

Sat. Mar 20, 2021

Room 4

Academic Program [Oral B] | 01. Education and History of Chemistry | Oral B

[A04-2pm] 01. Education and History of Chemistry

Chair: Kenji Katayama, Shinji Inomata

1:00 PM - 3:40 PM Room 4 (Online Meeting)

[A04-2pm-01] New Development of Microscale

Chemistry: International Partnership in
Microscale Chemistry○Kazuko Ogino¹ (1. Tohoku University)

1:00 PM - 1:20 PM

[A04-2pm-02] New developments in microscale chemistry
experiments

~Report from high school chemistry room~

○Kumiko Kataoka¹ (1. Seisen Junior & Senior
High School)

1:20 PM - 1:40 PM

[A04-2pm-03] A Proposal of Simple Mohr Method to
Deepen Understanding of Precipitation
Titration○Kazuyuki Yamada¹, Kumiko Kataoka² (1.
Seishin Gakuen High School · Junior High
School, 2. Seison Junior and Senior High
School)

1:40 PM - 2:00 PM

[A04-2pm-04] First-year university chemistry experiment
in Covid-19 using microscale experiments○Yasunao Kuriyama¹ (1. Yamagata University)

2:00 PM - 2:20 PM

[A04-2pm-05] New Development of Microscale

Chemistry: Introduction for the
undergraduate education○Kenji Katayama¹, Yuki Konno, Naomi Tsuchiya
(1. Chuo University)

2:20 PM - 2:40 PM

[A04-2pm-06] New Developments in Microscale

Experiments: Case Study of Experiments
Education for University and Teachers'
Licenses○Yumiko Takagi¹ (1. Kagawa University)

2:40 PM - 3:00 PM

[A04-2pm-07] Measurement of dissolved oxygen by small
scale Winkler's methodSugawara Kazuki¹, Matsuoka Shu¹, ○HideyukiSawatari¹ (1. Miyagi university of education)

3:00 PM - 3:20 PM

[A04-2pm-08] Improvement and execution of basic
chemical experiment class with considering
prevention of COVID-19 at Fukushima
University○Shinji Inomata¹, Hiromasa Ikuta¹, TsugikoTakase¹ (1. Fukushima Univ.)

3:20 PM - 3:40 PM

Room 2

Academic Program [Oral B] | 02. Theoretical Chemistry, Chemoinformatics,
and Computational Chemistry | Oral B[A02-2pm] 02. Theoretical Chemistry,
Chemoinformatics, and Computational
Chemistry

Chair: Mitutaka Okumura, Ryohei Kishi

1:00 PM - 2:40 PM Room 2 (Online Meeting)

[A02-2pm-01] Theoretical study on the spin-unrestricted

CC2 calculations of optical response
properties of open-shell singlet molecules○Ryohei Kishi^{1,2}, Masako Yokoyama¹, Wataru
Yoshida¹, Yosuke Shimizu¹, Masato Ikeuchi¹,
Jinki Shoda¹, Masayoshi Nakano^{1,2,3} (1. Grad.
Sch. Eng. Sci., Osaka Univ., 2. QIQB, Osaka Univ.,
3. CSRN, Osaka Univ.)

1:00 PM - 1:20 PM

[A02-2pm-02] Automatic fragmentation in the divide and
conquer quantum chemical calculations
with the energy error estimation○Toshikazu Fujimori¹, Masato Kobayashi^{2,3,4},
Tetsuya Taketsugu^{2,3,4} (1. Graduate School of
Chemical Sciences and Engineering, Hokkaido
University, 2. Faculty of Science, Hokkaido
University, 3. WPI-ICReDD, Hokkaido University,
4. ESICB, Kyoto University)

1:20 PM - 1:40 PM

[A02-2pm-03] Reaction-network-based analysis and
prediction on the coordination self-
assembly of Pd₃L₆ double-walled triangle○Satoshi Takahashi¹, Tomoki Tateishi¹, Yuya
Sasaki¹, Hirofumi Sato^{2,3,4}, Shuichi Hiraoka¹ (1.
Graduate School of Arts and Sciences, The Univ.
of Tokyo, 2. Department of Molecular
Engineering, Kyoto Univ., 3. ESICB, Kyoto Univ.,
4. Fukui Institute for Fundamental Chemistry,

Kyoto Univ.)

1:40 PM - 2:00 PM

[A02-2pm-04] Extrapolating molecular properties using machine learning models trained with small-size experimental databases

○Kan Hatakeyama-Sato¹, Kenichi Oyaizu¹ (1.

Waseda Univ.)

2:00 PM - 2:20 PM

[A02-2pm-05] Orbital Correlation Diagram for Understanding Surface Reactions

○Yuta Tsuji¹, Kazunari Yoshizawa¹ (1. Kyushu Univ.)

2:20 PM - 2:40 PM

Room 4

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

[A04-2am] 04. Physical Chemistry -Properties-

Chair:Tomoyuki Mochida, Taku Iiyama

9:00 AM - 10:20 AM Room 4 (Online Meeting)

[A04-2am-01] Structure of ion solvation and association and solvent water in an aqueous magnesium chloride solution under the gigapascal pressure range

○Toshio Yamaguchi¹, Nami Fukuyama¹, Koji Yoshida¹, Yoshinori Katayama² (1. Fukuoka University, 2. Synchrotron Radiation Research Center)

9:00 AM - 9:20 AM

[A04-2am-02] Molecular Dynamics Analysis of Hydration Properties inside the Nanochannels of Self-Assembled Ionic Liquid Crystals

○Yoshiki Ishii¹, Nobuyuki Matubayasi², Go Watanabe³, Yoshihisa Harada⁴, Takashi Kato⁴, Hitoshi Washizu¹ (1. Univ. of Hyogo, 2. Osaka Univ., 3. Kitasato Univ., 4. The Univ. of Tokyo)

9:20 AM - 9:40 AM

[A04-2am-03] Ionogels containing ruthenium-complexes and exhibiting ionic conductivity changes by application of external stimuli

○Ryo Sumitani¹, Tomoyuki Mochida^{1,2} (1. Graduate School of Science, Kobe University, 2. Research Center for Membrane and Film Technology)

9:40 AM - 10:00 AM

[A04-2am-04] Possibility of *ab initio* effective fragment

potential molecular dynamics simulations for predicting thermodynamic properties of the functional liquid materials

○Nahoko KUROKI¹, Hiroto MORI^{1,2} (1. Chuo Univ., 2. IMS)

10:00 AM - 10:20 AM

Room 3

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

[A03-2am] 04. Physical Chemistry -Properties-

Chair:Ken Onda, Takuya Okamoto

9:00 AM - 11:20 AM Room 3 (Online Meeting)

[A03-2am-01] Theoretical study on singlet fission

dynamics of symmetric hetero linear pentacene tetramer models

○Masayoshi Nakano^{1,2,3}, Hajime Miyamoto¹, Kazuaki Tokuyama¹ (1. Graduate School of Engineering Science, Osaka University, 2. Center for Spintronics Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

9:00 AM - 9:20 AM

[A03-2am-02] Theoretical Study on the Effect of Applying External Static Electric Field on Singlet Fission Dynamics of Pentacene Dimer Models

○Takayoshi Tonami¹, Ryota Sugimori¹, Ryota Sakai¹, Masayoshi Nakano^{1,2,3} (1. Osaka University, 2. Center for Spintronic Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

9:20 AM - 9:40 AM

[A03-2am-03] Theoretical study on third-order nonlinear optical properties for radical trimer cations

○Wataru Yoshida¹, Hiroshi Matsui², Hajime Miyamoto¹, Ryota Sugimori¹, Takayoshi Tonami¹, Ryohei Kishi^{1,3}, Masayoshi Nakano^{1,3,4} (1. Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 2. Osaka Institute of Public Health, 3. Center for Quantum Information and Quantum Biology, Osaka University, 4. Center for Spintronics Research Network, Osaka University)

9:40 AM - 10:00 AM

- [A03-2am-04] Theoretical study on structure, aromaticities and open-shell characters of π -trimers of antiaromatic molecules
 ○Masato Ikeuchi¹, Ryouhei Kishi³, Wataru Yoshida¹, Yousuke Shimizu¹, Jinaki Shouda¹, Masayoshi Nakano^{2,3} (1. Graduate School of Engineering Science, Osaka University, 2. Center for Spintronics Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

10:00 AM - 10:20 AM

- [A03-2am-05] Quantum Design of Curved π -Conjugated Molecules for Highly-Efficient Singlet Fission: Bending Effect of the Perylene/Peropyrene Backbones
 ○Kenji Okada¹, Ryota Sakai², Masayoshi Nakano^{1,3,4} (1. Graduate School of Engineering Science, Osaka Univ., 2. School of Engineering Science, Osaka Univ., 3. Center for Spintronics Research Network, Osaka Univ., 4. Quantum Information and Quantum Biology Division, Osaka Univ.)

10:20 AM - 10:40 AM

- [A03-2am-06] Theoretical study on singlet fission dynamics in pentacene ring-shaped aggregate models: Aggregate size and molecular configuration dependences
 ○Hajime Miyamoto¹, Kazuaki Tokuyama¹, Masayoshi Nakano^{1,2,3} (1. Graduate School of Engineering Science, Osaka University, 2. Center for Spintronics Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

10:40 AM - 11:00 AM

- [A03-2am-07] Quantitative prediction of singlet fission rates and molecular design of singlet fission materials
 ○Katsuyuki Shizu¹, Chihaya Adachi², Hironori Kaji¹ (1. Kyoto Univ., 2. Kyushu Univ.)

11:00 AM - 11:20 AM

Room 5

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

[A05-2pm] 05. Physical Chemistry -Chemical

Kinetics and Dynamics-

Chair: Takuya Horio, Masashi Arakawa, Fuminori Misaizu

1:00 PM - 3:20 PM Room 5 (Online Meeting)

- [A05-2pm-01] Capturing roaming molecular fragments of formaldehyde in real time

○Tomoyuki Endo^{1,2}, Simon P Neville³, Vicent Wanie², Samuel Beaulieu², Chen Qu⁴, Jude Deschamps², Philippe Lassonde², Bruno E Schmidt⁵, Hikaru Fujise⁶, Mizuho Fushitani⁶, Akiyoshi Hishikawa^{6,7}, Paul L Houston^{8,9}, Joel M Bowman¹⁰, Michael S Schuurman^{3,11}, François Légaré², Heide Ibrahim² (1. QST-KPSI, 2. INRS-EMT, 3. Univ. of Ottawa, 4. Univ. of Maryland, 5. few-cycle Inc., 6. Nagoya Univ. Dept. Chemistry, 7. Nagoya Univ. RCMS, 8. Cornell Univ., 9. Georgia Inst. of Tech., 10. Emory Univ., 11. NRC of Canada)

1:00 PM - 1:20 PM

- [A05-2pm-02] Ultrafast nuclear dynamics of electronically highly excited O_2^+ investigated by pump-probe measurements using near-infrared laser pulses and high-order harmonics

○Kana Yamada¹, Toshiaki Ando¹, Atsushi Iwasaki¹, Kaoru Yamanouchi¹ (1. The University of Tokyo)

1:20 PM - 1:40 PM

- [A05-2pm-03] Structural features in the growth of silver cluster cations observed by photodissociation/absorption spectroscopy

○Satoshi Kono¹, Shun Kawamura¹, Kensuke Morishita¹, Masashi Arakawa¹, Takuya Horio¹, Akira Terasaki¹ (1. Kyushu University)

1:40 PM - 2:00 PM

- [A05-2pm-04] NO dissociation ability of IX group clusters.

○Masato Yamaguchi¹, Yufei Zhang¹, Ken Miyajima¹, Joost M. Bakker², Olga V. Lushchikova², Fumitaka Mafuné¹ (1. Graduate School of Arts and Sciences, The University of Tokyo, 2. Radboud University)

2:00 PM - 2:20 PM

- [A05-2pm-05] Ion imaging of vibrational predissociation of Ar-tagged protonated water monomer and dimer

○Yuri Ito¹, Mizuhiro Kominato¹, Yuji Nakashima¹, Fuminori Misaizu¹ (1. Tohoku University)

2:20 PM - 2:40 PM

[A05-2pm-06] OPIG-DC Voltage-Revolved Collision-Induced Reactions of Bimolecular Ions

○Shinji Nonose¹, Satoko Kanamori¹, Saki Kitamura¹, Takaaki Iyama¹, Wataru Kadota¹, Juri MORishita¹, Yuto Yonebayashi¹, Hiroto Ohta¹, Satofumi Tago¹, Tomoya Yoshida¹ (1. Yokohama City University)

2:40 PM - 3:00 PM

[A05-2pm-07] Freezing process of micro droplets of pure water and water– ethylene glycol mixtures evaporatively cooled in a vacuum

○Tamon Kusumoto¹, Takefumi Handa¹, Masashi Arakawa¹, Takuya Horio¹, Akira Terasaki¹ (1. Kyushu University)

3:00 PM - 3:20 PM

Room 6

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

[A06-2pm] 08. Catalysts and Catalysis

Chair:Hiroshi Kominami, Haruno Murayama

1:00 PM - 3:20 PM Room 6 (Online Meeting)

[A06-2pm-01] Photocatalytic hydrogen production by hybrid photocatalyst composed of layered niobate nanoparticles with multilayered Ru(II) dyes in the presence of redox mediators

○Nobutaka Yoshimura¹, Atsushi Kobayashi², Masaki Yoshida², Tomoki Kondo³, Ryu Abe³, Masako Kato² (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. Graduate School of Science, Hokkaido University, 3. Graduate School of Engineering, Kyoto University)

1:00 PM - 1:20 PM

[A06-2pm-02] Photothermal Dry Reforming of Methane over Supported Rhodium Catalysts

○Daichi Takami¹, Akira Yamamoto^{1,2}, Hisao Yoshida^{1,2} (1. Kyoto Univ., 2. ESICB, Kyoto Univ.)

1:20 PM - 1:40 PM

[A06-2pm-03] Synthesis of porphyrin comprising nanodisks from covalent organic frameworks through mechanical stirring and investigation of their photocatalytic

activity

○XINXI LI¹, Yasuko Osakada¹, Mamoru Fujitsuka¹ (1. Osaka University)

1:40 PM - 2:00 PM

[A06-2pm-04] Water oxidation over gold plasmonic photocatalyst modified with hole-transferring cocatalyst

○Eri Fudo¹, Atsuhiko Tanaka^{1,2}, Hiroshi Kominami¹ (1. Kindai university, 2. JST PRESTO)

2:00 PM - 2:20 PM

[A06-2pm-05] Synthesis and Photocatalytic Properties of Iron Disilicide/TiO₂ Composite Powder

○Kensuke Akiyama¹, Sakiko Nojima¹, Hiroshi Irie² (1. Kanagawa Institute of Industrial Science and Technology, 2. University of Yamanashi)

2:20 PM - 2:40 PM

[A06-2pm-06] Photocatalytic O₂ Evolution under Visible Light on a Bismuth-based Layered Oxyhalide SrBi₃O₄Cl₃

○Daichi Ozaki¹, Hajime Suzuki¹, Osamu Tomita¹, Ryota Sakamoto¹, Ryu Abe¹ (1. Kyoto university)

2:40 PM - 3:00 PM

[A06-2pm-07] Development of a visible-light responsive photocatalyst by enhancing the functionality of Ti-MOF and its application to photocatalytic hydrogen peroxide production

○Yoshifumi Kondo¹, Yusuke Isaka¹, Yasutaka Kuwahara^{1,2,3}, Kohsuke Mori^{1,2}, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. PRESTO, JST)

3:00 PM - 3:20 PM

Room 7

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

[A07-2pm] 08. Catalysts and Catalysis

Chair:Satoru Takakusagi, Satoshi Muratsugu

1:00 PM - 3:40 PM Room 7 (Online Meeting)

[A07-2pm-01] Theoretical suggestion of selective benzene hydroxylation in aqueous solution by Keggin-type polyoxometalate

○Kei Ikeda¹, Yoshihito Shiota¹, Kazunari

Yoshizawa¹ (1. Institute for Materials
Chemistry and Engineering, Kyushu University)
1:00 PM - 1:20 PM

[A07-2pm-02] Preparation and Catalytic Selective
Oxidation Performances of Rutile-type IrO₂
Nanoparticles
○Satoshi Muratsugu¹, Takatoshi Sudoh¹, Satoru
Ikemoto¹, Mizuki Tada^{1,2} (1. Dept. Chem.
Nagoya Univ., 2. RCMS, Nagoya Univ.)
1:20 PM - 1:40 PM

[A07-2pm-03] High-density formation of metal/oxide
interfacial active sites on a supported Ru-V
catalyst prepared through hybrid clustering
○Shun Hayashi¹, Tetsuya Shishido^{1,2} (1. Tokyo
Metropolitan Univ., 2. ESICB, Kyoto Univ.)
1:40 PM - 2:00 PM

[A07-2pm-04] Grafting Method for Selective Formation of
Bis-grafted Surface Species
○Yusuke Ishizaka¹, Kazuhiro Matsumoto²,
Katsuhiko Takeuchi², Norihisa Fukaya², Kazuhiko
Sato², Jun-Chul Choi^{1,2} (1. University of
Tsukuba, 2. National Institute of Advanced
Industrial Science And Technology)
2:00 PM - 2:20 PM

[A07-2pm-05] Low Temperature Reduction of Subnano
Copper Oxides for Catalytic Hydrocarbon
Oxidations
○Kazutaka Sonobe¹, Makoto Tanabe², Takane
Imaoka^{1,2}, Wang Jae Chun³, Kimihisa
Yamamoto^{1,2} (1. Tokyo Institute of Technology,
2. JST-ERATO, 3. International Christian
University)
2:20 PM - 2:40 PM

[A07-2pm-06] Selective Hydroperoxygenation of Olefin
Realized by Coinage Multimetallic Sub-
nanocatalyst
○Tatsuya MORI¹, Takamasa TSUKAMOTO^{1,2},
Makoto TANABE², Tetsuya KANBE^{1,2}, Takane
IMAOKA^{1,2}, Kimihisa YAMAMOTO^{1,2} (1. Lab.
Chem. Life Sci., Tokyo Tech, 2. JST-ERATO)
2:40 PM - 3:00 PM

[A07-2pm-07] Prolonging catalytic lifetime in MTO
reaction over phosphorus-modified CHA
zeolite
○Nao Tsunoji¹, Ryora Osuga², Toshiyuki Yokoi²
(1. Hiroshima University, 2. Tokyo Institute of

Technology)
3:00 PM - 3:20 PM

[A07-2pm-08] Time-Resolved Dispersive-XAS Analysis of
Molybdenum Complex as Key Species
Toward Ammonia Formation
○Akira Yamamoto^{1,2}, Kazuya Arashiba³, Shimpei
Naniwa¹, Kazuo Kato⁴, Hiromasa Tanaka⁵,
Kazunari Yoshizawa⁶, Yoshiaki Nishibayashi³,
Hisao Yoshida^{1,2} (1. Kyoto Univ., 2. ESICB,
Kyoto Univ., 3. The Univ. of Tokyo, 4. JASRI, 5.
Daido University, 6. Kyushu Univ.)
3:20 PM - 3:40 PM

Room 13

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

[A13-2am] 09. Coordination Chemistry,
Organometallic Chemistry
Chair: Nobuhiro Yanai, Kazuya Otsubo, Ryuta Ishikawa
9:00 AM - 11:20 AM Room 13 (Online Meeting)

[A13-2am-01] Structures and Properties of
Supramolecular Assemblies Constructed by
Pyridine Derived Ligand
○Mikoto Uematsu¹, Ryuta Ishikawa¹, Satoshi
Kawata¹ (1. Fukuoka University)
9:00 AM - 9:20 AM

[A13-2am-02] Triboluminescence of pyridinophane
copper complexes in crystals and polymers
○ayumu karimata¹, Pradnya P Patil¹, Robert R
Fayzulin², Eugene Khaskin¹, Sebastien Lapointe¹,
Julia R Khusnutdinova¹ (1. okinawa institute of
science and technology, 2. Arbuzov Institute)
9:20 AM - 9:40 AM

[A13-2am-03] Space-through charge transfer interactions
in network complexes
○Marie Okuyama¹, Hiroyoshi Ohtsu¹, Masaki
Kawano¹ (1. Tokyo Institute of Technology)
9:40 AM - 10:00 AM

[A13-2am-04] Hyperpolarization of metal-organic
frameworks utilizing photoexcited triplet
electrons and its applications
○Saiya Fujiwara¹, Kenichiro Tateishi², Tomohiro
Uesaka², Keiko Ideta¹, Nobuo Kimizuka^{1,3},
Nobuhiro Yanai^{1,3,4} (1. Graduate School of
Engineering, Kyushu University, 2. RIKEN, 3.
Center for Molecular Systems, Kyushu University,

4. PRESTO, JST)

10:00 AM - 10:20 AM

- [A13-2am-05] Syntheses, crystal structures and photophysical properties of C60 incorporated zinc porphyrin dimers
[○]Kohei Ohwada¹, Minoru Mitsumi¹, Chiasa Urugami², Hideki Hashimoto² (1. Okayama Univ. of science, 2. Kwansei Gakuin Univ.)

10:20 AM - 10:40 AM

- [A13-2am-06] Fused Porphyrin-Based Porous Crystals
[○]Shun Sugimoto¹, Hiroshi Sato¹, Takuzo Aida^{1,2} (1. The Univ. of Tokyo, 2. Riken)

10:40 AM - 11:00 AM

- [A13-2am-07] A platinum-dimer based metal-organic framework having a pre-installed cationic guest for proton conduction
[○]Kazuya Otsubo¹, Shuya Nagayama¹, Kuniyoshi Sugimoto², Shogo Kawaguchi², Hiroshi Kitagawa¹ (1. Kyoto University, 2. JASRI/SPRING-8)

11:00 AM - 11:20 AM

Room 14

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

[A14-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Ryosuke Miyake, Toshiro Takao, Hisako Hashimoto
9:00 AM - 11:40 AM Room 14 (Online Meeting)

- [A14-2am-01] Synthesis and luminescence properties of silver(I) halogenido coordination polymers bridged by pyrazine, methylpyrazine, and aminopyrazine

Taiki Kuwahara¹, Hideki Ohtsu¹, [○]Kiyoshi Tsuge¹
(1. University of Toyama)

9:00 AM - 9:20 AM

- [A14-2am-02] Construction of Ni and Pd clusters using cyclooligosilane bearing aromatic substituents

[○]Kento Shimamoto¹, Yusuke Sunasa^{2,3} (1. The University of Tokyo, 2. IIS, The University of Tokyo, 3. JST PRESTO)

9:20 AM - 9:40 AM

- [A14-2am-03] Synthesis of multinuclear Pd clusters having [2.2]paracyclophane ligands
[○]Tsuyoshi Sugawa¹, Ayaka Hatano¹, Koji Yamamoto¹, Tetsuro Murahashi¹ (1. Tokyo

Institute of Technology)

9:40 AM - 10:00 AM

- [A14-2am-04] Creation of a series of lanthanide cubane clusters inside single-crystals of an anionic Rh₄Zn₄ complex with L-cysteinate

[○]Nobuto Yoshinari¹, Natthaya Meundaeng¹, Takumi Konno¹ (1. Osaka University)

10:00 AM - 10:20 AM

- [A14-2am-05] Metal-induced folding and assembly through three-crossing peptidic units

[○]Ami Saito¹, Tomohisa Sawada^{1,2}, Makoto Fujita^{1,3} (1. Grad. School of Engineering, The Univ. of Tokyo, 2. JST PRESTO, 3. Institute for Molecular Science)

10:20 AM - 10:40 AM

- [A14-2am-06] Creation of coordination polyhedra by collaborative metal-acetylene

 π -coordination[○]Yuya Domoto¹, Masahiro Abe¹, Kidai Yamamoto¹, Makoto Fujita^{1,2} (1. The University of Tokyo, 2. Institute for Molecular Science)

10:40 AM - 11:00 AM

- [A14-2am-07] Isolation of Mononuclear [Co(ligand)(CO)₃] Metalloradicals and Its H₂ Activation Mechanism

[○]Satoshi Takebayashi¹, Robert R. Fayzullin (1. Okinawa Institute of Science and Technology Graduate University)

11:00 AM - 11:20 AM

- [A14-2am-08] The Syntheses and Structures of Vanadium Complexes Bearing Triamidoamine Ligands with Bulky Substituents.

[○]Yoshiaki Kokubo¹, Yuji Kajita¹, Hideki Masuda¹ (1. Aichi Institute of Technology)

11:20 AM - 11:40 AM

Room 12

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

[A12-2am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Shogo Kuriyama, Hayato Tsurugi, Satoshi Abe
9:00 AM - 11:40 AM Room 12 (Online Meeting)

- [A12-2am-01] N-Methylation of Amines via Reductive Carbon Dioxide Fixation Catalyzed by Lanthanum Hydridotriarylborate

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

Chair: Yutaka Ie, Yasujiro Murata
9:00 AM - 11:40 AM Room 16 (Online Meeting)

Mechanism elucidation of the photomelting function

○Tomoaki Konishi¹, Yumi Nakaïke², Mitsuo Hara³, Wataru Yajima⁴, Ryo Shikata⁴, Masaki Hada^{5,6}, Shohei Saito¹ (1. Grad. Sch. of Sci., Kyoto Univ., 2. Grad. Sch. of Eng., Kyoto Univ., 3. Grad. Sch. of Eng., Nagoya Univ., 4. College of Eng. Sci., Univ of Tsukuba, 5. Grad. Sch. of Pure Appl. Sci., Univ of Tsukuba, 6. TREMS)

9:00 AM - 9:20 AM

○Haruki Sanematsu^{1,2}, Atsuro Takai², Masayuki Takeuchi^{1,2} (1. University of Tsukuba, 2. National Institute for Materials Science)

9:20 AM - 9:40 AM

○Takumi Sakamaki¹, Shang Rui¹, Eiich

○Koichi Shinohara¹, Hayato Tsurugi¹, Kazushi
Mashima¹ (1. Graduate School of Engineering
Science, Osaka Univ.)

9:00 AM - 9:20 AM

○Mariko Inoue¹, Mai Mizukami¹, Tokiya Teraishi¹,
Hayato Tsurugi¹, Kazushi Mashima¹ (1. Osaka
University)

9:20 AM - 9:40 AM

○Takayuki Itabashi¹, Kazuya Arashiba¹, Shogo Kuriyama¹, Yoshiaki Nishibayashi¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[○]Akihito Egi¹, Hiromasa Tanaka², Asuka Konomi¹,
 Yoshiaki Nishibayashi³, Kazunari Yoshizawa¹ (1.
 Institute for Materials Chemistry and
 Engineering, Kyushu University, 2. School of
 Liberal Arts and Science, Daido University, 3.
 School of Engineering, The University of Tokyo)

10:00 AM - 10:20 AM

○Hiroki Toda¹, Ken Sakata², Nishibayashi
Yoshiaki¹ (1. The University of Tokyo, 2. Toho
University)

10:20 AM - 10:40 AM

○Basudev Maity¹, Satoshi Abe¹, Eriko Nango²,
Rie Tanaka⁴, Mitsuo Shoji³, Yasuteru Shigeta³,
Takafumi Ueno¹ (1. Tokyo Institute of
Technology, 2. Tohoku University, 3. Tsukuba
University, 4. RIKEN, SPing8)

10:40 AM - 11:00 AM

Nakamura¹ (1. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[A16-2am-04] Spirohexaradical: Synthesis and Magnetic Properties○Takuya Kanetomo¹, Yusuke Fukushima¹, Yuta Takenouchi¹, Masaya Enomoto¹ (1. Tokyo Univ. of Sci.)

10:00 AM - 10:20 AM

[A16-2am-05] Alkyl Chain Length Effect in Organic Field-Effect Transistors of Tetrathienonaphthalenes○Motoki Kumeda¹, Kimiya Taniguchi¹, Atsushi Yamamoto¹, Yu Suenaga¹, Toshio Asada¹, Yasunori Matsui¹, Reitaro Hattori¹, Miho Higashinakaya¹, Takuya Ogaki¹, Eisuke Ohta¹, Hiroyoshi Naito¹, Hiroshi Ikeda¹ (1. Osaka Pref. Univ.)

10:20 AM - 10:40 AM

[A16-2am-06] Substituent dependent alignment of asymmetrically substituted π -extended aza[5]helicenes○Satoru Hiroto¹, Mana Wakita¹, Moeko Chujo¹ (1. Kyoto University)

10:40 AM - 11:00 AM

[A16-2am-07] Discovery of Flexible C-C Bond: Reversible Expansion and Contraction of an Extremely Elongated C-C Single Bond○Takuya Shimajiri¹, Takanori Suzuki¹, Yusuke Ishigaki¹ (1. Hokkaido Univ.)

11:00 AM - 11:20 AM

[A16-2am-08] Control of rotation in [2]rotaxanes○Yusuke Kawasaki¹, Hiroshi Koganezawa¹, Yuichiro Mutoh¹, Yusuke Yoshigoe¹, Shinichi Saito¹ (1. Faculty of Science, Tokyo University of Science)

11:20 AM - 11:40 AM

Room 8

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

[A08-2pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Ichiro Hisaki, Yoshimitsu Itoh

1:00 PM - 3:40 PM Room 8 (Online Meeting)

[A08-2pm-01] Kinetic control over the self-assembly of a Pd₆L₄ square-based pyramid○Tomoki Tateishi¹, Satoshi Takahashi¹, Keisuke Aratsu¹, Shuichi Hiraoka¹ (1. Graduate School of Arts and Sciences, The University of Tokyo)

1:00 PM - 1:20 PM

[A08-2pm-02] Structural control of a porous metal-macrocycle framework based on molecular adsorption to a local allosteric site○Ryunosuke Hayashi¹, Masahiro Asakura¹, Shinya Mitsui¹, Shohei Tashiro¹, Mitsuhiro Shionoya¹ (1. The University of Tokyo)

1:20 PM - 1:40 PM

[A08-2pm-03] Dynamic behavior of double-walled cages in the self-assembly and the guest recognition○Yukari Tamura¹, Hiroki Takezawa¹, Makoto Fujita¹ (1. The University of Tokyo)

1:40 PM - 2:00 PM

[A08-2pm-04] Highly Selective Heterochiral Supramolecular Polymerization of Thiophene-Fused Chiral [4n]Annulenes○Tsubasa Aoki¹, Michihisa Ueda¹, Takayuki Nakamuro², Eiichi Nakamura², Takuzo Aida^{1,3}, Yoshimitsu Itoh¹ (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. Grad. Sch. Sci., The Univ. of Tokyo, 3. CEMS, RIKEN)

2:00 PM - 2:20 PM

[A08-2pm-05] Rim-differentiated pillar[5]arenes: self-assembly and chirality control○Shixin Fa¹, Kouichi Egami¹, Keisuke Adachi¹, Kenichi Kato¹, Yoko Sakata², Shigehisa Akine², Tomoki Ogoshi^{1,2} (1. Kyoto University, 2. Kanazawa University)

2:20 PM - 2:40 PM

[A08-2pm-06] Generation of Porous Crystal of Triaryltriazine Derivative Based on CH- π Interaction○Eisuke Ohta¹, Haruka Izumi¹, Eriko Yasuzawa¹, Takuya Ogaki¹, Yasunori Matsui¹, Hiroyasu Sato², Hiroshi Ikeda¹ (1. Osaka Pref. Univ., 2. Rigaku)

2:40 PM - 3:00 PM

[A08-2pm-07] Creation of highly-crossed torus topologies by unique entangling nature of metal-peptide chains○Yuuki Inomata¹, Tomohisa Sawada^{1,2}, Makoto Fujita^{1,3} (1. Grad. School of Engineering, The University of Tokyo, 2. JST PRESTO, 3. IMS)

3:00 PM - 3:20 PM

[A08-2pm-08] Seeded Self-Assembly of Charge-Terminated Poly(3-hexylthiophene) Amphiphiles Based on the Energy Landscape

○Tomoya Fukui¹, Ian Manners² (1. CLS, Tokyo Tech., 2. Univ. of Victoria)

3:20 PM - 3:40 PM

Room 20

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

[A20-2am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Takashi Mino, Shuhei Kusumoto

9:00 AM - 11:40 AM Room 20 (Online Meeting)

[A20-2am-01] Controlled cyclization of arylalkynes through folding inside a molecular cage

○Hiroki Takezawa¹, Harumi Hayakawa¹, Makoto Fujita¹ (1. The Univ. of Tokyo)

9:00 AM - 9:20 AM

[A20-2am-02] Construction of the Difluoroglycine Core by Three-Component Coupling Reaction Predicted by Quantum Chemical Calculations

○Tsuyoshi Mita^{1,2}, Hiroki Hayashi^{1,2}, Hitomi Katsuyama^{1,2}, Yu Harabuchi^{1,2,3}, Satoshi Maeda^{1,2,3} (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

9:20 AM - 9:40 AM

[A20-2am-03] Heavy-Metal-Free Fischer–Tropsch Type Reaction

○Shrinwantu Pal¹, Andreas Phanopoulos¹, Takafumi Kawakami¹, Kyoko Nozaki¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[A20-2am-04] Asymmetric Synthesis of Silacyclopentanes and Silaoxanes

○Akihiro Kuroo², Kazunobu Igawa^{1,2}, Katsuhiko Tomooka^{1,2} (1. IMCE, Kyushu Univ., 2. Grad. Sch. Eng. Sci., Kyushu Univ.)

10:00 AM - 10:20 AM

[A20-2am-05] Chiral symmetry breaking of *meso*-diols involving dynamic crystallization

○Aoi Washio¹, Yasushi Yoshida¹, Takashi Mino¹,

Yoshio Kasashima², Masami Sakamoto¹ (1.

Graduated school of engineering, Chiba university, 2. Faculty of Creative Engineering, Chiba Institute of Technology)

10:20 AM - 10:40 AM

[A20-2am-06] Synthesis of Planar-chiral Glycine and Its Peptide

○Yuki Yoshida², Kazunobu Igawa^{1,2}, Katsuhiko Tomooka^{1,2} (1. IMCE, Kyushu Univ., 2. Grad. Sch. Eng. Sci., Kyushu Univ.)

10:40 AM - 11:00 AM

[A20-2am-07] Development of Well-Dispersed Trifluoromethanesulfonic Acid-Treated Metal Oxide

Nanoparticles Immobilized on Nitrogen-Doped Carbon

○Xi Yang¹, Tomohiro Yasukawa¹, Shu Kobayashi¹ (1. The University of Tokyo)

11:00 AM - 11:20 AM

[A20-2am-08] Enantioselective α -Halogenation of N-Acyl-3,5-Dimethylpyrazoles Catalyzed by Chiral π -Cu(II)- π Complexes

○Kazuki Nishimura¹, Yanzhao Wang, Yoshihiro Ogura, Kazuaki Ishihara¹ (1. Nagoya Univ.)

11:20 AM - 11:40 AM

Room 19

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

[A19-2am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Shuhei Higashibayashi, Taiga Yurino

9:00 AM - 11:40 AM Room 19 (Online Meeting)

[A19-2am-01] Development of Core/Shell-Type

Heterogeneous Supports and Structure-Activity Relationship

○Tatsuya Kuremoto¹, Ren Sadatsune¹, Tomohiro Yasukawa¹, Shu Kobayashi¹ (1. The University of Tokyo)

9:00 AM - 9:20 AM

[A19-2am-02] Application of N-doped Carbon

Incarcerated Copper Nanoparticle Catalysts to Sequential- and Continuous-flow Systems

○Fumiya Tobita¹, Tomohiro Yasukawa¹, Shū

Kobayashi¹ (1. The University of Tokyo)

9:20 AM - 9:40 AM

- [A19-2am-03] Micro-Raman imaging of fine chemical synthesis of imidazolium-based ionic liquids; *in situ* observation of molecular transformation and reaction temperature

○Hajime OKAJIMA^{1,2}, Akira SAKAMOTO¹ (1. Aoyama Gakuin University, 2. PRESTO, JST)

9:40 AM - 10:00 AM

- [A19-2am-04] Sulfonium ion-promoted traceless Schmidt reaction of alkyl azides

○Bayu Ardiansah¹, Hiroki Tanimoto², Kiyomi Kakiuchi¹ (1. Graduate School of Materials Science, Nara Institute of Science and Technology, 2. Faculty of Pharmaceutical Sciences, University of Toyama)

10:00 AM - 10:20 AM

- [A19-2am-05] The synthesis of substituted catechols by novel 1,2-rearrangement of *ortho*-quinols

○Riichi Hashimoto¹, Kengo Hanaya¹, Shuhei Higashibayashi¹, Takeshi Sugai¹ (1. Keio university)

10:20 AM - 10:40 AM

- [A19-2am-06] *N*-Difluoroalkylative Dearomatization of Pyridine Guided by Quantum Chemical Calculations

○Hiroki Hayashi^{1,2}, Hitoki Katsuyama^{1,2}, Tsuyoshi Mita^{1,2}, Yu Harabuchi^{1,2,3}, Satoshi Maeda^{1,2,3} (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

10:40 AM - 11:00 AM

- [A19-2am-07] Silyl Cyanopalladate-Catalyzed Friedel-Crafts-type Cyclization Affording 3-Aryloxindole Derivatives

○Hamdiye Ece^{1,3}, Taiga Yurino^{2,3}, Takeshi Ohkuma^{2,3} (1. Graduate School of Chemical Sciences and Engineering, 2. Faculty of Engineering, 3. Hokkaido University)

11:00 AM - 11:20 AM

- [A19-2am-08] 8π electrocyclic reaction of phosphonate derivatives

○HIROKI SAITO¹, Keiji Tanino² (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

11:20 AM - 11:40 AM

Room 1

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

[A01-2pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Go Hirai, Shigenobu Umemiya

1:00 PM - 3:40 PM Room 1 (Online Meeting)

- [A01-2pm-01] Live-Cell Protein Lysine Acylation Using Boronate-Assisted Hydroxamic Acid Catalyst

○Christopher Adamson¹, Shigehiro Kawashima¹, Kenzo Yamatsugu¹, Motomu Kanai¹ (1. The University of Tokyo)

1:00 PM - 1:20 PM

- [A01-2pm-02] Synthetic hyper acetylation of histones with a chemical catalyst system and its application to *Xenopus laevis* sperm chromatin

○Hidetoshi Kajino¹, Tomomi Nagatani², Miku Oi¹, Tomoya Kujirai^{3,4}, Hitoshi Kurumizaka^{3,4}, Atsuya Nishiyama², Makoto Nakanishi², Kenzo Yamatsugu¹, Shigehiro A Kawashima¹, Motomu Kanai¹ (1. The Univ. of Tokyo, 2. The Univ. of Tokyo, The Institute of Medical Science, 3. The Univ. of Tokyo, Institute of Quantitative Biosciences, 4. JST-ERATO)

1:20 PM - 1:40 PM

- [A01-2pm-03] *N*-GlycoAlbumin-Ru artificial metalloenzyme for therapeutic drug synthesis.

○Igor Nasibullin^{1,3}, Ivan Smirnov³, Katsunori Tanaka^{1,2,3} (1. RIKEN, Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2. Tokyo Institute of Technology, Department of Chemical Science and Engineering, School of Materials and Chemical Technology, 3. Kazan Federal University, Biofunctional Chemistry Laboratory, A. Butlerov Inst.)

1:40 PM - 2:00 PM

- [A01-2pm-04] Anticancer approach by a gold artificial metalloenzyme-catalyzed synthesis of quaternary ammonium derivatives via hydroamination

○Tsong-Che Chang¹, Tomoya YAMAMOTO¹,

Katsunori TANAKA^{1,2,3} (1. Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2. Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 3. Biofunctional Chemistry Laboratory, A. Butlerov Inst., Kazan Federal University)

2:00 PM - 2:20 PM

[A01-2pm-05] Rational design of a stapled JAZ peptide as the jasmonate-related transcription factor-selective inhibitor

○Yousuke Takaoka¹, Kaho Suzuki¹, Minoru Ueda^{1,2} (1. Tohoku Univ., Grad. Sci., 2. Tohoku Univ., Grad. Life Sciences)

2:20 PM - 2:40 PM

[A01-2pm-06] Tumor therapy using ruthenium catalytic reaction in mice

○Kyohei Muguruma¹, Peni Ahmadi², Tsung-che Chang², Katsunori Tanaka^{1,2,3} (1. Tokyo Institute of Technology, 2. RIKEN, 3. Kazan Federal University)

2:40 PM - 3:00 PM

[A01-2pm-07] Revealing Binding Position of Aplyronine A as A Protein-Protein Interaction Inducer

○Didik Huswo Utomo¹, Akari Fujieda¹, Maho Morita¹, Hideo Kigoshi², Masaki Kita¹ (1. Graduate School of Bioagricultural Sciences, Nagoya University, 2. Graduate School of Pure and Applied Sciences, University of Tsukuba)

3:00 PM - 3:20 PM

[A01-2pm-08] Reactivity of acrolein released from cancer cells: Application for selective cancer therapy and diagnosis

○Ambara Rachmat Pradipta¹, Peni Ahmadi², Tanaka Katsunori^{1,2,3} (1. Tokyo Tech., 2. RIKEN, 3. Kazan Univ.)

3:20 PM - 3:40 PM

Room 24

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

[A24-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Osami Shoji, Akira Onoda

1:00 PM - 3:40 PM Room 24 (Online Meeting)

[A24-2pm-01] Energy Analysis of Miniprotein by in Vivo Protein Crystallization

○Mariko Kojima¹, Yuki Hishikawa¹, Satoshi Abe¹, Tadaomi Huruta¹, Duy Phuoc Tran¹, Akio Kitao¹, Takafumi Ueno¹ (1. TokyoTech)

1:00 PM - 1:20 PM

[A24-2pm-02] Design of the dynamic assembly behaviors of artificial β -helical protein needles.

○Kosuke Kikuchi¹, Fukuyama Tatsuya², Basudev Maity¹, Tadaomi Furuta¹, Yusuke T Maeda², Takayuki Uchihashi³, Takafumi Ueno¹ (1. Tokyo Tech., 2. Kyusyu Univ., 3. Nagoya Univ.)

1:20 PM - 1:40 PM

[A24-2pm-03] Dual-surface functionalization of an artificial protein nanoparticle TIP60 using molecular-filtration effect of surface pores

○Erika Nasu¹, Norifumi Kawakami¹, Kenji Miyamoto¹ (1. Keio University)

1:40 PM - 2:00 PM

[A24-2pm-04] Star-shaped Supramolecular Assembly Formed by the Conjugation of Hexameric Tyrosine-coordinated Hemoprotein with Engineered Cytochrome *b*₅₆₂

○Julian Wong Soon¹, Koji Oohora¹, Shota Hirayama¹, Takashi Hayashi¹ (1. Osaka University)

2:00 PM - 2:20 PM

[A24-2pm-05] Development of SPIONs-conjugated Pt Nanoparticles-Latex Nanocomposite Beads for Immunochromatography Assay with Enhanced Sensitivity

Sizun He¹, The Son Le¹, Mari Takahashi¹, Yasushi Enomoto², Yasufumi Matsumura², ○Shinya Maenosono¹ (1. JAIST, 2. Nippon Steel Chem. Mater. Co., Ltd.)

2:20 PM - 2:40 PM

[A24-2pm-06] Evolutionary Engineering of a Cp*Rh(III)-linked Artificial Metalloenzyme with a Chimeric β -Barrel Protein Scaffold for Isoquinoline Synthesis via C(sp²)-H Bond Activation

○Shunsuke Kato¹, Akira Onoda², Ulrich Schwaneberg³, Takashi Hayashi¹ (1. Osaka University, 2. Hokkaido University, 3. RWTH Aachen University)

2:40 PM - 3:00 PM

[A24-2pm-07] Screening of Peptide Derivatives for the Activation of Wild-Type Cytochrome P450BM3 for Gaseous Substrates Hydroxylation

○Kai Yonemura¹, Sinya Ariyasu¹, Hiroshi Sugimoto^{2,4}, Yoshihito Watanabe³, Osami Shoji^{4,1} (1. Nagoya University, 2. RIKEN/SPRING-8, 3. RCMS Nagoya University, 4. JST CREST)
3:00 PM - 3:20 PM

[A24-2pm-08] Synthesis of Hemoglobin Oligomer Capable of Structural Changes in Response to O₂ Association and Dissociation

○Yoshitsugu Morita¹, Chinatsu Okuma¹, Teruyuki Komatsu¹ (1. Chuo University)
3:20 PM - 3:40 PM

Room 23

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

[A23-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Kohei Sato, Toshikazu Bando
1:00 PM - 3:40 PM Room 23 (Online Meeting)

[A23-2pm-01] Dual-Stimuli-Responsive Small Molecular Probes for Quantitative Detection of Both pH and Enzyme Activity

○Wenting Huo¹, Miki Koji¹, Daisuke Tokunaga¹, Huiying Mu¹, Masahiro Oe¹, Kouichi Ohe¹, Hiroshi Harada¹ (1. Kyoto Univ.)
1:00 PM - 1:20 PM

[A23-2pm-02] Transmembrane Anion Transport by Imidazolinium-based Multiblock Amphiphile

○Miki Mori¹, Kohei Sato¹, Toru Ekimoto², Shinichi Okumura², Mitsunori Ikeguchi^{2,3}, Kazuhito Tabata⁴, Hiroyuki Noji⁴, Kazushi Kinbara¹ (1. Sch. Life Sci. Tech., Tokyo Tech, 2. Grad. Sch. Med. Life Sci., Yokohama City Univ., 3. MIH, RIKEN, 4. Grad. Sch. Eng., The Univ. of Tokyo)
1:20 PM - 1:40 PM

[A23-2pm-03] Design and Synthesis of Supramolecular Phosphatases Functionalized with Lewis Acid Moieties for Catalytic Hydrolysis of Phosphate Monoester in Two-Phase Solvent System

○Shin Aoki^{1,2}, Akib Bin Rahman¹, Hirokazu Okamoto¹, Tomohiro Tanaka¹ (1. Faculty of Pharm. Sci., Tokyo Univ. Sci., 2. Research Inst. Sci. Tech., Tokyo Univ. Sci.)
1:40 PM - 2:00 PM

[A23-2pm-04] Improved photoswitching proteins for endogenous gene activation by near-infrared light

○Takahiro Nakajima^{1,2}, Moritoshi Sato² (1. KISTEC, 2. Grad. Sch. Arts and Sci., The Univ. of Tokyo)
2:00 PM - 2:20 PM

[A23-2pm-05] Sequence-Specific DNA Alkylation by a Chlorambucil-Conjugated Cyclic Pyrrole-Imidazole Polyamide

○Yuki Hirose¹, Kaori Hashiya¹, Toshikazu Bando¹, Hiroshi Sugiyama^{1,2} (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University)
2:20 PM - 2:40 PM

[A23-2pm-06] Transcription and replication control of mitochondrial DNA by sequence-specific DNA binders

○Takuya Hidaka¹, Ganesh Pandian Namasivayam², Toshikazu Bando¹, Hiroshi Sugiyama^{1,2} (1. Grad. Sch. of Sci., Kyoto Univ., 2. iCeMS, Kyoto Univ.)
2:40 PM - 3:00 PM

[A23-2pm-07] Construction of Intracellular Condition Responsive System Toward Cancer Cell Selective Therapeutics

- Development of the Intracellular Condition Responsive XNA and Disulfide Linkers -
○Seiya Ishizawa¹, Masahito Inagaki¹, Kenta Otake¹, Masaki Nishijima¹, Yasuyuki Araki¹, Wada Takehiko¹ (1. Tohoku University, IMRAM)
3:00 PM - 3:20 PM

[A23-2pm-08] Development of Reactions Constructing Novel Three-Dimensional Skeletons for Exploring New Chemical Space and Protein-Protein Interaction (PPI) Inhibitory Activity

○Hiroki Ueda^{1,2}, Peter Wipf³, Hiroyuki

Nakamura¹ (1. Tokyo Institute of Technology, Laboratory for Chemistry and Life Science, 2. Tokyo Institute of Technology, School of Life Science and Technology, 3. Univ. of Pittsburgh, Department of Chemistry)
3:20 PM - 3:40 PM

Room 25

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

[A25-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Yousuke Katsuda, Soyoung Park
1:00 PM - 3:40 PM Room 25 (Online Meeting)

[A25-2pm-01] Synthesis of a benzo[a]pyrene-modified oligonucleotide and its application to a fluorescent colorimetric detection of single base alterations of RNA sequences
○Yu Watari¹, Kaito Nakatani¹, Yui Ohtsuka¹, Tomonori Waku¹, Akio Kobori¹ (1. Kyoto Institute of Technology)
1:00 PM - 1:20 PM

[A25-2pm-02] A triplex-forming linear probe for sensitive and sequence-specific detection of duplex DNA
○Yanglingzhi Chen¹, Keiji Murayama¹, Hiroyuki Asanuma¹ (1. The Univ. of nagoya)
1:20 PM - 1:40 PM

[A25-2pm-03] Development of a fluorescent thymidine analog and construction of orientation-dependent FRET system
○Shingo Hirashima¹, Soyoung Park¹, Hiroshi Sugiyama¹ (1. Kyoto University)
1:40 PM - 2:00 PM

[A25-2pm-04] Development of Bio-Labile Protecting Groups for oligonucleotides
○Akira Ono¹, Takayuki Oota¹, Kousei Nakamura¹, Hisao Saneyoshi² (1. Kanagawa University, 2. Shiga University of Medical Science)
2:00 PM - 2:20 PM

[A25-2pm-05] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (65) : Microscopic analyses for elucidating molecular mechanisms at the interaction between berberine and bulged RNA
○Tamaki ENDOH¹, Sagar SATPATHI¹, Tatsuya

OHYAMA¹, Peter PODBEVŠEK², Janez PLAVEC^{2,3,4}, Naoki SUGIMOTO¹ (1. Konan University, 2. National Institute of Chemistry, 3. EN→FIST Centre of Excellence, 4. University of Ljubljana)
2:20 PM - 2:40 PM

[A25-2pm-06] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (66) : Effect of molecular crowding on replication along non-natural DNAs
○Shuntaro Takahashi¹, Piet Herdewijn², Naoki Sugimoto^{1,3} (1. Konan University, FIBER, 2. KU Leuven, 3. Konan University, FIRST)
2:40 PM - 3:00 PM

[A25-2pm-07] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (67): Effects of malignant alteration in cancer cells on the DNA G-quadruplexes and transcript mutations
○Hisae Tateishi-Karimata¹, Keiko Kawauchi², Tatsuya Ohyama¹, Naoki Sugimoto^{1,2} (1. FIBER, Konan University, 2. FIRST, Konan University)
3:00 PM - 3:20 PM

[A25-2pm-08] Development of a novel technology for gene suppression based on formation of RNA structure.
○Takuto Kamura¹, Yosuke Katsuda¹, Taishi Nakamura², Kenichi Tsujita³, Yusuke Kitamura¹, Masaki Hagihara⁴, Shin-ichi Sato⁵, Toshihiro Ihara¹ (1. Faculty of Advanced Science and Technology, Kumamoto University, 2. Department of Medical Information Sciences and Administration Planning, Kumamoto University Hospital, 3. Department of Cardiovascular Medicine, Faculty of Life Sciences, Kumamoto University, 4. Faculty of Science and Technology, Hirosaki University, 5. Institute for Chemical Research, Kyoto University)
3:20 PM - 3:40 PM

Room 10

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

[A10-2pm] 18. Polymer
Chair: Takuma Kureha, Yuuki Hata
1:00 PM - 3:20 PM Room 10 (Online Meeting)

- [A10-2pm-01] The relation between relaxation time and mechanical properties of supramolecular hydrogels.
 ○Subaru Konishi¹, Yu Kashiwagi¹, Go Watanabe², Motofumi Osaki^{1,3}, Takuya Katashima⁴, Osamu Urakawa¹, Hiroyasu Yamaguchi^{1,3}, Tadashi Inoue^{1,3}, Akira Harada⁵, Yoshinori Takashima^{1,3,6} (1. Grad. Sch. of Sci., Osaka Univ., 2. Sch. of Sci., Kitasato Univ., 3. PRC, Osaka Univ., 4. Sch. of Eng., The Univ. of Tokyo, 5. ISIR, Osaka Univ., 6. Institute for Advanced Co-Creation Studies, Osaka Univ.)
 1:00 PM - 1:20 PM
- [A10-2pm-02] Design and evaluation of mechanical properties of dissimilar polymer knitting materials with movable cross-links
 ○Ryohei Ikura¹, Shunsuke Murata², Yuka Ikemoto³, Motofumi Osaki^{1,4}, Hiroyasu Yamaguchi¹, Akira Harada⁵, Go Matsuba², Yoshinori Takashima^{1,4,6} (1. Grad. Sch. of Sci., Osaka Univ., 2. Grad. Sch. of Org. Mat. Eng., Yamagata Univ., 3. JASRI, 4. PRC., Osaka Univ., 5. Inst. for Advanced Co-Creation Studies., 6. The Inst. of Scientific and Industrial Res., Osaka Univ.)
 1:20 PM - 1:40 PM
- [A10-2pm-03] Mechanoresponsive PDMS that Reversibly Changes Fluorescence in Sub-MPa Stress
 ○Hidetsugu Kitakado¹, Shohei Saito¹ (1. Grad. Sch. of Sci., Kyoto Univ.)
 1:40 PM - 2:00 PM
- [A10-2pm-04] Gelation mechanism of freeze-crosslinked cellulose nanofiber gels with high compressive strength
 ○Daisuke Miura¹, Takuya Nankawa², Teppei Yamada³, Yurina Sekine² (1. Yamagata University, 2. Japan Atomic Energy Agency, 3. The University of Tokyo)
 2:00 PM - 2:20 PM
- [A10-2pm-05] Structural Properties Analysis of Temperature-responsive Hydrogels with Unique Nanodomains
 ○Takuma Kureha¹, Takuto Hirayama¹, Yuuki Takahashi¹, Hikaru Kida¹, Naoki Suda¹ (1. Hirosaki University)

2:20 PM - 2:40 PM

- [A10-2pm-06] Effect of excluded volume and overlap of dissolved polymers under dilute and crowding conditions on molecular crystallization
 ○Yuuki Hata¹, Xiang Li², Ung-il Chung², Takamasa Sakai² (1. National Defense Medical College, 2. The University of Tokyo)
 2:40 PM - 3:00 PM
- [A10-2pm-07] Second-order phase transition behavior in polymer glass transition
 ○Mitsuru Ishikawa¹, Masayoshi Yagishita¹, Yuya Hiramoto¹, Takayuki Uwada¹ (1. Josai University)
 3:00 PM - 3:20 PM

Room 28

Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B

[A28-2am] 20. Materials Chemistry -Basic and Application-

Chair:Hideo Sawada, Kazu Okumura

9:00 AM - 10:40 AM Room 28 (Online Meeting)

- [A28-2am-01] Coordination-Driven Self-Assembly on Polymer Surfaces for Efficient Synthesis of $[\text{Au}(\text{SPh})]_n$ Coordination Polymer-Based Films
 ○Takaaki Tsuruoka¹, Takashi Ohashi¹, Aude Demessence², Yohei Takashima¹, Kensuke Akamatsu¹ (1. Konan University, 2. Institute of Research on Catalysis and Environment of Lyon)
 9:00 AM - 9:20 AM
- [A28-2am-02] Optical luminescence from protein-directed Au_{-20} clusters upon hard X-ray irradiation
 ○Zuoyue Liu¹, Kyung Oh Jung², Ryo Takahata³, Masanori Sakamoto³, Toshiharu Teranishi³, Mamoru Fujitsuka¹, Guillem Pratx², Yasuko Osakada¹ (1. Osaka University, 2. Stanford University, 3. Kyoto University)
 9:20 AM - 9:40 AM
- [A28-2am-03] Structural Analysis of Silver Nanowires
 ○Yasunao Miyamura¹ (1. Showa Denko K.K.)
 9:40 AM - 10:00 AM
- [A28-2am-04] Characteristics of silicone rubber in the

joint on aluminum-silicone rubber joint
interface by chemical bonding

○DENG XUELIANG¹, JING SANG¹, SUMIO

AISAWA¹, Kastuhito Mori², HIDETOSHI

HIRAHARA¹ (1. Iwate University, 2. Sulfur

Chemical Laboratory Inc.)

10:00 AM - 10:20 AM

[A28-2am-05] Preparation of Paintable Hybrid Polymers

Showing Thermally-Stable White-Light

Emission Based on POSS

○Masayuki Gon¹, Satoru Saitome¹, Kazuo

Tanaka¹, Yoshiki Chujo¹ (1. Graduate School of

Engineering, Kyoto University)

10:20 AM - 10:40 AM

Room 29

Academic Program [Oral B] | 21. Energy and Related Chemistry, Geo and
Space Chemistry | Oral B

[A29-2pm] 21. Energy and Related Chemistry, Geo and Space Chemistry

Chair: Atsushi Wakamiya, Takaya Kubo

1:00 PM - 2:40 PM Room 29 (Online Meeting)

[A29-2pm-01] Unprecedentedly efficient overall water
splitting in acid with anisotropic metal
nanosheets

○DONGSHUANG WU¹, Kohei Kusada¹, Satoru

Yoshioka², Tomokazu Yamamoto², Takaaki

Toriyama², Syo Matsumura², Yanna Chen³,

Okkyun Seo³, Jaemyung Kim³, Chulho Song³,

Satoshi Hiroi³, Osami Sakata³, Toshiaki Ina⁴,

Shogo Kawaguchi⁴, Yoshiki Kubota⁵, Hirokazu

Kobayashi¹, Hiroshi Kitagawa¹ (1. Kyoto

university, 2. Kyushu university, 3. National

Institute for Materials Science, 4. Japan

Synchrotron Radiation Research Institute (JASRI),

SPRING-8, 5. Osaka Prefecture University)

1:00 PM - 1:20 PM

[A29-2pm-02] Silicon Carbide: A Promising Anode
Material to Lookout for Next Generation
Lithium Ion Batteries

○Ravi Nandan¹, Noriyuki Takamori¹, Koichi

Higashimine¹, Rajashekar Badam¹, Noriyoshi

Matsumi¹ (1. Japan Advanced Institute of

Science and Technology)

1:20 PM - 1:40 PM

[A29-2pm-03] Accelerated Lifetime Testing of Perovskite

Solar Cells

○Richard Murdey¹, Yuko Matsushige¹, Yasuhisa

Ishikura¹, Minh Anh Truong¹, Tomoya

Nakamura¹, Atsushi Wakamiya¹ (1. ICR, Kyoto

Univ.)

1:40 PM - 2:00 PM

[A29-2pm-04] Fabrication of High Purity Tin Perovskite
Films Realized by Tin(IV) Scavenging
Method

○Tomoya Nakamura¹, Minh Anh Truong¹,

Shuaifeng Hu¹, Kento Otsuka¹, Ruito

Hashimoto¹, Richard Murdey¹, Takahiro

Sasamori², Hyung Do Kim³, Hideo Ohkita³,

Taketo Handa¹, Yoshihiko Kanemitsu¹, Atsushi

Wakamiya¹ (1. ICR, Kyoto Univ., 2. Graduate

School of Science and Technology, Univ. of

Tsukuba, 3. Graduate School of Engineering,

Kyoto Univ.)

2:00 PM - 2:20 PM

[A29-2pm-05] Effect of ZnO Annealing Condition on the
Performance of PbS Quantum Dot/ZnO
Nanowire Solar Cells

○Haibin Wang¹, Yun XIAO¹, Jotaro NAKAZAKI¹,

Takaya KUBO¹, Hiroshi SEGAWA^{1,2} (1. RCAST,

The Univ. of Tokyo, 2. Grad. Sch. Arts and Sci.

The Univ. of Tokyo)

2:20 PM - 2:40 PM

Room 11

Academic Program [Oral B] | 22. Resources Utilization Chemistry,
Environmental and Green Chemistry | Oral B

[A11-2pm] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Chair: Kazuya Koumoto, Hironori Ogata

1:00 PM - 3:00 PM Room 11 (Online Meeting)

[A11-2pm-01] Structure and solid state properties of
charge-transfer salts using biomass-derived
molecules

○Hironori Ogata¹, Masaru Ide¹, Eiji Masai²,

Yuichiro Otsuka³, Masaya Nakamura³ (1. Hosei

Univ., 2. Nagaoka Univ. of Technol., 3. Forestry

and Forest Products Research Institute)

1:00 PM - 1:20 PM

[A11-2pm-02] Photoreforming of Lignocellulosic Biomass
into Hydrogen Utilizing the Entire Visible
Range of Light in the Presence of

Composite Photocatalyst

○Haruki Nagakawa¹, Morio Nagata¹ (1. Tokyo University of Science)

1:20 PM - 1:40 PM

[A11-2pm-03] Air quality diagnosis in two field studies with different dominant sources, according to radical chemistry and oxidative capacity
○Jiaru Li¹, Nanase Kohno¹, Kentaro Murano¹, Yosuke Sakamoto^{1,2}, Yoshizumi Kajii^{1,2} (1. Graduate School of Global Environmental Studies, Kyoto University, 2. National Institute for Environmental Studies)

1:40 PM - 2:00 PM

[A11-2pm-04] Influence of Support Characteristics of Resin-supported Formate Catalyst to its Activity for CO₂ Reduction with Hydrosilanes
○Ria Ayu Pramudita¹, Yuichi Manaka^{1,2}, Ken Motokura^{1,3} (1. Tokyo Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology, 3. JST PRESTO)

2:00 PM - 2:20 PM

[A11-2pm-05] Suzuki-Miyaura coupling reactions in water using aqueous betaine solutions as the solvent
○Tomoaki Wada¹, Riku Matsumoto¹, Kazuya Koumoto¹ (1. Konan Univ.)

2:20 PM - 2:40 PM

[A11-2pm-06] Extraction of organic compounds using aqueous two-phase system formed by betaines and salts
○Riku Matsumoto¹, Tomoaki Wada¹, Kazuya Koumoto¹ (1. Konan Univ.)

2:40 PM - 3:00 PM

Academic Program [Oral B] | 01. Education and History of Chemistry | Oral B**[A04-2pm] 01. Education and History of Chemistry**

Chair: Kenji Katayama, Shinji Inomata

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 4 (Online Meeting)

[A04-2pm-01] New Development of Microscale Chemistry: International Partnership in Microscale Chemistry○Kazuko Ogino¹ (1. Tohoku University)

1:00 PM - 1:20 PM

[A04-2pm-02] New developments in microscale chemistry experiments

~Report from high school chemistry room~

○Kumiko Kataoka¹ (1. Seisen Junior & Senior High School)

1:20 PM - 1:40 PM

[A04-2pm-03] A Proposal of Simple Mohr Method to Deepen Understanding of Precipitation Titration○Kazuyuki Yamada¹, Kumiko Kataoka² (1. Seishin Gakuen High School · Junior High School, 2. Seison Junior and Senior High School)

1:40 PM - 2:00 PM

[A04-2pm-04] First-year university chemistry experiment in Covid-19 using microscale experiments○Yasunao Kuriyama¹ (1. Yamagata University)

2:00 PM - 2:20 PM

[A04-2pm-05] New Development of Microscale Chemistry: Introduction for the undergraduate education○Kenji Katayama¹, Yuki Konno, Naomi Tsuchiya (1. Chuo University)

2:20 PM - 2:40 PM

[A04-2pm-06] New Developments in Microscale Experiments: Case Study of Experiments Education for University and Teachers' Licenses○Yumiko Takagi¹ (1. Kagawa University)

2:40 PM - 3:00 PM

[A04-2pm-07] Measurement of dissolved oxygen by small scale Winkler's methodSugawara Kazuki¹, Matsuoka Shu¹, ○Hideyuki Sawatari¹ (1. Miyagi university of education)

3:00 PM - 3:20 PM

[A04-2pm-08] Improvement and execution of basic chemical experiment class with considering prevention of COVID-19 at Fukushima University○Shinji Inomata¹, Hiromasa Ikuta¹, Tsugiko Takase¹ (1. Fukushima Univ.)

3:20 PM - 3:40 PM

マイクロスケール実験の新しい展開：国際的な連携を中心として

(東北大理) ○荻野 和子

New Development of Microscale Chemistry: International Partnership in Microscale Chemistry

(Graduate School of Science, Tohoku University) ○Kazuko Ogino

Microscale chemistry (MC; often referred as small-scale chemistry) is a teaching method working with small quantities of chemical substances. There are advantages such as environmental friendliness, shorter reaction times. The International Symposium on Microscale Chemistry (ISMC) started in 2000. Green Chemistry (GC) and Green & Sustainable Chemistry(GSC) is incorporated in the symposia. Thus, MC and GSC education have developed through international cooperation. The 9th ISMC was held in Sendai in 2017 and the 10th in South Africa 2019. International partnership has contributed to the development of chemistry education and education for sustainable development. At present, education at all levels has temporarily shifted to remote learning due to the COVID-19 pandemic, hobbling an integral component of chemistry courses: the laboratory. MC might be useful in some cases. International exchange of experiences and ideas could be useful.

Keywords : Microscale chemistry, International partnership, Green chemistry education, ESD , Covid-19 pandemic

化学の対象である物質は、原子・分子からできている。目に見えない小さな粒子の世界のイメージを描くには、目でみる、さらには自分で実験することが重要である。教育効果、環境への影響等多面的な観点から、化学実験の条件を最適にするとマイクロスケール実験(MC)に行きつく*。

MC は活発な国際連携により発展してきた。グリーンケミストリー教育をも包含して 2000 年以来国際マイクロスケールケミストリーシンポジウム (ISMC) が開催されてきた。2017 年仙台での第 9 回、2019 年南アでの第 10 回を経て、原則として隔年に開催されることとなった。第 11 回 ISMC は、2021 年 7 月に英国で Web 開催予定である。 [Home \(weebly.com\)](https://www.home-weebly.com) 参照

国により化学教育の在り方は異なるが、「化学教育における実験の重要性」、「GC・GSC の理念の導入」が、MC 研究者の共通認識である。

Covid-19 によるパンデミックで、現在我が国をはじめ多くの国の学校教育は、大きな影響を受けている。文科省は「感染のリスクが高い学習活動」として「児童生徒同士が近距離で活動する実験や観察」をあげている。私たちが開発した MC は、器具が安価で小さく、スペースをとらない、試薬も各人に配布するので、参加者は場所を移動することなく実験できる。この特徴を生かすと3密を避けた実験が可能である。実際清泉女学院中学高等学校の片岡久美子教諭は 2020 年 6 月からの授業に取り入れて実験している¹⁾。Covid-19 パンデミックのもとでの化学実験について、国際連携は有用であると考ええる。

*筆者が MC を始めたのは、1988 年の「金属イオンをつかまえる」の実験を 100 人近い小中高校生に実施したときである。イオン交換体のカラム3本とキレート樹脂のカラム2本を使い、クロマトグラフィーで数種の金属イオン混合物をそれぞれ分離する実験を行った。MC の技法により参加者は 20 種ほどの試薬を間違いなく使い分けた。

1) 清泉女学院中学高等学校 片岡久美子教諭からの私信

マイクロスケール実験の新たな展開 ～コロナ禍の高校化学室からの報告～

(清泉女学院中学高等学校) 片岡久美子

New developments in microscale chemistry experiments

~Report from high school chemistry room~

Seisen Junior & Senior High School Kumiko Kataoka

It was not possible to go to school from March 2020 because of COVID-19 infection, but it was possible to go to school from June. However, there were restriction on laboratory use and group work. Since I have been working on microscale chemistry experiments since 2003, I was able to have students conduct experiments at the same time as resuming school. In this report, as a new development of microscale chemistry experiments that have been conducted for many years, I report on the experiments conducted at the time of school reopening in June and their status.

Keywords : Microscale chemistry experiment

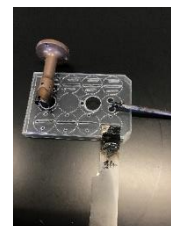
2020年3月2日から全国すべての小学校、中学校、高等学校、特別支援学校で新型コロナウイルス感染拡大のための臨時休校が続いていたが、神奈川県では、5月に神奈川県教育委員会から出された「県立学校の教育活動の再開等に関するガイドライン」に従って、6月からようやく分散登校が可能となった。しかしながら文部科学省から出された「学校における新型コロナウイルス感染症に関する衛生管理マニュアル～「学校の新しい生活様式」～2020.5.22Ver.1により、理科における「児童生徒同士が近距離で活動する実験や観察」には制限があった。筆者は2003年以降ESD (Education for Sustainable Development) 等の観点より¹⁾ マイクロスケール化学実験に取り組んで来た。そのことが思いがけず「学校の新しい生活様式」に対応しており、学校再開と同時に生徒実験を行わせるということができた。これは分散登校によりクラスの人数が半分であったことも大きい、それ以上にマイクロスケール化学実験の持つ新たな可能性を認識できたことが大きかった。本稿では長年行ってきたマイクロスケール化学実験の新たな展開として、6月の学校再開時以降に行った高校2年生対象の生徒実験とその状況について報告する。

新しい生活様式への対応方法	事例
1. マイクロスケール化学実験	・金属のイオン化傾向 ・各種電池 ・各種電気分解 ・銅/鉄イオンの性質
2. 仮想実験	・結晶格子 ・ヘスの法則
3. マイクロスケール化学実験による 実技テスト	・無機物質の定性

写真：少人数での実験を可能にするため、実験道具は急遽手作り
または100均で購入して数を確保した。

1) マイクロスケール化学実験—化学と教育：マイクロスケール
実験の広場から—

(社) 日本化学会 化学教育協議会 日本化学会 関東支部



マイクロスケール実験の新たな展開 沈殿滴定への理解を深める簡易モール法の提案

(清真学園高等学校・中学校¹ 清泉女学院中学高等学校²) ○山田 一幸¹・片岡 久美子²

A Proposal of Simple Mohr Method to Deepen Understanding of Precipitation Titration
(¹Seishin Gakuen High School and Junior High School, ²Seisen Junior and Senior High School)
○Kazuyuki Yamada,¹ Kumiko Kataoka²

As one of the methods for measuring the chloride ion concentration, there is a Mohr method in which an aqueous potassium chromate solution is used as an indicator and titrated with a silver nitrate solution. We will learn about the presence or absence of precipitation due to the difference in solubility product in "Soluble equilibrium and solubility product" in the unit of high school chemistry. Many questions using the Mohr method product have been asked in university entrance examinations in recent years. The word called by "Mohr method" is not mentioned in some textbooks. However, the Mohr method requires the use of brown burette, potassium chromate aqueous solution, and silver nitrate aqueous solution. Therefore, it is difficult to do it in high school.

The authors examined a simple Mohr method based on the idea of a microscale experiment that does not require special equipment and uses as few reagents as possible. As a result, we were able to establish a simple Mohr method in which the precision is the same as the chloride ion concentration obtained by the conventional method, and the amount of reagent can be suppressed to 1/10 or less of the conventional method.

Keywords : *Microscale; Mohr Method; Solubility Product;*

塩化物イオン濃度を測定する方法のひとつとして、クロム酸カリウム水溶液を指示薬として硝酸銀溶液で滴定するモール法がある。高等学校化学の単元で、「溶解平衡と溶解度積」で溶解度積の差による沈殿生成の有無について学習する。近年、モール法を使った問題は大学入試で多く出題されている。しかし、「モール法」という用語は、いくつかの教科書には記載されていない。褐色ビュレット、クロム酸カリウム水溶液、硝酸銀水溶液の使用が必須であるため、高等学校においてモール法の実験を行うことは難しく、多くは実施されていない。

そこで筆者らは特別な器具を必要とせず、また試薬は極力少なくするマイクロスケール実験の考えに基づいて、簡易的に行えるモール法を検討した。その結果、従来の方法によって得られる塩化物イオン濃度と精度が変わらず、また試薬量も従来の 1/10 以下まで抑えることができる簡易的なモール法が確立できた。

表 測定手法の違いによる塩化物イオン濃度の測定結果

測定手法	塩化物イオン濃度(mol/L)
褐色ビュレットを使うモール法	0.0200
マイクロスケール実験に基づく簡易的モール法	0.0199
測定誤差 0.456%	

マイクロスケールを用いたコロナ禍における大学初年次化学実験

(山形大理) ○栗山恭直

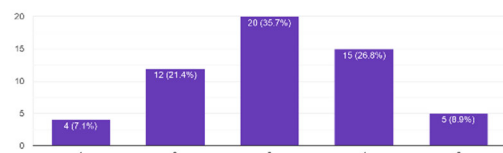
First-year university chemistry experiment in Covid-19 using microscale experiments
(School of Science, Yamagata University) ○Yasunao Kuriyama

We have been promoting microscale experiments and researching how to utilize them. This year, we report that we were able to carry out the experiment without the influence of corona by conducting the synthesis of methyl orange by microscale experiment in the situation where it is difficult to carry out the chemical experiment at the university due to the Covid-19.

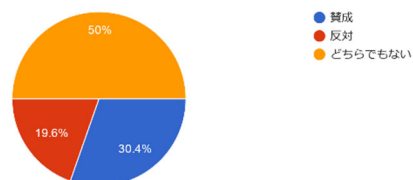
Keywords : *microscale experiments; first year university experiment; methyl orange synthesis; personal experiment;*

我々は、マイクロスケール実験の普及活動を行い¹⁾、その活用方法について研究してきた。今年はコロナ禍で大学での化学実験の実施が難しい状況の中で大学初年次の開講されている理学部学生対象の基礎化学実験でマイクロスケールを行ったので報告する。実験内容は、メチルオレンジの合成をマイクロスケール実験²⁾での個人実験。一人一人で行うことによりコロナの影響なく実験を実施できたので報告する。実験方法はスクリー間に試薬をプチボットの滴瓶より加えていき反応しメチルオレンジを合成する。合成したメチルオレンジを実際に用いて変色域を決定する。さらに身の回りの酸塩基やアルコールなどの未知資料の同定を行う。90分程度で終了する。

メチルオレンジの合成実験について質問します。実験は簡単でしたか。
56件の回答



今回は個人実験でしたが、個人で行う実験についてどう思いますか。
56件の回答



高校での理科選択の関係で難易度はばらつきがあった。今回のコロナの影響での個人実験に関しては、反対意見は2割程度であった。理由としては、他学生との交流を深めるためにも数人で実験するのがよいと考える、お互いに意見交換しながらやってみたかった、1人で実験行う場合、実験結果が変になったときにどこで間違えたかわからないからなどであった。肯定意見では、自分のペースで進めることができるから。個人で行うことにより、実験の予習や、考察をより真剣に行う人が増えると考えたため。コロナウイルスの流行のため、仕方ないと思う。

マイクロスケールでの個人実験の教育効果が高いことがわかった。

1) <http://microscale-exp.csj.jp/index.html> 2) 北海道教育センター研究紀要第23号 (2011) 小原伸彦「マイクロスケール実験によるメチルオレンジの合成」

マイクロスケール実験の新しい展開: 大学学部教育への展開

(中大理工¹) ○片山 建二¹・紺野 祐樹¹・土屋 尚美¹

New Development of Microscale Chemistry: Introduction for the undergraduate education
(¹Department of Applied Chemistry, Chuo University) ○Kenji Katayama,¹ Yuki Konno,¹
Naomi Tsuchiya¹

The concept of “small/micro-scale experiment,” indicates educational experiments for intuitive understanding of the intrinsic principle of chemical processes by visualization using simple equipment. Since less space, cost and chemicals are necessary, it has various advantages over the conventional educational experiments. We have developed series of experiments on chemical engineering and physical chemistry as education experiment series, and introduced in the course of our university. In this presentation, We will introduce various merits by using “small/micro-scale experiment.”

Keywords : Microscale (Smallscale) experiment; Undergraduate education;

マイクロ（スモール）スケール実験とは、少量の化学物質、コンパクトな実験器具を用いて実験を可視化することにより、学生の理解度を向上させる実験科学教育の総称である。小型の実験器具により、個別実験が可能となり、実験を体感しながら理解できる。我々は、マイクロスケール実験のコンセプトを大学学部生の物理化学・化学工学・教養化学実験に導入してきた。本発表では、我々の導入してきた実験及びそのメリットについて紹介する。

教養化学実験においては、陽イオンの定性・滴定・分離・有機合成などの実験操作にマイクロスケール実験の手法を導入し、試薬の90%、廃液の60%の削減に成功した。物理化学実験においては、⁽¹⁾ 気体の仕事・反応熱・凝固点降下・相図・平衡・起電力に関する実験を、化学工学実験においては、⁽²⁾ 流体・伝熱・高圧ガス・吸着・蒸留・ガス吸収・物質拡散の実験をマイクロスケール化することに成功した。マイクロスケールにすることで、個別の実験を可視化して行うことができるため、学生の理解度の向上に役立っている。本稿では、これらの実験の概略と中央大学での取り組みについて紹介する。

1) 栗原彰太・片山建二 化学と教育, 62, 94 (2014).

2) K. Katayama, et al. Chemrxiv, DOI: 0.26434/chemrxiv.9947474.v1

マイクロスケール実験の新しい展開:大学教育及び教員研修の実践

(香川大教育) ○高木 由美子

New Developments in Microscale Experiments: Case Study of Experiments Education for University and Teachers' Licenses (*Faculty of Education, Kagawa University*)
Yumiko Takagi

Microscale experiments have various advantages such as saving reaction and handling time, cutting costs and using reagents, reducing the amount of waste chemicals by setting an appropriate reaction system. Because of it does not use a laboratory and/or expensive equipment, it is a method that can utilize the ingenuity of the teachers and review the concept of the experimental education. We report on the practice the experimenter created and experimented with microscale experimental materials that can be expected to have new educational effects, with the aim of helping to design classroom experiment that the interesting for students to learn science.

Keywords : *Micro Scale Chemistry; Small Scale Chemistry; Teaching Materials*

マイクロスケール実験は、適切な反応系を設定することで、反応時間の短縮、試薬と経費の節約と廃棄物の少量化を図ることができるなど様々な利点がある。また、場所を選ばず、実験のコンセプトそのものをとらえ直すことのできる方法である。廃棄物が少量であるため、有毒物質が発生する場合でも、大気汚染に係る環境基準値以下で実験を行うことが可能であり、使用する水、電気などの容量を最小限に抑えることができることから、実験室設備がないところでも体験型の実験授業機会を確保することができ、また、一人一人が各自の実験器具で実験をすることを設定できるため、災害により実験室設備が整わない時、今回の COVID-19 禍の影響で、3密を避ける、自宅での学習を余儀なくされる場合でも、学習機会を確保することができるなど様々な長所を有している。さらに、一人ひとりが積極的に実験に参加する、指導側が一人ひとりの学習の進捗状況を適切に判断し、フィードバックを行うことができるなどの教育的効果、環境教育、誰一人取り残さない学習機会の確保などにも大きく貢献できることが見込まれる。

マイクロスケール実験の長所を生かし、新たな教育効果を期待できるマイクロスケール実験教材を作成・体験させることで理科への興味・関心を喚起できる授業設計に役立てることをねらいとして行った教育実践について報告する。

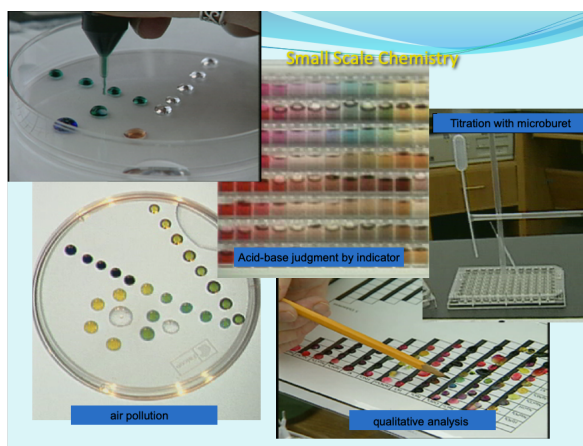


Figure 1 Example of Micro Scale Chemistry

スモールスケールでの Winkler 法による溶存酸素量の測定

(宮城教育大学¹⁾ 菅原 一貴¹・松岡 周¹・○猿渡 英之¹

Measurement of dissolved oxygen by small scale Winkler's method (¹Miyagi University of Education) Sugawara Kazuki,¹ Matsuoka Shu,¹ ○Hideyuki Sawatari¹

Measurement of dissolved oxygen (DO) in environmental water is important because it directly affects the live of organism in water. Recently, DO meter is widely used for DO measurement, but it is expensive and also requires exchange of its sensor due to deterioration. On the other hand, Winkler's method has long been used for DO measurement. In this method, manganese reacts with the oxygen in water and precipitate of manganese compounds is formed. Then, the precipitate is dissolved and determined by iodometric titration. In the conventional Winkler's method, sample water is taken in a glass made "oxygen bottle" and reagents are added to it, but the experimental procedures which requires some skills and occurring of waste containing manganese could be a problem.

Among the reports on the methods for the determination of DO with small amount of water samples, Ibanez *et al.*^{1),2)} utilized a disposable plastic syringe, in which water sample and reagents were introduced. Employing the method, current authors optimized the experimental conditions for better reproducibility and easier operation.

Keywords : *small scale experiment; measurement of dissolved oxygen; Winkler's method*

環境水中の溶存酸素量(dissolved oxygen, DO)は水生生物の生育の可否に直接関わる重要な指標である。DO の測定は溶存酸素計を用いて行われることが現在では多いが、高価である上にセンサー部の劣化による交換も要する。一方、古くから行われてきた方法として Winkler 法がある。これは、溶存酸素をマンガンと反応させて沈殿を生成し、それを溶解してヨウ化物イオンと反応させチオ硫酸ナトリウムで滴定する方法である。通常は 100 mL 程度の試料水を「酸素びん」と呼ばれる容器に採取し、そこに試薬を添加して沈殿の生成や溶解を行うが、操作に少々熟練を要し、またマンガンを含む廃液が多く発生することが課題である。

少量の試料による溶存酸素量測定法はいくつか報告されているが、Ibanez ら^{1),2)}はプラスチック製のディスポーザブルシリンジに試料水と試薬を吸い上げて反応させる方法を報告している。演者らはこれを用いて、再現性の良い値が容易な操作で得られるような実験方法の検討を行っており、その結果について報告する。

1) J. G. Ibanez, M. Hernandez-Esparza, C. Doria-Serrano, A. Fregoso-Infante, M. M .Singh, *Environmental Chemistry: Microscale Laboratory Experiments*. Springer, New York. (2008).

2) J. G. Ibanez(栗山恭直 訳), 水中の溶存酸素濃度を低価格で測定するマイクロスケール実験 溶存酸素の測定, 第9回国際マイクロスケール実験シンポジウム・マイクロスケールケミストリー第4回シンポジウムーグリーン化学実験ー論文・マニュアル集 (2017)

新型コロナウイルス感染症予防に配慮した化学実験授業の改良と実施について

(福島大共生システム理工) ○猪俣慎二・生田博将・高瀬つぎ子

Improvement and execution of basic chemical experiment class with considering prevention of COVID-19 at Fukushima Univ. (*Faculty of Symbiotic System Science, Fukushima University*)
○Shinji Inomata, Hiromasa Ikuta, Tsugiko Takase.

Basic chemical experiment class for our second-year college students was improved to prevent COVID-19 and then was implemented. One of the important changes was that the original one class divided to three classes and each class used individual experimental room. This distributed arrangement makes it easy to keep social distancing. Microscale experiments was introduced for qualitative analysis of some metal ions. This method was also effective for the prevention because each student uses a personal experimental set by him- or herself. We will also mention effective placement of teaching assistants and ingenuity for experiments that need to be carried out in pairs.

Keywords : *Microscale Chemistry; COVID-19; Chemical Experiment Class*

新型コロナウイルス感染症の予防のため、福島大学の前期授業のほとんどが対面授業ではなく、遠隔授業となった。共生システム理工学類の2年次学生が受講する化学実験Ⅰは一時的に延期となり、その後、夏休み期間中に集中講義形式(連続5日間、13時から18時)で行うことになった。通常なら週間授業15回(13時から18時)を実施すべきところであるので、大幅な時間の短縮を余儀なくされた。このため実施方法や実験テーマについて検討し、次のように対応した。まず、実施場所として通常使用する化学実験室(定員約90名)に加え、物理実験室(定員約90名)と生物学実験室(定員約60名)を借用し、履修者44名をほぼ3等分に振り分けた。これにより、実験台1台につき1人または2人での実験が可能となり、いわゆる3密をさけることができた。また、実験室入室時にはアルコールによる手指消毒を徹底させ、ゴーグル、マスクを着用させた。次に、授業時間が1/3に減少することから、実験内容について精査した。例えば、金属イオンの定性分析と系統分離に関する実験(5回分)はマイクロスケール実験で行うことで1回分とした。これにより系統分離は実施できなくなかったが、調べる金属イオンの種類が5種類(Fe^{3+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , Mg^{2+})から9種類($\text{Fe}^{2+/3+}$, Pb^{2+} , Cu^{2+} , Zn^{2+} , Ag^{+} , Ca^{2+} , Sr^{2+} , Ba^{2+})に増やすことができた。また、実験セットは試薬をつめた点眼ビンセットとセルカルチャープレート(24 ウエル)1枚、キムワイプ1箱、イオン交換水を入れた500 mL 洗淨びんで構成されており、本セットを学生1人ごとに配布して、1実験台で実施したので、感染予防に対しても効果的であったと思われる。この他、2人一組で実施する滴定実験や有機定性の分析実施方法、ティーチングアシスタントの配置等にもふれる。

[A02-2pm] 02. Theoretical Chemistry, Chemoinformatics, and Computational Chemistry

Chair: Mitutaka Okumura, Ryohei Kishi

Sat. Mar 20, 2021 1:00 PM - 2:40 PM Room 2 (Online Meeting)

[A02-2pm-01] Theoretical study on the spin-unrestricted CC2 calculations of optical response properties of open-shell singlet molecules

○Ryohei Kishi^{1,2}, Masako Yokoyama¹, Wataru Yoshida¹, Yosuke Shimizu¹, Masato Ikeuchi¹, Jinki Shoda¹, Masayoshi Nakano^{1,2,3} (1. Grad. Sch. Eng. Sci., Osaka Univ., 2. QIQB, Osaka Univ., 3. CERN, Osaka Univ.)

1:00 PM - 1:20 PM

[A02-2pm-02] Automatic fragmentation in the divide and conquer quantum chemical calculations with the energy error estimation

○Toshikazu Fujimori¹, Masato Kobayashi^{2,3,4}, Tetsuya Taketsugu^{2,3,4} (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University, 3. WPI-ICReDD, Hokkaido University, 4. ESICB, Kyoto University)

1:20 PM - 1:40 PM

[A02-2pm-03] Reaction-network-based analysis and prediction on the coordination self-assembly of Pd₃L₆ double-walled triangle

○Satoshi Takahashi¹, Tomoki Tateishi¹, Yuya Sasaki¹, Hirofumi Sato^{2,3,4}, Shuichi Hiraoka¹ (1. Graduate School of Arts and Sciences, The Univ. of Tokyo, 2. Department of Molecular Engineering, Kyoto Univ., 3. ESICB, Kyoto Univ., 4. Fukui Institute for Fundamental Chemistry, Kyoto Univ.)

1:40 PM - 2:00 PM

[A02-2pm-04] Extrapolating molecular properties using machine learning models trained with small-size experimental databases

○Kan Hatakeyama-Sato¹, Kenichi Oyaizu¹ (1. Waseda Univ.)

2:00 PM - 2:20 PM

[A02-2pm-05] Orbital Correlation Diagram for Understanding Surface Reactions

○Yuta Tsuji¹, Kazunari Yoshizawa¹ (1. Kyushu Univ.)

2:20 PM - 2:40 PM

スピン非制限 CC2 法による一重項開殻分子系の光応答物性計算についての理論研究

(阪大院基礎工¹・阪大基礎工²・阪大 QIQB³・阪大 CSRN⁴) ○岸 亮平^{1,3}・横山 麻紗子¹・吉田 航¹・清水 陽介¹・池内 雅登²・正田 迅己²・中野 雅由^{1,3,4}

Theoretical Study on the Spin-Unrestricted CC2 Calculations of Optical Response Properties of Open-Shell Singlet Molecules (¹Graduate School of Engineering Science, Osaka University, ²School of Engineering Science, Osaka University, ³QIQB, Osaka University, ⁴CSRN, Osaka University) Ryohei Kishi^{1,3}, Masako Yokoyama¹, Wataru Yoshida¹, Yosuke Shimizu¹, Masato Ikeuchi², Jinki Shoda², Masayoshi Nakano^{1,3,4}

Recently, open-shell molecules have attracted attention as novel optical functional materials. Generally, it is difficult to apply the spin-unrestricted (U)CCSD/CCSD(T) methods to the calculations of optical response properties of medium-/large-sized open-shell molecules, whereas applicability of DFT method to the problem has not been sufficiently clarified. In this study, we examine applicability of the UCC2 method, which is known as an approximation of UCCSD method, to the calculations of optical response properties of open-shell molecules.

Keywords: Open-Shell Molecules; Spin-Unrestricted CC2 Method; Optical Response Properties; (Hyper)Polarizability

近年、一重項開殻分子のジラジカル因子 (y) に基づく新奇光機能分子の設計に注目が集まっている。これらの系の合成・単離は未だ容易ではなく、理論・計算による物性予測や機構解明が不可欠である。しかし、機能発現が期待される大きなサイズの開殻分子系に対しては、高精度 *ab initio* 電子相関法である UCCSD/UCCSD(T)法の適用は困難であり、また各種 DFT 法の適用限界も十分調べられていない部分が多い。本研究では、UCCSD 法に対する近似である UCC2 法の開殻分子系の三次非線形光学物性計算への適用をもとに、中程度のサイズの系における各手法の適用性について比較検討した。まず、以前の研究で静的第二超分極率 (γ) の y 依存性について検討した、*p*-quinodimethane (*p*QM, Fig. 1a) の環外 C-C 結合を伸長させたモデル¹⁾で比較を行った。UCC2 レベルでの全エネルギーは CFOUR v2.1²⁾を用いて計算し、有限場法により静的 γ を算出した。Fig. 1b に各計算法の静的 γ の y (PUHF レベルで算出) 依存性を示す。これより、 y の小さな領域では絶対値で 2 倍程度の差が見られるものの、UCCSD/UCCSD(T)法で得られた y の中間領域でピークを持ちその後減少する傾向は¹⁾、UCC2 法でも再現されることがわかった。発表では、*p*QM 分子での比較の詳細や、より大きなサイズの開殻分子系における適用性についても議論する。

まず、以前の研究で静的第二超分極率 (γ) の y 依存性について検討した、*p*-quinodimethane (*p*QM, Fig. 1a) の環外 C-C 結合を伸長させたモデル¹⁾で比較を行った。UCC2 レベルでの全エネルギーは CFOUR v2.1²⁾を用いて計算し、有限場法により静的 γ を算出した。Fig. 1b に各計算法の静的 γ の y (PUHF レベルで算出) 依存性を示す。これより、 y の小さな領域では絶対値で 2 倍程度の差が見られるものの、UCCSD/UCCSD(T)法で得られた y の中間領域でピークを持ちその後減少する傾向は¹⁾、UCC2 法でも再現されることがわかった。発表では、*p*QM 分子での比較の詳細や、より大きなサイズの開殻分子系における適用性についても議論する。

1) Nakano M. et al., *J. Phys. Chem. A*, **2005**, 109, 885.

2) Matthews D. A. et al., *J. Chem. Phys.*, **2020**, 152, 214108.

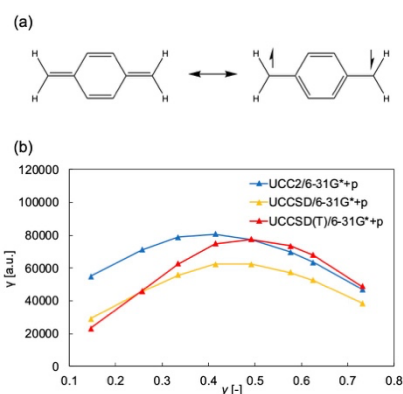


Fig. 1. *p*QM 分子 (a), 静的 γ の y 依存性 (b).

Automatic fragmentation in the divide and conquer quantum chemical calculations with the energy error estimation

(¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, ²Faculty of Science, Hokkaido University, ³WPI-ICReDD, Hokkaido University, ⁴ESICB, Kyoto University) ○Toshikazu Fujimori,¹ Masato Kobayashi,^{2,3,4} Tetsuya Taketsugu^{2,3,4}

Keywords: Hartree-Fock (HF) calculation; Second-order Møller-Plesset (MP2) calculation; Linear-scaling electronic structure calculation

Many fragmentation-based electronic structure methods such as the divide-and-conquer (DC) method¹ have been developed to reduce the computational time for calculations of large-scale systems. However, these methods result in introducing the energy errors associated with the fragmentation. In addition, most of these methods use parameters other than energy in the control of the energy errors. In this study, we report automatic error control schemes in the DC-HF and DC-MP2 calculations with the estimation of the energy variation associated with the fragment change, which is controlled with the buffer region in case of the DC method.

In the DC-HF calculation, we introduce the two-layered buffer region for each disjoint fragment (central region). The energy variation by transferring each atom in the outer buffer region into the inner buffer region can be estimated by means of the subsystem density matrix.² As for the DC-MP2 calculation, we derived the upper bound of the electron correlation energy contribution for each atom in the buffer regions based on the atomic orbital Laplace MP2 method and Schwarz inequality.³ With these estimated energy as the criterion, the appropriate buffer region can be automatically determined for each of the DC-HF and DC-MP2 methods.

The automated DC-MP2 calculation was performed for 100 water molecules (Table). From the average fragment size, the present method can effectively aid the selection of the appropriate buffer region for each subsystem in the DC-HF and DC-MP2 calculations. Consequently, the energy error was almost constant in any initial conditions.

Table. Initial DC-HF buffer-size (r_b^{in} and r_b^{out}) dependence of the automated DC-MP2 correlation energy ($E_{\text{corr}}^{(2)}$) and the major axis radius ($\langle I_{\text{HF}}^{\alpha} \rangle$ and $\langle I_{\text{corr}}^{\alpha} \rangle$) for 100 water cluster system.

$r_b^{\text{in}}/\text{\AA}$	$r_b^{\text{out}}/\text{\AA}$	$E_{\text{HF}}/E_{\text{h}}$	$E_{\text{corr}}^{(2)}/E_{\text{h}}$	(Diff.)/ $\mu E_{\text{h}} \text{ atom}^{-1}$	$\langle I_{\text{HF}}^{\alpha} \rangle/\text{\AA}$	$\langle I_{\text{corr}}^{\alpha} \rangle/\text{\AA}$
3.5	4.5	-7601.504443	-19.105142	(+8.37)	7.233	6.564
4.0	5.0	-7601.504613	-19.105141	(+8.37)	7.238	6.538
4.5	5.5	-7601.504342	-19.105031	(+8.74)	7.161	6.522
5.0	6.0	-7601.504417	-19.105000	(+8.84)	7.161	6.480
5.5	6.5	-7601.504467	-19.105185	(+8.23)	7.000	6.427
Standard MP2		-7601.504673	-19.107652			

1) M. Kobayashi *et al.*, *J. Chem. Phys.* **2007**, 127, 074103. 2) M. Kobayashi, T. Fujimori, T. Taketsugu, *J. Comput. Chem.* **2018**, 39, 909. 3) T. Fujimori *et al.*, ChemRxiv 13064225.v1.

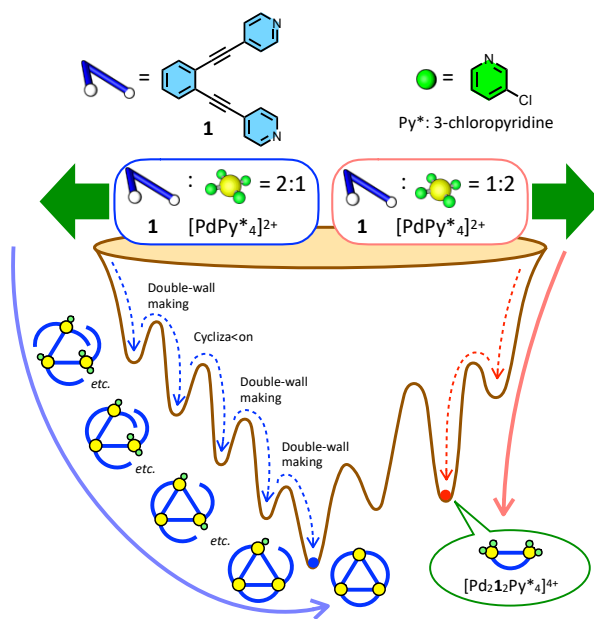
Reaction-network-based analysis and prediction on the coordination self-assembly of Pd₃L₆ double-walled triangle

(¹Department of Basic Science, The University of Tokyo, Japan, ²Department of Molecular Engineering, Kyoto University, Japan, ³ESICB, Kyoto University, Japan, ⁴Fukui Institute for Fundamental Chemistry, Kyoto University, Japan)

○Satoshi Takahashi,¹ Tomoki Tateishi,¹ Yuya Sasaki,¹ Hirofumi Sato,^{2,3,4} Shuichi Hiraoka¹

Keywords: Molecular self-assembly; Chemical master equation; Kinetic control

The self-assembly process of the [Pd₃**1**₆]⁶⁺ double-walled triangle (DWT)¹ was analyzed by our developed numerical analysis of self-assembly system (NASAP), which has already succeeded in obtaining detailed information of several coordination self-assemblies²⁻⁶. The self-assembly of the DWT, which takes place in a complicated reaction network consisting of multiple inter- and intramolecular reactions (oligomerization, cyclization, and double-wall making), is a good example not only to reveal general principles underlying complicated molecular self-assembly but also to demonstrate the power of numerical simulation to predict a suitable reaction condition under which a new molecular self-assembly is produced under kinetic control. The reaction network for the DWT composed of 161 chemical species that are connected by total 896 elementary reactions classified into 9 types of reversible reactions was established by the numerical search of 18-dimensional parameter space so that the time-development of the species would reproduce the corresponding experimental data obtained by quantitative analysis of self-assembly system (QASAP)⁷. NASAP led to the dominant reaction pathways, which are determined by the balance between inter- and intramolecular reactions. Besides, the numerical simulation predicted the formation of [Pd₂**1**₂Py*₄]⁴⁺ as a major product (#%) from **1** and [PdPy*₄]²⁺ in a 1:2 ratio under kinetic control, which was consistent with the experimental result (#%).



1) S. Takahashi *et al.*, *Phys. Chem. Chem. Phys.* **2020**, 22, 26614. 2) Y. Matsumura *et al.*, *Phys. Chem. Chem. Phys.* **2017**, 19, 20338. 3) S. Takahashi *et al.*, *Phys. Chem. Chem. Phys.* **2019**, 21, 6341. 4) S. Komine *et al.*, *J. Am. Chem. Soc.* **2019**, 141, 3178. 5) L. H. Foianesi-Takeshige *et al.*, *Commun. Chem.* **2019**, 2, 128. 6) T. Tateishi *et al.*, *J. Am. Chem. Soc.* **2019**, 141, 19669. 7) Reviews: a) S. Hiraoka, *Bull. Chem. Soc. Jpn.* **2018**, 91, 957. b) S. Hiraoka, *Isr. J. Chem.* **2019**, 59, 151. c) S. Hiraoka *et al.*, *Chem. Rec.* **2021**, 21, DOI: 10.1002/tcr.202000124.

小規模な実験データベースの機械学習に基づく有機分子の物性の外挿予測モデルの構築

(早大理工) ○畠山 歓・小柳津 研一

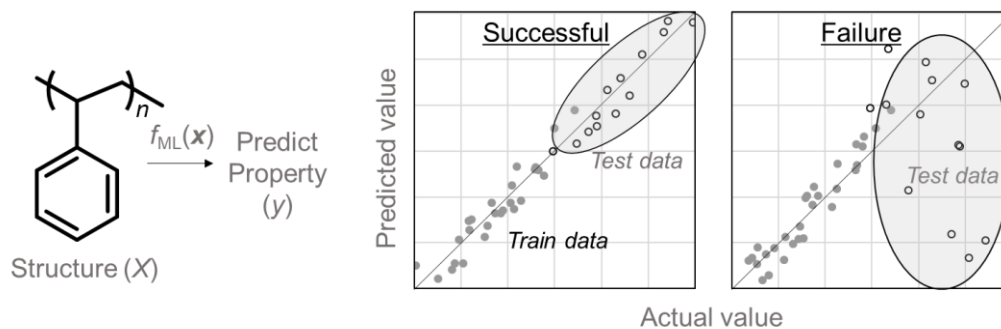
Extrapolating molecular properties using machine learning models trained with small-size experimental databases (*Department of Applied Chemistry, Waseda University*) ○Kan Hatakeyama-Sato, Kenichi Oyaizu

Materials informatics enables the estimation of material properties from their structures using machine learning models. Still, the prediction has been difficult, especially when small databases with missing data are used and when so-called extrapolation is pursued. Here, we introduce imputation techniques to cope with the issues. The demands of descriptors and models for the prediction will also be discussed in the presentation.

Keywords : *Materials Informatics, Organic Functional Materials, Machine Learning*

マテリアル・インフォマティクスの方法論の発展により、機械学習関数 f_{ML} をもとに材料構造(x)から所望の物性 y を予測する手法が開発されつつある^{1,2}。一方で未解決の課題として、主に実測データベースを扱う際の 1)学習データの件数不足、2)欠損値への対処や、予測したい物性が訓練データの範囲外にある 3)外挿予測時の精度低下などが残っている。

本報告では代入法(imputation)を回帰問題に応用し、小規模な実験データベース条件下での予測精度の改善を試みた。密度や分解温度等の物性値を予測するタスクにおいて、異なる物性データベースを統合し、更に欠損値を機械学習モデルで代入しながら回帰することで、多くの物性(>70%)で予測性能を上げられることが分かった。当日は内挿・外挿予測の為の学習モデルや記述子の選定法等についても、併せて議論する。



1 R. Ramprasad, R. Batra, G. Pilania, A. Mannodi-Kanakkithodi, C. Kim, *Npj Comput. Mater.* **2017**, 3, 54.

2 K. Hatakeyama-Sato, K. Oyaizu, *Commun. Mater.* **2020**, 1, article number: 49.

Orbital Correlation Diagram for Understanding Surface Reactions

(Institute for Materials Chemistry and Engineering, Kyushu University) ○ Yuta Tsuji, Kazunari Yoshizawa

Keywords: Band Calculations; Methane; C-H Bond Activation; Metal Oxides; Transition State

In this talk, an orbital correlation diagram is proposed for the purpose of understanding and predicting a surface reaction. To deal with the electronic structure of a surface, one may need to rely on a cluster model or a surface slab model. Band (crystal) orbitals calculated at the Γ point in the reciprocal space for the unit cell of the slab model with periodicity are found helpful for the construction of the correlation diagram. By using the diagram thus established, the C–H bond activation reaction of methane on an IrO_2 surface is investigated. The energy level of the d_{z^2} orbital of a coordinatively unsaturated Ir atom in the surface is found to be important for determining the activation barrier of the reaction. The activation energy can be reduced by lowering the energy level of the d_{z^2} orbital. Conversely, a rise in the energy of the d_{z^2} orbital leads to an increase in the activation barrier. To make the d_{z^2} orbital energy change, the concept of mixed-anion compounds is adopted. The replacement of an oxide with a different anion allows one to tune the crystal field splitting of metal oxides. IrO_2 doped with F as an axial ligand yields a lower-lying d_{z^2} orbital level, while the orbital goes up in energy when IrO_2 is doped with N. This trend is consistent with what is expected from the electronegativity of each dopant. A perfect inverse linear correlation is found between the activation energy of the reaction and the electronegativity as shown in Figure 1. By changing the dopant, one may have control over the reactivity of IrO_2 .¹⁾

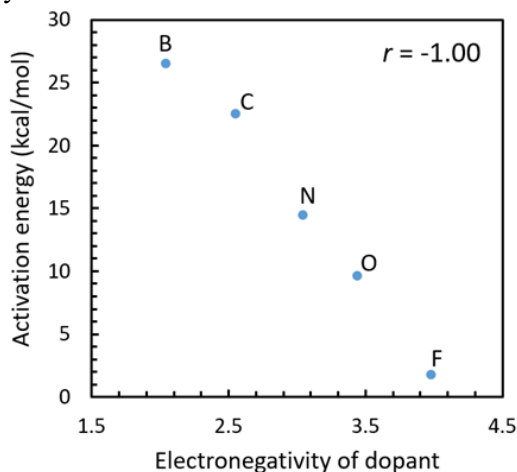


Figure 1. The activation energy of C–H bond dissociation of methane on doped IrO_2 is plotted as a function of the electronegativity of the dopant (Pauling's scale). r denotes the Pearson's correlation coefficient. O corresponds to the undoped system.

1) Tsuji, Y.; Yoshizawa, K. *J. Phys. Chem. C* **2020**, *124*, 17058.

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

[A04-2am] 04. Physical Chemistry -Properties-

Chair: Tomoyuki Mochida, Taku Iiyama

Sat. Mar 20, 2021 9:00 AM - 10:20 AM Room 4 (Online Meeting)

[A04-2am-01] Structure of ion solvation and association and solvent water in an aqueous magnesium chloride solution under the gigapascal pressure range

○Toshio Yamaguchi¹, Nami Fukuyama¹, Koji Yoshida¹, Yoshinori Katayama² (1. Fukuoka University, 2. Synchrotron Radiation Research Center)

9:00 AM - 9:20 AM

[A04-2am-02] Molecular Dynamics Analysis of Hydration Properties inside the Nanochannels of Self-Assembled Ionic Liquid Crystals

○Yoshiki Ishii¹, Nobuyuki Matubayasi², Go Watanabe³, Yoshihisa Harada⁴, Takashi Kato⁴, Hitoshi Washizu¹ (1. Univ. of Hyogo, 2. Osaka Univ., 3. Kitasato Univ., 4. The Univ. of Tokyo)

9:20 AM - 9:40 AM

[A04-2am-03] Ionogels containing ruthenium-complexes and exhibiting ionic conductivity changes by application of external stimuli

○Ryo Sumitani¹, Tomoyuki Mochida^{1,2} (1. Graduate School of Science, Kobe University, 2. Research Center for Membrane and Film Technology)

9:40 AM - 10:00 AM

[A04-2am-04] Possibility of *ab initio* effective fragment potential molecular dynamics simulations for predicting thermodynamic properties of the functional liquid materials

○Nahoko KUROKI¹, Hiroto Mori^{1,2} (1. Chuo Univ., 2. IMS)

10:00 AM - 10:20 AM

Structure of Ion Solvation and Association and Solvent Water in an Aqueous Magnesium Chloride Solution under the Gigapascal Pressure Range

(¹*Faculty of Science, Fukuoka University*, ²*Synchrotron Radiation Research Center, National Institutes for Quantum and Radiological Science*) ○Toshio Yamaguchi,¹ Nami Fukuyama,¹ Koji Yoshida,¹ Yoshinori Katayama²

Keywords: Ion Solvation; Ion Association; Water; High Pressure; X-ray Diffraction

Ion solvation and water structure under high pressure at the molecular level are essential issues in various scientific topics, such as the geological processes in the Earth's upper mantle, pressure-induced protein denaturation in chemical biology and biotechnology, and salty ice formation in planetary science. So far, we have reported the structure of pure water,¹ aqueous sodium chloride² and calcium chloride³ solutions in the gigapascal (GPa) pressure range by X-ray and neutron diffraction combined with empirical potential structure refinement (EPSR) modeling.

Here, we present the structure of a 2 *m* (=mol/kg) magnesium chloride aqueous solution at 1 GPa/300 K, 1 GPa/500 K, 2 GPa/500K, and 3.8 GPa/500 K, as well as at an ambient condition, determined by synchrotron X-ray diffraction measurements combined with EPSR modeling. When the solution is pressurized to the GPa pressure range, the ice-like hydrogen-bonded water network at 300 K/0.1 MPa is drastically perturbed to give rise to a simple liquid-like water molecules arrangement of a mean coordination number of 13. Interestingly, the first-neighbor tetrahedral moiety of solvent water is maintained even in the GPa pressure range, but the second and outer shells are collapsed. The mean coordination number of the chloride ion increases from around eight at 0.1 MPa to about 17 at 3.8 GPa, accompanied by the evolution of the extended solvation shells. On the other hand, the magnesium ion has a mean coordination number of five water molecules and does not change significantly with pressure. The mean coordination number of the contact ion-pairs between the magnesium and chloride ions varies within the range of 0.3 and 0.9, dependent on pressure and temperature.

1) T. Yamaguchi, K. Fujimura, K. Uchi, K. Yoshida, Y. Katayama, *J. Mol. Liq.* **2012**, 176, 44. 2) T. Yamaguchi, N. Fukuyama, K. Yoshida, Y. Katayama, *J. Phys. Chem. Lett.* **2021**, 12, 250. 3) T. Yamaguchi, M. Nishino, K. Yoshida, M. Takumi, K. Nagata, T. Hattori, *Eur. J. Inorg. Chem.* **2019**, 1170.

自己組織化イオン液晶のナノチャネルにおける水和様態の分子動力学解析

(兵庫県大院シミュ¹・阪大院基礎工²・北里大理³・東大物性研⁴・東大院工⁵)
 ○石井 良樹¹・松林 伸幸²・渡辺 豪³・原田 慈久⁴・加藤 隆史⁵・鷺津 仁志¹
 Molecular Dynamics Analysis of Hydration Properties inside the Nanochannels of Self-Assembled Ionic Liquid Crystals (¹*Graduate School of Simulation Studies, University of Hyogo*, ²*Graduate School of Engineering Science, Osaka University*, ³*School of Science, Kitasato University*, ⁴*The Institute for Solid State Physics, The University of Tokyo*, ⁵*School of Engineering, The University of Tokyo*) ○Yoshiki Ishii,¹ Nobuyuki Matubayasi,² Go Watanabe,³ Yoshihisa Harada,⁴ Takashi Kato,⁵ Hitoshi Washizu¹

Self-assembled ionic liquid crystals can transport water and ions via the hydrophilic nanochannels, and these materials are promising candidates as water-treatment membranes. In this study, we investigated structural and transport properties of water molecules confined in the nanochannels of self-assembled ionic liquid crystals via all-atom molecular dynamics (MD) simulation. The molecular models of ionic liquid crystals were prepared with the self-consistent modeling scheme combining MD and density functional theory. In the self-assembled ionic liquids observed by the MD simulation, water molecules are stabilized by forming the hydration shell of hydrogen-bonding network. In the nanoconfined environment, we found that the entropic effect of solvation free energy plays an important role for the water transport, and furthermore, the anisotropic diffusion of water molecules can be observed with an increase of the water concentration.

Keywords : *Molecular Dynamics; Ionic Liquid Crystals; Self Assembly; Nanochannels; Hydration*

自己組織化イオン液晶は、親水性の官能基が形成するナノチャネルを用いて、水やイオンを輸送することができることから、水処理膜への応用が期待されている¹⁻³⁾。そこで本研究では、全原子分子動力学 (MD) 計算を用いて、自己組織化イオン液晶のナノチャネルがもつ水和構造と水分子の輸送特性を調べた。イオン液晶の分子モデルは、MD 法と密度汎関数法を組み合わせた self-consistent scheme⁴⁾を用いて構築した。その全原子モデルを用いた MD 計算から、ナノチャネル内では水分子は水素結合ネットワークによる水和圏を形成することで安定化し、エントロピー的な振る舞いが重要な役割を示すこと、また水の濃度上昇によって水分子の異方的な拡散機構が誘起されることを明らかにした⁵⁾。

- 1) T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno, M. Funahashi, *Nat. Rev. Mater.* **2017**, 2, 17001.
- 2) M. Henmi, K. Nakatsuji, T. Ichikawa, H. Tomioka, T. Sakamoto, M. Yoshio, T. Kato, *Adv. Mater.* **2012**, 24, 2238.
- 3) T. Sakamoto, T. Ogawa, H. Nada, K. Nakatsuji, M. Mitani, B. Soberats, K. Kawata, M. Yoshio, H. Tomioka, T. Sasaki, M. Kimura, M. Henmi, T. Kato, *Adv. Sci.* **2018**, 5, 1700405.
- 4) Y. Ishii, N. Matubayasi, *J. Chem. Theory Comput.* **2020**, 16, 651.
- 5) Y. Ishii, N. Matubayasi, G. Watanabe, T. Kato, H. Washizu, *submitted*.

Ionogels Containing Ruthenium-Complexes and Exhibiting Ionic Conductivity Changes by Application of External Stimuli

(Graduate School of Science, Kobe University) ○Ryo Sumitani, Tomoyuki Mochida

Keywords: Ionic liquids; Ruthenium complexes; Photochemical reaction; Gels; Ionic conductivity

We have synthesized photoreactive ionic liquids (ILs) containing sandwich-type Ru complexes. IL **1** reversibly transforms into a coordination polymer upon UV photoirradiation and heating (**Fig. 1a**).¹⁾ Based on this mechanism, reversible control of ionic conductivity and viscoelasticity by light and heat treatments were realized.²⁻⁴⁾

In this study, to develop ionogels that exhibit changes in their physical properties through the application of external stimuli, we synthesized ionogels comprised of Ru-containing ILs and low molecular weight gelators (**Fig. 1b**). Addition of gelator **A** or **B** (5 wt%) to IL **1** produced ionogels **1A** and **1B**, which were pale yellow soft gels. The ionic conductivity of ionogel **1A** was $2.7 \times 10^{-6} \text{ S cm}^{-1}$, which was one order of magnitude lower than that of IL **1**. The ionogel formed an orange solid coordination polymer upon UV photoirradiation, the ionic conductivity decreased by two orders of magnitude and the elastic modulus increased by one order of magnitude. The solid returned to the original ionogel upon heating. These photochemical and thermal reactions were reversible. On the other hand, ionogel **1B** exhibited a similar photochemical reaction, but the photoproduct turned into a pale yellow liquid upon heating, not returning to the gel, owing to the coordination of the gelator to the Ru center.

We also prepared ionogel **2A**, comprised of IL **2** and gelator **A** (**Fig. 1c**). The gel reversibly formed oligomers by light and heat treatments. The photoreaction rate was much faster than that of ionogel **1A**.

We thank Prof. M. Yamanaka (Meiji pharmaceutical university) for providing gelator **B**.

1) Y. Funasako, S. Mori, T. Mochida, *Chem. Commun.*, **52**, 6277 (2016). 2) R. Sumitani, H. Yoshikawa, T. Mochida, *Chem. Commun.*, **56**, 6189 (2020). 3) R. Sumitani, T. Mochida, *Macromolecules*, **53**, 6968 (2020). 4) R. Sumitani, T. Mochida, *Soft Matter*, **16**, 9946 (2020).

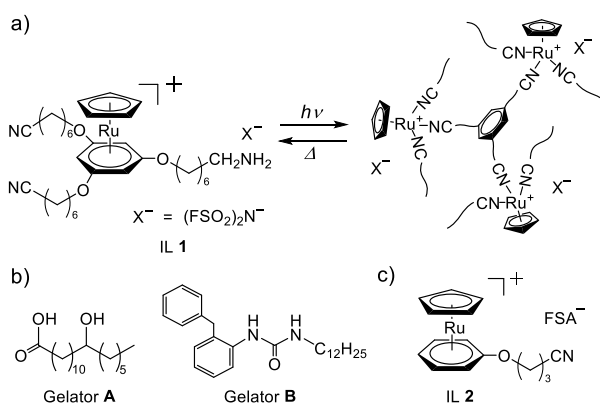


Fig. 1. (a) Reversible transformation between IL and coordination polymer by the application of light and heat. Structural formulae of the (b) gelators and (c) IL **2** used in this study.

Possibility of *Ab Initio* Effective Fragment Potential Molecular Dynamics Simulations for Predicting Thermodynamic Properties of the Functional Liquid Materials

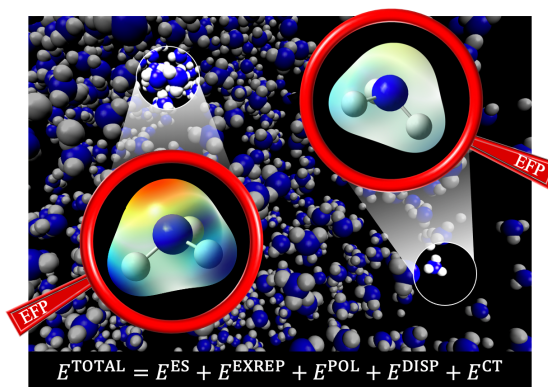
(¹Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, ²JST ACT-X, ³Department of Theoretical and Computational Molecular Science, Institute for Molecular Science) ○Nahoko Kuroki,^{1,2} Hirotooshi Mori^{1,3}

Keywords: Functional Liquid Materials; *Ab Initio* Molecular Dynamics; Effective Fragment Potential; Intermolecular Interaction

For designing optimal solvents for chemical engineering processes such as fluid transportation, separation extraction, and gas absorption, it is mandatory to predict the thermodynamic properties of the candidate solvents by *ab initio* molecular simulations. However, the computational costs of the *ab initio* molecular simulations are too high to make practical applications within enough short time. In the field of chemical engineering, it has been forced to perform non-efficient experimental tasks including try and error.

With the background, in recent years, we have developed a novel molecular simulation method based on fragment-based molecular theory (Effective Fragment Potential Molecular Dynamics; EFP-MD), which is promising for *ab initio* prediction of thermodynamic properties of functional liquid materials.¹⁻³ In the EFP theory, which was originally developed by Day *et al.*,^{4,5} macroscopic thermodynamic properties of the functional liquids are expanded by a set of compact wave functions of the component "Fragment" molecules. We have shown that liquid structures, excess functions, and diffusion constants of functional liquid materials (ionic liquids, mixed solvents, and supercritical fluids) can be at least qualitatively well described by our EFP-MD simulations. We have also succeeded in predicting equilibrium thermodynamic properties of the functional liquids by combining the fragment-based molecular theory with machine learning techniques.

In this talk, we'll show the way to screen functional liquid materials with enough prediction speed and chemical accuracy. The corresponding experimental validations with small costs will be also presented.



1) N. Kuroki, H. Mori, *Chem. Lett.* **2016**, 45, 1009. 2) N. Kuroki, H. Mori, *Chem. Phys. Lett.* **2018**, 694, 82. 3) N. Kuroki, H. Mori, *J. Phys. Chem. B* **2019**, 123, 194. 4) P. N. Day, *et al. J. Chem. Phys.* **1996**, 105, 1968. 5) M. S. Gordon, *et al. Chem. Rev.* **2012**, 112, 632.

[A03-2am] 04. Physical Chemistry -Properties-

Chair: Ken Onda, Takuya Okamoto

Sat. Mar 20, 2021 9:00 AM - 11:20 AM Room 3 (Online Meeting)

[A03-2am-01] Theoretical study on singlet fission dynamics of symmetric hetero linear pentacene tetramer models

○Masayoshi Nakano^{1,2,3}, Hajime Miyamoto¹, Kazuaki Tokuyama¹ (1. Graduate School of Engineering Science, Osaka University, 2. Center for Spintronics Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

9:00 AM - 9:20 AM

[A03-2am-02] Theoretical Study on the Effect of Applying External Static Electric Field on Singlet Fission Dynamics of Pentacene Dimer Models

○Takayoshi Tonami¹, Ryota Sugimori¹, Ryota Sakai¹, Masayoshi Nakano^{1,2,3} (1. Osaka University, 2. Center for Spintronic Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

9:20 AM - 9:40 AM

[A03-2am-03] Theoretical study on third-order nonlinear optical properties for radical trimer cations

○Wataru Yoshida¹, Hiroshi Matsui², Hajime Miyamoto¹, Ryota Sugimori¹, Takayoshi Tonami¹, Ryohei Kishi^{1,3}, Masayoshi Nakano^{1,3,4} (1. Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 2. Osaka Institute of Public Health, 3. Center for Quantum Information and Quantum Biology, Osaka University, 4. Center for Spintronics Research Network, Osaka University)

9:40 AM - 10:00 AM

[A03-2am-04] Theoretical study on structure, aromaticities and open-shell characters of π -trimers of antiaromatic molecules

○Masato Ikeuchi¹, Ryouhei Kishi³, Wataru Yoshida¹, Yousuke Shimizu¹, Jinnki Shouda¹, Masayoshi Nakano^{2,3} (1. Graduate School of Engineering Science, Osaka University, 2. Center for Spintronics Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

10:00 AM - 10:20 AM

[A03-2am-05] Quantum Design of Curved π -Conjugated Molecules for Highly-Efficient Singlet Fission: Bending Effect of the Perylene/Peropyrene Backbones

○Kenji Okada¹, Ryota Sakai², Masayoshi Nakano^{1,3,4} (1. Graduate School of Engineering Science, Osaka Univ., 2. School of Engineering Science, Osaka Univ., 3. Center for Spintronics Research Network, Osaka Univ., 4. Quantum Information and Quantum Biology Division, Osaka Univ.)

10:20 AM - 10:40 AM

[A03-2am-06] Theoretical study on singlet fission dynamics in pentacene ring-shaped aggregate models: Aggregate size and molecular configuration dependences

○Hajime Miyamoto¹, Kazuaki Tokuyama¹, Masayoshi Nakano^{1,2,3} (1. Graduate School of Engineering Science, Osaka University, 2. Center for Spintronics Research Network, Osaka University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

University, 3. Center for Quantum Information and Quantum Biology, Osaka University)

10:40 AM - 11:00 AM

[A03-2am-07] Quantitative prediction of singlet fission rates and molecular design of singlet fission materials

○Katsuyuki Shizu¹, Chihaya Adachi², Hironori Kaji¹ (1. Kyoto Univ., 2. Kyushu Univ.)

11:00 AM - 11:20 AM

対称ヘテロ直鎖状ペンタセン 4 量体モデルのシングレットフィッションダイナミクスの理論研究

(阪大院基礎工¹・阪大基礎工²・阪大 CSRN³・阪大 IQIB⁴) ○中野 雅由^{1,3,4}・宮本 孟¹・徳山 和明²

Theoretical Study on Singlet Fission Dynamics of Symmetric Hetero Linear Pentacene Tetramer Models (¹Graduate School of Engineering Science, Osaka University, ²School of Engineering Science, Osaka University, ³CSRN, Osaka University, ⁴IQIB, Osaka University) ○Masayoshi Nakano,^{1,3,4} Hajime Miyamoto,¹ Kazuaki Tokuyama²

Singlet fission (SF) is a photochemical process, where a singlet exciton splits into two triplet excitons, and has recently attracted much attention from the viewpoint of improving the photoelectric conversion efficiency of solar cells. In this study, we investigate the SF dynamics in a symmetric hetero linear tetramer model composed of two kinds of pentacene dimers with different intermolecular distances (r_i), where $r_1 = 4.0$ Å for the outer dimer and $r_2 = 4.0$ to 3.4 Å for the inner dimer, by numerical simulations based on the quantum master equation. The effect of the heterogeneity originating from the difference in these intermolecular interactions on the dynamics was clarified. The results show the usual increase in the population of the correlated triplet pair (TT), except for the middle $r_2 = 3.675$ Å, where the SF rate increases for $r_2 = 3.4$ Å compared to 4.0 Å. For the middle $r_2 = 3.675$ Å, however, it is found that there is a peculiar time evolution, where the TT population increases rapidly to 0.65 within 200 fs and then increases very slowly to 0.85 over 10 ps. From the relative relaxation factor analysis, it is found that this is due to the large superposition of singlet excitation and TT components in the region showing intermediate heterogeneity (around $r_2 = 3.675$ Å).

Keywords : Singlet Fission; Hetero Linear Molecular Aggregate; Quantum Master Equation; Pentacene; Exciton Dynamics

一重項分裂(SF)は、一重項励起子が2つの三重項励起子に分裂する光化学過程であり、太陽電池の光電変換効率向上の観点から近年注目されている。本研究では、分子間距離(r_i)の異なる2種類のペンタセン2量体からなる対称ヘテロ線形4量体モデル(外側の2量体では $r_1 = 4.0$ Åに固定、内側の2量体では $r_2 = 4.0$ から 3.4 Åまで変化)におけるSFダイナミクスを、量子マスター方程式に基づく数値シミュレーション¹⁾により調べ、これらの分子間相互作用の違いに由来するヘテロ性がダイナミクスに与える影響を明らかにした。その結果、中間のヘテロ性をもつ $r_2 = 3.675$ Å付近を除いて、通常の相関三重項対(TT)のポピュレーション増加を示し、 $r_2 = 3.4$ Åの場合は 4.0 Åの場合に比べてSFレートが増加したが、中間の $r_2 = 3.675$ Å付近では、TTポピュレーションが200fs以内に0.65まで急激に増加し、その後10psかけて0.85まで非常に緩やかに増加するという特異な時間発展が見られた。相対緩和因子解析より、これは、中間ヘテロ性を示す領域($r_2 = 3.675$ Å付近)で、一重項励起成分とTT成分の大きな重ね合わせが生じることが原因であることが判明した。

1) M. Nakano et al. *J. Comput. Chem.* **2019**, 40, 89.; *J. Chem. Phys.* **2019**, 150, 234305.

Theoretical Study on the Effect of Applying External Static Electric Field on Singlet Fission Dynamics of Pentacene Dimer Models

(¹Graduate School of Engineering, Osaka University, ²Center for Spintronic Research Network, Osaka University, ³Center for Quantum Information and Quantum Biology, Osaka University)
 ○Takayoshi Tonami,¹ Ryota Sugimori,¹ Ryota Sakai,¹ Masayoshi Nakano^{1,2,3}

Keywords: Singlet Fission; External Static Electric Field; Pentacene; Quantum Chemical Calculation; Quantum Dynamics

Singlet fission (SF) is a photophysical process generating two triplet excitons ($T_1 + T_1$) through the spin-allowed process from a singlet exciton (S_1S_0) to a correlated triplet pair (TT) state.¹ The important factors governing SF dynamics are: (i) energy gap between S_1 and $2 \times T_1$ states ($E(S_1) \geq 2E(T_1)$) or diradical character,² (ii) intermolecular electronic coupling, and (iii) vibronic coupling.^{1,2} So far, a lot of molecular designs and syntheses have been conducted to realize efficient SF by controlling these factors. It is also predicted that application of an external static electric field changes the excitation energies and electronic couplings, and then affects the SF dynamics, which is expected to be a novel physical control way for efficient SF.

In this study, we investigate the effect of applying an external static electric field (F) on SF dynamics of pentacene dimer model (Fig. 1) using quantum chemical calculations and quantum dynamics simulations.³ Fig.2a shows the variations of excitation energies of $S_1S_0(S_0S_1)$, TT, cation-anion pair (CA), and anion-cation pair (AC) states related to the SF process by applying F in the x direction. It is found that excitation energies of CA and AC states are increased and decreased, respectively, because these states have large dipole moment amplitudes. Fig.2b shows the variations of the SF rate and TT yield by applying F . It is found that the SF rate and TT yield are increased and decreased, respectively, with increasing $|F|$. Detailed analysis results will be given in the presentation.

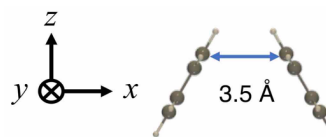


Fig. 1. Pentacene dimer model

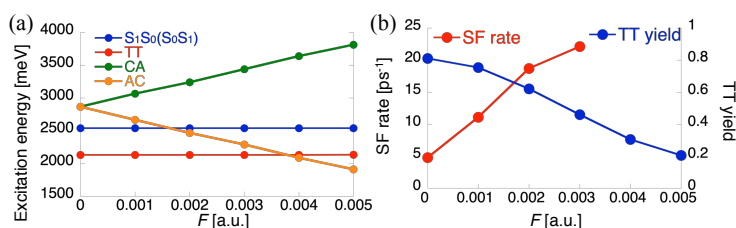


Fig. 2. Variations of excitation energies of S_1S_0 (S_0S_1), TT, CA, and AC states (a) and SF rate and TT yield (b) by applying F in the x direction

1) M. B. Smith, J. Michl *Chem. Rev.* **2010**, *110*, 6891. 2) (a) T. Minami, M. Nakano, *J. Phys. Chem. Lett.* **2012**, *3*, 145. (b) S. Ito et al. *J. Photochem. Photobiol. C: Photochem. Rev.* **2018**, *34*, 85. 3) (a) M. Nakano et al. *J. Phys. Chem. C* **2016**, *120*, 22803. (b) M. Nakano, *J. Comput. Chem.* **2019**, *40*, 89.

モノラジカル分子三量体カチオンの三次非線形光学物性に関する理論研究

(阪大院基礎工¹・大安研²・阪大 QIQB³・阪大 CSRN⁴) ○吉田 航¹・松井 啓史²・宮本 孟・杉森 亮太¹・當波 孝凱¹・岸 亮平^{1,3}・中野 雅由^{1,3,4}

Theoretical study on third-order nonlinear optical properties for radical trimer cations
(¹Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, ²Osaka Institute of Public Health, ³Center for Quantum Information and Quantum Biology, Osaka University, ⁴Center for Spintronics Research Network, Osaka University) ○Wataru Yoshida,¹ Hiroshi Matsui,² Hajime Miyamoto,¹ Ryota Sugimori,¹ Takayoshi Tonami,^{1,3} Ryohei Kishi,^{1,3,4} Masayoshi Nakano

Molecular design guidelines for controlling the amplitude and sign of the second hyperpolarizability γ (third-order nonlinear optical property at the molecular scale) have been desired for applications in photonics and optoelectronics. Nakano et al. theoretically investigated the relationship between the open-shell character y_s ($0(\text{closed-shell}) \leq y_s \leq 1$ (pure open-shell)) and γ (y_s - γ correlation), and found that open-shell singlet systems with intermediate y_s (referred to as diradicaloids) exhibit larger γ than closed-shell or pure open-shell analogues. They have also reported H_3^+ model – an example of hole-doped diradicaloids – exhibits a negative monotonic increase in γ with increasing y_s , but realistic hole-doped diradicaloids have not been fully examined. In this study, we theoretically clarify the y_s - γ correlation for 1,2,3,5-dithiadiazolyl trimer cation ($DTDA_3^+$). It is found that γ exhibits a negative increase up to the middle y_s , after which the amplitude of γ decreases and the sign of γ changes from negative to positive, which is different from y_s - γ correlation of the H_3^+ model.

Keywords: Nonlinear Optics; Open-Shell Singlet; Molecular Aggregate; Charged States; Valence-Bond Configuration Interaction Model

第二超分極率 γ は分子レベルでの三次非線形光学(NLO)物性を特徴づける物性量であり、フォトニクス、光エレクトロニクス分野への応用のために、 γ の大きさと符号を制御するための分子設計指針が求められている。近年、中野らにより、中間的なジラジカル因子 y ($0(\text{閉殻}) \leq y_s \leq 1(\text{完全開殻})$) を有する分子 (ジラジカロイド) が優れた γ を示すという y_s - γ 相関が理論的に見出された¹⁾。また、ホールドーピングジラジカロイドである H_3^+ モデルにおいて y_s の増加に対して γ が負に単調増加するという y_s - γ 相関が予測されたが²⁾、現実的な系での検討は十分に行われていない。本研究では、実在分子 (1,2,3,5-dithiadiazolyl (DTDA) ラジカル) の 3 量体カチオン ($DTDA_3^+$) における y - γ 相関を量子化学計算により調べた。その結果、 $DTDA_3^+$ では、中間的な y において γ の符号が負から正に反転を伴う H_3^+ モデルと異なる y_s - γ 相関を示すことが明らかとなった。

1) M. Nakano, et al., *J. Phys. Chem. A* **109**, 885 (2005).

2) A. Takebe, M. Nakano, et al., *Chem. Phys. Lett.* **451**, 111 (2008).

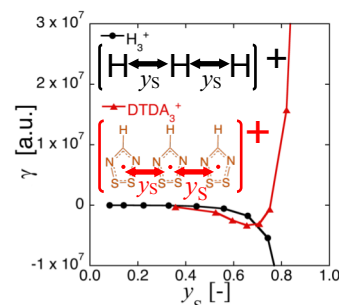


Fig.1. y_s - γ correlation for H_3^+ and $DTDA_3^+$

反芳香族分子の π 三量体における構造、芳香族性、開殻性に関する理論研究

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Theoretical study on structure, aromaticities and open-shell characters of π -trimers of antiaromatic molecules (¹*School of Engineering Science, Osaka University*, ²*Graduate School of Engineering Science, Osaka University*, ³*CSRN, Osaka University*, ⁴*QIQB, Osaka University*) ○Masato Ikeuchi¹, Ryohei Kishi^{2,4}, Wataru Yoshida², Yosuke Shimizu², Jinki Shoda¹, Masayoshi Nakano^{2,3,4}

Intermolecular-Interaction-Induced aromatic character in the π -stacked antiaromatic molecules is known as three-dimensional(3D)-aromaticity. Even though 3D-aromaticity in π -dimers have been investigated so far for several model and realistic π -dimers, details of 3D-aromaticity in π -multimers have not been clarified yet. In this study, we discuss the relationship between the structures, aromaticities, open-shell characters and optical response properties of π -trimer models of several antiaromatic molecules by quantum chemical calculations.

Keywords : 3D-aromaticity; Cyclooctatetraene; π -Trimer; Quantum Chemical Calculation

反芳香族分子の π 積層系において、分子間の軌道相互作用により誘起される芳香族的性質は三次元芳香族性と呼ばれる¹⁾。これまで、種々のモデルおよび実在の反芳香族分子の π 二量体において、三次元芳香族性発現の機構解明に関する研究が理論、実験両面からなされてきたが¹⁻³⁾、多量体における発現機構については未解明な点が多い。また近年、反芳香族分子において発現する一重項開殻性の電子構造にも注目が集まっている。そこで本研究では、シクロオクタテトラエン (COT) をもとにした反芳香族分子の π 三量体モデルにおける構造、芳香族性、開殻性の関係を量子化学計算に基づき議論する。

COT の基底状態の安定構造は、 D_{2d} 対称性の折れ曲がった舟型構造を取り、平面構造で結合交代のある D_{4h} 対称性、および正八員環構造の D_{8h} 対称性の構造はポテンシャル曲面における鞍点である。一方近年、化学修飾により平面化された COT 誘導体を合成する研究も盛んに行われている。本研究ではまず、各対称性の制限下で COT 単量体の構造を最適化し、図 1 に示すように等しい分子間距離 (D) で配置した π 三量体モデルを構築する。 D を種々に変化させ、分子軌道相関図、開殻性の指標であるジラジカル因子、芳香族性の指標である磁気遮蔽定数や磁場誘導電流密度などを量子化学計算により検討し、単量体の構造が、両端と中央の構成分子、および三量体全体における電子構造や芳香族性に与える影響を議論する。

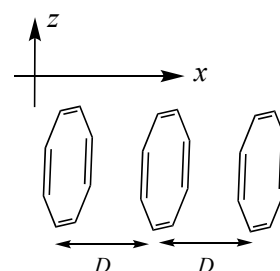


図 1. COT(D_{4h}) π 三量体モデル (完全重なり型)

1) Corminboeuf, C. et al., *Org. Lett.*, **2007**, 9, 3263; Bean, D. E. et al., *Org. Lett.* **2008**, 10, 5573.

2) Nozawa R. et al., *Nat. Commun.*, **2016**, 7, 13620; Nozawa R. et al., *Nat. Commun.*, **2019**, 10, 3576.

高効率シングレットフィッションのための湾曲 π 共役分子系の量子設計：ペリレン/ペロピレン骨格の屈曲効果

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Quantum Design of Curved π -Conjugated Molecules for Highly-Efficient Singlet Fission: Bending Effect of the Perylene/Peropyrene Backbones (¹Graduate School of Engineering Science, Osaka University, ²School of Engineering Science, Osaka University, ³Center for Spintronics Research Network (CSRN), Osaka University, ⁴Quantum Information and Quantum Biology Division (QIQB), Osaka University) ○Kenji Okada,¹ Ryota Sakai,² Masayoshi Nakano^{1,3,4}

Singlet fission (SF) is a photophysical process, where a singlet exciton splits into two triplet excitons. SF has recently attracted intensive attention due to its potential of improving the efficiency of solar cells. For designing efficient SF materials, it is essential to tune the singlet and triplet excitation energies. In this study, we theoretically clarify the correlation between structure and the SF energy level matching condition in the curved π -conjugated systems including perylene and peropyrene derivatives, and design novel curved π -conjugated SF molecules. In summary, it is found that bending of the perylene and peropyrene skeletons reduce and increase the positive $\Delta E_{\text{SF}} (= 2E(\text{T}_1) - E(\text{S}_1))$, respectively,. Details will be reported in the presentation.

Keywords : Singlet fission; Quantum Chemical Calculation; Diradicaloid; Exciton; Curved π -Conjugated System

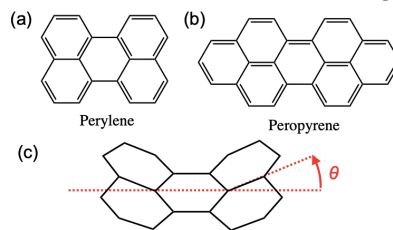


Figure 1. Molecular structures of perylene (a) and peropyrene (b), and the curved perylene model (c).

シングレットフィッション(SF)は一つの一重項励起子が二つの励起子に分裂する過程であり、高効率有機太陽電池への応用が期待されている¹⁾。SF材料の設計には、第一に分子の一重項・三重項励起エネルギーについて、 $\Delta E_{\text{SF}} = 2E(\text{T}_1) - E(\text{S}_1)$ を負（発熱）または0（等熱）に近づけることが必要である。本研究では分子骨格の歪みに着目し、ペリレン・ペロピレン誘導体の骨格の屈曲とSFエネルギー準位整合条件の関係を理論的に解明し、新規の湾曲 π 共役 SF 分子の設計を提案する。屈曲型ペリレンモデル (Figure 1) より、ペリレンでは θ の増大に従い $E(\text{S}_1)$ と $E(\text{T}_1)$ が同程度低下し、これは吸熱的なSF条件を発熱的または等熱的に転じさせる設計に利用できると考えられる。他方、ペロピレン骨格における湾曲効果は逆に作用し、平面において正の ΔE_{SF} をさらに増大させることが予測された。しかし、分子歪みとそれを実現するための化学修飾は不可分であり、いくつかのボウル型ペロピレン類縁体において軌道相互作用のために $\Delta E_{\text{SF}} \approx 0$ の達成が可能であることが明らかとなった。詳細は当日報告する。

1) (a) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891. (b) S. Ito, T. Nagami, M. Nakano, *J. Photochem. Photobiol. C: Photochem. Rev.* **2018**, *34*, 85. (c) T. Minami, M. Nakano, *J. Phys. Chem. Lett.* **2012**, *3*, 145.

ペンタセン環状分子集合系モデルのシングレットフィッションダイナミクスに関する理論研究：集合系サイズおよび分子配向依存性

(阪大院基礎工¹・阪大基礎工²・阪大 CSRN³・阪大 QIQB⁴) ○宮本 孟¹・徳山 和明²・中野雅由^{1,3,4}

Theoretical Study on Singlet Fission Dynamics in Pentacene Ring-Shaped Aggregate Models: Aggregate Size and Molecular Configuration Dependences (¹*Graduate School of Engineering Science, Osaka University*, ²*School of Engineering Science, Osaka University*, ³*Center for Spintronics Research Network, Osaka University*, ⁴*Center for Quantum Information and Quantum Biology, Osaka University*)○Hajime Miyamoto,¹ Kazuaki Tokuyama,² Masayoshi Nakano^{1,3,4}

Singlet fission (SF) is a photophysical process, where one singlet exciton splits into two triplet excitons in organic aggregates, is expected to have a potential for improving the photoelectric conversion efficiency in organic solar cells. Since aggregate structure has a crucial role in SF dynamics, we have investigated the size and molecular configuration dependences of SF dynamics in ring-shaped aggregate models shown in Figure 1 named J-, H-, and slip-stack-like aggregate models, respectively, using the quantum master equation method. **Keywords** : Singlet Fission; Quantum Master Equation; Ring-Shaped Molecular Aggregate; Exciton Dynamics; Pentacene

シングレットフィッション(SF)は有機分子集合系内で一重項励起子 S_1 が、相関三重項対 TT を経て二つの三重項励起子に分裂する現象であり、太陽電池の光電変換効率向上への可能性から盛んに研究されている¹。本研究では、図 1(a)–(c)のペンタセン環状集合系モデル(鏡映対称な J 型・H 型²及び非対称な slip-stack-like 型モデル)における SF ダイナミクスを量子マスター方程式法に基づき解析し、SF 速度 k と TT 収率 a の分子配向および構成分子数(N)依存性について検討した。各 N についての結果(図 2)より、slip-stack-like 型モデルでは中間的な N において、H 型環状集合系モデルと比較して速度・収率ともに増大することが明らかになった。詳細は当日報告する。

1) (a) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891. (b) S. Ito, T. Nagami, M. Nakano, *J. Photochem. Photobiol. C: Photochem. Rev.* **2018**, *34*, 85. (c) M. Nakano et al. *J. Comput. Chem.* **2019**, *40*, 89. 2) H. Miyamoto, M. Nakano, *ChemPhotoChem* **2020**, *4*, 5249.

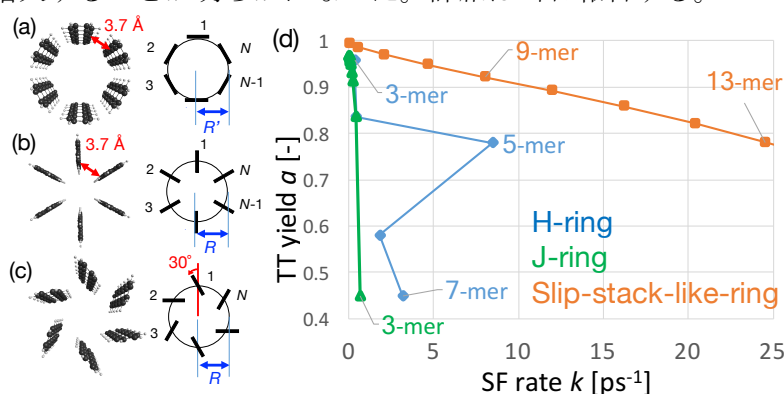


図 1. ペンタセン J 型(a), H 型(b), slip-stack-like 型(c)集合系の構造モデルおよび各モデルの SF 速度 k 、TT 収率 a の集合系サイズ N 依存性(d)。

一重項励起子分裂速度の定量的予測と分子設計

(京大化研¹・九大 OPERA²・JST ERATO³・九大 I2CNER⁴) ○志津 功将¹・
安達 千波矢^{2,4}・梶 弘典¹

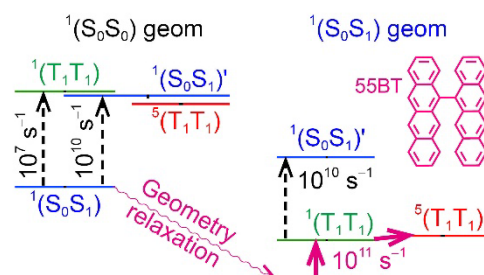
Quantitative prediction of singlet fission rates and molecular design of singlet fission materials
(¹*Institute for Chemical Research, Kyoto University*, ²*Center for Organic Photonics and Electronics Research (OPERA), Kyushu University*, ³*Japan Science and Technology Agency (JST), ERATO*, ⁴*International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University*) ○Katsuyuki Shizu,¹ Chihaya Adachi,^{2,4} Hironori Kaji¹

Singlet fission (SF) generates two triplet excitons from one singlet exciton. SF has been used to increase the number of triplet excitons and exciton-generation efficiency in organic solar cells and organic light-emitting diodes. SF materials with high triplet energy have been required to increase versatility of SF in optoelectronic devices¹⁾. Recently, we have developed a theoretical method based on RAS-2SF calculation and the Fermi golden rule to quantitatively predict intramolecular and intermolecular SF rates^{2,3)}. In this study, we briefly review the theoretical method and apply it to molecular design for an intramolecular SF material with high triplet energy, 5,5'-bitetracene⁴⁾ (55BT).

Keywords : Singlet Fission; Tetracene; Vibronic Coupling; Configuration Interaction; the Fermi Golden Rule

一重項励起子分裂 (Singlet Fission, SF) は1つの一重項励起子が2つの三重項励起子に分裂する現象であり、SF が持つ三重項励起子の増感効果は、有機太陽電池や有機 EL 素子の特性向上に役立てられてきた。光電子デバイスにおける SF の有用性を高めるため、高い三重項エネルギーを持つ SF 材料の開発が求められている¹⁾。著者らは、SF 材料の分子設計を目的として、RAS-2SF 法と Fermi の黄金律に基づいて、分子内および分子間 SF の速度を定量的に予測できる理論手法を開発してきた^{2,3)}。

本研究では、開発した理論手法を 5,5'-bitetracene (55BT) の分子設計に応用した例を示す⁴⁾。理論計算の結果から、55BT は 1.26 eV の高い T₁ エネルギーを持ち、励起一重項状態 ¹(S₀S₁) における構造緩和の後、10¹¹ s⁻¹ の速度で内部転換を起こすことで、効率よく三重項励起子のペア ¹(T₁T₁) を生成すると予想される。



1) Spatial Separation of Triplet Excitons Drives Endothermic Singlet Fission. N. V. Korovina, C. H. Chang, J. C. Johnson, *Nat. Chem.* **2020**, 12, 391. 2) Effect of Vibronic Coupling on Correlated Triplet Pair Formation in the Singlet Fission Process of Linked Tetracene Dimers. K. Shizu, C. Adachi, H. Kaji, *J. Phys. Chem. A* **2020**, 124, 3641. 3) Visual Understanding of Vibronic Coupling and Quantitative Rate Expression for Singlet Fission in Molecular Aggregates. K. Shizu, C. Adachi, H. Kaji, *Bull. Chem. Soc. Jpn.* **2020**, 93, 1305. 4) Correlated Triplet Pair Formation Activated by Geometry Relaxation in Directly Linked Tetracene Dimer (5,5'-Bitetracene). K. Shizu, C. Adachi, H. Kaji, *ACS Omega*. DOI: 10.1021/acsomega.0c04809.

[A05-2pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Takuya Horio, Masashi Arakawa, Fuminori Misaizu

Sat. Mar 20, 2021 1:00 PM - 3:20 PM Room 5 (Online Meeting)

[A05-2pm-01] Capturing roaming molecular fragments of formaldehyde in real time

○Tomoyuki Endo^{1,2}, Simon P Neville³, Vicent Wanie², Samuel Beaulieu², Chen Qu⁴, Jude Deschamps², Philippe Lassonde², Bruno E Schmidt⁵, Hikaru Fujise⁶, Mizuho Fushitani⁶, Akiyoshi Hishikawa^{6,7}, Paul L Houston^{8,9}, Joel M Bowman¹⁰, Michael S Schuurman^{3,11}, François Légaré², Heide Ibrahim² (1. QST-KPSI, 2. INRS-EMT, 3. Univ. of Ottawa, 4. Univ. of Maryland, 5. few-cycle Inc., 6. Nagoya Univ. Dept. Chemistry, 7. Nagoya Univ. RCMS, 8. Cornell Univ., 9. Georgia Inst. of Tech., 10. Emory Univ., 11. NRC of Canada)

1:00 PM - 1:20 PM

[A05-2pm-02] Ultrafast nuclear dynamics of electronically highly excited O₂⁺ investigated by pump-probe measurements using near-infrared laser pulses and high-order harmonics

○Kana Yamada¹, Toshiaki Ando¹, Atsushi Iwasaki¹, Kaoru Yamanouchi¹ (1. The University of Tokyo)

1:20 PM - 1:40 PM

[A05-2pm-03] Structural features in the growth of silver cluster cations observed by photodissociation/absorption spectroscopy

○Satoshi Kono¹, Shun Kawamura¹, Kensuke Morishita¹, Masashi Arakawa¹, Takuya Horio¹, Akira Terasaki¹ (1. Kyushu University)

1:40 PM - 2:00 PM

[A05-2pm-04] NO dissociation ability of IX group clusters.

○Masato Yamaguchi¹, Yufei Zhang¹, Ken Miyajima¹, Joost M. Bakker², Olga V. Lushchikova², Fumitaka Mafuné¹ (1. Graduate School of Arts and Sciences, The University of Tokyo, 2. Radboud University)

2:00 PM - 2:20 PM

[A05-2pm-05] Ion imaging of vibrational predissociation of Ar-tagged protonated water monomer and dimer

○Yuri Ito¹, Mizuhiro Kominato¹, Yuji Nakashima¹, Fuminori Misaizu¹ (1. Tohoku University)

2:20 PM - 2:40 PM

[A05-2pm-06] OPIG-DC Voltage-Revolved Collision-Induced Reactions of Bimolecular Ions

○Shinji Nonose¹, Satoko Kanamori¹, Saki Kitamura¹, Takaaki Iyama¹, Wataru Kadota¹, Juri MOrishita¹, Yuto Yonebayashi¹, Hiroto Ohta¹, Satofumi Tago¹, Tomoya Yoshida¹ (1. Yokohama City University)

2:40 PM - 3:00 PM

[A05-2pm-07] Freezing process of micro droplets of pure water and water– ethylene glycol mixtures evaporatively cooled in a vacuum

○Tamon Kusumoto¹, Takefumi Handa¹, Masashi Arakawa¹, Takuya Horio¹, Akira Terasaki¹ (1. Kyushu University)

3:00 PM - 3:20 PM

Capturing roaming molecular fragments of formaldehyde in real time

(¹Kansai Photon Science Institute, National Institutes for Quantum and Radiological Science and Technology, ²Centre Énergie Matériaux Télécommunications, Institut National de la Recherche Scientifique, ³Department of Chemistry and Biomolecular Sciences, University Ottawa, ⁴Department of Chemistry and Biochemistry, University of Maryland, ⁵few-cycle Inc., ⁶Department of Chemistry, Nagoya University, ⁷Research Center for Materials Science, Nagoya University, ⁸Department of Chemistry and Chemical Biology, Cornell University, ⁹School of Chemistry and Biochemistry, Georgia Institute of Technology, ¹⁰Department of Chemistry and Cherry L. Emerson Center for Scientific Computation, Emory University, ¹¹National Research Council of Canada) ○Tomoyuki Endo,^{1,2} Simon P. Neville,³ Vincent Wanie,² Samuel Beaulieu,² Chen Qu,⁴ Jude Deschamps,² Philippe Lassonde,² Bruno E. Schmidt,⁵ Hikaru Fujise,⁶ Mizuho Fushitani,⁶ Akiyoshi Hishikawa,^{6,7} Paul L. Houston,^{8,9} Joel M. Bowman,¹⁰ Michael S. Schuurman,^{3,11} François Légaré,² Heide Ibrahim²

Keywords: Molecular Dynamics, roaming process, Intense laser fields, Ultrafast spectroscopy, Coulomb explosion imaging

In conventional (molecular/radical) dissociation reactions, molecules go through the minimum energy path from reactants to products. Alternative dissociation pathway called “roaming” was discovered in the dissociation of formaldehyde (H_2CO)¹. In the roaming reaction, the roaming fragment (H atom) walks around the remaining HCO. Footprints of roaming were reported in various molecular systems. However, a roaming fragment itself has not been observed directly because of a stochastic nature of roaming process. Recently, we have successfully captured roaming fragments in real time by using a combination of Coulomb explosion imaging and quasi-classical trajectory analysis.²

Ultraviolet pump pulses ($\lambda = 304$ nm) were used to populate deuterated formaldehyde (D_2CO) to the electronically excited S_1 state. After the relaxation to the vibrationally hot S_0 state, D_2CO can follow dissociation pathways including roaming. Time-delayed few-cycle intense probe pulses ($\lambda = 750$ nm, 8 fs) were used to ionize dissociating D_2CO to D_2CO^{3+} . The three-dimensional momenta of pairs of fragment ions (D^+ , D^+ , CO^+) were measured by using a Coulomb explosion imaging technique.

The measured momentum distribution shows a clear dependence on pump-probe time-delay reflecting the dissociation of D_2CO on the S_0 state. The contribution of the roaming pathway has been successfully distinguished from other pathways by comparison with theoretical calculation including all the critical experimental steps (relaxation, dynamics on the S_0 state, and Coulomb explosion). Moreover, the S_1/S_0 relaxation process, that is five-orders of magnitude faster than previously reported process, has been observed.

1) D. Townsend et al., *Science* **2004**, 306, 1158. 2) T. Endo et al., *Science* **2020**, 370, 1072.

Ultrafast nuclear dynamics of electronically highly excited O_2^+ investigated by pump-probe measurements using near-infrared laser pulses and high-order harmonics

(¹*School of Science, The University of Tokyo*) ○Kana Yamada,¹ Toshiaki Ando,¹ Atsushi Iwasaki,¹ Kaoru Yamanouchi

Keywords: High-order harmonics; Oxygen molecular ion; Pump-probe measurement; Electronically highly excited states

When molecules are ionized by extreme ultraviolet (XUV) light pulses, ions are created in the electronically highly excited states, and the ions show a variety of nuclear dynamics depending on the shapes of the potential energy surfaces. O_2^+ is one of the diatomic molecules whose nuclear dynamics have been intensively studied. By a pump-probe experiment performed up to the delay time of 2 ps, it was reported that the yield of O^+ fragments exhibits oscillation with the period of 40 fs, corresponding to the vibrational frequency of O_2^+ prepared in the $a^4\Pi_u$ state.¹ On the other hand, it was shown by a photoelectron-photoion coincidence measurement that O_2^+ prepared in the $3^2\Pi_u$ state either predissociates into the 3rd dissociation continuum or dissociates directly into the 5th dissociation continuum depending on the prepared vibrational levels.² In the present study, we probe the nuclear dynamics of the electronically highly excited $a^4\Pi_u$ and $3^2\Pi_u$ states of O_2^+ in real-time by performing pump-probe measurements using few-cycle near-infrared (near-IR) laser pulses and high-order harmonics in the XUV region in the delay-time range up to 100 fs.

We find that the delay-time dependence of the kinetic energy distribution of O^+ exhibits oscillatory and curved-line structures. In order to assign the observed structures, we simulate the delay-time dependence of the kinetic energy distribution of O^+ fragments by assuming that O_2^+ is first prepared in an electronically highly excited state by the high-order harmonics and is further excited by the near-IR laser pulse to a dissociative electronic state of O_2^+ . Based on the numerical simulation, we assign the oscillatory structure to the O^+ fragments produced through the dissociation of O_2^+ in the $f^4\Pi_g$ state, which is prepared by the photoexcitation of O_2^+ in the $a^4\Pi_u$ state by the near-IR laser pulse, and that the oscillation reflects the vibrational motion of O_2^+ in the $a^4\Pi_u$ state. Based on the numerical simulation of the delay-time dependence of the kinetic energy distribution of O^+ and the delay-time dependent angular distribution of O^+ , we assign the curved-line structure to the O^+ fragments produced through the dissociation of O_2^+ in the $7^2\Sigma_u$ and $8^2\Sigma_g$ states, both of which are prepared by the photoexcitation of O_2^+ in the $3^2\Pi_u$ state by the near-IR pulse, and that the delay-time dependence of the curved-line structure reflects the direct dissociation of O_2^+ in the $3^2\Pi_u$ state to the 5th dissociation continuum.

1) P. Cörlin *et al.*, *Phys. Rev. A* **2015**, 91, 043415. 2) X. Tang *et al.*, *J. Chem. Phys.* **2018**, 148, 124309.

Structural Features in the Growth of Silver Cluster Cations Observed by Photodissociation/Absorption Spectroscopy

(Kyushu University) ○ Satoshi Kono, Shun Kawamura, Kensuke Morishita, Masashi Arakawa, Takuya Horio, Akira Terasaki

Keywords: Silver Cluster; Photodissociation Spectroscopy; Cavity Ring-Down Spectroscopy; Size Dependence; Geometric Structure

A silver nanoparticle shows optical absorption originating from collective excitation of free electrons, so-called surface plasmon resonance, which attracts much attention due to an enhanced electric field inherent in the optical process that allows various applications. This optical response of a nanoparticle should be contrasted with that of a silver atom, where only one electron participates in the transition between atomic orbitals. Therefore, it is expected that the collective excitation emerges in the cluster regime of several to several hundreds of atoms. We have been tackling this basic problem by spectroscopic studies on size-selected free silver cluster cations, Ag_N^+ . Here we extend our previous experiments¹ on $N = 2\text{--}70$ to even larger sizes. The series of photodissociation/absorption spectra reveals systematic changes in the geometry of silver clusters as a function of size.

Size-selected Ag_N^+ clusters, which were produced by a magnetron-sputter cluster-ion source coupled with a quadrupole mass filter, were introduced into a linear ion trap to prepare high-density sample clusters. The trapped clusters were irradiated with a pulsed OPO laser to induce dissociation upon photoabsorption. The dissociation yield, as monitored by a second quadrupole mass filter, was normalized by the photon flux of the incident laser. The measurement was performed as a function of photon energy between 3.5 and 4.1 eV (355–302 nm in wavelength) to obtain a photodissociation spectrum.

A part of the results is shown in Fig. 1. A double-peak profile is observed at $N = 71$, implying an ellipsoidal structure; the higher-energy peak is attributed to an oscillation of electrons along the two shorter axes of the cluster, while the other peak corresponds to the longer axis. In contrast, only one peak shows up at $N = 92$, indicating a spherical symmetry. Spectral features similar to those of nanoparticles/nanorods thus appeared at these sizes in the cluster regime. We will present complete results of photodissociation up to $N = 92$ along with photoabsorption measurement performed by a cavity-enhanced technique that is in progress.

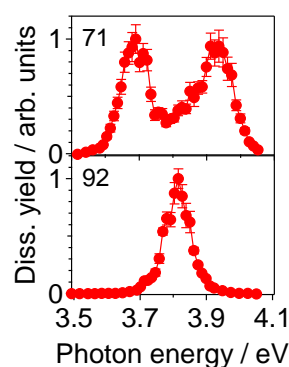


Fig. 1. Photodissociation spectra of Ag_N^+ ($N = 71$ and 92).

1) Fujimoto, Kono, Arakawa, Horio, Yasuike, Terasaki, The 99th CSJ Annual Meeting, 2D3-31 (2019); Kono, Arakawa, Horio, Terasaki, The 100th CSJ Annual Meeting, 1D2-39 (2020).

IX 族クラスターの NO 解離能

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NO dissociation ability of IX group clusters. (¹School of Arts and Sciences, The University of Tokyo, ²Radboud University) ○Masato Yamaguchi¹, Yufei Zhang¹, Ken Miyajima¹, Joost M. Bakker², Olga V. Lushchikova², Fumitaka Mafuné¹

The geometrical structures of metal clusters containing Rh and Ir, which are known as precious metal of IX group, were determined using the combination of infrared multiple photon dissociation (IRMPD) spectroscopy and quantum calculations. In the experiments, MNOAr^+ ($\text{M} = \text{Rh}_5\text{Ta}$, Ir_6) clusters were generated by laser ablation method in the presence of Ar/He carrier gas. By irradiating the IR laser, IRMPD signals were obtained as the Ar desorption on the mass spectra.^{1,2} In previous studies, it was suggested that NO on the Rh_6^+ cluster existed as the molecular form on the cluster predominantly.³ In contrast, NO on the Rh_5Ta^+ alloy cluster were dissociated after adsorption reaction without any geometrical isomers. The geometrical structure of Ir_6NO^+ were also investigated and it was suggested that at least three isomers coexisted in the products we observed. To evaluate the ability of NO bond cleavage, binding energies of O and N on these metal clusters were investigated. As the result, oxophilicity of metal clusters seems to have relation with NO dissociation (Fig. 1). We will discuss adsorption forms of NO molecules and NO dissociation ability of clusters in detail.

Keywords : Gas phase cluster, Infrared multiple photon dissociation, Rhodium, Iridium, Tantalum

IX 族原子に属する Rh, Ir を含むクラスターと NO の反応について, その幾何構造を赤外多光子解離分光法と量子化学計算を用いて決定した[1, 2]. 実験では Ar と He の混合ガスをキャリアガスに用い, 目的の金属をレーザー蒸発することで MNOAr^+ ($\text{M} = \text{Rh}_5\text{Ta}$, Ir_6) クラスターを生成した. 生成したクラスターに赤外光を照射することで Ar の脱離を誘起し, IRMPD スペクトルを取得した. 先行研究である Rh_6^+ クラスターに対する NO の吸着形態は分子吸着が支配的であるのに対し[3], Rh を 1 原子 Ta に置き換えた Rh_5Ta^+ 合金クラスターは NO を解離吸着することが示された. また, Ir_6^+ と NO の反応では NO の分子吸着と解離吸着を含む, 少なくとも 3 つの異性体が共存することが示唆された. 量子化学計算によってこれら金属クラスターに対する O, N 原子との結合エネルギーを調べたところ, 酸素原子親和性と NO 解離能力の間に一定の関係が見られた (Fig.1). 発表では幾何構造の決定と解離能力の評価について議論する.

[1] M. Yamaguchi et al., *J. Phys. Chem. C* **123** (2019) 3476–3481

[2] M. Yamaguchi et al., *J. Phys. Chem. C* **11** (2020) 4408–4412

[3] T. Nagata et al., *J. Phys. Chem. C* **121** (2017) 27417–27426

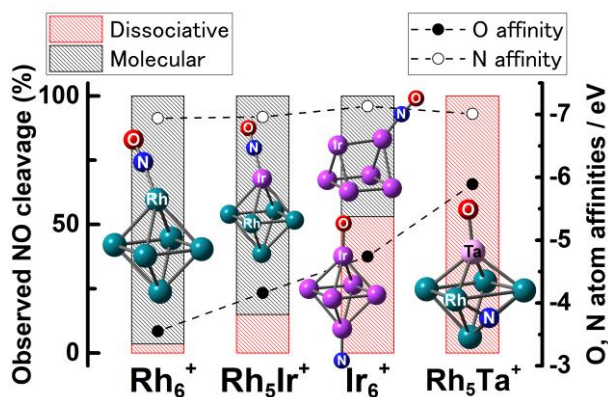


Figure 1 Ratios between dissociatively vs. molecularly adsorbed NO molecule on Rh_6^+ , Rh_5Ir^+ , Ir_6^+ and Rh_5Ta^+ clusters. Left vertical axis indicates NO cleavage percentage while right vertical axis indicates adsorption energies of O or N atom.

Ion imaging of vibrational predissociation of Ar-tagged protonated water monomer and dimer

(Graduate School of Science, Tohoku University) ○Yuri Ito, Mizuhiro Kominato, Yuji Nakashima, Fuminori Misaizu

Keywords: vibrational predissociation; ion imaging; hydrogen bonding; mass spectrometry; cluster ion

Infrared photodissociation of gas-phase molecular clusters has been widely studied to understand intra- and intermolecular vibrational relaxation processes. In this study, vibrational predissociation processes of Ar-tagged protonated water monomer ($\text{H}_3\text{O}^+\text{-Ar}$) and dimer ($\text{H}^+(\text{H}_2\text{O})_2\text{-Ar}$) were investigated by using an ion imaging apparatus designed for photodissociation of mass-selected ionic species.¹

Ar-tagged protonated water cluster cations were generated by electron impact ionization of an $\text{H}_2\text{O}/\text{Ar}$ gas mixture. After mass separation, $\text{H}_3\text{O}^+\text{-Ar}$ and $\text{H}^+(\text{H}_2\text{O})_2\text{-Ar}$ were irradiated with a linearly polarized infrared laser, which resonantly excited some of the OH-stretching modes.² Photofragment ions produced by Ar predissociation were then observed as images to determine translational energy (E_t) distributions.

Fig. 1 shows the E_t distributions plotted against E_t fractions of available energies (E_{avl}). In $\text{H}_3\text{O}^+\text{-Ar}$, the E_t distribution for the bound-OH excitation obviously broadened toward larger E_t/E_{avl} as compared to the free-OH excitation. On the other hand, $\text{H}^+(\text{H}_2\text{O})_2\text{-Ar}$ exhibited some different features. First, the E_t fraction for the bound-OH excitation was smaller than that for $\text{H}_3\text{O}^+\text{-Ar}$, indicating a propensity for internal excitation in the photofragment $\text{H}^+(\text{H}_2\text{O})_2$. Second, the E_t distribution for bound-OH excitation was almost identical to that for the free-OH excitation of the other H_2O molecule. Thus, mode dependence disappeared in the E_t distributions for $\text{H}^+(\text{H}_2\text{O})_2\text{-Ar}$. These observed features will be discussed in terms of the number of internal degrees of freedom in the photofragment ions.

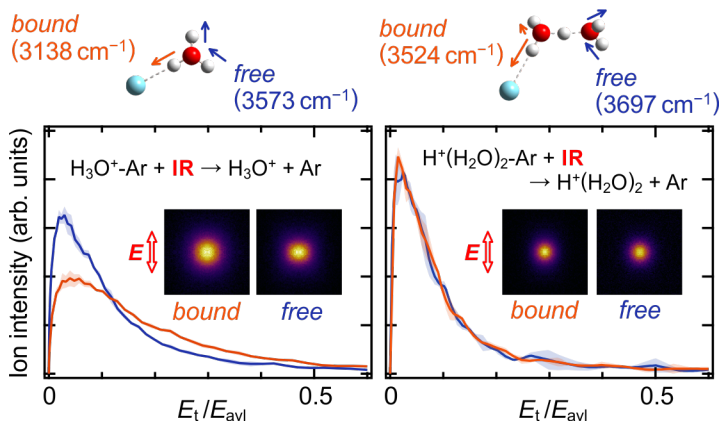


Fig. 1: Illustrations for OH-stretching modes of $\text{H}_3\text{O}^+\text{-Ar}$ and $\text{H}^+(\text{H}_2\text{O})_2\text{-Ar}$ (top), the corresponding ion images and the E_t distributions plotted against E_t/E_{avl} ratio (bottom). E is a polarization direction of the dissociation laser.

- 1) K. Okutsu *et al.*, *Rev. Sci. Instrum.* **88**, 053105 (2017).
- 2) J. M. Headrick *et al.*, *Science* **308**, 1765 (2005).

生体分子イオンの衝突誘起反応における OPIG-DC 電圧依存性

(横浜市立大学生命ナノ¹) ○野々瀬真司¹・金森怜子¹・北村佐樹¹・井山貴瑛¹・角田渉¹・森下樹里¹・米林優人¹・太田寛人¹・田子智郁¹・吉田智哉¹

OPIG-DC Voltage-Resolved Collision-Induced Reactions of Biomolecular Ions (¹Graduate School of Nanobioscience, Yokohama City University) ○Shinji Nonose,¹ Satoko Kanamori,¹ Saki Kitamura,¹ Takaaki Iyama,¹ Wataru Kadota,¹ Julie Morishita,¹ Yuto Yonebayashi,¹ Hiroto Ota,¹ Satofumi Tago,¹ Tomoya Yoshida¹

Time-, temperature-, and OPIG-DC voltage-resolved proton transfer reactions of peptide and protein ions to 1,4-butanedi-amine and 1-hexylamine (Hx) were examined in the gas phase. Collision-induced dissociation of cluster ions including guanine or guanosine with a sodium or a potassium atom were also studied. Absolute reaction rate constants for proton transfer were determined from intensities of precursor and product ions in the mass spectra. With changes of direct current (DC) voltage to put octapole ion guide (OPIG) in the collision cell, V_{DC} , remarkable change was observed for distribution of product ions and reaction rate constants of proton transfer. The results indicate that conformation changes on ions at OPIG-DC voltage range, which relate with complex formation. In collision-induced dissociation of guanine or guanosine cluster ions, sequential decompositions proceeded, which would relate to specific stability of G-quadruplex. An issue that is attracting considerable attention is their conformations might resemble structural evolution that originated from internal energy in the gas phase.

Keywords : Biomolecular ion; Proton transfer reaction; OPIG-DC

気相中でペプチドおよびタンパク質の多電荷イオンと 1,4-butanedi-amine および 1-hexylamine (Hx) とのプロトン移動反応に関して研究した。プロトン移動の反応速度を指標として、反応温度、反応時間、およびオクタポールイオンガイド(OPIG)の直流電圧(OPIG-DC)である V_{DC} を変化させることによって、イオンの立体構造と反応に関して検討した。図1に melittin イオン、 $[M+4H]^{4+}$ と Hx とのプロトン移動反応の V_{DC} 依存性に関する質量スペクトルを示す。(A)はESIによってイオンを生成した場合、(B)は $[M+4H]^{4+}$ のみを選別した場合、(C)~(G)は衝突反応セルに Hx を導入して、プロトン移動反応を誘起した場合をそれぞれ表す。(C)から(G)への順で、 V_{DC} が増加している。 V_{DC} の増加に伴って、 $[M+3H]^{3+}$ の割合が減少し $[M+4H]^{4+}$ の割合が増加した。ところが、 V_{DC} の値が 170V 付近では $[M+4H]^{4+}$ の割合が減少し $[M+3H]^{3+}$ の割合が増加した。

- 1) Temperature-Resolved Proton Transfer Reactions of Biomolecular Ions, S. Nonose, *Mass Spectrometry*, **2020**, 9, A0083.

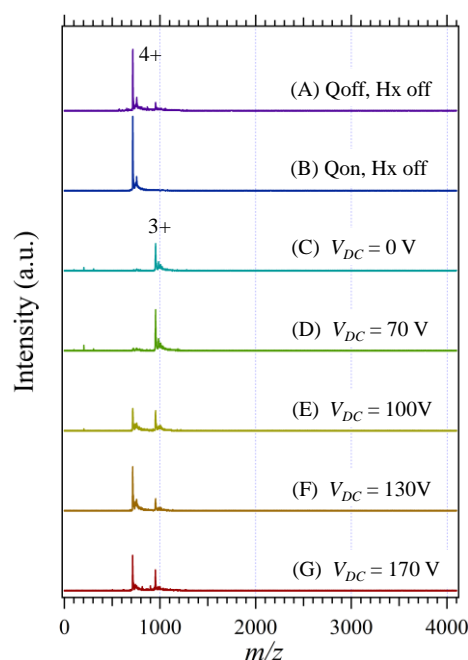


Figure 1. Mass spectra of melittin ion, $[M+4H]^{4+}$, reacted with Hx in various V_{DC} .

真空下での蒸発冷却による水および水-エチレングリコール混合液滴の凍結過程

(九大院理) ○楠本多聞・飯田岳史・荒川雅・堀尾琢哉・寺寄亨

Freezing Process of Micro Droplets of Pure Water and Water–Ethylene Glycol Mixtures Evaporatively Cooled in a Vacuum (*Graduate School of Science, Kyushu University*) ○Tamon Kusumoto, Takefumi Handa, Masashi Arakawa, Takuya Horio, Akira Terasaki

We have been studying freezing processes of water and ethylene-glycol (EG) droplets in a vacuum, focusing on thermodynamics upon evaporative cooling. We reported previously that water droplets freeze at deeply supercooled states,¹⁾ while EG droplets retain the liquid phase owing to heating by the thermal radiation at room temperature.²⁾ In the present study, we extend these studies toward the following two directions. (1) Size dependence of water droplets: We observed freezing processes of water droplets of 36–51 μm in diameter, which are smaller than 49–71 μm of the previous study.¹⁾ It was found with the aid of numerical simulation that smaller droplets freeze faster as well as at lower temperatures. (2) Effects of EG addition to water droplets: Addition of EG is expected to slow down the freezing. The present experiment on 38- μm droplets showed that the freezing time is 5.9, 10.3, and beyond 15 ms for pure water, a 1.3% EG mixture, and a 4.8% mixture, respectively (Fig. 1). This significant delay cannot be attributed only to depression of the vapor pressure but implies that changes in the heat capacity and the nucleation rate should be taken into account upon EG addition.

Keywords: Water Droplet; Evaporative Cooling; Freezing; Water–Ethylene Glycol Mixture

真空下で急速に蒸発冷却される液滴の熱力学過程に注目し、水液滴とエチレングリコール (EG) 液滴を取り上げて、凝固に至るまでの時間 (凍結時間) や凝固時の相転移温度について実験研究を行っている。これまでに、水液滴が過冷却深部で凝固すること¹⁾、一方で蒸気圧の低い EG 液滴は蒸発冷却と室温輻射の加熱効果が拮抗して液相を保つこと²⁾、などを見出した。本研究は、これら先行研究を次の2点について拡張した。(1) 水液滴のサイズ依存性: 直径 38 μm の水液滴は、Fig. 1 中の黒線 (凍結曲線) のように、発生後 5.9 ms で全体の 5 割が凍結した。同様の実験で、従来の 49–71 μm に加えて 36–51 μm の小さな水液滴の凍結過程を新たに観察した。その結果、時々刻々の温度変化の数値シミュレーションと合わせて、小さな液滴ほど短時間かつ低温で凝固することを見出した。(2) 水液滴への EG 混合効果: 短時間で凝固する水液滴に EG を添加すると、凍結が遅くなると予想される。この検証を目的に EG 混合水液滴を実験した結果、Fig. 1 のように、モル分率 1.3% では 5 割の凍結に 10.3 ms を要した。添加量を増すと凍結はさらに遅くなり、4.8% では 15 ms 後にも液相が保たれた。微量の混合が大きく影響した本結果は、EG 添加による蒸気圧の降下だけでは説明できず、比熱や凍結核生成速度の変化も考慮した考察を進めている。

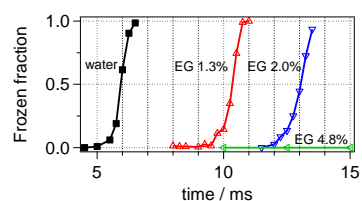


Fig. 1 Freezing curves of 38- μm droplets of pure water and EG mixtures. Molar fractions of EG are 0% (pure), 1.3%, 2.0%, and 4.8% for black, red, blue, and green plots, respectively.

1) K. Ando et al., *Phys. Chem. Chem. Phys.* **2018**, 20, 28435. 2) K. Ando et al., *Chem. Lett.* **2016**, 45, 961.

[A06-2pm] 08. Catalysts and Catalysis

Chair: Hiroshi Kominami, Haruno Murayama

Sat. Mar 20, 2021 1:00 PM - 3:20 PM Room 6 (Online Meeting)

- [A06-2pm-01] Photocatalytic hydrogen production by hybrid photocatalyst composed of layered niobate nanoparticles with multilayered Ru(II) dyes in the presence of redox mediators**
○Nobutaka Yoshimura¹, Atsushi Kobayashi², Masaki Yoshida², Tomoki Kondo³, Ryu Abe³, Masako Kato² (1. Graduate School of Chemical Science and Engineering, Hokkaido University, 2. Graduate School of Science, Hokkaido University, 3. Graduate School of Engineering, Kyoto University)
1:00 PM - 1:20 PM
- [A06-2pm-02] Photothermal Dry Reforming of Methane over Supported Rhodium Catalysts**
○Daichi Takami¹, Akira Yamamoto^{1,2}, Hisao Yoshida^{1,2} (1. Kyoto Univ., 2. ESICB, Kyoto Univ.)
1:20 PM - 1:40 PM
- [A06-2pm-03] Synthesis of porphyrin comprising nanodisks from covalent organic frameworks through mechanical stirring and investigation of their photocatalytic activity**
○XINXI LI¹, Yasuko Osakada¹, Mamoru Fujitsuka¹ (1. Osaka University)
1:40 PM - 2:00 PM
- [A06-2pm-04] Water oxidation over gold plasmonic photocatalyst modified with hole-transferring cocatalyst**
○Eri Fudo¹, Atsuhiko Tanaka^{1,2}, Hiroshi Kominami¹ (1. Kindai university, 2. JST PRESTO)
2:00 PM - 2:20 PM
- [A06-2pm-05] Synthesis and Photocatalytic Properties of Iron Disilicide/TiO₂ Composite Powder**
○Kensuke Akiyama¹, Sakiko Nojima¹, Hiroshi Irie² (1. Kanagawa Institute of Industrial Science and Technology, 2. University of Yamanashi)
2:20 PM - 2:40 PM
- [A06-2pm-06] Photocatalytic O₂ Evolution under Visible Light on a Bismuth-based Layered Oxyhalide SrBi₃O₄Cl₃**
○Daichi Ozaki¹, Hajime Suzuki¹, Osamu Tomita¹, Ryota Sakamoto¹, Ryu Abe¹ (1. Kyoto university)
2:40 PM - 3:00 PM
- [A06-2pm-07] Development of a visible-light responsive photocatalyst by enhancing the functionality of Ti-MOF and its application to photocatalytic hydrogen peroxide production**
○Yoshifumi Kondo¹, Yusuke Isaka¹, Yasutaka Kuwahara^{1,2,3}, Kohsuke Mori^{1,2}, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. PRESTO, JST)
3:00 PM - 3:20 PM

Photocatalytic hydrogen production by hybrid photocatalyst composed of layered niobate nanoparticles with multilayered Ru(II) dyes in the presence of redox mediators

(¹Hokkaido University, ²Kyoto University) ○Nobutaka Yoshimura,^{1*} Atsushi Kobayashi,¹ Masaki Yoshida,¹ Tomoki Kondo,² Ryu Abe,² Masako Kato¹

Keywords: Solar Water Splitting; Layered Metal Oxide Nanoparticle; Ru(II) Photosensitizer; Multilayering; Redox Mediator

Solar water splitting has attracted considerable attention as the promising reaction to generate clean and renewable energy resources such as H₂. High photo-induced charge separation efficiency is strongly required for the Z-scheme type photocatalysis involving redox-reversible electron mediator, to achieve highly efficient H₂ production. Herein, we prepared three types of Pt-cocatalyst-loaded layered niobium oxide K_xH_{4-x}Nb₆O₁₇ (LNO) nanoparticle (NP) photocatalysts¹⁾ with double-layered Ru(II) photosensitizers (PS)²⁾; Zr⁴⁺-phosphonate exposed type NP (Fig. 1; **ZrP-2Ru@LNO**), phosphonic acid exposed type NP (**P-2Ru@LNO**), and bipyridine exposed type NP (**2Ru@LNO**). The photocatalytic H₂ production was evaluated in the presence of KI or [Co(bpy)₃]SO₄ as the redox-reversible electron source in the aqueous solution under blue light irradiation (pH = 2, λ = 470 nm).

The **ZrP-2Ru@LNO** exhibited the highest activity (11.2 μmol / 6 h) in 0.5 M KI aq. (Fig. 2a), whereas **P-2Ru@LNO** was the best photocatalyst (11.8 μmol / 6 h) in 16 mM [Co(bpy)₃]SO₄ aq. (Fig. 2b). Zeta potential measurements suggested that the electrostatic interaction between the nanoparticle surface and electron donor is a key factor determining the photo-induced electron transfer kinetics. Details will be discussed.

1) R. Abe, *et al.*, *J. Am. Chem. Soc.* **2013**, 135, 16872

2) N. Yoshimura, *et al.*, *Chem. Eur. J.* **2020**, 26, 16939-16946.

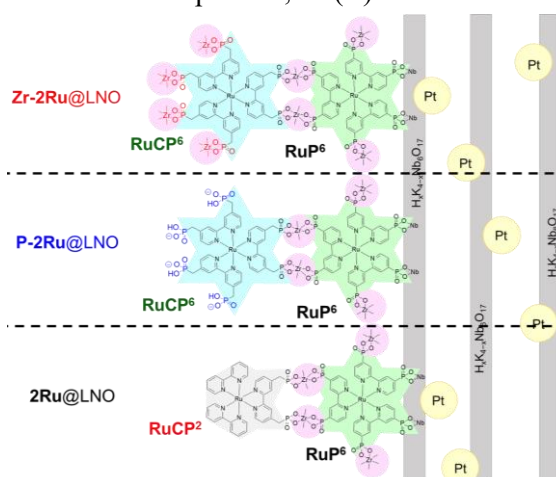


Fig. 1 Schematic structures of **X-2Ru@LNO**.

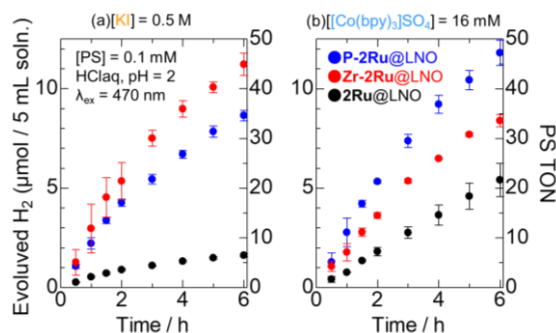


Fig. 2 Results of photocatalytic H₂ evolution by **X-2Ru@LNO** nanoparticles in (a) 0.5 M KI aq. and (b) 16mM [Co(bpy)₃]SO₄ aq.

担持ロジウム触媒による光熱変換型メタンドライリフォーミング反応

(京大人環¹・京大 ESICB²) ○高見 大地¹・山本 旭^{1,2}・吉田 寿雄^{1,2}

Photothermal Dry Reforming of Methane over Supported Rhodium Catalysts (¹Graduate School of Human and Environmental Studies, Kyoto University, ²Elements Strategy Initiative for Catalysts and Batteries, Kyoto University) ○Daichi Takami,¹ Akira Yamamoto,^{1,2} Hisao Yoshida^{1,2}

In terms of recycling of carbon dioxide, dry reforming of methane (DRM, $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$) is one of the promising technologies. However, it requires high temperature conditions around 1073 K to obtain the high conversion. Recently, light-driven DRM reaction has been investigated to utilize solar energy instead of the thermal energy from the heater. In this study, we found that supported rhodium catalysts showed high activity in the DRM reaction under visible and near-infrared light irradiation¹⁾. Besides, we performed the temperature evaluation of rhodium nanoparticles during the reaction using operant dispersive XAS measurements under light irradiation. As a result, the temperature of rhodium nanoparticles reached to over 600 K immediately after the start of the light irradiation (Fig. 1).

Keywords : Dry reforming of methane; Visible light; Photothermal; Rhodium; XAS

二酸化炭素の資源化の観点でメタンドライリフォーミング(DRM)反応は有用な反応である。一方で、高い転化率で反応を進行させるためには 1073 K 程度の高温条件を必要とする。このエネルギーを太陽光で賄うことを目指し、近年では光照射下での DRM 反応が研究されている。本研究では、可視・近赤外光照射下で担持ロジウム触媒が DRM 反応に高い活性を示すことを明らかにし¹⁾、反応中の金属ロジウムの温度を光照射下での Operant Dispersive XAS 測定から見積もることに成功した。Fig. 1 には、光照射下での触媒活性と温度測定の結果を示す。光照射開始から金属ロジウムの温度の急激な増加が確認された。光照射により、活性点である金属ロジウムが 600 K 以上まで高温化することが分かった。また、光照射開始と共に、生成物である CO と H₂ の生成が確認され、高温状態となった金属活性点を反応サイトとして DRM 反応が進行するものと考えられる。

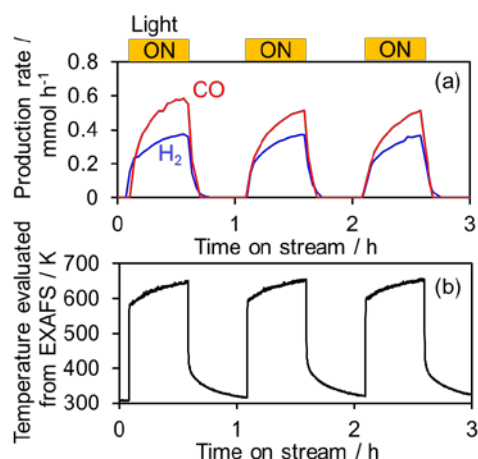


Fig. 1 The time profile of (a) the production rates of CO and H₂ and (b) the temperature evaluated from EXAFS spectra.

1) D. Takami, A. Yamamoto and H. Yoshida, *Catal. Sci. Technol.*, **2020**, 10, 5811.

Synthesis of porphyrin comprising nanodisks from covalent organic frameworks through mechanical stirring and investigation of their photocatalytic activity

(¹The Institute of Scientific and Industrial Research, Osaka University) ○Xinxi Li,¹ Yasuko Osakada,¹ Mamoru Fujitsuka¹

Keywords: Porphyrin; Covalent Organic Frameworks; Two-Dimensional Polymer; Photocatalysis; Nanomaterials

Two-dimensional (2D) materials such as graphene are attractive for applications in materials science, biology, energy storage, and photocatalysis. One of the simplest methods to synthesize 2D materials such as nanodisks from layered materials is liquid-phase exfoliation. In liquid phase exfoliation for the synthesis of 2D polymers, covalent organic frameworks (COFs) are commonly used as an exfoliating material because of their layered structure. In the previous studies, COFs with benzene or triphenylbenzene as core units were exfoliated by immersion or mechanical sonication in common solvents.¹ However, exfoliation of COFs containing porphyrin-like- π -conjugated molecular units is still difficult. Herein, we investigated the liquid-phase exfoliation of porphyrin-containing COFs using common solvents, and found that mechanical stirring is crucial for efficient exfoliation to obtain porphyrin-containing nanodisks (Figure 1).

Porphyrin-containing COFs were synthesized as previously reported by Banerjee *et al.*² The COFs and solvent (water, methanol, nitrobenzene, pyridine, etc.) were added into a flask and stirred for 20 hours at boiling point or room temperature to obtain the black samples (e-CONs(solvent)). We observed a considerable acceleration in hydrogen evolution reaction, 2 mmol g⁻¹ h⁻¹ of H₂ was generated from water using e-CONs(H₂O) as a photocatalyst, which is nearly five times higher than that by the original COFs.³

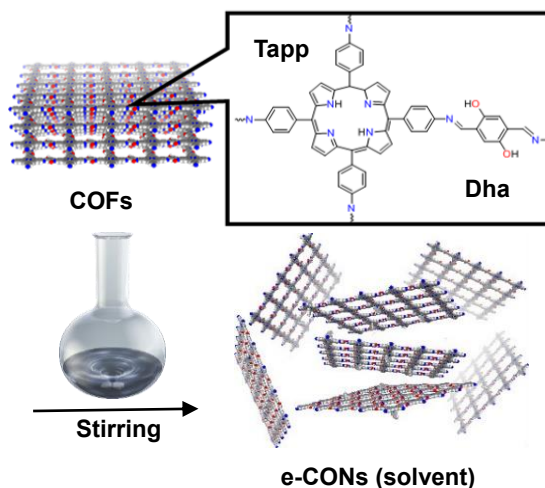


Figure 1. Structure of COFs and synthesis of e-CONs(solvent).

1) D.N. Bunck, W.R. Dichtel, *J. Am. Chem. Soc.*, **2013**, 135, 14952. 2) S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine, R. Banerjee, *Angew. Chem., Int. Ed.* **2013**, 52, 13052. 3) X. Li, T. Goto, K. Nomura, M. Zhu, T. Sekino, Y. Osakada, *Appl. Surf. Sci.*, **2020**, 513, 145720.

Water oxidation over gold plasmonic photocatalyst modified with hole-transferring cocatalyst

(¹ Graduate School of Science and Engineering, Kindai University, ² Faculty of Science and Engineering, Kindai University, ³ JST PRESTO) ○Eri Fudo,¹ Atsuhiko Tanaka,^{2, 3} Hiroshi Kominami²

Keywords: Water oxidation; Surface plasmon resonance; Au nanoparticles

In the water splitting system, it is known that water is a source of electrons for H₂ evolution. Therefore, it is especially important to improve photocatalytic activity of water oxidation for efficient artificial photosynthesis. A plasmonic photocatalyst is a new type of photocatalyst responding to visible light and shows photoabsorption at around 550 nm due to surface plasmon resonance (SPR). We achieved water oxidation over TiO₂ modified with Au and Pt NPs (Au/TiO₂-Pt) in the presence of an electron donor under irradiation of visible light.¹⁾ However, their photocatalytic activities were not high because of rapid recombination of holes and electrons. In the field of photoelectrochemistry, it is reported that TiO₂-Au-Ni(OH)₂ and TiO₂-Au-CrO_x photoelectrodes show efficient plasmon-induced charge separation under visible light and accumulate positive charges released from resonant Au nanoparticles.²⁾ In this study, we investigated whether a hole transfer cocatalyst is effective for the H₂O oxidation process over an Au plasmonic photocatalyst in a powder suspension system. We chose chromium(III) species (identified as Cr(OH)₃ in this study) as the hole transfer cocatalyst.

Figure 1 shows the rates of O₂ evolution over various samples in the presence of Ag⁺ as an electron scavenger. No O₂ was produced over TiO₂ and Cr(OH)₃/TiO₂ because no band-gap excitation occurred under irradiation of visible light. On the other hand, water was oxidized over Au/TiO₂ under visible light irradiation, resulting in plasmonic O₂ evolution, as was reported previously in the presence of another electron scavenger. We noted that introduction of Cr(OH)₃ increases the rate by two fold (0.38 to 0.78 μmol h⁻¹), *i.e.*, Cr(OH)₃ strongly contributes to the water oxidation over Au/TiO₂. In plasmonic oxidation of Pb²⁺, PbO₂ was deposited on Cr(OH)₃/Au, indicating that Cr(OH)₃ effectively works as a hole transfer cocatalyst.

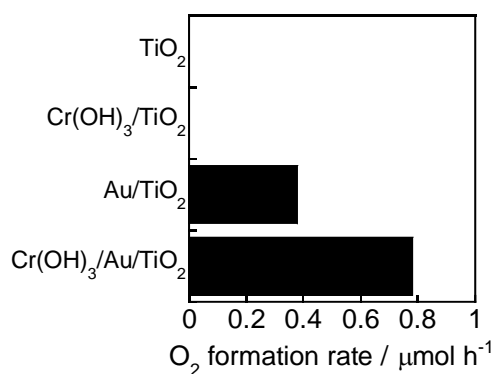


Figure 1 Rates of O₂ formation in aqueous suspensions of various photocatalysts under irradiation of visible light from a Xe lamp equipped with a Y48 cut-filter.

- 1) Tanaka *et al.*, *ACS Catal.*, **3**, 1886 (2013).
- 2) Kao *et al.*, *ChemNanoMat*, **5**, 1021 (2019).

鉄シリサイド／ルチル型酸化チタン複合粒子の光触媒効果による水分解

(神奈川産技総研¹・山梨大クリーンエネ研²) ○秋山賢輔¹・本泉 佑¹・長沼康弘¹・入江 寛²

Synthesis and Photocatalytic Properties of Iron Disilicide/TiO₂ Composite Powder

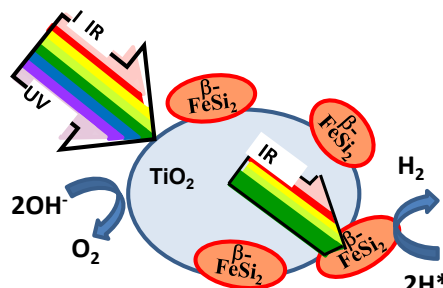
(¹ Kanagawa Institute of Industrial Science and Technology, ² University of Yamanashi, Clean Energy Research Center;) ○Kensuke Akiyama,¹ Yu Motoizumi,¹ Hiroshi Irie,²

Photocatalytic water-splitting is an ideal method for solar energy harvesting. Some photocatalysts that can split water under UV light have been discovered. However, development of visible-light sensitive photocatalysts is indispensable due to the effective utilization of incoming solar energy. On the other hand, semiconducting iron disilicide (β -FeSi₂) has a band gap of approximately 0.80 eV and a very large optical absorption coefficient over 1×10^5 /cm at 1 eV. Moreover, it has recently been reported that this semiconducting material acts as a hydrogen evolution photocatalyst. As a hydrogen-evolution photocatalyst, β -FeSi₂ is expected to enable the use of infrared light longer than 1300nm, which is the longest wavelength of light to be utilized. In this paper, we report on the novel fabrication method of β -FeSi₂ and rutile TiO₂ composite powder.

Keywords : Iron disilicide; Composite Powder; Photocatalysis

β -FeSi₂ は水素発生光触媒材料として報告されているが、バンドギャップが 0.8eV と小さいため単一粒子での水分解は困難である¹⁾。このため報告者は SiC 粒子表面に β -FeSi₂ ナノ結晶粒を合成した複合粒子を作製し、酸化犠牲剤のホルムアルデヒドを添加した水溶液中での光触媒効果による水素発生を報告した²⁾。本研究ではスパッタ法を用いてルチル型酸化チタン (TiO₂) 表面に β -FeSi₂ ナノ結晶粒が分散した複合粒子 (図 1) を作製し、この複合粒子を純水中で紫外光及びキセノン光照射により水素、及び酸素の発生を確認した。

Fig.1. Schematic diagram of β -FeSi₂/TiO₂ composite powder.



- 1) M. Yoshimizu, R. Kobayashi, M. Saegusa, T. Takashima, H. Funakubo, K. Akiyama, Y. Matsumoto and H. Irie, Chem. Comm., 51 (2015) 2818.
- 2) K. Akiyama, Y. Motoizumi, T. Okuda, H. Funakubo, H. Irie and Y. Matsumoto, MRS Advances 2 (2017) 471.

ビスマス系層状酸ハロゲン化物光触媒 $\text{SrBi}_3\text{O}_4\text{Cl}_3$ による可視光 O_2 生成反応

(京大院工) ○尾崎 大智・鈴木 肇・富田 修・坂本 良太・阿部 竜

Photocatalytic O_2 Evolution under Visible Light on a Bismuth-based Layered Oxyhalide $\text{SrBi}_3\text{O}_4\text{Cl}_3$ (*Graduate School of Engineering, Kyoto University*) ○Daichi Ozaki, Hajime Suzuki, Osamu Tomita, Ryota Sakamoto, Ryu Abe

Bismuth-based layered oxyhalides have recently emerged as promising photocatalysts for visible-light-induced water splitting.¹ Herein we disclose that a Sillén-type layered oxyhalide $\text{SrBi}_3\text{O}_4\text{Cl}_3$ (Fig. 1a) is a promising photocatalyst for visible-light-driven O_2 evolution. Previously reported SrBiO_2Cl and BiOCl , having single-halide and double-halide layers, respectively, absorb only UV light (Fig. 1b). In contrast, $\text{SrBi}_3\text{O}_4\text{Cl}_3$ with alternating single- and double-halide layers can absorb visible light. $\text{RuO}_2/\text{SrBi}_3\text{O}_4\text{Cl}_3$ exhibits stable activity for O_2 evolution under visible light (Fig. 1c), allowing visible-light-driven Z-scheme water splitting.

Keywords : Artificial Photosynthesis; O_2 Evolution Reaction; Z-scheme Water Splitting; Mixed-anion Compound; Oxyhalide

最近、ビスマス系層状酸ハロゲン化物群が可視光水分解用光触媒として有望であることが見出されている¹。本研究では、Sillén型の層状酸ハロゲン化物に着目し、ハライド層の積層パターンによってバンドギャップが大きく変化することを見出した。1層あるいは2層のハライド層しかもたない SrBiO_2Cl や BiOCl が紫外光しか吸収できないのに対し、1層と2層のハライド層が共存した $\text{SrBi}_3\text{O}_4\text{Cl}_3$ (Fig. 1a) は特異的に可視光吸収が可能であることが示された (Fig. 1b)。 $\text{SrBi}_3\text{O}_4\text{Cl}_3$ は可視光照射下で O_2 生成光触媒として機能し、特に $\text{RuO}_2/\text{SrBi}_3\text{O}_4\text{Cl}_3$ は、 Fe^{3+} 水溶液からの O_2 生成反応において、繰り返しほぼ量論量の O_2 生成が可能であった (Fig. 1c)。 $\text{RuO}_2/\text{SrBi}_3\text{O}_4\text{Cl}_3$ を O_2 生成系光触媒とし、可視光二段階励起型水分解を達成した。

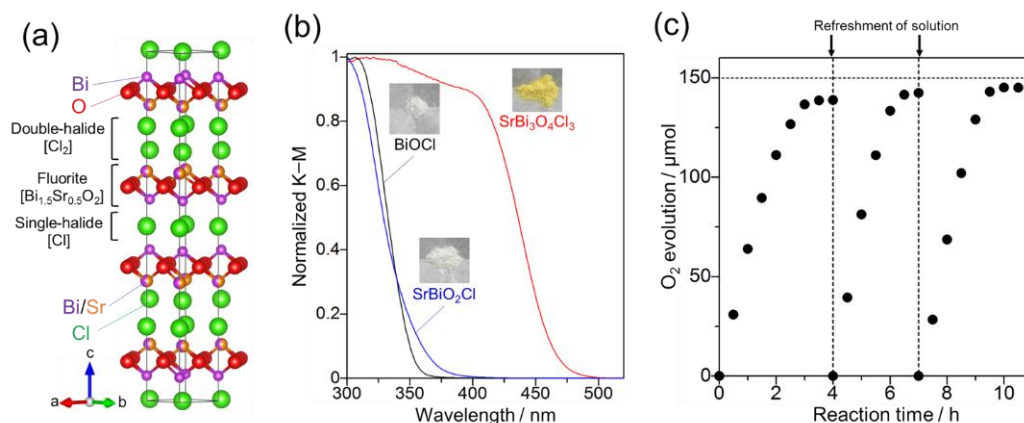


Fig. 1 (a) Crystal structure of $\text{SrBi}_3\text{O}_4\text{Cl}_3$. (b) UV-vis diffuse reflectance spectra of $\text{SrBi}_3\text{O}_4\text{Cl}_3$, SrBiO_2Cl and BiOCl . (c) O_2 evolution on $\text{RuO}_2/\text{SrBi}_3\text{O}_4\text{Cl}_3$ (100 mg) from $\text{Fe}_2(\text{SO}_4)_3(\text{aq})$ (5 mM as Fe^{3+} , 120 mL, pH 2.4) under visible light ($400 < \lambda < 800$ nm).

1) H. Fujito, H. Kageyama, R. Abe et al., *J. Am. Chem. Soc.* **2016**, *138*, 8.

Ti-MOF 高機能化による可視光応答型光触媒の創成と光触媒的過酸化水素生成への応用

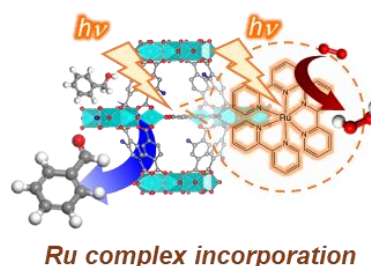
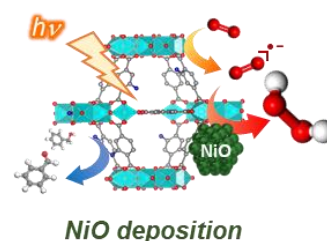
(阪大院工¹・京大 ESICB²・JST さきがけ³) ○近藤 吉史¹、井坂 祐輔¹、
桑原 泰隆^{1,2,3}、森 浩亮^{1,2}、山下 弘巳^{1,2*}

Development of a visible-light responsive photocatalyst by enhancing the functionality of Ti-MOF and its application to photocatalytic hydrogen peroxide production (¹Graduate School of Engineering, Osaka University, ²Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, ³JST PRESTO) ○Yoshifumi Kondo,¹ Yusuke Isaka,¹ Yasutaka Kuwahara,^{1,2,3} Kohsuke Mori,^{1,2} Hiromi Yamashita^{1,2}

Amine-functionalized Ti-based MOF, MIL-125-NH₂, was used as a photocatalytic material and applied to hydrogen peroxide production and benzyl alcohol oxidation under visible-light irradiation^{1,2}. Hydrogen peroxide was photocatalytically generated under visible-light irradiation utilizing MIL-125-NH₂. NiO deposited on MIL-125-NH₂ significantly enhanced the catalytic activity because of the ability of NiO to enhance the selectivity for the two-electron reduction of O₂ to H₂O₂. In addition, Ru complex incorporated into MIL-125-NH₂ (Ru(bpy)₃@MIL-125-NH₂) was synthesized and applied to benzyl alcohol oxidation under visible-light irradiation. The amount of produced benzaldehyde was much enhanced utilizing Ru(bpy)₃@MIL-125-NH₂ than the physical mixture of Ru complex and MIL-125-NH₂. The incorporation of Ru complex into MIL-125-NH₂ is indispensable to enhance the photocatalytic activity.

Keywords : Metal-Organic Framework; Photocatalyst

本研究ではアミノ基修飾 MOF の 1 つである MIL-125-NH₂ を光触媒材料とし、可視光照射下での H₂O₂ 生成やベンジルアルコール酸化を行った^{1,2}。MIL-125-NH₂ を用いた場合、可視光照射下で H₂O₂ が光触媒的に生成することを見出した。また、NiO を MIL-125-NH₂ に担持したところ、触媒活性が大幅に向上した。これは担持した NiO が酸素の 2 電子還元を選択性を向上させたためであると推察される。さらに MIL-125-NH₂ の細孔内に Ru 錯体を内包した光触媒材料を調製し、可視光照射下でベンジルアルコール酸化反応を行った。酸化生成物のベンズアルデヒド生成量は Ru 錯体と MIL-125-NH₂ の物理混合よりも大幅に増加した。つまり、Ru 錯体を MIL-125-NH₂ に内包することにより、優れた触媒活性を示すことが分かった。



1) Y. Isaka, Y. Kondo, Y. Kawase, Y. Kuwahara, K. Mori, H. Yamashita, *Chem. Commun.* **2018**, 54, 9270.

2) Y. Isaka, Y. Kondo, Y. Kuwahara, K. Mori, H. Yamashita, *Catal. Sci. Technol.* **2019**, 9, 1511.

[A07-2pm] 08. Catalysts and Catalysis

Chair: Satoru Takakusagi, Satoshi Muratsugu

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 7 (Online Meeting)

[A07-2pm-01] Theoretical suggestion of selective benzene hydroxylation in aqueous solution by Keggin-type polyoxometalate○Kei Ikeda¹, Yoshihito Shiota¹, Kazunari Yoshizawa¹ (1. Institute for Materials Chemistry and Engineering, Kyushu University)

1:00 PM - 1:20 PM

[A07-2pm-02] Preparation and Catalytic Selective Oxidation Performances of Rutile-type IrO₂ Nanoparticles○Satoshi Muratsugu¹, Takatoshi Sudoh¹, Satoru Ikemoto¹, Mizuki Tada^{1,2} (1. Dept. Chem. Nagoya Univ., 2. RCMS, Nagoya Univ.)

1:20 PM - 1:40 PM

[A07-2pm-03] High-density formation of metal/oxide interfacial active sites on a supported Ru-V catalyst prepared through hybrid clustering○Shun Hayashi¹, Tetsuya Shishido^{1,2} (1. Tokyo Metropolitan Univ., 2. ESICB, Kyoto Univ.)

1:40 PM - 2:00 PM

[A07-2pm-04] Grafting Method for Selective Formation of Bis-grafted Surface Species○Yusuke Ishizaka¹, Kazuhiro Matsumoto², Katsuhiko Takeuchi², Norihisa Fukaya², Kazuhiko Sato², Jun-Chul Choi^{1,2} (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science And Technology)

2:00 PM - 2:20 PM

[A07-2pm-05] Low Temperature Reduction of Subnano Copper Oxides for Catalytic Hydrocarbon Oxidations○Kazutaka Sonobe¹, Makoto Tanabe², Takane Imaoka^{1,2}, Wang Jae Chun³, Kimihisa Yamamoto^{1,2} (1. Tokyo Institute of Technology, 2. JST-ERATO, 3. International Christian University)

2:20 PM - 2:40 PM

[A07-2pm-06] Selective Hydroperoxygenation of Olefin Realized by Coinage Multimetallic Sub-nanocatalyst○Tatsuya MORI¹, Takamasa TSUKAMOTO^{1,2}, Makoto TANABE², Tetsuya KANBE^{1,2}, Takane IMAOKA^{1,2}, Kimihisa YAMAMOTO^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech, 2. JST-ERATO)

2:40 PM - 3:00 PM

[A07-2pm-07] Prolonging catalytic lifetime in MTO reaction over phosphorus-modified CHA zeolite○Nao Tsunoji¹, Ryora Osuga², Toshiyuki Yokoi² (1. Hiroshima University, 2. Tokyo Institute of Technology)

3:00 PM - 3:20 PM

[A07-2pm-08] Time-Resolved Dispersive-XAS Analysis of Molybdenum Complex as Key Species Toward Ammonia Formation

○Akira Yamamoto^{1,2}, Kazuya Arashiba³, Shimpei Naniwa¹, Kazuo Kato⁴, Hiromasa Tanaka⁵, Kazunari Yoshizawa⁶, Yoshiaki Nishibayashi³, Hisao Yoshida^{1,2} (1. Kyoto Univ., 2. ESICB, Kyoto Univ., 3. The Univ. of Tokyo, 4. JASRI, 5. Daido University, 6. Kyushu Univ.)

3:20 PM - 3:40 PM

Theoretical suggestion of selective benzene hydroxylation in aqueous solution by Keggin-type polyoxometalate

(Institute for Materials Chemistry and Engineering, Kyushu University) ○Kei Ikeda, Yoshihito Shiota, Kazunari Yoshizawa

Keywords: ruthenium-substituted Keggin-type polyoxometalate, benzene hydroxylation, Density functional theory, Orbital interaction, push-pull effect

Owing to the high toxicity of benzene and its derivatives, it is necessary to develop catalysts that decompose them in aqueous solution. Previously, Ru-oxyl complex catalyzing the oxidative cracking of benzene have been reported,¹ but there is a serious problem that Ru-oxyl species decomposes organic aromatic ligands itself and/or other Ru-oxyl complexes. Herein we focused on the benzene hydroxylation by Ru-substituted Keggin-type polyoxometalate $[\text{Ru}(\text{O})\text{XW}_{12}\text{O}_{39}]^{n-}$, namely **Ru^VOX**, (X = heteroatoms such as Al, Ga, Si, Ge, P, As and S) having robustness in aqueous solution and the oxidative-tolerant ligand. Since **Ru^VOX** also can catalyze water oxidation,² leading to the decreasing the selectivity of benzene hydroxylation in aqueous solution, we considered both reaction paths.

We found that the energy level of the unoccupied π^* orbital in $\text{Ru}^{\text{V}}=\text{O}$ acting as the frontier orbital in benzene hydroxylation reaction is stabilized by heteroatoms substitution (Figure (a) and (b)), leading to the decreasing of the activation energy for benzene hydroxylation reaction but not water oxidation. This stabilization is not “electron push-pull effect” but “geometrical push-pull effect” due to the depending on the bond distance between Ru and O_i ($\text{Ru}-\text{O}_i$) changed by the bond distance between heteroatoms and O_i . In addition, we confirmed the reaction rate ratio between benzene hydroxylation and water oxidation reactions ($r_{\text{B}}/r_{\text{W}}$) and found a good liner correlation ($R^2 = 0.98$) between $\log(r_{\text{B}}/r_{\text{W}})$ and distance in $\text{Ru}-\text{O}_i$ (Figure (c)). Our results demonstrated that **Ru^VOS** is the candidate of the selective benzene hydroxylation catalyst in aqueous solutions.³

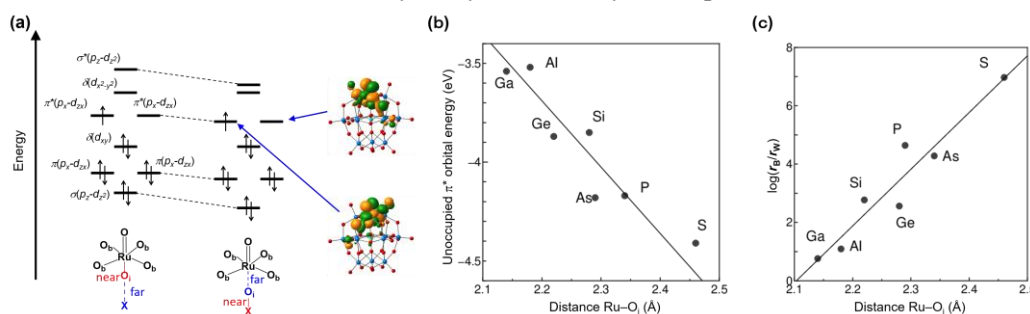


Figure. (a) Schematic orbital energy levels in $\text{Ru}^{\text{V}}=\text{O}$ species and π^* orbitals. Distance in $\text{Ru}-\text{O}_i$ versus (b) energies of unoccupied π^* orbitals ($R^2 = 0.88$) and (c) $\log(r_{\text{B}}/r_{\text{W}})$ values ($R^2 = 0.98$).

1) Y. Shimoyama, T. Ishizuka, H. Kotani, T. Kojima, *ACS Catal.* **2019**, 9, 671. 2) M. Murakami, D. Hong, T. Suenobu, S. Yamaguchi, T. Ogura, S. Fukuzumi, *J. Am. Chem. Soc.* **2011**, 133, 11605. 3) K. Ikeda, Y. Shiota, K. Yoshizawa, *to be submitted*.

Preparation and Catalytic Selective Oxidation Performances of Rutile-type IrO₂ Nanoparticles

(¹Graduate School of Science, Nagoya University, ²Research Center for Materials Science, Nagoya University) ○Satoshi Muratsugu,¹ Takatoshi Sudoh,¹ Satoru Ikemoto,¹ Mizuki Tada^{1,2}

Keywords: Iridium Oxide; Nanoparticle; Rutile; Selective Oxidation; O₂ Activation

The (110) surface of rutile-type IrO₂ is reported to be active for C-H bond activation (methane, propane, and cyclopropane oxidation)^[1-3] and NO oxidation^[4]; however, these researches are from the fields of surface chemistry^[1,3] and theoretical chemistry^[2,4]. We prepared rutile-type IrO₂ nanoparticles with (110) surfaces as real catalyst materials, and investigated their catalytic performances (selective oxidation performances using molecular O₂ as an oxidant).

The rutile-type nanoparticles were successfully prepared from iridium acetate as a starting material. XRD patterns revealed that the bulk phase was single rutile type structure with the existence of (110) surface, as was observed from TEM. BET surface area was ca. 20 m²g⁻¹, indicating that the size of the prepared rutile-type IrO₂ nanoparticles was much smaller than the commercially available rutile-type bulk IrO₂ (Wako Chemicals Co. Ltd.).

The catalytic selective oxidation performances using molecular oxygen were investigated on the prepared IrO₂ nanoparticles. The prepared rutile-type IrO₂ nanoparticles exhibited higher catalytic activity on the selective oxidation of xanthene (Conversion: >99%; Reaction conditions: xanthene (0.25 mol L⁻¹), IrO₂ (0.167 mmol), nonane (1.5 mL), IrO₂/xanthene/dodecane (internal standard) = 1/50/12.5 (molar ratio), O₂ (0.1 MPa), 373 K, 12 h) with 100% selectivity to xanthone compared to the commercially available rutile-type bulk IrO₂ (Wako Chemicals Co. Ltd.) (Conversion: 2%). This activity was also superior to the activity of the commercially available amorphous IrO₂ (Alfa Aesar Co. Ltd.) with similar surface area (Conversion: 56%). Facts that the reaction did not proceed only in the supernatant after the separation from the solid phase, and that Ir species was not leached in the supernatant after the complete conversion, suggested that the prepared rutile-type IrO₂ nanoparticles worked heterogeneously. The O₂ activation mechanism on the surface of the prepared rutile-type IrO₂ nanoparticles will also be presented.

1) Z. Liang, *et al. Science*, **2017**, 356, 299. 2) Y. Tsuji, *et al. J. Phys. Chem. C* **2018**, 122, 15359. 3) R. Martin, *et al. Phys. Chem. Chem. Phys.* **2018**, 20, 29264. 4) H. Yuan, *et al. ACS Catal.* **2018**, 8, 10864.

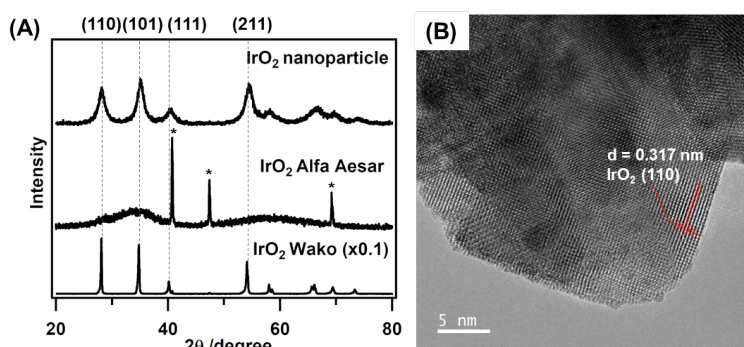


Figure 1. (A) XRD pattern (*: peaks attributed to Ir) and (B) TEM image of the prepared rutile-type IrO₂ nanoparticles.

High-density formation of metal/oxide interfacial active sites on a supported Ru-V catalyst prepared through hybrid clustering

(¹Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, ²ESICB, Kyoto University) ○Shun Hayashi,¹ Tetsuya Shishido^{1,2}

Keywords: Ruthenium, Vanadium, Hybrid cluster, Metal/oxide interface

The catalytic activities of heterogeneous catalysts depend not only on the intrinsic properties of the active (metal) species but also on the adjacent oxide species. Since the catalytic reactions prefer to take place at the interface between metals and oxides, forming a high density of metal/oxide interfaces is key to improving the activities. We focus on the possibility of hybrid clusters as catalyst precursors. The hybrid clusters are formulated as $[(M^1L)_xM^2_yO_n]$, in which metal ions (M^1) are bound to metal oxide clusters ($M^2_yO_n$) in the presence of organic ligands (L),¹ and thus can be viewed as the minimal building blocks of a metal/oxide interface. Therefore, we expected that catalysts prepared from the hybrid clusters would have a high density of metal/oxide interfaces. In this study, a supported Ru-V catalyst was prepared from a Ru-V hybrid cluster, $[\{Ru(cym)\}_4V_6O_{19}]$ (cym = *p*-cymene),² as a precursor. The effects of the preparation method on the local structures and catalytic performance are discussed with reference to typical Ru-V based catalysts.

The catalytic activity of Ru-V catalyst prepared through hybrid clustering was compared with conventional Ru-V catalysts using *N*-alkylation of amines with alcohols as a test reaction. The activity of the carbon-supported Ru-V catalysts depended on the mixing method (Figure 1). The physical mixing of V/C did not increase the activity of pristine Ru/C, suggesting that the formation of Ru/VO_x interface is essential for a high activity. The catalyst prepared through hybrid clustering showed higher activity than that prepared by co-impregnation of Ru(acac)₃ and VO(acac)₂ (acac = acetylacetonate) by one order of magnitude. These results suggest that the reaction likely takes place at the Ru/VO_x interface and hybrid clustering is the most efficient method of forming a high density of such interfaces. The local structures and the formation mechanism of the Ru/VO_x interfaces will be discussed orally according to *in-situ* X-ray absorption spectroscopy.

1) Putaj, P. *et al. Coord. Chem. Rev.* **2011**, 255, 1642. 2) Süss-Fink, G. *et al. Polyhedron* **1998**, 17, 2817.

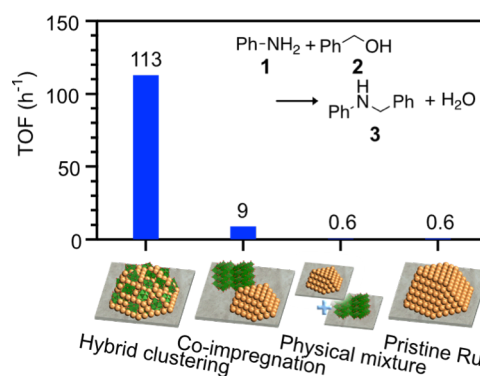


Figure 1. Effect of mixing method on the activity of Ru-V catalysts for *N*-alkylation of aniline (**1**) with benzylalcohol (**2**). Reaction condition: **1** (0.5 mmol), **2** (1.0 mmol), *p*-xylene (1 mL), catalyst (0.2 mol% Ru, V/Ru = 1.5), 413 K, 4 h, 1 atm Ar. All catalysts were prepared by calcination under an air flow at 573 K, followed by reduction under an H₂ flow at 573 K. TOF = $[3]/([Ru]_{total} \cdot \text{Time})$

Grafting Method for Selective Formation of Bis-grafted Surface Species

(¹Graduate School of Pure and Applied Sciences, University of Tsukuba, ²Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)) ○Yusuke Ishizaka,¹ Kazuhiro Matsumoto,² Katsuhiko Takeuchi,² Norihisa Fukaya,² Kazuhiko Sato,² Jun-Chul Choi^{1,2}

Keywords: Bis-grafted surface species; Surface organometallic chemistry; Platinum; Disilicate ligand; Substitution on ligand

Surface organometallics chemistry (SOMC) has been developed as one of attractive approaches to understand surface species in single-site heterogeneous catalysts.¹ In the SOMC, organometallic complexes often grafted by ligand exchange reactions with surface hydroxyl groups on oxide supports (Figure 1, top). However, by this grafting method, the heterogeneity on surface of oxide supports sometimes causes a formation of multiple surface species, which make the characterization of individual surface species difficult. To obtain single surface species, highly dehydroxylated oxide supports, which consist mostly of isolated hydroxyl groups, are frequently used to acquire mono-grafted surface species (Figure 1, bottom). On the other hand, the selective formation of bis-grafted surface species, which are assumed to exhibit different reactivities, have not been accomplished via SOMC.

In order to selectively form bis-grafted surface species on oxide supports, we designed a “pre-grafted precursor” (PGP) bearing a bidentate tetra-*tert*-butoxy disilicate ligand, $-\text{OSi}(\text{O}^t\text{Bu})_2\text{OSi}(\text{O}^t\text{Bu})_2\text{O}-$, which was grafted at silicon atom in the disilicate ligand (Figure 2). Two types of PGP platinum complex were synthesized and identified by NMR spectroscopy and X-ray crystallographic study. Thus-obtained PGPs were grafted on silica supports which were dried at 120 °C in vacuum to remove physisorbed water and the chemical structure of the surface species was evaluated by solid-state NMR spectroscopy. ¹³C CP/MAS NMR spectra showed peaks corresponding to a COD ligand, comparison of chemical shift values to those in a previous report indicated the selective formation of the desired bis-grafted surface species.²

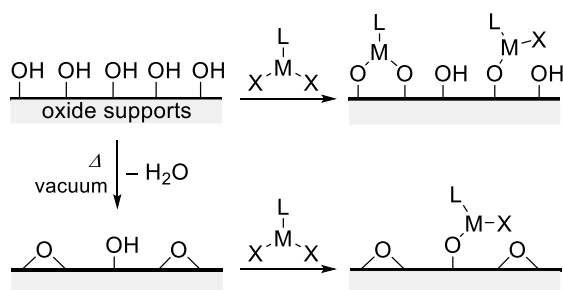


Figure 1. Conventional method to obtain single surface species.

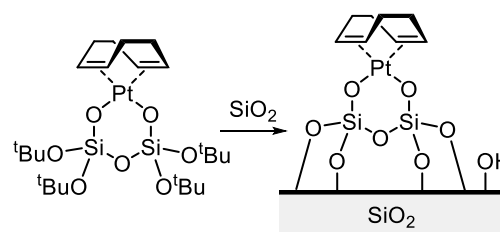


Figure 2. Grafting of pre-grafted precursor.

- 1) C. Copéret *et al.*, *Chem. Rev.* **2016**, *116*, 323. 2) C. Copéret *et al.*, *Dalton Trans.* **2013**, *42*, 238.

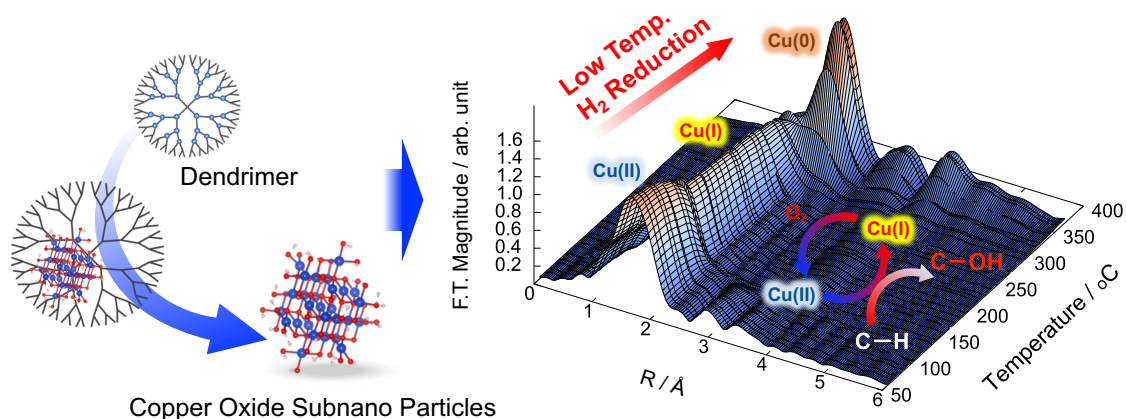
Low-Temperature Reduction of Subnano Copper Oxides for Catalytic Hydrocarbon Oxidations

(¹Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, ²JST-ERATO in Tokyo Institute of Technology, ³Department of Natural Sciences, International Christian University) ○Kazutaka Sonobe,¹ Makoto Tanabe,² Takane Imaoka,^{1,2} Wang Jae Chun,³ Kimihisa Yamamoto^{1,2}

Keywords: Subnanoparticles; Copper Oxide; Dendrimer; Catalytic Oxidation; Hydrocarbon

Metal oxide subnanoparticles have been attracted attention as remarkable active species in the catalytic property due to the large surface area and the irregular electronic polarization. Especially, the metal oxide subnanoparticles are expected as new active catalysts for hydrocarbon oxidations, which is one of the challenging issue in industrial chemistry. However, it is difficult to synthesize size-selected metal oxide subnanoparticles with conventional methods. Dendritic poly(phenylazomethine)s (DPA G4) exhibit an electronic gradient property from the core to terminal sites via the π -conjugated branched systems, which are suitable for the synthesis of subnano copper oxide particles in atomic-level precision.¹⁾ In recent work, we reported smallest size subnanoparticle (Cu_{12}O_x) achieved a large number of TON (= 3597) for 5 h, which was enhanced by particle size effect²⁾. In this work, we fabricate them by using the dendritic template and revealed their reactivity for basic redox reactions.

The STEM observation of the atom-specific copper oxide subnanoparticles shows that the particle sizes were maintained in c.a. 1.0 nm with narrower size distribution. The redox properties of the particles was revealed using *in-situ* X-ray absorption spectroscopy (XAFS), and copper oxide subnanoparticles shows steeply reduction of Cu(II) into Cu(I) at lower temperature than bulk or nanoparticle of copper oxides. This significant stabilization of Cu(I) state was only discovered in a subnano region.



1) K. Yamamoto, T. Imaoka, *Acc. Chem. Res.* **2014**, 47, 1127. 2) K. Sonobe, M. Tanabe, K. Yamamoto, *ACS Nano* **2020**, 14, 1804

Selective Hydroperoxygation of Olefin Realized by Coinage Multimetallic Sub-nanocatalyst

(¹ Lab. Chem. Life Sci., Tokyo Tech., ² JST-ERATO) ○ Tatsuya Moriai,¹ Takamasa Tsukamoto,^{1,2} Makoto Tanabe,² Tetsuya Kambe,^{1,2} Takane Imaoka,^{1,2} Kimihisa Yamamoto^{1,2}

Keywords: Dendrimer; Sub-nanoparticle; Coinage Metal; Hydroperoxygation Reaction; Catalyst

Although particles on a sub-nanometer (~ 1 nm) scale have attracted worldwide attention, precise synthesis of them has been difficult especially for multimetallic sub-nanoparticles (SNPs). For this obstacle, we recently developed the ‘atom-hybridization method (AHM)’ using the 4th generation phenylazomethine dendrimer (DPA G4) as a multiligand template¹. This macromolecule possesses the unique intramolecular potential gradient, thereby accumulates metal salts into its imine units from the inner layer stepwise. Subsequently, synthesis of SNPs with a controlled size is achieved by chemical reduction of metal salts assembled on the DPA G4. The synthesis of multimetallic SNPs is also realized by co-accumulation of various metal salts to each layer of the DPA G4.

In this study, we focused on exploring the reactivity of SNPs through a catalytic reaction². First, three types of coinage metals (Au, Ag, and Cu) were precisely co-accumulated to the DPA G4. Then, we succeeded in the synthesis of mono-, bi-, trimetallic SNPs with desired sizes and compositions (Fig. 1a and b). Finally, the catalytic activity of SNPs was systematically evaluated through the cyclohexene oxidation. As a result, Cu SNPs showed high catalytic performance even under the mild condition in contrast to conventional Cu catalysts (Fig. 1c). Moreover, the hybridization of Au and Ag to the Cu SNPs remarkably activated the catalytic activity, realizing the high selective hydroperoxygation of the cyclohexene. In conclusion, the unique chemical reactivity of 1-nm catalysts was revealed by the bottom-up synthetic approach applying dendrimer.

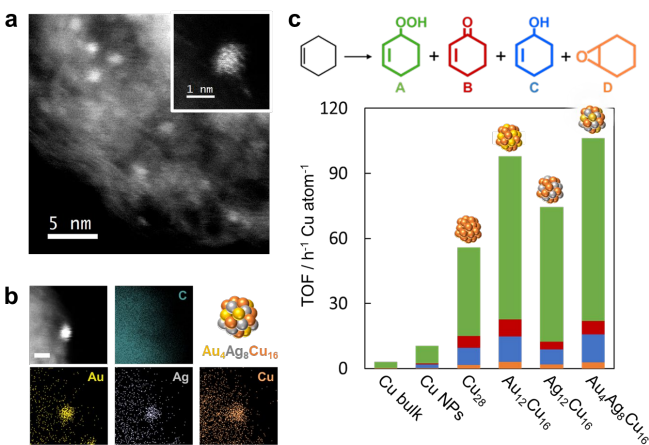


Fig. 1. **a** STEM images and **b** STEM/EDS mapping (scale bar: 2 nm) of the Au₄Ag₈Cu₁₆ SNPs supported on carbon. **c** Reaction products and TOFs per Cu atom of SNP catalysts obtained from the cyclohexene oxidation.

- 1) T. Tsukamoto, T. Kambe, A. Nakao, T. Imaoka, K. Yamamoto, *Nature Commun.* **2018**, 9, 3873.
- 2) T. Moriai, T. Tsukamoto, M. Tanabe, T. Kambe, K. Yamamoto, *Angew. Chem. Int. Ed.* **2020**, 59, 23051–23055.

リン修飾 CHA ゼオライトによる MTO 反応の触媒寿命延長

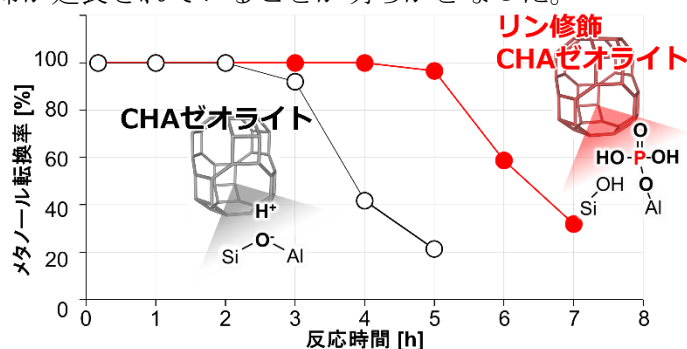
(広島大¹・東工大²) ○津野地 直¹・大須賀 遼太²・横井 俊之²

Prolonging catalytic life-time in methanol-to-olefin reaction by phosphorus-modified CHA zeolite (¹*Graduate School of Advanced Science and Engineering, Hiroshima University,* ²*Institute for Innovative Research, Tokyo Institute of Technology,*) ○Nao Tsunoji,¹ Ryota Osuga,² Toshiyuki Yokoi,²

By direct phosphorus modification using tetraethylphosphonium as a phosphorus-modifying agent (P-MA), phosphorus-modified CHA zeolite was synthesized and its catalytic performance for the methanol-to-olefin (MTO) reaction was investigated. We characterized the obtained samples with different degree of phosphorus modification using elemental analysis, X-ray diffraction (XRD), nitrogen adsorption, magic angle spinning NMR spectroscopy, and temperature-programmed desorption (TPD) with ammonia. Comparative catalytic testing demonstrated the effectiveness of the phosphorus modification for prolonging the catalyst lifetime while retaining the high light olefin selectivity. The relative amount of non-aromatic carbons retained in the zeolite catalysts after the MTO reaction increased with increasing degree of phosphorus modification, demonstrating that the suppression of excess oligomerization of the hydrocarbon species results in a prolonged lifetime.

Keywords : CHA zeolite; phosphorus modification; methanol to olefin reaction

テトラエチルホスホニウムを用いた直接リン修飾^{1,2}によって、リン修飾 CHA ゼオライトを合成し、その MTO 触媒特性を評価した。合成条件検討によってリン修飾度の異なる触媒を合成し、その触媒反応前後の物性評価を、元素分析、XRD、窒素吸着、マジック角回転 NMR および NH₃-TPD 測定により行った。いずれの触媒も高い低級オレフィンの選択性を示した一方で、リン修飾による触媒寿命の延長が明確に確認された。触媒反応後の析出炭素種の分析結果から、リン修飾度の増加に伴って、触媒中の炭素成分の芳香族性が低下しており、炭化水素種の過度なオリゴマー化が抑制されることで触媒寿命が延長されていることが明らかとなった。



1) Y. Yamasaki, N. Tsunoji, Y. Takamitsu, M. Sadakane, T. Sano, *Micropore. Mesopore. Mater.* **2016**, 223, 129.

2) Y. Kakiuchi, T. Tanigawa, N. Tsunoji, Y. Takamitsu, M. Sadakane, T. Sano, *Appl. Catal. A* **2019**, 575, 357.

室温アンモニア生成反応に有効な PNP 型ピンサー配位子を有する Mo 錯体触媒の時分割 Dispersive XAS 分析

(京大院人環¹・京大触媒電池²・東大院工³・JASRI⁴・大同大⁵・九大先導研⁶)

○山本 旭^{1,2}・荒芝 和也³・浪花 晋平¹・加藤 和男⁴・田中 宏昌⁵・吉澤 一成⁶・

西林 仁昭³・吉田 寿雄^{1,2}

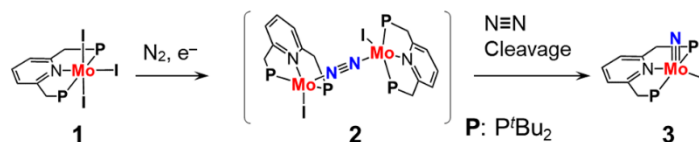
Time-Resolved Dispersive-XAS Analysis of Molybdenum-Dinitrogen Complex as Key Species toward Ammonia Formation (¹*Graduate School of Human and Environmental Studies, Kyoto University*, ²*Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University*, ³*Department of Applied Chemistry, School of Engineering, The University of Tokyo*, ⁴*Japan Synchrotron Radiation Research Institute (JASRI)*, ⁵*School of Liberal Arts and Sciences, Daido University*, ⁶*Institute for Materials Chemistry and Engineering, Kyushu University*)

○Akira Yamamoto,^{1,2} Kazuya Arashiba,³ Shimpei Naniwa,¹ Kazuo Kato,⁴ Hiromasa Tanaka,⁵ Kazunari Yoshizawa,⁶ Yoshiaki Nishibayashi,³ Hisao Yoshida^{1,2}

The molybdenum complex catalysts have been reported to be effective for the ammonia synthesis from dinitrogen at room temperature and ambient pressure in the presence of reductants and proton sources.^{1,2)} However, the key structure for the cleavage of the nitrogen–nitrogen triple bond (N≡N) of dinitrogen has not been experimentally elucidated. In this work, we performed a structural analysis of a reactive molybdenum complex bearing a PNP-type pincer ligand in the transformation of molybdenum triiodide complex ([MoI₃(PNP)], **1**; PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine) to the corresponding nitride complex ([Mo(≡N)I(PNP)], **3**) involving the cleavage of N≡N by *in-situ* dispersive XAS spectroscopy. We successfully obtained the spectrum of an unstable Mo complex at a low temperature of 198 K, and proposed the molecular structure based on the simulation results.³⁾

Keywords : Molybdenum complex; Ammonia Synthesis; Dispersive XAS; Low temperature

本研究では、PNP 型ピンサー配位子を有するモリブデン錯体触媒を用いた室温でのアンモニア合成反応^{1,2)}において、窒素分子の三重結合 (N≡N) の開裂の鍵となるモリブデン中間体錯体の構造を明らかにすることを目的として、SPring-8 での波長分散型 X 吸収分光法 (Dispersive XAS) を用いたモリブデン錯体のその場分析を行った。窒素分子の N≡N の開裂を伴うモリブデントリヨード錯体 (**1**) から対応するニトリド錯体 (**3**) への化学量論的な変換反応 (Scheme 1) 中の Mo K-edge XAS 分析から、198 K の低温条件でのみ観測されるモリブデン錯体のスペクトルを得ることに成功した。得られたスペクトルから、窒素分子の開裂における鍵中間体の構造を提案した。³⁾



Scheme 1. Proposed reaction mechanism of the N≡N cleavage of dinitrogen.

- 1) K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.*, **2011**, 3, 120.
- 2) Y. Ashida, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Nature*, **2019**, 568, 536.
- 3) A. Yamamoto, K. Arashiba, S. Naniwa, K. Kato, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, H. Yoshida, *Phys. Chem. Chem. Phys.*, **2020**, 22, 12368.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[A13-2am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Nobuhiro Yanai, Kazuya Otsubo, Ryuta Ishikawa

Sat. Mar 20, 2021 9:00 AM - 11:20 AM Room 13 (Online Meeting)

[A13-2am-01] Structures and Properties of Supramolecular Assemblies Constructed by Pyrizine Derived Ligand○Mikoto Uematsu¹, Ryuta Ishikawa¹, Satoshi Kawata¹ (1. Fukoka University)

9:00 AM - 9:20 AM

[A13-2am-02] Triboluminescence of pyridinophane copper complexes in crystals and polymers○ayumu karimata¹, Pradnya P Patil¹, Robert R Fayzulin², Eugene Khaskin¹, Sebastien Lapointe¹, Julia R Khusnutdinova¹ (1. okinawa institute of science and technology, 2. Arbuzov Institute)

9:20 AM - 9:40 AM

[A13-2am-03] Space-through charge transfer interactions in network complexes○Marie Okuyama¹, Hiroyoshi Ohtsu¹, Masaki Kawano¹ (1. Tokyo Institute of Technology)

9:40 AM - 10:00 AM

[A13-2am-04] Hyperpolarization of metal-organic frameworks utilizing photoexcited triplet electrons and its applications○Saiya Fujiwara¹, Kenichiro Tateishi², Tomohiro Uesaka², Keiko Ideta¹, Nobuo Kimizuka^{1,3}, Nobuhiro Yanai^{1,3,4} (1. Graduate School of Engineering, Kyushu University, 2. RIKEN, 3. Center for Molecular Systems, Kyushu University, 4. PRESTO, JST)

10:00 AM - 10:20 AM

[A13-2am-05] Syntheses, crystal structures and photophysical properties of C60 incorporated zinc porphyrin dimers○Kohei Ohwada¹, Minoru Mitsumi¹, Chiasa Uragami², Hideki Hashimoto² (1. Okayama Univ. of science, 2. Kwansei Gakuin Univ.)

10:20 AM - 10:40 AM

[A13-2am-06] Fused Porphyrin-Based Porous Crystals○Shun Suginome¹, Hiroshi Sato¹, Takuzo Aida^{1,2} (1. The Univ. of Tokyo, 2. Riken)

10:40 AM - 11:00 AM

[A13-2am-07] A platinum-dimer based metal- organic framework having a pre-installed cationic guest for proton conduction○Kazuya Otsubo¹, Shuya Nagayama¹, Kuniyoshi Sugimoto², Shogo Kawaguchi², Hiroshi Kitagawa¹ (1. Kyoto University, 2. JASRI/SPRING-8)

11:00 AM - 11:20 AM

Structures and Properties of Supramolecular Assemblies Constructed by Pyrizine Derived Ligand

(¹*Faculty of Science, Fukuoka University*) ○ Mikoto Uematsu,¹ Ryuta Ishikawa,¹ Satoshi Kawata¹

Keywords: Hydrogen Bond; Supramolecule

Crystal engineering, a study of manipulating packing structures of crystalline materials, has an aspect as a derivation of functionalities or physical properties. Especially, supramolecular coordination assemblies with hydrogen bonding network have often shown fascinating structures, dynamics, or functionalities. It is not only these individual factors but also correlations among them that attract most researchers.

One of the most effective strategies to obtain hydrogen bonding network in packing is to select a ligand with numerous hydrogen bonding acceptor sites in its structure. tdpd^{2-} (tdpd^{2-} = 2,3-dicyano-5,6-pyrazinediolate) is a pyrizine derived ligand with six hydrogen bonding acceptor sites in its structure, and, on account of these sites, numerous supramolecular assemblies have been generated.¹⁻³ In this research, six unprecedented supramolecular coordination assemblies constructed by tdpd^{2-} have been synthesized.

The obtained compounds can be divided into two types; tdpd mono formed systems (**1-4**) and bis formed systems (**5**, **6**). For mono formed systems, each has different assembled structures with different dimension; 1-D chain, 2-D sheet, and 3-D network, without hydrogen bonding network by H_2O molecules. Especially, for the 3-D network system, including Cu^{II} as a central metal ion, the EPR spectroscopic measurement indicates magnetic interaction among localized spins ($S = 1/2$) of Cu^{II} ions. On the other hand, both of the bis formed systems have hydrogen bonding networks by H_2O molecules in the 2D sheet-like assembled structure (Fig. 1) and along the 1D chains (Fig. 2), for **5** and **6**, respectively. To observe behaviors of H_2O molecules in the packings and structural dynamics of **5** and **6**, proton conductivities and water adsorption properties have been investigated. Proton conductivities at RH = 100% are $\sigma_{363\text{K}} = 4.493 \times 10^{-7} \text{ S cm}^{-1}$ with $E_a = 0.180 \text{ eV}$ and $\sigma_{363\text{K}} = 7.243 \times 10^{-7} \text{ S cm}^{-1}$ with $E_a = 0.139 \text{ eV}$ for **5** and **6**, respectively, and these values of E_a are attributed to Grothuss mechanism. Furthermore, the isotherm of **6** shows that the H_2O uptake increases with multi steps in the adsorption process, indicating structural changes with soaking H_2O molecules.

1) Y. Sugiyama, *CrystEngComm*, **2000**, 32, 1. 2) K. Adachi, *Chem. Chem. J.* **2005**, 11, 6616. 3) H. Kumagai, *Inorganics*, **2018**, 6, 115.

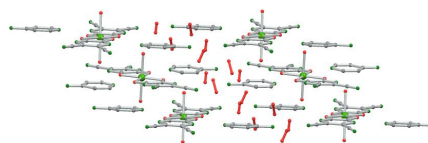


Fig.1 2D-Supramolecular Structure of **5**

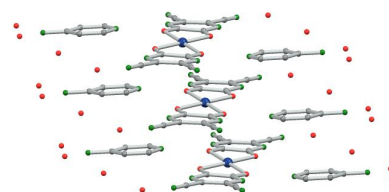


Fig.2 1D-Supramolecular Structure of **6**

Triboluminescence of pyridinophane copper complexes in crystals and polymers

(¹Okinawa Institute of Science and Technology, ²Arbuzov Institute) ○Ayumu karimata¹, Pradnya P Patil¹, Robert R Fayzulin², Eugene Khaskin¹, Sebastien Lapointe¹, Julia R Khusnutdinova¹

Keywords: Copper, Photoluminescence, Polymer, Triboluminescence, Mechanoresponsive materials

Triboluminescence (TL) is known as a light-emission caused by applying mechanical force on a material without photo-excitation. Many Eu and Tb complexes have been reported to show TL, while, there are extremely limited examples on triboluminescent Cu^I complexes. Our research group has studied luminescent pyridinophane (N4) Cu^I complexes¹ and their mechanoresponse in polymers². Recently new family of luminescent (N4)Cu^I(NHC)]X complexes **1**, **2**, and **3a–d** were prepared (Figure 1). The crystals show good photoluminescence efficiency (0.66–0.83) in the crystals and bright TL by grinding them even under air³. Piezoelectricity of crystal has been previously discussed in the literature as a factor to cause strong electric field that leads to excitation of molecule in crystal. However, TL of this luminescent Cu^I complex series is observed in both centrosymmetric and non-centrosymmetric crystals, as well as even in amorphous PMMA films. TL spectra of PMMA films containing 1 wt% of complex **1** were measured by rubbing the surface of the film using glass tube

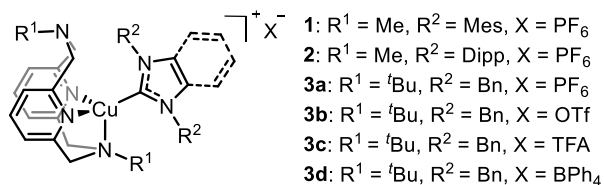


Figure 1. Chemical structure of N4Cu^I(NHC) **1**, **2**, and **3a–d**.

under atmosphere of various gases. In N₂, Ar, and He, intense gas discharge emission was observed (Fig. 2c), which was not observed in the crystal. TL is observed even under CO₂ and in vacuum, while emission is extremely weak or absent in SF₆ gas, implying that gas discharge mechanisms is involved in the excitation of the Cu^I complex in PMMA.

1) Patil, P. H.; Filonenko, G. A.; Lapointe, S.; Fayzullin, R. R.; Khusnutdinova, J. R. *Inorg. Chem.* **2018**, 57 (16), 10009. 2) A. Karimata, P. H. Patil, E. Khaskin, S. Lapointe, R. R. Fayzullin, P. Stampoulis, J. R. Khusnutdinova, *Chem. Commun.* **2020**, 56, 50. 3) A. Karimata, P. H. Patil, R. R. Fayzullin, E. Khaskin, S. Lapointe, J. R. Khusnutdinova, *Chem. Sci.* **2020**, 11, 10814.

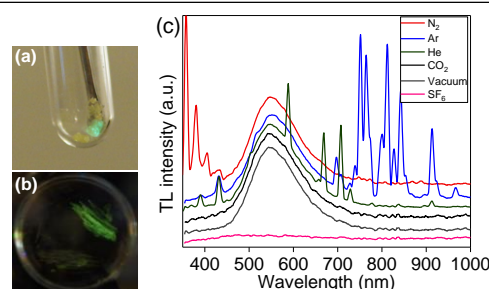


Figure 2. Images of TL of **1** (a) crystal and (b) PMMA film (10 wt%). (c) TL spectra of **1** in PMMA film under different gas (1 wt%).

ネットワーク錯体における空間を介した電荷移動相互作用の解明

(東工大理¹) ○奥山 万理恵¹・大津 博義¹・河野 正規¹

Space-through charge transfer interactions in network complexes

(¹*Department of Chemistry, School of Science, Tokyo Institute of Technology*) ○ Marie Okuyama,¹ Hiroyoshi Ohtsu,¹ Masaki Kawano²

Complexes including copper halides are interested in their luminescence behavior depends on the structure. If this unit is implemented into coordination network, it is expected to have high luminescence. In this study, by using T_d symmetric ligand TPPM= tetra-4-(4-pyridyl)phenylmethane and copper bromide cubane complex $[\text{Cu}_4\text{Br}_4(\text{PPh}_3)_4]$, two types of network complexes was obtained (**Network 1, 2**). Furthermore, a highly luminescent network complex (**Network 3**) was obtained by phase transition induced by heat. Crystal structure analysis revealed that the structure of highly luminescent network **3** have Cu(I) coordinated by four pyridyl unit of TPPM with tetrahedral geometry in its skeleton, in which $[\text{CuBr}_2]^-$ exists as a counter anion. We could also obtain the same network with other halides than Br⁻ which can be used for comparison of the nature of host guest interactions. The through space charge transfer was clarified from spectroscopic experiment and quantum chemical calculations.

Keywords : Coordination Networks; Through-space charge transfer; Copper halides

銅ハロゲンを含む錯体は構造に起因した発光挙動の変化に興味を持たれ、細孔性ネットワークを利用することで剛直な性質を生かした高発光性が期待される。本研究では T_d 対称配位子 TPPM = tetra-4-(4-pyridyl)phenylmethane と臭化銅キューバン型錯体 $[\text{Cu}_4\text{Br}_4(\text{PPh}_3)_4]$ を用いることで2種類のネットワーク錯体(**Network 1, 2**) が、さらに温度による相転移により新たな高発光性のネットワーク錯体(**Network 3**)が得られた。その高発光を示す構造は結晶構造解析により、 $[\text{CuBr}_2]^-$ がカウンターアニオンとして存在する、銅1価4配位構造を骨格に持つネットワーク錯体ということが分かった。このカウンターアニオンを別ハロゲン種のもものと比較し、空間を介した電荷移動遷移を有することを分光実験的、量子化学計算の両側面から明らかにした。

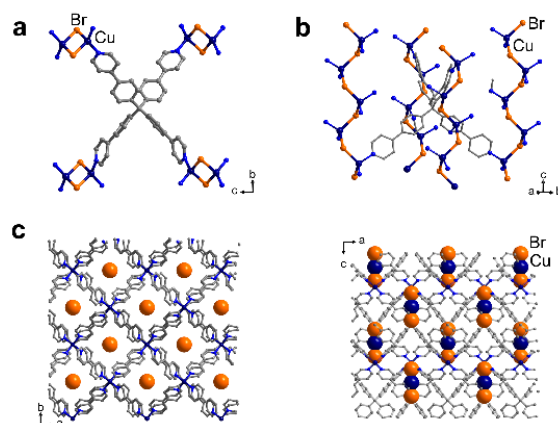


Figure 1. The crystal structure of (a) Network 1, (b) Network 2, and (c), (d) Network 3

Hyperpolarization of metal-organic frameworks utilizing photoexcited triplet electrons and its applications

(¹Graduate School of Engineering, Kyushu University, ²Center for Molecular Systems, Kyushu University, ³PRESTO, JST, ⁴RIKEN Nishina Center for Accelerator-Based Science)

○Saiya Fujiwara,¹ Kenichiro Tateishi,⁴ Tomohiro Uesaka,⁴ Keiko Ideta,¹ Nobuo Kimizuka,^{1,2} Nobuhiro Yanai,^{1,2,3}

Keywords: Dynamic nuclear polarization; Excited triplet state; Metal-organic framework

Nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) are versatile methods in modern chemistry and biology fields. Nevertheless, they suffer from intrinsically limited sensitivity due to the low nuclear spin polarization at ambient temperature. One of the promising methods to overcome this limitation is triplet dynamic nuclear polarization (triplet-DNP), which uses polarized triplet electrons produced by photo-excitation at room temperature. Triplet-DNP has provided high nuclear polarization enhancements, mainly in dense organic crystals such as *p*-terphenyl.¹ However, it remains difficult for such organic crystals to accommodate target molecules to be hyperpolarized.

To develop a triplet-DNP system with accessibility for a wide range of polarizing targets, we employ metal-organic frameworks (MOFs) as new host materials. We have reported the first example of triplet-DNP of prototypical MOF ZIF-8 at room temperature, proving the concept of using MOFs as ‘porous’ and ‘rigid’ hosts for triplet-DNP.² Recently, we have focused on the porous MOF MIL-53 showing guest-induced breathing behavior as a candidate to hyperpolarize small molecules of interest in NMR and MRI. In this presentation, we will report the generation of electron spin polarization in the MOF then discuss the triplet-DNP and nuclear polarization transfer from MOF to accommodated guest molecules.

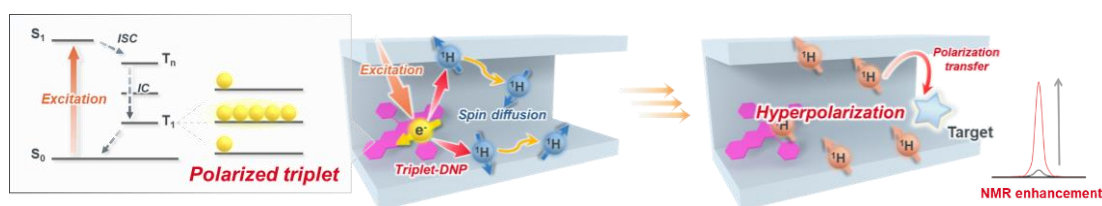


Figure 1. Schematic illustration of triplet-DNP in MOFs. Photoexcitation of the polarizing agent is followed by spin-selective intersystem crossing (ISC). The resulting electron spin polarization is transferred to nuclear spin.²

- 1) K. Tateishi, M. Negoro, S. Nishida, A. Kagawa, Y. Morita, M. Kitagawa, *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 7527–7530.
- 2) S. Fujiwara, M. Hosoyamada, K. Tateishi, T. Uesaka, K. Ideta, N. Kimizuka, N. Yanai, *J. Am. Chem. Soc.*, **2018**, *140*, 15606–15610.

フラーレン内包多孔性亜鉛ポルフィリンダイマーの合成, 結晶構造, 光物性

(岡山理科大院理¹・関西学院大院理工²) ○大和田晃平¹・満身 稔¹・浦上千藍紗²・橋本秀樹²

Syntheses, crystal structures and photophysical properties of C₆₀ incorporated zinc porphyrin dimers (¹Graduate School of Science, Okayama University of science, ² Graduate School of Science and Technology, Kwansei Gakuin University) ○Kohei Ohwada,¹ Minoru Mitsumi,¹ Chiasa Urugami,² Hideki Hashimoto²

To develop a photo charge-separation system with lifetime of the order of microseconds based on a porous metal complex, we are conducting developments of porous metal porphyrins with an acceptor incorporated in the pores. In this study, two types of zinc porphyrin dimers were synthesized to incorporate C₆₀ in the channel formed by self-assembled porphyrin dimers. We report syntheses, crystal structures, and photophysical properties of a C₆₀ incorporated zinc porphyrin dimer.

Keywords : Metal Organic Framework (MOF), Zinc porphyrin

当研究では, 多孔性金属錯体に基づくマイクロ秒オーダーの寿命を持つ光電荷分離システムの開発を目指し, アクセプターを内包した多孔性金属ポルフィリン錯体の合成と光物性評価を行なっている. これまでに, 多孔性亜鉛ポルフィリン錯体の細孔内にアクセプターとして C₆₀ を導入したフラーレン内包多孔性亜鉛ポルフィリン錯体の結晶化と X 線結晶構造解析に成功するとともに, その電荷分離寿命が 0.25 nsであることを明らかにしている¹⁾. 本研究では, 電荷分離の長寿命化を目指して, 亜鉛ポルフィリン錯体が形成するチャンネル内で C₆₀ を内包するために, 二種類の亜鉛ポルフィリンダイマー $\mathbf{1}, \mathbf{2}$ を新規に合成した(図1). 亜鉛ポルフィリンダイマー $\mathbf{1}, \mathbf{2}$ を用いて C₆₀ 内包多孔性亜鉛ポルフィリンダイマーの結晶化を行なったところ, 図2に示す $\mathbf{1} \cdot \text{C}_{60}$ を得ることができた. 本発表では, 二種類の亜鉛ポルフィリンダイマー $\mathbf{1}, \mathbf{2}$ の合成とともに, C₆₀ 内包多孔性亜鉛ポルフィリンダイマー $\mathbf{1} \cdot \text{C}_{60}$ の合成, 結晶構造解析, 光物性評価について報告する.

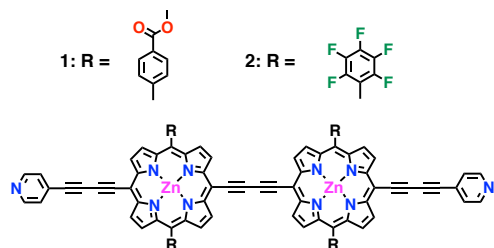


図1. 亜鉛ポルフィリンダイマー $\mathbf{1}, \mathbf{2}$.

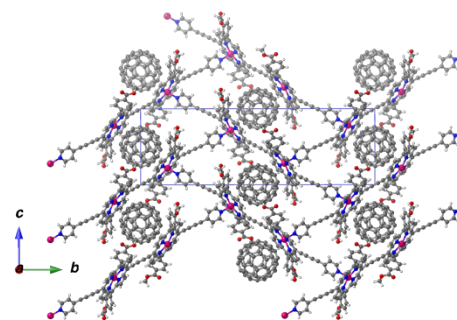


図2. $\mathbf{1} \cdot \text{C}_{60}$ の結晶構造.

1) 堀内ら, 錯体化学討論会第 65 回討論会, 3Fa-03, 2015.

Fused Porphyrin-Based Porous Crystals

(¹*School of Engineering, The University of Tokyo*, ²*JST-PRESTO*, ³*CEMS, RIKEN*) ○
Shun Sugimoto,¹ Hiroshi Sato,^{1,2} Takuzo Aida^{1,3}

Keywords: Porous Crystal; Metal–Organic Framework; Fused Porphyrin; π -Conjugation; Near Infrared Responsive

Porous crystals comprising extended π -conjugated systems have been actively studied in recent years.^{1,2} We have developed “adaptive nanographene MOF” which exhibits unique structural phase transition by cooperatively rotating its large and planer π -system upon guest uptake.¹

Among extended π -conjugated systems, fused porphyrins are attractive candidates for further developing adaptive porous crystals taking advantage of their multiple coordination sites as well as absorption in the near infrared (NIR) region.³ Herein, we will report the novel porous crystals composed of triply linked fused porphyrin and their NIR light responsive behavior.⁴

We newly synthesized a fused porphyrin-based dicarboxylic acid ligand (^{Fuse}LH₂, Fig. 1a). Dark purple colored ^{Fuse}MOF crystals were obtained by the reaction of ^{Fuse}LH₂ with Zn(NO₃)₂·6H₂O in *N,N*-diethylformamide. The single crystal structure of ^{Fuse}MOF revealed that ^{Fuse}L²⁻ is mutually connected with hexatopic Zn₄O clusters to form its cubic lattice (Fig. 1b). Interestingly, despite the use of the extremely long ligand, interpenetration doesn't take place due to the bulky substituents, affording huge void spaces corresponding to 86% of the crystal volume.

We carried out *in situ* microscopic observation upon NIR laser irradiation (Fig. 2). Surprisingly, a single crystal of ^{Fuse}MOF dispersed in DMF immediately shrank by 18% in volume upon NIR irradiation, and then it recovered the original size and shape, reversibly. We will present in detail about this intriguing phenomenon.

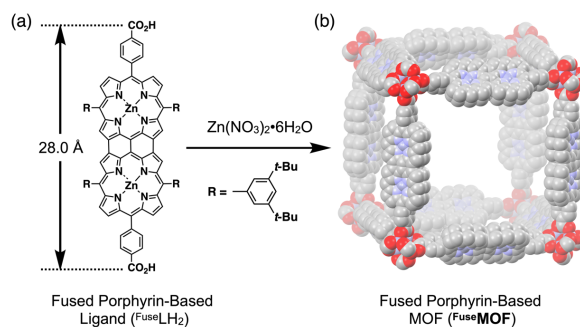


Fig. 1 (a) Structure of ^{Fuse}LH₂. (b) Crystal structure of ^{Fuse}MOF.

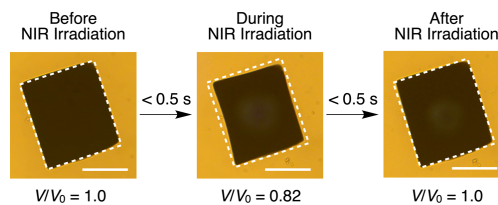


Fig. 2 Microscopic observation of ^{Fuse}MOF upon NIR laser irradiation (scale bar: 100 μ m).

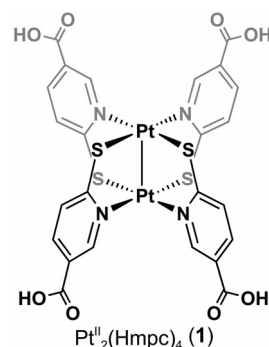
1) S. Sugimoto *et al.* *J. Am. Chem. Soc.* **2019**, *141*, 15649. 2) H. C. Zhou *et al.* *J. Am. Chem. Soc.* **2019**, *141*, 2054. 3) A. Tsuda and A. Osuka, *Science* **2001**, *293*, 79. 4) S. Sugimoto *et al.* to be submitted.

A platinum-dimer based metal–organic framework having a pre-installed cationic guest for proton conduction

(¹Grad. Sch. Sci., Kyoto Univ., ²JASRI/SPRING-8) ○Kazuya Otsubo,¹ Shuya Nagayama,¹ Kuniyoshi Sugimoto,² Shogo Kawaguchi,² Hiroshi Kitagawa¹

Keywords: Metal–Organic Frameworks; Proton Conduction; Platinum Dimer Complex; Synchrotron X-ray Diffraction

Solid-state proton conductors have been of particular interest of researchers because of its potential use for fuel cells. Among them, metal–organic frameworks (MOFs), which have networked structure made from metal ions and organic ligands have provided diverse research platform for proton conduction in recent years. In this work, we have newly synthesized a novel MOF based on the divalent platinum dimer complex with free carboxyl group, $\text{Pt}^{\text{II}}_2(\text{Hmpc})_4$ (**1**; H_2mpc = 6-mercaptopyridine-3-carboxylic acid).



Title MOF (**2**) was synthesized according to following reaction:

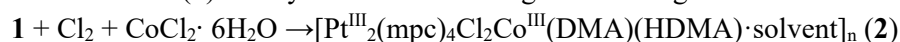


Figure 1 shows the X-ray crystal structure of **2** at 100 K. **2** crystallizes in monoclinic space group $P2_1/n$ ($a = 17.822(2)$, $b = 9.0411(8)$, $c = 30.291(3)$ Å, $\beta = 106.966(1)^\circ$, $V = 4668.4(8)$ Å³). In this framework, Co(III) ions are coordinated with three fourth of the carboxyl groups of the platinum dimer unit to form the 2D-layer structure. In addition, a dimethylammonium cation (HDMA) is trapped as a guest inside the pore through hydrogen bonding network with free carboxyl group of the ligand. Alternate current impedance measurement revealed a high proton conduction of 10^{-3} Scm^{-1} . Details are presented.

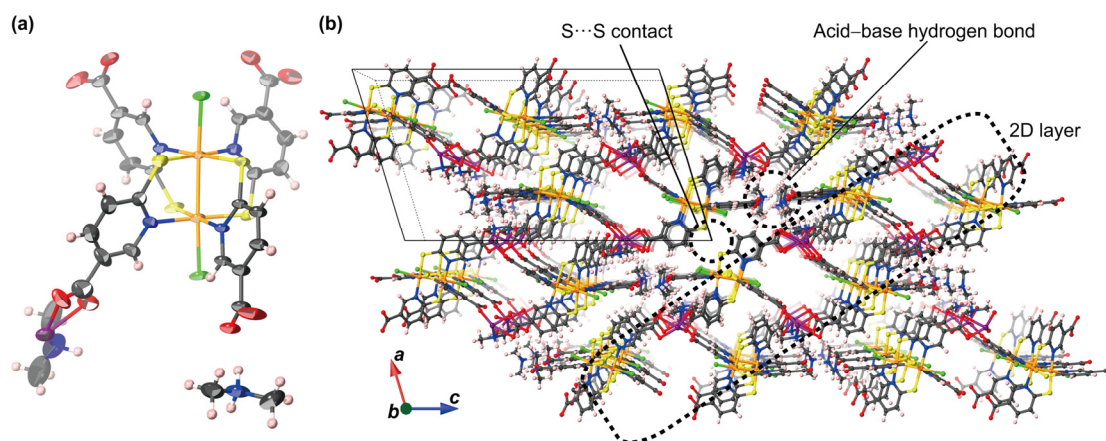


Figure 1. Crystal structure of **2** at 100 K. (a) Asymmetric unit of **2**. (b) 3D packing structure along the b -axis. Platinum, chlorine, carbon, nitrogen, oxygen, and hydrogen atoms are shown in orange, green, grey, blue, red and pink, respectively.

(1) H. Furukawa *et al.*, *Science*, **2013**, 341, 123044. (2) M. Sadakiyo, T. Yamada, H. Kitagawa, *J. Am. Chem. Soc.*, **2009**, 131, 9906. (3) G.K.H. Shimizu, J.M. Taylor, S. Kim, *Science*, **2013**, 41, 354. (4) M. Sadakiyo, T. Yamada, H. Kitagawa, *ChemPlusChem*, **2016**, 81, 691.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[A14-2am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Ryosuke Miyake, Toshiro Takao, Hisako Hashimoto

Sat. Mar 20, 2021 9:00 AM - 11:40 AM Room 14 (Online Meeting)

[A14-2am-01] Synthesis and luminescence properties of silver(I) halogenido coordination polymers bridged by pyrazine, methylpyrazine, and aminopyrazineTaiki Kuwahara¹, Hideki Ohtsu¹, Kiyoshi Tsuge¹ (1. University of Toyama)

9:00 AM - 9:20 AM

[A14-2am-02] Construction of Ni and Pd clusters using cyclooligosilane bearing aromatic substituentsKento Shimamoto¹, Yusuke Sunasa^{2,3} (1. The University of Tokyo, 2. IIS, The University of Tokyo, 3. JST PRESTO)

9:20 AM - 9:40 AM

[A14-2am-03] Synthesis of multinuclear Pd clusters having [2.2]paracyclophane ligandsTsuayoshi Sugawa¹, Ayaka Hatano¹, Koji Yamamoto¹, Tetsuro Murahashi¹ (1. Tokyo Institute of Technology)

9:40 AM - 10:00 AM

[A14-2am-04] Creation of a series of lanthanide cubane clusters inside single-crystals of an anionic Rh₄Zn₄ complex with L-cysteinateNobuto Yoshinari¹, Natthaya Meundaeng¹, Takumi Konno¹ (1. Osaka University)

10:00 AM - 10:20 AM

[A14-2am-05] Metal-induced folding and assembly through three-crossing peptidic unitsAmi Saito¹, Tomohisa Sawada^{1,2}, Makoto Fujita^{1,3} (1. Grad. School of Engineering, The Univ. of Tokyo, 2. JST PRESTO, 3. Institute for Molecular Science)

10:20 AM - 10:40 AM

[A14-2am-06] Creation of coordination polyhedra by collaborative metal–acetylene π -coordinationYuya Domoto¹, Masahiro Abe¹, Kidai Yamamoto¹, Makoto Fujita^{1,2} (1. The University of Tokyo, 2. Institute for Molecular Science)

10:40 AM - 11:00 AM

[A14-2am-07] Isolation of Mononuclear [Co(ligand)(CO)₃] Metalloradicals and Its H₂ Activation MechanismSatoshi Takebayashi¹, Robert R. Fayzullin (1. Okinawa Institute of Science and Technology Graduate University)

11:00 AM - 11:20 AM

[A14-2am-08] The Syntheses and Structures of Vanadium Complexes Bearing Triamidoamine Ligands with Bulky Substituents.Yoshiaki Kokubo¹, Yuji Kajita¹, Hideki Masuda¹ (1. Aichi Institute of Technology)

11:20 AM - 11:40 AM

Synthesis and Luminescence Properties of Silver(I) Halogenido Coordination Polymers Bridged by Pyrazine, Methylpyrazine, and Aminopyrazine

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

Keywords: Silver; Luminescence; Charge-transfer Transition; π - π^* Transition

Though luminescent Ag^{I} complexes have been prepared using various ligands, their number is still less than that of relating Cu^{I} complexes and characters of their emissive excited states (ESs) have not been well documented because of energetic competition between several possible emissive ESs. Here, aiming at the Ag^{I} complexes showing charge-transfer (CT) type emission, we utilized pyrazine (pyz), methylpyrazine (Mepyz) and aminopyrazine (ampyz) bearing a low-lying π^* orbital to obtain Ag^{I} complexes with the formula of $[\text{Ag}_2\text{X}_2(\text{PPh}_3)_2(\mu\text{-L})]_n$ (**AgX-L**: X = I, Br; L = pyz, Mepyz, ampyz).¹⁾

AgX-L were prepared as colorless single crystals by the reaction of AgX, PPh_3 , and excess amount of L in a mixed-solvent of CH_3CN and DMF. X-ray crystal structure analysis showed that the complexes are composed of $\{\text{Ag}_2\text{X}_2(\text{PPh}_3)_2\}$ units connected by L. All the complexes were strongly emissive at room temperature (Φ : 0.4 – 0.7) with the λ_{max} at around 500 nm (Table 1 and Figure 1). The blue-shift of the emission bands of **AgX-Mepyz** compared to those of **AgX-pyz** and their μs -order lifetimes imply that their emissive ESs are charge-transfer (CT) transitions from the $\{\text{Ag}_2\text{X}_2\}$ core to a π^* orbital of L. On the other hand, the ms-order lifetimes of **AgX-ampyz** indicated that their emissive ESs were not similar CT transitions although the blue-shift of their emission bands compared to those of **AgX-pyz** and **AgX-Mepyz** were expected one for CT type transitions. Because the emissive ESs of **AgX-bpy** (X = I, Br, Cl; bpy: 4,4'-bipyridine) have also been ascribed to the π - π^* transition in bpy,²⁾ those of **AgX-ampyz** were similarly ascribed to the π - π^* transition in ampyz. Due to the destabilization of the π^* orbital of the pyz ring by the amino group, the CT ES of **AgX-ampyz** was raised, which resulted in switching the lowest ES from CT to π - π^* one.

1) T. Kuwahara, *et al. Inorg. Chem. in print.* 2) M. Dosen, *et al. Inorg. Chem.* **2019**, 58, 8419.

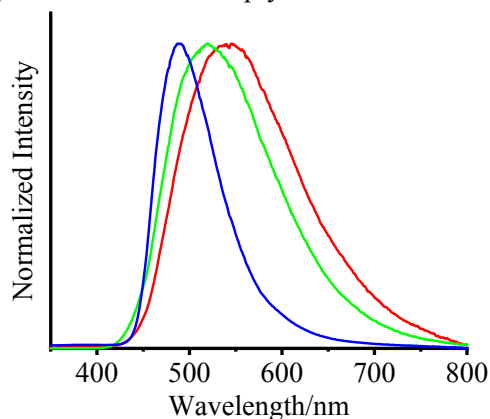


Figure 1. Emission spectra of **AgI-L** (L = pyz: red, L = Mepyz, green, L = ampyz; blue).

Table 1. Photophysical properties of **AgX-L**

L	X = I		X = Br	
	$\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$	$\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$
pyz	530	1.5	530	3.9
Mepyz	515	1.4	515	4.5
ampyz	490	1.0×10^3	490	5.4×10^3

Construction of Ni and Pd Clusters Using Cyclooligosilane Bearing Aromatic Substituents

(¹*School of Engineering, and* ²*Institute of Industrial Science, The University of Tokyo, ³JST PRESTO*) ○Kento Shimamoto¹, Yusuke Sunada^{2,3}

Keywords: Cluster, Organosilicon Compounds, Oxidative Addition

Transition metal clusters have attracted much attentions due to their characteristic reactivities realized by cooperative functions induced by multiple metal atoms. Thus a number of metal clusters have been synthesized, and unique reactions including activation of unreactive molecules have been described so far. In our research group, it was found that a series of palladium clusters can be facily constructed by the sequential insertion of palladium species into the multiple Si-Si bonds of organosilicon compounds. For instance, reaction of [Pd(CN^{*t*}Bu)₂]₃ with oligosilanes such as Ph₂ClSi-SiClPh₂ or bicyclic ladder polysilane led to the selective formation of Pd₆ or Pd₁₁ clusters, respectively.¹

In this presentation, we wish to report that treatment of cyclotetrasilane with nickel(0) precursor afforded a pentanuclear nickel cluster. The molecular structure determined by X-ray diffraction analysis revealed that unique bond activation reaction took place in the course of this reaction.

Cyclotetrasilane

bearing Ph groups as the substituents, Si₄Ph₈, was chosen as the oligosilane. Then, 5:7 mixture of Ni(cod)₂ and CN^{*t*}Bu was treated with Si₄Ph₈ in toluene at 60 °C for 48 h (Scheme 1). Dark red crystals of **1** was obtained after recrystallization from hexamethyldisiloxane, and the molecular structure of **1** was determined by X-ray diffraction analysis (Figure 1). Apparently, cluster **1** consists of five nickel atoms as well as four SiPh₂ moieties. It was found that C≡N bond of a CN^{*t*}Bu ligand was cleaved, and subsequent formation of a C=C bond occurred to form cluster **1**.

Scheme 1. Synthesis of **1**.

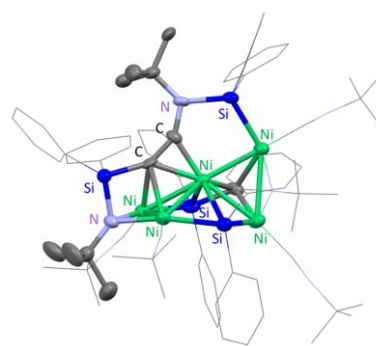
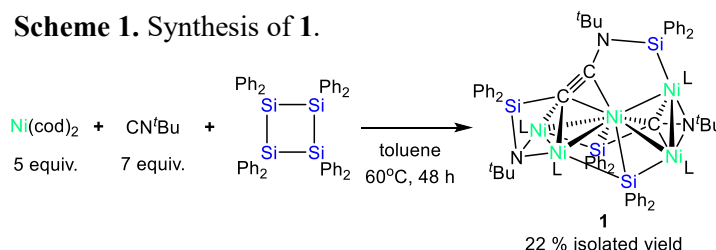


Figure 1. ORTEP view of **1**.

- 1) (a) Sunada, Y.; Haige, R.; Otsuka, K.; Kyushin, S.; Nagashima, H. *Nat. Commun.* **2013**, 4, 3014/1–3014/7; (b) Shimamoto, K.; Sunada, Y. *Chem. Eur. J.* **2019**, 25, 3761-3765.

Synthesis of multinuclear Pd clusters having [2.2]paracyclophane ligands

(School of Materials and Chemical Technology, Tokyo Institute of Technology) ○Tsuyoshi Sugawa, Ayaka Hatano, Koji Yamamoto, Tetsuro Murahashi

Keywords: Coordination chemistry, Palladium, Sandwich complex, Multinuclear cluster

Our group has developed the method to control the structures of metal clusters by using aromatic bridging ligands. For example, our group revealed that [2.2]paracyclophane behaves as the excellent bridging ligand for Pd₃ sandwich cluster (Figure 1, left).¹ Our group also recently reported synthesis of three-dimensional sandwich nanocube compounds supported by cycloheptatrienyl ligands (Figure 1, right).²

Herein we report synthesis and structure of three-dimensional multinuclear palladium clusters stabilized by [2.2]paracyclophane ligands.

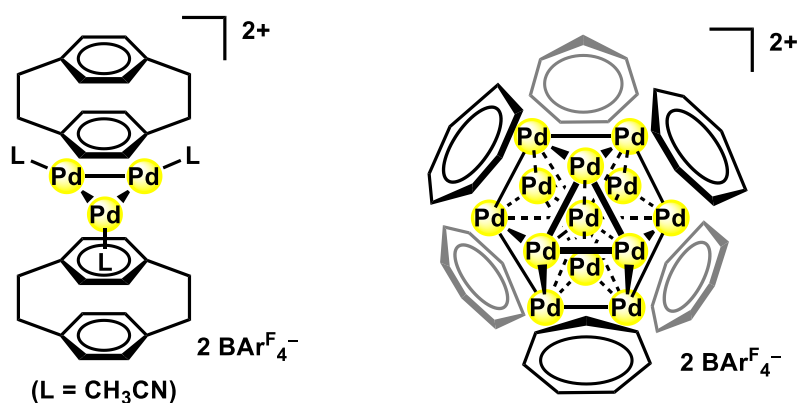


Figure 1. Pd₃ clusters supported by [2.2]paracyclophane ligands and Pd₁₃ cluster supported by cycloheptatrienyl

1) T. Murahashi, *et al.*, *Angew. Chem. Int. Ed.* **2007**, 46, 5440. 2) T. Murahashi, *et al.* *J. Am. Chem. Soc.* **2018**, 140, 12682.

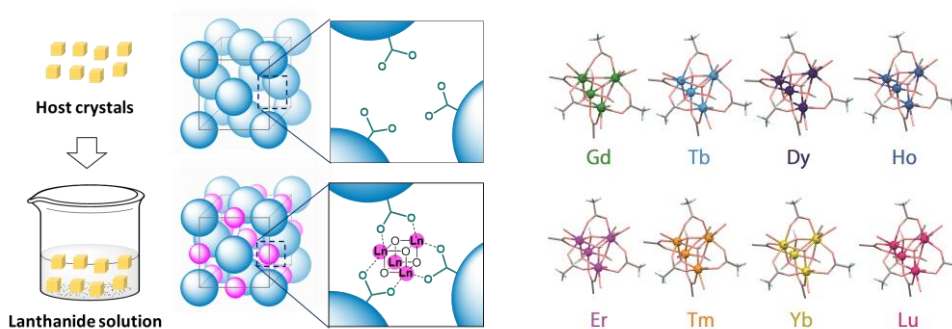
Creation of a series of lanthanide cubane clusters inside single-crystals of an anionic Rh_4Zn_4 complex with L-cysteinate

(¹Graduate School of Science, Osaka University) ○Nobuto Yoshinari,¹ Natthaya Meundaeng,¹ Takumi Konno¹

Keywords: Single-Crystal-to-Single-Crystal Conversion; Lanthanide Ion; Metal Hydroxide Clusters

The post-synthetic modification (PSM) of crystalline-materials has long attracted synthetic chemists and material scientists because it allows creating new compounds that are difficult to synthesize by conventional processes. Usually, such a solid-to-solid conversion needs a robust crystal lattice. Hence infinite materials, such as Zeolites and metal-organic-frameworks (MOFs), are widely explored as the host crystals. However, the PSM for the supramolecular crystals is relatively less explored due to their inherent instability. In this work, we report the creation of lanthanide cubane clusters inside a supramolecular crystal through PSM.¹⁾

As the host crystals, we employed the potassium salt of an octanuclear $\text{Rh}^{\text{III}}_4\text{Zn}^{\text{II}}_4$ complex anion with L-cysteine, $\text{K}_6[\text{Rh}_4\text{Zn}_4(\text{L-cys})_{12}\text{O}]\cdot n\text{H}_2\text{O}$.²⁾ Freshly prepared single-crystals of $\text{K}_6[\mathbf{1}]$ were immersed in an excess amount of $\text{Ln}(\text{OAc})_3$ ($\text{Ln} = \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Er}^{\text{III}}, \text{Ho}^{\text{III}}, \text{Tm}^{\text{III}}, \text{Yb}^{\text{III}}, \text{Lu}^{\text{III}}$) solution at room temperature. While the initial crystals $\text{K}_6[\mathbf{1}]$ were well-soluble in water, the resulting crystals $\mathbf{2}_{\text{Ln}}$ became insoluble in water with keeping single-crystallinity. Single-crystal X-ray analysis indicates that $\mathbf{2}_{\text{Ln}}$ involves cubane-type lanthanide hydroxide clusters, $[\text{Ln}_4(\mu_3\text{-OH})_4(\mu_2\text{-OAc})_3(\text{H}_2\text{O})_x]^{5+}$ and $[\mathbf{1}]^{6-}$ in a 1:1 ratio. Each lanthanide clusters are bound by three free carboxylate groups from $[\mathbf{1}]^{6-}$ through COO-Ln coordination bonds. As a result, the 3,3-connected **srs-b** type MOF structure is constructed. As far as we know, this is the first example of PSM from supramolecular crystals to MOFs by the installation of cationic species.



- 1) N. Yoshinari, N. Meundaeng, H. Tabe, Y. Yamada, S. Yamashita, Y. Nakazawa, T. Konno, *Angew. Chem. Int. Ed.* **2020**, *59*, 18048. 2) N. Yoshinari, S. Yamashita, Y. Fukuda, Y. Nakazawa, T. Konno, *Chem. Sci.* **2019**, *10*, 587.

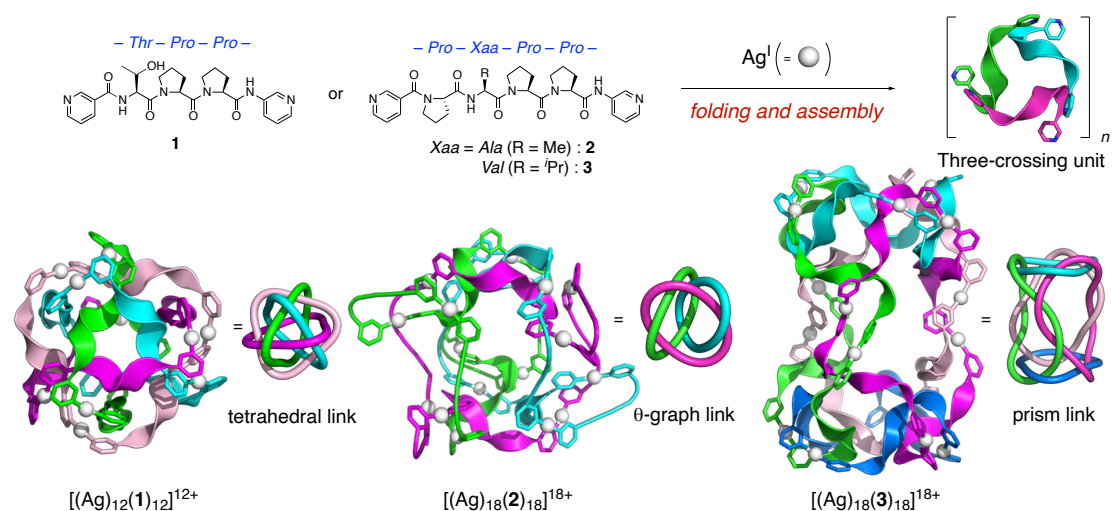
Metal-induced folding and assembly through three-crossing peptidic units

(¹Grad. School of Engineering, The University of Tokyo, ²JST PRESTO, ³Institute for Molecular Science) ○Ami Saito¹; Tomohisa Sawada^{1,2}; Makoto Fujita^{1,3}

Keywords: peptide, self-assembly, folding, metal complex, silver ion

In the field of molecular topologies, it has still been challenging to synthesize a molecular *polyhedral link*, which is a framework of multiple macrocycles interlocking in a polyhedral manner. In this work, we constructed such molecular polyhedral links by using a peptide-based three-crossing unit. During the course of studies on the folding-and-assembly method,^[1] which utilizes concomitant processes of short peptides folding and their metal-directed self-assembly, we found the combination of Ag(I) ions and a bis-pyridyl appended peptide ligand of the Thr-Pro-Pro sequence (**1**) gave a *tetrahedral link* framework based on a three-crossing unit. Moreover, we developed a series of polyhedral links by extending the peptide sequence.

First, complexation of ligand **1** and Ag(I) ions gave a self-assembled $[\text{Ag}_{12}(\mathbf{1})_{12}]^{12+}$ structure. Crystallographic study revealed the formation of a *tetrahedral link* framework, where four units of the three-crossing motif (**1**)₃ were self-assembled in *T* symmetry.^[2] We then designed the tetrapeptide sequences, Pro-Ala-Pro-Pro (**2**) and Pro-Val-Pro-Pro (**3**). Complexation of Ag(I) ions and ligands **2** and **3** gave the $[\text{Ag}_{18}(\mathbf{2})_{18}]^{18+}$ and $[\text{Ag}_{18}(\mathbf{3})_{18}]^{18+}$ complexes, respectively. Crystallographic studies revealed the formation of a *θ-graph link* that includes two units of three-crossing motif (**2**)₃ and a *triangular prism link* that consists of six units of three-crossing motif (**3**)₃, respectively. Thus, we succeeded in construction of a series of polyhedral links by extending the peptide sequence via the three-crossing unit design.



1) T. Sawada and M. Fujita, *Chem*, **2020**, 6, 1861–1876. 2) T. Sawada, A. Saito, K. Tamiya, K. Shimokawa, Y. Hisada, and M. Fujita, *Nat. Commun.*, **2019**, 10, 921.

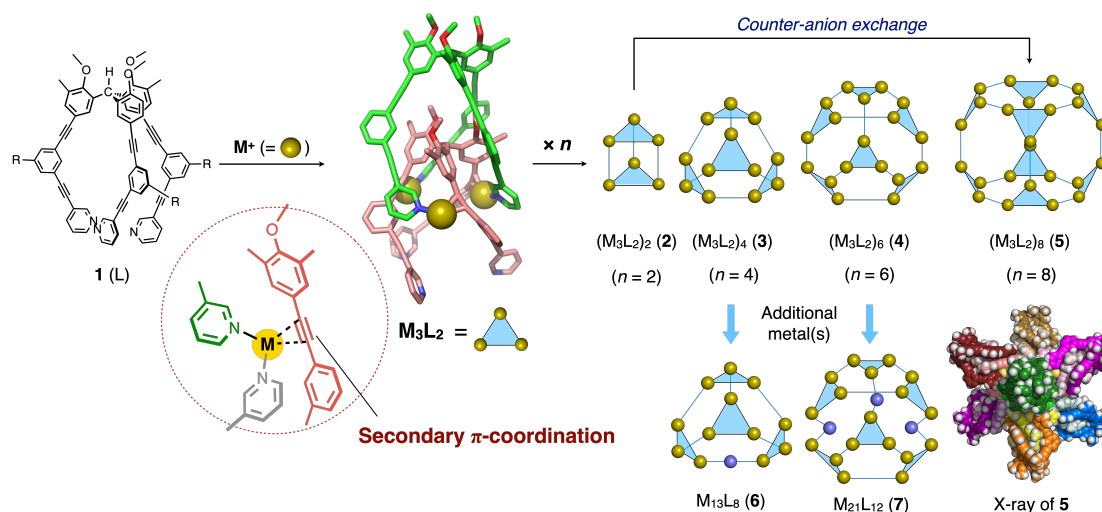
Creation of Coordination Polyhedra by Collaborative Metal–Acetylene π -coordination

(¹Graduate School of Engineering, The University of Tokyo, ²Institute for Molecular Science) ○Yuya Domoto,¹ Masahiro Abe,¹ Kidai Yamamoto,¹ Makoto Fujita^{1,2}

Keywords: Self-Assembly; π -coordination; Acetylenes; Silver Complexes; Molecular Cages

Acetylene π -coordination is a well-known weak interaction working in diverse organometallic transformations, while it has seldom been applied to metal-directed self-assembly in contrast to other coordination bonds such as relatively strong pyridyl or carboxylate coordination. We have recently elucidated that the self-assembly of propeller-shaped ligand **1** (L, R = H) and metal ions (M = Cu^I, Ag^I) afforded highly-entangled coordination polyhedra (M₃L₂)_n (**2-4**; $n = 2, 4, 6$), based on a key role of the acetylene spacers in **1** as weak secondary coordination sites upon metal binding at the primary pyridyl sites.^[1,2] Furthermore, the larger (M₃L₂)₈ (**5**) with a truncated cubic framework was also selectively constructed by post-assembly counter-anion exchange (BF₄ to NO₃) of (M₃L₂)₂ cage **2**. Flexible nature of acetylene π -coordination with weak directionality would realize the formation of a series of cage structures with high structural complexity, which emerge as a promising strategy for the construction of new classes of nanostructures.

We will also present (i) construction of hybridized cage frameworks (M₁₃L₈ (**6**) and M₂₁L₁₂ (**7**)) by additional metal insertion to (M₃L₂)_n polyhedra, and (ii) helicity control of the inherently chiral cage structures via accumulation of small chiral functional groups (R = (*S*)-2-alkoxy groups) on the frameworks, which also contain highly entangled substructures.



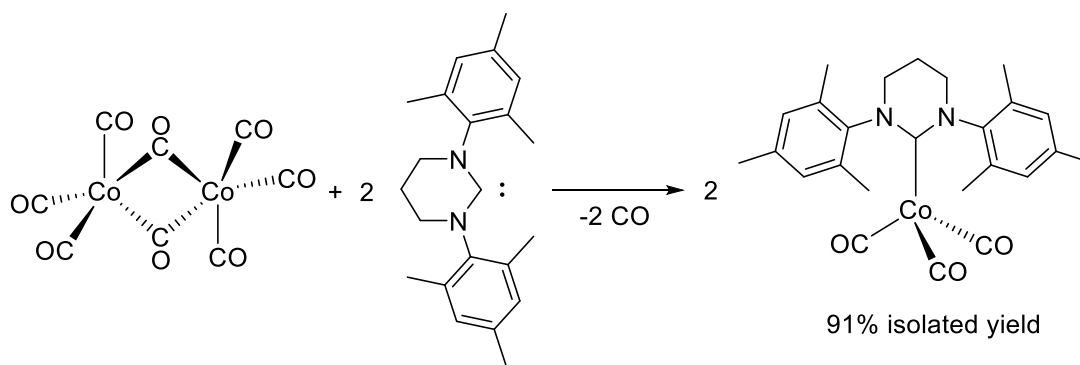
1) a) Y. Domoto, M. Abe, T. Kikuchi, M. Fujita, *Angew. Chem. Int. Ed.* **2020**, 59, 3450. b) Y. Domoto, M. Abe, K. Yamamoto, T. Kikuchi, M. Fujita, *Chem. Sci.* **2020**, 11, 10457.

Isolation of Mononuclear [Co(ligand)(CO)₃] Metalloradicals and Its H₂ Activation Mechanism

(¹Science and Technology Group, Okinawa Institute of Science and Technology Graduate University, ²Arbuzov Institute of Organic and Physical Chemistry) ○Satoshi Takebayashi,¹ Robert Fayzullin²

Keywords: Cobalt; NHC; Metalloradical; H₂ activation; Hydroformylation.

The dimeric cobalt (0) complexes [Co(ligand)(CO)₃]₂ (ligand = CO or PR₃) have been known as one of the most useful organometallic catalysts in industry since 1940s. Nowadays, long-chain alcohols are produced using [Co(PR₃)(CO)₃]₂-catalyzed hydroformylation of long-chain olefins.¹ [Co(ligand)(CO)₃]₂ is known to exist in equilibrium with a monomeric 17-electron metalloradical complex, [Co(ligand)(CO)₃], based on spectroscopic studies.² The termolecular reaction between two molecules of this metalloradical species and H₂ is proposed as a pathway to generate a key catalytic intermediate [HCo(ligand)(CO)₃].^{2,3} However, synthesis and isolation of the monomeric [Co(ligand)(CO)₃] is unknown, and because of that its reactivity towards H₂ have not been clarified. In this talk, I will present the first synthesis and isolation of the monomeric [Co(ligand)(CO)₃] complexes using N-heterocyclic carbene (NHC) ligands, as well as its H₂ activation mechanism.⁴



(1) Hebrard, F.; Kalck, P., *Chem. Rev.* **2009**, *109*, 4272-4282.

(2) Klingler, R. J.; Chen, M. J.; Rathke, J. W.; Kramarz, K. W., *Organometallics* **2007**, *26*, 352-357.

(3) Capps, K. B.; Bauer, A.; Kiss, G.; Hoff, C. D., *J. Organomet. Chem.* **1999**, *586*, 23-30.

(4) Takebayashi, S.; Fayzullin, R. R., *Organometallics* **2021**, DOI: 10.1021/acs.organomet.0c00765

Syntheses and Structures of Divanadium Complexes Bearing Triamidoamine Ligands with Bulky Substituents

(Faculty of Engineering, Aichi Institute of Technology) ○Yoshiaki Kokubo, Yuji Kajita, Hideki Masuda

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

The catalytic conversion reaction of atmospheric dinitrogen into ammonia using dinitrogen complexes has been attracted attention. We previously reported syntheses and characterizations of some dinitrogen-divanadium complexes with triamidoamine ligands bearing bulky substituents ($[\{V(L^R)\}_2(\mu-N_2)]$ ($R = iBu$ (**1**), $EtBu$ (**2**), iPr_2Bn (**3**), Bn (**4**), and $MeBn$ (**5**)).^{1,2} Their crystal structures revealed to be a divanadium complex with a bridging N_2 ligand. The protonation reactions of these complexes in the presence of reductant and proton source showed ammonia generation. However, the substituent effect for ammonia generations was not observed. Therefore, we have synthesized three triamidoamine ligands with isopropyl (**6**), 3-pentyl (**7**) or dicyclohexyl (**8**) groups as a bulkier substituent in order to examine the substituent effect on the coordinated N_2 . And we prepared three novel divanadium complexes by reacting $[VCl_3THF_3]$ with these ligands in Et_2O under N_2 . These complexes were obtained as dark green crystals by recrystallization from Et_2O or hexane under N_2 . Also, we carried out ammonia generation reactions using these complexes. For complex **6**, the crystal structure revealed a divanadium complex with a bridging N_2 ligand. The coordination geometry around each vanadium center is trigonal bipyramidal and the τ -value is 1.00. The $V-N_{N_2}$ and $N-N$ bond lengths are 1.7655(18) and 1.218(4) Å, respectively, whose bond lengths, when compared with those of **2** ($V-N_{N_2}$ (1.768(2) Å) and $N-N$ (1.221(4) Å)), indicated similar values despite a smaller number of C atoms. In the same way, complexes **7** and **8** were characterized by NMR, IR, and UV-vis spectroscopic and X-ray structure analyses. In this presentation, the syntheses and characterizations of divanadium complexes with a bulkier triamidoamine ligand will be described in detail.

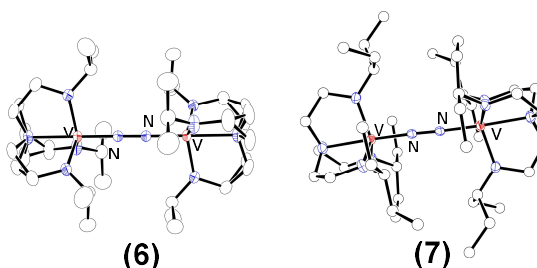
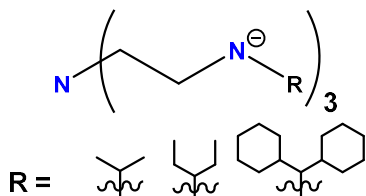


Figure 1. Structures of ligands prepared Figure 2. Crystal structures of complexes **6** and **7**

1) Y. Kokubo et al., *Inorg. Chem.* **2018**, 57, 11884-11894. 2) Y. Kokubo et al., *Eur. J. Inorg. Chem.* **2020**, 15, 1456-1464.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[A12-2am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Shogo Kuriyama, Hayato Tsurugi, Satoshi Abe

Sat. Mar 20, 2021 9:00 AM - 11:40 AM Room 12 (Online Meeting)

[A12-2am-01] *N*-Methylation of Amines *via* Reductive Carbon Dioxide Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes bearing a Nitrogen Tridentate Ligand○Koichi Shinohara¹, Hayato Tsurugi¹, Kazushi Mashima¹ (1. Graduate School of Engineering Science, Osaka Univ.)

9:00 AM - 9:20 AM

[A12-2am-02] Hydroaminoalkylation of Alkenes Using Titanium-Aluminum Catalysts○Mariko Inoue¹, Mai Mizukami¹, Tokiya Teraishi¹, Hayato Tsurugi¹, Kazushi Mashima¹ (1. Osaka University)

9:20 AM - 9:40 AM

[A12-2am-03] Development of C-N bond formation reactions from molybdenum-nitride complex with carbon-centered electrophiles directed toward formation of organonitrogen compounds○Takayuki Itabashi¹, Kazuya Arashiba¹, Shogo Kuriyama¹, Yoshiaki Nishibayashi¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[A12-2am-04] Theoretical Study on Nitrogen Fixation Catalyzed by Dinitrogen-Bridged Dimolybdenum Complexes Bearing Pincer-Type Ligands○Akihito Egi¹, Hiromasa Tanaka², Asuka Konomi¹, Yoshiaki Nishibayashi³, Kazunari Yoshizawa¹ (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. School of Liberal Arts and Science, Daido University, 3. School of Engineering, The University of Tokyo)

10:00 AM - 10:20 AM

[A12-2am-05] Manganese-catalyzed oxidative conversion of ammonia into dinitrogen○Hiroki Toda¹, Ken Sakata², Nishibayashi Yoshiaki¹ (1. The University of Tokyo, 2. Toho University)

10:20 AM - 10:40 AM

[A12-2am-06] Observation of CO release reaction in a crystalline Lysozyme-Mn(CO)₃ scaffold○Basudev Maity¹, Satoshi Abe¹, Eriko Nango², Rie Tanaka⁴, Mitsuo Shoji³, Yasuteru Shigeta³, Takafumi Ueno¹ (1. Tokyo Institute of Technology, 2. Tohoku University, 3. Tsukuba University, 4. RIKEN, SPring8)

10:40 AM - 11:00 AM

[A12-2am-07] Mechanistic study on rhenium-catalyzed ammonia formation from dinitrogen under mild reaction conditions○FANQIANG MENG¹, SHOGO KURIYAMA¹, HIROMASA TANAKA³, AKIHITO EGI², KAZUNARI YOSHIKAWA², YOSHIKI NISHIBAYASHI¹ (1. School of Engineering, The University of Tokyo, 2. Institute for Materials Chemistry and Engineering, Kyushu University, 3. School of Liberal Arts and Sciences, Daido University)

11:00 AM - 11:20 AM

[A12-2am-08] Durable photocatalytic reduction of carbon dioxide using ionic liquids

○Yasuomi Yamazaki¹, Yoshiyuki Asai¹, Riku Maruyama¹, Taro Tsubomura¹ (1. Seikei Univ.)

11:20 AM - 11:40 AM

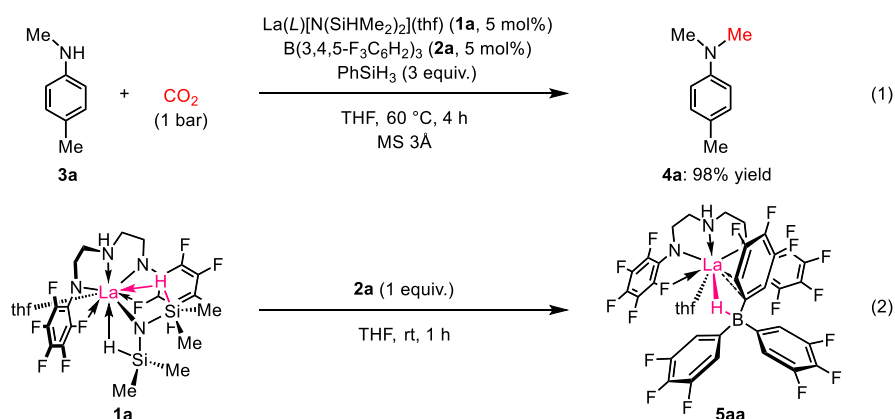
N-Methylation of Amines *via* Reductive Carbon Dioxide Fixation Catalyzed by Lanthanum Hydridotriarylborate Complexes bearing a Nitrogen Tridentate Ligand

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

Keywords: Carbon dioxide; Reduction; Lanthanum catalyst; Methylation; *N*-Methylaniline

Carbon dioxide is an inexpensive and nontoxic C1 resource for producing various chemical compounds. Reductive transformation of carbon dioxide have been developed by using many kinds of reductants, such as hydrosilanes, hydroboranes, and dihydrogen, to give formic acid, methanol, and methane.¹ Another transformation is the reduction of carbon dioxide in the presence of amines for accessing to *N*-methylamines.² Herein, we report that lanthanum complexes bearing *N,N'*-bis(pentafluorophenyl)diethylenetriamine dianion and a hydridotriarylborate anion serve as catalysts for the hydrosilylation of CO₂ in the presence of *N*-methylanilines to give the corresponding *N,N*-dimethylanilines.

We used La(*L*)[N(SiHMe₂)₂](thf) (**1a**: *L* = *N,N'*-bis(pentafluorophenyl)diethylenetriamine dianion) and an equimolar amount of various triarylboranes **2** for a catalytic *N*-methylation of *N*-methyl-*p*-toluidine (**3a**) under atmospheric pressure of CO₂ with PhSiH₃ (3 equiv.) in the presence of MS 3Å to afford *N,N*-dimethyl-*p*-toluidine (**4a**). After screening triarylboranes for the catalytic reaction, B(3,4,5-F₃C₆H₂)₃ (**2a**) was found to be the best in terms of catalytic activity and selectivity to afford **4a** in 98% yield (eq. 1). Concerning to a reaction mechanism, we conducted a stoichiometric reaction of **1a** with **2a** to yield a lanthanum hydridotriarylborate complex, La(*L*)[HB(3,4,5-F₃C₆H₂)₃](thf) (**5aa**), which showed almost the same catalytic activity as the *in-situ* mixture catalyst system (eq. 2). We disclose substrate scope as well as the influence of Lewis acidity of triarylboranes toward the catalytic activity.



1) F. J. Fernández-Alvarez, A. M. Aitani, L. A. Oro, *Catal. Sci. Technol.* **2014**, 4, 611. 2) Y. Li, X. Fang, K. Junge, M. Beller, *Angew. Chem., Int. Ed.* **2013**, 52, 9568.

Hydroaminoalkylation of Alkenes Using Titanium-Aluminum Catalysts

(Graduate School of Engineering Science, Osaka University)

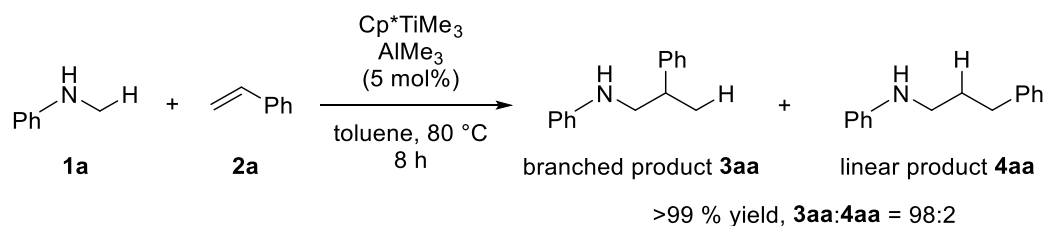
○Mariko Inoue, Mai Mizukami, Tokiya Teraishi, Hayato Tsurugi, and Kazushi Mashima

Keywords: Hydroaminoalkylation, Alkyltitanium, Alkylaluminum, C–H bond functionalization

β -Branched alkylamines are synthetically useful building blocks for producing biologically active compounds. One of ideal synthetic methods is metal-catalyzed branch selective hydroaminoalkylation of α -olefins *via* α -C–H bond activation of alkylamines. Homoleptic amidometal complexes of group 4 and 5 metals were reported by Nugent *et al.* as the first catalysts for the branch-selective hydroaminoalkylation of 1-pentene with HNMe_2 ,¹ and then various catalysts of group 4 and 5 metals have been developed; however, these catalysts often needed high temperature and elongated reaction time.² We here report that a combination of Cp^*TiMe_3 and AlMe_3 became an active catalyst with a high branch-selectivity for hydroaminoalkylation of alkenes with *N*-methylaniline derivatives.

Treatment of styrene and *N*-methylaniline in toluene at 80 °C in the presence of catalytic amounts of Cp^*TiMe_3 (5 mol%) and AlMe_3 (5 mol%) gave the corresponding β -branched hydroaminoalkylation product **3aa** and the corresponding linear product **4aa** in 98:2 ratio (Scheme 1). Trimethylaluminum plays an important role in both catalytic efficiency and selectivity; in the absence of AlMe_3 , we found low yield (12%) and low selectivity (branch:linear = 64:36) for hydroaminoalkylated products **3aa** and **4aa** even if Cp^*TiMe_3 (10 mol%) was employed. Other trialkylaluminum reagents such as AlEt_3 and Al^iBu_3 served well as effective additives with keeping a high branch-selectivity, whereas AlClEt_2 and $\text{Al}(\text{OEt})\text{Et}_2$ resulted in low activity and poor selectivity. We applied this $\text{Cp}^*\text{TiMe}_3/\text{AlMe}_3$ catalyst system for various 1-alkenes and 1,3-dienes, selectively producing the corresponding β -branched amines.

Scheme 1. Hydroaminoalkylation of Alkenes Catalyzed by Cp^*TiMe_3 and AlMe_3



[1] Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, 2, 161–162. [2](a) Chong, E.; Garcia, P.; Schafer, L. L. *Synthesis* **2014**, 46, 2884–2896. (b) Edwards, P. M.; Schafer, L. L. *Chem. Commun.* **2018**, 54, 12543–12560.

Development of C-N bond formation reactions from molybdenum-nitride complex with carbon-centered electrophiles directed toward formation of organonitrogen compounds

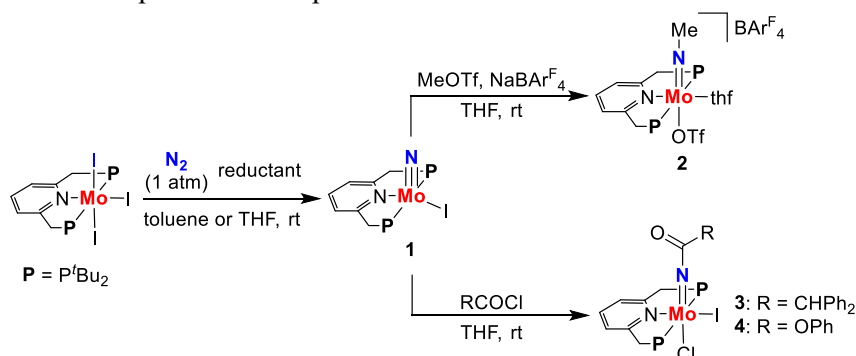
(Graduate School of Engineering, The University of Tokyo,) ○Takayuki Itabashi, Kazuya Arashiba, Shougo Kuriyama, Yoshiaki Nishibayashi,

Keywords: Molybdenum complex; Nitride complex; Pincer ligand; Nitrogen fixation; C-N bond formation

Transition metal nitride complexes are known to be as key intermediates in biological and chemical nitrogen fixation and as nitrogen atom transfer reagents for C-N bond formation reaction. Therefore, transformation of nitride complexes derived from dinitrogen into organonitrogen compounds is one of the promising routes to achieve C-N functionalization with dinitrogen.¹

Recently, we have found that molybdenum complexes bearing pincer type ligand cleaved the triple bond of the bridging dinitrogen ligand afforded terminal nitride complexes which worked as catalysts toward ammonia formation under ambient reaction conditions.² Focused on the molybdenum-nitride complex **1** derived from dinitrogen, we have investigated the reaction of complex **1** with carbon-centered electrophiles directed toward the formation of organonitrogen compounds other than ammonia.

Methylation of complex **1** with methyl triflate gave methylimide complex **2** in 58% yield. This result suggested that the terminal nitride ligand of nitride complex **1** has nucleophilic character and motivated us to use other electrophiles. Acylation of **1** with diphenylacetyl chloride and phenyl chloroformate afforded acetylimide complex **3** in 51% yield and carbamate complex **4** in 76% yield, respectively. Further transformation of these complexes will be explained in this presentation.



- 1) Masero, F.; Perrin, M. A.; Dey, S.; Mougel, V. *Chem. Eur. J.* **2020**, doi.org/10.1002/chem.202003134 2) a) Arashiba, K.; Eizawa, A.; Tanaka, H.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1111. b) Arashiba, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. *Chem. Eur. J.* **2020**, *26*, 13383.

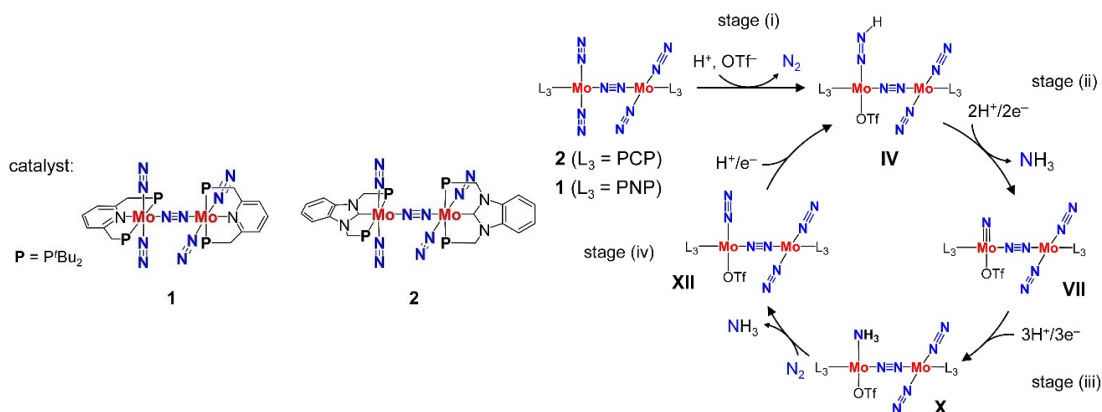
Theoretical Study on Nitrogen Fixation Catalyzed by Dinitrogen-bridged Dimolybdenum Complexes Bearing Pincer-Type Ligands

(¹*Institute for Materials Chemistry and Engineering, Kyushu University*, ²*School of Liberal Arts and Sciences, Daido University*, ³*School of Engineering, The University of Tokyo*)

○Akihito Egi,¹ Hiromasa Tanaka,² Asuka Konomi,¹ Yoshiaki Nishibayashi,³ Kazunari Yoshizawa¹

Keywords: Nitrogen Fixation; Molybdenum Complex; Density Functional Calculations; Bimetallic Complex, Ammonia

Density-functional-theory (DFT) calculations are carried out for the proposal of a theoretically-plausible reaction pathway for nitrogen fixation catalyzed by dinitrogen-bridged dimolybdenum complexes bearing pincer-type PCP and PNP ligands. The free energy profiles of the entire reaction pathway calculated with a dispersion-corrected functional provide a catalytic mechanism energetically more efficient than the previously proposed one.¹ In the newly-proposed mechanism, the dinuclear Mo–N≡N–Mo structure should be maintained during the catalytic cycle.² In spite of the coordination of the triflate (OTf) group with a strong electron-withdrawing ability, dinitrogen coordinated to a Mo^I center has higher reactivity with a proton donor than that coordinated to an electron-rich Mo⁰ center. This result enables us to propose a shortcut pathway, in which the regeneration of the dimolybdenum Mo⁰Mo⁰ complex is not required. Intermetallic electron transfer between two Mo cores induced by protonation effectively enhances the reactivity of coordinate N₂ with a proton donor. Our calculations reveal that the synergy of the Mo cores at the protonation step is essential for the catalytic performance of the dimolybdenum system.



1) H. Tanaka, K. Arashiba, S. Kuriyama, A. Sasada, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2014**, 5, 3737.

2) A. Egi, H. Tanaka, A. Konomi, Y. Nishibayashi, K. Yoshizawa, *Eur. J. Inorg. Chem.* **2020**, 1490-1498.

Manganese-catalyzed oxidative conversion of ammonia into dinitrogen

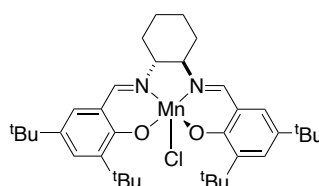
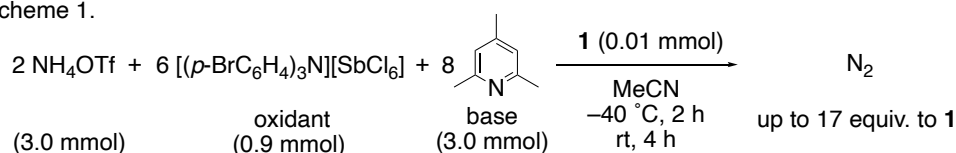
(¹Graduate School of Engineering, The University of Tokyo. ²Faculty of Pharmaceutical Sciences, Toho University.) ○Hiroki, Toda,¹ Ken Sakata,² Yoshiaki Nishibayashi¹

Keywords : Ammonia Oxidation; Catalytic Reaction; Energy Carriers; Manganese Complexes

Ammonia is a desirable candidate as an energy carrier toward a sustainable society because of its advantages such as easiness of handling, high energy density, and a carbon-free fuel.¹ Recently, for extraction of energy from ammonia, a few examples of catalytic oxidation of ammonia into dinitrogen using transition metal complexes have been reported.² To utilize ammonia as an energy carrier, oxidative conversion of ammonia into dinitrogen by base metal catalyst is an important transformation. Toward this goal, we have focused on manganese complexes bearing salen ligand (salen: *N,N'*-ethylene-bis(salicyldeneamine)) because these complexes have catalytic activity for several oxidation reactions such as epoxidation of olefins, benzylic oxidation, and sulfide oxidation.³

Herein, we report catalytic ammonia oxidation into dinitrogen by Mn(salen) complexes under chemical and electrochemical oxidation conditions (Scheme 1). A detailed reaction mechanism was investigated by the synthesis of intermediates and stoichiometric reactions using manganese intermediates, which suggests the formation of hydrazine complexes via attack of ammonia on monometallic imide complexes as key reactive intermediates. In addition, we also confirmed that proton-coupled electron transfer (PCET) occurs in the first oxidation step from electrochemical study.

Scheme 1.



1

[1] Guo, J.; Chen, P. *Chem* **2017**, *3*, 709. [2] a) Habibzadeh, F.; Miller, S. L.; Hamann, T. W.; Smith, M. R. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 2849. b) Bhattacharya, P.; Heiden, Z. M.; Chambers, G. M.; Johnson, S. I.; Bullock, R. M.; Mock, M. T. *Angew. Chem., Int. Ed.* **2019**, *58*, 11618. c) Nakajima, K.; Toda, H.; Sakata, K.; Nishibayashi, Y. *Nat. Chem.* **2019**, *11*, 702. d) Zott, M. D.; Garrido-Barros, P.; Peters, J. C. *ACS Catal.* **2019**, *9*, 10101. [3] Katsuki, T. *Synlett* **2003**, *3*, 281.

Observation of CO release reaction in a crystalline Lysozyme-Mn(CO)₃ scaffold

(¹Tokyo Institute of Technology; ²Tohoku University; ³Tsukuba University; ⁴RIKEN SPring-8 Center; ⁵MRC laboratory of molecular biology) ○ Basudev Maity,¹ Satoshi Abe,¹ Eriko Nango,² Mitsuo Shoji,³ Fangjio Luo⁴, Takanori Nakane⁵, Rie Tanaka,⁴ Yasuteru Shigeta,³ Takafumi Ueno¹

Keywords: Serial crystallography; Lysozyme protein crystal; CO release reaction.

Direct observation of a chemical reaction is important to explore the mechanism of the reaction. Current studies on this includes spectroscopy, structure determination and isolation of intermediates. However, it becomes complicated if the intermediate is transient or short-lived. Although ultrafast spectroscopic studies provide information about such species, structural assignments in those studies are mostly based on the theoretical spectrum of the model structures. Therefore, a suitable methodology is needed to see the reaction dynamics in real time and space. Recently, serial femtosecond crystallography has attracted significant attention for its ability to capture structural changes of proteins/enzymes up to femtosecond time intervals.¹⁻³ Such time-resolved serial crystallography has potential to study a chemical reaction with capturing short-lived intermediates or transient structural changes. However, the methodology has been applied mostly to explore the mechanism of natural protein/enzymes reactions and not extended to any synthetic chemistry reactions due to less diffraction spots, low solvent content, rigidity etc. of the small-molecules crystals. In order to overcome such issues associated with small-molecule reactions, we have fixed the reaction into a porous protein crystal to study their reactions by time-resolved serial crystallography. This presentation will describe the structural changes during the progress of a CO release reaction from an organometallic Mn-carbonyl complex fixed into the lysozyme protein crystal (Figure 1). Such methodology is expected to be applied to study the mechanism of less-explored reactions involved in synthetic chemistry as well as artificial metalloenzyme reactions.

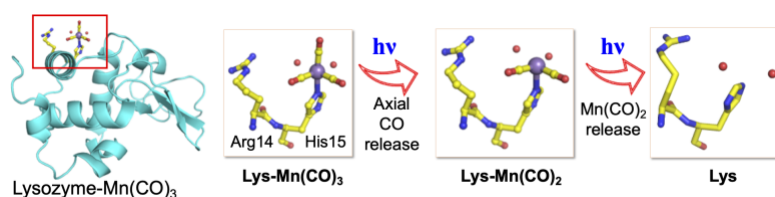


Figure 1: Structure of Lys-Mn(CO)₃ and CO release reaction pathway.

- 1) P. Fromme, *Nat. Chem. Bio.* **2015**, *11*, 895-899.
- 2) E. Nango, A. Royant, M. Kubo, T. Nakane, C. Wickstrand, T. Kimura, T. Tanaka, T. Kensuke, C. Song, R. Tanaka et al. *Science*, **2016**, *354*, 1552-1557.
- 3) T. Tosha, T. Nomura, T. Nishida, N. Saeki, K. Okubayashi, et al. *Nat. Commun.* **2017**, *8*, 1585.

Mechanistic Study on Rhenium-Catalyzed Ammonia Formation from Dinitrogen under Mild Reaction Conditions

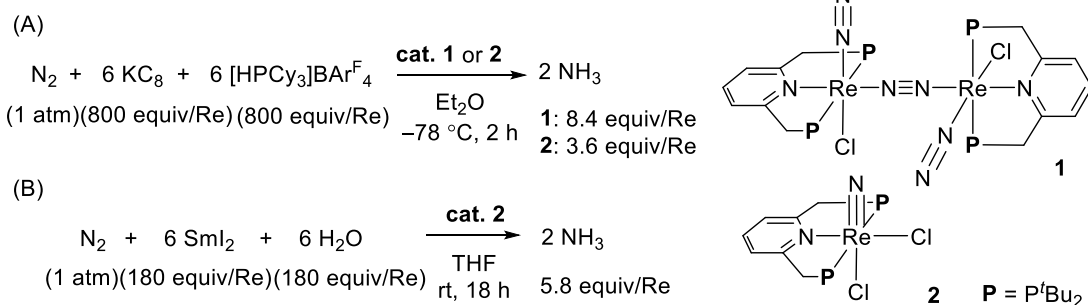
(¹The University of Tokyo, ²Daido University, ³Kyushu University) ○Fanqiang MENG,¹ Shogo KURIYAMA,¹ Hiromasa TANAKA,² Akihito EGI,³ Kazunari YOSHIZAWA,³ Yoshiaki NISHIBAYASHI¹

Keywords: Rhenium complex; Nitrogen fixation; Ammonia; Pincer ligand; Dinitrogen Complex

Catalytic reduction of dinitrogen under mild conditions represents a green and efficient methodological possibility for future ammonia production. To date, several transition metal-complexes have shown catalytic activities toward nitrogen fixation under mild reaction conditions.¹ Recently, we have reported that a dinitrogen-bridged dirhenium complex bearing PNP-type pincer ligands [$\{\text{ReCl}(\text{N}_2)(\text{PNP})\}_2(\mu\text{-N}_2)$] (**1**, PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) worked as a catalyst for the reaction of dinitrogen (1 atm) with KC_8 as a reductant and $[\text{HPCy}_3]\text{BAR}^{\text{F}}_4$ (Ar^{F} = 3, 5-bis(trifluoromethyl)phenyl) as a proton source at -78°C to produce 8.4 equiv of ammonia based on the rhenium atom of the catalyst (Scheme 1A).² Here, we have carried out extensive studies to get mechanistic information for this catalytic system.

When complex **1** was treated with KC_8 and triflic acid at -78°C , the formation of a rhenium nitride complex bearing a dinitrogen-bridged dirhenium structure was observed but the dinuclear rhenium nitride complex was not isolated as a pure form. On the other hand, a mononuclear nitride complex $[\text{Re}(\text{N})\text{Cl}_2(\text{PNP})]$ (**2**), which was prepared from the reaction of $[\text{ReCl}_3(\text{PPh}_3)_2(\text{MeCN})]$ with PNP at 80°C , also catalyzed the formation of ammonia at -78°C (Scheme 1A). These results suggest a rhenium-nitride species as a key intermediate in the rhenium-catalyzed nitrogen fixation. We also found that dinitrogen (1 atm) reacted with SmI_2 as a reductant and water as a proton source in the presence of **2** at room temperature for 18 h to give 5.8 equiv of ammonia based on the rhenium atom of the catalyst (Scheme 1B).

Scheme 1



1) Chalkley, M.; Drover, M.; Peters, J. *Chem. Rev.* **2020**, *120*, 5582. 2) Meng, F.; Kuriyama, S.; Tanaka, H.; Egi, A.; Yoshizawa, K.; Nishibayashi, Y. *ChemRxiv* **2020**, DOI:10.26434/chemrxiv.12162270.

Durable Photocatalytic Reduction of Carbon Dioxide Using Ionic Liquids

(¹Faculty of Science and Technology, Seikei University) ○Yasuomi Yamazaki,¹ Yoshiyuki Asai,¹ Riku Maruyama,¹ Taro Tsubomura¹

Keywords: Metal Complexes, Photocatalytic Reactions, CO₂ Reduction, Ionic Liquids, Solvent Effect

Metal complexes have attracted global attention since *fac*-Re(N[^]N)(CO)₃X-type complexes (N[^]N = diimine ligand, X = Cl⁻, Br⁻) were reported as a visible-light-driven photocatalyst in *N,N*-dimethylformamide (DMF) containing amines firstly by Lehn and co-workers, because of their high reaction selectivity and efficiency.¹ A large variety of photosensitizers, catalysts, and electron donors have been synthesized to improve turnover numbers and quantum yields.² The solvents, in contrast, have barely been changed from the first system; the best durability and efficiencies of the photocatalytic reactions were recorded when using DMF or *N,N*-dimethylacetamide (DMA) as a main solvent and triethanolamine (TEOA) as an additive for promoting photocatalysis. Aiming to diversify photocatalytic systems for CO₂ reduction using metal complexes, this study investigated the use of various ionic liquids as reaction solvents (Figure 1).³ The photophysical properties of a photosensitizer complex and the photocatalytic ability of mixed systems consisting of the photosensitizer and a Re(I) catalyst in twelve kinds of ionic liquids were systematically investigated by comparison with those in DMA. Even though the photophysical properties of the photosensitizer complex in ionic-liquid solutions were quite similar to those in DMA, both the photosensitizing ability and the photocatalytic abilities of the systems strongly depended on the structures of the ionic liquids. Several ionic liquids were successfully used as new solvents for the photocatalytic systems showing durability similar to or higher than DMA solutions. Moreover, we found that some of the ionic liquids are also useful as an additive to increase the durability of photocatalytic systems because of decrease in the overpotential for the catalytic reaction on the Re(I) complexes. When using a Ru(II) diimine complex as a photosensitizer and a Re(I) complex as a catalyst in a mixture of DMA and [bmim][Tf₂N] (3:1 v/v), the turnover number of CO formation became 1.5 times that in DMA-TEOA mixed solution.

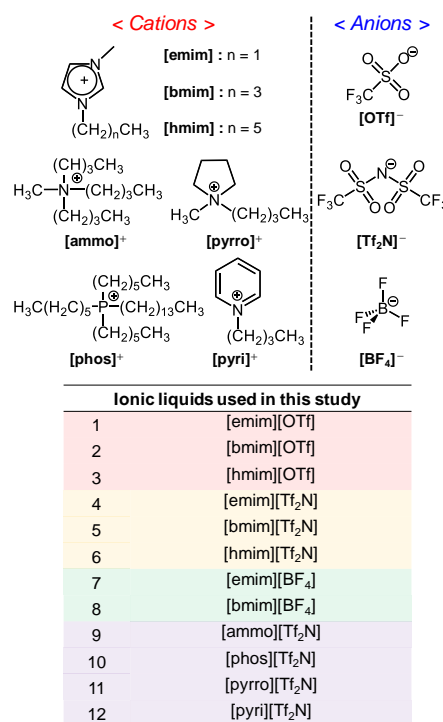


Figure 1. Structures and abbreviations of the ionic liquids used in this study.

1) J. Hawecker, J.-M. Lehn, R. Ziessel, *Helv. Chim. Acta.*, **1986**, 69, 1990. 2) Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol., C*, **2015**, 25, 106. 3) Y. Asai, H. Katsuragi, K. Kita, T. Tsubomura, Y. Yamazaki, *Dalton Trans.*, **2020**, 49, 4277.

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[A16-2am] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair:Yutaka Ie, Yasujiro Murata

Sat. Mar 20, 2021 9:00 AM - 11:40 AM Room 16 (Online Meeting)

[A16-2am-01] Baird aromatic light-melt adhesive: Mechanism elucidation of the photomelting function

○Tomoaki Konishi¹, Yumi Nakaike², Mitsuo Hara³, Wataru Yajima⁴, Ryo Shikata⁴, Masaki Hada^{5,6}, Shohei Saito¹ (1. Grad. Sch. of Sci., Kyoto Univ., 2. Grad. Sch. of Eng., Kyoto Univ., 3. Grad. Sch. of Eng., Nagoya Univ., 4. College of Eng. Sci., Univ of Tsukuba., 5. Grad. Sch. of Pure Appl. Sci., Univ of Tsukuba, 6. TREMS)

9:00 AM - 9:20 AM

[A16-2am-02] Divergent Synthesis of Amino-Functionalized Aromatic Diimides by Quantitative and Catalyst-Free Hydroamination

○Haruki Sanematsu^{1,2}, Atsuro Takai², Masayuki Takeuchi^{1,2} (1. University of Tsukuba, 2. National Institute for Materials Science)

9:20 AM - 9:40 AM

[A16-2am-03] B₂N₂-Doped Dibenzorubicene; Synthesis and Properties

○Takumi Sakamaki¹, Shang Rui¹, Eiich Nakamura¹ (1. The Univ. of Tokyo)

9:40 AM - 10:00 AM

[A16-2am-04] Spirohexaradical: Synthesis and Magnetic Properties

○Takuya Kanetomo¹, Yusuke Fukushima¹, Yuta Takenouchi¹, Masaya Enomoto¹ (1. Tokyo Univ. of Sci.)

10:00 AM - 10:20 AM

[A16-2am-05] Alkyl Chain Length Effect in Organic Field-Effect Transistors of Tetrathienonaphthalenes

○Motoki Kumeda¹, Kimiya Taniguchi¹, Atsushi Yamamoto¹, Yu Suenaga¹, Toshio Asada¹, Yasunori Matsui¹, Reitaro Hattori¹, Miho Higashinakaya¹, Takuya Ogaki¹, Eisuke Ohta¹, Hiroyoshi Naito¹, Hiroshi Ikeda¹ (1. Osaka Pref. Univ.)

10:20 AM - 10:40 AM

[A16-2am-06] Substituent dependent alignment of asymmetrically substituted π -extended aza[5]helicenes

○Satoru Hiroto¹, Mana Wakita¹, Moeko Chujo¹ (1. Kyoto University)

10:40 AM - 11:00 AM

[A16-2am-07] Discovery of Flexible C-C Bond: Reversible Expansion and Contraction of an Extremely Elongated C-C Single Bond

○Takuya Shimajiri¹, Takanori Suzuki¹, Yusuke Ishigaki¹ (1. Hokkaido Univ.)

11:00 AM - 11:20 AM

[A16-2am-08] Control of rotation in [2]rotaxanes

○Yusuke Kawasaki¹, Hiroshi Koganezawa¹, Yuichiro Mutoh¹, Yusuke Yoshigoe¹, Shinichi Saito¹ (1. Faculty of Science, Tokyo University of Science)

11:20 AM - 11:40 AM

励起状態芳香族性を示す新型ライトメルト接着材料の開発と光応答メカニズムの解明

(京大院理¹・京大院工²・名大院工³・筑波大応理⁴・筑波大院数理(TREMS)⁵) ○小西智暉¹・中池由美²・原 光生³・矢嶋 渉⁴・四方 諒⁴・羽田真毅⁵・齊藤尚平¹

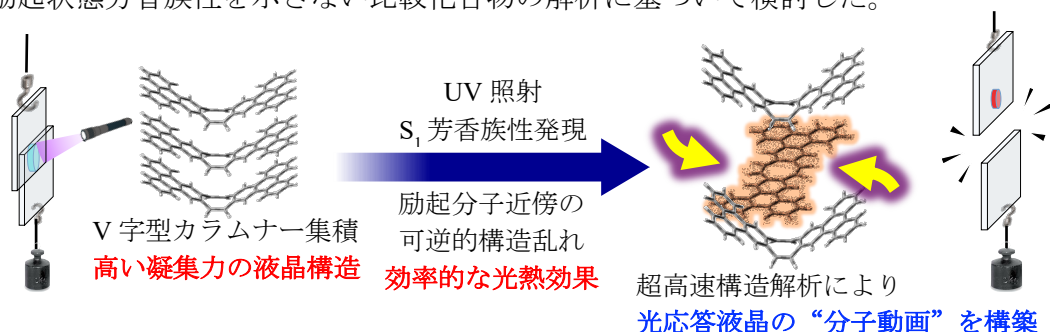
Baird aromatic light-melt adhesive: Mechanism elucidation of the photomelting function

(¹Graduate School of Science, Kyoto University, ²Graduate School of Engineering, Kyoto University, ³Graduate School of Engineering, Nagoya University, ⁴College of Engineering Science, University of Tsukuba, ⁵Tsukuba Research Center for Energy Material Science, Graduate School of Pure and Applied Science, University of Tsukuba) ○Tomoaki Konishi,¹ Yumi Nakaike², Mitsuo Hara³, Wataru Yajima⁴, Ryo Shikata⁴, Masaki Hada⁵, Shohei Saito¹

We have developed a transparent columnar liquid-crystal adhesive that can be melt by UV irradiation. Unlike previously reported light-melt adhesive based on anthracene unit¹⁾, the adhesive does not require a photoreaction for the photomelting event, but shows excited-state aromaticity. The adhesive strength is restored simply by stopping the light irradiation. Here, molecular-level mechanism of the macroscopic photomelting behavior is discussed based on femtosecond electron diffraction analysis.

Keywords: Triphenylene; Excited state aromaticity; Columnar liquid crystal; Adhesive; Femtosecond electron diffraction

光で剥がせる透明なカラムナー液晶の接着材料を開発した。羽ばたくトリフェニレン液晶分子 (TP-FLAP) は、凝集力の高い V 字型集積構造を形成し、紫外光を照射すると励起状態芳香族性を発現して平面型へと構造緩和する。平面型構造での S_1 励起状態から S_0 基底状態への遷移は禁制であり、励起エネルギーを効率的に熱へ変換できる。従来のライトメルト接着材料¹⁾は光照射によるアントラセン骨格の二量化を利用して光剥離したが、TP-FLAP は光反応を必要とせず、光照射を止めるだけで接着力が回復する。分子レベルの光剥離メカニズムについて、フェムト秒電子線回折実験や、励起状態芳香族性を示さない比較化合物の解析に基づいて検討した。



- 1) S. Saito, S. Nobusue, E. Tsuzaka, *et al. Nat. Commun.* **2016**, 7, 12094.

Divergent Synthesis of Amino-Functionalized Aromatic Diimides by Quantitative and Catalyst-Free Hydroamination

(¹Faculty of Pure and Applied Sciences, University of Tsukuba, ²Molecular Design and Function Group, National Institute for Materials Science: NIMS) ○Haruki Sanematsu,^{1,2} Atsuro Takai,² Masayuki Takeuchi^{1,2}

Keywords: Hydroamination; Aromatic Diimide; Electron-Deficient π -System; Catalyst-Free Click Reaction; π -Electron Material

Aromatic diimides such as naphthalenediimide (NDI) and perylenediimides (PDI) are representative π -systems having excellent optoelectronic properties and electron-accepting ability, and, as such, have been extensively studied in the fields of organic electronics, fluorescence sensors, and so forth. Functionalization of the diimide π -core is known to induce significant changes in its conformation and physicochemical properties. It often requires, however, numerous synthetic efforts and metal catalysts to attach functional groups to the π -core.¹⁾ Recently, we reported catalyst-free functionalization of an ethynyl substituted aromatic diimides with various amines that proceed almost quantitatively.²⁾ Nonetheless, the synthesis of multi-amino-functionalized π -systems and polymers has still been difficult. In this work, we designed novel aromatic diimides in which hydroamination occurs simultaneously to afford multi amine adducts and polymers.

We synthesized a series of vinyl-substituted NDIs and PDIs that reacted with amines simultaneously and quantitatively without an external catalyst (Fig.1). Hydroamination of the two vinyl groups of an aromatic diimide with a diamine and a 2 eq. of monoamine respectively afforded an amino-bridged macromolecule and an amine bisadduct. The resulting amino-functionalized aromatic diimides, especially the PDI derivative exhibited remarkable fluorescence switching by reversible interconversion between amine protonated/deprotonated forms in response to the addition of Brønsted acid/base.³⁾

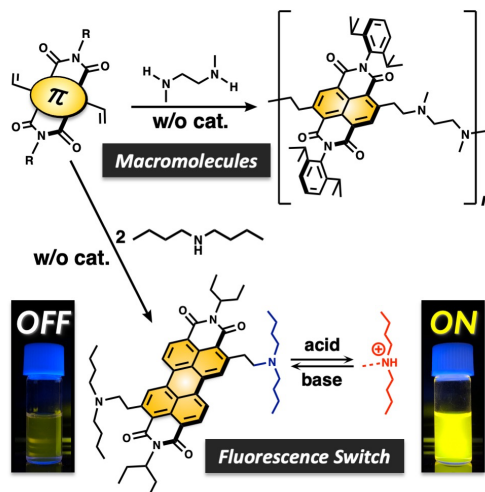


Fig.1 Catalyst-free synthesis of an amino-bridged NDI macromolecule and an acid/base responsive fluorescent PDI.

1) a) F. Würthner and co-workers, *Org. Chem. Front.* **2019**, 6, 1272. b) S. Matile and co-workers, *Chem. Commun.* **2010**, 46, 4225. 2) a) A. Takai, M. Takeuchi, *Bull. Chem. Soc. Jpn.* **2018**, 91, 44. b) K. Nakano, H. Sanematsu, Y. Kaji, A. Takai, K. Tajima, *Chem. Eur. J.* **2020**, 26, 15931. 3) H. Sanematsu, Y. Matsushita, M. Takeuchi, A. Takai, *Chem. Eur. J.* **2021**, 27, 934.

B₂N₂-Doped Dibenzorubicene; Synthesis and Properties

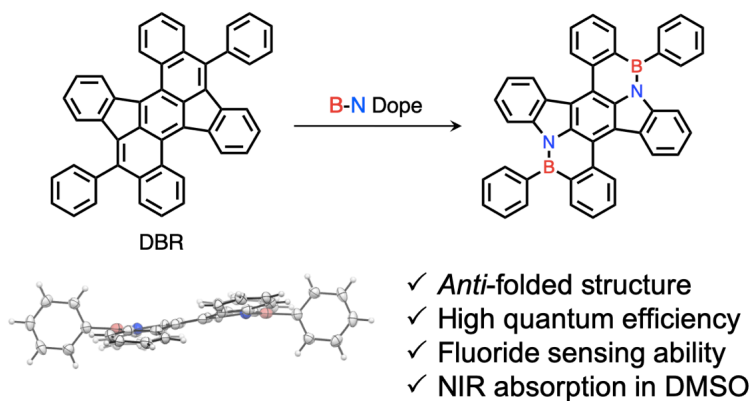
(School of Science, The University of Tokyo)

○Takumi, Sakamaki; Rui, Shang; Eiichi, Nakamura

Keywords: Isoelectronic analogues; Heteroaromatics

Abstract: Curved π -conjugated molecular have attracted much interest because they have good solubility and unique properties compared to planar π -conjugated system. On the other hands, doping boron-nitrogen (B-N) unit into π -conjugated system is effective strategy to tune optical and physical properties. Considering the isoelectronic relationship between C=C and B-N bonds, replacement of the C=C units in π -skeletons with the corresponding B-N units would create a new type of heteroarene that maintains the structural similarity. For example, BN doped π -conjugated system usually have high luminescence due to dipolar nature BN unit. With boron atom has Lewis acidic property because of vacant p-orbital.

In this work, We designed and synthesized a new BN-doped molecule based on these two strategies. The dibenzorubicene (DBR) backbone has nonplanar structure and high charge carrier mobility, which can be used for optoelectronic devices,¹ but it has low quantum efficiency. By doping BN unit properly located in a nonplanar molecule, the fluorescence quantum yields of compounds were up to 88%. In addition, high sensitivity of fluoride ion was achieved maintaining strong fluorescence, indicating the efficient emission properties of these materials. Achiral *anti*-folded backbone of BN compound was revealed by single-crystal X-ray structure analysis. Interestingly, When BN compound was dissolved in DMSO, near infrared (NIR) absorption could be observed. The application of these materials in various organic devices is expected.



1) X. Gu, X. Xu, H. Li, Q. Miao, *J. Am. Chem. Soc.* **2015**, *137*, 16203–16208.

スピロヘキサラジカルの合成と磁性

(東理大理¹) ○金友 拓哉¹・福島 雄佑¹・竹之内 佑太¹・榎本 真哉¹Spirohexaradical: Synthesis and Magnetic Properties (¹Tokyo Univ. of Sci.) ○ Takuya Kanetomo,¹ Yusuke Fukushima,¹ Yuta Takenouchi,¹ Masaya Enomoto¹

The spin polarization and/or molecular symmetry are an effective approach in order to develop a high-spin oligoradical. In this study, we have synthesized a novel hexaradical, which is 2,2',7,7'-tetra(*N*-*tert*-butylaminoxyl)-9,9'(10*H*,10'*H*)-spirobiacridine-10,10'-dioxyl (**1**, Fig. 1a). Hexaradical **1** has two acridine rings with ferrimagnetic-coupled triradical ($S' = 1/2$), and the total spin state of **1** has been expected to show the ground triplet state ($S_{\text{total}} = 1$) owing to the D_{2d} molecular symmetry. In fact, the results of $\chi_m T$ vs. T for **1** as shown in Fig. 1b indicate the presence of intramolecular ferromagnetic coupling between two acridine rings.

Keywords : Organic radical; Molecular magnetism; Spiro compound

1つの分子内に複数のラジカル電子を有する有機ラジカル化合物は、分子内の磁氣的相互作用を制御することで金属イオンに匹敵する磁気モーメントを示す。そのため、金属フリーな磁性材料のビルディングブロックとして有用である。分子内のスピンの同一方向に配列した状態 (高スピン状態) を得るには、スピン分極則と分子の対称性に着目した設計指針が有効である。これまで2つの設計を組み合わせた高スピン分子の合成例は少ない。本研究ではスピロビアカリジン母骨格に、アカリジン環上でのスピン分極とスピロ骨格 (D_{2d} 対称性) を組み合わせて高スピン分子の獲得を目指している。

今回、spirobiacridine-*N,N'*-dioxyl を母骨格に、2,2',7,7'位へ4つの *tert*-butyl nitroxide 部位を挿入したスピロヘキサラジカル (**1**) を合成した (Fig. 1a)。2つのアカリジン環はそれぞれ3つのラジカル部位を持ち、スピン分極則より、1つのアカリジン環はフェリ磁性的なスピン状態 ($S' = 1/2$) として振る舞う。さらに、**1** のスピロ骨格 (D_{2d} 対称) は直交する2つのアカリジン環の間に強磁性的相互作用をもたらすことが期待できる ($S_{\text{total}} = 1$)。実際、**1** の磁気測定の結果は分子内強磁性的相互作用の存在を示唆した (Fig. 1b)。

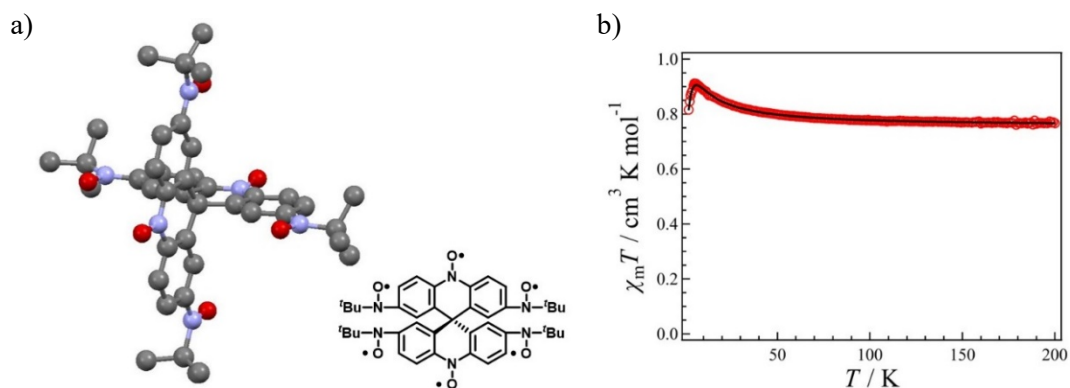


Fig. 1. (a) Crystal structure and structural formula of **1**. (b) $\chi_m T$ vs. T for **1** measured at 10 kOe.

テトラチエノナフタレンの有機電界効果トランジスタにおけるアルキル鎖長効果

(阪府大) ○久米田元紀・谷口公哉・山本惇司・末永 悠・麻田俊雄・松井康哲・服部励太郎・東中屋美帆・大垣拓也・太田英輔・内藤裕義・池田 浩

Systematic Investigation of Alkyl Chain Length Effect in Organic Field Effect Transistors of Tetrathienonaphthalenes (*Osaka Pref. Univ.*) ○Motoki Kumeda, Taniguchi Kimiya, Atsushi Yamamoto, Yu Suenaga, Toshio Asada, Yasunori Matsui, Reitaro Hattori, Miho Higashinakaya, Takuya Ogaki, Eisuke Ohta, Hiroyoshi Naito, Hiroshi Ikeda

Molecules with large π -planes have the potential of high-performance semiconductors for organic field-effect transistors owing to the large π -overlap in the solid state.¹ In this work, we synthesized various alkyl derivatives of a large π -plane compound, tetrathienonaphthalene (Fig. a), and investigated the relationship between the crystal structures and the hole mobility μ_h in thin film transistors (Fig. b).² As a result, it turns out that a thin film of the pentyl derivative TTN-5 formed a two-dimensional π -stacking structure and exhibited a relatively high μ_h of $> 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The cause is thought to be that the thin film of TTN-5 has large crystal grains with high transfer integrals in two directions (Fig. c,d).

Keywords: Organic Semiconductor; Organic Field-effect Transistors; Two-dimensional π -Stacking; Tetrathienonaphthalene; Hole Mobility; Transfer Integral

広い π 平面をもつ分子は固体状態で π 軌道の大きな重なりを形成し、有機電界効果トランジスタの高性能半導体となる可能性がある¹。本研究では広い π 平面を有するテトラチエノナフタレンの種々のアルキル誘導体 (Fig. a) を合成し、それらの結晶構造と薄膜トランジスタにおける正孔移動度 μ_h との関連性を評価した (Fig. b)²。その結果、ペンチル誘導体 TTN-5 は2次元で π スタックする結晶構造を形成し、移動度 $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ の比較的高い μ_h を示すことが分かった。その理由は、TTN-5 の薄膜が2方向に高い電荷移動積分を示す大きな結晶粒を有するためと考えられる (Fig. c,d)。

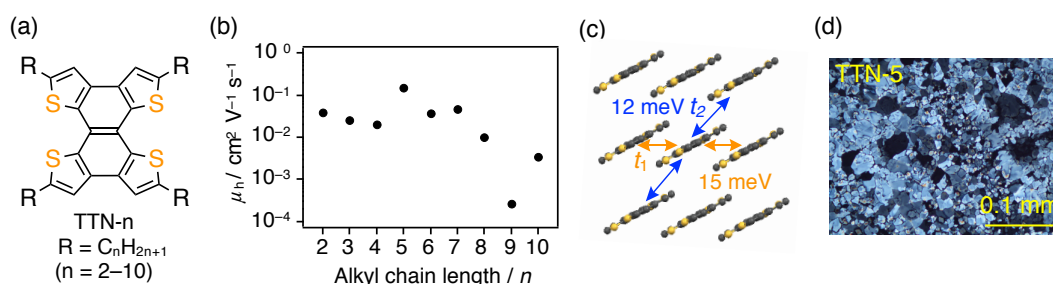


Fig. (a) Molecular structures of TTN-n. (b) μ_h of TTN-n. (c) t of TTN-5. (d) Polarization microscope image of TTN-5.

- 1) Zhang, L.; Cao, Y.; Colella, S. N.; Liang, Y.; Brédas, J.-L.; Houk, K. N.; Briseno, A. L. *Acc. Chem. Res.* **2015**, *48*, 500.
- 2) Yamamoto, A.; Matsui, Y.; Asada, T.; Kumeda, M.; Takagi, K.; Suenaga, Y.; Nagae, K.; Ohta, E.; Sato, H.; Koseki, S.; Naito, H.; Ikeda, H. *J. Org. Chem.* **2016**, *81*, 3168.

非対称 π 拡張アザヘリセンの合成と置換基による配列制御

(京大院人環¹) ○廣戸 聡¹・脇田 真奈¹・中條 萌絵子¹

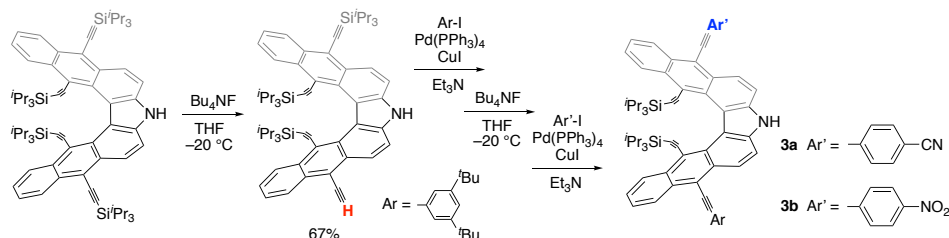
Substituent dependent alignment of asymmetrically substituted π -extended aza[5]helicenes (¹*Graduate School of Human and Environmental Studies, Kyoto University*) ○Satoru Hiroto,¹ Mana Wakita,¹ Moeko Chujo¹

Helicenes have attracted considerable attention due to their helical structures and chiral features. Recently, we have achieved regioselective substitutions of various aryl substituents to π -extended aza[5]helicenes. According to this protocol, we succeeded in synthesis of donor-acceptor type aza[5]helicenes with asymmetric structures. The absorption and emission spectra of these products exhibited solvent-dependent behaviors, indicating the presence of intramolecular charge-transfer interaction. The asymmetric helicenes were unambiguously characterized by X-ray diffraction analysis. In crystal, two molecules were aligned in face-to-face fashion. Interestingly, their ordering proved dependent on the external substituents. In particular, triisopropylsilyl substituted helicenes exhibited parallel alignments, constructing one-dimensional columnar packing.

Keywords : *Helicene; Desilylation; Charge-transfer; Spontaneous polarization*

ヘリセンは螺旋構造および光学活性な性質から新たな材料として注目されている。ヘリセンを積層させることで、円偏光発光の増強の他、キラルな反応場が形成できると期待できる。最近、我々は発光特性に優れたアザ[5]ヘリセンに対し、様々な置換基を選択的に導入できる手法を最近開発した^{1,2)}。今回、この手法を活用することで非対称に置換基を導入したアザ[5]ヘリセンの合成に成功した。

実際に、アザヘリセンに対し、フッ化セシウムを室温で作用させることで、外側のシリル基が一つ脱離した生成物を良好な収率で得ることに成功した。この基質に対し、様々なハロゲン化アリールと菌頭カップリングを行うことで、螺旋の外側に異なる電子効果をもつアザヘリセンの合成に成功した。得られたアザヘリセンはいずれも溶バトクロミズムを示し、特に、極性溶媒中で蛍光の消光が見られたことから、分子内移動相互作用の存在が示唆された。X線構造解析を行ったところ、結晶中で二分子が π スタックしている構造を構築していることがわかった。特に、トリイソプロピルシリル基をもつアザヘリセンでは、双極子モーメントを揃える向きに配列し、結晶中で一次元カラム構造を形成していることを明らかにした。



1) A. Ushiyama, H. Shinokubo, S. Hiroto *Chem. Lett.* **2019**, 48, 1069.

2) S. Hiroto *Bull. Chem. Soc. Jpn.* **2020**, 93, 1334.

Discovery of Flexible C-C Bond: Reversible Expansion and Contraction of an Extremely Elongated C-C Single Bond

(¹ Department of Chemistry, Faculty of Science, Hokkaido University)

○Takuya Shimajiri,¹ Takanori Suzuki,¹ Yusuke Ishigaki¹

Keywords: long bond, photoisomerization, thermal isomerization, X-ray analysis, single-crystalline reaction

Carbon–carbon (C–C) covalent bonds represent the most fundamental concept in organic chemistry. Elucidation of their nature is of great importance for further understanding of chemical phenomena; for instance, to understand what happens at the limits of a bond. Since deviation from the standard causes a large loss of bonding energy, generally C–C bond does not exhibit expansion or contraction. With regard to the C–C single bond, which has a standard length of 1.54 Å, three approaches have been taken to increase the bond length in neutral organic compounds to beyond 1.7 Å: (i) diamondoid dimers,¹ (ii) fused or clamped hexaphenylethanes,^{2,3} and (iii) diaminocarboranes.⁴ Among them, we focused on the approach (ii) while adopting the intramolecular core-shell strategy which affects the stability of the compound with a weak and elongated bond. Based on the core-shell strategy, we previously designed dispiro[dibenzocycloheptatriene (DBCHT)] derivatives **1a–1c** and reported that **1a–1c** have an extremely elongated C–C single bond whose length is greater than 1.7 Å. Especially, **1c** recorded 1.806(2) Å at 400 K, which is the greatest value among neutral hydrocarbons. The presence of the bond was demonstrated based on the observation of bonding electron by X-ray analysis and of C–C stretching vibration by Raman spectroscopy.⁵

Such a weak and elongated bond should exhibit a unique bond “flexibility”, which is a reversible expansion and contraction induced by external stimuli such as light or heat. Herein, we are focusing on DBCHT-dimer substructure in **1** since DBCHT-dimer⁶ has been known to show [2+2] photocycloaddition reaction to the caged molecule. If [2+2] photocycloaddition reaction occurs between DBCHT units in **1**, changes not only in physical properties but also in the bond length of the central C–C bond should be observed (Figure 1). Thus, we photoirradiated a solution of **1** at ambient temperature and found that [2+2] photocyclization proceeded quantitatively in **1** to produce caged molecules **2**. Then, we conducted the X-ray analyses at 400 K to determine the C–C bond lengths. As a result of the formation of cyclobutane ring, the neighboring central C–C single bond was certainly contracted. Especially, **2c** shows the largest change in the bond length [1.7146(19) Å] from **1c**, which is up to 5% contraction of the bond. In addition, heating of **2** in a solid state, long-bonded compounds **1** were quantitatively regenerated by thermal cycloreversion.

These results revealed the bond “flexibility”, a new facet of elongated C–C single bonds.⁷ In addition to expansion and contraction of the central bond, interconversion between **1** and **2** causes a large shift in HOMO level.

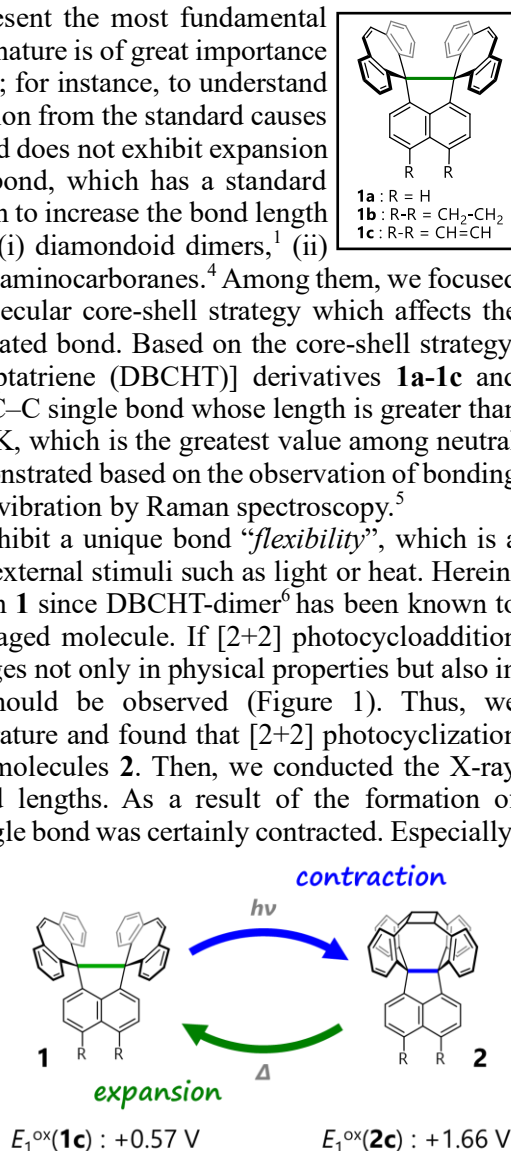


Figure 1. Interconversion between **1** and **2**.

- 1) P. R. Schreiner *et al.*, *Nature*, **2011**, 477, 308.; 2) R. Herges *et al.*, *Angew. Chem. Int. Ed.* **1997**, 36, 1757.; 3) F. Toda *et al.*, *Tetrahedron*, **2001**, 57, 3761.; 4) X.-Q. Xiao *et al.*, *Angew. Chem. Int. Ed.* **2019**, 58, 1397.; 5) Y. Ishigaki, T. Shimajiri, T. Takeda, R. Katoono, T. Suzuki, *Chem*, **2018**, 4, 795.; 6) G. Dyker *et al.*, *J. Org. Chem.* **2009**, 74, 8355.; 7) T. Shimajiri, T. Suzuki, Y. Ishigaki, *Angew. Chem. Int. Ed.* **2020**, 59, 22252.

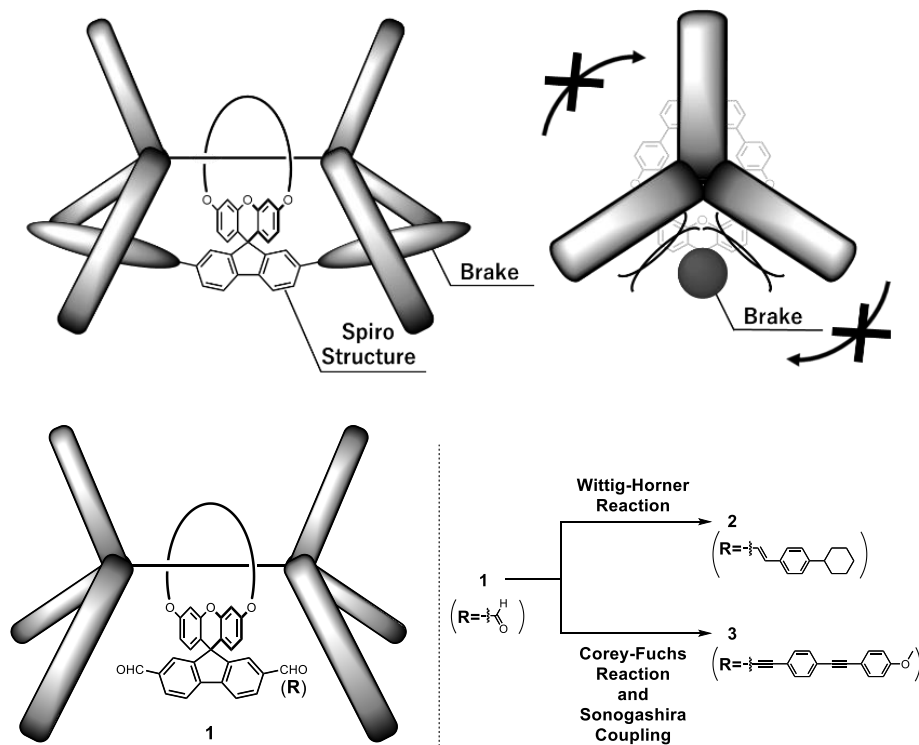
[2]ロタキサンにおける回転運動の制御

(東理大理) ○川寄 祐介・小金澤 寛・武藤 雄一郎・吉越 裕介・斎藤 慎一
Control of rotation in [2]rotaxanes (*Faculty of Science, Tokyo University of Science*) ○Yusuke
Kawasaki, Hiroshi Koganezawa, Yuichiro Mutoh, Yusuke Yoshigoe, Shinichi Saito

Interlocked compound such as rotaxane or catenane is expected to be applied to molecular machines because the movement of the components could be controlled easily. In the previous study, we utilized the catalytic activity of the macrocyclic phenanthroline-Cu complex to synthesize [2]rotaxanes by the oxidative dimerization of terminal alkynes. In this study, we achieved the synthesis of [2]rotaxanes which consist of the macrocyclic phenanthroline component with spiro skeleton and short axle component. A large and rigid side chain was introduced to the rotaxane, and the rotation of the axle moiety was examined.

Keywords : Rotaxane, Interlocked Compound, Spiro Compound, Dynamic Behavior

ロタキサンやカテナンといったインターロック化合物は、各構成要素が独立して運動を行うために分子マシンとしての応用を期待されている。当研究室ではこれまでに大環状フェナントロリン-銅錯体を触媒とする末端アルキンの二量化反応を用いたロタキサンの合成法を開発している。本研究において我々はスピロ骨格を導入した環構造と短い軸構造を有する[2]ロタキサン **1** の合成に成功した。このロタキサン環構造に環構造に剛直かつ大きな側鎖を導入することで **2** 及び **3** を得た。さらに合成したロタキサン **2,3** において、軸構造の回転運動が阻害される可能性について検討した。



[A08-2pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Ichiro Hisaki, Yoshimitsu Itoh

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 8 (Online Meeting)

[A08-2pm-01] Kinetic control over the self-assembly of a Pd₆L₄ square-based pyramid

○Tomoki Tateishi¹, Satoshi Takahashi¹, Keisuke Aratsu¹, Shuichi Hiraoka¹ (1. Graduate School of Arts and Sciences, The University of Tokyo)

1:00 PM - 1:20 PM

[A08-2pm-02] Structural control of a porous metal– macrocycle framework based on molecular adsorption to a local allosteric site

○Ryunosuke Hayashi¹, Masahiro Asakura¹, Shinya Mitsui¹, Shohei Tashiro¹, Mitsuhiro Shionoya¹ (1. The University of Tokyo)

1:20 PM - 1:40 PM

[A08-2pm-03] Dynamic behavior of double-walled cages in the self-assembly and the guest recognition

○Yukari Tamura¹, Hiroki Takezawa¹, Makoto Fujita¹ (1. The University of Tokyo)

1:40 PM - 2:00 PM

[A08-2pm-04] Highly Selective Heterochiral Supramolecular Polymerization of Thiophene-Fused Chiral [4*n*]Annulenes

○Tsubasa Aoki¹, Michihisa Ueda¹, Takayuki Nakamuro², Eiichi Nakamura², Takuzo Aida^{1,3}, Yoshimitsu Itoh¹ (1. Grad. Sch. Eng., The Univ. of Tokyo, 2. Grad. Sch. Sci., The Univ. of Tokyo, 3. CEMS, RIKEN)

2:00 PM - 2:20 PM

[A08-2pm-05] Rim-differentiated pillar[5]arenes: self-assembly and chirality control

○Shixin Fa¹, Kouichi Egami¹, Keisuke Adachi¹, Kenichi Kato¹, Yoko Sakata², Shigehisa Akine², Tomoki Ogoshi^{1,2} (1. Kyoto University, 2. Kanazawa University)

2:20 PM - 2:40 PM

[A08-2pm-06] Generation of Porous Crystal of Triaryltriazine Derivative Based on CH- π Interaction

○Eisuke Ohta¹, Haruka Izumi¹, Eriko Yasuzawa¹, Takuya Ogaki¹, Yasunori Matsui¹, Hiroyasu Sato², Hiroshi Ikeda¹ (1. Osaka Pref. Univ., 2. Rigaku)

2:40 PM - 3:00 PM

[A08-2pm-07] Creation of highly-crossed torus topologies by unique entangling nature of metal– peptide chains

○Yuuki Inomata¹, Tomohisa Sawada^{1,2}, Makoto Fujita^{1,3} (1. Grad. School of Engineering, The University of Tokyo, 2. JST PRESTO, 3. IMS)

3:00 PM - 3:20 PM

[A08-2pm-08] Seeded Self-Assembly of Charge-Terminated Poly(3-hexylthiophene) Amphiphiles Based on the Energy Landscape

○Tomoya Fukui¹, Ian Manners² (1. CLS, Tokyo Tech., 2. Univ. of Victoria)

3:20 PM - 3:40 PM

Kinetic control over the self-assembly of a Pd₆L₄ square-based pyramid

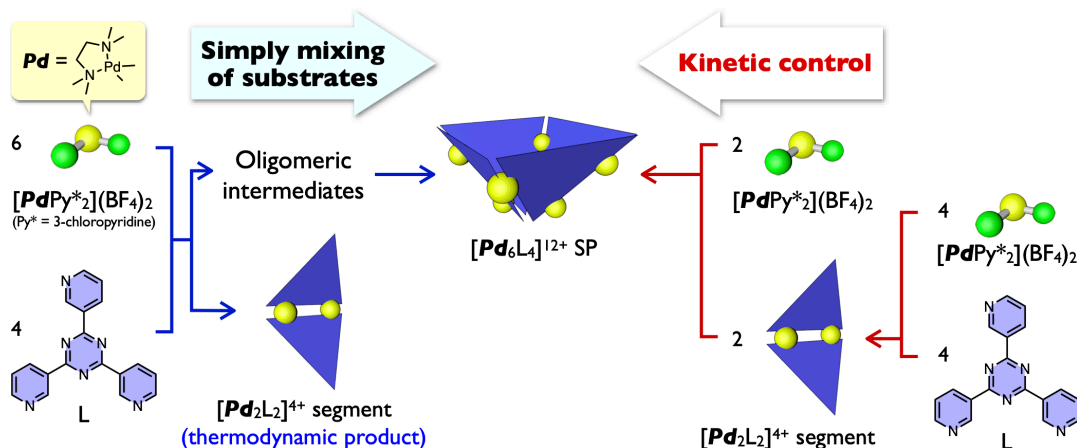
(¹Graduate School of Arts and Sciences, The University of Tokyo)

○Tomoki Tateishi,¹ Satoshi Takahashi,¹ Keisuke Aratsu,¹ Shuichi Hiraoka¹

Keywords: self-assembly; kinetic control; Pd(II) complex; selectivity; reaction design

The self-assembly of the [Pd'L₄]¹²⁺ square-based pyramid (SP), where Pd' indicates a *cis*-protected Pd(ethylenediamine), in water was reported by Fujita and his coworkers.¹ They proposed that the self-assembly of the SP would take place through a [Pd'₂L₂]⁴⁺ segment, which was supported by the isolation of a [Pd''₂L₂]⁴⁺ segment, where Pd'' indicates Pd(2,2-bipyridine).

In this work, the time-development of self-assembly process of the [Pd₆L₄]¹²⁺ SP, where Pd indicates a *cis*-protected Pd(*N,N,N',N'*-tetramethylethylenediamine)², was investigated in organic solvent by QASAP³ and NASAP^{2,4}. To our surprise, the [Pd₂L₂]⁴⁺ segment was produced as a thermodynamically most stable, major product (66%) with the [Pd₆L₄]¹²⁺ SP in only 17% yield. QASAP and NASAP indicate that the [Pd₆L₄]¹²⁺ SP is not produced mainly through the [Pd₂L₂]⁴⁺ segment but through chain-like oligomers without bridging. It was found that the [Pd₆L₄]¹²⁺ SP was produced in 69% yield by the reaction between the presynthesized [Pd₂L₂]⁴⁺ segment and [PdPy*₂](BF₄)₂ under kinetic control.



- 1) Fujita, M.; Yu, S.-Y.; Kusakawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem. Int. Ed.* **1998**, *37*, 2082–2085. 2) Komine, S.; Takahashi, S.; Kojima, T.; Sato, H.; Hiraoka, S. *J. Am. Chem. Soc.* **2019**, *141*, 3178–3186. 3) (a) Tsujimoto, Y.; Kojima, T.; Hiraoka, S. *Chem. Sci.* **2014**, *5*, 4167–4172. (b) Hiraoka, S. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 957–978. (c) Hiraoka, S. *Isr. J. Chem.* **2019**, *59*, 151–165. 4) (a) Matsumura, Y.; Hiraoka, S.; Sato, H. *Phys. Chem. Chem. Phys.* **2017**, *19*, 20338–20342. (b) Takahashi, S.; Sasaki, Y.; Hiraoka, S.; Sato, H. *Phys. Chem. Chem. Phys.* **2019**, *21*, 6341–6347. (c) Hiraoka, S.; Takahashi, S.; Sato, H. *Chem. Rec.* **2020**, DOI: 10.1002/tcr.202000124.

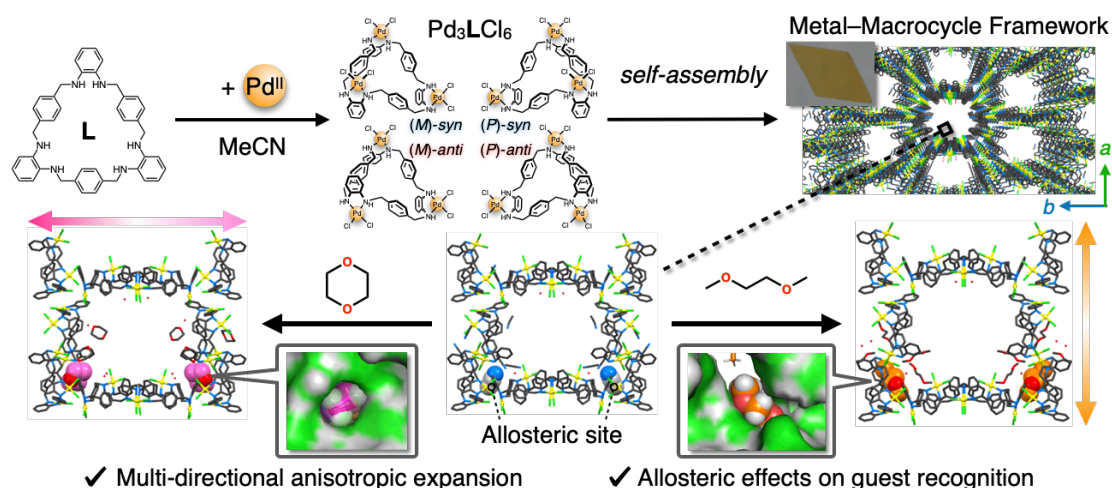
Structural control of a porous metal–macrocycle framework based on molecular adsorption to a local allosteric site

(Graduate School of Science, The University of Tokyo) ○Ryunosuke Hayashi, Masahiro Asakura, Shinya Mitsui, Shohei Tashiro, Mitsuhiro Shionoya

Keywords: Molecular recognition; Porous crystal; Supramolecular metal complex; Single-crystal X-ray diffraction; Allosteric effects

Dynamic conformational changes in biomacromolecules driven by molecular recognition at an allosteric site are essential for the precise regulation of their activity, and it is challenging to artificially design such elaborate systems. Previously, our group has developed a Pd^{II}-macrocycles-based porous molecular crystal, metal–macrocycle framework (MMF). It has five different guest recognition sites on one-dimensional nano-channels and site-selectively adsorbs various molecules.^[1]

In this study, we found a multi-directional anisotropic transformation of the channel structure by introducing small effector molecules. For example, expansion along the *a*-axis was induced in 1,2-dimethoxyethane, whereas the expansion was observed along *b*-axis in 1,4-dioxane. Single-crystal XRD analysis revealed that one of the guest recognition pockets of the Pd^{II}-macrocycle was specifically deformed depending on the effector contained. Therefore, it was shown that this pocket could function as an allosteric site to determine the entire crystal structure, where molecular encapsulation led to the rearrangement of Pd^{II}-macrocycle inducing the cell transformation. As a result, the crystal structure can be reversibly controlled in various directions depending on the effector molecules. In addition, we demonstrated allosteric effects of conversion on the guest adsorption to other free binding pockets. The guest recognition ability can be regulated allosterically based on the dynamic structural changes.



1) S. Tashiro, R. Kubota, M. Shionoya, *J. Am. Chem. Soc.* **2012**, 134, 2461.

Dynamic behavior of double-walled cages in the self-assembly and the guest recognition

(Graduate School of Engineering, University of Tokyo)

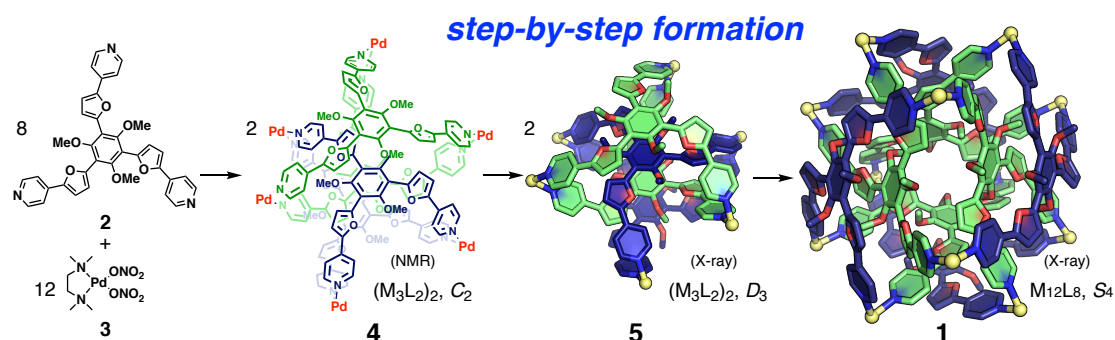
○Yukari Tamura, Hiroki Takezawa, Makoto Fujita

Keywords: double-walled interlocked structure; host-guest; guest adaptive; molecular recognition; step-by-step formation

Dynamic behavior in self-assembly and guest recognition processes is vital to develop a complex chemical network. Recently, we have reported that the coordination cage with a double-walled interlocked structure **1** exhibits guest-adaptive molecular recognition and dynamic guest exchange.¹ Here, we validated the guest inclusion through the portal expansion by using a robust Pt analog of the double-walled cage.² We also found that the semi-flexible ligand for the cage exhibits dynamic behavior in the self-assembly process and enables step-by-step formations of double-walled interlocked structures.

A Pt analog of double-walled cage **1** was synthesized from a 2:3 mixture of the ligand **2** and a Pt(II) complex by heating at 100 °C for 18 d in the presence of an excess amount of CCl₄ as a template. Kinetic studies in the guest inclusion showed similar kinetics between Pd double-walled cage and the Pt analog, revealing the guest inclusion through adaptive portal expansion.

The dynamic nature in self-assembly of **1** was also investigated. (M₃L₂)₂ **4** with C₂ symmetry was formed when a 2:3 mixture of ligand **2** (20 mM) and a Pd(II) complex **3** (30 mM) in CD₃OD was stirred in at room temperature for 5 min. By adding D₂O and CD₃CN to change the solvent system to CD₃OD/CD₃CN/D₂O = 1:1:8 and stirring at 60 °C for 5 h, **4** was converted to another isomer of (M₃L₂)₂ **5** with D₃ symmetry. Both products **4** and **5** have *pseudo*-hexapodal ligands composed of a stacked dimer of tripodal ligand **2**. After stirring at 100 °C for 25 h, **5** was totally converted to **1**. The results emphasize that the self-recognition of the ligand is essential for the formation of double-walled structures.



1) Y. Tamura, H. Takezawa, M. Fujita, *J. Am. Chem. Soc.* **2020**, *142*, 5504. 2) Y. Tamura, H. Takezawa, M. Fujita, *Chem. Lett.* **2020**, *49*, 912.

Highly Selective Heterochiral Supramolecular Polymerization of Thiophene-Fused Chiral [4n]Annulenes

(¹Grad. Sch. of Eng., The Univ. of Tokyo, ²Grad. Sch. of Sci., The Univ. of Tokyo, ³CEMS, RIKEN) ○Tsubasa Aoki,¹ Michihisa Ueda,¹ Takayuki Nakamuro,² Eiichi Nakamura,² Takuzo Aida,^{1,3} Yoshimitsu Itoh¹

Keywords: Chirality; Supramolecular Polymers; Heterochiral Sequence; [4n]Annulene

In nature, the stereochemistry that we can find for amino acids is L-form. This is a typical example of “homochirality” in nature. On the other hand, in the crystallization of racemic mixtures, more than 90% are racemates (heterochiral), and less than 10% are conglomerates (homochiral). Interestingly, in the case of supramolecular polymers,¹ where reversible non-covalent bonds connect the monomer units, it is known that they prefer a homochiral 1D arrangement due to the formation of helical assemblies.²

Here we report the first example of a highly selective heterochiral supramolecular polymer of thiophene-fused chiral [4n]annulene derivatives.³ Upon mixing the two optically resolved monomers, a white precipitate was observed. A microcrystal electron crystallography, combined with analytical HPLC, AFM, and various spectroscopic measurements suggested that the precipitate has a structure of 1D heterochiral supramolecular polymer. Interestingly, the origin of high stereoselectivity was attributable to strong antiparallel dipole interactions between the polarized conjugated planar moieties. This is a novel motif for driving supramolecular polymerization compared to conventional ones that prefer homochiral monomer sequences via hydrogen-bonding arrays. Besides, our previous studies have also shown that this monomer can be racemized upon photoirradiation by the emergence of Baird aromaticity.⁴ Based on this understanding, we succeeded in photopolymerization in a spatiotemporal manner.

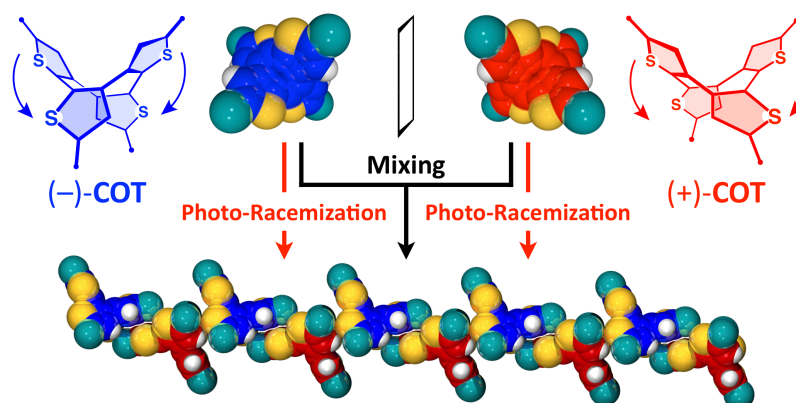


Fig. Heterochiral 1D Supramolecular Polymerization by Racemization

1) T. Aida *et al.*, *Science* **2012**, 335, 813. 2) a) Y. Ishida *et al.*, *JACS* **2002**, 124, 14017. b) K. Sato *et al.*, *Chem. Sci.* **2014**, 5, 136. 3) M. Ueda, T. Aoki *et al.*, *submitted*. 4) M. Ueda *et al.*, *Nature Commun.* **2017**, 8, 346.

Rim-differentiated pillar[5]arenes: self-assembly and chirality control

(¹Graduate School of Engineering, Kyoto University, ²WPI-NanoLSI, Kanazawa University)
 ○Shixin Fa,¹ Kouichi Egami,¹ Keisuke Adachi,¹ Kenichi Kato,¹ Yoko Sakata,² Shigehisa Akine,² Tomoki Ogoshi^{1,2}

Keywords: Pillar[n]arenes, Self-Assembly, Chirality, Non-Covalent Interactions, Nanotubes

As a rising star in supramolecular macrocyclic chemistry, pillar[n]arenes inherently combine many excellent characteristics of traditional macrocycles: easy to synthesis and functionalize, hydrophobic cavity with controllable size, and more importantly, high symmetrical structures.¹ Previous research on pillar[n]arenes was mainly based on their high symmetry due to synthesis limitations. Research on symmetry breaking of pillar[n]arenes remains underexplored.²

Herein, we synthesized rim-differentiated pillar[5]arenes bearing benzoic acids and alkyl chains on two rims.³ Self-assembled dimeric and trimeric nanotubes based on the rim-differentiated pillar[5]arenes showed well defined shape, length and diameter (Fig. 1a). The planar chirality of these rim-differentiated pillar[5]arenes could be induced by chiral amines and controlled precisely via achiral regulators, producing a ternary chiral induction and memory system (Fig. 1c). In addition, chiral nanotubes with either *pS* or *pR* chirality were constructed by introducing stereogenic carbons on the alkyl chains (Fig. 1b).

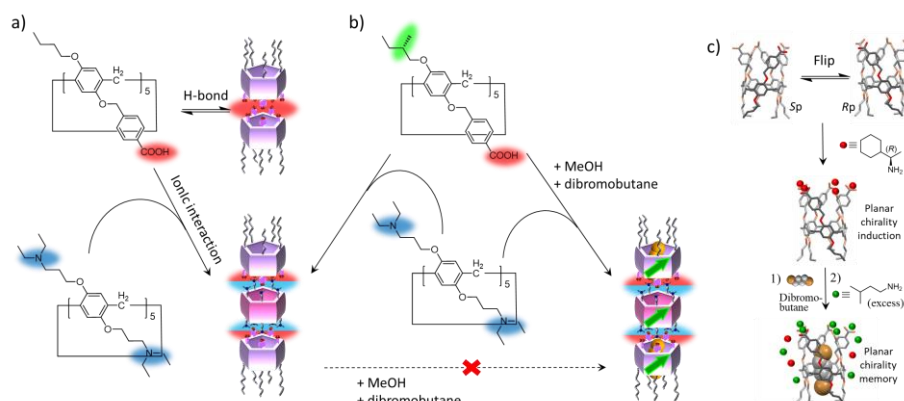


Fig. 1 Self-assembly and chirality control of rim-differentiated pillar[5]arenes. (a) Racemic and (b) chiral nanotubes formation. (c) Chiral induction and regulation.

1) T. Ogoshi, T. Yamagishi, Y. Nakamoto, *Chem. Rev.* **2016**, *116*, 7937. 2) M. Guo, X. Wang, C. Zhan, P. Demay-Drouhard, W. Li, K. Du, M. A. Olson, H. Zuilhof, A. C.-H. Sue, *J. Am. Chem. Soc.* **2018**, *140*, 74. 3) a) S. Fa, Y. Sakata, S. Akine, T. Ogoshi, *Angew. Chem. Int. Ed.* **2020**, *59*, 9309. b) S. Fa, K. Egami, K. Adachi, K. Kato, T. Ogoshi, *Angew. Chem. Int. Ed.* **2020**, *59*, 20353.

トリアリールトリアジン誘導体の CH- π 相互作用による多孔性結晶の生成

(阪府大¹・リガク²) ○太田英輔¹・泉 遥¹・安澤英利子¹・大垣拓也¹・
松井康哲¹・佐藤寛泰²・池田 浩¹

Generation of Porous Crystal of Triaryltriazine Derivative Based on CH- π Interaction
(¹Osaka Pref. Univ., ²Rigaku) ○Eisuke Ohta,¹ Haruka Izumi,¹ Eriko Yasuzawa,¹ Takuya Ogaki,¹
Yasunori Matsui,¹ Hiroyasu Sato,² Hiroshi Ikeda¹

The crystal structures of triaryltriazine derivatives possessing three acridinyl or anthryl groups were elucidated. It was found that the acridinyl derivative crystallizes in a densely packed manner while the anthryl one forms a porous crystal in which molecules are arranged keeping long intermolecular distances as a result of CH- π interactions of anthryl groups.

Keywords: Molecular Porous Crystal; Clathrate Crystal; Fullerene; Crystal Engineering

近年、有機多孔性材料の新たな種類として、再結晶化により構造を再構築できる多孔性分子結晶が注目を集めている。しかし、一般に分子は結晶化で密に詰まろうとするため、大きな空孔をもつ多孔性分子結晶を得るのは未だ困難な課題である。本研究では、3つのアクリジニル基またはアンスリル基をもつトリアリールトリアジン誘導体 **1** および **2** (Fig. 1a) の結晶構造を解析し、**2** が極めて大きな空孔をもつ多孔性分子結晶を形成することを見出した。

化合物 **1** および **2** をトルエンおよびクロロホルムから再結晶し、X線結晶構造解析を行った。その結果、**1** は結晶中で分子が密に充填したパッキング構造を形成するのに対し、**2** の結晶のパッキング構造は疎であり、分子が互いに離れて一次元チャンネルが生ずることがわかった (Fig. 1b)。これは、**2** が結晶を形成するときにアンスリル部位が集合して4,5,10位の3点において強いCH- π 相互作用を発現するためと考えられる。また、C₆₀の存在下で**2**を結晶化したところ、複数のC₆₀分子をチャンネルに含む包接結晶が得られることもわかった (Fig. 1c)。

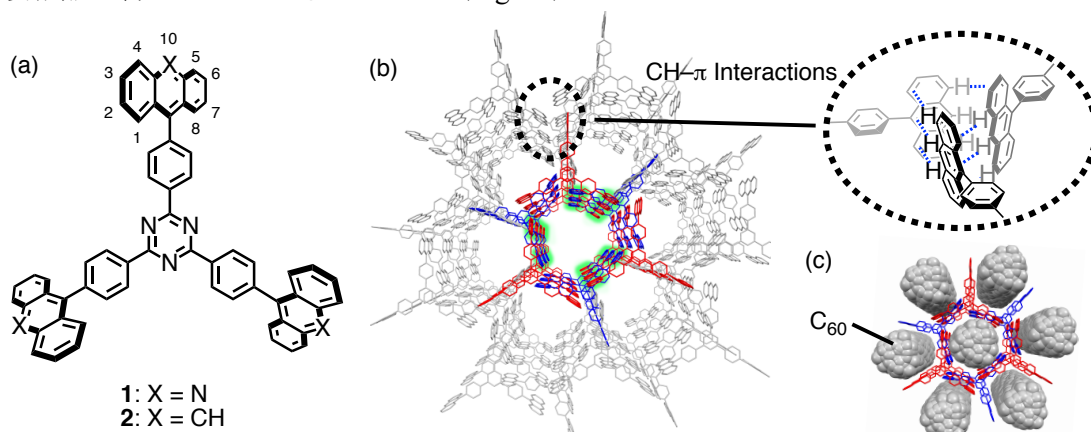


Fig. 1. (a) Molecular structures of **1** and **2**. (b) Packing structures of the crystal of **2** and (c) C₆₀-containing crystal of **2** determined by X-ray crystallographic analyses.

金属連結ペプチド鎖の絡まり特性を利用した高次トーラス分子トポロジーの創出

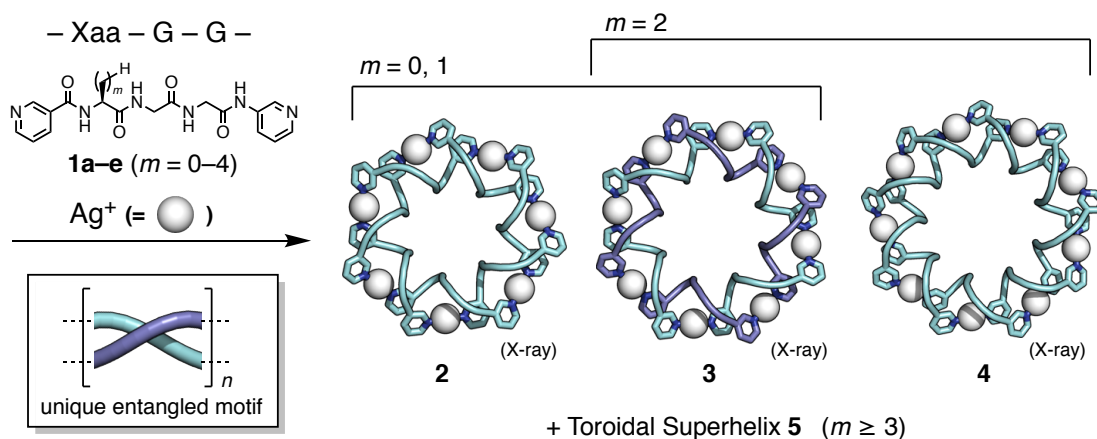
(東大院工¹・JST さきがけ²・分子研³) ○猪俣 祐貴¹・澤田 知久^{1,2}・藤田 誠^{1,3}

Creation of highly-crossed torus topologies by unique entangling nature of metal-peptide chains (¹*Grad. School of Engineering, The University of Tokyo*, ²*JST PRESTO*, ³*IMS*) ○Yuuki Inomata,¹ Tomohisa Sawada,^{1,2} Makoto Fujita^{1,3}

In this work, we succeeded in constructing highly entangled torus molecules by utilizing latent entangling nature of a metal-peptide chain, which consists of a flexible ditopic tripeptide ligand and Ag⁺ ions. In solution, triglycine ligand **1a** and Ag⁺ self-assembled to two highly symmetric species in equilibrium state. The crystals of 7-crossing knot **2** and 8-crossing analogue **3** were obtained respectively, and successfully characterized by X-ray analysis. These molecules were constructed in high regio- and stereoselective manner. Moreover, introduction of longer sidechains filling up the torus cavity (ligands **1b-e**) afforded 9-crossing torus knot **4** and toroidal superhelix **5**, an infinite form of torus knots, with retaining the same entangled motifs.

Keywords : self-assembly; peptide; knot; catenane; double helix

本研究では、柔軟なペプチド配位子と銀イオンの自己集合により、金属連結ペプチド鎖の潜在的に絡まりやすい性質を見出し、高次トーラス分子トポロジーの構築に成功した。トリグリシン配位子 (**1a**) と銀イオンをニトロメタン溶媒中で混合すると、対称性の高い 2 種類の構造が溶液中で生成し、それぞれ 7,8 交点のトーラス結び目分子 (**2, 3**) が高い位置・立体選択性で構築されることを各種 NMR 測定および X 線構造解析により確認した¹⁾。さらに、トーラス構造の空孔を埋めるように側鎖の炭素長を増すと (**1b-e**)、配位子 **1a** と銀イオンからなるペプチド鎖で特異的にみられる絡まり部分構造を維持したまま、9 交差の結び目構造 (**4**) や、トーラス結び目が無限に伸長した超らせん構造 (**5**) が生成することも見出した²⁾。



1) Y. Inomata, T. Sawada, M. Fujita, *Chem* **2020**, 6, 294. 2) *Manuscript in preparation*.

エネルギーランドスケープに基づく両親媒性ポリチオフェンミセルの精密合成

(東工大化生研¹・ビクトリア大学²) ○福井 智也¹・Ian Manners²

Seeded Self-Assembly of Charge-Terminated Poly(3-hexylthiophene) Amphiphiles Based on the Energy Landscape (¹Laboratory for Chemistry and Life Science, Tokyo Institute of Technology; ²Department of Chemistry, University of Victoria) ○Tomoya Fukui,¹ Ian Manners²

Control over self-assembly approaches to well-defined crystalline 1D nanostructures is a significant for applications in optoelectronics and biomedicine. We synthesized charge-terminated amphiphilic polythiophene homopolymers [PT_nP]I which self-assembled into colloiddally stable fiber-like micelles in solution. In-depth studies of the self-assembly behavior permitted the unveiling of the energy landscape of the self-assembly process. On the basis of the kinetic and thermodynamic insight provided, we have been able to achieve an unprecedented level of control over the length of fiber-like micelles from 40 to 2800 nm¹. Furthermore, the fiber-like micelles exhibited an exceptionally high exciton diffusion constant which is 1000 times higher than that of conventional polythiophene homopolymers².

Keywords : Polythiophene; Self-assembly; Living crystallization-driven self-assembly; Crystalline micelles; Energy landscape

分子・高分子の自己集合過程を制御し、ナノ構造体を精密に構築することは、優れた光電子的機能の発現のために必要不可欠である。本研究では、ポリマー末端にカチオン部位を導入した両親媒性ポリチオフェン [PT_nP]I を新たに合成し、溶液中においてファイバー状ミセルを形成することを明らかにした。さらに、ミセル形成過程のエネルギーランドスケープを明らかにし、その理解に基づき自己集合過程を速度論的に制御することで、ミセルの長さを 2800 nm まで制御することに成功した¹。この結晶性ミセルを用いて作製したフィルムは、一般的なポリチオフェンの約 1000 倍となる巨大な励起子拡散係数を示すことを明らかにした²。

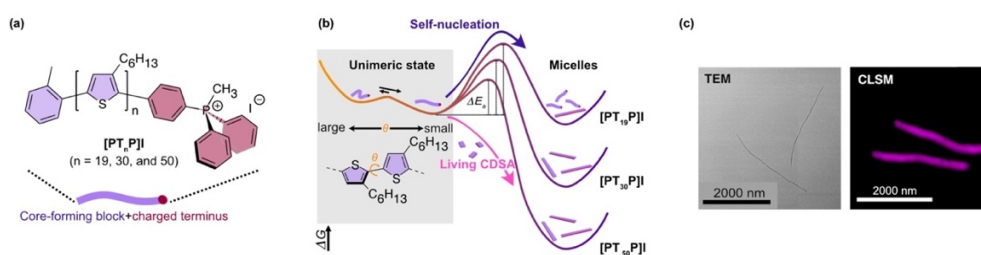


Figure (a) Structure of [PT_nP]I (b) Schematic representation of the energy landscape on self-assembly of [PT_nP]I in solution (c) TEM and confocal laser scanning microscopy images of fiber-like micelles.

- [1] T. Fukui, J. D. Garcia-Hernandez, L. R. MacFarlane, S. Lei, G. R. Whittell, I. Manners, J. Am. Chem. Soc. 142, 15038-15048 (2020).
- [2] A. J. Sneyd[†], T. Fukui[†] *et al.*, Submitted; arXiv:2009.05989. [†]These authors contributed equally to this work.

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

[A20-2am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Takashi Mino, Shuhei Kusumoto

Sat. Mar 20, 2021 9:00 AM - 11:40 AM Room 20 (Online Meeting)

[A20-2am-01] Controlled cyclization of arylalkynes through folding inside a molecular cage

○ Hiroki Takezawa¹, Harumi Hayakawa¹, Makoto Fujita¹ (1. The Univ. of Tokyo)

9:00 AM - 9:20 AM

[A20-2am-02] Construction of the Difluoroglycine Core by Three-Component Coupling Reaction Predicted by Quantum Chemical Calculations

○ Tsuyoshi Mita^{1,2}, Hiroki Hayashi^{1,2}, Hitomi Katsuyama^{1,2}, Yu Harabuchi^{1,2,3}, Satoshi Maeda^{1,2,3} (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

9:20 AM - 9:40 AM

[A20-2am-03] Heavy-Metal-Free Fischer– Tropsch Type Reaction

○ Shrinwantu Pal¹, Andreas Phanopoulos¹, Takafumi Kawakami¹, Kyoko Nozaki¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[A20-2am-04] Asymmetric Synthesis of Silacyclopentanes and Silaoxanes

○ Akihiro Kuroo², Kazunobu Igawa^{1,2}, Katsuhiko Tomooka^{1,2} (1. IMCE, Kyushu Univ., 2. Grad. Sch. Eng. Sci., Kyushu Univ.)

10:00 AM - 10:20 AM

[A20-2am-05] Chiral symmetry breaking of *meso*-diols involving dynamic crystallization

○ Aoi Washio¹, Yasushi Yoshida¹, Takashi Mino¹, Yoshio Kasashima², Masami Sakamoto¹ (1. Graduated school of engineering, Chiba university, 2. Faculty of Creative Engineering, Chiba Institute of Technology)

10:20 AM - 10:40 AM

[A20-2am-06] Synthesis of Planar-chiral Glycine and Its Peptide

○ Yuki Yoshida², Kazunobu Igawa^{1,2}, Katsuhiko Tomooka^{1,2} (1. IMCE, Kyushu Univ., 2. Grad. Sch. Eng. Sci., Kyushu Univ.)

10:40 AM - 11:00 AM

[A20-2am-07] Development of Well-Dispersed Trifluoromethanesulfonic Acid-Treated Metal Oxide

Nanoparticles Immobilized on Nitrogen-Doped Carbon

○ Xi Yang¹, Tomohiro Yasukawa¹, Shu Kobayashi¹ (1. The University of Tokyo)

11:00 AM - 11:20 AM

[A20-2am-08] Enantioselective α -Halogenation of N-Acyl-3,5-Dimethylpyrazoles Catalyzed by Chiral π -Cu(II)- π Complexes

○ Kazuki Nishimura¹, Yanzhao Wang, Yoshihiro Ogura, Kazuaki Ishihara¹ (1. Nagoya Univ.)

11:20 AM - 11:40 AM

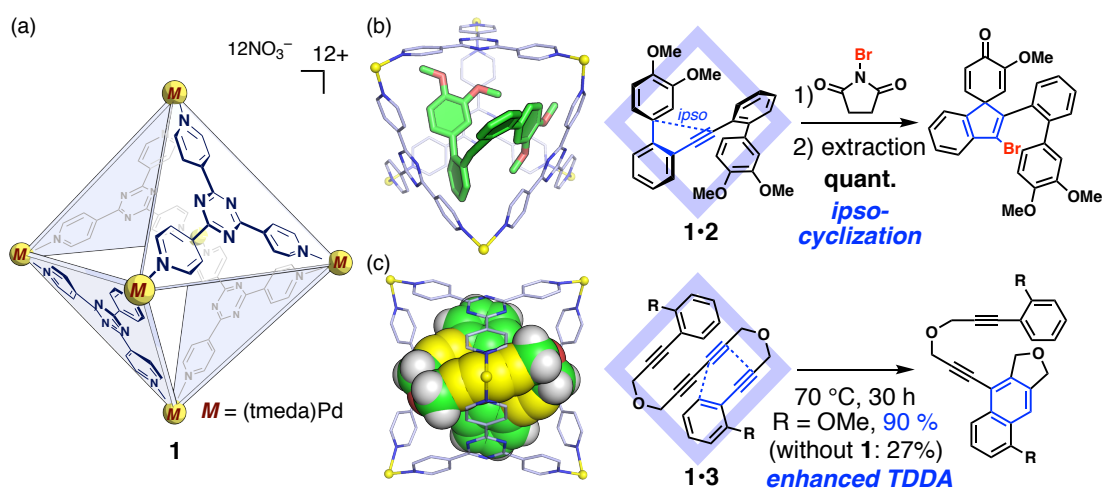
Controlled Cyclization of Arylalkynes through Folding inside a Molecular Cage

(Graduate School of Engineering, The University of Tokyo) ○Hiroki Takezawa, Harumi Hayakawa, Makoto Fujita

Keywords: Arylalkyne; Cyclization Reaction; Confined Cavity; Host–Guest; Inclusion Compound

Intramolecular cyclization involving ene and yne moieties is versatile for construction of polycyclic hydrocarbons from a linear precursor. However, the flexibility of the linear precursor hampers the control of the conformation, which causes low reactivity and selectivity in the cyclization. Here, we achieved controlled cyclization reactions of linear arylalkyne precursors by folding inside a molecular cage. The confined cavity of cage **1** forces the precursors to adopt a fixed fold conformation which is advantageous to the selective electrophilic or thermal cyclization reactions (Fig. a).

When bis(biphenyl)acetylene **2** (1.4 equiv) was suspended in an aqueous solution of cage **1** (10 mM) and heated at 80 °C for 1 h, 80% of the cage formed inclusion complex **1·2** (Fig. b). The folded conformation of **2** in cage **1** was revealed by X-ray crystallographic analysis. The fixed conformation resulted in an unusual *ipso*-cyclization with an electrophile. Cage **1** also induced folded conformation of oligoalkyne **3** to accelerate thermal tetradehydro-Diels-Alder (TDDA) type cyclization (Fig. c). We also achieved site-selective TDDA reactions with non-symmetric arylalkynes, which produced sterically hindered biaryl compounds.



計算科学主導によるジフルオログリシンの骨格構築法の開発とその応用研究

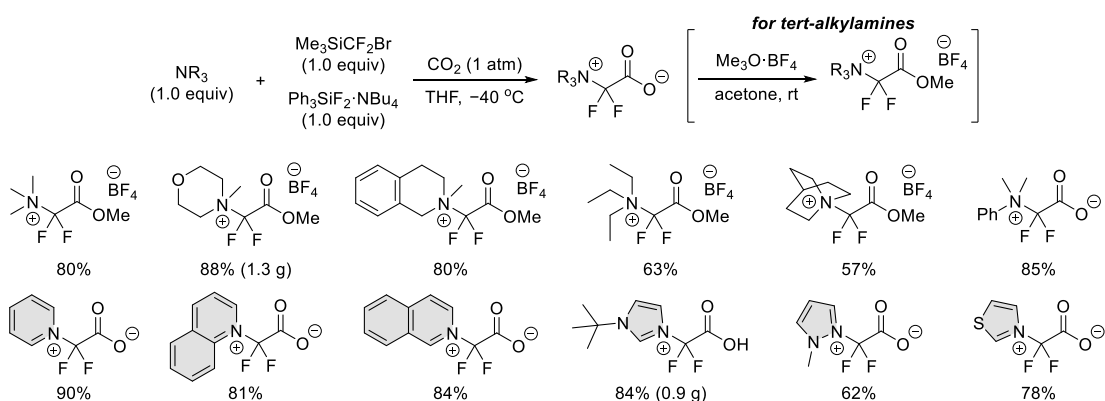
(北大 WPI-ICReDD¹・JST-ERATO²・北大院理³) ○美多 剛^{1,2}・林 裕樹^{1,2}・勝山 瞳^{1,2}・原渕 祐^{1,2,3}・前田 理^{1,2,3}

Construction of the Difluoroglycine Core by Three-Component Coupling Reaction Predicted by Quantum Chemical Calculations (¹WPI-ICReDD, Hokkaido Univ., ²JST-ERATO, ³Fac. of Sci., Hokkaido Univ.) ○Tsuyoshi Mita,^{1,2} Hiroki Hayashi,^{1,2} Hitomi Katsuyama,^{1,2} Yu Harabuchi,^{1,2,3} Satoshi Maeda^{1,2,3}

The AFIR (Artificial Force Induced Reaction) method, a core technology of ICRDD, proposed a new reaction pathway for α,α -difluoroglycine, which is thought to be a potential bioisostere of natural glycine. Following the computational prediction, we conducted the chemical synthesis of difluoroglycine derivatives from simple three starting materials such as NR_3 , $:\text{CF}_2$ (difluorocarbene), and CO_2 . In addition to the substrate scope, the synthetic application of difluoroglycine derivatives will be disclosed.

Keywords : Artificial Force Induced Reaction; Amino Acids; Carbon Dioxide; Fluorine; Multi-Component Reaction

ICReDD の基幹技術である人工力誘起反応法 (AFIR 法) により、 α,α -ジフルオログリシンの新しい合成経路を量子化学計算で予測した。提案された出発原料であるアミン、ジフルオロカルベン (反応系中で発生)、および二酸化炭素を用いて合成化学実験を行ったところ、これら単純な三成分からのジフルオログリシン誘導体の化学合成に成功した。^{1,2} 本発表ではさらなる基質適用範囲の検討に加え、本手法で合成したジフルオログリシン誘導体の合成化学的な応用研究を中心に紹介する。³



1) Mita, T.; Harabuchi, Y.; Maeda, S. *Chem. Sci.* **2020**, *11*, 7569-7577.

2) 美多 剛 “計算科学による α -アミノ酸の合成経路予測と実験科学による具現化” 月刊 機能材料 **2020**, *40* (11 月号), 23-32.

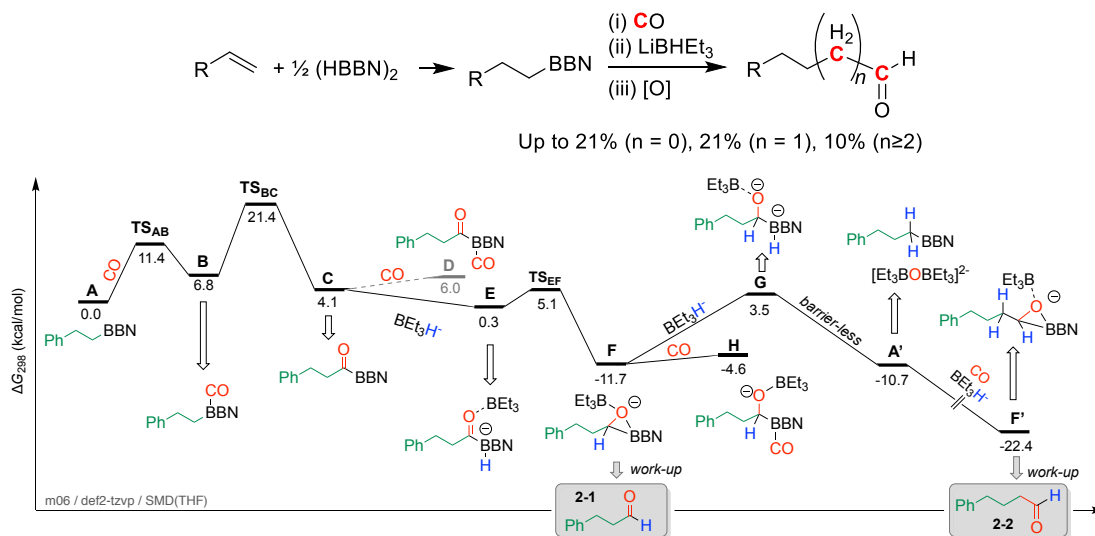
3) Hayashi, H.; Takano, H.; Katsuyama, H.; Harabuchi, Y.; Maeda, S.; Mita, T. *Manuscript in preparation*.

Heavy-Metal-Free Fischer–Tropsch Type Reaction

(¹Graduate School of Engineering, The University of Tokyo) ○Shrinwantu Pal,¹ Andreas Phanopoulos,¹ Takafumi Kawakami,¹ Kyoko Nozaki¹

Keywords: Fischer-Tropsch Reaction, Homologation,

The Fischer–Tropsch processes¹ are a type of chemical reaction that convert a mixture of CO and H₂ to liquid hydrocarbons. Typically, such reactions are mediated by transition-metal catalysts and require high temperatures and pressures. Here we report the low-temperature, heavy-metal-free homologation of a carbon chain using CO as a C1-source showing for the first time that transition-metal catalysts are not required for Fischer–Tropsch type reactivity. Reaction of an alkylborane (9-(2-phenethyl)-BBN) in the presence of either LiHBEt₃ or LiAlH₄ resulted in multiple sequential CO insertion/reduction events to afford elongated chains by more than two methylene (–CH₂–) units, affording aldehyde products upon oxidative aqueous workup.² Theoretical and experimental mechanistic studies indicate that the boron terminus is responsible for CO incorporation (via a coordination-insertion mechanism reminiscent of transition-metal catalysis³), as well as sequential hydride delivery leading to reduction of acylborane intermediates to alkylboranes.



References:

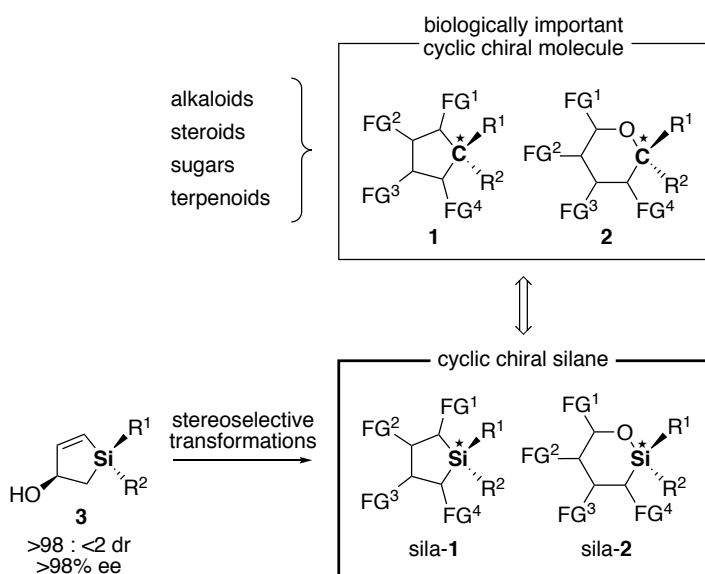
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2. Phanopoulos, A.; Pal, S.; Kawakami, T.; Nozaki, K. *J. Am. Chem. Soc.* **2020**, *142*, 14064–14068
3. Shultz, C. S.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 9172–9173

Asymmetric Synthesis of Silacyclopentanes and Silaoxanes

(¹*Institute for Materials Chemistry and Engineering, and* ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Akihiro Kuroo,² Kazunobu Igawa,^{1,2} Katsuhiko Tomooka^{1,2}

Keywords: *Chiral Silicon Molecule; Asymmetric Synthesis; Silacyclopentane; Silaoxane; Stereoselective Transformation*

Functionalized chiral cyclopentane skeleton **1** and oxane skeleton **2** with asymmetric carbons are key components in many biologically important natural products such as alkaloids, steroids, sugars, and terpenoids. As a part of our chiral silicon molecule chemistry, we have recently designed sila-**1** and sila-**2** as potential candidates for unnatural bioactive molecules in which the asymmetric carbon was replaced with an asymmetric silicon. As a result, sila-**1** and sila-**2** were successfully synthesized from previously developed silacyclopentenol **3** via stereoselective transformations.^{1,2} The details of the reactions and their biological activities will be presented.



1) K. Igawa, D. Yoshihiro, Y. Abe, K. Tomooka, *Angew. Chem. Int. Ed.* **2016**, 55, 5814.

2) K. Igawa, A. Kuroo, D. Yoshihiro, Y. Yamanaka, K. Tomooka, *Synlett* **2017**, 28, 2445.

動的晶出過程を伴うメソジオール類の対称性の破れ

(千葉大院工¹・千葉工大創造工²) ○鷲尾 葵¹・吉田 泰志¹・三野 孝¹・笠島 義夫²・坂本 昌巳¹ Chiral symmetry breaking of meso-diols involving dynamic crystallization (¹Graduate School of Engineering, Chiba University, ² Faculty of Creative Engineering, Chiba Institute of Technology) ○Aoi Washio¹, Yasushi Yoshida¹, Takashi Mino¹, Yoshio Kasashima², Masami Sakamoto¹

Dynamic crystallization is a highly efficient optical resolution compared to conventional methods, since the method provides optically active compounds without external chiral sources. In this study, we attempted to desymmetrization of *meso*-diols involving dynamic crystallization (**Figure 1**). Several monoacylated diols **3** were synthesized by the reaction of *meso*-diols **1** with aroyl chloride **2**. Among them, **3a**, **3b**, and **3c** were found to be conglomerates with a chiral space group. We investigated the optical resolution of **3** by dynamic crystallization. In a sealed tube, racemic **3** was suspended with glass beads in a small amount of toluene with a catalytic amount of DBU. After a few days, all three substrates were converted to enantiomorphic crystals in 99% ee. **Keywords** : *Meso*-diols; Desymmetrization; Dynamic crystallization; Chiral symmetry breaking; Homochirality

キラル結晶の分子配列を不斉源とする動的結晶化法は化学的不斉源を用いることなく光学活性体を得ることができるため、従来の手法と比べ、非常に高効率な光学分割法である¹⁾。本研究では、動的結晶化法を用いて、メソジオール類の非対称化を試みた(**Figure 1**)。メソジオール類の非対称化は、アシル化酵素のリパーゼを始め、世界中で研究が行われている²⁾。

メソジオール類 **1** と塩化アロイル **2** を反応させ、モノアシル化ジオール **3** を合成した。そのうち、**3a**, **3b**, **3c** がキラル空間群を有するコングロメレートであることが明らかになった。次に、**3a-3c** のラセミ化条件の検討を行った。その結果、塩基性条件下にて **3** のラセミ化が確認できた。以上の結果を踏まえ、動的結晶化にて **3** の光学分割を試みた。耐圧管に少量のトルエンと **3** を加え、触媒量の DBU の存在下、60 °C でガラスビーズと共に懸濁、撹拌を行った。徐々にシグモイド状の対称性の破れが進行し、数日後には、全ての **3** において 99% ee 以上の光学純度でデラセミ化を達成した。

1) M. Sakamoto, Asymmetric Synthesis Involving Dynamic Enantioselective Crystallization, in *Advances in Organic Crystal Chemistry, Comprehensive Reviews 2020*, M. Sakamoto, H. Uekusa eds, Springer, **2020**, 433. 2) R. Schreiner *et al*, *Angew. Chem. Int. Ed.*, **2011**, 50, 6012-6042.

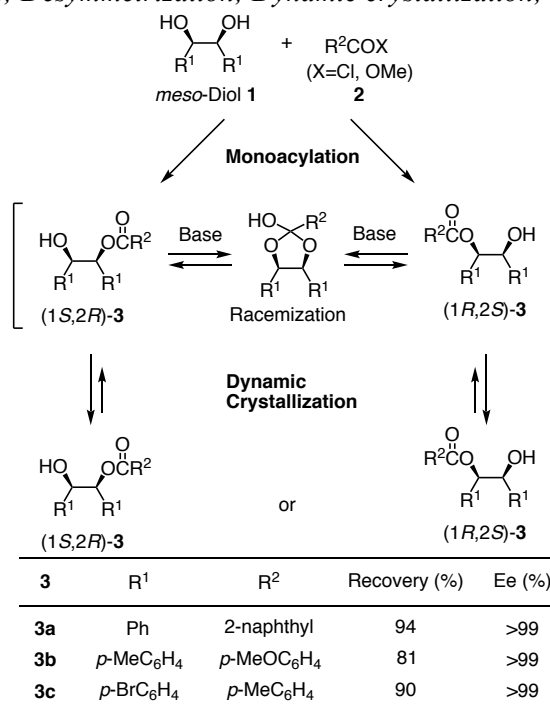


Figure 1. Chiral symmetry breaking of *meso*-diols involving dynamic crystallization. (This work)

面不斉グリシンの創製とそのペプチド合成

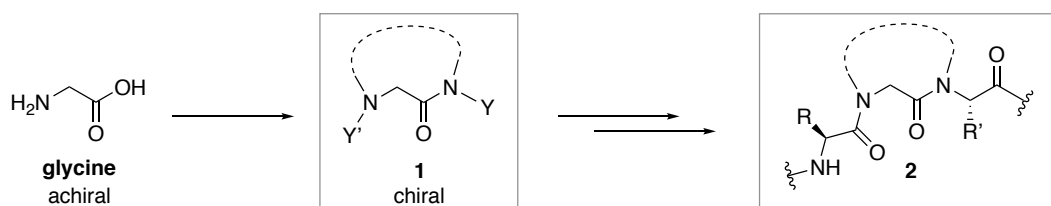
(九大先導研¹・九大院総理工²) ○吉田 祐樹²・井川 和宣^{1,2}・友岡 克彦^{1,2}

Synthesis of Planar-chiral Glycine and Its Peptide (¹*Institute for Materials Chemistry and Engineering, and* ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Yuki Yoshida,² Kazunobu Igawa,^{1,2} Katsuhiko Tomooka^{1,2}

As a novel chiral amino acid, we have newly designed and synthesized planar-chiral glycine derivative **1** having medium-sized cyclic skeleton. As we expected, **1** has stable planar chirality at ambient temperature. Moreover, we synthesized peptide **2** containing **1**. Herein, we wish to present the details of the synthesis of **1** and **2**, and stereochemical behavior of **1**.

Keywords : Planar Chirality; Amino Acid; Glycine; Stereochemical Behavior; Peptide

面不斉分子の研究¹の一環として今回、面不斉アミノ酸の開発を指向し、適切な中員環骨格にグリシンを組み込んだ分子 **1** を設計、合成した²。各種分析の結果、**1** が室温下安定な面不斉を有することが明らかになった。さらに **1** をペプチド鎖に組み込んだ **2** の合成にも成功し、その生物活性も評価した。講演時には、それらの合成と立体化学的安定性の詳細、生物活性評価の結果について議論する。



- 1) a) K. Tomooka, N. Komine, D. Fujiki, T. Nakai, S. Yanagitsuru, *J. Am. Chem. Soc.* **2005**, *127*, 12182.
 b) K. Tomooka, M. Suzuki, M. Shimada, S. Yanagitsuru, K. Uehara, *Org. Lett.* **2006**, *8*, 963.
 c) K. Tomooka, T. Ezawa, H. Inoue, K. Uehara, K. Igawa, *J. Am. Chem. Soc.* **2011**, *133*, 1754.
 d) K. Tomooka, C. Iso, K. Uehara, M. Suzuki, R. Nishikawa-Shimono, K. Igawa, *Angew. Chem. Int. Ed.* **2012**, *51*, 10355.
 e) K. Tomooka, S. Miyasaka, S. Motomura, K. Igawa, *Chem. Eur. J.* **2014**, *20*, 7598.
- 2) a) 日本化学会第 99 春季年会講演予稿集, 3F1-51 (2019).
 b) 日本化学会第 100 春季年会講演予稿集, 2B5-32 (2020).

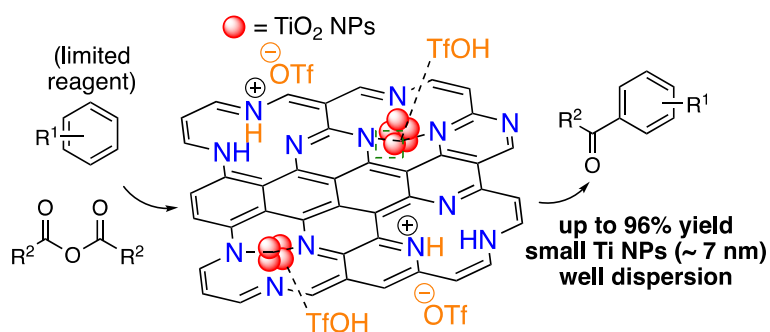
Development of Well-Dispersed Trifluoromethanesulfonic Acid-Treated Metal Oxide Nanoparticles Immobilized on Nitrogen-Doped Carbon

(School of Science, The Univ. of Tokyo) ○ Xi YANG, Tomohiro YASUKAWA, Shū KOBAYASHI

Keywords: Heterogeneous catalyst; Nitrogen-doped carbon; Friedel-Craft acylation; Titanium nanoparticle; Solid acid catalyst

Solid acid catalysts are widely used for various organic transformations due to their noncorrosive and nontoxic nature and reusability. One of the most prominent catalysts is sulfated metal oxides, such as zirconia and titania, for their significant acidity. However, these catalysts usually have a limited density of acidic sites and low surface areas. To increase their surface area, construction of metal oxide nanoparticles and incorporation of porous structures have been examined. However, particle agglomeration during catalyst preparation was commonly observed, leading to compromised catalytic activity.

Our group previously developed nitrogen-doped carbon incarcerated (NCI) metal nanoparticle (NP) catalysts, which demonstrated outstanding robustness and excellent stability with small particle sizes.¹⁾ Furthermore, the active species with small NP sizes in NCI metal NP catalysts could tolerate strong acid treatment.²⁾ Inspired by our previous results, we constructed heterogeneous trifluoromethanesulfonic acid immobilized NCI titanium nanoparticle (NP) catalysts with well-dispersed, small Ti NPs (ca 7 nm) that are otherwise difficult to achieve using acid-treated metal oxides. The catalysts showed high activity for Friedel–Crafts acylation with low titanium loading (2 mol%, <1 mg of metal for 1 mmol of substrate). A range of microscopic, spectroscopic and physicochemical studies revealed that the nitrogen-doped carbon immobilized the trifluoromethanesulfonic acid and that the addition of metals further changed the nature of the acidic species and enhanced catalytic activity.



1) S. Kobayashi. *et al. Org. Lett.* **2018**, 20, 5172. 2) S. Kobayashi. *et al. J. Org. Chem.* **2020**, 85, 7543. 3) T. Yasukawa, S. Kobayashi, *et al. Chem. Asian J.* in press, DOI: 10.1002/asia.202001274.

Enantio α -Halogenation of *N*-Acyl-3,5-dimethylpyrazoles Catalyzed by Chiral π -Cu(II)- π Complexes

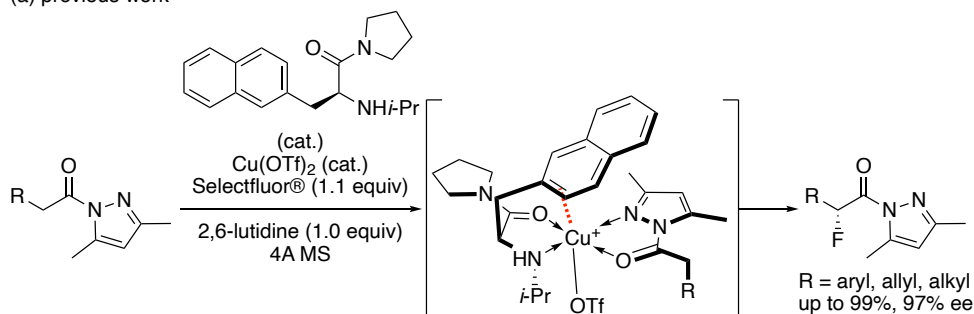
(Graduate School of Engineering, Nagoya University) ○Kazuki Nishimura, Yanzhao Wang, Yoshihiro Ogura, Kazuaki Ishihara

Keywords: Halogenation Reaction; Lewis Acid Catalyst; *N*-Acylpyrazole; π -Cation Interaction

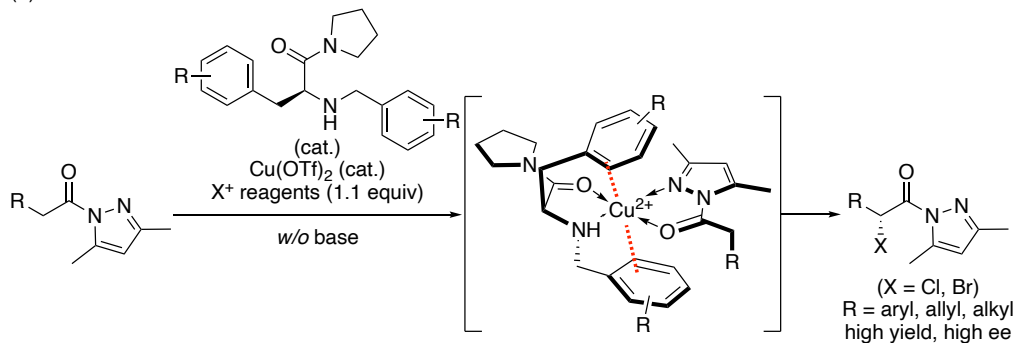
We have already developed the enantioselective α -fluorination reaction of *N*-acylpyrazoles catalyzed by chiral π -Cu(II) catalysts.¹⁾ Here, we developed the enantioselective α -halogenation reaction of *N*-acylpyrazoles catalyzed by chiral π -Cu(II)- π complexes, which were prepared *in situ* from copper(II) triflate and (*S*)-arylalanine amides. Although there are vast reports of α -halogenation reaction, the carbonyl substrates for these are limited to aldehydes, ketones, and 1,3-dicarbonyl compounds that have relatively low pK_a values associated with the α -hydrogen atoms. Against this background, here the development of highly efficient enantioselective α -halogenation of *N*-acylpyrazoles is described.

The double π -cation interaction between the two unsaturated bonds on the chiral ligand and Cu(II) center might play a critical role in the construction of chiral cavity as well as high catalytic activity. The corresponding *N*-(α -haloacyl)pyrazoles were obtained in high yield with high enantioselectivity without the addition of base. We would like to propose a possible transition state based on X-ray diffraction analysis of the key intermediates.

(a) previous work



(b) This work



1) Ishihara, K.; Nishimura, K.; Yamakawa, K. *Angew. Chem. Int. Ed.* **2010**, 59, 17641.

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

[A19-2am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Shuhei Higashibayashi, Taiga Yurino

Sat. Mar 20, 2021 9:00 AM - 11:40 AM Room 19 (Online Meeting)

[A19-2am-01] Development of Core/Shell-Type Heterogeneous Supports and Structure-Activity Relationship

○Tatsuya Kuremoto¹, Ren Sadatsune¹, Tomohiro Yasukawa¹, Shu Kobayashi¹ (1. The University of Tokyo)

9:00 AM - 9:20 AM

[A19-2am-02] Application of N-doped Carbon Incarcerated Copper Nanoparticle Catalysts to Sequential- and Continuous-flow Systems

○Fumiya Tobita¹, Tomohiro Yasukawa¹, Shū Kobayashi¹ (1. The University of Tokyo)

9:20 AM - 9:40 AM

[A19-2am-03] Micro-Raman imaging of fine chemical synthesis of imidazolium-based ionic liquids; *in situ* observation of molecular transformation and reaction temperature

○Hajime OKAJIMA^{1,2}, Akira SAKAMOTO¹ (1. Aoyama Gakuin University, 2. PRESTO, JST)

9:40 AM - 10:00 AM

[A19-2am-04] Sulfonium ion-promoted traceless Schmidt reaction of alkyl azides

○Bayu Ardiansah¹, Hiroki Tanimoto², Kiyomi Kakiuchi¹ (1. Graduate School of Materials Science, Nara Institute of Science and Technology, 2. Faculty of Pharmaceutical Sciences, University of Toyama)

10:00 AM - 10:20 AM

[A19-2am-05] The synthesis of substituted catechols by novel 1,2-rearrangement of *ortho*-quinols

○Riichi Hashimoto¹, Kengo Hanaya¹, Shuhei Higashibayashi¹, Takeshi Sugai¹ (1. Keio university)

10:20 AM - 10:40 AM

[A19-2am-06] N-Difluoroalkylative Dearomatization of Pyridine Guided by Quantum Chemical Calculations

○Hiroki Hayashi^{1,2}, Hitoki Katsuyama^{1,2}, Tsuyoshi Mita^{1,2}, Yu Harabuchi^{1,2,3}, Satoshi Maeda^{1,2,3} (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

10:40 AM - 11:00 AM

[A19-2am-07] Silyl Cyanopalladate-Catalyzed Friedel– Crafts-type Cyclization Affording 3-Aryloxindole Derivatives

○Hamdiye Ece^{1,3}, Taiga Yurino^{2,3}, Takeshi Ohkuma^{2,3} (1. Graduate School of Chemical Sciences and Engineering, 2. Faculty of Engineering, 3. Hokkaido University)

11:00 AM - 11:20 AM

[A19-2am-08] 8π electrocyclic reaction of phosphonate derivatives

○HIROKI SAITO¹, Keiji Tanino² (1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, 2. Faculty of Science, Hokkaido University)

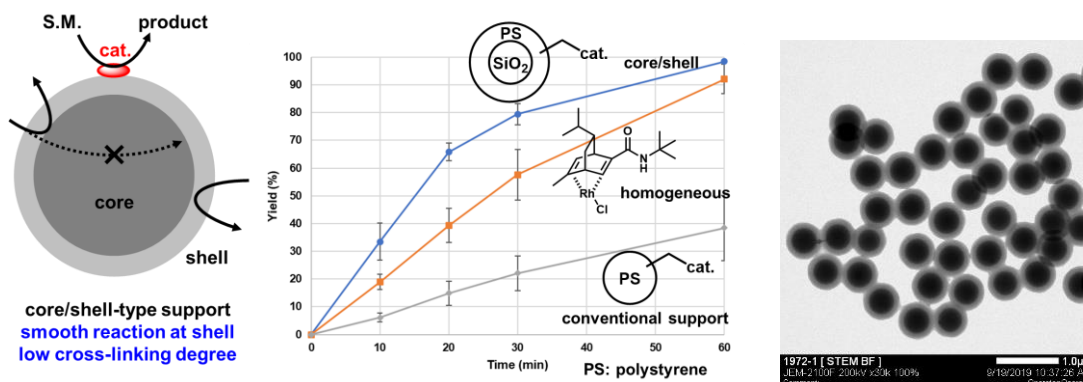
11:20 AM - 11:40 AM

Development of Core/Shell-Type Heterogeneous Supports and Structure-Activity Relationship

(School of Science, The Univ. of Tokyo) ○ Tatsuya KUREMOTO; Ren SADATSUNE; Tomohiro YASUKAWA; Shū KOBAYASHI,

Keywords: Heterogeneous catalyst; Immobilized catalyst; Asymmetric reaction; Flow reaction; Core/shell-type polymer

Immobilization of homogeneous catalyst facilitates catalyst separation from reaction mixtures and recovery/reuse of catalysts. However, a major common problem in current immobilized catalysts is the lower catalytic activities compared with the corresponding homogeneous catalysts, which sometimes hamper the application of immobilized catalysts to industry.¹⁾ It is acknowledged that active sites of immobilized catalysts have limited accessibility, which leads to diminished performance. While a high degree of cross-linking leads to decreased mass transport efficiency, there is a lower limit of a cross-linking degree below which the material becomes more soluble and mechanically less stable. To address the issue, we designed a core/shell-type support in which low-cross-linking degree polystyrene is attached on a rigid core material to keep high mass transport efficiency and make the whole support insoluble, stable, and easy to handle. Next, we immobilized chiral diene-Rh catalyst on core/shell-type support and investigated in detail the relationship between the structure of supports and the catalytic activity, and found that the major factor to control the activity was the cross-linking degree. The catalyst showed superior catalytic activity to conventional immobilized catalysts, and reached almost the same level as the corresponding homogeneous catalyst. We believe this strategy would be applicable to other immobilized catalysts and the catalytic activity could be improved.



1) Hayler, J. D.; Hickey, M. R. et al. *Green Chem.* **2018**, 5082–5103.

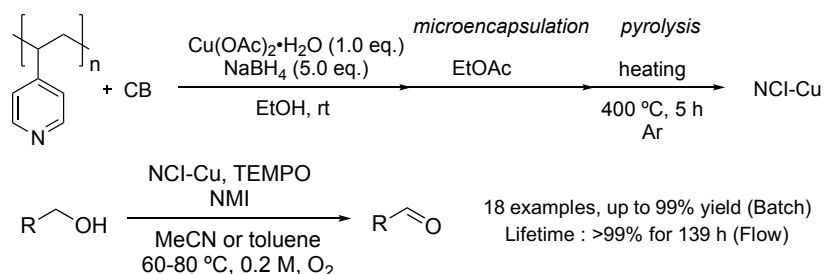
Application of N-doped Carbon Incarcerated Copper Nanoparticle Catalysts to Sequential- and Continuous-flow Systems

(School of Science, The Univ. of Tokyo) OFumiya TOBITA, Tomohiro YASUKAWA, Shū KOBAYASHI

Keywords: Heterogeneous catalyst, Nitrogen-doped carbon, Aerobic oxidation reaction, Cu nanoparticle, Flow reaction

Oxidation of alcohols to the corresponding aldehydes is one of the most crucial organic reactions. Co-catalyst systems of Cu complexes and *N*-oxyl radicals such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) are known as convenient oxidation systems of alcohols.¹⁾ Immobilization of metal catalysts for these reactions is desirable because metals are toxic and may interrupt following reactions when applied to tandem reactions. There are many reports of heterogeneous copper catalysts for these reactions; however, tedious processes to prepare catalysts are required and applications to aliphatic alcohols are limited in most cases.

We hypothesized that activation of Cu species by ligands was necessary to construct highly active catalysts considering that successful homogeneous catalyst systems utilized bipyridine ligands. Herein, we report nitrogen-doped carbon supported Cu nanoparticle catalysts (NCI-Cu) for aerobic oxidation of alcohols to aldehydes including aliphatic ones. The catalysts were prepared from poly-4-vinylpyridine by pyrolysis of the polymer encapsulated Cu nanoparticles.²⁾ Nitrogen dopants were crucial for high catalytic activity indicating that they might work as solid-state ligands to activate Cu species. XPS analysis revealed that the temperature in the pyrolysis process was crucial to prepare active Cu catalysts and influenced the component of *N*-doped carbon. The catalysts showed high activity for various substrates including aliphatic ones and the activity was kept in five reuses at least in a batch system. Furthermore, its lifetime in flow system was over 139 h. By applying the catalysts, 2-step continuous- and sequential-flow synthesis of unsaturated carbonyl compounds were demonstrated.



1) S. Stahl *et al.* *J. Am. Chem. Soc.* **2011**, 133, 16901.

2) S. Kobayashi *et al.* *Org. Lett.* **2018**, 20, 5172.

Micro-Raman Imaging of Fine Chemical Synthesis of Imidazolium-Based Ionic Liquids: *In situ* Observation of Molecular Transformation and Reaction Temperature

(¹*Coll. Sci. Eng., Aoyama Gakuin Univ.*, ²*PRESTO, JST*) ○Hajime Okajima,^{1,2} Akira Sakamoto¹

Keywords: Raman Microspectroscopy; Raman Imaging; Raman Temperature; Microreactor; Ionic Liquids

Microreactors attract much attention as flow chemical reaction devices. Thanks to the efficient heat removal and rapid mixing in these devices, many exothermic reactions are precisely controlled. However, the actual reaction process (mass diffusions, molecular transformations, heat generations, and heat removals) in such a small device is difficult to be confirmed experimentally. Micro-Raman imaging is a promising method for *in situ* label-free reaction monitoring. So far, we have observed mixing process¹, rotational isomerization², heating/cooling of water flow³, and molecular conversion⁴ by using Raman spectroscopy. Here, we demonstrate the detection of a hot spot in fine chemical synthesis of 1-ethyl-3-methylimidazolium ethyl sulfate (**1**) from 1-methylimidazole (**2**) and diethyl sulfate (**3**). Although this exothermic reaction ($\Delta H = -100 \text{ kJ mol}^{-1}$) would raise the reaction temperature to over 200 °C in macro-scale mixing, microreactors with sub-mm depth channels can thermally control the reaction and prevent the formation of byproducts⁶. To determine the reaction temperature inside a microreactor, we investigate Stokes and anti-Stokes Raman spectra of the reacting solution. **Fig. 1 (a)** shows a schematic of our experimental setup. We used a T-shaped microreactor (depth; 0.2 mm, width; 0.5 mm) with four inlets (two inlets connected to a reaction channel, others to reference channels) and measured the inside by a confocal Raman spectrometer (objective; $\times 40$, excitation; 532 nm). **Fig. 1 (b)** shows the band intensities and temperatures, which were determined from the anti-Stokes Stokes intensity ratios of the Raman bands. We found that the product **1** formed near the contacting surface of the reactants (**2** and **3**), and the temperature at the same place increases over 30 °C (at 2-mm downstream from the junction). Although the efficient heat removals of microreactors are expected to help the thermal control of this reaction, the temperature near the reaction surface is still higher than those at other positions. Experimental detection of such μm -scale hot spots becomes possible by using micro-Raman imaging.

1) *Annual Meeting Jpn. Soc. Mol. Sci.* **2017**, 2P019. 2) *CSJ Annual Meeting* **2019**, 4A3-12. 3) *ICAVS* **2019**, P295. 4) *CSJ Annual Meeting* **2020**, 3B8-19. 5) N. Shen *et al.*, *J. Mol. Liq.* **2016**, 222, 622.

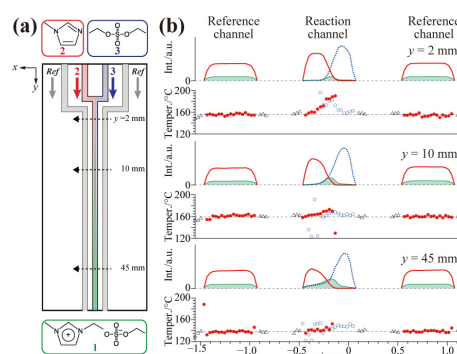


Fig. 1 (a): A schematic of the microfluidic reaction of **1**. The reference channels (gray colored) were filled with mixture of **1** and **2**.

(b): Raman intensities and Raman temperatures inside the channels. The results at 2, 10, and 45-mm downstream from the junction are shown (corresponding to 0.2, 1.0, and 4.5-sec residence times). Raman bands at 598, 668, and 509 cm^{-1} were used as marker bands of **1**, **2**, and **3**, respectively. Red solid lines and closed circles indicate intensities and temperatures of **2**, respectively, blue broken lines and open circles indicate those of **3**, and green filled lines indicate intensities of **1**. Open triangles are the temperatures of channel media (quartz glass) determined from the low-frequency Raman spectra³.

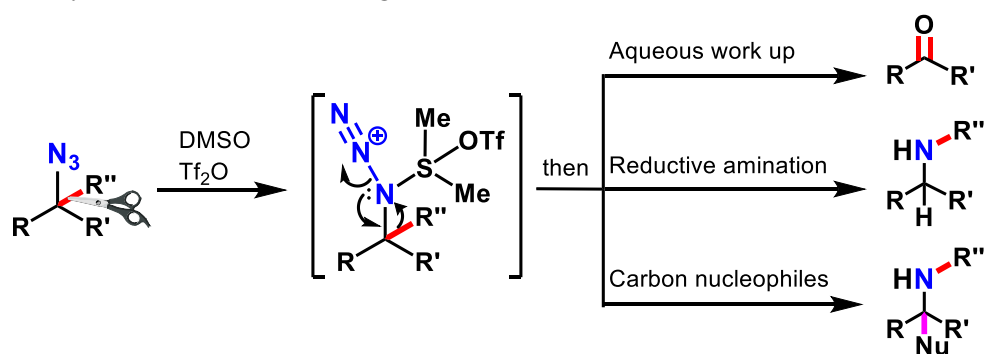
Sulfonium Ion-Promoted Traceless Schmidt Reaction of Alkyl Azides

(¹*Division of Materials Science, Nara Institute of Science and Technology*, ²*Faculty of Pharmaceutical Sciences, University of Toyama*) ○ Bayu Ardiansah,¹ Hiroki Tanimoto,² Kiyomi Kakiuchi¹

Keywords: Schmidt Reaction; Organic Azides; Chemical Bond Cleavage; Sulfonium Ion

Renovating the structures of organic compounds through activation of unreactive chemical bonding such as carbon-hydrogen and carbon-carbon bonds enables dramatic development of potent pharmaceuticals and chemical probes connected with bioactive compounds. For this purpose, organic azides have long been recognized to show attractive characters to disconnect inert chemical bonding.¹ Although Schmidt reaction is one of the well-known methods for these conversions, activation of azido groups requires excess strong acids or elevated temperature even at highly reactive positions (allylic or benzylic).² Moreover, for the chemical bond activation, Schmidt reaction usually requires unremovable substituents in the products such as acyl groups.³ These limitations have driven us to develop traceless activation of organic azides, which lead to versatile modification of molecules without residue in the products.

With *in-situ* prepared sulfonium ion as reactive species, carbon-hydrogen bond activation of primary and secondary alkyl azides was successfully achieved to give corresponding aldehydes and ketones in up to 92% yield after hydrolysis. Furthermore, treatment of tertiary alkyl azides allowed carbon-carbon bond migration forming carbon-nitrogen bonds, including ring expansion, to give *N*-alkylimines. These intermediates were successfully delivered to substituent-removed ketones by aqueous work-up for hydrolysis, and to *N,N*-disubstituted amines by one-pot reduction in moderate to good yields. Moreover, addition of carbon nucleophiles to the iminium intermediates gave substituent-rearranged *tert*-alkylamines without any trace of the activator reagent.



1) H. Tanimoto, K. Kakiuchi, *Nat. Prod. Commun.* **2013**, 8, 1021. 2) a) A. Wroblewski, J. Aubé, *J. Org. Chem.* **2001**, 66, 886. b) N. Jiao, *et al.*, *Nat. Chem.* **2019**, 11, 71. 3) J. Aubé, G. L. Milligan, *J. Am. Chem. Soc.* **1991**, 113, 8965.

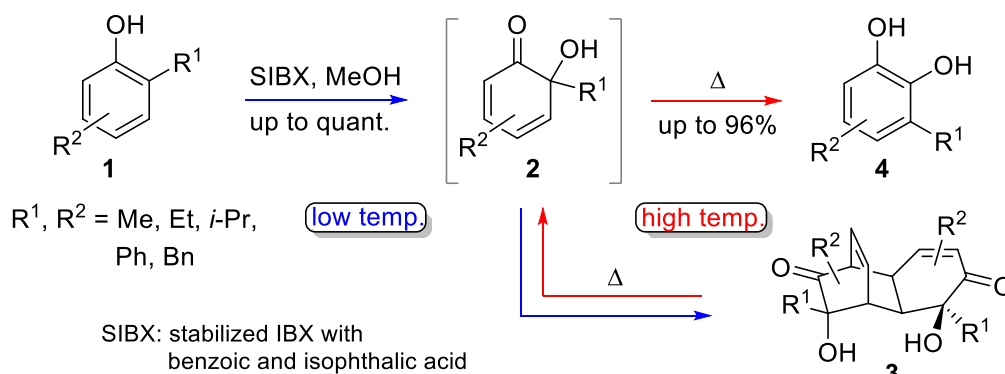
The synthesis of substituted catechols by 1,2-rearrangement of *ortho*-quinols

(¹*Faculty of Pharmacy, Keio University*) ○ Riichi Hashimoto,¹ Kengo Hanaya,¹ Shuhei Higashibayashi,¹ Takeshi Sugai¹

Keywords: *ortho*-Quinols; Thermal 1,2-rearrangement; Substituted catechols

para-Quinols are used as precursors for substituted polyphenols,¹⁾ since it is known that 1,2-rearrangement of *para*-quinols gives substituted phenols under acidic or basic conditions. On the other hand, the utility of *ortho*-quinols has been limited owing to mainly three problems. First, the synthesis of *ortho*-quinols from 2-alkylphenols requires site-selective hydroxylation.²⁾ Second, *ortho*-quinols cause the dimerization easily by Diels-Alder reaction.³⁾ Third, it has been recognized that *ortho*-quinols does not undergo 1,2 rearrangement over 60 years. Instead, other reactions such as acyloin rearrangement and cyclohexadienone ring-opening proceeded under acidic or basic conditions.^{4,5)} Here, we overcome these three problems, and achieved the successive conversion from substituted phenols **1** to catechols **4** through site-selective hydroxylation and 1,2-rearrangement of *ortho*-quinols **2** generated by retro Diels-Alder reaction of *ortho*-quinol dimer **3**.

Site-selective hydroxylation of 2-alkylphenols **1** was achieved by IBX oxidation. Thus generated *ortho*-quinols **2** rapidly underwent Diels-Alder reaction in one pot, giving the dimers **3** in high yield. Under heating condition, retro Diels-Alder reaction of dimers **3** took place to show the equilibrium with monomers **2**. We found that at a high temperature under neutral condition promoted 1,2-rearrangement of *in situ* generated **2**, giving the thermodynamically favored catechols **4**. Under the optimized conditions, catechols **4** were obtained from phenols **1** in high yields up to 87% in 2 steps. The reaction mechanism and energy profile were analyzed by DFT calculation.



- 1) K. A. Parker and Y. Koh, *J. Am. Chem. Soc.*, **1994**, *116*, 11149.; 2) S. Quideau *et al.*, *J. Org. Chem.*, **2007**, *72*, 6280.; 3) S. Quideau *et al.*, *Synlett.*, **2008**, *4*, 467.; 4) P. Klezl *et al.*, *Tetrahedron*, **1958**, *4*, 49.; 5) H. Budzikiewicz *et al.*, *Mh. Chem. Bd.*, **1959**, 609.

N-ジフルオロアルキル化を伴うピリジンの脱芳香族化反応の計算科学による予測と具現化

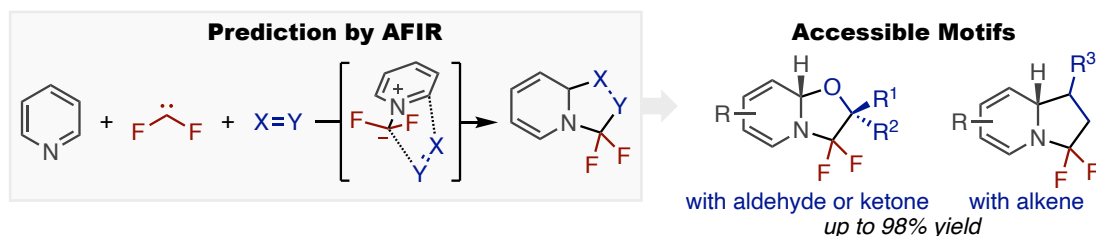
(北大 WPI-ICReDD¹・JST-ERATO²・北大院理³) ○林 裕樹^{1,2}・勝山 瞳^{1,2}・美多 剛^{1,2}・原渕 祐^{1,2,3}・前田 理^{1,2,3}

N-Difluoroalkylative Dearomatization of Pyridine Guided by Quantum Chemical Calculations (¹WPI-ICReDD, Hokkaido Univ., ²JST-ERATO, ³Fac. of Sci., Hokkaido Univ.) ○Hiroki Hayashi,^{1,2} Hitomi Katsuyama,^{1,2} Tsuyoshi Mita,^{1,2} Yu Harabuchi,^{1,2,3} Satoshi Maeda^{1,2,3}

Fluorinated nitrogen-containing heterocycles are privileged motifs in bioactive compounds and materials. Although numerous methods for synthesis of the structure have been developed extensively, the construction of heterocycle bearing an α,α -difluoromethylene unit adjacent to a nitrogen atom has been less explored presumably due to their inherent instability. Here, we describe computational prediction by quantum chemical calculations and experimental demonstration that identifies a multicomponent reaction to access these compounds. The automated search of reaction pathway by artificial force induced reaction (AFIR)¹ predicted that the three-component reaction of pyridine, difluorocarbene and an electrophile such as an aldehyde or an alkene proceeded through the pyridinium ylide-mediated 1,3-dipolar cycloaddition to give a dearomatized heterocyclic product. Based on this scenario, the predicted reaction could be performed successfully to afford the desired fluorinated *N*-heterocycles.

Keywords : *N*-Heterocycles; Quantum Chemical Calculation; Multi-Component Reaction; Difluoroalkylation; Dearomatization

フッ素化された含窒素ヘテロ環構造は様々な医薬品に含まれる分子骨格であり、これまでに数多くの合成手法が報告されてきた。しかし、窒素原子に隣接する炭素に2つのフッ素原子を有する *N*- α,α -ジフルオロ含窒素ヘテロ環の構築手法は非常に限られている。今回我々は、量子化学計算を用いる人工力誘起反応 (AFIR: Artificial Force Induced Reaction) 法¹によって、同骨格構築に有効な三成分連結反応をゼロから予測し、実験での合成に成功した。まず、AFIR 法による計算から、ピリジン、ジフルオロカルベン、アルデヒドまたはアルケンのような求電子剤を基質とする、ピリジニウムイリドを経由する脱芳香族化を伴う 1,3-双極子環化付加反応が進行することが示唆された。得られた計算結果を指針として本反応の具現化を検討した結果、*N*- α,α -ジフルオロアルキル骨格を持つ含窒素ヘテロ環生成物を高収率で得ることに成功した。



- 1) Maeda, S.; Harabuchi, Y.; Takagi, M.; Taketsugu, T.; Morokuma, K. *Chem. Rec.* **2016**, *16*, 2232.
- 2) Hayashi, H.; Katsuyama, H.; Mita, T.; Harabuchi, Y.; Maeda, S. *manuscript in preparation*.

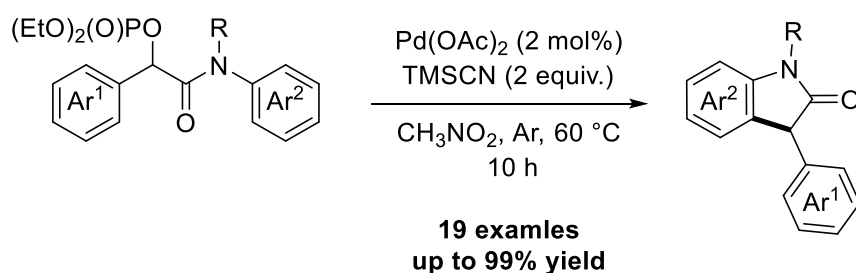
Silyl Cyanopalladate-Catalyzed Friedel–Crafts-type Cyclization Affording 3-Aryloxindole Derivatives

(¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, ²Faculty of Engineering, Hokkaido University, ³Frontier Chemistry Center, Hokkaido University) ○ Hamdiye Ece,¹ Taiga Yurino,^{2,3} Takeshi Ohkuma^{2,3}

Keywords: Friedel–Crafts-type cyclization, silyl Lewis acid, cyanopalladate complex

It is well known that thermodynamically stable metal cyanide ($M(CN)_n$) species are formed due to the strong interaction between transition metal salt (MX_n) and C-terminus of cyanide (CN^-). In the presence of the excess amount of trimethylsilyl cyanide (TMSCN), a part of the metal cyanide is converted into the corresponding silyl cyanometallates ($TMS[M(CN)_{n+1}]$) in equilibrium. Recently, we have focused on the Lewis acidic properties of silyl cyanometallates generated *in situ* from catalytic amount of Pd and/or Ag salts and stoichiometric amount of TMSCN. The complexes, $(TMS)[Pd(CN)_3]$ and $(TMS)[Ag(CN)_2]$, can activate allylic phosphates as Lewis acid catalysts to promote Friedel–Crafts-type reaction affording C-allylated phenol and anisole, respectively.¹ Herein, we report that 3-aryloxindoles are successfully synthesized through silyl cyanopalladate catalyzed Friedel–Crafts-type cyclization.

The diethylphosphates of *N*-arylmandelamides were catalytically cyclized in CH_3NO_2 by the combination of $Pd(OAc)_2$ (2 mol%) and TMSCN (2 equiv) under Ar atmosphere. In most cases, the target compounds were obtained in around 99% yield. Formation of six-membered lactam from *N*-benzylmandelamide derivative was completed under the same conditions without any problem. The gram-scale reaction also gave the product quantitatively. For the application of the product, 3-arylation of the oxindole to afford the 3,3-diaryloxindoles with two different aryl groups were successfully performed.



1) Yurino, T.; Ece, H.; Ohkuma, T. *Asian J. Org. Chem.* **2020**, *9*, 557.

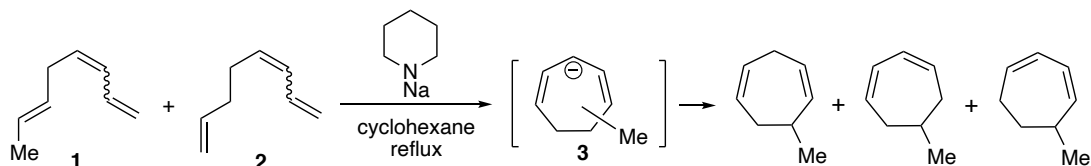
8 π electrocyclic reaction of phosphonate derivatives

(¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, ²Faculty of Science, Hokkaido University) ○Hiroki Saito,¹ Keiji Tanino²

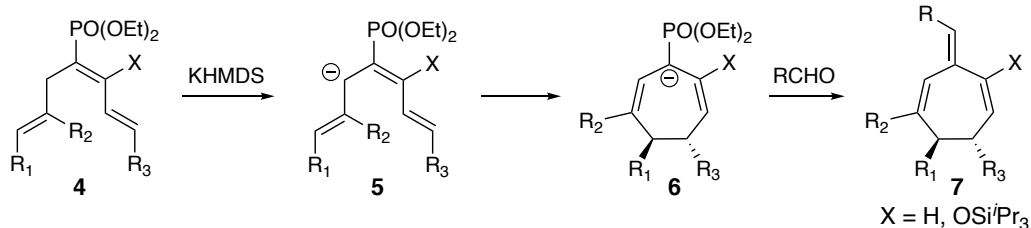
Keywords: Seven-membered carbocycle; Phosphonate; 8 π electrocyclic reaction; Horner-Wadsworth-Emmons reaction

The development of an efficient method for the construction of seven-membered carbocycles is an important object which would contribute natural product synthesis. Various methods have been developed so far, but few examples using an 8 π electrocyclic reaction of a heptatrienyl anion have been reported due to the difficulty in controlling the regiochemistry of the double bonds in the product. For example, Kleinschmidt *et al.* reported that a mixture of octatriene **1** and **2** underwent a cyclization reaction upon treatment with a base in refluxing cyclohexane, resulting in formation of a mixture of three regioisomers of cycloheptadiene. Herein, we report an 8 π electrocyclic reaction of phosphonate derivative **4**, which affords a seven-membered product **7** as a single regioisomer possessing three alkene moieties. The reaction proceeds through generation of a heptatrienyl anion species **5**, an 8 π electrocyclic reaction to give cycloheptadienyl anion **6**, and Horner-Wadsworth-Emmons (HWE) reaction with an aldehyde, giving rise to a 3-alkylidene-1,4-cycloheptadiene derivative. The new cyclization reaction provided a variety of substituted cycloheptadiene derivatives involving enol silyl ethers.

Previous work (Kleinschmidt, 1986)



This work



1) Zuech, E. A.; Crain, D. L.; Kleinschmidt, R. F. *J. Org. Chem.* **1986**, *33*, 771-775. 2) 卯田祥子, 土門大祐, 谷野圭持, 日本化学会第 97 春季年会 2017, 4E5-30, 日吉.

Academic Program [Oral B] | 16. Natural Products Chemistry, Chemical Biology | Oral B**[A01-2pm] 16. Natural Products Chemistry, Chemical Biology**

Chair: Go Hirai, Shigenobu Umemiya

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 1 (Online Meeting)

[A01-2pm-01] Live-Cell Protein Lysine Acylation Using Boronate-Assisted Hydroxamic Acid Catalyst○Christopher Adamson¹, Shigehiro Kawashima¹, Kenzo Yamatsugu¹, Motomu Kanai¹ (1. The University of Tokyo)

1:00 PM - 1:20 PM

[A01-2pm-02] Synthetic hyper acetylation of histones with a chemical catalyst system and its application to *Xenopus laevis* sperm chromatin○Hidetoshi Kajino¹, Tomomi Nagatani², Miku Oi¹, Tomoya Kujirai^{3,4}, Hitoshi Kurumizaka^{3,4}, Atsuya Nishiyama², Makoto Nakanishi², Kenzo Yamatsugu¹, Shigehiro A Kawashima¹, Motomu Kanai¹ (1. The Univ. of Tokyo, 2. The Univ. of Tokyo, The Institute of Medical Science, 3. The Univ. of Tokyo, Institute of Quantitative Biosciences, 4. JST-ERATO)

1:20 PM - 1:40 PM

[A01-2pm-03] N-GlycoAlbumin-Ru artificial metalloenzyme for therapeutic drug synthesis.○Igor Nasibullin^{1,3}, Ivan Smirnov³, Katsunori Tanaka^{1,2,3} (1. RIKEN, Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2. Tokyo Institute of Technology, Department of Chemical Science and Engineering, School of Materials and Chemical Technology, 3. Kazan Federal University, Biofunctional Chemistry Laboratory, A. Butlerov Inst.)

1:40 PM - 2:00 PM

[A01-2pm-04] Anticancer approach by a gold artificial metalloenzyme-catalyzed synthesis of quaternary ammonium derivatives via hydroamination○Tung-Che Chang¹, Tomoya YAMAMOTO¹, Katsunori TANAKA^{1,2,3} (1. Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2. Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 3. Biofunctional Chemistry Laboratory, A. Butlerov Inst., Kazan Federal University)

2:00 PM - 2:20 PM

[A01-2pm-05] Rational design of a stapled JAZ peptide as the jasmonate-related transcription factor-selective inhibitor○Yosuke Takaoka¹, Kaho Suzuki¹, Minoru Ueda^{1,2} (1. Tohoku Univ., Grad. Sci., 2. Tohoku Univ., Grad. Life Sciences)

2:20 PM - 2:40 PM

[A01-2pm-06] Tumor therapy using ruthenium catalytic reaction in mice○Kyohei Muguruma¹, Peni Ahmadi², Tung-che Chang², Katsunori Tanaka^{1,2,3} (1. Tokyo Institute of Technology, 2. RIKEN, 3. Kazan Federal University)

2:40 PM - 3:00 PM

[A01-2pm-07] Revealing Binding Position of Aplyronine A as A Protein-Protein Interaction Inducer○Didik Huswo Utomo¹, Akari Fujieda¹, Maho Morita¹, Hideo Kigoshi², Masaki Kita¹ (1.

Graduate School of Bioagricultural Sciences, Nagoya University , 2. Graduate School of Pure and Applied Sciences, University of Tsukuba)

3:00 PM - 3:20 PM

[A01-2pm-08] Reactivity of acrolein released from cancer cells: Application for selective cancer therapy and diagnosis

○Ambara Rachmat Pradipta¹, Peni Ahmadi², Tanaka Katsunori^{1,2,3} (1. Tokyo Tech., 2. RIKEN, 3. Kazan Univ.)

3:20 PM - 3:40 PM

Live-Cell Protein Lysine Acylation Using Boronate-Assisted Hydroxamic Acid Catalyst

¹Graduate School of Pharmaceutical Sciences, The University of Tokyo

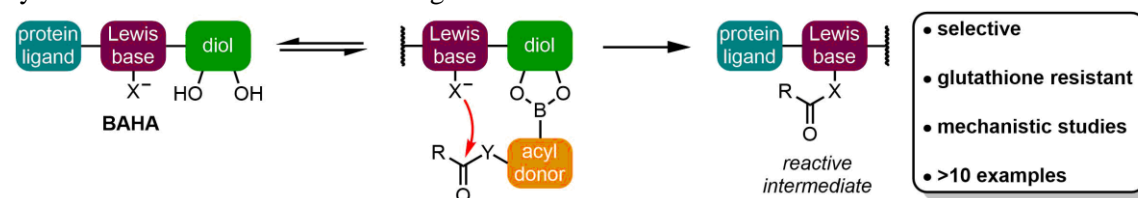
○ Christopher Adamson¹, Shigehiro Kawashima¹, Kenzo Yamatsugu¹, Motomu Kanai¹

Keywords: catalysis, post-translational modification, boronic acids

Eukaryotic cell processes including signal transduction, regulation of enzyme activity, and transcriptional regulation are tightly regulated via protein post-translational modifications (PTMs). Thus, chemical methods to install PTMs within living cells should prove useful as tools for manipulating these phenomena. Our research group has reported regioselective protein lysine acylation using the DSH catalyst system.¹ However, competition between the DSH catalyst and glutathione (GSH) leads to a lower concentration of the reactive intermediate. This necessitated millimolar concentrations of thioester acyl donor. However, exposure of cells to thioester reagents at millimolar concentrations leads to considerable off-target acylation.

To overcome this problem, we devised the boronate-assisted hydroxamic acid (BAHA) catalyst system (Figure). In this system, the catalyst's diol module reversibly binds to a boronic acid-containing acyl donor. The subsequent intramolecular acyl transfer to a Lewis base moiety thus benefits from a local molarity effect. A more rapid pathway to the reactive intermediate increases the concentration of the reactive intermediate, thus enabling a high yielding reaction even at micromolar reagent concentrations. Critically, this process is not significantly inhibited by GSH.

To showcase this methodology, we demonstrated the installation of naturally occurring and abiotic lysine acylation within HEK293T cells. As off-target protein acylation is very low when compared to precedent methods, the BAHA system constitutes a minimally invasive tool for lysine PTM installation within living cells.



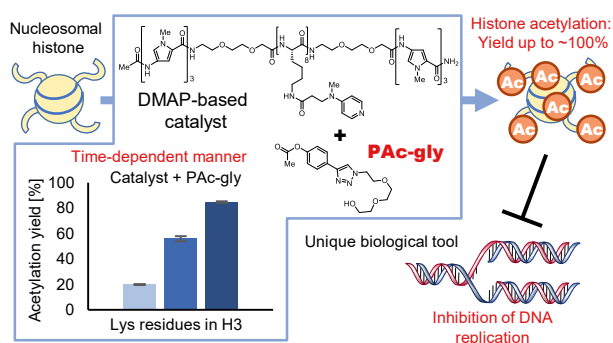
Synthetic hyper acetylation of histones with a chemical catalyst system and its application to *Xenopus laevis* sperm chromatin

(¹Graduate School of Pharmaceutical Sciences, The University of Tokyo, ²The Institute of Medical Science, The University of Tokyo, ³Institute of Quantitative Biosciences, The University of Tokyo, ⁴JST-ERATO) ○Hidetoshi Kajino,¹ Tomomi Nagatani,² Miku Oi,¹ Tomoya Kujirai,^{3,4} Hitoshi Kurumizaka,^{3,4} Atsuya Nishiyama,² Makoto Nakanishi,² Kenzo Yamatsugu,¹ Shigehiro A. Kawashima,¹ Motomu Kanai¹

Keywords: Protein modification; Catalyst; Acetylation; Histone; *Xenopus laevis*

Post-translational modifications of histones are a critical chemical process in epigenetics. Chemical approaches to modulating post-translational modifications of histones under physiological conditions provide unique tools for elucidation of epigenetic mechanisms and for therapeutic purposes. Here, we report combinations of a DMAP-based catalyst¹ (PDP or 16DMAP) and a phenyl acetate with optimal electron density (PAC-gly) as a new chemical system for high-yield, selective synthetic acetylation of histone lysine residues. Although PAC-gly itself caused little background protein acetylation and underwent little unproductive hydrolysis, the DMAP-based catalysts promoted almost quantitative histone acetylation. This high reactivity is likely due to a stabilized transition state of the rate-determining acyl pyridinium-formation step through a ternary complex composed of the catalyst, the acetyl donor, and the reacting lysine.

We applied this chemical system to *Xenopus laevis* sperm chromatin (XSC). XSC is unreactive to histone acetyl transferase-mediated acetylation, but was approximately 90% acetylated under our reaction conditions. Acetylated XSC strongly inhibited DNA replication in the *Xenopus* egg extract system, suggesting the importance of a proper level of histone acetylation for cell cycle progression.²



1) Ishiguro, T.; Amamoto, Y.; Tanabe, K.; Liu, J.; Kajino, H.; Fujimura, A.; Aoi, Y.; Osakabe, A.; Horikoshi, N.; Kurumizaka, H.; Yamatsugu, K.; Kawashima, S. A.; Kanai, M. *Chem*, **2017**, 2, 840-859. 2) Kajino, H.; Nagatani, T.; Oi, M.; Kujirai, T.; Kurumizaka, H.; Nishiyama, A.; Nakanishi, M.; Yamatsugu, K.; Kawashima, S. A.; Kanai, M. *RSC Chem. Biol.*, **2020**, 1, 56-59.

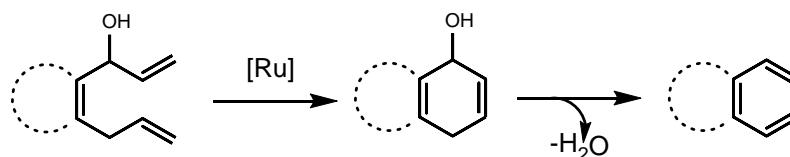
N-Glycoalbumin-Ru artificial metalloenzyme for therapeutic drug synthesis.

(¹RIKEN, Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, ²Tokyo Institute of Technology, Department of Chemical Science and Engineering, School of Materials and Chemical Technology, ³Kazan Federal University, Biofunctional Chemistry Laboratory, A. Butlerov Inst.) ○Igor Nasibullin^{1,3}, Ivan Smirnov³, and Katsunori Tanaka^{1,2,3}

Keywords: Ring-closing metathesis; Artificial metalloenzyme; N-glycan; Albumin

Artificial metalloenzymes (ArM) are the most promising systems for catalysis of the new-to-nature reactions in biological environments. In order to design a biocompatible ArM we hypothesized that natural non-metal proteins acting as carriers of small molecules in living organisms, might be an efficient basis for using in creation of the ArM. Due to protein stability and ability to bind with various hydrophobic molecules, metal catalyst with appropriate hydrophobic anchor can tightly bind with protein at the desired binding site.

In our study, we have designed an efficient albumin-based Ru-type metalloenzyme suitable for therapeutic *in vivo* drug synthesis via ring-closing metathesis reaction.^{1,2} In particular, high activity has been found for aromatization reaction by sequential cyclization/dehydration steps. The catalytic synthesis of various carbo- and heteroaromatic compounds was performed. Acyclic precursor (prodrug) of anticancer drug has been developed to reduce the biological activity, as well as the side effects of the anticancer drug. Site-selective catalytic cyclization of a biologically inactive prodrug caused a significant inhibitory effect on the cancer cells growth.



1) S. Eda, I. Nasibullin, K. Vong, N. Kudo, M. Yoshida, A. Kurbangalieva, K. Tanaka, *Nature Catal.* **2019**, 2, 780.

2) K. Vong, S. Eda, Y. Kadota, I. Nasibullin, T. Wakatake, S. Yokoshima, K. Shirasu, K. Tanaka, *Nature Commun.* **2019**, 10, 5746.

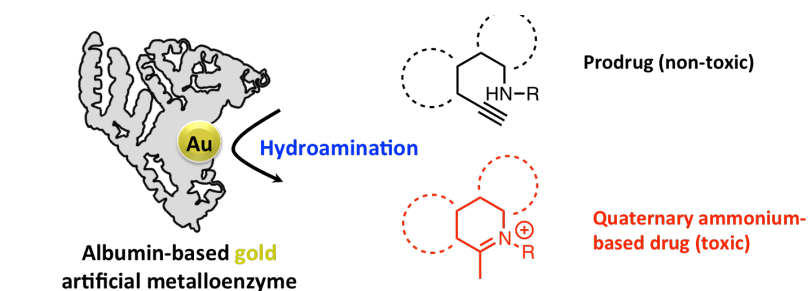
Anticancer approach by a gold artificial metalloenzyme-catalyzed synthesis of quaternary ammonium derivatives via hydroamination

(¹Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, ²Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, ³Biofunctional Chemistry Laboratory, A. Butlerov Inst., Kazan Federal University) ○Tsung-Che Chang,¹ Tomoya Yamamoto,¹ Katsunori Tanaka^{1,2,3}

Keywords: Gold catalyst; Artificial metalloenzyme; Prodrug; Anticancer drug

One of the most common treatments for cancer is chemotherapy, which is defined as the use of drugs to destroy cancer cells. This approach has demonstrated significant curative effects. However, because chemotherapy is not perfectly specific for cancer cells, it has significant side effects on rapidly dividing healthy cells.¹ An emerging approach in the field of targeted drug delivery is establishment of abiotic metal-triggered prodrug mechanisms that can control the release of bioactive drugs.² This approach is advantageous because of the bioorthogonality of abiotic metals. Currently, design of prodrugs that use abiotic metals as a trigger relies heavily on uncaging strategies.

This work introduces a strategy based on a gold-catalyzed synthesis of a quaternary ammonium-based anticancer drug from a prodrug in good turnover number (over 100) via hydroamination under physiological conditions. To make the prodrug strategy biocompatible, a human serum albumin-based gold artificial metalloenzyme^{3,4} (ArM), rather than of the free gold metal complex, was used as a trigger for prodrug activation. The albumin-based gold ArM protected the catalytic activity of a bound gold metal even in the presence of up to 1 mM glutathione *in vitro*. The synthesized drug via the gold ArM exerted a therapeutic effect in cell-based assays, highlighting the potential usefulness of the gold ArM in anticancer approaches.



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ジャスモン酸関連転写因子選択的なステープル JAZ ペプチドの開発

(東北大院理¹・東北大院生命²) ○高岡 洋輔¹・鈴木 華穂¹・上田 実^{1,2}

Rational design of a stapled JAZ peptide as the jasmonate-related transcription factor-selective inhibitor (¹*Graduate School of Science, Tohoku University*, ²*Graduate School of Life Science, Tohoku University*) ○Yousuke Takaoka,¹ Kaho Suzuki,¹ Minoru Ueda^{1,2}

Plant hormone jasmonate (JA) induces protein-protein interaction between F-box protein COI1 and transcriptional repressor JAZ, and causes plant defense responses as well as growth inhibition. In the absence of JA, JAZ binds to and represses the MYC transcription factors. Upon JA biosynthesis, JA recruits JAZ to COI1 for JAZ degradation, and then, the derepressed MYC upregulates the expression of JA-related genes. Here, we successfully developed a MYC-selective peptide inhibitor based on the crystal structure of MYC-JAZ complex. This designed stapled JAZ peptide selectively inhibited MYC-mediated gene expression in *Arabidopsis thaliana*, whereas it has almost no affinity with COI1.

Keywords : Plant hormone; Chemical Biology; Transcription factor; Stapled peptide

ジャスモン酸 (JA) は、F-box タンパク質 COI1 と転写リプレッサー JAZ との共受容体に認識され、植物の生長や免疫などを制御する重要な植物ホルモンである。定常状態で JAZ は主要転写因子 MYC などに結合して機能を抑制するが、JA 活性本体 JA-Ile を介して JAZ が COI1 と結合するとユビキチン化され、分解される。続いて JAZ による抑制が解除された転写因子 (TF) が活性化され、様々な JA 関連遺伝子の発現が誘起される。シロイヌナズナに JAZ は 13 種、JA 関連 TF は 25 種以上が発現しており、それぞれの下流を複雑に制御すると考えられているが、詳細は不明な点が多い。

結晶構造解析から、JAZ は MYC との結合時には結合ドメイン全体がヘリックス構造を形成するのに対し、COI1/JA-Ile との三者複合体形成時には同じドメインの一部をランダムループ構造に変化させることが分かっている (Fig. 1)。そこで本研究では、JA 関連 TF 選択的なツール開発を目指し、JAZ の構造を MYC 結合型ヘリックス構造に固定したステープルペプチド (JAZst) を開発した¹⁾。まず JAZst は、

COI1 には全く結合せず MYC 選択的に結合すること、及び MYC との結合がステープル化によって 50 倍向上することなどを確認した。さらにシロイヌナズナに JA と JAZst を共投与すると、JA による MYC 下流の遺伝子発現が顕著に抑制されることが示唆された。JAZst は複雑な JA 応答を制御する新規ケミカルツールとして期待される。

1) K. Suzuki, Y. Takaoka, M. Ueda, *RSC Chem. Biol.* in press.

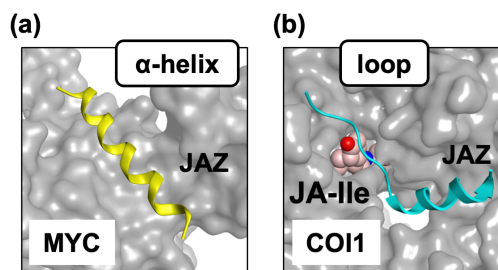


Fig. 1. (a) MYC3 及び (b) COI1 と JAZ との共結晶構造 (PDB ID: 4RS9, 3OGL) .

マウス体内でのルテニウム触媒反応によるがん治療

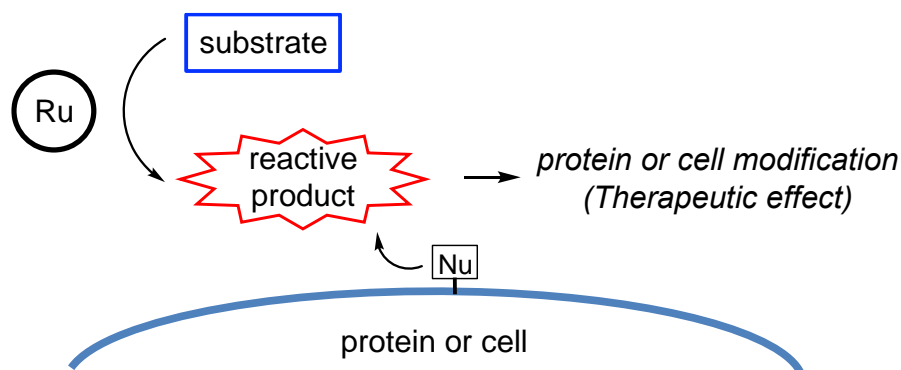
(東工大物質理工¹・理研 開拓研究本部 田中生体研²・カザン大 A.ブトレーロフ研 生体研³) ○六車 共平¹・Ahmadi Peni²・張宗哲²・田中 克典^{1,2,3}

Tumor therapy using ruthenium catalytic reaction in mice (¹*School of Materials and Chemical Technology, Tokyo Institute of Technology*, ²*Biofunctional Synthetic Chemistry Laboratory, CPR, RIKEN*, ⁴*Biofunctional Chemistry Laboratory, Alexander Butlerov Institute of Chemistry, Kazan Federal University*) ○ Kyohei Muguruma,¹ Peni Ahmadi,² Chang Tsung-che,² Katsunori Tanaka^{1,2,3}

The function of cell or protein can be artificially regulated by chemically modification of their surfaces. In this study, we developed a modification reaction of protein and cell surfaces by using a highly reactive and biocompatible ruthenium catalyst. In the use of proapoptotic peptide as a substrate in this reaction, tumor cells were significantly killed by conjugation of the peptide onto cell surface in the presence of ruthenium catalyst. In addition, a single administration of substrate and metal-protein complex (ruthenium catalyst and metal carrier) from the tail vein to a tumor-bearing mouse successfully suppressed the tumor growth. In summary, our ruthenium catalyzed reaction using proapoptotic peptide can be applied to in vivo condition and exhibit significant therapeutic effect against tumor tissues.

Keywords : Ruthenium; Cell surface modification; Catalytic reaction, In vivo synthetic chemistry

タンパク質や細胞表面を様々な分子により化学修飾することで、人為的にそれらの機能を改変することが行われている。本研究では、高い反応性および生体適合性を有するルテニウム触媒を用い、タンパク質や細胞表面の化学修飾法を開発した。アポトーシス誘導性ペプチドを反応基質として、本反応をがん細胞に対して行うことで、触媒の存在下においてのみ有意な殺細胞活性を示した。さらに、基質とキャリアに担持したルテニウム触媒を担がんマウスに尾静注することで、がんの増殖を抑制することに成功した。すなわち、本反応は生体内においても進行し、がん治療に応用することが可能である。



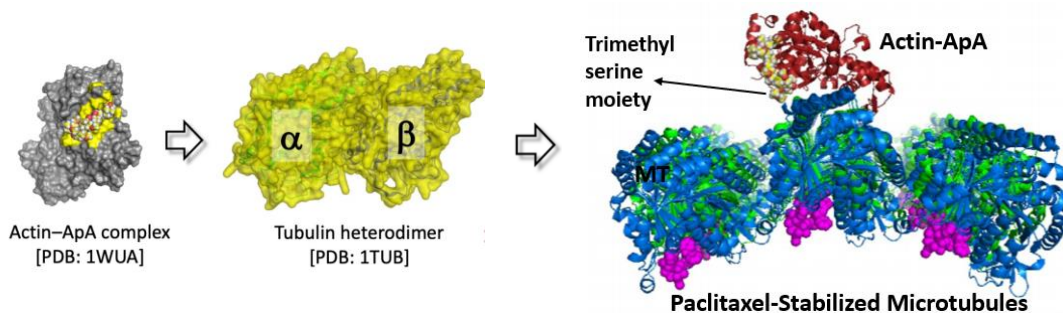
Revealing Binding Position of Aplyronine A as a Protein-Protein Interaction Inducer

(¹Graduate School of Bioagricultural Sciences, Nagoya University; ²Graduate School of Pure and Applied Sciences, University of Tsukuba) ○Didik Huswo Utomo¹, Akari Fujieda¹, Maho Morita¹, Hideo Kigoshi², Masaki Kita¹

Keywords: Aplyronine A, protein-protein interaction, actin, tubulin, ternary complex

Aplyronine A (ApA) is an antitumor macrolide that stabilizes the protein-protein interaction between actin and tubulin¹. This study aims to evaluate the binding position of actin-aplyronine A (ApA) complex on tubulin and microtubule (MT) lattice. 3D structure of actin-ApA (1WUA) and tubulin (1TUB) were retrieved from PDBJ.org^{2,3}. Protein-protein docking technique in Molecular Operating Environment (MOE.2019.1) was employed for determining the binding position of actin-ApA complex on tubulin. These results showed that actin-ApA complex had 10 possible binding models on tubulin heterodimers with the best affinity of -81.7 kcal/mol. The protein-protein interaction was clearly mediated by ApA and the stable ternary complex was supported by hydrogen bonds and hydrophobic interactions. Predicted ternary complex revealed that actin-ApA complex preferred the Helix-11 (H11) and Helix-12 (H12) for its binding position on tubulin.

Furthermore, reaction of actin-ApA with paclitaxel-stabilized MT was conducted at 37 °C for 1 hour, and their interactions were evaluated after multi-ultracentrifugation strategy (58.000 rpm and 120.000 rpm) using SDS-PAGE. Negative stain in electron microscopy showed that actin-ApA complex directly broke paclitaxel-stabilized MT. Most of the tubulin became a ternary complex, and some short fragments were broken when interacted with actin-ApA complex. This finding will be further validated by 3D-cryo-EM.



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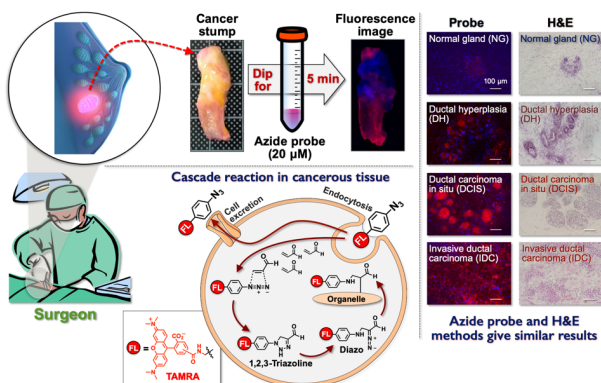
Reactivity of acrolein released from cancer cells: Application for selective cancer therapy and diagnosis

(¹*School of Materials and Chemical Technology, Department of Chemical Science and Engineering, Tokyo Institute of Technology*, ²*Biofunctional Synthetic Chemistry Laboratory, RIKEN Cluster for Pioneering Research*, ³*Biofunctional Chemistry Laboratory, A. Butlerov Institute of Chemistry, Kazan Federal University*) ○Ambara R. Pradipta,¹ Peni Ahmadi,² Katsunori Tanaka^{1,2,3}

Keywords: Acrolein, Cancer, Drug delivery, 1,3-Dipolar cycloaddition, Aryl Azide

Acrolein, a highly toxic α,β -unsaturated aldehyde, occurs as a pollutant in the environment (*e.g.*, tobacco smoke and exhaust gas) and is ubiquitously generated in biosystems (*e.g.*, lipid peroxidation process and metabolism of polyamines). High accumulation of acrolein in biosystems is often linked pathologically with several diseases, including cancer and Alzheimer's disease. Accordingly, acrolein holds great potential as a biomarker, and its direct measurement in biological samples is essential to provide information for diagnosis and therapeutic purposes.

Recently, we discovered 1,3-dipolar cycloaddition reaction between aryl azide and acrolein, which proceeds without a catalyst to give 4-formyl-1,2,3-triazoline derivative. The reaction proceeds with high reactivity and selectivity even under physiological conditions. We have successfully utilized the acrolein-azide click reaction as a robust method for detecting and visualizing acrolein generated by live cells.¹ Furthermore, we found that a high level of acrolein is expressed in cancer cells, whereas only a negligible amount is expressed in healthy cells. Herein, we utilized the azide-acrolein click reaction to discriminate breast cancer lesion from the normal breast gland, which resected from breast cancer patients.^{2,3} This method can be used not only to visualize the cancer tissues rapidly but also to distinguish morphology of the resected tissues. Thus, it has a potential clinical application for breast-conserving surgery. Furthermore, the ability to perform chemical reactions with cancer metabolites only at the desired cancer site is highly advantageous for cancer therapy.



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[A24-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Osami Shoji, Akira Onoda

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 24 (Online Meeting)

[A24-2pm-01] Energy Analysis of Miniprotein by in Vivo Protein Crystallization○Mariko Kojima¹, Yuki Hishikawa¹, Satoshi Abe¹, Tadaomi Huruta¹, Duy Phuoc Tran¹, Akio Kitao¹, Takafumi Ueno¹ (1. TokyoTech)

1:00 PM - 1:20 PM

[A24-2pm-02] Design of the dynamic assembly behaviors of artificial β -helical protein needles.○Kosuke Kikuchi¹, Fukuyama Tatsuya², Basudev Maity¹, Tadaomi Furuta¹, Yusuke T Maeda², Takayuki Uchihashi³, Takafumi Ueno¹ (1. Tokyo Tech., 2. Kyusyu Univ., 3. Nagoya Univ.)

1:20 PM - 1:40 PM

[A24-2pm-03] Dual-surface functionalization of an artificial protein nanoparticle TIP60 using molecular-filtration effect of surface pores○Erika Nasu¹, Norifumi Kawakami¹, Kenji Miyamoto¹ (1. Keio University)

1:40 PM - 2:00 PM

[A24-2pm-04] Star-shaped Supramolecular Assembly Formed by the Conjugation of Hexameric Tyrosine-coordinated Hemoprotein with Engineered Cytochrome b_{562} ○Julian Wong Soon¹, Koji Oohora¹, Shota Hirayama¹, Takashi Hayashi¹ (1. Osaka University)

2:00 PM - 2:20 PM

[A24-2pm-05] Development of SPIONs-conjugated Pt Nanoparticles-Latex Nanocomposite Beads for Immunochromatography Assay with Enhanced SensitivitySizun He¹, The Son Le¹, Mari Takahashi¹, Yasushi Enomoto², Yasufumi Matsumura², ○Shinya Maenosono¹ (1. JAIST, 2. Nippon Steel Chem. Mater. Co., Ltd.)

2:20 PM - 2:40 PM

[A24-2pm-06] Evolutionary Engineering of a Cp*Rh(III)-linked Artificial Metalloenzyme with a Chimeric β -Barrel Protein Scaffold for Isoquinoline Synthesis via C(sp²)-H Bond Activation○Shunsuke Kato¹, Akira Onoda², Ulrich Schwaneberg³, Takashi Hayashi¹ (1. Osaka University, 2. Hokkaido University, 3. RWTH Aachen University)

2:40 PM - 3:00 PM

[A24-2pm-07] Screening of Peptide Derivatives for the Activation of Wild-Type Cytochrome P450BM3 for Gaseous Substrates Hydroxylation○Kai Yonemura¹, Sinya Ariyasu¹, Hiroshi Sugimoto^{2,4}, Yoshihito Watanabe³, Osami Shoji^{4,1} (1. Nagoya University, 2. RIKEN/SPring-8, 3. RCMS Nagoya University, 4. JST CREST)

3:00 PM - 3:20 PM

[A24-2pm-08] Synthesis of Hemoglobin Oligomer Capable of Structural Changes in Response to O₂ Association and Dissociation○Yoshitsugu Morita¹, Chinatsu Okuma¹, Teruyuki Komatsu¹ (1. Chuo University)

3:20 PM - 3:40 PM

Energy Analysis of Miniprotein by in Vivo Protein Crystallization

(¹Graduate School of Life-Science and Technology, Tokyo Institute of Technology)

○Mariko Kojima,¹ Yuki Hishikawa,¹ Satoshi Abe,¹ Tadaomi Furuta,¹ Duy Phuoc Tran,¹ Akio Kitao,¹ Takafumi Ueno¹

Keywords: Protein crystal engineering; In vivo protein crystallization; Metastable state; Molecular dynamics simulation

X-ray crystal structure analysis is the most essential structure determination method to gain reliable structural information of proteins at the atomic level. However, crystallization remains a bottleneck because of the difficulty in optimizing crystallization conditions to gain high-quality diffracted crystals. Protein crystal engineering to enhance crystallizability and improve crystal stability has been achieved. In recent years, immobilizing the target molecule at well-defined positions in an existing host lattice of protein crystal attracts attention as a high-versatile crystallization of the target molecule.¹ One of the challenging studies using host protein crystal is experimentally capturing the 3D structure of the target molecules in an unstable state, which is difficult to obtain in solution.

In this study, we attempted X-ray crystal structure analysis and energy analysis of miniprotein with ten amino acids, CLN025 immobilized in the loop region of polyhedra crystal (PhC) that realize high-resolution crystal structure analysis (Fig. 1a,c).^{2,3} CLN025 folds to remarkably stable β -hairpin structure in solution. We designed five types of CLN025 fused PhCs with different fusion site and linker. X-ray crystal structure analysis revealed that the electron density of the full length of CLN025 was observed in one of the mutants, Δ L1-CLN-2-PhC in which CLN025 was inserted between Y71 and N77 (Fig. 1b). The structure indicates that the structure of CLN025 immobilized in Δ L1-CLN-2-PhC was an unstable helical structure that has not been observed experimentally (Fig. 1d). The energy analysis of CLN025 obtained in this measurement by the simulation is carried out at present.

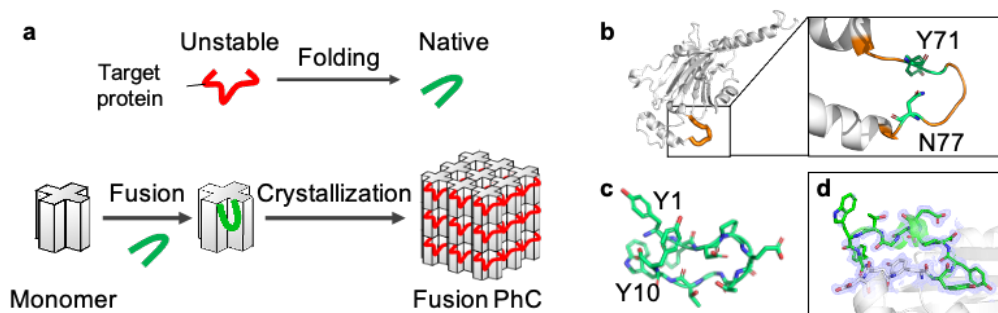


Fig. 1 a) Scheme of immobilization of unstable state target in fusion mutant PhC. b) Fusion site in loop region of Δ L1-CLN-2-PhC. c) Structure of CLN025 (PDB ID: 5aw1). d) Structure and electron density map of CLN025 observed in Δ L1-CLN-2-PhC.

1) Z. S. Derewenda, *Acta Crystallogr. Sect. D Biol. Crystallogr.* **2010**, 66, 604. 2) S. Honda, *et al.*, *J. Am. Chem. Soc.* **2008**, 130, 15327. 3) F. Coulibaly, *et al.*, *Nature*, **2007**, 446, 97.

β-ヘリックス人工分子針の動的集合設計

(東工大生命理工¹・九大理²・名大理²) ○菊池 幸祐¹・福山 達也²・Maity Basudev¹・古田 忠臣¹・前多 裕介²・内橋 貴之³・上野 隆史¹

Design of the dynamic assembly behaviors of artificial β -helical protein needles (¹*School of Life Science and Technology, Tokyo Institute of Technology*, ²*Department of Physics, Kyusyu University*, ³*Department of Physics, Nagoya University*) ○ Kosuke Kikuchi,¹ Tatsuya Fukuyama,² Basudev Maity,¹ Tadaomi Furuta,¹ Yusuke T. Maeda,² Takayuki Uchihashi,³ Takafumi Ueno¹

Recent progress on structural analysis and computational methods has allowed the accurate design of protein assemblies. However, the dynamic behavior of molecules in their assembly process remains unclear. In this study, we investigated the assembly mechanism of artificial β -helical protein needles (PN) derived from bacteriophage T4. We regulated the two-dimensional assembly behaviors of PN by engineering the tip domain and observed the dynamic behaviors directly by high-speed atomic force microscopy (HS-AFM).

Keywords : Protein Assembly; β -helix; High-speed Atomic Force Microscopy; Single-molecule Analysis; Monte Carlo Simulation

タンパク質は自発的な集合によって複雑な構造体を形成可能であり、なかでもその二次元集合体は機能性材料として注目されてきた。近年では構造解析や計算科学手法の発達によりタンパク質集合体の精密設計が可能となってきたものの、分子の動的特性にもとづいた集合体設計指針

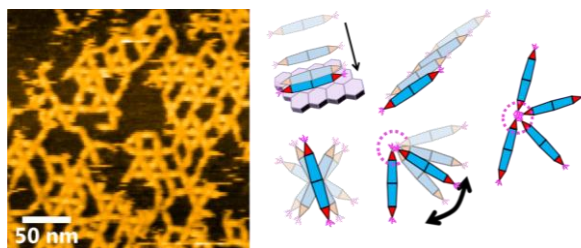


Figure 1. マイカ基板上 PN 二次元パターン形成および集合体構築を誘起する PN 単分子の動的挙動。

は確立されていない。それは、会合状態から規則構造形成に至る過程の直接観察が困難であり、分子集合化の動的メカニズムの理解が進んでいないためである。タンパク質の会合体が秩序パターン構造へと変換される際の分子の協同的な運動を追跡することができれば、集団的挙動に基づいた集合体設計が可能になると期待できる。そこで本研究では、バクテリオファージ T4 由来の β ヘリックス人工分子針 (Protein Needle, PN) に着目した¹。高速原子間力顕微鏡 (HS-AFM) による PN の動的挙動の単分子レベル追跡²にもとづき、その動的挙動制御による二次元集合体形成を試みた。HS-AFM 観察の結果からマイカ基板上において PN は動的な正三角形モザイクパターンを形成することが示され、モンテカルロシミュレーションによって PN の単分子での運動性が秩序だった集合構造形成に必要なことが明らかとなった (Figure 1)。

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- 2) Ueno, T.; Niwase, K.; Tsubokawa, D.; Kikuchi, K.; Takai, N.; Furuta, T.; Kawano, R.; Uchihashi, T. *Nanoscale* **2020**, *12*, 8166–8173.

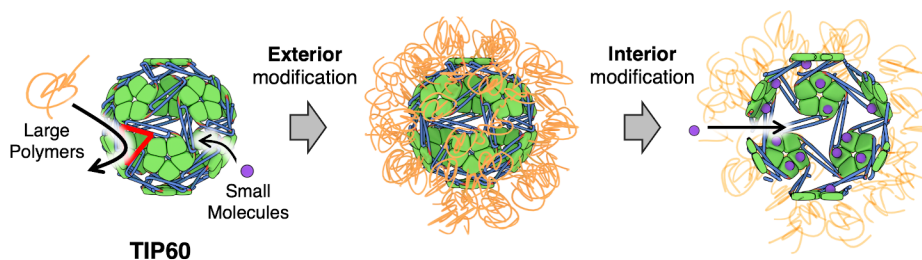
Dual-surface functionalization of an artificial protein nanoparticle TIP60 using molecular-filtration effect of surface pores

(¹*Department of Biosciences and Informations, Keio University*) ○Erika Nasu,¹ Norifumi Kawakami,¹ Kenji Miyamoto¹

Keywords: Protein Nanoparticles; Porous Materials; Dual-surface Modification

Hollow protein nanocages, which can incorporate cargo molecules in their inner cavity, are attractive materials for various applications such as drug-delivery systems and catalysis¹. We produced an artificial protein nanoparticle designated as TIP60 by designing fusion proteins composed of a pentamer protein and dimer protein². The TIP60 is a hollow nanoparticle with 20 pores on its surface. The serine residues on the interior and exterior surface of TIP60 can be replaced with cysteine residues as functional groups for site-specific chemical modification. We performed modification experiments using mutants of TIP60 introduced cysteine residues on the interior surface of TIP60 and size-different polymer molecules with maleimide groups specifically reacting with thiols. The polymers smaller than the size of the pores on the TIP60 modified cysteine residues on the interior surface, while the larger polymers could not modify them. This result suggested that the pores on the surface of TIP60 functioned as size-dependent molecular filters, which allowed only molecules smaller than the pore size to penetrate into the inner cavity of TIP60.

Motivated by the finding of size-dependent molecular discriminations by the pores on TIP60, we performed dual-surface modifications of TIP60 by size-different molecules. A double mutant of TIP60 with cysteine residues on both interior and exterior surfaces was first modified by polymer molecules larger than the pore size. These large molecules could modify cysteine residues on the exterior surface. The remained interior cysteine residues were modified by thiol-containing small molecules. We also demonstrated that the redox-responsive release of thiol-containing small molecules from the dual-surface modified TIP60.



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Star-shaped Supramolecular Assembly Formed by the Conjugation of Hexameric Tyrosine-coordinated Hemoprotein with Cytochrome *b*₅₆₂

(Graduate School of Engineering, Osaka University) ○ Julian Wong Soon, Koji Oohora, Shota Hirayama, Takashi Hayashi

Keywords: Supramolecular assembly; Cytochrome *b*₅₆₂; Hexameric Tyrosine-coordinated Hemoprotein; Heme

Various artificial supramolecular protein assemblies have emerged within the past decade due to its variety in structures and bio-functionalities which can be used for applications.¹ Biological and chemical strategies are used to create such artificial assembly systems driven by the naturally existing protein–protein, protein–ligand/cofactor, protein–compound, and receptor–ligand interactions.² In this context, we have successfully reported a number of protein-assembling system using hemoproteins such as cytochrome *b*₅₆₂ (Cyt *b*₅₆₂), and hexameric tyrosine-coordinated hemoprotein (HTHP) with a highly symmetric structure.

In our recent studies, the attachment of an artificial heme onto the surface of the Cyt *b*₅₆₂ mutant, followed by removal of the prosthetic heme provided a rigid linear assembly via heme–heme pocket interaction and secondary hydrogen bond interaction.³ In this work, we focused on the conjugation of this Cyt *b*₅₆₂ assembly with the apo-form of HTHP towards a star-shaped protein assembly (Figure 1). Initially, the transfer of the heme cofactors from Cyt *b*₅₆₂ into the apo-form of HTHP was observed by the mixing of these two proteins, showing the possibility of this strategy. Sequentially, the reaction mixture of the heme-mediated linear Cyt *b*₅₆₂ assembly and apo-HTHP at 45 °C forms a new assembly, which is confirmed by size exclusion chromatography. The further evaluation and analysis of the resulting assembly were carried out by SDS PAGE, UV-Vis spectroscopy, and dynamic light scattering.

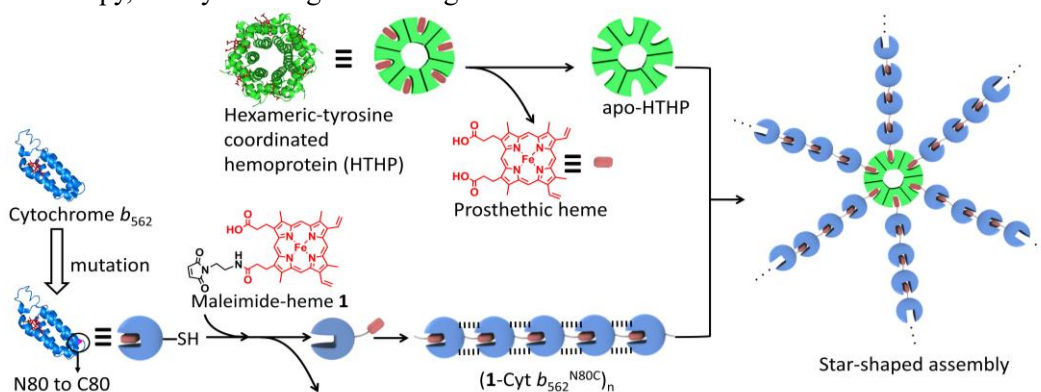


Figure 1. Schematic representation of star-shaped assembly of hemoproteins.

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イムノクロマトの超高感度化に向けた SPIONs 結合 Pt ナノ粒子-ラテックスナノコンポジットビーズの開発

(北陸先端大院¹・日鉄ケミカル&マテリアル(株)²) Sizun He¹・The Son Le¹・高橋 麻里¹・榎本 靖²・松村 康史²・○前之園 信也¹

Development of SPIONs-conjugated Pt Nanoparticles-Latex Nanocomposite Beads for Immunochromatography Assay with Enhanced Sensitivity (¹*School of Materials Science, JAIST*, ²*Nippon Steel Chem. Mater. Co., Ltd.*) Sizun He¹, The Son Le¹, Mari Takahashi¹, Yasushi Enomoto², Yasufumi Matsumura², ○Shinya Maenosono¹

Recently we have developed metal (Au or Pt) nanoparticle-loaded latex (P2VP) beads as probes for immunochromatographic test (ICT) strips with enhanced sensitivity.¹ The naked-eye detection sensitivities were enhanced by more than 64- and 16-fold for the strips with Au-P2VPs and Pt-P2VPs, respectively, compared with that using conventional colloidal gold. In this study, superparamagnetic iron oxide nanoparticles (SPIONs) were further conjugated on the metal nanoparticle-loaded latex beads in order to further improve the ICT sensitivity enabling the probes to enrich a target analyte from a sample *via* magnetic separation. Structure, magnetic property and colloidal stability of the SPION-conjugated Pt-P2VPs were investigated. In addition, the performance of the beads as probes for ICT was evaluated.

Keywords : Immunochromatographic Assay; Nanocomposite; Superparamagnetic Iron Oxide

最近我々は、イムノクロマトグラフィックテスト (ICT) の飛躍的な高感度化を可能にする新奇プローブとして、金属 (Au あるいは Pt) ナノ粒子を担持させたラテックス (P2VP) 粒子を創製した (Fig. 1)。¹ 汎用されている金ナノ粒子プローブに比べ、Au-P2VP は 64 倍、Pt-P2VP は 16 倍の感度向上が達成された。本研究では、この金属ナノ粒子担持ラテックスプローブに超常磁性酸化鉄ナノ粒子 (SPIONs) を結合させて磁性を付与することで、サンプルから標的検体を磁気濃縮することで感度のさらなる向上を図った (Fig. 2)。本講演では、SPION 結合 Pt-P2VP プローブの構造、磁気特性、コロイド安定性、および ICT プローブとしての性能評価の結果について紹介する。

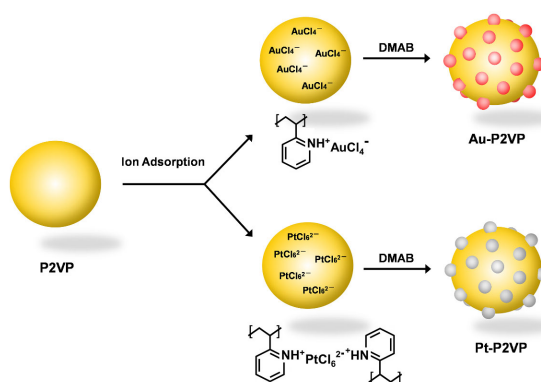


Fig. 1. Schematic illustration of the synthesis of Au-P2VPs and Pt-P2VPs.

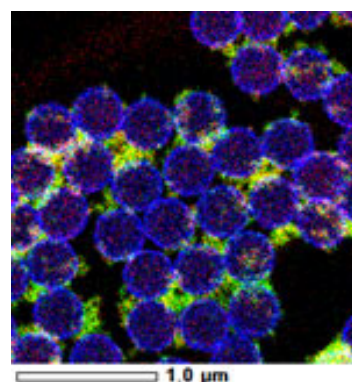


Fig. 2. EDS mapping image of SPION-conjugated Pt-P2VPs (green: Fe, blue: Pt).

1) Metal (Au, Pt) Nanoparticle-Latex Nanocomposites as Probes for Immunochromatographic Test Strips with Enhanced Sensitivity. Y. Matsumura *et al.*, *ACS Appl. Mater. Interfaces* **2018**, *10*, 31977.

Evolutionary Engineering of a Cp*Rh(III)-linked Artificial Metalloenzyme with a Chimeric β -Barrel Protein Scaffold for Isoquinoline Synthesis via C(sp²)-H Bond Activation

(¹Graduate School of Engineering, Osaka University, ²Graduate School of Environmental Science, Hokkaido University, ³Institute of Biotechnology, RWTH Aachen University)

○ Shunsuke Kato,¹ Akira Onoda,² Schwaneberg Ulrich,³ Takashi Hayashi¹

Keywords: Artificial Metalloenzyme; Biohybrid Catalyst; Directed Evolution; Rhodium

Artificial metalloenzymes consisting of a synthetic metal cofactor within a protein scaffold have emerged as a new type of catalyst which combines attractive features of transition metal catalysts and biocatalysts. Our group has previously reported a Cp*Rh(III)-linked artificial metalloenzyme (NB-Rh), in which a Cp*Rh(III) cofactor was covalently incorporated into the hydrophobic cavity of nitrobindin (NB).¹ NB-Rh and its engineered variants efficiently promoted cycloaddition of acetophenone oximes with alkynes to produce isoquinolines via C-H bond activation.² To further improve its catalytic activity, we here conducted an evolutionary engineering of the NB protein scaffold. With the aim of providing a custom-designed and confined active site for the artificial metalloenzyme, a helix-loop-helix (HLH) domain of fatty acid binding protein (FABP) were genetically recombined with the β -barrel structure of NB to generate a chimeric protein scaffold NB^{HLH} (Figure 1a). After optimization of the amino acid sequence based on directed evolution methodology, a promising variant, NB^{HLH1}(A119/P149), with high stability was identified. Moreover, further directed evolution of NB^{HLH1}(A119/P149) with the Cp*Rh complex afforded an evolved artificial metalloenzyme with a 40-fold increase in the catalytic efficiency relative to original NB-Rh (Figure 1b). Herein, we will present the construction of the chimeric protein scaffold as a host for the Cp*Rh(III)-linked artificial metalloenzymes and its directed evolution for the cycloaddition reactions.

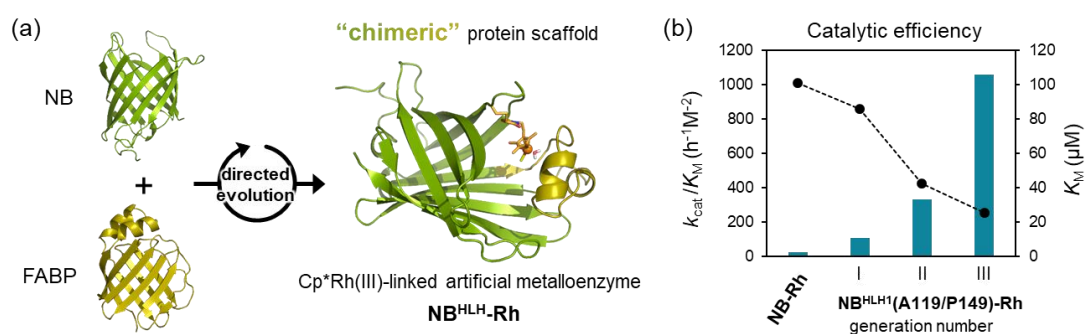


Figure 1. (a) Construction of a Cp*Rh(III)-linked artificial metalloenzyme with chimeric protein scaffold. (b) Michaelis-Menten parameters of the evolved NB^{HLH}-Rh variants for the cycloaddition reaction.

1) S. Kato, A. Onoda, A. R. Grimm, U. Schwaneberg, T. Hayashi, *Inorg. Chem.* **2020**, 59, 14457-14463.

2) S. Kato, A. Onoda, N. Taniguchi, U. Schwaneberg, T. Hayashi, *ChemBioChem.* **2020**, in press.

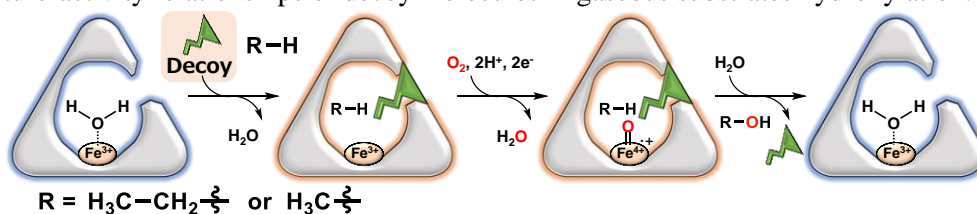
Screening of Peptide Derivatives for the Activation of Wild-Type Cytochrome P450BM3 for Gaseous Substrates Hydroxylation

(¹Graduate School of Science, Nagoya University, ²Riken/SPring-8, ³RCMS Nagoya University, ⁴JST CREST) ○ Kai Yonemura,¹ Shinya Ariyasu,¹ Hiroshi Sugimoto,^{2,4} Yoshihito Watanabe,³ Osami Shoji^{1,4}

Keywords: Hydroxylation, Cytochrome P450BM3, Decoy molecule, Gaseous substrate, Screening

The monooxygenase cytochrome P450BM3 (P450BM3) is a heme enzyme which catalyzes hydroxylation of long chain fatty acids at an extremely high rate. Despite its advantageous catalytic activity, P450BM3 does not catalyze hydroxylation of non-native substrates such as benzene due to its high substrate specificity. However, we have achieved benzene hydroxylation catalyzed by wild-type P450BM3 by adding amino acid derivatives.¹ We named such functional molecules “decoy molecules.” Decoy molecules activate P450BM3 by binding to P450BM3 in a similar manner to native substrates. However, decoy molecules themselves are not hydroxylated because of shortage of chain length. The small reaction space for non-native substrate hydroxylation is therefore formed at the catalytic site (Figure). The structure of decoy molecules has been improved to enhance catalytic activity of P450BM3. Recently, we demonstrated that screening of dipeptide derivatives is effective way to discover more effective decoy molecules in benzene hydroxylation.²

Herein, we adopted systematic screening strategy to examine hydroxylation activity of bromoethane and bromomethane catalyzed by P450BM3 in the presence of decoy molecules. Haloalkanes were chosen as surrogate substrates of gaseous alkanes for easy detection of aldehydes formed after α -elimination of HBr upon hydroxylation by colorimetric purpald assay.³ Previously reported decoy molecule library (containing over 160 molecules) and newly prepared library (containing over 20 molecules) were screened. Through the screening, specialized decoy molecules for haloalkanes hydroxylation by wild-type P450BM3 were discovered. Moreover, detectable amount of ethanol and methanol by GC-MS analysis was formed after catalytic ethane and methane hydroxylation under high pressure. Furthermore, the catalytic activity was improved using novel decoy molecules with mutated P450BM3. Based on the results of the screening, we discuss the structure-activity relationships of decoy molecules in gaseous substrates hydroxylation.



1) O. Shoji et al., *Angew. Chem. Int. Ed.* **2017**, 56, 10324–10329. 2) K. Yonemura et al., *ACS Catal.* **2020**, 10, 9136–9144. 3) H. B. Hopps, *Aldrichimica Acta*, **2000**, 33, 28–30.

Synthesis of Hemoglobin Oligomer Capable of Structural Changes in Response to O₂ Association and Dissociation

(Faculty of Science and Engineering, Chuo University) ○Yoshitsugu Morita¹, Chinatsu Okuma, Teruyuki Komatsu

Keywords: Smart Polymers, O₂ Response, Hemoglobin, Protein Assembly, Supramolecular Polymer

Considerable interest has arisen recently in protein assemblies as functional biomaterials. We have recently reported a linear coordination polymer of recombinant hemoglobin [rHb(β C93A/ β K120C)].¹⁾ Hb consists of an $\alpha_2\beta_2$ tetramer with dissociation equilibrium to two $\alpha\beta$ dimers. Hb Kansas [rHb(β N102T)] has unique transformation. The dissociation is promoted by O₂ association because Asn- β N102 which stabilizes the quaternary structure of oxy Hb is lacked in the protein. In this paper, we report synthesis and dynamic structural changes of a rHb(β C93A/ β N102T/ β K120C) [rHb(2)] oligomer in response to O₂ association and dissociation (Fig. 1).

First, we expressed rHb(di- α / β C93A/ β K120C) [rHb(1)] using *Pichia* yeast²⁾ and combined rHb(1) with a bismaleimide crosslinker, yielding a robust rHb(1) oligomer. Size exclusion chromatography and dynamic light scattering indicated that the oligomer consists of average 8 rHb(1) molecules. In contrast, combining rHb(2) with the same crosslinker yielded XL[$\alpha\beta$ (2)]₂. Interestingly, XL[$\alpha\beta$ (2)]₂ was polymerized under anaerobic condition to form the similar oligomer made of average 8 rHb(2) molecules. Upon addition of O₂, the oligomer dissociated to XL[$\alpha\beta$ (2)]₂. The structural changes were observed reversibly for three cycles. The rHb(2) oligomer is an unique functional biomaterial capable of structural changes in response to O₂ association and dissociation.

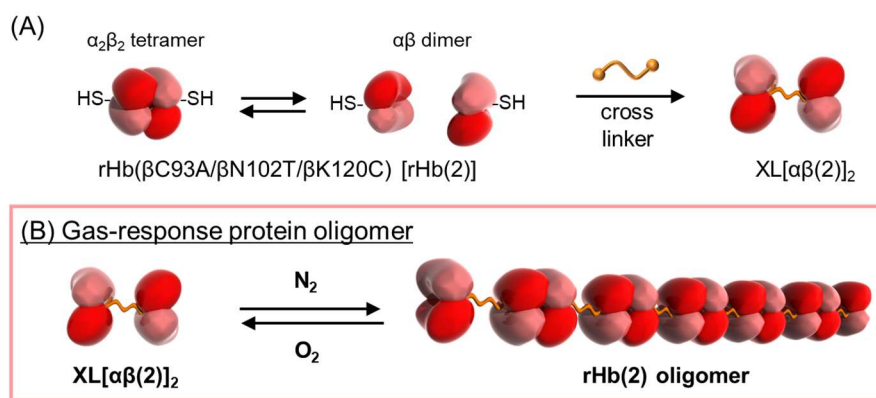


Fig. 1 (A) Synthetic scheme and (B) structural changes of the rHb(2) oligomer.

1) R. Adachi, S. Suzuki, T. Mitsuda, Y. Morita, T. Komatsu, *Chem. Commun.* **2020**, 56, 15585.

2) Y. Morita, A. Saito, J. Yamaguchi, T. Komatsu, *RSC Chem. Biol.* **2020**, 1, 128

[A23-2pm] 17. Biofunctional Chemistry, Biotechnology

Chair: Kohei Sato, Toshikazu Bando

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 23 (Online Meeting)

[A23-2pm-01] Dual-Stimuli-Responsive Small Molecular Probes for Quantitative Detection of Both pH and Enzyme Activity○Wenting Huo¹, Miki Koji¹, Daisuke Tokunaga¹, Huiying Mu¹, Masahiro Oe¹, Kouichi Ohe¹, Hiroshi Harada¹ (1. Kyoto Univ.)

1:00 PM - 1:20 PM

[A23-2pm-02] Transmembrane Anion Transport by Imidazolinium-based Multiblock Amphiphile○Miki Mori¹, Kohei Sato¹, Toru Ekimoto², Shinichi Okumura², Mitsunori Ikeguchi^{2,3}, Kazuhito Tabata⁴, Hiroyuki Noji⁴, Kazushi Kinbara¹ (1. Sch. Life Sci. Tech., Tokyo Tech, 2. Grad. Sch. Med. Life Sci., Yokohama City Univ., 3. MIH, RIKEN, 4. Grad. Sch. Eng., The Univ. of Tokyo)

1:20 PM - 1:40 PM

[A23-2pm-03] Design and Synthesis of Supramolecular Phosphatases Functionalized with Lewis Acid Moieties for Catalytic Hydrolysis of Phosphate Monoester in Two-Phase Solvent System○Shin Aoki^{1,2}, Akib Bin Rahman¹, Hirokazu Okamoto¹, Tomohiro Tanaka¹ (1. Faculty of Pharm. Sci., Tokyo Univ. Sci., 2. Research Inst. Sci. Tech., Tokyo Univ. Sci.)

1:40 PM - 2:00 PM

[A23-2pm-04] Improved photoswitching proteins for endogenous gene activation by near-infrared light○Takahiro Nakajima^{1,2}, Moritoshi Sato² (1. KISTEC, 2. Grad. Sch. Arts and Sci., The Univ. of Tokyo)

2:00 PM - 2:20 PM

[A23-2pm-05] Sequence-Specific DNA Alkylation by a Chlorambucil-Conjugated Cyclic Pyrrole-Imidazole Polyamide○Yuki Hirose¹, Kaori Hashiya¹, Toshikazu Bando¹, Hiroshi Sugiyama^{1,2} (1. Department of Chemistry, Graduate School of Science, Kyoto University, 2. Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University)

2:20 PM - 2:40 PM

[A23-2pm-06] Transcription and replication control of mitochondrial DNA by sequence-specific DNA binders○Takuya Hidaka¹, Ganesh Pandian Namasivayam², Toshikazu Bando¹, Hiroshi Sugiyama^{1,2} (1. Grad. Sch. of Sci., Kyoto Univ., 2. iCeMS, Kyoto Univ.)

2:40 PM - 3:00 PM

[A23-2pm-07] Construction of Intracellular Condition Responsive System Toward Cancer Cell Selective Therapeutics - Development of the Intracellular Condition Responsive XNA and Disulfide Linkers -○Seiya Ishizawa¹, Masahito Inagaki¹, Kenta Otake¹, Masaki Nishijima¹, Yasuyuki Araki¹, Wada Takehiko¹ (1. Tohoku University, IMRAM)

3:00 PM - 3:20 PM

[A23-2pm-08] Development of Reactions Constructing Novel Three-Dimensional
Skeletons for Exploring New Chemical Space and Protein-Protein
Interaction (PPI) Inhibitory Activity

○Hiroki Ueda^{1,2}, Peter Wipf³, Hiroyuki Nakamura¹ (1. Tokyo Institute of Technology,
Laboratory for Chemistry and Life Science, 2. Tokyo Institute of Technology, School of Life
Science and Technology, 3. Univ. of Pittsburgh, Department of Chemistry)

3:20 PM - 3:40 PM

Dual-Stimuli-Responsive Small Molecular Probes for Quantitative Detection of Both pH and Enzyme Activity

(¹Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, ²Laboratory of Cancer Cell Biology, Graduate School of Biostudies, Kyoto University) ○ Wenting Huo,¹ Koji Miki,¹ Daisuke Tokunaga,¹ Huiying Mu,¹ Masahiro Oe,¹ Hiroshi Harada,² Kouichi Ohe¹

Keywords: Photoluminescence; Dual-Responsive Probe; Bipyridyl; Quantification

Determination and quantification of multiple analytes are important for better understanding those physiological functions which involve the coincidence of multiple chemical events. However, very few probes that respond to multiple stimuli, especially to an enzyme, have been reported. In this contest, we have developed the first dual-responsive probe for quantitative detection of pH as well as enzyme activity in an unknown sample. 3,3'-Dihydroxy-2,2'-bipyridyl derivative **3** whose molecular weight is less than 200 is easy to be functionalized. Because two sterically demanding substituents at oxygen functionality of bipyridine induced its twisted structure, probe **1** is non-emissive. However, the removal of a

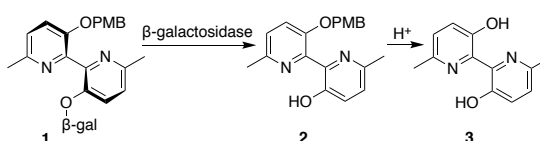


Figure 1. Activation process of probe **1**.

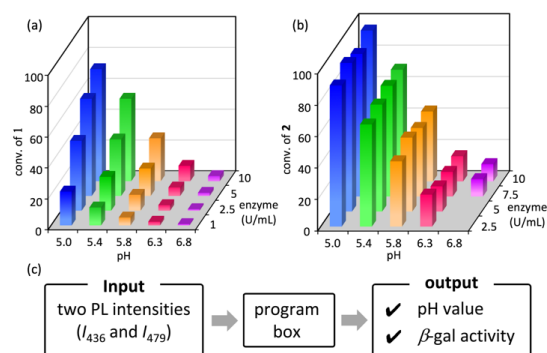


Figure 2. (a) and (b): Three-dimensional graphs of the conversion of **1** and **2** with pH values and enzyme activities. (c) Flow chart of the calculation program.

β -galactosyl (β -gal) moiety followed by the deprotection of *p*-methoxybenzyl (PMB) group gave emissive **3** through intermediate **2** whose emission is different from **3** (Figure 1). Moreover, probe **1** could emit strong photoluminescent signals in ovarian cancer cells OVK-18, while it emitted negligible photoluminescence in normal human cells HUVEC. Three-dimensional graphs of the conversion of **1** and **2** with pH values and β -galactosidase's activities (Figure 2a and 2b) allowed us to build up a calculation program (Figure 2c). Inputting the photoluminescence (PL) intensity at 436 nm and 479 nm into the program box automatically produces outputs of calculated pH value and enzyme activity with high accuracy. Relative errors of the pH and the β -galactosidase activity between the calculated value and the experimental value were below $0.6\% \pm 0.1\%$ and $7\% \pm 2\%$, respectively. Therefore, this dual-responsive probe will earn a place in bioimaging area for monitoring multiple analytes with high efficiency.

Transmembrane Anion Transport by Imidazolinium-based Multiblock Amphiphile

(¹*School of Life Science and Technology, Tokyo Institute of Technology*, ²*Graduate School of Medical Life Science, Yokohama City University*, ³*Medical Sciences Innovation Hub Program, RIKEN*, ⁴*Graduate School of Engineering, University of Tokyo*) ○Miki Mori,¹ Kohei Sato,¹ Toru Ekimoto,² Shinichi Okumura,² Mitsunori Ikeguchi,^{2,3} Kazuhito Tabata,⁴ Hiroyuki Noji,⁴ Kazushi Kinbara¹

Keywords: Multiblock amphiphile; Anion transport; Lipid bilayer membranes; Imidazolinium

Preservation and regulation of ion-concentration gradients across the biological membranes is important in cellular events, such as apoptosis and proliferation. In nature, ion transport across the membranes is realized by membrane transporters embedded in the lipid bilayer membranes. Meanwhile, dysregulation of ion transport, especially that of anion transport, is considered to cause serious diseases such as cystic fibrosis.

Previously, our group has reported that multiblock amphiphiles, consisting of alternately aligned hydrophobic aromatic units and hydrophilic oligo (ethylene glycol) chains, can transport ions across the lipid bilayer membranes¹⁾. In this study, we newly developed an imidazolinium-based multiblock amphiphile (**IMA**), which bears imidazolinium ion at the center of hydrophobic unit as an anion recognition site (**Figure**).

We investigated the ion transport activity of **IMA** using liposomes as model membranes. Interestingly, **IMA** transported anions as a mobile carrier, with selectivity for nitrate. ¹H NMR titration experiment in solution indicated that **IMA** recognizes anions via (C–H)⁺⋯X[–] hydrogen bond of imidazolinium ring. Furthermore, the results of all-atom molecular dynamics simulation were consistent with experimental results, suggesting that the **IMA** forms dimeric species during anion transport²⁾.

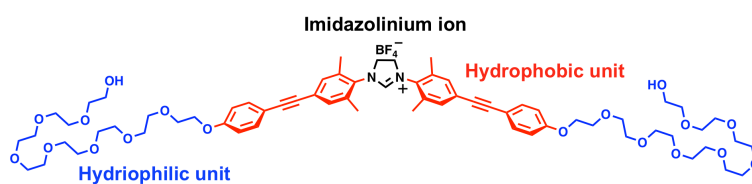


Figure. Molecular structure of **IMA**

1) T. Muraoka, T. Shima, T. Hamada, M. Morita, M. Takagi, K. V. Tabata, H. Noji and K. Kinbara *J. Am. Chem. Soc.*, **2012**, *134*, 19788. 2) M. Mori, K. Sato, T. Ekimoto, S. Okumura, M. Ikeguchi, K. V. Tabata, H. Noji and K. Kinbara, *Chem. Asian J.*, published online (<https://doi.org/10.1002/asia.202001106>).

Synthesis of Supramolecular Phosphatases Functionalized with Lewis Acid Moieties for Catalytic Hydrolysis of Phosphate Monoester in Two-Phase Solvent System

(¹*Faculty of Pharmaceutical Sciences, Tokyo University of Science*, ²*Research Institute for Science and Technology, Tokyo University of Science*) ○Shin Aoki,^{1,2} Akib Bin Rahman,¹ Hirokazu Okamoto,¹ Yuya Miyazawa

Keywords: Supramolecular Phosphatases; Self-Assembly; Zinc; Copper; Potassium

The phosphorylation and dephosphorylation of proteins are essential regulatory systems that can significantly alter the structures, subcellular localization, stability and biological activity of proteins and related biomolecules. Although some artificial compounds which mimic the active center of metallophosphatases have been reported, very few of them function as catalysts for the hydrolysis of phosphate monoesters such as mono(4-nitrophenyl) phosphate (MNP), because phosphate monoesters are generally less reactive than phosphate diesters and triesters.

A supramolecular strategy based on the self-assembly of molecular building blocks represents a potentially useful strategy for the construction of artificial chemical architectures that exhibit higher and more specific chemical reactivity.¹⁾ We previously reported the supramolecular complexes formed by the 2:2:2 self-assembly of bis(Zn²⁺-cyclen) complexes (cyclen = 1,4,7,10-terazacyclododecane) having a 2,2'-bipyridyl (bpy) linker and one or two long alkyl (C₂₂) chains (Zn₂L² and Zn₂L³, respectively), with the functionalized barbitol (Bar) derivatives and Cu²⁺ in two-phase solvent system (CHCl₃/H₂O) accelerate the hydrolysis of MNP.²⁻⁴ In this paper, we report new supramolecular complexes formed by the 2:2:2:4 self-assembly of Zn₂L², Bar-18-crown-6 ether conjugate, Cu²⁺ and alkaline metal, that have a higher MNP hydrolysis activity in the presence of K⁺ than that in the presence of Li⁺, Na⁺, Rb⁺, and Mg²⁺.⁵⁾

- 1) S. Aoki, M. Zulkefeli, Y. Hisamatsu, M. Kitamura, in *Synergy in Supramolecular Chemistry*, 2015, pp 33 (T. Nabeshima, Ed., CRC, Boca Raton).
- 2) M. Zulkefeli, Y. Hisamatsu, A. Suzuki, Y. Miyazawa, M. Shiro, S. Aoki, *Chem. Asian J.*, **2014**, *9*, 2831.
- 3) A. B. Rahman, H. Imafuku, Y. Miyazawa, A. Kafle, H. Sakai, Y. Saga, S. Aoki. *Inorg. Chem.*, **2019**, *58*, 5603.
- 4) a) Y. Hisamatsu, Y. Miyazawa, T. Yoneda, M. Miyauchi, M. Zulkefeli, S. Aoki, *Chem. Pharm. Bull.*, **2016**, *64*, 451. b) Y. Miyazawa, A. B. Rahman, Y. Saga, H. Imafuku, Y. Hisamatsu, S. Aoki, *Micromachines* **2019**, *10*, 452 (24 pages).
- 5) A. B. Rahman, H. Okamoto, Y. Miyazawa, S. Aoki, *Eur. J. Inorg. Chem.*, **2021**, in press.

近赤外光スイッチタンパク質によるゲノム遺伝子活性化システム

(KISTEC¹・東大院総文²) ○中嶋 隆浩^{1,2}・佐藤 守俊²

Improved photoswitching proteins for endogenous gene activation by near-infrared light (¹Kanagawa Institute of Industrial Science and Technology, ²Graduate School of Arts and Sciences, The University of Tokyo) ○Takahiro Nakajima^{1,2}, Moritoshi Sato²

Photoswitching proteins, which can dimerize by illumination with light, are core components of optogenetic tools. So far, several excellent photoswitching proteins that can dimerize by blue-light illumination have facilitated the development of a variety of blue-light optogenetic tools. However, in order to manipulate biological functions in deep tissues in living animals, NIR-light activatable optogenetic tools are highly needed, because light between 650 nm and 900 nm, called NIR window, can efficiently penetrate into biological tissues. Here, we found the cause of the serious problem that the existing NIR-light photoswitching proteins have. To overcome the problem, we engineered the existing NIR-light photoswitching proteins by introducing mutations and developed the improved photoswitching proteins. Using the improved photoswitching proteins, we developed the NIR-light activatable endogenous gene activation system that is based on CRISPR–Cas9 technology. We demonstrated that a mouse endogenous gene can be activated by NIR-light illumination in living mouse livers. Our NIR-light photoswitching proteins will facilitate to develop a variety of NIR-light optogenetic tools for *in vivo* in deep tissues.

Keywords : Optogenetics; Photoswitching proteins; Near-infrared light; CRISPR–Cas9; Endogenous gene activation

光スイッチタンパク質とは、光照射によって結合・解離を自在にコントロールできるタンパク質ペアであり、オプトジェネティクス・光操作技術を支える基盤技術である。青色の光スイッチタンパク質には優れたものがあるので、それらを用いて青色の光操作ツールが今まで多数開発されてきた。しかし、生体内で光操作を行うためには、青色でなく、組織透過性が高い近赤外色の光操作ツールが強く望まれている。今回我々は、近赤外色の光スイッチタンパク質が持っている重篤な問題点およびその原因を見つけ出し、これをアミノ酸変異を施すことで改良した。そしてこの改良型光スイッチタンパク質と CRISPR-Cas9 技術を融合して、近赤外光によってゲノム遺伝子を活性化できる光操作ツールを開発した。我々は、この光操作ツールによって、生きているマウスの肝臓内でゲノム遺伝子を活性化できることを示した(図)。我々の近赤外光スイッチタンパク質は、様々な近赤外光操作ツールの開発を促進するであろう。

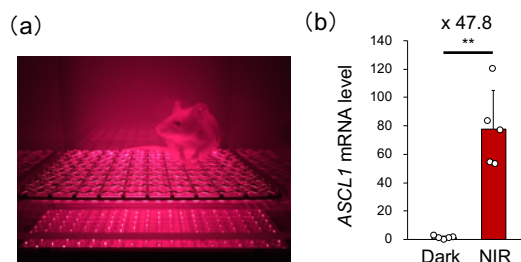


図 (a) 生きたマウスへの近赤外光照射の様子。(b) 近赤外光照射によるマウスゲノム遺伝子(ASCL1)発現の活性化。光操作ツールのプラスミドDNAをマウス肝臓に導入する。その後、(a)のように光照射するか(NIR)、または暗所に置く(Dark)。肝臓からmRNAを抽出し、ASCL1遺伝子のmRNAをqPCRにより定量した。

Sequence-Specific DNA Alkylation by a Chlorambucil-Conjugated Cyclic Pyrrole–Imidazole Polyamide

(¹Graduate School of Science, Kyoto University, ²Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University) ○ Yuki Hirose,¹ Kaori Hashiya,¹ Toshikazu Bando,¹ Hiroshi Sugiyama,^{1,2}

Keywords: Pyrrole–imidazole polyamide; DNA alkylating agent; Anticancer drug

DNA alkylating agents, such as nitrogen mustard analogs and duocarmycin derivatives, form covalent bonds with DNA and inhibit DNA replication and cell proliferation. While some DNA alkylating agents have been used as anticancer agents taking advantage of their high cytotoxicity, side effects due to non-specific alkylation have been a problem. In order to solve this problem, sequence-specific DNA alkylating agents have been developed by conjugating DNA alkylating agents to pyrrole–imidazole polyamides (PIPs), which bind to DNA in a sequence-specific manner.

In this study, we conjugated DNA alkylator chlorambucil (Chb) to a cyclic PIP (cPIP)¹, which is known to have a higher DNA-binding affinity than a well-studied hairpin PIP (hPIP), and we evaluated its alkylating property. Capillary electrophoresis using long DNA strands and HPLC product analysis using short DNA fragments indicated that a cPIP–Chb selectively alkylated the N3 position of purine bases around the target sequences with higher DNA alkylation activity than hPIP–Chbs. Besides, cytotoxicity assays using LNCaP prostate cancer cells showed that cPIP–Chb exhibited cytotoxicity comparable to that of hPIP–Chb.² While some issues, such as side effects and working mechanisms, need to be clarified, these results indicated the potential of cPIP–Chbs for anticancer drug applications.

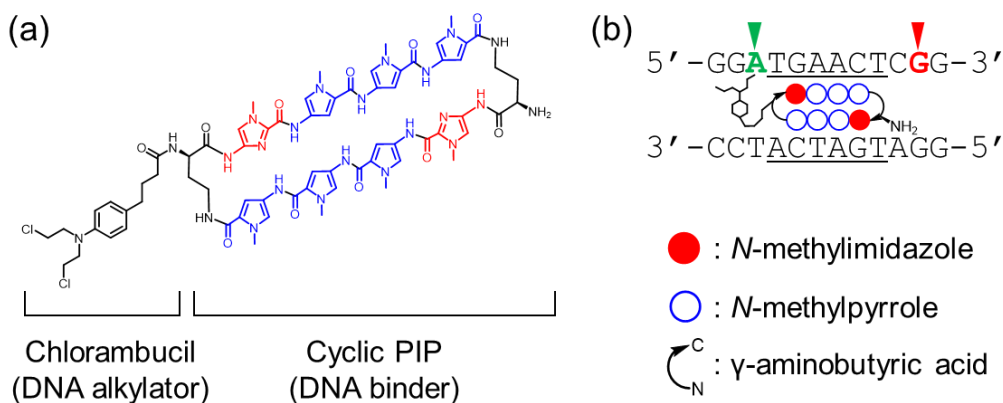


Figure 1. (a) The chemical structure of cPIP–Chb. (b) One of the alkylation sites of cPIP–Chb.

1) Y. Hirose, S. Asamitsu, T. Bando, H. Sugiyama, *J. Am. Chem. Soc.* **2019**, *141*, 13165.

2) Y. Hirose, K. Hashiya, T. Bando, H. Sugiyama, *Chem. Eur. J.* *in press*.

塩基配列選択的 DNA 結合性化合物を用いたミトコンドリア DNA の転写・複製制御

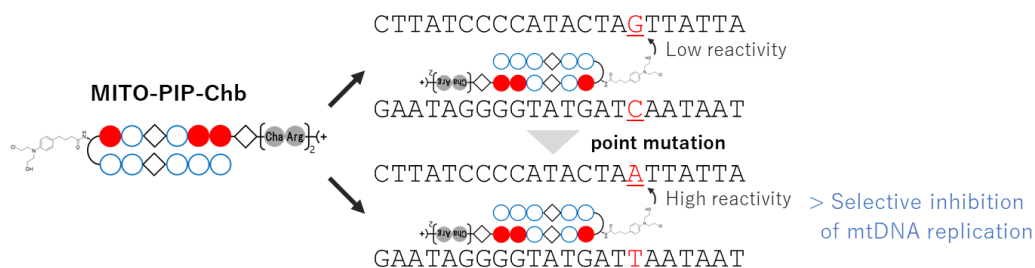
(京大院理¹・京大 iCeMS²) ○日高 拓也¹・NAMASIVAYAM Ganesh Pandian²・板東 俊和¹・杉山 弘^{1,2}

Transcription and replication control of mitochondrial DNA by sequence-specific DNA binders (¹Graduate School of Science, Kyoto University, ²Institute for Integrated Cell-Material Sciences, Kyoto University) ○Takuya Hidaka,¹ NAMASIVAYAM Ganesh Pandian,² Toshikazu Bando,¹ Hiroshi Sugiyama^{1,2}

Mitochondria possess their own DNA (mtDNA) encoding 37 essential genes for mitochondrial function and mutations in mtDNA cause genetic disorders named mitochondrial diseases. To cure the diseases, we need approaches to eliminate mutated mtDNA from cells. Although this has been achieved by biological tools like zinc finger nuclease and TALEN, the usage of viral vectors is major concern. To provide a chemical approach, we developed MITO-PIPs, synthetic molecules which can recognize specific mtDNA sequence, and reported promoter-specific transcription control.¹⁾ Recently, we focus on conjugates of MITO-PIP and DNA alkylating reagent (chlorambucil) to inhibit replication of mutated mtDNA selectively (see the figure below). In this presentation, we want to show our chemical approach toward a gene therapy of mitochondrial diseases with recent data.

Keywords : Pyrrole-Imidazole Polyamide, Mitochondria Penetrating Peptide, Mitochondrial DNA, Mitochondria, Mitochondrial Diseases

ミトコンドリア DNA(mtDNA)は、ミトコンドリア機能に必須な 37 種類の遺伝子をコードしているため、その変異はミトコンドリア病と呼ばれる遺伝性疾患を引き起こす。その根本的治療には変異 mtDNA を減らす手法が必要であり、zinc finger nuclease や TALEN といった分子生物学的ツールが応用されてきた。しかしこれらはウイルスベクターを用いるため、その安全性が議論されている。そこで我々はミトコンドリア病治療を見据え、塩基配列選択的に mtDNA に結合する化合物 MITO-PIP を開発し、プロモーター選択的な転写制御を報告した。¹⁾ これを変異 mtDNA 選択的複製阻害に応用するため、我々は MITO-PIP と DNA アルキル化剤 (クロランブシル) のコンジュゲートに着目し研究を行っている(下図)。本発表では、ミトコンドリア病の遺伝子治療実現に向けた我々の化学的アプローチを、最近の結果と併せて紹介したい。



1) T. Hidaka, H. Sugiyama, *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 8444.

がん細胞選択的薬効発現を指向した細胞内環境応答型システムの構築 – 新規細胞内環境応答型人工核酸ならびにジスルフィドリンカー系の開発 –

(東北大多元研) ○石澤誠也・稲垣雅仁・大竹健太・西嶋政樹・荒木保幸・和田健彦
Construction of Intracellular Condition Responsive System Toward Cancer Cell Selective Therapeutics - Development of the Intracellular Condition Responsive XNA and Disulfide Linkers - (IMRAM, Tohoku University)○Seiya Ishizawa, Masahito Inagaki, Kenta Otake, Masaki Nishijima, Yasuyuki Araki, Wada Takehiko

Oligonucleotide therapeutics (ONT) has received much attention as a promising candidate for next-generation molecular targeted drugs. Despite the very attractive features, there still remains a major issue to be improved; i.e., the expression of therapeutic effect on non-target normal cells called off-target effects. We have reported a series of novel artificial nucleic acids, named Peptide Ribonucleic Acids (PRNAs), as promising candidates for target hypoxic cell-specific ONT molecules. For applying hypoxic cell-specific ONT, PRNAs containing phenylboronic acid (PRNA-PBA) were synthesized and the detailed properties have been reported. In this study, we tried to extend this strategy and concept to natural phosphodiester backbone type artificial nucleic acid with threoninol derivatives.

Keywords : Oligonucleotide Therapeutics; Artificial Nucleic Acids; Disulfide Linkers; Drug Delivery Systems; Off-target Effects

現在医薬品の主流となっている抗体医薬に次ぐ分子標的医薬として、従来治療法がなかった筋ジストロフィーの治療薬として認可された核酸医薬が非常に注目され、現在精力的に研究推進されている。しかし、標的 RNA の類似塩基配列を有する非標的核酸との複合体形成に基づく、オフターゲット効果と呼ばれる副作用発現が改善すべき重大な課題として指摘されている。本課題改善に向け、増幅期の癌など虚血性疾患では細胞質 pH が低下していることに注目し、“細胞内環境応答型”人工核酸として、ペプチドリボ核酸(PRNA)を設計・合成し、分子内にフェニルボロン酸を導入することで細胞内 pH 変化に対応して、薬効発現の *off-on* 制御可能であることを明らかにした(図 1)。一方、癌細胞では細胞内グルタチオン濃度が正常細胞に比較して非常に高いことも知られており、我々はこのグルタチオン濃度の差異をトリガーとする薬効発現制御法開発にも取り組んできた。

本研究では、上記 PRNA で得た知見を、リン酸ジエステル骨格人工核酸への展開を目指し、Threoninol 誘導体の合成に取り組んだ。加えて、細胞内グルタチオン濃度差に基づく癌細胞選択的薬効発現型 DDS (図 2)開発に取り組んだ。

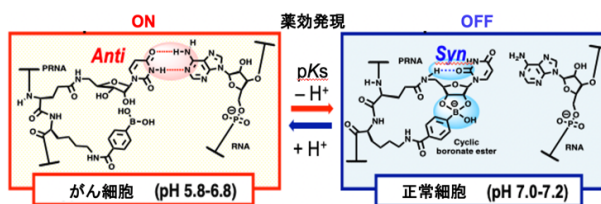


図 1. ペプチドリボ核酸 (PRNA)

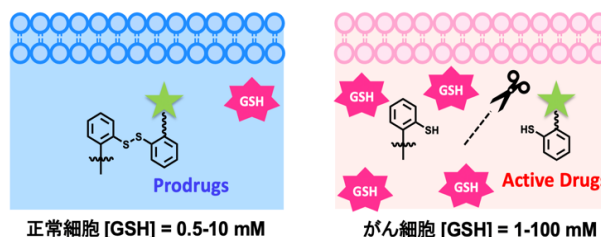


図 2. GSH 濃度差対応型ジスルフィドリンカー

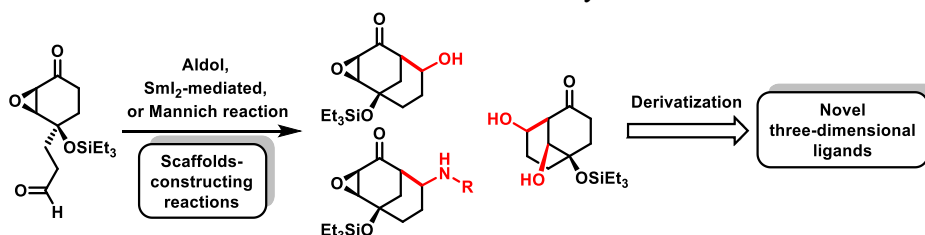
Development of Reactions Constructing Novel Three-Dimensional Skeletons for Exploring New Chemical Space and Protein-Protein Interaction (PPI) Inhibitory Activity

(¹Tokyo Institute of Technology, Laboratory for Chemistry and Life Science, ²Tokyo Institute of Technology, School of Life Science and Technology, ³Univ. of Pittsburgh, Department of Chemistry) ○Hiroki Ueda,^{1,2} Peter Wipf,³ Hiroyuki Nakamura¹

Keywords: Chemical Space; Aldol Reaction; Samarium Iodide; Protein-Protein Interaction

Recently, protein-protein interactions (PPIs) have been investigated for their potential to discover more specific drugs.^{1,2} Currently, most approved drugs have a stick-like or planar structure. To target PPIs, three-dimensional ligands are necessary for the mimicry of the secondary structures of interacting peptides. However, due to their structural nature mentioned above, conventional drugs are not suitable for PPI inhibition. Nevertheless, recent progress in sp^2 - sp^2 coupling reactions has further increased the proportion of sp^2 carbons in drug candidates.³ Moreover, there are few reactions that can be used to construct a three-dimensional structure. Advantages of three-dimensional small molecules include that, generally, such molecules have higher specificity in protein binding.^{4,5} Also, it is reported that the fraction of sp^3 carbons in the drug candidates correlates with the stages successfully passed in clinical trials.⁶ We envisioned to design reactions yielding new three-dimensional molecules.

We previously reported bicyclo[3.3.1]nonanes as hypoxia-inducible factor inhibitors.⁷ To obtain compounds with a similar carbon skeleton more concisely, we designed ketoepoxides substrates having an aldehyde group and tried to construct diverse three-dimensional skeletons with different functionalities through an aldol reaction, SmI_2 -mediated reductive cyclization or Mannich reaction. We envisioned that it is possible to access diverse products by introducing sidechains to the scaffolds. Herein, we report the results of key cyclization reactions, derivatizations and the evaluation of three-dimensionality.



- 1) J. A. Wells, C. L. McClendon, *Nature* **2007**, 450, 1001. 2) X. Ran, J. E. Gestwicki, *Curr. Opin. Chem. Biol.* **2018**, 44, 75. 3) W. P. Walters, J. Green, J. R. Weiss, M. A. Murcko, *J. Med. Chem.* **2011**, 54, 6405. 4) P. A. Clemons, N. E. Bodycombe, H. A. Carrinski, J. A. Wilson, A. F. Shamji, B. K. Wagner, A. N. Koehler, S. L. Schreiber, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, 107, 18787. 5) F. Lovering, *Medchemcomm* **2013**, 4, 515. 6) F. Lovering, J. Bikker, C. Humblet, *J. Med. Chem.* **2009**, 52, 6752. 7) H. Ueda, A. Yoshimori, H. Nakamura, *Bioorganic Med. Chem.* **2018**, 26, 3345.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[A25-2pm] 17. Biofunctional Chemistry, Biotechnology**

Chair: Yousuke Katsuda, Soyoung Park

Sat. Mar 20, 2021 1:00 PM - 3:40 PM Room 25 (Online Meeting)

[A25-2pm-01] Synthesis of a benzo[a]pyrene-modified oligonucleotide and its application to a fluorescent colorimetric detection of single base alterations of RNA sequences○Yu Watari¹, Kaito Nakatani¹, Yui Ohtsuka¹, Tomonori Waku¹, Akio Kobori¹ (1. Kyoto Institute of Technology)

1:00 PM - 1:20 PM

[A25-2pm-02] A triplex-forming linear probe for sensitive and sequence-specific detection of duplex DNA○Yanglingzhi Chen¹, Keiji Murayama¹, Hiroyuki Asanuma¹ (1. The Univ. of nagoya)

1:20 PM - 1:40 PM

[A25-2pm-03] Development of a fluorescent thymidine analog and construction of orientation-dependent FRET system○Shingo Hirashima¹, Soyoung Park¹, Hiroshi Sugiyama¹ (1. Kyoto University)

1:40 PM - 2:00 PM

[A25-2pm-04] Development of Bio-Labile Protecting Groups for oligonucleotides○Akira Ono¹, Takayuki Oota¹, Kousei Nakamura¹, Hisao Saneyoshi² (1. Kanagawa University, 2. Shiga University of Medical Science)

2:00 PM - 2:20 PM

[A25-2pm-05] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (65) : Microscopic analyses for elucidating molecular mechanisms at the interaction between berberine and bulged RNA○Tamaki ENDOH¹, Sagar SATPATHI¹, Tatsuya OHYAMA¹, Peter PODBEVŠEK², Janez PLAVEC^{2,3,4}, Naoki SUGIMOTO¹ (1. Konan University, 2. National Institute of Chemistry, 3. EN→FIST Centre of Excellence, 4. University of Ljubljana)

2:20 PM - 2:40 PM

[A25-2pm-06] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (66) : Effect of molecular crowding on replication along non-natural DNAs○Shuntaro Takahashi¹, Piet Herdewijn², Naoki Sugimoto^{1,3} (1. Konan University, FIBER, 2. KU Leuven, 3. Konan University, FIRST)

2:40 PM - 3:00 PM

[A25-2pm-07] Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (67): Effects of malignant alteration in cancer cells on the DNA G-quadruplexes and transcript mutations○Hisae Tateishi-Karimata¹, Keiko Kawauchi², Tatsuya Ohyama¹, Naoki Sugimoto^{1,2} (1. FIBER, Konan University, 2. FIRST, Konan University)

3:00 PM - 3:20 PM

[A25-2pm-08] Development of a novel technology for gene suppression based on formation of RNA structure.○Takuto Kamura¹, Yosuke Katsuda¹, Taishi Nakamura², Kenichi Tsujita³, Yusuke Kitamura¹, Masaki Hagihara⁴, Shin-ichi Sato⁵, Toshihiro Ihara¹ (1. Faculty of Advanced Science and

Technology, Kumamoto University, 2. Department of Medical Information Sciences and Administration Planning, Kumamoto University Hospital, 3. Department of Cardiovascular Medicine, Faculty of Life Sciences, Kumamoto University, 4. Faculty of Science and Technology, Hirosaki University, 5. Institute for Chemical Research, Kyoto University)
3:20 PM - 3:40 PM

Synthesis of a benzo[a]pyrene-modified oligonucleotide and its application to the fluorescent colorimetric detection of single base alterations of RNA sequences

(Graduate School of Science and Technology, Kyoto Institute of Technology) ○Yu Watari, Kaito Nakatani, Yui Ohtsuka, Tomonori Waku, Akio Kobori

Keywords: Benzo[a]pyrene; Pyrene; RNA; Single base alteration

The analytical methods for detection of single base alterations of RNA sequences are essential for diagnosis and treatment of serious diseases such as cancers. Previously, we reported facile detection of single base alterations of RNA sequences using a pyrene-modified oligonucleotide, OMU_{py}2.¹ OMU_{py}2 contains two 2'-*O*-pyrenylmethyluridine (U_{py}) units in the middle of 2'-*O*-methyl RNA sequences. OMU_{py}2 produces strong fluorescence only in the presence of complementary RNAs. In addition, OMU_{py}2 is capable of discrimination between RNAs and DNAs.

In this work, we report the synthesis and photophysical properties of a novel fluorescent oligonucleotide, OMCbpyU_{py} where a 2'-*O*-benzo[a]pyrenylmethylcytidine (Cbpy) unit and a U_{py} unit are consecutively introduced (**Figure 1a**). The oligonucleotides with a Cbpy unit may be useful for biological applications such as RNA imaging with confocal laser microscopy since benzo[a]pyrene exhibits an absorption band corresponded to canonical laser wavelength. The Cbpy phosphoramidite unit was synthesized in four steps from cytidine in 18% total yield and successfully incorporated into the 2'-*O*-methyl RNA sequences via solid-phase synthesis (**Figure 1b**). The fluorescence spectra of **OMCbpyU_{py}1** were measured at an excitation wavelength of 405 nm (**Figure 1c**). **OMCbpyU_{py}1** showed strong fluorescent signals at 500 nm in the presence of **Kras G12D**. The fluorescent intensity at 500 nm of **OMCbpyU_{py}1** in the presence of **Kras G12D** was 28-fold higher than that in the absence of **Kras G12D**. On the other hand, **OMCbpyU_{py}1** showed weak fluorescent signals at 500 nm in the presence of **Kras WT**. It is notable that the fluorescent intensity at 500 nm of the **OMCbpyU_{py}1** in the presence of **Kras WT** was one-sixth that of the **OMCbpyU_{py}1** in the presence of **Kras G12D**. Furthermore, the emission colors of these duplexes were clearly distinguished by naked eyes under UV irradiation. These results suggest that **OMCbpyU_{py}1** is applicable to facile analytical methods for detection of single base alterations of RNA sequences.

1) A. Mahara, *et al.*, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3648-3650.

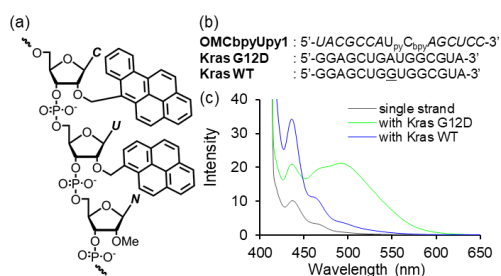


Figure 1. (a) Chemical structure of OMCbpyU_{py}. (b) The sequences of the oligonucleotides used in this work. Italic and capital letters represent 2'-*O*-Me RNAs and RNAs, respectively. (c) Fluorescence spectra of **OMCbpyU_{py}1** in the presence of **Kras G12D** and **Kras WT** and in the absence of RNAs.

A triplex-forming linear probe for sensitive and sequence-specific detection of duplex DNA

(Graduate School of Engineering, Nagoya University) ○ Yanglingzhi Chen, Keiji Murayama, Hiroyuki Asanuma

Keywords: Sensitive DNA detection; Artificial nucleic acid; Perylene derivative; Polymerase chain reaction; Perylene derivatives

Most of the strategies for detection of target DNA have relied on the denaturation of double-strand DNA (dsDNA) into single strands, which prevents a simple detection. In this study, we report a triplex-forming linear probe tethering multiple fluorophores at intervals of native oligonucleotides with D-threoninol as scaffold, which allows simple detection of the dsDNA without denaturation. The principle of the linear probe is schematically illustrated in Figure 1 on the left: At single-stranded state, it self-quenches due to hydrophobic interaction among fluorophores, while it sequence-specifically forms triplex with dsDNA via Hoogsteen base-pairing.¹ As a result, fluorescence remarkably recovers because weakly stacked fluorophores are separated by their intercalation between the base-pairs.

By the incorporation of perylene derivative L and anthraquinone derivative gQ, we have successfully designed an optimal probe 3L1gQ, targeting human Androgen Receptor (AR) gene. Signal/background ratio of 3L1gQ was as high as 278 (Figure on the right). Moreover, the melting temperature of the triplex with this linear probe (61.9 °C) was much higher than that of native DNA (40.0 °C), suggesting remarkable improvement on triplex stability. As possible application, detection of PCR products was performed: 3L1gQ showed clear light-up in the presence of product-dsDNA containing target site after PCR reaction, only by the addition of the probe to PCR solution (data not shown). These results demonstrate remarkable ability as a fluorescent probe for detecting dsDNA, and its possibility for applying to dsDNA-targeted diagnosis in cell.

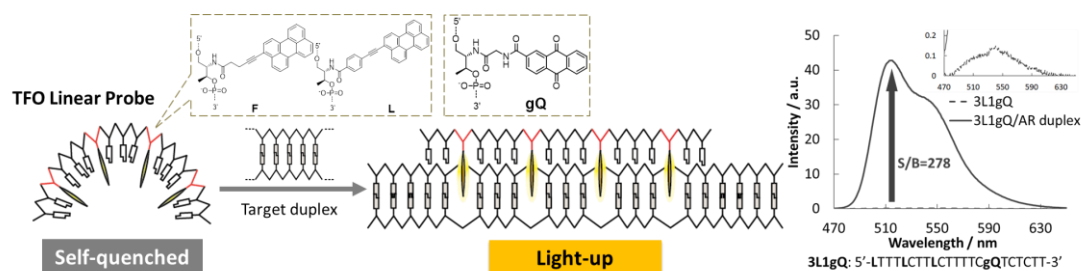


Figure. Schematic illustration of the linear probe (left panel) and its light-up in the presence of target dsDNA (right panel).

1) Y. Chen *et al.*, *Chem. Commun.*, **2020**, 56, 5358-5361.

Development of a fluorescent thymidine analog and construction of orientation-dependent FRET system

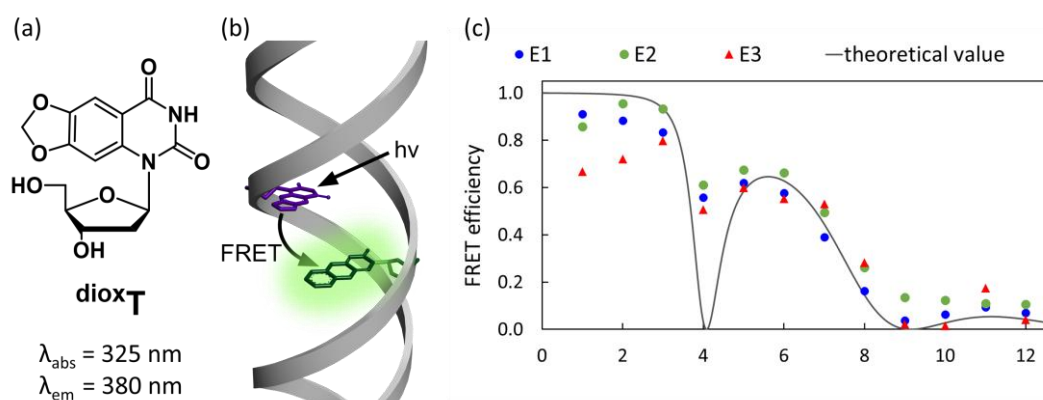
(Graduate School of Science, Kyoto University)

○Shingo Hirashima, Hiroshi Sugiyama, Soyoung Park

Keywords: DNA, fluorescent nucleic acid, thymidine analogue, FRET

Fluorescent nucleosides are useful tools for investigating the structures and interactions of nucleic acids. As a new bright thymidine analogue and a donor in nucleobase analog FRET pair, we developed ^{diox}T, which consists of a quinazoline derivative attached with 1,3-dioxolane moiety.¹ Thermal denaturation experiment showed that ^{diox}T formed the most stable base pair with adenine. The photophysical property of ^{diox}T was fully investigated considering all combinations of nearest neighboring bases. We found a high quantum yield (0.20) of ^{diox}T when incorporated into double-stranded DNA. This value is relatively high among reported emissive U/T analogues.

Förster resonance energy transfer, FRET has been used as a molecular ruler to monitor the distance between or within biomolecules. A distance- and orientation-dependent FRET system can be a more powerful tool than conventional ones because of higher spatial sensitivity. Such FRET pairs have been developed using DNA scaffolds. We constructed a FRET pair using ^{diox}T,² since no FRET pair has used isomorphous U/T analog. We measured experimental FRET efficiencies by steady-state fluorescence and time-resolved fluorescence. The experimental value showed local minimum suggesting the orientation dependency. In comparison of experimental and theoretical FRET efficiency, they showed similar tendency.



(a) Chemical structure of ^{diox}T and its absorption and emission wavelengths. (b) Schematic illustration of our FRET system. (c) Experimental FRET efficiencies based on steady-state fluorescence of donor (E1) and acceptor (E2), and time-resolved fluorescence of donor (E3). Theoretical value (gray).

1) Hirashima, S.; Han, J. H.; Tsuno, H.; Tanigaki, Y.; Park, S.; Sugiyama, H. *Chem. Eur. J.* **2019**, 25, 9913. 2) Hirashima, S.; Sugiyama, H.; Park, S. *J. Phys. Chem. B* **2020**, 124, 8794.

細胞内反応によって脱離するオリゴヌクレオチドの保護期の開発

(神奈川大学工¹・滋賀医科大学医²) 小野 晶¹・○太田 貴之¹・中村 康大¹・實吉 尚郎²

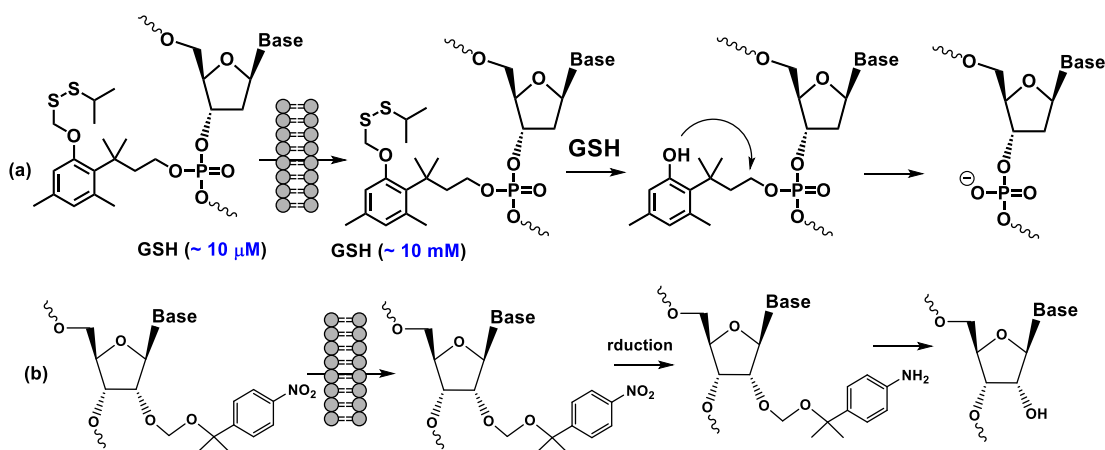
Development of Bio-Labile Protecting Groups for oligonucleotides

(¹Faculty of Engineering, Kanagawa University, ²School of Medicine, Shiga University of Medical Science) ○Akira Ono,¹ Takayuki Ohta,¹ Kodai Nakamura,¹ Hisao Saneyoshi²

Efficient delivery of these oligonucleotide-based drugs to their sites of action remains a major challenge. A prodrug approach for oligonucleotides was proposed for improving cell membrane permeability and nuclease resistance. This strategy employs biolabile protecting groups for neutralizing the anionic charges of phosphodiester moieties. Here, we report two types of bio-labile protecting groups for oligonucleotides. The protecting groups on the phosphodiester moieties were cleaved in a buffer containing 10 mM glutathione, which was used as a model of intracellular fluid. The bioreduction labile protecting group of the 2'-hydroxyl group in RNA is deprotected by reduction of the nitro group.

Keywords : Nucleic Acid Medicine; Prodrug; Oligonucleotide synthesis; glutathione; biolabile protecting group

プロドラッグ型核酸医薬には、生体内反応で脱離する保護基が必要である。本発表では2種類の保護基を報告する。一つは、グルタチオンによって脱保護される保護基である。グルタチオンは細胞の外部と内部で濃度が大きく異なる。細胞外濃度(～10 μM)では安定で、細胞内濃度(～10 mM)のグルタチオンによって除去されるリン酸ジエステル部の保護基を合成した。もう一つは、還元環境で除去されるRNAの2'-水酸基の保護基である。還元状態にある細胞中で、保護基上のニトロ基がアミノ基に還元されることで脱離することが期待される。



(a) H. Saneyoshi, *et al.*, *Org. Lett.*, **2019**, 21, 862–866. <https://doi.org/10.1021/acs.orglett.8b03501>

(b) H. Saneyoshi, *et al.*, *Org. Lett.*, **2020**, 22, 15, 6006–6009. <https://doi.org/10.1021/acs.orglett.0c02086>

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (65): Microscopic analyses for elucidating molecular mechanisms at the interaction between berberine and bulged RNA

(¹FIBER, Konan University, ²Slovenian NMR Centre, National Institute of Chemistry, ³EN→FIST Centre of Excellence, ⁴Faculty of Chemistry and Chemical Technology, University of Ljubljana, ⁵FIRST, Konan University) ○Tamaki Endoh¹, Sagar Satpathi¹, Tatsuya Ohyama¹, Peter Podbevšek², Janez Plavec^{2,3,4}, and Naoki Sugimoto^{1,5}

Keywords: RNA; Interaction, Alkaloid, Berberine, NMR

Phytochemicals (PCs) show a broad spectrum of biological activities such as antioxidant, antibacterial, and antitumor properties. The biological activities of PCs are thought to be provided by affecting protein functions in cells. In contrast, by considering the chemical structural properties of PCs, which contain multiple heterocycles with nitrogen atoms, it corresponds to those of chemicals that tend to interact with RNAs rather than proteins.¹ Thus, some of the biological activities of PCs are likely to be resulted from their interaction with RNAs. However, the biological importance of PCs is still not evident in the context of their influence on the functions of RNAs.

In this study, to verify the biological activities of PCs mediated by direct interaction with particular RNA unit, an integrated investigation based on physicochemical and structural analyses was demonstrated using a berberine (BRB) as a model PC. BRB is one of the biologically active chemicals in medicinally important plants. An approach to identify RNA motifs interacting with BRB was performed using RNA-capturing microsphere particles (R-CAMPs), which we have originally established to optimize functional RNA aptamers.² A minimal RNA motif consisting of a cytosine bulge with UA and GU neighbouring base pairs was found for the interaction with BRB. Detailed analyses of the interaction were performed by NMR-based structure determination followed by molecular dynamics simulation and physicochemical analyses, such as UV melting and ITC, highlighting importance of electrostatic and stacking interactions for the stabilization of the RNA upon BRB interaction (Figure). The results suggest the potential biological activities of PCs mediated by their interaction with RNAs. In addition, the basic knowledge of the chemical properties for the RNA recognition by PCs would be useful for the development of therapeutic drugs that target functional RNAs.

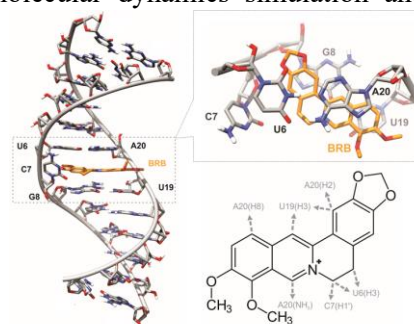


Figure. Tertiary structure and interactions between BRB and RNA.

1) C. S. Eubanks, A. E. Hargrove, *Biochemistry*, **2019**, 58, 199. 2) T. Endoh, T. Ohyama, N. Sugimoto, *Small*, **2019**, 15, 1805062.

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (66) : Effect of molecular crowding on replication along non-natural DNAs

(¹FIBER, Konan University, ²KU Leuven, ³FIRST, Konan University) ○Shuntaro Takahashi¹, Piet Herdewijn², and Naoki Sugimoto^{1,3}

Keywords: Unnatural nucleic acids; DNA replication; Hydrogen bonding; Stacking interaction; Molecular crowding

Unnatural nucleic acids are promising materials to expand genetic information beyond the natural bases.¹ During replication, substrate nucleotide incorporation should be strictly controlled for optimal base pairing with template strand bases. Base-pairing interactions occur via hydrogen bonding and base stacking, which could be perturbed by the chemical environment.² However, the chemical environmental effect on the replication of unnatural nucleic acids is less understood. In this study, we investigated the effect of molecular crowding on the efficiency and preference of single primer extension with native dNTPs along a template containing different unnatural bases (inosine, 5-methyl-isocytosine, and isoguanine) and different sugars (DNA, hexitol nucleic acids, and arabinose nucleic acids).³ Although dNTPs were non-cognate substrate against the unnatural nucleobases on the template, Klenow Fragment (KF) DNA polymerase preferred to polymerize a certain dNTP. Interestingly, the trend of polymerization basically indicated the high efficiency of the incorporation of preferred pyrimidine dNTPs with low fidelity but the low efficiency of the incorporation of preferred purine dNTPs with high fidelity. However, in the presence of 20 wt% PEG 200 (average molecular weight 200), the efficiency of the incorporation of preferred pyrimidine dNTPs decreased, whereas that of preferred purine dNTPs increased, resulting in all the efficiencies showing almost similar levels irrespective of the chemical structure of the templates (Figure). These findings indicate that preferred pyrimidine dNTPs depend on hydrogen bond formation, which was destabilized by molecular crowding due to a decrease in the water activity. However, the incorporation of preferred purine dNTPs through base-stacking interaction was facilitated by molecular crowding. Our finding suggests that the crowding conditions in a solution and in an enzyme could be key factors determining the efficiency and fidelity of DNA polymerization along unnatural nucleosides.

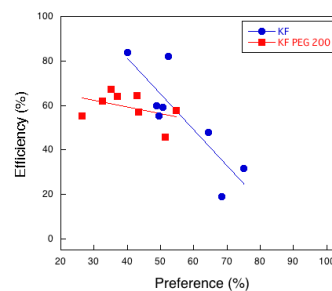


Figure. Plots of the efficiency versus preference of the primer extension by KF in the absence and presence of PEG 200.

1) P. Herdewijn, P. Marliere, *Chem. Biodiversity* **2009**, 6, 791. 2) S. Takahashi, N. Sugimoto, *Chem. Soc. Rev.* **2020**, 49, 8439. 3) S. Takahashi, P. Herdewijn, N. Sugimoto, *Molecules* **2020**, 25, 4120.

Nucleic Acids Chemistry beyond the Watson-Crick Double Helix (67): Effects of malignant alteration in cancer cells on the DNA G-quadruplexes and transcript mutations

(¹FIBER, Konan University, ²FIRST, Konan University) ○Hisae Tateishi-Karimata¹, Keiko Kawauchi², Tatsuya Ohyama,¹ and Naoki Sugimoto^{1,2}

Keywords: Transcript mutation; Cancer cell; Malignant alteration; G-quadruplex; Potassium concentration

The DNA sequences with the potential to form G-quadruplexes locate in oncogenes or proto-oncogenes. We previously showed that the frequency of transcript mutations depends on the stability of the G-quadruplexes formed in the template DNAs.¹ The G-quadruplex formation is highly responsive to surrounding conditions, particularly K^+ concentration. Malignant cancer cells have a much lower K^+ concentration than normal cells because of overexpression of a K^+ channel; thus, G-quadruplexes may be unstable in cancer cells.

Here, we investigated physicochemically how changes of intracellular chemical environments influence G-quadruplex formation and transcription during tumor progression in cells. We designed template DNAs with a G-quadruplex (D1, D2, D3, or D4) and without G-quadruplex (Linear). Thermodynamic analysis showed that the G-quadruplexes in D2 and D4 were very stable. The effect of the G-quadruplex stability on the production of run-off transcripts was also estimated. In a normal cell (NIH3T3 cell), the transcription efficiency inversely correlated with G-quadruplex stability (Figure 1a). Interestingly, higher transcript levels were produced from templates with G-quadruplex-forming potential in the Ras-transformed cell with highly metastatic properties than in the normal cell (Figure 1b). These results suggest that in normal cell, K^+ ions attenuate the transcription of certain oncogenes by stabilizing G-quadruplex structures.² In our presentation, we will discuss how the stability of G-quadruplexes in cell is changed during tumor progression.

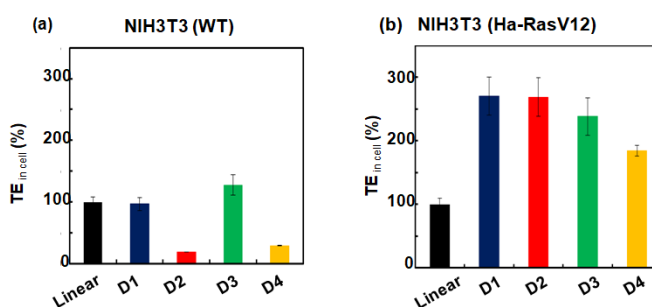


Figure 1. Effect of the G-quadruplex stability on the production of run-off transcripts (transcription efficiency in cell: TE_{in cell}). The TE_{in cell} values from each template encoded on a plasmid in (a) NIH3T3 and (b) NIH3T3 (Ha-RasV12) cells. qRT-PCR was performed to quantify run-off transcripts.

1) H. Tateishi-Karimata, N. Isono, N. Sugimoto, *PLoS ONE*. **2014**, *9*, e90580

2) H. Tateishi-Karimata, K. Kawauchi, N. Sugimoto, *J. Am. Chem. Soc.* **2018**, *140*, 642.

Development of a novel technology for gene suppression based on formation of RNA structure

(¹Faculty of Advanced Science and Technology, Kumamoto University, ²Department of Medical Information Sciences and Administration Planning, Kumamoto University Hospital, ³Department of Cardiovascular Medicine, Faculty of Life Sciences, Kumamoto University, ⁴Faculty of Science and Technology, Hirosaki University, ⁵Institute for Chemical Research, Kyoto University) ○Takuto Kamura¹, Yousuke Katsuda¹, Taishi Nakamura², Kenichi Tsujita³, Yusuke Kitamura¹, Masaki Hagihara⁴, Shin-ichi Sato⁵, Toshihiro Ihara¹

Keywords: *RNA G-quadruplex; Staple oligomer; Off-target effect; Nucleic acid analogue; Nucleic acid medicine*

Nucleic acid-based therapeutics, such as antisense and small interfering RNA (siRNA), are promising strategies against a large number of diseases. As many diseases are caused by abnormal gene expression, a temptation to remediate the aberrant expression of the cognate mRNA or protein has arisen to restore the proper function of relevant cellular machinery. An easy way to achieve this goal is to use siRNA or antisense nucleic acid to repress the expression of the specific gene. Although we need to use the nucleic acid analogues such as XNAs in these techniques to elongate their detention time in cell, it would result in the loss of repression activity since the translational machinery could not recognize the non-native structures in the duplexes containing XNAs because these techniques required cooperative reaction with enzymes.

Here, we introduce a simple method for target gene suppression by induction of a G-quadruplex structure in the relevant mRNA using single strand XNA (and native DNA or RNA) named staple oligomer (**Fig. 1**). RNA G-quadruplex structure is known to block protein synthesis. The role of the staple oligomer is just a trigger or inducer of the G-quadruplex structure in mRNA. We expected that this technology would be a “Next-Generation” Nucleic Acid Medicine. In this presentation, we show the results of the experiments representing the effective suppression of the target genes by the staple oligomers *in vitro* and *in vivo* (**Fig. 2**).

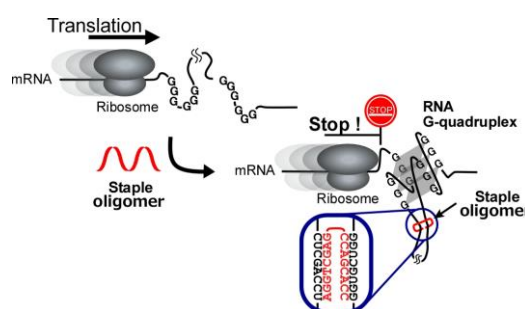


Fig. 1 Schematic illustration of translational inhibition caused by staple-induced G-quadruplex

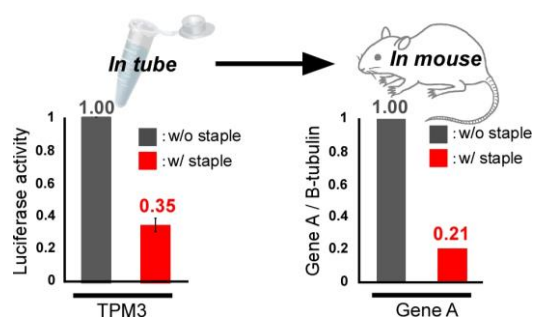


Fig. 2 Evaluation of translational suppression efficiency *in vitro* and *in vivo*.

[A10-2pm] 18. Polymer

Chair: Takuma Kureha, Yuuki Hata

Sat. Mar 20, 2021 1:00 PM - 3:20 PM Room 10 (Online Meeting)

[A10-2pm-01] The relation between relaxation time and mechanical properties of supramolecular hydrogels.

○Subaru Konishi¹, Yu Kashiwagi¹, Go Watanabe², Motofumi Osaki^{1,3}, Takuya Katashima⁴, Osamu Urakawa¹, Hiroyasu Yamaguchi^{1,3}, Tadashi Inoue^{1,3}, Akira Harada⁵, Yoshinori Takashima^{1,3,6} (1. Grad. Sch. of Sci., Osaka Univ., 2. Sch. of Sci., Kitasato Univ., 3. PRC, Osaka Univ., 4. Sch. of Eng., The Univ. of Tokyo, 5. ISIR, Osaka Univ., 6. Institute for Advanced Co-Creation Studies, Osaka Univ.)

1:00 PM - 1:20 PM

[A10-2pm-02] Design and evaluation of mechanical properties of dissimilar polymer knitting materials with movable cross-links

○Ryohei Ikura¹, Shunsuke Murata², Yuka Ikemoto³, Motofumi Osaki^{1,4}, Hiroyasu Yamaguchi¹, Akira Harada⁵, Go Matsuba², Yoshinori Takashima^{1,4,6} (1. Grad. Sch. of Sci., Osaka Univ., 2. Grad. Sch. of Org. Mat. Eng., Yamagata Univ., 3. JASRI, 4. PRC, Osaka Univ., 5. Inst. for Advanced Co-Creation Studies, 6. The Inst. of Scientific and Industrial Res., Osaka Univ.)

1:20 PM - 1:40 PM

[A10-2pm-03] Mechanoresponsive PDMS that Reversibly Changes Fluorescence in Sub-MPa Stress

○Hidetsugu Kitakado¹, Shohei Saito¹ (1. Grad. Sch. of Sci., Kyoto Univ.)

1:40 PM - 2:00 PM

[A10-2pm-04] Gelation mechanism of freeze-crosslinked cellulose nanofiber gels with high compressive strength

○Daisuke Miura¹, Takuya Nankawa², Teppei Yamada³, Yurina Sekine² (1. Yamagata University, 2. Japan Atomic Energy Agency, 3. The University of Tokyo)

2:00 PM - 2:20 PM

[A10-2pm-05] Structural Properties Analysis of Temperature-responsive Hydrogels with Unique Nanodomains

○Takuma Kureha¹, Takuto Hirayama¹, Yuuki Takahashi¹, Hikaru Kida¹, Naoki Suda¹ (1. Hirosaki University)

2:20 PM - 2:40 PM

[A10-2pm-06] Effect of excluded volume and overlap of dissolved polymers under dilute and crowding conditions on molecular crystallization

○Yuuki Hata¹, Xiang Li², Ung-il Chung², Takamasa Sakai² (1. National Defense Medical College, 2. The University of Tokyo)

2:40 PM - 3:00 PM

[A10-2pm-07] Second-order phase transition behavior in polymer glass transition

○Mitsuru Ishikawa¹, Masayoshi Yagishita¹, Yuya Hiramoto¹, Takayuki Uwada¹ (1. Josai University)

3:00 PM - 3:20 PM

The Relation between Relaxation Time and Mechanical Properties of Supramolecular Hydrogels

(¹Graduate School of Science, Osaka University, ²School of Science, Kitasato University, ³Project Research Center for Fundamental Sciences, Osaka University, ⁴School of Engineering, The University of Tokyo, ⁵The Institute of Science and Industrial Research, Osaka University, ⁶Institute for Co-Creation Studies, Osaka University, ⁷Institute for Open and Transdisciplinary Research Initiatives, Osaka University) ○ Subaru Konishi,¹ Yu Kashiwagi,¹ Go Watanabe,² Motofumi Osaki,^{1,3} Takuya Katashima,⁴ Osamu Urakawa,¹ Hiroyasu Yamaguchi,^{1,3} Tadashi Inoue,^{1,3} Akira Harada,⁵ Yoshinori Takashima^{1,3,6,7}

Keywords: Reversible cross-link; Host-guest interaction; Viscoelasticity; Relaxation time; Fracture energy

Design of cross-links makes great impacts on mechanical properties and functionality of polymeric materials. In particular, reversible cross-links constructed by noncovalent bonds have been used as a mechanism for dissipating mechanical energy to improve toughness.¹ Herein, we prepared supramolecular hydrogels cross-linked by host-guest interactions using cyclodextrins (CDs) and cation-terminated alkyl guest units (**Fig. 1**).² We investigated the relation between the second-order relaxation time ($\langle\tau\rangle_w$) and fracture energy (G_f) of the hydrogels with the purpose of establishing a general strategy for tough materials.

Linear viscoelastic measurements revealed that $\langle\tau\rangle_w$ of the hydrogels was controlled by the kinetics of host-guest interactions derived from potential barrier of cation units.^{3,4} Mechanical properties was evaluated by tensile tests, and the α CD-PyC11 hydrogel showed highest G_f . We investigated the effect of the viscoelastic behavior of the reversible cross-links on G_f using product of $\langle\tau\rangle_w$ and strain rate ($\dot{\epsilon}_c$) (**Fig. 2**). G_f within $\dot{\epsilon}_c\langle\tau\rangle_w$ of 1~10 showed a local maximum, indicating that the viscoelastic behavior of the reversible cross-links improved G_f of the α CD-R hydrogels.

- 1) X. Zhao, *Soft Matter* **2014**, *10*, 672–687.
- 2) S. Konishi, *et al.*, *Polym. Chem.* **2020**, *11*, 6811–6820.
- 3) Yonemura, H. *et al.* *J. Phys. Chem.* **1992**, *96*, 5765–5770.
- 4) A. Harada, *J. Am. Chem. Soc.* **2000**, *122*, 3797–3798.

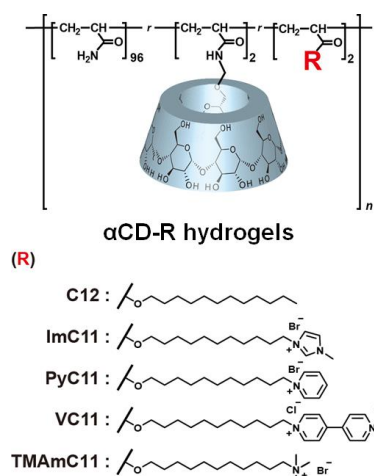


Figure 1. Chemical structures of the α CD-R hydrogels.

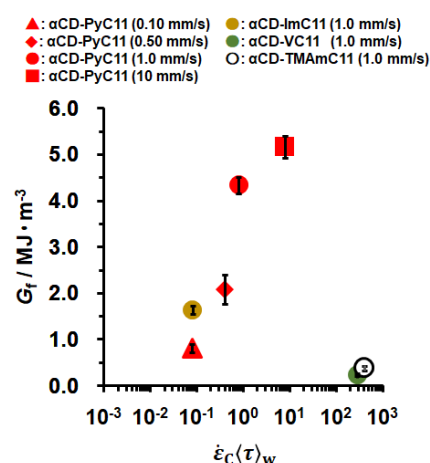


Figure 2. The relation between G_f and $\dot{\epsilon}_c\langle\tau\rangle_w$ of the α CD-R hydrogels.

Design and evaluation of mechanical properties of dissimilar polymer knitting materials with movable cross-links

(¹Graduate School of Science, Osaka University, ²Graduate School of Organic Material Engineering, Yamagata University, ³JASRI, ⁴PRC, Osaka University, ⁵ISIR, Osaka University, ⁶Institute for Advanced Co-Creation Studies, Osaka University, ⁷OTRI, Osaka University) ○Ryohei Ikura,¹ Shunsuke Murayama,² Yuka Ikemoto,³ Motofumi Osaki,^{1,4} Hiroyasu Yamaguchi,¹ Akira Harada,⁵ Go Matsuba,² Yoshinori Takashima^{1,4,6,7}

Keywords: Cyclodextrin; Supramolecular elastomer; Host-guest interaction; Movable cross-linking; Polymer blending

[Introduction] A design of cross-links affects mechanical properties of polymeric materials. Previously, the movable cross-links were formed during the bulk polymerization between cyclodextrin (CD) monomer and main chain monomer¹. Herein, we designed the materials where movable cross-links connect between dissimilar polymers, and evaluated their mechanical properties.

[Result] The dissimilar polymer knitting materials with movable cross-links (pBA-PACyCD (x, y)⊃pEA (z)) were obtained by bulk polymerization of ethyl acrylate (EA) in the presence of the peracetylated-γCD modified poly(butyl acrylate) (pBA-PACyCD). For evaluation of mechanical properties, tensile tests were carried out (Fig. 1). The polymer blend materials without cross-linking (pEA / pBA (10, 90): comparison) exhibited low fracture energy and plastic deformation. On the other hand, pBA-PACyCD (10, 1)⊃pEA (89) showed higher fracture energy and clear fracture point. These results indicated that CD unit acts as cross-linking point to improve the fracture energy. In addition, the fracture energy of pBA-PACyCD (10, 1)⊃pEA (89) is 1.9 times larger than that of the copolymer of EA and BA with movable cross-links (p(BA-EA)-PACyCD (10, 89, 1): comparison). To evaluate stress dispersion property, we observed stress relaxation of test pieces stretched at 400%. As a result, the stress of pBA-PACyCD (10, 1)⊃pEA (89) decreased faster than that of p(BA-EA)-PACyCD (10, 89, 1). The sliding of CD units in p(BA-EA)-PACyCD (10, 89, 1) were limited by another CD units as bulk stopper. pBA-PACyCD (10, 1)⊃pEA (89) have more space over which CD unit can slide, leading effective stress dispersion to realize higher fracture energy.

1) R. Ikura, J. Park, M. Osaki, H. Yamaguchi, A. Harada, Y. Takashima, *Macromolecules* **2019**, 52, 6953-6962

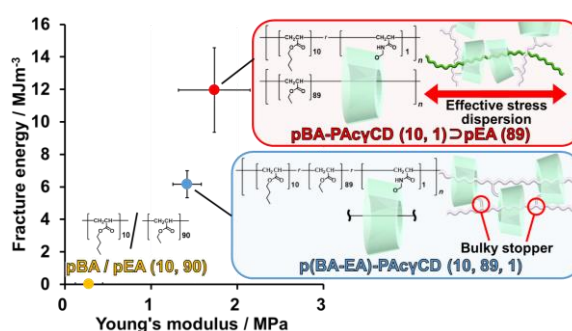


Figure 1. Plots of fracture energy vs Young's modulus for pBA-PACyCD (10, 1)⊃pEA (89), p(BA-EA)-PACyCD (10, 89, 1), and pBA / pEA (10, 90).

Mechanoresponsive PDMS that Reversibly Changes Fluorescence in Sub-MPa Stress

(Graduate School of Science, Kyoto University) ○Hidetsugu Kitakado, Shohei Saito

Keywords: Poly(dimethylsiloxane); Force probe; Ratiometric fluorescence; Stress-strain curve; Viscoelasticity

PDMS is a widely used polymer in biotechnology and electronics fields due to its biocompatibility, flexibility, transparency, and easy processability. In this study, we have developed PDMS elastomers that can quantitatively evaluate weak sub-MPa stress by ratiometric fluorescence analysis. In the PDMS, a flexible fluorescent force probe (FLAP) was chemically introduced into cross-linking positions of the polymer chain network. The FLAP molecule changes its fluorescent spectrum quickly and reversibly by its conformational change, thus FLAP can be used for real-time analysis of nanoscale stress concentration¹⁾. Stress-strain curve and viscoelasticity of PDMS with different compositions are analyzed, and then the relationship between mechanical properties and fluorescence response was investigated. In addition, by monitoring the fluorescence response associated with compression as well as stretching, the nanoscale stress concentration of PDMS will be analyzed.

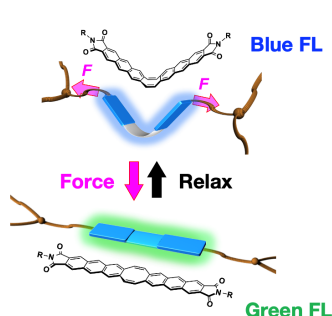


Fig. 1. Force-responsive fluorescence change of FLAP force probe.

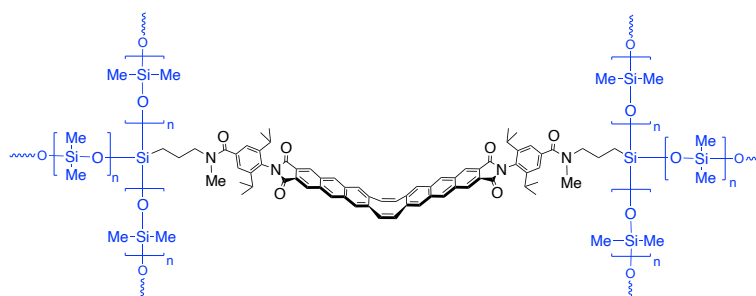


Fig. 2. Chemical structure of PDMS elastomer introduced with FLAP molecule at crosslinking points.

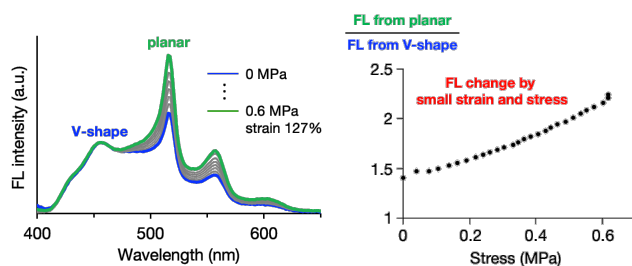


Fig. 3. Fluorescence changes and ratiometric fluorescent analysis of PDMS elastomer during elongational test.

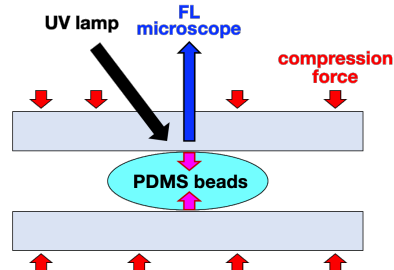


Fig. 4. Fluorescent stress analysis in PDMS beads during compression.

- 1) R. Kotani, S. Yokoyama, S. Nobusue, S. Yamaguchi, A. Osuka, H. Yabu, S. Saito, arXiv:2011.00202 (2020).

Gelation mechanism of freeze-crosslinked cellulose nanofiber gels with high compressive strength

(¹Faculty of science, Yamagata University, ²Japan Atomic Energy Agency, ³Graduate School of Science, The University of Tokyo) ○¹ Daisuke Miura, ² Takuya Nankawa, ³ Teppei Yamada, ² Yurina Sekine

Keywords: Cellulose nanofibers, Freeze cross-linking, Organic acid, Hierarchical structure

Cellulose nanofibers (CNFs) derived from natural polymers and their applications are promising raw materials, especially for medical and environmental applications. Developments of gelation methods of cellulose nanofibers, which are eco-friendly, non-toxic, and easily, are required for these applications. Recently, we developed a freeze crosslinking method to obtain a physically crosslinked hydrogel with high compressive strength and high compressive recoverability from carboxymethyl cellulose nanofiber (CMCF) and citric acid (CA)¹⁾. The freeze crosslinked CMCF hydrogel was formed by adding an aqueous CA solution to a frozen CMCF sol and then thawing the sol. Without the freeze crosslinking method, the CMCF sol and CA complex produced hydrogels, which easily collapsed under compressive stress. The compressive strength of the freeze crosslinked CMCF hydrogel was approximately 200,000 times higher than that of the non-freeze crosslinked CMCF hydrogel. The result indicates that freezing is an important procedure to create a high strength hydrogel.

In this study, we investigated the gelation mechanism of the freeze crosslinked CMCF hydrogel by SEM observations, IR spectroscopy, and XRD methods using CMCF-CA mixtures during the gelation process. The samples were prepared by adding an aqueous CA solution to a frozen CMCF sol and then thawing the sol for 5 to 1440 min. The reaction between CMCF and CA was stopped by immersing the sample in a large amounts of distilled water. From the SEM images of the samples, it was observed that CMCF bound to each other to form a larger ribbon-like structure with the reaction time. The IR spectra and XRD results also showed that the microscopic structure of CMCF changed due to the reaction with CA. We also demonstrated that the freeze crosslinked CMCF hydrogels are formed using other organic acids such as malic acid, ascorbic acid, succinic acid, and maleic acid. The results showed that the reaction between frozen CMCF sol and an organic acid solution created a ribbon-like structure that contributes to the high strength of the CMCF hydrogels.



1) Y. Sekine *et al.*, *ACS Appl. Polym. Mater.* **2020**, 2(12), 5842.

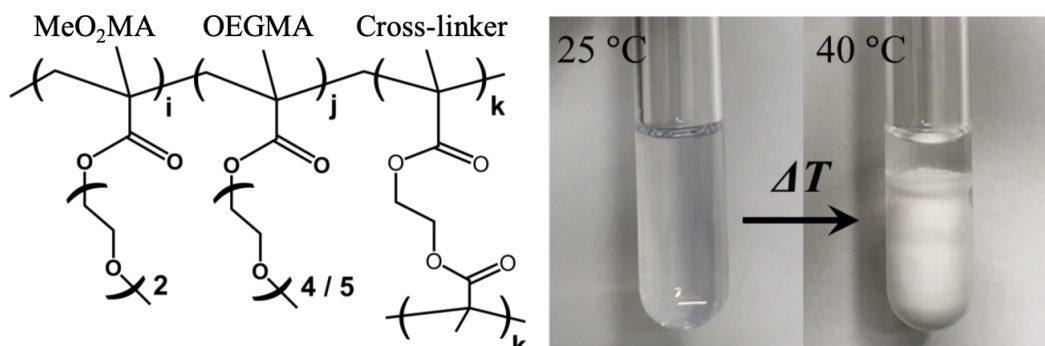
Structural Properties Analysis of Temperature-responsive Hydrogels with Unique Nanodomains

(¹Graduate School of Science and Technology, Hirosaki University) ○Takuma Kureha,¹ Takuto Hirayama,¹ Yuuki Takahashi,¹ Hikaru Kida,¹ Naoki Suda¹

Keywords: Hydrogels; Dynamic light scattering; Temperature-responsiveness; Small-angle neutron scattering

Recently, poly(oligo ethylene glycol methacrylate) (POEGMA)-based polymers have been developed as a new type of thermo-responsive polymer. They offer a potential alternative to the use of thermo-responsive polymers and PEG for the design of hydrogels for biomedical applications. POEGMA-based polymers can be synthesized via facile free radical polymerization and they display a lower critical solution temperature (LCST) in water that is governed by the ethylene oxide chain length (n) of the OEGMA monomer. Through the statistical copolymerization of diethylene glycol methacrylate (MeO₂MA, $n = 2$) and OEGMA ($n = 4$ or 5), copolymers can be prepared that display the LCST ranging anywhere from ~ 20 °C to ~ 63 °C (Figure). Although, many researchers have developed POEGMA-based gels for use in advanced biomedical applications, such as bioconjugates, coatings, microspheres, and injectable gels, very few studies have been reported on the physical properties of POEGMA-based gels, especially for the volume transition during changes in temperature. In this study, the structural properties of hydrogels with ethylene glycol units in their side chains were characterized by dynamic light scattering (DLS), dynamic viscoelasticity measurements, and small-angle neutron scattering (SANS).

We found that the polymer aggregate domains were formed in the gels and grew by increasing the temperature, which was observed by the dynamics of polymer networks.¹ Furthermore, the viscoelasticity of the gels was increased as the nanodomain grew, and it depended on copolymerization ratio of MeO₂MA and OEGMA.² From SANS analysis, we also discovered that the distance between the nanodomains was determined by the ethylene oxide chain length (n).



1) T. Kureha et al., *Macromolecules* **2018**, 51, 8932. 2) T. Kureha et al., *Soft Matter* **2020**, in press.

高分子クラウディングおよび希薄環境下での分子結晶化における排除体積と重なり合いの効果

(防衛医大研セ¹・東大物性研²・東大院工³) ○秦 裕樹¹・Xiang Li²・鄭 雄一³・酒井 崇匡³

Effect of excluded volume and overlap of dissolved polymers under dilute and crowding conditions on molecular crystallization (¹National Defense Medical College Research Institute, ²Institute for Solid State Physics, The University of Tokyo, ³Graduate School of Engineering, The University of Tokyo) ○Yuuki Hata,¹ Xiang Li,² Ung-il Chung,³ Takamasa Sakai³

Synthetic polymer solutions have been used as in vitro models of in vivo crowding conditions composed of biomacromolecules in a folded state. However, the differences between in vitro and in vivo crowding have rarely been demonstrated. In this study, we explored caffeine crystallization in poly(ethylene glycol) (PEG) solutions and found that the crystallization behavior was drastically changed depending on whether the polymer concentration was below or above the overlap concentration.¹ This result highlights the uniqueness of in vitro solutions of polymers in a random coil state, that is, the interpenetration of polymers under concentrated conditions.

Keywords: Molecular Self-Assembly; Crystallization; Macromolecular Crowding; Overlap Concentration; Depletion Attraction

ランダムコイル状態の合成高分子の溶液は、折りたたみ状態のタンパク質等からなる生体内クラウディング環境の模倣として用いられるが、両者の違いにはほとんど焦点が当てられてこなかった。本研究では、ランダムコイルに特徴的な重なり合いが、分子結晶化挙動を方向づけることを明らかにした¹⁾。PEG 溶液中でのカフェインの結晶化を調査した結果、PEG が希薄領域では高分子量ほど結晶化を促進した (Figure 1a)。これは高分子の排除体積に由来する枯渇引力によって結晶核形成が促進されるためと推察される。一方で、重なり濃度 (c^*) 以上では結晶化速度に PEG 分子量依存性がなかった (Figure 1b)。これは、高分子溶液の特徴サイズが、準希薄領域では分子量依存性のないブロッブとなるためと考えられる。この結果は、折りたたみ状態の生体高分子からなるクラウディングとの対比において、コイル状態の合成高分子は重なり合うことが特徴であることを示している。

1) Hata, Y.; Li, X.; Chung, U.; Sakai, T. Molecular crystallization directed by polymer size and overlap under dilute and crowded macromolecular conditions. *Polym. J.* **2021**, accepted.

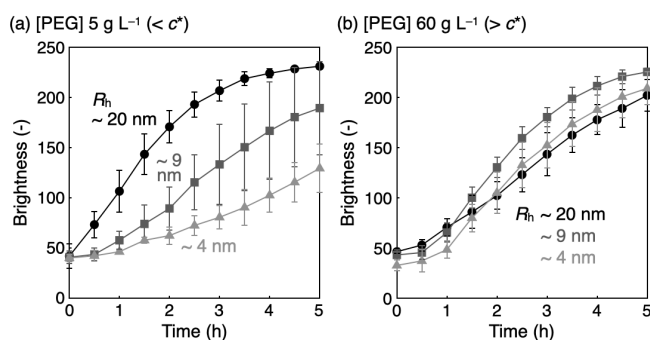


Figure 1. Photograph brightness time-lapse for samples containing caffeine and PEG at (a) 5 and (b) 60 g L⁻¹. PEGs with various hydrodynamic radius (R_h) were used, and c^* was ~ 40 g L⁻¹ for $R_h \sim 4$ nm. An increase in y-axis brightness indicates formation of caffeine particulate crystals.

Second-order phase transition behavior in polymer glass transition

(¹Department of Chemistry, Josai University) ○Mitsuru Ishikawa,¹ Masayoshi Yagishita,¹ Yuya Hiramoto,¹ Takayuki Uwada¹

Keywords: Glass Transition; Second-order Phase Transition; Critical Phenomena

Glass transition was primarily considered to be not phase transition. Recent single-molecule spectroscopy (SMS) developments have prompted re-investigating polymer glass transition at the microscopic scale, revealing that glass transition includes phenomena similar to second-order phase transition.¹ They are characterized by microscopic collective polymer motion and discontinuous changes in temperature dependent relaxation times within a temperature window that includes the polymer calorimetric glass transition temperature T_g .

We selected poly(vinyl acetate): PVAC10 (MW 100,000)¹; PVAC50 (MW 500,000) and poly(ethyl methacrylate): PEMA05 (MW 50,000). Viscosity-sensitive fluorescence probe Cy3 used in SMS shows enhanced fluorescence intensity with increased polymer viscosity and *vice versa*. Thus, changes in Cy3 fluorescence intensity report us thermally driven polymer dynamics or relaxation. SMS was carried out with a video microscope equipped with a CCD camera and an image intensifier making it possible observe single molecule Cy3 covalently immobilized on a quartz surface with a polymer overlay. The single molecule Cy3 was irradiated with a CW 532-nm laser using evanescent excitation geometry. Sample temperatures were controlled with a hot plate for microscope use from room temperature (23–25 °C) to 90 °C, within which we evaluated T_g (36.5 for PVAC10, 37.9 for PVAC50, and 65.8 °C for PEMA05) by DSC.

We observed autocorrelation functions $C(\tau)$ and power spectra $J(\nu)$ from individual single Cy3 fluorescence trajectories $I_i(t)$, and then evaluated average relaxation time $\langle\tau_R\rangle$ from 20–30 $C(\tau)$ at the above noted temperatures controlled with a hot plate.

Figure 1 illustrates the key to the present research to contrast it with the conventional idea of glass-forming material relaxations. The present work elucidated enhanced $\langle\tau_R\rangle$ above T_g . This observation looks critical slowing down as a critical phenomenon in the

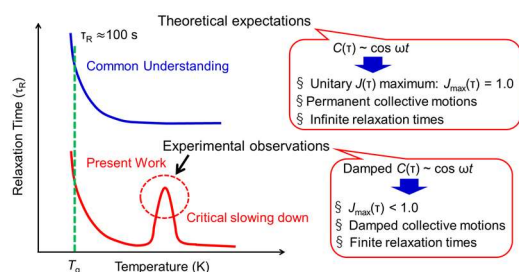


Figure 1. Schematic of the present work summary.

second-order phase transition. Enhanced $\langle\tau_R\rangle$ simultaneously occurred together with oscillatory $C(\tau)$, the latter of which provides evidence for polymer collective motion around single Cy3 molecules. Thus, both enhanced $\langle\tau_R\rangle$ and oscillatory $C(\tau)$ above T_g evidenced second-order phase transition behavior in polymer glass transition.

1) M. Ishikawa et al., *ChemRxiv* **2020**, 12696020.

Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B**[A28-2am] 20. Materials Chemistry -Basic and Application-**

Chair:Hideo Sawada, Kazu Okumura

Sat. Mar 20, 2021 9:00 AM - 10:40 AM Room 28 (Online Meeting)

[A28-2am-01] Coordination-Driven Self-Assembly on Polymer Surfaces for Efficient Synthesis of $[\text{Au}(\text{SPh})]_n$ Coordination Polymer-Based Films

[○]Takaaki Tsuruoka¹, Takashi Ohashi¹, Aude Demessence², Yohei Takashima¹, Kensuke Akamatsu¹ (1. Konan University, 2. Institute of Research on Catalysis and Environment of Lyon)

9:00 AM - 9:20 AM

[A28-2am-02] Optical luminescence from protein-directed Au_{-20} clusters upon hard X-ray irradiation

[○]Zuoyue Liu¹, Kyung Oh Jung², Ryo Takahata³, Masanori Sakamoto³, Toshiharu Teranishi³, Mamoru Fujitsuka¹, Guillem Pratx², Yasuko Osakada¹ (1. Osaka University, 2. Stanford University, 3. Kyoto University)

9:20 AM - 9:40 AM

[A28-2am-03] Structural Analysis of Silver Nanowires

[○]Yasunao Miyamura¹ (1. Showa Denko K.K.)

9:40 AM - 10:00 AM

[A28-2am-04] Characteristics of silicone rubber in the joint on aluminum-silicone rubber joint interface by chemical bonding

[○]DENG XUELIANG¹, JING SANG¹, SUMIO AISAWA¹, Kastuhito Mori², HIDETOSHI HIRAHARA¹ (1. Iwate University, 2. Sulfur Chemical Laboratory Inc.)

10:00 AM - 10:20 AM

[A28-2am-05] Preparation of Paintable Hybrid Polymers Showing Thermally-Stable White-Light Emission Based on POSS

[○]Masayuki Gon¹, Satoru Saotome¹, Kazuo Tanaka¹, Yoshiki Chujo¹ (1. Graduate School of Engineering, Kyoto University)

10:20 AM - 10:40 AM

Coordination-Driven Self-Assembly on Polymer Substrates for Efficient Synthesis of $[\text{Au}(\text{SPh})]_n$ Coordination Polymer-Based Films

(¹FIRST, Konan University, ²IRCELYON) ○Takaaki Tsuruoka,¹ Takashi Ohhashi,¹ Aude Demessence,² Yohei Takashima,¹ Kensuke Akamatsu¹

Keywords: Au Coordination Polymer; Self-Assembly; Interfacial Reaction

Recently, increasing efforts have been devoted to the preparation of coordination polymers (CPs) with specific optical and electrical properties because of the development of flexible, lightweight, and portable solid state optoelectronic devices with high efficiency. In spite of significant advances in the research of 3D CPs-based thin films, all approaches for fabricating low-dimensional (1D or 2D) CPs practically rely on the layer-by-layer approach. Therefore, facile synthetic approaches to fabricate thin films of CPs on flexible substrates are in significant demand, such as the in situ one-pot synthesis of CPs on substrates under mild reaction conditions.

This approach involves the adsorption of Au ions into nylon substrate, a sequential reaction with reduction of Au(III) ions, and complexation of Au(I) ions and SPh at the interface between the nylon surface and the reaction solution containing only thiophenol (HSPh) molecules (**Figure**). $[\text{Au}(\text{SPh})]_n$ CPs with high crystallinity can be formed directly on the nylon substrate using this approach. In addition, we demonstrate that initially formed amorphous $[\text{Au}(\text{SPh})]_n$ aggregates are transformed to crystalline $[\text{Au}(\text{SPh})]_n$ CPs through the rearrangement of components during the reaction. Our study not only provides fundamental aspects of the crystal formation of CP on the substrate but also a pathway toward formation of continuous free-standing CP crystal films; this was achieved via the control over growth kinetics.

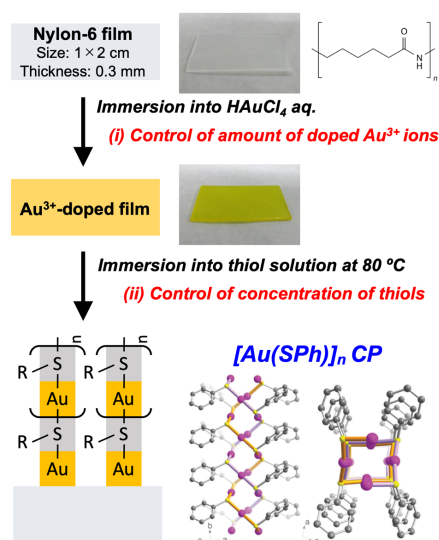


Figure. Schematic illustration of the developed interfacial approach for formation of $[\text{Au}(\text{SPh})]_n$ CPs on a substrate.

1) T. Tsuruoka et al., *Cryst. Growth Des.* **2020**, *20*, 1961-1968.

Optical luminescence from protein-directed Au₂₀ clusters upon hard X-ray irradiation

(¹Osaka University, ²Stanford University, ³Kyoto University) ○Zuoyue Liu,¹ Kyung Oh Jung,² Ryo Takahata,³ Masanori Sakamoto,³ Toshiharu Teranishi,³ Mamoru Fujitsuka,¹ Guillem Pratx,² Yasuko Osakada¹

Keywords: Hard X-ray irradiation; Protein; Au clusters; Luminescence

Hard X-ray excited optical luminescence (hXEOL) is promising in bio-imaging field, but development of contrast agents is limited. Previously, we used protein-directed Au₂₅ clusters as the contrast agent for hXEOL.¹ Recently, protein-directed Au₂₀ clusters were found to have higher emission quantum yield (15%) than Au₂₅ clusters (4%).² In this study, we employed protein-directed Au₂₀ clusters as the contrast agent and investigated their luminescent properties under hard X-ray irradiation (60 kVp), both in solutions and films.³

Three kinds of proteins were used for the synthesis of Au₂₀ clusters, namely, bovine serum albumin (BSA), human serum albumin (HSA) and lactoferrin. Upon hard X-ray irradiation, clear emission was observed from the solutions of protein-directed Au₂₀ clusters (Fig. 1a and 1b). When embedded in films (PEG/PVA), we observed red emission from HSA-directed Au₂₀ clusters under UV light irradiation (Fig. 1c). Furthermore, the HSA-directed Au₂₀ clusters in the films displayed clear emission under hard X-ray irradiation compared to the control films (Fig. 1d). These results demonstrated potential application of protein-directed Au₂₀ clusters in bio-imaging field.

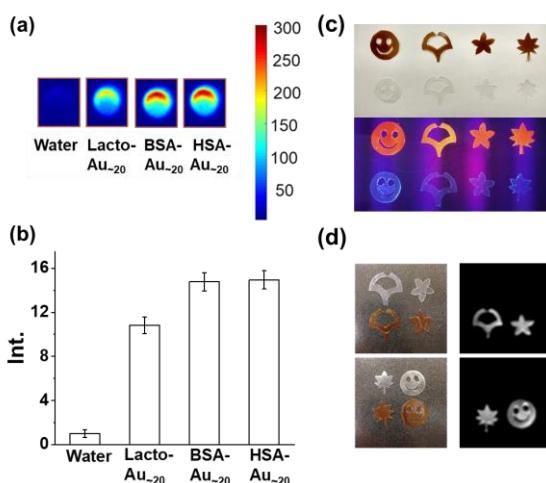


Figure 1. (a) hXEOL images and (b) signal of water, lactoferrin-, BSA- and HSA-directed Au₂₀ clusters. (c) Images of HSA-directed Au₂₀ clusters embedded films and control films under natural light (top) and UV light (365 nm, bottom) irradiation. (d) Images of HSA-directed Au₂₀ clusters embedded films and control films under natural light (left) and hard X-ray irradiation (right).

- 1) Y. Osakada, G. Pratx, C. Sun, M. Sakamoto, M. Ahmad, O. Volotskova, Q. Ong, T. Teranishi, Y. Harada, L. Xing, B. Cui, *Chem. Commun.* **2014**, 50, 3549.
- 2) P. Zhang, X. Yang, Y. Wang, N. Zhao, Z. Xiong, C. Huang, *Nanoscale*, **2014**, 6, 2261.
- 3) Z. Liu, K.O. Jung, R. Takahata, M. Sakamoto, T. Teranishi, M. Fujitsuka, G. Pratx, Y. Osakada, *RSC. Adv.* **2020**, 10, 13824.

銀ナノワイヤの構造解析

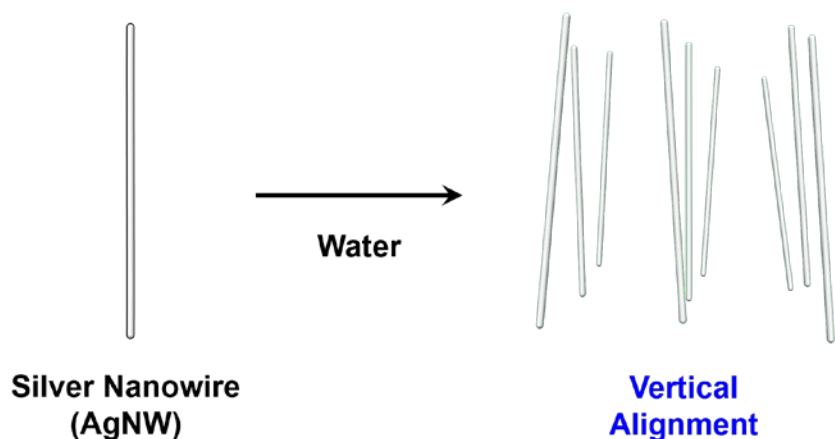
(昭和電工株式会社¹⁾ ○宮村泰直¹・門脇靖¹・山竹邦明¹・竹下聡一郎¹・原真尚¹・山木繁¹・大籬英樹¹

Structural Analysis of Silver Nanowires (¹Showa Denko K.K.) ○Yasunao Miyamura,¹ Yasushi Kadowaki,¹ Kuniaki Yamatake,¹ Masanao Hara,¹ Shigeru Yamaki,¹ Hideki Ohata¹

Silver nanowires (AgNWs) possess both transparency and conductivity, which are indispensable traits for electric materials such as transparent conductive films (TCF). For these applications, precise control of the alignment of AgNW in suspension is one of the most crucial keys to the fabrication of TCF, since alignment of AgNWs can induce anisotropic electric and photonic characteristics. During the investigation of AgNWs' alignments, we have found when dispersed in water, AgNWs spontaneously form anisotropic phase in suspension so that long axis of AgNWs direct perpendicular to the ground. We will present structural analysis of AgNW forming anisotropic phase in aqueous suspension, which can be fixed within gel and polymer matrices.

Keywords : Silver Nanowires, AgNW

銀ナノワイヤ (AgNW) は透明導電フィルム (TCF) 作製に必要な透明性と導電性を有する電子材料である。TCF 作製においては AgNW の配向に伴い異方的電気特性および異方的光学特性が発現するため、精密な配向制御が重要となる。こうした配向検討の過程において我々は AgNW が水分散液中で自発的に鉛直配向し異方相を形成することを明らかにした。本報告では水分散液中およびゲル・ポリマー中に固定化された配向 AgNW 構造について報告する。



アルミニウムとシリコンゴム複合体の接合界面でのシリコンゴム物性の影響に関する研究

(岩大院工¹・株式会社いおう化学研究所²) ○鄧 学良¹・桑 静¹・會澤 純雄¹・森 克仁²・平原 英俊¹

Characteristics of silicone rubber in the joint on aluminum-silicone rubber joint interface by chemical bonding

(¹ Department of Frontier Materials and Function Engineering, Graduate School of Engineering, Iwate University, ² Sulfur Chemical Institute) ○Xueliang Deng,¹ Jing Sang,¹ Sumio Aisawa, Katsuhito Mori,² Hidetoshi Hirahara¹

The interface bonding and adhesion mechanism of metal and polymer are very important for polymer composites. However, it is difficult to evaluate the chemical and physical characteristics of the bonded interface or elucidate the bonding mechanism using the non-destructive method of the bonded interface. In this study, a triazine-based silane coupling agent is used to treat aluminum (Al) and silicone rubber (Q) to make interface chemical bonding. The bonding strength test, swelling experiment, rubber curing degree and dynamic mechanical analysis of the Al/Q with different thicknesses were carried out to reveal the molecular motion behavior. The results show that bonded Al/Q interface has increased co-operation of molecular motion corresponding to stress relaxation compared to unbonded Q, because bonded rubber molecules constrain the molecular motility.

Keywords : *Interface molecular motion, Interface chemical bonding, Direct adhesion, Swelling*

金属とポリマーの接合は産業分野で広く使用され、その界面結合のメカニズムは非常に重要である。しかしながら、接合した界面の非破壊法による接合界面の化学的、物理的特性の評価、または接合メカニズムの解明は困難である¹⁾。シミュレーション以外の実験手法による界面結合分子特性に関する研究報告はほとんどない。

本研究では、トリアジン系シランカップリング剤を使用してアルミニウム (Al) とシリコンゴム (Q) を表面処理することによって、化学結合による金属とポリマーを結合させた。Al 基板に異なる厚さの Q を結合させ、その複合体の膨潤実験および動的粘弾性分析から、化学結合によって Al/Q 界面の物性と Q の分子運動制御を明らかにした。Al と Q の間の界面結合は、界面の付近だけでなく、Q のある厚さまで影響することが明らかになった。また、膨潤試験の結果から、同じゴムの厚さで、Al/Q/Al 両面接合サンプルの膨潤率は Al/Q 片面接合サンプルの膨潤率よりも小さいことが明かとなった。これは、界面化学結合が Q 分子が束縛されたためと考えられる。

- 1) Depth resolved compositional analysis of aluminium oxide thin film using non-destructive soft x-ray reflectivity technique. Sinha, M.; Modi, M. H, Applied Surface Science, **2017**, 419, 311.

Preparation of Paintable Hybrid Polymers Showing Thermally-Stable White-Light Emission Based on POSS

(Graduate School of Engineering, Kyoto University)

○Masayuki Gon, Satoru Saotome, Kazuo Tanaka, Yoshiki Chujo

Keywords: polyhedral oligomeric silsesquioxane; organic–inorganic hybrid; white-light emission; silicon; π -conjugated polymer

Polymeric materials with white-light emission have great attention as a promising candidate for paper-type illumination. In principle, combinations of two or three-types of different colors are necessary for generating white light. Therefore, the key point in the material design is to maintain a color balance suitable for white emission. In particular, since the material performance consisting of several components is often spoiled by temperature changes due to activation of molecular motion followed by phase separation, it is important not only to produce mixing state but also to maintain the original state. Herein, to realize thermoresistant white-light emission, we prepared hybrid polymers with a polyhedral oligomeric silsesquioxane (POSS) and a π -conjugated polymer having high thermal stability. POSS has a cubic structure composed of Si–O bonds and is used as an “element block” to create organic–inorganic hybrid materials at the molecular level (Figure 1).¹⁾

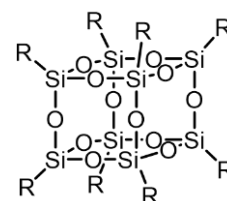


Figure 1. The structure of POSS.

Figure 2 shows the chemical structures of two luminophores, **TPE-POSS** and **MEH-PPV**. We were able to prepare homogeneous hybrid films with a spin-coating method from chloroform solutions containing **TPE-POSS** and **MEH-PPV** at arbitrary ratios. Figure 3 shows one of the resulting thin films showing white-light emission composed of **TPE-POSS** 95 wt% and **MEH-PPV** 5 wt%. From the variable temperature (VT) photoluminescence (PL) spectra and their CIE diagrams, it was clearly observed that the film maintained the color balance from 300 to 425 K. In summary, hybridization with the POSS and π -conjugated polymer is promised to be a simple and versatile method to create thermally stable light-emitting materials.

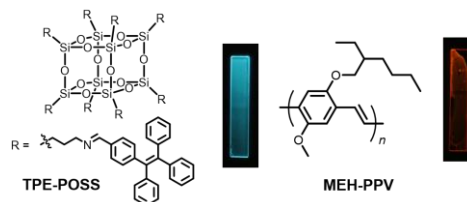


Figure 2. The structures and photos in films irradiated by UV lamp (365 nm) of mixed two components.

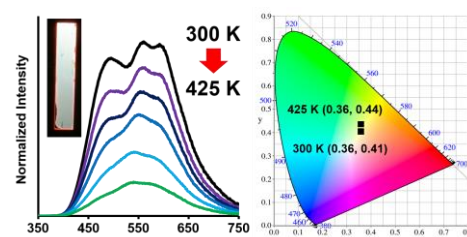


Figure 3. The resulted white-light emissive thin film composed of **TPE-POSS** 95 wt% and **MEH-PPV** 5 wt% and their VT PL spectra and CIE diagrams.

1) Chujo, Y.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **2015**, 88, 633.

Academic Program [Oral B] | 21. Energy and Related Chemistry, Geo and Space Chemistry | Oral B**[A29-2pm] 21. Energy and Related Chemistry, Geo and Space Chemistry**

Chair: Atsushi Wakamiya, Takaya Kubo

Sat. Mar 20, 2021 1:00 PM - 2:40 PM Room 29 (Online Meeting)

[A29-2pm-01] Unprecedentedly efficient overall water splitting in acid with anisotropic metal nanosheets

○DONGSHUANG WU¹, Kohei Kusada¹, Satoru Yoshioka², Tomokazu Yamamoto², Takaaki Toriyama², Syo Matsumura², Yanna Chen³, Okkyun Seo³, Jaemyung Kim³, Chulho Song³, Satoshi Hiroi³, Osami Sakata³, Toshiaki Ina⁴, Shogo Kawaguchi⁴, Yoshiki Kubota⁵, Hirokazu Kobayashi¹, Hiroshi Kitagawa¹ (1. Kyoto university, 2. Kyushu university, 3. National Institute for Materials Science, 4. Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 5. Osaka Prefecture University)

1:00 PM - 1:20 PM

[A29-2pm-02] Silicon Carbide: A Promising Anode Material to Lookout for Next Generation Lithium Ion Batteries

○Ravi Nandan¹, Noriyuki Takamori¹, Koichi Higashimine¹, Rajashekar Badam¹, Noriyoshi Matsumi¹ (1. Japan Advanced Institute of Science and Technology)

1:20 PM - 1:40 PM

[A29-2pm-03] Accelerated Lifetime Testing of Perovskite Solar Cells

○Richard Murdey¹, Yuko Matsushige¹, Yasuhisa Ishikura¹, Minh Anh Truong¹, Tomoya Nakamura¹, Atsushi Wakamiya¹ (1. ICR, Kyoto Univ.)

1:40 PM - 2:00 PM

[A29-2pm-04] Fabrication of High Purity Tin Perovskite Films Realized by Tin(IV) Scavenging Method

○Tomoya Nakamura¹, Minh Anh Truong¹, Shuaifeng Hu¹, Kento Otsuka¹, Ruito Hashimoto¹, Richard Murdey¹, Takahiro Sasamori², Hyung Do Kim³, Hideo Ohkita³, Taketo Handa¹, Yoshihiko Kanemitsu¹, Atsushi Wakamiya¹ (1. ICR, Kyoto Univ., 2. Graduate School of Science and Technology, Univ. of Tsukuba, 3. Graduate School of Engineering, Kyoto Univ.)

2:00 PM - 2:20 PM

[A29-2pm-05] Effect of ZnO Annealing Condition on the Performance of PbS Quantum Dot/ZnO Nanowire Solar Cells

○Haibin Wang¹, Yun XIAO¹, Jotaro NAKAZAKI¹, Takaya KUBO¹, Hiroshi SEGAWA^{1,2} (1. RCAST, The Univ. of Tokyo, 2. Grad. Sch. Arts and Sci. The Univ. of Tokyo)

2:20 PM - 2:40 PM

Unprecedentedly efficient overall water splitting in acid with anisotropic metal nanosheets

(¹Graduate School of Science, Kyoto University, ²Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, ³Synchrotron X-ray Group and Synchrotron X-ray Station at SPring-8, National Institute for Materials Science, ⁴Research & Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, ⁵Department of Physical Science, Graduate School of Science, Osaka Prefecture University.) ○DONGSHUANG WU,¹ Kohei Kusada,¹ Satoru Yoshioka,² Tomokazu Yamamoto,² Takaaki Toriyama,² Syo Matsumura,² Yanna Chen,³ Okkyun Seo,³ Jaemyung Kim,³ Chulho Song,³ Satoshi Hiroi,³ Osami Sakata,³ Toshiaki Ina,⁴ Shogo Kawaguchi,⁴ Yoshiki Kubota,⁵ Hirokazu Kobayashi,¹ Hiroshi Kitagawa¹

Keywords: Nanomaterials; Alloys; Ruthenium; Electrochemistry; Water splitting

Water electrolysis is among the most wanted techniques to produce hydrogen, however, it accounts for only 4% of global hydrogen production.¹ One of the reasons is the high cost and low performance of catalysts promoting the anodic oxygen evolution reaction (OER). OER is an uphill energy transformation process involving four-proton and -electron transfers per oxygen molecule, which typically requires catalysts to work under high overpotentials and counteracts the long-term operation of catalysts. Currently, only Ir oxides show moderate stability for OER in acid,² but still require high overpotentials (generally over 300 mV). In contrast, Ru is the most active OER catalyst and is nearly 5~16 times cheaper than Ir these five years, however, Ru cannot be practically used because of serious degradation problem.³

We report a highly efficient catalyst in acid, that is solid-solution Ru-Ir nanosized-coral (**RuIr-NC**) consisting of 3 nm-thick sheets with only 6 at.% of Ir (Figure (a, b)). **RuIr-NC** achieves high mass activity and specific activity for OER, which are 1-2 orders of magnitude higher than the reported highly active catalysts. An overall water-splitting cell using **RuIr-NC** as both electrodes can reach 10 mA/cm² at 1.485 V for 120 h without noticeable degradation (Figure (c)), which outperforms the known cells. Operando spectroscopy and atomic-resolution electron microscopy indicated that the high performance results from the ability of the preferentially exposed {0001} facets to resist the formation of dissolvable metal oxides and to transform ephemeral Ru into a long-lived catalyst.

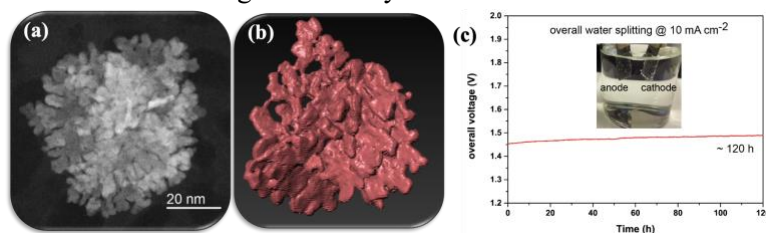


Figure (a) High-angle annular dark-field-Scanning transmission electron microscopy image of RuIr-NC (b) an image from 3D tomographic reconstructions showing coral-like morphology. (c) Chronopotentiometric curves of **RuIr-NC** || **RuIr-NC** full cell at 10 mA cm⁻²_{geo}. The inset shows the two-electrode configuration with bubbles on both electrodes.

1) a) Z. Seh et al., *Science* **2017**, 355, 4998. b) M. Schalenbach et al., *Int. J. Electrochem. Sci.* **2018**, 13, 1173. 2) a) L. Seitz et al. *Science* **2016**, 353, 1011. b) H. Nong et al. *Nat. Catal.* **2018**, 1, 841. 3) a) T. Reier et al. *ACS Catal.* **2012**, 2, 1765. b) H. Over et al. *Chem. Rev.* **2012**, 112, 3356.

Silicon Carbide: A Promising Anode Material to Lookout for Lithium Ion Batteries

○Ravi Nandan,¹ Noriyuki Takamori,¹ Koichi Higashimine,² Rajashekar Badam,¹ Noriyoshi Matsumi^{1,*}

(¹Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, ²Center for Nano Materials and Technology, Japan Advanced Institute of Science and Technology, *E-mail: - matsumi@jaist.ac.)

Keywords: Silicon Carbide; Anode; Lithium-ion Battery; Reversible Capacity

Despite promising specific capacity (~ 3579 mAh/g) of silicon, its adoption in lithium-ion batteries (LIB) as anode material has delayed due to its accelerated capacity fading owing to aggressive volume change during alloying/dealloying with lithium.¹ Developing a facile methodology for rational designing of a robust Si and carbon-based anode systems for realization of high-performance LIB is much needed. In this line, inspired by the attractive structural features in combination with promising thermal stability of silicon carbide (SiC),² we have devised a user-friendly facile methodology to develop SiC based anode materials which does not require any sophisticated instrumentation or very high temperature treatment. To study the adeptness of this method we have selected two synthesis temperature in a window of 550 – 1100 °C and samples were named as SiC-1 and SiC-2, respectively. The SiC nanoparticle embedded carbon-based anode materials when employed in anodic-half cell configuration offered a high reversible capacity (~ 1230 mAh/g @ 250 cycles, Figure 1), in conjunction with a promising capacity retention. The study pointed out that SiC based systems were electrochemically active for lithiation/delithiation and can be explored as an efficient anode material for LIB.

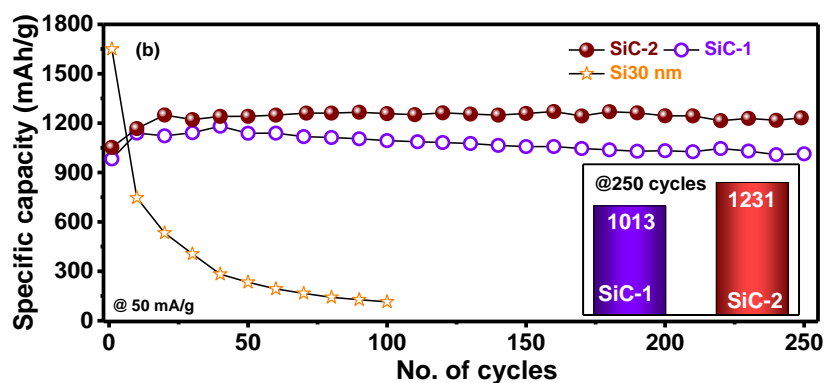


Figure 1. Comparative cycling study of SiC-1, SiC-2 and Si based anodic half-cells.

1) M. Ashuri et.al. *Nanoscale* **2016**, 8, 74. 2) A. L. Lipson et.al. *J. Phys. Chem. C* **2012**, 116, 20949.

Acknowledgement- Authors acknowledge JST-Mirai Program (Grant No. JP18077239) for financial support.

ペロブスカイト太陽電池の効率的な安定性評価

(京大化研) ○Richard Murdey・松重 優子・石倉 靖久・Minh Anh Truong・中村 智也・若宮 淳志 Accelerated Lifetime Testing of Perovskite Solar Cells (*Institute for Chemical Research, Kyoto University*) ○Richard Murdey, Yuko Matsushige, Yasuhisa Ishikura, Minh Anh Truong, Tomoya Nakamura, Atsushi Wakamiya

An accelerated test protocol for mixed composition metal halide perovskite solar cells is established in order to investigate the device stability under dark storage condition. With this test, called the stability accelerated lifetime test (SALT), the time for the device to reach 80% output (T_{80}) is reduced to the order of a few days, allowing fast, iterative evaluation of material and device stability. The accelerated test results of perovskite devices with stabilizing PEAI or 4F-PEAI additive are linked to real-world storage lifetimes^{1,2)} with the aid of a model rate equation and supporting analytical framework.

Keywords : Solar Cell, Metal Halide Perovskite, Device, Stability, Testing

金属ハライドペロブスカイト太陽電池の安定性を評価するための、独自の加速試験手法 (Stability Accelerated Lifetime Test; SALT) の開発を行った。本手法により、太陽電池素子の出力が最初の 80% に低下するまでの時間 (T_{80}) を数日程度まで短縮でき、素子の安定性を速やかに評価することが可能になった。独自の反応速度モデルを用いた解析により、SALT 法の加速試験結果を実際の劣化^{1,2)}の経時変化へと対応させることができた。

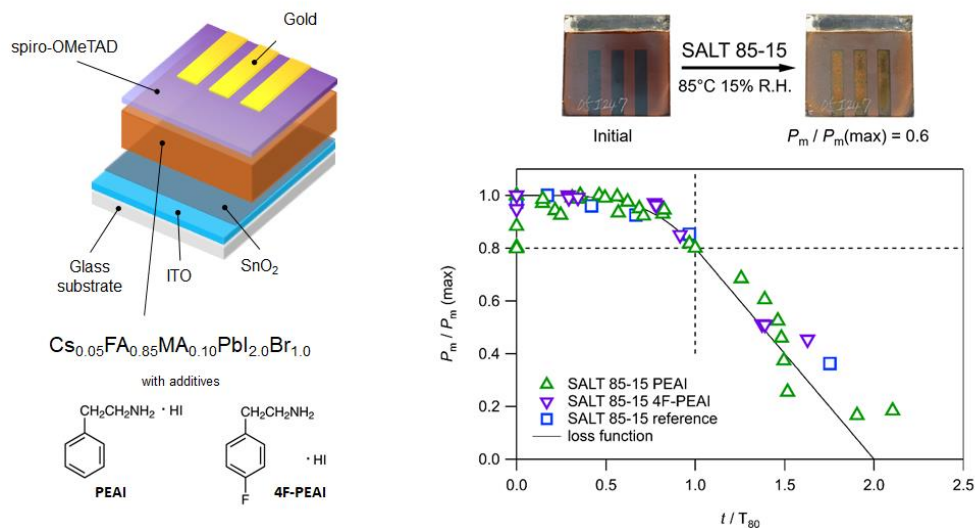


Figure 1. The perovskite test cells and stability accelerated lifetime test (SALT) results at 85 °C and 15% relative humidity (R.H.).

- 1) L. N. Quan, M. Yuan, R. Comin, et al., *J. Am. Chem. Soc.*, **2016**, 138, 2649.
- 2) D. S. Lee, J. S. Yun, J. Kim, et al., *ACS Energy Lett.*, **2018**, 3, 647.

Sn(IV)スカベンジャー法を用いた高純度スズ系ペロブスカイト半導体膜の作製

(京大化研¹・筑波大院数理物質²・京大院工³) ○中村 智也¹・Minh Anh Truong¹・Shuaifeng Hu¹・大塚 健斗¹・橋本 隼人¹・Richard Murdey¹・笹森 貴裕²・Hyung Do Kim³・大北 英生³・半田 岳人¹・金光 義彦¹・若宮 淳志¹

Fabrication of High Purity Tin Perovskite Films Realized by Tin(IV) Scavenging Method (¹*Institute for Chemical Research, Kyoto University*, ²*Graduate School of Science and Technology, University of Tsukuba*, ³*Graduate School of Engineering, Kyoto University*) ○Tomoya Nakamura,¹ Minh Anh Truong,¹ Shuaifeng Hu,¹ Kento Otsuka,¹ Ruito Hashimoto,¹ Richard Murdey,¹ Takahiro Sasamori,² Hyung Do Kim,³ Hideo Ohkita,³ Taketo Handa,¹ Yoshihiko Kanemitsu,¹ Atsushi Wakamiya¹

The performance of tin-based perovskite solar cells is strongly affected by defects arising from the facile oxidation of Sn(II) to Sn(IV). Here, we show that the selective reduction of SnF₂ by a dihydropyrazine derivative generates tin nanoparticles, which can scavenge Sn(IV) impurities. Perovskite films fabricated using this Sn(IV) scavenging method are essentially free of Sn(IV) species, and exhibit strong photoluminescence with prolonged decay lifetimes. The maximum power conversion efficiency was 11.5% (certified value: 11.2%).

Keywords : Semiconductor; Perovskite; Solar Cells; Nanoparticles; Reducing Agent

スズ系ペロブスカイト太陽電池において、材料中の Sn(II)が容易に酸化されて Sn(IV)種が混在してしまうことが性能向上のボトルネックになっていた。我々は、ジヒドロピラジン体が SnF₂ を高選択的に還元することを利用して系中で 0 価のスズナノ粒子を発生させ、Sn(IV)種を完全に捕捉除去する「スカベンジャー法」を開発した (Figure 1a)。今回の手法を用いて作製した「Sn(IV)フリー」のスズペロブスカイト半導体薄膜は、従来よりも 3 倍以上長い蛍光寿命など優れた光物性を示し、光吸収層として用いた太陽電池デバイスにおいて、スズペロブスカイト太陽電池で世界最高水準のエネルギー変換効率 (11.5%, 認証値 11.2%) を得ることができた (Figure 1b) ¹⁾。

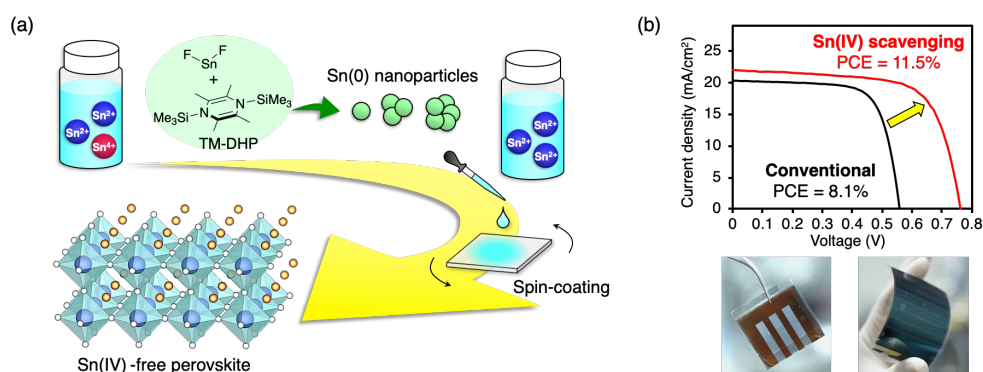


Figure 1. (a) Illustration of the Sn(IV) scavenging method and (b) performance of solar cell devices.

1) T. Nakamura, S. Yakumaru, M. A. Truong, K. Kim, J. Liu, S. Hu, K. Otsuka, R. Hashimoto, R. Murdey, T. Sasamori, H. D. Kim, H. Ohkita, T. Handa, Y. Kanemitsu, A. Wakamiya, *Nat. Commun.* **2020**, *11*, 3308.

Effect of ZnO Annealing Condition on the Performance of PbS Quantum Dot/ZnO Nanowires Solar Cells

(¹*RCAST, The University of Tokyo*, ²*Graduate School of Arts and Science, The University of Tokyo*) ○Haibin Wang,¹ Yun Xiao,¹ Jotaro Nakazaki,¹ Takaya Kubo,¹ Hiroshi Segawa^{1,2}

Keywords: Solar cell; ZnO nanowire; Annealing; Colloidal quantum dot; Lead(II) sulfide;

ZnO nanowires (NW) as an electron acceptor have been a critical component in increasing power conversion efficiency (PCE) of PbS quantum dot (QD) solar cell, by improving charge collection and light absorption in near-infrared region simultaneously.¹ However, PbS QD/ZnO NW devices tend to show open-circuit voltage (V_{oc}) lower than that of the planar device formed by simply depositing PbS QD layers on top of flat ZnO layers. The reduced V_{oc} is believed to result mainly from defect-related interfacial recombination because of larger surface-to-volume ratio of ZnO NWs. To solve this problem, metal oxide surface passivation and hydrogen plasma treatments were reported useful to reduce the surface defects of ZnO NWs. In this study, we investigated how the annealing atmosphere of ZnO NWs influenced the performance of the PbS QD/ZnO-NW solar cells.

ZnO nanowires (~650 nm) were formed on FTO (F-doped SnO₂) glass substrates by a hydrothermal method. The ZnO NWs were annealed at 200°C, 300°C, 400°C for 30 minutes in O₂ and N₂ atmosphere, respectively. PbS QD/ZnO NW solar cells were fabricated with iodide ion ligand exchanged PbS by a dip-coating method (Fig. 1a inset).

The anneal treatment increased the crystallinity of the ZnO NWs as confirmed by XRD, and reduced the defect states of ZnO NWs as indicated by the reduction of defect-related photoluminescence in the visible region. However, the solar cell performance (J_{sc} , V_{oc} and PCE) of N₂-annealed solar cells decreased with increasing annealing temperature. In contrast, although J_{sc} values of the O₂-annealed devices were reduced by annealing (Fig. 1a), V_{oc} values (except for 400°C O₂ annealed one) are almost the same values independent of annealing temperature (Fig. 1b). Notably, FF increased from 59.6% for the untreated devices to 71.0% for 300°C O₂ annealed ones (Fig. 1c): an FF of 71.0% is the highest value to date for PbS QD/ZnO NW solar cells. Such a high FF can counterbalance the decreased J_{sc} values, yielding a PCE of approximately 8.2%.

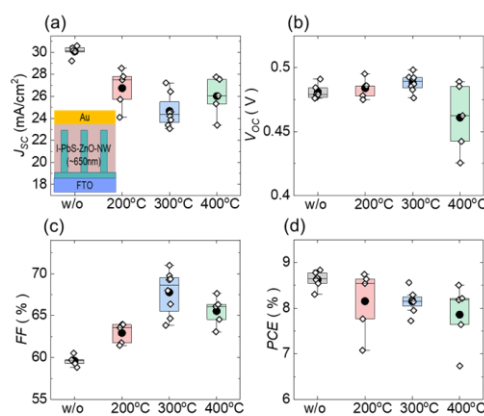


Fig. 1. (a) J_{sc} , (b) V_{oc} , (c) FF and (d) PCE of PbS QD/ZnO-NW solar cells fabricated with as-prepared ZnO NWs and ones annealed at different temperatures in O₂ atmosphere.

- 1) H. Wang, T. Kubo, J. Nakazaki, H. Segawa, *ACS Energy Lett.*, **2017**, 2, 2110.

[A11-2pm] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Chair: Kazuya Koumoto, Hironori Ogata

Sat. Mar 20, 2021 1:00 PM - 3:00 PM Room 11 (Online Meeting)

[A11-2pm-01] Structure and solid state properties of charge-transfer salts using biomass-derived molecules

○Hironori Ogata¹, Masaru Ide¹, Eiji Masai², Yuichiro Otsuka³, Masaya Nakamura³ (1. Hosei Univ., 2. Nagaoka Univ. of Technol., 3. Forestry and Forest Products Research Institute)

1:00 PM - 1:20 PM

[A11-2pm-02] Photoreforming of Lignocellulosic Biomass into Hydrogen Utilizing the Entire Visible Range of Light in the Presence of Composite Photocatalyst

○Haruki Nagakawa¹, Morio Nagata¹ (1. Tokyo University of Science)

1:20 PM - 1:40 PM

[A11-2pm-03] Air quality diagnosis in two field studies with different dominant sources, according to radical chemistry and oxidative capacity

○Jiaru Li¹, Nanase Kohno¹, Kentaro Murano¹, Yosuke Sakamoto^{1,2}, Yoshizumi Kajii^{1,2} (1. Graduate School of Global Environmental Studies, Kyoto University, 2. National Institute for Environmental Studies)

1:40 PM - 2:00 PM

[A11-2pm-04] Influence of Support Characteristics of Resin-supported Formate Catalyst to its Activity for CO₂ Reduction with Hydrosilanes

○Ria Ayu Pramudita¹, Yuichi Manaka^{1,2}, Ken Motokura^{1,3} (1. Tokyo Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology, 3. JST PRESTO)

2:00 PM - 2:20 PM

[A11-2pm-05] Suzuki-Miyaura coupling reactions in water using aqueous betaine solutions as the solvent

○Tomoaki Wada¹, Riku Matsumoto¹, Kazuya Koumoto¹ (1. Konan Univ.)

2:20 PM - 2:40 PM

[A11-2pm-06] Extraction of organic compounds using aqueous two-phase system formed by betaines and salts

○Riku Matsumoto¹, Tomoaki Wada¹, Kazuya Koumoto¹ (1. Konan Univ.)

2:40 PM - 3:00 PM

バイオマス由来分子を用いた電荷移動塩の構造と物性

(法政大院理工¹・長岡技科大²・森林総研³)

○緒方 啓典¹・井手 克¹・政井 英司²・大塚 祐一郎³・中村 雅哉³

Structure and solid state properties of charge-transfer salts using biomass-derived molecules (¹Graduate School of Sci. and Engin., Hosei University, ²Department of Bioengineering, Nagaoka University of Technology, ³Forest Research and Management Organization) ○THironori Ogata,¹ Masaru Ide,¹ Eiji Masai,² Yuichiro Otsuka,³ Masaya Nakamura³

Lignin, which accounts for about 15-30% of the cell wall components of trees in woody biomass, is partly used as a fragrance. However, its effective utilization method has not yet been fully established. If lignin can be converted into high-value-added organic materials, it is expected to greatly contribute to the formation of a recycling-oriented society. In 2006, a technology for producing 2-pyrone-4,6-dicarboxylic acid (PDC), which is an intermediate metabolite of lignin, was developed using the lignin metabolism system of the bacterial SYK-6(1). Focusing on the high electron acceptability of PDCs, we have developed various charge transfer salts based on PDCs and investigated their structures and electrical properties. As a result, it was clarified that these compounds have characteristics reflecting the characteristics of the unique molecular structure of PDC.

In this study, we report on the characteristics of the electrical properties of these compounds based on the results of low-temperature crystal structure analysis. We also report the correlation between the structural characteristics of these compounds and their electrical properties.

Keywords : Biomass; Lignin; 2-Pyrone-4,6-dicarboxylic acid; Charge transfer salts

木質系バイオマスのなかでも樹木の細胞壁成分の約 15-30%を占めるリグニンは、一部が香料等として利用されているものの、その有効なその利用方法については未だ十分に確立されていない。リグニンを付加価値の高い有機材料に変換することができれば、循環型社会の形成に大きく貢献することが期待されている。2006 年にバクテリア SYK-6 株のリグニン代謝系を利用したリグニンの中間代謝物である 2-pyrone-4,6-dicarboxylic acid (PDC)の生産技術が開発された。PDC は、生分解性ポリマー材料やキレート剤等への応用の可能性が報告されている。我々は、PDC の電子受容性に着目し、PDC をベースとした各種電荷移動塩の開発を行い、その電気的性質について調べてきた。その結果、PDC の特異な分子構造の特徴を反映した特徴を有することを明らかにした。本研究では、これらの化合物の物性の特徴について報告するとともに、新たに低温結晶構造解析を行った結果を元に、これらの化合物の構造上の特徴と物性の相関について明らかになった結果について報告する。

1) Y.Otsuka *et al.*, *Appl. Microbiol. Biotechnol.*, **2006**, 71, 608.

2) M. Hishida *et al.*, *Polymer Journal*, **2009**, 41, 297.

3) T. Michinobu, *et al.*, *Chem.Lett.*, **2010**, 39, 400-401.

Photoreforming of Lignocellulosic Biomass into Hydrogen Utilizing the Entire Visible Range of Light in the Presence of Composite Photocatalyst

(¹*Graduate School of Engineering, Tokyo University of Science*) ○Haruki Nagakawa,¹ Morio Nagata¹

Keywords: Photocatalytic Reaction; Photoreforming; Lignocellulose; Hydrogen Production; Composite Photocatalyst

The most significant challenges of the 21st century are related to energy exhaustion and global warming. To overcome these challenges, it is necessary to develop sustainable energy sources. In this regard, energy production from biomass is among the promising strategies; moreover, it has less hazardous impacts on the environment. The most abundant form of biomass is lignocellulose, which refers to organic matter such as grass, wood, paper and agricultural crop residues. In recent years, the photocatalytic photoreforming of biomass has been attracting significant attention. Compared to conventional chemocatalytic methods, photocatalytic reactions are conducted under ambient atmospheric pressure and temperature. Furthermore, hydrogen fuel could be produced using light energy by combining photoreforming of biomass and water splitting. The photoreforming of biomass is advantageous because the energy required for the reaction is smaller than that required by the conventional photocatalytic water splitting processes.

In this study, we realized highly efficient hydrogen production from lignocellulose in an alkaline solution at a high temperature under simulated sunlight,¹ using a CdS/SiC composite photocatalyst. The photocatalyst was stable against light irradiation in an alkaline solution at a high temperature. CdS/SiC absorbs the entire visible range of light, and the photocatalytic reaction proceeds with light of wavelengths shorter than 580 nm. Our previous study suggested that light of wavelengths longer than 580 nm absorbed by SiC is not used in the photocatalytic reactions,² and therefore, the absorbed light must be emitted as heat. The alkaline solution was maintained at a high temperature by the heat emitted from SiC. The dissolution of lignin and swelling of cellulose were promoted in this solution, and the photocatalytic reaction could proceed more easily. In the CdS/SiC composite, the recombination was suppressed by electron transfer between CdS and SiC, and the hydrogen production activity increased by ~20 times compared with those in the presence of any simple photocatalyst. Furthermore, the photoreforming activity of this system was evaluated in detail using α -cellulose. Indeed, quantum yields of 19.6% at 380 nm and 2.0% at 420 nm were achieved, which significantly exceeded the highest apparent quantum yield reported thus far.³

1) H. Nagakawa, M. Nagata, *ACS Appl. Energy Mater.* **2021**, in press. 2) H. Nagakawa, T. Ochiai, Y. Takekuma, S. Konuma, M. Nagata, *ACS Omega* **2018**, 3, 12770. 3) D. W. Wakerley, M. F. Kuehnelt, K. L. Orchard, K. H. Ly, T. E. Rosser, E. Reisner, *Nat. Energy* **2017**, 2, 17021.

Air quality diagnosis in two field studies with different dominant sources, according to radical chemistry and oxidative capacity

(¹Graduate School of Global Environmental Studies, Kyoto University, ²National Institute of Environmental Studies) ○ Jiaru Li,¹ Nanase Kohno,¹ Yosuke Sakamoto,^{1,2} Yoshizumi Kajii^{1,2}

Keywords: Field studies; Total OH reactivity; NO_x–HO_x–VOCs chemistry; Oxidative capacity

With the development of urbanization and industrialization, air quality has become a major issue in many places in particular in urban areas. Ozone, as the representative of oxidant, has been reported with an increasing tendency recently in Japan regardless of the precursors (VOCs & NO_x) have been mitigated. Such a “puzzle” has been closely related to radical chemistry initiated from hydroxyl radicals (OH). Therefore, it is essential to disclose the mechanism between radical reactions and ozone production procedure. Particularly field studies that dominated by different pollution sources should be lumped to provide unequivocal information. In atmospheric chemistry, OH radicals can react with countless OH-reactants, i.e. the trace species in the air, and products further react with NO_x to form secondary products and ozone. Therefore, OH reactivity (the inverse of OH lifetime) is the key to investigate the air quality and give clues to photochemical processes.

Two field observations were conducted in suburban area in Tsukuba (summer in 2017) and Keihin coastal industrial area in Yokohama (summer in 2019), where different dominant sources have been expected. Total OH reactivity (OHR) in both sites was continuously measured by laser-pump and laser induced fluorescence (LP-LIF)¹. Trace species including ozone were concurrently measured by commercial instrumentations including GC-MS, PTR-MS, and so on. The average OHR was determined as 12.9 s⁻¹ in Tsukuba and 35% remains to be missing reactivity after specifying the contributions of measured trace species². Measurement in Yokohama contains only 5% of missing among 11.6 s⁻¹ OHR. The average ozone concentrations in Tsukuba and Yokohama were detected as 31.1±20.4, and 15.5±12.4 ppbv, respectively. After exploring the source of missing reactivity, we found that it mainly came from secondary products in Tsukuba in which both biogenic and anthropogenic VOCs as primary emissions were importantly existed. Active photochemical procedure existed in Tsukuba and high level of missing OH reactivity boosted oxidative capacity. However, compared to that, Yokohama suffered mainly from primary emissions, the elevated NO_x constrained radical reactions and lead to inert oxidative capacity.

1. Sadanaga, Y. *et al.* Development of a measurement system of peroxy radicals using a chemical amplification/laser-induced fluorescence technique. *Rev. Sci. Instrum.* **75**, 864–872 (2004).
2. Li, J. *et al.* Total hydroxyl radical reactivity measurements in a suburban area during AQUAS–Tsukuba campaign in summer 2017. *Sci. Total Environ.* **740**, 139897 (2020).

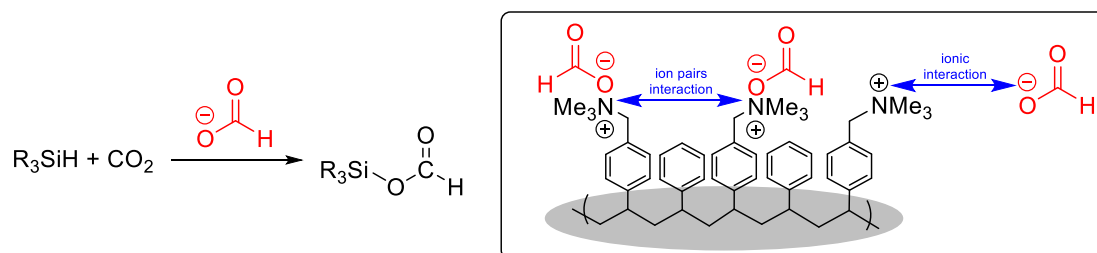
Influence of Support Characteristics of Resin-supported Formate Catalyst to its Activity for CO₂ Reduction with Hydrosilanes

(¹*School of Materials and Chemical Technology, Tokyo Institute of Technology*, ²*Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology*, ³*JST PRESTO*) ○Ria Ayu Pramudita,¹ Yuichi Manaka,^{1,2} Ken Motokura,^{1,3}

Keywords: Carbon Dioxide; Heterogeneous Catalysis; Hydrosilylation; Organocatalysts; Polymer Support

To decelerate the impact of climate change and to provide a cheap alternative to fossil resources, the utilization of carbon dioxide (CO₂) in the atmosphere has been considered as a promising solution. However, due to its high stability, the adoption of CO₂ as a C1 synthon is difficult and a catalyst is needed to help accelerate its reduction. Formate anion is shown as an excellent catalyst for CO₂ reduction with hydrosilanes,¹ without any requirements of metal catalyst that can potentially harm the environment. Heterogeneous formate catalyst was prepared from widely available anion exchange resin, where formate anion was paired with alkylammonium cation supported by the copolymer of polystyrene and divinylbenzene, through a simple anion exchange reaction.

Various resin-supported formate catalysts were synthesized, characterized with elemental analysis, FT-IR, and solid-state ¹³C CP-MAS NMR spectroscopy, and applied as catalysts for CO₂ hydrosilylation reactions. Among the prepared resin-supported formate catalysts, it was found that the catalyst with higher activity for CO₂ hydrosilylation had a lower wavenumber of aldehydic C—H stretching peaks observed in the FT-IR spectra of the pure catalyst. A similar observation was found in the homogeneous catalytic system as well. Additionally, the observation of elemental and solid-state ¹³C NMR analyses suggested that the ion-pair density might also influence the catalytic activity, where an increase of ion-pair density above an optimum value had a detrimental effect on the activity of resin-supported formate catalyst for the hydrosilylation of CO₂.²



- 1) K. Motokura, C. Nakagawa, R.A. Pramudita, Y. Manaka, *ACS Sustainable Chem. Eng.* **2019**, 7, 11056. 2) R.A. Pramudita, Y. Manaka, K. Motokura, *Chem. Eur. J.* **2020**, 26, 7939.

ベタイン水溶液を溶媒とした鈴木-宮浦カップリング反応

(甲南大¹⁾) ○和田 朋晃¹・松本 陸¹・甲元 一也¹

Suzuki-Miyaura coupling reactions in water using aqueous betaine solutions as the solvent
(¹Konan University) ○Tomoaki Wada¹, Riku Matsumoto,¹ Kazuya Koumoto¹

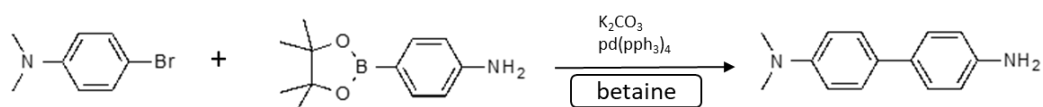
Keywords : Green chemistry; Organic synthesis; Betaine; Suzuki-Miyaura coupling reactions; Solubilization

Organic syntheses in water instead of using organic solvents have focused attractive attentions in recent years. Our recent study revealed that aqueous betaine solution can dissolve various poorly water-soluble substances at a high concentration. Therefore, we hypothesized that the solution enables to be used as a solvent for various organic synthesis. In this study, to investigate the function and characteristics of the aqueous betaine solution as the solvent, Suzuki-Miyaura coupling reactions were carried out in the solution.

The coupling reactions shown in the scheme (*vide infra*) were performed and compared in both homogeneous and two-phase systems. The yields in water or in water/organic solvent two-phase systems was considerably low (less than 40%). On the other hand, the yield in betaine solution, water/water two-phase system, was significantly high. It was suggested that this was influenced not only by the improvement of the water solubility of the substances, but also by the distribution characteristics of the substances, catalysts and salts. Moreover, in comparison to surfactants, generally used as solubilizer for the substances, it was revealed that the betaine solution was superior in the viewpoint of scarce foaming and high reactivity.

近年、有機溶媒を使用せず、水中で行う有機合成に注目が集まっている¹⁾。ベタイン誘導体を含む水溶液は、難水溶性物質を高濃度で溶解できることが明らかとなっており、水系有機溶媒において種々の原料物質を反応させる溶媒として適していることが考えられる。そこで本研究ではベタイン水溶液を反応溶媒とし、鈴木-宮浦カップリング反応を行い、その溶媒としての機能、特徴について検討した。

鈴木-宮浦カップリング反応は均一相、二相のどちらでも行われるが、以下の反応を水中や二相系で行ったところ、収率が40%以下と低くなった。一方、ベタイン水溶液では水-水二相系となったが反応収率は大幅に高まった。これは、反応原料の水溶性の向上だけでなく、反応原料や触媒、塩の分配特性も影響していることが示唆された。また、汎用性の界面活性剤との比較では、泡立ちや反応性においてベタイン水溶液に優位性も確認された。



1) R. A. Sheldon, *Green Chem.*, 2005, 7, 267.

ベタインと塩が形成する水性二相系を利用した有機物の抽出

(甲南大¹⁾) ○松本 陸¹・和田 朋晃¹・甲元 一也¹

Extraction of organic compounds using aqueous two-phase system formed by betaines and salts
(Konan University) ○Riku Matsumoto, Tomoaki Wada, Kazuya Koumoto

Aqueous two-phase systems (ATPS), which are formed by mixing additives such as polymers with salts, have been investigated for the separation of proteins, nucleic acids, and low-molecular-weight compounds as an environmental-friendly liquid-liquid extraction medium.¹ There involve problems on increase in viscosity of additive phase,² however, it is desired to develop new additives to facilitate extraction. In this study, we evaluated the applicability of betaine derivatives as additives for ATPS.

We found that betaine **4** and **5** showed great phase separation ability when mixed with salts whose anions have high cosmotropic properties. Furthermore, we compared the extraction ability of the ATPS to various low-molecular-weight compounds varied the water-solubility, proteins and DNAs. It was revealed that betaine **5**, being different from PEG and other additives, can extract various low- and high-molecular-weight compounds efficiently without any precipitation.

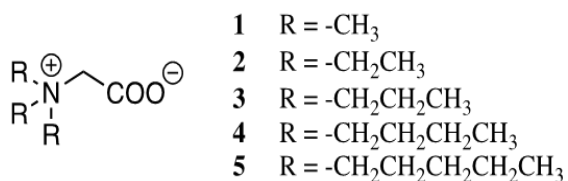
Keywords : Green Chemistry, Aqueous Two-Phase System, Betaine, Salts, Extraction

ポリマーなどの添加剤と塩との混合によって形成される水性二相系(ATPS)は、環境負荷の少ない液-液抽出媒体としてタンパク質や核酸、低分子化合物の分離への応用が検討されている¹⁾。しかし、添加剤による粘度上昇などの課題もあり²⁾、これを改善する新たな添加剤の開発が望まれている。我々は図1に示すベタイン誘導体に特異な塩排他特性があることを見出しており、本研究ではこのベタイン誘導体の ATPS 添加剤への適用性を評価、検討した。

その結果、ベタイン **4**、**5** とアニオンのコスモトロピー性が高い塩との混合で高い相分離能が発現することが明らかとなった。さらに、ベタイン **5** と硫酸ナトリウムが形成する ATPS を使って水溶性に差があ

る低分子化合物やタンパク質、DNA の分配挙動を比較したところ、ベタイン **5** は PEG や他の添加剤と異なって沈殿を生じることなく種々の低分子、高分子を

高効率で抽出できることが明らかとなった。図1 ベタイン誘導体の化学構造



1) M. Iqbal, Y. Tao, S. Xie, Y. Zhu, D. Chen, X. Wang, L. Huang, D. Peng, A. Sattar, M. A. B. Shabbir, H. I. Hussain, S. Ahmed, and Z. Yuan, *Biol. Proced. Online*. **2016**, 18, 18.

2) S. Saita, Y. Mieno, Y. Kohno, and H. Ohno, *Chem. Commun.* **2014**, 50, 15450.