to analyze sequences of peptide nucleic acids (PNA).

Keywords : Xeno nucleic acid; Serinol nucleic acid; Peptide nucleic acid; Sequencing

高い酵素耐性や化学的安定を持つことから人工核酸による酵素やアプタマーが近年注目されている。しかしながら、従来の配列解析法は酵素による伸長反応を利用していたため、適用可能な人工核酸の化学構造に大幅な制限があるという問題点があった。そこで、本研究では人工核酸の配列を解析する新しい手法の開発を目指した。具体的には、二重鎖形成を利用することで人工核酸の配列情報をDNAに“転写”し、DNAを配列解析することで人工核酸の配列を明らかにすることを目指した。

まず、我々が開発した人工核酸であるセリノール核酸 (SNA; Fig. 1)¹⁾の配列解析を試みた。末端をビオチン修飾した10merのSNAとランダム配列を持つDNAを二重鎖形成させ、磁気ビーズ上に固定化した。その後、二重鎖形成したDNA配列を溶出し、PCRで増幅して次世代シーケンサーによって配列解析を行った。その結果、元のSNA配列に相補的なDNA配列が得られた。すなわち、本手法を利用することでSNAの配列解析が可能であることが分かった。また、同様の手法を利用することでペプチド核酸 (PNA)²⁾の配列解析も可能であることがわかった。本手法は二重鎖形成のみを利用しているため、様々な人工核酸の配列解析や修飾塩基導入核酸の配列解析も可能であるという特長がある。本講演では鎖長や配列の影響などについても詳細に報告する予定である。

- 1) H. Kashida, K. Murayama, T. Toda, H. Asanuma, *Angew. Chem. Int. Ed.*, **2011**, *50*, 1285-1288.
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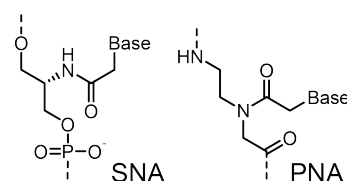


Fig. 1. Chemical structures of SNA and PNA.

完全キャップ化メッセンジャーRNAの製造を可能にする共転写用 *PureCap* アナログの開発

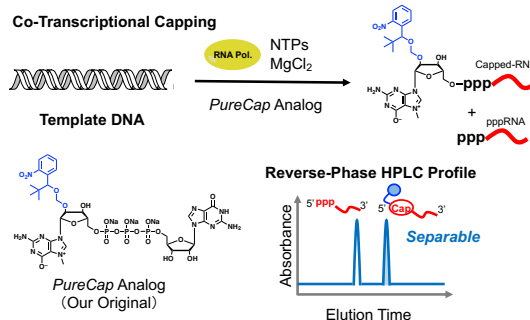
(名大院理¹・名大物国センター²・京府大医大³・iCONM⁴・JST-CREST⁵・iGCORE⁶)
 ○稲垣 雅仁¹・阿部 奈保子¹・Zhenmin Li¹・中嶋 裕子^{1,2}・Susit Acharyya¹・小川 和哉¹・川口 大輔¹・平岡 陽花¹・坂野 文香¹・Zheyu Meng¹・多田 瑞紀¹・石田 竜真¹・Pingxue Lyu¹・小久保 建吾¹・村瀬 裕貴¹・橋谷 文貴²・木村 康明¹・内田 智士^{3,4}・阿部 洋^{1,2,5,6}
 Development of *PureCap* Analogs for Co-transcriptional Capping Enable Synthesis of Fully Capped Messenger RNA (¹Graduate School of Science, Nagoya University, ²Research Center for Materials Science, Nagoya University, ³Graduate School of Medicinal Science, Kyoto Prefectural University of Medicine, ⁴iCONM, ⁵JST-CREST, ⁶iGCORE) ○Masahito Inagaki,¹ Naoko Abe,¹ Zhenmin Li,¹ Yuko Nakashima,^{1,2} Susit Acharyya,¹ Kazuya Ogawa,¹ Daisuke Kawaguchi,¹ Haruka Hiraoka,¹ Ayaka Banno,¹ Zheyu Meng,¹ Mizuki Tada,¹ Tatsuma Ishida,¹ Pingxue Lyu,¹ Kengo Kokubo,¹ Hirotaka Murase,¹ Fumitaka Hashiya,² Yasuaki Kimura,¹ Satoshi Uchida,^{5,6} Hiroshi Abe^{1,2,5,6}

With the spread of the COVID-19 pandemic, the importance of research and development on messenger RNA (mRNA) therapeutics is strongly demanded. One of the characteristic structures of mRNA therapeutics is the 5'-Cap structure. The purity of the Cap structure strongly affects the activity of mRNA therapeutics. An in vitro transcription, co-transcriptional capping, with nucleoside triphosphate (NTPs) and cap analogs, ARCA or CleanCap®, are applied for the general production of mRNA therapeutics. The cap analogs and NTPs are competitively incorporated into the 5'-end RNA, and the resulting transcript mRNA is a mixture of the capped form and the terminal triphosphate form. Since mRNA therapeutics are relatively longer nucleic acids, it is difficult to isolate and purify only the capped form. The Cap purity of mRNA therapeutics is 55-80%, which varies from lot to lot. In this study, we achieved the production of completely capped mRNA by co-transcriptional capping using a novel cap analog, "*PureCap* analog", which was originally developed in our group. In addition, we have also succeeded in producing high-purity mRNA having the "Cap2 structure," which was difficult to synthesize with commercially available cap analogs.

Keywords : Cap Structures; *PureCap* Analogs; mRNA Therapeutics; Photo-Cleavable Hydrophobic Protecting Groups; In Vitro Transcription

新型コロナウイルス感染症の蔓延に伴い、mRNA 医薬に関する研究開発の重要性が増大している。mRNA 医薬に特徴的な構造として、5'末端キャップ構造が挙げられ、そのキャップ構造の純度が mRNA 医薬の活性に大きく影響することから、高純度のキャップ化 mRNA を製造する手法の確立は喫緊の課題である。一般的な mRNA 医薬の製造においては、「キャップアナログ (ARCA、CleanCap®)」を一定割合で含む NTP 溶液中で RNA ポリメラーゼによる転写反応 (共転写法) が用いられる。したがって、5'末端にはキャップアナログと NTP が競合して取り込まれ、得られる転写物 mRNA は、キャップ化体と末端トリリン酸体の混合物となる。mRNA 医薬は非常に長い核酸であるため、キャップ化体のみを単離精製することは困難であり、実際に用いられている mRNA 医薬のキャップ化純度は 55~80%とロット間でのばらつきがある。本研究では、独自に開発した新規キャップアナログである「*PureCap* アナログ」を用いた共転写法により、完全キャップ化 mRNA の製造を達成した。また、既存のキャップアナログでは合成が困難であった「Cap2 構造」を有する mRNA の高純度製造にも成功したので、それらの詳細を報告する。

Reference: Cap analogs with a hydrophobic photocleavable tag enable facile purification of fully capped mRNA with various cap structures, M. Inagaki, N. Abe, Z. Li, Y. Nakashima, S. Acharyya, K. Ogawa, D. Kawaguchi, H. Hiraoka, A. Banno, Z. Meng, M. Tada, T. Ishida, P. Lyu, K. Kokubo, H. Murase, F. Hashiya, Y. Kimura, S. Uchida, H. Abe, *ChemRxiv*. 2022, Submitted (Sep. 29)



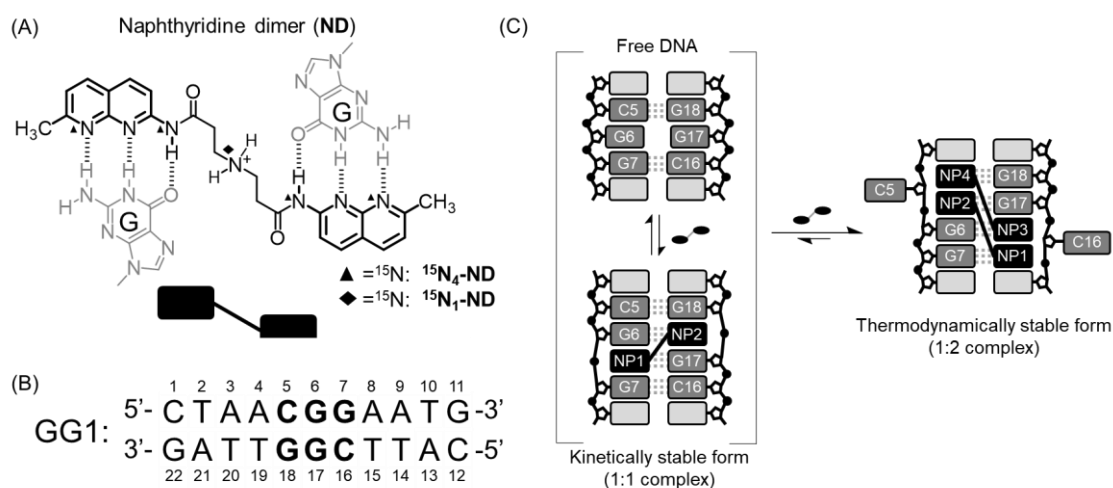
NMR analysis of mismatch base pair recognition mechanism by naphthyridine derivative

(¹*Institute for Protein Research, Osaka University*, ²*SANKEN, Osaka University*, ³*Yokohama National University*) ○Shuhei Sakurabayashi^{1,2}, Kyoko Furuita¹, Noriaki Sugiura², Takeshi Yamada², Toshimichi Fujiwara¹, Kazuhiko Nakatani², Chojiro Kojima^{1,3}

Keywords: NMR, structural analysis, naphthyridine, isotope labelling, mismatch

Repeat expansion diseases are caused by expansions of simple sequence repeats in the human genome. The aberrant CGG repeat expansions in an *FMR1* gene induce fragile X syndrome. A synthetic small molecule naphthyridine dimer (**ND**, Fig. 1A, ref. 1) binds to d(CG_nG) triad, a structural motif found in the hairpin structure in CGG repeat.

In this study, the interaction between a small molecule **ND** that binds to the CGG sequence and double-stranded DNA (dsDNA) containing the d(CG_nG) sequence (**GG1**, Fig. 1B) was analyzed by NMR, accompanied by the synthesis of ¹⁵N-labeled **NDs** (Fig. 1A). **ND** was found to form two types of complexes with **GG1**: a kinetically stable (dsDNA : **ND**) 1:1 complex and a thermodynamically stable 1:2 complex (Fig. 1C). Analysis of the ³¹P NMR spectrum revealed that the phosphate backbone of the 1:1 complex is unwound, whereas in the 1:2 complex can release the strain in the backbone by flip-outs of cytosines (C5 and C16).



(A) The binding mode of **ND** to d(CG_nG) triad. (B) the 1:2 complex structure of d(CG_nG) triad and **ND** determined by NMR. (C) 1D ¹H-NMR spectrum of the binding intermediate of imino proton region.

(ref. 1) K. Nakatani, S. Sando, H. Kumasawa, J. Kikuchi and I. Saito, *J. Am. Chem. Soc.*, 2001, **123**, 12650–12657

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (86): Intracellular multicolor detection of multiple chemicals using signaling light-up aptamers

(¹FIBER, Konan University, ²Sun Yat-sen University, ³FIRST, Konan University) ○Tamaki Endoh¹, Jia-Heng Tan,² Shuo-Bin Chen², Naoki Sugimoto^{1,3}

Keywords: RNA, aptamer, imaging, fluorophore, orthogonality

Various chemical probes that output fluorescence signals have been developed to visualize molecules in living cells. Recently, RNA-based mimics of fluorescent proteins, which are known as light-up aptamers consisting of an RNA aptamer and a fluorogen, have been developed. Light aptamers can be converted into so-called signaling aptamers, which enable fluorometric detection and quantification of small molecules. Detection of small chemicals such as metabolites in living cells has been reported using the signaling aptamers.

Although light-up aptamers that fluoresce at different wavelengths have been developed, only a single target chemical has been detected at a time in cells. In this study, we demonstrate RNA selection based on the sequence of a pioneering light-up aptamer, Broccoli, to create orthogonal light-up aptamers, each of which recognizes a different fluorogen and emits fluorescence at a different wavelength. We obtained these orthogonal light-up aptamers using RNA-capturing microsphere particles (R-CAMPs), which enable selection of RNAs interacting with a molecule of interest emitting fluorescence.¹ In addition, based on the orthogonal light-up aptamers, we have designed signaling light-up aptamers for fluorometric detection of multiple chemicals (Figure 1). We succeeded simultaneous detection of theophylline and *S*-adenosyl methionine in cells by blue and green fluorescence.² The results demonstrated here provides a simple strategy for rational designing of the signaling aptamers for multicolor detection of intracellular chemicals.

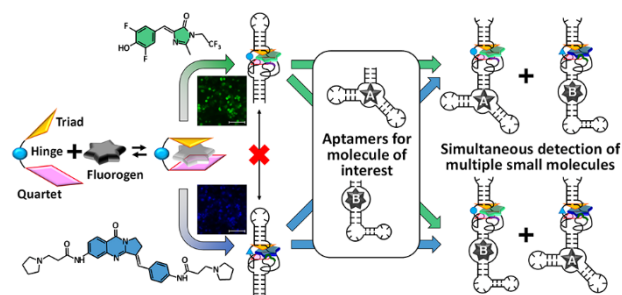


Figure 1. Construction of signaling aptamers targeting multiple small chemicals.²

1) a) T. Endoh, T. Ohya, N. Sugimoto, *Small* **2019**, *15*, 1805062; b) T. Endoh, N. Sugimoto, *Anal. Chem.* **2020**, *92*, 7955; c) S. Satpathi, T. Endoh, P. Podbevšek, J. Plavec, N. Sugimoto, *Nucleic Acids Res.* **2021**, *49*, 8449; d) T. Endoh, S. Takahashi, N. Sugimoto, *Chem. Commun.* **2023**, in press, DOI: 10.1039/D2CC05858H. 2) T. Endoh, J.-H. Tan, S.-B. Chen, N. Sugimoto, *Anal. Chem.* **2023**, in press, DOI: 10.1021/acs.analchem.2c03598.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[E1661-1vn] 17. Biofunctional Chemistry, Biotechnology**

Chair: Koji Oohora, Nobutaka Fujieda

Wed. Mar 22, 2023 4:10 PM - 6:40 PM E1661 (1611, Bldg. 16 [1F])

[E1661-1vn-01] Proposed BciC enzymatic hydrolysis and decarboxylation mechanism○Mitsuaki Hirose¹, Jiro Harada², Yuichiro Kashiama³, Hitoshi Tamiaki¹ (1. Ritsumeikan Univ., 2. Kurume Univ., 3. Fukui Univ. of Technol.)

4:10 PM - 4:30 PM

[E1661-1vn-02] Fabrication of Oil-in-Water (O/W) emulsions using enzyme reactive self-assembling peptides○Ayato Higuchi¹, Rie Wakabayashi¹, Masahiro Goto^{1,2}, Noriho Kamiya^{1,2} (1. The Univ. of Kyushu, 2. Center for Future Chemistry, The Univ. of Kyushu)

4:30 PM - 4:50 PM

[E1661-1vn-03] Dispersion of protein nanoparticle in water/DMSO mixed solvent○Maika Yamashita¹, Norifumi Kawakami¹, Kenji Miyamoto¹ (1. Keio University)

4:50 PM - 5:10 PM

[E1661-1vn-04] Studies on the association character and structural analysis of antibody light chain that tetramerizes by domain swapping○Takahiro Sakai¹, Shohei Yamaguchi¹, Tsuyoshi Mashima¹, Naoya Kobayashi¹, Hideaki Ogata⁴, Emi Hifumi², Taizo Uda³, Shun Hirota¹ (1. Nara Inst. Sci. Tech., 2. Oita Univ., 3. ISIT, 4. University of Hyogo)

5:10 PM - 5:30 PM

[E1661-1vn-05] Development of Artificial Metalloenzymes with 2-His-1-Carboxylate Facial Triad toward Stereoselective Michael Addition Reaction○Ryusei Matsumoto¹, Saho Yoshioka², Yoshitsugu Morita¹, Nobutaka Fujieda^{1,2} (1. Osaka Metropolitan University, 2. Osaka Prefecture University)

5:40 PM - 6:00 PM

[E1661-1vn-06] Catalytic C–H bond amination by engineered hemoproteins containing iron porphycene as an artificial cofactor○Yoshiyuki Yoshiyuki¹, Koji Oohora¹, Takashi Hayashi¹ (1. Osaka University)

6:00 PM - 6:20 PM

[E1661-1vn-07] Directed Evolution of Myoglobin Reconstituted with an Iron Corrole Complex: Development of Artificial Peroxidase with Enhanced Catalytic Activity○Koki Takeuchi¹, Shunsuke Kato¹, Takashi Hayashi¹ (1. Graduate School of Engineering, Osaka University)

6:20 PM - 6:40 PM

Proposed BciC enzymatic hydrolysis and decarboxylation mechanism

(¹Graduate School of Life Sciences, Ritsumeikan University, ²Kurume University School of Medicine, ³Graduate School of Engineering, Fukui University of Technology) ○Mitsuaki Hirose,¹ Jiro Harada,² Yuichiro Kashiya,³ Hitoshi Tamiaki¹
 Keywords: BciC; Chlorophyll; Decarboxylation; Enzyme; Hydrolysis

Chlorophylls are molecularly designed to optimize various roles in photosynthesis (sunlight absorption, excited energy transfer, and charge separation) by enzymatic modifications of their peripheral functional groups as well as the core skeleton.

Most photosynthetic antennas are formed by complexation of pigments with proteins, but the core part of chlorosomes, the main light-harvesting antennae of green photosynthetic bacteria, consists solely of bacteriochlorophyll (BChl) *c*, *d*, and *e* molecules (Fig. 1, left drawing). These BChl-*c/d/e* have common structural motifs, namely, the presence of a hydroxy group at the C3¹-position and the absence of a methoxycarbonyl group at the C13²-position. A BciC enzyme catalyzed the removal of a methoxycarbonyl group in chlorophyllide-*a* at the C13²-position, which reduced the steric hindrance around the 13-keto-carbonyl group.¹ Therefore, the BciC is one of the most important enzymes in the biosynthesis of BChl-*c/d/e*. The *in vivo* BciC-catalyzed reaction mechanism would occur via the two sequential steps:^{2,3} (1) enzymatic hydrolysis of the C13²-methyl ester [Fig. 1, right, step (i)], followed by (2) quick, spontaneous decarboxylation in the resulting carboxylic acid [Fig. 1, right, step (ii)]; however, the possibility that the C13²-decarboxylation enzymatically proceeded, could not be ruled out. We conducted docking simulations of a computationally predicted BciC protein conformation and the precursor, as well as *in vitro* assays of mutated BciC with a zinc-complexed model substrate. Thus, we discussed BciC-catalyzed hydrolysis and decarboxylation.

1) T. Oba, H. Tamiaki, *Photosynth. Res.* **1999**, 61, 23. 2) M. Hirose, J. Harada, H. Tamiaki, *Biochemistry* **2020**, 59, 4622. 3) M. Hirose, J. Harada, H. Tamiaki, *Bioorg. Med. Chem. Lett.* **2021**, 40, 127931.

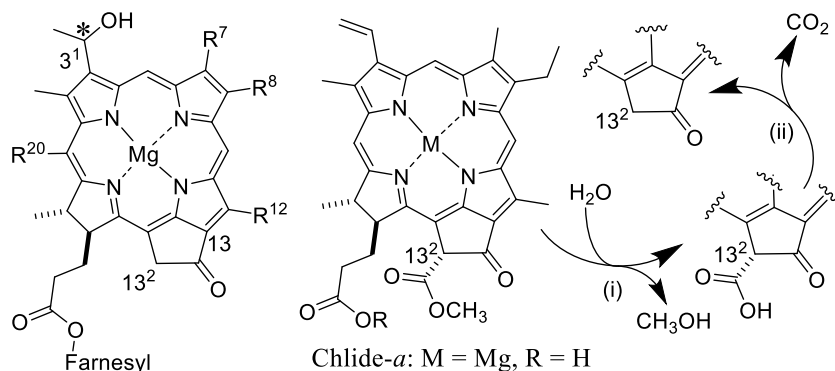


Figure 1. Molecular structures of farnesylated BChl-*c/d/e* homologs; BChl-*c*: R⁷ = R²⁰ = CH₃; BChl-*d*: R⁷ = CH₃, R²⁰ = H; BChl-*e*: R⁷ = CHO, R²⁰ = CH₃; R⁸ = CH₂CH₃, CH₂CH₂CH₃, or CH₂CH(CH₃)₂, CH₂C(CH₃)₃; R¹² = CH₃ or CH₂CH₃. The asterisk (*) shows the 3¹-chirality (left drawing). A (mutated) BciC enzymatic reaction mechanism via two successive reactions: (i) BciC-catalyzed hydrolysis of the C13²-methoxycarbonyl group in Chlide-*a*/Zn-Me-Pheide-*a* and (ii) decarboxylation of the C13²-carboxy group (right drawing).

酵素反応性自己組織化ペプチドを用いた O/W エマルションの創製

(九大院工) ○樋口 亜也斗・若林 里衣・後藤 雅宏・神谷 典穂

Fabrication of Oil-in-Water (O/W) emulsions using enzyme reactive self-assembling peptides
(Graduate School of Engineering, Kyushu University)

○Ayato Higuchi, Rie Wakabayashi, Masahiro Goto, Noriho Kamiya

In this study, we aimed to fabricate highly effective Oil-in-Water (O/W) emulsions for potential vaccine applications. To achieve this goal, self-assembling peptides, Fmoc-XL₂QG (X = 20 natural amino acids), having reactivity to microbial transglutaminase (MTG) enzyme were synthesized and investigated^[1, 2]. Among the 20 self-assembling peptides, those having charged or hydrophilic amino acids at the X position showed both self-assembling ability and MTG reactivity, and stabilized the interface of O/W emulsions. The study on antigen uptake into dendritic cells (DC2.4) using enhanced green fluorescent protein (EGFP) as a model antigen showed that the higher uptake by O/W emulsion formulations than EGFP alone.

Keywords : Peptide Amphiphile; Emulsion; Enzymatic reaction; Self-assembly; Vaccine.

本研究はワクチンへの応用が可能な O/W エマルションの作製を目指し、そのために微生物由来トランスグルタミナーゼ (MTG) 反応性を有する自己組織化ペプチド Fmoc-XL₂QG (X = 任意のアミノ酸) の利用を提案している。MTG 反応により抗原タンパク質を直接自己組織化ペプチド上に提示した抗原修飾ファイバーを O/W エマルションの界面安定化剤として用いることで、これが可能になると考えた (Fig. 1a)^[1, 2]。ペプチド配列の探索を行った結果、X に荷電性、親水性アミノ酸を導入したペプチドが自己組織化能と MTG 反応性を併せ持ち、エマルション界面を安定化することが明らかとなった。また、モデル抗原として緑色蛍光タンパク質 (EGFP) を選択し、樹状細胞 (DC2.4) への抗原の取り込みを評価した結果、EGFP のみと比較して O/W エマルションにより取り込みが向上することが確認された (Fig. 1b)。

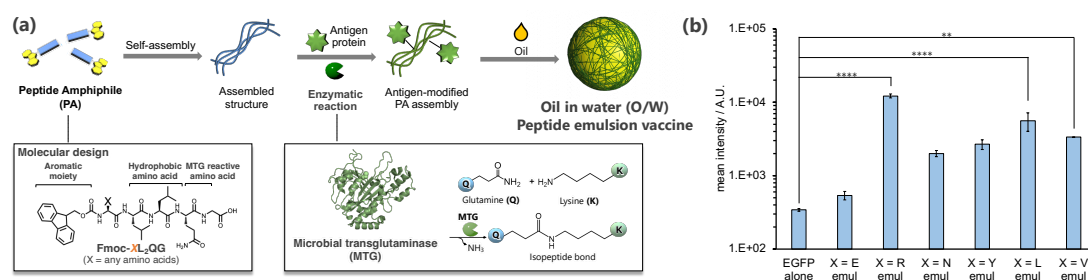


Fig. 1 (a) Conceptual diagram of this study.

(b) Mean EGFP fluorescence intensities of DC2.4 cells treated with EGFP samples. N = 3, mean \pm SD, ** $p < 0.01$, **** $p < 0.0001$.

[1] R. Wakabayashi, A. Suehiro, M. Goto, N. Kamiya, *Chem. Commun.* **55**, 640 (2019).

[2] R. Wakabayashi, A. Higuchi, H. Obayashi, M. Goto, N. Kamiya, *Int. J. Mol. Sci.*, **22**, 3459 (2021).

Dispersion of Protein Nanoparticle in Water/DMSO Mixed Solvent

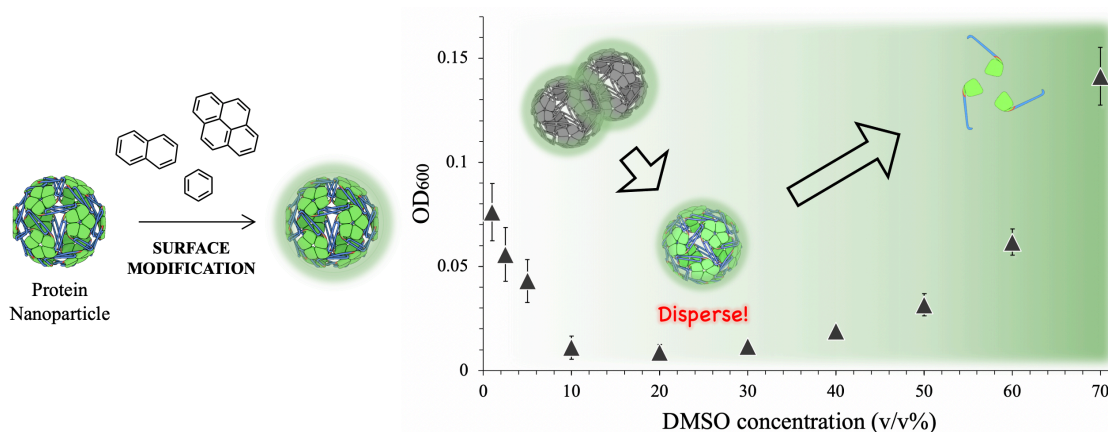
(¹ Keio University) ○Maika Yamashita,¹ Norifumi kawakami,¹ Kenji Miyamoto¹

Keywords: Protein Nanoparticles; Dimethyl Sulfoxide; TIP60; Hydrophobic Effect; Chemical Modification

Proteins that fold in organic solvents will be attractive materials for applications. Possible approaches to obtain such proteins are designing the sequence by computational simulation or experimentally exploring the sequence by random mutagenesis. However, combinations of various organic solvents and large sequence space of proteins make it difficult for the sequence design in simulation approaches. The random mutagenesis approach is also inefficient because proteins are generally synthesized in an aqueous biological environment, requiring purifications and subsequent refolding in organic solvents. In this study, as the first step for designing the protein folded in organic solvent, we propose an alternative approach to design the soluble protein based on our designed protein nanocage TIP60^{1,2} in organic solvents as following two steps.

First, the exterior surface of TIP60 was chemically modified with aromatic compounds, and then the solubility in the different concentration ratios of water/ DMSO mixed solvent was observed by monitoring the light scattering (Figure). As a result, although the modified protein was aggregated in water, the dispersibility was improved under a specific concentration of DMSO. The optimal ratio of mixed solvent was different depending on the size of the aromatic rings of modified groups.

Second, we prepared the mutant having hydrophobic amino acids at the position where the aromatic compound was modified. The mutant showed that the protein yield was improved compared to that of TIP60 without mutation in the optimized ratio of mixed solvent. These data suggested that our method may provide a basis for designing hydrophobic proteins.



1) N. Kawakami *et al.*, *Angew. Chem. Int. Ed.* **2018** 2) J. Obata *et al.*, *Chem. Commun.*, **2021**

Studies on the association character and structural analysis of antibody light chain that tetramerizes by domain swapping

(¹Div. Mat. Sci., NAIST, ²Grad. Sch. Sci., Univ. Hyogo, ³Inst. Res. Mgmt., Oita Univ., ⁴Nanotech Lab., ISIT) ○ Takahiro Sakai,¹ Shohei Yamaguchi,¹ Tsuyoshi Mashima,¹ Naoya Kobayashi,¹ Hideaki Ogata,² Emi Hifumi,³ Taizo Uda,⁴ Shun Hirota¹

Keywords: Antibody light chain; Domain swapping; Oligomerization; Thermodynamic parameters; Variable region

Catalytic antibody is an antibody exhibiting catalytic activity. Its activity has been reported to increase by oligomerization. In this research, we investigated an oligomeric catalytic antibody light chain #4 variant, #4C214A, in which the

Cys residue that forms a disulfide bond with Cys of the heavy chain is replaced with Ala (Fig. 1). According to size exclusion chromatography (SEC) analysis, #4C214A exists in equilibrium between monomeric and tetrameric forms. The standard enthalpy change by dissociation of the tetramer to monomers calculated from the dissociation constants decreased by increasing the temperature (4–45°C). It indicates that #4C214A forms a tetramer through hydrophobic interactions. Additionally, the dissociation rate of the #4C214A tetramer was much slower than those of typical protein complexes, indicating that relatively large structural changes occur during dissociation of the tetramer.

In order to investigate whether the variable or constant region contributes to the oligomerization, we prepared a variant with a TEV protease recognition site introduced between the variable and constant regions of #4C214A. The purified samples were then cleaved with a TEV protease. According to SEC analysis, the variable region of #4, #4VL, existed in equilibrium between monomeric and tetrameric forms. Two domain-swapped dimers of #4VL constructed a tetramer in the crystal structure (Fig. 2). Many hydrophobic residues were located at the dimer–dimer interface, supporting our hypothesis that hydrophobic interactions contribute to the tetramerization.



Fig. 1. Schematic representation of equilibrium between monomeric and tetrameric forms of a catalytic antibody light chain.

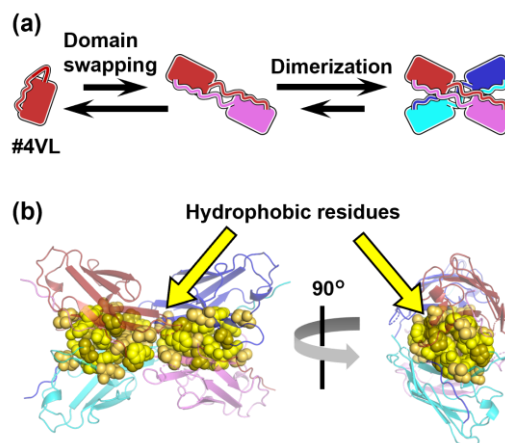


Fig. 2. (a) Schematic diagram of #4VL tetramerization. (b) #4VL tetrameric structure and hydrophobic residues between #4VL domain-swapped dimers.

2-His-1-Carboxylate Facial Triad 構造を有する人工金属酵素の開発

(¹大阪公大院農、²阪府大院生命) ○松本隆聖¹・吉岡紗穂²・森田能次¹・藤枝伸宇^{1,2}
Development of Artificial Metalloenzymes with 2-His-1-carboxylate Facial Triads toward Stereoselective Michael Addition Reaction

(¹Graduate School of Agriculture, Osaka Metropolitan University, ²Graduate School of Life and Environmental Sciences, Osaka Prefecture University)

○Ryusei Matsumoto, Saho Yoshioka, Yoshitsugu Morita, Nobutaka Fujieda

Lately, artificial metalloenzymes have garnered significant interest as emerging hybrid catalysts endowing chemical catalyst with stereoselectivity in biomolecule. TM1459 from *Thermotoga maritima* has high thermal stability and contains a metal binding site consisting of 4-histidine tetrad. By using this protein as metal ligands, we have recently developed the artificial metalloenzymes. In this study, we attempted to construct enzymes with high stereoselectivity by mutating four histidines, at this metal binding site, to alanine or metal-chelating glutamate to build 2-his-1-carboxylate facial triad. We screened thus obtained library of mutants in the asymmetric Michael addition reaction, and further characterized the several mutants that showed high stereoselectivity.

Keywords : Artificial Metalloenzymes, Macromolecular Ligands, Stereodivergent reaction

近年、タンパク質に金属錯体を結合させたハイブリッド触媒である人工金属酵素の構築が注目を集めている。当研究室では超好熱菌由来の TM1459 タンパク質を用い、4 つのヒスチジン残基からなる金属結合部位に直接金属イオンを結合させることで、より簡便に人工金属酵素を構築する手法を開発してきた¹。本研究では、この 4 つのヒスチジン残基のうち 2 つをそれぞれ、カルボン酸を側鎖に持つアミノ酸とアラニンに変異させることで 2-His-1-Carboxylate Facial Triad 構造を活性中心に構築した。これらに硫酸銅を導入することで不斉マイケル付加反応のスクリーニングを行なった。

モデル反応として、2-アザカルコンをアクセプター、アセト酢酸メチルをドナーとして、反応(Fig 1)を行なった。構築した変異体をライブラリーとしてスクリーニングしたところ、H52A/H58E 変異体を添加した際に鏡像体過剰率が 96 %を示し、立体選択性が見られた。本発表ではこれらの詳細に加え、さらなる変異導入によるライブラリーの拡充と、それらの結晶構造をもとにした機能解析について議論する²。

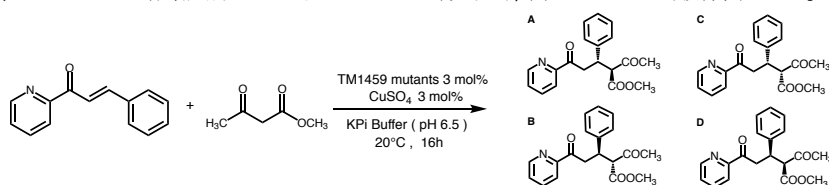


Fig 1. Model reaction employed in this study

1) (a) Fujieda, N.; Itoh, S. et al., *J. Am. Chem. Soc.*, **2017**, 139, 5149. (b) Fujieda, N.; Itoh, S. et al., *Angew. Chem. Int. Ed.*, **2020**, 59, 7717. 2) Matsumoto, R.; Fujieda, N. et al., *ChemRxiv*, **2022**, 10.26434/chemrxiv-2022-5sh4j.

Catalytic C–H bond amination by engineered hemoproteins containing iron porphycene as an artificial cofactor

(Graduate School of Engineering, Osaka University) ○Yoshiyuki Kagawa, Koji Oohora, Takashi Hayashi

Keywords: Iron Porphycene; Artificial Metalloenzyme; Hemoprotein; C–H Bond Amination; Nitrene Transfer

Artificial metalloenzymes afforded by combination of protein scaffolds and metal complexes have emerged as a promising catalyst to realize new-to-nature reactions. Recently, hemoprotein-based artificial metalloenzymes for C–H bond amination have been demonstrated by directed evolution¹ and substitution of the metal center of heme.² Our group has previously reported that myoglobins reconstituted with metal complexes of porphycene, a constitutional isomer of porphyrin, catalyze C–H bond hydroxylation³ and olefin cyclopropanation⁴. In this work, we investigated the catalytic activity of the hemoprotein reconstituted with metalporphycene toward C–H bond aminations (Fig. 1).

First, reconstituted myoglobins with Mn-, Fe- and Co-porphycenes (rMb-MnPc, rMb-FePc, rMb-CoPc) were prepared. rMb-FePc outperforms other reconstituted myoglobins and native myoglobin (nMb) for the intramolecular C–H bond amination of 2,4,6-triisopropylbenzenesulfonyl azide. Kinetic studies revealed that k_{cat} value of rMb-FePc ($k_{\text{cat}} = 55 \text{ s}^{-1}$) was higher than that of nMb ($k_{\text{cat}} = 14 \text{ s}^{-1}$), whereas both K_{m} values were almost the same. These results indicate that the catalytic activity was improved by the substitution of heme with iron porphycene in myoglobin. Next, the C–H bond amination by rMb-FePc mutants were evaluated. The H64A mutant promotes the C–H bond amination of 2,4,6-triethylbenzenesulfonyl azide with TON of 23 with 27%ee, whereas rMb-FePc and nMb show lower activities (TON = 7 and 2, respectively) and no enantioselectivity. Further investigation using other protein scaffolds and the mutants is now in progress.

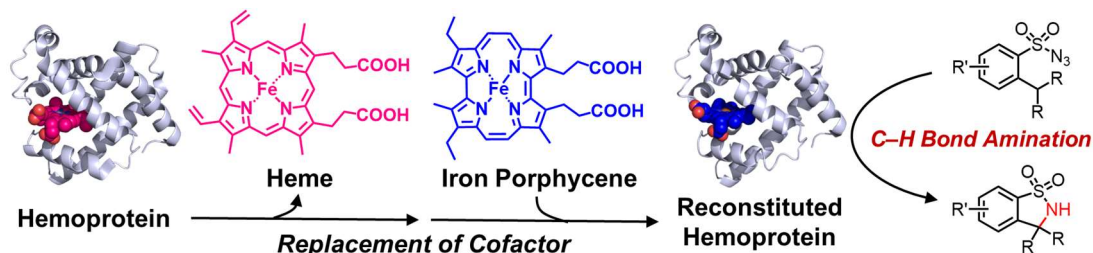


Fig. 1. Intramolecular C–H bond amination by reconstituted hemoprotein.

- 1) F. H. Arnold *et al.*, *Nat. Chem.* **2017**, 9, 629. 2) J. F. Hartwig *et al.*, *J. Am. Chem. Soc.* **2017**, 139, 1750.
 3) K. Oohora, T. Hayashi *et al.*, *J. Am. Chem. Soc.* **2013**, 135, 17282. 4) K. Oohora, T. Hayashi *et al.*, *J. Am. Chem. Soc.* **2017**, 139, 18460.

Directed Evolution of Myoglobin Reconstituted with an Iron Corrole Complex: Development of Artificial Peroxidase with Enhanced Catalytic Activity

(Graduate School of Engineering, Osaka University) ○Koki Takeuchi, Shunsuke Kato, Takashi Hayashi

Keywords: Directed evolution; High-throughput screening; Iron corrole complex; Myoglobin; Artificial peroxidase

Artificial metalloenzymes (ArMs), where a synthetic metal cofactor is incorporated into a protein scaffold, have received much attention due to their unique properties. ArMs hold a great potential to combine attractive features of natural enzymes and transition metal catalysts. The non-natural catalytic activities of ArMs can be systematically tuned by a series of genetic engineering techniques, such as directed evolution. Our group has previously reported an ArM, termed Mb-1, in which myoglobin (Mb) is reconstituted with an Fe corrole complex **1**.¹ Since the trianionic character of corrole ligand could stabilize high-valent iron-oxo intermediates, Mb-1 was found to show higher H₂O₂-dependent catalytic peroxidase activity toward oxidation of phenolic compounds compared to native Mb. Based on this promising result, we here set out to perform directed evolution of Mb-1 to further improve its peroxidase activity.

Development of an accurate high-throughput screening (HTS) platform is necessary to realize the directed evolution campaign for the ArMs (Figure 1). In this study, we first developed a new HTS platform for the directed evolution of Mb-1 based on an affinity purification system using maltose binding protein-tag.² The HTS platform enabled us to quickly purify the protein scaffolds and assemble the target ArMs efficiently in the 96-well format. Using this HTS platform, we next carried out the screening of protein library generated via site-saturation mutagenesis for the amino acid residues located in the active site of Mb. Through three rounds of the library screening, an L89F/I99L/I107F variant was found to show 14-fold higher initial rate for ABTS oxidation. Herein, we will present the details of the directed evolution campaign and the kinetic experiments on the evolved artificial metalloenzyme.

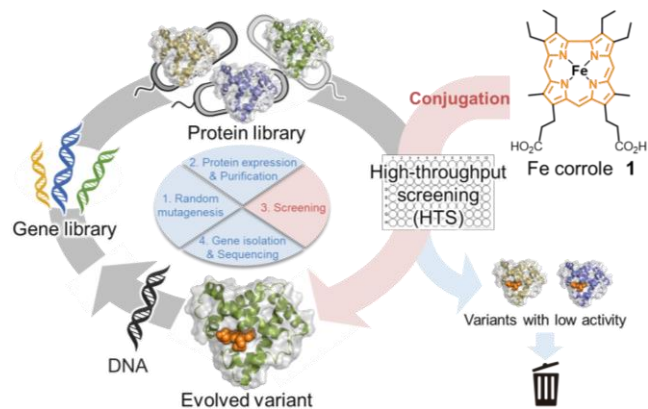


Figure 1. Directed evolution of Mb-1.

1) T. Hayashi *et al.*, *J. Am. Chem. Soc.* **2009**, *131*, 15124. 2) T. Hayashi *et al.*, *ChemBioChem*, **2021**, *22*, 679.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[E1662-1vn] 17. Biofunctional Chemistry, Biotechnology**

Chair: Masayasu Taki, Yoshitaka Koseki

Wed. Mar 22, 2023 4:10 PM - 6:40 PM E1662 (1612, Bldg. 16 [1F])

[E1662-1vn-01] Design and application of functional oligonucleotides encoding the information of intracellular target metabolite○Yuto Motohashi¹, Shuhei Moritani¹, Tatsuya Nishihara¹, Kazuhito Tanabe¹ (1. Aoyama Gakuin University)

4:10 PM - 4:30 PM

[E1662-1vn-02] Functional Thin-Layer Chromatography for Tissue Glutathione Imaging○Tatsuya Nishihara¹, Koki Nishida¹, Rika Tsukame¹, Kazuhito Tanabe (1. Aoyama Gakuin University)

4:30 PM - 4:50 PM

[E1662-1vn-03] Development of prodrug nanoparticles with highly selective drug release in cancer cells○Aki Shibata¹, Yoshitaka Koseki¹, Keita Tanita¹, Ryuju Suzuki¹, Anh T.N. Dao^{1,2}, Hitoshi Kasai¹ (1. IMRAM, Tohoku University, 2. Nagasaki University)

4:50 PM - 5:10 PM

[E1662-1vn-04] Synthesis of β -lactamase-mediated activation of an SN-38-cephalosporin conjugate and their anticancer properties○Yoshitaka Koseki¹, Mitsuki Uehara¹, Ryuuju Suzuki¹, Anh Thi Ngoc Dao², Hitoshi Kasai¹ (1. Tohoku Univ., 2. Nagasaki Univ.)

5:10 PM - 5:30 PM

[E1662-1vn-05] Viscosity-Responsiveness and Melanosomal Visualization in Living Cells using Water-Soluble Fluorescent Probe○Junya Adachi¹, Haruka Oda¹, Toshiaki Fukushima¹, Hiroka Sugai², Kohei Sato¹, Hiroshi Kimura¹, Kazushi Kinbara¹ (1. Tokyo Inst. Tech., 2. Univ. of Tsukuba)

5:40 PM - 6:00 PM

[E1662-1vn-06] Structure-property relationships of NIR-emissive phosphorhodamine dyes and their utilization in cell imaging○Yoshiki Tanaka¹, Masayasu Taki², Shigehiro Yamaguchi^{1,2} (1. Graduate school of science, Nagoya University, 2. ITbM, Nagoya University)

6:00 PM - 6:20 PM

[E1662-1vn-07] Design, synthesis, and chiroptical properties of figure-eight shaped macrocycles composed of bispyrrolidinoindoline alkaloidal scaffold○Tasuku Honda¹, Daiji Ogata², Makoto Tsurui³, Takahiro Muraoka⁴, Yuichi Kitagawa³, Yasuchika Hasegawa³, Junpei Yuasa², Hiroki Oguri¹ (1. The University of Tokyo, 2. Tokyo University of Science, 3. Hokkaido University, 4. Tokyo University of Agriculture and Technology)

6:20 PM - 6:40 PM

細胞内の標的代謝物情報をコード可能にする機能性人工核酸の開発と応用

(青山学院大理工) ○本橋 優人・盛谷 周平・西原 達哉・田邊 一仁

Design and application of functional oligonucleotides encoding the information of intracellular target metabolite (*Graduate School of Science and Engineering, Aoyama Gakuin University*)

○Yuto Motohashi, Shuhei Moritani, Tatsuya Nishihara, Kazuhito Tanabe

Intracellular metabolite and mRNA are changed according to the disease status. The conventional metabolite analysis methods such as liquid chromatography-mass spectrometry (LC-MS) could analyze multicomponent metabolites. However, it is difficult to analyze other omics such as transcriptome simultaneously. In this study, we attempted to construct a molecular system to encode the information of target metabolite into the DNA sequence and quantify each DNA sequence including cDNA. As a proof of concept, we succeeded in the quantification of intracellular GSH and mRNA (HO-1) changes under hydrogen peroxide exposure using qPCR.

Keywords : Functional oligonucleotide; Metabolites; mRNA

細胞内で産生される代謝物は疾病の進行に応じて大きく変化するため、疾病バイオマーカーとしての活用が期待されている。これまでに、液体クロマトグラフィー質量分析法 (LC-MS) に代表される代謝物解析法が報告されてきたが、多様な代謝物を解析できる一方で、トランスクリプトーム等とのトランスオミクス解析を指向した場合、それぞれ独立した分析手法を用いる必要があり、時間とコストが大幅にかかってしまう点が大きな課題となってきた。

以上を踏まえ、本研究では、検体中に含まれる標的代謝物の種類、及び存在量を DNA にコードする方法論の構築を目指した。本方法論の検証に向け、標的代謝物としてグルタチオン (GSH) を選択し、システムの構築を試みた。詳細なシステムを図に示した。GSH のコード化にはジスルフィド結合を介してビオチンを修飾した DNA を用いた。本 DNA を積載したストレプトアビジン標識磁性ビーズに対して、GSH を含むサンプルを添加することで、GSH 量に依存してジスルフィド結合の開裂反応を進行させた。続いて、遊離した DNA を回収・定量し、GSH を定量することとした。実際に、定量 PCR、及び次世代シーケンサーを用いて、細胞中に含まれる GSH 量の定量したところ、33 fmol/cell であることがわかった。また、過酸化水素 (H_2O_2) を A549 細胞に曝露した結果、GSH 量の減少、及び酸化ストレスマーカーであるヘムオキシゲナーゼ (HO-1) の有意な増加を定量 PCR にて確かめた。以上の結果から、代謝物と mRNA を同時解析できることが示された。

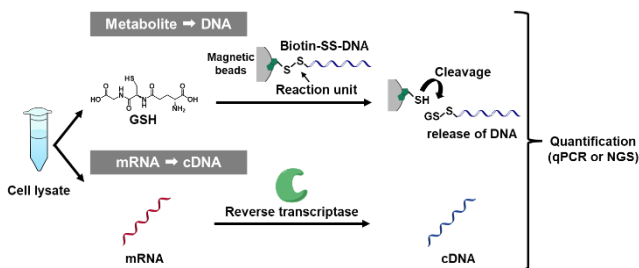


Figure 1. Schematic illustration to quantify GSH and mRNA using DNA encoding strategy.

組織内グルタチオンイメージングを指向した機能性薄層クロマトグラフィーの開発

(青山学院大理工) ○西原 達哉・西田 光輝・塚目 莉加・田邊 一仁

Functional Thin-Layer Chromatography for Tissue Glutathione Imaging (*Graduate School of Science and Engineering, Aoyama Gakuin University*) ○Tatsuya Nishihara, Koki Nishida, Rika Tsukame, Kazuhito Tanabe

Distribution of glutathione (GSH) in the tissues is an important indicator for disease assessment. However, imaging MS has limitation to image GSH distribution in the tissue slice such as time-consuming steps and expensive equipment. To solve these limitations, in this study, we employed the thin layer chromatography coated with fluorescent labeling agent to image GSH distribution in the frozen tissue slice. This method enabled simple and rapid imaging of GSH distribution in several tissues.

Keywords : Metabolite; Molecular probe; TLC

グルタチオン (GSH) は、細胞内に豊富に含まれる小分子のチオール化合物であり、抗酸化剤として重要な機能を果たしている。また、グルタチオン抱合を通じて薬物代謝に寄与している。さらに、GSH のホメオスタシスの変動は、種々の疾病と関連することが報告されている。そのため、組織内における GSH の分布解析は、生命機能や疾病における分子メカニズムの理解において非常に重要である。

組織内に含まれる生体分子の分布解析にあたり、イメージング MS が有用な方法論の一つとして挙げられる。イメージング MS は、高い空間分解能で解析が可能である一方で、測定、及び解析に膨大な時間を要する点が課題として挙げられる。また、GSH などの反応性の高い官能基を有する生体分子の検出には、前処理 (マスクキング) を必要とする。

以上を踏まえ、本研究では、安価、かつ簡便に組織内に含まれる GSH をイメージング可能にする新たな方法論の構築を目指した。具体的には、標的分子 GSH と選択的に反応する蛍光プローブ (GLA) を塗布した機能化薄層クロマトグラフィー (fTLC) を用いることとした。Figure 1 に示した通り、機能化 TLC に対して、凍結組織切片をスタンプする。この際、組織内に含まれる GSH と TLC に塗布した蛍光プローブとの間で反応が進行する。GLA と GSH 付加体 (GLA-GSH) の極性が大きく変化するため、TLC により展開することで未反応分子を容易に除去可能となる。UV 照射後、GLA-GSH 由来の蛍光発光からイメージングを行う。実際に、各種組織 (肝臓、腎臓、脳) 中の GSH イメージングに成功した。

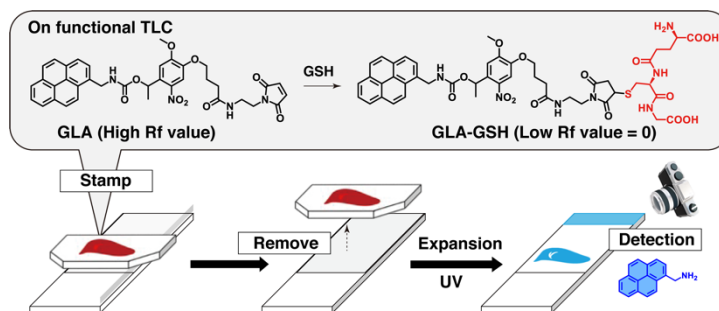


Figure 1. Schematic illustration to image GSH distribution in the frozen tissue slice

Development of prodrug nanoparticles with highly selective drug release in cancer cells

(¹*Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University*, ²*Nagasaki University*) ○Aki Shibata¹, Yoshitaka Koseki¹, Keita Tanita¹, Ryuju Suzuki¹, Anh Thi Ngoc Dao^{1,2}, Hitoshi Kasai¹

Keywords: drug delivery system; anticancer agent; tertiary hydroxy group; prodrug; nanoparticle

In the field of anticancer agent development, prodrug nanoparticles (NPs), which are composed of only prodrug molecules, have been actively studied to reduce the side effects. Although the NPs are expected to accumulate in tumor tissues *via* the enhanced permeability and retention (EPR) effect,¹⁾ the conventional prodrug molecules that construct the NPs would be hydrolyzed by the esterases existing abundantly inside the body before reaching tumor tissues. To avoid this limitation, we aimed to develop the NPs that are stable against esterases and can selectively release drugs in cancer cells, in which prodrugs with sterically hindered esters derived from tertiary hydroxy groups are the component.

From this background, we synthesized the prodrugs (CPT-TML) composed of two types of trimethyl lock (TML) groups, which has esterase-sensitive acetyl ester or esterase-insensitive ethyl ether as the protecting group (PG), linked to the tertiary hydroxy group of the anticancer drug camptothecin (CPT) (Figure 1), and fabricated their NPs with a particle size within 100 nm using the reprecipitation method.²⁾ In the evaluation of release kinetics in mouse serum at 37°C, CPT-TML-OEt NPs, which has ethyl ether as the PG, could not release CPT. In contrast, CPT-TML-OAc NPs, which has acetyl ester as the PG, smoothly released CPT owing to the strong lactone formation tendency of the TML group (Figure 2). These results revealed that sterically hindered esters derived from tertiary hydroxy groups have low susceptibility to esterase-catalyzed hydrolysis owing to large steric hindrance and the trigger for CPT release is the removal of the PG in the TML group. We are investigating the synthesis of a prodrug that can remove the PG in the TML group in response to the tumor-specific triggers.

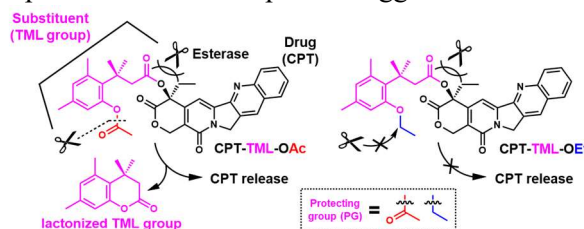


Figure 1. Molecular design of CPT-TML prodrugs and proposed CPT release mechanism.

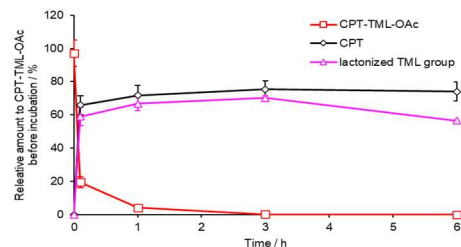


Figure 2. Release kinetics of CPT-TML-OAc NPs in mouse serum at 37°C.

1) SK. Golombek *et al.*, *Adv. Drug Deliv. Rev.* **2018**, 130, 17. 2) H. Kasai *et al.*, *Jpn. J. Appl. Phys.*, **1992**, 31, L1132.

β -ラクタマーゼにより活性化される SN-38-セファロスポリン誘導体の合成と抗がん活性評価

(東北大多元研¹・長崎大院工²) ○小関 良卓¹・上原 満季¹・鈴木 龍樹¹・Anh T.N. Dao²・笠井 均¹

Synthesis of β -lactamase-mediated activation of an SN-38-cephalosporin conjugate and their anticancer properties (¹*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, ²*Graduate School of Engineering, Nagasaki University*) Kensuke Kiyokawa,¹ ○ Yoshitaka Koseki¹, Mitsuki Uehara¹, Ryuju Suzuki¹, Anh T.N. Dao², Hitoshi Kasai¹

This study aimed to develop a new prodrug to improve the anticancer drug treatment by reducing side effects caused by the hydrolysis of ester or urethane bonds outside of the target area. We designed a prodrug of SN-38, an anticancer drug compound, modified with a cephalosporin (Fig. 1). Cephalosporins are β -lactam antibiotics, and drugs are released when the lactam ring is hydrolyzed by β -lactamase (BlaC). As shown in Fig. 2, SN-38-ceph-OH was assayed using human breast cancer cells (MCF-7) and found to have increased activity when treated with BlaC, likely due to the quantity of SN-38 released by the enzymatic reaction of BlaC within the cells.

Keywords : Aziridine; Iminoiodinane; Metal Free; Iodine; Ammonium Iodide

近年、副作用軽減を目指した抗がん剤に関する研究が盛んに行われており、その一つにプロドラッグが挙げられる。既存のプロドラッグは主に薬物をエステル結合やウレタン結合により化学修飾されるため、がん細胞以外でも容易に加水分解を受け、副作用発現の原因となる。そこで本研究では、加水分解に安定なエーテル結合によって抗がん剤へ置換基を導入した新規プロドラッグを開発することを目的とした。抗がん剤として SN-38 をモデル化合物に選択し、置換基としてセファロスポリンを選択した。セファロスポリンは β -ラクタム系抗生物質であり、 β -ラクタム環が β -ラクタマーゼ (BlaC) により加水分解されると失活する。本研究では、この BlaC による開環反応を利用して SN-38 を放出させる機構を考案し、プロドラッグ分子 SN-38-ceph-OH を合成した (Fig.1)。ヒト乳がん細胞 (MCF-7) に BlaC を添加し、培養後、SN-38-ceph-OH または SN-38 を投与し、細胞生存率を比較したところ、BlaC の添加に伴う活性向上が確認された (Fig.2)。この結果は、プロドラッグががん細胞内において BlaC により活性化されたことに起因すると考えられる。

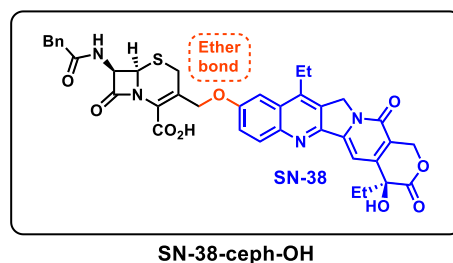


Fig.1 プロドラッグの分子構造

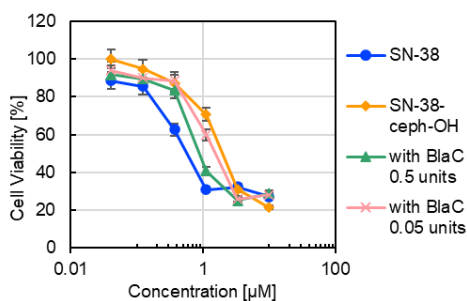


Fig.2 細胞増殖抑制活性試験

Viscosity-Responsiveness and Melanosomal Visualization in Living Cells using Water-Soluble Fluorescent Probe

(¹Tokyo Institute of Technology, ²University of Tsukuba) ○Junya Adachi¹, Haruka Oda¹, Toshiaki Fukushima¹, Hiroka Sugai², Kohei Sato¹, Hiroshi Kimura¹, Kazushi Kinbara¹

Keywords: Fluorescent probe, Viscosity responsiveness, Melanosome, Living cell imaging, Anthracene

The intracellular microviscosity of living cells has attracted significant interest due to its influence on various biologically relevant processes. To visualize the viscosity in living cells, several types of viscosity-responsive fluorescent probes have been developed. However, such probes currently in use still have limitations in certain situations, and there are continuing needs for further investigations on the elaborate functions of the probes.

At the last annual meeting, we have reported fundamental properties of **AN-PEG8** (Figure 1a), which has been developed based on 9,10-bis(*N,N*-dialkylamino)anthracene¹ as a probe applicable to living cell systems.² Namely, **AN-PEG8** showed viscosity-responsive emission in aqueous environments and allowed for lysosome-targeting visualization in HeLa cells.

Subsequently, we aimed to observe the staining behavior of water-soluble **AN-PEG8**, that reflects its viscosity-responsiveness in living cells. As a result, we found that the emission intensity of **AN-PEG8** varied in response to the changes in the osmotic pressure of the cell culture medium, which is considered to alter lysosomal viscosity³ (Figure 1b). Additionally, this probe can visualize melanosome, the densest organelle in melanoma cell.⁴ These results seemed due to the viscosity-responsive properties of **AN-PEG8**, which may help in the design of functional fluorescent probes for biological applications.

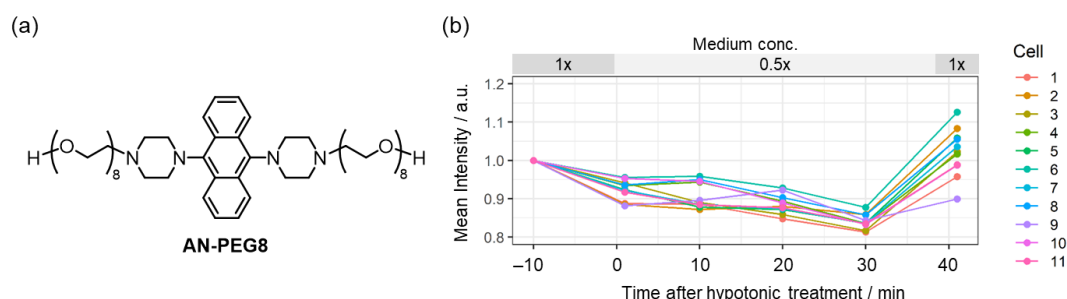


Figure 1. (a) Molecular structure of **AN-PEG8**. (b) Changes in emission intensity of **AN-PEG8** caused by osmotic pressure of culture medium.

(1) Morokuma, K.; Konishi, G.-i. *et al. J. Am. Chem. Soc.* **2016**, *138*, 8194–8206. (2) Adachi, J.; Fukushima, T.; Kinbara, K. *et al. ChemRxiv* **2022**, preprint. DOI: 10.26434/chemrxiv-2022-p8jq4 (3) Li, P. *et al. Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 29155–29165. (4) Ahmad, I. *et al. Photodiagnosis Photodyn. Ther.* **2021**, *33*, 102096.

Structure-property relationships of NIR-emissive phospho-rhodamine dyes and utilization in cell imaging

(¹Graduate School of Science, Nagoya University, ²²Institute of Transformative Bio-Molecules (ITbM), Nagoya University) ○Yoshiki Tanaka,¹Masayasu Taki,² Shigehiro Yamaguchi^{1,2}

Keywords: Near infrared (NIR) fluorescent probe, HaloTag ligand, Structure-property relationship, Live-cell imaging, STED microscopy

Protein-tag system has been a widely used technique to label target proteins with organic fluorescent dyes. Although various labeling reagents are available, the development of near-infrared (NIR) fluorescent ligands with membrane permeability, high chemical stability, and photostability are still demanded. In this study, we have developed a series of HaloTag ligands that consists of NIR-emissive phospho-rhodamine dyes and systematically investigated the structure-property relationships in terms of intramolecular spirocyclization equilibrium, fluorescent wavelength, and cell membrane permeability. Introduction of a five-membered thiophene ring with a carboxy group results in the formation of spirocyclic lactams, which makes the dye permeable to the cell membrane (Figure 1). With reducing the number of alkyl groups on the terminal amino groups, the absorption and emission spectra were hypsochromically shifted, and a larger equilibrium constant for the intramolecular spirocyclization was obtained. All of compounds **1**~**3** were successfully employed to stain target organelles in cells expressing HaloTag fusion protein. Moreover, compound **2** was applicable for STED imaging equipped with a 775 nm depletion laser (Figure 2), allowing us to perform two-color STED imaging in far-red to NIR region in the presence of a SiR dye with minimal crosstalk. Compound **4** bearing a sulfonamide group on the thiophene ring was also synthesized, in which the ring-closed form was stabilized, and membrane permeability was dramatically improved, resulting in significant decrease in labelling time. It enabled to stain live cells under physiological conditions. As a result, tracking the dynamics of organelles for a long period was achieved.

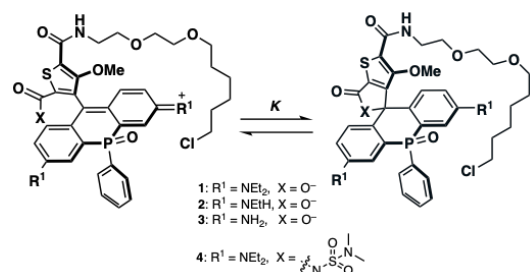


Figure 1 Chemical structures and spirocyclic equilibrium of dyes conjugated with a HaloTag ligand.

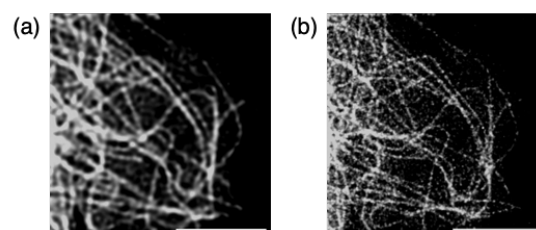


Figure 2 (a) Confocal and (b) STED image of live COS7 β -Tul-Halo-expressing cell stained with compound **2**. Scale bar, 2 μm .

Design, synthesis, and chiroptical properties of figure-eight shaped macrocycles composed of bispyrrolidinoindoline alkaloidal scaffold

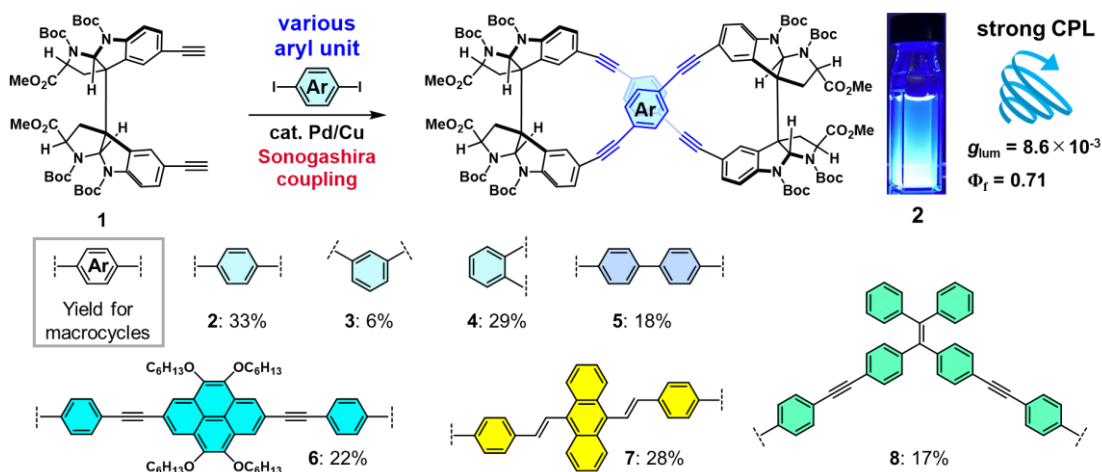
(¹Graduate School of Science, The University of Tokyo, ²Graduate School of Science, Tokyo University of Science, ³Graduate School of Chemical Sciences and Engineering, Hokkaido University, ⁴Graduate School of Engineering, Tokyo University of Agriculture and Technology, ⁵Faculty of Engineering, Hokkaido University)

○ Tasuku Honda,¹ Daiji Ogata,² Makoto Tsurui,³ Takahiro Muraoka,⁴ Yuichi Kitagawa,⁵ Yasuchika Hasegawa,⁵ Junpei Yuasa,² Hiroki Oguri¹

Keywords: Indole alkaloids; Bispyrrolidinoindoline; Macrocyclic oligomer; Circularly Polarized Luminescence; Aggregation-induced Emission

The figure-eight shaped macrocycles bearing D_2 -symmetry have been attracting attention as the privileged scaffold for displaying strong circularly polarized luminescence (CPL).¹ Most of the reported studies employ chiral C_2 -symmetric aromatic scaffolds, such as helicene, binaphthyl, para-cyclophane, to induce chirality of the π -conjugated macrocycles.² In contrast to these synthetic investigations that require optical resolutions to provide enantiopure macrocycles, we are exploring an alternative approach utilizing chiral C_2 -symmetric alkaloid scaffold, bispyrrolidinoindoline (BPI),^{3, 4} for rapid asymmetric synthesis of the figure-eight shaped macrocycles bearing π -conjugated systems.

In this study, we designed and synthesized figure-eight shaped macrocycles based on the BPI unit bearing terminal acetylenes **1**, and the chiral C_2 -symmetric scaffold **1** can be readily synthesized from L-tryptophane on gram scale.⁴ Modular assembly of **1** with various diiodo aromatic compounds allowed rapid synthesis of macrocycles **2-8** up to 33% yield. Notably, figure-eight shaped macrocycle **2** exhibited good CPL properties ($\Phi_f = 0.71$, $g_{lum} = 8.6 \times 10^{-3}$). Relationships between structure and chiroptical properties of macrocycles will be reported.



- 1) Kubo, H.; Shimizu, D.; Hirose, T.; Matsuda, K. *Org. Lett.* **2020**, 22, 9276; 2) Hasegawa, M.; Nojima, Y.; Mazaki, Y. *ChemPhotoChem* **2021**, 5, 1; 3) Wada, M.; Murata, T.; Oikawa, H.; Oguri, H. *Org. Biomol. Chem.* **2014**, 12, 298; 4) Taniguchi, T.; Tsubouchi, A.; Imai, Y.; Yuasa, J.; Oguri, H. *J. Org. Chem.* **2018**, 83, 15284.

[K301-1pm] 18. Polymer

Chair: Hiroharu Ajiro, Takeshi Yamamoto

Wed. Mar 22, 2023 1:20 PM - 3:40 PM K301 (K301, Lecture Hall Bldg. [3F])

[K301-1pm-01] Extrapolation performance Improvement by quantum chemical calculations for machine learning-based predictions of flow-synthesized binary copolymers.

○Shogo Takasuka¹, Shunto Oikawa¹, Takayoshi Yoshimura², Sho Ito¹, Yosuke Harashima¹, Tomoaki Takayama¹, Shigehito Asano³, Akira Kurosawa³, Tetsunori Sugawara³, Miho Hatanaka², Tomoyuki Miyao¹, Takamitsu Matsubara¹, Yuya Ohnishi³, Hiroharu Ajiro¹, Mikiya Fujii¹ (1. Nara Institute of Science and Technology, 2. Keio University, 3. JSR Corporation)

1:20 PM - 1:40 PM

[K301-1pm-02] Synthesis of heat-resistant polymer particles by dispersion polymerization and RAFT precipitation polymerization of styrene with maleimide derivatives

○Shun Yamazaki¹, Daisuke Aoki¹, Tatsuo Taniguchi¹, Takashi Karatsu¹, Takeshi Wakiya², Koki Okura² (1. Chiba university, 2. Sekisui Chemical Company)

1:40 PM - 2:00 PM

[K301-1pm-03] Monomer Sorting and Parallel Polymerization in Bichannel MOFs

○Keat Beamsley¹, Nobuhiko Hosono¹, Takashi Uemura¹ (1. Grad. Sch. of Eng., The Univ. of Tokyo)

2:00 PM - 2:20 PM

[K301-1pm-04] Synthesis of double-stranded polymers via controlled crosslinking in coordination nanospaces

○Masahiro Abe¹, Tomohito Mori², Yuki Kametani³, Takashi Uemura³ (1. Graduate School of Frontier Sciences, The University of Tokyo, 2. School of Engineering, The University of Tokyo, 3. Graduate School of Engineering, The University of Tokyo)

2:20 PM - 2:40 PM

[K301-1pm-05] Highly efficient polymerization behavior using molecular flow field induced by scanning wave photopolymerization

○Takuto Ishiyama¹, Hirona Nakamura¹, Miho Aizawa^{1,2}, Kyohei Hisano¹, Shoichi Kubo¹, Atsushi Shishido¹ (1. Tokyo Institute of Technology, 2. PRESTO, JST)

2:40 PM - 3:00 PM

[K301-1pm-06] Development of Alternating Copolymerization by Ring-Opening Metathesis Polymerization of Fluoroalkenes

○Kaoru Tashiro¹, Midori Akiyama¹, Kimiaki Kashiwagi², Takashi Okazoe^{1,2} (1. The Univ. of Tokyo, 2. AGC Inc.)

3:00 PM - 3:20 PM

[K301-1pm-07] Screw-Sense Induction to Poly(quinoxaline-2,3-diyl) Bearing Achiral Amino Groups by Addition of Chiral Acids in Water

○Tomonori Yamawaki¹, Ren Hirano¹, Takeshi Yamamoto¹, Michinori Sugimoto¹ (1. Kyoto university)

3:20 PM - 3:40 PM

フロー合成したコポリマーに対する機械学習予測の量子化学計算による外挿性向上

(奈良先端科学技術大学院大学¹・慶應義塾大学²・JSR 株式会社³) ○高須賀 聖五¹・及川 駿登¹・吉村 誠慶²・伊藤 翔¹・原嶋 庸介¹・高山 大鑑¹・浅野 重人³・黒澤 哲³・菅原 哲徳³・畑中 美穂²・宮尾 知幸¹・松原 崇充¹・大西 裕也³・網代 広治¹・藤井 幹也¹

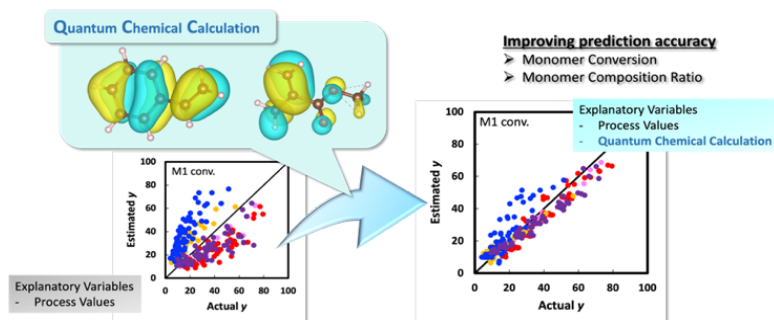
Extrapolation performance improvement by quantum chemical calculations for machine learning-based predictions of flow-synthesized binary copolymers (¹Nara Institute of Science and Technology, ²Keio University, ³JSR Corporation) ○Shogo Takasuka¹, Shunto Oikawa¹, Takayoshi Yoshimura², Sho Ito¹, Yosuke Harashima¹, Tomoaki Takayama¹, Shigehito Asano³, Akira Kurosawa³, Tetsunori Sugawara³, Miho Hatanaka², Tomoyuki Miyao¹, Takamitsu Matsubara¹, Yuya Ohnishi³, Hiroharu Ajiro¹, Mikiya Fujii¹

The properties of polymers are highly dependent on the combination and composition ratio of the monomers used to prepare them; however, the large number of available monomers makes an exhaustive investigation of all the possible combinations difficult. In this study, a machine learning model was constructed using experimental data of copolymers radical polymerized by flow reactor, and the prediction performance of monomer conversion and monomer composition ratio in polymers was verified. High prediction accuracy was achieved even in the molecular extrapolation region by including not only the process conditions but also the quantum chemical calculation values as explanatory variables. In particular, we found that molecular orbital energy and orbital energy gap are important factors for improving accuracy.

Keywords : Machine Learning, Materials Informatics, Polymer Science, Flow Synthesis, Quantum Chemical

ポリマーの特性は、モノマーの組合せおよび構成比率に大きく依存するが、モノマーの種類は無数にあり、全ての組合せを網羅的に探索することは困難である。本研究では、フロー合成装置にてラジカル重合したコポリマーの実験データを用いて機械学習モデルを構築し、モノマー転化率およびポリマー中モノマー組成比の予測性能について検証を行った。プロセス条件のみを用いた学習モデルでは取得データ近傍にたいしてのみにしか予測性能を有しないが、量子化学計算値を説明変数に含むことで分子外挿領域でも高い予測精度を示すことがわかった。特に、予測には分子軌道エネルギーおよびラジカル

の軌道エネルギー差が精度向上に重要な因子であることを見出した。当日はモデル化の詳細について報告する。



スチレンとマレイミド誘導体の分散重合および RAFT 沈殿重合による耐熱性高分子微粒子の合成

(千葉大院工¹・積水化学工業²) ○山崎 駿¹・青木 大輔¹・谷口 竜王¹・唐津 孝¹・大倉 滉生²・脇屋 武司²

Synthesis of heat-resistant polymer particles by dispersion polymerization and RAFT precipitation polymerization of styrene with maleimide derivatives (¹Graduate School of Engineering, Chiba University, ²Sekisui Chemical) ○Shun Yamazaki¹, Daisuke Aoki¹, Tatsuo Taniguchi¹, Takashi Karatsu¹, Koki Okura², Takeshi Wakiya²

Polymer particles with large specific surface area are one of the most important industrial dispersion materials. However, most of polymer particles have poor heat resistance and mechanical strength, which still limit their application in automotive and electronic products. In this study, heat-resistant polymer particles were synthesized by conventional dispersion polymerization and reversible addition fragmentation chain transfer (RAFT) precipitation polymerization (RAFTPP) of styrene with *N*-phenylmaleimide (*N*-PMI). Monodisperse spherical solid particles were obtained by dispersion polymerization and RAFTPP in methyl ethyl ketone/methanol mixture. Elemental analysis revealed that the composition ratio of St to *N*-PMI in the copolymer is 1:1. Thermogravimetric analysis results showed that the 5 % weight loss temperature increased by about 30°C compared to that of PSt particles, indicating improved heat resistance. Furthermore, surface modification was also demonstrated by surface-initiated RAFT polymerization using the RAFT residues exposed on the surface of particles prepared by RAFTPP.

Keywords : Heat-resistant polymer particles; dispersion polymerization; RAFT polymerization; RAFT precipitation polymerization; *N*-phenylmaleimide

大きな比表面積を有する高分子微粒子は、重要な工業用分散材料のひとつである。しかし、一般的な高分子微粒子の多くは耐熱性や機械的強度に乏しく、自動車製品や電子機器製品への応用には未だ制限がある。本研究では、分散重合および可逆的付加開裂連鎖移動(RAFT)沈殿重合により、剛直な構造を持つ *N*-フェニルマレイミド(*N*-PMI)をスチレン(St)と共重合した耐熱性高分子微粒子を合成した。メチルエチルケトン/メタノールの混合溶媒中における分散重合および RAFTPP により、単分散な真球状中実粒子を得ることができた。元素分析により、共重合体における St と *N*-PMI の組成比が 1:1 であることが明らかになった。熱重量分析により PSt 粒子と比較して 5% 重量減少温度が約 30°C 上昇していたことから、耐熱性向上を達成した。さらに、RAFTPP で調製した粒子表面に露出した RAFT 残基を利用した表面開始 RAFT 重合による表面修飾も検討した。

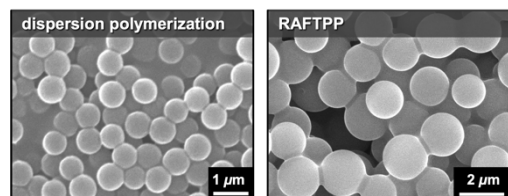


Figure 1. SEM images of particles prepared by dispersion polymerization and RAFTPP of St and *N*-PMI.

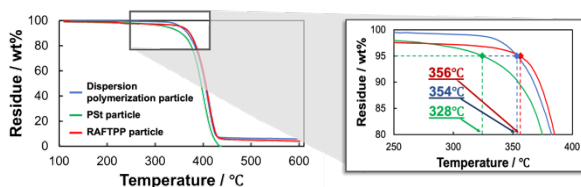


Figure 2. TGA curves of particles prepared by dispersion polymerization and RAFTPP.

Monomer Sorting and Parallel Polymerization in Bichannel MOFs

○Keat Beamsley,¹ Nobuhiko Hosono,¹ Takashi Uemura¹ (¹*Graduate School of Engineering, The University of Tokyo*)

Keywords: Metal-Organic Frameworks; Inclusion Polymerization; Nanopores; Assembly Structures

Organic polymers have, up to this point, been largely left out of the conversation in favor of rigid inorganic species when it comes to engineering materials at the sub-nanometer scale. This is because their entangled and disordered nature in the bulk phase has traditionally limited the scale of nanostructural features they can retain, with the noted exception of assemblies on surfaces. In light of this, our group has found success in developing templated polymerization methods whereby the nanopores of metal-organic frameworks (MOFs) are used as reaction vessels for polymerization. The properties of these nanopores are reflected by the polymers made inside them, enacting rational design at the sub-nanoscale such as two-dimensional pores producing polymer nanosheets of unimolecular thickness¹ and one-dimensional pores bearing immobilized monomers controlling the compositional sequence of individual monomer units in copolymers.²

In this work, we used a type of MOF bearing two distinct one-dimensional pores (a “Bichannel MOF”) and were able to further evolve our method by achieving self-sorting of two different monomers into two respective pore types, where they could be separately polymerized in adjacent pores (“parallel polymerization”) (Figure 1). The MOF focused on here, [Cu(5-methylisophthalate)]_n, has hydrophilic and hydrophobic pores arranged in alternating fashion, and thus sorts vinyl monomers based on their polarity. Polymers which would normally undergo phase separation in the bulk state are therefore formed intercalated with each other on a single-chain level by way of the sub-nanometer alternation pattern of channels in the MOF crystal.

Further, crosslinking through the MOF walls was investigated using divinylated ligands as part of the MOF structure. The two-polymer assemblies formed are unprecedented array structures where two types of polymer chain alternate on the molecular level, and are anticipated as next-generation functional materials.

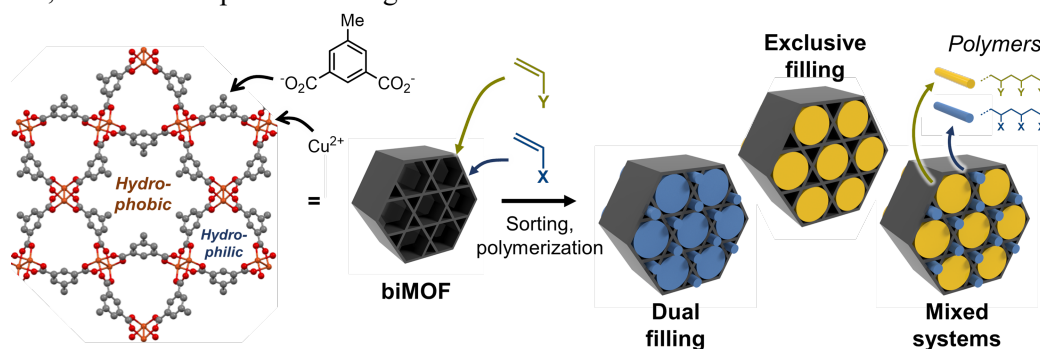


Figure 1. Schematic of the monomer sorting and parallel polymerization in a bichannel MOF.

1) Hosono, N. et al. *Nat. Commun.* **2020**, *11*, 3573. 2) Mochizuki, S. et al. *Nat. Commun.* **2018**, *9*, 329.

Synthesis of double-stranded polymers via controlled crosslinking reaction in coordination nanospaces

(¹Graduate School of Frontier Sciences, the University of Tokyo, ²School of Engineering, the University of Tokyo, ³Graduate School of Engineering, the University of Tokyo)

○Masahiro Abe,¹ Tomohiro Mori,² Yuki Kametani,² Takashi Uemura,³

Keywords: Radical Polymerization; Metal–Organic Frameworks; Crosslinking; Topology; Post-Polymerization Modification

Double-stranded polymers, including DNA, RNA, and polysaccharides, are commonly found and play a vital role in biosystems. Inspired by their elegant structures and functions, several approaches for the preparation of synthetic polymer duplexes have been developed. However, the previous strategies usually require elaborated monomer designs to achieve selective crosslinking between two polymer chains. Herein, we report a versatile methodology to synthesize double-stranded polymers even from common vinyl monomers.^[1] Crosslinking polymerization was conducted within metal–organic frameworks (MOFs), in which the diameter of nanopores was comparable to the two vinyl polymer chains (**Figure 1**). The effective spatial constraint inhibits the unfavorable random crosslinks among multiple polymers, fabricating polymer duplexes.

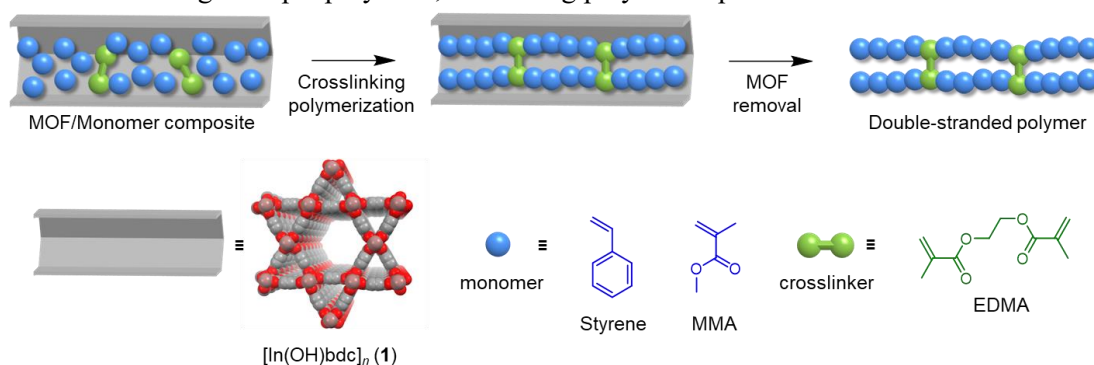


Figure 1. Scheme image for the preparation of double-stranded polymers in nanochannels of **1**.

[In(OH)(bdc)]_n (MIL-68^[2], bdc = 1,4-benzenedicarboxylate, **1**) was employed as a host framework possessing suitable one-dimensional pores to demonstrate our strategy. Vinyl monomers, such as styrene and methyl methacrylate, were encapsulated in **1** with a crosslinker and initiator. The crosslinking radical polymerization within the nanochannel was performed by heating the composite at 120 °C for 24 hours. Soluble crosslinked polymers were obtained after the decomposition of **1** by chelating agents. The double-stranded topology endows the polymers with atypical properties, such as lower intrinsic viscosity and higher glass transition temperature compared to their single-stranded counterparts.

[1] M. Abe, Y. Kametani, T. Uemura, *J. Am. Chem. Soc.* *accepted*. [2] M. Latroche, *et al.*, *Inorg. Chem.* **2008**, 47, 11892–11901.

Highly Efficient Polymerization Behavior Using Molecular Flow Field Induced by Scanning Wave Photopolymerization

(¹Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, ²PRESTO, JST)
 ○Takuto Ishiyama,¹ Hirona Nakamura,¹ Miho Aizawa,^{1,2} Kyohei Hisano,¹ Shoichi Kubo,¹
 Atsushi Shishido¹

Keywords: Photopolymerization; Flow Field; Polymerization Behavior; Molecular Alignment

The existence of macromolecules became widely recognized in the 1930s with the acceptance of Staudinger's macromolecular theory. Since then, the effects of external forces on polymers have been actively studied. Mechanical force and flow fields applied to polymers was considered the main cause of the degradation of polymers. In recent years, the relationship between polymers and external forces has been reevaluated as a source for the functionalization of polymers. For example, mechanical force changes the color of mechanophores, and the flow field accelerates the crystallization of polymers.^{1,2} Recently we have developed a novel photopolymerization process with spatiotemporal photoirradiation, termed scanning wave photopolymerization (SWaP), which induces molecular diffusion and flow during the polymerization.³ This photoinduced flow aligns the polymer main chains and side chains along the flow direction, allowing the creation of various functional materials. Since polymerization proceeds in the flow field induced by polymerized molecules themselves, this method has the potential to cause distinct polymerization behavior. In this study, we investigated the effect of molecular flow on polymerization reaction and found specific polymerization behaviors.

A photopolymerizable sample was prepared by mixing an anisotropic methacrylate monomer and a photoinitiator Irgacure 651. The mixture was injected into a glass cell, and irradiated with a scanned UV slit light or static UV

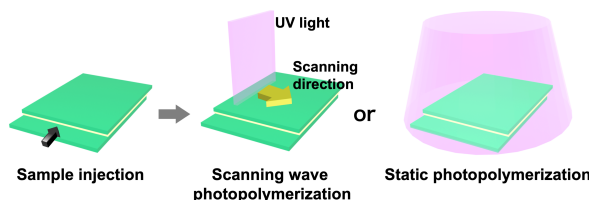


Figure 1. Schematic illustration of a photopolymerization process.

light throughout the cell (**Figure 1**). Finally, polymer films were obtained by rapid cooling. Molecular weight and monomer conversion of the obtained polymers under various exposure energies were evaluated by size exclusion chromatography. As a result, the exposure energy of SWaP to reach 95% conversion was ten times lower than that of static polymerization. Furthermore, SWaP synthesized polymers with larger molecular weights than static polymerization at the same conversion. These results strongly suggest that molecular flow induced by SWaP enhances polymerization efficiency dramatically and yields high molecular weight polymers. Furthermore, we applied SWaP to commodity monomers and investigated the versatility of this specific polymerization behavior.

1) K. Imato, H. Otsuka, *et al.*, *ACS Macro Lett.* **2015**, 4, 1307. 2) Z. Wang, L. Li, *et al.*, *Macromolecules* **2016**, 49, 1505. 3) K. Hisano, A. Shishido, *et al.*, *Sci. Adv.* **2017**, 3, e1701610.

フルオロアルケンの開環メタセシス重合による交互共重合の開発

(東大院工¹・AGC(株)²) ○田代 薫¹・秋山 みどり¹・柏木 王明²・岡添 隆^{1,2}

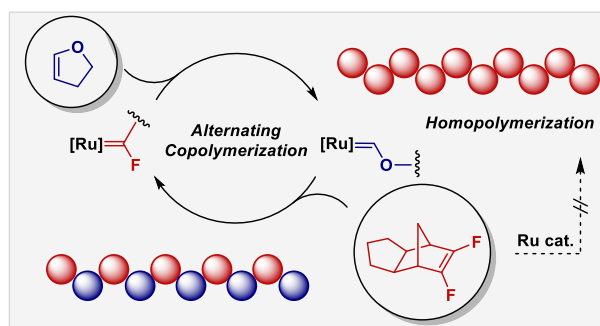
Development of Alternating Copolymerization by Ring-Opening Metathesis Polymerization of Fluoroalkenes

(¹Graduate School of Engineering, The University of Tokyo, ²AGC Inc.) ○Kaoru Tashiro,¹ Midori Akiyama,¹ Kimiaki Kashiwagi,² Takashi Okazoe^{1,2}

Ring-opening metathesis polymerization (ROMP) has become one of the most powerful methods to synthesize diverse functional polymers from cycloalkenes. Norbornene derivatives (NBEs) are highly strained and therefore commonly used as substrates for not only homopolymerization but also copolymerization. Alternating copolymerization is distinguished by the ability to control the sequence of two monomers, a beneficial feature which allows the polymer bulk properties to be adjusted according to the sequence order. To the best of our knowledge, completely alternating ROMP of NBEs has not been reported, though other highly-strained cycloalkenes (cyclobutene,¹⁾ cyclopropene,²⁾ and oxanorbornene³⁾) have been used for alternating ROMP. In the present study, inspired by the cross metathesis of fluoroalkenes and enol ethers,⁴⁾ copolymerization of fluorinated NBEs and dihydrofuran was conducted. The introduction of fluorine atoms at the carbon-carbon double bond prevents homopolymerization of NBEs, thereby ensuring a completely alternating sequence.

Keywords : Ring-Opening Metathesis Polymerization, Alternating Copolymerization

開環メタセシス重合は、環状アルケンから多様な機能性ポリマーを合成する最も有力な方法の一つである。ノルボルネン誘導体は、その大きな環歪みゆえに多くの単独重合に加え共重合にも利用される。中でも交互共重合は二種類のモノマーの規則的な配列を実現することで物性を制御できる優れた手法と言える。シクロブテン¹⁾、シクロプロペン²⁾、オキサノルボルネン³⁾の交互開環メタセシス重合が報告される一方で、ノルボルネン誘導体の完全な交互開環メタセシス重合は報告例がない。本研究では、フルオロアルケンとエノールエーテルのクロスメタセシスに着想を得て⁴⁾、炭素-炭素二重結合にフッ素原子を導入することによりノルボルネン誘導体の単独重合を抑え、ジヒドロフランとの開環メタセシス重合により完全な交互共重合体を合成した。



1) Song, A.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2009**, *131*, 3444–3445. 2) Elling, B. R.; Xia, Y. *J. Am. Chem. Soc.* **2015**, *137*, 9922–9926. 3) Pal, S.; Alizadeh, M.; Kong, P.; Kilbinger, A. F. M. *Chem. Sci.* **2021**, *12*, 6705–6711. 4) Mori, K.; Akiyama, M.; Inada, K.; Imamura, Y.; Ishibashi, Y.; Takahira, Y.; Nozaki, K.; Okazoe, T. *J. Am. Chem. Soc.* **2021**, *143*, 20980–20987.

アキラルアミン側鎖を有するポリキノキサリンの合成とキラル酸添加による水中らせん不斉誘起

(京大院工) ○山脇 大昇・平野 蓮・山本 武司・杉野目 道紀

Screw-Sense Induction to Poly(quinoxaline-2,3-diyl) Bearing Achiral Amino Groups by Addition of Chiral Acids in Water (*Graduate School of Engineering, Kyoto University*) ○Tomonori Yamawaki, Ren Hirano, Takeshi Yamamoto, Michinori Suginome

In this work, we synthesized poly(quinoxaline-2,3-diyl)s (PQXs) bearing achiral ammonium group, and investigated the screw-sense induction by adding chiral acids in water. The screw-sense induction to PQXs (**P1** and **P2**) having ammonium side chains with different alkyl chain lengths was achieved by addition of chiral acids (10 mM) such as carboxylic acid **1**, hydroxy acid **2**, and sulfonic acid **3** (Fig. 1). Perfect screw-sense induction was observed in aqueous solution of **2** by increasing the degree of polymerization of **P1** and **P2**.

Keywords : Helical Polymer; Circularly Dichroism; Helical Chirality; Chirality Detection; Water-Soluble Polymer

近年、新たなキラル機能性材料の開発を目指し、アキラルな高分子の主鎖らせん不斉制御に注目が集まっている。我々はこれまでにアキラルなカルボン酸側鎖を有するポリ(キノキサリン-2,3-ジイル) (PQX)に少量のキラルアミンを添加することで、水中での完全な一方向巻きらせん不斉誘起を達成している¹⁾。本研究ではアキラルなアンモニウム側鎖を有する水溶性 PQX を合成し、種々のキラル酸添加による水中らせん不斉誘起について検討した。

アキラルアンモニウム側鎖を有する PQX として、アルキル鎖長の異なる **P1** および **P2** を合成し、種々のキラル酸水溶液 (10 mM) 中において誘起されるらせん不斉を円偏光二色性スペクトルから評価した (Fig. 1)。カルボン酸(**1**)、ヒドロキシ酸(**2**)、スルホン酸(**3**)の添加によりそれぞれらせん不斉誘起が確認された。**P1**、**P2**のいずれにおいても、マンデル酸誘導体(**2**)の添加では左巻きの、カンファースルホン酸(**3**)の添加では右巻きのらせん不斉が誘起された。一方、テトラヒドロフロ酸(**1**)の存在下では**P1**で左巻き、**P2**で右巻きのらせん不斉が誘起された。また、重合度を40量体から100量体へと増加させることでらせん不斉の誘起効率が向上し、**P1**、**P2**ともに**2**の水溶液中において完全な一方向巻きらせん不斉を誘起することができた。

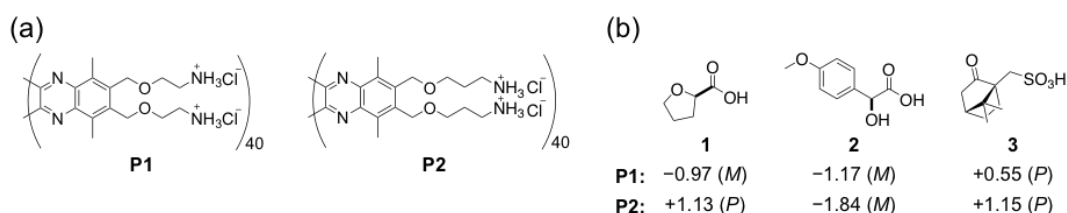


Fig.1. (a) Structures of **P1** and **P2**. (b) Chiral additives and measured CD intensity (g_{abs} ($\Delta\epsilon/\epsilon$) at 370 nm) at 20 °C. Induced screw-sense are shown in parenthesis.

1) Yamawaki, T.; Kuroda, T.; Nagata, Y.; Suginome, M. The 102nd CSJ Annual Meeting, **2022**, C203-1pm-01.

Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B**[B445-1am] 19. Colloid and Interface Chemistry**

Chair: Masaki Saruyama, Yosuke Okamura

Wed. Mar 22, 2023 9:00 AM - 11:30 AM B445 (445, Bldg. 4 [4F])

[B445-1am-01] Reversible control of dispersibility of cubic gold nanoparticles induced by visible light irradiation○Koichiro Saito¹, Keegan McGehee^{1,2}, Yasuo Norikane^{1,2} (1. AIST, 2. Univ. of Tsukuba)
9:00 AM - 9:20 AM**[B445-1am-02] Sonication-induced nanocrystallization of a gold cluster enabled by encapsulation in micelles**○Yuki Saito¹, Ayano Suda², Maki Sakai², Yukatsu Shichibu^{1,2}, Katsuaki Konishi^{1,2} (1. Fac. of Env. Earth Sci., Hokkaido Univ., 2. Grad. Sch. of Env. Sci., Hokkaido Univ.)
9:20 AM - 9:40 AM**[B445-1am-03] Fabrication and Unique Characterization of Polymeric Nanofiber Suspension as Novel Anisotropic Nanomaterials.**○Hayato Yokose¹, Naoya Ichihara¹, Yosuke Okamura^{1,2} (1. Grad. Sch. of Eng., Tokai Univ., 2. Micro/Nano Tech. Center, Tokai Univ.)
9:40 AM - 10:00 AM**[B445-1am-04] Structure– Function Relationship Studies of Hydrophobic Ligands for Stable Colloidal Nanoparticles**○Tatsuya Sudo¹, Shohei Yamashita¹, Hidehiro Kamiya¹, Yohei Okada (1. Tokyo University of Agriculture and Technology)
10:00 AM - 10:20 AM**[B445-1am-05] Dispersibility Study of Surface-modified TiO₂ Nanoparticles: Thermodynamics of Dispersion and Agglomeration in Less-polar Solvents**○Shohei Yamashita¹, Yukina Ito¹, Tatsuya Sudo¹, Hidehiro Kamiya¹, Yohei Okada¹ (1. Tokyo University of Agriculture and Technology)
10:30 AM - 10:50 AM**[B445-1am-06] Anisotropic control of three-dimensional nanoparticle superlattices**○Masaki Saruyama¹, Toshiharu Teranishi¹ (1. Kyoto Univ.)
10:50 AM - 11:10 AM**[B445-1am-07] Colloidal synthesis of coherent InP/ZnS core/shell nanocrystals and their optoelectronic applications**○Kazuhiro Nemoto¹, Naoto Shirahata^{1,2,3} (1. National Institute for Materials Science, 2. Hokkaido University, 3. Chuo University)
11:10 AM - 11:30 AM

可視光照射による可逆的な金ナノキューブの分散制御

(産総研¹・筑波大²) ○斎藤 滉一郎¹・Keegan McGehee^{1,2}・則包 恭央^{1,2}

Reversible control of dispersibility of cubic gold nanoparticles induced by visible light irradiation (¹*National Institute of Advanced Industrial Science and Technology (AIST)*, ²*Graduate School of Science and Technology, University of Tsukuba*) ○Koichiro Saito,¹ Keegan McGehee,^{1,2} Yasuo Norikane^{1,2}

Plasmonic gold and silver nanoparticles change their properties based on the assembled state. Various applications such as catalytic reaction and photothermal therapy using self-assembled plasmonic nanoparticles have been reported. Since light is a noninvasive stimulus, many methods for controlling the self-assembly of plasmonic nanoparticles using light have been studied.¹⁾ However, nonspherical particles are rarely targeted, and ultraviolet light is mainly used. In this study, we succeeded in controlling the dispersibility of porous gold nanocubes using a novel water-soluble azobenzene derivative, which photoisomerizes under visible light (Fig. 1a).²⁾ Light-induced changes in the average particle size determined by dynamic light scattering (DLS) suggests that the gold nanocubes were aggregated under blue light irradiation and redispersed under green light irradiation (Fig. 1b).

Keywords : Metal Nanoparticles; Plasmon Resonance; Self-assembly; Azobenzene; Photoisomerization

プラズモン共鳴を示す金や銀のナノ粒子は、凝集状態に応じて特性が変化する。そのため、自己組織化したナノ粒子を用いた触媒反応や光熱療法など、さまざまな応用が報告されている。光は非侵襲的な刺激であるため、これまでに光を利用して自己組織化を制御する多様な手法が研究されてきた¹⁾。しかし、非球状粒子を対象とした報告は少なく、使用される光も主に紫外線であることが更なる発展を妨げていた。本研究では、可視光下で光異性化する水溶性アゾベンゼン誘導体を用いることで、多孔質な金ナノキューブの分散性を制御することに成功した(図 1a)²⁾。動的な光散乱(DLS)によって測定した平均粒子径が光照射によって可逆に変化したことから、金ナノキューブが青色光照射下で凝集、緑色光照射下で再分散することが示された(図 1b)。

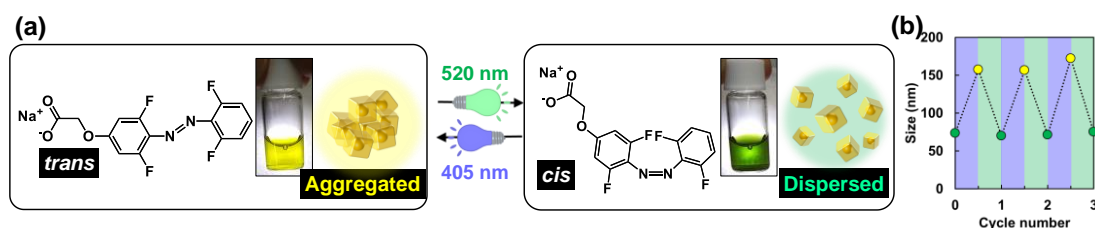


Figure 1. (a) Schematic illustration of the visible-light-induced reversible self-assembly of gold nanocubes. (b) Visible-light-induced change of the average size of the assembled gold nanocubes measured by DLS.

1) T. Bian, Z. Chu, R. Klajn, *Adv. Mater.* **2020**, 32, 1905866. 2) K. Saito, K. McGehee, Y. Norikane, *Part. Part. Syst. Charact.* **2022**, 39, 2200123.

ミセルへの内包による金クラスターの超音波ナノ結晶化

(北大院地球環境¹・北大院環境²) ○齋藤結大¹・須田綾乃²・酒井麻希²・七分勇勝^{1,2}・小西克明^{1,2}

Sonication-induced nanocrystallization of a gold cluster enabled by encapsulation in micelles (¹*Faculty of Environmental Earth Science, Hokkaido University*, ²*Graduate School of Environmental Science, Hokkaido University*) ○Yuki Saito,¹ Ayano Suda,² Maki Sakai,² Yukatsu Shichibu,^{1,2} Katsuaki Konishi^{1,2}

Sonication-induced crystallization (Sono-crystallization) is a promising method to enhance photoluminescence (PL) intensities of AIE molecules. However, conventional sono-crystallization methods have difficulty in controlling the growth of generated crystal seeds, and especially it is challenging to obtain nanosized molecular crystals. In this work, we present size-selective sono-crystallization of $[\text{Au}_8(\text{dppp})_4(\text{CN})_2]^{2+}$ cluster enabled by the encapsulation of clusters into SDS micelles (**Figure 1**). Our approach using a surfactant would be applicable to other molecules rather than gold clusters and is expected to be a powerful method to control arrangements and physical properties of aggregated molecules.

Keywords : Cluster, Sono-crystallization, Micelle, AIE, Molecular assembly

超音波は、そのキャビテーション効果によって分子の結晶化を促進することが出来る。超音波結晶化と呼ばれるこの手法は多方面での活用が期待されており、中でも AIE 特性を示す分子の結晶化によって発光強度を劇的に高める手法が注目を集めている。しかし、これまでの超音波結晶化は、生成した結晶核の成長を抑制することは難しく、ナノサイズの結晶を選択的かつ安定に取り出すことは困難だった。本研究では、AIE 性の金クラスターである $[\text{Au}_8(\text{dppp})_4(\text{CN})_2]^{2+}$ を用いて、SDS から成るミセルの内部への取り込み後に超音波を照射することで、サイズ選択的にナノ結晶を得る手法を考案した。ミセルへの取り込みは超音波結晶化を促進するだけでなく、生成した結晶核の成長を抑制する効果があることを見出した。ナノ結晶化した Au₈ クラスターは著しい発光強度の増大を示し、ランダムに凝集した状態と比較して量子収率が 4 倍以上に増強された。本講演ではこの詳細について発表する。

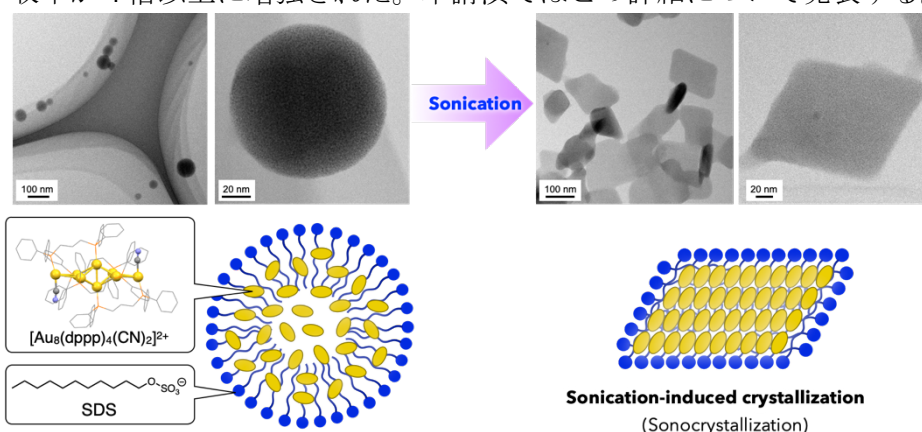


Figure 1. STEM images and schematic illustration of the sono-crystallization of Au₈ clusters in SDS micelles.

新規異方性材料としての高分子ナノファイバー分散体の創製とユニークな特性

(東海大院工¹・東海大マイクロ・ナノ研²) ○横瀬 颯人¹・市原 直弥¹・岡村 陽介^{1,2}
Fabrication and Unique Characterization of Polymeric Nanofiber Suspension as Novel Anisotropic Nanomaterials (¹*Graduate School of Engineering, Tokai University*, ²*Micro/Nano Technology Center, Tokai University*) ○Hayato Yokose,¹ Naoya Ichihara,¹ Yosuke Okamura^{1,2}

Anisotropic particles exhibit unique properties compared to isotropic ones; *e.g.* the disc-shaped particles exhibit higher viscosity and enhance aggregation ability than spherical particles¹⁾. Polymeric nanofibers, widely used in the fields such as environment and biomedical applications, are one of the anisotropic materials with high aspect ratio between narrow diameter and length of the fibers²⁾. In this study, we propose a fabrication procedure of fragmented nanofibers dispersed stably in water, and their application to novel carriers for turbidimetric immunoassay. Fragmented nanofibers composed of polystyrene (PS) were fabricated by the electrospinning method and mechanical fragmentation. To improve the dispersion stability of the fragmented nanofibers and to introduce functional groups, bovine serum albumin (BSA) was physically adsorbed to the surface of the fragmented nanofibers. Antibodies were conjugated by chemical cross-linking via amino groups of the BSA on the fragmented nanofibers. When antigen was added to the dispersion, nanofibers were specifically aggregated by the antigen-antibody reaction. In fact, nanofiber dispersion was found to aggregate at a wider range of antigen concentrations compared to microspheres with the same surface area.

Keywords: *Polymeric nanofibers, Anisotropic nanomaterials, Aggregation and dispersion*

異方性を有した形状の微粒子は、等方性のものと比較してユニークな特性を発現する。例えば円盤のような面を有する微粒子は、界面における接触面積の増大によって接着力や反応性が向上し、これに伴って、分散液の粘性や凝集特性などが顕著に向上する結果が得られている¹⁾。我々は、新たな異方性微粒子として、ナノファイバーに着目した。ナノファイバーとは、ナノレベルの直径を有した繊維材料であり、その極細径を活かして環境や医学などの分野にて活用が期待されている²⁾。本研究では、水に安定に分散する高分子ナノファイバー分散体を創製するとともに、その形状に由来する高い凝集特性を活用して、新規凝集比濁用担体としての応用を目指す。

電界紡糸法によってポリスチレンからなるナノファイバーを調製し、機械攪拌にて裁断した。次に、分散安定性の向上と官能基の導入を指向して、分散体の表面にウシ血清アルブミン(BSA)を物理吸着させ、裁断化ナノファイバー分散体を得た。ナノファイバー分散体の表面の BSA がもつアミノ基を標的として、化学架橋にて抗体を結合させた。抗原抗体反応による特異的な凝集を惹起したところ、調製したナノファイバー分散体は同表面積の真球上微粒子と比較してより低濃度かつ広範囲の抗原濃度にて凝集する様子が確認された。

1) Zhang H. *et al. ACS Appl. Polym. Mater.* 2, 3355-3364 (2020).

2) 谷岡明彦 監修『ナノファイバー実用化技術と用途展開の最前線』, CMC 出版 (2012).

疎水性溶媒中へのナノ粒子分散におけるリガンドの構造機能相関

(東農工大) ○須藤 達也・山下 翔平・神谷 秀博・岡田 洋平

Structure-Function Relationship Studies of Hydrophobic Ligands for Stable Colloidal Nanoparticles (Tokyo University of Agriculture and Technology) ○Tatsuya Sudo, Shohei Yamashita, Hidehiro Kamiya, Yohei Okada

Nanoparticles have specific physicochemical properties that differ from bulk materials and are attracting attention as functional materials such as electronic components and optical devices. Since nanoparticles are prone to aggregation, surface modification with ligands is widely used to enhance the dispersibility of nanoparticles. However, structure-function relationships of ligands are still controversial. In this study, ligands with slightly different molecular structures were synthesized based on ligands with oleic acid structures, which are frequently used as hydrophobic ligands, and their ability to disperse nanoparticles was evaluated. The results revealed that the presence of a double bond in the center of ligand molecule enhances the dispersibility of the nanoparticles in hydrophobic solvents.

Keywords : Nanoparticles; Ligands; Dispersibility; Hydrophobic solvents

ナノ粒子はバルク固体とは異なる特異的な物理化学的特性を有していることから、電子部材や光学デバイスの高機能化を達成できる材料として注目されている。ナノ粒子は高い凝集性を有しており、そのままナノ粒子固有の特性を十分に発現することができない。したがって、リガンドと呼ばれる有機分子を粒子表面に修飾することでナノ粒子の分散性を高める手法が多用されている。ところが、リガンドの分子構造と粒子分散性の相関は十分に解明されておらず、経験則に頼ってリガンド分子を選定しているのが実情である¹⁾。

そこで本研究では、疎水性リガンドとして多用されるオレイン酸構造のリガンドを基軸として分子構造がわずかに異なるリガンドを合成し、その分散機能性を比較・評価することで、疎水性溶媒中へのナノ粒子分散においてリガンドが高い機能性を発現するための構造的条件を検証した。その結果、リガンド分子中央の二重結合の存在がナノ粒子の分散性を高めるために重要な要素であることが示された²⁾(図)。

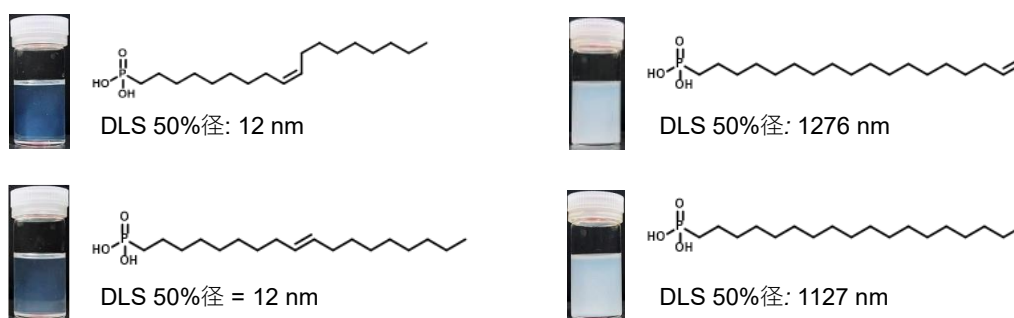


図 TiO₂ ナノ粒子のデカン分散液の見た目と DLS 測定結果 (粒子径 $d_{50} = 7$ nm)

1) Yang, Y. *et al.*, *Nano Lett.* **2016**, *16*, 2127 – 2132, 2) Sudo, T. *et al.*, *Chem. Eur. J.* **2022**, accepted

表面修飾 TiO₂ ナノ粒子の分散性評価：疎水性溶媒中における分散－凝集の熱力学

(東農工大) ○山下翔平・伊藤友紀奈・須藤達也・神谷秀博・岡田洋平

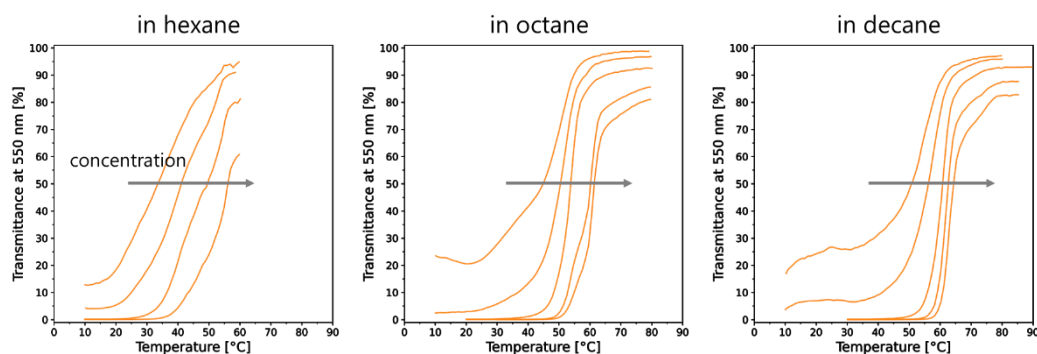
Dispersibility Study of Surface-modified TiO₂ Nanoparticles: Thermodynamics of Dispersion and Agglomeration in Less-polar Solvents (*Tokyo University of Agriculture and Technology*)

○Shohei Yamashita, Yukina Ito, Tatsuya Sudo, Hidehiro Kamiya, Yohei Okada

Fundamental understanding of solution properties of ligand-nanoparticle complexes is of importance for their application. In particular, the relationships between the structure of surface ligands and the dispersibility of the complexes in less-polar solvents has recently been the subject of controversy. We have previously reported the effect of chain length¹⁾ and regio- and stereochemistries of C=C double bonds²⁾ of surface ligands on the dispersibility of hydrophobic phosphonate-capped TiO₂ nanoparticles. In this study, we attempted to discuss the dispersibility of various hydrophobic phosphonate-capped TiO₂ nanoparticles in less-polar solvents from a thermodynamic point of view. Examples of stearylphosphonate-capped TiO₂ nanoparticles are shown in the figure. Visible light transmittance revealed that the thermo-responsive dispersion-agglomeration transition varied with ligand structure, solvent, and concentration of nanoparticles.

Keywords : Nanoparticles; Phosphonic acid; Dispersibility; Thermo-responsiveness

リガンド－ナノ粒子複合体の応用には、溶液中での特性の理解が重要である。特に近年、リガンドの構造と疎水性溶媒中における複合体の分散性の相関が議論の渦中にある。我々はこれまでに、疎水性ホスホン酸被覆 TiO₂ ナノ粒子の分散性について、表面リガンドの鎖長¹⁾や二重結合の位置および立体化学²⁾が影響をおよぼすことを報告してきた。本研究では、さまざまな疎水性ホスホン酸被覆 TiO₂ ナノ粒子について、疎水性溶媒中における分散性を熱力学の観点から議論することを試みた。ステアシルホスホン酸被覆 TiO₂ ナノ粒子の例を図に示す。可視光透過率測定から、熱応答性の分散凝集遷移は、リガンド構造、溶媒、粒子濃度によって変化することがわかった。



1) Yamashita, S.; Sudo, T.; Kamiya, H.; Okada, Y. *Chem. Eur. J.* **2022**, 28, e202201560.

2) Sudo, T.; Yamashita, S.; Koike, N.; Kamiya, H.; Okada, Y. *Chem. Eur. J.* **2022**, accepted.

ナノ粒子三次元超格子の構造異方性制御

(京大化研¹) ○猿山 雅亮¹・寺西 利治¹

Anisotropy Control of 3-Dimensional Nanocrystal Superlattice (¹*Institute for Chemical Research, Kyoto University*) ○Masaki Saruyama,¹ Toshiharu Teranishi¹

We show the formation and structural control of three-dimensional superlattice of Cu_{2-x}S nanocrystals (NCs). During the synthesis of Cu_{2-x}S NCs in liquid solution, monodisperse Cu_{2-x}S NCs were self-assembled into highly-ordered 3D superlattices through van der Waals attractive forces. The shape of superlattice depends on the amine ligand concentration in the synthesis, in which higher amine concentration yielded anisotropic rod-shaped superlattice while lower concentration gave highly-symmetric fcc-based superlattice. TEM observation revealed that the shape of each Cu_{2-x}S NC component determines the overall structure of the superlattice. We conducted the synchrotron-based in-situ small-angle X-ray scattering measurements to monitor the overall process of the reaction, including the nucleation and growth of NCs and the formation of superlattices in various amine concentration.

Keywords : Nanoparticles; Self-assembly; Superlattice; Anisotropy

無機ナノ粒子の集合体は、近接するナノ粒子間の相互作用等により分散状態の単一ナノ粒子では発現しない協奏的物性を示す。その特性はナノ粒子の配列に大きく影響を受けるため、その配列様式を制御する方法の開発は重要である。本発表では、液相での Cu_{2-x}S ナノ粒子成長過程における三次元超格子の自発形成と、その形状異方性の制御について報告する。塩化銅とアルキルアミン存在下でジスルフィドを注入すると Cu_{2-x}S ナノ粒子が核形成し、その後のサイズ成長の間にファンデルワールス引力によって凝集が生じた。この凝集物は均一形状の Cu_{2-x}S ナノ粒子が規則配列した三次元超格子であることが分かった。その構造はアミン濃度によって大きく変化し、アミン濃度が大きいときは一方向に伸長した異方形状になり、アミン濃度が小さいときは等方的な多面体となった (Fig.)。TEM 観察により、超格子を構成する Cu_{2-x}S ナノ粒子の形状異方性がアミン濃度によって変化したことで超格子全体の構造が大きく変化したことを明らかにした。

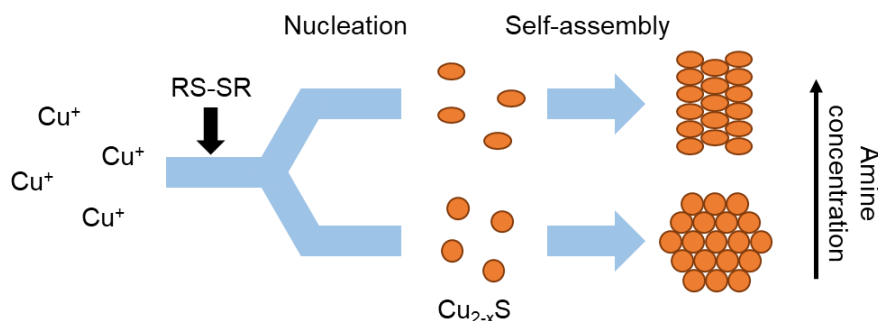


Fig. Schematic formation process of Cu_{2-x}S nanocrystal superlattices in colloidal synthesis.

コヒーレントコアシェル構造を有する InP/ZnS ナノ結晶の合成と応用

(NIMS¹・北大院理²・中大院理工³) ○根本 一宏¹・白幡直人^{1,2,3}

Colloidal synthesis of coherent InP/ZnS core/shell nanocrystals and their optoelectronic applications (¹*International Center for Materials Nanoarchitectonics, National Institute for Materials Science*, ²*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, ³*Graduate School of Chemical Sciences and Engineering, Chuo University*)

○Kazuhiro Nemoto,¹ Naoto Shirahata^{1,2,3}

We report that coherent growth of zinc sulfide (ZnS) on a colloidal indium phosphide (InP) nanocrystal (NC) yields a InP/ZnS core/shell structure with a single lattice constant of 0.563 nm. Compared to the bulk crystal of zinc-blend InP, the lattice of core NC is compressed by 4.1%. To the contrary, the lattice of shell expands by 4.1% relative to bulky ZnS crystal throughout the core/shell NC if the shell is thinner than or equal to 0.81 nm and the diameter of the core QD is smaller than 2.64 nm. Under these conditions, the coherent NCs showed the superior optical properties. Furthermore, we fabricated a PD device using coherent InP/ZnS QD as the active layer and showed superior photoresponse characteristics. The time required for the rise and fall of the signal waveform was 4 msec and 9 msec, respectively, indicating the fastest response time among Cd-free QD system PDs reported so far.

Keywords: Indium phosphide; Zinc sulfide; Photodiode; Photodetector; Nanocrystal

リン化インジウム(InP)ナノ結晶(NC)は有害なカドミウム(Cd)の代替材料としてオプトエレクトロニクス分野で研究が進められている。本研究では InP NC に硫化亜鉛 (ZnS) をコヒーレント成長させると、単一格子定数 0.563 nm の InP/ZnS コア/シェル構造が得られることを報告する¹。InP のバルク結晶と比較すると、コア NC の格子は等方的に 4.1% 圧縮され、逆に、シェルの厚さが 0.81 nm 以下で、コア NC の直径が 2.64 nm より小さい場合、シェルの格子は等方的に 4.1%

膨張し、あたかも単結晶のコア/シェル結晶粒子を得た。この粒子は優れた光学特性を示した。さらに図 1 が示すようにコヒーレント InP/ZnS NC を活性層に具備するフォトダイオード(PD)素子の作製を行い、優れた光応答特性を示した²。信号波形の立ち上がり時間は 4 msec、立ち下がり時間は 9 msec で、応答時間の速さは従来報告された Cd フリーNC 系 PD の中で最速であった。

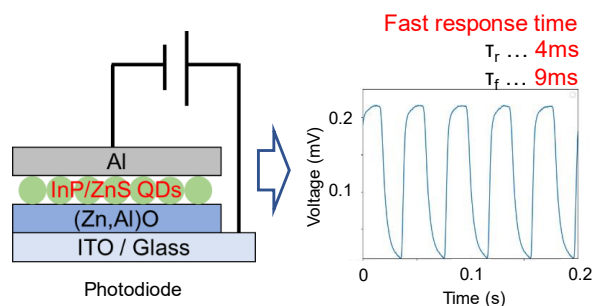


図 1 フォトダイオードの構造と応答時間

1 K. Nemoto, J. Watanabe, H.-T. Sun and N. Shirahata, *Nanoscale*, 2022, **14**, 9900–9909.

2 K. Nemoto, J. Watanabe, H. Yamada, H.-T. Sun and N. Shirahata, *Nanoscale Adv.*, DOI: 10.1039/d2na00734g