

Wed. Mar 23, 2022

F203

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

[F203-1pm] 04. Physical Chemistry -Properties-

Chair: Kazuyuki Takahashi, Michio-M. Matsushita

1:20 PM - 3:40 PM F203 (Online Meeting)

[F203-1pm-01] Dope – Non-dope transitions of new organic conductors, β'' -(BEDT-TTF)₂XC₂H₄SO₃ (X = Cl, Br)○Hiroki Akutsu¹, Yasuhiro Nakazawa¹ (1. Osaka University)

1:20 PM - 1:40 PM

[F203-1pm-02] Novel planar nickel dithiolene complexes with electron-donating substituents: structure, optical and FET properties○Masatoshi Ito¹, Tomoko Fujino¹, So Yokomori¹, Lei Zhang¹, Toshiki Higashino², Rie Makiura³, Kanokwan Takeno³, Hatsumi Mori¹ (1. ISSP, the Univ. of Tokyo, 2. AIST, 3. Grad. Sch. Engineer., OPU)

1:40 PM - 2:00 PM

[F203-1pm-03] Ferroelectric Organic Semiconductor: Structural and Physical Properties of Alkylamide Substituted BTBT Derivatives○Kohei Sambe¹, Takashi Takeda^{1,2}, Norihisa Hoshino^{1,2}, Wakana Matsuda³, Kanae Tsujita¹, Shingo Maruyama¹, Shunsuke Yamamoto¹, Shu Seki³, Yuji Matsumoto¹, Tomoyuki Akutagawa^{1,2} (1. Graduate School of Engineering, Tohoku University, 2. IMRAM, Tohoku University, 3. Graduate School of Engineering, Kyoto University)

2:00 PM - 2:20 PM

[F203-1pm-04] Magneto-Elastic Behavior of Two-Dimensional Organic-Inorganic Hybrid Perovskites with Ferroelasticity○Naoto Tsuchiya¹, Tatsuya Ishinuki¹, Saya Aoki¹, Yuki Nakayama¹, Glouven Cosquer^{1,2,3}, Sadafumi Nishihara^{1,2,3,4}, Katsuya Inoue^{1,2,3} (1. Graduate School of Advanced Science and Engineering, Hiroshima Univ., 2. Chirality Research Center (CResCent), Hiroshima Univ., 3. Institute for Advanced Materials Research, Hiroshima Univ., 4. PRESTO, JST)

2:20 PM - 2:40 PM

[F203-1pm-05] Photomagnetic effects in low-dimensional copper octacyanidometallate assemblies○Olaf Stefanczyk¹, TingYun Pai¹, Kunal Kumar¹, Corine Mathoniere², Barbara Sieklucka³, Shin-ichi Ohkoshi¹ (1. The Univ. of Tokyo, Sch. of Sci., Dept. of Chem., 2. Univ. Bordeaux, CNRS - CRPP, France, 3. Jagiellonian Univ., Fac. of Chem., Poland)

2:40 PM - 3:00 PM

[F203-1pm-06] Two Dimensional Crystals of Ferromagnetic [MnCr(oxalate)₃] Layer Alternately Stacked with Supramolecular Cations of (2-(x-phenyl)ethan-1-aminium)⁺[18]crown-6 (x = H, *o*-fluoro, *m*-fluoro, and *p*-fluoro)○Jiabing Wu¹, Ruikang Huang^{1,2}, Kiyonori Takahashi^{1,2}, Kenta Kokado^{1,2}, Takayoshi Nakamura^{1,2} (1. Grad. School of Environ. Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ.)

3:00 PM - 3:20 PM

[F203-1pm-07] Contribution of intermolecular interactions to spin crossover transition behaviors of isostructural Fe(III) complexes by means of computational analysis of intermolecular interaction energies○Kazuyuki Takahashi¹, Ryosuke Azuma¹, Takahiro Sakurai², Hitoshi Ohta³ (1. Graduate School of Science, Kobe University, 2. Research Facility Center for Science and Technology, Kobe University, 3. Molecular Photoscience Research Center, Kobe University)

3:20 PM - 3:40 PM

F102

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

[F102-1pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Tatsuya Tukuda, Mizuho Fushitani

1:00 PM - 3:40 PM F102 (Online Meeting)

[F102-1pm-01] Suggestion of the reaction mechanism of HFO-1123 disproportionation reaction based on the reaction products analysis and the model simulation○Sae Fujita¹, Hikaru Murakami², Hirotaka

Kitagawa², Takahiko Hashimoto², Yukio Nakano¹ (1. Tokyo Gakugei University, 2. Panasonic Corporation)

1:00 PM - 1:20 PM

- [F102-1pm-02] Development of HFO-1123 disproportionation reaction inhibitor
 ○Hikaru Murakami¹, Takahiko Hashimoto¹, Hirotaka Kitagawa¹, Sae Fujita², Yukio Nakano² (1. Panasonic Corporation, 2. Tokyo Gakugei University)

1:20 PM - 1:40 PM

- [F102-1pm-03] Electron-ion coincidence laser tunneling ionization imaging of O₂ with auxiliary dissociation pulses
 ○Daimu Ikeya¹, Hikaru Fujise¹, Akitaka Matsuda¹, Mizuho Fushitani¹, Akiyoshi Hishikawa^{1,2} (1. Dept. of Chemistry, Nagoya University, 2. RCMS, Nagoya University)

1:40 PM - 2:00 PM

- [F102-1pm-04] Attosecond optical and Ramsey-type interferometry using high-order harmonics
 ○Takuya Matsubara^{1,2}, Yasuo Nabekawa¹, Kenichi L. Ishikawa³, Kaoru Yamanouchi², Katsumi Midorikawa¹ (1. RAP, RIKEN, 2. Sch. Sci., The Univ. of Tokyo, 3. Grad. Sch. Eng., The Univ. of Tokyo)

2:00 PM - 2:20 PM

- [F102-1pm-05] Electron-Impact Promoted Selective [2 + 2] Cycloaddition Mediated by Carbon Nanotube
 ○Dongxin Liu¹, Satori Kowashi¹, Takayuki Nakamuro¹, Dominik Lungerich¹, Kaoru Yamanouchi¹, Koji Harano¹, Eiichi Nakamura¹ (1. The University of Tokyo)

2:20 PM - 2:40 PM

- [F102-1pm-06] Ultrafast spectral diffusion dynamics of molecular excitons in ultrathin organic films
 ○Tatsuya Yoshida¹, Kazuya Watanabe¹ (1. Faculty of Science, Kyoto University)

2:40 PM - 3:00 PM

- [F102-1pm-07] Single Pd Atom Doping into Au₂₄ Cluster Stabilized by PVP: Synthesis, Structural Analysis, and Catalysis
 ○Shingo Hasegawa¹, Shinya Masuda¹, Shinjiro Takano¹, Koji Harano¹, Tatsuya Tsukuda^{1,2} (1.

Grad. Sch. Sci., The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)

3:00 PM - 3:20 PM

- [F102-1pm-08] Inter-cluster electron transfer $X^{2-} + X^0 \rightarrow 2X^-$ ($X = \text{PtAu}_{24}(\text{SC}_n\text{H}_{2n+1})_{18}$): effect of alkyl chain length of thiolate ligands on reaction rate
 ○Megumi Suyama¹, Shinjiro Takano¹, Tatsuya Tsukuda^{1,2} (1. Grad. Sch. of Sci., The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)

3:20 PM - 3:40 PM

D201

Academic Program [Oral B] | 06. Analytical Chemistry | Oral B

[D201-1pm] 06. Analytical Chemistry

Chair: Kosei Ueno, Rintaro Shimada

2:20 PM - 3:40 PM D201 (Online Meeting)

- [D201-1pm-01] Control of fluorescence signals by the infrared Purcell effect
 Yuto Kitajima¹, Yuto Shikama¹, Keisuke Imaeda¹, ○Kosei Ueno¹ (1. Hokkaido Univ.)

2:20 PM - 2:40 PM

- [D201-1pm-02] Deconstruction of Obscure Features in SVD Spectral Components for Biological Raman Imaging Applications
 ○Ashok Zachariah Samuel², Shumpei Horii¹, Masahiro Ando², Haruko Takeyama¹ (1. Waseda University, 2. Research Organization for Nano and Life Innoovation, Waseda University.)

2:40 PM - 3:00 PM

- [D201-1pm-03] Composition analysis of multivariate Raman spectral data with independent component analysis
 ○Rintaro Shimada¹ (1. Aoyama Gakuin Univ.)

3:00 PM - 3:20 PM

- [D201-1pm-04] Development of portable gas chromatograph using ball surface acoustic wave sensor for monitoring manned space environment
 ○Takamitsu Iwaya¹, Shingo Akao¹, Kazushi Yamanaka¹, Tatsuhiro Okano¹, Nobuo Takeda¹, Yusuke Tsukahara¹, Toru Oizumi¹, Fukushi Hideyuki¹, Tomoki Tanaka¹, Maki Sugawara¹,

Toshihiro Tsuji¹, Akinobu Takeda¹, Asuka Shima², Satoshi Matsumoto², Haruna Sugahara², Takeshi Hoshino², Tetsuya Sakashita² (1. Ball Wave Inc., 2. JAXA)
3:20 PM - 3:40 PM

B304

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

[B304-1 am] 08. Catalysts and Catalysis

Chair: Takane Imaoka, Jun-Chul Choi

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

[B304-1 am-01] Development of durable high entropy alloy nanoparticle catalysts for CO₂ hydrogenation

○Naoki Hashimoto¹, Kohsuke Mori^{1,2}, Naoto Kamiuchi¹, Hideto Yoshida¹, Hisayoshi Kobayashi³, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. Kyoto Inst. of Tech.)

9:00 AM - 9:20 AM

[B304-1 am-02] Bifunctional heterogeneous silica-supported imidazolium salt and silver catalyst for efficient chemical fixation of carbondioxide

○Sangita Karanjit¹, Emiko Tanaka¹, Masaya kashihara¹, Lok Kumar Shrestha², Atsushi Nakayama¹, Katsuhiko Ariga^{2,3}, Kosuke Namba¹ (1. Tokushima University, 2. National Institute for Materials Science (NIMS), 3. The University of Tokyo)

9:20 AM - 9:40 AM

[B304-1 am-03] The role of potassium additive on the catalytic performance of cobalt for CO₂-FTS

○Shohei Harada¹, Shigeo Satokawa², Masaru Ogura¹ (1. The University of Tokyo, 2. Seikei University)

9:40 AM - 10:00 AM

[B304-1 am-04] CO₂ hydrogenation to methanol using Pt-loaded molybdenum sub-oxide catalyst

○Yasutaka Kuwahara^{1,2,3}, Koji Hamahara¹, Takashi Mihogi¹, Hisayoshi Kobayashi^{1,4}, Hiromi Yamashita^{1,2} (1. Osaka Univ., 2. Kyoto Univ. ESICB, 3. PRESTO, 4. Kyoto Inst. Tech.)

10:00 AM - 10:20 AM

[B304-1 am-05] Experimental investigation of CO₂ catalytic behavior in a supercritical CO₂ state for CO₂ stabilization into geological storage

○Takashi Fujii¹, Kenta Asahina¹, Masateru Nishioka¹ (1. National Institute of Advanced Industrial Science and Technology)

10:20 AM - 10:40 AM

[B304-1 am-06] Selective oxidation of methane over iron oxide subnanocluster supported catalysts using a diiron-introduced polyoxometalate as a precursor

○Keiju Wachi¹, Tomohiro Yabe¹, Takaaki Suzuki¹, Kentaro Yonesato¹, Kosuke Suzuki¹, Kazuya Yamaguchi¹ (1. The University of Tokyo)

10:40 AM - 11:00 AM

[B304-1 am-07] Oxygen Evolution Reaction Driven by Charge-Transfer from Cr-complex to Co-Containing Polyoxometalate in a Porous Ionic Crystal

○Yuto Shimoyama¹, ZHEWEI WENG¹, Naoki Ogiwara¹, Sayaka Uchida¹ (1. The University of Tokyo)

11:00 AM - 11:20 AM

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

[B304-1 pm] 08. Catalysts and Catalysis

Chair: Tomohiro Yabe, Satoshi Muratsugu

1:20 PM - 3:40 PM B304 (Online Meeting)

[B304-1 pm-01] Precise Synthesis of Nickel Sub-nano Particles for Greenhouse Gas Conversion

○Tatsuya Moriai¹, Takamasa Tsukamoto^{1,2,3}, Makoto Tanabe², Tetsuya Kambe^{1,2}, Takane Imaoka^{1,2}, Kimihisa Yamamoto^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-ERATO, 3. JST-PRESTO)

1:20 PM - 1:40 PM

[B304-1 pm-02] Preparation and Evaluation of Redox Performance/Catalytic Ammoxidation Performance of Copper and Ruthenium Incorporated Ceria

○Chaoqi Chen¹, Satoru Ikemoto¹, Satoshi Muratsugu¹, Mizuki Tada^{1,2} (1. Dept.Chem., Nagoya Univ., 2. RCMS, Nagoya Univ.)

1:40 PM - 2:00 PM

[B304-1pm-03] Phosphonate-type pseudo-grafted precursor for efficient surface modification of silica

○Yusuke Ishizaka^{1,2}, Kazuhiro Matsumoto², Kazuhiko Sato², Jun-Chul Choi^{1,2} (1.

University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

2:00 PM - 2:20 PM

[B304-1pm-04] Development of a new in-situ UV-vis reflection spectroscopy system for the formic acid dehydrogenation

○Risheng Li^{1,2}, Hajime Kawanami^{1,2}, Tetsuya Kodaira² (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology)

2:20 PM - 2:40 PM

[B304-1pm-05] Frontier Orbital Theory of Molecular Adsorption on TiO₂ Surface

○Takashi Kamachi Kamachi^{1,5}, Nobutsugu Hamamoto¹, Toshinobu Tatsumi¹, Motoshi Takao², Toyao Takashi^{2,5}, Yoyo Hinuma³, Zen Maeno², Satoru Takakusagi², Shinya Furukawa^{2,5}, Ichigaku Takigawa⁴, Ken-ichi Shimizu² (1. Fukuoka Institute of Technology, 2. Hokkaido Univ., 3. National Institute of Advanced Industrial Science and Technology, 4. RIKEN, 5. ESICB)

2:40 PM - 3:00 PM

[B304-1pm-06] Synthesis of Pt/TiO_{2-x} Photocatalyst via Reduction Assisted by Hydrogen Spillover and Formation Mechanism of Surface-exposed Ti³⁺

○Yukari Yamazaki¹, Kohsuke Mori^{1,2}, Yasutaka Kuwahara^{1,2,3}, Hisayoshi Kobayashi⁴, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. JST PRESTO, 4. Kyoto Inst. of Tech.)

3:00 PM - 3:20 PM

[B304-1pm-07] Unraveling Hydrogen Spillover Pathways over Reducible Metal Oxide

○Kohsuke MORI^{1,2}, Kazuki Shun¹, Shinya Masuda¹, Naoki Hashimoto¹, Hisayoshi Kobayashi³, Hiromi Yamashita^{1,2} (1. Osaka University, 2. ESICB Kyoto University, 3. Kyoto Institute of Technology)

3:20 PM - 3:40 PM

J202

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

[J202-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaki Kawano, Tomoji Ozeki

1:00 PM - 3:40 PM J202 (Online Meeting)

[J202-1pm-01] A Pseudorotaxane Structure with γ -Cyclodextrin Controlled by Chiral Recognition of an Au^I₆Ag^I₃Cu^{II}₃ Molecular Cap

○Tatsuhiro Kojima¹, Hiroto Takeda¹, Naoto Kuwamura¹, Takumi Konno¹ (1. Osaka University)

1:00 PM - 1:20 PM

[J202-1pm-02] Slow magnetic relaxations of an S=1/2 copper(II) ion incorporated into the nuclear-spin-free Keggin-type tungstosilicate

○Toshiharu Ishizaki¹, Tomoji Ozeki¹ (1. Nihon University)

1:20 PM - 1:40 PM

[J202-1pm-03] New Ligand for Metal-Organic Frameworks based on Tetrabenzo Chichibabin Hydrocarbons with Potential Close Shell-Diradical Transition

○Zhongyue Zhang¹, Kunio Awaga¹ (1. Nagoya University)

1:40 PM - 2:00 PM

[J202-1pm-04] Study of luminescent Cu(I)-pyridinophane-arylamide complexes and their incorporation into polymer films: towards the development of mechanoresponsive materials

○Tatiana Gridneva¹, Ayumu Karimata¹, Julia Khusnutinova¹ (1. Okinawa Institute of Science and Technology)

2:00 PM - 2:20 PM

[J202-1pm-05] Study of Multi-dimensional Transformations with Successive Reaction in Cu(II) Coordination Polymer

○Yao Jing¹, Yukihiro Yoshida¹, Shintaro Kobayashi², Shogo Kawaguchi², Hiroshi Kitagawa¹ (1. Kyoto Univ., 2. Japan

Synchrotron Radiation Research Institute
(JASRI))

2:20 PM - 2:40 PM

[J202-1pm-06] Energy-efficient olefin separation by coordination networks using tetrahedral ligands.

○JOONSIK KIM¹, Pavel M Usov¹, Yuki Wada¹, Hiroyoshi Ohtsu¹, Takaya Matsumoto^{1,2}, Masaki Kawano¹ (1. Tokyotech, 2. ENEOS Corporation)

2:40 PM - 3:00 PM

[J202-1pm-07] Temperature-dependent Wiggling of a Cu(II) Ion in Hydrogen-bonded Networks of a Zr– Mo Cluster

○Ryoji Mitsuhashi¹, Yuya Imai¹, Sugiarto Sugiarto¹, Yuji Kikukawa¹, Yoshihito Hayashi¹ (1. Kanazawa Univ.)

3:00 PM - 3:20 PM

[J202-1pm-08] Design of Isolated Spaces for Selective CO₂ Adsorption

○Terumasa Shimada¹, Pavel Usov¹, Yuki Wada¹, Hiroyoshi Ohtsu¹, Taku Watanabe², Takaya Matsumoto^{1,2}, Masaki Kawano¹ (1. Tokyo Institute of Technology, 2. ENEOS Corporation)

3:20 PM - 3:40 PM

J403

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

[J403-1pm] 09. Coordination Chemistry,
Organometallic Chemistry

Chair: Masaya Enomoto, Hisashi Shimakoshi

1:00 PM - 3:40 PM J403 (Online Meeting)

[J403-1pm-01] Guest-selective Gate-Opening Behavior of Flexible Porous Coordination Polymer with Hydrogen-bond Keylock

○Ken-ichi Otake¹, Yifan Gu¹, Jia-jia Zheng¹, Susumu Kitagawa¹ (1. Kyoto University)

1:00 PM - 1:20 PM

[J403-1pm-02] Direct EXSY NMR observation of reversible Co-Co bond homolysis

○Satoshi Takebayashi¹, Robert Fayzullin², Richa Bansal¹ (1. Okinawa Institute of Science and Technology Graduate University, 2. Arbuzov Institute of Organic and Physical Chemistry)

1:20 PM - 1:40 PM

[J403-1pm-03] Study on a Spin-Crossover Behavior for a Cobalt(II) Complex with a hydrogen-bonded network

○Takuya Kanetomo¹, Zhen Ni¹, Masaya Enomoto¹ (1. Tokyo University of Science)

1:40 PM - 2:00 PM

[J403-1pm-04] Adaptable water networks for capturing bioactive molecules inside the pores of a coordination network

○Yuki Wada¹, Pavel M Usov¹, Hiroyoshi Ohtsu¹, Masaki Kawano¹ (1. Tokyo Tech)

2:00 PM - 2:20 PM

[J403-1pm-05] Photochemical Hydrogen Evolution from Alkaline Water Catalyzed by Co-NHC Complexes

○Kosei Yamauchi¹, Yasunobu Wakafuji¹, Ken Sakai¹ (1. Kyushu University)

2:20 PM - 2:40 PM

[J403-1pm-06] Photochemical Hydrogen Production based on HCOOH/CO₂ cycle Catalyzed by Pentanuclear Cobalt Complex

○Takuya Akai¹, Yutaka Saga¹, Mio Kondo^{1,2}, Shigeyuki Masaoka¹ (1. Osaka University, 2. JST PRESTO)

2:40 PM - 3:00 PM

[J403-1pm-07] Bulky and non-bulky PNP complexes with earth-abundant metals and their hydrogenation reactivity

○Dilip Kumar Pandey¹, Robert R. Fayzullin², Julia Khusnutdinova¹ (1. Okinawa Institute of Science and Technology, 2. Arbuzov Institute of Organic and Physical Chemistry)

3:00 PM - 3:20 PM

[J403-1pm-08] Synthesis and Characterization of Ligand Modified Vitamin B₁₂ and Evaluation of the Catalytic Activities

○Keita Shichijo¹, Yoshio Hisaeda¹, Hisashi Shimakoshi¹ (1. Kyushu Univ.)

3:20 PM - 3:40 PM

J402

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

[J402-1pm] 09. Coordination Chemistry,
Organometallic Chemistry

Chair: Michito Yoshizawa, Keishiro Tahara
1:00 PM - 3:40 PM J402 (Online Meeting)

[J402-1pm-01] *trans-cis* isomerism of Pt complex with *o*-aminobenzenethiol ligand

○Pingping HUANG¹, Yukihiro YOSHIDA¹,
Hiroshi KITAGAWA¹ (1. Kyoto Univ.)

1:00 PM - 1:20 PM

[J402-1pm-02] Small-Molecule Activation Driven by Metal-Metal Cooperation in Pt/Base Metal Complexes

○GOVINDARAJAN RAMADOSS¹, Shubham Deolka¹, Eugene Khaskin¹, Robert R. Fayzullin², Shrinwantu Pal³, Rumpa Pal¹, Julia R. Khusnutdinova¹ (1. Okinawa Institute of

Science and Technology Graduate University, 2. Abuzov Institute of Organic and Physical Chemistry FRC Kazan Scientific Center of RAS Arbuzov Street, Kazan 420088 (Russian Federation), 3. Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan)

1:20 PM - 1:40 PM

[J402-1pm-03] The intramolecular charge transfer properties of a

benzothienobenzothiophene derivative complexed with a bulky Lewis acid

○TAKASHI IKEDA¹, Keishiro Tahara¹, Toshikazu Ono², Yoshiki Ozawa¹, Masaaki Abe¹ (1. Univ. of Hyogo, 2. Kyushu Univ)

1:40 PM - 2:00 PM

[J402-1pm-04] Heterometallic interaction emerges from resonant inelastic X-ray scattering in luminescent Tb–Pt molecules.

○Takefumi Yoshida¹, Yasuhiro Iwasawa¹, Masahiro Yamashita² (1. The University of Electro-Communications, 2. Tohoku University)

2:00 PM - 2:20 PM

[J402-1pm-05] Two Steps One-dimensional Reaction of Platinum-Rhodium Dinuclear Complexes and Several Metal Species

○Kazuhiro Uemura¹, Yuya Ikeda², Atsushi Takamori³, Tomoyuki Takeyama⁴ (1. Faculty of Engineering, Gifu University, 2. Graduate School of Natural Science and Technology, Gifu

University, 3. Graduate School of Engineering, Gifu University, 4. Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology)

2:20 PM - 2:40 PM

[J402-1pm-06] Synthesis and physical properties of a functionalized

cyclohexanedithiocarboxylate-based MMX-chain complex

○Hayato Moriyama¹, Kazuya Otsubo¹, Kuniyoshi Sugimoto², Hiroshi Kitagawa¹ (1. Kyoto University, 2. JASRI/SPring-8)

2:40 PM - 3:00 PM

[J402-1pm-07] A Polyaromatic Capsule Solid as a Vapor Adsorbent for Benzene Derivatives

○Ryuki Sumida¹, Michito Yoshizawa¹ (1. Lab. for Chem. & Life Sci., Tokyo Inst. of Tech.)

3:00 PM - 3:20 PM

[J402-1pm-08] Vapor-controlled Assembly/Disassembly of an Anionic Pt(II) Complex Loaded on a Cationic Nanosheet

○Masaki Yoshida¹, Tamami Morimoto¹, Atsushi Kobayashi¹, Masako Kato^{1,2} (1. Hokkaido University, 2. Kwansei Gakuin University)

3:20 PM - 3:40 PM

D202

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

[D202-1pm] 10. Organic Chemistry -Organometallic Compounds-

Chair: Naoki Ishida, Kei Muto

1:00 PM - 3:40 PM D202 (Online Meeting)

[D202-1pm-01] Deacylative Coupling Reaction through Claisen-Retro-Claisen Condensation

○Ryota Isshiki¹, Hikaru Nakahara¹, Keiichi Iizumi¹, Masayuki Kubo¹, Kei Muto¹, Junichiro YAMAGUCHI¹ (1. Waseda University)

1:00 PM - 1:20 PM

[D202-1pm-02] Development of a Dehydrogenative Coupling Reaction of Phenols with Aldehydes

○Tairin Kawasaki¹, Tomohiro Tosaki¹, Naoki Ishida¹, Masahiro Murakami¹ (1. Graduate School of Engineering, Kyoto University)

1:20 PM - 1:40 PM

- [D202-1pm-03] Copper(I)- and Palladium(II)-Catalyzed Carboboration of *gem*-Disubstituted Allenes
 ○Yu Ozawa¹, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)
 1:40 PM - 2:00 PM
- [D202-1pm-04] The Iridium (III)-Catalyzed Carbon(sp²)-Hydrogen Bond Amidation of 2-Aroylimidazoles: A Direct Observations of Kinetic and Thermodynamic Mechanistic Tunability
 ○Sanjit Kumar Mahato¹, Naoto Chatani¹ (1. Faculty of Engineering, Osaka University)
 2:00 PM - 2:20 PM
- [D202-1pm-05] Mechanochemical synthesis of aryl manganese(II) reagents by ball milling
 ○Rina Takahashi¹, Koji Kubota^{1,2}, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)
 2:20 PM - 2:40 PM
- [D202-1pm-06] Rhodium-Catalyzed Formal [4+1] Cycloaddition between Benzocyclobutenones and Styrenes as a Carbenoid Equivalent
 ○Shusuke Ochi¹, Zining Zhang¹, Ying Xia¹, Guangbin Dong¹ (1. The University of Chicago)
 2:40 PM - 3:00 PM
- [D202-1pm-07] Rh-Catalyzed Oxidative Carbon-Hydrogen Alkylation of Aniline Derivatives with Allylic Alcohol
 ○Shrikant Manmathappa Khake¹, Naoto Chatani¹ (1. Faculty of Engineering, Osaka University)
 3:00 PM - 3:20 PM
- [D202-1pm-08] Pd-Catalyzed Deoxygenative Coupling of Aromatic Compounds
 ○Miki B Kurosawa¹, Mizuho Watanabe¹, Kenta Kato¹, Kei Muto¹, Junichiro Yamaguchi¹ (1. Waseda University)
 3:20 PM - 3:40 PM

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

[K3-1pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Tomohiko Nishiuchi, Sayaka Hatano
 1:00 PM - 3:40 PM K3 (Online Meeting)

- [K3-1pm-01] Luminescent Chromism with Reversible Coordination Number of Hypervalent Tin(IV) Complexes
 ○Masayuki Gon¹, Kazuo Tanaka¹, Yoshiki Chujo¹ (1. Grad. Sch. of Eng., Kyoto Univ.)
 1:00 PM - 1:20 PM
- [K3-1pm-02] Crystallization-Induced Emission Enhancement of Low Energy Gap Boron Complexes
 ○Masashi Nakamura¹, Masayuki Gon¹, Kazuo Tanaka¹ (1. Graduate School of Engineering, Kyoto University)
 1:20 PM - 1:40 PM
- [K3-1pm-03] The syntheses and properties of diazazethrene bisimide and its dimer
 ○Keita Tajima¹, Norihito Fukui¹, Hiroshi Shinokubo¹ (1. The Univ. of Nagoya)
 1:40 PM - 2:00 PM
- [K3-1pm-04] Synthesis and long-wavelength-absorption of indenoperylene and its π -extended derivatives
 Masaki Kato¹, ○Norihito Fukui^{1,2}, Hiroshi Shinokubo¹ (1. Nagoya Univ., 2. JST PRESTO)
 2:00 PM - 2:20 PM
- [K3-1pm-05] Synthesis, Structure and Properties of π -Expanded Carbohelicenes
 ○Michihisa Toya¹, Hideto Ito¹, Kenichiro Itami^{1,2} (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University)
 2:20 PM - 2:40 PM
- [K3-1pm-06] Perfluorocycloparaphenylenes: Fully fluorinated carbon nanorings by Ni-mediated one-pot synthesis
 ○Hiroki Shudo¹, Motonobu Kuwayama¹, Masafumi Shimasaki², Taishi Nishihara², Youhei Takeda³, Takuya Kuwabara¹, Akiko Yagi¹, Yasutomu Segawa⁴, Kenichiro Itami¹ (1. Nagoya University, 2. Kyoto University, 3. Osaka University, 4. Institute for Molecular Science)
 2:40 PM - 3:00 PM

[K3-1pm-07] Synthesis of phenine nanocarbon molecules via a polygon-assembling strategy
 ○Tatsuru Mio¹, Koki Ikemoto¹, Sota Sato¹, Hiroyuki Isobe¹ (1. Department of Chemistry, the University of Tokyo)
 3:00 PM - 3:20 PM

[K3-1pm-08] Synthesis of aromatic ladder polymer utilizing coordination nanospaces
 ○Takumi Miura¹, Takashi Kitao^{1,2}, Takashi Uemura¹ (1. Grad. Sch. of Eng. The Univ. of Tokyo, 2. JST-PRESTO)
 3:20 PM - 3:40 PM

K1

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

[K1-1pm] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Aiko Fukazawa, Wataru Setaka
 1:20 PM - 3:40 PM K1 (Online Meeting)

[K1-1pm-01] Synthesis of Calix[3]pyrrole and Its Strain-induced Reaction
 ○Yuya Inaba¹, Jenny Pirillo², Yuh Hijikata², Yasuhide Inokuma^{1,2} (1. Grad. Sch. Eng., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ.)
 1:20 PM - 1:40 PM

[K1-1pm-02] Structure and Properties of Silylene-Coordinated Si=B Bonded Species
 ○Taichi Koike¹, Takeaki Iwamoto¹ (1. Tohoku University)
 1:40 PM - 2:00 PM

[K1-1pm-03] Design and synthesis of a phenine nanocage with chirality
 ○Toshiya M. Fukunaga¹, Takahide Kato¹, Koki Ikemoto¹, Hiroyuki Isobe¹ (1. The University of Tokyo)
 2:00 PM - 2:20 PM

[K1-1pm-04] Structural Control of [3]Catenanes Composed of Cyclic Porphyrin Dimers via Complexation with Amine Templates
 ○Yuki Oka¹, Hiroshi Masai¹, Jun Terao¹ (1. Graduate School of Arts and Science, The University of Tokyo)
 2:20 PM - 2:40 PM

[K1-1pm-05] Synthesis and characteristics of well-defined and flexible foldamers

○Takuma Morozumi^{1,2}, Masayuki Takeuchi^{1,2} (1. University of Tsukuba, 2. National Institute for Materials Science (NIMS))
 2:40 PM - 3:00 PM

[K1-1pm-06] Design and synthesis of benzo[*de*]isoquinolino[1,8-*gh*]quinoline diamides π -electron systems
 ○Craig P. Yu¹, Akito Yamamoto², Shohei Kumagai¹, Hiroyuki Ishii³, Jun Takeya^{1,4}, Toshihiro Okamoto^{1,5,6} (1. The University of Tokyo, 2. Daicel Corporation, 3. University of Tsukuba, 4. National Institute for Materials Science (NIMS), 5. PRESTO, JST, 6. CREST, JST)
 3:00 PM - 3:20 PM

[K1-1pm-07] Synthesis of Pyrrole-Based Quinoidal Molecules with Open-Shell Structures
 ○Shinya Sugiura¹, Hiromitsu Maeda¹ (1. Ritsumeikan Univ.)
 3:20 PM - 3:40 PM

H301

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

[H301-1pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Yukatsu Shichibu, Yoko Sakata
 1:00 PM - 3:40 PM H301 (Online Meeting)

[H301-1pm-01] Generation of a Monomerically Dispersed C₆₀ Monolayer Templated by a Two-Dimensional Crystal of Macrocycles
 ○Shin-ichiro Kawano¹, Masato Nakaya², Atsuki Ishiguro¹, Masaaki Saitow³, Takeshi Yanai⁴, Jun Onoe², Kentaro Tanaka¹ (1. Nagoya University, Graduate School of Science, 2. Nagoya University, Graduate School of Engineering, 3. Nagoya University, Research Center for Materials Science, 4. Nagoya University, ITbM)
 1:00 PM - 1:20 PM

[H301-1pm-02] Size-sensitive recognition of nanometer-sized Guests by Rim-Extended Cyclodextrins
 ○Takato Ogata¹, Hiroki Hanayama¹, Koji Harano¹, Eiichi Nakamura¹ (1. Grad. Sch. of Sci., The Univ. of Tokyo)
 1:20 PM - 1:40 PM

- [H301-1pm-03] Optical Properties and Molecular Recognition of a Sumanene-Based Chemosensor
 ○Hiroaki Mizuno¹, Hironobu Nakazawa², Akihisa Miyagawa³, Yumi Yakiyama², Hidehiro Sakurai², Gaku Fukuhara¹ (1. Dept. of Chem., Tokyo Tech, 2. Dept. of Appl. Chem., Osaka Univ., 3. Dept. of Chem., Univ. of Tsukuba)
 1:40 PM - 2:00 PM
- [H301-1pm-04] Guest Encapsulation Behavior of Covered Fluorine-modified Hollow-type Metal Oxide Cluster {Mo₁₃₂}
 ○Chinatsu Murata¹, Yukatsu Shichibu^{1,2}, Katsuaki Konishi^{1,2} (1. Grad. Sch. Env. Sci., Hokkaido Univ., 2. Fac. Env. Earth Sci., Hokkaido Univ.)
 2:00 PM - 2:20 PM
- [H301-1pm-05] Self-assembly process of a supramolecular square built in paddle-wheel-type dinuclear rhodium(II) complex as a corner unit
 ○Atsushi Okazawa¹, Satoshi Takahashi², Shuichi Hiraoka² (1. Nihon Univ. Sch. Med., 2. Dept. of Basic Sci., The Univ. of Tokyo)
 2:20 PM - 2:40 PM
- [H301-1pm-06] Kinetically Controlled Coordination Self-assembly: Approaches to Pathway Selection
 ○Shuichi Hiraoka¹, Naoki Sanada¹, Satoshi Takahashi¹, Tomoki Tateishi¹, Isamu Kikuchi¹ (1. the University of Tokyo)
 2:40 PM - 3:00 PM
- [H301-1pm-07] Recognition of Aromatic Compounds Using Crystal of Tetraphenylethene Derivatives
 ○Takahiro Kakuta¹, Yuki Sugimoto¹, Ryota Nakanishi¹, Shigehisa Akine¹, Tada-aki Yamagishi¹ (1. Kanazawa University)
 3:00 PM - 3:20 PM
- [H301-1pm-08] Size-selective Guest Recognition and the Open/Close Control of Macrocyclic Cobalt(III) Dinuclear Metallohosts Having Bulky Bridging Ligands
 ○Ryo Sudo¹, Yoko Sakata^{1,2}, Shigehisa Akine^{1,2} (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life

Science Institute, Kanazawa University)

3:20 PM - 3:40 PM

H201

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

[H201-1pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Tomoki Yoneda, Yumi Yakiyama

1:20 PM - 3:40 PM H201 (Online Meeting)

- [H201-1pm-01] Synthesis of Monodisperse Polyketones and Chain Length Dependent Crystallinity Changes
 ○Yumehiro Manabe¹, Kilingaru I. Shivakumar², Jenny Pirillo², Yuh Hijikata², Tomoki Yoneda¹, Yuki Ide², Yasuhide Inokuma^{1,2} (1. Grad. Sch. Eng., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ.)
 1:20 PM - 1:40 PM
- [H201-1pm-02] The noncovalent approach in the design of luminescent crystalline rotors
 ○Alexander Mikherdov¹, Mingoo Jin^{1,2}, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)
 1:40 PM - 2:00 PM
- [H201-1pm-03] Construction of hydrogen-bonded organic frameworks with naphthoic acid groups and its structural transition behavior
 ○Yuto Suzuki¹, Ryusei Oketani¹, Ichiro Hisaki¹ (1. Osaka university)
 2:00 PM - 2:20 PM
- [H201-1pm-04] Stumuri-responsive Single Crystals of Pyrene-introduced Indanedione Dimers
 ○Yumi Yakiyama^{1,2}, Ryotaro Seki¹, Hidehiro Sakurai^{1,2} (1. Osaka University, 2. ICS-OTRI, Osaka University)
 2:20 PM - 2:40 PM
- [H201-1pm-05] Development of crystalline molecular gears by utilizing tri-phenyl triazine based rotors
 ○Mingoo Jin^{1,2}, Ryosukei Kitsu¹, Natsumi Hanmyo¹, Motohiro Mizuno³, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido

University, 3. NanoMaterials Research Institute,
Kanazawa University)

2:40 PM - 3:00 PM

[H201-1pm-06] Topology control and properties of the
porous organic salts composed of
modified triphenylmethylenes and
tetrahedral sulfonic acid.

○Hiroi Sei¹, Norimitsu Tohnai¹ (1. Osaka
university)

3:00 PM - 3:20 PM

[H201-1pm-07] Hydrogen-bonded inorganic frameworks:
aromatic molecules parallelly stacked in
the nano-honeycomb pore

○Masayasu Igarashi¹, Takeshi Nozawa¹,
Tomohiro Matsumoto¹, Fujio Yagihashi¹,
Takashi Kikuchi², Kazuhiko Sato¹ (1. National
Institute of Advanced Industrial Science and
Technology (AIST), 2. Rigaku Corporation)

3:20 PM - 3:40 PM

K6

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

[K6-1pm] 13. Organic Chemistry -Reaction
Mechanism, Photochemistry,
Electrochemistry-

Chair: Yasunori Matsui, Hajime Maeda

1:40 PM - 3:40 PM K6 (Online Meeting)

[K6-1pm-01] Titanium-Catalyzed Intermolecular Radical
Addition to Ketones via sp^3 C-H Bond
Activation

○Xue Peng¹, Yuki Hirao¹, Shunsuke Yabu²,
Hirofumi Sato², Masahiro Higashi², Harunobu
Mitsunuma¹, Motomu Kanai¹ (1. The University
of Tokyo, 2. Kyoto University)

1:40 PM - 2:00 PM

[K6-1pm-02] Hydrogenation and Borylation of Alkyl
Chlorides using Zirconocene and
Photoredox Catalysis

○Toshimasa Okita¹, Keisuke Tanaka¹, Kazuhiro
Aida¹, Eisuke Ota¹, Junichiro Yamaguchi¹ (1.
Waseda University)

2:00 PM - 2:20 PM

[K6-1pm-03] Hybridization of triplets and organic radicals
towards photo-driven hyperpolarization

○Koki Nishimura¹, Kenichiro Tateishi³, Tomohiro

Uesaha³, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,2,4}

(1. Grad. Sch. Eng., Kyushu Univ., 2. CMS,
Kyushu Univ., 3. RIKEN Nishina Center for
Accelerator-Based Science, 4. PRESTO, JST)

2:20 PM - 2:40 PM

[K6-1pm-04] Development of oxygen-containing
heterocyclic compounds synthesis using
visible light responsiveness of main group
elements

○Saki Maejima¹, Eiji Yamaguchi¹, Akichika Itoh¹
(1. Gifu Pharmaceutical University)

2:40 PM - 3:00 PM

[K6-1pm-05] Development of Carbazole Dendrimers with
Luminescent Radical Core

○XIAOTIAN XIAOTIAN¹, Wataru Ota², Tohru
Sato^{3,4,5}, Yasuo Nakayama⁶, Minoru Furukori⁷,
Takuya Hosokai⁷, Eri Hisamura⁸, Andrew P
Monkman⁹, Ken Albrecht^{8,10} (1. Grad. Sch. Eng.
Sci., Kyushu Univ., 2. MOLFEX, Inc, 3. Fukui
Institute for Fundamental Chemistry, Kyoto
University, 4. Department of Molecular
Engineering, Graduate School of Engineering,
Kyoto University, 5. Elements Strategy Initiative for
Catalysts & Batteries (ESICB), Kyoto University, 6.
Department of Pure and Applied Chemistry,
Faculty of Science and Technology, Tokyo
University of Science, 7. National Institute of
Advanced Industrial Science and Technology
(AIST), 8. IMCE, Kyushu Univ., 9. Univ. Durham,
10. JST-PRESTO)

3:00 PM - 3:20 PM

[K6-1pm-06] Photon Upconversion in Polymer Media
Utilizing Energy Harvesting and
Intramolecular TTA

○Yasunori Matsui^{1,2}, Takumi Takahashi¹, Masaya
Kano¹, Takuya Ogaki^{1,2}, Eisuke Ohta^{1,2}, Hiroshi
Ikeda^{1,2} (1. Grad. Sch. of Eng., Osaka Pref. Univ.,
2. RIMED, Osaka Pref. Univ.)

3:20 PM - 3:40 PM

K4

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

[K4-1pm] 14. Organic Chemistry -Aromatic,
Heterocyclic, and Heteroatom
Compounds-

Chair: Taiki Morita, Takeshi Nanjo
1:00 PM - 3:40 PM K4 (Online Meeting)

[K4-1pm-01] Synthesis of Isoxazoloazaborines via Gold(I)-Catalyzed Propargyl Aza-Claisen Rearrangement/Borylative Cyclization Cascade and Methylene Insertion of Zinc Carbenoid into N-O Bond of Isoxazoles
○Masato Tsuda¹, Taiki Morita^{1,2}, Hiroyuki Nakamura^{1,2} (1. School of Life Science and Technology, Tokyo Institute of Technology, 2. Laboratory for Chemistry and Life Science, Tokyo Institute of Technology)

1:00 PM - 1:20 PM

[K4-1pm-03] Photouncaging-induced amide formation by red light irradiation to indolizines
○Kenji Watanabe¹, Asuka Kuratsu¹, Takashi Niwa^{1,2}, Takamitsu Hosoya^{1,2} (1. RIKEN BDR, 2. TMDU IBB)

1:40 PM - 2:00 PM

[K4-1pm-04] Deaminative borylation of aromatic amines based on photoinduced electron transfer
○Akira Shiozuka², Kohei Sekine^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

2:00 PM - 2:20 PM

[K4-1pm-05] Development of Organophotocatalyst Enabling Substrate Recognition by Pyridine Moiety for C-C Bond Forming Reaction
○Natsuki Kato¹, Takeshi Nanjo¹, Yoshiji Takemoto¹ (1. Grad. Sch. Pharm. Sci., Kyoto Univ.)

2:20 PM - 2:40 PM

[K4-1pm-06] Dearomative Dicarboxylation of Heteroaromatic Compounds Using CO₂ Radical Anion
○Tsuyoshi Mita^{1,2}, Yong You^{1,2}, Wataru Kanna³, Hideaki Takano^{1,2}, Hiroki Hayashi^{1,2}, Satoshi Maeda^{1,2,3} (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

2:40 PM - 3:00 PM

[K4-1pm-07] Synthesis of polysubstituted imidazoles using α , γ -diazido- α , β -unsaturated esters
○Keita Matsushima¹, Shota Tanaka¹, Taisei Koide¹, Ikuro Sasaki¹, Hideyuki Sugimura¹ (1.

Aoyama Gakuin University)

3:00 PM - 3:20 PM

[K4-1pm-08] Synthesis of iptycenes Using Ambident Anthracene

○Mizuki Hyodo¹, Takayuki Iwata², Mitsuru Shindo²

(1. Interdis. Grad. Sch. Eng. Sci., Kyushu Univ., 2.

IMCE, Kyushu Univ.)

3:20 PM - 3:40 PM

K307

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

[K307-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Hiromichi Egami, Ryo Yazaki

1:00 PM - 3:40 PM K307 (Online Meeting)

[K307-1pm-01] Direct Catalytic Enantioselective Hydrophosphonylation of N-Unprotected Ketimines

○Yuta Kondo¹, Koki Yamada¹, Tetsuya Kadota¹, Hiroyuki Morimoto¹, Takashi Ohshima¹ (1.

Graduate School of Pharmaceutical Sciences, Kyushu University)

1:00 PM - 1:20 PM

[K307-1pm-02] Asymmetric fluorination of allylic amides using diatonic phase-transfer catalyst and its mechanistic insight

○Hiromichi Egami¹, Tomoki Niwa¹, Kousuke Nishibashi¹, Hitomi Sato¹, Kiyoshi Ujiie¹, Kenji Yamashita¹, Yoshitaka Hamashima¹ (1. Univ. of Shizuoka)

1:20 PM - 1:40 PM

[K307-1pm-03] Enantioselective Radical Cation [2+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Mechanistic Insight into the Effect of Photoirradiation

○Kei Katagiri¹, Shuhei Ohmura¹, Takahiro Horibe¹, Kazuaki Ishihara¹ (1. Nagoya University)

1:40 PM - 2:00 PM

[K307-1pm-04] Enantioselective Oxidative Dearomatization of Arenols Using High-performance Hypohalite Catalysis

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

2:00 PM - 2:20 PM

[K307-1pm-05] Ammonium Hypoiodite-catalyzed

Oxidative Umpolung of Indoles for Dearomatization

○Hiroki Tanaka¹, Muhammet Uyanik¹, Kazuaki Ishihara¹ (1. Nagoya University)

2:20 PM - 2:40 PM

[K307-1pm-06] Convuluted Polymer-Supported-Cobalt-

Catalyzed Regioselective

Cyclotrimerization of Aryl Alkynes

○Abhijit Sen¹, Takuma Sato¹, Aya Ohno¹, Heeyoel Baek¹, Yoichi M. A. Yamada¹ (1. Green Nano Catalysis Research Team)

2:40 PM - 3:00 PM

[K307-1pm-07] Homologation of Aryl aldehydes Using

Nitromethane as a C1 Source with

Nitrogen-doped Carbon Supported

Palladium Catalysts

○Tomohiro Yasukawa¹, Yasuhiro Yamashita¹, Shu Kobayashi¹ (1. The University of Tokyo)

3:00 PM - 3:20 PM

[K307-1pm-08] Development of Chiral Lewis Acid

Complexes with High Hydrophobicity as Self-healing Catalysts for Reactions in Water

○Fangqiu Lu¹, Taku Kitanosono¹, Yasuhiro Yamashita¹, Shū Kobayashi¹ (1. The Univ. of Tokyo)

3:20 PM - 3:40 PM

K5

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

[K5-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Eiko Yasui, Hiroyuki Miyamura

1:20 PM - 3:40 PM K5 (Online Meeting)

[K5-1pm-01] Nitrogen-Doped Carbon-Incarcerated Zinc

Catalysts as Less Sacrificial Electrodes for Electrochemical Allylation Reactions

○Ryusuke Masuda¹, Tomohiro Yasukawa¹, Yasuhiro Yamashita¹, Shu Kobayashi¹ (1. The University of Tokyo)

1:20 PM - 1:40 PM

[K5-1pm-02] Development of reductive cleavage of aryl

ethers using cooperative catalytic systems of heterogeneous metal nanoparticles and Lewis acids

○Hiroyuki Miyamura¹, Shu Kobayashi¹ (1. The Univ. of Tokyo)

1:40 PM - 2:00 PM

[K5-1pm-03] Development of Solid Base Catalysts for

Hydroxypyrazine Synthesis in Water

○Tomoya Hisada¹, Taku Kitanosono¹, Yasuhiro Yamashita¹, Shū Kobayashi¹ (1. University of Tokyo)

2:00 PM - 2:20 PM

[K5-1pm-04] Highly Selective Synthesis of α -Aminoamide

Utilizing an Umpolung Reaction and

Characteristics of α -Hydrazonoester○Isao Mizota¹ (1. Mie University)

2:20 PM - 2:40 PM

[K5-1pm-05] Synthestic study of arenicolides

-construction of complete carbon framework-

○Reo Hirao¹, Yoshinori Kawano¹, Eiko Yasui¹, Shinji Nagumo¹ (1. Kogakuin University)

2:40 PM - 3:00 PM

[K5-1pm-06] Chemo-, Regio- and Diastereoselective Ring-

Opening of Epoxy by Utilizing Sulfenate

Anions: An Efficient Access to β -Hydroxy Sulfoxides○Jian Zhang¹, Vipul Vithal Betkekar¹, Keisuke Suzuki², Ken Ohmori¹ (1. Department of Chemistry, School of Science, Tokyo Institute of Technology., 2. Institute of Innovative Research, Tokyo Institute of Technology.)

3:00 PM - 3:20 PM

[K5-1pm-07] Reductive Dimerization of Styrenes Enabled

by Flow Microreactors

○Jiang Yiyuan¹, Yorimitsu Hideki¹ (1. Graduate School of Science, Kyoto University)

3:20 PM - 3:40 PM

B104

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

[B104-1pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Yousuke Takaoka, Yuichiro Hori

1:00 PM - 3:40 PM B104 (Online Meeting)

[B104-1pm-01] A therapeutic approach for cancers with special genetic mutations using in vivo synthetic chemistry

○Tsung-Che Chang¹, Igor Nasibullin¹, Katsunori Tanaka^{1,2,3} (1. RIKEN, 2. Tokyo Institute of Technology, 3. Kazan Federal University)

1:00 PM - 1:20 PM

[B104-1pm-02] Fungal toxin fusicochin enhances plant growth by promoting stomatal opening

○Hironaru Kiriya¹, Satoru Kinoshita², Yuki Hayashi², Toshinori Kinoshita², Shigemitsu Kasuga¹, Hiroki Irieda¹, Junko Ohkanda¹ (1. Shinshu Univ., 2. Nagoya Univ.)

1:20 PM - 1:40 PM

[B104-1pm-03] Analyses and regulation of protein-protein interactions caused by jasmonate-related transcription factors

○Yousuke Takaoka¹, Suzuki Kaho¹, Ueda Minoru^{1,2} (1. Tohoku Univ, Grad. Sci., 2. Tohoku Univ, Grad. Life Sci.)

1:40 PM - 2:00 PM

[B104-1pm-04] Development of a Fulgimide-Fluorophore Dyad Molecule for Fluorescence Photoswitching in Cellular Imaging

○Kenji Torii¹, Yuichiro Hori^{1,2}, Kazuya Kikuchi^{1,2} (1. Graduate School of Engineering, Osaka University, 2. Immunology Frontier Research Center, Osaka University)

2:00 PM - 2:20 PM

[B104-1pm-05] Display-based discovery of N-methylated cyclic peptide inhibitors of prokaryotic iPGMs

○Renier Herman Pieter van Neer¹, Patricia Dranchak², Mahesh Aitha², Laurence Lamy², Hiroyuki Kimura¹, Scott Lovell³, Takayuki Katoh¹, James Inglese², Hiroaki Suga¹ (1. Graduate school of Science, Department of Chemistry, University of Tokyo, 2. National Center for Advancing Translational Sciences, National Institutes of Health, 3. Protein Structure Laboratory, Structural Biology Center, University of Kansas)

2:20 PM - 2:40 PM

[B104-1pm-06] Development of activatable fluorescence probe for carboxypeptidase activity to

visualize cancer

○Minoru Kawatani¹, Mako Kamiya¹, Hirohisa Iwaki¹, Kyoko Yamamoto¹, Yasuteru Urano^{1,2} (1. Grad. Sch. Med., The Univ. of Tokyo, 2. Grad. Sch. Pharm. Sci., The Univ. of Tokyo)

2:40 PM - 3:00 PM

[B104-1pm-07] Site-selective Cleavage of Protein by Cysteine Formylation

○Naoki Zenmyo¹, Akihiro Yasuda¹, Yuya Matsumoto², Shohei Uchinomiya¹, Naoya Shindo¹, Kaori Tabata¹, Akio Ojida¹ (1. Grad. Sch. Phar. Sci., The Univ. of Kyushu, 2. The Univ. of Kyushu, Phar. Sci.)

3:00 PM - 3:20 PM

[B104-1pm-08] Exploration of Biomolecularly Transparent IR Region for Structural Identification Using VCD

○Zarif Zubir¹, Nurul Fajry Maulida, Tohru Taniguchi², Kenji Monde² (1. Hokkaido U., Graduate School of Life Science, 2. Hokkaido U., Faculty of Advanced Life Science)

3:20 PM - 3:40 PM

G201

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

[G201-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Tomonori Tamura, Kazutoshi Iijima

9:00 AM - 11:40 AM G201 (Online Meeting)

[G201-1am-01] A novel antidotal system for a fire gas poisoning using artificial hemoglobin model complexes

Qiyue Mao¹, Xuansu Zhao², Yasutaka Fukuda³, Akiko Kiriya⁴, Shigeru Negi⁴, Hideki Yoshioka², ○Hiroaki Kitagishi¹ (1. Doshisha University, 2. Building Research Institute, 3. Better Living, 4. Doshisha Women's College of Liberal Arts)

9:00 AM - 9:20 AM

[G201-1am-02] Development of photo-responsive cell scaffold for control of cellular function

○Hiroki Miyajima¹, Saeka Kato¹, Kazutoshi Iijima¹ (1. Yokohama National Univ.)

9:20 AM - 9:40 AM

[G201-1am-03] Controlling IEDDA Reaction with

Macrocyclic Tetrazines

○Ira Novianti¹, Toshiyuki Kowada¹, Shin Mizukami¹ (1. Tohoku University)

9:40 AM - 10:00 AM

[G201-1am-04] Development of Functional Anthracene-Based Multiblock Fluorophore for

Visualization of Biological Environment

○Junya Adachi¹, Kohei Sato¹, Kazushi Kinbara¹ (1. Tokyo Tech.)

10:00 AM - 10:20 AM

[G201-1am-05] Evaluation of the properties of a cyclic pyrrole–imidazole polyamide, which specifically binds to CAG/CTG repeat DNA

○Yuki Hirose¹, Tomo Ohno¹, Sefan Asamitsu², Kaori Hashiya¹, Toshikazu Bando¹, Hiroshi Sugiyama^{1,3} (1. Graduate School of Science, Kyoto University, 2. RIKEN Center for Biosystems Dynamics Research, 3. Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University)

10:20 AM - 10:40 AM

[G201-1am-06] Development of selective Cu⁺-responsive protein labeling reagent towards conditional proteomics

○Rong Cheng¹, Tomonori Tamura¹, Itaru Hamachi^{1,2} (1. Kyoto University, 2. ERATO, JST)

10:40 AM - 11:00 AM

[G201-1am-07] Expanding the detectable pH range of DNA nanostructure-based fluorescent pH sensors

○Khongorzul Gerelbaatar¹, Eiji Nakata¹, Hisaaki Hirose², Shiroh Futaki², Takashi Morii¹ (1. Institute of Advanced Energy Science, Kyoto University, 2. Institute of Chemical Research, Kyoto University)

11:00 AM - 11:20 AM

[G201-1am-08] Selection of macrocyclic peptides against SARS-CoV2 spike protein from Tyr, Trp, Pro-rich macrocyclic peptide library

○Tomoshige Fujino¹, Ryogo Sonoda¹, Taiga Sumi¹, Hiroshi Murakami¹ (1. Nagoya Univ.)

11:20 AM - 11:40 AM

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

[G202-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Takashi Matsuo, Hiroshi Murakami

9:00 AM - 11:40 AM G202 (Online Meeting)

[G202-1am-01] Preparation of super-catalytic antibody against the conserved region of influenza virus hemagglutinin molecule and the biochemical features

○Emi Hifumi¹, Tamami Nonaka¹, Ayuka Tanaka¹, Taizo Uda² (1. Oita university, 2. ISIT)

9:00 AM - 9:20 AM

[G202-1am-02] Improvement of neutralizing activity of monobody against SARS-CoV-2 by affinity maturation

○Taishi Kondo¹, Kazuhiro Matsuoka², Tomoshige Fujino¹, Shun Umemoto¹, Gosuke Hayashi¹, Yasumasa Iwatani^{2,3}, Hiroshi Murakami^{1,4} (1. Graduate School of Engineering, Nagoya University, 2. Department of Infectious Diseases and Immunology, Clinical Research Center, National Hospital Organization Nagoya Medical Center, 3. Division of Basic Medicine, Graduate School of Medicine, Nagoya University, 4. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)

9:20 AM - 9:40 AM

[G202-1am-03] Activity regulation for adenylate kinase through conformational change trapping with antibody proteins

Ibuki Nakamura¹, Hiroshi Amesaka², Kento Yonezawa¹, Hironari Kamikubo¹, Shunichi Tanaka², ○Takashi Matsuo¹ (1. Nara Inst. Sci. Tech., 2. Kyoto Pref. Univ.)

9:40 AM - 10:00 AM

[G202-1am-04] A rapid, convenient, and highly sensitive electrochemical detection of human hemoglobin in serum using a high-affinity bivalent antibody-enzyme complex

○Daimei Miura¹, Hayato Kimura¹, Wakako Tsugawa¹, Koji Sode², Kazunori Ikebukuro¹, Ryutaro Asano¹ (1. Tokyo University of Agriculture and Technology, 2. Joint

Department of Biomedical Engineering, The University of North Carolina at Chapel Hill and North Carolina State University)

10:00 AM - 10:20 AM

- [G202-1am-05] Thiazolidine ring-opening by 2-aminobenzamide-based formaldehyde scavengers for one-pot multiple peptide ligation
 ○Koki Nakatsu¹, Hiroshi Murakami^{1,2}, Gosuke Hayashi¹, Akimitsu Okamoto^{3,4} (1. Department of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ., 3. Graduate School of Engineering, The Univ. of Tokyo, 4. Research Center for Advanced Science and Technology, The Univ. of Tokyo)
 10:20 AM - 10:40 AM
- [G202-1am-06] Ribosomal synthesis of peptide libraries containing cyclic γ -amino acids for drug screening
 ○Takashi Miura¹, Takayuki Katoh¹, Hiroaki Suga¹ (1. The University of Tokyo)
 10:40 AM - 11:00 AM
- [G202-1am-07] A chemi-genetic Ca²⁺ indicator based on a synthetic chelator and a fluorescent protein
 ○Wenchao Zhu¹, Takuya Terai¹, Yusuke Nasu¹, Robert Earl Campbell^{1,2} (1. The University of Tokyo, 2. The University of Albert)
 11:00 AM - 11:20 AM
- [G202-1am-08] Development of Split-Luciferase Probes for Monitoring Endogenous RNAs in Living Cells
 ○Masatoshi Eguchi¹, Hideaki Yoshimura¹, Yoshibumi Ueda¹, Takeaki Ozawa¹ (1. School of Science, The University of Tokyo)
 11:20 AM - 11:40 AM

C202

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

[C202-1pm] 18. Polymer

Chair: Takeharu Haino, Yasuhiro Kohsaka

1:20 PM - 3:40 PM C202 (Online Meeting)

- [C202-1pm-01] Synthesis of novel perfluoropolyethers using hexafluoropropylene oxide
 ○Minoru Koyama¹, Midori Akiyama¹, Kimiaki

Kashiwagi², Kyoko Nozaki¹, Takashi Okazoe^{1,2}
 (1. Graduate School of Engineering, The University of Tokyo, 2. AGC Inc.)

1:20 PM - 1:40 PM

- [C202-1pm-02] Synthesis of unimolecularly-thick polyelectrolyte networks using MOF templates
 ○Ami Saito¹, Yuki Hayashi¹, Marta Ximenes¹, Nobuhiko Hosono¹, Takashi Uemura¹ (1. The University of Tokyo, Graduate School of Engineering)
 1:40 PM - 2:00 PM
- [C202-1pm-03] Self-Assembling Behavior and Negative Non-Linear Dependence of Hydrogen-Bonded Tris(phenylisoxazolyl)benzene Dimers
 ○Yudai Ono¹, Takehiro Hirao¹, Takeharu Haino¹ (1. Hiroshima University)
 2:00 PM - 2:20 PM
- [C202-1pm-04] Vinyl polymers degradable through main chain scission by retro-aldol reaction over the backbone and pendants
 ○Akane Kazama¹, Patrick Théato³, Yasuhiro Kohsaka^{1,2} (1. Faculty of Textile Science and Technology, Shinshu University, 2. Research Initiative for Supra-Materials (RISM), Shinshu University, 3. Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology)
 2:20 PM - 2:40 PM
- [C202-1pm-05] Synthesis of π -Conjugated Organometallic Polymers Containing Fused Titanacycle and Thiophene Units
 ○Alvin Tanudjaja¹, Ryoyu Hifumi¹, Shinsuke Inagi¹, Ikuyoshi Tomita¹ (1. Tokyo Institute of Technology)
 2:40 PM - 3:00 PM
- [C202-1pm-06] Improvement of Hydrolysis Resistance for PET by Copper Catalyzed Decarboxylation of Terminal Carboxylic Acid
 ○Masato Akahira¹, Hirokazu Komatsu¹, Koji Yamauchi¹ (1. Toray Industries, Inc.)
 3:00 PM - 3:20 PM
- [C202-1pm-07] Synthesis of supramolecular polysulfide polymers using hydrogen bonds and

coordination bonds

○Yuichiro Kobayashi¹, Yuki Yamagishi¹,
Akiyoshi Horiguchi¹, Daiki Kitano¹, Hiroyasu
Yamaguchi^{1,2} (1. Osaka University, 2. ISC-
OTRI)

3:20 PM - 3:40 PM

C203

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

[C203-1pm] 18. Polymer

Chair: Kenichi Kato, Yoshinori Takashima

1:20 PM - 3:40 PM C203 (Online Meeting)

[C203-1pm-01] Carboxyl-substituted Poly(quinoxaline-
2,3-diyl) for Quantification of a Small
Enantiomeric Imbalance of Chiral Amines
by CD Spectroscopy in Water

○Tomonori Yamawaki¹, Takuma Kuroda¹,
Yuuya Nagata¹, Michinori Sugimoto¹ (1.
Kyoto Univ.)

1:20 PM - 1:40 PM

[C203-1pm-02] Construction of Donor-Acceptor Type
Conjugated Polymers Based on
Pillar[5]arene Units

○Keisuke Wada¹, Shunsuke Ohtani¹, Kenichi
Kato¹, Shixin Fa¹, Tomoki Ogoshi^{1,2} (1. Grad.
Sch. of Eng., Kyoto Univ., 2. Kanazawa
University WPI-NanoLSI)

1:40 PM - 2:00 PM

[C203-1pm-03] Synthesis of boratrane-pendant polymers
and their specific properties changes
through side chain reactions

○Akira Takahashi¹, Masahiro Yamanishi¹,
Atsushi Kameyama¹ (1. Kanagawa Univ.)

2:00 PM - 2:20 PM

[C203-1pm-04] Increasing the strength of temperature-
responsive polymer gels

○Kazunari Yoshida¹, Naofumi Fujiwara¹ (1.
Yamagata Univ.)

2:20 PM - 2:40 PM

[C203-1pm-05] Low-voltage-driven hydrogel actuator
using hydrophobic interaction between
poly(ethylene glycol) and iodine

○Hongyao Zhou¹, Teppei Yamada¹ (1. The
Univ. of Tokyo)

2:40 PM - 3:00 PM

[C203-1pm-06] Functional design of polymeric materials
based on movable cross-links and
application for strain-sensor

○Ryohei Ikura¹, Shunsuke Murayama³, Junsu
Park¹, Yuka Ikemoto⁴, Motofumi Osaki^{1,5},
Hiroyasu Yamaguchi^{1,6}, Akira Harada⁷, Go
Matsuba³, Yoshinori Takashima^{1,2,5,6} (1. Grad.
Sch. of Sci., Osaka Univ., 2. Inst. for Advanced
Co-Creation Studies, Osaka Univ., 3. Grad. Sch.
of Org. Mater. Eng., Yamagata Univ., 4. JASRI,
5. PRC, Osaka Univ., 6. OTRI, Osaka Univ., 7.
ISIR, Osaka Univ.)

3:00 PM - 3:20 PM

[C203-1pm-07] Novel Reticular Polymeric
Nanomembranes Formed within
Unconventional Electric Double Layer:
Synthesis and Functions

○Yoshimitsu Itoh^{1,2}, Tengfei FU¹, Pier-Luc
CHAMPAGNE¹, Takuzo AIDA^{1,3} (1. Graduate
School of Engineering, The University of Tokyo,
2. JST PRESTO, 3. RIKEN CEMS)

3:20 PM - 3:40 PM

A202

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

[A202-1pm] 19. Colloid and Interface Chemistry

Chair: Hideyuki Mitomo, Hiroyasu Nishi

1:00 PM - 3:40 PM A202 (Online Meeting)

[A202-1pm-01] Room-Temperature Coalescence of Metal
Nanoparticles by Ligand Exchange with
Tri-*n*-Octylphosphine Oxide and
Subsequent Dipping into an Organic
Solvent Containing a Sintering Agent

○Soichiro Okada¹, Yoshio Nakahara¹, Mitsuru
Watanabe², Toshiyuki Tamai², Yasuyuki
Kobayashi², Setsuko Yajima¹ (1. Faculty of
Systems Engineering, Wakayama University, 2.
Osaka Research Institute of Industrial Science
and Technology)

1:00 PM - 1:20 PM

[A202-1pm-02] Platinum-Group-Metal High-Entropy-Alloy
Nanoparticles

○DONGSHUANG WU¹, Kohei Kusada¹, Hiroshi
Kitagawa¹ (1. Kyoto university)

1:20 PM - 1:40 PM

[A202-1vn] 19. Colloid and Interface Chemistry

Chair: Yuta Uetake, Masashi Mizukami

4:10 PM - 6:50 PM A202 (Online Meeting)

[A202-1pm-03] The effects of Hofmeister series of salts for the aggregation of polyion complex particles composed of polysaccharides

○Makoto Yamazaki¹, Makoto Yabe², Kazutoshi Iijima¹ (1. Yokohama National Univ., 2. Mol Processing)

1:40 PM - 2:00 PM

[A202-1pm-04] Generation of Hydroxyl radical by Ultrasound-Excited Titanium Dioxide Nanoparticles - Gold Nanocluster Loading Effect-

○Hideya Kawasaki¹, Atsuya Ikeda³, Ken Yamamoto² (1. Kansai University, 2. Kansai University, 3. Kansai University)

2:00 PM - 2:20 PM

[A202-1pm-05] Preparation of smart core-shell gel particles having hydrophilic core and temperature-responsive shell

○Akifumi Kawamura^{1,2}, Mitsuhide Sasaoka¹, Takashi Miyata^{1,2} (1. Fac. Chem. Mater. Bioeng., Kansai University, 2. ORDIST, Kansai University)

2:20 PM - 2:40 PM

[A202-1pm-06] Role of Surface Ligand Structure in the Colloidal Stability of TiO₂ Nanoparticles

○Shohei Yamashita¹, Hidehiro Kamiya¹, Yohei Okada² (1. Tokyo University of Agriculture and Technology, 2. Tokyo University of Agriculture and Technology)

2:40 PM - 3:00 PM

[A202-1pm-07] Acid-controlled reactivities of ligand-protected gold nanoclusters

○Wataru Suzuki¹, Ryo Takahata¹, Toshiharu Teranishi¹ (1. Institute for Chemical Research, Kyoto University)

3:00 PM - 3:20 PM

[A202-1pm-08] Type I collagen-stabilized gold nanoparticles produced by pulsed laser ablation in liquids and γ -ray irradiation

○Nazgul Assan¹, Tomoyuki Suezawa, Satoshi Seino¹, Yuta Uetake^{1,2}, Michiya Matsusaki^{1,2}, Hidehiro Sakurai^{1,2} (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

3:20 PM - 3:40 PM

[A202-1vn-01] Solvent effects on pulsed laser ablation in liquids (PLAL) using microchip laser for preparation of gold nanoparticles

○Barana Sandakelum Hettiarachchi¹, Yuta Uetake^{1,2}, Yumi Yakiyama^{1,2}, Hidehiro Sakurai^{1,2} (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

4:10 PM - 4:30 PM

[A202-1vn-02] Site-Selective Introduction of Metal Oxide Co-catalysts through Plasmon-Induced Charge Separation and Galvanic Replacement

○Hiroyasu Nishi¹, Kangseok Kim¹, Tetsu Tatsuma¹ (1. The University of Tokyo)

4:30 PM - 4:50 PM

[A202-1vn-03] Liquid-Crystalline Organic-Inorganic Hybrid Dendron-Modified Fe₃O₄ Nanoparticles: Characterization of the Self-organized Structure

○Takehiro Yachi¹, Masaki Matsubara^{1,2}, Xiangbing Zeng³, Goran Ungar³, Atsushi Muramatsu¹, Kanie Kiyoshi¹ (1. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, 2. National Institute of Technology, Sendai College, 3. The University of Sheffield)

4:50 PM - 5:10 PM

[A202-1vn-04] Construction of Ultra-thin Pt Layers on Ni Substrates for Highly Efficient Oxygen Reduction Reaction Catalysts

○Dilnigeer Dilixiati¹, Yuka Araki¹, Toshihiro Kondo¹ (1. Ochanomizu University)

5:10 PM - 5:30 PM

[A202-1vn-05] Validation of a quantitative analysis for intramolecular vibrations of electrolytes in the heterophase system by the near-infrared spectroscopy

○Jingchao Xu¹, Hideshi MAKI¹, Minoru MIZUHATA^{1,2} (1. Kobe University, 2. Jagiellonian University)

5:30 PM - 5:50 PM

[A202-1vn-06] Synthesis and characterization of porous boron nitride having specific gas adsorption properties

○Takahiro Ohkubo¹, Jun Kimura¹, Kai Egami¹, Masato Yamashita¹, Yasushige Kuroda¹ (1. Okayama Univ.)

5:50 PM - 6:10 PM

[A202-1vn-07] Direct Determination of Structure of Concentrated Polymer Brushes by Surface Forces Measurement

○Yutaka Takahashi¹, Masashi Mizukami¹, Yoshinobu Tsujii², Kazue Kurihara¹ (1. Tohoku University, 2. Kyoto University)

6:10 PM - 6:30 PM

[A202-1vn-08] Development of a long-term stabilization method of chlorosilane in air and its application to superhydrophobic materials with self-healing ability by the reconstruction of surface morphologies

○Satoshi Nakamura¹, Atsushi Hozumi¹ (1. AIST)

6:30 PM - 6:50 PM

C205

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

[C205-1pm] 20. Materials Chemistry -Basic and Application-

Chair: Masahiko Nakamoto, Shun-ichi Tamaru
1:40 PM - 3:40 PM C205 (Online Meeting)

[C205-1pm-01] Polypeptide Responsive Out-of-Equilibrium Volume Change of Hydrogel-Enzyme Hybrid

○Masahiko Nakamoto¹, Shiro Kitano^{1,2}, Michiya Matsusaki¹ (1. Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2. Technical Research Institute, TOPPAN INC.)

1:40 PM - 2:00 PM

[C205-1pm-02] Production of a hybrid hydrogel consisting of synthetic polymers and artificial protein nanocages

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

2:00 PM - 2:20 PM

[C205-1pm-03] Programmed Porous Nanostructures with

Biomolecular Machines and Nanoparticles

○Kiyoshi Morishita¹, P. K. Hashim¹, Haruaki Yanagisawa¹, Masahide Kikkawa¹, Tatsuya Niwa², Hideki Taguchi², Takuzo Aida^{1,3} (1. The University of Tokyo, 2. Tokyo Institute of Technology, 3. RIKEN Center for Emergent Matter Science)

2:20 PM - 2:40 PM

[C205-1pm-05] Screw Dislocation-Induced Mirror Symmetry-Breaking in Bulk Metal-Organic Crystals

○Gangfeng CHEN^{1,2} (1. The University of Tokyo, 2. RIKEN Centre for Emergent Matter Science)

3:00 PM - 3:20 PM

[C205-1pm-06] Formation of novel concave surface structures by patterned photopolymerization induced molecular diffusion

○Sayuri Hashimoto¹, Norihisa Akamatsu¹, Shoichi Kubo¹, Atsushi Shishido¹ (1. Tokyo Institute of Technology)

3:20 PM - 3:40 PM

C204

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

[C204-1pm] 20. Materials Chemistry -Basic and Application-

Chair: Takeshi Maeda, Osamu Tsutsumi
1:40 PM - 3:40 PM C204 (Online Meeting)

[C204-1pm-01] Triboluminescence of luminophores in blended polymers: Simple preparation method for triboluminescent films

○ayumu karimata¹, Robert R Fayzullin², Julia R Khusnutdinova¹ (1. OIST, 2. Arbuzov Institute)

1:40 PM - 2:00 PM

[C204-1pm-02] Synthesis and Near-Infrared Photoluminescence Properties of Novel D- π -A-Type Pyridinium Betaine Dyes Based on Thiophene-Derived π -Skeleton

○Ami Morimoto¹, Mao Saikusa¹, Naoya Suzuki¹, Takeshi Maeda¹, Shigeyuki Yagi¹, Seiji Akiyama² (1. Osaka Prefecture University, 2.

Mitsubishi Chemical Corporation)

2:00 PM - 2:20 PM

[C204-1pm-03] 3-Dimensional Control of Nanostructure of Chiral-Nematic Liquid-Crystals in Monodispersed Polymeric Microparticles

○Tomoki Shigeyama¹, Kyohei Hisano¹, Osamu Tsutsumi¹ (1. Ritsumeikan Univ.)

2:20 PM - 2:40 PM

[C204-1pm-04] Aggregation-induced room-temperature phosphorescence from mesogenic gold(I) complexes

○Andriani Furoida¹, Kyohei Hisano¹, Osamu Tsutsumi¹ (1. Ritsumeikan University)

2:40 PM - 3:00 PM

[C204-1pm-06] High-Speed Bending of Salicylideneaniline Crystals by Photothermal-Induced Natural Vibration

○Shodai Hasebe¹, Yuki Hagiwara¹, Toru Asahi¹, Hideko Koshima¹ (1. Waseda Univ.)

3:20 PM - 3:40 PM

J401

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

[J401-1vn] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Chair: Yoshito Ando, Takeru Ohe

4:10 PM - 6:10 PM J401 (Online Meeting)

[J401-1vn-01] Relationship between coloration of chrome-tanned leathers reacted by glucose oxides and their mechanical strength

○Takeru Ohe¹, Yurika Yoshimura¹ (1. Osaka Research Institute of Industrial Science and Technology)

4:10 PM - 4:30 PM

[J401-1vn-02] Removal, Separation and Recovery of Cs, Co, and Sr from the Mixed Solution Using *Arthrobacter* Cells

○Takehiko Tsuruta¹, Jun Tachibana¹, Kazuya Yokoyama¹, Takahiro Nagane¹, Yuya Koseki¹, Akira Shiga¹ (1. Hachinohe Institute of technology)

4:30 PM - 4:50 PM

[J401-1vn-03] New separation technology of Ni and Co in solution by chelating resin for resource recovery from waste lithium-ion batteries.

○Jiro Kondo^{1,2}, Aono Hiromichi², Tsugita

Yasuhiro¹ (1. EGS.,co.Ltd, 2. The Univ. of Ehime)

4:50 PM - 5:10 PM

[J401-1vn-04] Design of thermoplastic materials using cellulose as a base matrix

○RUOZHU WANG¹, Yoshito Andou¹ (1. Kyushu Institute of Technology)

5:10 PM - 5:30 PM

[J401-1vn-05] Conductive Properties of Oxygen Deficient Titanium Dioxide by In-liquid Plasma Treatment

○Kai Takagi¹, Yuta Fujii², Haruo Kuriyama¹, Takenori Hayakawa¹, Izumi Serizawa¹, Naoya Ishida², Chiaki Terashima², Akira Fujishima² (1. ORC MANUFACTURING CO., LTD, 2. Tokyo University of Science)

5:30 PM - 5:50 PM

[J401-1vn-06] Complete mineralization of fluorinated ionic liquids using low-temperature superheated water

○Hisao Hori¹, Satomi Oishi¹ (1. Kanagawa Univ.)

5:50 PM - 6:10 PM

[F203-1pm] 04. Physical Chemistry -Properties-

Chair: Kazuyuki Takahashi, Michio-M. Matsushita

Wed. Mar 23, 2022 1:20 PM - 3:40 PM F203 (Online Meeting)

[F203-1pm-01] Dope – Non-dope transitions of new organic conductors, β'' -(BEDT-TTF)₂XC₂H₄SO₃ (X = Cl, Br)○Hiroki Akutsu¹, Yasuhiro Nakazawa¹ (1. Osaka University)

1:20 PM - 1:40 PM

[F203-1pm-02] Novel planar nickel dithiolene complexes with electron-donating substituents: structure, optical and FET properties○Masatoshi Ito¹, Tomoko Fujino¹, So Yokomori¹, Lei Zhang¹, Toshiki Higashino², Rie Makiura³, Kanokwan Takeno³, Hatsumi Mori¹ (1. ISSP, the Univ. of Tokyo, 2. AIST, 3. Grad. Sch. Engineer., OPU)

1:40 PM - 2:00 PM

[F203-1pm-03] Ferroelectric Organic Semiconductor: Structural and Physical Properties of Alkylamide Substituted BTBT Derivatives○Kohei Sambe¹, Takashi Takeda^{1,2}, Norihisa Hoshino^{1,2}, Wakana Matsuda³, Kanae Tsujita¹, Shingo Maruyama¹, Shunsuke Yamamoto¹, Shu Seki³, Yuji Matsumoto¹, Tomoyuki Akutagawa^{1,2} (1. Graduate School of Engineering, Tohoku University, 2. IMRAM, Tohoku University, 3. Graduate School of Engineering, Kyoto University)

2:00 PM - 2:20 PM

[F203-1pm-04] Magneto-Elastic Behavior of Two-Dimensional Organic-Inorganic Hybrid Perovskites with Ferroelasticity○Naoto Tsuchiya¹, Tatsuya Ishinuki¹, Saya Aoki¹, Yuki Nakayama¹, Glouven Cosquer^{1,2,3}, Sadafumi Nishihara^{1,2,3,4}, Katsuya Inoue^{1,2,3} (1. Graduate School of Advanced Science and Engineering, Hiroshima Univ., 2. Chirality Research Center (CResCent), Hiroshima Univ., 3. Institute for Advanced Materials Research, Hiroshima Univ., 4. PRESTO, JST)

2:20 PM - 2:40 PM

[F203-1pm-05] Photomagnetic effects in low-dimensional copper octacyanidometallate assemblies○Olaf Stefanczyk¹, TingYun Pai¹, Kunal Kumar¹, Corine Mathoniere², Barbara Sieklucka³, Shin-ichi Ohkoshi¹ (1. The Univ. of Tokyo, Sch. of Sci., Dept. of Chem., 2. Univ. Bordeaux, CNRS - CRPP, France, 3. Jagiellonian Univ., Fac. of Chem., Poland)

2:40 PM - 3:00 PM

[F203-1pm-06] Two Dimensional Crystals of Ferromagnetic [MnCr(oxalate)₃]⁻ Layer Alternately Stacked with Supramolecular Cations of (2-(*x*-phenyl)ethan-1-aminium)⁺[18]crown-6 (*x* = H, *o*-fluoro, *m*-fluoro, and *p*-fluoro)○Jiabing Wu¹, Ruikang Huang^{1,2}, Kiyonori Takahashi^{1,2}, Kenta Kokado^{1,2}, Takayoshi Nakamura^{1,2} (1. Grad. School of Environ. Sci., Hokkaido Univ., 2. RIES, Hokkaido Univ.)

3:00 PM - 3:20 PM

[F203-1pm-07] Contribution of intermolecular interactions to spin crossover transition behaviors of isostructural Fe(III) complexes by means of

computational analysis of intermolecular interaction energies

○Kazuyuki Takahashi¹, Ryosuke Azuma¹, Takahiro Sakurai², Hitoshi ohta³ (1. Graduate School of Science, Kobe University, 2. Research Facility Center for Science and Technology, Kobe University, 3. Molecular Photoscience Research Center, Kobe University)

3:20 PM - 3:40 PM

新規有機伝導体 β'' -(BEDT-TTF) $_2$ XC $_2$ H $_4$ SO $_3$ (X = Cl, Br)における Dope - Non-dope 転移

(阪大院理) ○ 坪 広樹・中澤 康浩

Dope – Non-dope transitions of new organic conductors, β'' -(BEDT-TTF) $_2$ XC $_2$ H $_4$ SO $_3$ (X = Cl, Br) (Graduate School of Science, Osaka University) ○ Hiroki Akutsu, Yasuhiro Nakazawa

The title new organic conductors show novel Doped – Non-doped transitions, which we report here. The Cl salt is a non-doped salt at room temperature. At 210 K a structural phase transition was observed, below which the salt was in the interlayer charge disproportionation state, namely the donor layers were doped by tilts of dipole moments of the anions. The Br salt, which is isostructural to the low temperature phase of the Cl salt and therefore which appears to be doped, becomes non-doped after applying 1 kbar of static pressure.

Keywords : Organic Conductors; BEDT-TTF; Dope; Interlayer Charge Disproportionation; Metal-Insulator Transition

我々是对イオン層の分極による特異な電子構造を持つ有機伝導体を報告して来た。今回は β'' -(ET) $_2$ ClC $_2$ H $_4$ SO $_3$ (**1**) を報告する。抵抗率(図 1)に降温 210 K、昇温 260 K で跳びがある。室温の結晶構造($P2_1/m$)では、ET 1 分子と鏡面に位置した ClC $_2$ H $_4$ SO $_3^-$ の半分が結晶学的に独立で、-SO $_3^-$ 基は回転 disorder している。低温相($P\bar{1}$)では鏡面が無くなってアニオン 1 分子が独立になり、-SO $_3^-$ 基は order していた。アニオンの双極子モーメント μ は 6.9 D であり、元の鏡面からの傾き(θ)は 9°であり伝導面垂直方向に分極成分が現れ、ドナー A 層はマイナス側に B 層はプラス側に囲まれていた。分極を電位(E_e)に直すと 0.45 eV となり、-0.45 V が A 層に、+0.45 V が B 層にかかっていることになり、A 層から B 層に電子が移るはずである。実際、100 K での ET の価数を結合距離から計算すると、A : +0.36、B : +0.64 価であり、予想通り電子移動、層間電荷分離、部分ドーピングが示唆され、温度による非ドーピング – ドーピング転移が起きたと言える。

β'' - β'' -(ET) $_2$ BrC $_2$ H $_4$ SO $_3$ (**2**) は以前報告していて、70 K で金属-絶縁体転移を示す。室温の構造が **1** の低温相と同形で、この塩でも層間電荷分離が期待される。 $\mu = 9.9$ D、 $\theta = 5.5^\circ$ 、 $E_e = 0.35$ eV であった。しかし、150 K での ET の価数は A : +0.492、B : +0.508 価であり、0.008 価のドーピングがあると計算されるが、この経験式の誤差が ± 0.1 よりドーピングは無いと言える。ところが、抵抗率(図 1)を見ると、絶縁化後 4.2 K までに 12 倍しか抵抗が増加せず、ドーピングの存在が示唆された。この塩に 1 kbar の静水圧を印加すると、転移温度が 10 K ほど上昇し、抵抗上昇は 1.1 万倍になり、ドーピングがなくなったと言え、圧力誘起のドーピング – 非ドーピング転移が起こったことが示唆された。圧力によりアニオンの傾きが無くなったためと考えている。当日は磁化率の結果も報告する。

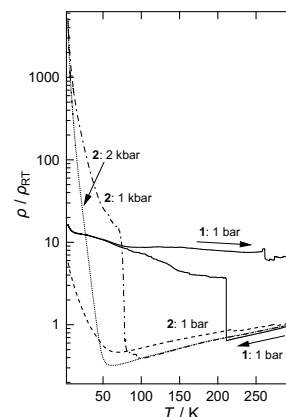


図 1. **1** および **2** の抵抗率

電子供与性置換基を有する平面型新規ニッケルジチオレン錯体： 構造・光学特性・電界効果トランジスタの特性

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Novel Planar Nickel Dithiolene Complexes with Electron-donating Substituents: Structure, Optical and FET Properties (¹ISSP, The Univ. of Tokyo, ²AIST, ³Grad. Sch. Engineer., OPU) ○ Masatoshi Ito,¹ Tomoko Fujino,¹ So Yokomori,¹ Lei Zhang,¹ Toshiki Higashino,² Rie Makiura,³ Kanokwan Takeno,³ Hatsumi Mori¹

Ambipolar semiconductors are next-generation semiconducting materials. However, stringent electronic requirements such as narrow HOMO-LUMO gap and deep LUMO level still limit the number of successful examples. Herein, we designed and synthesized novel three planar nickel bis-dithiolene complexes (**1a**, **1b**, and **1c**) with alkoxy substituents of a different chain length. Interestingly, single crystal structure analyses revealed that **1a** exhibits a one-dimensional stacking structure, while **1b** and **1c** exhibit a two-dimensional, herringbone-like stacking structure, maintaining relatively strong intermolecular orbital interactions by a highly planar d/ π -conjugated framework structure. In this presentation, we will discuss the optical properties and FET characteristics fabricated by solution-coating process.

Keywords : Nickel Complexes; Dithiolene Complexes; Optical Conductivity; Field-effect Transistor; FET

アンバイポーラ半導体は、正孔と電子の双方を伝導する次世代の半導体材料として期待されている。しかし、狭い HOMO-LUMO ギャップや深い LUMO 準位といった電子構造上の厳しい要請により、大気下で安定に駆動する材料は依然限られている。最近、数例のニッケルビスジチオレン錯体がこの要件を満足し、アンバイポーラ特性の大気下における発現が報告されている¹が、そのキャリア移動度はごく低い水準にとどまっている。これは、嵩高い置換基による捻じれた分子構造に起因する、有効なトランスファー積分の欠如によるものと考えられる。本研究では、 π - π 相互作用などによる強い分子間相互作用を確保しうる平面型錯体構造によるキャリア移動度向上を指向し、鎖長の異なるアルコキシ置換基を導入した3種の新規平面型ニッケルビスジチオレン錯体 (**1a**, **1b**, **1c**) を合成した (図 1a)。

単結晶構造解析とこれに基づく理論計算により、置換基鎖長の差による分子積層構造の変化、並びに分子間相互作用との相関を調査した。興味深いことに、**1a** は1次元的積層構造を示した一方、**1b** および **1c** は平面的な d/ π 共役系骨格構造によって比較的強い分子間軌道相互作用を維持しながら、ヘリングボーン状の2次元的積層構造を示した (図 1b)。本発表では、各錯体の光学特性に加え、溶液プロセスを応用して作製した FET の特性評価についても報告する。

1) T. D. Anthopoulos *et al.*, *Adv. Mater.*, **2006**, 18, 1900; T. D. Anthopoulos *et al.*, *Appl. Phys. Lett.*, **2007**, 90, 122105; G. C. Papavassiliou *et al.*, *Crystals*, **2012**, 2, 762.

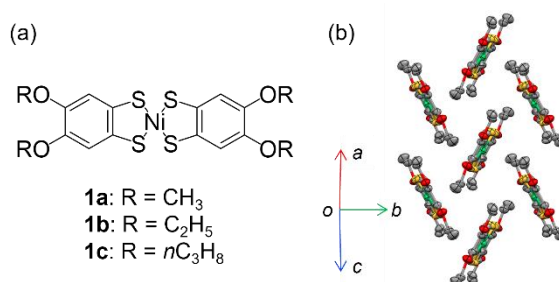


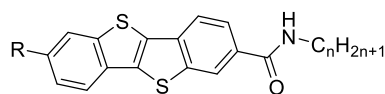
図 1 (a) **1** の分子構造。 (b) **1b** の 2 次元的積層構造。

Ferroelectric Organic Semiconductor: Structural and Physical Properties of Alkylamide Substituted BTBT Derivatives

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Keywords: [1]Benzothieno[3,2-*b*][1]benzothiophene; Alkylamide; Organic semiconductor; Ferroelectricity; Hydrogen-bond

[1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT) derivatives can form the 2D electronic structure and organic field-effect transistors (OFET) with high hole mobility.¹ On the other hand, alkylamide-substituted π -electronic molecules can show ferroelectric behavior accompanying by the dipole inversion at hydrogen



- | | | |
|------------|------------------------------------|--------|
| 1 : | R = C ₈ H ₁₇ | n = 3 |
| 2 : | R = C ₈ H ₁₇ | n = 14 |
| 3 : | R = H | n = 3 |
| 4 : | R = H | n = 14 |

Fig. 1. R-BTBT-CONHC_nH_{2n+1}

bonding (HB) sites of alkylamide units.² Such polarization change has a potential to affect the semiconducting behavior. Herein, we synthesized alkylamide-substituted R-BTBT-CONHC_nH_{2n+1} (**Fig. 1**), which semiconducting behavior, ferroelectricity, and molecular assembly structures were examined. Single-crystal X-ray structural analyses of **1** and **3** revealed the formation of herringbone arrangement of BTBT skeleton and the 1D HB chains of alkylamide groups (**Fig. 2**). The thin-films of **2** were fabricated for channel layer of a top-contact type OFET device and its μ_{FET} and V_{Th} values were observed at 0.021 cm² V⁻¹ s⁻¹ and -9.7 V, respectively (**Fig. 3**). Based on the DSC and XRD measurements, **2** formed the SmE phase above 369 K followed by the melting at 469 K. The ferroelectric hysteresis behavior of **2** was observed in the *P*-*E* curve at the SmE phase with $E_c = 5.65$ V μm^{-1} and $P_r = 2.21$ $\mu\text{C cm}^{-2}$ at 413 K and 0.1 Hz, respectively (**Fig. 4**).

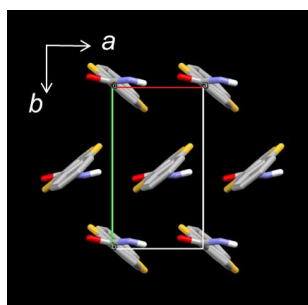


Fig. 2. Crystal structure of **1**.

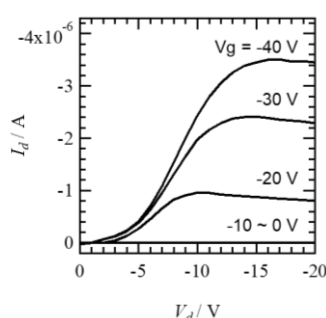


Fig. 3. Output curves of **2**.

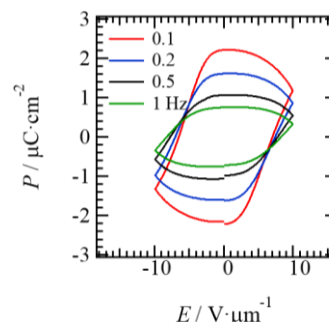


Fig. 4. *P*-*E* curves of **2**.

- 1) K. Takimiya, I. Osaka, T. Mori, M. Nakano, *Acc. Chem. Res.* **2014**, *47*, 1493.
- 2) H. Anetai, T. Takeda, N. Hoshino, H. Kobayashi, N. Saito, M. Shigeno, M. Yamaguchi, T. Akutagawa, *J. Am. Chem. Soc.* **2019**, *141*, 2391.

Magneto-Elastic Behavior of Two-Dimensional Organic-Inorganic Hybrid Perovskites with Ferroelasticity

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Keywords: Multiferroic; Magnetic Properties; Ferroelasticity; Structural Phase Transition

Multiferroic properties show that two or more ferroic orders such as ferromagnetism, ferroelectricity, and ferroelasticity are co-exist.¹ For example, magnetoelectric effect, in which the polarization is induced by applying magnetic field or the magnetization is induced by applying electric field, has been reported in both theoretically and experimentally. On the other hand, the cross-correlation between ferroelasticity and ferromagnetism or ferroelectricity has been rarely studied. In this study, we investigate the cross-correlation between ferroelasticity and ferromagnetism using two-dimensional organic-inorganic hybrid perovskites with a layered structure of organic ammonium cations and metal halide ions.

Previously, we found that the magnetization shift, characterized by a vertical shift in the origin of the hysteresis, was observed when cooled in a magnetic field from above magnetic critical temperature in perovskite-type compound (PEA)₂Fe^{II}Cl₄ (PEA = 2-phenylethylammonium) with ferroelasticity and canted antiferromagnetism (Fig. 1).² We synthesized a series of hybrid perovskites, (PEA)₂M^{II}Cl₄ (*M* = Mn, Ni, Cu) to investigate the effect of magnetization shift due to differences in the transition metals. X-ray crystal structure investigations show that they have a similar structure to that of the iron compound (Fig. 2). In (PEA)₂Cu^{II}Cl₄, ferroelastic domains were observed by polarized microscopy observation. Magnetic properties exhibit ferromagnetic behavior below 9.4 K. In this presentation, we report magnetic and elastic properties of (PEA)₂M^{II}Cl₄, and discuss the magneto-elastic behavior.

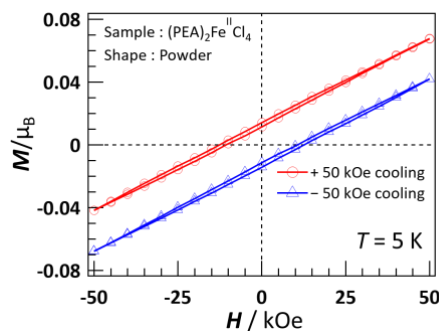


Figure 1. *M* vs *H* plots of (PEA)₂Fe^{II}Cl₄ after field cooling in + 50 kOe (red) and – 50 kOe (blue).

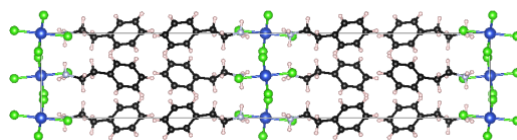


Figure 2. The crystal structure of a series of metal substituted (PEA)₂M^{II}Cl₄ viewed along *b*-axis.

- 1) C. N. R. Rao, K. Rao, *J. Solid State Chemistry: Compounds* (Eds.: P. Day, A.K. Cheetham), Oxford University Press, Oxford **1992**, pp. 281 – 284.
- 2) Y. Nakayama, S. Nishihara, K. Inoue, T. Suzuki, M. Kurmoo, *Angew. Chem., Int. Ed.* **2017**, 56, 9367.

Photomagnetic effects in low-dimensional copper octacyanidometallate assemblies

(¹The Univ. of Tokyo, Sch. of Sci., Dept. of Chem., ²Univ. Bordeaux, CNRS – CRPP, France, ³Jagiellonian Univ., Fac. of Chem., Poland) ○Olaf Stefanczyk,¹ TingYun Pai,¹ Kunal Kumar,¹ Corine Mathoniere,² Barbara Sieklucka,³ Shin-ichi Ohkoshi¹

Keywords: Molecular Magnetism, Photomagnetic Effect, Switchable Materials, Functional Materials, Metal Complexes

Research on new photomagnetic materials – compounds which magnetic properties can be switched by irradiation, are of great interest in the study of magnetochemistry. Two main classes of photomagnetic materials have been broadly studied: electron transfer and spin crossover photomagnets. Much attention was drawn to the $\text{Cu}^{\text{II}}\text{--}[\text{Mo}^{\text{IV}}(\text{CN})_8]$ assemblies due to their ability to reveal the light-induced metal-to-metal charge-transfer (MMCT) effect: $\text{Cu}^{\text{II}}(S=1/2)\text{--}\text{Mo}^{\text{IV-LS}}(S=0)\text{--}\text{Cu}^{\text{II}}(S=1/2) \rightarrow \text{Cu}^{\text{I}}(S=0)\text{--}[\text{Mo}^{\text{V-LS}}\text{--}\text{Cu}^{\text{II}}](S_{\text{total}}=1)$ and/or the light-induced excited spin-state trapping (LIESST) phenomenon in the $\text{Mo}(\text{IV})$ centre: $\text{Cu}^{\text{II}}(S=1/2)\text{--}\text{Mo}^{\text{IV-LS}}(S=0)\text{--}\text{Cu}^{\text{II}}(S=1/2) \rightarrow [\text{Cu}^{\text{II}}\text{--}\text{Mo}^{\text{IV-HS}}\text{--}\text{Cu}^{\text{II}}](S_{\text{total}}=2)$.¹

In this presentation we will summarize research on two new ionic systems:

$\{[\text{Cu}(\text{tren})_2(\mu\text{-tn})]\cdot[\text{Mo}(\text{CN})_8]\cdot 7.5\text{H}_2\text{O}$ (**1**) and $\{[\text{Cu}(\text{tren})_2(\mu\text{-tn})]\cdot[\text{Mo}(\text{CN})_8]\cdot\{[\text{Cu}(\text{tren})_2[\text{Mo}(\text{CN})_8]\}\cdot 9\text{H}_2\text{O}$ (**2**), where tren = (tris(2-aminoethyl)amine and tn = 1,3-diaminopropane, and two trinuclear reference samples:

$[\text{Cu}(\text{tn})_2]_2[\text{Mo}(\text{CN})_8]\cdot 2\text{H}_2\text{O}$ (**3**) and $[\text{Cu}(\text{tren})_2][\text{Mo}(\text{CN})_8]\cdot 5.25\text{H}_2\text{O}$ (**4**).² Optical spectroscopy, supported by quantum chemical calculations, confirmed the presence of the $\text{Mo}(\text{IV})$ to $\text{Cu}(\text{II})$ charge transfer bands for CN-bridged compounds (**2** – **4**). Additionally, detailed descriptions of energy level diagrams of **1** – **4** with the frontier molecular orbitals and possible optical transitions were made. Magnetic studies indicated paramagnetic behaviour with weak antiferromagnetic interactions at low temperature. Finally, photomagnetic studies of **1** – **4** showed the increase of magnetization after irradiation with 473 and 410 nm light at 10 K. Data analysis suggests that the photomagnetic effect in **1** has the LIESST origin, while other cyanido-bridged compounds prefer the MMCT mechanism.

1) O. Stefanczyk, K. Nakabayashi, S. Ohkoshi, *Springer Series in Chemical Physics*, **2021**, 125, 149. 2) T. Pai, O. Stefanczyk, K. Kumar, C. Mathonière, B. Sieklucka, S. Ohkoshi, *Inorg. Chem. Front.*, **2022**, DOI: 10.1039/D1QI01469B

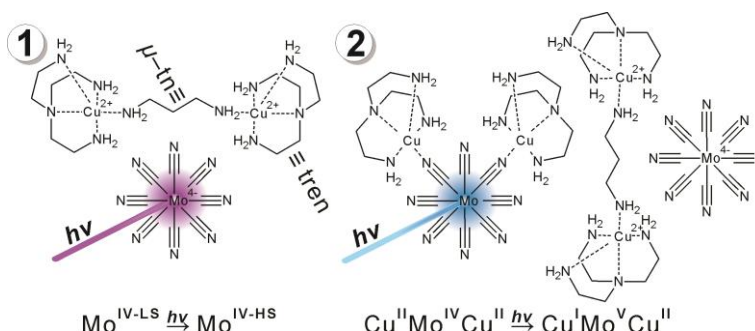


Figure 1. Scheme of structure and photomagnetic effect in **1** and **2**.

Two Dimensional Crystals of Ferromagnetic $[\text{MnCr}(\text{oxalate})_3]^-$ Layer Alternately Stacked with Supramolecular Cations of (2-(*x*-phenyl)ethane-1-aminium) $^+$ [18]crown-6 (*x* = H, *o*-fluoro, *m*-fluoro, and *p*-fluoro)

(¹*Grad. School of Environ. Sci., Hokkaido University*, ²*RIES, Hokkaido University*) ○Jiabing Wu,¹ Ruikang Huang,^{1,2} Kiyonori Takahashi,^{1,2} Kenta Kokado,^{1,2} Takayoshi Nakamura^{1,2}

Keywords: Ferromagnetic; Magnetoelectric materials; 2D crystals; Supramolecule

The magnetoelectric (ME) effect in multiferroics is a prominent cross correlation phenomenon, in which the electric field controls the magnetization, and the magnetic field rules the electric polarization. A strategy for inducing ME effect in hybrid crystals is that enhancing the correlation between two relatively independent units, which rule the electric or magnetic order respectively.^[1]

Here we introduced the supramolecular cations of (2-(*x*-phenyl)ethane-1-aminium) $^+$ [18]crown-6 (*x* = H, *o*-fluoro, *m*-fluoro, and *p*-fluoro) as a possible ferroelectric moiety between ferromagnetic honeycomb layer of $[\text{MnCr}(\text{oxalate})_3]^-$ to obtained four hybrid crystals **1-4**. As shown in Figure 1, crystals exhibited 2D layered structures, where cations of ((2-phenyl)ethane-1-aminium) $^+$ in **1** and (2-(*o*-fluorophenyl)ethane-1-aminium) $^+$ in **2** partly

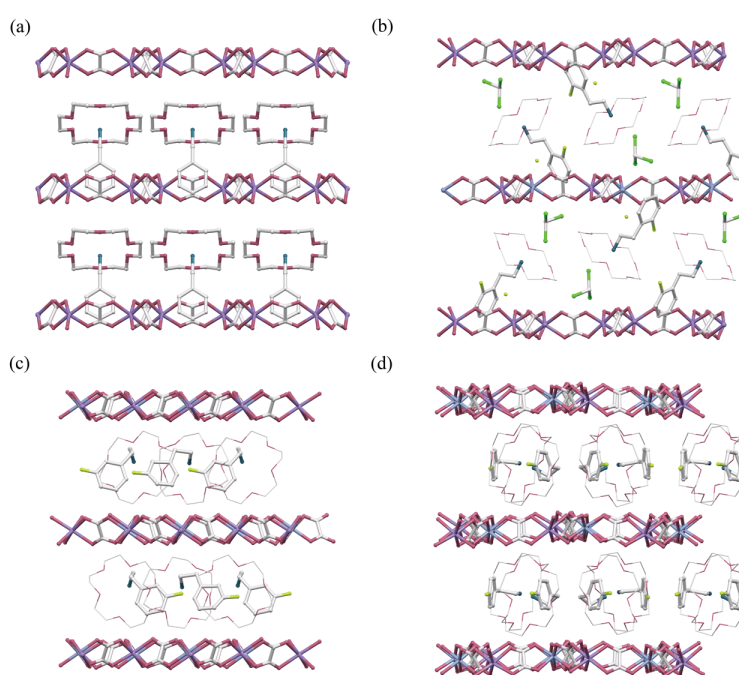


Figure 1. Crystal structures of (a) **1**, (b) **2**, (c) **3**, and (d) **4**

injected into the layer of $[\text{MnCr}(\text{oxalate})_3]^-$. The presence of fluorine substituents on *m*- and *p*-positions hindered cations intersperse $[\text{MnCr}(\text{oxalate})_3]^-$ layer in crystal **3** and **4**, resulting in relatively independent layered structures. The crystal structures, dielectric, and magnetic properties of **1-4** will be discussed in detail.

1) Lee J H, Fang L, Vlahos E, et al. *Nature*, **2010**, 466, 7309.

エネルギー計算に基づく同形鉄(III)錯体のスピントロクロオーバー転移に与える分子間相互作用の効果

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Contribution of intermolecular interactions to spin crossover transition behaviors of isostructural Fe(III) complexes by means of computational analysis of intermolecular interaction energies (¹Graduate School of Science, Kobe University, ²Research Facility Center for Science and Technology, Kobe University, ³Molecular Photoscience Research Center, Kobe University) ○Kazuyuki Takahashi,¹ Ryosuke Azuma,¹ Takahiro Sakurai,² Hitoshi Ohta³

The control of phase transition behaviors is important from a point of view of both fundamentals and applications. We reported that the spin crossover (SCO) transition enthalpies of neutral heteroleptic Fe(III) complexes were affected by not only the nearest-neighbor interactions but also the next-nearest-neighbor interactions. To clarify the effect of electrostatic interaction on the SCO transition behaviors, we investigate the structures and properties of new isostructural Fe(III) SCO complexes with various octahedral anions. Intermolecular interaction energies are computed using the temperature-dependent crystal structures of isostructural Fe(III) SCO complexes. The comparison of the temperature dependence of intermolecular interaction energies between isostructural complexes reveals that electrostatic interaction can give no significant effect on the SCO transition.

Keywords : Spin crossover; Intermolecular interaction; Iron(III) complex; Electrostatic interaction; Isostructural complex

スピントロクロオーバー (SCO) をはじめとした相転移挙動の制御は基礎的な面に限らず、応用の観点からも重要である。我々は中性ヘテロレプティック鉄(III)SCO 錯体の転移エンタルピーが最近接分子間相互作用ばかりでなく直接コンタクトのない次近接分子間相互作用の変化も大きな役割を果たしていることを分子間相互作用のエネルギー計算と熱力学パラメータとの比較から明らかにした¹⁾。今回、アニオンが異なるものの同形構造を取る新規イオン性鉄(III)錯体 $[\text{Fe}(\text{qsal})_2]\text{X}$ ($\text{Hqsal} = N$ -(8-quinoyl)salicylaldimine, $\text{X} = \text{PF}_6, \text{AsF}_6, \text{SbF}_6$)を比較することで、静電相互作用の SCO 転移挙動に与える効果を明らかにすることを目的とした。各鉄(III)錯体はアニオン交換反応を用い拡散法により得た。磁化の温度依存性からいずれの錯体も SCO を示すことがわかった (Fig. 1)。各錯体の結晶構造の温度変化から、各温度での分子間相互作用を様々なエネルギー計算より求めた。分子間相互作用エネルギーの温度変化の錯体間の比較から静電相互作用はスピン転移へ大きな影響を与えないことが明らかとなった。

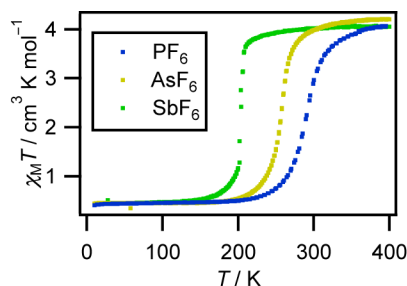


Fig. 1 The $\chi_M T$ vs. T products of the Fe complexes

1) A. Miyawaki, K. Takahashi et al., *Inorg. Chem.* **2020**, 59, 12295.

[F102-1pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Tatsuya Tukuda, Mizuho Fushitani

Wed. Mar 23, 2022 1:00 PM - 3:40 PM F102 (Online Meeting)

- [F102-1pm-01] Suggestion of the reaction mechanism of HFO-1123 disproportionation reaction based on the reaction products analysis and the model simulation**
 ○Sae Fujita¹, Hikaru Murakami², Hirotaka Kitagawa², Takahiko Hashimoto², Yukio Nakano¹ (1. Tokyo Gakugei University, 2. Panasonic Corporation)
 1:00 PM - 1:20 PM
- [F102-1pm-02] Development of HFO-1123 disproportionation reaction inhibitor**
 ○Hikaru Murakami¹, Takahiko Hashimoto¹, Hirotaka Kitagawa¹, Sae Fujita², Yukio Nakano² (1. Panasonic Corporation, 2. Tokyo Gakugei University)
 1:20 PM - 1:40 PM
- [F102-1pm-03] Electron-ion coincidence laser tunneling ionization imaging of O₂ with auxiliary dissociation pulses**
 ○Daimu Ikeya¹, Hikaru Fujise¹, Akitaka Matsuda¹, Mizuho Fushitani¹, Akiyoshi Hishikawa^{1,2} (1. Dept. of Chemistry, Nagoya University, 2. RCMS, Nagoya University)
 1:40 PM - 2:00 PM
- [F102-1pm-04] Attosecond optical and Ramsey-type interferometry using high-order harmonics**
 ○Takuya Matsubara^{1,2}, Yasuo Nabekawa¹, Kenichi L. Ishikawa³, Kaoru Yamanouchi², Katsumi Midorikawa¹ (1. RAP, RIKEN, 2. Sch. Sci., The Univ. of Tokyo, 3. Grad. Sch. Eng., The Univ. of Tokyo)
 2:00 PM - 2:20 PM
- [F102-1pm-05] Electron-Impact Promoted Selective [2 + 2] Cycloaddition Mediated by Carbon Nanotube**
 ○Dongxin Liu¹, Satori Kowashi¹, Takayuki Nakamuro¹, Dominik Langerich¹, Kaoru Yamanouchi¹, Koji Harano¹, Eiichi Nakamura¹ (1. The University of Tokyo)
 2:20 PM - 2:40 PM
- [F102-1pm-06] Ultrafast spectral diffusion dynamics of molecular excitons in ultrathin organic films**
 ○Tatsuya Yoshida¹, Kazuya Watanabe¹ (1. Faculty of Science, Kyoto University)
 2:40 PM - 3:00 PM
- [F102-1pm-07] Single Pd Atom Doping into Au₂₄ Cluster Stabilized by PVP: Synthesis, Structural Analysis, and Catalysis**
 ○Shingo Hasegawa¹, Shinya Masuda¹, Shinjiro Takano¹, Koji Harano¹, Tatsuya Tsukuda^{1,2} (1. Grad. Sch. Sci., The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)
 3:00 PM - 3:20 PM
- [F102-1pm-08] Inter-cluster electron transfer $X^{2-} + X^0 \rightarrow 2X^-$ ($X = \text{PtAu}_{24}(\text{SC}_n\text{H}_{2n+1})_{18}$): effect of alkyl chain length of thiolate ligands on reaction rate**
 ○Megumi Suyama¹, Shinjiro Takano¹, Tatsuya Tsukuda^{1,2} (1. Grad. Sch. of Sci., The Univ. of Tokyo, 2. ESICB, Kyoto Univ.)
 3:20 PM - 3:40 PM

反応生成物の分析とシミュレーションに基づいた HFO-1123 の不均化反応の反応機構の提案

(東京学芸大学¹・パナソニック株式会社²) ○藤田 紗江¹、村上 光²、北川 浩崇²、橋元 任彦²、中野 幸夫¹

Suggestion of the reaction mechanism of HFO-1123 disproportionation reaction based on the reaction products analysis and the model simulation (Tokyo Gakugei University¹, Panasonic Corporation²) ○Sae Fujita¹, Hikaru Murakami², Hirotaka Kitagawa², Takahiko Hashimoto², Yukio Nakano¹

Some laws in Japan will restrict the use of some F-gases (fluorinated greenhouse gases) currently used. HFO-1123 (CF₂CFH) with very low GWP is one of the most promising candidates for alternative of F-gases currently used. However, external factors such as electric discharge for HFO-1123 under conditions of high temperature and pressure are known to be triggered the explosive decomposition with rapid and large increase of temperature and pressure which is commonly called disproportionation. Therefore, to practical use of HFO-1123 as refrigerant, it is necessary to understand the disproportionation reaction and then suppress it. The results of GC/MS measurements of the gaseous components after the disproportionation reaction of HFO-1123 show that some products are formed by F and CF₂. In addition, the results of FTIR measurements show the molar ratios of HFO-1123 and some products formed by F in the gaseous components after the reaction. In this study, by combining these results and the changes in Gibbs free energies of the reactions predicted be occurred, the reaction mechanism of the disproportionation of HFO-1123 was constructed. For compounds of which thermal parameters have not reported, those thermal parameters were calculated using *ab initio* calculations. Then the constructed reaction mechanism was verified by results of chemical kinetics simulation using Chemkin. Due to space limitations, details will be explained in this presentation.

Keywords : Refrigerant, HFO-1123, Disproportionation reaction, Reaction Mechanism, Simulation

空調機器等で使用される冷媒は、法律によって環境への負担が少ないものへと移行されている。HFO-1123 (CF₂CFH) は GWP が非常に低いため、新規冷媒の有力な候補であるが、高温・高圧条件下において放電などの外部因子により、温度・圧力が急激に上昇する不均化反応と呼ばれる爆発的な自己分解反応を起こす。よって冷媒として実用化するには、この反応を理解し、抑制する必要がある。現在、不均化反応後の気体成分の GC/MS による測定の結果から、反応中に F 原子や CF₂ ラジカルにより生成する化合物があることがわかった。また、FTIR による測定結果から反応後の気体成分の HFO-1123 や F 原子によって生成される化合物の物質質量比がわかっている。本研究では、これらの実験結果から考えられる素反応と、その反応の反応前後のギブス自由エネルギーを用いることで、HFO-1123 の不均化反応の反応機構を構築した。この時、エンタルピーなどの文献値がないものは分子軌道計算を用いて計算を行った。その後、構築した反応機構の妥当性を Chemkin で化学反応シミュレーションを行い、検証を行った。紙面の都合上、詳細は本発表で説明する。

HFO-1123 不均化反応抑制剤の開発

(パナソニック株式会社¹・東京学芸大学²) ○村上 光¹・橋元 任彦¹・北川 浩崇¹
藤田 紗江²・中野 幸夫²

Development of HFO-1123 disproportionation reaction inhibitor (¹ Panasonic Corporation, ² Tokyo gakuhei university) ○Hikaru Murakami¹, Takahiko Hashimoto¹, Hirotaka Kitagawa¹, Sae Fujita², Yukio Nakano²

In recent years, various environmental regulations have called for the development of refrigerant with low global warming potential (GWP). HFO-1123 (CF₂CFH) is one of the most promising candidates as a new refrigerant because of its small GWP of 0.3. However, HFO-1123 has not been put into practical use because it causes disproportionation reaction in which the temperature and pressure rise rapidly due to external factors such as electronic discharge under high temperature and pressure conditions, and there is a need for technology to suppress the disproportionation reaction. We succeeded in reproducing the disproportionation reaction experimentally and estimated that the disproportionation reaction proceeds by polymerization reaction and radical chain reaction using product analysis after the disproportionation reaction, spectroscopic analysis during the reaction, and chemical kinetics simulation¹⁾. Based on these reaction mechanisms, iodine compounds such as iododifluoromethane (CF₂HI) and hydrocarbons such as propane (C₃H₈) were selected as reaction inhibitors that can suppress the disproportionation reaction. It was confirmed that the disproportionation reaction could be suppressed by adding them to HFO-1123, and the concentration of the reaction inhibitor required to suppress the reaction was measured in the temperature range of 298K-423 K. In this presentation, we will present the effectiveness and suppression mechanism of reaction inhibition.

Keywords : Refrigerant; HFO-1123; Disproportionation; Radical; Inhibitor

近年、様々な環境規制により地球温暖化係数 (GWP) の低い冷媒の開発が求められている。HFO-1123 (CF₂CFH) は GWP が 0.3 と小さいため、新規冷媒として最も有力な候補の 1 つである。しかし、HFO-1123 は高温・高圧条件下において放電等の外部要因により、温度・圧力が急激に上昇する不均化反応を引き起こすことから実用化されておらず、不均化反応を抑制する技術が求められている。我々はこの不均化反応を実験的に再現することに成功し、不均化反応後の生成物分析、反応中の分光解析、計算シミュレーションを用いて重合反応やラジカル連鎖反応により不均化反応が進行すると推定した¹⁾。これらの反応メカニズムを基に不均化反応を抑制できる反応抑制剤として、ヨードジフルオロメタン (CF₂HI) をはじめとするヨウ素化合物と、プロパン (C₃H₈) をはじめとする炭化水素を選定した。これらを HFO-1123 に添加することで不均化反応が抑制できることを確認し、298K~423 K の温度範囲で反応抑制に必要な反応抑制剤添加濃度を測定した。本発表では反応抑制剤の有効性と反応抑制メカニズムについて報告する。

1) 藤田紗江ほか, 第 15 回分子科学討論会, 3A12 (2021)

Electron-ion coincidence laser tunneling ionization imaging of O₂ with auxiliary dissociation pulses

(¹Dept. of Chemistry, Nagoya University, ²RCMS, Nagoya University)

○Daimu Ikeya¹, Hikaru Fujise¹, Akitaka Matsuda¹, Mizuho Fushitani¹, Akiyoshi Hishikawa^{1,2}

Keywords: Laser tunneling ionization, Electron-ion coincidence measurement, Auxiliary dissociation pulse, Intense laser field, O₂

Intense laser fields ($\sim 10^{14}$ W/cm²) distort electron binding potentials of molecules and induce tunneling ionization. Since the rate is governed by characteristics of molecules, tunneling ionization provides a unique tool to investigate molecular properties, such as distributions of electrons within molecules. Molecular frame photoelectron angular distribution (MFPAD) measurement in circularly polarized intense laser fields is a powerful method for molecular imaging using tunneling ionization [1,2]. On the other hand, since this method requires both ionization and molecular dissociation for electron-ion coincidence detection, it can only be applied to molecules susceptible to dissociation in circularly polarized laser fields. In this study, we demonstrated a new approach, where auxiliary dissociation pulses are introduced to circumvent the difficulty.

The output of Ti:Sapphire laser system (ω , 800 nm, 45 fs) was split into two beams by a beam splitter. One was converted into circularly polarized pulses by a quarter wave plate. The other was introduced into a β -BBO crystal and converted into UV pulses (2ω , 400 nm, 60 fs). The two pulses were introduced into an ultrahigh vacuum chamber and focused on O₂ by a concave mirror. The UV pulses were delayed by 80 fs and blocked every other shot by an optical chopper. The ions and photoelectrons were accelerated toward separate position sensitive detectors by a static electric field and detected in coincidence. Momenta of each particle were calculated from the time of flight (t) and detected positions (x, y).

Figure 1 shows the kinetic energy release (KER) spectra of O₂. The spectrum with the ionization pulses alone (1.7×10^{14} W/cm²) has two peaks, which are observed in the previous study [2]. On the other hand, when introducing the auxiliary pulses (2ω on), a new peak emerged. The net KER spectrum (purple) was peaked at 0.7 eV. Since this peak agrees with a previous study for photodissociation (395 nm) of O₂⁺ beam [3], it was assigned to the dissociation pathway via ionization from HOMO-1 (π_u). The corresponding MFPAD shows a larger distribution in perpendicular to the molecular axis, supporting the assignment.

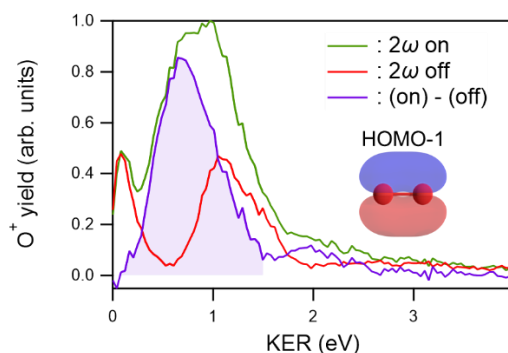


Fig. 1: The kinetic energy release spectra of O₂ obtained with 2ω pulse on (green), 2ω pulse off (red), and the net signal (purple).

- [1] A. Staudte *et al.*, Phys. Rev. Lett. **103**, 033004 (2009).
- [2] H. Liu *et al.*, Phys. Rev. A **88**, 061401(R) (2013).
- [3] M. Zohrabi *et al.*, Phys. Rev. A **83**, 053405 (2011).

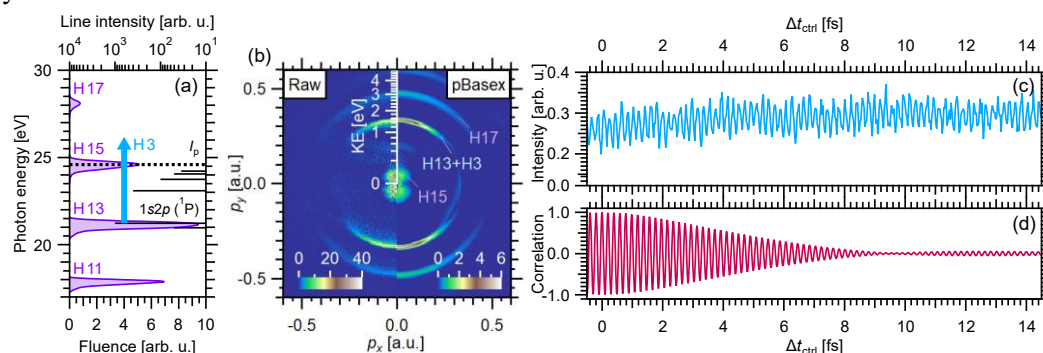
Attosecond optical and Ramsey-type interferometry using high-order harmonics

(¹RIKEN Attosecond Science Research Team, ²School of Science, The University of Tokyo, ³Graduate School of Engineering, The University of Tokyo) ○Takuya Matsubara,^{1,2} Yasuo Nabekawa,¹ Kenichi L. Ishikawa,³ Kaoru Yamanouchi,² Katsumi Midorikawa¹

Keywords: Attosecond science, High-order harmonics, Ramsey-type interferometry, Electronic wavepackets

An investigation of coherent superpositions of electronic states in atoms, i.e., electronic wavepackets (EWP), gives us an opportunity to deepen our understanding of the charge dynamics and achieve the control of quantum states. Ramsey-type interferometry, by which we monitor the quantum interference between two EWP created by a pair of phase-locked pulses, has been developed recently using extreme ultraviolet (XUV) pulses whose delay time is controlled in attosecond time scale.¹⁻³ In the present study, we demonstrate attosecond Ramsey-type interferometric measurements using ~20 fs XUV pulses and the split-and-delay interferometer⁴ after the generation of XUV pulses as high-order harmonics (HHs) of near-IR femtosecond laser pulses.

The spectrum of the generated XUV pulses is shown in Fig. 1(a) with the absorption lines of He. The irradiation of a pair of the 13th harmonic components in the XUV pulses generates a coherent superposition of the ground $1s^2$ state and the excited $1s2p$ state in He. A third harmonic pulse (266 nm) passing through a Mach-Zehnder interferometer is used as a probe pulse, by which He in the excited $1s2p$ state is ionized. The momentum image of the resultant photoelectrons is shown in Fig. 1(b). The yield of the electron plotted as a function of the delay time between the two XUV pulses Δt_{ctrl} in the range between -0.5 and 14.5 fs (Fig. 1(c)) exhibits an oscillation with the period of 195 as, corresponding to the excitation energy from the ground $1s^2$ state to the $1s2p$ state. The oscillation after $\Delta t_{\text{ctrl}} \sim 10$ fs can be interpreted as the Ramsey-type quantum interference because the optical interference disappears beyond the delay time of $\Delta t_{\text{ctrl}} \sim 10$ fs as in Fig. 1(d). The interferometric method we have developed in the present study can also be applied to the investigation of ultrafast dynamics of a vibrational and electronic wavepacket of molecular systems.



- 1) I. Lontos, *et al.*, *Opt. Lett.* **35**, 832 (2010).
- 2) Y. Hikosaka, *et al.*, *Nat. Commun.* **10**, 4988 (2019).
- 3) A. Wituscheck, *et al.*, *Nat. Commun.* **11**, 883 (2020).
- 4) Y. Nabekawa, *et al.*, *Phys. Rev. Lett.* **97**, 153904 (2006).

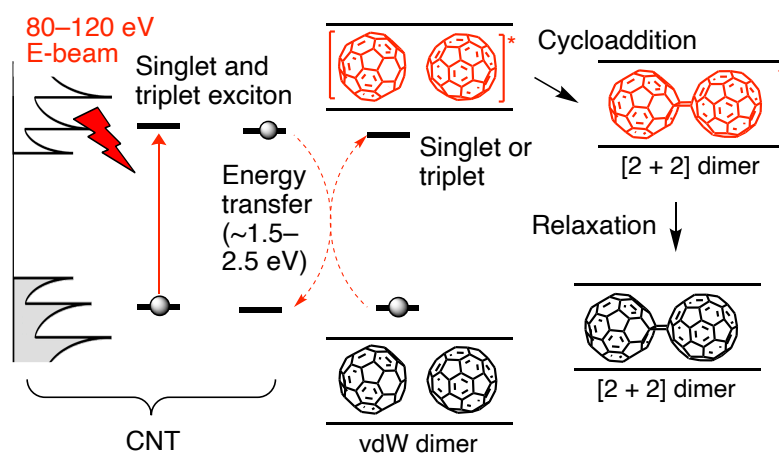
Electron-Impact Promoted Selective [2 + 2] Cycloaddition Mediated by Carbon Nanotube

(¹Department of Chemistry, The University of Tokyo, ²Center for Nanomedicine, Institute for Basic Science, ³Graduate Program of Nano Biomedical Engineering, Advanced Science Institute, Yonsei University) ○Dongxin Liu,¹ Satori Kowashi,¹ Takayuki Nakamuro,¹ Dominik Lungerich,^{1,2,3} Kaoru Yamanouchi,¹ Koji Harano,¹ Eiichi Nakamura¹

Keywords: Excited State Chemistry; Radiation Chemistry; Radical Cation; Fullerene; Transmission Electron Microscopy

Attention toward chemical applications of transmission electron microscopy (TEM) has been increasing but such studies are often plagued by radiation damage, which occurs via ionization (radiolysis) for organic matters.¹ Although radiolysis is highly important in the field of TEM, previous studies on radiolysis have largely been descriptive and qualitative due to the lack of methods to probe molecular mechanism. Here, we adopted chemically well-defined system to study radiolysis.

We chose thermally-forbidden [2 + 2] cycloaddition of a van der Waals dimer of [60]fullerene (C₆₀) to C₁₂₀ in a carbon nanotube (CNT) that proceeds under electron beam (e-beam) irradiation² and conducted variable-temperature³ and variable-voltage (VT/VV)⁴ study to investigate reaction paths and effects of e-beam. With the VT/VV study, we identified five reaction pathways that serve as mechanistic models of radiolysis damage, which demonstrate the importance of VT/VV kinetic analysis in the studies of radiation damage.



1) R. F. Egerton *Micron* **2019**, 119, 72. 2) M. Koshino *et al. Nat. Chem.* **2010**, 2, 117. 3) S. Okada *et al. J. Am. Chem. Soc.* **2017**, 139, 18281. 4) D. Liu *et al. arXiv*, arXiv:2110.02530.

有機超薄膜中の超高速スペクトル拡散ダイナミクス

(京大院理¹) ○吉田 龍矢¹・渡邊 一也¹

Ultrafast spectral diffusion dynamics of molecular excitons in ultrathin organic films
(¹Graduate School of Science, Kyoto University) ○Tatsuya Yoshida,¹ Kazuya Watanabe¹

Spectral diffusion immediately after photoexcitation reflects the vibronic coupling in the photoexcited system. In this work, we study spectral diffusion of molecular excitons in thin films of tetracene [1] and 3,4,9,10-perylenetetracarboxylic-diimide (PTCDI) [2] by using two-dimensional electronic spectroscopy (2DES). The samples were prepared in ultrahigh vacuum (UHV) chamber by thermal depositions of the molecules on graphene and measurements have been carried out under the UHV condition. Temperature dependence of the spectral diffusion is studied from 96 to 471 K by analyzing the 2DES signal. Significant acceleration of spectral diffusion with increasing the temperature is observed which cannot be explained by a linear system-bath coupling model with a harmonic bath. We propose an anharmonic coupling model in which the exciton energy gap fluctuations by a high-frequency intramolecular vibration are enhanced by the coupling with a low-frequency phonon mode.

Keywords : Exciton; Two-dimensional electronic spectroscopy; Organic thin film

有機固体中の励起子において、光励起直後にフェムトからピコ秒で進行する超高速スペクトル拡散には熱浴との振電結合が反映されている。本研究では二次元電子分光法(2DES)を超高真空下 ($<3.0 \times 10^{-8}$ Pa) の Graphene/Ir(111)基板上に作製したテトラセンおよび PTCDI の薄膜に適用し、励起子スペクトル拡散挙動を調べた。Fig. 1 および Fig. 2 に示す 2DES 信号の温度依存性から、スペクトル拡散が温度上昇によって加速していることがわかった。この加速を引き起こす機構としては高周波数振動モードと低周波数振動モード間の非調和結合が考えられる。

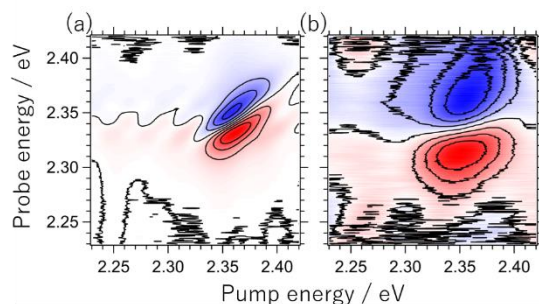


Fig. 1 2DES spectra of tetracene thin films at (a) 96 K and (b) 186 K. The delay times are 200 fs.

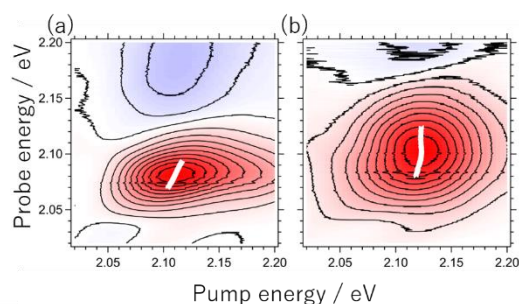


Fig. 2 2DES spectra of PTCDI thin films at (a) 105 K and (b) 298 K. The Delay times are 200 fs.

[1] T. Yoshida, K. Watanabe, M. Petrović, M. Kralj, *J. Phys. Chem. Lett.*, **11**, 5248 (2020).

[2] T. Yoshida, K. Watanabe, *J. Phys. Chem. B.*, **125**, 9350 (2021).

Single Pd Atom Doping into Au₂₄ Cluster Stabilized by PVP: Synthesis, Structural Analysis, and Catalysis

(¹Graduate School of Science, The University of Tokyo, ²Elements Strategy Initiative for Catalysts and Batteries, Kyoto University) ○Shingo Hasegawa,¹ Shinya Masuda,¹ Shinjiro Takano,¹ Koji Harano,¹ Tatsuya Tsukuda^{1,2}

Keywords: Au Cluster; PVP; Single Atom Doping; Aerobic Oxidation; Catalyst

Gold clusters smaller than a critical dimension of ~2 nm exhibit size-specific catalysis for oxidation reactions.¹ Control of the size with atomic precision is essential for elucidating the origin and optimizing the catalysis. Recently, we have achieved atomically precise synthesis of an unprecedented magic number cluster, Au₂₄ stabilized by polyvinylpyrrolidone (Au₂₄:PVP), by the kinetic control of cluster formation process.² In this study, we have successfully synthesized Au₂₃Pd₁:PVP by co-reduction method and revealed the geometrical structure of Au₂₃Pd₁ and single Pd atom doping effect on catalysis.

Au₂₃Pd₁:PVP was prepared by mixing an aqueous solution of HAuCl₄ and Na₂PdCl₄ (Au : Pd = 23 : 1) with that of NaBH₄ in the presence of PVP using a micromixer. Selective formation of Au₂₃Pd₁ cluster was confirmed by MALDI mass spectrometry (**Figure 1a**). Curve fitting analysis of Pd K-edge EXAFS revealed that the coordination number of Pd–Au bond was 6.1 ± 0.7 , indicating that the doped Pd atom was exposed on the cluster surface. As a result of structural search of bare Au₂₃Pd₁ cluster by DFT calculations, several stable isomers with 6-coordinated Pd atoms were obtained and reproduced some of TEM images of Au₂₃Pd₁:PVP (**Figures 1b–d**). Au₂₃Pd₁:PVP exhibited significantly higher activity than undoped Au₂₄:PVP for benzyl alcohol oxidation: the apparent activation energy was estimated to be 45 ± 2 and 56 ± 3 kJ mol^{−1} for Au₂₃Pd₁:PVP and Au₂₄:PVP, respectively. Kinetic isotope effect indicated that hydride elimination from the α -carbon by cluster surface was rate-determining step for both catalysts. It was proposed that the Pd dopant located on the cluster surface acts as a reaction site for hydride elimination with reduced activation energy.

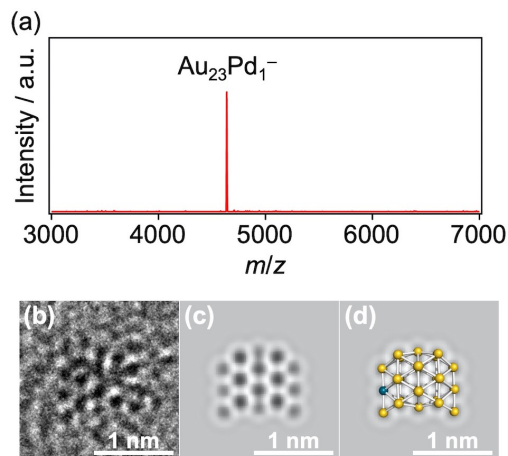


Figure 1 (a) MALDI mass spectrum and (b) a representative TEM image of Au₂₃Pd₁:PVP. (c) Simulated TEM image and (d) model structure of Au₂₃Pd₁.

1) S. Yamazoe, K. Koyasu, T. Tsukuda, *Acc. Chem. Res.* **2014**, *47*, 816. 2) S. Hasegawa, S. Takano, K. Harano, T. Tsukuda, *JACS Au* **2021**, *1*, 660.

Inter-cluster electron transfer $X^{2-} + X^0 \rightarrow 2X^-$ ($X = \text{PtAu}_{24}(\text{SC}_n\text{H}_{2n+1})_{18}$): effect of alkyl chain length of thiolate ligands on reaction rate

(¹Graduate School of Science, The University of Tokyo, ²ESICB, Kyoto University) ○Megumi Suyama,¹ Shinjiro Takano,¹ Tatsuya Tsukuda^{1,2}

Keywords: Ligand-protected metal cluster; Electron transfer; Inter-cluster reaction

It has been thought that metal clusters protected by ligands retain their identity as distinct entities even in the presence of other clusters. However, recent studies have revealed their dynamic nature in solution, where they exchange constituent metals and ligands.^{1,2} We have recently found that $[\text{PtAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^-$ (denoted as X^-) having an icosahedral $\text{Pt@Au}_{12}(7\text{e})$ core was spontaneously formed via electron transfer (ET) from $[\text{PtAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^{2-}$ (X^{2-}) to $[\text{PtAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^0$ (X^0) with $\text{Pt@Au}_{12}(6\text{e})$ and $\text{Pt@Au}_{12}(8\text{e})$ cores, respectively (Fig. 1).³ $X^{2-} + X^0 \rightarrow 2X^-$. In this study, we systematically determined the ET rates (k_{ET}) from $[\text{PtAu}_{24}(\text{SC}_n\text{H}_{2n+1})_{18}]^{2-}$ (X_n^{2-}) to $[\text{PtAu}_{24}(\text{SC}_m\text{H}_{2m+1})_{18}]^0$ (X_m^0) with $n, m = 2-16$.

Figure 2 shows the k_{ET} values for $X_n^{2-} + X_m^0 \rightarrow X_n^- + X_m^-$ determined by analyzing time dependent UV-Vis absorption spectra of the mixture of X_n^{2-} and X_m^0 . The k_{ET} values decreased with increase in the $n+m$ values in the range of 4–12, but increased in the range of 12–32. The former behavior can be explained in such a manner that the overlap of the superatomic orbitals required for ET is hindered by longer alkyl chains. In contrast, the latter counterintuitive behavior implies that the overlap of the superatomic orbitals is promoted due to the formation of long-lived dimer by vdW interaction between the alkyl chain. This hypothesis was supported by the observation of $(X_n \cdot X_m)^{2-}$ by electrospray ionization mass spectrometry of the mixture of X_n^{2-} and X_m^0 .

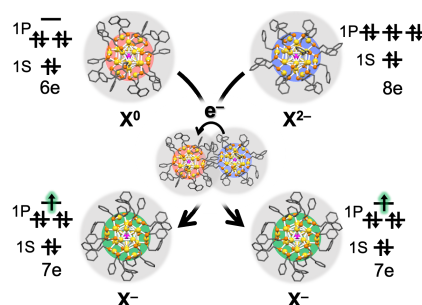


Fig. 1. Inter-cluster ET reaction from X^{2-} to X^0 ($X = \text{PtAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}$).

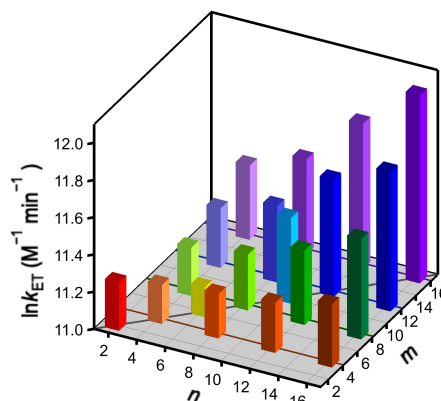


Fig. 2. ET rate constants as a function of (n, m) .

1) Y. Niihori *et al.* *J. Phys. Chem. C* **2019**, *123*, 13324–13329. 2) M. Neumaier *et al.* *J. Am. Chem. Soc.* **2021**, *143*, 6969–6980. 3) M. Suyama *et al.* *J. Am. Chem. Soc.* **2019**, *141*, 14048–14051.

Academic Program [Oral B] | 06. Analytical Chemistry | Oral B**[D201-1pm] 06. Analytical Chemistry**

Chair: Kosei Ueno, Rintaro Shimada

Wed. Mar 23, 2022 2:20 PM - 3:40 PM D201 (Online Meeting)

[D201-1pm-01] Control of fluorescence signals by the infrared Purcell effectYuto Kitajima¹, Yuto Shikama¹, Keisuke Imaeda¹, [○]Kosei Ueno¹ (1. Hokkaido Univ.)

2:20 PM - 2:40 PM

[D201-1pm-02] Deconstruction of Obscure Features in SVD Spectral Components for Biological Raman Imaging Applications[○]Ashok Zachariah Samuel², Shumpei Horii¹, Masahiro Ando², Haruko Takeyama¹ (1. Waseda University, 2. Research Organization for Nano and Life Inoovation, Waseda University.)

2:40 PM - 3:00 PM

[D201-1pm-03] Composition analysis of multivariate Raman spectral data with independent component analysis[○]Rintaro Shimada¹ (1. Aoyama Gakuin Univ.)

3:00 PM - 3:20 PM

[D201-1pm-04] Development of portable gas chromatograph using ball surface acoustic wave sensor for monitoring manned space environment[○]Takamitsu Iwaya¹, Shingo Akao¹, Kazushi Yamanaka¹, Tatsuhiko Okano¹, Nobuo Takeda¹, Yusuke Tsukahara¹, Toru Oizumi¹, Fukushi Hideyuki¹, Tomoki Tanaka¹, Maki Sugawara¹, Toshihiro Tsuji¹, Akinobu Takeda¹, Asuka Shima², Satoshi Matsumoto², Haruna Sugahara², Takeshi Hoshino², Tetsuya Sakashita² (1. Ball Wave Inc., 2. JAXA)

3:20 PM - 3:40 PM

赤外 Purcell 効果による蛍光分子の発光制御

(北大院総化¹・北大院理²) 北島 雄人¹・志釜 優斗¹・今枝 佳祐²・○上野 貢生²
Control of fluorescence signals by the infrared Purcell effect (¹Graduate School of Chemical Sciences and Engineering, ²Faculty of Science, Hokkaido University) Yuto Kitajima,¹ Yuto Shikama,¹ Keisuke Imaeda,² ○Kosei Ueno²

The gold nanorod with a relatively longer length and the gold nanochain structure in which the gold nanoblocks are linearly connected indicate localized surface plasmon resonances and a high electromagnetic field enhancement effect in the mid-infrared region. When the fluorescence of fluorescent molecules was measured in a strong near field in the mid-infrared region, a decrease in the fluorescence signal and a shortening of the fluorescence lifetime were obviously observed. In this study, we investigated the relationship between the enhancement of optical phonons based on the infrared Purcell effect and the non-radiation process of fluorescence molecules.

Keywords : Localized surface plasmon resonances; Mid-infrared; IR Purcell effect; Optical phonons; Vibrational spectroscopy

近年、プラズモンの光電場増強効果を利用した蛍光法による高感度分子検出技術が注目されている。蛍光増強は、可視域にプラズモン共鳴を有する金属ナノ微粒子近傍に存在する分子の輻射速度が Purcell 効果によって促進され、蛍光の量子収率が増大することにより誘起される。一方、我々は、中赤外域において高い光電場増強効果を示す金ナノチェーン構造と分子振動モードとの相互作用が蛍光やラマン散乱分光特性に与える影響について関心を持って研究を行っている。本研究では、中赤外域においてプラズモン共鳴波数を厳密に制御して蛍光分子を配置し、蛍光シグナルが変調される現象を系統的に明らかにすることを目的とする。

ガラス基板上に電子ビームリソグラフィ／リフトオフ法により中赤外波長において局在表面プラズモン共鳴を示す金ナノチェーン構造を作製した¹⁾。作製した構造体基板のプラズモン共鳴スペクトルを顕微 FT-IR 装置を用いて測定し、金ナノチェーン構造の長さによって中赤外域においてプラズモン共鳴波数を厳密に制御できることを明らかにした。蛍光分子 Eosin Y を構造体基板上に配置すると、再現性良く蛍光強度が減少し、蛍光寿命が短寿命化することが明らかになった。特筆すべき点は、分子の官能基の吸収波数と赤外プラズモンの共鳴波数が一致したときに、蛍光強度が減少することが定性的に示され、赤外 Purcell 効果により光学フォノンが増強して蛍光シグナルが減少したものと考えられる。光学フォノンの位相緩和ダイナミクスを追跡するため、現在コヒーレント光学フォノン計測系を構築して、プラズモン増強場における分子振動緩和ダイナミクスの変調や強結合等による振動状態の変調の有無について検討を行っている。

1) K. Ueno et al. *Opt. Express*, **24**, 17728-17737 (2016).

Deconstruction of Obscure Features in SVD Spectral Components for Biological Raman Imaging Applications

(¹Research Organization for Nano and Life Innovations, Waseda University, ²Department of Advanced Science Engineering, Waseda University, ³Computational Bio Big-Data Open Innovation Laboratory, AIST-Waseda University, ⁴Department of Life Science and Medical Bioscience, Waseda University, ⁵Institute for Advanced Research of Biosystem Dynamics, Waseda Research Institute for Science and Engineering, Graduate School of Advanced Science and Engineering, Waseda University) ○ Ashok Zachariah Samuel,¹ Shumpei Horii,^{2,3} Masahiro Ando,¹ and Haruko Takeyama^{1,2,4,5}

Keywords: Raman spectroscopy; DSAM; *Penicillium chrysogenum*; Multivariate curve resolution; single cell imaging

Raman spectroscopy is an optical spectroscopy technique with applications in biology and medicine.¹ Different functional biomolecules bear characteristic functional groups and hence their optical responses come at different frequencies in the Raman spectrum. This opens a possibility of simultaneous detection of multiple biomolecules in single cell microorganisms. However, highly overlapped signatures in the collected Raman data defy an easy analysis. Singular-value decomposition (SVD) and principal component analysis (PCA) are routinely used for analyzing Raman images. Often, as a general strategy, classification of specimens based on overall spectral variance explained by specific spectral vectors have been adopted. Consequently, such analysis methods unfortunately destroy the molecular information in the Raman data. This often leads to speculative interpretations based on the relative intensities of the bands in the SVD/PCA vectors. To circumvent this problem, we have developed a combined multivariate approach, *viz.*, deconstruction of SVD vectors applying MCR (DSAM).³ By applying this methodology, we have extracted the contribution of five biomolecular constituents of the *Penicillium chrysogenum* filamentous cell⁴ to the SVD vectors. Our study showed complex mixing of Raman spectra and the background, which makes relative intensities in the SVD spectral vectors difficult to interpret. We also show that the relative intensity ratio of biomolecule specific bands in SVD components, if observed clearly, are not reflective of their relative contributions. Similarly, image contrast in the SVD-decomposed Raman images from *Penicillium chrysogenum* was also misleading. However, by applying DSAM, we succeeded in accurately interpreting SVD spectra and images in molecular terms.

1) Samuel, A. Z.; Miyaoka, R.; Ando, M.; Gaebler, A.; Thiele, C.; Takeyama, H. *Commun. Biol.* **2020**, 3, 372. 2) Guo, S.; Rösch, P.; Popp, J.; Bocklitz, T. *J. Chemom.* **2020**, 34, e3202. 3) Samuel, A. Z.; Horii, S.; Ando, M.; Takeyama, H. *Anal. Chem.* **2021**, 93, 12139. 4) Horii, S.; Ando, M.; Samuel, A. Z.; Take, A.; Nakashima, T.; Matsumoto, A.; Takahashi, Y.; Takeyama, H. *J. Nat. Prod.* **2020**, 83, 3223.

独立成分分析による多変量ラマン信号成分分解の検討

(¹青学大) ○島田 林太郎¹

Composition analysis of multivariate Raman spectral data with independent component analysis (¹Aoyama Gakuin University) ○Rintaro Shimada¹

Independent Component Analysis (ICA) is applied to the composition analysis of a Raman spectral data set obtained from an inhomogeneous mixture of various chemical species. Systematic study of artificially prepared model Raman spectra data sets revealed that spectral preprocessing through numerical differentiation enhanced the statistical independence of components' spectra. Hence, ICA on a differentiated Raman data set yielded improved resolution. Application to experimentally obtained Raman data sets from the biological specimen are also demonstrated.

Keywords : Spectral Analysis; Multivariate Analysis; Raman Spectroscopy

細胞など非常に複雑な化学系を非侵襲 *in situ* 分析する手法の一つとしてラマン分光法は非常に強力である。しかし、多数の化学成分の混合したラマンスペクトルの解析は簡単ではなく、その定量・定性的な解析には専門的な分光学的知識が必須であった。本研究では、統計的独立性をもとに重畳した信号を複数の構成成分信号へと分離する手法である独立成分分析(ICA)を用いて、不均一混合物から得られた混合ラマンスペクトルを簡便に成分スペクトルへ分離する方法について検討した。

まず、人工的に準備したモデル成分スペクトルを用い、ラマン信号への ICA の適用可能性を調べたところ、ラマンスペクトルそのものは統計的独立性が低く、そのまま ICA の適用は困難であった。そこでスペクトルの独立性を向上させる前処理を検討したところ、スペクトル微分により成分スペクトル間の独立性は大きく向上することが明らかとなった。一方で、スペクトル中のノイズが ICA への適用性を著しく低下させる要因となることも判明した。以上の結果から、本研究では図 1 に示すスキームに基づく新たなスペクトル成分分解法を提案する。(1) 多変量混合ラマンデータ \mathbf{A} に対し、主成分分析により次元削減及びノイズの低減を行う。(2)主成分ローディングスペクトルを数値微分し(\mathbf{P}')、さらに ICA を用いて成分分解のための分離行列 \mathbf{W} を決定する。(3)微分は線形処理であるため、微分前の主成分ローディングスペクトル \mathbf{P} に直接分離行列 \mathbf{W} を適用し、独立(化学)成分スペクトル \mathbf{P}_{chem} を得る。(4)主成分スコア \mathbf{T} に分離行列の逆行列を作用させ、独立(化学)成分のスコア(定量情報) \mathbf{T}_{chem} を得る。講演では、生体試料由来の実測データへ本手法を適用した結果について報告し、その適用範囲や限界について議論する。

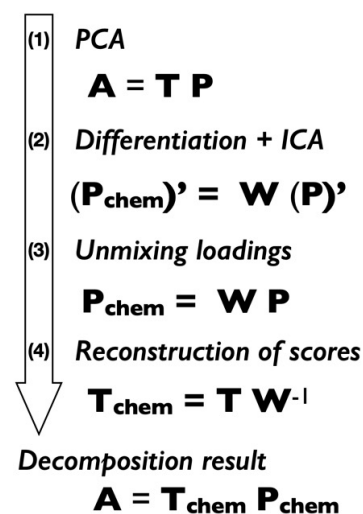


図 1 解析スキーム

有人宇宙環境モニタリングのためのボール SAW センサを用いた可搬型ガスクロマトグラフの開発

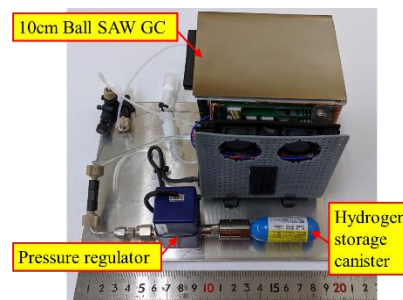
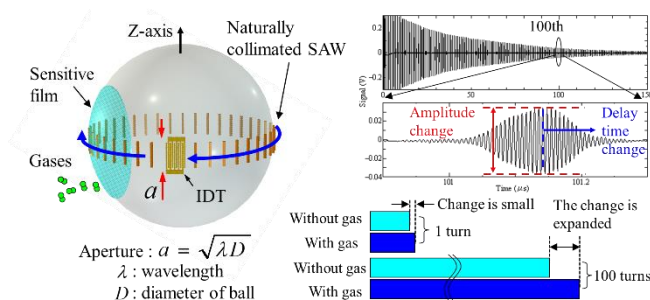
(ボールウェーブ¹・宇宙航空研究開発機構²) ○岩谷隆光¹・赤尾慎吾¹・山中一司¹・岡野達広¹・竹田宣生¹・塚原祐輔¹・大泉透¹・福士秀幸¹・田中智樹¹・菅原真希¹・辻俊宏¹・武田昭信¹・島明日香²・松本聡²・菅原春菜²・星野健²・坂下哲也²

Development of portable gas chromatograph using ball surface acoustic wave sensor for monitoring manned space environment (¹Ball Wave Inc., ²JAXA) ○Takamitsu Iwaya¹, Shingo Akao¹, Kazushi Yamanaka¹, Tatsuhiro Okano¹, Nobuo Takeda¹, Yusuke Tsukahara¹, Toru Oizumi¹, Hideyuki Fukushi¹, Tomoki Tanaka¹, Maki Sugawara¹, Toshihiro Tsuji¹, Akinobu Takeda¹, Asuka Shima², Satoshi Matsumoto², Haruna Sugahara², Takeshi Hoshino², and Tetsuya Sakashita²

Gas chromatograph (GC) is useful for atmospheric monitoring in a manned space environment, but GC is usually large and difficult to carry. We have developed a compact and highly sensitive ball surface acoustic wave (SAW) sensor¹ (Fig.1) that utilizes the phenomenon that SAW on spherical elements make multiple roundtrips under specific condition and have developed a portable ball SAW GC² using the ball SAW sensor as a detector. In this study, a prototype of 10 cm square, 762 g ball SAW GC shown in Fig. 2 was developed. We succeeded in separation and detection of 10 kinds of gases selected from a list of airborne contaminants in spacecraft³ using the prototyped GC.

Keywords : Gas Chromatograph; SAW Sensor; MEMS Column; Environment Monitoring

有人宇宙環境の大気モニタリングには多種類のガスを分析できるガスクロマトグラフ(GC)が有用であるが、通常 GC は大型で持ち運びが困難である。我々は、球状素子上の弾性表面波(surface acoustic wave; SAW)が特定条件で多重周回する現象を利用した小型で高感度なボール SAW センサ¹ (Fig.1)を開発し、これを検出器として用いた可搬型のボール SAW GC²を開発してきた。本研究では、Fig.2 に示す 10 cm 角、762 g のボール SAW GC の試作機を開発した。この試作機を用いて宇宙機における空中汚染物質のリスト³より選定した 10 種の有害ガスの分離・検出に成功した。



- 1) K. Yamanaka, S. Ishikawa, N. Nakaso, N. Takeda, D-Y. Sim, T. Mihara, A. Mizukami, I. Satoh, S. Akao and Y. Tsukahara: IEEE Trans. UFFC. **53** (2006) 793.
- 2) Y. Yamamoto, S. Akao, H. Nagai, T. Sakamoto, N. Nakaso, T. Tsuji, and K. Yamanaka: Jpn. J. Appl. Phys. **49** (2010) 07HD14.
- 3) <https://standards.nasa.gov/standard/jsc/jsc-20584>

[B304-1am] 08. Catalysts and Catalysis

Chair: Takane Imaoka, Jun-Chul Choi

Wed. Mar 23, 2022 9:00 AM - 11:20 AM B304 (Online Meeting)

[B304-1am-01] Development of durable high entropy alloy nanoparticle catalysts for CO₂ hydrogenation

○Naoki Hashimoto¹, Kohsuke Mori^{1,2}, Naoto Kamiuchi¹, Hideto Yoshida¹, Hisayoshi Kobayashi³, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. Kyoto Inst. of Tech.)

9:00 AM - 9:20 AM

[B304-1am-02] Bifunctional heterogeneous silica- supported imidazolium salt and silver catalyst for efficient chemical fixation of carbondioxide

○Sangita Karanjit¹, Emiko Tanaka¹, Masaya kashihara¹, Lok Kumar Shrestha², Atsushi Nakayama¹, Katsuhiko Ariga^{2,3}, Kosuke Namba¹ (1. Tokushima University, 2. National Institute for Materials Science (NIMS), 3. The University of Tokyo)

9:20 AM - 9:40 AM

[B304-1am-03] The role of potassium additive on the catalytic performance of cobalt for CO₂-FTS

○Shohei Harada¹, Shigeo Satokawa², Masaru Ogura¹ (1. The University of Tokyo, 2. Seikei University)

9:40 AM - 10:00 AM

[B304-1am-04] CO₂ hydrogenation to methanol using Pt-loaded molybdenum sub-oxide catalyst

○Yasutaka Kuwahara^{1,2,3}, Koji Hamahara¹, Takashi Mihogi¹, Hisayoshi Kobayashi^{1,4}, Hiromi Yamashita^{1,2} (1. Osaka Univ., 2. Kyoto Univ. ESICB, 3. PRESTO, 4. Kyoto Inst. Tech.)

10:00 AM - 10:20 AM

[B304-1am-05] Experimental investigation of CO₂ catalytic behavior in a supercritical CO₂ state for CO₂ stabilization into geological storage

○Takashi Fujii¹, Kenta Asahina¹, Masateru Nishioka¹ (1. National Institute of Advanced Industrial Science and Technology)

10:20 AM - 10:40 AM

[B304-1am-06] Selective oxidation of methane over iron oxide subnanocluster supported catalysts using a diiron-introduced polyoxometalate as a precursor

○Keiju Wachi¹, Tomohiro Yabe¹, Takaaki Suzuki¹, Kentaro Yonesato¹, Kosuke Suzuki¹, Kazuya Yamaguchi¹ (1. The University of Tokyo)

10:40 AM - 11:00 AM

[B304-1am-07] Oxygen Evolution Reaction Driven by Charge-Transfer from Cr-complex to Co-Containing Polyoxometalate in a Porous Ionic Crystal

○Yuto Shimoyama¹, ZHEWEI WENG¹, Naoki Ogiwara¹, Sayaka Uchida¹ (1. The University of Tokyo)

11:00 AM - 11:20 AM

CO₂ 水素化反応を高耐久に駆動するハイエントロピー合金ナノ粒子触媒の開発

(阪大院工¹・京大 ESICB²・阪大産研³・京工繊大⁴) ○橋本 直樹¹・森 浩亮^{1,2}・神内 直人³・吉田 秀人³・小林 久芳⁴・山下 弘巳^{1,2}

Development of Durable High Entropy Alloy Nanoparticle Catalysts for CO₂ Hydrogenation (¹Graduate School of Engineering, Osaka University, ²Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, ³SANKEN, Osaka University, ⁴Kyoto Institute of Technology) ○Naoki Hashimoto¹, Kohsuke Mori^{1,2}, Naoto Kamiuchi³, Hideto Yoshida³, Hisayoshi Kobayashi⁴, Hiromi Yamashita^{1,2}

High entropy alloys (HEAs), which are novel class of metallic materials are attracting much interest from various fields including catalysis due to their unique properties such as specific strength, thermal stability etc. Herein, we developed novel synthetic method of HEA nanoparticles (NPs) catalysts supported on TiO₂. The CoNiCuRuPd HEA NPs on TiO₂ produced in this work were found to be both active and extremely durable during the CO₂ hydrogenation reaction. These results suggest the HEA materials have potential practical applications as an ideal heterogeneous catalyst.

Keywords : High entropy alloy, Hydrogen spillover, CO₂ hydrogenation

ハイエントロピー合金(HEA)は①5 種類以上の元素を含有②ほぼ等原子組成比③单相の固溶体という 3 つの条件を満たす新規材料である。この HEA は従来の合金材料と比較して高い高温安定性や腐食耐性を発現することが報告されており、注目を集めている。しかし、触媒分野での応用を志向した HEA ナノ粒子はその合成法が十分に確立されていない。本研究では二酸化チタン(TiO₂)上での水素スピルオーバー現象を利用することで 400 °C という比較的低温かつ水素還元という簡便な手法で HEA ナノ粒子を合成可能であることを見出した¹⁾。本研究では Co, Ni, Cu, Ru, Pd からなる HEA ナノ粒子を合成した。H₂-TPR, HAADF-STEM, in situ XAFS などのキャラクタリゼーションから、5 元素がナノ粒子内において原子レベルで混合していることが示唆された(Figure1)。この触媒を CO₂ 水素化反応による CO, CH₄ 生成反応へ応用したところ、Pd 単元素触媒よりも高い CO₂ 転化率を示し、加えて非常に高い耐久性を持つことが明らかとなった。これらの特性は HEA に特有な「カクテル効果」と「低拡散効果」に由来することが示唆された。

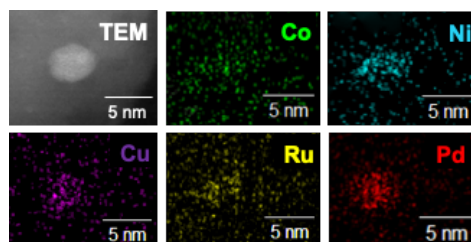


Figure1 HAADF-STEM image and EDX mappings of HEA nanoparticle.

1) K. Mori, N. Hashimoto, N. Kamiuchi, H. Yoshida, H. Kobayashi, H. Yamashita, *Nat. Commun.*, **2021**, 12, 3884

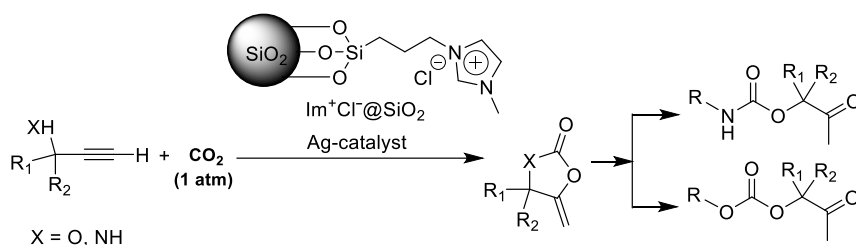
Bifunctional heterogeneous silica-supported imidazolium salt and silver catalyst for efficient chemical fixation of carbondioxide

(¹Tokushima University, ²National Institute for Materials Science (NIMS), ³The University of Tokyo) ○Sangita Karanjit¹, Emiko Tanaka¹, Masaya kashihara¹, Lok Kumar Shrestha², Atsushi Nakayama¹, Katsuhiko Ariga^{2,3}, Kosuke Namba¹

Keywords: heterogeneous catalyst, carbondioxide conversion, Silver catalyst

Carbondioxide (CO₂) has attracted considerable attention in recent years due to the environmental degradation and global warming caused by its emission. Great efforts have been implemented to reduce CO₂ levels in the atmosphere. Conversely, this gas has been regarded as a nontoxic, abundant, nonflammable, and renewable one-carbon (C1) feedstock for the synthesis of a variety of value-added chemicals. The reactions of CO₂ with unsaturated alcohols and amines to afford carbonates and carbamates through carboxylative cyclization process is one of the most promising green routes to convert CO₂. Silver has the potential to activate alkynes and has been extensively studied for chemical transformation of CO₂. Most of the studies have concentrated on homogeneous catalysis using relatively large amounts of Ag-based catalysts¹. However, in general, harsh reaction condition and sophisticated process for catalyst preparation are required for these reactions.

Compared to homogeneous systems, heterogeneous system is advantageous for the development of green and sustainable society in terms of good activity and reusability. To date, very few heterogeneous catalysts for this transformation including Cu and Ag are reported. In this context, solid catalysis with ammonium salts by covalent grafting (supported ionic liquids, SILs) could be an ideal choice because of the fact that in SILs, ammonium salts are used in small amounts, while their efficiencies are similar or sometimes even much better than non-supported ones. In this work, we prepared a silica-supported bifunctional heterogeneous catalytic system based on imidazolium salt where the Im⁺Cl⁻@SiO₂ activated both Ag-catalyst and substrate for carboxylative cyclization reaction of propargyl alcohols by efficient utilization of CO₂ with excellent yields of the corresponding carbonates and carbamates under mild reaction condition. We also confirmed the reusability of catalyst up to five cycles.



1) S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H.-M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn.* **2011**, 84, 698–717.

Role of potassium additive on the catalytic performance of cobalt for CO₂-FTS

(¹ School of Engineering, The University of Tokyo, ² Department of Materials and Life Science, Seikei University, ³ Institute of Industrial Science, The University of Tokyo) ○Shohei Harada,¹ Shigeo Satokawa,² Masaru Ogura³

Keywords: CO₂ hydrogenation, Fischer-Tropsch synthesis, Cobalt catalyst

Fischer-Tropsch Synthesis (FTS) using CO₂ (CO₂-FTS) is one of the potential technologies to transform atmospheric CO₂ to a liquid synthetic fuel.¹ Cobalt-based catalysts have been used in FTS, and long-chain hydrocarbons are produced on a commercial scale. On the other hand, the catalyst is known to form methane dominantly (>90%) along with short-chain gaseous hydrocarbons (C₂-C₄) in CO₂-FTS.² Adding potassium in the Co catalyst has been demonstrated to reduce the methane selectivity to 55%, and to increase carbon chain growth to form liquid hydrocarbons (C₅+).³ The promotive effect of K is promising for CO₂-FTS, however still now it has not been clarified in detail yet. In this work, the role of K is investigated by combination of FT-IR, XPS, and STEM from the viewpoints of location and interaction to Co catalysts.

The catalytic activity of K-Co/SiO₂ resulted in a low methane selectivity and a high C₂₋₄ and C₅₊ selectivity. The liquid phase products included not only n-alkanes from C₅ to C₈ but also C₂₊ alcohols and acetic acid. Probe FT-IR and XPS spectra of Co2p regions reveal that potassium keeps the oxidized Co surface even after reduction prior to the FTS. Potassium is possible to exist on the cobalt surface of K-Co/SiO₂, and the oxidized Co surface supplies a weakly basic site for promoting CO₂ adsorption. Therefore, the role of potassium in CO₂-FTS is maintaining the oxidized Co species to promote CO₂ activation by locating on the Co surface.

This study is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Table 1. Catalytic activities for CO₂-FTS at 300 °C under 1 MPa

Catalyst	CO ₂ conversion / %	CO selectivity / %	Hydrocarbon selectivity / %		
			CH ₄	C ₂₋₄	C ₅₊ [*]
Co/SiO ₂	21	10	90	0.6	9.1
K-Co/SiO ₂	16	31	56	27	16
Co/Na-Y	25	8.9	91	1.0	8.0
Co-Y	3.0	< 0.1	< 0.1	< 0.1	< 0.1

^{*} Including C₂₊ alcohols and acetic acid

1) M. D. Porosoff, B. H. Yan, J. G. G. Chen, *Energy Environ. Sci.* **2016**, 9, 62. 2) C. G. Visconti, L. Lietti, E. Tronconi, P. Forzatti, R. Zennaro and E. Finocchio, *APPL. CATAL. A-GEN.* **2009**, 355, 61. 3) R. A. Iloy, K. Jalama, *Catalysis* **2019**, 9, 18.

Pt 担持モリブデン亜酸化物触媒を用いた CO₂ 水素化によるメタノール合成反応

(阪大院工¹・京大 ESICB²・JST さきがけ³・京都工繊大⁴) ○桑原泰隆^{1,2,3}・浜原幸治¹・三保木隆志¹・小林久芳^{1,4}・山下弘巳^{1,2}

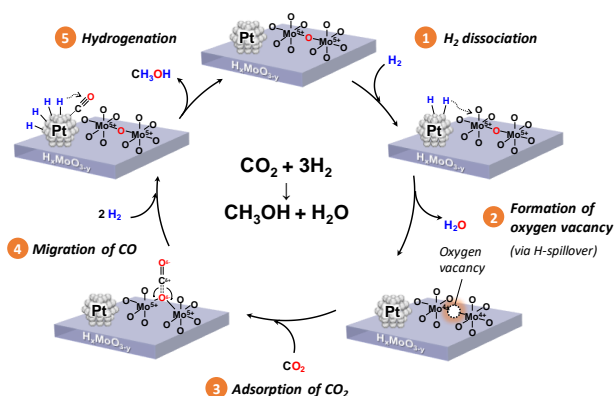
CO₂ Hydrogenation to Methanol using Pt-loaded Molybdenum Sub-oxide Catalyst (¹Graduate School of Engineering, Osaka University, ²Unit of Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, ³JST PRESTO, ⁴Kyoto Institute of Technology)

○Yasutaka Kuwahara,^{1,2,3} Koji Hamahara,¹ Takashi Mihogi,¹ Hisayoshi Kobayashi,^{1,4} Hiromi Yamashita^{1,2}

Production of methanol from CO₂ is a promising chemical process that can alleviate both the environmental burden and the dependence on fossil fuels. We herein report that oxygen-defective molybdenum sub-oxide coupled with Pt nanoparticles (Pt/H_xMoO_{3-y}) affords high methanol yield in liquid-phase CO₂ hydrogenation under relatively mild reaction conditions (total 4.0 MPa, 200 °C), outperforming other oxide-supported Pt catalysts in terms of both the yield and selectivity for methanol. Experiments and comprehensive analyses reveal that abundant surface oxygen vacancies in H_xMoO_{3-y} confer the catalyst with enhanced adsorption and activation capability to transform CO₂ to CO, and the Pt nanoparticles act as hydrogenation sites for the CO intermediate to afford methanol. Based on the experimental and computational studies, an oxygen-vacancy-mediated “reverse Mars–van Krevelen” mechanism is proposed.

Keywords : CO₂ Hydrogenation; Methanol Synthesis; Molybdenum Oxide; Oxygen Vacancy

CO₂をメタノールへと直接変換することができれば、地球温暖化問題と資源枯渇問題を同時に解決できる有効な技術となり得る。本研究では、Pt ナノ粒子を固定化したモリブデン亜酸化物(Pt/H_xMoO_{3-y})触媒が、比較的温和な反応条件(4.0 MPa, 200 °C)での液相 CO₂ 水素化反応において、他の酸化物担持 Pt 触媒よりも高いメタノール収率を与えることを見出した¹⁾。実験および種々のキャラクタリゼーションから、モリブデン酸化物中に導入された酸素欠陥²⁾が CO₂を吸着・活性化することで CO 中間体を生成し、Pt ナノ粒子が水素化サイトとして機能することで最終的にメタノールが生成するものと推察された。実験および DFT 計算から、酸素欠陥を介した逆 Mars-van Krevelen 機構により反応が進行するものと推察された。



1) Y. Kuwahara, T. Mihogi, K. Hamahara, K. Kusu, H. Kobayashi, H. Yamashita, *Chem. Sci.*, **2021**, *12*, 9902. [Selected as Inside Front Cover]

2) Y. Kuwahara, Y. Yoshimura, K. Haematsu, H. Yamashita, *J. Am. Chem. Soc.*, **2018**, *140*, 9203.

短期 CO₂ 地中固定化開発のための超臨界 CO₂ 条件下での触媒による CO₂ 転換挙動に関する実験的研究

((国研) 産総研^{1,2}) ○藤井 孝志¹・朝比奈 健太¹・西岡 将輝²

Experimental investigation of CO₂ catalytic behavior in a supercritical CO₂ state for a rapid CO₂ stabilization into geological storage (¹*Research Institute of Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology (AIST)*,² *Research Institute Chemical Process Technology, AIST*) ○Takashi Fujii,¹ Kenta Asahina,¹ Masateru Nishioka,²

CO₂ capture and storage (CCS) technology is a vital tool for deep reduction of anthropogenic CO₂ emissions from CO₂ large point sources (e.g., power generation). Long-term stabilization of storing CO₂ into storage reservoirs is a critical step for safe implementation of this technology. Indeed, majority of the CO₂ will remain as an immiscible phase of CO₂ in its supercritical state, which is not dissolved into formation water. With respect to such challenge, we propose a novel CCS technology through CO₂-nanocatalyst injection, which directly converted the CO₂ into hydrocarbon compounds within storage reservoirs. Our results showed that under conditions of CO₂ geological storage, the presence of Ni nanocatalyst with a little water provided sufficient catalytic activity regarding CO₂ hydrogenation to afford various long-chain n-alkanes.

Keywords : CCS, catalytic conversion, Ni, nanocatalyst, supercritical CO₂

有力な CO₂ 削減方法の一つに、CO₂ 回収・貯留 (CCS) 技術が挙げられる。本技術は、主に、火力発電所や製鉄所などの大規模 CO₂ 排出源からの CO₂ を直接地中に貯留するものであり、想定される地中貯留条件下では超臨界状態となる。安全な CCS 技術の実施のためには、圧入した CO₂ を長期にわたり安定的に貯留することが必要不可欠である。しかしながら、大部分の CO₂ が、地層水に溶解しない、つまり超臨界 CO₂ 状態のまま存在することが予想¹⁾ されている。本研究では、CO₂ の早期固定化を目的に、CO₂ 圧入時にナノ触媒を添加することで、地中貯留層内で CO₂ を直接安定な固体や液体の炭化水素に転換するための技術開発を行っている。これまで、地下 1km の模擬 CO₂ 地中貯留条件 (40~50℃、約 10MPa) 下で、Ni ナノ触媒と少量の水を用いて CO₂ 転換反応実験を行ったところ、CO₂ の一部が、様々な長鎖飽和炭化水素化合物に転換することが明らかとなった。

1) Reactive transport modelling of CO₂ storage in saline aquifers to elucidate fundamental processes, trapping mechanisms and sequestration partitioning. J. W. Johnson, J. J. Nitao, K. G. Knauss, *Geological Society Special Publication* **2004**, 233, 107.

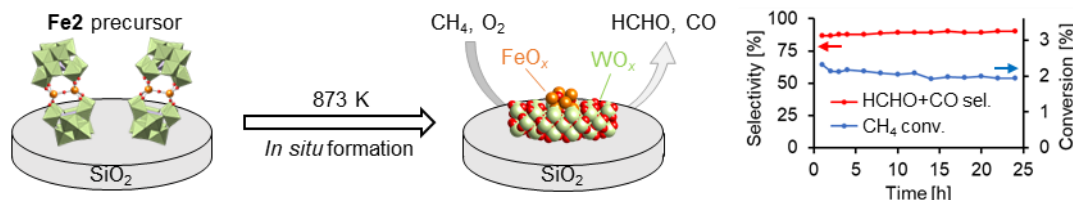
Selective Oxidation of Methane over Iron Oxide Subnanocluster Supported Catalysts Using a Diiron-introduced Polyoxometalate as a Precursor

(School of Engineering, The University of Tokyo) ○Keiju Wachi, Tomohiro Yabe, Takaaki Suzuki, Kentaro Yonesato, Kosuke Suzuki, Kazuya Yamaguchi

Keywords: methane oxidation; polyoxometalate; iron oxide subnanocluster; thermal stability

Selective oxidation of methane into value-added C1 products such as HCHO and CO remains challenging due to high stability of methane and facile overoxidation of C1 products into CO₂.¹ Iron oxide cluster catalysts are promising since they selectively convert methane into HCHO and CO with low activation energy.² However, our preliminary test revealed that SiO₂-supported iron oxide clusters were agglomerated and deactivated under methane oxidation conditions at 873 K. In this study, we used a diiron-introduced polyoxometalate (**Fe2**) as a precursor to form thermally stable iron oxide subnanoclusters. **Fe2** has the structure that iron dinuclear core is encapsulated in lacunary polyoxometalate (**POM**) frameworks composed of WO₆ units. Although the lacunary polyoxometalate frameworks are supposed to be decomposed into tungsten oxide at 873 K, the *in situ* formed tungsten oxide is expected to have a protecting effect on iron oxide cluster active sites.

Firstly, **Fe2** was synthesized by stoichiometric reaction of a divacant lacunary silicotungstate₇ and iron(III) acetylacetonate. Then, **Fe2** was dispersed on SiO₂ using an incipient wetness method to prepare **Fe2**/SiO₂. **Fe2**/SiO₂ exhibited high selectivity to HCHO and CO (41% and 46%, respectively) at 2.3% methane conversion at 873 K (CH₄:O₂:Ar = 2:1:7, total flow rate: 50 mL min⁻¹), and maintained its catalytic activity even after 24 h. Moreover, several control experiments elucidated that iron species introduction into the lacunary polyoxometalate in advance plays a key role to maintain the catalytic activity. Fe K-edge and W L₃-edge XAFS analyses revealed that, in **Fe2**/SiO₂, **Fe2** precursor was decomposed into iron oxide subnanoclusters and tungsten oxide nanoclusters. Furthermore, STEM-EDS analysis indicated that iron oxide subnanoclusters were dispersed in tungsten oxide nanoclusters. Thus, we concluded that the *in situ* formed tungsten oxide protected iron oxide subnanoclusters from agglomeration by using **Fe2** as a precursor.



- 1) J. Tian, J. Tan, Z. Zhang, P. Han, M. Yin, S. Wan, J. Lin, S. Wang, Y. Wang, *Nat. Commun.* **2020**, 11, 5693. 2) Q. Zhang, Y. Li, D. An, Y. Wang, *Appl. Catal. A* **2009**, 356, 103.

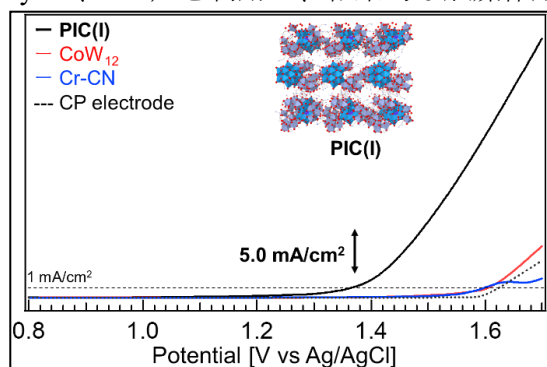
Oxygen Evolution Reaction Driven by Charge-Transfer from Cr-complex to Co-Containing Polyoxometalate in a Porous Ionic Crystal

○Yuto Shimoyama¹, ZHEWEI WENG¹, Naoki Ogiwara¹, Sayaka Uchida¹ (1. The University of Tokyo)

Considerable efforts have been devoted to developing oxygen evolution reaction (OER) catalysts based on transition metal oxides. Polyoxometalates (POMs) can be regarded as model compounds of transition metal oxides, and cobalt-containing POMs (Co-POMs) have received significant interest as candidates. Nanocomposites based on Co-POMs have been reported to show high OER activity due to synergistic effects among the components, while the role of each component is unclear due to its complex structure. Herein, we utilize porous ionic crystals (PICs) based on Co-POMs, which enable the establishment of a composition–structure–function relationship to understand the origin of the synergistic catalysis. Specifically, a Keggin-type POM [α -CoW₁₂O₄₀]⁶⁻ and a Cr-complex [Cr₃O(OOCCH₂CN)₆(H₂O)₃]⁺ are implemented as building blocks of PIC for OER under non-basic conditions. The PIC exhibits efficient and sustained OER catalytic activity while each building block is inactive. Electrochemical and spectroscopic studies clearly show that the synergistic catalysis originates from the charge transfer from the Cr-complex to [α -CoW₁₂O₄₀]⁶⁻; the increased electron density of [α -CoW₁₂O₄₀]⁶⁻ may increase its basicity and accelerate proton abstraction as well as enhance electron transfer to stabilize reaction intermediates adsorbed on [α -CoW₁₂O₄₀]⁶⁻.

Keywords : Oxygen evolution reaction, Polyoxometamate, Ionic crystal, electrochemical catalysis, Porous materials

遷移金属酸化物を用いた酸素発生反応（Oxygen Evolution Reaction, OER）触媒の開発が盛んに行われている。Polyoxometalate (POM) は、アニオン性の遷移金属酸化物クラスターであり、特にコバルト含有 POM (Co-POM) は OER 触媒の候補として注目されている。Co-POM を用いたナノコンポジット材料が構成ユニット間の相乗効果により高い OER 活性を示すことが報告されているが、その複雑な構造から各成分の役割は不明である。本研究では、組成-構造-機能の関係を確立できる Co-POM をベースにした多孔性イオン結晶（Porous Ionic Crystal、PIC）を利用し、相乗的な触媒作用の起源を理解することを目指した。Keggin 型 POM [α -CoW₁₂O₄₀]⁶⁻ とクロム錯体 [Cr₃O(OOCCH₂CN)₆(H₂O)₃]⁺ を構成ユニットとした PIC で相乗的な OER 触媒活性が発現することを見出した。電気化学的および分光学的研究により、この相乗的な触媒活性は Cr 錯体から [α -CoW₁₂O₄₀]⁶⁻ への電荷移動に起因することを明らかにした。



1) **Shimoyama Y.**; Ogiwara N.; Weng Z.; Uchida S., Oxygen Evolution Reaction Driven by Charge-Transfer from Cr-Complex to Co-Containing Polyoxometalate in a Porous Ionic Crystal. *J. Am. Chem. Soc.*, *accepted*.

[B304-1pm] 08. Catalysts and Catalysis

Chair: Tomohiro Yabe, Satoshi Muratsugu

Wed. Mar 23, 2022 1:20 PM - 3:40 PM B304 (Online Meeting)

[B304-1pm-01] Precise Synthesis of Nickel Sub-nano Particles for Greenhouse Gas Conversion○Tatsuya Moriai¹, Takamasa Tsukamoto^{1,2,3}, Makoto Tanabe², Tetsuya Kambe^{1,2}, Takane Imaoka^{1,2}, Kimihisa Yamamoto^{1,2} (1. Lab. Chem. Life Sci., Tokyo Tech., 2. JST-ERATO, 3. JST-PRESTO)

1:20 PM - 1:40 PM

[B304-1pm-02] Preparation and Evaluation of Redox Performance/Catalytic Ammonoxidation Performance of Copper and Ruthenium Incorporated Ceria○Chaoqi Chen¹, Satoru Ikemoto¹, Satoshi Muratsugu¹, Mizuki Tada^{1,2} (1. Dept.Chem., Nagoya Univ., 2. RCMS, Nagoya Univ.)

1:40 PM - 2:00 PM

[B304-1pm-03] Phosphonate-type pseudo-grafted precursor for efficient surface modification of silica○Yusuke Ishizaka^{1,2}, Kazuhiro Matsumoto², Kazuhiko Sato², Jun-Chul Choi^{1,2} (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

2:00 PM - 2:20 PM

[B304-1pm-04] Development of a new in-situ UV-vis reflection spectroscopy system for the formic acid dehydrogenation○Risheng Li^{1,2}, Hajime Kawanami^{1,2}, Tetsuya Kodaira² (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology)

2:20 PM - 2:40 PM

[B304-1pm-05] Frontier Orbital Theory of Molecular Adsorption on TiO₂ Surface○Takashi Kamachi Kamachi^{1,5}, Nobutsugu Hamamoto¹, Toshinobu Tatsumi¹, Motoshi Takao², Toyao Takashi^{2,5}, Yoyo Hinuma³, Zen Maeno², Satoru Takakusagi², Shinya Furukawa^{2,5}, Ichigaku Takigawa⁴, Ken-ichi Shimizu² (1. Fukuoka Institute of Technology, 2. Hokkaido Univ., 3. National Institute of Advanced Industrial Science and Technology, 4. RIKEN, 5. ESICB)

2:40 PM - 3:00 PM

[B304-1pm-06] Synthesis of Pt/TiO_{2-x} Photocatalyst via Reduction Assisted by Hydrogen Spillover and Formation Mechanism of Surface-exposed Ti³⁺○Yukari Yamazaki¹, Kohsuke Mori^{1,2}, Yasutaka Kuwahara^{1,2,3}, Hisayoshi Kobayashi⁴, Hiromi Yamashita^{1,2} (1. Grad. Eng., Osaka Univ., 2. ESICB, Kyoto Univ., 3. JST PRESTO, 4. Kyoto Inst. of Tech.)

3:00 PM - 3:20 PM

[B304-1pm-07] Unraveling Hydrogen Spillover Pathways over Reducible Metal Oxide○Kohsuke MORI^{1,2}, Kazuki Shun¹, Shinya Masuda¹, Naoki Hashimoto¹, Hisayoshi

Kobayashi³, Hiromi Yamashita^{1,2} (1. Osaka University, 2. ESICB Kyoto University, 3.
Kyoto Institute of Technology)

3:20 PM - 3:40 PM

Precise Synthesis of Nickel Sub-nano Particles for Greenhouse Gas Conversion

(¹Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, ²JST-ERATO, ³JST-PRESTO) ○Tatsuya Moriai,¹ Takamasa Tsukamoto,^{1,2,3} Makoto Tanabe,² Tetsuya Kambe,^{1,2} Takane Imaoka,^{1,2} Kimihisa Yamamoto^{1,2}

Keywords: Dendrimer; Sub-nano particle; Nickel; Greenhouse gas; Catalyst

Sub-nano particles (SNPs) have attracted worldwide attention due to the high reactivity and the unique property beyond the extension of the bulk and nanoparticles. Our research group has achieved the precise synthesis of various SNPs showing the higher catalytic performance than that of conventional materials by the template method using a dendrimer.^{1,2} In this work, we succeeded to synthesize 4 types of nickel SNPs and applied them to greenhouse gas conversion as catalysts.

Following accumulation of nickel salts to dendrimers, 4 types of nickel SNPs were prepared by reduction of these complexes. The dendrimer applied in this work possesses intramolecular potential gradient, thereby the precise synthesis of nickel SNPs with defined atomicity such as Ni₄, Ni₁₂, Ni₂₈, and Ni₆₀ was realized. (Fig. 1a) This stepwise complexation behavior was monitored by UV-vis absorption spectroscopy. STEM observation and EDX analysis demonstrated that SNPs with a diameter of around 1 nm composed of nickel atoms were loaded on silica and graphene supports. (Fig. 1b) The oxidation state and H₂-reduction temperature of nickel SNPs were evaluated by XPS, H₂-TPR, and XAFS measurements. Remarkably, it was indicated that nickel SNPs had the higher catalytic performance than conventional materials and the outstandingly durability for the greenhouse gas conversion reaction. It was theoretically suggested that this result originated from the structure peculiar to SNP with the unique active sites.

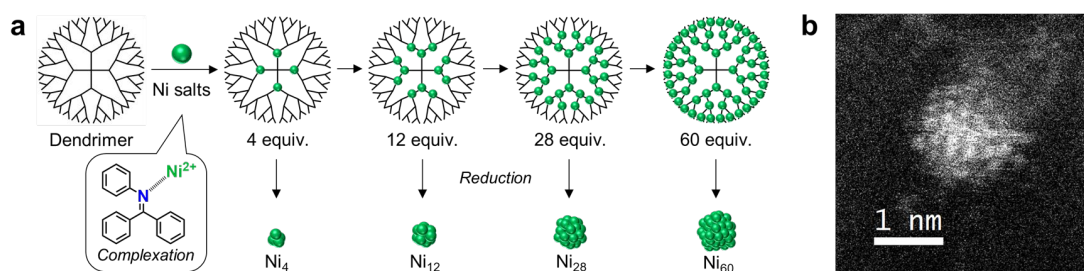


Fig. 1. **a** The scheme for stepwise complexation of Ni salts into a dendrimer and synthesis of 4 types of Ni SNPs. **b** A STEM image of Ni₂₈ on graphene at atomic resolution.

1) T. Tsukamoto *et al.* *Nat. Commun.* **2018**, 9, 3873. 2) T. Moriai *et al.*, *Angew. Chem. Int. Ed.* **2020**, 59, 23051-23055.

Preparation and Evaluation of Redox Performance/Catalytic Ammoxidation Performances of Copper and Ruthenium Incorporated Ceria

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

Keywords: Mixed Metal Oxide; Ceria; Copper; Ruthenium; Ammoxidation

We previously reported the incorporation of Cr and Rh ions to the ceria achieved high redox performance below 423 K and exhibited high catalytic activity toward alcohol oxidation.¹ In this study, we report a ceria-based mixed oxide by adjusting the incorporated metal ions to Cu and the trace amount of Ru. The mixed cerium oxide with Cu and Ru was found to exhibit redox performance at low temperature and high catalytic activity and selectivity for the ammoxidation of benzyl alcohol.

Prepared mixed cerium oxide with Cu and Ru incorporation (denoted as Cu_{0.18}Ru_{0.05}CeO_z) was characterized by XRD and TEM and it was found that Cu_{0.18}Ru_{0.05}CeO_z had fluorite structure of ceria with dispersed Cu and Ru on the surface. TPR/TPO showed that Cu_{0.18}Ru_{0.05}CeO_z exhibited the reversible redox performance below 423 K. *In situ* XANES measurement during the reduction process demonstrated the three metal species of Cu, Ru and Ce contributed in the redox behavior, and this multi-reduction behavior was elucidated by the reduced Ru at first with subsequently promoted reduction of Cu and Ce species.

Cu_{0.18}Ru_{0.05}CeO_z significantly promoted the conversion of benzyl alcohol (95%) to benzonitrile (90% yield) (conditions: Ru/Cu/benzyl alcohol/NH₃ = 1/3.5/100/191, [benzyl alcohol] = 1.93 mol, NH₃: 0.32 MPa, O₂: 1 MPa, toluene: 1.0 mL, 423 K, 24 h) compared with Cu_{0.18}CeO_z without Ru, Ru_{0.04}CeO_z without Cu, and CeO₂ (Table 1). Several control reaction experiments (N₂ 1 MPa instead of O₂, with/without NH₃) suggested that Ru efficiently processed the oxidation of benzyl alcohol to form benzaldehyde and Cu worked as active site for the cyanation of benzaldehyde to benzonitrile. The catalytic performances of the ammoxidation and the role of each metal in the catalyst will be presented.

[1] Ikemoto, S. *et al. Phys. Chem. Chem. Phys.* 2019, 21, 20868-20877.

Table 1. Catalytic Performances of Cu_{0.18}Ru_{0.05}CeO_z for Ammoxidation of Benzyl Alcohol^a

Entry	Catalyst	Conv. %	Benzonitrile	
			Selec. %	Yield %
1 ^b	Cu _{0.18} Ru _{0.05} CeO _z	95	95	90
2 ^c	Cu _{0.18} CeO _z	70	78	55
3 ^d	Ru _{0.04} CeO _z	91	29	27
4 ^e	CeO ₂	77	10	8
5	Blank	0	0	0
6 ^f	Cu _{0.18} Ru _{0.05} CeO _z	20	0	0

^a Reaction conditions: **Benzyl alcohol (BA)**: 1.93 mmol (1.61 mol L⁻¹), toluene: 1.0 mL, dodecane (internal standard): 0.07 mL (1.98 mmol), NH₃: 0.32 MPa (3.7 mmol), O₂: 1.0 MPa, 423 K, 24 h. ^b Cu_{0.18}Ru_{0.05}CeO_z: 74 mg (Ru: 0.019 mmol, Cu 0.068 mmol), Ru/Cu/BA/NH₃/dodecane = 1/3.5/100/191/100. ^c Cu_{0.18}CeO_z: 77 mg (Cu: 0.068 mmol), Cu/BA/NH₃/dodecane = 1/29/58/29. ^d Ru_{0.04}CeO_z: 72 mg (Ru: 0.019 mmol), Ru/BA/NH₃/dodecane = 1/100/191/100. ^e CeO₂ 74 mg, BA/NH₃/dodecane = 1/1.91/1. ^f N₂ 1.0 MPa (instead of O₂). The major product was *N*-Benzylidenebenzamine (Selec.: >99%, Yield 22%)

Phosphonate-Type Pseudo-Grafted Precursor for Efficient Surface Modification of Silica

(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,^{1,2} Kazuhiro Matsumoto,² Kazuhiko Sato,² Jun-Chul Choi^{1,2}

Keywords: Silyl Phosphonate; Surface Modification; Silica; Grafting; Solid-State NMR

Surface modification of inorganic metal oxides by grafting of phosphonic acids and its derivatives is an attractive approach to obtain tailored organic-inorganic hybrid materials, which can be utilized as heterogeneous catalysts, sensors, etc. However, silica surface is difficult to modify compared to other oxide supports because phosphonic acid derivatives are grafted by slow formation of P–O–Si bonds. On the other hand, we have recently developed “pseudo-grafted precursor” (PGP) bearing disilicate moiety –OSi(O^tBu)₂OSi(O^tBu)₂O–. PGP can be grafted on silica surface by substitution reaction at the silicon atoms of the disilicate moiety involving the formation of Si–O–Si bonds.¹

In this work, we developed phosphonate-type pseudo-grafted precursor (P-PGP) to effectively modify the silica surface.² P-PGP was synthesized by a reaction of [(^tBuO)₂Si(OH)]₂O with O=P(C₆H₄OMe)Cl₂, and grafted on fumed silica (AEROSIL300) to acquire P-PGP@SiO₂. The phosphorous content of P-PGP@SiO₂ determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) was 0.40 wt%, which was higher than that of a sample grafting the corresponding phosphonic acid O=P(C₆H₄OMe)(OH)₂ (0.12 wt%). Based on characterization of surface species by solid-state NMR measurement and detection of ^tBuOH and isobutene as side-products during the grafting, we propose that the grafting of P-PGP proceeds through the formation of Si–O–Si bonds rather than P–O–Si bonds, which enables the effective surface modification of silica supports.

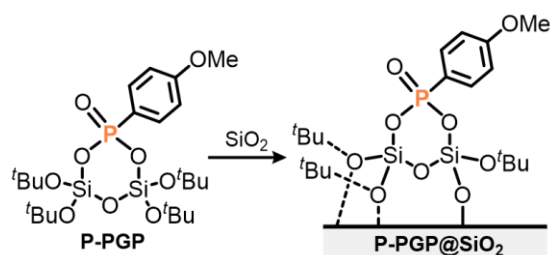


Table 1. phosphorous contents of grafted P-PGP and corresponding phosphonic acid.

Samples	Loaded P (wt%)	Grafted P (wt%)
P-PGP@SiO ₂	0.50	0.40
O=P(C ₆ H ₄ OMe)(OH) ₂ @SiO ₂	0.50	0.12

1)) Y. Ishizaka, N. Arai, K. Matsumoto, H. Nagashima, K. Takeuchi, N. Fukaya, H. Yasuda, K. Sato, J.-C. Choi, *Chem. Eur. J.* **2021**, 27, 12069. 2) Y. Ishizaka, K. Matsumoto, K. Sato, J.-C. Choi, *Chemistry-Methods*, DOI:10.1002/cmt.202100080.

Development of a New In Situ UV-vis Reflection Spectroscopy System for the Formic Acid Dehydrogenation

(¹Graduate School of Science and Technology, University of Tsukuba, ² National Institute of Advanced Industrial Science and Technology) ○Risheng Li,^{1,2} Tetsuya Kodaira,² Hajime Kawanami^{1,2}

Keywords: In-situ monitoring, UV-vis, homogeneous Ir catalyst.

In recent decades, formic acid (FA) has attracted significant attention and is regarded as one of the most promising liquid organic hydrogen carriers (LOHC).^{1,2} Although many efficient catalysts for FA dehydrogenation (FADH) are developed³⁻⁵, little research has been reported on the reaction mechanisms by “*in situ*” measurements.⁶ Herein, we developed a new *in situ* UV-Vis reflection spectroscopy system, as shown in Figure 1, to monitor FADH catalyzed by Ir homogenous complexes (Ir-4DHBP) in gas-liquid mixed phase. In this system, instead of detecting the transmittance intensity conventionally, the incident light was led to the sample solution, then diffusely reflected by homogeneously scattered inorganic particles (α -Al₂O₃) in the sample solution, then diffuse reflected light was collected by the concave mirror, and finally detected by the spectrometer. When the UV-Vis transmitted spectrum during FADH was measured, we could not obtain any peaks of the solution (Figure 2, green line). Whereas, by applying this method, we succeeded to obtain the stable UV-Vis spectrum with low S/N during FADH (Figure 2, black line), in which the curve shape is consistent with the conventional UV-vis spectra of Ir complex (Ir-4DHBP) in 0.01M sulfuric acid aqueous solution (Figure 2, blue line). In this presentation, we will discuss FADH with the UV-Vis spectra by our system.

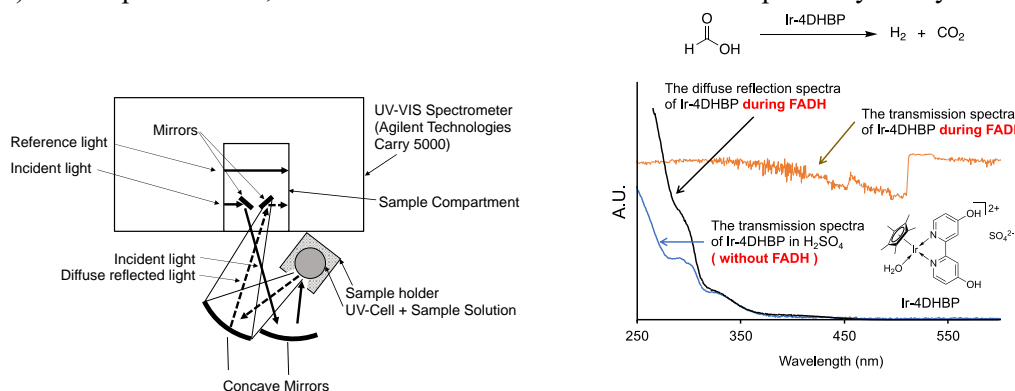


Figure 1 UV-Vis Diffuse Reflection System. **Figure 2** Obtained Spectrum under various conditions.

1) Kawanami, H. et. al, Adv. Inorg. Chem, **2017**, 70, 395-427. 2) Züttel, A. et. al, Hydrogen as a future energy carrier, **2008**. 3) Himeda, Y., Green Chem., **2009**, 11, 2018. 4) Zhong, S. et. al, ACS Appl. Mater. Interfaces, **2021**, 13, 46749. 5) Patra, S. et. al, Inorg. Chem., **2021**, 60, 14275. 6) Aghmiz, A. et. al., J. Mol. Catal. A: Chemical, **2003**, 195, 113.

TiO₂ 表面上の分子吸着に関するフロンティア軌道理論

(福工大工¹・北大触媒科学研²・産総研³・理研⁴・京大元素戦略拠点⁵) ○蒲池 高志^{1,5}・濱本 信次¹・巽 俊暢¹・高尾 基史²・鳥屋尾 隆^{2,5}・日沼 洋陽³・前野 禅²・高草木 達²・古川 森也^{2,5}・瀧川 一学⁴・清水 研一^{2,5}

Frontier Orbital Theory of Molecular Adsorption on TiO₂ Surface (¹Fukuoka Institute of Technology, ²Hokkaido Univ., ³National Institute of Advanced Industrial Science and Technology, ⁴RIKEN, ⁵ESICB) ○Takashi Kamachi Kamachi^{1,5}, Nobutsugu Hamamoto¹, Toshinobu Tatsumi¹, Motoshi Takao², Toyao Takashi^{2,5}, Yoyo Hinuma³, Zen Maeno², Satoru Takakusagi², Shinya Furukawa^{2,5}, Ichigaku Takigawa⁴, Ken-ichi Shimizu²

Frontier orbital theory has played an important role in the interpretation of various chemical phenomena thus far. This theory has been fundamentally applied in the design of molecular systems but has not been fully utilized for solid catalysts because of the complexity of the interactions. In this study, we use first-principles calculations and regression analyses to investigate the behavior of frontier orbital for molecular adsorption on solid catalysis, which is a critical step in the initial stage of a catalytic reaction. We adopt the anatase (101) and rutile (110) TiO₂ surfaces as research targets.

Keywords : molecular adsorption, TiO₂, Frontier Molecular Orbital Theory

故福井謙一教授がフロンティア軌道(FMO)理論[1]を発表してから既に 70 年近く経過したが、あらゆる化学現象を俯瞰的に理解するための基本的な概念として現在も広く受け入れられている。本研究では TiO₂ 表面における分子吸着に焦点をあて、網羅的な DFT 計算と最新のインフォマティクス手法を用いて、複雑な表面での相互作用を FMO 理論からどの程度評価できるのか明らかにした[2]。

最安定なアナターゼ(101)面とルチル(110)面への 41 種類の分子の吸着エネルギーを周期的密度汎関数法により見積もった。汎関数は PBEsol を使い、吸着エネルギーを正確に見積もるために Grimme の分散力補正を加えた。

図 1 のようにアナターゼ(101)面における吸着エネルギーと HOMO のエネルギー準位とのあいだに高い相関が見られた。一方で、LUMO との相関は見られなかった。表面の吸着においても、FMO 理論が示すとおりフロンティア軌道が重要であり、特に HOMO のエネルギー準位が重要な役割を果たしていることを示している。さらに、分子を炭化水素とヘテロ原子を含む化合物にグループ分けするとさらに高い相関関係があることが判明した。炭化水素はファンデルワールス力が主な物理吸着、ヘテロ原子を含む化合物は表面 Ti 原子への結合生成を伴う化学吸着と表面との相互作用が本質的に異なるため、グループ分けによる相関の向上につながったものと考えられる。

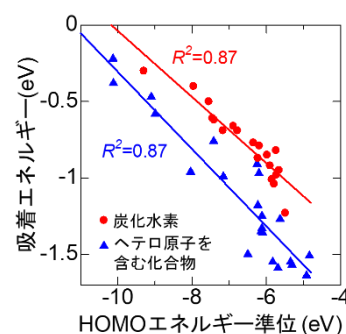


図 1. アナターゼ(101)面における吸着エネルギーと HOMO 準位の相関関係。

- 1) K. Fukui, T. Yonezawa, H. Shingu, *J. Chem. Phys.* **1952**, *20*, 722.
- 2) T. Kamachi, T. Tatsumi, T. Toyao, Y. Hinuma, Z. Maeno, S. Takakusagi, S. Furukawa, I. Takigawa, K. Shimizu, *J. Phys. Chem. C* **2019**, *123*, 20988.
- 3) N. Hamamoto, T. Tatsumi, M. Takao, T. Toyao, Y. Hinuma, Shimizu, T. Kamachi, *J. Phys. Chem. C.*, **2021**, *125*, 3827.

Synthesis of Pt/TiO_{2-x} Photocatalyst via Reduction Assisted by Hydrogen Spillover and Formation Mechanism of Surface-exposed Ti³⁺

(¹Graduate School of Engineering, Osaka University, ²Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, ³JST PRESTO, ⁴Kyoto Institute of Technology) ○Yukari Yamazaki,¹ Kohsuke Mori,^{1, 2} Yasutaka Kuwahara,^{1, 2, 3} Hisayoshi Kobayashi,⁴ Hiromi Yamashita^{1, 2}

Keywords: Reduced titanium dioxide, Hydrogen spillover, Photocatalyst

Defect engineering is one of the important strategies in the field of heterogeneous catalysts. Reduced metal cation and concomitant oxygen vacancy (V_O) in semiconductor oxide, as represented by TiO_{2-x} including Ti³⁺ and V_O, play an important role in various catalytic and photocatalytic reactions.¹ In the application of TiO_{2-x} photocatalyst, the introduced defects form donor level below the conduction band, thereby providing remarkable photocatalytic performance by improvement of the electron conductivity and narrowing its inherent bandgap. Although the effect of defects on the photocatalytic activity and the development of facile reduction method is one of the hot topics of research, the formation mechanism of defects has caught less attention.

In this study, we synthesized Pt deposited TiO_{2-x} photocatalyst via a reduction treatment assisted by hydrogen spillover from rutile, anatase, or brookite TiO₂ as a starting material.² As a result of ESR measurement, surface-exposed Ti³⁺ and V_O were observed in rutile and brookite Pt/TiO_{2-x} after the reduction treatment. Notably, rutile Pt/TiO_{2-x} included a more amount of defects, therefore photocatalytic activity was enhanced by the reduction treatment. In contrast, anatase Pt/TiO_{2-x} included V_O but not surface-exposed Ti³⁺. During the reduction treatment, Ti⁴⁺ was reduced to Ti³⁺ by an electron donation from spillover H atom to TiO₂ conduction band and V_O formation occurred via dehydration (Fig. 1). The obtained results suggest that the depth of the inherent midgap states, depending on the crystal phases, influences the formation of surface-exposed Ti³⁺.

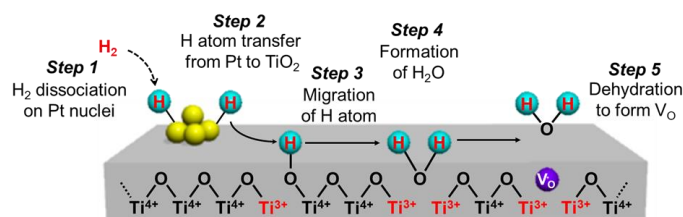


Fig. 1. Possible scheme of defect formation by the reduction assisted by hydrogen spillover.

1) Y. Yamazaki, T. Toyonaga, N. Doshita, K. Mori, Y. Kuwahara, S. Yamazaki, H. Yamashita, *ACS Appl. Mater. Interfaces*. DOI: 10.1021/acsami.1c20148. 2) Y. Yamazaki, K. Mori, Y. Kuwahara, H. Kobayashi, H. Yamashita, *ACS Appl. Mater. Interfaces* **2021**, 13, 48669.

還元性金属酸化物における水素スピルオーバー経路の解明

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Unraveling Hydrogen Spillover Pathways over Reducible Metal Oxide (¹Graduate School of Engineering, Osaka University, ²ESICB Kyoto University, ³Kyoto Institute of Technology)

○Kohsuke Mori,^{1,2} Shun Kazuki,¹ Shinya Masuda,¹ Naoki Hashimoto,¹ Hisayoshi Kobayashi,³ Hiromi Yamashita^{1,2}

Hydrogen spillover in typical reducible metal oxides, such as TiO₂, CeO₂, and WO₃, was elucidated by combining systematic characterization methods involving various *in situ* techniques and kinetic analysis. TiO₂ and CeO₂ were proven to be promising platforms for the synthesis of non-equilibrium RuNi binary solid solution alloy nanoparticles displaying a synergistic promotional effect in the hydrolysis of ammonia borane. Such behavior was driven by the simultaneous reduction of both cations under a H₂ atmosphere over TiO₂ and CeO₂, in which hydrogen spillover favorably occurred over their surfaces rather than within their bulk phases. Conversely, hydrogen atoms were found to preferentially migrate within the bulk prior to the surface over WO₃. Thus, the reductions of both cations occurred individually on WO₃, which resulted in the formation of segregated NPs with no activity enhancement.

Keywords : *Hydrogen Spillover; Alloy Nanoparticle; Reducible Metal Oxide*

水素スピルオーバーとは、金属粒子上で解離吸着した水素原子が触媒担体へと流れる現象である¹⁾。これまで我々は Ru³⁺と Ni²⁺を担持した TiO₂ に水素昇温還元を施すと水素スピルオーバーが発現し、その強い還元駆動力によって非平衡 RuNi 合金粒子が形成することを見出してきた^{2,3)}。本研究では、この RuNi 合金粒子が各種還元性酸化物担体上で形成するかどうかを指標とすることで、それぞれの水素スピルオーバー機構の解明を目指した。

アンモニアボランからの水素生成反応において、RuNi/TiO₂、RuNi/CeO₂ はともに Ru のみを担持した触媒と比べて合金効果により高い活性を示した。一方、RuNi/WO₃ では合金効果が発現せず Ru/WO₃ と同等の活性を示した。H/D 交換反応を利用した *in-situ* DRIFT 測定では、TiO₂ の場合 50 °C で、CeO₂ では 50~150 °C の間で 2600-2700 cm⁻¹ 付近に δ_{O-D} 基が観察された。すなわち TiO₂ や CeO₂ では表面のスピルオーバーが優先的に起こり、それゆえ Ru と Ni の合金化が促進されたと言える。一方、WO₃ では 150~250 °C の間でピークが確認されたことから内部のスピルオーバーが優先的に進行するため合金が生成しなかったと言える。

1) K. Mori, N. Hashimoto, N. Kamiuchi, H. Yoshida, H. Kobayashi, H. Yamashita, *Nat. Commun.*, **2021**, 12, 3884–3893

2) K. Mori, K. Miyawaki, H. Yamashita, *ACS Catal.*, **2016**, 6, 3128–3135.

3) S. Masuda, K. Shun, K. Mori, Y. Kuwahara, H. Yamashita, *Chem. Sci.*, **2020**, 11, 4194–4203.

[J202-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Masaki Kawano, Tomoji Ozeki

Wed. Mar 23, 2022 1:00 PM - 3:40 PM J202 (Online Meeting)

[J202-1pm-01] A Pseudorotaxane Structure with γ -Cyclodextrin Controlled by Chiral Recognition of an $\text{Au}^{\text{I}}_6\text{Ag}^{\text{I}}_3\text{Cu}^{\text{II}}_3$ Molecular Cap○Tatsuhiro Kojima¹, Hiroto Takeda¹, Naoto Kuwamura¹, Takumi Konno¹ (1. Osaka University)

1:00 PM - 1:20 PM

[J202-1pm-02] Slow magnetic relaxations of an $S=1/2$ copper(II) ion incorporated into the nuclear-spin-free Keggin-type tungstosilicate○Toshiharu Ishizaki¹, Tomoji Ozeki¹ (1. Nihon University)

1:20 PM - 1:40 PM

[J202-1pm-03] New Ligand for Metal-Organic Frameworks based on Tetrabenzo Chichibabin Hydrocarbons with Potential Close Shell-Diradical Transition○Zhongyue Zhang¹, Kunio Awaga¹ (1. Nagoya University)

1:40 PM - 2:00 PM

[J202-1pm-04] Study of luminescent Cu(I)-pyridinophane-arylamide complexes and their incorporation into polymer films: towards the development of mechanoresponsive materials○Tatiana Gridneva¹, Ayumu Karimata¹, Julia Khusnutinova¹ (1. Okinawa Institute of Science and Technology)

2:00 PM - 2:20 PM

[J202-1pm-05] Study of Multi-dimensional Transformations with Successive Reaction in Cu(II) Coordination Polymer○Yao Jing¹, Yukihiro Yoshida¹, Shintaro Kobayashi², Shogo Kawaguchi², Hiroshi Kitagawa¹ (1. Kyoto Univ., 2. Japan Synchrotron Radiation Research Institute (JASRI))

2:20 PM - 2:40 PM

[J202-1pm-06] Energy-efficient olefin separation by coordination networks using tetrahedral ligands.○JOONSIK KIM¹, Pavel M Usov¹, Yuki Wada¹, Hiroyoshi Ohtsu¹, Takaya Matsumoto^{1,2}, Masaki Kawano¹ (1. Tokyotech, 2. ENEOS Corporation)

2:40 PM - 3:00 PM

[J202-1pm-07] Temperature-dependent Wiggling of a Cu(II) Ion in Hydrogen-bonded Networks of a Zr– Mo Cluster○Ryoji Mitsuhashi¹, Yuya Imai¹, Sugiarto Sugiarto¹, Yuji Kikukawa¹, Yoshihito Hayashi¹ (1. Kanazawa Univ.)

3:00 PM - 3:20 PM

[J202-1pm-08] Design of Isolated Spaces for Selective CO₂ Adsorption○Terumasa Shimada¹, Pavel Usov¹, Yuki Wada¹, Hiroyoshi Ohtsu¹, Taku Watanabe², Takaya Matsumoto^{1,2}, Masaki Kawano¹ (1. Tokyo Institute of Technology, 2. ENEOS Corporation)

3:20 PM - 3:40 PM

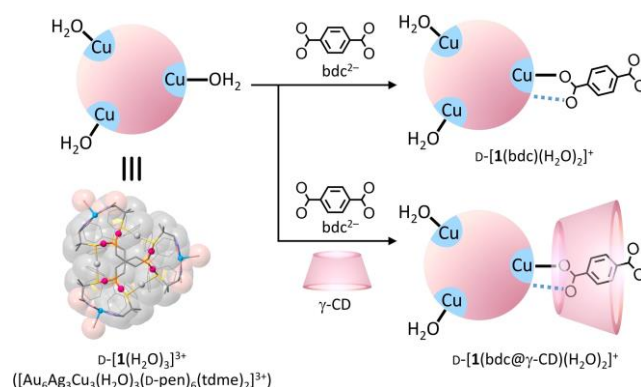
A Pseudorotaxane Structure with γ -Cyclodextrin Controlled by Chiral Recognition of an $\text{Au}^{\text{I}}_6\text{Ag}^{\text{I}}_3\text{Cu}^{\text{II}}_3$ Molecular Cap

(¹Graduate School of Science, Osaka University) ○Tatsuhiro Kojima,¹ Hiroto Takeda,¹ Naoto Kuwamura,¹ Takumi Konno¹

Keywords: Pseudorotaxane; γ -Cyclodextrin; Multinuclear Complex

Pseudorotaxane is a well-known supramolecule in which a macrocyclic molecular ring is threaded by a rod-shaped molecular axle, with its terminal position connected to a bulky molecular cap. The use of cyclodextrins (CDs) as molecular rings has been a target of intensive studies in recent decades because of their versatile molecular recognition abilities. Although the evaluation of intermolecular interactions between ring and axle molecules is essential to understand molecular recognition, most previous studies on pseudorotaxanes containing CDs as a molecular ring have been performed mainly via NMR spectroscopy in solution rather than X-ray crystallography in the solid state, and reports on the X-ray crystal structures of this class of supramolecules are scarce. In this presentation, we report a pseudorotaxane system with γ -CD controlled by chiral recognition of $[\text{Au}_6\text{Ag}_3\text{Cu}_3(\text{H}_2\text{O})_3(\text{D-pen})_6(\text{tdme})_2]^{3+}$ ($\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$; pen^{2-} = penicillamate, tdme = 1,1,1-tris(diphenylphosphinomethyl)ethane), the structure of which was established by single-crystal X-ray crystallography.¹

Soaking crystals of $\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$ in aqueous Na_2bdc (bdc^{2-} = 1,4-benzenedicarboxylate) yielded crystals containing $\text{D-}[\mathbf{1}(\text{bdc})(\text{H}_2\text{O})_2]^+$ due to the replacement of a terminal aqua ligand in $\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$ by a monodentate bdc^{2-} ligand. When γ -CD was added to aqueous Na_2bdc , $\text{D-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$ was transformed to $\text{D-}[\mathbf{1}(\text{bdc}@ \gamma\text{-CD})(\text{H}_2\text{O})_2]^+$, where a γ -CD ring was threaded by a bdc^{2-} molecule to construct a pseudorotaxane structure. While the use of dicarboxylates with an aliphatic carbon chain instead of bdc^{2-} afforded analogous pseudorotaxanes, such pseudorotaxane species were not formed when crystals of $[\text{Au}_6\text{Ag}_3\text{Cu}_3(\text{H}_2\text{O})_3(\text{L-pen})_6(\text{tdme})_2]^{3+}$ ($\text{L-}[\mathbf{1}(\text{H}_2\text{O})_3]^{3+}$) were soaked in aqueous Na_2bdc and γ -CD, affording only crystals containing $\text{L-}[\mathbf{1}(\text{bdc})(\text{H}_2\text{O})_2]^+$.



1) T. Kojima, H. Takeda, N. Kuwamura, T. Konno, *Chem. Eur. J.* **2021**, 27, 15981.

Slow magnetic relaxations of an $S=1/2$ copper(II) ion incorporated into the nuclear-spin-free Keggin-type tungstosilicate

(¹College of Humanities and Sciences, Nihon University) ○Toshiharu Ishizaki,¹ Tomoji Ozeki¹

Keywords: Slow magnetic relaxations, $S=1/2$, Copper(II) complex, Polyoxometalate.

Recently, slow magnetic relaxations of $S=1/2$ systems after removal of an applied magnetic field are expected as the spin qubit for quantum information processing device.¹ In order to increase relaxation times, it is important to suppress the fast quantum tunneling relaxations which facilitated by dipolar interactions and hyperfine interactions in this system. From this point of view, large, rigid and nuclear-spin-free polyoxometalates would be useful for the ligand toward the potential spin qubits.² However, reported examples of slow relaxation behaviors, especially complexes with only one spin center are very limited. Here we report, slow magnetic relaxations of copper(II) ion incorporated in the large, rigid and nuclear-spin-free tungstosilicate are presented.

The tetrabutylammonium salt $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Cu}]]$ (**1**) was prepared from the potassium salt.³ The X-band ESR spectrum of powder form of **1** showed well separated four peaks originated by the copper(II) ion. The g -value was decreasing and A -value was increased compared with the potassium salt, which would indicate decreasing coordination number from six to five by removing terminal water ligand.⁴ DC magnetic susceptibility measurements indicated $S=1/2$ state of **1**. AC magnetic susceptibility measurements revealed that **1** shows slow magnetic relaxations in an applied static magnetic field (H_{DC}). The temperature- and static-field-dependences of extracted relaxation times of 5 % magnetically diluted **1** $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Cu}_{0.05}\text{Zn}_{0.95}]]$ (**dil.1**) collected in $H_{\text{DC}}=3000$ Oe and at 1.8 K, respectively, were successfully reproduced by simultaneously fitting of direct, Raman and quantum tunneling processes.⁵ From the analyses, Raman relaxation process is dominated at all measured temperatures in $H_{\text{DC}}=3000$ Oe. The utilization of nuclear-spin-free polyoxometalate ligand seems to have reduced the contribution of quantum tunneling process even at low temperatures.

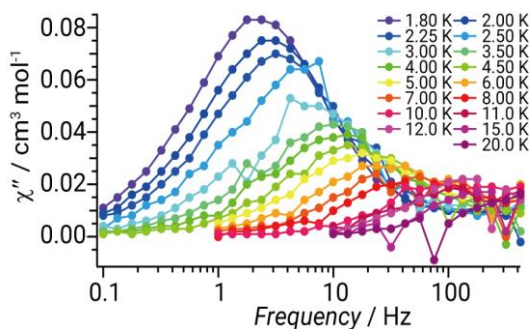


Fig.1 Frequency dependence of out-of-phase susceptibilities of **dil.1** in $H_{\text{DC}}=3000$ Oe at indicated temperatures.

1) R. Sessoli *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 2154. 2) E. Coronado *et al.*, *Chem. Soc. Rev.*, **2012**, *41*, 7464. 3) L.-N. He *et al.*, *Green Chem.* **2016**, *18*, 282. 4) A. M. V. Cavaleiro *et al.*, *Polyhedron* **1999**, *18*, 1163. 5) T. Ishizaki *et al.*, *Chem. Eur. J.* **2021**, *27*, 12686.

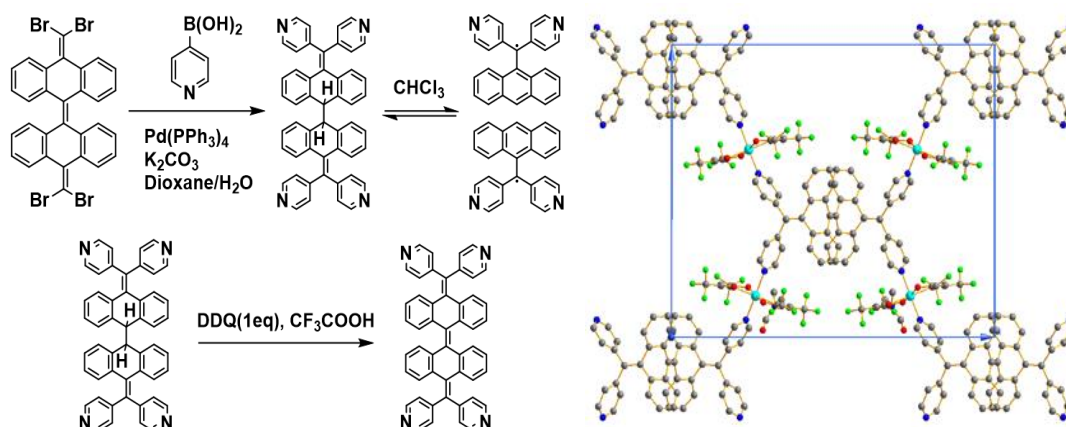
New Ligand for Metal-Organic Frameworks based on Tetrabenzo Chichibabin Hydrocarbons with Potential Close Shell-Diradical Transition

(¹Research Center for Materials Science, Nagoya University, ²Graduate School of Science, Nagoya University) ○Zhongyue Zhang,¹ Kunio Awaga,²

Keywords: Tetrabenzo Chichibabin Hydrocarbon; Diradical; Metal-Organic Frameworks; Redox Activity

The transition between the close-shell ground state and diradical state of organic compounds has been of interest in the past decade, especially when the spin-state transition is accompanied with a structural configuration alternation. To date, most such transitions are reported to occur in a solution state, which allows a rapid relaxation of the excited diradical state to the diamagnetic ground state. As a result, it is intriguing to explore the behavior of such diradicals in solid-state by incorporating such diradical unit into metal-organic frameworks (MOFs).

To achieve this target, a well-known diradical precursor, namely tetrabenzo Chichibabin hydrocarbon is selected and synthetically modified with four pyridine antennas. (4py-tbCH). Using the literature method to prepare the 4py-tbCH molecule, however, unprecedently yielded 2H-4py-tbCH, which exhibits a monomer-dimer equilibrium in solution. Oxidation to the 4py-tbCH could be achieved by Scholl reaction, and the MOF containing this ligand were obtained by diffusive mixing the solution of 4py-tbCH and Cu(hfac)₂. Solid-state cyclic voltammetry and electrochemistry, as well as the *ex situ* magnetometry and EPR measurements will be carried on the obtained MOF to evaluate the spin-state transition of the ligand upon the electrochemical oxidation or reduction.



References:

- 1) Zebing Zeng, *et al*, *J. Am. Chem. Soc.* **2012**, 134, 14513–14525.

Study of luminescent Cu(I)-pyridinophane-arylamide complexes and their incorporation into polymer films: towards the development of mechanoresponsive materials

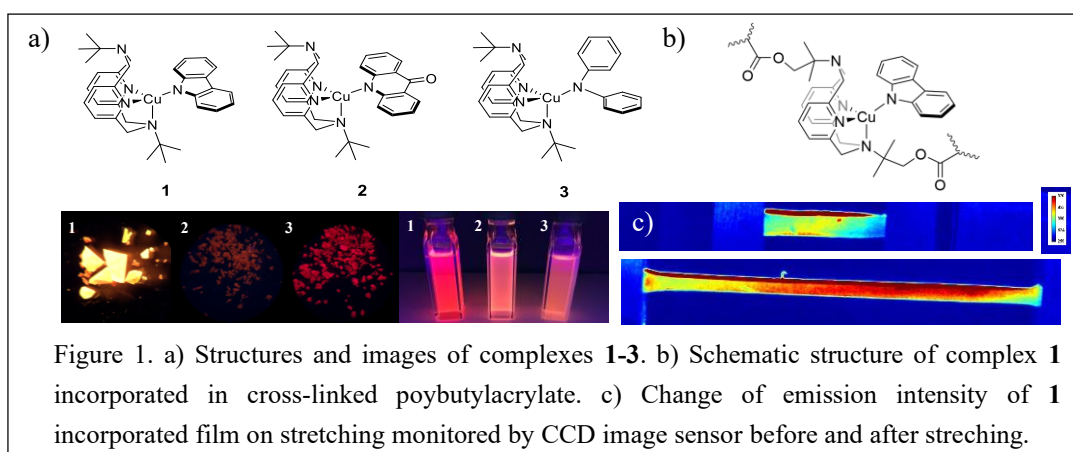
(¹Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology)

○Tatiana Gridneva,¹ Ayumu Karimata,¹ Julia Khusnutdinova¹

Keywords: Photoluminescent metal complexes, Mechanoresponsive materials, Cu(I)-emitters

Mechanoresponsive materials which change their optical properties in response to applied mechanical force are important for stress and damage sensing. Previously in our group, polybutylacrylate films incorporating photoluminescent copper(I)-NHC complexes as cross-linkers were developed.¹ The films show highly sensitive change of photoluminescent intensity upon stretching. The change is reversible and non-sacrificial, and the mechanism is considered to be suppression of the nonradiative decay by restricting the mobility of the complexes when stretching. However, there are still challenges such low miscibility of the complex in the polymer, which might arise from the cationic nature of the complex.

In this work, copper(I)-pyridinophane complexes bearing neutral arylamide ligands were synthesized as new mechanophores. The complexes show orange to red photoluminescence with the maximum wavelength up to 693 nm, representing limited examples of copper(I) red emitters. The properties of the complexes largely depend on the arylamide ligands, with the trend of complexes with more electron-donating ligands to give longer wavelength emission. The cross-linked polybutylacrylate films incorporating the complex **1** were prepared and found to show reversible change in photoluminescence intensity on stretching and releasing.



1. Karimata, A.; Patil, P. H.; Khaskin E.; Lapointe, S.; Fayzullin, R. R.; Khusnutdinova, J. R. *Chem. Commun.* **2020**, 56, 50-53

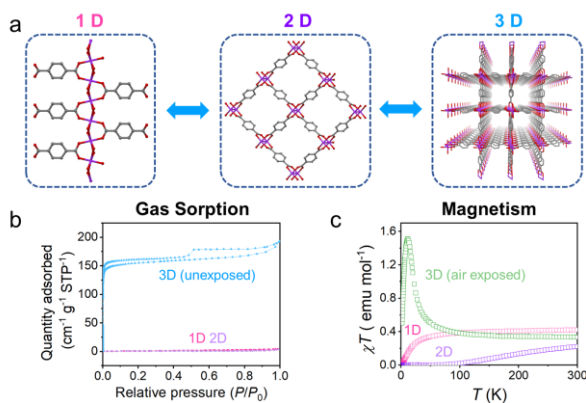
Study of Multi-dimensional Transformations with Successive Reaction in Cu(II) Coordination Polymer

(¹Graduate School of Science, Kyoto University, ²Japan Synchrotron Radiation Research Institute) ○Yao Jing,¹ Yukihiro Yoshida,¹ Shintaro Kobayashi,² Shogo Kawaguchi,² Hiroshi Kitagawa¹

Keywords: Coordination polymer; Multi-dimensional transformations; Successive reaction; Gas sorption; Magnetism

Dimensionality of atomic or molecular arrangements through chemical bonds plays a crucial role in determining the electronic properties of solids. Coordination polymers (CPs) are a promising platform for investigating dimensional transformations, because the coordination bonds ($100\text{--}300\text{ kJ mol}^{-1}$), which are generally weaker than covalent bonds ($200\text{--}800\text{ kJ mol}^{-1}$), possess thermodynamically stable but kinetically labile metal-ligand interactions. Although considerable efforts are being undertaken to develop CPs with the dimensional transformation,¹ a multi-dimensional 1D/2D/3D reversible transformation has not been accomplished.

In this study, we succeeded in realizing the 1D/2D/3D reversible transformation for the first time in CPs comprising Cu(II) ions and bidentate terephthalate (BDC^{2-}). The 2D layered coordination framework in 2D Cu-BDC² was reversibly transformed into 1D chains due to the dissociation of the Cu(II) paddlewheels induced by water coordination (Figure a). The kinetics of 2D to 1D successive transformation passing through an intermediate phase was investigated in situ by synchrotron XRD. The 2D-to-3D transformation was achieved by removing DMF followed by the connection of the 2D sheets (Figure a). These dimensional transformations significantly changed chemical and physical properties such as gas sorption and magnetism. Although the nitrogen gas uptake in open-framework 1D and 2D Cu-BDC was insignificant, pronounced absorption was observed for 3D Cu-BDC (Figure b). Drastic difference in magnetic behavior is consistent with their coordination structures; uniform 1D chain of Cu(II) in 1D Cu-BDC and 2D sheet based on Cu(II)-paddlewheel dimers in 2D Cu-BDC. Ferromagnetic behavior observed in air-exposed 3D Cu-BDC is mainly attributed to the 3D structure formed by the connection of 2D sheets (Figure c).



- 1) a) M. Edgar *et al.*, *Chem. Eur. J.* **2001**, 7, 5168. b) R. Medishetty *et al.*, *Chem. Eur. J.* **2015**, 21, 11948.
2) C. Carson *et al.*, *Eur. J. Inorg. Chem.* **2009**, 2009, 2338.

Energy-efficient olefin separation by coordination networks using tetrahedral ligands

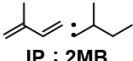
(¹*School of Science, Tokyo Institute of Technology*, ²*ENEOS Corporation*) ○Joonsik Kim,¹ Pavel M Usov,¹ Yuki Wada,¹ Hiroyoshi Ohtsu,¹ Takaya Matsumoto,^{1,2} Masaki Kawano¹

Keywords: Metal-organic frameworks; Hydrocarbon separation; X-ray crystallography

Unsaturated hydrocarbons are widely used in industry as raw materials, but they typically require the use of extractive distillation processes for purification, which consume large amounts of energy. To address this challenge, several metal-organic frameworks (MOFs) based on copper iodide were developed.¹ The presence of accessible pores inside these frameworks could be used for separating and isolating specific molecules from hydrocarbon mixtures.² However, there have not been many studies on the separation of olefin mixtures, especially including diene. Therefore, several pyridyl-based ligands were employed for MOF formation, providing promising candidates with high selectivity for olefins.

Currently, we succeeded in obtaining two types of MOF structures, which were investigated for their ability to separate olefin mixtures. Specifically, two ligands containing a rigid tetrahedral core were synthesized, and then combined with copper iodide to generate two MOFs comprised of helical copper iodide chains (denoted as MOF1 and MOF2). These materials were activated using two-step solvent exchange and vacuum treatment prior to guest sorption measurements. The mixture adsorption isotherms were calculated from the single component data using IAST (ideal adsorbed solution theory), which was used to determine guest selectivity. Remarkably, MOF1 showed a 327-fold selectivity of isoprene over 2-methylbutane (Table 1), which is considerably higher than previous studies.³

Table 1. Guest uptake and selectivity of each MOFs.

Material	Isoprene uptake, mmol/g	IAST Selectivity at 50 kPa	Reference
		 IP : 2MB	
MOF1	0.65	327 : 1	This work
MOF2	1.4	9.5 : 1	This work
MIL-125	4.4	1.1 : 1	3
NH ₂ -MIL-125	4.6	1.1 : 1	3

1) R. Robson, *J. Am. Chem. Soc.* **1989**, *111*, 5962-5964. 2) O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186-2187. 3) S. Kim, W. Ahn, *Catalysis Today*. **2013**, *204*, 85-93.

Temperature-dependent Wiggling of a Cu(II) Ion in Hydrogen-bonded Networks of a Zr–Mo Cluster

(¹*Institute of Liberal Arts and Science, Kanazawa University*, ²*Graduate School of Natural Science and Technology, Kanazawa University*) ○ Ryoji Mitsuhashi,¹ Yuya Imai,² Sugiarto,² Yuji Kikukawa,² Yoshihito Hayashi²

Keywords: Zr–Mo Cluster; Hydrogen-bonding Interactions

Coordination compounds with a degenerate energy state are known to distort spontaneously to remove its degeneracy owing to Jahn–Teller effect. A typical example of Jahn–Teller distortion in first-row transition metal ion is a hexacoordinated Cu(II) complex, which often exhibits a tetragonal elongation.¹ On the other hand, a trigonal distortion is difficult for Cu(II) complexes because the degeneracy will not be removed in this symmetry. We recently reported a Ti–Mo cluster, $[\text{Ti}\{\text{MoO}_3(\text{tacn})\}_6]^{4+}$ ($\text{tacn} = 1,4,7\text{-triazacyclononane}$).² This cluster spontaneously takes trigonal symmetry by intramolecular hydrogen-bonds and can propagate the symmetry over the crystal by intermolecular hydrogen-bonds. In this study, we focused on putting the simplest hexacoordinated Cu(II) complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in trigonal coordination environment by incorporating in hydrogen-bonded networks of $[\text{Zr}\{\text{MoO}_3(\text{tacn})\}_6]^{4+}$ (**ZrMO6**⁴⁺), which is analogous to the Ti–Mo cluster, and ClO_4^- .

A double salt of $[\text{Cu}(\text{H}_2\text{O})_6]\text{ZrMO6}(\text{ClO}_4)_6$ was prepared by a reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $[\text{MoO}_3(\text{tacn})]$ and $\text{Cu}(\text{ClO}_4)_2$. At 100 K, single-crystal X-ray analysis revealed that $[\text{Cu}(\text{H}_2\text{O})_6]\text{ZrMO6}(\text{ClO}_4)_6$ was crystallized in a trigonal system, and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ was successfully located at the crystallographic trigonal axis. At room temperature, on the other hand, the Cu(II) ions exhibited a positional disorder to form an aggregated compound with the Zr–Mo cluster (Figure 1). This positional disorder was observed even when the same crystal was employed for the measurements at both temperatures. This indicates that a Cu(II) ion is moving back and forth between two positions even in the crystal at high temperature. This temperature-dependent wiggling of the Cu(II) ion is further supported by variable temperature EPR measurements. This unique solid-state dynamic disorder for Cu(II) ion is presumably due to the frustrated secondary coordination sphere which enforces $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cation in trigonal symmetry.

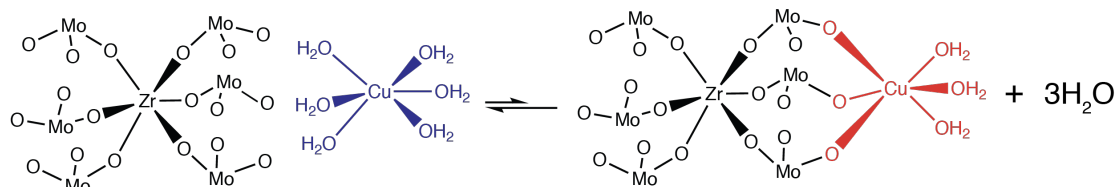


Figure 1. Schematic view of temperature-dependent wiggling of Cu(II) ion in the crystal.

1) M. A. Halcrow, *Chem. Soc. Rev.* **2013**, 42, 1748. 2) Sugiarto et al., *Inorg. Chim. Acta* **2020**, 509, 119691.

選択的 CO₂ 吸着のための孤立空間の設計

(東工大理¹・ENEOS (株)²) ○嶋田 光将¹・Pavel Usov¹・和田 雄貴¹・大津 博義¹・渡邊 卓²・松本 隆也^{1,2}・河野 正規¹

Design of Isolated Spaces for Selective CO₂ Adsorption (¹*School of Science, Tokyo Institute of Technology*, ²*ENEOS Corporation*) ○Terumasa Shimada,¹ Pavel Usov,¹ Yuki Wada,¹ Hiroyoshi Ohtsu,¹ Taku Watanabe,² Takaya Matsumoto,^{1,2} Masaki Kawano¹

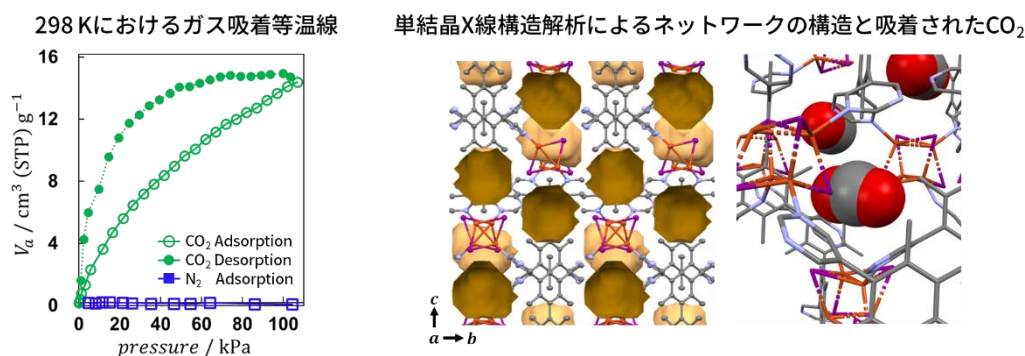
In this work, a novel porous coordination network was synthesized by combining a tetrahedral¹ ligand and copper(I) iodide. Although the network has isolated pores with no clear exterior access, it was able to selectively adsorb CO₂ at rt and maintain it for more than one week while exposed to atmosphere, as revealed by adsorption isotherms, IR spectra, and single crystal X-ray diffraction measurements. Furthermore, we determined the adsorption energy of CO₂ and its diffusion mechanism throughout the network using MatlantisTM, a high-speed versatile atomic-scale simulator. The calculations helped explain the adsorption mechanism, which was in good agreement with the experimental results. In conclusion, a novel design strategy for CO₂ sorbents based on isolated spaces was proposed.

Keywords : Metal-Organic Frameworks; Gas Adsorption; Carbon dioxide; X-ray Structure Analysis; Deep Learning

本研究では四面体型の配位構造¹⁾を持つピリミジン配位子とヨウ化銅(I)の組み合わせにより、新規の細孔性ネットワーク錯体を合成した。ネットワークは細孔として外部との接点を持たない孤立空間のみを有していたにもかかわらず、室温でCO₂を選択的に吸着し、加えて、空気中で1週間以上CO₂を貯蔵可能であることが吸着等温線およびIRスペクトル、単結晶X線回折の測定によって明らかになった。

さらに、汎用原子シミュレーターMatlantisTMを用いて、CO₂のネットワークに対する吸着エネルギー、およびネットワーク中のCO₂の拡散経路を計算した。それにより孤立空間へのCO₂の吸着メカニズムが説明され、実験結果との良い一致を示した。

以上から、孤立空間を利用したCO₂吸着材の新たな設計戦略を提案する。



1) Xiu-Liang Lv, Shuai Yuan, Lin-Hua Xie, Hannah F. Darke, Ya Chen, Tao He, Chen Dong, Bin Wang, Yong-Zheng Zhang, Jian-Rong Li, and Hong-Cai Zhou, *J. Am. Chem. Soc.* **2019**, 141, 26, 10283–10293

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[J403-1pm] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Masaya Enomoto, Hisashi Shimakoshi

Wed. Mar 23, 2022 1:00 PM - 3:40 PM J403 (Online Meeting)

[J403-1pm-01] Guest-selective Gate-Opening Behavior of Flexible Porous Coordination Polymer with Hydrogen-bond Keylock○Ken-ichi Otake¹, Yifan Gu¹, Jia-jia Zheng¹, Susumu Kitagawa¹ (1. Kyoto University)

1:00 PM - 1:20 PM

[J403-1pm-02] Direct EXSY NMR observation of reversible Co-Co bond homolysis○Satoshi Takebayashi¹, Robert Fayzullin², Richa Bansal¹ (1. Okinawa Institute of Science and Technology Graduate University, 2. Arbuzov Institute of Organic and Physical Chemistry)

1:20 PM - 1:40 PM

[J403-1pm-03] Study on a Spin-Crossover Behavior for a Cobalt(II) Complex with a hydrogen-bonded network○Takuya Kanetomo¹, Zhen Ni¹, Masaya Enomoto¹ (1. Tokyo University of Science)

1:40 PM - 2:00 PM

[J403-1pm-04] Adaptable water networks for capturing bioactive molecules inside the pores of a coordination network○Yuki Wada¹, Pavel M Usov¹, Hiroyoshi Ohtsu¹, Masaki Kawano¹ (1. Tokyo Tech)

2:00 PM - 2:20 PM

[J403-1pm-05] Photochemical Hydrogen Evolution from Alkaline Water Catalyzed by Co-NHC Complexes○Kosei Yamauchi¹, Yasunobu Wakafuji¹, Ken Sakai¹ (1. Kyushu University)

2:20 PM - 2:40 PM

[J403-1pm-06] Photochemical Hydrogen Production based on HCOOH/CO₂ cycle Catalyzed by Pentanuclear Cobalt Complex○Takuya Akai¹, Yutaka Saga¹, Mio Kondo^{1,2}, Shigeyuki Masaoka¹ (1. Osaka University, 2. JST PRESTO)

2:40 PM - 3:00 PM

[J403-1pm-07] Bulky and non-bulky PNP complexes with earth-abundant metals and their hydrogenation reactivity○Dilip Kumar Pandey¹, Robert R. Fayzullin², Julia Khusnutdinova¹ (1. Okinawa Institute of Science and Technology, 2. Arbuzov Institute of Organic and Physical Chemistry)

3:00 PM - 3:20 PM

[J403-1pm-08] Synthesis and Characterization of Ligand Modified Vitamin B₁₂ and Evaluation of the Catalytic Activities○Keita Shichijo¹, Yoshio Hisaeda¹, Hisashi Shimakoshi¹ (1. Kyushu Univ.)

3:20 PM - 3:40 PM

水素結合をキーロックとする柔軟な多孔性配位高分子のゲスト選択的ゲートオープン挙動

(京大 iCeMS¹) 大竹 研一¹、Yifan Gu¹、Jia-jia Zheng¹、北川 進¹

Guest-selective Gate-Opening Behavior of Flexible Porous Coordination Polymer with Hydrogen-bond Keylock (¹*Institute for Integrated Cell-Material Sciences, Kyoto University*) ○Ken-ichi Otake¹, Yifan Gu¹, Jia-jia Zheng¹, Susumu Kitagawa¹

Flexible porous coordination polymers (PCPs) have been extensively investigated because of their interesting gas adsorption properties such as gate opening behavior and shape-memory effect. In this work, we developed a novel PCP that exhibits highly selective gate-opening behavior toward a specific target molecule, by utilizing hydrogen-bond keylock design. This PCP has an interdigitated 2D sheet-type structure and exhibits reversible structural changes upon CO₂ sorption. The PCP design, syntheses, crystal structures, gas sorption behaviors, and theoretical characterization were investigated. Details of this study are reported.

Keywords : Porous Coordination Polymers; Crystal Structures; Gas sorption

柔軟な多孔性配位高分子 (PCP) は、ゲートオープン挙動や形状記憶効果などの興味深いガス吸着特性を持つことから、広く研究されている。報告者らは、様々なガス/蒸気に対する PCP の吸着・分離選択能に関して系統的な知見を得ることを目的として、一連の PCP 群の設計・合成を行い、その構造柔軟性とガス吸着特性について調べてきた。本研究では、水素結合のキーロックデザインを利用して、特定の標的ガス分子に対して高選択的なゲートオープン挙動を示す新規なフレキシブル多孔性配位を開発した。その中で非常に高い選択制を持って CO₂ 吸着特性を示す新規の PCP、**PCP-X** を見出した。PCP の設計、合成、結晶構造、ガス吸着挙動、および理論的な特性を調べた。**PCP-X** は、合成時には三次元ネットワーク構造を有している。

PCP-X は、熱活性化処理によって構造が大きく変化して、interdigitated 型二次元シート積層構造を持つ **PCP-X-act** となることが単結晶構造解析により明らかになった(図 1 左)。また、**PCP-X-act** は配位フリーの水酸基やピリジン基を骨格に有しており、各シート間が水素結合によって連結されていることもわかった。ガス吸着特性を調べたところ、**PCP-X** が可逆的な構造変化を伴いながら、CO₂ の吸着を行うことも明らかになった(図 1 右)。詳細は当日報告する。

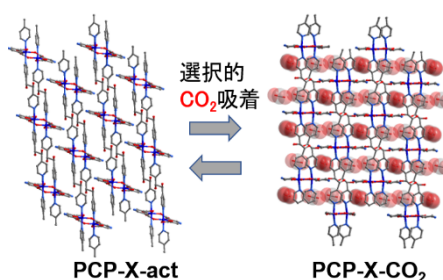


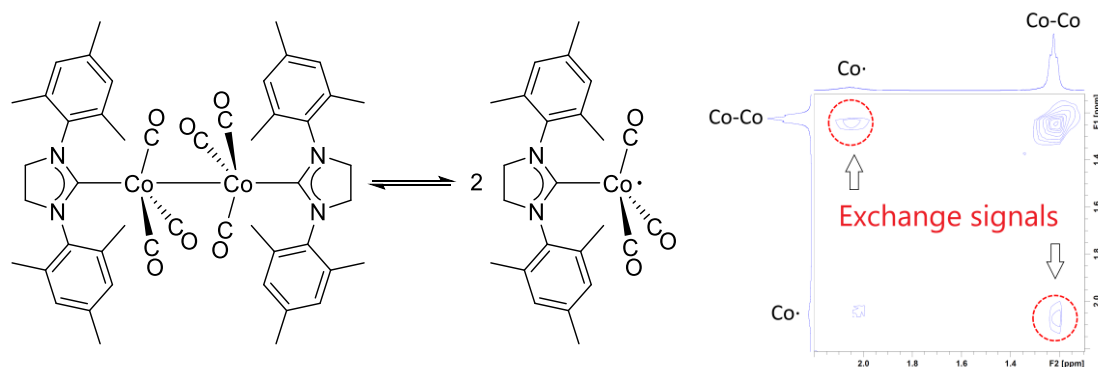
図 1. **PCP-X** の結晶構造の変化。Co:青色,C:灰色、N:水色,O:赤色で示した。CO₂ 吸着構造(**PCP-X-CO₂**)では、吸着された CO₂ 分子を半透明の vdW モデルで示した。

Direct EXSY NMR observation of reversible Co-Co bond homolysis

(¹Science and Technology Group, Okinawa Institute of Science and Technology Graduate University, ²Arbuzov Institute of Organic and Physical Chemistry) ○Satoshi Takebayashi,¹ Robert Fayzullin,² Richa Bansal¹

Keywords: Cobalt; Homolysis; NHC; Metalloradical; EXSY NMR

Bond homolysis is one of the two most fundamental bond breaking mechanisms in chemistry. Majority of bond homolysis is reversible reaction that favors recombination of the generated transient radical species. Steric crowding around radical center and delocalization of spin density shift this equilibrium towards generation of persistent radical species,¹ and by virtue of this stabilization, many radical species have been isolated.²⁻⁴ Conventionally, this reversibility is observed as a temperature dependent reversible change of spectra, however real-time observation of reversible bond homolysis is unknown. Two-dimensional exchange NMR (2D EXSY NMR) and 2D IR spectroscopies are powerful methods to observe real-time chemical exchanges. Large number of chemical exchanges with wide range of exchange time scales have been studied using these methods however, it's application to observe reversible homolytic bond cleavage is unknown. *In this talk, we report the first real-time 2D EXSY NMR observation of reversible homolytic bond cleavage using dimeric cobalt complexes.*



- (1) Griller, D. & Ingold, K. U. Persistent carbon-centered radicals. *Acc. Chem. Res.* **9**, 13-19 (1976).
- (2) Sakamaki, D., Ghosh, S. & Seki, S. Dynamic covalent bonds: approaches from stable radical species. *Mater. Chem. Front.* **3**, 2270-2282 (2019).
- (3) Hoff, C. D. Thermodynamic and kinetic studies of stable low valent transition metal radical complexes. *Coord. Chem. Rev.* **206-207**, 451-467 (2000).
- (4) Takebayashi, S. & Fayzullin, R. R. [Co(NHC)(CO)₃]: Isolation and Reactivity Study of a Model 17-Electron Species in the Oxo Process. *Organometallics* **40**, 500-507 (2021).

水素結合ネットワークを有した Co(II)金属錯体におけるスピントロソオーバー挙動の解明

(東理大理¹) ○金友 拓哉¹・倪 真¹・榎本 真哉¹

Study on a Spin-Crossover Behavior for a Cobalt(II) Complex with a Hydrogen-Bonded Network (¹Tokyo University of Science) ○Takuya Kanetomo,¹ Zhen Ni,¹ Masaya Enomoto¹

Hydrogen-bonded metal-organic frameworks (H-MOFs) are formed by a metal complex as a building block through the H-bond and have been applied to flexible porous molecular materials. In this study, we synthesized a terpyridine-based ligand, 5,5''-dicarboxy-2,2':6',2''-terpyridine (H₂5tpybCO₂) and a cobalt complex with two H₂5tpybCO₂ ligands, [Co^{II}(H₂5tpybCO₂)₂](H₂O)_{2.4}(DMF)_{1.2} (**1**·solv). Compound **1**·solv exhibited a 4-fold interpenetrating H-bonded diamond framework (Fig. 1a). The desolvated **1** showed a spin-crossover (SCO) behaviour with an asymmetric thermal hysteresis (Fig. 1b).

Keywords : Cobalt(II) complexes; Spin crossover; Hydrogen-bonded metal-organic frameworks

水素結合性金属有機構造体 (H-MOF) は金属錯体を構成単位として水素結合で連結した構造体であり、柔軟な分子性多孔質材料として近年研究が進められている。本研究では、2,2':6',2''-テルピリジンの5,5''位にカルボキシ基を導入した H₂5tpybCO₂ を配位子に H-MOF の開発を試みた。中心金属には Co²⁺ イオンを採用し、外場応答による可逆的なスピン状態の変化 (SCO 現象) を導入する。これにより、磁気スイッチング現象を伴う H-MOF の開発が期待できる。

新奇に合成した錯体 **1**·solv は、構造解析より、末端カルボキシ/カルボキシレート部位を介した分子間水素結合が存在する。これにより、錯体ユニットは4つの方向へ伸展したダイヤモンド格子を形成する (図 1a)。また、その格子は4重に相互貫入しており、1次元の空孔を与える。結晶溶媒はその空孔を占有しており、加熱による溶媒の脱離を熱分析から確認した。また、その脱離時に構造変化を示した。錯体 **1**·solv は室温以下で高スピン状態のみ示したが、脱溶媒後の **1** は 200–400 K の範囲で非対称な熱ヒステリシスループを伴う SCO 挙動を示した (図 1b)。

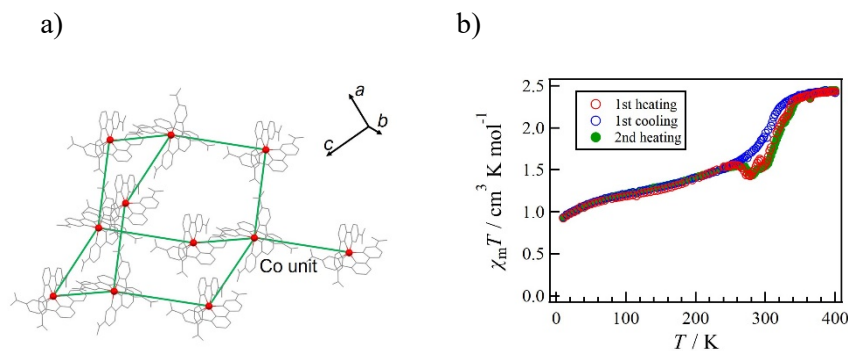


Fig. 1. (a) The H-bonded diamond framework of **1**. (b) $\chi_m T$ vs. T for the desolvated **1**.

Adaptable water networks for capturing bioactive molecules inside the pores of a coordination network

(School of Science, Tokyo Institute of Technology)

○Yuki Wada, Pavel M Usov, Hiroyoshi Ohtsu, Masaki Kawano

Keywords: Coordination networks; Host-guest interactions; Single crystal analysis; Structure determination; Bioactive compounds

X-ray analysis of compounds incorporated into the pores of coordination networks could not only reveal important information about the guest structures¹ and host-guest interactions,² but also monitor reaction intermediates³ and detect metastable species.⁴ However, to date, only a handful of host networks have been identified to be compatible for a wide range of substrates since guest capture and stabilization is typically promoted by a series of finely-balanced host-guest interactions, which are difficult to rationally design.

In this study, a coordination network with hexaazaphenalenyl based ligands was used for the encapsulation and structural characterization of several bioactive compounds. The single crystal analysis revealed that guest binding was facilitated by hydrogen-bonded water networks and clusters inside the pores, which adapted depending on the guest molecule, providing clearly defined crystallographic sites (Fig. 1). As a result, the guest structures could be determined with high resolution, and limited number of constraints and restraints.

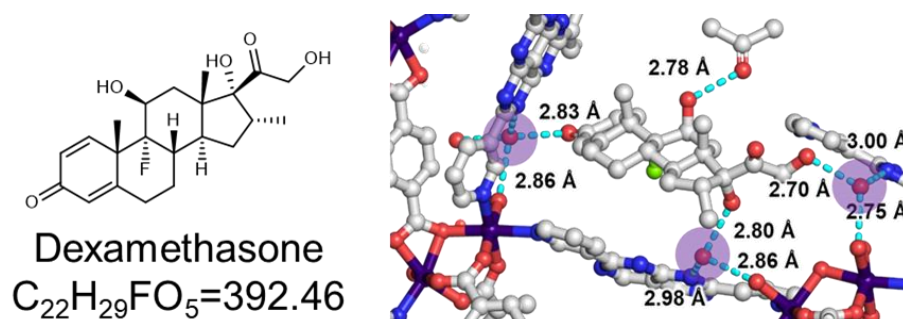


Fig. 1 Dexamethasone structure (left) and a crystal structure of encapsulated dexamethasone showing key hydrogen bonding interactions and their corresponding distances (right). Purple circles highlight water molecules that act as binding sites.

1) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita, *Nature*, **2013**, 495, 461–466. 2) Y. Wada, H. Ohtsu, P. M. Usov, B. Chan, K. Deekomwong, M. Kawano, *Inorg. Chem.*, **2021**, 60, 17858-17864. 3) T. Kawamichi, T. Haneda, M. Kawano, M. Fujita, *Nature*, **2009**, 461, 633-635. 4) H. Kitagawa, H. Ohtsu, A. J. Cruz-Cabeza, M. Kawano, *IUCrJ.* **2016**, 3, 232-236.

Photochemical Hydrogen Evolution from Alkaline Water Catalyzed by Co-NHC Complexes

(Department of Chemistry, Faculty of Science, Kyushu University)

○Kosei Yamauchi, Yasunobu Wakafuji, Ken Sakai

Keywords: artificial photosynthesis; hydrogen evolution; alkaline water splitting; cobalt complex; NHC

In order to realize overall water-splitting reaction ($2\text{H}_2\text{O} + 4h\nu \rightarrow 2\text{H}_2 + \text{O}_2$) on the basis of molecular systems, it is crucial to ensure sufficient driving force for both H_2 and O_2 evolution reactions (HER and OER). We have previously studied on molecular photosystems in which HER is driven by oxidative quenching of $[\text{Ru}^*(\text{bpy})_3]^{2+}$, but the reaction rates and turnover numbers were relatively low when **Co-NHC1** and other molecular catalysts were employed.^{1,2} On the other hand, the reductive quenching of $[\text{Ru}^*(\text{bpy})_3]^{2+}$ provides large driving force for HER but insufficient driving force for OER in the acidic to neutral pH range. In this study, we focus on a new strategy to maintain the driving force for both HER and OER by carrying out the reductive quenching process of $[\text{Ru}^*(\text{bpy})_3]^{2+}$ under highly alkaline conditions.

A large amount of H_2 (TON = 40000 at pH = 12.8) evolved when using a $[\text{Ru}(\text{bpy})_3]^{2+}$ /ascorbate photochemical system in the presence of a newly synthesized **Co-NHC3** catalyst for HER even under highly alkaline conditions (Figure 1). Furthermore, it was found that **Co-NHC3** is more durable than **Co-NHC1**. More interestingly, as the pH increased, sustained evolution of H_2 took place in larger amounts (pH < 12.8). We are now carefully investigating the factors correlating with this unusual pH response toward the catalytic activity. In the presentation, we will show the overall picture for photocatalytic cycle of HER by **Co-NHC3** and **Co-NHC1**.

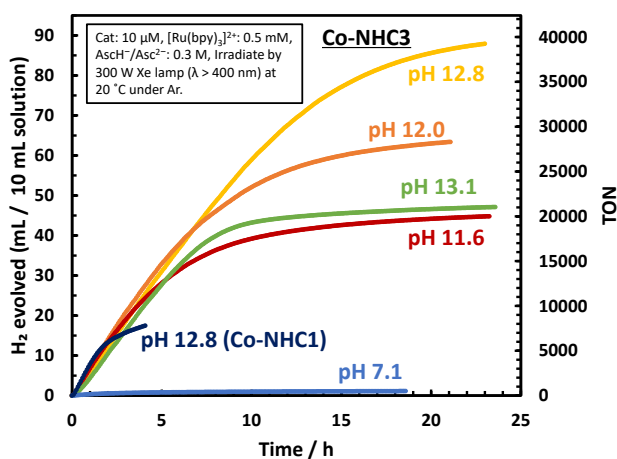
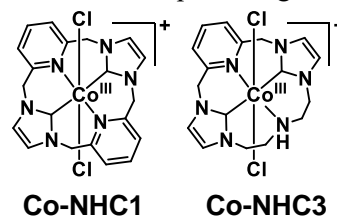


Figure 1. Photochemical H_2 Evolution from Alkaline Water Catalyzed by Co-NHC complexes.

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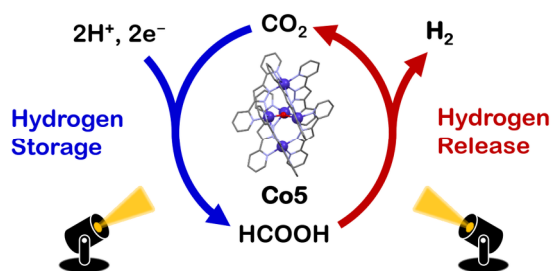
Photochemical Hydrogen Production based on HCOOH/CO₂ cycle Catalyzed by Pentanuclear Cobalt Complex

(¹Graduate School of Engineering, Osaka University, ²JST PRESTO) ○Takuya Akai,¹ Yutaka Saga,¹ Mio Kondo,^{1,2} Shigeyuki Masaoka¹

Keywords: Multinuclear Metal Complex; Photoreaction; CO₂ Reduction; Formic Acid Dehydrogenation

With the increasing demand for energy and the rapid depletion of fossil fuels, the development of renewable and environmentally friendly energy sources has become essential. Given this background, significant research efforts have focused on the liquid organic hydrogen carrier formic acid, which is a low-toxicity liquid under ambient conditions. Therefore, efficient catalysts for the production of formic acid and its conversion into hydrogen are required for utilisation of formic acid as a hydrogen carrier.

In this work, we developed a novel pentanuclear cobalt complex ($[\text{Co}_5\text{OH}(\text{bpp})_6]^{3+}$, **Co5**, Hbpp = 3,5-bis(2-pyridyl)pyrazole) and investigated its photocatalytic activity for the production and dehydrogenation of formic acid (**Fig.**). The photoirradiation of a solution containing **Co5**, a photosensitizer and a sacrificial electron donor in a CO₂ atmosphere resulted in the formation of formic acid, carbon monoxide, and hydrogen.¹ Surprisingly, the evolution of hydrogen was completely suppressed in an Ar atmosphere, indicating that CO₂ is required for the generation of hydrogen. The photoirradiation of a solution containing **Co5**, a photosensitizer, a sacrificial electron donor and formic acid in an Ar atmosphere resulted in the formation of hydrogen and CO₂. Therefore, the first catalytic cycle for hydrogen production based on the photochemical two-electron reduction of CO₂ and the dehydrogenation of formic acid was demonstrated.² Under the optimized conditions, the turnover frequency (TOF) of **Co5** for the dehydrogenation reaction of formic acid was higher (229 h⁻¹) than those reported for other molecular catalysts that operate under photoirradiation at ambient temperature. In addition, mechanistic studies were performed to elucidate the underlying mechanism of the catalytic cycle.



1) T. Akai, M. Kondo, S. K. Lee, H. Izu, T. Enomoto, M. Okamura, Y. Saga and S. Masaoka, *Dalton Trans.*, **2020**, 49, 1384.

2) T. Akai, M. Kondo, Y. Saga and S. Masaoka, *Chem. Commun.*, **2022**, accepted, DOI: 10.1039/D1CC06445B.

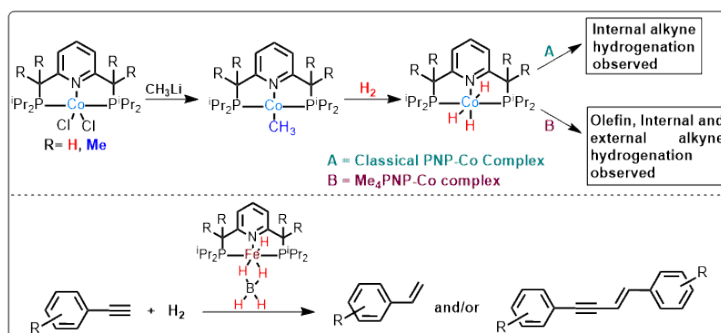
Bulky and non-bulky PNP complexes with earth abundant metals and their hydrogenation reactivity

(¹Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, Okinawa, ²Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Russian Federation) ○ Dilip K. Pandey,¹ Robert R. Fayzullin,² and Julia R. Khusnutdinova¹

Keywords: PNP Pincer; Cobalt complexes; hydrogen activation; Hydrogenation; Alkenes and alkynes

Precious transition metal complexes with PNP-pincer ligand backbone have exhibited substantial catalytic activity in a variety of hydrogenation and dehydrogenation reactions. Recent efforts are being made on the substitution of precious transition metals with cheaper, first row transition metals.¹

In this regard, cobalt and iron complexes with pincer ligands came up as potential solution for catalyzing the hydrogenation of alkenes, alkynes, ketones, aldehydes, and imines, etc. in presence of molecular hydrogen.² We



have previously developed a novel bulky PNP ligand, in which metal-ligand cooperation is disabled by methylation of the CH_2 arms, leading to unusual reactivity with Ni complexes.³ Herein, we report Co and Fe complexes with tetramethylated and classical PNP ligands and compare their reactivity in hydrogenation of alkenes and alkynes. We found that cobalt pincer complexes supported by the bulky tetramethylated PNP ligand $\text{Me}_4\text{PNP}^{\text{R}}$ ($\text{R} = ^i\text{Pr}$) are highly reactive towards H_2 and show catalytic activity in hydrogenation of alkenes and alkynes.⁴ The studies of the model systems show that in the case of Co(I) methyl complex as a precatalyst, the hydrogenation reactivity occurs via a sequence of two-electron oxidative addition and reductive elimination steps. This led to the development of catalytic protocol for alkene and alkyne hydrogenation. Finally, we will also discuss and compare the reactivity of Fe complexes with classical and tetramethylated PNP ligands in alkyne hydrogenation.

1) J. Wen et. Al, *Chem. Soc. Rev.* **2021**, 50, 3211. 2) K. Junge et. Al, *Chem. Eur. J.* **2019**, 25, 122. 3) a) S. Lapointe, E. Khaskin, R. R. Fayzullin, and J. R. Khusnutdinova, *Organometallics* **2019**, 38, 1581. And *Organometallics* **2019**, 38, 4433. 4) S. Lapointe, D. K. Pandey, J. M. Gallagher, J. Osborne, R. R. Fayzullin, E. Khaskin, and J. R. Khusnutdinova *Organometallics* **2021**, 40, 3617.

Synthesis and Characterization of Ligand Modified Vitamin B₁₂ and Evaluation of the Catalytic Activities

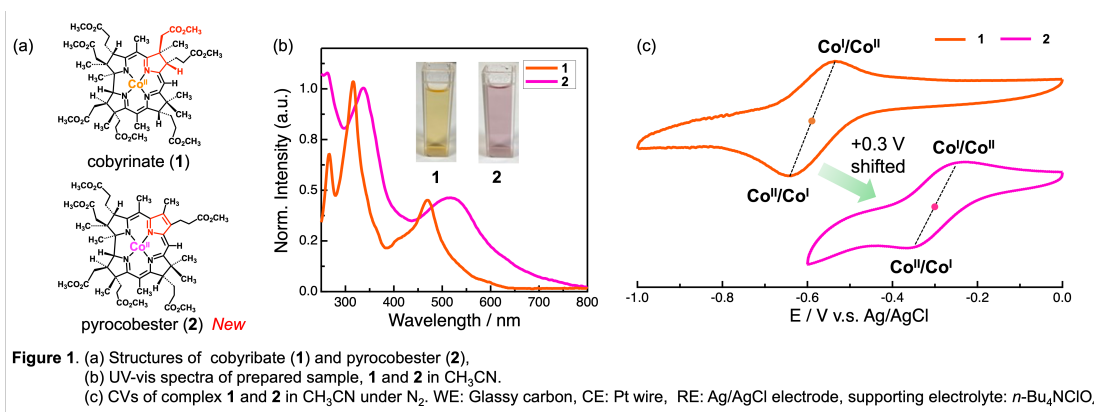
(Graduate School of Engineering, Kyushu University) ○Keita Shichijo, Yoshio Hisaeda, Hisashi Shimakoshi

Keywords: Vitamin B₁₂; Metal complex; Co-C complex; Catalytic reaction

Vitamin B₁₂ is a unique metal complex which has the cobalt ion and the corrin as a centered metal and a ligand, respectively. The Co(I) state of the vitamin B₁₂ reacts alkyl halide to form alkylated complex by the S_N2 type reaction and proceed the several catalytic reactions via alkyl radicals formed by homolysis of the cobalt-carbon bond.¹ Based on these characters of the vitamin B₁₂, many B₁₂-inspired reactions have been developed.² In general, many researchers have used the cobyrinate complex (**1**) as the B₁₂ derivatives. In this work, we succeeded the synthesis and characterization of the Co(II) state of pyrocobester (**2**) with π -expanded structure. Moreover, we clarified the catalytic reactivities of the complex.

The pyrocobester was synthesized by the pyrolysis of the cobyrinate.³ The absorption of the pyrocobester showed efficiently red-shift compared to the cobyrinate because of the conjugated corrin ligand (**Figure 1. (b)**). Furthermore, Co(II)/Co(I) redox potentials were +0.3 V shifted (**Figure 1. (c)**). In addition, the spectrum was changed after adding the CH₃I as the substrate. It is suggested that Co(I) state of pyrocobester reacted with CH₃I and alkylated complex (CH₃-Co(III)) was formed.

We constructed the eco-friendly photocatalytic system composed of the pyrocobester as the active center and tungsten oxide (WO₃) as visible light responsive photocatalyst. In this system, Co(I) species was formed under visible light irradiation by using water (or methanol) as electron source. In this presentation, we will report experimental detail of pyrocobester chemistry.



1) D. Gryko et al., *Chem. Soc. Rev.*, **2015**, 44, 3391. 2) H. Shimakoshi, Y. Hisaeda, *Chem. Rec.*, **2021**, 21, 2080. 3) B. Kräutler et al., *Helv. Chim. Acta.*, **1983**, 66, 1493.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[J402-1pm] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Michito Yoshizawa, Keishiro Tahara

Wed. Mar 23, 2022 1:00 PM - 3:40 PM J402 (Online Meeting)

[J402-1pm-01] *trans-cis* isomerism of Pt complex with *o*-aminobenzenethiol ligand○Pingping HUANG¹, Yukihiro YOSHIDA¹, Hiroshi KITAGAWA¹ (1. Kyoto Univ.)

1:00 PM - 1:20 PM

[J402-1pm-02] Small-Molecule Activation Driven by Metal-Metal Cooperation in Pt/Base Metal Complexes○GOVINDARAJAN RAMADOSS¹, Shubham Deolka¹, Eugene Khaskin¹, Robert R. Fayzullin², Shrinwantu Pal³, Rumpa Pal¹, Julia R. Khusnutdinova¹ (1. Okinawa Institute of Science and Technology Graduate University, 2. Abuzov Institute of Organic and Physical Chemistry FRC Kazan Scientific Center of RAS Arbuzov Street, Kazan 420088 (Russian Federation), 3. Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan)

1:20 PM - 1:40 PM

[J402-1pm-03] The intramolecular charge transfer properties of a benzothienobenzothiophene derivative complexed with a bulky Lewis acid○TAKASHI IKEDA¹, Keishiro Tahara¹, Toshikazu Ono², Yoshiki Ozawa¹, Masaaki Abe¹ (1. Univ. of Hyogo, 2. Kyushu Univ)

1:40 PM - 2:00 PM

[J402-1pm-04] Heterometallic interaction emerges from resonant inelastic X-ray scattering in luminescent Tb–Pt molecules.○Takefumi Yoshida¹, Yasuhiro Iwasawa¹, Masahiro Yamashita² (1. The University of Electro-Communications, 2. Tohoku University)

2:00 PM - 2:20 PM

[J402-1pm-05] Two Steps One-dimensional Reaction of Platinum-Rhodium Dinuclear Complexes and Several Metal Species○Kazuhiro Uemura¹, Yuya Ikeda², Atsushi Takamori³, Tomoyuki Takeyama⁴ (1. Faculty of Engineering, Gifu University, 2. Graduate School of Natural Science and Technology, Gifu University, 3. Graduate School of Engineering, Gifu University, 4. Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology)

2:20 PM - 2:40 PM

[J402-1pm-06] Synthesis and physical properties of a functionalized cyclohexanedithiocarboxylate-based MMX-chain complex○Hayato Moriyama¹, Kazuya Otsubo¹, Kunihiisa Sugimoto², Hiroshi Kitagawa¹ (1. Kyoto University, 2. JASRI/SPring-8)

2:40 PM - 3:00 PM

[J402-1pm-07] A Polyaromatic Capsule Solid as a Vapor Adsorbent for Benzene Derivatives○Ryuki Sumida¹, Michito Yoshizawa¹ (1. Lab. for Chem. & Life Sci., Tokyo Inst. of Tech.)

3:00 PM - 3:20 PM

[J402-1pm-08] Vapor-controlled Assembly/Disassembly of an Anionic Pt(II)
Complex Loaded on a Cationic Nanosheet

○Masaki Yoshida¹, Tamami Morimoto¹, Atsushi Kobayashi¹, Masako Kato^{1,2} (1. Hokkaido University, 2. Kwansei Gakuin University)

3:20 PM - 3:40 PM

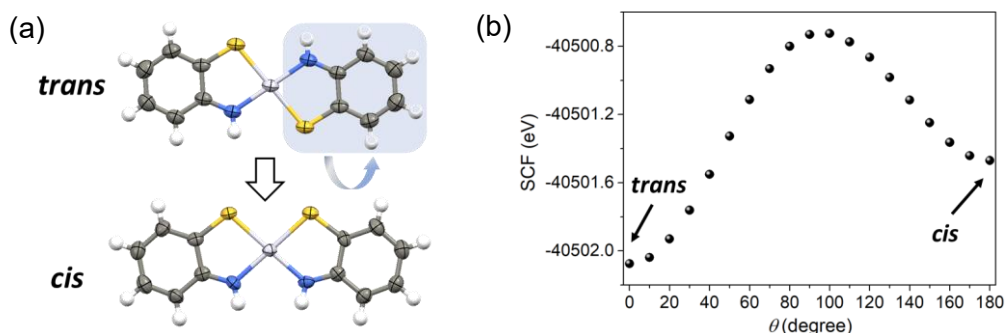
Trans-cis Isomerism of Pt Complexes with *o*-Aminobenzenethiol Ligand

(¹Graduate School of Science, Kyoto University) ○ Pingping Huang,¹ Yukihiro Yoshida,¹ Hiroshi Kitagawa¹

Keywords: π -planar Pt complexes; *trans-cis* isomerism; DFT; proton–electron coupling

Trans and *cis* isomers of Pt complexes have received widespread acceptance as a clinical drug for the treatment of various diseases.¹ In this study, a N,S-donor ligand, *o*-aminobenzenethiol, was reacted with Pt(II) salt in aqueous methanol solution under ambient atmosphere.² The neutral π -planar complexes, *trans*- and *cis*-Pt(itsq)₂ (itsq^{•−} represents the *o*-iminothiosemiquinonate π -radical; Figure a), were simultaneously harvested as dark-blue solids. Equilibrium dynamics for the *trans-cis* isomerization of the Pt complexes was evaluated by ¹H NMR spectroscopy in five kinds of organic solvents. It is found that the *trans* isomer is dynamically more stable than the *cis* isomer in most solvents and that the isomerization process is entropically controlled possibly *via* a solvent association mechanism. In addition, DFT calculations predicted that the *trans* isomer is 0.60 eV more stable than the *cis* isomer with a rotational barrier of 1.35 eV (Figure b).

Proton-coupled electron transfer (PCET) plays a pivotal role in biological and chemical processes.³ Molecules with π -electron systems, where the π -conjugation can be reconstructed by attaching or detaching protons, have been investigated to realize the PCET behavior. Metal complexes with π -ligands bearing Lewis acidic/basic sites are of great interest in understanding the PCET. In this study, we address the PCET behavior of the Pt complexes based on the pH-dependent absorption and electrochemical spectra in solution state. Given that the *trans* and *cis* isomers have different two-dimensional layered structures, i.e., those based on monomer and dimer units, respectively, the present system may provide a feasible platform for investigating the effect of molecular packing on the proton-electron coupled electron conduction and magnetism. The results are also discussed in detail.



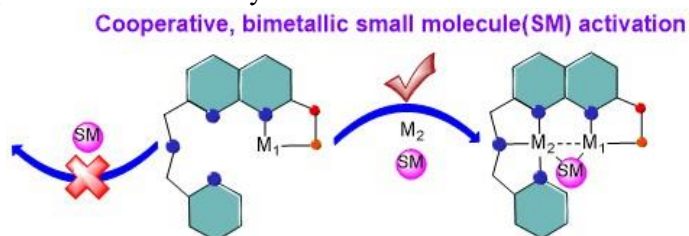
1) M. J. Abrams, B. A. Murrer, *Science* **1993**, 261, 725. 2) K. Matsumoto, I. Fukutomi, I. Kinoshita, S. Ooi, *Inorg. Chim. Acta* **1989**, 158, 201. 3) a) T. Mitani, G. Saito, H. Urayama, *Phys. Rev. Lett.* **1988**, 60, 2299. b) M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, 107, 5004.

Small-Molecule Activation Driven by Metal-Metal Cooperation in Pt/Base Metal Complexes

(¹Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, ² Arbuzov Institute of Organic and Physical Chemistry, FCR Kazan Scientific Center, Russian Academy of Sciences, ³ Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan) ○ Govindarajan Ramadoss,¹ Shubham Deolka,¹ Eugene Khaskin,¹ Robert R. Fayzullin,² Shrinwantu Pal,³ Julia R. Khusnutdinova*¹

Keywords: Heterobimetallic, Naphthyridine, Metal-metal cooperation, Small-molecule activation.

The design and exploration of a multimetallic complex has gained much interest owing to their great potential in catalysis and small molecule activation via cooperation of two or more metal centers. In particular, heterobimetallic complexes play a crucial role in small molecule activation since two different metal centers in proximity may allow facile activation of small and inert molecules.¹ However, the synthesis of selective heterobimetallic complexes is highly challenging due to unselective binding of two metal ions by the ligand core; in many cases scrambling of metal ions can occur. To overcome this synthetic difficulty our group has recently started working on the synthesis of unsymmetrical ligand scaffolds by functionalizing naphthyridine core at 2 and 7 positions, where one of the side arms has a soft phosphine donor and the opposite arm has a hard nitrogen donor. Such a ligand design allowed us to form selective heterobimetallic complex via stepwise synthesis. As a result, we previously reported metal-metal cooperative B-C and C-H bond activation by Pt/Cu heterobimetallic complexes,² Herein, we report the selective stepwise synthesis of heterobimetallic complexes where Pt showing close interaction with other non-transition, base metals in unsymmetrical 1,8-naphthyridine ligand core. This talk will cover the aspects about metal-metal cooperation and how the potential synergistic interaction between Pt and a base metal influence the reactivity towards H₂, Si-H, B-H and C-H activation of alkynes, while such reactivity is not observed when Pt alone or base metal alone are present. The presence of Pt-base metal interaction will be analyzed by QTAIM and NBO analyses.



- 1) A. N. Desnoyer, A. Nicolay, P. Rios, M. S. Ziegler, T. D. Tilley, *Acc. Chem. Res.* **2020**, *53*, 1944.
- 2) S. Deolka, O. Rivada, S. L. Aristizábal, R. R. Fayzullin, S. Pal, K. Nozaki, E. Khaskin, J. R. Khusnutdinova, *Chem.Sci.* **2020**, *11*, 5494.

かさ高いルイス酸と複合化したベンゾチエノベンゾチオフェン誘導体の分子内電荷移動特性の評価

(兵庫県立大院理¹・九大院工²) ○池田 貴志¹・田原 圭志朗¹・小野 利和²・小澤 芳樹¹・阿部 正明¹

The intramolecular charge transfer properties of a benzothienobenzothiophene derivative complexed with a bulky Lewis acid (¹Graduate School of Science, University of Hyogo, ²Graduate School of Engineering, Kyushu University)○Takashi Ikeda¹, Keishiro Tahara¹, Toshikazu Ono², Yoshiki Ozawa¹, Masaaki Abe¹

Recently, organic semiconductors have attracted great attention as organic materials because they have high flexibility and processability. We report the synthesis of a new benzothienobenzothiophene (BTBT) derivative by covalently introducing a pyridyl group. The BTBT derivative was bound with tris(pentafluorophenyl)borane as Lewis acid through the B-N bond formation. The obtained complex showed a red shift in the intramolecular charge transfer emission from BTBT to pyridyl moieties compared to the emission of the pyridyl derivatives. The photoluminescence quantum yields increased from 7.7 to 50% upon complexation. The complex crystallized in two forms containing π -stack columns and dimers, giving different emission properties.

Keyword : [1]benzothieno[3,2-b][1]benzothiophene, Intramolecular charge transfer, Luminescence, Crystalline polymorphs, Organic semiconductor

π 共役分子は優れた光機能特性や導電特性を有しており、有機エレクトロニクスを始めとする機能性材料の領域で注目を集めている。特に p 型有機半導体であるベンゾチエノベンゾチオフェン(BTBT)は高い正孔移動度と大気安定性を有していることから、機能性材料の優れた骨格として知られている。導電性に注目し、BTBT 誘導体を配位子とした配位高分子¹や金属錯体の自己組織化単分子膜²が報告されている。本研究では、光学特性に注目し、有機半導体の導電性と発光特性を兼ね備えた機能性分子材料の開発を目的とした。

BTBT に電子アクセプターであるピリジン部位を共有結合で導入し、BTBT-py を合成した。BTBT-py は、BTBT 部位からピリジン部位への分子内電荷移動(ICT)遷移による吸収と発光を示した。かさ高いルイス酸であるトリス(ペンタフルオロフェニル)ボラン(TPFB)と複合化を行い、BTBT-py-TPFB を合成した(図 1a)。複合化に伴う LUMO の低下により、トルエン溶液中で発光波長が 392 nm から 451 nm にレッドシフトし、蛍光量子収率が 7.7%から 50%に増大した。固体状態では、2 種類の結晶多形が得られ、BTBT 骨格が π スタックしたカラム構造とダイマー構造を含んでいた(図 1b)。カラム構造を含む結晶は、基底状態での会合に起因して、ダイマー($\lambda_{em} = 476$ nm)に比べ発光がレッドシフトした($\lambda_{em} = 516$ nm)。カラム構造は TPFB 部位に覆われ、他のカラムから孤立しており、積層方向への電気伝導と ICT 特性を組合わせた機能発現が期待される。

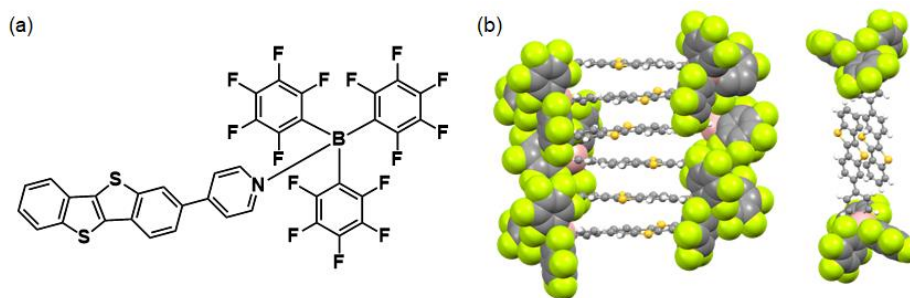


図 1. (a) BTBT-py-TPFB の化学構造. (b)結晶構造に含まれる π スタックカラム及びダイマー.

1) S. Koyama, H. Iguchi *et al.*, *Chem. Lett.*, 2019, **48**, 756–759.

2) K. Tahara, Y. Ashihara, T. Ikeda, T. Kadoya, M. Abe *et al.*, *Inorg. Chem.*, 2020, **59**, 17945–17957.

Heterometallic interaction emerges from resonant inelastic X-ray scattering in luminescent Tb–Pt molecules.

(¹The University of Electro-Communications, ²Tohoku University) ○Takefumi Yoshida,¹ Yasuhiro Iwasawa,¹ Masahiro Yamashita²

Keywords: resonant inelastic X-ray scattering; heterometallic interaction; platinum; terbium.

The heterometallic complexes have been utilized in a variety of researches such as luminescence, catalysis, and magnetism. Luminescence has received particular interests from viewpoints of luminescence devices, bio-imaging, photosensitizers, etc. Moreover, heterometallic interaction is also an important issue in the luminescence event of heterometallic complexes, and great efforts have been devoted to the design of various intermetallic interactions. Although high-resolution X-ray diffraction can visualize the electron density of bonds,¹ theoretical calculation dominates the method to examine intermetallic interactions. We synthesized the heterometallic Ln–Pt complexes: $\text{NEt}_4\{\text{Pt}(\text{PhSAc})_4\}\text{Ln}[(\text{PhSAc})_4\text{Pt}]\cdot 2\text{DMF}$ ($\text{Ln} = \text{Gd}$ (**1**), Tb (**2**), Dy (**3**); $\text{PhSAc} = \text{benzothioacetate}$, $\text{NEt}_4 = \text{tetraethylammonium}$), in which both diamagnetic Pt(II) ions interact with the central Ln(III) ion. Pt- L_{III} resonant inelastic X-ray scattering (RIXS)² was used to experimentally to prove the unique role of the Ln–Pt interaction in the luminescence property of the Tb–Pt molecule. RIXS enabled to identify the distinguishing factors in the coordination environment and the existence of heterometallic interaction with implications to the observed luminescence.

The two-dimensional (2D) RIXS mapping which has a higher sensitivity to bonding interaction over XANES allowed us to observe the Pt–Ln interactions in **1**, **2** and **3** but not in $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ (Fig. 1). The electronic structures revealed by the 2D RIXS mapping are different in the appearance with $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ and **1-3**. **1-3** showed a clear shoulder peak along the direction of energy transfer (y axis) (Fig. 1). The difference arises from the difference in the coordination structure around Pt ions, where $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ has a square planer structure and the complexes **1-3** have a square pyramidal structure. The details of the results of RIXS and luminescence will be presented in the talk. The RIXS confirmed the interaction between Ln and Pt ions, where the difference in the coordination environment of Pt complexes such as $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ and $\text{NEt}_4\{\text{Pt}(\text{PhSAc})_4\}\text{Ln}[(\text{PhSAc})_4\text{Pt}]\cdot 2\text{DMF}$ was successfully visualized.

1) J. Overgaard, *et. al.*, *Appl. Crystal.*, 2020, **53**, 635. 2) J. Mizuki, *et. al.*, *ACS Catal.*, 2015, **5**, 1112.

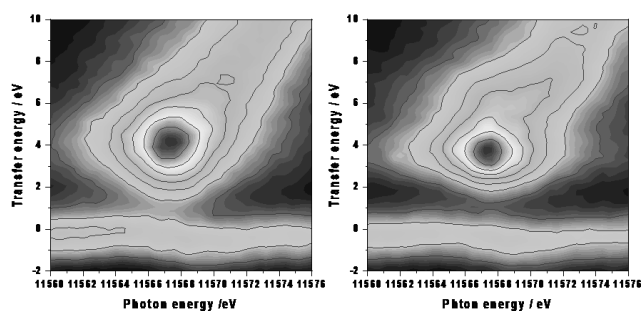


Fig. 1. 2D RIXS of (left) $2\text{NBt}_4[\text{Pt}(\text{dmit})_2]$ and (right) **2**.

白金-ロジウム複核錯体と種々の金属との2段階一次元多核化反応

(岐阜大工¹・岐阜大院自然科学²・岐阜大院工³・東工大院物質⁴)

○植村 一広¹・池田 友哉²・高森 敦志³・竹山 知志⁴

Two Steps One-dimensional Reaction of Platinum-Rhodium Dinuclear Complexes and Several Metal Species (¹*Faculty of Engineering, Gifu University*, ²*Graduate School of Natural Science and Technology, Gifu University*, ³*Graduate School of Engineering, Gifu University*, ⁴*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*) ○Kazuhiro Uemura,¹ Yuya Ikeda,² Atsushi Takamori,³ Tomoyuki Takeyama⁴

[PtRhCl₂(NH₃)₂(piam)₂PPh₃][PF₆] (piam = pivalamidate) has dinuclear structure where platinum and rhodium atoms are bridged by two piam ligands, and rhodium is axially coordinated by PPh₃. This dinuclear complex is possible to bind several metals with Pt–M bonds. In this study, we will show the results of one-dimensional pentanuclearization with Pt, Pd, and Cu, discussing the binding constants based on crystal structures and DFT calculations. **Keywords** : Multinuclear Complex; Binding Constant; One-dimensional; Hetero-metal

我々が合成に成功している白金-ロジウム複核錯体の[PtRhCl₃(NH₃)₂(piam)₂] (**1**, piam = pivalamidate) は、白金とロジウムが2つのピバロアミダートによって架橋された構造をとる¹⁾。金属酸化数はPt(+2)–Rh(+3)で、両金属 d_z² 軌道による σ* 軌道に LUMO をもつので、d_z² 軌道に HOMO をもつ金属錯体と金属結合で一次元伸長化できる²⁾。PPh₃を加えると、ロジウムのアキシシャル位に配位し、[PtRhCl₂(NH₃)₂(piam)₂PPh₃][PF₆] (**2**) となり、白金のアキシシャル位で金属結合可能となる。例えば、平面性の[PtCl₄]²⁻と混合すると、2:1 で反応し、[Ph–Pt]–[Pt]–[Pt–Rh]と並んだ一次元状五核錯体 (**2-Pt-2**) となる。本研究では、定量的に反応を追跡し、会合定数を算出したので報告する。

(Bu₄N)₂[PtCl₄]の0.3 mM CH₂Cl₂溶液に、0.2 等量ずつ **2**を加えて、UV-vis 測定した。(図1) **2**を加えると、1.0 等量まで413 nmの吸収が増大し、続いて、2.2 等量まで452 nmの吸収が増大した。413 nmの吸収は、[Ph–Pt]–[Pt]と並んだ三核錯体 (**2-Pt**)の金属 σ 性軌道間の遷移に由来し、**2** → **2-Pt** → **2-Pt-2**と二段階で一次元多核化していることがわかった。一段階目と二段階目の会合定数を K₁と K₂とすると、K₁ = 6.8 × 10⁷ mol⁻¹L、K₂ = 7.2 × 10⁵ mol⁻¹Lであった。¹H NMRとDFT計算の結果、(Bu₄N)₂[PdCl₄]、(Bu₄N)₂[CuCl₄]、(Bu₄N)Clとの会合についても議論する予定である。

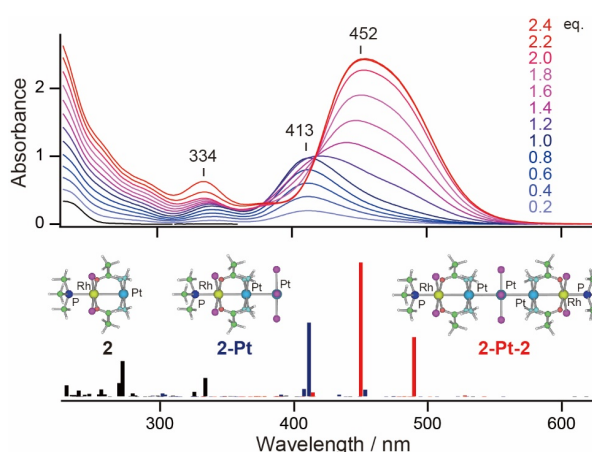


図1. UV-vis 測定と TD-DFT 計算の結果.

1) *Eur. J. Inorg. Chem.*, **2007**, 809. 2) *Dalton Trans.*, **2017**, 46, 5474.

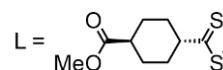
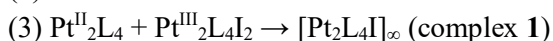
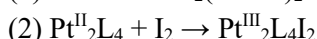
Synthesis and physical properties of a functionalized cyclohexane-dithiocarboxylate-based MMX-chain complex

(¹Graduate School of Science, Kyoto University, ²JASRI/SPring-8) ○Hayato Moriyama,¹ Kazuya Otsubo,¹ Kuniyasa Sugimoto,² Hiroshi Kitagawa¹

Keywords: Polynuclear complex; Structural chemistry; Mixed-valence compound; Electronic state

One-dimensional halogen-bridged mixed-valence dinuclear metal complexes (MMX-chains) show a wide variety of electronic states depending on the external stimuli such as temperature and pressure due to the high degrees of freedom of the charge polarization in dimerized metal unit. In particular, some dithiocarboxylate-based MMX-chains exhibit metallic conductivity¹. However, only the effect of alkyl chain length of the ligand has been systematically studied in this system. In this study, we have aimed to investigate the electronic states by introducing a rigid moiety to a dithiocarboxylate ligand.

The MMX-chain $\text{Pt}_2\text{L}_4\text{I}$ (complex **1**) based on *trans*-4-(methoxycarbonyl)cyclohexanedithiocarboxylate (L) as a ligand was synthesized by the following reactions:



The crystal structure of complex **1** was determined by the single crystal X-ray structural analysis at 100 K (Fig. 1(a)). Based on the observed $\text{Pt} \cdots \text{I}$ distances, the electronic state in a chain is in the charge-polarization state (CP state: $-\text{Pt}^{2+}-\text{Pt}^{3+}-\text{I}^-$). The electrical conductivity was measured by a two-terminal method along the chain direction. As the temperature increased, the conductivity changed from increasing to decreasing around 323 K, suggesting a structural phase transition at 323 K (Fig. 1(b)). From the variable temperature single crystal X-ray structure analysis, the bridging iodide ions exist at the midpoint between platinum dimer units above 323 K. This suggests that the electronic state in a chain is in the averaged-valence state (AV state: $-\text{Pt}^{2.5+}-\text{Pt}^{2.5+}-\text{I}^-$). Details are discussed.

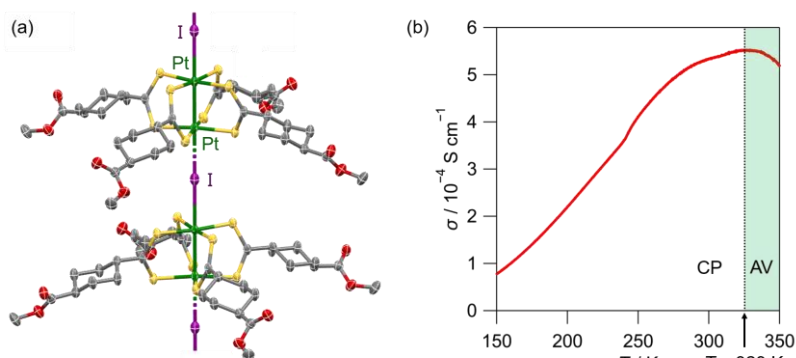


Fig. 1 (a) Molecular structure of complex **1** at 100 K. Hydrogen atoms are omitted for clarity. (gray: C, red: O, yellow: S, green: Pt, purple: I) (b) Electrical conductivity of complex **1**.

1) M. Mitsumi *et al*, *J. Am. Chem. Soc.* **2001**, 123, 11179-11192

A Polyaromatic Capsule Solid as a Vapor Adsorbent for Benzene Derivatives

(Lab. for Chem. & Life Sci., Tokyo Tech) Ryuki Sumida, Michito Yoshizawa

Keywords: Porous solid; Volatile compound; Adsorption; Polyaromatic capsule; Reusability

Porous materials, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), are useful solids for adsorption, separation, and storage of molecules.^[1] Most of these materials possess infinite cavities and windows in subnanometer to nanometer size. In contrast, polyaromatic capsule **1**, composed of eight anthracene panels and two metal ions, provides a finite, large cavity with four small windows.^[2] Here we report that capsule solid (**1**)_n displays adsorption ability for benzene derivatives as a new vapor adsorbent.

Capsule solid (**1**)_n was put in a sealed vessel including benzene (BN), toluene (TL), and *o*-xylene (oXL) without direct host-guest and guest-guest contact (Figure 1a). After standing at r.t. for 1 h, the resultant solid (**1**)_n•(BN)_x•(TL)_y•(oXL)_z was subjected to reduced pressure and dissolved in CD₃CN. ¹H NMR analysis of the product solution revealed that 3.3 equivalent of the benzene derivatives (based on **1**) are bound by solid (**1**)_n, with >80% oXL selectivity (Figure 1b, left). In the same way, solid (**1**)_n bound oXL from a mixture of three xylene isomers with 53% selectivity (Figure 1b, right). The volatilization of the adsorbed molecules was suppressed by solid (**1**)_n even at 100 °C for 1 h (Figure 1c). Furthermore, solid (**1**)_n could be reused at least five times with the same adsorption ability for three xylene isomers (Figure 1d).

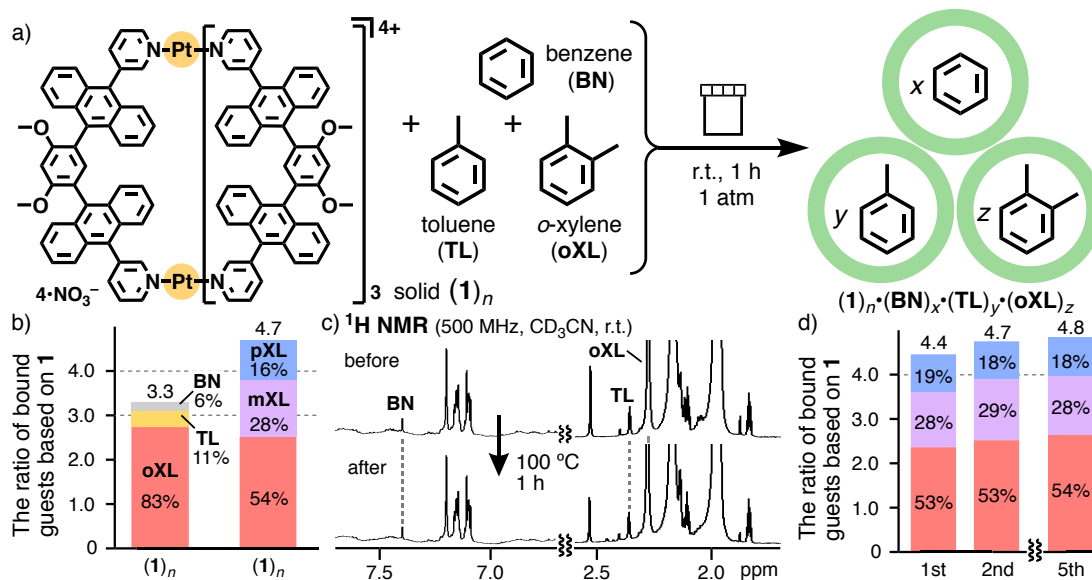


Figure 1. a) Selective vapor adsorption by solid (**1**)_n. b) Guest ratios and % after binding experiments. c) ¹H NMR spectra of (**1**)_n•(BN)_x•(TL)_y•(oXL)_z before/after heating. d) Reusability of solid (**1**)_n.

[1] G. Zhang, B. Hua, A. Dey, M. Ghosh, B. A. Moosa, N. M. Khashab, *Acc. Chem. Res.* **2021**, *54*, 155–168. [2] N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441.

Vapor-controlled Assembly/Disassembly of an Anionic Pt(II) Complex Loaded on a Cationic Nanosheet

(¹Faculty of Science, Hokkaido University, ²School of Biological and Environmental Sciences, Kwansei Gakuin University) ○Masaki Yoshida,¹ Tamami Morimoto,¹ Atsushi Kobayashi,¹ Masako Kato^{1,2}

Keywords: Vapochromism; Nanosheet; Intermolecular interactions; Luminescence; Cyclometalated Pt(II) complex

Layered double hydroxides (LDHs; Fig. 1(a)), which consist of positively charged nanosheet-like structures and interlayer anions, are well-known to electrostatically load anionic molecules. In this work, we have focused on the controlled assembly of electrostatically loaded anionic molecules on the LDH by external stimuli. Here we report a stimuli-responsive nanohybrid material based on an anionic Pt(II) complex [Pt(CN)₂(ppy)][−] (Fig. 1(b); Hppy = 2-phenylpyridine) and the LDH consisting of Mg²⁺ and Al³⁺ ions (Mg-Al LDH), in which the Pt(II) complex was found to assemble on the LDH under water vapor, causing vapochromic luminescence.

The Pt(II)-loaded Mg-Al LDH nanoparticles (hereafter termed as **Pt-LDH**) have been synthesized by heating K[Pt(CN)₂(ppy)] together with MgCl₂·6H₂O, AlCl₃·6H₂O, and tris(hydroxymethyl)aminomethane. Importantly, the obtained **Pt-LDH** exhibited obvious vapochromism. As shown in Fig. 2, dry **Pt-LDH** displayed green emission consisting of several vibronic satellite bands ($\lambda_{\text{em}}^{\text{max}} = 480$ and 520 nm; RH 0% in Fig. 2), while the emission color changed to orange under water vapor ($\lambda_{\text{em}}^{\text{max}} = 604$ nm; RH 97% in Fig. 2). The variable-temperature emission lifetime measurements revealed that the luminescence of the dry **Pt-LDH** originated from the ligand-centered ³ $\pi\pi^*$ luminescence of discrete [Pt(CN)₂(ppy)][−], whereas the luminescence of **Pt-LDH** under water vapor originated from the assembled state. Thus, these results indicate that the assembly of Pt(II) complex molecules was controlled on the LDH nanosheets by water vapor adsorption. The detailed vapochromic mechanism will be discussed in detail based on differential scanning calorimetry (DSC) and water vapor adsorption measurements.

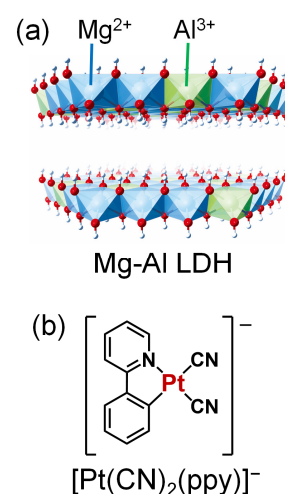


Fig. 1 (a) Mg-Al LDH and (b) [Pt(CN)₂(ppy)][−].

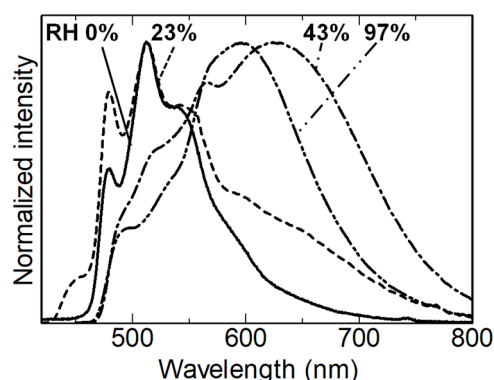


Fig. 2 Emission spectra of **Pt-LDH** under various relative humidity (RH).

Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds- | Oral B**[D202-1pm] 10. Organic Chemistry -Organometallic Compounds-**

Chair: Naoki Ishida, Kei Muto

Wed. Mar 23, 2022 1:00 PM - 3:40 PM D202 (Online Meeting)

[D202-1pm-01] Deacylative Coupling Reaction through Claisen-Retro-Claisen Condensation○Ryota Isshiki¹, Hikaru Nakahara¹, Keiichiro Iizumi¹, Masayuki Kubo¹, Kei Muto¹, Junichiro YAMAGUCHI¹ (1. Waseda University)

1:00 PM - 1:20 PM

[D202-1pm-02] Development of a Dehydrogenative Coupling Reaction of Phenols with Aldehydes○Tairin Kawasaki¹, Tomohiro Tosaki¹, Naoki Ishida¹, Masahiro Murakami¹ (1. Graduate School of Engineering, Kyoto University)

1:20 PM - 1:40 PM

[D202-1pm-03] Copper(I)- and Palladium(II)-Catalyzed Carboboration of *gem*-Disubstituted Allenes○Yu Ozawa¹, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

1:40 PM - 2:00 PM

[D202-1pm-04] The Iridium (III)-Catalyzed Carbon(sp²)-Hydrogen Bond Amidation of 2-Aroylimidazoles: A Direct Observations of Kinetic and Thermodynamic Mechanistic Tunability○Sanjit Kumar Mahato¹, Naoto Chatani¹ (1. Faculty of Engineering, Osaka University)

2:00 PM - 2:20 PM

[D202-1pm-05] Mechanochemical synthesis of aryl manganese(II) reagents by ball milling○Rina Takahashi¹, Koji Kubota^{1,2}, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

2:20 PM - 2:40 PM

[D202-1pm-06] Rhodium-Catalyzed Formal [4+1] Cycloaddition between Benzocyclobutenones and Styrenes as a Carbenoid Equivalent○Shusuke Ochi¹, Zining Zhang¹, Ying Xia¹, Guangbin Dong¹ (1. The University of Chicago)

2:40 PM - 3:00 PM

[D202-1pm-07] Rh-Catalyzed Oxidative Carbon-Hydrogen Alkylation of Aniline Derivatives with Allylic Alcohol○Shrikant Manmathappa Khake¹, Naoto Chatani¹ (1. Faculty of Engineering, Osaka University)

3:00 PM - 3:20 PM

[D202-1pm-08] Pd-Catalyzed Deoxygenative Coupling of Aromatic Compounds○Miki B Kurosawa¹, Mizuho Watanabe¹, Kenta Kato¹, Kei Muto¹, Junichiro Yamaguchi¹ (1. Waseda University)

3:20 PM - 3:40 PM

クライゼン-レトロクライゼン縮合を利用した芳香族ケトンの脱アシル型カップリング反応

(早大院先進理工¹・早大高等研²)

○一色 遼大¹・中原 輝¹・飯泉 慶一朗¹・久保 真之¹・武藤 慶²・山口 潤一郎¹

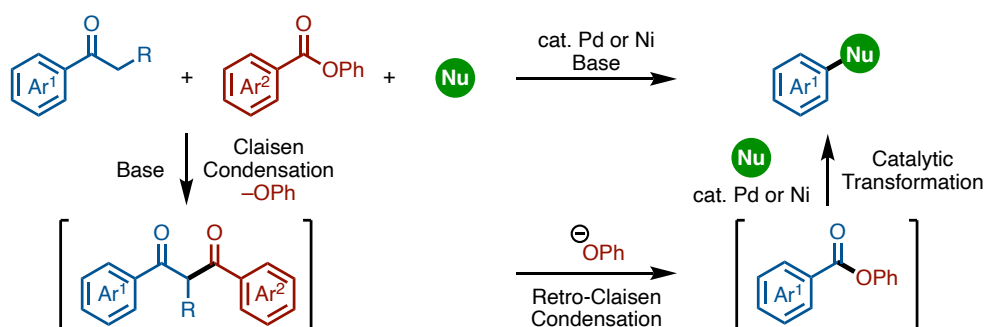
Deacylative Coupling Reaction through Claisen-Retro-Claisen Condensation (¹*Graduate School of Advanced Science and Engineering, Waseda University*, ²*Institute for Advanced Study, Waseda University*) ○Ryota Isshiki,¹ Hikaru Nakahara,¹ Keiichiro Iizumi,¹ Masayuki Kubo,¹ Kei Muto,² Junichiro Yamaguchi¹

We have developed Ni- or Pd-catalyzed deacylative couplings of aromatic ketones. A key for these reaction are a functional group metathesis between aromatic ketones ($\text{Ar}^1\text{-COR}$) and aromatic esters ($\text{Ar}^2\text{-CO}_2\text{R}$) *via* sequential Claisen/retro-Claisen condensation, giving aromatic esters ($\text{Ar}^1\text{-CO}_2\text{R}$). Merging the functional group metathesis and various decarbonylative couplings of aromatic esters in a one-pot manner, a formal deacylative couplings of aromatic ketones can be realized.

Keywords : Nickel; Palladium; Aromatic Ketones; Deacylative Coupling; Functional Group Metathesis

芳香族分子の構造修飾法として遷移金属触媒を用いたハロアレーンと求核剤のカップリング反応が知られる。遷移金属触媒化学の発展に伴い、ハロアレーンの代替としてフェノール類や芳香族エステルなどが適用可能になった。しかし、芳香族ケトンを実効求電子剤とする脱アシル型カップリング反応は報告例が少なく、化学量論量の遷移金属を要する、配向基をもつ芳香族ケトンに限られるなどの課題がある¹⁾。

今回我々は、ニッケルもしくはパラジウム触媒を用いた芳香族ケトンの脱アシル型カップリング反応を開発した。塩基存在下、芳香族ケトン($\text{Ar}^1\text{-COR}$)と芳香族エステル($\text{Ar}^2\text{-CO}_2\text{R}$)を反応させるとクライゼン縮合とレトロクライゼン縮合が進行し、芳香族エステル($\text{Ar}^1\text{-CO}_2\text{R}$)が得られることを見いだした。この反応と芳香族エステルの種々の脱カルボニル型変換反応²⁾を同一容器内で行うことで、形式的な脱アシル型カップリング反応を可能とした。



1) [a] Lu, H.; Yu, T.-Y.; Xu, P.-F.; Wei, H. *Chem. Rev.* **2021**, *121*, 365–411. [b] Li, H.; Ma, M.; Liu, Q.-S.; Wang, M.-L.; Wang, Z.-Y.; Xu, H.; Li, L.-J.; Wang, X.; Dai, H.-X. *Angew. Chem., Int. Ed.* **2020**, *59*, 14388–14393. 2) Takise, R.; Muto, K.; Yamaguchi, J. *Chem. Soc. Rev.* **2017**, *46*, 5864–5888.

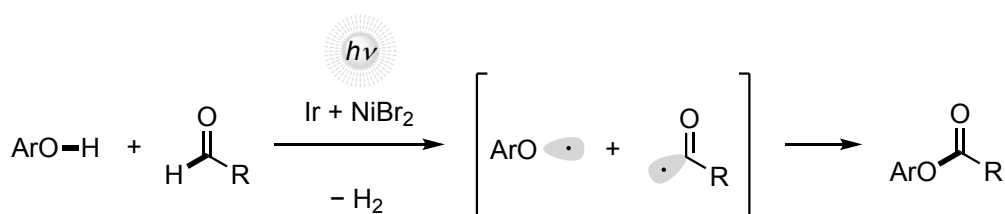
Development of a Dehydrogenative Coupling Reaction of Phenols with Aldehydes

(¹Graduate School of Engineering, Kyoto University) ○ Tairin Kawasaki,¹ Tomohiro Tosaki,¹ Naoki Ishida,¹ Masahiro Murakami¹

Keywords: Dehydrogenative Reaction; Coupling Reaction; Photoredox Catalysis; Nickel Catalysis; Hydrogen Atom Transfer

Herein is reported a convenient method to acylate phenolic hydroxyl groups with aldehydes.¹ We recently reported a photo-induced dehydrogenative coupling reaction of alkylarenes with aldehydes, which was facilitated by collaboration of an iridium photoredox catalyst and a nickel catalyst.² When the reaction conditions were applied to a solution of 4-*tert*-butylphenol and varelaldehyde, 4-*tert*-butylphenyl pentanoate was obtained in 96% yield, involving gaseous hydrogen. Results of mechanistic studies implied that a phenoxy radical and an acyl radical cross-coupled. A phenolic hydroxy group was selectively acylated in preference to alkyl-substituted hydroxy groups, probably thanks to the unique reaction mechanism.

The dehydrogenative coupling of phenols and aldehydes was extended to a dehydrogenative coupling reaction of primary alcohols with phenols.³ A primary alcohol was initially dehydrogenated by the visible light/iridium/nickel dibromide system to generate transiently the corresponding aldehyde that sequentially coupled with a phenol forming the phenyl ester.



1) T. Kawasaki, N. Ishida, M. Murakami, *Angew. Chem. Int. Ed.* **2020**, 59, 18267. 2) T. Kawasaki, N. Ishida, M. Murakami, *J. Am. Chem. Soc.* **2020**, 142, 3366. 3) T. Kawasaki, T. Tosaki, N. Ishida, M. Murakami, *Org. Lett.* **2021**, 23, 7683.

銅(I)およびパラジウム(II)触媒を用いた *gem*-二置換アレン類のカルボホウ素化反応の開発

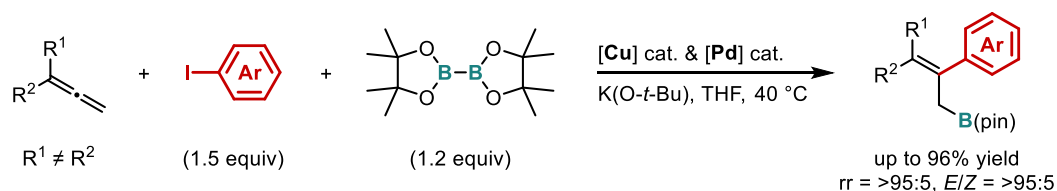
(北大院工¹・WPI-ICReDD²) ○小澤 友¹・伊藤 肇^{1,2}

Copper(I)- and Palladium(II)-Catalyzed Carboboration of *gem*-Disubstituted Allenes
(¹Graduate School of Engineering, Hokkaido University, ²WPI-ICReDD, Hokkaido University)
○Yu Ozawa,¹ Hajime Ito^{1,2}

Allylic boronates are versatile building blocks for synthesis of complex molecules in organic and pharmaceutical research. Recently, our group developed a regio- and stereoselective alkylboration reaction of *gem*-disubstituted allenes using a copper(I)/diboron catalytic system.¹ The alkylation of the alkenyl copper(I) intermediates with alkyl electrophiles furnished the multisubstituted allylic boronates bearing tetrasubstituted alkene moiety. Thus, we anticipated that the use of the other electrophiles, instead of the alkyl electrophiles, can expand the product structure versatility. Here, we describe the development of a copper(I)/palladium(II)-catalyzed arylboration reaction of *gem*-disubstituted allenes.² The transmetalation between the alkenyl copper(I) intermediates and aryl palladium(II) species, and the following reductive elimination gave the corresponding multisubstituted allylic boronates in high yield with high regio- and stereoselectivity (up to 96%, *rr* = >95:5, *E/Z* = >95:5).

Keywords : Copper(I) catalyst, Palladium(II) catalyst, Diboron reagent, Allylic boronates, Carboboration reaction

多置換アリルホウ素化合物は立体的に混雑した複雑な有機分子の合成に有用な合成中間体である。最近、当研究室では、銅(I)/ジボロン触媒系とアルキル求電子剤を用いた *gem*-二置換アレン類のアルキルホウ素化反応を開発し、四置換アルケン構造を有するアリルホウ素化合物の合成を達成した¹。この反応では、アルケニル銅(I)中間体のアルキル化によって四置換アルケン構造が構築される。そこで、このアルケニル銅(I)中間体に別の求電子剤を作用させることができれば、前報とは異なる構造の多置換アリルホウ素化合物が得られると考えた。本研究では、パラジウム(II)触媒存在下でアリール求電子剤を用いることでアルケニル銅(I)中間体のアリール化が可能であることを見出した²。これによって、スチレン骨格を有する多置換アリルホウ素化合物が高収率かつ高位置・立体選択的に得られた (up to 96%, *rr* = >95:5, *E/Z* = >95:5)。



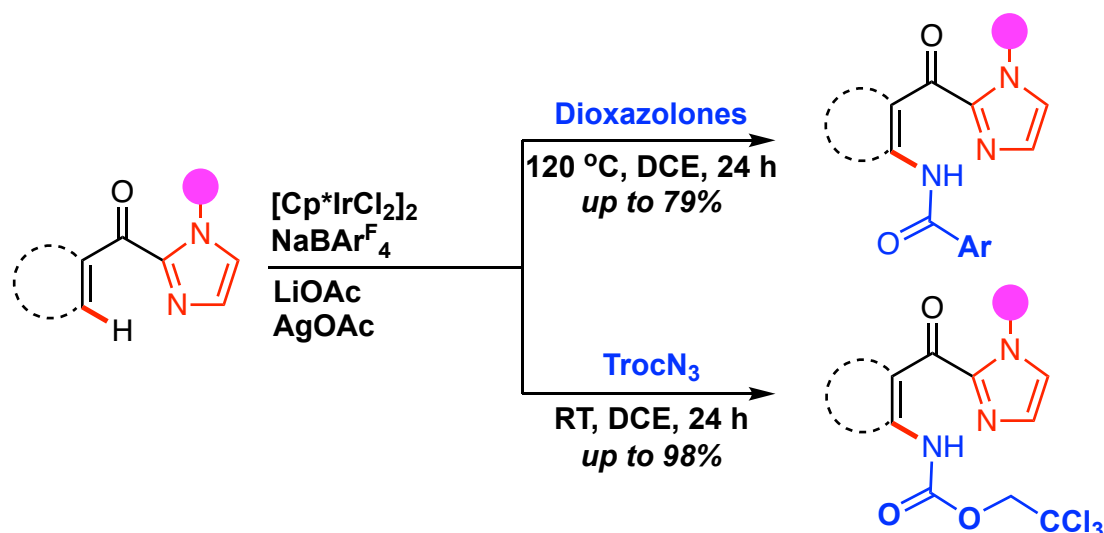
- Ozawa, Y.; Endo, K.; Ito, H. *J. Am. Chem. Soc.* **2021**, *143*, 13865.
- Copper(I)- and palladium(II)-catalyzed arylboration reactions of multiple bonds were pioneered by the Nakao and Semba group. a) Semba, K.; Nakao, Y. *J. Am. Chem. Soc.* **2014**, *136*, 7567. b) Semba, K.; Nakao, Y. *Tetrahedron*, **2019**, *75*, 709.

The Iridium (III)-Catalyzed C(sp²)-H Bond Amidation of 2-Aroylimidazoles: A Direct Observations of Kinetic and Thermodynamic Mechanistic Tunability

(Graduate School of Engineering, Osaka University) ○Sanjit Kumar Mahato, Naoto Chatani

Keywords: Carbon-Hydrogen Bond Cleavage; Nitrene Intermediate; Iridium Catalyst; Amidation; Thermodynamic and Kinetic Control

The transition metal catalyzed direct C-N bond formation *via* nitrene insertion plays crucial role to easily access to highly functionalized amides, which are encountered in many natural products and have key factors in screening preclinical drug candidates.¹ Thus, metal catalyzed direct C-H amidation has attracted much attention by organic chemists due to its atom- and step-economical process as it does not require any preactivation of the reactants.^{1b-c} Here, we report an Ir(III)-catalyzed direct C(sp²)-H amidation of 2-arylimidazoles² with dioxazolones and 2,2,2-trichloroethyl azides (TrocN₃) as nitrene sources. Although these two nitrene precursors differ greatly in reactivity and react through different mechanism only by changing the temperature under the same reaction conditions. This methodology is applicable for a wide of substituted aromatic and heterocyclic substrates to produce amido aroylimidazoles in good yields.



1) (a) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400. (b) Ju, M.; Schomaker, J. M. *Nat. Rev. Chem.* **2021**, *5*, 580. (c) Hong, S.Y.; Kim, D.; Chang, S. *Nat. Catal.* **2021**, *4*, 79.

2) (a) Mahato, S. K.; Chatani, N. *ACS Catal.*, **2020**, *10*, 5173. (b) Mahato, S. K.; Ohara, N.; Khake, S. M.; Chatani, N. *ACS Catal.*, **2021**, *11*, 7126. (c) Ohara, N.; Das, A.; Mahato, S. K.; Chatani, N. *Chem. Lett.* **2021**, *50*, 1722.

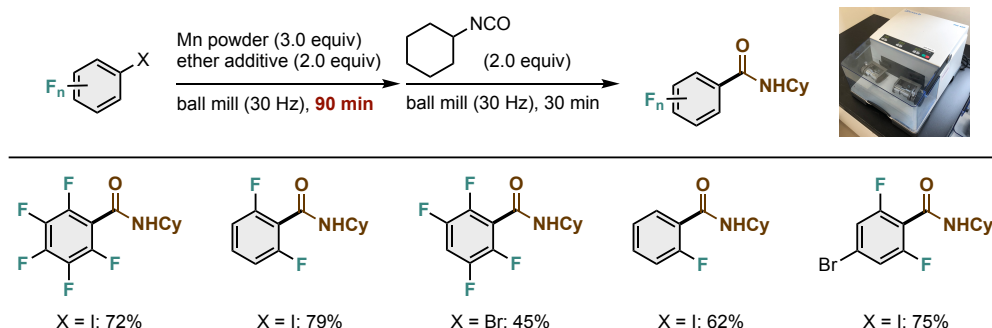
ボールミルを用いたアリールマンガン試薬のメカノケミカル合成

(北大院工¹・北大 WPI-ICReDD²) ○高橋 里奈¹・久保田 浩司^{1,2}・伊藤肇^{1,2}
 Mechanochemical synthesis of aryl manganese(II) reagents by ball milling (¹*Graduate School of Engineering, Hokkaido University*, ²*WPI-ICReDD, Hokkaido University*) ○ Rina Takahashi,¹ Koji Kubota,^{1,2} Hajime Ito^{1,2}

Organomanganese reagents have been used for C–C bond-forming reactions as a soft alternative of Grignard reagents because of their high chemoselectivity. Although organomanganese reagents are generally prepared by transmetalation from the corresponding organolithium or organomagnesium reagents, it is difficult to synthesize functionalized organomanganese reagents. Direct insertion of Mn(0) into organic halides has also been studied but requires strong metal reductants for the activation of Mn metal or additives for promoting an electron transfer process. Herein, we developed a fast and efficient generation of aryl manganese reagents via direct insertion of Mn powder into aryl halides using ball milling without the activation agents. This reaction was applicable to polyfluoroaryl bromides and iodides. The selective Mn insertion was achieved in *ortho*-position to fluorine atom of aryl halides with multiple reaction sites. Additionally, mechanochemically-prepared aryl manganese reagents can react with various electrophiles in a one-pot fashion.

Keywords : Organomanganese Reagents; Carbon Nucleophiles; Polyfluoroarylation; Mechanochemistry; Ball Milling

有機マンガン試薬はその高い化学選択性のため、ソフトな Grignard 試薬として C–C 結合形成反応に用いられる¹。しかし、その主な合成法は対応する有機リチウムまたはマグネシウム試薬を用いたトランスメタル化で、この場合は官能基許容性が低下する。0 価マンガンと有機ハロゲン化物からも合成可能だが、この方法は還元力の高い金属によるマンガンの活性化、または塩化鉛などの電子移動を促進する添加剤を必要とする。本研究ではボールミルを用いたメカノケミカル条件下、活性化剤を必要とせず迅速にアリールマンガン試薬を合成する手法を開発した。本反応は反応点のオルト位にフッ素原子を有するアリールハライドに適用でき、複数の反応点を有するアリールハライドを用いた場合はフッ素原子の近傍で選択的に反応が進行した。合成したアリールマンガン試薬は種々の求電子剤とワンポットで反応させることができる。



1) Cahiez, G.; Duplais, C.; Buendia, J. *Chem. Rev.* **2009**, *109*, 1434.

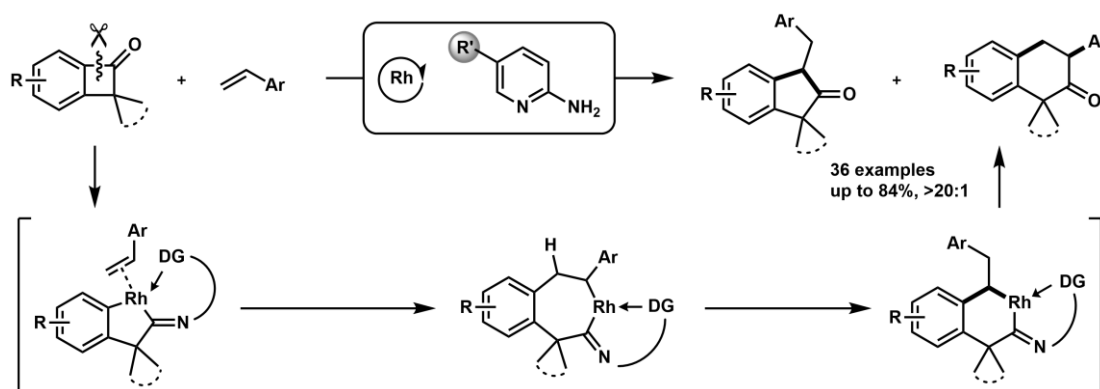
Rhodium-Catalyzed Formal [4+1] Cycloaddition between Benzocyclobutenones and Styrenes as a Carbenoid Equivalent

(¹Department of Chemistry, The University of Chicago) ○Shusuke Ochi,¹ Zining Zhang,¹ Ying Xia,¹ Guangbin Dong¹

Keywords: [4+1] annulation; C–C activation; ketones; 2-indanones; carbene equivalent

“Cut-and-sew” transformations, in which the selective cleavage of a carbon–carbon (C–C) bond and subsequent 2π -insertion is catalyzed by a transition metal catalyst, have been developed as robust ring-expansion reactions.¹ On the other hand, one-carbon insertion after transition metal-catalyzed C–C bond activation is very challenging due to incompatibility between highly reactive metal carbenes and inert C–C bonds. We previously discovered that allenes can serve as a one-carbon unit in the intramolecular [4+1] cycloaddition with cyclobutanones enabled by a β -H elimination and reinsertion process,² which is very common in 1,1-difunctionalization of olefins.³ Taking advantage of this key reactivity of metallacycle intermediates, we envisioned that olefins could behave as a “carbenoid equivalent” during the similar, but more challenging intermolecular “cut-and-sew” process.

When benzocyclobutenones were treated with styrenes in the presence of a rhodium catalyst and 2-aminopyridine-based co-catalyst, 2-indanones and 2-tetralones were obtained in up to 84% total yield and >20:1 selectivity. This method afforded multi-substituted 2-indanones with wide-ranging functional group tolerance. Excellent selectivity toward 2-tetralone formation could be described by DFT calculations, which indicated the facile β -H elimination of a seven-membered rhodacycle intermediate. This reaction was scalable to gram-scale, and the 2-indanone was derivatized to synthetically valuable compounds.



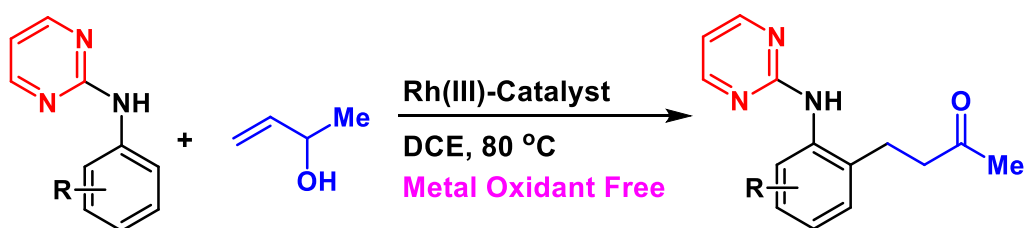
1) P.-H. Chen, B. A. Billett, T. Tsukamoto, G. Dong, *ACS Catal.* **2017**, 7, 1340. 2) X. Zhou, G. Dong, *J. Am. Chem. Soc.* **2015**, 137, 13715. 3) Y. Li, D. Wu, H.-G. C, G. Yin, *Angew. Chem., Int. Ed.* **2019**, 59, 7990.

Rh-Catalyzed Oxidative Carbon-Hydrogen Alkylation of Aniline Derivatives with Allylic Alcohol

(Graduate School of Engineering, Osaka University) ○Shrikant Manmathappa Khake, Naoto Chatani

Keywords: Rhodium Catalyst; Carbon-Hydrogen Bond Cleavage; Oxidative C-H Alkylation; Pyrimidinyl Directing Group; Allylic Alcohol

The transition metal catalyzed direct C–H bond functionalization *via* chelation assistance is one of the most attractive fields in organic chemistry because of its step economical applications in synthetic field.¹ In last decades, transition metal catalyzed direct C–H alkylation reaction has emerged as a powerful tool to access various pharmaceutical precursors, complex organic molecules and drug compounds in step and atom economical manner.² Recently, allyl alcohol have been widely used as alkylating reagent because of their commercially availability, low cost, and easy preparation and handling. Transition metals, such as Co, Rh, Ru have shown great advancement in the C–H bond alkylation of arenes and heteroarenes with allyl alcohols using directing group strategy.³ Among all these reports, the reaction requires a stoichiometric amount of oxidants or metal salts to achieve oxidative C–H alkylation products, which consequently generates metal waste. In this context, the development of mild and efficient catalytic system for C–H alkylation with allyl alcohol without use of oxidants or metal salt is highly desirable. Herein, we present the Rh(III)-catalyzed oxidative C–H alkylation of aniline derivatives with allylic alcohol using a pyrimidinyl group as a directing group without use of oxidant or metal salts. This reaction provides broad substrate scope for aniline derivatives. In addition, the reaction tolerates various important functional groups. Preliminary mechanistic studies have been carried out to understand the reaction mechanism.



1) (a) Khake, S. M.; Chatani, N. *Trends in Chem.* **2019**, *1*, 524. (b) Rej, S.; Ano, Y.; Chatani, N. *Chem. Rev.* **2020**, *120*, 1788.

2) Han, S. M.; Choi, M.; Jeong, T.; Sharma, S.; Mishra, N. M.; Park, J. Oh, J. S.; Kim, W. J.; Lee, J. S.; Kim, I. S. *J. Org. Chem.* **2015**, *80*, 11092.

3) (a) Kalsi, D.; Laskar, R. A.; Barsu, N.; Premkumar, J. R.; Sundararaju, B. *Org. Lett.* **2016**, *18*, 4198. (b) Sun, J.-S.; Wang, Y.-Y.; Liu, M.; Zhang, J.; Liu, C.-F.; Xu, Y.-J.; Dong, L. *Org. Chem. Front.* **2019**, *6*, 2713. (c) Kumar, S. G.; Chand, T.; Singh, D.; Kapur, M. *Org. Lett.* **2018**, *20*, 4934.

Pd-Catalyzed Deoxygenative Coupling of Aromatic Compounds

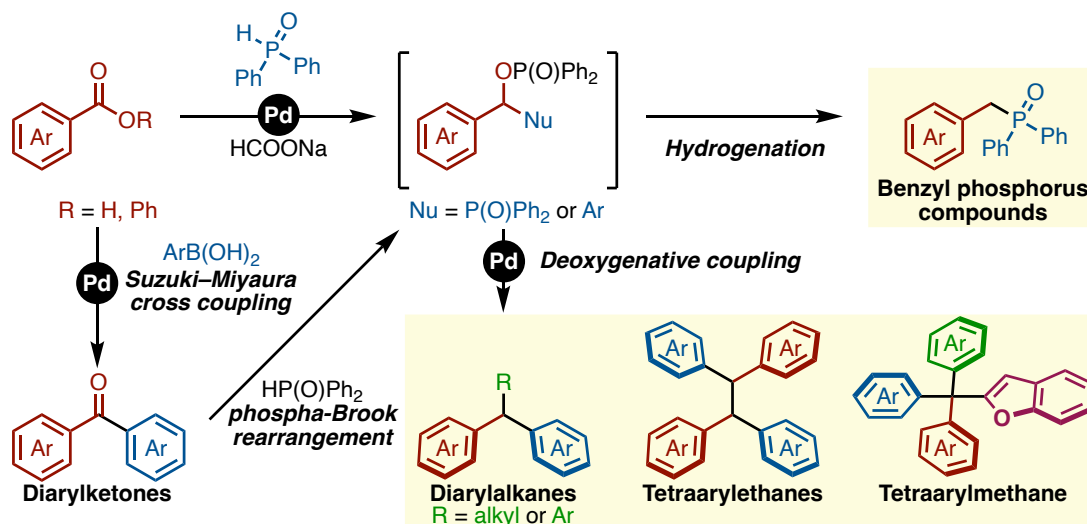
(¹Graduate School of Advanced Science and Engineering, Waseda University, ²Institute for Advanced Study, Waseda University)

○Miki B. Kurosawa,¹ Mizuho Watanabe,¹ Kenta Kato,¹ Kei Muto,² Junichiro Yamaguchi¹

Keywords: Palladium; Reductive Reaction; Phospha-Brook Rearrangement; Deoxygenative Reaction; Aromatic Compounds

Aromatic compounds such as carboxylic acids and esters are frequently used as abundant, inexpensive chemical feedstock in organic synthesis and can be derived into various aromatics. For example, nucleophilic acyl substitutions have been used as classical transformation of aromatic esters. Recently, transition-metal-catalyzed decarbonyl transformation of aromatic esters with various carbon/hetero-nucleophiles has received attention as an emerging method in synthetic organic chemistry.¹

Herein, we have developed a palladium-catalyzed deoxygenative couplings as a new type transformation reaction between aromatic carboxylic acids and esters.¹ Aromatic esters can be function as benzylating agents to give the corresponding benzyl phosphorus compounds. Mechanistic studies of this reaction revealed that the deoxygenative reaction proceed through the phospha-Brook rearrangement. As an application to this coupling we also developed unified synthesis of multi-arylated alkanes by catalytic deoxygenative transformation of diarylketones. Diarylketones, which are readily prepared by aromatic carboxylic acids could be converted to diarylmethanes, diarylethane, triarylmethanes, triarylethane, tetraarylmethane and tetraarylethanes via diarylmethylphosphinates generated by the phospha-Brook rearrangement.



- 1) Kurosawa, M. B.; Isshiki, R.; Muto, K.; Yamaguchi, J. *J. Am. Chem. Soc.* **2020**, *142*, 7386–7392.
- 2) Halima, T. B.; Zhang, W.; Yalaoui, I.; Hong, X.; Yang, Y.-F.; Houk, K. N.; Newman, S. G. *J. Am. Chem. Soc.* **2017**, *139*, 1311–1318.

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[K3-1pm] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Tomohiko Nishiuchi, Sayaka Hatano

Wed. Mar 23, 2022 1:00 PM - 3:40 PM K3 (Online Meeting)

[K3-1pm-01] Luminescent Chromism with Reversible Coordination Number of Hypervalent Tin(IV) Complexes○Masayuki Gon¹, Kazuo Tanaka¹, Yoshiki Chujo¹ (1. Grad. Sch. of Eng., Kyoto Univ.)

1:00 PM - 1:20 PM

[K3-1pm-02] Crystallization-Induced Emission Enhancement of Low Energy Gap Boron Complexes○Masashi Nakamura¹, Masayuki Gon¹, Kazuo Tanaka¹ (1. Graduate School of Engineering, Kyoto University)

1:20 PM - 1:40 PM

[K3-1pm-03] The syntheses and properties of diazazethrene bisimide and its dimer○Keita Tajima¹, Norihito Fukui¹, Hiroshi Shinokubo¹ (1. The Univ. of Nagoya)

1:40 PM - 2:00 PM

[K3-1pm-04] Synthesis and long-wavelength-absorption of indenoperylene and its π -extended derivativesMasaki Kato¹, ○Norihito Fukui^{1,2}, Hiroshi Shinokubo¹ (1. Nagoya Univ., 2. JST PRESTO)

2:00 PM - 2:20 PM

[K3-1pm-05] Synthesis, Structure and Properties of π -Expanded Carbohelicenes○Michihisa Toya¹, Hideto Ito¹, Kenichiro Itami^{1,2} (1. Graduate School of Science, Nagoya University, 2. Institute of Transformative Bio-Molecules, Nagoya University)

2:20 PM - 2:40 PM

[K3-1pm-06] Perfluorocycloparaphenylenes: Fully fluorinated carbon nanorings by Ni-mediated one-pot synthesis○Hiroki Shudo¹, Motonobu Kuwayama¹, Masafumi Shimasaki², Taishi Nishihara², Youhei Takeda³, Takuya Kuwabara¹, Akiko Yagi¹, Yasutomo Segawa⁴, Kenichiro Itami¹ (1. Nagoya University, 2. Kyoto University, 3. Osaka University, 4. Institute for Molecular Science)

2:40 PM - 3:00 PM

[K3-1pm-07] Synthesis of phenine nanocarbon molecules via a polygon-assembling strategy○Tatsuru Mio¹, Koki Ikemoto¹, Sota Sato¹, Hiroyuki Isobe¹ (1. Department of Chemistry, the University of Tokyo)

3:00 PM - 3:20 PM

[K3-1pm-08] Synthesis of aromatic ladder polymer utilizing coordination nanospaces○Takumi Miura¹, Takashi Kitao^{1,2}, Takashi Uemura¹ (1. Grad. Sch. of Eng. The Univ. of Tokyo, 2. JST-PRESTO)

3:20 PM - 3:40 PM

Luminescent Chromism with Reversible Coordination Number of Hypervalent Tin(IV) Complexes

(Graduate School of Engineering, Kyoto University)

○Masayuki Gon, Kazuo Tanaka, Yoshiki Chujo

Keywords: tin; hypervalent bond; luminescence; chromism; π -conjugated system

Luminescent chromism can be applied to highly sensitive chemical sensor. To achieve clear responsiveness of luminescent π -conjugated molecules, it is significant to keep the π -conjugated systems before and after sensing. However, that is difficult because the luminescent color change induced by external stimuli often accompanies structural distortion or alteration. Herein, we found that hypervalent bonds were effective in controlling energy levels of π -conjugated systems preserving the shape of the frontier molecular orbitals (FMOs). Concretely, stable luminescent chromisms both in solution and solid states were realized by using reversible coordination-number control of hypervalent tin(IV)-fused azobenzene complexes.¹⁾

Figure 1 shows the chemical structures and luminescent chromism of **TAz-F** with five- and six-coordinate forms in solution and solid states. In non-coordinating solvent such as toluene, **TAz-F** had the five-coordinate geometry showing orange emission. Meanwhile, in DMSO, the oxygen atom of DMSO molecule was attached to the tin atom of **TAz-F** and the resulted six-coordinate complex exhibited yellow emission. In solid state, reversible crystal-crystal transition between five- and six-coordinate structures occurred by heating and exposure of DMSO vapor, and the resulted solids showed deep-red and orange emissions, respectively. We confirmed preservation of the shape of FMOs during reversible coordination-number change of tin atom by theoretical calculation. Those chromisms were attributed to variation of electronic states of the π -conjugated systems constructed by azobenzene and hypervalent bonds around the tin atom.

Our findings propose that the hypervalent system is expected to open the field of clear sensing system with color-tunable π -conjugated system.

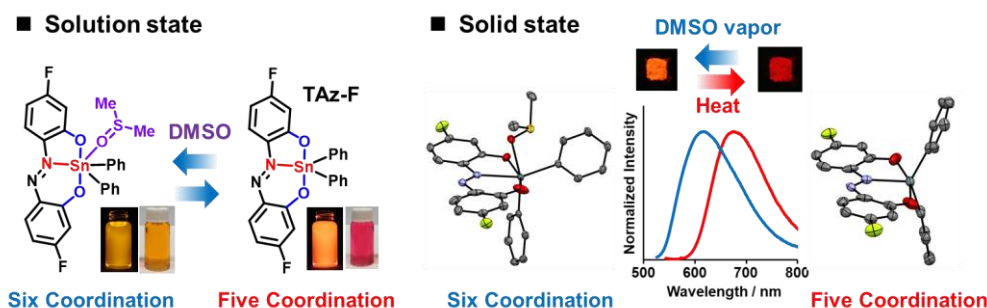


Figure 1. The luminescent chromism of **TAz-F** with DMSO in solution and solid states.

1) Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, 27, 7561.

Crystallization-Induced Emission Enhancement of Low Energy Gap Boron Complexes

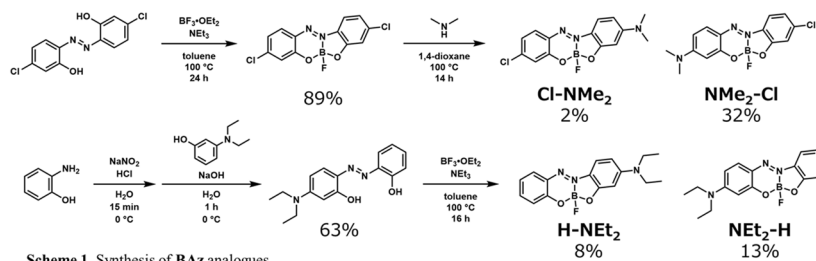
(¹Graduate School of Engineering, Kyoto University)

○Masashi Nakamura,¹ Masayuki Gon,¹ Kazuo Tanaka¹

Keywords: Boron; Azobenzene; Crystal; Luminescence; Conjugated system

Crystallization-induced emission enhancement (CIEE) is a unique photophysical phenomenon in which the compound shows no or weak luminescence in amorphous state but becomes strongly emissive in crystalline states.¹⁾ CIEE-active organic luminogens have received attracting attention in the application areas of light emitting diodes, optical waveguides, and organic lasers. However, there are very few reports of CIEE compounds because design strategies have not yet been established. In addition, most of them have twisted structures which make their emission blue-shifted. Therefore, it is quite difficult to realize the CIEE phenomenon in a longer wavelength region such as deep-red or near-infrared range. Recently, we reported that four-coordinate boron-fused azomethine complexes (**BAm**) exhibited CIEE property in yellow region.²⁾ Furthermore, boron-fused azobenzene complexes (**BAz**) showed bright solid-state emission in red region (Figure 1).³⁾ In this work, we developed several kinds of **BAz** derivatives introduced amino groups to achieve the CIEE phenomenon in further longer wavelength range.

We synthesized four kinds of **BAz** analogues according to Scheme 1. Among them, **H-NEt₂** and **NMe₂-Cl** exhibited CIEE behaviors in deep-red region (Figure 2). Furthermore, we found that there were clear differences between optical properties of each two isomers with different substitution positions in crystal.



Scheme 1. Synthesis of **BAz** analogues.

1) Tang, B. Z. *et al. Chem. Commun.* **2007**, 3255. 2) Chujo, Y. *et al. Chem. Eur. J.* **2017**, 23, 11827.

3) Chujo, Y. *et al. Macromol. Rapid Commun.* **2021**, 42, 2000566.

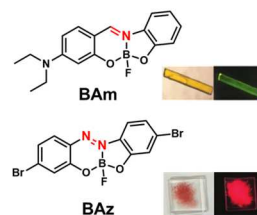


Figure 1. Chemical structures of **BAm** and **BAz**.

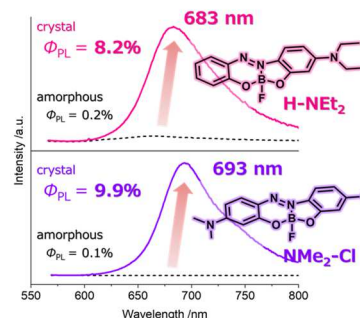


Figure 2. Photoluminescence spectra of **H-NEt₂** and **NMe₂-Cl** in crystalline state.

ジアザゼトレンビスイミドおよびその二量体の合成と物性

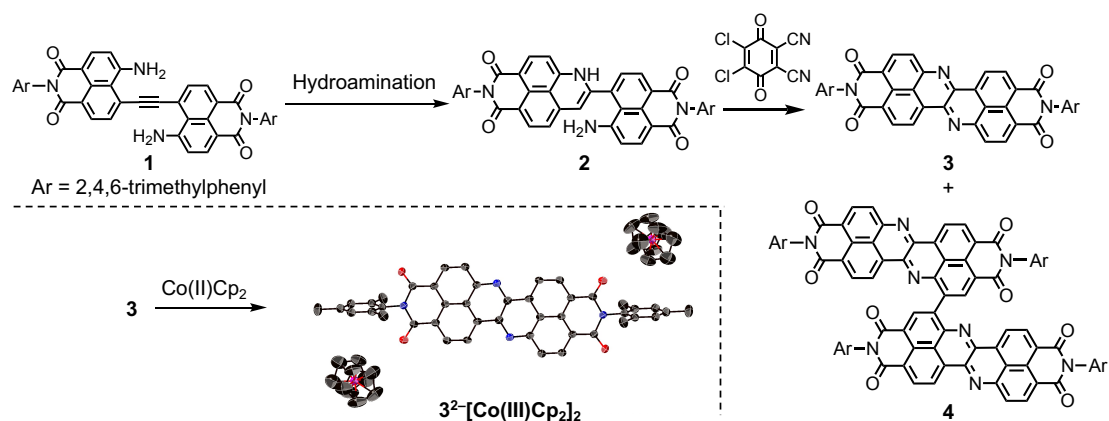
(名大院工) ○田島 慶太・福井 識人・忍久保 洋

Synthesis and Properties of diazazethrene bisimides (*Graduate School of Engineering, Nagoya University*) ○Keita Tajima, Norihito Fukui, Hiroshi Shinokubo

Zethrene is a redox-active polycyclic aromatic hydrocarbon consisting of two phenalene units. The electronic modulation of zethrene by structural modification should be promising to achieve novel π -conjugated molecules with excellent redox activity. Here, we report the synthesis and properties of diazazethrene bisimides (DAZBIs), which are zethrene derivatives containing two imide groups and two imine-type nitrogen atoms. Notably, its dianion exhibited remarkable stability under ambient conditions.

Keywords : Aza-polycyclic aromatic hydrocarbon, Electron deficient π -system, Zethrene, Radical anion, Dianion

最近我々は、ナノグラフェンへの電子求引基のイミドと電気陰性な窒素原子の導入を指針とすることで、優れた電子受容性を持つ機能性 π 共役分子の創出に成功した¹⁾。一方、2つのフェナレンが縮環した構造をもつゼトレンは、電子受容性に長けている。本研究では上記の指針をゼトレンに適用することで、さらに高い電子受容性をもつ π 共役分子の創製を目指した。アルキンで架橋されたアミノナフタレンモノイミド **1** に対して分子内ヒドロアミノ化を行うことで、アザフェナレン中間体 **2** を合成した。興味深いことに、化合物 **2** にジクロロジシアノベンゾキノンを用いたところ、化合物 **3** のみならずその二量体 **4** も得られた。電気化学測定の結果、化合物 **3** および **4** は非常に高い電子受容性を有することがわかった。この高い電子受容性に注目し、化合物 **3** に2当量のコバルトセンを用いたところ、対応するジアニオンの単離に成功した。ジアニオンは大気下で取り扱えるほど安定であった。



1) Tajima, K.; Matsuo, K.; Yamada, H.; Seki, S.; Fukui, N.; Shinokubo, H. *Angew. Chem. Int. Ed.* **2021**, *60*, 14060.

インデノペリレンおよびその π 拡張誘導体の合成と長波長吸収特性

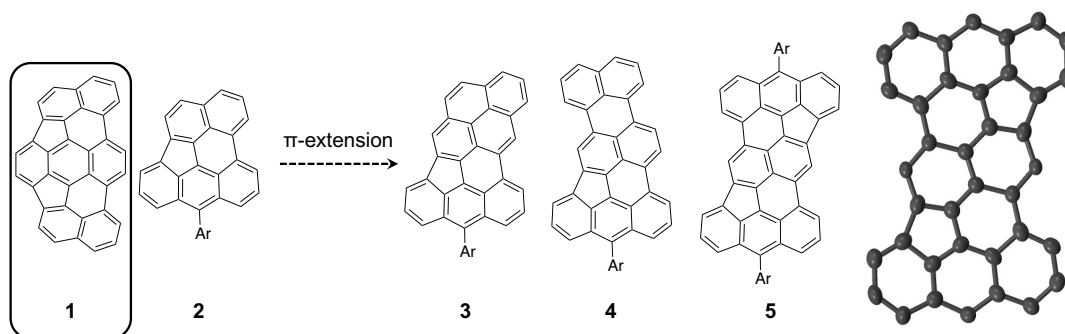
(名大院工) 加藤 将輝、○福井 識人、忍久保 洋

Synthesis and long-wavelength-absorption of indenoperylene and its π -extended derivatives
(Graduate School of Engineering, Nagoya University) Masaki Kato, Norihito Fukui, Hiroshi Shinokubo

Polycyclic aromatic hydrocarbons (PAHs) with a narrow HOMO–LUMO gap are attractive research targets. These molecules exhibit intriguing properties including near-infrared (NIR) absorption and reversible redox activity. Recently, we have reported *as*-indacenoterrylene, a bowl-shaped PAH that exhibits near-infrared absorption. In this presentation, we report its substructure, indenoperylene. The absorption of indenoperylene covered entire visible region despite its medium-sized structure. We also synthesized its π -extended derivatives, which exhibited near-infrared absorption.

Keywords : polycyclic aromatic hydrocarbons; indenoperylene; five-membered ring; near-infrared absorption; π -extension

狭い HOMO–LUMO ギャップをもつ多環芳香族炭化水素 (PAH) は、近赤外吸収や可逆的な酸化還元活性といった魅力的な電子的特性を示すため、近年注目されている。ごく最近、我々は近赤外領域までの吸収を示すお椀型 PAH であるインダセノテルリレン **1** を合成した^[1]。本研究では、その部分骨格であるインデノペリレン **2** を合成した。インデノペリレン **2** は中程度のサイズを有する PAH でありながら可視光全域を吸収した^[2]。また、インデノペリレンの π 拡張体 **3**、**4**、**5** を合成した。化合物 **4** と **5** はさらに長波長化した吸収を示し、その末端は近赤外領域まで及んでいた。



1. Tanaka, Y.; Fukui, N.; Shinokubo, H. *Nat Commun* **2020**, *11*, 3873.
2. Kato, M.; Fukui, N.; Shinokubo, H. *Chem. Eur. J.* **2021**, *in press*.

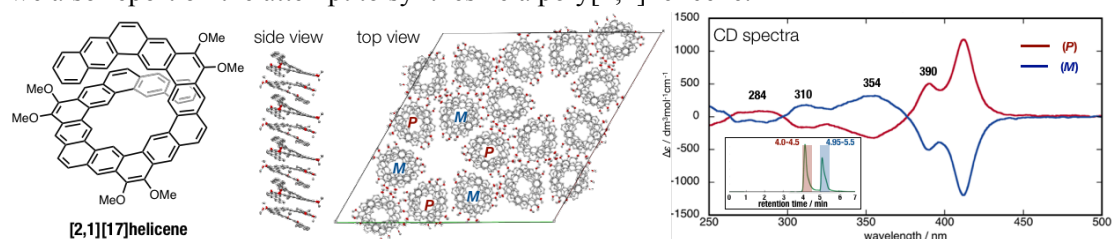
Synthesis, Structure and Properties of π -Expanded Carbohelicenes

(¹Graduate School of Science, Nagoya University, Nagoya University, ²Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University) ○ Michihisa Toya,¹ Hideto Ito,¹ Kenichiro Itami,^{1,2}

Keywords: Expanded Helicene; π -Conjugated Molecule; Ladder Molecule; Optical Resolution; Helical Polymer

Helicene represents one of the non-planar aromatics with a helical structure. The development of helicene chemistry has diversified by elongation, conjugation of multi-helicene, and laterally π -elongation of the helicene structure.¹ In particular, expanded helicenes with a larger diameter of the shaft are one of great interests in this field and materials science.² They are expected to exhibit the molecular encapsulation ability taken advantage of their vacancies, and larger π -conjugation and π - π overlapping between helical pitches than conventional helicenes, resulting in novel electrical, optical, and chiroptical properties. Particularly, [2,1]helicenes, kekulene-like-shaped expanded helicenes, have attracted much attention due to those simple and beautiful structures and unique physical and electronic properties.^{2a,b,c} However, the chemistry of [2,1]helicenes are still in its infancy and only shorter racemic analogues with 13 benzene rings were reported so far.

Herein, we report the synthesis of novel expanded [2,1]carbohelicenes composed of 15 and 17 benzene rings. The stepwise Wittig elongation of dibromo phenanthrene units having aldehyde and phosphonium salt and subsequent ring closure by Yamamoto coupling successfully afforded up to [2,1][17]helicene. The structural and photophysical evaluations by NMR and X-ray crystallographic analyses and conventional spectroscopic analyses were also performed. Furthermore, we succeeded in the optical resolution of right- and left-handed helicenes for the first time in the related molecules, and clarified those chiroptical properties by circular dichroism (CD). The racemization process and photophysical properties were also estimated by computational studies. In the presentation, we also report on the attempt to synthesize a poly[2,1]helicene.



- 1) a) Shen, Y.; Chen, C.-F. *Chem. Rev.* **2012**, *112*, 1463. b) Li, C.; Yang, Y.; Miao, Q. *Chem. Asian J.* **2018**, *13*, 884. 2) a) Porsev, V. V.; Bandura, A. V.; Lukyanov, S. I.; Evarestov, R. A. *Carbon* **2019**, *152*, 755. b) Kiel, G. R.; Patel, S. C.; Smith, P. W.; Levine, D. S.; Tilley, T. D. *J. Am. Chem. Soc.* **2017**, *139*, 18456. c) Nakanuki, Y.; Hirose, T.; Matsuda, K. *J. Am. Chem. Soc.* **2018**, *140*, 15461. d) Fujise, K.; Tsurumaki, E.; Wakamatsu, K.; Toyota, S. *Chem. Eur. J.* **2021**, *27*, 4548. e) Fujise, K.; Tsurumaki, E.; Fukuhara, G.; Hara, N.; Imai, Y.; Toyota, S. *Chem. Asian J.* **2020**, *15*, 2456.

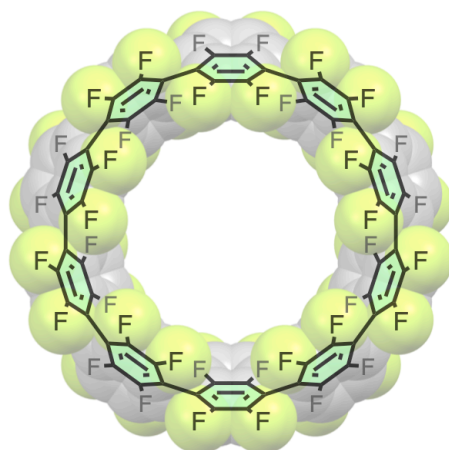
Perfluorocycloparaphenylenes: Fully fluorinated carbon nanorings by Ni-mediated one-pot synthesis

(¹Graduate School of Science, Nagoya University, ²Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, ³Institute of Advanced Energy, Kyoto University, ⁴Graduate School of Engineering, Osaka University, ⁵Institute for Molecular Science, ⁶SOKENDAI)

○Hiroki Shudo,¹ Motonobu Kuwayama,² Masafumi Shimasaki,³ Taishi Nishihara,³ Youhei Takeda,⁴ Takuya Kuwabara,^{1,2} Akiko Yagi,^{1,2} Yasutomo Segawa,^{5,6} Kenichiro Itami^{1,2}

Keywords: Perfluorinated compounds; Cycloparaphenylenes; Nickel complex; Perfluorocycloparaphenylenes

Perfluorinated aromatic compounds, the so-called *perfluoroarenes*, are widely used in materials science owing to their high electron affinity and characteristic intermolecular interactions. However, methods to synthesize highly strained perfluoroarenes have remained elusive so far,¹ which greatly limits their structural diversity. Herein, we report the synthesis and isolation of perfluorocycloparaphenylenes (PFCPPs) as a class of ring-shaped perfluoroarenes.² Using macrocyclic nickel complexes, we succeeded in synthesizing PF[n]CPPs ($n = 10, 12, 14, 16$) in one-pot without noble metals. The molecular structures of PF[n]CPPs ($n = 10, 12, 14$) were determined by X-ray crystallography to confirm their tubular alignment. Photophysical and electrochemical measurements revealed that PF[n]CPPs ($n = 10, 12, 14$) exhibit wide HOMO–LUMO gaps, high electron affinity, and strong phosphorescence at low temperature. PFCPPs are not only useful as electron-accepting organic semiconductors but can also be used for accelerating the creation of topologically unique molecular nanocarbon materials.



- 1) a) Sakamoto, Y.; Suzuki, T. *J. Org. Chem.* **2017**, 82, 8111. b) Troyanov, S. I.; Kemnitz, E. *Curr. Org. Chem.* **2012**, 16, 1060.
- 2) Shudo, H.; Kuwayama, M.; Shimasaki, M.; Nishihara, T.; Takeda, Y.; Kuwabara, T.; Yagi, A.; Segawa, Y.; Itami, K. *ChemRxiv*, **2021**, DOI: 10.33774/chemrxiv-2021-7kd63

多角形組立戦略によるフェナインナノカーボン分子の合成

(東大院理¹) ○美尾樹¹, 池本晃喜¹, 佐藤宗太¹, 磯部寛之¹

Synthesis of Phenine Nanocarbon Molecules via a Polygon-Assembling Strategy (¹*Department of Chemistry, The University of Tokyo*) ○Tatsuru Mio,¹ Koki Ikemoto,¹ Sota Sato,¹ Hiroyuki Isobe¹

For the synthesis of large nanocarbon molecules comprising 1,3,5-trisubstituted benzene (phenine), we devised a polygon-assembling strategy where preformed polygons of phenine are assembled. As the first demonstration of this strategy, the synthesis of hemispherical phenine nanocarbon ($C_{180}H_{220}$) was accomplished by assembling two types of phenine pentagons (**1** and **2**) by Suzuki-Miyaura coupling, followed by "stitching" biaryl bonds at the periphery. Despite the presence of 220 protons in the structure of hemispherical phenine nanocarbon, only 11 resonances were observed in the 1H NMR spectrum, suggesting a highly symmetric structure. On the other hand, single-crystal X-ray diffraction analysis revealed an ovaly-deformed geometry of the molecule. With the aid of theoretical calculations and a geometric measure developed as curved phenine normal vectors (CPNV), the origin of the structural deformation was ascribed to fluctuations of inter-phenine dihedral angles.

Keywords : Hemispheres; Polygons; Macrocycles; Flexibility; Coupling reactions

1,3,5-三置換ベンゼン (フェナイン) を用いた巨大ナノカーボン分子設計を展開し, フェナイン多角形ユニットを組み合わせ, より巨大な分子の簡便合成を可能とする「多角形組立」戦略を考案した¹. この戦略に基づき, 2種類の五角形ユニット (**1** and **2**) を鈴木-宮浦カップリングによる連結し, 周縁部を縫い上げることで, 半球型フェナインナノカーボン ($C_{180}H_{220}$) を合成した (Figure 1). 1H NMR スペクトルから, 分子中の 220 個の水素原子に対し, 11 本のピークのみが観測され, C_{5v} の高い対称性を有していることが示唆された. 一方, 単結晶 X 線回折構造は楕円型に変形していた. 理論計算に加え, フェナインナノカーボンの構造評価指標として Curved Phenine Normal Vector (CPNV) を新たに導入することで², 歪んだ構造がフェナインユニット間の二面角のゆらぎに由来することを明らかにした.

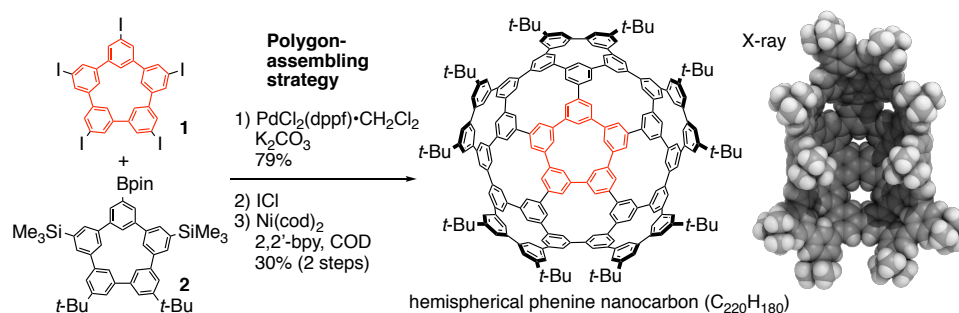


Figure 1. Polygon-assembling strategy for the synthesis of hemispherical phenine nanocarbon
1) T. Mio, K. Ikemoto, S. Sato, H. Isobe, *Angew. Chem. Int. Ed.* **2020**, *59*, 6567-6571. 2) T. Mio, K. Ikemoto, H. Isobe, *Chem. Asian J.* **2020**, *15*, 1355-1359.

錯体ナノ空間を用いた芳香族ラダー高分子の合成

(東大院工¹・JST さきがけ²) ○三浦 匠¹・北尾 岳史^{1,2}・植村 卓史¹

Synthesis of aromatic ladder polymer utilizing coordination nanospaces

(¹Graduate School of Engineering, The University of Tokyo, ²JST-PRESTO) ○Takumi Miura,¹ Takashi Kitao,^{1,2} Takashi Uemura¹

Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings. Since the carrier mobility of acenes increases with the number of benzene rings, effective methods for synthesis of long acenes have been highly required. Here, we report the synthesis of acenes with infinitely fused benzene rings, namely polyacene, utilizing metal-organic frameworks (MOFs) as a template.

We performed polymerization of a naphthalene derivative within one-dimensional nanochannels of the MOFs. In contrast to the bulk condition, unfavorable crosslinking reaction was effectively suppressed within the MOFs, providing the precursor polymer with 71 linearly fused rings. Subsequently, dehydro-aromatization reaction was performed by heating the nanocomposite of the MOF including the precursor polymer.

Keywords : Metal-Organic Framework; Ladder polymer; Annulation reaction

ベンゼン環が直線状に縮環したアセンは、高いキャリア移動度を有するため、次世代ナノデバイスの基幹材料として注目されている。アセンは環の個数の増加に従いキャリア移動度が大きくなるため、長いアセン(=ポリアセン)の合成手法の開発が強く求められている。多孔性金属錯体(MOF)は、その構成要素を適切に選択することで、細孔構造を原子レベルで緻密に設計できる。そのため、MOF が有するナノ空間を高分子合成の場として用いることで、得られる高分子の構造を精密に制御することが可能である。本研究では、MOF の一次元ナノ細孔を多環芳香族炭化水素の重合場として用いることで、架橋反応を抑制し、ポリアセンを合成した。

高い熱安定性を持つ MOF の 1 次元細孔内でナフタレン誘導体を重合した。モノマーのみを加熱した場合、分子間の架橋反応が進行し、枝分かれ構造を有する生成物が確認された。それに対して、MOF から単離した前駆体の IR・¹³C-NMR・MALDI-TOF MS 測定から、MOF 細孔内では一次元的に重合反応が進行し、長いもので環が 71 個連結した前駆体高分子が形成されていることが分かった(**Fig. 1**)。続いて、MOF と前駆体高分子複合体を加熱処理することで、MOF の細孔内で脱水素芳香化反応を行った。

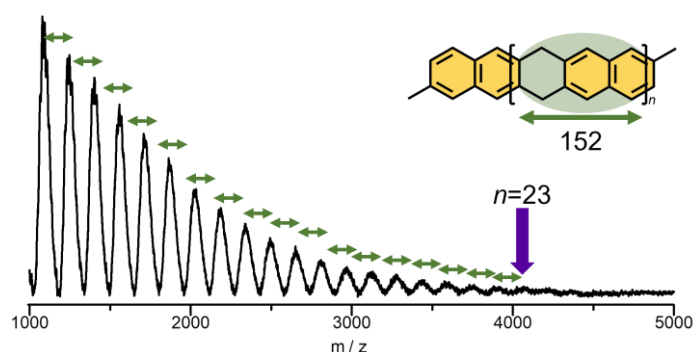


Fig. 1 MALDI-TOF MS spectrum of precursor polymer.

Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry- | Oral B**[K1-1pm] 11. Organic Chemistry -Structural Organic Chemistry-**

Chair: Aiko Fukazawa, Wataru Setaka

Wed. Mar 23, 2022 1:20 PM - 3:40 PM K1 (Online Meeting)

[K1-1pm-01] Synthesis of Calix[3]pyrrole and Its Strain-induced Reaction○Yuya Inaba¹, Jenny Pirillo², Yuh Hijikata², Yasuhide Inokuma^{1,2} (1. Grad. Sch. Eng., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ.)

1:20 PM - 1:40 PM

[K1-1pm-02] Structure and Properties of Silylene-Coordinated Si=B Bonded Species○Taichi Koike¹, Takeaki Iwamoto¹ (1. Tohoku University)

1:40 PM - 2:00 PM

[K1-1pm-03] Design and synthesis of a phenine nanocage with chirality○Toshiya M. Fukunaga¹, Takahide Kato¹, Koki Ikemoto¹, Hiroyuki Isobe¹ (1. The University of Tokyo)

2:00 PM - 2:20 PM

[K1-1pm-04] Structural Control of [3]Catenanes Composed of Cyclic Porphyrin Dimers via Complexation with Amine Templates○Yuki Oka¹, Hiroshi Masai¹, Jun Terao¹ (1. Graduate School of Arts and Science, The University of Tokyo)

2:20 PM - 2:40 PM

[K1-1pm-05] Synthesis and characteristics of well-defined and flexible foldamers○Takuma Morozumi^{1,2}, Masayuki Takeuchi^{1,2} (1. University of Tsukuba, 2. National Institute for Materials Science (NIMS))

2:40 PM - 3:00 PM

[K1-1pm-06] Design and synthesis of benzo[*de*]isoquinolino[1,8-*gh*]quinoline diamides π -electron systems○Craig P. Yu¹, Akito Yamamoto², Shohei Kumagai¹, Hiroyuki Ishii³, Jun Takeya^{1,4}, Toshihiro Okamoto^{1,5,6} (1. The University of Tokyo, 2. Daicel Corporation, 3. University of Tsukuba, 4. National Institute for Materials Science (NIMS), 5. PRESTO, JST, 6. CREST, JST)

3:00 PM - 3:20 PM

[K1-1pm-07] Synthesis of Pyrrole-Based Quinoidal Molecules with Open-Shell Structures○Shinya Sugiura¹, Hiromitsu Maeda¹ (1. Ritsumeikan Univ.)

3:20 PM - 3:40 PM

Synthesis of Calix[3]pyrrole and Its Strain-Induced Reaction

(¹Grad. Sch. Eng., Hokkaido Univ., ²WPI-ICReDD, Hokkaido Univ.) ○Yuya Inaba,¹ Jenny Pirillo,² Yuh Hijikata,² Yasuhide Inokuma^{1,2}

Keywords: Calix[*n*]pyrrole; Ring Strain; Ring Expansion Reaction; Anion Binding; Carbonyl Compound

Tetrapyrrolic macrocycles such as porphyrins can be selectively obtained by condensation reaction of pyrrole and carbonyl compounds, whereas corresponding tripyrrolic macrocycles have been never observed except boron complex obtained by template synthesis. Calix[3]pyrrole, a tripyrrolic macrocycle bearing three *sp*³ carbon linkage, might hold a key to explain the absence of macrocycle with three pyrrole subunits. In this work, we synthesized calix[3]pyrrole **1** and discovered its strain-induced ring expansion reaction.¹ Besides, core-modified analogues of **1** having different strain energies were prepared to investigate the substrate scope and reaction mechanism of the strain-induced ring expansion reaction.

Calix[3]pyrrole **1** (**Figure 1a**) was obtained from aliphatic hexaketone compound via cyclization and Paal-Knorr pyrrole formation reaction. Crystal structure of **1** have shown its strained structure, which was also indicated by computational analysis. This strain caused **1** a rapid ring expansion reaction under acidic conditions to give calix[6]pyrrole **2** within 30 seconds (**Scheme 1**). This result helps us to explain the absence of tripyrrolic macrocycles in classical acid-catalyzed condensation reactions.

To gain a better understanding about this ring expansion reaction, calix[*n*]furan[3–*n*]pyrrole **3–5** (*n* = 1–3, **Figure 1b**) were synthesized in a manner similar to **1**. Presumed from crystal structures and theoretical calculations, the ring strain increases as the number of inner NH sites increases. Under acidic conditions, calix[1]furan[2]pyrrole **3** caused regioselective ring expansion reaction to give macrocycle **6** over 5 minutes, while less-strained **4** and **5** were stable. Although **4** was inert, *N*-methylation of **4** impelled the ring expansion reaction and enabled the isolation of linear reaction intermediate which gives a clue to explain a reaction mechanism. This unique reactivity of calix[3]-type macrocycles could provide access to new larger pyrrolic macrocycles.

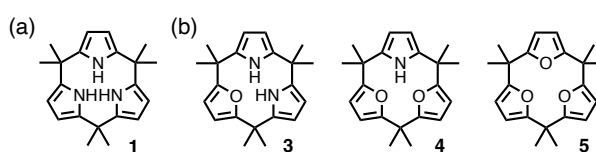
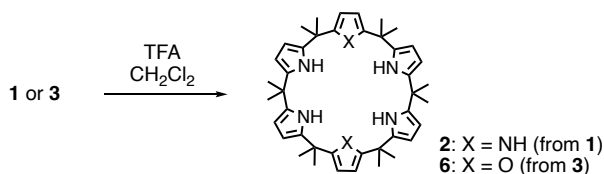


Figure 1. (a) Structure of **1** and (b) its analogues **3–5**.



Scheme 1. Ring expansion reaction of **1** and **3**.

1) Y. Inaba, Y. Nomata, Y. Ide, J. Pirillo, Y. Hijikata, T. Yoneda, A. Osuka, J. L. Sessler, Y. Inokuma, *J. Am. Chem. Soc.*, **2021**, *143*, 12355–12360.

Structure and Properties of Silylene-Coordinated Si=B Bonded Species

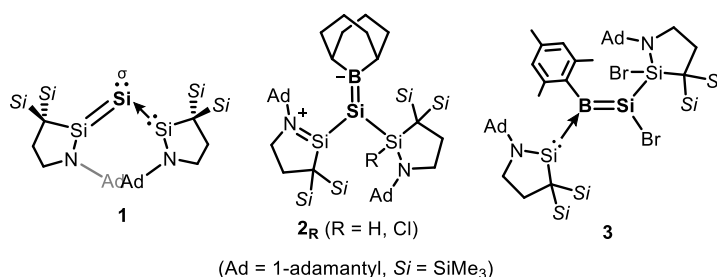
(Graduate School of Science, Tohoku University) ○Taichi Koike, Takeaki Iwamoto

Keywords: Silicon, Boron, Silicon-Boron Double Bond, Silylene, Main-Group-Element Chemistry

Heavier multiply bonded species of p-block elements have attracted interest not only due to their unique optical properties attributed to the narrow HOMO-LUMO gap, but due to their ability to activate small molecules such as H₂ and CO.¹ While the structures and reactivities of homoatomic doubly bonded species of silicon (disilenes) and boron (diborenes) have been extensively investigated, the studies on their heteroatomic counterpart, Si=B double-bonded species, remain scarce.²

Recently, our group reported the synthesis of the cyclic (alkyl)(amino)silylene (CAASi)-stabilized monoatomic silicon complex **1** which exhibits a π -delocalized-ylidene structure in solution (Chart 1).³ Spectroscopic studies and DFT calculations revealed the high electron density on the central silicon atom as well as the highly polarized Si=Si double bond character of silylone **1** which brought us to think that **1** could be an adequate precursor to access new silicon-containing π -electron systems. Herein, we report the facile synthesis of CAASi-stabilized zwitterionic boratasilenes **2_R** and borasilene **3** (Chart 1) by the treatment of **1** towards various hydro/haloboranes at ambient conditions. In this presentation, the synthesis, structure, and unique electronic properties of the Si=B bonded species will be discussed.

Chart 1.



1) T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608–3680. 2) N. Nakata, A. Sekiguchi, *J. Am. Chem. Soc.* **2006**, *128*, 422–423; Y. Suzuki, S. Ishida, S. Sato, H. Isobe, T. Iwamoto, *Angew. Chem. Int. Ed.* **2017**, *56*, 4593–4597. 3) T. Koike, T. Nukazawa, T. Iwamoto, *J. Am. Chem. Soc.* **2021**, *143*, 14332–14341.

Design and synthesis of a phenine nanocage with chirality

(¹Department of Chemistry, The University of Tokyo) ○Toshiya M. Fukunaga,¹ Takahide Kato,¹ Koki Ikemoto,¹ Hiroyuki Isobe¹

Keywords: diamond twin; carbon; chirality; helicity; stereoisomerism

The chemistry of sp^2 -hybridized carbon atoms started from the studies of its two-dimensional networks with benzene/graphite/graphene. Types of the sp^2 -network were further expanded by the discovery of curved variants such as fullerene and carbon nanotubes. The discovery of these carbon allotropes ignited interests of chemists in exploring unique nanocarbon molecules with large sp^2 -networks via organic syntheses. In our group, the nanocarbon molecules are being diversified by a synthetic strategy that adopts "phenine (1,3,5-trisubstituted benzene)" as a fundamental trigonal planar unit to be assembled.¹ Herein, the phenine strategy is expanded to design a nanometer-sized cage **1** with chirality (Figure 1a). Phenine nanocage **1** possessed 14 phenine vertices, and the synthesis was completed by forming 15 edges between them via coupling reactions. The synthetic route was versatile enough to introduce various substituents, and nanocage **2** with 26 phenine units was also synthesized to install radiating phenine substituents on the cage. The atomic-level structure of the phenine nanocage **1** was revealed by X-ray diffraction analysis of a single crystal (Figure 1b). Although there were potentially 5600 isomeric structures arising from (*R*)/(*S*) atropisomerism at 15 biaryl edges, phenine nanocage **1** existed as a singly pair of enantiomers in the crystal. The chirality of **1** originates from the helicity around the major C_3 axis, and we propose the stereochemistry to be described with "(*P*)" and "(*M*)" descriptors. Although stereochemical non-rigidity of **1** and **2** obscured their chirality, structural rigidification with a dimethylated linkage allowed for the chiral resolution of the enantiomers of phenine nanocages. Our perspective over the chiral phenine nanocage will be disclosed and discussed in the presentation.

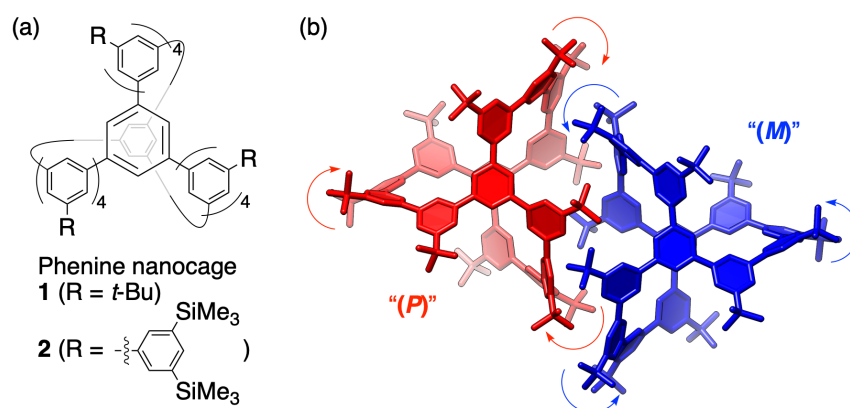


Figure 1. Phenine nanocages. (a) Chemical structures. (b) Crystal structures of **1**.

1) K. Ikemoto, H. Isobe, *Bull. Chem. Soc. Jpn.* **2021**, 94, 281.

(¹Graduate School of Arts and Science, The University of Tokyo) ○Yuki Oka¹, Hiroshi Masai¹, Jun Terao¹

Keywords: Mechanically Interlocked Molecule; Porphyrin; Non-Covalent Bonding; Template Synthesis; Host Guest

Catenanes have the potential for applications such as molecular machines owing to the unique motility among mechanically interlocked cyclic components.¹ So far, most of catenanes functionalized by switching between the only two states of their supramolecular structures to change the motility of cyclic components. For further extension of higher-order functionalized catenanes, it is desired to develop methodologies for manipulating the more complicated motilities of cyclic components and to output the controlled motility as the functionality of catenanes. In this work, we achieved three-states switching of motility of cyclic components by synthesizing [3]catenane **1** composed of three cyclic porphyrin dimers (**Fig 1**). The [3]catenane **1** formed different supramolecular structures **2** and **3** utilizing coordination bonds between Ru or Zn porphyrins and multidentate amine ligands **L1** or **L2**. In case of **2**, all of three cyclic components were connected through Zn–N and Ru–N coordination bonding with **L1**. On the other hand, in **3**, only two cyclic components were connected via complexation with **L2**. Thus formed different supramolecular structures of [3]catenanes that had different motility of cyclic components depending on how cyclic components were connected through coordination bonds. Furthermore, fluorescence measurements revealed that the manipulation of cyclic component motilities leads to the regulation of communication among multiple cyclic components of [3]catenane.

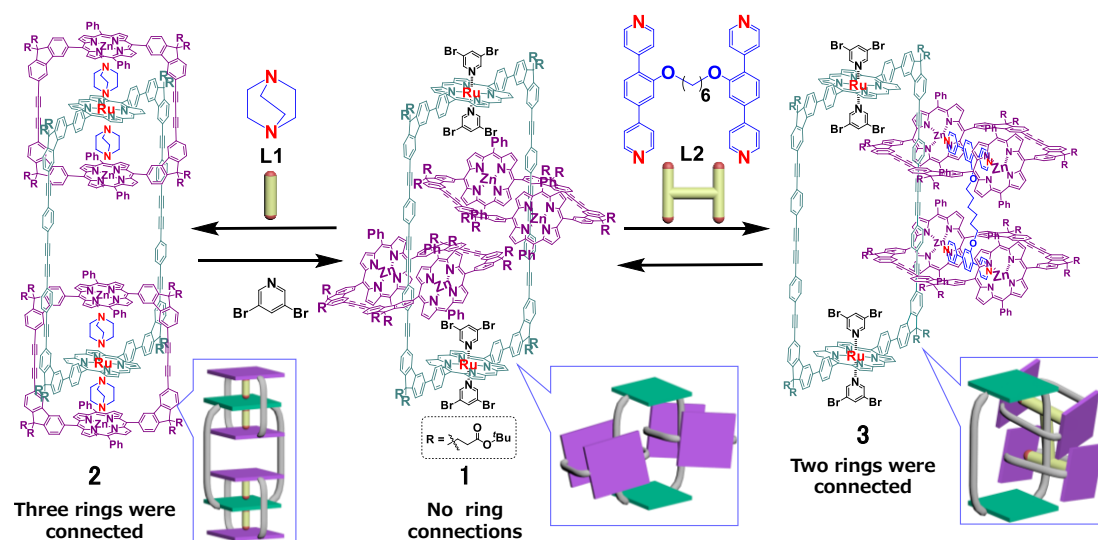


Figure 1. Structure of the [3]catenane **1** and switching of its supramolecular structures.

1) Gil-Ramírez, G.; Leigh, D.A.; Stephens, A. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 6110.

高分子の主鎖間配向を模したフォルダマーの合成と電子物性の制御

(筑波大院理工情報数理物質¹・物質・材料研究機構 (NIMS)²) ○両角 拓磨^{1,2}・竹内正之^{1,2}

Synthesis and characteristics of well-defined and flexible foldamers (¹*Faculty of Pure and Applied Sciences, University of Tsukuba*; ²*National Institute for Materials Science (NIMS)*)

○Takuma Morozumi,^{1,2} Masayuki Takeuchi^{1,2}

In semiconductor polymers, the design has been focused on the electronic structure and/or high crystallinity; recently, it has been revealed that the control over the orientation of main chains, such as the angle, distance, or dihedral angle between polymer main chains, is important.¹ We herein report the design and synthesis of new foldamers and cyclophane as a model of polymer stacking structure. The foldamers are designed to take well-defined structures which enable them to change their orientations upon external perturbation. This design is meant to imitate crystalline solid structures of π -extended polymers. Using various measurements, the foldamers were revealed to adopt the folded structures, where the direction of the BT11s was aligned; in addition, the temperature dependence on fluorescence intensity was reversed by solvent. We infer that this dependence was derived from change for population of dimer-like and monomer-like conformation.

Keywords : Foldamer; π -electronic properties; Orientation control

有機半導体高分子の研究においては、かつてはモノマー、ポリマーの電子構造や結晶性の高さに重点が置かれてきた。近年、その性能を調節するためには分子鎖間の配列数・角度・距離・ずれ・ドメインサイズなど、分子鎖間の情報を含んだ高次構造やそれを制御するプロセスも重要であることが認識されている¹⁾。我々は、BTTTモノマーの積層構造を維持しつつも柔軟に層間距離や角度が可変なフォルダマー群およびシクロファンを新規に合成した。構造解析の結果、合成した分子は全てのBTTTが同一方向に揃い折りたたまれた構造をしていることが示唆された。またこのフォルダマー群は蛍光強度の温度依存性が溶媒によって逆転する現象などを示し、積層構造に対する摂動の結果生じる様々な現象を見出した。

1) R. C. Smith, *Macromol. Rapid Commun.* **2009**, 30, 2067.

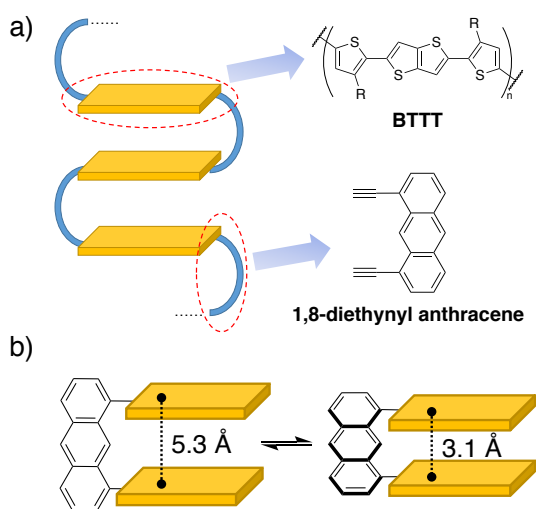


Figure 1: a) Molecular design of flexible and well-defined foldamer. b) Schematic representation for the valuable distance of an anthracene linker.

Design and synthesis of benzo[de]isoquinolino[1,8-gh]quinoline diamides π -electron systems

(¹Graduate School of Frontier Sciences, The University of Tokyo, ²Daicel Corp., ³University of Tsukuba, ⁴WPI-MANA, NIMS, ⁵PRESTO, JST, ⁶CREST, JST)

○Craig P. Yu,¹ Akito Yamamoto,² Shohei Kumagai,¹ Hiroyuki Ishii,³ Jun Takeya,^{1,4} Toshihiro Okamoto^{1,5,6}

Keywords: n-type organic semiconductors; nitrogen-containing π -electron system; molecular design; molecular assembly; organic field-effect transistors

Synthetically versatile electron-deficient π -electron systems are urgently needed for organic electronic applications, yet their design and synthesis are challenging due to the low reactivity from large electron affinities.¹ The high-performance benzo[de]isoquinolino[1,8-gh]quinolinetetracarboxylic diimide (BQQDI) n-type organic semiconductors² (Figure 1) possess deep-lying lowest unoccupied molecular orbital (LUMO) levels that are necessary for air-stable electron transports in transistors, but this very electronic feature limits their synthetic and application versatilities. In the current molecular design, we remove a CO group from each imide of the BQQDI to introduce the novel benzo[de]isoquinolino[1,8-gh]quinoline diamide (BQQDA) π -electron system (Figure 1).³ The push-pull nature of the condensed amide moieties as opposed to the strongly electron-deficient imide provide versatility in chemical functionalization to tailor the BQQDA π -electron system for various electronic applications.

We demonstrate an effective synthetic method to furnish the target amide-containing BQQDA parent structure via organocatalysis, and highly selective functionalization can

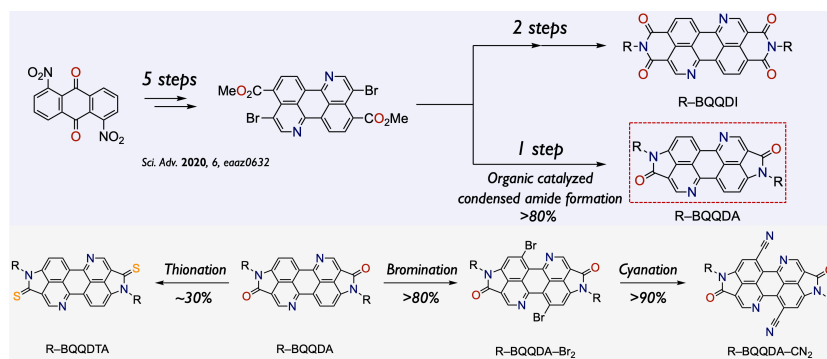


Figure 1 The synthetic routes for R-BQQDI, R-BQQDA and various chemical modifications of the BQQDI π -electron system.

moieties as well as on the *bay* positions of the nitrogen-containing skeleton. Fine-tuning of the fundamental properties and supramolecular packing motifs are achieved via chemical modifications (Figure 1), and the cyanated BQQDA organic semiconductor demonstrates a high air-stable electron-carrier mobility. Besides their uses in transistors, the photochemical properties of the BQQDA π -electron systems also show promise for optoelectronic applications.

- 1) Usta, H. *et al.*, *Acc. Chem. Res.* **2011**, 44, 501–510.
- 2) Okamoto, T. *et al.*, *Sci. Adv.* **2020**, 6, eaaz0632.
- 3) Yu, C. P. *et al.* *Submitted*.

ピロール架橋型キノンの合成と開殻系への展開

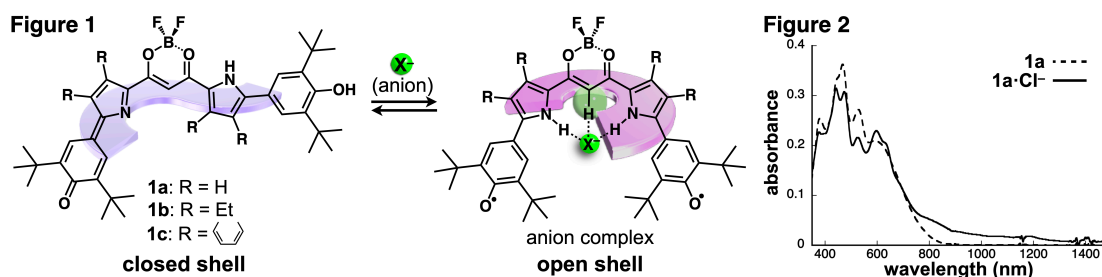
(立命館大生命科学) ○杉浦 慎哉・前田 大光

Synthesis of Pyrrole-Bridged Quinoidal Molecules with Open-Shell Structures (*College of Life Sciences, Ritsumeikan University*) ○Shinya Sugiura, Hiromitsu Maeda

π -Extended quinoid molecules, exhibiting diradical properties and near-infrared absorptions, have been of interest in various fields. Controlling electronic and optical properties of quinoid units exhibiting tautomerism would provide materials responsive to external stimuli. In the previous work, pyrrole-bridged quinones were synthesized for the evaluations of their tautomeric behaviors depending on external stimuli. In this study, quinoidal pyrrole-based anion-responsive π -electronic systems were synthesized for exhibiting diradical properties, which can be controlled by anion binding. Quinoidal anion-responsive molecules were obtained by oxidative reaction of corresponding precursors with PbO_2 , and ^1H NMR signals showed only closed-shell forms in CDCl_3 . Furthermore, UV/vis absorption spectrum was changed upon the addition of Cl^- , suggesting that the tautomer ratios, which are correlated with diradical properties, could be controlled by Cl^- binding.

Keywords : π -conjugated systems; pyrrole derivatives; quinone; tautomerism; diradical property

拡張 π 電子系キノン誘導体は、ジラジカル特性や長波長領域の吸収を示すことから、広い分野で注目されている。互変異性によるキノイド分子の電子・光物性を制御できれば、刺激応答性材料への展開が期待できる。われわれは、ピロール架橋したキノン誘導体を新たに合成し、外部刺激によって互変異性の制御が可能であることを見出した。¹⁾ 以上をふまえ、本研究では、ピロールからなるアニオン応答性 π 電子系にキノンユニットを導入することで、アニオン会合によるジラジカル性の制御を検討した (Figure 1)。対応するフェノール前駆体に対し PbO_2 を用いた酸化によって **1a–c** の合成に成功し、 ^1H NMR からいずれも CDCl_3 中で閉殻構造を形成することが明らかになった。さらに、**1a** は CH_2Cl_2 中で Cl^- 添加により近赤外領域に吸収帯が観測されたことから、アニオン会合による互変異性の変調にともなうジラジカル性の発現が示唆された (Figure 2)。²⁾



1) Sugiura, S.; Maeda, H. *Chem. Commun.* **2021**, 57, 6983.

2) Sugiura, S.; Maeda, H. to be submitted.

[H301-1pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Yukatsu Shichibu, Yoko Sakata

Wed. Mar 23, 2022 1:00 PM - 3:40 PM H301 (Online Meeting)

- [H301-1pm-01] Generation of a Monomerically Dispersed C₆₀ Monolayer Templated by a Two-Dimensional Crystal of Macrocycles
○Shin-ichiro Kawano¹, Masato Nakaya², Atsuki Ishiguro¹, Masaaki Saitow³, Takeshi Yanai⁴, Jun Onoe², Kentaro Tanaka¹ (1. Nagoya University, Graduate School of Science, 2. Nagoya University, Graduate School of Engineering, 3. Nagoya University, Research Center for Materials Science, 4. Nagoya University, ITbM)
1:00 PM - 1:20 PM
- [H301-1pm-02] Size-sensitive recognition of nanometer-sized Guests by Rim-Extended Cyclodextrins
○Takato Ogata¹, Hiroki Hanayama¹, Koji Harano¹, Eiichi Nakamura¹ (1. Grad. Sch. of Sci., The Univ. of Tokyo)
1:20 PM - 1:40 PM
- [H301-1pm-03] Optical Properties and Molecular Recognition of a Sumanene-Based Chemosensor
○Hiroaki Mizuno¹, Hironobu Nakazawa², Akihisa Miyagawa³, Yumi Yakiyama², Hidehiro Sakurai², Gaku Fukuhara¹ (1. Dept. of Chem., Tokyo Tech, 2. Dept. of Appl. Chem., Osaka Univ., 3. Dept. of Chem., Univ. of Tsukuba)
1:40 PM - 2:00 PM
- [H301-1pm-04] Guest Encapsulation Behavior of Covered Fluorine-modified Hollow-type Metal Oxide Cluster {Mo₁₃₂}
○Chinatsu Murata¹, Yukatsu Shichibu^{1,2}, Katsuaki Konishi^{1,2} (1. Grad. Sch. Env. Sci., Hokkaido Univ., 2. Fac. Env. Earth Sci., Hokkaido Univ.)
2:00 PM - 2:20 PM
- [H301-1pm-05] Self-assembly process of a supramolecular square built in paddle-wheel-type dinuclear rhodium(II) complex as a corner unit
○Atsushi Okazawa¹, Satoshi Takahashi², Shuichi Hiraoka² (1. Nihon Univ. Sch. Med., 2. Dept. of Basic Sci., The Univ. of Tokyo)
2:20 PM - 2:40 PM
- [H301-1pm-06] Kinetically Controlled Coordination Self-assembly: Approaches to Pathway Selection
○Shuichi Hiraoka¹, Naoki Sanada¹, Satoshi Takahashi¹, Tomoki Tateishi¹, Isamu Kikuchi¹ (1. the University of Tokyo)
2:40 PM - 3:00 PM
- [H301-1pm-07] Recognition of Aromatic Compounds Using Crystal of Tetraphenylethene Derivatives
○Takahiro Kakuta¹, Yuki Sugimoto¹, Ryota Nakanishi¹, Shigehisa Akine¹, Tada-aki Yamagishi¹ (1. Kanazawa University)
3:00 PM - 3:20 PM

[H301-1pm-08] Size-selective Guest Recognition and the Open/Close Control of
Macrocyclic Cobalt(III) Dinuclear Metallohosts Having Bulky
Bridging Ligands

○Ryo Sudo¹, Yoko Sakata^{1,2}, Shigehisa Akine^{1,2} (1. Graduate School of Natural Science
and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa
University)

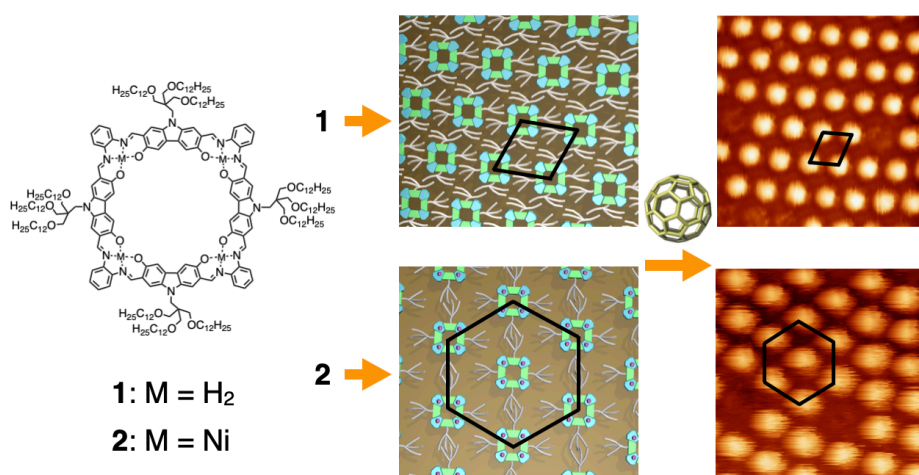
3:20 PM - 3:40 PM

Generation of a Monomerically Dispersed C₆₀ Monolayer Templated by a Two-Dimensional Crystal of Macrocycles

(¹Graduate School of Science, Nagoya University, ²Graduate School of Engineering, Nagoya University, ³Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University) ○ Shin-ichiro Kawano,¹ Masato Nakaya,² Atsuki Ishiguro,¹ Masaaki Saitow,¹ Takeshi Yanai,³ Jun Onoe,² Kentaro Tanaka¹

Keywords: Supramolecular Chemistry; Host–Guest Chemistry; Macrocycle; Nanospace; Scanning Tunneling Microscopy

An integrated array of monomerically dispersed fullerenes on an electrode surface hold tremendous promise for exploration of a new class of exotic organic devices such as monomolecular transistors and molecular memories. A periodic monolayer array of discrete C₆₀s was generated on an atomically flat Au(111) surface with the aid of a template adlayer. As the template, we employed 2D crystals on the surface composed of a shape-persistent macrocycle and its metal complex.¹ The macrocycle was made by 4:4 alternative condensation between carbazole and phenylenediamine precursors and has a 1 nm hollow. Therefore, the macrocycles formed periodic arrays of molecular pits on the surface to capture a fullerene in each pit. Scanning tunneling microscopy (STM) imaging under ultra-high vacuum (UHV) revealed that the square-shaped macrocycles, with 1.5 nm sides, were arranged with a periodicity of approximately 4 nm spacings on the Au(111) surface. The periodic pattern of C₆₀s on the surface was prepared by sublimation onto the surface. C₆₀s were accommodated in the pits and the complex was thermally stabilized up to about 200 °C by CH- π interaction with the inner edge of the pit and by interaction with the gold surface which was observed in a scanning tunneling spectroscopy measurement.²



1) S. Kawano, Y. Ishida, K. Tanaka, *J. Am. Chem. Soc.* **2015**, 137, 2295. 1) S. Kawano, M. Nakaya, A. Ishiguro, M. Saitow, T. Yanai, J. Onoe, K. Tanaka, submitted.

Size-sensitive Recognition of Nanometer-sized Guest by Rim-extended Cyclodextrins

(¹Department of Chemistry, The University of Tokyo)

○Takato Ogata,¹ Hiroki Hanayama,¹ Koji Harano,¹ Eiichi Nakamura¹

Keywords: Cyclodextrin; Macrocyclic molecules; Transmission electron microscopy; Carbon nanotubes; Molecular recognition

Size-selective guest inclusion to a cavity of a macrocyclic molecule is widely applied in separation chemistry and supramolecular chemistry. In contrast to the size-selective recognition of a single atom ion and a small molecule, size-selective recognition of a nm-sized guest is still difficult due to the general difficulty in synthesizing a large macrocyclic host and a large entropy loss associated with the guest binding. Our group recently reported structural identification of the binding of cyclodextrins (CD) to various sizes of hydrophobic tips of conical carbon nanotubes (NTs) by single-molecule atomic-resolution time-resolved electron microscopy (SMART-EM)¹. CDs recognize guests by size-sensitive binding using the two rims (narrow and wide rims) in addition to the cavity (Fig. a left). We surmise that the nm-size selectivity in guest binding can be achieved by enhancing the wide rim binding (wRB) over narrow rim binding (nRB) and suppressing the cavity binding (CB) by modification of the wide rim with hydrophobic groups (Fig. a right). For this purpose, we designed rim-extended γ -CD, in which secondary hydroxy groups at the wide rim are partially acylated to maintain water solubility (Fig. b).

We synthesized three rim-extended CDs (Ac- γ -CD, Pn- γ -CD, and Php- γ -CD) bearing different hydrophobic groups and examined the binding of these CDs to the NT library by SMART-EM. The overall shape of CD in an EM image matches well with the structural model based on wRB of rim-modified γ -CDs (Fig. c). The radius-selectivity data of γ -CD and the rim-extended γ -CDs shows that binding-selectivity spectrum shifts to larger guests by introduction of longer substituents due to enhanced hydrophobic and van der Waals interactions with NTs (Fig. d). Elongation of the alkyl group (Pn- γ -CD) completely suppressed the CB binding by the steric hindrance, and installation of phenyl group (Php- γ -CD) further enhances the CD-NT interaction to show unimodal distribution ranging from 6 to 9 Å in NT diameter by rim binding.

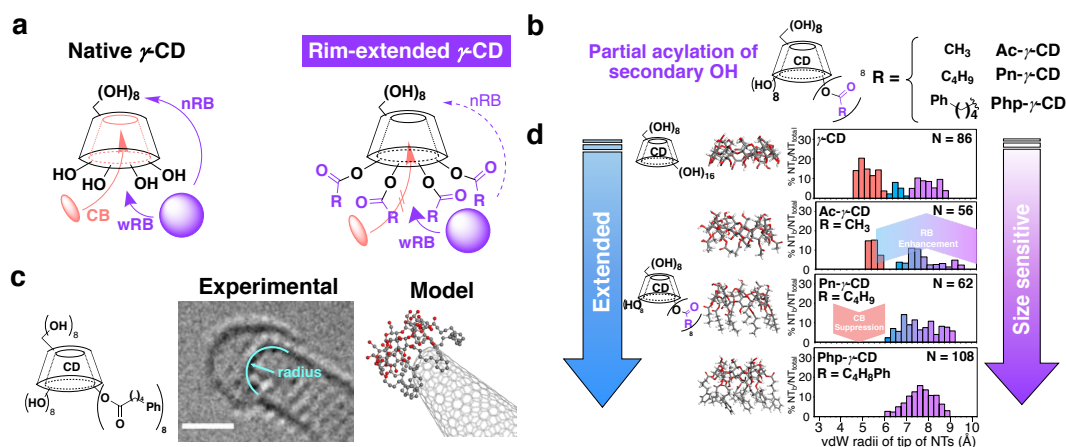


Figure. Molecular recognition by rim-extended CDs. a) Control of guest binding by acylation of secondary hydroxy groups at the wide rim. b) Chemical structure of rim-extended γ -CDs. c) TEM image of Php- γ -CD on an NT in wRB mode (left, exposure time = 250 ms Scale bar: 1 nm) and the corresponding atomic-number-correlated molecular model² (right). d) Histograms of the percentage of CD-bound NT per total number of NTs.

1) H. Hanayama *et al.*, *J. Am. Chem. Soc.* **2021**, 143, 5786. 2) J. Xing, *et al.*, *ArXiv*, 2107, 01490

Optical Properties and Molecular Recognition of a Sumanene-Based Chemosensor

(¹Department of Chemistry, Tokyo Institute of Technology, ²Department of Applied Chemistry, Osaka University, ³Department of Chemistry, University of Tsukuba) ○Hiroaki Mizuno,¹ Hironobu Nakazawa,¹ Akihisa Miyagawa,³ Yumi Yakiyama,² Hidehiro Sakurai,² Gaku Fukuhara¹

Keywords: Sumanene; Supramolecular Polymer; Molecular Recognition

In this study, we chose sumanene¹⁾ (**1**) as a signal-amplification moiety and indole as a fluorescence reporter and also a molecular-recognition site, and thus conjugated each part to afford a sumanene chemosensor (**2**), shown in Fig. 1a.

The chemosensor **2** shows intriguing optical properties. The fluorescence lifetime decays of **2** gave three excited species including a rise component. This rise was not observed in a chromophoric reference compound, indicating that the indole chromophores on the sumanene scaffold intermolecularly interact on each other. Upon the gradual addition of guests examined, fluorescence intensities of **2** were quenched (see the example of benzoate in Fig. 1b). Surprisingly, a binding constant of **2** upon the complexation of benzoate was enhanced by a factor of up to 200, comparing to that obtained from the reference compound. This amplification behavior may reasonably be explained due to the sumanene scaffold; the three indole moieties cooperatively interact with benzoate.²⁾ The results of a stack-induced amplification sensing will also be discussed.

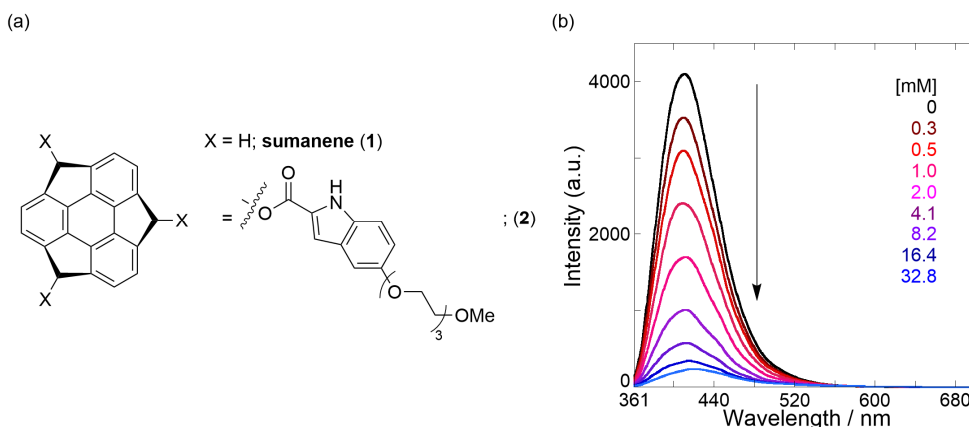


Figure 1. (a) Chemical structures of sumanene (**1**) and its chemosensor (**2**). (b) Fluorescence spectra of **2** (468 μM: black) upon the gradual addition of benzoate (0.3–32.8 mM: from brown to sky blue) in CH₂Cl₂ at 25 °C.

1) (a) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878. (b) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580. 2) Bates, G. W.; Triyanti; Light, M. E.; Albrecht, M.; Gale, P. A. *J. Org. Chem.* **2007**, *72*, 8921.

Guest Encapsulation Behavior of Covered Fluorine-modified Hollow-type Metal Oxide Cluster $\{\text{Mo}_{132}\}$

(¹Grad. Sch. Env. Sci., Hokkaido Univ., ²Fac. Env. Earth Sci., Hokkaido Univ.) ○Chinatsu Murata¹, Yukatsu Shichibu^{1,2}, Katsuaki Konishi^{1,2}

Keywords: Polyoxometalate; Fluorine modified

Hollow-type metal oxide cluster $\{\text{Mo}_{132}\text{O}_{372}(\text{H}_2\text{O})_{72}(\text{L})_{30}\}^{n-}$ ($\text{L} = \text{AcO}^-$, SO_4^{2-} , etc.; denoted by $\{\text{Mo}_{132}\text{-L}\}$) has a porous spherical structure^[1]. It has a molybdenum-oxide based framework, and ligands (L) are coordinated to the inside. In addition, guest molecules can be encapsulated through pores on the surface^[2]. However, modification of the inner environment, leading to the tuning of selectivity for guest molecules, had not been established. In this work, we examined the structure and inclusion behavior of a trifluoroacetate (TFA) modified cluster $\{\text{Mo}_{132}\text{-TFA}\}$, and the behavior was compared to that of $\{\text{Mo}_{132}\text{-OAc}\}$.

$\{\text{Mo}_{132}\text{-TFA}\}$ was obtained via ligand exchange reaction of $\{\text{Mo}_{132}\text{-OAc}\}$ with TFA in water. Single crystal X-ray diffraction revealed that it had a spherical structure in which CF_3 groups were introduced on the inner surface. Retention of the spherical structure after the reaction was confirmed by NMR, FT-IR and UV-Vis spectra. The inner environment of $\{\text{Mo}_{132}\text{-TFA}\}$ was then investigated from the encapsulation behavior of cyclic organic molecules. Encapsulations of these molecules into two types of $\{\text{Mo}_{132}\}$ hosts were shown by NMR analyses, and the number of included guest molecules were determined from quantitative NMR. As for five-membered rings, each of them was basically more efficiently encapsulated into $\{\text{Mo}_{132}\text{-TFA}\}$ than $\{\text{Mo}_{132}\text{-OAc}\}$ (Fig. 1).

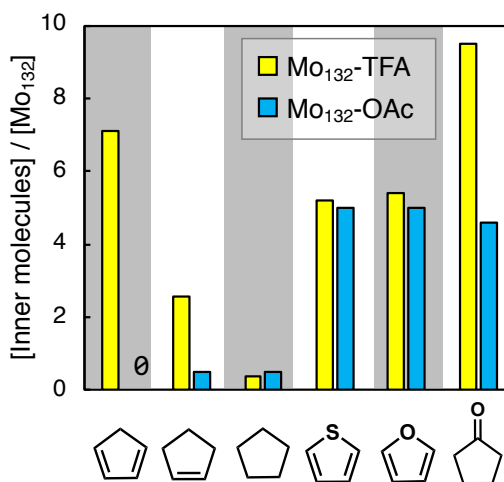


Fig. 1 Inclusion ability of $\{\text{Mo}_{132}\}$ for five-membered rings.

[1] A. Müller *et al.*, *Chem. Soc. Rev.* **2012**, 41, 7431.

[2] R. Neumann *et al.*, *Chem. Eur. J.* **2016**, 22, 15231.

Paddle-wheel 型ロジウム(II)二核錯体をコーナー素子とする超分子四角形の自己集合過程

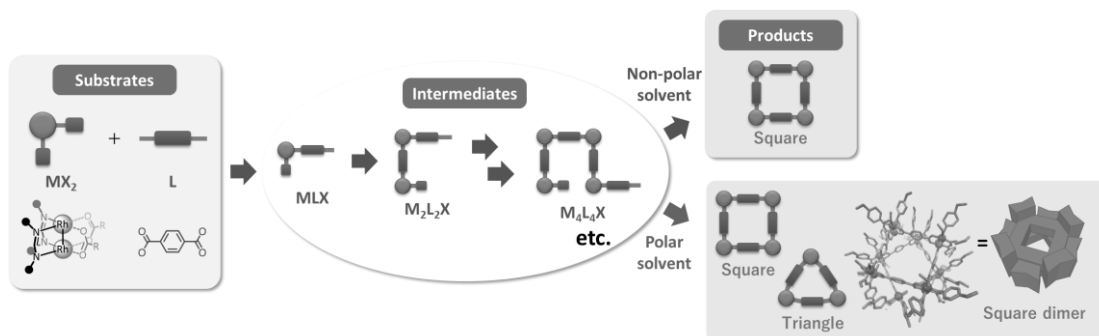
(日大医¹・東大院総合文化²) ○岡澤 厚¹・高橋 聡²・平岡 秀一²

Self-assembly process of a supramolecular square built in paddle-wheel-type dinuclear rhodium(II) complex as a corner unit (¹*Nihon University School of Medicine*, ²*Graduate School of Arts and Sciences, The University of Tokyo*) ○Atsushi Okazawa,¹ Satoshi Takahashi,² Shuichi Hiraoka²

Paddle-wheel-type coordination geometry is a dinuclear coordination motif found in various transition-metal ions, and useful as building blocks for forming metal-organic frameworks and molecular self-assembly systems. Among such dinuclear compounds, Rh₂(II, II) complexes have been attracted as catalysts, photosensitizers, and dyes for solar cells. Cotton *et al.* have reported the self-assembly of supramolecules built in paddle-wheel-type *cis*-protected dinuclear rhodium(II) complexes as a corner unit.¹⁾ However, their self-assembly processes have been unclear. In this work, we revealed the self-assembly process of a supramolecular square by quantitative analysis based on ¹H NMR measurement (QASAP) and numerical analysis based on reaction models (NASAP). Solvent effect on the formation process was also investigated and it was found that the supramolecular square dimerizes in polar solvent.

Keywords : *Molecular Self-Assembly; Rh(II) Complex; Reaction Mechanism; Quantitative NMR*

Paddle-wheel 型構造は多くの遷移金属イオンに見られる二核配位様式で、金属有機構造体(MOF)や自己組織化分子システムのビルディングブロックとして利用される。特に、Rh₂(II, II)錯体は触媒、光増感剤、太陽電池用色素として着目されている。シス位を保護した paddle-wheel 型ロジウム(II)二核錯体をコーナー素子とした超分子構造は Cotton らによって精力的に研究されてきたが、その自己集合過程の詳細は明らかになっていない¹⁾。そこで我々は、[Rh₂]コーナー素子と架橋配位子からなる自己集合四角形分子の形成過程を¹H NMR 測定による定量解析(QASAP)²⁾および反応モデルを用いた数値解析(NASAP)²⁾により明らかにした。形成過程に及ぼす溶媒効果も調べ、極性溶媒中で超分子四角形が二量化することも見出した。



1) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759.

2) S. Hiraoka, S. Takahashi, H. Sato, *Chem. Rec.* **2020**, *21*, 443.

Kinetically Controlled Coordination Self-assembly: Approaches to Pathway Selection

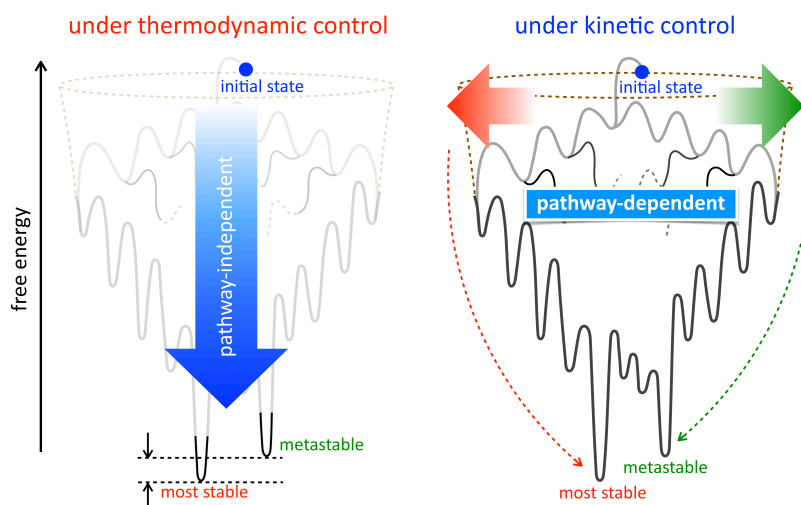
(¹Graduate School of Arts and Sciences, The University of Tokyo)

○Shuichi Hiraoka,¹ Naoki Sanada,¹ Satoshi Takahashi,¹ Tomoki Tateishi,¹ Isamu Kikuchi¹

Keywords: Molecular Self-assembly; Kinetic Control; Palladium Ion

In most cases, molecular self-assembly proceeds under thermodynamic control to reach equilibrium, which makes a great advantage in that wrong connection between the building blocks can be corrected so that the thermodynamically most stable assembly is dominantly produced. Considering that in such a molecular self-assembly the products should Boltzmann distribute, we notice that there are limitations in thermodynamically controlled molecular self-assembly. The first is that the most stable assemblies cannot be produced more than the Boltzmann distribution though they are always the major product under thermodynamic control. The second is that as is often the case with multicomponent self-assembly where various assemblies with similar thermodynamic stability tend to be produced, a single assembly cannot be selected under thermodynamic control. Furthermore, the selective production of a metastable assembly is impossible. These difficulties arise from the fact that equilibrium

reactions obey the thermodynamic law. In contrast, if the self-assembly is controlled by kinetics, we have a chance to produce desired assemblies in higher yield and selectivity than those under thermodynamic control.



Here, we present two approaches to pathway selection which enable us to produce thermodynamically stable assemblies and metastable ones beyond the Boltzmann distribution. These are based on the idea that even though the elementary reactions in molecular self-assembly are reversible, we can make a situation where self-assembly proceeds under kinetic control: global irreversibility with local reversibility (GILOR) on the energy landscape. We will discuss these approaches applied to Pd(II) coordination self-assembly systems as a proof-of-principle.

テトラフェニルエテン誘導体の結晶による芳香族分子の認識

(金沢大¹) ○角田 貴洋¹・杉本 祐綺¹・中西 良太¹・秋根 茂久¹・山岸 忠明¹
 Recognition of Aromatic Compounds Using Crystal of Tetraphenylethene Derivatives (¹
Kanazawa University) ○Takahiro Kakuta,¹ Yuki Sugimoto,¹ Ryota Nakanishi,¹ Shigehisa
 Akine,¹ Tada-aki Yamagishi¹

Tetraphenylethene (TPE) is a famous compound to exhibit aggregation-induced emission. The luminescence properties of TPE in the solid state are changed between the crystalline and amorphous states. In this study, TPE derivatives with various alkoxy substituent groups (CnTPE; n is denoted carbon number of alkoxy groups) were synthesized in three steps. The C1TPE showed blue and green emission color in the crystalline and amorphous state, respectively. On the other hand, the C2TPE exhibited green color emission regardless of crystalline state. By X-ray diffraction analysis, the crystal structure of C2TPE was only difference in other alkoxy groups. In addition, TPE derivatives showed recognition properties in response to aromatic molecules.

Keywords : Tetraphenylethene, Alkoxy groups, Aromatic compounds, Naphthalene

テトラフェニルエテン (TPE) は、凝集誘起発光 (AIE) を示す。TPE は、結晶状態による発光挙動変化を示す一方、非晶状態の分子状態を把握するのは困難である。本研究では、鎖長の異なるアルコキシ基を修飾した TPE (CnTPE, n はアルキル鎖の炭素数) を合成し、物性評価した。CnTPE は、アルキル鎖長により結晶状態が変化した。また C2TPE は、他の置換基と異なり、結晶状態に依存しない発光挙動を示した。

各 CnTPE は、3 段階の反応により合成した (Figure 1)。Figure 2 には、C1TPE と C2TPE の固体状態での発光色を示す。C1TPE が結晶状態とアモルファス状態で発光色が青色から緑色に変化した一方、C2TPE は、結晶状態でもアモルファス状態でも緑色発光を示した。アルキル鎖長による変化を評価するため、結晶状態の CnTPE を用いて発光波長を測定した。C2TPE のみ緑色発光 (487 nm) を示し、n = 3 以上では約 450 nm に発光極大を示した。粉末 X 線回折 (PXRD) を行った結果、n = 1、n = 2、n ≥ 3 で異なる回折ピークを示した。そこで、単結晶 X 線構造解析により、n = 1, 2, 6, 9 の結晶構造を調査した結果、それぞれ異なる結晶系が確認された。これら発光挙動の変化は、アルキル鎖の相互作用や CH/π 相互作用による結晶構造変化が影響すると考えられる。C2TPE 結晶へナフタレン誘導体を混合させ、結晶化を行った。混合物は、XRD の回折パターンが変化し、原料以外のピークを示した。加えて、ナフタレンの種類により蛍光色が変わった。

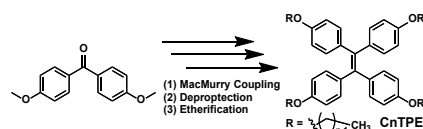


Figure 1. Synthesis scheme of CnTPE.



Figure 2. Emission behaviors of TPE modified methoxy (C1TPE) and ethoxy groups (C2TPE) depending on crystalline state.

かさ高い架橋配位子を導入した環状コバルト(III)二核メタロホストのサイズ選択的ゲスト認識とその開閉の制御

(金沢大院自然¹・金沢大 NanoLSI²) ○須藤 涼¹・酒田 陽子^{1,2}・秋根 茂久^{1,2}

Size-selective Guest Recognition and the Open/Close Control of Macrocyclic Cobalt(III) Dinuclear Metallohosts Having Bulky Bridging Ligands (¹Graduate School of Natural Science and Technology, Kanazawa University, ²Nano Life Science Institute, Kanazawa University)

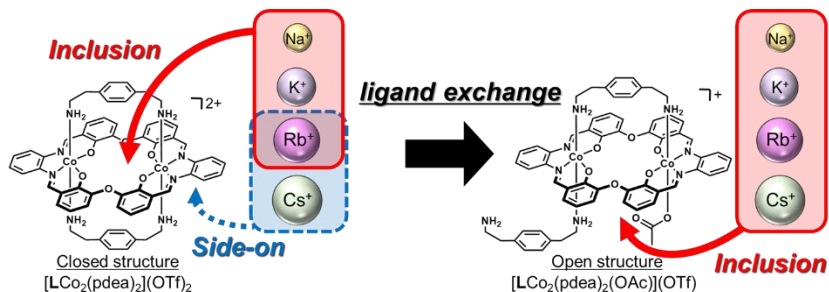
○Ryo Sudo,¹ Yoko Sakata,^{1,2} Shigehisa Akine^{1,2}

Closing/opening the apertures of macrocyclic hosts is expected to control the guest release and uptake. We synthesized a doubly-bridged macrocyclic metallohost having a bis(saloph) macrocyclic ligand by the reaction of the corresponding piperidine complex with *p*-phenylenediethanamine (pdea). While smaller guests (Na⁺, K⁺, Rb⁺) formed the inclusion complex with the host, large guest (Cs⁺) exclusively formed the side-on complex. This doubly-bridged metallohost was converted into a singly-bridged structure by ligand exchange, which formed inclusion complex with the larger guests as well as the small guests.

Keywords : Guest Recognition; Ligand Exchange; Metallohost; Bridging Ligand; Alkali Metal

環状ホスト分子の空孔の開口部を状況に応じて開閉したり、事後修飾したりすることができれば、認識能などのチューニングが可能な高機能性ホストとしての応用が期待される。我々は、二つの saloph 部位を有する環状二核コバルト(III)メタロホストを開発し、この軸位に単座配位子や二座配位子を導入したメタロホストを用いて、ゲストである金属イオンの取り込み速度や認識能の制御について報告してきた¹⁻³。本研究では、このメタロホストの開口部にかさ高い架橋配位子として、*p*-フェニレンジエタナミン(pdea)を導入し、ゲスト取り込み速度や認識能の制御を試みた。

二重架橋錯体 [LCo₂(pdea)₂](OTf)₂ は軸位にピペリジンを導入した錯体 [LCo₂(pip)₄](OTf)₂ (pip = piperidine) と pdea との配位子交換によって合成した。この錯体はゲストサイズに応じて、イオン半径の小さいイオンを空孔内に包接し、大きいイオンとは空孔外で side-on 錯体を形成することが明らかになった。また、配位子交換により開口部が開いた単架橋構造に変換することで、大きいゲストとも包接体を形成させることに成功した。



- 1) Sakata, Y.; Murata, C.; Akine, S. *Nat. Commun.* **2017**, *8*, 16005.
- 2) Sakata, Y.; Okada, M.; Akine, S. *Chem. Eur. J.* **2020**, *26*, 7595-7601.
- 3) Sakata, Y.; Okada, M.; Akine, S. *Chem. Eur. J.* **2021**, *27*, 2284-2288.

[H201-1pm] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Tomoki Yoneda, Yumi Yakiyama

Wed. Mar 23, 2022 1:20 PM - 3:40 PM H201 (Online Meeting)

[H201-1pm-01] Synthesis of Monodisperse Polyketones and Chain Length Dependent Crystallinity Changes

○Yumehiro Manabe¹, Kilingaru I. Shivakumar², Jenny Pirillo², Yuh Hijikata², Tomoki Yoneda¹, Yuki Ide², Yasuhide Inokuma^{1,2} (1. Grad. Sch. Eng., Hokkaido Univ., 2. WPI-ICReDD, Hokkaido Univ.)

1:20 PM - 1:40 PM

[H201-1pm-02] The noncovalent approach in the design of luminescent crystalline rotors

○Alexander Mikherdov¹, Mingoo Jin^{1,2}, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University)

1:40 PM - 2:00 PM

[H201-1pm-03] Construction of hydrogen-bonded organic frameworks with naphthoic acid groups and its structural transition behavior

○Yuto Suzuki¹, Ryusei Oketani¹, Ichiro Hisaki¹ (1. Osaka university)

2:00 PM - 2:20 PM

[H201-1pm-04] Stumuri-responsive Single Crystals of Pyrene-introduced Indanedione Dimers

○Yumi Yakiyama^{1,2}, Ryotaro Seki¹, Hidehiro Sakurai^{1,2} (1. Osaka University, 2. ICS-OTRI, Osaka Univeristy)

2:20 PM - 2:40 PM

[H201-1pm-05] Development of crystalline molecular gears by utilizing tri-phenyl triazine based rotors

○Mingoo Jin^{1,2}, Ryouusukei Kitsu¹, Natsumi Hanmyo¹, Motohiro Mizuno³, Hajime Ito^{1,2} (1. Graduate School of Engineering, Hokkaido University, 2. WPI-ICReDD, Hokkaido University, 3. NanoMaterials Research Institute, Kanazawa University)

2:40 PM - 3:00 PM

[H201-1pm-06] Topology control and properties of the porous organic salts composed of modified triphenylmethylenamines and tetrahedral sulfonic acid.

○Hiroi Sei¹, Norimitsu Tohnai¹ (1. Osaka university)

3:00 PM - 3:20 PM

[H201-1pm-07] Hydrogen-bonded inorganic frameworks: aromatic molecules parallelly stacked in the nano-honeycomb pore

○Masayasu Igarashi¹, Takeshi Nozawa¹, Tomohiro Matsumoto¹, Fujio Yagihashi¹, Takashi Kikuchi², Kazuhiko Sato¹ (1. National Institute of Advanced Industrial Science and Technology (AIST), 2. Rigaku Corporation)

3:20 PM - 3:40 PM

Synthesis of Monodisperse Polyketones and Chain Length Dependent Crystallinity Changes

(¹Grad. School of Eng., Hokkaido Univ., ²WPI-ICReDD, Hokkaido Univ.) ○ Yumehiro Manabe,¹ Killingar I. Shivakumar,² Jenny Pirillo,² Yuh Hijikata,² Tomoki Yoneda,¹ Yuki Ide,² Yasuhide Inokuma^{1,2}

Keywords: Monodispersity; Polyketone; Crystallinity; X-ray Crystallography

Monodisperse oligomers enables to elucidate the precise correlations of their structure and molecular weights in comparison with the corresponding polydisperse polymers.¹ Here we report the synthesis of monodisperse aliphatic polyketones up to 20 mer and revealed their chain length dependent crystallinity changes.

Monodisperse aliphatic polyketones up to **10 mer** were iteratively synthesized by repeating terminal-selective silylation and subsequent silver(I) oxide mediated homo- or cross-coupling reactions from an acetylacetone derivative as a monomer.² Further longer polyketones **12**, **16** and **20 mer** were obtained by polymerization reaction of bis-silylated tetramer¹ and preparative recycling GPC separation in 7%, 6%, and 5% yields, respectively (**Figure 1a**).

The crystallinity transition of the aliphatic polyketones upon their chain length elongation was investigated by single- and powder X-ray diffraction analysis. While polyketones until **4 mer** have their own conformations in the single crystal structures², the conformations above **5 mer** were estimated to be converged into the helical conformation (**Figure 1b**). This crystallinity changes were estimated by comparing the powder X-ray patterns of polyketones with the calculated crystal structure of the polyketones.

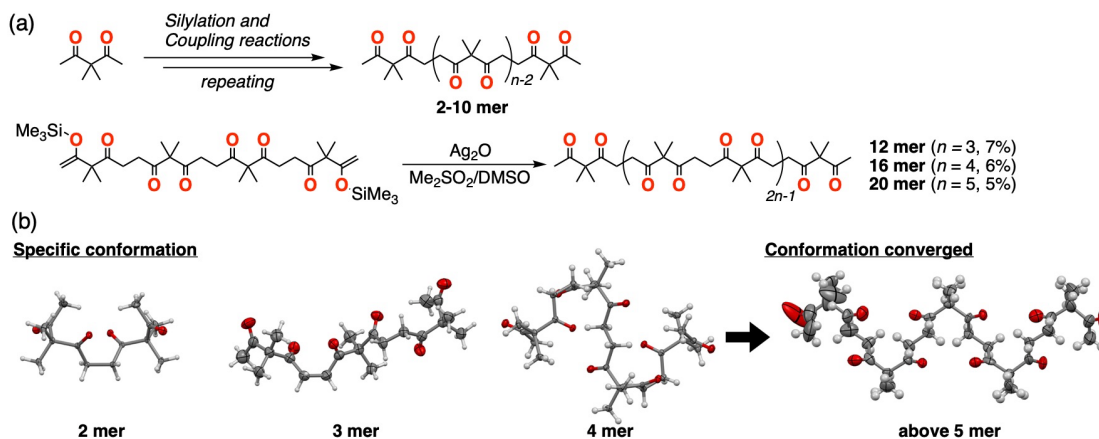


Figure 1. (a) Synthesis of monodisperse aliphatic polyketones **2-10**, **12**, **16**, and **20 mer**; (b) Chain length dependent crystal structure transitions of the polyketones.

1) S. Binauld, D. Damiron, L. A. Connal, C. J. Hawker, E. Drockenmuller, *Macromol. Rapid Commun.*, **2011**, 32, 147; 2) (a) M. Uesaka, Y. Saito, S. Yoshioka, Y. Domoto, M. Fujita, Y. Inokuma, *Commun. Chem.*, **2018**, 1, 23; (b) Y. Manabe, M. Uesaka, T. Yoneda, Y. Inokuma, *J. Org. Chem.*, **2019**, 84, 9957.

The Noncovalent Approach in The Design of Luminescent Crystalline Rotors

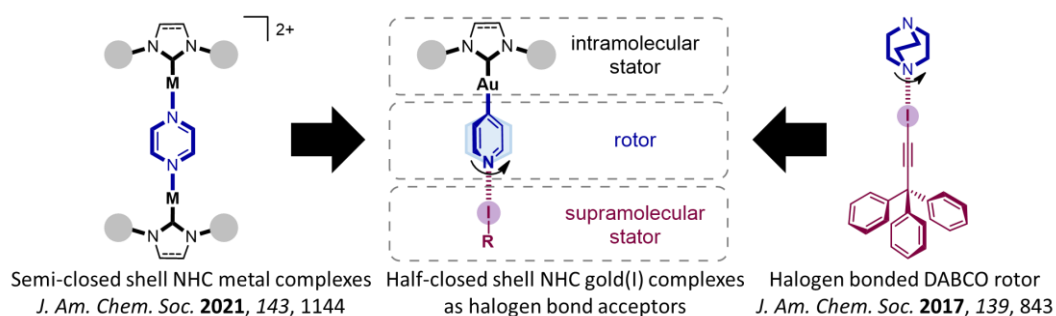
(¹Graduate School of Engineering, Hokkaido University, ²WPI-ICReDD, Hokkaido University)

○ Alexander Mikherdov,¹ Mingoo Jin,^{1,2} Hajime Ito^{1,2}

Keywords: Molecular Dynamics, Crystalline Rotors, Halogen Bonding, Organometallic Luminophores

This work is aimed at the development of amphidynamic luminescent co-crystals based on the principles of the rational design of organometallic luminophores and noncovalent crystal engineering to produce materials that combine both luminescence and rotational motion. In pursuit of a new concept in the development of amphidynamic crystalline materials, we implemented the strategy of encapsulation of molecular rotor by two types of stators: intramolecular organometallic stator and supramolecular halogen bonding stator. The background of this work is based on the encapsulation approach utilized previously for semi-closed shell NHC metal complexes¹ and halogen bonding crystal engineering of DABCO-based molecular rotors.²

Therefore, we have developed the half-closed NHC gold(I) aryl complexes which could act as halogen bond acceptors and co-crystallized them with three types of organic halogen bond donors: iodopentafluorobenzene, 1,4-diiodotetrafluorobenzene, 1,3,5-triiodotrifluorobenzene. The several co-crystals with different ratios of components were obtained and characterized by single-crystal X-ray diffraction and luminescence spectroscopy in the solid state. All co-crystals display the strong dependence of the luminescence intensity on temperature which suggests the presence of rotational dynamics in the solid state.



1) M. Jin, R. Ando, M. J. Jellen, M. A. Garcia-Garibay, H. Ito, *J. Am. Chem. Soc.* **2021**, *143*, 1144. 2) a) L. Catalano, S. Pérez-Estrada, Hs.-H. Wang, A. J.-L. Ayitou, S. I. Khan, G. Terraneo, P. Metrangolo, S. Brown, M. A. Garcia-Garibay *J. Am. Chem. Soc.* **2017**, *139*, 843. b) L. Catalano, S. Pérez-Estrada, G. Terraneo, T. Pilati, G. Resnati, P. Metrangolo, M. A. Garcia-Garibay *J. Am. Chem. Soc.* **2015**, *137*, 15386.

Construction of hydrogen-bonded organic frameworks with naphthoic acid groups and its structural transition behavior

(¹ Osaka University) ○Yuto Suzuki,¹ Ryusei Oketani,¹ Ichiro Hisaki¹

Keywords: *Hydrogen-bonded organic framework, Porous structure, Carboxylic acid, dibenzo[*g,p*]chrysene, non-planer π -conjugated molecule.*

Hydrogen-bonded organic frameworks (HOFs) are attractive materials as high-crystalline and regeneratable porous organic materials, but have some problems regarding stability and designability of the porous structure. The construction of stable HOFs with permanent porosity has been reported in recent years, and we also have reported that dibenzo[*g,p*]chrysene (DBC) tetracarboxylic acid derivative, namely **CPDBC**, formed a stable HOF.¹⁾ This stability is resulting from the assembling that non-planer π -conjugated skeletons stacked uniformly (shape-fitted docking). However, the designability of other skeletons is not clear.

In this work, we constructed isostructural DBC HOFs applying analogs with 4'-carboxybiphenyl-4-yl, 4-carboxynaphthalen-1-yl or 6-carboxynaphthalen-2-yl derivatives (**CBPDBC**, **C1NDBC** or **C2NDBC**, respectively, Figure 1a) and investigated the effect of peripheral functional groups. These carboxylic acids were crystallized by the solvent evaporation method with various aromatic solvents as guest molecules. **CBPDBC** and **C1NDBC** were only yield microcrystals. According to the PXRD measurement, both were formed the isostructural HOFs as **CPDBC**. On the other hand, plate crystals of **C2NDBC** were yielded under various poor solvent conditions. From the crystals using

5-*tert*-butyl-*m*-xylene or methyl benzoate, the obtained structures were isostructural HOFs as DBC derivatives (Figure 1b). **C1NDBC** and **C2NDBC** showed different behaviors in the introduction and removal of molecules. Only **C1NDBC** shows reversible structural change.

In this presentation, we will show the obtained crystal structure, the behavior of the structural change, the stability of the structure and the porosity.

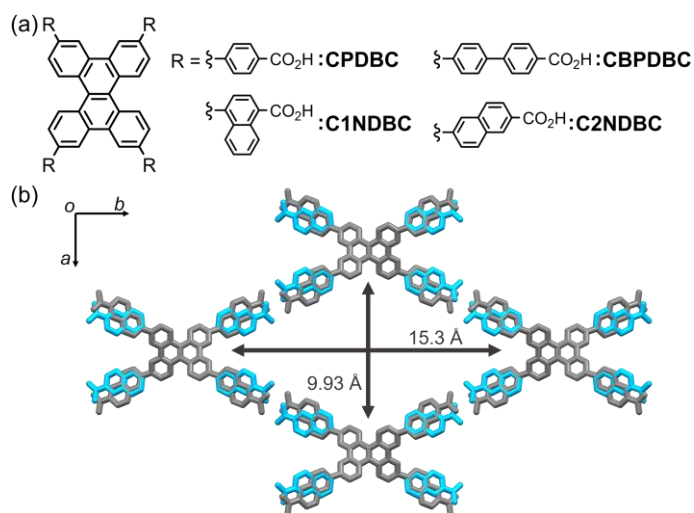


Figure 1. (a) Chemical structures of **C1NDBC** and **C2NDBC**. (b) Obtained crystal structure of **C2NDBC**. Naphthyl groups are disordered in 2 positions, major (gray) and minor (cyan).

1) Y. Suzuki, N. Tohnai, A. Saeki, I. Hisaki, *Chem. Commun.* **2020**, 56, 13369-13372.

Stimuli-responsive Single Crystals of Pyrene-introduced Indanedione Dimers

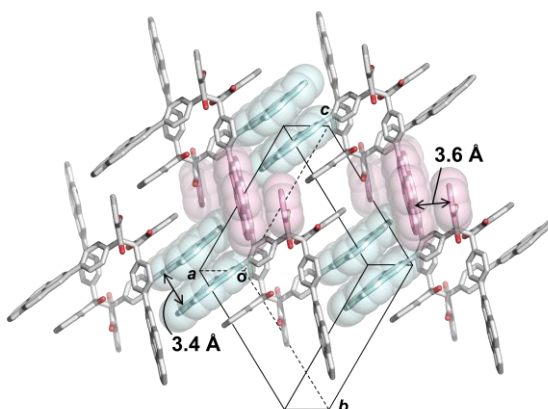
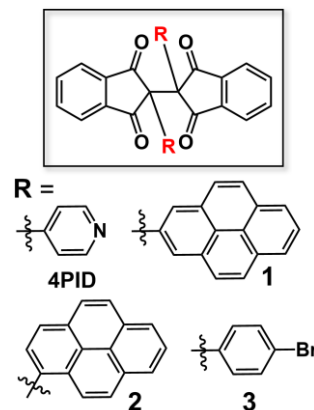
(¹Graduate School of Engineering, Osaka University, ²ICS-OTRI, Osaka University)

○Yumi Yakiyama,^{1,2} Ryotaro Seki,¹ Hidehiro Sakurai^{1,2}

Keywords: Pyrene; Stimulus responsiveness; Structural Phase Transition

In general, molecular crystals are constructed by weak intramolecular interactions and tend to have poor structural stability to external stimuli. However, in recent years, many examples of molecular crystals that flexibly change their structures and physical properties in response to the outer stimuli are reported. In this context, we also have great interest on the stimuli-responsive soft crystals and focused on X-shaped indanedione dimers as their building units.¹⁾ Their unique X-shape enables the solvent-included channel formation in the crystalline state and provides the flexibility to the framework. These features resulted in the preparation of sponge-like crystalline system of **4PID** in which two structures, 1D-channel holding **OPEN** form and tightly packed **CLOSE** form are interconvertible by the guest solvent adsorption/removal with keeping the crystallinity.^{1a)} On the basis of this result, here we designed and synthesized two new indanedione dimers **1** and **2** in which pyrene unit was introduced as the fluorophore.

The desired products **1** and **2** were prepared from bis(bromophenyl)indanedione dimer **3** by Suzuki-Miyaura cross coupling reaction with corresponding pyreneboronic acid. Both solution- and solid-state emission spectra of **1** showed emission band from pyrene monomer at around 400 nm. In addition to that, the solid sample also showed the emission attributable to pyrene excimer while the dense solution did not. On the other hand, diluted solution of **2** showed the emission band derived from pyrene monomer and the concentrated one gave pyrene excimer emission, though the solid sample did not show any emission. Single crystal X-ray analysis of **1** revealed the formation of two types of π - π interactions, between two pyrene skeletons (3.4 Å) and between the pyrene and indanedione skeletons (3.6 Å) (Figure). Interestingly, this crystal of **1** showed the phase transition by heating to show the structure and emission property changes.



1) a) Y. Yakiyama, T. Fujinaka, M. Nishimura, R. Seki, H. Sakurai, *Chem. Commun.* **2020**, 56, 9687.

b) Y. Yakiyama, T. Fujinaka, M. Nishimura, R. Seki, H. Sakurai, *Asian J. Org. Chem.* **2021**, 10, 2690.

トリアジン骨格を有する分子ローターを用いた結晶内の分子間ギア運動の開発とその精密制御

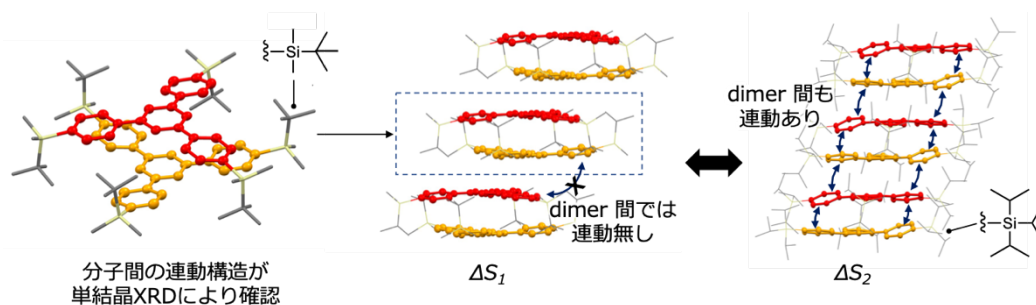
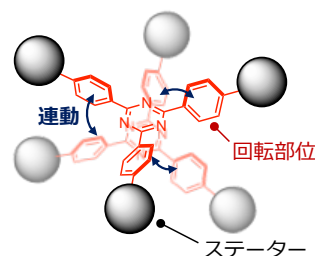
(北大院工¹・北大 WPI-ICReDD²・金沢大マテリアル研³) ○陳旻究^{1,2}・吉津龍之介¹・半妙夏海¹・水野元博³・伊藤肇^{1,2}

Development of crystalline molecular gears by utilizing tri-phenyl triazine based rotors (¹Graduate School of Engineering, Hokkaido University, ²WPI-ICReDD, Hokkaido University, ³NanoMaterials Research Institute, Kanazawa University) ○Mingoo Jin,^{1,2} Ryunosuke Kitsu,¹ Natsumi Hamnyo,¹ Motohiro Mizuno,³ Hajime Ito^{1,2}

Crystalline molecular gear showing molecular correlated-rotation in crystalline media have attracted many interests because of the high potential for application to molecular machines.¹⁾ However, it is difficult to design the molecular gears in crystal due to unpredictable crystal packing. Recently, we have developed a crystalline molecular gear by utilizing inter-molecular packing manner of a 2,4,6-triaryl-1,3,5-triazine molecular rotors in crystal. In this work, we have designed and investigated the series of triazine-based crystalline molecular gears, which consist of phenyl-rings as a rotator with bulky silyl groups as a stator. The molecular rotors formed inter-locked dimer structure in crystal, having the correlated geometry between the phenylenes, confirmed by single crystal XRD. Interestingly, introducing different silyl-group could alter the inter-dimer packing manner. The geared rotations were observed by several solid-state NMR studies and the DFT calculation, which will be described in the presentation.

Keywords : Aziridine; Iminoiodinane; Metal Free; Iodine; Ammonium Iodide

結晶中で分子やその一部が隣り合う分子と互いに連動してギア運動を示す結晶を結晶性分子ギアと言う。この結晶は分子マシンへの応用が期待されているが、その設計指針は未だない¹⁾。本研究では、トリアリールトリアジン骨格を有する分子が結晶内で分子間の連動回転を示すことおよびその連動構造を精密に調整することに成功した(右図と下図)。本発表では、その分子間連動運動の詳細および関連する結晶構造について報告する。



1) Liepuoniute, I.; Jellen, M. J.; Garcia-Garibay, M. A. *Chem. Sci.* **2020**, *11*, 12994.

修飾トリフェニルメチルアミンと四面体型スルホン酸による多孔質構造のトポロジー制御とその物性

(阪大院工) ○施 宏居・藤内 謙光

Topology control and properties of the porous organic salts composed of modified triphenylmethylenamines and tetrahedral sulfonic acid.

(Graduate School of Engineering, Osaka University) ○Hiroi Sei, Norimitsu Tohnai

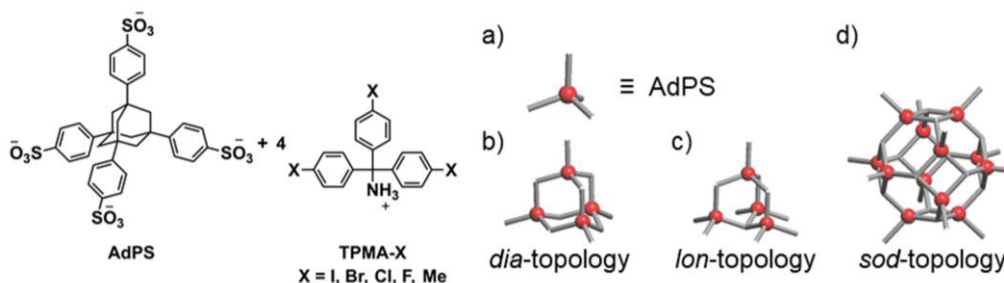
Controlling the network topology of porous materials heavily changes the pore size and shape, and would improve structural stability and gas adsorption properties. We have reported on the construction of porous structures with organic salts composed of various sulfonic acids and bulky amines such as triphenylmethylenamine (TPMA). Sulfonic acids and amines are self-assembled by strong charge-assisted hydrogen bonding to form supramolecular clusters, and then they are connected to construct the porous structure with various network topologies.

In the current work, we prepared the organic salts with the tetrahedral tetrasulfonic acid with adamantane core and TPMA-X (X=I, Br, Cl, F, Me) to control the topology and constructed porous structures with different topologies by the substituents X. Furthermore, TPMA-Me salt formed three type topologies and changed gas adsorption properties.

Keywords : Hydrogen bond; Organic salt; Porous structure; Topology

多孔質材料のネットワークトポロジーは、空孔径や形状を大きく変化させ、多孔質材料の構造安定性やガス吸着特性などの性能を向上させることが期待されている。我々はこれまで種々の芳香族スルホン酸とトリフェニルメチルアミン(TPMA)などの嵩高いアミンによる多孔質有機塩を報告してきた。スルホン酸とアミンが強固な電荷補助型水素結合によって自己集合した超分子クラスターを形成し、それらが様々なネットワークトポロジーで繋がることで多孔質構造を構築している。

本研究では、トポロジーの制御を目的に、アダマンタン中心を持つ四面体型スルホン酸と置換基を導入した TPMA-X (X= I, Br, Cl, Me)の有機塩(Scheme 1)を作製し、置換基の嵩高さによってトポロジーの異なる多孔質構造を構築した。さらに TPMA-Me 塩では再結晶溶媒を変えるだけで容易に 3 種のトポロジー(Figure 1)を作り分け、ガス吸着特性を変化させることに成功した。



Scheme 1

Figure 1. a) A schematic representation of AdPS. The topology of TPMA-Me salt, b) dia-topology, c) lon-topology, d) sod-topology.

水素結合性無機構造体内に平行にスタックした芳香族化合物

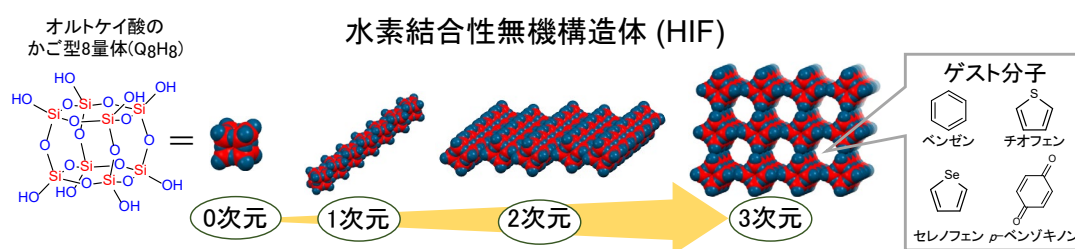
(産総研触媒化学融合セ¹・リガク²) ○五十嵐正安¹・野澤竹志¹・松本朋浩¹・八木橋不二夫¹・菊池貴²・佐藤一彦¹

Hydrogen-bonded inorganic frameworks: aromatic molecules parallelly stacked in the nano-honeycomb pore (¹*Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)*, ²*Rigaku Corporation*) ○ Masayasu Igarashi¹, Takeshi Nozawa¹, Tomohiro Matsumoto¹, Fujio Yagihashi¹, Takashi Kikuchi², Kazuhiko Sato¹

We apply the hydrogen-bonded organic frameworks (HOFs) strategy to inorganic materials science using the cubic octamer of orthosilicic acid, $[\text{Si}_8\text{O}_{12}][\text{OH}]_8$, as a building block, and find various types of hydrogen-bonded inorganic frameworks (HIFs). We succeed in parallel π -stacking pure benzene, thiophene, selenophene, *p*-benzoquinone, thiophene-*p*-benzoquinone, and benzene-*p*-benzoquinone polymers in the nano-honeycomb pores.

Keywords : *Hydrogen-bonded Inorganic Frameworks (HIFs); Orthosilicic Acid; Single-crystal X-ray Analysis; Aromatic Molecules; Parallel π -Stacking*

我々はこれまでに、オルトケイ酸 ($\text{Si}(\text{OH})_4$) と、その 2 量体、環状 3 量体、環状 4 量体、かご型 8 量体 ($[\text{Si}_8\text{O}_{12}][\text{OH}]_8$, Q_8H_8) の単離に成功している^{1,2)}。 Q_8H_8 を水素結合を介しネットワーク化させることで、種々の水素結合性無機構造体 (HIFs) 結晶を得ることに成功した。 Q_8H_8 が 3 次元状に水素結合ネットワーク化したナノハニカム細孔内に、ベンゼンやチオフェン、セレンフェンなどの芳香族化合物や *p*-ベンゾキノンを平行に積層させることに成功し、それらの構造を X 線結晶構造解析により明らかにした³⁾。ベンゼンがナノハニカム細孔に詰まった結晶の蛍光スペクトルを測定した結果、エキシマー発光が観測されたことから、ナノハニカム細孔内において、ベンゼン分子同士は π - π 相互作用ができる状態であることを明らかにした。



謝辞：この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構 (NEDO) の委託業務の結果得られたものです。

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- 2) T. Nozawa, T. Matsumoto, F. Yagihashi, T. Beppu, K. Sato, M. Igarashi, *Chem. Lett.* **2018**, 47, 1530.
- 3) M. Igarashi, T. Nozawa, T. Matsumoto, F. Yagihashi, T. Kikuchi, K. Sato, *Nat. Commun.* **2021**, 12, 7025.

[K6-1pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Yasunori Matsui, Hajime Maeda

Wed. Mar 23, 2022 1:40 PM - 3:40 PM K6 (Online Meeting)

[K6-1pm-01] Titanium-Catalyzed Intermolecular Radical Addition to Ketones via sp^3 C-H Bond Activation

[○]Xue Peng¹, Yuki Hirao¹, Shunsuke Yabu², Hirofumi Sato², Masahiro Higashi², Harunobu Mitsunuma¹, Motomu Kanai¹ (1. The University of Tokyo, 2. Kyoto University)

1:40 PM - 2:00 PM

[K6-1pm-02] Hydrogenation and Borylation of Alkyl Chlorides using Zirconocene and Photoredox Catalysis

[○]Toshimasa Okita¹, Keisuke Tanaka¹, Kazuhiro Aida¹, Eisuke Ota¹, Junichiro Yamaguchi¹ (1. Waseda University)

2:00 PM - 2:20 PM

[K6-1pm-03] Hybridization of triplets and organic radicals towards photo-driven hyperpolarization

[○]Koki Nishimura¹, Kenichiro Tateishi³, Tomohiro Uesaha³, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,2,4} (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. RIKEN Nishina Center for Accelerator-Based Science, 4. PRESTO, JST)

2:20 PM - 2:40 PM

[K6-1pm-04] Development of oxygen-containing heterocyclic compounds synthesis using visible light responsiveness of main group elements

[○]Saki Maejima¹, Eiji Yamaguchi¹, Akichika Itoh¹ (1. Gifu Pharmaceutical University)

2:40 PM - 3:00 PM

[K6-1pm-05] Development of Carbazole Dendrimers with Luminescent Radical Core

[○]XIAOTIAN XIAOTIAN¹, Wataru Ota², Tohru Sato^{3,4,5}, Yasuo Nakayama⁶, Minori Furukori⁷, Takuya Hosokai⁷, Eri Hisamura⁸, Andrew P Monkman⁹, Ken Albrecht^{8,10} (1. Grad. Sch. Eng. Sci., Kyushu Univ., 2. MOLFEX, Inc, 3. Fukui Institute for Fundamental Chemistry, Kyoto University, 4. Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, 5. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 6. Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 7. National Institute of Advanced Industrial Science and Technology (AIST), 8. IMCE, Kyushu Univ., 9. Univ. Durham, 10. JST-PRESTO)

3:00 PM - 3:20 PM

[K6-1pm-06] Photon Upconversion in Polymer Media Utilizing Energy Harvesting and Intramolecular TTA

[○]Yasunori Matsui^{1,2}, Takumi Takahashi¹, Masaya Kanoh¹, Takuya Ogaki^{1,2}, Eisuke Ohta^{1,2}, Hiroshi Ikeda^{1,2} (1. Grad. Sch. of Eng., Osaka Pref. Univ., 2. RIMED, Osaka Pref. Univ.)

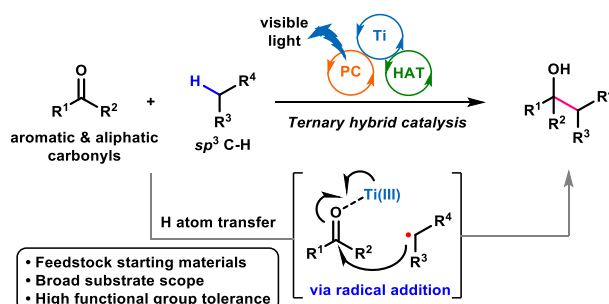
3:20 PM - 3:40 PM

Titanium-Catalyzed Intermolecular Radical Addition to Ketones via sp^3 C-H Bond Activation

(¹The University of Tokyo, ²Kyoto University) ○Xue Peng¹, Yuki Hirao¹, Shunsuke Yabu², Hirofumi Sato², Masahiro Higashi², Harunobu Mitsunuma¹, Motomu Kanai¹

Keywords: Photoredox catalysis, HAT catalyst, Titanium complex catalyst, Late-stage functionalization, Radical addition

Tertiary alcohols exist widely in natural products, pharmaceuticals, pesticides, and ligands. Traditional synthesis of tertiary alcohols utilizes nucleophilic addition of organometallic reagents to ketones developed in the previous century. However, they exhibit low functional group tolerance, require stoichiometric quantities of organometallic reagents, and generate stoichiometric quantities of metal salt side products. Therefore, the interest in developing novel, safer and more sustainable reactions is growing within the scientific community, especially for the late-stage functionalization. In comparison of nucleophilic addition, direct radical addition of ketones can be an ideal approach due to the high functional group compatibility of radical species. However, radical addition to carbonyl groups is a thermodynamically uphill process.¹ Therefore, successful radical addition is only possible if the alkoxy radical can be intercepted via a subsequent fast event.² In particular, there are no reported radical addition of ketones with simple transient radicals derived from hydrocarbon feedstocks or natural products via C-H bond activation. Here we report a ternary hybrid catalysis composed of an acridinium photoredox catalyst, a thiophosphoric imide (TPI) catalyst, and a titanium complex catalyst. This catalytic system realized direct sp^3 C-H addition of organic molecules such as toluene, benzyl alcohol, alkenes, aldehydes, and THF to various ketones and aldehydes. The key for this transformation is the intrinsically unfavorable radical addition step promoted by single-electron reduction of the intermediate alkoxy radical by catalytically generated titanium(III) species which is supported by mechanistic studies. Due to the mildness and high functional group compatibility, the reaction is applicable to late-stage functionalization of biologically active compounds.³



1) P. Gray, A. Williams, *Chem. Rev.* **1959**, 59, 239. 2) a) P. Devin, L. Fensterbank, M. Malacria, *Tetrahedron Lett.* **1999**, 40, 5511. b) M. Saladrigas, C. Bosch, G. V. Saborit, J. Bonjoch, B. Bradshaw, *Angew. Chem., Int. Ed.* **2018**, 57, 182. c) B. Wu, R. Zhu, *ACS Catal.* **2020**, 10, 510. 3) **X. Peng**, Y. Hirao, S. Yabu, H. Sato, M. Higashi, H. Mitsunuma, M. Kanai, manuscript in preparation.

Hydrogenation and Borylation of Alkyl Chlorides using Zirconocene and Photoredox Catalysis

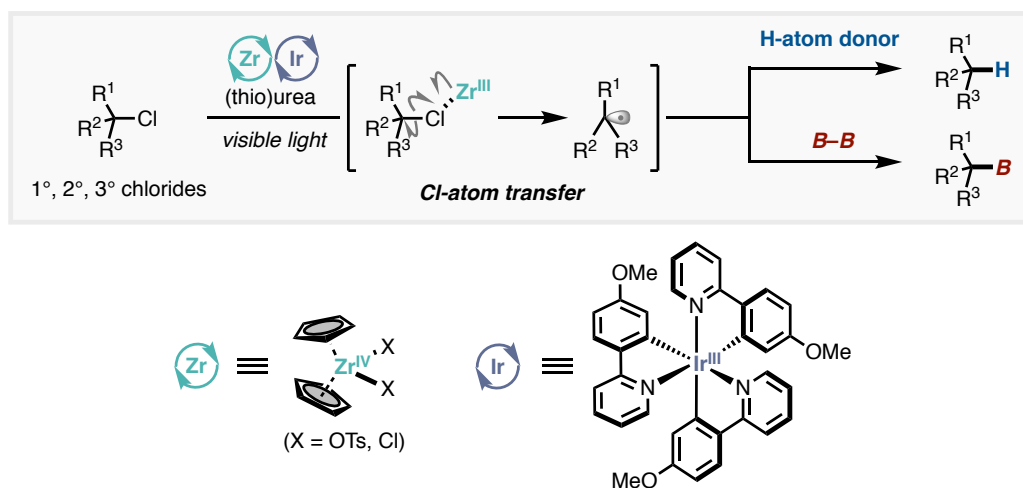
(Graduate School of Advanced Science and Engineering, Waseda University)

○Toshimasa Okita, Keisuke Tanaka, Kazuhiro Aida, Eisuke Ota, Junichiro Yamaguchi

Keywords: Zirconocene; Photoredox catalyst; Alkyl chlorides; Radical; Borylation

Homolysis of C–Cl bond is one of the fundamental transformations generating alkyl radical intermediates from versatile and abundant alkyl chlorides. However, the C–Cl bond cleavage remains unexplored due to requirement of high negative potential and bond dissociation energy (BDE) compared with alkyl bromides and alkyl iodides. Although synthetically useful approaches utilizing stoichiometric metal reductants,^{1a} titanocene,^{1b} and photoredox catalyst^{1c,1d} can activate alkyl chlorides, some drawbacks remain such as requiring strong reductants, heating with high temperature, and lack of substrate generality.

Herein, we have developed a C–Cl bond cleavage of alkyl chlorides using zirconocene and photoredox catalysts. Catalytically generated zirconocene(III)² enabled chlorine atom transfer from an alkyl chloride to furnish a corresponding alkyl radical. The resulting radical successfully underwent hydrogenation or borylation by employing hydrogen atom donor or diboron as radical trapping agents. These reactions are facilitated by the addition of (thio)urea as a co-catalyst. This reaction has been applied to various alkyl chlorides including derivatives of natural products and medicinal agents under mild conditions.



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- 2) Aida, K.; Hirao, M.; Funabashi, A.; Sugimura, N.; Ota, E.; Yamaguchi, J. *ChemRxiv.* **2021**, DOI: 10.26434/chemrxiv.14605392

光駆動型超核偏極を志向したトリプレットとラジカルの複合化

(1. 九大院工、2. 九大 CMS、3. 理研仁科セ、4. JST さきがけ) ○西村 亘生¹、立石 健一郎³、上坂 友洋³、君塚 信夫^{1,2}、楊井 伸浩^{1,2,4}

Hybridization of triplets and organic radicals towards photo-driven hyperpolarization (1. Grad. Sch. Eng., Kyushu Univ., 2. CMS, Kyushu Univ., 3. RIKEN Nishina Center for Accelerator-Based Science, 4. PRESTO, JST) ○Koki Nishimura¹, Kenichiro Tateishi³, Tomohiro Uesaha³, Nobuo Kimizuka^{1,2}, Nobuhiro Yanai^{1,2,4}

Dynamic nuclear polarization (DNP) is one of the powerful methods to improve the NMR sensitivity, however, there are some problems for the applications. The photo-driven Overhauser DNP can be achieved by light irradiation only using the reaction between the photo-excited triplets and the radicals. However, the efficiency of dynamic electron polarization, the most important process, is quite low. Here we synthesized several novel triplet-radical hybrid systems and observed hyperpolarized electron spins from time-resolved ESR. We will discuss the design guideline for efficient photo-driven Overhauser DNP.

Keywords : *Dynamic nuclear polarization; Dynamic electron polarization; Photo-excited triplet state; Magnetic resonance; Overhauser effect*

NMR の感度を改善する技術として動的核偏極 (DNP) は強力な手法である一方で課題も多い。光駆動型のオーバーハウザー DNP は光励起三重項とラジカルの反応を用いて光照射のみで駆動するものの、報告例は限られており、電子偏極生成効率の低さが課題となっている^{1)~4)}。そこで、種々の色素と安定有機ラジカルを複合した分子を合成し、電子偏極生成効率を評価した。

ポルフィリン誘導体と安定有機ラジカルであるニトロキシラジカルを連結した分子を合成した。この分子を 1 mM 含むトルエン溶液を調製し、室温・脱気下で時間分解 ESR 測定を行ったところ、ラジカル由来の時間減衰する ESR 信号が得られた。他の連結様式の結果も総合し、高効率な光駆動型 DNP の実現に向けた偏極源分子の設計指針について議論する。

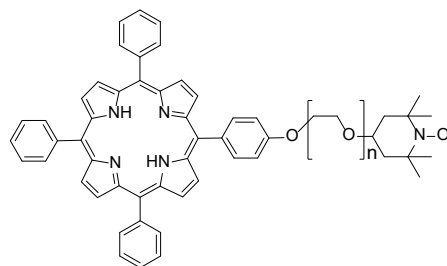


Fig. 1 Molecular structure

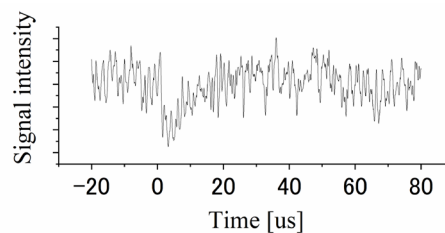


Fig. 2 ESR signal decay (n = 2)

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典型元素の可視光応答性を利用した含酸素-複素環化合物合成法の開発

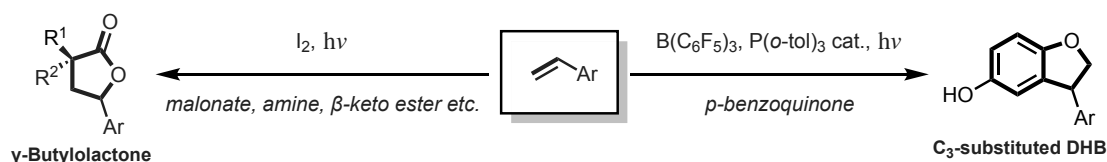
(岐阜薬大¹) ○前島 咲¹・山口 英士¹・伊藤 彰近¹

Development of oxygen-containing heterocyclic compounds synthesis using visible light responsiveness of main group elements (¹Gifu Pharmaceutical University) ○Saki Maejima,¹ Eiji Yamaguchi,¹ Akichika Itoh¹

We have developed the diversity-oriented synthesis methodologies for various lactones via biofunctionalization of olefins mediated by molecular iodine and visible light. That is to say, we developed some methodologies leading to various lactone derivatives such as γ -butyrolactones,^{1,2} spirolactones,³ and iminolactones⁴ by forming C-C/C-O bond in the intermolecular reaction. In addition, we have recently developed a regioselective synthesis of C₃-substituted dihydrobenzofuran (DHB) via biofunctionalization of olefins under visible light irradiation by using the classical photochemical reaction, so-called the Paternò-Büchi reaction. Specifically, we developed a rare-metal free regioselective methodology leading to C₃-substituted DHBs by forming intermolecular C-C/C-O bonds between *p*-benzoquinones (*p*-BQs) and α -olefins in the presence of B(C₆F₅)₃ as a Lewis acid catalyst under 450 nm LED light irradiation. Interestingly, the use of Lewis base catalyst such as phosphine was also found to improve the yield. In this conference, the details of rapid photosynthesis methodology for oxygen-containing heterocyclic compounds are comprehensively reported.

Keywords : Photo-reaction; Main group element; Heterocycles; Biofunctionalization of olefin, Paternò-Büchi reaction

演者は、典型元素の可視光応答性を利用しオレフィン類の二官能基化を経る、種々のラクトン類の多様性指向型合成法の体系化を達成した。具体的には、オレフィン類と分子状ヨウ素が反応することにより生成する高反応性のハロアルキル種に対し、種々の反応剤を組み合わせることで C-C/C-O 結合の新規形成を介したラクトン骨格構築法を開発した。さらに、近年は古典的な光化学反応であるパテルノ-ビュッヒ反応を活用することで、可視光照射下、オレフィンの二官能基化を介した 3 位置換ジヒドロベンゾフランの位置選択的合成法も見出している。具体的には、オレフィン類と *p*-ベンゾキノン に対して B(C₆F₅)₃ を触媒として用い可視光を外部照射することで、Paternò-Büchi 反応を介して 3 位置換ジヒドロベンゾフランが効率的に得られることが分かった。さらに興味深いことに、ホスフィンなどのルイス塩基触媒を併用することで、収率が大幅に向上することも判明した。本学会では、それらの開発した含酸素-複素環化合物の迅速光合成法について網羅的に報告する。



- 1) S. Maejima, E. Yamaguchi, A. Itoh, *Adv. Synth. Catal.* **2017**, 359, 3883-3887. 2) S. Maejima, E. Yamaguchi, A. Itoh, *ACS Omega* **2019**, 4, 4856-4870. 3) S. Maejima, E. Yamaguchi, A. Itoh, *J. Org. Chem.* **2019**, 84, 9519-9531. 4) S. Maejima, E. Yamaguchi, A. Itoh, *J. Org. Chem.* **2020**, 85, 10709-10718.

発光ラジカルをコアとするカルバゾールデンドリマーの創製

(九大院総理工¹・MOLFEX²・京大福セ³・京大院工⁴・京大 ESICB⁵・東理大理工⁶・産総研 物質計測標準⁷・九大先導研⁸・ダラム大⁹・JST-さがけ¹⁰) Rui Xiaotian¹・大田 航²・佐藤 徹^{3,4,5}・中山 泰生^{6,7}・古郡 美紀^{6,7}・細貝 拓也⁷・久村 絵理⁸・Andrew Monkman⁹・アルブレヒト 建^{8,10}

Creation of carbazole dendrimer with luminescent radical as core (Grad. Sch. Eng. Sci., Kyushu Univ.¹・MOLFEX, Inc.²・FIFC, Kyoto Univ Univ.³・Grad. Sch. Eng. Sci., Kyoto Univ.⁴・ESICB, Kyoto Univ.⁵・Faculty of Science and Technology, Tokyo University of Science⁶・AIST⁷・IMCE, Kyushu Univ.⁸・Univ. Durham⁹・JST-PRESTO¹⁰) Xiaotian Rui¹・Wataru Ota²・Tohru Sato^{3,4,5}・Yasuo Nakayama^{6,7}・Minoru Furukori^{6,7}・Takuya Hosokai⁸・Andrew P Monkman⁹・Ken Albrecht^{8,10}

Doublet luminescent materials are attracting attention because 100% exciton utilization efficiency can be achieved in organic light-emitting diodes (OLEDs). However, it has severe problems such as poor stability. This research introduces a radical core dendrimer design strategy to construct a stable radical molecule. A series of carbazole dendronized tri(2,4,6-trichlorophenyl)methyl (TTM) radicals were synthesized. The photophysical properties of all generations of radical dendrimers were compared to understand the structure-property relationship systematically. The photoluminescence quantum yield (PLQY) increased with the generation increase, and the fourth generation (G4TTM) in cyclohexane solution showed PLQY as high as 80% with wavelength at 627 nm in deep red region due to the low non-radiative decay rate constant. The dendron modification strategy has also significantly increased the photostability compared to the bare TTM radical.

Keywords : Excited Doublet State; Stable Radical; Dendrimer; Luminescent Materials

発光ラジカルを有機 EL の発光層として用いることで 100%の励起子利用効率が実現出来るため注目されている。しかし、安定性などに問題がある。嵩高いデンドロンの導入により、ラジカルを電子的、立体的に安定化することで課題であった安定性を解決できると考えた。本研究では発光ラジカルの構造特性相関を体系的に理解するため、TTM をコアとする各世代 (G1-G4) のカルバゾールデンドリマーの合成とその発光特性を報告する。発光量子収率 (PLQY) は世代の増加とともに増加し、G4TTM では無輻射減衰速度定数が急激に減少するため、波長 627 nm で 80%の PLQY を示した(シクロヘキサン中)。TTM ラジカルと比較して光安定性も大幅に向上した。

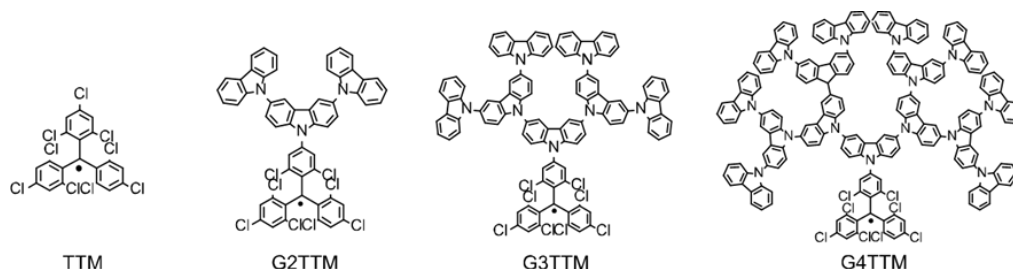


Fig.1 Structure of carbazole dendronized TTM radicals.

ポリマー媒体におけるエネルギー捕集と分子内 TTA を利用した光アップコンバージョン

(阪府大院工¹・阪府大 RIMED²)

○松井康哲^{1,2}・高橋拓海¹・加納雅也¹・大垣拓也^{1,2}・太田英輔^{1,2}・池田 浩^{1,2}

Photon Upconversion in Polymer Media Utilizing Energy Harvesting and Intramolecular TTA
(¹Grad. Sch. Eng., Osaka Pref. Univ., ²RIMED, Osaka Pref. Univ.) ○Yasunori Matsui,^{1,2}
Takumi Takahashi,¹ Masaya Kanoh,¹ Takuya Ogaki,^{1,2} Eisuke Ohta,^{1,2} Hiroshi Ikeda^{1,2}

Photon upconversion (UC) is a molecular technology that converts a low-energy light to a higher-energy light by employing triplet energy transfer from an energy donor (D) and triplet-triplet annihilation (TTA) of energy acceptors (A). To realize UC in the solid state, efficient triplet energy harvesting and suppression of fluorescence resonance energy-transfer quenching are required. For this purpose, we prepared solution-processed polymer composites containing D, an energy mediator (M), and an DPA-linked dyad DPA-Ad-DPA as A (Fig. 1), and further showed that the composites exhibit efficient TTA-UC.

Keywords : Delayed Fluorescence; Energy Transfer; Triplet-Triplet Annihilation; Polymer Gel

フォトンアップコンバージョン (UC) とは、エネルギードナー (D) の三重項エネルギー移動とエネルギーアクセプター (A) の三重項-三重項消滅 (TTA) を利用して低エネルギー光子を高エネルギー光子に変換する技術である。固体中で高効率な TTA-UC を実現するには、励起エネルギーの効率的な捕集と蛍光共鳴エネルギー移動消光の抑制が必要となる。そこで本研究では、ポリマー媒体においてメディエータ (M) を介したエネルギー捕集と分子内 TTA^{1,2} を利用した、3 成分系 UC を検討した。具体的には、D として白金オクタエチルポルフィリン (PtOEP, Fig. 1), M としてジ(*t*-ブチル)フェニルアントラセン (DBPA), A として DPA 連結ダイアド (DPA-Ad-DPA^{1,2}) を含むポリマー複合体を溶液プロセスにより作製した (Fig. 2)。その結果、硬いポリマー媒体であるポリメタクリル酸メチルやポリメタクリル酸エチルでは、分子が拡散しにくく分子間エネルギー移動がおこりにくい、柔らかい媒体であるポリウレタンでは分子間エネルギー移動がおこり、TTA-UC が観測されることがわかった (Fig. 3)。

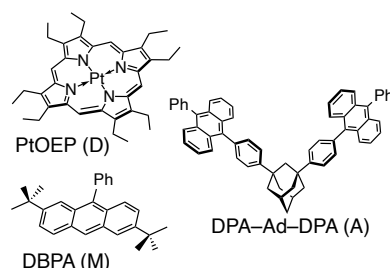


Fig. 1. Chemical structures of PtOEP, DBPA, and DPA-Ad-DPA.

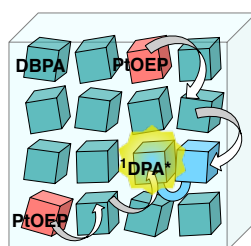


Fig. 2. A schematic representation of polymer composites containing PtOEP, DBPA, and DPA-Ad-DPA.

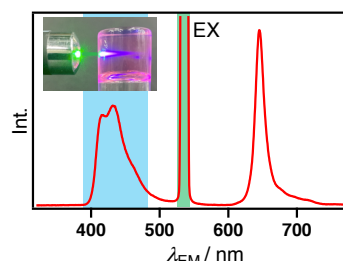


Fig. 3. UC emission spectrum of the polyurethane gel ($\lambda_{\text{EX}} = 535 \text{ nm}$).

- 1) Kanoh, M.; Matsui, Y.; Ogaki, T.; Ikeda, H. *et al. J. Phys. Chem. B*, **2021**, 125, 4831–4837.
- 2) Matsui, Y.; Kanoh, M.; Ikeda, H. *et al. J. Photochem. Photobiol. A: Chem.*, **2020**, 387, 112107.

[K4-1pm] 14. Organic Chemistry -Aromatic, Heterocyclic, and Heteroatom Compounds-

Chair: Taiki Morita, Takeshi Nanjo

Wed. Mar 23, 2022 1:00 PM - 3:40 PM K4 (Online Meeting)

[K4-1pm-01] Synthesis of Isoxazoloazaborines via Gold(I)-Catalyzed Propargyl Aza-Claisen Rearrangement/Borylative Cyclization Cascade and Methylene Insertion of Zinc Carbenoid into N-O Bond of Isoxazoles

○Masato Tsuda¹, Taiki Morita^{1,2}, Hiroyuki Nakamura^{1,2} (1. School of Life Science and Technology, Tokyo Institute of Technology, 2. Laboratory for Chemistry and Life Science, Tokyo Institute of Technology)

1:00 PM - 1:20 PM

[K4-1pm-03] Photouncaging-induced amide formation by red light irradiation to indolizines

○Kenji Watanabe¹, Asuka Kuratsu¹, Takashi Niwa^{1,2}, Takamitsu Hosoya^{1,2} (1. RIKEN BDR, 2. TMDU IBB)

1:40 PM - 2:00 PM

[K4-1pm-04] Deaminative borylation of aromatic amines based on photoinduced electron transfer

○Akira Shiozuka², Kohei Sekine^{1,2}, Yoichiro Kuninobu^{1,2} (1. Institute for Materials Chemistry and Engineering, Kyushu University, 2. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

2:00 PM - 2:20 PM

[K4-1pm-05] Development of Organophotocatalyst Enabling Substrate Recognition by Pyridine Moiety for C-C Bond Forming Reaction

○Natsuki Kato¹, Takeshi Nanjo¹, Yoshiji Takemoto¹ (1. Grad. Sch. Pharm. Sci., Kyoto Univ.)

2:20 PM - 2:40 PM

[K4-1pm-06] Dearomative Dicarboxylation of Heteroaromatic Compounds Using CO₂ Radical Anion

○Tsuyoshi Mita^{1,2}, Yong You^{1,2}, Wataru Kanna³, Hideaki Takano^{1,2}, Hiroki Hayashi^{1,2}, Satoshi Maeda^{1,2,3} (1. WPI-ICReDD, Hokkaido Univ., 2. JST-ERATO, 3. Fac. of Sci., Hokkaido Univ.)

2:40 PM - 3:00 PM

[K4-1pm-07] Synthesis of polysubstituted imidazoles using α, γ -diazido- α, β -unsaturated esters

○Keita Matsushima¹, Shota Tanaka¹, Taisei Koide¹, Ikuo Sasaki¹, Hideyuki Sugimura¹ (1. Aoyama Gakuin University)

3:00 PM - 3:20 PM

[K4-1pm-08] Synthesis of iptycenes Using Ambident Anthracene

○Mizuki Hyodo¹, Takayuki Iwata², Mitsuru Shindo² (1. Interdis. Grad. Sch. Eng. Sci., Kyushu Univ., 2. IMCE, Kyushu Univ.)

3:20 PM - 3:40 PM

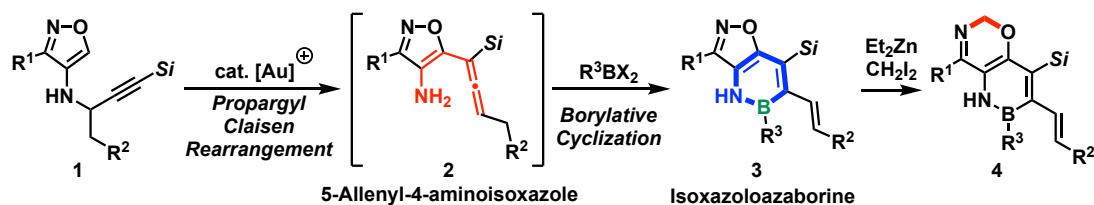
Synthesis of Isoxazoloazaborines via Gold(I)-Catalyzed Propargyl Aza-Claisen Rearrangement/Borylative Cyclization Cascade and Methylene Insertion of Zinc Carbenoid into N-O Bond of Isoxazoles

(¹*School of Life Science and Technology, Tokyo Institute of Technology*, ²*Laboratory for Chemistry and Life Science, Tokyo Institute of Technology*) ○Masato Tsuda,¹ Taiki Morita,^{1,2} Hiroyuki Nakamura^{1,2}

Keywords: Isoxazole; Azaborine; Gold Catalyst; Propargyl Claisen Rearrangement; Zinc Carbenoid

Heterocycles containing boron and nitrogen atoms in their ring systems, represented by 1,2-azaborine as a BN isostere of benzene, have recently attracted much attention in various research fields.¹⁾ Although recent synthetic studies have yielded numerous BN-embedded polycyclic aromatic compounds, there are still few examples of heteroarene-fused 1,2-azaborines because of the limited synthetic approaches to the ring system. In general, heteroarene-fused 1,2-azaborines have been synthesized by treating 2-aminostyrenes with electrophilic boron agents.

Recently, we reported the synthesis of 5-allenyl-4-aminoisoxazoles **2** by cationic gold(I) catalyzed propargyl aza-Claisen rearrangement of 4-*N*-propargylaminoisoxazoles **1**.²⁾ Although the allenic amine intermediates have been considered to be generated by conventional propargyl aza-Claisen rearrangement, they had never been used in further reactions because of their rapid intramolecular cyclization.³⁾ Herein, we report the synthesis of an unprecedented BN-heterocycle, isoxazoloazaborine **3** using 5-allenyl-4-aminoisoxazole **2**. The adjacent amino group and allene moiety of isoxazole **2** were successfully engaged in electrophilic borylative cyclization to give fused azaborine **3**. This is the first report of 1,2-azaborine synthesis utilizing allene functionality. Moreover, studies on derivatization of product **3** led us to find ring-expansion of isoxazoles through N-O bond insertion of zinc carbenoid to give oxazine-fused azaborine **4**.⁴⁾



1) Giustra, Z. X.; Liu, S.-Y. *J. Am. Chem. Soc.* **2018**, *140*, 1184-1194. 2) Tsuda, M.; Morita, T.; Fukuhara, S.; Nakamura, H. *Org. Biomol. Chem.* **2021**, *19*, 1358-1364. 3) Saito, A.; Konishi, T.; Hanzawa, Y. *Org. Lett.* **2010**, *12*, 372-374. 4) Tsuda, M.; Morita, T.; Nakamura, H. *Chem. Commun.* **2022**, DOI:10.1039/D1CC07002A.

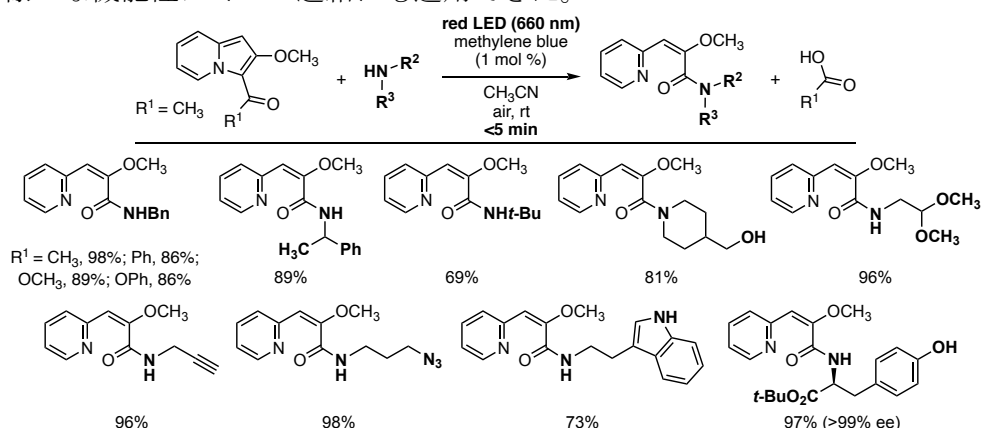
インドリジンへの赤色光照射によるアンケーシング誘起アミド形成

(理研 BDR¹・東医歯大 IBB²) ○渡邊 賢司¹・倉津 飛鳥¹・丹羽 節^{1,2}・細谷 孝充^{1,2}
 Photouncaging-induced amide formation by red light irradiation to indolizines (¹RIKEN BDR,
²TMDU IBB) ○Kenji Watanabe,¹ Asuka Kuratsu,¹ Takashi Niwa,^{1,2} Takamitsu Hosoya^{1,2}

Recently, we reported a photo-uncaging system of carboxylic acids via photooxidation of 3-acylindolizines triggered by a biopermeable red light (660 nm) in the presence of a photosensitizer.^{1,2} In this reaction, β -pyridylacrylic acids or the corresponding esters are also obtained as photooxidation products through the reaction with a solvent molecules, such as water or alcohols. Based on this result, we considered that an efficient linkage between indolizines and amines is achievable under the photoreaction conditions. Indeed, irradiation of 3-acylindolizines with a red light for a short time (<5 min) in the presence of amines (1.5 equiv) and a photosensitizer afforded acrylamide derivatives in high yields. This result demonstrates that a simple light stimulation of 3-acylindolizines in the presence of amines enables rapid release of carboxylic acids and immediate amide bond formation.

Keywords : Indolizine; Amine; Amide; Photooxidation; Uncaging

最近我々は、3-アシルインドリジンが触媒量の光増感剤の存在下、赤色光の照射によって、様々なカルボン酸やアルコールを短時間で放出することを報告した^{1,2)}。本反応では、インドリジンの光酸化分解物に溶媒の水分子やアルコールが結合した生成物を与える。そこで、求核性の高いアミン存在下で光反応を行うことで、インドリジンとアミンとの間で迅速な結合形成が行えるのではないかと考えた。実際に、3-アシルインドリジンにアミン（1.5 当量）と光増感剤の存在下で赤色光を短時間（<5 分）照射すると、アクリルアミド誘導体が高収率で得られた。すなわち、3-アシルインドリジンの光反応は、アシル基由来の化合物を放出するだけでなく、アミノ基との共有結合形成によって分子を連結できることが分かった。本反応は高い官能基許容性を示し、様々な機能性アミンの連結にも適用できた。



1) Watanabe, K.; Terao, N.; Kii, I.; Nakagawa, R.; Niwa, T.; Hosoya, T. *Org. Lett.* **2020**, 22, 5434.

2) Watanabe, K.; Terao, N.; Niwa, T.; Hosoya, T. *J. Org. Chem.* **2021**, 86, 11822.

光誘起電子移動を鍵とする芳香族アミンの C–N 結合切断を伴うボリル化反応の開発

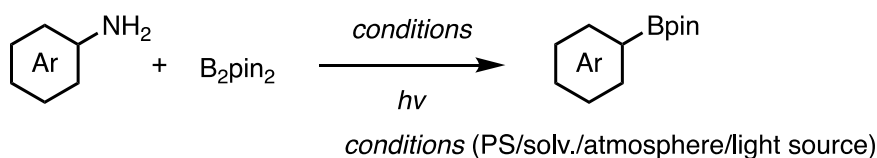
(九大先導研¹・九大院総理工²) ○塩塚朗²・関根康平^{1,2}・國信洋一郎^{1,2}

Deaminative borylation of aromatic amines based on photoinduced electron transfer (¹*Institute for materials Chemistry and Engineering, Kyushu University*, ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Akira Shiozuka,² Kohei Sekine,^{1,2} Yoichiro Kuninobu^{1,2}

We found that the deaminative borylation of aromatic amines proceeded in the presence of bis(pinacolato)diboron (B₂pin₂) under light irradiation. This reaction system can be applied to various aromatic amines. Deaminative borylation for secondary and tertiary amines in cyclopentyl methyl ether (CPME) with pyrene as a photosensitizer upon photoirradiation at 365 nm proceeded smoothly. On the other hand, the reaction of primary amines in dimethylcarbonate (DMC) under air upon photoirradiation at 427 nm gave the desired products in high yields.

Keywords : Aromatic Amine; Borylation; C–N Bond Cleavage; Photoinduced Electron Transfer; Concerted Reaction

光照射下で芳香族アミンに対してビス(ピナコラート)ジボロン(B₂pin₂)を作用させると、脱アミノ化を伴うボリル化反応が進行することを見出した。本反応は、用いる基質に対して最適な反応条件を付すことで、種々の芳香族アミンに適用可能である。芳香族第二級、第三級アミンに対しては、光増感剤としてピレンを用い、シクロペンチルメチルエーテル(CPME)溶媒中、紫外光(365 nm)を照射することで反応が円滑に進行することがわかった¹⁾。一方、芳香族第一級アミンに対しては、空気雰囲気下、可視光(427 nm)を照射することで、効率よくボリル化反応が進行することを見出した。



secondary and tertiary amines: pyrene, CPME, CO₂ (balloon), 365 nm

primary amines: none, DMC, air (open), 427 nm

PS: photosensitizer, CPME: cyclopentyl methyl ether, DMC: dimethyl carbonate.

1) Shiozuka, A.; Sekine, K.; Kuninobu, Y. *Org. Lett.* **2021**, 23, 4774.

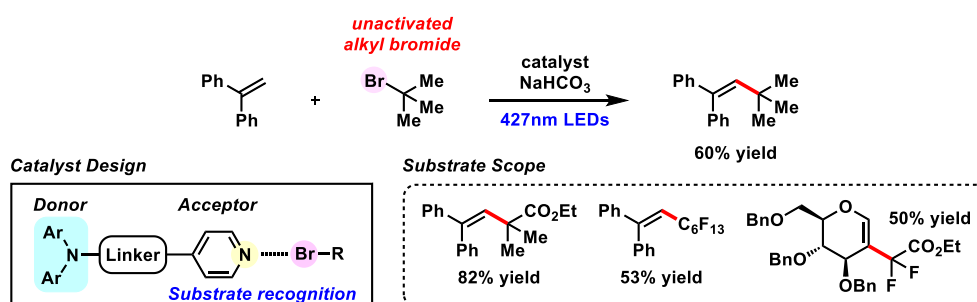
A Pyridine-based Organophotocatalyst Enabling Substrate Recognition for C-C Bond Forming Reaction

(Graduate School of Pharmaceutical Sciences, Kyoto University) ○Natsuki Kato, Takeshi Nanjo, Yoshiji Takemoto

Keywords: Organo-photocatalyst, Substrate recognition, Donor-Acceptor molecules, Pyridine, Halogen bonding

Photoredox catalysis has emerged as a powerful tool enabling radical-mediated transformations under mild conditions and a wide variety of transition metal complexes and organic molecules has been developed as a photocatalyst exhibiting different photochemical properties.¹ Recently, several research groups started to introduce the substrate-binding site into catalyst molecules in order to achieve stereoselective reaction,² and in the course of the investigation to develop higher reactive catalysts, we envisaged that the design of an organic molecule bearing a substrate recognition site on donor-acceptor core would provide a stronger reductive catalyst for single electron transfer reaction.

On the basis of the concept, we designed and synthesized a series of pyridine-based donor-acceptor molecules, which are expected to bind with alkyl halides through halogen bonding, and investigated the C–C bond formation reaction between alkene and alkyl bromide, which is recognized as a useful radical precursor. As a result, donor-acceptor molecules bearing diarylamine as a donor moiety exhibits high reactivity and even an unactivated alkyl bromide such as *t*-BuBr bearing high redox potential ($E_{\text{red}} = \text{ca.} -2.0 \text{ V}$ vs SCE)³ provided the desired product in 60% yield, despite of the lower redox potential of the catalyst. Several experimental analyses suggested that there is the interaction between a catalyst and alkyl bromide in solution and it would be the key to achieve the high reactivity of the catalyst.



1) MacMillan, D. W. C. *et al. J. Org. Chem.* **2016**, *81*, 6898. 2) (a) Meggers, E. *et al. Nature* **2014**, *515*, 100. (b) Yoon, T. P. *et al. J. Am. Chem. Soc.* **2017**, *139*, 17186. (c) Bach, T. *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 6640. (d) Melchiorre, P. *et al. Nat. Chem.* **2013**, *5*, 750. 3) a) Fry, J. A. *et al. J. Org. Chem.* **1976**, *41*, 54. b) Leonori, D. *et al. Science* **2020**, *367*, 102.

CO₂ ラジカルアニオンを用いるヘテロ芳香環の脱芳香族ダブルカルボキシル化：計算化学を取り入れた反応開発

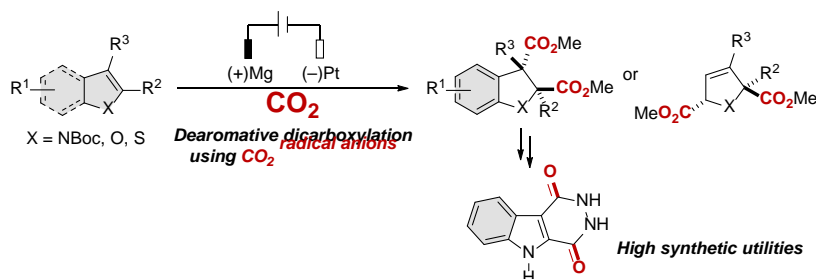
(北大 WPI-ICReDD¹・JST-ERATO²・北大院理³) ○美多 剛^{1,2}・游 勇^{1,2}・神名 航³・高野 秀明^{1,2}・林 裕樹^{1,2}・前田 理^{1,2,3}

Dearomative Dicarboxylation of Heteroaromatic Compounds Using CO₂ Radical Anion (¹WPI-ICReDD, Hokkaido Univ., ²JST-ERATO, ³Fac. of Sci., Hokkaido Univ.) ○Tsuyoshi Mita,^{1,2} Yong You,^{1,2} Wataru Kanna,³ Hideaki Takano,^{1,2} Hiroki Hayashi,^{1,2} Satoshi Maeda^{1,2,3}

The dearomative dicarboxylation of stable heteroaromatics using CO₂ is highly challenging but represents a significantly powerful method for producing synthetically useful dicarboxylic acids. However, these types of transformations are still underdeveloped, and concise methodologies with high efficiency have not been reported. We herein describe a new electrochemical protocol using the CO₂ radical anion ($E_{1/2}$ of CO₂ = -2.2 V in DMF and -2.3 V in CH₃CN vs SCE) that produces unprecedented *trans*-oriented 2,3-dicarboxylic acids from several heteroaromatics such as *N*-Ac-, Boc-, Ph-indoles, benzofuran, benzothiophene, electron-deficient furans, thiophenes, 1,3-diphenylisobenzofuran, and *N*-Boc-pyrazole with their reduction potentials more positive than -3 V. The dicarboxylated products thus obtained can be derivatized into useful synthetic intermediates for biologically active compounds in few steps.

Keywords: *Electrochemical Carboxylation; Carbon Dioxide; Heteroaromatics; Dearomatization; Dicarboxylation*

二酸化炭素を一電子還元することにより生じるラジカルアニオンを用いることで、これまでに報告例のないヘテロ芳香環の CO₂ による電解ダブルカルボキシル化に成功した。すなわち、CO₂ よりも還元電位が大きく、一般的な還元条件では還元が難しいとされるインドール誘導体、ベンゾフラン、ベンゾチオフェン、電子求引基が導入されたフラン、チオフェンを用いた際に、脱芳香族化を伴うダブルカルボキシル化が進行することがわかった。これらの基質は通常の -2.5 V 以上の還元電位があるため、CO₂ の方が優先的に一電子還元される。ただし、その後、ヘテロ芳香環の 2 位に対して、一電子還元で生じた CO₂ ラジカルアニオンが付加し最初のカルボキシル化が進行することを DFT 計算で明らかにした。加えて、反応が進行する基質は概ね還元電位が -3 V 以内であることを計算化学と実験化学の両面から見出した。



You, Y.; Kanna, W.; Takano, H.; Hayashi, H.; Maeda, S.; Mita, T. *under review*.

α,γ -ジアジド- α,β -不飽和エステルを利用した多置換イミダゾールの合成

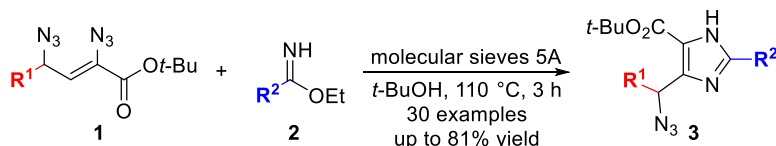
(青山学院大院理工¹⁾) ○松島 佳汰¹・田中 勝太¹・小出大晟¹・佐々木 郁雄¹・杉村 秀幸¹

Synthesis of polysubstituted imidazoles using α,γ -diazido- α,β -unsaturated esters (¹*Graduate School of Science and Engineering, Aoyama Gakuin University*) ○Keita Matsushima,¹ Shota Tanaka,¹ Taisei Koide,¹ Ikuo Sasaki,¹ Hideyuki Sugimura¹

Compounds containing imidazole ring possess various biological activities, and the substitution patterns of the imidazole ring have a huge impact on biological activities of the resultant molecules. Therefore, various synthetic methods of polysubstituted imidazoles have been developed. In 2015, Yu *et al.* reported the synthetic method using vinyl azides and imidates¹⁾. In our laboratory, the synthetic method of α,γ -diazido- α,β -unsaturated esters **1** containing a vinyl azide moiety was reported²⁾. In this study, we applied Yu's method to the diazide compounds **1** and optimized the reaction conditions. As a result, it was found that the polysubstituted imidazole **3** was obtained in good yield when the reaction was performed in the presence of molecular sieves 5A as an additive in *t*-BuOH at 110 °C for 3 h. With the optimized conditions in hand, the substrate scope was investigated. Furthermore, to demonstrate the synthetic utility, transformations of the azido group of the obtained polysubstituted imidazoles were carried out.

Keywords : *Heteroaromatic Compounds; Imidazoles; Vinyl Azides; Imidates*

イミダゾール環を含む化合物は様々な生物活性を示し、その置換様式は生物活性に大きく影響を与えることから、今までに様々な多置換イミダゾールの合成法が開発されてきた。2015年には、Yu らによってビニルアジドとイミデートを利用した多置換イミダゾールの合成法が報告された¹⁾。一方、当研究室ではビニルアジド構造を持つ α,γ -ジアジド- α,β -不飽和エステル **1** の合成法を報告している²⁾。そこで、本研究ではこのジアジド化合物 **1** に対して Yu らの多置換イミダゾールの合成法を適用し、反応条件の最適化を行ったところ、添加剤として molecular sieves 5A を用い *t*-BuOH 中、110 °C で3時間反応を行うと、多置換イミダゾール **3** が良好な収率で得られることが分かった。さらに、この最適反応条件を用いて基質適用範囲の調査を行った。また、この合成法の有用性を示すために、得られた多置換イミダゾールが有するアジド基の変換反応の検討を行った。



1) Y. Yu *et al.* *RSC Adv.* **2015**, 5, 55808-55811.

2) H. Sugimura *et al.* *Tetrahedron Lett.* **2015**, 56, 2813-2816.

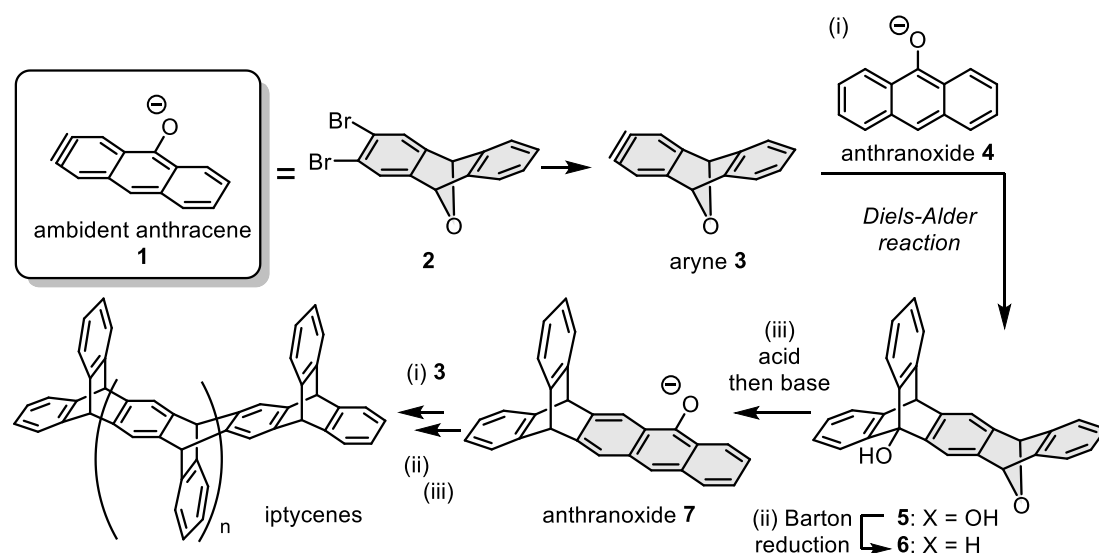
▪ Synthesis of Iptycenes Using Ambident Anthracene

(¹*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*, ²*Institute for Materials Chemistry and Engineering, Kyushu University*) ○ Mizuki Hyodo,¹ Takayuki Iwata,² Shindo Mitsuru²

Keywords : Iptycene, Anthracene, Benzyne, Diels-Alder reaction, Triptycene

Iptycenes are aromatic compounds in which arenes are fused with barrelene scaffold. Based on the unique and rigid structure, iptycenes have been used in the fields of supramolecular chemistry, molecular machine, materials science, etc. However synthetic methods of iptycenes, in particular large iptycenes which have more than seven benzene rings, are very limited. We have recently developed a novel synthetic methods of triptycenes utilizing Diels-Alder reaction between arynes and electron-rich anthranoxides derived from anthrones.¹ In this presentation, we will report synthesis of iptycenes using “ambident anthracene **1**”, which has both aryne and arynophile moieties.

2,3-Dibromo-9,10-dihydro-9,10-epoxyanthracene (**2**) was used as an equivalent of ambident anthracene **1**. The strategy to synthesize iptycenes comprises of three steps; (i) formation of aryne **3** and *in situ* Diels-Alder reaction with anthranoxide **4** to construct triptycene scaffold, (ii) removal of the bridgehead hydroxy group by Barton deoxygenation (**5** to **6**), and (iii) formation of anthranoxide **7** by ring-opening of the ether ring system and subsequent deprotonation. Arynophile **7** was further treated with aryne **3** and repeating these steps successfully provided large undeciptycene bearing up to eleven benzene rings.



(1) T. Iwata, M. Hyodo, T. Fukami, Y. Shiota, K. Yoshizawa, M. Shindo, *Chem. Eur. J.* **2020**, *26*, 8506.

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

[K307-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Hiromichi Egami, Ryo Yazaki

Wed. Mar 23, 2022 1:00 PM - 3:40 PM K307 (Online Meeting)

[K307-1pm-01] Direct Catalytic Enantioselective Hydrophosphonylation of N-Unprotected Ketimines

○Yuta Kondo¹, Koki Yamada¹, Tetsuya Kadota¹, Hiroyuki Morimoto¹, Takashi Ohshima¹
(1. Graduate School of Pharmaceutical Sciences, Kyushu University)

1:00 PM - 1:20 PM

[K307-1pm-02] Asymmetric fluorination of allylic amides using diatonic phase-transfer catalyst and its mechanistic insight

○Hiromichi Egami¹, Tomoki Niwa¹, Kousuke Nishibashi¹, Hitomi Sato¹, Kiyoshi Ujiie¹, Kenji Yamashita¹, Yoshitaka Hamashima¹ (1. Univ. of Shizuoka)

1:20 PM - 1:40 PM

[K307-1pm-03] Enantioselective Radical Cation [2+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Mechanistic Insight into the Effect of Photoirradiation

○Kei Katagiri¹, Shuhei Ohmura¹, Takahiro Horibe¹, Kazuaki Ishihara¹ (1. Nagoya University)

1:40 PM - 2:00 PM

[K307-1pm-04] Enantioselective Oxidative Dearomatization of Arenols Using High-performance Hypohalite Catalysis

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

2:00 PM - 2:20 PM

[K307-1pm-05] Ammonium Hypoiodite-catalyzed Oxidative Umpolung of Indoles for Dearomatization

○Hiroki Tanaka¹, Muhammet Uyanik¹, Kazuaki Ishihara¹ (1. Nagoya University)

2:20 PM - 2:40 PM

[K307-1pm-06] Convuluted Polymer-Supported-Cobalt-Catalyzed Regioselective Cyclotrimerization of Aryl Alkynes

○Abhijit Sen¹, Takuma Sato¹, Aya Ohno¹, Heeyoel Baek¹, Yoichi M. A. Yamada¹ (1. Green Nano Catalysis Research Team)

2:40 PM - 3:00 PM

[K307-1pm-07] Homologation of Aryl aldehydes Using Nitromethane as a C1 Source with Nitrogen-doped Carbon Supported Palladium Catalysts

○Tomohiro Yasukawa¹, Yasuhiro Yamashita¹, Shu Kobayashi¹ (1. The University of Tokyo)

3:00 PM - 3:20 PM

[K307-1pm-08] Development of Chiral Lewis Acid Complexes with High Hydrophobicity as Self-healing Catalysts for Reactions in Water

○Fangqiu Lu¹, Taku Kitanosono¹, Yasuhiro Yamashita¹, Shū Kobayashi¹ (1. The Univ. of Tokyo)

3:20 PM - 3:40 PM

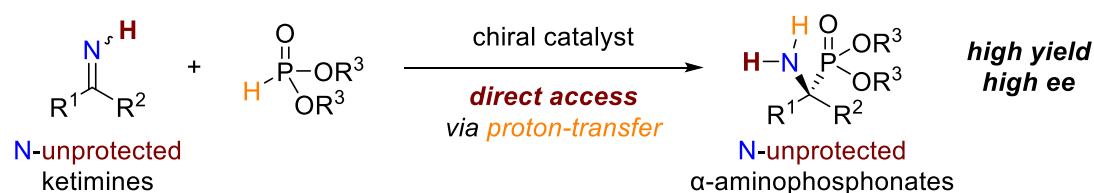
Direct Catalytic Enantioselective Hydrophosphonylation of N-Unprotected Ketimines

(Graduate School of Pharmaceutical Sciences, Kyushu University) ○Yuta Kondo, Koki Yamada, Tetsuya Kadota, Hiroyuki Morimoto, Takashi Ohshima

Keywords: Asymmetric Reaction; Catalytic Reaction; N-Unprotected Ketimine; Hydrophosphonylation; α -Aminophosphonate

α -Aminophosphonates are useful α -amino acid analogs and important building blocks for bioactive and pharmaceutical compounds. One of the most efficient methods for synthesizing enantioenriched α -aminophosphonates is direct catalytic enantioselective hydrophosphonylation of imines.¹ In particular, hydrophosphonylation of ketimines is useful for synthesizing α -tetrasubstituted α -aminophosphonates. Nevertheless, all the reported reactions use N-protected ketimines for controlling stability, reactivity, and stereoselectivity and require protection/deprotection steps for obtaining N-unprotected α -aminophosphonates.

To circumvent the problem, our group is recently interested in the use of N-unprotected ketimines as a substrate because N-unprotected amines are directly obtained without such protection/deprotection steps, which can contribute to the Sustainable Development Goals (SDGs).² To this end, herein we report direct catalytic enantioselective hydrophosphonylation of N-unprotected ketimines.³ By choosing the appropriate chiral catalyst and reaction conditions, we achieved the direct synthesis of N-unprotected α -aminophosphonates in high yield and high enantioselectivity. Detailed reaction conditions and substrate scope will be disclosed in this presentation.



- (1) For reviews of enantioselective hydrophosphonylation of imines, see: (a) P. Merino, E. Marqués-López, R. P. Herrera, *Adv. Synth. Catal.* **2008**, 350, 1195–1208; (b) M. Ordóñez, H. Rojas-Cabrera, C. Cativiela, *Tetrahedron* **2009**, 65, 17–49.
- (2) For a review, see: (a) K. Morisaki, H. Morimoto, T. Ohshima, *ACS Catal.* **2020**, 10, 6924–6951. For selected our contributions, see: (b) R. Yonesaki, Y. Kondo, W. Akkad, M. Sawa, K. Morisaki, H. Morimoto, T. Ohshima, *Chem. Eur. J.* **2018**, 24, 15211–15214; (c) T. Kadota, M. Sawa, Y. Kondo, H. Morimoto, T. Ohshima, *Org. Lett.* **2021**, 23, 4553–4558.
- (3) Y. Kondo, K. Yamada, T. Kadota, H. Morimoto, T. Ohshima, *manuscript in preparation*.

ジアニオン型相間移動触媒を用いるアリルアミドの不斉フッ素化反応とその反応機構に関する研究

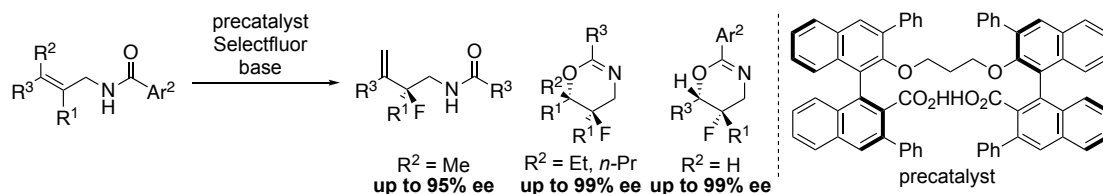
(静岡県大薬) ○江上 寛通・丹羽 智紀・西橋 幸佑・佐藤 瞳・氏家 清・山下 賢二・濱島 義隆

Asymmetric Fluorination of Allylic Amides Using Dianionic Phase-Transfer Catalyst and Its Mechanistic Insight (*School of Pharmaceutical Sciences, University of Shizuoka*) ○Hiromichi Egami, Tomoki Niwa, Kousuke Nishibashi, Hitomi Sato, Kiyoshi Ujiie, Kenji Yamashita, Yoshitaka Hamashima

Fluorine is an element of interest in life science field, because biological activity is often improved by introduction of fluorine into an organic molecule at an appropriate position. Since each enantiomer usually has different bioactivity due to chiral environment in nature, asymmetric control in fluorine incorporation is an important subject. In this context, we recently developed dicarboxylate phase-transfer catalyst and demonstrated the asymmetric fluorofunctionalizations of alkenes and dearomatizing fluorinations of aromatic compounds. This time, we examined allylic amides having various substitution pattern using the catalyst, and we noticed the stereochemistry depends on substitution pattern. Based on the mechanistic studies, it was found that active catalytic species were altered in the presence or absence of R² substituent. In this presentation, we will discuss the details.

Keywords : Fluorine; phase-transfer catalyst; asymmetric reaction; alkene; reaction mechanism

有機分子の適切な位置にフッ素を導入することでその生物活性がしばしば向上することから、生命科学研究においてフッ素は関心の高い元素である。生体内がキラルな環境下にあるため光学異性体は生体内で異なる作用を示すことから、フッ素導入における不斉制御は重要な課題である。当研究室では最近、キラルなジカルボキシレート型相間移動触媒の開発に成功し¹⁾、アルケン類の不斉フッ素官能基化および芳香族化合物の脱芳香環化型フッ素化反応の優れた触媒となることを明らかにしてきた。今回様々なアリルアミド類を検討したところ、その生成物および立体化学が基質の置換パターンに応じて異なることがわかった。そこで反応機構解析を行ったところ、アルケン部位の R² 置換基の有無によりその活性種が変化することが明らかとなった²⁾。本発表ではその詳細について報告する。



- 1) H. Egami, T. Niwa, H. Sato, R. Hotta, T. Rouno, Y. Kawato, Y. Hamashima, *J. Am. Chem. Soc.* **2018**, *140*, 2785.
- 2) T. Niwa, K. Nishibashi, H. Sato, K. Ujiie, K. Yamashita, H. Egami, Y. Hamashima, *J. Am. Chem. Soc.* **2021**, *143*, 16599.

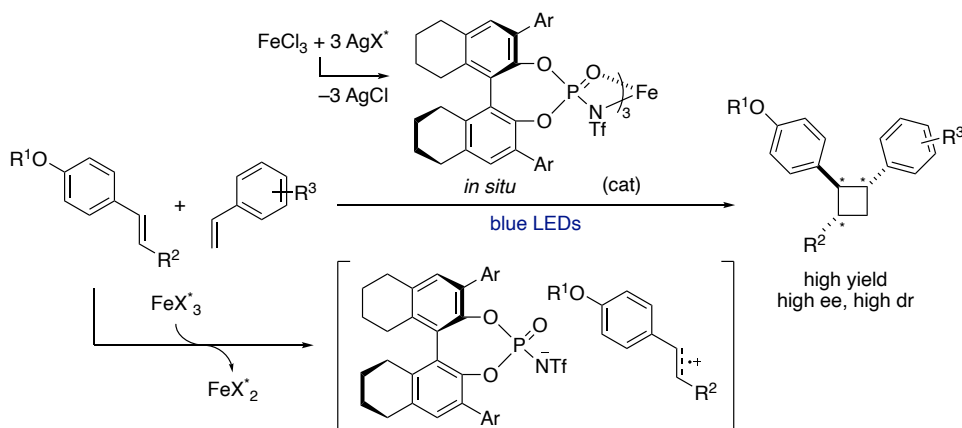
Enantioselective Radical Cation [2+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Mechanistic Insight into the Effect of Photoirradiation

(Graduate School of Engineering, Nagoya University) ○ Kei Katagiri, Shuhei Ohmura, Takahiro Horibe, Kazuaki Ishihara

Keywords: Radical Cation; [2+2] Cycloaddition; Chiral Iron(III) Salt; Chiral Counter Anion; Photoirradiation

Radical cation [2+2] cycloaddition of anetholes with styrenes is of interest because it is one of the most straightforward methods to synthesize 1,2-diarylcyclobutanes, which are present in various natural products and pharmaceuticals. Generally, the reaction commences with the oxidation of an anethole derivative to provide an anethole radical cation intermediate. To generate such a reactive intermediate, great progress has been made on the development of several initiators over the past few decades. However, enantioselective variants of this type of reaction have been still challenging because those require precisely stereoselective control for labile radical cation intermediates.¹

We previously developed radical cation [2+2] cycloadditions initiated by iron(III) salts as effective one-electron oxidants.² Here, we developed a chiral iron(III) salt, which could be prepared *in situ* from an iron(III) chloride and chiral silver *N*-triflyl phosphoramides, for enantioselective radical cation [2+2] cycloaddition. Several anetholes could be oxidized, and the resulting radical cation intermediates bearing chiral *N*-triflyl phosphoramide reacted with styrenes affording the [2+2] cycloadducts stereoselectively. Intriguingly, irradiation with blue LEDs dramatically improved the yield. As a result, the products were obtained in high yield with high enantioselectivity and diastereoselectivity. To elucidate the effect of photoirradiation, several control experiments and spectroscopy analyses were conducted.



- 1) P. D. Morse, T. M. Nguyen, C. L. Cruz, D. A. Nicewicz, *Tetrahedron* **2018**, 74, 3266. 2) T. Horibe, K. Katagiri, K. Ishihara, *Adv. Synth. Catal.* **2020**, 362, 960.

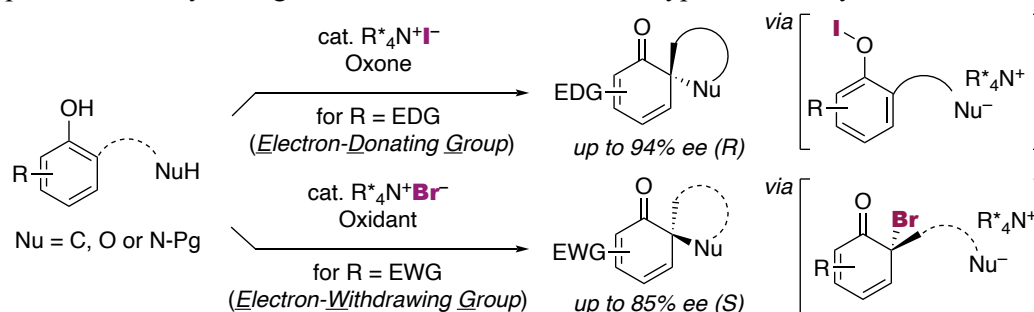
Oxidative Dearomatization of Arenols Using High-performance Hypohalite Catalysis

(Graduate School of Engineering, Nagoya University) ○Takehiro Kato, Muhammet Uyanik, Kazuaki Ishihara

Keywords: Chiral Hypohalite Catalysts; Oxidative Dearomatization; Phenol; Enantioselective; Oxone

Enantioselective oxidative dearomatization of arenols is an important tool for the synthesis of several biologically important compounds. To date, many elegant strategies have been developed using transition metal or hypervalent iodine catalysts or reagents.¹ In this regard, we have developed chiral quaternary ammonium hypoiodite-catalyzed enantioselective oxidative dearomatization of 1-naphthols.² In this catalytic system, hypoiodite active species were generated *in situ* from the corresponding quaternary ammonium iodides in the presence of hydrogen peroxide as an environmentally benign oxidant. However, the substrate scope was limited to 1-naphthols, and, in most cases, long times were required to complete the reactions, even for these highly reactive substrates.

Here, we developed a high-performance ammonium hypohalite catalysis for the enantioselective oxidative dearomatization reactions. Hypohalite catalytic active species could be generated *in situ* from the corresponding chiral quaternary ammonium halides with oxone as an environmentally benign oxidant. Only inorganic wastes were generated from the oxidant used. By using hypoiodite catalysis, the oxidation of a wide range of naphthols and electron-rich phenols could proceed under mild conditions to afford the corresponding spirolactones with high enantioselectivity.^{3,4} On the other hand, by using hypobromite catalysis, intra- or intermolecular oxidative dearomatization of electron-deficient phenols, which were hardly reactive using the hypoiodite catalysis, readily proceeded to give the corresponding adducts. Control experiments revealed that the reaction mechanism of hypobromite catalysis might be different from that of the hypoiodite catalysis.



- 1) S.-L. You, *Asymmetric Dearomatization Reactions*, John Wiley & Sons, Hoboken, **2016**.
- 2) M. Uyanik, N. Sasakura, E. Kaneko, K. Ohori, K. Ishihara, *Chem. Lett.* **2015**, 44, 179.
- 3) M. Uyanik, T. Kato, N. Sahara, O. Katade, K. Ishihara, *ACS Catal.* **2019**, 9, 11619.
- 4) M. Uyanik, N. Sahara, O. Katade, K. Ishihara, *Org. Lett.* **2020**, 22, 560.

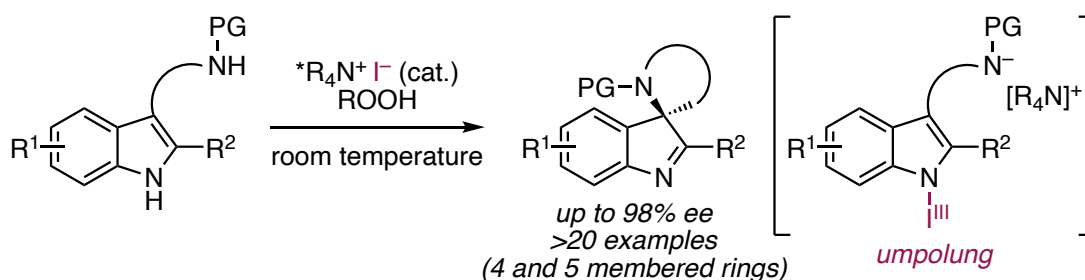
Ammonium Hypoiodite-catalyzed Oxidative Umpolung of Indoles for Dearomatization

(Graduate School of Engineering, Nagoya University) ○Hiroki Tanaka, Muhammet Uyanik, Kazuaki Ishihara

Keywords: Hypoiodite Catalysis; Oxidation; Cyclization; Indole; Umpolung

Indole derivatives are key structural units of several biologically active compounds. To date, numerous synthetic methods for those compounds have been developed. Among them, the dearomatization of indoles is one of the most powerful tools for the synthesis of substituted or polycyclic indole derivatives.¹ In most dearomatization strategies, indoles have been utilized as nucleophiles due to the high nucleophilicity of the indole nucleus at C-3. Only a few methods using C-3 electrophilic indoles have been reported.² On the other hand, in our laboratory, quaternary ammonium hypoiodite salt catalysis has been developed for environmentally benign oxidative coupling reactions.³ In this catalytic oxidation system, hypoiodite salts are generated *in situ* from the corresponding quaternary ammonium iodides in the presence of hydrogen peroxide or alkyl hydroperoxides as an environmentally benign oxidant.

Here, we describe the hypoiodite-catalyzed oxidative dearomatization of indole derivatives.^{4,5} Mechanistic studies suggest umpolung reactivity of the C-3 position of indoles by iodination of the indole nitrogen atom. In addition, enantioselective dearomative spirocyclization of indoles using chiral quaternary ammonium iodide as a catalyst gave the corresponding spiroindolenines with high enantioselectivity. Moreover, site-selective spirocyclization of tryptamine at C-3 position was achieved to give the difficult-to-access spiroazetidine in an enantioselective manner. We anticipated that this unusual “electrophilic indole” strategy would allow improving the synthetic portfolio for indole manipulation significantly.



- 1) C. Zheng, S.-L. You, *Nat. Prod. Rep.* **2019**, 36, 1589.
- 2) M. Bandini, *Org. Biomol. Chem.* **2013**, 11, 5206.
- 3) M. Uyanik, K. Ishihara, *ChemCatChem* **2012**, 4, 177.
- 4) M. Uyanik, H. Tanaka, K. Ishihara, *Org. Lett.* **2020**, 22, 8049.
- 5) M. Uyanik, H. Tanaka, K. Ishihara, *Asian J. Org. Chem.* **2021**, 10, 164.

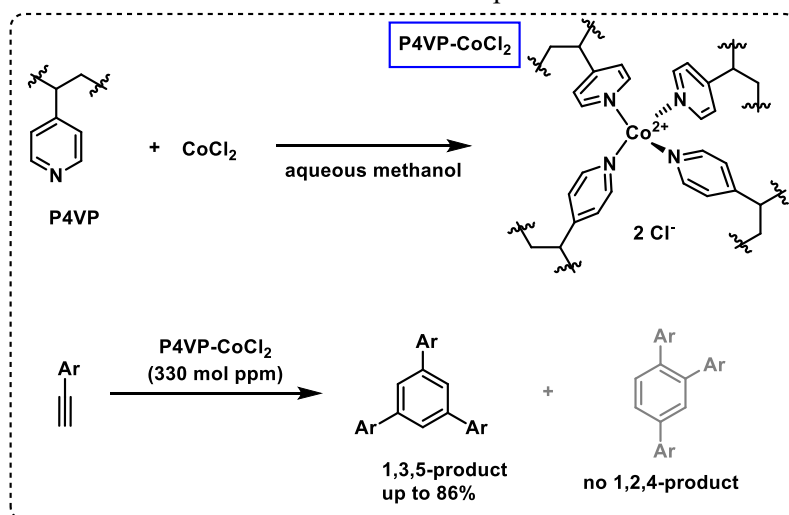
Convoluting Polymer-Supported-Cobalt-Catalyzed Regioselective Cyclotrimerization of Aryl Alkynes

(¹CSRS, RIKEN) ○Abhijit Sen,¹ Takuma Sato,¹ Aya Ohno,¹ Heeyoel Baek,¹ Yoichi, M. A. Yamada¹

Keywords: Poly(4-vinylpyridine); Cobalt catalysis; Heterogeneous catalysis; Regioselective reaction; Cyclotrimerization

Transition metal-catalyzed cyclotrimerization of aryl alkyne is a well-known reaction.¹ Among the transition metals, cobalt is one of the most commonly used metals.² The cobalt catalyzed cyclotrimerization usually afforded a mixture of 1,2,4-triarylbenzene and 1,3,5-triarylbenzene where 1,3,5-triarylbenzene is obtained as a minor product. Contrarily, these C₃-symmetric 1,3,5-triarylbenzenes are useful because of their application as polycyclic aromatic hydrocarbons (PAHs) and functional materials.³ Unfortunately, used cobalt catalysts are not reusable and required high catalyst loading.

This time, we developed a poly(4-vinylpyridine), P4VP-self-supported novel, stable, and heterogeneous cobalt catalyst P4VP-CoCl₂ by using our molecular convolution method.⁴ The structure was determined based on theoretical and experimental calculation. When the reaction of aryl acetylenes was carried out with 330 mol ppm of P4VP-CoCl₂ under neat conditions, exclusive 1,3,5-selective cyclotrimerization proceeded with up to 86% yield whereas no 1,2,4-selective product was obtained. The catalyst was recoverable and reusable. The catalyst tolerates gram-scale reactions. Functional materials were also synthesized. Details on substrate scope and mechanistic studies will be discussed in the presentation.



1) Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* **2011**, *40*, 3430. 2) Hilt, G.; Hengst, C.; Hess, W. *Eur. J. Org. Chem.* **2008**, 2293. 3) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817. 4) Sen, A.; Sato, T.; Ohno, A.; Baek, H.; Muranaka, A.; Yamada, Y. M. A. *JACS Au*, **2021**, *1*, 2080.

Homologation of Aryl aldehydes Using Nitromethane as a C1 Source with Nitrogen-doped Carbon Supported Palladium Catalysts

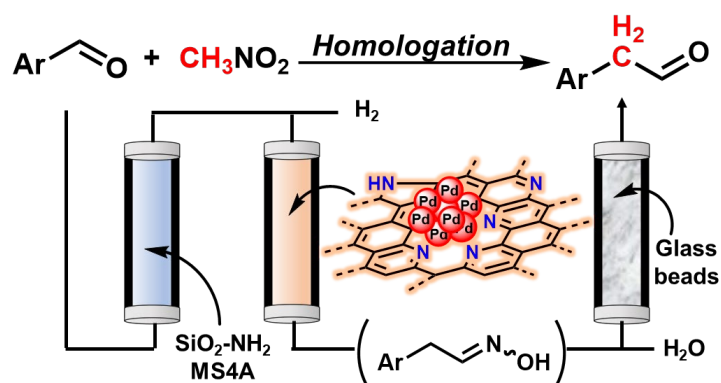
(GSC Social Cooperation Lab., The Univ. of Tokyo; School of Science, The Univ. of Tokyo) OTomohiro YASUKAWA, Yasuhiro YAMASHITA, Shū KOBAYASHI

Keywords: Heterogeneous Catalyst; Hydrogenation; Homologation Reaction; Flow Reaction; Nitrogen-doped Carbon

Homologation of aryl aldehydes provides useful synthetic intermediates. However, such a process requires multistep reactions with reactive reagents, which generates a significant amount of wastes and limits the scope. We designed such reactions using nitromethane as a C1 source via nitroolefin formation, partial hydrogenation to oximes, and hydration of oximes. To achieve this process, chemoselective hydrogenation reactions are needed. However, examples of selective hydrogenation of nitroolefins to oximes are very limited as it can produce several possible products. Reported systems required harsh conditions such as high pressure (10-20 bar) and substrate scope was limited.^{1), 2)}

We recently developed nitrogen-doped carbon incarcerated palladium nanoparticle catalysts for selective hydrogenation of nitroolefins to oximes.³⁾ The catalyst showed almost perfect selectivity, high activity, and reusability under ambient pressure. The nitrogen-dopants were essential to control the selectivity while dopant-free carbon-supported palladium catalysts gave a complex mixture.

Using the above-mentioned catalysts, three-step homologation reactions in both batch and flow systems were performed with only one purification step. Amino silica was used for the first nitroolefin formation step and the columns packed with heterogeneous catalysts were used for the flow reaction. A sequential continuous-flow system particularly worked efficiently to afford the product in high yield for more than two days.



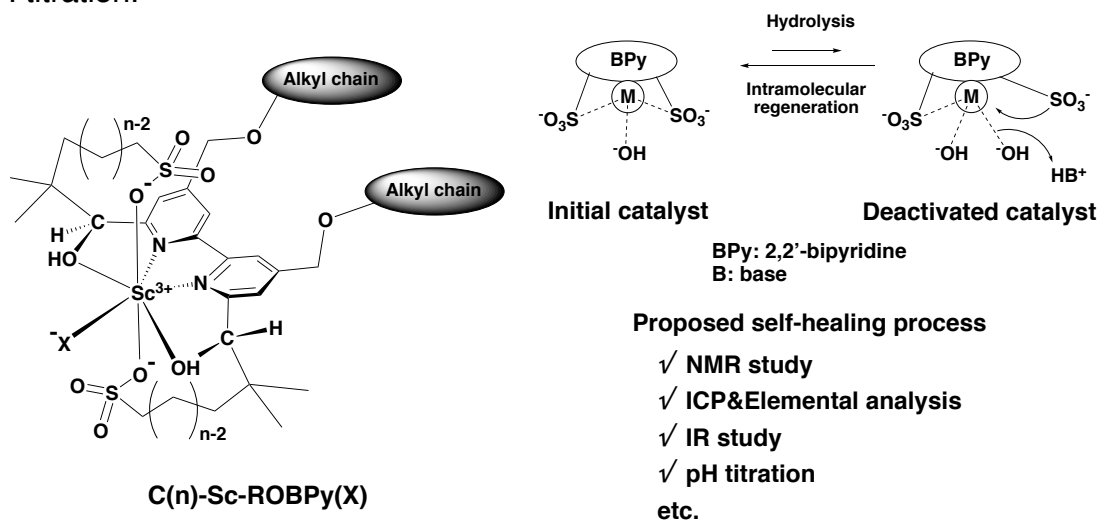
1) A. Corma, *et al. JACS*, **2007**, 129, 6358; 2) A. Wang, T. Zhang, *et al. Chem. Commun.* **2017**, 53, 1969; 3) T. Yasukawa, S. Kobayashi, The 100th CSJ Annual Meeting, 4B8-37, 2020.

Development of Chiral Lewis Acid Complexes with High Hydrophobicity as Self-healing Catalysts for Reactions in Water

(School of Science, The Univ. of Tokyo) ○ Fangqiu LU, Taku KITANOSONO,*
Yasuhiro YAMASHITA, Shū KOBAYASHI*

Keywords: Self-healing; Asymmetric Synthesis; Reaction in Water; Lewis Acid Catalyst; Hydrolysis

Organic reactions in water have attracted a great deal of attention due to advantages of safety and environmental harmony. Nowadays, chiral Lewis acid-catalyzed reactions in water have been well developed and widely applied.¹ However, there remains a problem of hydrolysis of central metal, which limits catalyst lifetime and sustainability. To solve such problems, we proposed an anionic chiral ligand by modifying a chiral 2,2'-bipyridine ligand (C(n)-Sc-ROBPy(X)).² It may repair itself continuously without external energy source and activation. It is supposed to have extremely long catalyst lifetime. This property can be defined as “self-healing”. We expected that alkyl chains substituted on 4,4'-position of a bipyridine will provide a high hydrophobicity to realize efficient enantioselective reactions in water. We evaluated the catalyst activity in water and studied the self-healing ability by several analytical methods such as NMR study, ICP analysis, elemental analysis, IR study and pH titration.



1) Kobayashi, S. *et al.* In *Book Chiral Lewis Acids in Organic Synthesis*, ed. by J. Mlynarski, Wiley-VCH, **2017**, 299-344.

2) Kobayashi, S. *et al.* 日本化学会第100回春季年会, 2B4-12.

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

[K5-1pm] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Eiko Yasui, Hiroyuki Miyamura

Wed. Mar 23, 2022 1:20 PM - 3:40 PM K5 (Online Meeting)

[K5-1pm-01] Nitrogen-Doped Carbon-Incarcerated Zinc Catalysts as Less Sacrificial Electrodes for Electrochemical Allylation Reactions

○Ryusuke Masuda¹, Tomohiro Yasukawa¹, Yasuhiro Yamashita¹, Shu Kobayashi¹ (1. The University of Tokyo)

1:20 PM - 1:40 PM

[K5-1pm-02] Development of reductive cleavage of aryl ethers using cooperative catalytic systems of heterogeneous metal nanoparticles and Lewis acids

○Hiroyuki Miyamura¹, Shu Kobayashi¹ (1. The Univ. of Tokyo)

1:40 PM - 2:00 PM

[K5-1pm-03] Development of Solid Base Catalysts for Hydroxypyrazine Synthesis in Water

○Tomoya Hisada¹, Taku Kitanosono¹, Yasuhiro Yamashita¹, Shū Kobayashi¹ (1. University of Tokyo)

2:00 PM - 2:20 PM

[K5-1pm-04] Highly Selective Synthesis of α -Aminoamide Utilizing an Umpolung Reaction and Characteristics of α -Hydrazonoester

○Isao Mizota¹ (1. Mie University)

2:20 PM - 2:40 PM

[K5-1pm-05] Synthestic study of arenicolides

-construction of complete carbon framework-

○Reo Hirao¹, Yoshinori Kawano¹, Eiko Yasui¹, Shinji Nagumo¹ (1. Kogakuin University)

2:40 PM - 3:00 PM

[K5-1pm-06] Chemo-, Regio- and Diastereoselective Ring-Opening of Epoxy by Utilizing Sulfenate Anions: An Efficient Access to β -Hydroxy Sulfoxides

○Jian Zhang¹, Vipul Vithal Betkekar¹, Keisuke Suzuki², Ken Ohmori¹ (1. Department of Chemistry, School of Science, Tokyo Institute of Technology., 2. Institute of Innovative Research, Tokyo Institute of Technology.)

3:00 PM - 3:20 PM

[K5-1pm-07] Reductive Dimerization of Styrenes Enabled by Flow Microreactors

○Jiang Yiyuan¹, Yorimitsu Hideki¹ (1. Graduate School of Science, Kyoto University)

3:20 PM - 3:40 PM

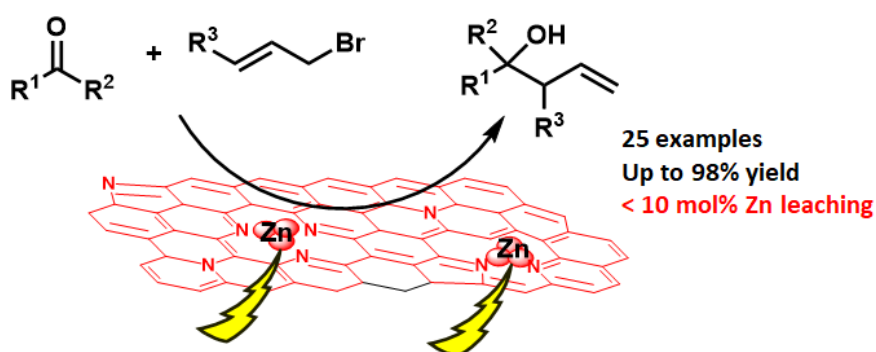
Nitrogen-Doped Carbon-Incarcerated Zinc Catalysts as Less Sacrificial Electrodes for Electrochemical Allylation Reactions

(School of Science, The Univ. of Tokyo) ORyusuke MASUDA, Tomohiro YASUKAWA, Yasuhiro YAMASHITA, Shū KOBAYASHI

Keywords: Heterogeneous Catalyst; Metal Nanoparticle Catalyst; Nitrogen-Doped Carbon; Electrochemical Reaction; Allylation Reaction

Metal nanoparticle catalysts have been of great interest because they can show unique activity and selectivity that differ from those obtained with bulk metals and metal complexes. The use of nitrogen-doped carbon (NDC) as a support would overcome many of limitations of metal nanoparticle catalysis for organic synthesis such as metal leaching because of strong interactions between nitrogen dopants and metals.¹⁾ However, electrochemical organic transformation, especially C–C bond-formation reactions, using electrodes prepared from NDC-supported metal catalysts remain challenging. These reactions are known to be clean and powerful redox processes that use electrons as traceless reagents. Indeed, bulk base metals such as zinc or iron are often consumed, and repeated use of such electrodes is still difficult. Recently, electrochemical allylation of carbonyl compounds in water using a zinc electrode has been developed with a catalytic amount of zinc consumed.²⁾ Nevertheless, a large amount (ca. 25 mol%) of zinc still leached out and an excess amount of zinc was used in terms of substrate amount. Moreover, the system required a divided cell and substrate scope was limited.

We have developed electrochemical allylation reactions of carbonyl compounds using cathodes prepared from NDC-incarcerated zinc catalysts. A range of aldehydes and ketones afforded the desired allylic alcohols in high yields with <10 mol% zinc leaching. NDC-stabilized zinc nanoparticle species showed advantages in terms of scope for heteroaromatic substrates compared with bulk zinc electrodes and enabled to use an undivided cell. Heterogeneous nature of active species was suggested by the hot filtration test.



✓ low equivalent of Zn ✓ reuse of electrode ✓ heterogeneous nature

1) M. Beller, *et al. Angew. Chem. Int. Ed.* **2016**, 55, 12582. 2) J. M. Huang, *et al. Chem. Commun.* **2010**, 46, 2286.

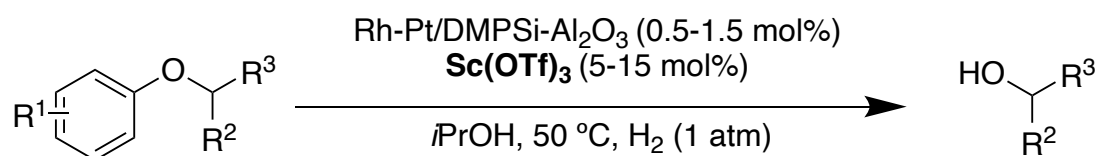
Development of Reductive Cleavage of Aryl Ethers Using Cooperative Catalytic Systems of Heterogeneous Metal Nanoparticles and Lewis Acids

(School of Science, The Univ. of Tokyo) ○ Hiroyuki MIYAMURA, Shū KOBAYASHI

Keywords: Heterogeneous Catalyst; Metal Nanoparticle; Lewis Acid; Cooperative Catalysis; Ether Cleavage

We have developed Rh-Pt bimetallic nanoparticles immobilized on a composite support of polydimethylsilane and alumina (Rh-Pt/DMPSi-Al₂O₃) as highly active catalysts for arene hydrogenation.¹⁾ It was also found that a significant rate acceleration occurred by cooperative catalytic systems of Rh-Pt/DMPSi-Al₂O₃ and Lewis acids compared to the case without use of Lewis acids, and that sterically hindered substrates could be hydrogenated under mild conditions.²⁾

In this study, we found that aryl alkyl ethers gave the corresponding aliphatic alcohols under reductive conditions using the cooperative catalytic systems. The reaction proceeded under very mild conditions; 50 °C and atmospheric hydrogen. Interestingly, aryl alkyl ethers containing bulkier aryl groups gave high selectivity toward reductive cleavage. Wide scope of alkyl groups in the ether was demonstrated under the optimized reaction conditions. We also investigated mechanistic studies and obtained insight about intermediates during the reductive cleavage reactions. To the best of our knowledge, this is unprecedented general reductive cleavage of aryl alkyl ethers to afford the corresponding aliphatic alcohols in high yields. We opened new methods to use aryl ethers as robust protecting groups, which can be deprotected catalytically under very mild conditions.



1) Miyamura, H. Kobayashi, S. *et al. J. Am. Chem. Soc.* **2018**, *140*, 11325.

2) Miyamura, H. Kobayashi, S. *submitted*.

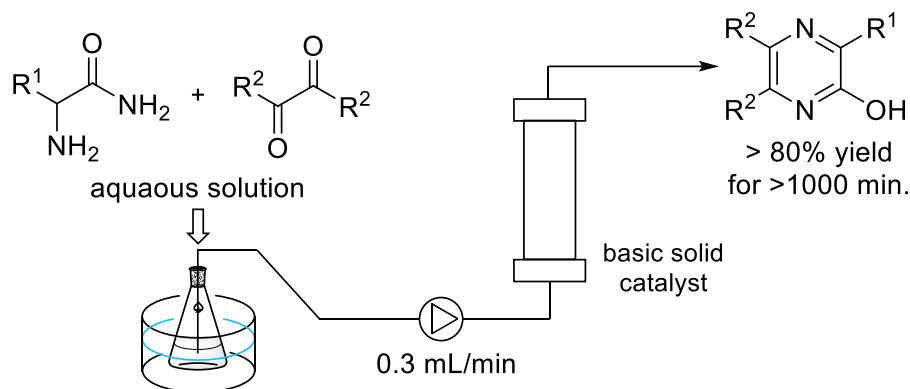
Development of Solid Base Catalysts for Hydroxypyrazine Synthesis in Water

(School of Science, The Univ. of Tokyo) OTomoya HISADA, Taku KITANOSONO,*
Yasuhiro YAMASHITA, Shū KOBAYASHI*

Keywords: Reaction in Water; Hydroxypyrazine; Flow Synthesis; A-type Zeolite; Basic Magnesium Salt

Hydroxypyrazine is an important structure in pharmaceuticals, and there is a need to establish an efficient method for the synthesis. Conventional synthetic methods require a large amount of phosphate buffer solution and an excessive amount of strong base, as well as a large amount of acid for quenching, which possess safety and waste problems.¹ The use of solid base catalysts can solve these problems, but there are few reports of solid base catalysts that can be used in water. On the other hand, our laboratory reported a heterocyclic formation reaction in water using a solid catalyst as environmentally friendly synthesis.² Here, we develop a solid base catalyst that can be used for hydroxypyrazine cyclization in water.

A-type zeolite and basic magnesium salts were found to catalyze the cyclization reaction of α -amino acid amides with glyoxal in water. This method can be applied to continuous-flow synthesis without use of any organic solvent. When a mixture of 2-aminomalonamide and glyoxal was pumped through a column packed with A-type zeolite, 3-hydroxypyrazinecarboxamide, a precursor of favipiravir (an antiviral drug), was obtained in good yields.³ Basic magnesium salts showed higher catalytic activity, catalyzing the cyclization reaction even at 5 mol% of loading under batch conditions. In addition, life time of basic magnesium salts was longer than that of A-type zeolites.



1) 富山化学工業株式会社. 特許第5739618号. 2015-05-01.

2) Kitanosono, T.; Cho, S.; Kobayashi, S. *Tetrahedron*. **2018**, 74, 7237.

3) Hisada, T.; Kitanosono, T.; Yamashita, Y.; Kobayashi, S. *Bull. Chem. Soc. Jpn.* **2021**, 94, 1757.

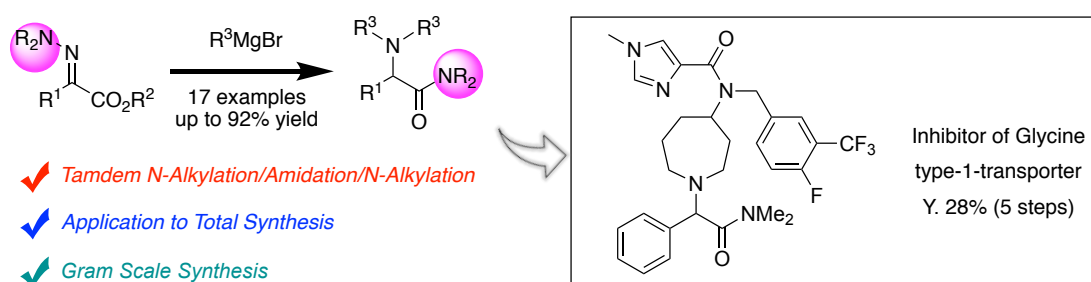
Highly Selective Synthesis of α -Aminoamide Utilizing an Umpolung Reaction and Characteristics of α -Hydrazonoester

(Graduate School of Engineering, Mie University) ○Isao Mizota, Yusuke Nakamura, Shunsuke Mizutani, Nanami Mizukoshi, Shunya Terasawa, Makoto Shimizu

Keywords: α -Hydrazonoester; Umpolung Reaction; *N*-Alkylation; Tandem Reaction; Amidation

Hydrazones are versatile synthetic intermediates in organic chemistry such as Wolff-Kishner reduction, Shapiro reaction, and Bamford-Stevens reaction. Since their C=N moieties behave as electrophiles of moderate reactivity with an availability of their chiral versions, e. g., SAMP and RAMP hydrazones, they have received considerable attention as stable and versatile imine derivatives and the development of various synthetic methodologies has been desired. During our research into α -iminoester,¹ we have been interested in the reactivity of oxime derivatives as stable and useful substrates for the S_N2 type reaction at the nitrogen atom and for the subsequent umpolung reactions to introduce plural substituents at the nitrogen.²

During the exploration into the S_N2 type reaction at the nitrogen atom, we focused on a relatively strong N-N bond of the hydrazone moiety and found that once the N-N bond was cleaved, the cleaved nitrogen moiety behaved as a good nucleophile for the ester part to convert it to an amide. Herein, we would like to report an intriguing α -aminoamide synthesis using an S_N2 type reaction at the nitrogen atom followed by the subsequent amide formation and the second *N*-alkylation. Further extension of the present reaction to the synthesis of an inhibitor of the glycine type-1-transporter was also successfully carried out in an efficient manner.³



- 1) I. Mizota, M. Shimizu, *Chem. Rev.* **2016**, 16, 688.
- 2) I. Mizota, M. Maeda, M. Shimizu, *Tetrahedron* **2015**, 71, 5793.
- 3) I. Mizota, Y. Nakamura, S. Mizutani, N. Mizukoshi, S. Terasawa, M. Shimizu, *Org. Lett.* **2021**, 23, 4168.

Arenicolide 類の骨格合成

(工学院大学¹)○平尾 玲生¹、川野 嘉矩¹、安井 英子¹、南雲 紳史¹

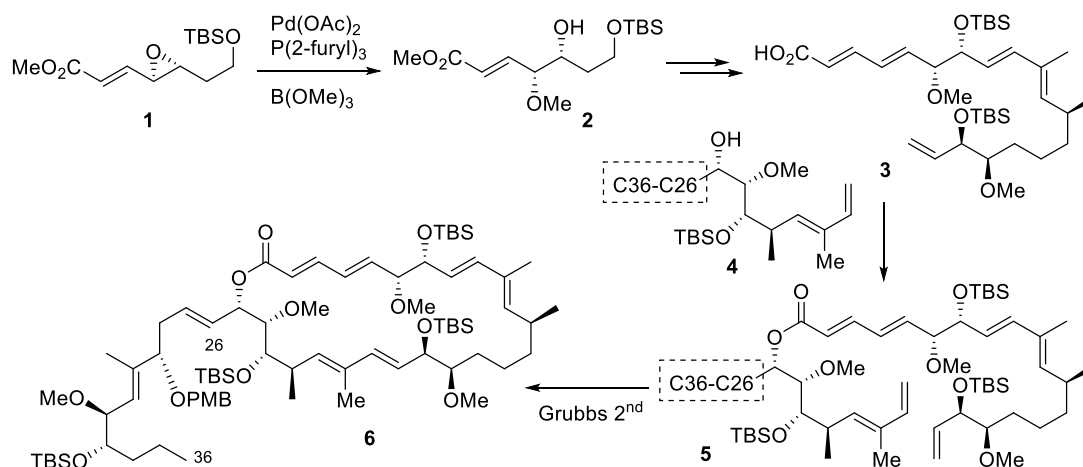
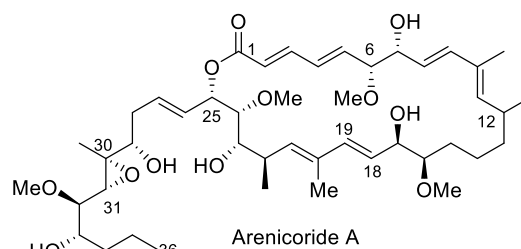
Synthetic study of arenicolides

-construction of complete carbon framework- (¹Kogakuin University) ○Reo Hirao¹, Yoshinori Kawano¹, Eiko Yasui¹, Shinji Nagumo¹

Arenicolide A is a 26-membered macrolide isolated from a marine actinomycete, *Salinispora arenicola* and exhibits inhibitory activity against colon cancer cells. It has four consecutively arranged hydroxyl and methoxy groups and three conjugated dienes. The total synthesis has been not reported so far and the configuration of the methyl group at the C12 has been not determined. We report here the synthesis of the precursor **6** having a complete carbon framework based on an alkoxy substitution of epoxy unsaturated ester **1** and ring closing metathesis.

Keywords : Macrolide; Ring Closing Metathesis; Marine Actinomycete

Arenicolide A は海洋放線菌 *Salinispora arenicola* の大規模発酵から単離、構造決定されたマクロライドであり、結腸ガン細胞に対する阻害作用を有する。その構造中には水酸基とメトキシ基が隣接したユニットが4か所、共役ジエンが3か所ある。これまでに全合成の報告はなく、C12位のメチル基の立体配置は未決定である。今回、エポキシ不飽和エステルアルコキシ置換反応と閉環メタセシス反応を基軸として Arenicolide A の完全炭素骨格を構築した。パラジウム触媒存在下、**1**に B(OMe)₃を作用させ **2**を得た。ここから炭素鎖伸長とセグメント連結を行うことで **3**を合成した。別に合成した **4**と縮合して **5**に導き、最後に第二世代 Grubbs 触媒による閉環メタセシスで **6**を合成した。

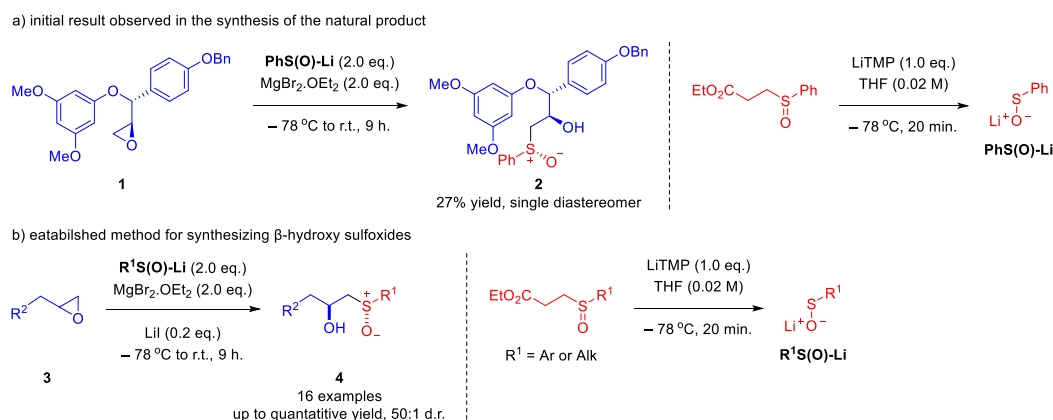


Chemo-, Regio- and Diastereoselective Ring-Opening of Epoxide by Utilizing Sulfenate Anions: An Efficient Access to β -Hydroxy Sulfoxides

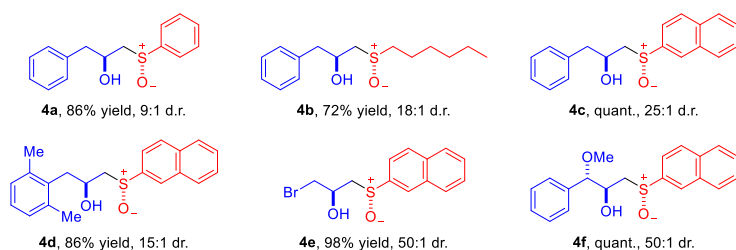
(¹Department of Chemistry, Tokyo Institute of Technology, ²Institute of Innovative Research, Tokyo Institute of Technology) ○Jian Zhang,¹ Vipul, V. Betkekar,¹ Keisuke Suzuki,² Ken Ohmori¹

Keywords: β -Hydroxy Sulfoxides, Epoxide, Sulfenate Anions, MgBr_2 .

During a course of our synthetic study on a natural product, we found that epoxide **1** allows the nucleophilic attack of sulfenate species to generate β -hydroxy sulfoxide **2** with *anti*-stereochemistry, albeit in 27% yield (Scheme 1a). Inspired by this promising result, demonstrating stereoselective transformation, we continued our efforts to develop new synthetic method and strategy. We first applied this reaction conditions to simple epoxide **3**, giving the corresponding β -hydroxy sulfoxide in 77% yield with 7.7:1 d.r. (Scheme 1b). After screening reaction conditions including base, Lewis acid, additive, temperature and solvents, the optimized one could be settled. We also found that addition of catalytic LiI promotes the reaction. We next examined a scope and limitation of this reaction, proving its broad applicability (Scheme 2). A computational study gave us important insights into the reaction mechanism and also its stereoselectivity. Details will be discussed in this presentation.



Scheme 1. initial result observed in the synthesis of the natural product and established methodology



Scheme 2. Substrate Scope

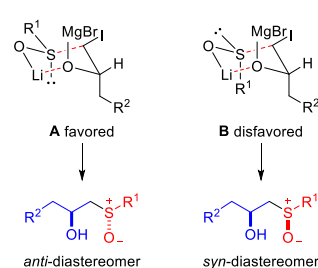


Fig 1. proposed intermediate

Reductive Dimerization of Styrenes Enabled by Flow Microreactors

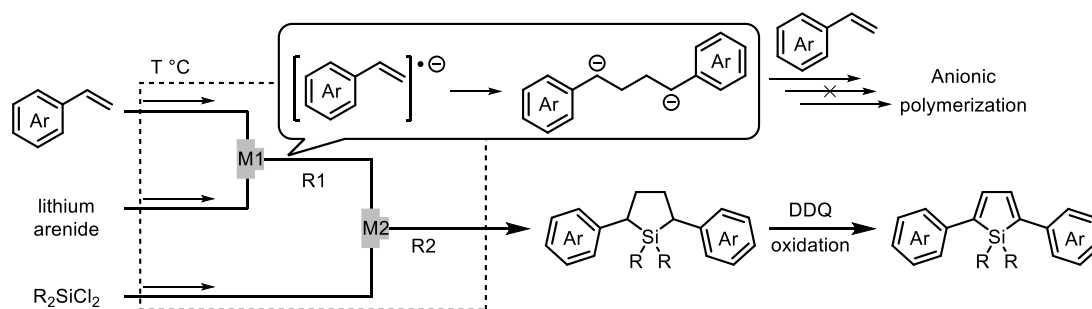
(Graduate School of Science, Kyoto University) ○Yiyuan Jiang, Hideki Yorimitsu

Keywords: Microreactor; Reductive Dimerization; Dianion; Silole

Although 1,4-dianions are useful precursors to cyclic skeletons, the generation of the dianions is limited to classical methods, such as reduction and halogen-lithium exchange of 1,4-dihaloalkanes. The dimerization of styrene by one-electron reduction can also generate dianions, but the highly reactive dianions easily undergo anionic polymerization.¹

Herein, we report the reaction of styrenes with lithium arenides in a flow microreactor leads to the instantaneous generation of a styryl radical anion and subsequent dimerization yields 1,4-diaryl-1,4-dianions. The efficiency was greatly improved by increasing the flow rate and decreasing the inner diameter of the mixer. Therefore, fast mixing is considered to be essential in this reaction. The efficiency and selectivity of this reductive dimerization was proved to be low in batch-type reactors.

This method is capable of generating the dianions of various styrenes. Furthermore, the generated dianions can react with various electrophiles. Notably, 3,4-unsubstituted 2,5-diarylsiloles can be conveniently synthesized by the reaction of the generated dianion species with dialkyldichlorosilanes followed by oxidation with DDQ. Although siloles have attracted a great deal of attention as a new class of functional materials due to their high electron-accepting and fluorescent properties, the synthetic methods for 3,4-unsubstituted 2,5-diarylsiloles are limited.²



1) M. Szwarc, M. Levy, R. Milkovich, *J. Am. Chem. Soc.* **1956**, 78, 2656.

2) S. Santra, *ChemistrySelect* **2020**, 5, 9034.

[B104-1pm] 16. Natural Products Chemistry, Chemical Biology

Chair: Yousuke Takaoka, Yuichiro Hori

Wed. Mar 23, 2022 1:00 PM - 3:40 PM B104 (Online Meeting)

[B104-1pm-01] A therapeutic approach for cancers with special genetic mutations using in vivo synthetic chemistry○Tsung-Che Chang¹, Igor Nasibullin¹, Katsunori Tanaka^{1,2,3} (1. RIKEN, 2. Tokyo Institute of Technology, 3. Kazan Federal University)

1:00 PM - 1:20 PM

[B104-1pm-02] Fungal toxin fusicoccin enhances plant growth by promoting stomatal opening○Hironaru Kiriya¹, Satoru Kinoshita², Yuki Hayashi², Toshinori Kinoshita², Shigemitsu Kasuga¹, Hiroki Irieda¹, Junko Ohkanda¹ (1. Shinshu Univ., 2. Nagoya Univ.)

1:20 PM - 1:40 PM

[B104-1pm-03] Analyses and regulation of protein-protein interactions caused by jasmonate-related transcription factors○Yousuke Takaoka¹, Suzuki Kaho¹, Ueda Minoru^{1,2} (1. Tohoku Univ, Grad. Sci., 2. Tohoku Univ, Grad. Life Sci.)

1:40 PM - 2:00 PM

[B104-1pm-04] Development of a Fulgimide-Fluorophore Dyad Molecule for Fluorescence Photoswitching in Cellular Imaging○Kenji Torii¹, Yuichiro Hori^{1,2}, Kazuya Kikuchi^{1,2} (1. Graduate School of Engineering, Osaka University, 2. Immunology Frontier Research Center, Osaka University)

2:00 PM - 2:20 PM

[B104-1pm-05] Display-based discovery of N-methylated cyclic peptide inhibitors of prokaryotic iPGMs○Renier Herman Pieter van Neer¹, Patricia Dranchak², Mahesh Aitha², Laurence Lamy², Hiroyuki Kimura¹, Scott Lovell³, Takayuki Katoh¹, James Inglese², Hiroaki Suga¹ (1. Graduate school of Science, Department of Chemistry, University of Tokyo, 2. National Center for Advancing Translational Sciences, National Institutes of Health, 3. Protein Structure Laboratory, Structural Biology Center, University of Kansas)

2:20 PM - 2:40 PM

[B104-1pm-06] Development of activatable fluorescence probe for carboxypeptidase activity to visualize cancer○Minoru Kawatani¹, Mako Kamiya¹, Hirohisa Iwaki¹, Kyoko Yamamoto¹, Yasuteru Urano^{1,2} (1. Grad. Sch. Med., The Univ. of Tokyo, 2. Grad. Sch. Pharm. Sci., The Univ. of Tokyo)

2:40 PM - 3:00 PM

[B104-1pm-07] Site-selective Cleavage of Protein by Cysteine Formylation○Naoki Zenmyo¹, Akihiro Yasuda¹, Yuya Matsumoto², Shohei Uchinomiya¹, Naoya Shindo¹, Kaori Tabata¹, Akio Ojida¹ (1. Grad. Sch. Phar. Sci., The Univ. of Kyushu, 2. The Univ. of Kyushu, Phar. Sci.)

3:00 PM - 3:20 PM

[B104-1pm-08] Exploration of Biomolecularly Transparent IR Region for Structural Identification Using VCD

○Zarif Zubir¹, Nurul Fajry Maulida, Tohru Taniguchi², Kenji Monde² (1. Hokkaido U., Graduate School of Life Science, 2. Hokkaido U., Faculty of Advanced Life Science)

3:20 PM - 3:40 PM

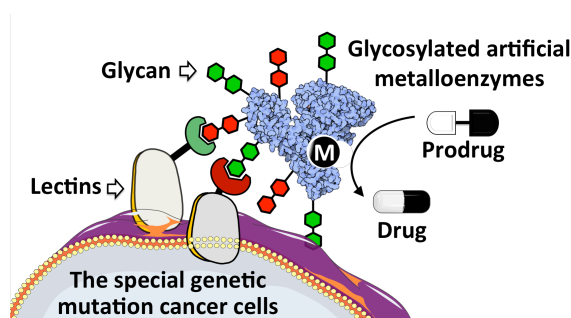
A therapeutic approach for cancers with special genetic mutations using in vivo synthetic chemistry

(¹Biofunctional Synthetic Chemistry Laboratory, Cluster for Pioneering Research, RIKEN, ²School of Materials and Chemical Technology, Tokyo Institute of Technology, ³Biofunctional Chemistry Laboratory, Alexander Butlerov Institute of Chemistry, Kazan Federal University) ○Tsung-Che Chang,¹ Igor Nasibullin,¹ Katsunori Tanaka^{1,2,3}

Keywords: Therapeutic in vivo synthetic chemistry; Glycotargeting; Artificial metalloenzymes; Genetic mutant cancers; Prodrug

A special gene mutation is present in approximately 25% of tumors, making it one of the most common gene mutations linked to cancer. There are currently no effective targeting methods or treatments available for patients with these special genetically modified cancers. One of the major components that drives cell-to-cell interactions is glycan recognition with lectins. Since most types of malignant cells compared to healthy cells have altered their glycan patterns, this represents a potential targeting mechanism for targeting the special genetic mutant cancers.

We have found several kinds of glycoproteins that enable effective targeting of the special genetic mutant cancer cells. Through adapting the targeting glycoproteins to become the glycosylated artificial metalloenzymes (GARMs)¹⁻⁵, the prodrug therapy activated by the GARMs exerted excellent anticancer activity in cell-based assays. Furthermore, in vivo drug synthesis via the GARMs was found to induce a reduction in implanted special genetic mutant tumor growth in mice.



1) S. Eda, I. Nasibullin, K. Vong, N. Kudo, M. Yoshida, A. Kurbanalieva, K. Tanaka, *Nat. Catal.* **2019**, 2, 780. 2) K. Vong, S. Eda, Y. Kadota, I. Nasibullin, T. Wakatake, S. Yokoshima, K. Shirasu, K. Tanaka, *Nat. Commun.* **2019**, 10, 5746. 3) T.-C. Chang, K. Vong, T. Yamamoto, K. Tanaka, *Angew. Chem. Int. Ed.* **2021**, 60, 12446. 4) K. Vong, T. Tahara, S. Urano, I. Nasibullin, K. Tsubokura, Y. Nakao, A. Kurbanalieva, H. Onoe, Y. Watanabe, K. Tanaka, *Sci. Adv.* **2021**, 7, eabg4038. 5) P. Ahmadi, K. Muguruma, T.-C. Chang, S. Tamura, K. Tsubokura, Y. Egawa, T. Suzuki, N. Dohmae, Y. Nakao, K. Tanaka, *Chem. Sci.* **2021**, 12, 12266.

植物病原菌二次代謝産物フシコキシンの気孔開口による成長促進効果の検証

(信州大農¹・名大院理²) ○桐山 寛生¹、木下 悟²、林 優紀²、木下 俊則²、春日 重光¹、入枝 泰樹¹、大神田 淳子¹

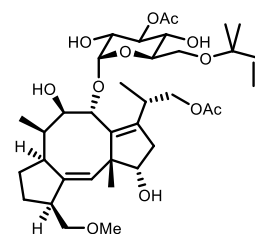
Fungal toxin fusicoccin enhances plant growth by promoting stomatal opening (¹*Academic Assembly, Institute of Agriculture, Shinshu Univ.*, ²*Graduate School of Science, Nagoya Univ.*)
○Hironaru Kiriya¹, Satoru Kinoshita², Yuki Hayashi², Toshinori Kinoshita², Shigemitsu Kasuga¹, Hiroki Irieda¹, Junko Ohkanda¹

Stomata are the pores in the plant epidermis surrounded by a pair of guard cells and are responsible for gas exchange. Through the stomata, plants optimize the concentration of carbon dioxide for photosynthesis in the leaf and minimize water loss. In 2014, Kinoshita et al. reported that overexpression of a plasma membrane (PM) H⁺-ATPase in *Arabidopsis* guard cells enhances the stomatal opening, carbon dioxide uptake, and the rate of photosynthesis, promoting plant growth.[1] These results indicate that control of stomatal opening greatly increases plant growth efficiency. In this study, we demonstrated that fusicoccin (FC), a fungal phytotoxin that stabilizes protein-protein interaction between the C-terminal phosphorylation region of PM H⁺-ATPase and 14-3-3, promotes stomatal opening, enhances carbon dioxide uptake and photosynthesis activity, and thereby promotes plant growth under the condition of sufficient supply of water and light. The experimental details will be discussed.

Keywords : fusicoccin; stoma; plant growth regulator; PM H⁺-ATPase; 14-3-3

気孔は、植物の表皮に存在し、1対の孔辺細胞とその周辺の細胞から構成され、ガス交換を担う。植物は気孔を通じ、光合成に必要な二酸化炭素の葉内濃度を最適化し、蒸散による水分損失を最小化している。2014年木下らにより、孔辺細胞に細胞膜(PM) H⁺-ATPaseを過剰発現した形質転換シロイヌナズナでは気孔開度、CO₂吸収量と光合成速度が増加し、植物がより成長すると報告された[1]。このことは、気孔開度の制御が植物の成長効率を大きく増加させることを示している。本研究では、PM H⁺-ATPaseのC末端リン酸化領域と14-3-3とのタンパク質間相互作用(PPI)を安定化して気孔開口を促進し、最終的に植物を枯死させる植物毒として知られる植物病原菌二次代謝産物フシコシン(FC)に着目し、遺伝子組換えに頼らない有機分子による気孔開口制御を目指した。詳細な検討の結果、光と水分が十分に供給された適切な環境下において、天然型FC-AはPM H⁺-ATPaseのC末端リン酸化領域と14-3-3とのPPIを安定化し気孔開度を増加させ、二酸化炭素吸収と光合成活性を亢進することを明らかにした。さらに、FC-Aの継続的な投与によりシロイヌナズナの植物成長が最大30%促進することを明らかにし、従来の通説と相反する活性を見出した。FCの植物成長促進効果は栽培植物であるコマツナやセロリでも確認できた。真菌のバイオ生産により大量取得可能なFCの農業利用により、食糧生産効率の改善やCO₂削減による低炭素社会の実現が可能になると期待される。

[1] Y. Wang et al., *Proc. Natl. Acad. Sci.* **2014**, *111*, 533.



Fusicoccin-A

ジャスモン酸関連転写因子が引き起こすタンパク質間相互作用の解析と制御

(東北大院理¹・東北大院生命科学²) ○高岡 洋輔¹・鈴木 華穂¹・上田 実^{1,2}
Analyses and regulation of protein-protein interactions caused by jasmonate-related transcription factors (¹*Graduate School of Science, Tohoku University*, ²*Graduate School of Life Sciences, Tohoku University*) ○Yousuke Takaoka,¹ Kaho Suzuki,¹ Minoru Ueda^{1,2}

A network of various protein-protein interactions (PPI) is involved in the repression and activation of (+)-7-*iso*-jasmonoyl-L-isoleucine (JA-Ile) signaling, a plant hormone which regulates plant defense responses as well as plant growth. In the absence of JA-Ile, transcriptional repressor JAZ represses transcription factors including a master regulator MYC. In contrast, when JA-Ile is accumulated, JAZ is degraded and then derepressed MYC able to interact with the transcriptional mediator MED25, resulting in upregulation of the JA-responsive gene expression. We herein performed a comprehensive analysis of the PPI between MYC-JAZ or MYC-MED25 *in vitro*. These results further illuminate the transcriptional machinery responsible for JA signaling.

Keywords : Plant hormone; Jasmonate; Protein-protein interaction; Transcription factor

植物防御や生長などを制御する植物ホルモン、ジャスモン酸イソロイシン (JA-Ile) に関連する主要転写因子 MYC は、定常状態では JA-Ile 受容体の一つであるリプレッサー JAZ によって機能が抑制されているが、活性化の際は転写メディエーター MED25 に結合して転写複合体を形成し、様々な遺伝子発現を誘導する (Fig. 1)。ただし、これらジャスモン酸シグナル伝達機構に関連するタンパク質間相互作用 (PPI) には分子レベルでは不明な点が残されている。本研究では、MYC 活性化において重要な MYC3 と MED25 との PPI を詳細に解析することで MED25 の MYC3 相互作用ドメインを同定し、MYC-JAZ、MYC-MED25 間の定量的な親和性を得ることなどに成功した¹⁾。これらの知見は、ジャスモン酸シグナル伝達機構の理解と、その機能制御等につながる事が期待される。

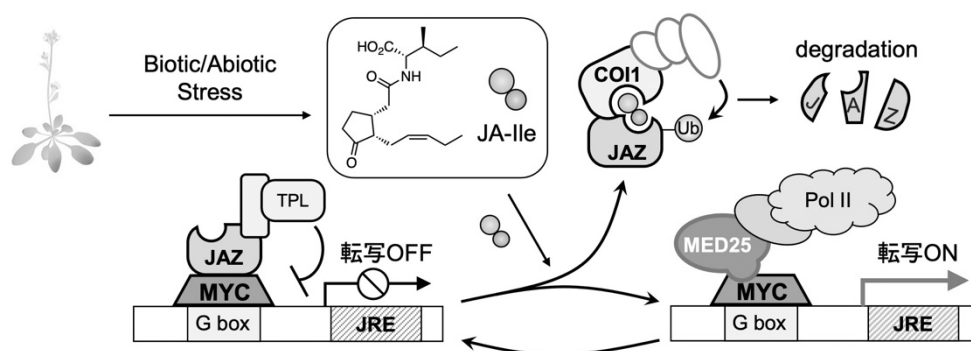


Figure 1. ジャスモン酸シグナル伝達の概要図 (JRE: ジャスモン酸応答性遺伝子).
1) Y. Takaoka, M. Ueda, *et al. J. Biol. Chem.*, **298**, 101504 (2022).

Development of a Fulgimide-Fluorophore Dyad Molecule for Fluorescence Photoswitching in Cellular Imaging

(¹Graduate School of Engineering, Osaka University, ²Immunology Frontier Research Center, Osaka University) ○Kenji Torii,¹ Yuichiro Hori,^{1,2} Kazuya Kikuchi^{1,2}

Keywords: FRET; photochromism; fulgimide; bioconjugation

Photoswitchable fluorescent molecules (PSFMs) whose fluorescence intensities are reversibly changed by light irradiation are biologically important tools for intracellular imaging. Reversibly photoswitchable fluorescent proteins¹ are widely applied as PSFMs to pulse-chase analysis and super-resolution imaging; however, these proteins suffer from photobleaching. Although, in recent years, synthetic PSFMs² have been developed to improve photostability, live-cell imaging using these molecules still has been challenging.

Herein, we developed a PSFM, named FF-TMR, containing a photochromic compound, furylfulgimide (FF)³, and a photostable fluorophore, tetramethylrhodamine (TMR). FF undergoes quantitative photoisomerization between open- and closed-ring forms and is used as a fluorescence quencher based on FRET whose efficiency can be controlled by change in its absorption spectra (Figure 1). As expected, the fluorescence intensity of FF-TMR is changed upon light irradiation. Moreover, the sophisticated molecular design of FF-TMR enables the preparation of the FF-TMR bioconjugates exhibiting reversible and fast fluorescence photoswitching in an aqueous solution. Supporting this result, in fixed cells, the fluorescence intensity of FF-TMR that labeled anti-tubulin antibody was repetitively modulated. In this conference, we will report on the detailed molecular design and photoswitching properties of FF-TMR and its bioconjugates.

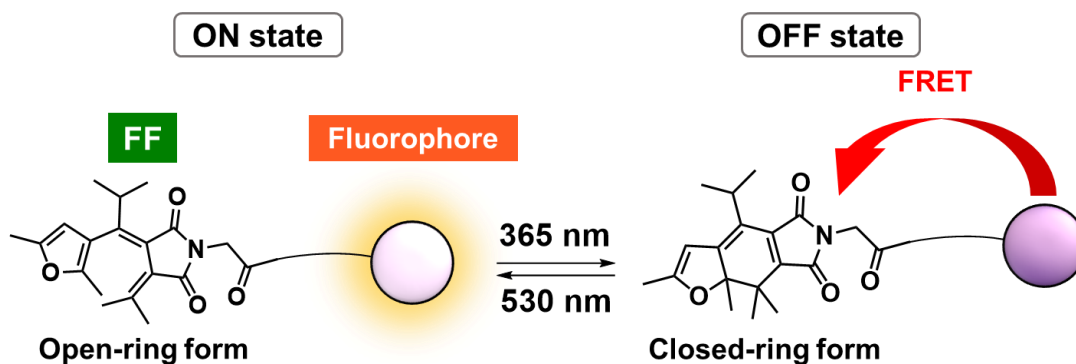


Figure 1. Fluorescence switching strategy of FF-TMR.

- 1) a) T. Grotjohann, *et al. Nature* **2011**, 478, 204. b) S. Habuchi, *et al. PNAS* **2005**, 102, 9511. 2) a) K. Uno, *et al. J. Am. Chem. Soc.* **2019**, 141, 16471. b) K. Torii, *et al. Bull. Chem. Soc. Jpn* **2020**, 93, 821. 3) Y. Yokoyama, *et al. Chem. Rev.* **2000**, 100, 1717.

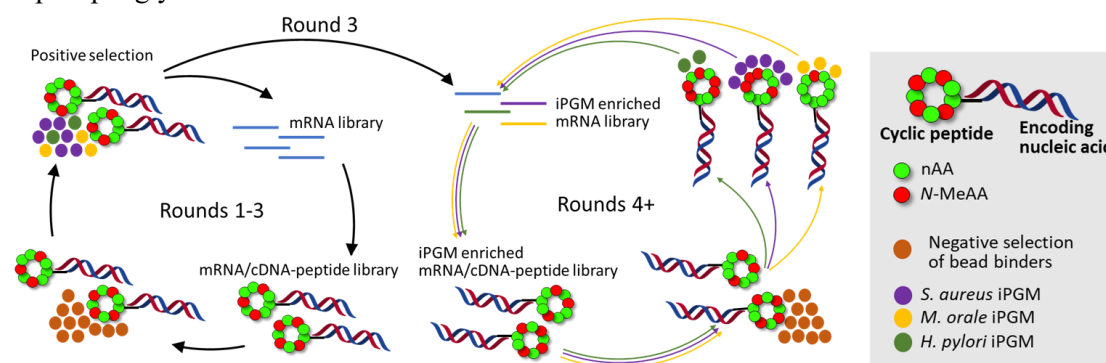
Affinity selection discovery of *N*-methylated cyclic peptide inhibitors of prokaryotic glycolytic mutases

(¹Graduate School of Science, University of Tokyo, ²National Center for Advancing Translational Sciences, National Institutes of Health, ³Structural Biology Center, University of Kansas ⁴New York Structural Biology Center, Brookhaven National Laboratory ⁵National Human Genome Research Institute, National Institutes of Health)

○R.H.P. van Neer¹, P.K. Dranchak², L. Liu³, M. Aitha², B. Queme², K. P. Battaile⁴, H. Kimura¹, T. Katoh¹, S. Lovell³, J. Inglese^{2,5*} and H. Suga^{1*}

Keywords: Peptides, Affinity selection, Isoenzymes, Antimicrobials, Crystallography.

N-methylated amino acids (*N*-MeAA) are privileged residues in natural bioactive peptides critical to bioactivity and metabolic stability¹. However, *de novo* discovery of these peptides through utilizing affinity selection methodologies is limited by low EF-Tu affinity of the *N*-methyl-aminoacyl-tRNA, causing poor ribosomal incorporation of *N*-methylated amino acids into the nascent peptide chain². By modifying the tRNA's T-stem region to compensate and tune the EF-Tu affinity³, we conducted a mRNA display-based screen using a macrocyclic peptide (MCP) library that contains six different *N*-MeAAs. Utilizing a “pool-and-split” enrichment strategy (see figure) we identified *N*-methylated MCPs against three orthologues of prokaryotic, metal ion-dependent phosphoglycerate mutases⁴. The identified MCPs reached upwards to 57% *N*-methylation in the random region with up to three consecutively incorporated *N*-MeAAs, rivalling natural products. Potent nanomolar inhibitors strongly mediated by *N*-methylation and ranging in ortholog-selectivity were identified. Co-crystal structures reveal both an active site metal ion-coordinating cysteine lariat-shaped MCP, architecturally similar to ipglycermide Ce-2⁵⁻⁶, however, functionally dependent on two trans *N*-Me backbone amides, as well as a metal ion-independent inhibitor chemotype that acts as a 3-phosphoglycerate mimetic.



- 1) Chatterjee, J. et al., *Angew. Chem. Int. Ed.* **2012**, 52, 1, 254-269.
- 2) Zhang, B. et. al., *J. Am. Chem. Soc.*, **2007**, 129, 37, 11316–11317.
- 3) Iwane, Y. et. al., *Nucleic Acids Res.* **2021**, 49, 19, 10807–10817.
- 4) Roychowdhury, A. et al., *FEBS J.* **2015**, 282, 1097-1110.
- 5) Yu, H. et al., *Nat. Commun.* **2017**, 8, 14932.
- 6) Wiedmann, M. et al., *J. Biol. Chem.* **2021**, 296, 100628.

Development of activatable fluorescence probe for carboxypeptidase activity to visualize cancer

(¹Graduate School of Medicine, The University of Tokyo, ²Graduate School of Pharmaceutical Science, The University of Tokyo) ○Minoru Kawatani,¹ Mako Kamiya,¹ Hirohisa Iwaki,¹ Kyoko Yamamoto,¹ Yasuteru Urano^{1,2}

Keywords: Carboxypeptidase; Fluorescence probe; Cancer; Fluorescence imaging; Photoinduced electron transfer

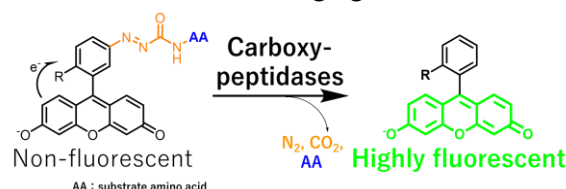
[Introduction] Carboxypeptidases (CPs) are enzymes that are up-regulated in some cancer cells, thus fluorescence detection of a specific CP activity allows visualization of cancer. However, only a few activatable fluorescent probes targeting CPs activities have been developed, as it is difficult to translate the chemical reaction from amide to carboxylate by CPs into the change in fluorescence intensity. In this study, we aimed to develop new activatable fluorescent probes that can detect CP activities with high sensitivity in live cells.

[Molecular design] We designed and synthesized molecules in which an azoformyl (AF) group and a substrate amino acid were introduced into the benzene moiety of fluorescein scaffold. The probe is weakly fluorescent before reaction with CP due to photoinduced electron transfer from fluorophore to the benzene moiety, but is converted to strongly fluorescent scaffold fluorophore upon reaction with CP.

[PSMA probe]¹⁾ We developed an activatable fluorescent probe, 5GluAF-2MeTG, which targets prostate cancer-specific membrane antigen (PSMA), a CP that is upregulated in prostate cancer, by introducing glutamate (Glu) as a substrate amino acid into membrane-permeable TokyoGreen (TG) scaffold. 5GluAF-2MeTG successfully visualized the tumor sites in resected specimens from prostate cancer patients, including milli-meter size tumors that are difficult to detect with the naked eye.

[CPM probe]²⁾ By incorporating basic amino acid (arginine; Arg) as a substrate amino acid into fluorescein diacetate (FDA) scaffold, we developed a fluorescent probe 5ArgAF-FDA with improved intracellular retention that targets Carboxypeptidase M (CPM), which is upregulated in breast cancer. By using 5ArgAF-FDA, we succeeded in visualizing the different CPM activity of different cell lines at the single cell level.

[Conclusion] We established a molecular design strategy of activatable fluorescent probes that can detect CPs with high sensitivity and succeeded in developing activatable fluorescent probes that are useful for cancer imaging.



1) M. Kawatani, *J. Am. Chem. Soc.* **2019**, *141*, 10409. 2) H. Iwaki, *Anal. Chem.* **2021**, *93*, 3470.

S-ホルミル化を利用した標的タンパク質の化学選択的切断法の開発

(九大院薬¹・九大薬²) ○善明 直輝¹・安田 斉弘¹・松本 侑也²・内之宮 祥平¹・進藤 直哉¹・田畑 香織¹・王子田 彰夫¹

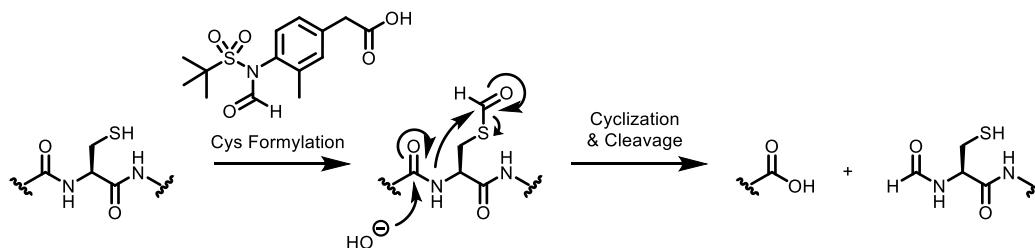
Site-selective Protein Cleavage by Cysteine Formylation (¹*Graduate School of Pharmaceutical Science, Kyushu University*, ²*Pharmaceutical Science, Kyushu University*)

○Naoki Zenmyo¹, Akihiro Yasuda¹, Yuya Matsumoto², Shohei Uchinomiya¹, Naoya Shindo¹, Kaori Tabata¹, Akio Ojida¹

In functional analysis of proteins, chemical modification with small molecule is useful for function analysis and regulation of protein of interest (POI). Although a number of selective protein labeling method have been reported, chemical protein cleavage method has been poorly developed. In this presentation, we report a novel chemical method enabling functional regulation of protein by cleavage reaction. We found that formylation of Cysteine residue induces cleavage of amide bond of peptide backbone. We evaluated the sequence selectivity and found that Asp-Cys and Asn-Cys sequence were cleaved in high efficiency. We also achieved sequence selective cleavage of Proteins by using formylation affinity probe.

Keywords : Protein Cleavage, Chemical Modification, Warhead, Cysteine Formylation

タンパク質を低分子により化学的に修飾する手法は、標的タンパク質の機能化・機能制御が可能であり、タンパク質研究において広く利用されている。一方で、タンパク質配列を化学的に切断することでその機能を制御する報告例はほとんどない。本研究では、タンパク質の切断を誘起可能な新しい化学的手法の探索を行い、システイン側鎖の S-ホルミル化によりタンパク質のアミド主鎖が切断される新しい知見を見出した。まずモデルペプチドを用いて配列選択性について検討を行い、Asp-Cys 配列および Asn-Cys 配列を有する基質で切断反応が効率的に進行することを明らかにした。さらに、S-ホルミル化分子の Cys 反応性のチューニングを行いタンパク質リガンドに導入することで、標的配列選択的なアフィニティー切断に成功したので報告を行う。

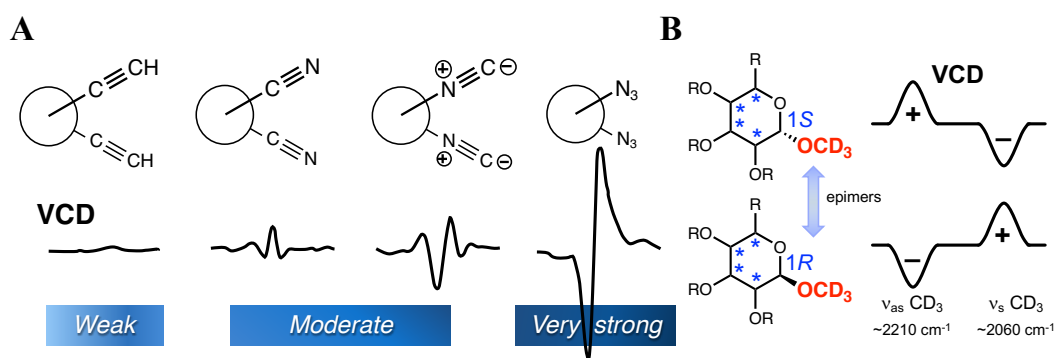


Exploration of Biomolecularly Transparent IR Region for Structural Identification Using VCD

(¹Graduate School of Life Science, Hokkaido University, ²Faculty of Advanced Life Science, Hokkaido University) ○ Mohamad Zarif Mohd Zubir,¹ Nurul Fajry Maulida,¹ Tohru Taniguchi,² Kenji Monde²

Keywords: Chirality, VCD Spectroscopy, Deuterium, Azide

The stereostructure of biomolecules significantly influences their roles in biological processes. Thus, a comprehensive knowledge of their structural properties is the key to fully understand and regulate their functions. However, stereostructure elucidation of biomolecules is rather challenging because of the limitation of conventional analytical methods. Vibrational circular dichroism (VCD) spectroscopy has proven to be a precise and powerful tool for molecular stereostructural characterization. First, we studied the applicability of nitrile, isonitrile, alkyne, and azido groups to identify suitable chromophores that exhibit VCD couplets in the 2300-1900 cm^{-1} region by using a chiral binaphthyl scaffold. Azido group is the most promising for extracting structural information from biomolecules because it showed the most simple and strong VCD signals whose pattern is readily predicted by harmonic DFT calculations (Figure A).¹ Second, we utilize the C-D stretching in this region to explore the practicality of CD_3 groups for obtaining the local chirality. A series of pyranosides was used as a model study. The epimeric pairs agreeably presented almost mirror-image VCD patterns in the 2300-1900 cm^{-1} region irrespective of other chiral centers (Figure B). The application of this concept was further demonstrated to other complex systems by studying the VCD spectra of the C-1 epimeric pairs of a disaccharide gentiobiose, 6-lauroylated surfactant, and 5-membered glucofuranosides.²



1) T. Taniguchi, M. Z. M. Zubir, N. Harada, K. Monde, *Phys. Chem. Chem. Phys.*, **2021**, 23, 27525.

2) M. Z. M. Zubir, N. F. Maulida, Y. Abe, Y. Nakamura, M. Abdelrasoul, T. Taniguchi, K. Monde, *Org. Biomol. Chem.*, **2022**, <https://doi.org/10.1039/D1OB02317A>.

[G201-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Tomonori Tamura, Kazutoshi Iijima

Wed. Mar 23, 2022 9:00 AM - 11:40 AM G201 (Online Meeting)

[G201-1am-01] A novel antidotal system for a fire gas poisoning using artificial hemoglobin model complexesQiyue Mao¹, Xuansu Zhao², Yasutaka Fukuda³, Akiko Kiriya⁴, Shigeru Negi⁴, Hideki Yoshioka², [○]Hiroaki Kitagishi¹ (1. Doshisha University, 2. Building Research Institute, 3. Better Living, 4. Doshisha Women's College of Liberal Arts)

9:00 AM - 9:20 AM

[G201-1am-02] Development of photo-responsive cell scaffold for control of cellular function[○]Hiroki Miyajima¹, Saeka Kato¹, Kazutoshi Iijima¹ (1. Yokohama National Univ.)

9:20 AM - 9:40 AM

[G201-1am-03] Controlling IEDDA Reaction with Macrocyclic Tetrazines[○]Ira Novianti¹, Toshiyuki Kowada¹, Shin Mizukami¹ (1. Tohoku University)

9:40 AM - 10:00 AM

[G201-1am-04] Development of Functional Anthracene-Based Multiblock Fluorophore for Visualization of Biological Environment[○]Junya Adachi¹, Kohei Sato¹, Kazushi Kinbara¹ (1. Tokyo Tech.)

10:00 AM - 10:20 AM

[G201-1am-05] Evaluation of the properties of a cyclic pyrrole–imidazole polyamide, which specifically binds to CAG/CTG repeat DNA[○]Yuki Hirose¹, Tomo Ohno¹, Sefan Asamitsu², Kaori Hashiya¹, Toshikazu Bando¹, Hiroshi Sugiyama^{1,3} (1. Graduate School of Science, Kyoto University, 2. RIKEN Center for Biosystems Dynamics Research, 3. Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University)

10:20 AM - 10:40 AM

[G201-1am-06] Development of selective Cu⁺-responsive protein labeling reagent towards conditional proteomics[○]Rong Cheng¹, Tomonori Tamura¹, Itaru Hamachi^{1,2} (1. Kyoto University, 2. ERATO, JST)

10:40 AM - 11:00 AM

[G201-1am-07] Expanding the detectable pH range of DNA nanostructure-based fluorescent pH sensors[○]Khongorzul Gerelbaatar¹, Eiji Nakata¹, Hisaaki Hirose², Shiroh Futaki², Takashi Morii¹ (1. Institute of Advanced Energy Science, Kyoto University, 2. Institute of Chemical Research, Kyoto University)

11:00 AM - 11:20 AM

[G201-1am-08] Selection of macrocyclic peptides against SARS-CoV2 spike protein from Tyr, Trp, Pro-rich macrocyclic peptide library[○]Tomoshige Fujino¹, Ryogo Sonoda¹, Taiga Sumi¹, Hiroshi Murakami¹ (1. Nagoya Univ.)

11:20 AM - 11:40 AM

人工ヘモグロビンモデル錯体による火災ガス中毒解毒剤の開発

(同志社大理工¹・建築研²・ベターリビング³・同志社女子大薬⁴) ○毛 齊悦¹・趙玄素²・福田 泰孝³・喜里山 暁子⁴・根木 滋⁴・吉岡 英樹²・北岸 宏亮¹

A novel antidotal system for a fire gas poisoning using artificial hemoglobin model complexes (¹*Faculty of Science and Engineering, Department of Molecular Chemistry and Biochemistry, Doshisha University*, ²*Building Research Institute*, ³*Center for Better Living*, ⁴*Faculty of Pharmaceutical Science, Doshisha Women's College of Liberal Arts*)

○Qiyue Mao,¹ Xuansu Zhao,² Yasutaka Fukuda,³ Akiko Kiriya,⁴ Shigeru Negi,⁴ Hideki Yoshioka,² Hiroaki Kitagishi¹

Carbon monoxide (CO) and hydrogen cyanide (HCN) are regarded as the primary toxic constituents of fire toxic gases. In this work, we developed an antidote that efficiently detoxifies CO and HCN gases at the same time. For practical applications as pharmaceuticals, it would be necessary to maintain the safety and reduced cost. Here, we have developed artificial hemoglobin model complexes that capture CO and cyanide ions *in vivo*. In animal experiments using mice, we proved that our heme protein model complexes are very effective as an antidote for fire toxic gases containing CO/HCN.

Keywords : Porphyrin; Cyclodextrin; Hemeprotein model; Gas poisoning; Animal experiment

火災ガスの中で毒性の高い成分は一酸化炭素(CO)とシアン化水素(HCN)である。これら2種のガス中毒に対する解毒法はそれぞれ開発されているが、COおよびHCNに対する同時に解毒効果を示す薬剤は未だ報告されていない。今回、我々は以前に報告した人工ヘモグロビンモデル錯体

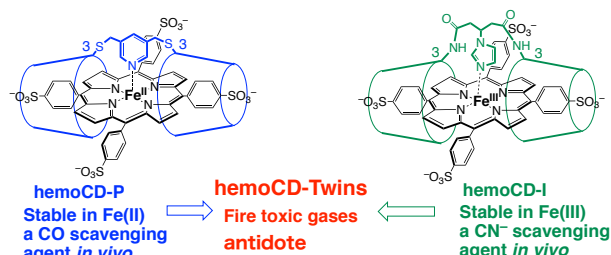


Figure 1. **hemoCD-Twins** composed of **hemoCD-P** and **hemoCD-I**.

(**hemoCD-P**, **hemoCD-I**) (Figure 1)¹⁾を混合して、CO/HCNを同時に効率よく解毒する薬剤(**hemoCD-Twins**)を開発した。**hemoCD-P**は体内で鉄(II)で安定であり、COを捕捉する。一方、**hemoCD-I**は鉄(III)で安定であり、CN⁻に対して高い結合親和性を示す。還元剤 Na₂S₂O₄により鉄(III)の **hemoCD-Twins** 溶液を鉄(II)へと還元した後、マウスに腹投与した。30分後、排出された尿に含まれた **hemoCD** を分析したところ、鉄(II)と鉄(III)の割合が同等であったことから、**hemoCD-P**は体内で鉄(II)で、COを捕捉する。一方、**hemoCD-I**は体内で酸化されて鉄(III)となり、CN⁻を捕捉することが可能であった。この結果からは **hemoCD-Twins** は生体内で CO/CN⁻を同時に捕捉できることが示唆された。さらにアクリルクロスの燃焼ガスをマウスに吸わせて、毒ガス中毒になったマウスに **hemoCD-Twins** を投与したところ、**hemoCD-Twins** を投与していないコントロールと比べて、マウスの生存率および回復率を著しく改善したことがわかった。

1) Kitagishi, H.; Kano, K. *Chem. Commun.*, **2021**, 57, 148–173.

細胞機能制御を目指した光応答性細胞足場の開発

(横国大院工¹・横国大理工²) ○宮島 浩樹¹・加藤 朗佳²・飯島 一智¹

Development of Photo-responsive Cell Scaffold for Control of Cellular Function (¹*Faculty of Engineering, Yokohama National University*, ²*College of Engineering Science, Yokohama National University*) ○Hiroki Miyajima,¹ Saeka Kato,² Kazutoshi Iijima¹

Photo-responsive materials have been studied as cell scaffolds or drug carriers owing to spatiotemporal control of their property with light stimuli. In this study, we developed a cell scaffold of hydrogel with a photo-responsive monomer to release a substance that can control cellular function in response to a light stimulus. Ortho-nitrobenzyl acrylate (*o*-NBA) known as a photo-responsive monomer was synthesized according to literature, and hydrogel was prepared after polymerization of *o*-NBA with gelatin methacrylate (GelMA) which was a gelatin derivative. The obtained hydrogel was irradiated by light, immersed in DMSO, and then the compounds extracted from the gel in DMSO were detected with UV-Vis spectroscopy. Detected UV-Vis spectra of hydrogel immersed in DMSO were different by light irradiation. From the results, *o*-NBA introduced into hydrogel would be decomposed by photo irradiation and the decomposed substance was released from the hydrogel.

Keywords : Cell Scaffold; Photo-responsive; Hydrogel

[緒言] 光刺激に応答する材料は特定箇所を任意の時間で制御できる材料であり、細胞足場や薬剤キャリアとしての応用が研究されている¹⁾。本研究では、光応答性モノマーを導入したハイドロゲルを作製し、光刺激に応答して任意の物質を放出し、細胞の機能制御を可能にする細胞足場の開発を目指した。

[手順] 光応答性モノマーとして知られているオルトニトロベンジルアクリレート (*o*-NBA)²⁾を合成し、ゼラチン誘導体であるゼラチンメタクリレート (GelMA)³⁾と重合することで、ハイドロゲルを作製した。得られたハイドロゲルに波長 365 nm の光を一定時間照射したのち、DMSO に 1 晩浸漬した。浸漬後の DMSO の UV-Vis スペクトルを測定することで、ハイドロゲルより放出された化合物の評価・解析を行った。

[結果と考察] ハイドロゲルを浸漬した DMSO 溶液の UV-Vis スペクトルにおいて、光照射の有無で UV-Vis スペクトルに差異が見られた。ハイドロゲルを形成する高分子鎖に導入された *o*-NBA が光照射によって分解し、その光分解物が検出されたものと考えられる。*o*-NBA はカルボキシ基を介して様々な分子を結合可能であり、光刺激に応答して種々の生理活性分子を放出することで細胞機能を制御する細胞足場としての応用が期待される。

1) L. Li, J. M. Scheiger, P. A. Levkin, *Adv.Mater.* **2019**, 31, 1807333.

2) A. M Kloxin, M. W Tibbitt, K. S Anseth, *Nat Protoc.* **2010**, 5(12) 1867-1887.

3) J. W. Nichol, S. T. Koshy, H. Bae, C. M. Hwang, S. Yamanlar, A. Khademhosseini, *Biomaterials* **2010**, 31, 5536-5544.

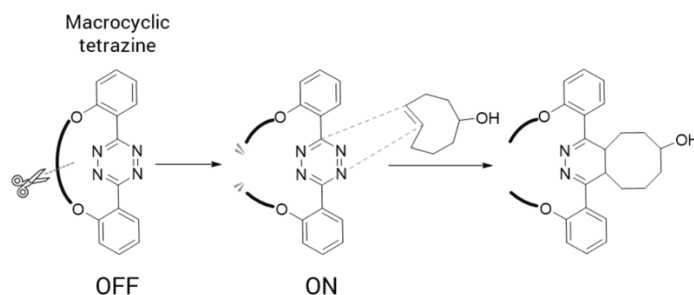
Controlling IEDDA Reaction with Macrocyclic Tetrazine

(¹Graduate School of Life Sciences, Tohoku University, ²Institute of Multidisciplinary Research of Advanced Materials, Tohoku University) ○ Ira Novianti,¹ Toshiyuki Kowada,^{1,2} Shin Mizukami^{1,2}

Keywords: Bioorthogonal Reaction, Click Chemistry, Tetrazines

Tetrazine cycloaddition refers to the reactions between tetrazines and dienophiles via inverse electron-demand Diels-Alder (IEDDA). Owing to its exceptionally fast kinetics and excellent biocompatibility, this bioorthogonal reaction has been applied in various fields spanning from material sciences to biomedicine and has been utilized for therapeutic in humans^{1,2}. This otherwise spontaneous reaction can be controlled by developing activatable tetrazines or activatable dienophiles. However, all activatable tetrazines have only been based on the oxidation of dihydrotetrazine into tetrazine^{3,4}, while tetrazine activation that relies on controlling tetrazine reactivity has yet to be developed.

Here we showed that connecting the two phenyl substituents of 3,6-diphenyltetrazine by a chemical bridge (macrocyclic tetrazine) can make it unreactive towards one of the most reactive dienophiles, *trans*-cyclooctene (TCO). Our theoretical study revealed that the suppressed reactivity was mainly attributed to the high distortion energy of the macrocyclic tetrazine that was originated from the rigid conformation. Furthermore, we also demonstrated the first example of tetrazine activation based on the cleavage reaction of the chemical bridge in macrocyclic tetrazine.



1) Oliveira, B. L.; Guo, Z.; Bernardes, G. J. L. *Chem. Soc. Rev.* **2017**, 46 (16), 4895–4950. 2) Mark, P. Click chemistry sees first use in humans. 3) Zhang, H.; Trout, W. S.; Liu, S.; Andrade, G. A.; Hudson, D. A.; Scinto, S. L.; Dicker, K. T.; Li, Y.; Lazowski, N.; Rosenthal, J.; Thorpe, C.; Jia, X.; Fox, J. M. *J. Am. Chem. Soc.* **2016**, 138 (18), 5978–5983. 4) Ehret, F.; Wu, H.; Alexander, S. C.; Devaraj, N. K. *J. Am. Chem. Soc.* **2015**, 137 (28), 8876–8879.

Development of Functional Anthracene-Based Multiblock Fluorophore for Visualization of Biological Environment

(School of Life Science and Technology, Tokyo Tech.) ○Junya Adachi, Kohei Sato, Kazushi Kinbara

Keywords: Anthracene; Visualization; Biological Environment

Phase separation is a ubiquitous phenomenon in biological systems such as lipid raft and liquid-liquid phase separation, where the environment is slightly different from the surroundings. Recently, this phenomenon has been revealed to play important roles in biological activities and attracts a great deal of attention not only in biology but also in chemistry.¹ However, details of this phenomenon remain unexplored, and there is a need to investigate the behavior of relevant molecules in the biological environment.

Our research group has developed a series of multiblock molecules, which form supramolecular assemblies in the lipid bilayer membranes and exhibit functions.² This functionality takes advantage of the environmental characteristics of the lipid bilayer membranes that have hydrophobic region surrounded by aqueous phases. By leveraging our experience of developing the functional molecules sensitive to the surrounding environment, we aimed to develop novel molecules that are able to sense a biological environment with phase separation.

Here, we designed anthracene-based multiblock fluorophores which successfully showed characteristic emission depending on the physical parameters of the surrounding environment, and applied them for visualization of the phase-separated substances related to the biological environment. The details of the chemical properties of these fluorophores will be presented at the conference.

1) Kamimura, Y. R.; Kanai, M. Chemical Insights into Liquid-Liquid Phase Separation in Molecular Biology. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 1045–1058.

2) Sato, K.; Muraoka, T.; Kinbara, K. Supramolecular Transmembrane Ion Channels Formed by Multiblock Amphiphiles. *Acc. Chem. Res.* **2021**, *54*, 3700–3709.

Evaluation of the properties of a cyclic pyrrole–imidazole polyamide, which specifically binds to CAG/CTG repeat DNA

(¹Graduate School of Science, Kyoto University, ²RIKEN Center for Biosystems Dynamics Research, ³Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University)
 ○Yuki Hirose,¹ Tomo Ohno,¹ Sefan Asamitsu,² Kaori Hashiya,¹ Toshikazu Bando,¹ Hiroshi Sugiyama^{1,3}

Keywords: CAG repeat; CTG repeat; Triplet repeat; Pyrrole–imidazole polyamide; DNA ligand

Trinucleotide repeat sequences widely exist in the human genome. And abnormal expansion of the repeat often leads to a variety of diseases.¹ The abnormal elongation of CAG/CTG repeat sequences causes Huntington's disease, spinocerebellar ataxia, and myotonic dystrophy. In order to develop therapeutic methods for these diseases, many compounds targeting CAG/CTG repeat sequences have been developed.² Our group have been studied hairpin pyrrole–imidazole polyamides (hPIPs), which sequence specifically bind to the minor groove of CAG/CTG sequences.³

Although hPIPs have been mainly used in many studies, cyclic PIPs (cPIPs) have been developed and reported to have higher DNA-binding affinity and sequence specificity than the corresponding hPIPs.⁴ Therefore, we have developed a CAG/CTG-targeting cPIP in this study. We evaluated its DNA-binding property by using double-stranded DNA melting temperature (T_m) measurements and surface plasmon resonance (SPR) assays. Additionally, the next-generation sequencing study revealed the high sequence specificity of the cPIP.⁵ The results of each experiment will be reported in detail in the presentation.

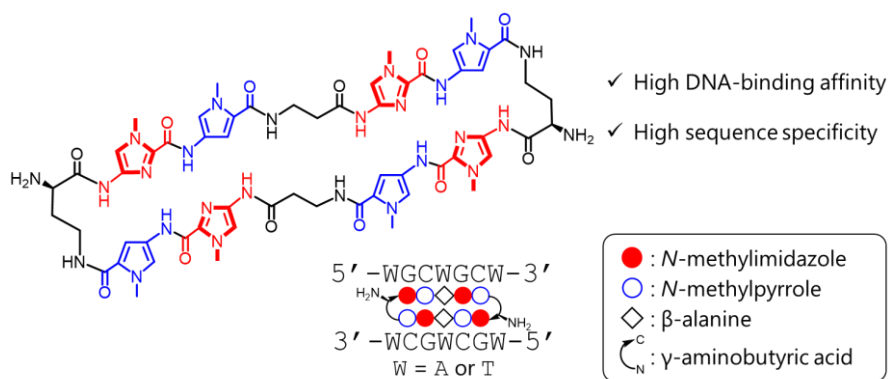


Figure. The chemical structure and ball-and-stick notation of the cPIP.

1) Mirkin, S. M. *Nature* **2007**, 447, 932. 2) Nakamori, M. *et al. Nat. Genet.* **2020**, 52, 146. 3) Asamitsu, S. *et al. Bioorg. Med. Chem.* **2014**, 22, 4646. 4) Herman, D. M. *et al.* **1999**, 121, 1121. 5) Hirose, Y. *et al. ChemBioChem in press.*

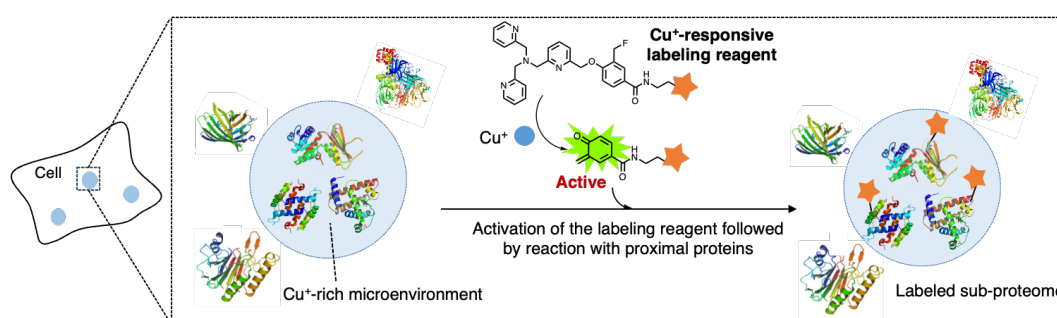
Development of selective Cu⁺-responsive protein labeling reagent towards conditional proteomics

(¹Graduate School of Engineering, Kyoto University, ²ERATO, JST) ○ Rong Cheng,¹ Tomonori Tamura,¹ Itaru Hamachi^{1,2}

Keywords: Cu⁺-responsive protein labeling reagent

Copper (Cu) is one of the most essential metals in all living systems, and its dynamics are precisely regulated in cells to maintain various physiological responses.¹ Cu⁺-responsive probes have emerged as powerful tools in tracking the dynamic changes in Cu⁺ to characterize its contribution to health and disease states.² However, most probes are diffusible hence the spatiotemporal resolution is limited, and they are incapable of identifying the proteins at Cu⁺-rich sites.

The conditional proteomics approach has emerged as a powerful method for identifying proteins in specific condition-rich microenvironments and mapping the localization of those microenvironments. This strategy has been applied to the proteome profiling of zinc ion- and hydrogen peroxide-rich regions in live cells.³ In this presentation, we report a Cu⁺-responsive protein labeling strategy for the detection of Cu⁺ with preserved spatial information and the identification of proteins at Cu⁺-rich sites in living cells. Specifically, we designed quinone methide (QM) precursor-based fluorescent reagents that undergo Cu⁺-dependent oxidative cleavage to release a highly electrophilic QM for subsequent labeling of proximal proteins *in situ*. The Cu⁺-responsiveness of these reagents was evaluated by *in vitro* assay, and the optimal reagent showed high selectivity for Cu⁺ over other biological metal ions and reactive oxygen species. The capability of this reagent in cellular contexts was demonstrated by Cu-dependent protein modification in HeLa cells overexpressing copper transporter 1.



1) Kardos, J et al., *Cell Commun. Signal.* **2018**, 16(1), 71. 2) Cotruvo, J. A et al., *C. J. Chem. Soc. Rev.* **2015**, 44(13), 4400. 3) a) Miki, T et al., *Nat. Methods.* **2016**, 13(11), 931. b) Zhu, H et al., *JACS.* **2020**, 142(37), 15711.

Expanding the detectable pH range of DNA nanostructure-based fluorescent pH sensors

(¹*Institute of Advanced Energy, Kyoto University*, ²*Institute for Chemical Research, Kyoto University*) ○Khongorzul Gerelbaatar¹, Eiji Nakata¹, Hisaaki Hirose², Shiroh Futaki², Takashi Morii¹

Keywords: fluorescent pH sensor; DNA nanostructure; DNA origami; ratiometric detection

Cellular processes are mediated through intertwined complex chemical and physical interactions of biological molecules. Therefore, analytical devices that simultaneously monitor the change of the concentration and the location of biologically important molecules, and the change of cellular environment indicated by various physical parameters will give a comprehensive understanding of molecular mechanisms underlying of various cellular processes.

Compared to the conventional sensors comprised of a single sensing molecule, assembling several kinds of fluorescent sensors on a DNA scaffold has advantages in monitoring different targets at the same time within the same nanospace by combining individual functions of fluorescent sensors. A single DNA scaffold allows the assembly of multiple fluorophores, with different responses towards pH changes, to be localized in a defined space, enabling ratiometric detection and the expansion of the detectable pH range.

We have developed a ratiometric pH sensor by constructing a DNA nanostructure labeled by two types of fluorophores based on a DNA origami method¹. The combination of a pH sensitive fluorophore fluorescein (CF) with pK_a of 6.5² and tetramethylrhodamine (CR), a pH insensitive fluorophore under the physiological conditions, assembled on a DNA origami scaffold had resulted in a reliable ratiometric pH detection in test tube. The sensor was successfully applied for real-time sensing of cellular pH changes throughout its internalization by its fluorescence signal variation under microscopic conditions.³ In this study, Oregon Green 488 (OG) with pK_a of 4.8² was coassembled with CF and CR on a DNA origami scaffold. The pH monitoring was carried out in a test tube by the ratiometric fluorescent pH sensor to successfully realize an expanded detectable pH range.

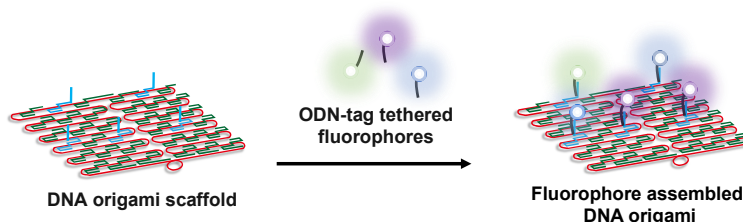


Fig. Illustration of fluorophores assembled DNA origami scaffold for intracellular pH monitoring

1) P. W. K. Rothemund, *Nature* **2006**, 440, 297. 2) J. Han and K. Burgess, *Chem. Rev.* **2010**, 110, 2709. 3) E. Nakata, *et al.*, *Chem. Sci.* **2021**, 12, 8231.

Tyr, Trp, Pro-rich 環状ペプチドライブラリの構築と SARS-CoV2 に対する環状ペプチドの選択

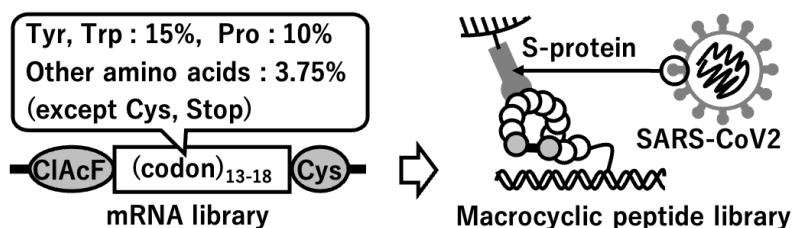
(名大院工¹・名大ナノライフ²) ○藤野 公茂¹・園田 凌吾¹・鷲見 大河¹・村上 裕^{1,2}

Selection of macrocyclic peptides against SARS-CoV2 spike protein from Tyr, Trp, Pro-rich macrocyclic peptide library (¹Graduate School of Engineering, Nagoya University, ²Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University) ○ Tomoshige Fujino,¹ Ryogo Sonoda,¹ Taiga Sumi,¹ Hiroshi Murakami^{1,2}

In this work, we constructed a macrocyclic peptide library with a high content of Tyr, Trp, and Pro residues by direct codon synthesis method¹⁾. We focused on these three amino acids because Tyr is rich in the complementarity determining region (CDR) of mammalian IgG²⁾, Trp is rich in the peptide binders selected in previous studies, and Pro is expected to contribute to a rigid structure of macrocyclic peptides. From this library, we successfully selected peptides that bind to the receptor-binding domain (RBD) of spike proteins of six strains of SARS-CoV2 (the original Wuhan strain, α , β , γ , δ , and κ variants) using TRAP-display³⁾. We also obtained a peptide that inhibits the interaction between RBD (the original, α , β , and γ variants) and human angiotensin-converting enzyme 2 (ACE2), which serves as the cellular receptor for SARS-CoV2 infection.

Keywords : Directed evolution; Peptide library; SARS-CoV2

本研究では、コドンをも1つの単位とする核酸合成を利用することで¹⁾、各アミノ酸の比率を制御し、Tyr, Trp, Pro の出現頻度の高い環状ペプチドライブラリを構築した。Tyr は、哺乳類の抗体 CDR において出現頻度が高いこと²⁾、Trp は、過去に取得された環状ペプチドの配列中の出現頻度が高かったことから比率を上げた。さらに、Pro は環状ペプチドの安定な構造形成に有効であると考えた。このライブラリから、進化分子工学的手法である TRAP 提示法を利用し³⁾、SARS コロナウイルス 2 の変異株 6 種 (武漢、 α 、 β 、 γ 、 δ 、 κ 株) のスパイクタンパク質受容体結合ドメイン(RBD)を標的とし、これに結合する環状ペプチドの選択を試みた。その結果、全ての変異株 RBD に結合する環状ペプチドを取得することに成功した。さらに、武漢、 α 、 β 、 γ 株の RBD に対しては、感染の際に受容体として働く、ヒトアンジオテンシン変換酵素 2 (ACE2) との結合を阻害することのできるペプチドについても取得に成功した。



1) B. Virnekäs et.al., *Nucleic Acids Res.* **1994**, 22(25), 5600. 2) M. Zemlin et.al., *J. Mol. Biol.* **2003**, 334(4), 733. 3) T. Ishizawa et.al., *J. Am. Chem. Soc.* **2013**, 135(14), 5433.

[G202-1am] 17. Biofunctional Chemistry, Biotechnology

Chair: Takashi Matsuo, Hiroshi Murakami

Wed. Mar 23, 2022 9:00 AM - 11:40 AM G202 (Online Meeting)

[G202-1am-01] Preparation of super-catalytic antibody against the conserved region of influenza virus hemagglutinin molecule and the biochemical features○Emi Hifumi¹, Tamami Nonaka¹, Ayuka Tanaka¹, Taizo Uda² (1. Oita university, 2. ISIT)

9:00 AM - 9:20 AM

[G202-1am-02] Improvement of neutralizing activity of monobody against SARS-CoV-2 by affinity maturation○Taishi Kondo¹, Kazuhiro Matsuoka², Tomoshige Fujino¹, Shun Umemoto¹, Gosuke Hayashi¹, Yasumasa Iwatani^{2,3}, Hiroshi Murakami^{1,4} (1. Graduate School of Engineering, Nagoya University, 2. Department of Infectious Diseases and Immunology, Clinical Research Center, National Hospital Organization Nagoya Medical Center, 3. Division of Basic Medicine, Graduate School of Medicine, Nagoya University, 4. Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University)

9:20 AM - 9:40 AM

[G202-1am-03] Activity regulation for adenylate kinase through conformational change trapping with antibody proteinsIbuki Nakamura¹, Hiroshi Amesaka², Kento Yonezawa¹, Hironari Kamikubo¹, Shunichi Tanaka², ○Takashi Matsuo¹ (1. Nara Inst. Sci. Tech., 2. Kyoto Pref. Univ.)

9:40 AM - 10:00 AM

[G202-1am-04] A rapid, convenient, and highly sensitive electrochemical detection of human hemoglobin in serum using a high-affinity bivalent antibody-enzyme complex○Daimei Miura¹, Hayato Kimura¹, Wakako Tsugawa¹, Koji Sode², Kazunori Ikebukuro¹, Ryutaro Asano¹ (1. Tokyo University of Agriculture and Technology, 2. Joint Department of Biomedical Engineering, The University of North Carolina at Chapel Hill and North Carolina State University)

10:00 AM - 10:20 AM

[G202-1am-05] Thiazolidine ring-opening by 2-aminobenzamide-based formaldehyde scavengers for one-pot multiple peptide ligation○Koki Nakatsu¹, Hiroshi Murakami^{1,2}, Gosuke Hayashi¹, Akimitsu Okamoto^{3,4} (1. Department of Engineering, Nagoya Univ., 2. Institute of Nano-Life-Systems, Nagoya Univ., 3. Graduate School of Engineering, The Univ. of Tokyo, 4. Research Center for Advanced Science and Technology, The Univ. of Tokyo)

10:20 AM - 10:40 AM

[G202-1am-06] Ribosomal synthesis of peptide libraries containing cyclic γ -amino acids for drug screening○Takashi Miura¹, Takayuki Katoh¹, Hiroaki Suga¹ (1. The University of Tokyo)

10:40 AM - 11:00 AM

[G202-1am-07] A chemi-genetic Ca^{2+} indicator based on a synthetic chelator and a fluorescent protein

○Wenchao Zhu¹, Takuya Terai¹, Yusuke Nasu¹, Robert Earl Campbell^{1,2} (1. The University of Tokyo, 2. The University of Albert)

11:00 AM - 11:20 AM

[G202-1am-08] Development of Split-Luciferase Probes for Monitoring Endogenous RNAs in Living Cells

○Masatoshi Eguchi¹, Hideaki Yoshimura¹, Yoshibumi Ueda¹, Takeaki Ozawa¹ (1. School of Science, The University of Tokyo)

11:20 AM - 11:40 AM

インフルエンザウイルス・ヘマグルチニン分子の保存領域に対するスーパー抗体酵素の作製とその生化学的性質

(大分大研究機構¹・大分大院工²・九州先端研³) ○一二三恵美¹・野中玲実¹・田中歩佳²・宇田泰三³

Preparation of super-catalytic antibody against the conserved region of influenza virus hemagglutinin molecule and the biochemical features (¹Research Promotion Institute, Oita University, ²Graduate School of Engineering, Oita University, ³Nanotechnology Laboratory, ISIT,) ○Emi Hifumi,¹ Tamami Nonaka,¹ Ayuka Tanaka,² Taizo Uda³

Hemagglutinin molecule of influenza virus is essential for viral infection. The frequent mutations occurred in this molecule have made numerous subtypes of influenza virus, and the vaccination inoculated every year is necessarily. In this study, in order to solve this problem, we developed a new method to make the super-catalytic antibody targeting the conserved region of the hemagglutinin molecule, in whose region the mutation hardly takes place. By mutating a part of the light chain of InfA-15 mAb, we could produce the effective super-catalytic antibody to suppress the infection of influenza virus *in vitro*. The chemical and biochemical features investigated in this study will be reported in detail.

Keywords : Catalytic antibody; Influenza virus; Hemagglutinin

【目的】インフルエンザウイルス・ヘマグルチニン分子(HA 分子)はウイルスの感染に必須である。一般に、この分子に頻繁に変異が入るためにインフルエンザウイルス(Flu virus)には多数の亜型が存在し、かつ、毎年のワクチン接種も余儀なくされている。本研究では、この問題を解決するために、どの型のウイルスにも対抗できる技術を開発するために HA 分子の保存領域を標的にしたスーパー抗体酵素を作製する手法を開発し、その化学的及び生化学的性質を詳細に調べたので報告する。

【実験手法】抗体軽鎖への変異導入には KOD-Plus-Mutagenesis Kit (TOYOBO)を用いた。酵素活性は市販の合成基質 Arg-pNA(R-pNA)、および特別に作製した FRET-InfA ペプチドを用いて評価した。Flu virus に対する感染抑制試験は H1N1 型ウイルスを用いて MDCK 細胞に感染させる Plaque assay を行った。

【結果と考察】演者等はすでに HA 分子の保存領域ペプチド(GMVDGWYG)に対するマウス型モノクローナル抗体(InfA-3, -6, -9, -10, -15, -18mAb)を取得している¹⁾。この中で InfA-15 抗体は Flu virus の H1(スペイン型)、H3 (香港型)、および H5 型 (トリ型) のどの HA にも反応する興味ある抗体である。しかしながら、InfA-15 抗体およびその軽鎖は抗原分解活性を有しておらず、Flu virus に対する感染抑制能は全く見られなかった。ところが、演者等が見出した抗体に変異導入法により²⁾、InfA-15 ほか複数の抗体軽鎖に酵素機能を付与することが出来、HA 保存領域ペプチドに対する分解能や Flu virus に対する感染抑制能を付与することに成功した。これは変異が多い SARS-CoV-2 の感染予防にも役立つ新技術として期待出来る。

1) E. Hifumi et al., *J. Biosci. Bioeng.*, **109**(6), 598-608(2010). 2) E. Hifumi et al., *Science Advances*, **6**(13), eaay6441(2020).

新型コロナウイルスに対する人工抗体 Monobody の親和性成熟による中和活性の向上

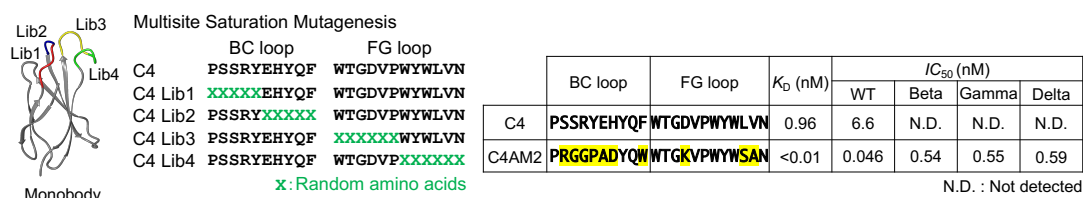
(名大院工¹・国立病院機構名古屋医療センター²・名大院医³・名大ナノライフ⁴) ○近藤 太志¹、松岡 和弘²、藤野 公茂¹、梅本 駿¹、林 剛介¹、岩谷 靖雅^{2,3}、村上 裕^{1,4}

Improvement of neutralizing activity of monobody against SARS-CoV-2 by affinity maturation (¹Graduate School of Engineering, Nagoya University, ²Department of Infectious Diseases and Immunology, Clinical Research Center, National Hospital Organization Nagoya Medical Center, ³Division of Basic Medicine, Graduate School of Medicine, Nagoya University, ⁴Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University) ○Taishi Kondo¹, Kazuhiro Matsuoka², Tomoshige Fujino¹, Shun Umemoto¹, Gosuke Hayashi¹, Yasumasa Iwatani^{2,3}, Hiroshi Murakami^{1,4}

We report affinity maturation of monobodies against the RBD of SARS-CoV-2 and the neutralization activity against SARS-CoV-2 wild-type as well as variants of concerns. We selected matured monobodies from multiple-site saturation libraries by using the *in vitro* selection method, the TRAP display. One of the clones showed high affinity ($K_D < 0.01$ nM) against the RBD of SARS-CoV-2. Furthermore, the monobody C4-AM2 efficiently neutralized wild-type SARS-CoV-2 ($IC_{50} = 46$ pM, 0.62 ng/ml) as well as the Alfa ($IC_{50} = 1.0$ ng/ml), the Beta ($IC_{50} = 7.2$ ng/ml), and the Gamma ($IC_{50} = 7.4$ ng/ml) variants infection to the host cells. **Keywords** : Directed Evolution; Neutralizing antibody; SARS-CoV-2; Antibody-like proteins

我々は 10 kDa 程度と小さい Monobody 人工抗体骨格を用いて TRAP 提示法によって、スパイクタンパク質に対して高い親和性を持つ 7 種類の Monobody を 4 日間で選択することに成功している¹⁾。その中のクローン C4 は細胞を用いた中和活性測定で SARS-CoV-2 に対して $IC_{50} = 6.6$ nM と強い中和活性を示した。

そこで、C4 の中和活性の向上を目指して、親和性成熟を行なった。C4 の BC、FG ループの 5,6 残基をランダム化した mRNA ライブラリを構築し、スパイクタンパク質に対してセレクションを行なった。その結果、各ライブラリで出現割合が高かった配列を用いた C4-AM1 では、解離定数が $K_D = 0.11$ nM と約 9 倍に向上した。さらに、よく保存されていた部分を固定し、その他の部分をランダム化した第二世代ライブラリを構築し、より厳しい条件で選択を行なった。その結果、得られた C4-AM2 は、解離定数 10 pM 以下となり、中和活性も $IC_{50} = 46$ pM, 0.62 ng/ml、変異株でもアルファ 1.0 ng/ml、ベータ 7.2 ng/ml、ガンマ 7.4 ng/ml、デルタ 8.0 ng/ml と大幅に向上した。



1) Kondo, T., et al, *Sci. Adv.* **2020**, 6 (42), eabd3916.

抗体タンパク質を用いた構造変化トラップによるアデニル酸キナーゼの活性制御

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Activity regulation for adenylate kinase through conformational change trapping with antibody proteins (¹*Division of Materials Science, Nara Institute of Science and Technology*, ²*Department of Biomolecular Chemistry, Kyoto Prefectural University*) Ibuki Nakamura,¹ Hiroshi Amesaka,² Kento Yonezawa,¹ Hironari Kamikubo,¹ Shun-ichi Tanaka,² ○Takashi Matsuo¹

Conformational trapping for biomacromolecules is a promising strategy of the function regulation for enzymes with large conformational changes. Accordingly, we attempted to regulate the activity of adenylate kinase (Adk), a phosphoryl transfer-mediating enzyme between ATP/ADP/AMP with the conformational interconversion of OPEN/CLOSED form, using low-molecular-weight antibody mimetics (“monobodies”) that recognize each conformation of Adk. Monobodies binding specifically to the OPEN form of Adk were found to decrease the Adk catalytic activity. Small angle X-ray scattering spectroscopic analysis for one of the monobodies complexed with Adk displayed the complexation fashion at the hinge part of Adk, not at its active site. The result indicates that the conformation trapping strategy is applicable for the enzymatic activity regulation without direct influences to the active site of the targeted enzyme.

Keywords : *Antibody; Conformational change trapping; Adenylate kinase; Function regulation; Small-angle X-ray scattering*

機能発揮時に大きな構造変化を伴うタンパク質に対して、その構造変化過程をトラップする手法は、活性部位への摂動に基づく方法と並ぶ有用な機能制御戦略であり、ウイルス感染防御や細胞工学への応用も期待される。そこで、OPEN⇌CLOSEDの構造変化を伴って ATP/ADP/AMP 間のリン酸基転移を触媒するアデニル酸キナーゼ (Adk) をモデル例として、Adk の OPEN/CLOSED 構造それぞれを特異的に認識し、ヒトフィブロネクチンタイプ III ドメインを分子骨格にもつ低分子抗体ミメティック「モノボディ」を調製し、Adk の活性制御、Adk-モノボディ複合体の構造評価を試みた。Adk に対するモノボディについては、M13 ファージを用いたファージディスプレイライブラリから、CLOSED 型に結合するものを 1 種類 (CL-1)、OPEN 型に結合するものを 3 種類 (OP-2, 3, 4) 取得できた。このうち、エピトープが重複しない OP-2 と 4 について、Adk 活性に対する影響を評価したところ、OP-2、4 とともに、酵素反応の初期過程が減速する傾向が観測された。一方、CL-1 による Adk 活性への効果は見られなかった。さらに、OP-4 について、X 線小角散乱で Adk との複合体構造を解析したところ、OP-4 は、構造が開閉するヒンジ部分に結合しているという結果が得られた。つまり、基質結合部位ではなく、酵素表面のヒンジ領域への摂動で酵素活性に必須の構造変化をトラップするというユニークな活性制御機構が明らかとなった。

A rapid, convenient, and highly sensitive electrochemical detection of human hemoglobin in serum using a high-affinity bivalent antibody-enzyme complex

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Keywords: Antibody-enzyme complex, Immunosensor, Catcher/Tag reaction, Glucose dehydrogenase, Anti-hemoglobin single-chain antibody

Antibody-enzyme complexes (AECs) are ideal sensing elements for immunosensors due to their bifunctionality. We have recently established a convenient, universal, and homogeneous preparation method of a bivalent AEC using Catcher/Tag system¹. EGFR, one of cancer marker, was successfully detected using the AEC as a sensing element, but its sensitivity was not meet clinically required range². The bivalent AEC could not exert avidity effects for EGFR with monomeric structure at lower target concentration. Here, we hypothesized that higher sensitivity can be achieved for multimeric target. Human hemoglobin (Hb) has tetrameric structure and is a biomarker for hematologic diseases. An extremely low level of Hb in blood immediately leads to hypoxia. Thus, rapid, convenient, and sensitive Hb detection is highly required.

In this research, a bivalent AEC composed of two anti-Hb single-chain antibodies (scFvs) and a glucose dehydrogenase was prepared using Catcher/Tag system, and applied to wash-free and electrochemical immunosensor. The bivalent AEC retained high enzymatic activity even after AEC formation. Whereas, an affinity to Hb of the bivalent AEC ($K_D = 4.3$ nM) was remarkably improved compared to scFv itself (13 nM) as we expected. This is due to synergic effect of the bivalency of AEC and the multimeric structure of Hb. Using the bivalent AEC combined with a magnet and magnetic beads, we tried to detect Hb in diluted human serum (Fig.). As a result, Hb-dependent current increase was observed within 25 min of manipulation time. The linear range was 0.97-28 g/dL, which completely covered clinically required range. Hemolysis reagents are often used for pre-treatment of Hb detection and can be considered as contaminants on electrochemical detection, however, in our system there were no influences of the hemolysis reagents. These results strongly suggested that we successfully developed a novel Hb detection system and it can be applied to detection of other multimeric biomarkers.

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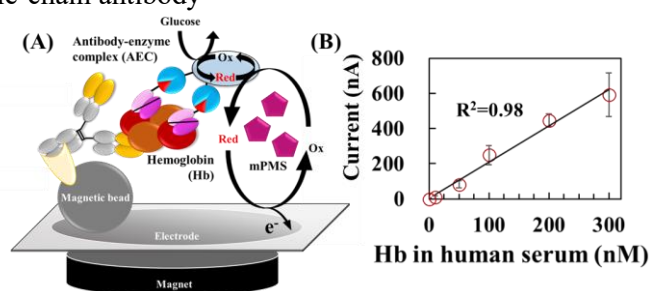


Fig. (A) A schematic illustration of wash-free Hb detection system. (B) Hb detection in human serum.

1) H. Kimura, R. Asano, N. Tsukamoto, W. Tsugawa, K. Sode, *Anal. Chem.*, **2018**, *90*, 14500. 2) H. Kimura, D. Miura, W. Tsugawa, K. Ikebukuro, K. Sode, R. Asano, *Biosens. Bioelectron.*, **2021**, *175*, 112885. (3) D. Miura, H. Kimura, W. Tsugawa, K. Ikebukuro, K. Sode, R. Asano, *Talanta*, **2021**, *234*, 122638.

Thiazolidine ring-opening by 2-aminobenzamide-based formaldehyde scavengers for one-pot multiple peptide ligation

(¹Graduate School of Engineering, Nagoya University, ²Institute of Nano-Life-Systems, Nagoya University, ³Graduate School of Engineering, The University of Tokyo, ⁴Research Center for Advanced Science and Technology, The University of Tokyo) ○ Koki Nakatsu¹, Hiroshi Murakami^{1,2}, Gosuke Hayashi¹, Akimitsu Okamoto^{3,4}

Keywords: Chemical Protein Synthesis; Native Chemical Ligation; Thiazolidine; 2-aminobenzamide; One-pot peptide ligation

In chemical protein synthesis, native chemical ligation (NCL)¹ is a promising strategy to ligate two unprotected peptide segments between an N-terminal cysteinyl peptide and a C-terminal peptide thioester. For multiple peptide segment condensation, the reactivity of the N- or C-terminus of internal segments should be controlled appropriately to avoid self-ligation and cyclization. For this purpose, 1,3-thiazolidine-4-carbonyl (Thz) was employed as a precursor of reactive Cys residue in many previous reports. Thz ring opens when methoxyamine is added at acidic condition.² However, due to its high nucleophilicity, methoxyamine attacks thioester moieties and produces a methoxyamine adduct during NCL (Figure 1a).

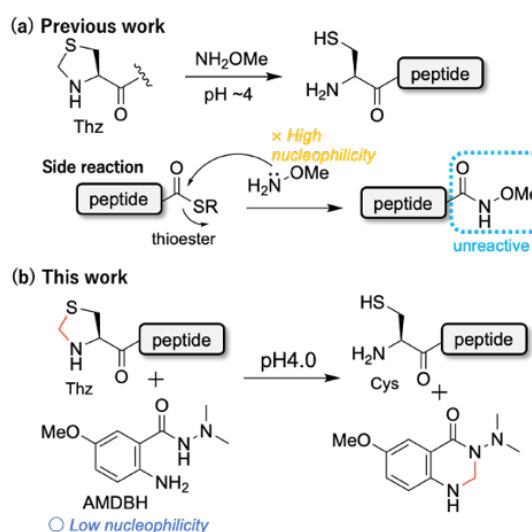


Figure 1. (a) Thz deprotection by methoxyamine. (b) Thz deprotection by AMDBH.

In this presentation, we will report a new Thz ring-opening method using 2-aminobenzamide-type formaldehyde scavengers. These scavengers have a weak nucleophile moiety at the *o*-position of the amine group, and after imine formation with aldehyde, a ring-closing reaction occurs and stable products is produced.³ After screening some derivatives, we found that 2-amino-5-methoxy-*N,N'*-dimethylbenzohydrazide (AMDBH) efficiently scavenged formaldehyde and converted Thz to Cys in NCL buffer (pH4.0) (Figure 1b). Due to the lower nucleophilicity of AMDBH, this scavenger did not affect thioester and ligation reaction at pH~7. Using AMDBH-mediated Thz ring-opening, we developed a one-pot four segments peptide ligation method. We applied this method to the chemical synthesis of monoubiquitinated histone H2A.Z (209 amino acids, 23 kD).

1) P. E. Dawson, T. W. Muir, I. Clark-Lewis, S. B. Kent, *Science* **1994**, 266, 776–779. 2) D. Bang, S. B. H. Kent, *Angew. Chem. Int. Ed Engl.* **2004**, 43, 2534–2538. 3) P. I. Kitov, D. F. Vinals, S. Ng, K. F. Tjhung, R. Derda, *J. Am. Chem. Soc.* **2014**, 136, 8149–8152.

Ribosomal synthesis of peptide libraries containing cyclic γ -amino acids for drug screening

(¹Graduate School of Science, The University of Tokyo) ○Takashi Miura,¹ Takayuki Katoh,¹ Hiroaki Suga¹

Keywords: *gamma amino acid; unnatural amino acid; macrocyclic peptide; translation; drug discovery*

γ -Amino acids can induce unique secondary structures of peptides, such as C₁₄-helix, C_{12/10}-helix, and C₁₂-turn.^[1] γ -amino acids are found in some natural bioactive peptides and play important roles in their biological activities and proteolytic stability.^[2] Especially, cyclic $\gamma^{2,4}$ -amino acids (c γ AA, Figure) are ideal building blocks that stabilize structures of peptides, and thereby can improve binding affinity to target proteins due to their constrained rigid conformations. Therefore, incorporation of c γ AAs into a random peptide library and its application to in vitro selection of active ligands would be powerful approach for developing novel therapeutic peptides.

Recently, our group reported the ribosomal incorporation of c γ AAs into nascent peptide chains using a reconstituted translation system assisted by Flexizyme technology, referred to as the Flexible In vitro Translation (FIT) system.^[3] Here we report the ribosomal synthesis of macrocyclic peptide libraries containing two c γ AAs, *cis*- and *trans*-3-aminocyclobutane carboxylic acid by means of the FIT system, and its application to an in vitro screening methodology, referred to as the Random nonstandard Peptides Integrated Discovery (RaPID) system.^[4] Consequently, we obtained inhibitor peptides against interferon-gamma receptor 1 (IFNGR1) that showed strong binding affinity and inhibitory activity with low nM *K_D* and IC₅₀ values. Moreover, the peptides containing c γ AA exhibited up to 27-fold longer half-lives in human serum than their alanine-substituted mutants.

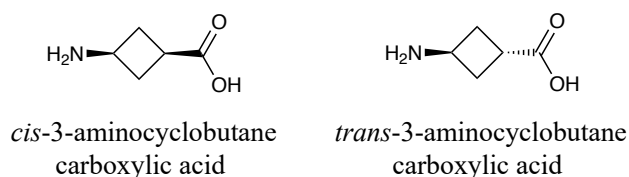


Figure Cyclic γ -amino acids used in this study

[1] Hintermann, T., Gademann, K., Jaun, B., Seebach, D., *Helv. Chim. Acta* **1998**, *81*, 983.

[2] Frackenpohl, J., Arvidsson, P.I., Schreiber, J.V., Seebach, D., *Chembiochem*, **2001**, *2*, 445.

[3] Katoh, T.; Suga, H. *J. Am. Chem. Soc.* **2020**, *142*, 4965.

[4] Yamagishi, Y.; Shoji, I.; Miyagawa, S.; Kawakami, T.; Katoh, T.; Goto, Y.; Suga, H. *Chem. Biol.* **2011**, *18*, 1562.

A chemi-genetic Ca^{2+} indicator based on a synthetic chelator and a fluorescent protein

(¹Graduate School of Science, The University of Tokyo, ²Department of Chemistry, The University of Alberta)

○Wenchao Zhu¹, Takuya Terai¹, Yusuke Nasu¹, Robert E. Campbell^{1,2}

Keywords: Fluorescence sensor, Calcium ion imaging, Protein chemistry, HaloTag

Metal ions (e.g., Ca^{2+} , Na^+) are crucial for cell signaling. For example, the Ca^{2+} concentration inside cells controls various processes, such as the release of neurotransmitters and muscle contraction. Fluorescent indicators are widely used for dynamic imaging of biological systems to understand their detailed mechanisms. The main classes of indicators are small molecule-based¹ and protein-based² indicators. A small molecule sensor consists of a synthetic fluorophore and a recognition motif, and a protein-based biosensor is made of a fluorescent protein (FP) and an ion-binding protein. Relative to small molecule-based indicators, protein-based indicators are inherently biological compatible and can be expressed with specific localization in cells or tissues. However, since protein-based biosensors rely on the ion-binding proteins, for ions for which suitable binding proteins have not been discovered (e.g., Mg^{2+} , Na^+), the development of a biosensor is impossible.

To combine the advantages of synthetic molecules and proteins in a single indicator, we conceived a new indicator design based on integrating a synthetic chelator and a FP. In this work, we set out to construct a Ca^{2+} indicator based on a combination of green FP (GFP), a self-labeling protein (HaloTag) which can covalently bind with a chloroalkane ligand, and a Ca^{2+} chelator BAPTA (1,2-bis(o-aminophenoxy) ethane-*N,N,N,N'*-tetraacetic acid) (**Fig. 1**). After combining ten types of BAPTA ligands and 32 types of GFP-HaloTag proteins, we eventually identified a prototype sensor with a 1.4-fold fluorescence change. We then performed many rounds of rational and random optimization to reach the final variant with a 10-fold fluorescence increase upon binding to Ca^{2+} . We demonstrated that this sensor is applicable to cell-based imaging experiments.

We hope our work serves as the archetype for a new class of chemi-genetic indicator with ion- or molecular-specificities that have not yet been realized with fully protein-based biosensors.

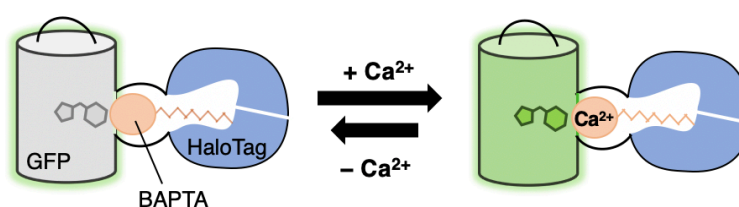


Fig 1. Schematic illustration of the chemi-genetic Ca^{2+} indicator developed in this work.

1) *Curr. Opin. Chem. Biol.* **2008**, 12, 515. 2) *Nat. Methods.* **2019**, 16, 649.

Development of Split-Luciferase Probes for Monitoring Endogenous RNAs in Living Cells

(Department of Chemistry, School of Science, The University of Tokyo)

○Eguchi, Masatoshi; Yoshimura, Hideaki; Yoshibumi, Ueda; Ozawa, Takeaki

Keywords: Luminescent imaging, Single cell analysis, Protein engineering

Gene expression plays essential roles in physiological and pathophysiological phenomena. Gene expression patterns upon external stimuli cause phenotypic changes such as cancer, differentiation, and pluripotency. Temporal gene expression alteration includes important clues for comprehension of the mechanisms in the phenotypic changes. In addition to the temporal properties, the intracellular localization of RNAs plays essential roles in inducing the physiological phenomena. Bioimaging approach in live cells for the RNAs will be useful to provide information on the time course and intracellular localization of target molecules for elucidating mechanisms of the physiological phenomena. A new analysis and imaging technology in living cells are required to reveal the temporal changes in RNA abundance in living cells. In this study, we aim to develop probes for temporal monitoring of a specific RNA as the target gene expression product in single living cells by luminescence observation. We developed a luminescence-based RNA probe which consists of two fusion proteins with each different domain; One is an RNA recognition domain that binds to a specific RNA sequence, and the other is a split luciferase domain. The probe emits a luminescence signal through luciferase reconstitution by responding to the presence of target RNAs.

Firstly, to assess the reversible reaction of the probe to target RNAs, we monitored luminescence of purified probe solution. The luminescence of the probe was weak in the absence of the target RNA. Upon addition of the RNA, the luminescence intensity increased, and following RNase treatment of the sample decreased the luminescence. Thus, the probe worked reversibly upon addition and digestion of target RNA. The time lapse luminescence images of living cells expressing the probes and target RNA were acquired under a luminescence microscope. The time-lapse luminescence images of probe-expressing cells were acquired under a luminescence microscope. The sample cells express the fluorescence protein gene fused with the target RNA sequence so that the fluorescence protein works as an indicator of the expression of the target RNA in these cells. The time-lapse images suggest the potential of the probe to detect and quantify the target RNAs in single living cells. The luminescence imaging of primary hippocampal neurons was also performed to detect endogenous RNA for confirming the applicability to the detection of endogenous RNA *in vivo*. This result suggested the ability of the present RNA probe to visualize subcellular localization and dynamics of the target RNA separately from the protein produced by translation of the RNA in living cells.

These results totally suggest that the probes have potential to monitor target RNA abundance in single living cells over time. In addition, the probe reversibly changed its luminescence in response to an increase or decrease in the target RNA. It was able to monitor the time course of gene expression using luminescence signals by this probe. These properties of the RNA probe indicate that the RNA probe will provide a practical methodology for visualization and quantification of RNAs to analyze time-course gene expression in living cells to explore characteristic gene expression patterns for various physiological events.

[C202-1pm] 18. Polymer

Chair: Takeharu Haino, Yasuhiro Kohsaka

Wed. Mar 23, 2022 1:20 PM - 3:40 PM C202 (Online Meeting)

[C202-1pm-01] Synthesis of novel perfluoropolyethers using hexafluoropropylene oxide○Minoru Koyama¹, Midori Akiyama¹, Kimiaki Kashiwagi², Kyoko Nozaki¹, Takashi Okazoe^{1,2} (1. Graduate School of Engineering, The University of Tokyo, 2. AGC Inc.)

1:20 PM - 1:40 PM

[C202-1pm-02] Synthesis of unimolecularly-thick polyelectrolyte networks using MOF templates○Ami Saito¹, Yuki Hayashi¹, Marta Ximenis¹, Nobuhiko Hosono¹, Takashi Uemura¹ (1. The University of Tokyo, Graduate School of Engineering)

1:40 PM - 2:00 PM

[C202-1pm-03] Self-Assembling Behavior and Negative Non-Linear Dependence of Hydrogen-Bonded Tris(phenylisoxazolyl)benzene Dimers○Yudai Ono¹, Takehiro Hirao¹, Takeharu Haino¹ (1. Hiroshima University)

2:00 PM - 2:20 PM

[C202-1pm-04] Vinyl polymers degradable through main chain scission by retro-aldol reaction over the backbone and pendants○Akane Kazama¹, Patrick Théato³, Yasuhiro Kohsaka^{1,2} (1. Faculty of Textile Science and Technology, Shinshu University, 2. Research Initiative for Supra-Materials (RISM), Shinshu University, 3. Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology)

2:20 PM - 2:40 PM

[C202-1pm-05] Synthesis of π -Conjugated Organometallic Polymers Containing Fused Titanacycle and Thiophene Units○Alvin Tanudjaja¹, Ryoyu Hifumi¹, Shinsuke Inagi¹, Ikuyoshi Tomita¹ (1. Tokyo Institute of Technology)

2:40 PM - 3:00 PM

[C202-1pm-06] Improvement of Hydrolysis Resistance for PET by Copper Catalyzed Decarboxylation of Terminal Carboxylic Acid○Masato Akahira¹, Hirokazu Komatsu¹, Koji Yamauchi¹ (1. Toray Industries, Inc.)

3:00 PM - 3:20 PM

[C202-1pm-07] Synthesis of supramolecular polysulfide polymers using hydrogen bonds and coordination bonds○Yuichiro Kobayashi¹, Yuki Yamagishi¹, Akiyoshi Horiguchi¹, Daiki Kitano¹, Hiroyasu Yamaguchi^{1,2} (1. Osaka University, 2. ISC-OTRI)

3:20 PM - 3:40 PM

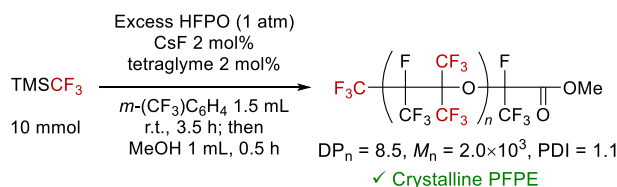
Synthesis of novel perfluoropolyethers using hexafluoropropylene oxide

(¹Graduate School of Engineering, The University of Tokyo, ²AGC Inc.) ○ Minoru Koyama,¹ Midori Akiyama,¹ Kimiaki Kashiwagi,² Kyoko Nozaki,¹ Takashi Okazoe^{1,2}
Keywords: Fluorine; Epoxide; Fluorinated polymer; Perfluoropolyether

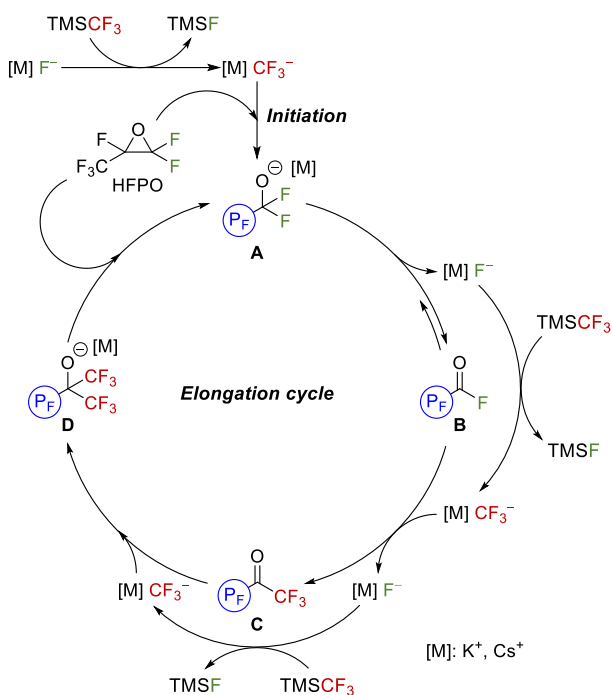
Organofluorine compounds have unique properties, and fluorinated polymers show significantly different physical properties from other polymers. Therefore, fluorinated polymers have received considerable attention in material chemistry.

In this study, the synthesis of a CF₃-rich perfluoropolyether (PFPE) has been achieved via the fluoride-catalyzed reaction of hexafluoropropylene oxide (HFPO) with (trifluoromethyl)trimethylsilane (TMSCF₃) (Scheme 1). Repetition of the sequence afforded a new PFPE as a solid, whose structure was confirmed using ¹⁹F NMR spectroscopy and GC-MS analysis. Thermal analysis and X-ray diffraction analysis revealed its crystalline character. To the best of our knowledge, this is the first example of crystalline PFPE. From contact angle measurements, the critical surface tension of this solid PFPE was determined to be 13.4 mN m⁻¹; this value demonstrated the higher water- and oil-repellency of the CF₃-rich PFPE compared to that of PTFE (18.5 mN m⁻¹).^[1]

A plausible reaction mechanism is shown in Scheme 2. Nucleophilic addition of a CF₃ anion to HFPO affords an acyl fluoride **B** via the ring-opening of HFPO followed by fluoride elimination. Further addition of CF₃ anions to the acyl fluoride **B** gives tertiary perfluoroalkoxide **D**, which attacks HFPO to regenerate an acyl fluoride.



Scheme 1. The synthesis of a CF₃-rich PFPE



Scheme 2. Proposed reaction mechanism

1) H. W. Fox, W. A. Zisman, *J. Colloid Sci.* **1950**, 6, 514–531.

MOF を鋳型とした単分子厚高分子電解質ネットワークの合成

(東大院工¹⁾) ○齋藤 杏実¹・林 柚希¹・Marta Ximenis¹・細野 暢彦¹・植村 卓史¹

Synthesis of unimolecularly-thick polyelectrolyte networks using MOF templates (¹*Graduate School of Engineering, The University of Tokyo*) ○Ami Saito,¹ Yuki Hayashi,¹ Marta Ximenis,¹ Nobuhiko Hosono¹, Takashi Uemura¹

Two-dimensional (2D) polymer possesses an anisotropic network topology, which is expected to show unique properties based on the specific morphology. We have developed the synthetic method for unimolecular-thick 2D polymer networks using nanosized slits of a metal-organic framework¹⁾. In this work, we performed the synthesis of 2D poly(methyl methacrylic acid) (PMAA) networks by polymerization of methyl methacrylate (MMA) and crosslinker in the MOF slits with 0.8-nm width, followed by MOF removal and hydrolysis (see *Figure*). The compound with the larger amount of polyanion (methyl methacrylic acid) composition shows the higher glass transition temperature. In the aqueous solution, the pH-responsive change of the particle size was observed.

Keywords: Two-dimensional polymer; Metal-Organic frameworks; Polyelectrolyte.

2次元高分子は、平面状に広がったネットワーク構造をもち、そのトポロジーと異方性から従来の直鎖状高分子とは異なる物性の発現が期待されている。私たちは、多孔性金属錯体 (MOF) のスリット状細孔を鋳型として、単分子厚の2次元高分子ネットワークを合成する手法を開発している¹⁾。本研究では、0.8 nm 幅の細孔内にモノマーとしてメタクリル酸メチル (MMA) と架橋剤を導入して重合を行った後に、MOF から取り出し、加水分解することで2次元ポリアニオンネットワークを合成した (下図)。加水分解率を調整でき、ポリアニオン組成 (メタクリル酸組成) の大きい化合物ほど高いガラス転移点を示した。また、水溶液中では、2次元ポリアニオンネットワークの粒子サイズに pH 応答性が見られた。

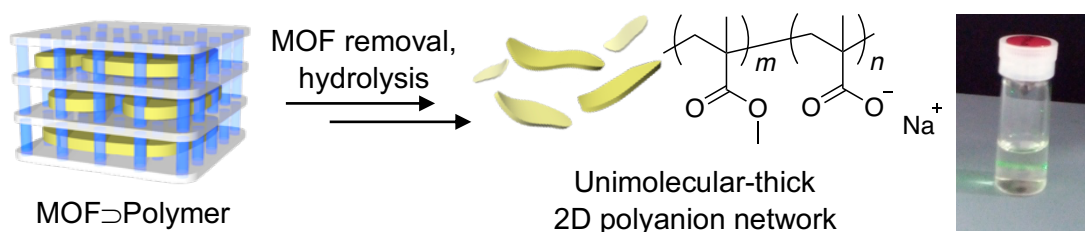


Figure. Synthesis of unimolecular-thick 2D PMAA (polyanion) and the aqueous solution showing a Tyndall effect.

1) N. Hosono, S. Mochizuki, Y. Hayashi and T. Uemura, *Nat. Commun.* **2020**, *11*, 3573.

Self-Assembling Behavior and Negative Non-Linear Dependence of Hydrogen-Bonded Tris(phenylisoxazoly)benzene Dimers

(Graduate School of Advanced Science and Engineering, Hiroshima University) ○Yudai Ono, Takehiro Hirao, Takeharu Haino

Keywords: Self-Assembly; Chirality; Circular Dichroism

Ureido-pyrimidinone (UPy) motif forms a quadruple hydrogen-bonded dimeric pair with a dimerization association constant of $K_{\text{dim}} > 1.0 \times 10^7 \text{ L mol}^{-1}$.¹⁾ Our group reported that tris(phenylisoxazoly)benzene derivatives with chiral side chains were stacked in a columnar fashion to form one-handed helical supramolecular polymers.²⁾ Here, we report the self-assembly behavior of UPy-appended tris(phenylisoxazoly)benzene (*S*)- and (*R*)-**1** in a mixture of CHCl_3 /methylcyclohexane (MCH) (Figure 1a). When the content of MCH was increased to 60%, a strong CD signal with a dissymmetry factor g_{abs} of 0.027 was observed (Figure 1b). On the other hand, no CD signal was observed in the pure CHCl_3 solutions of (*S*)-**1**.

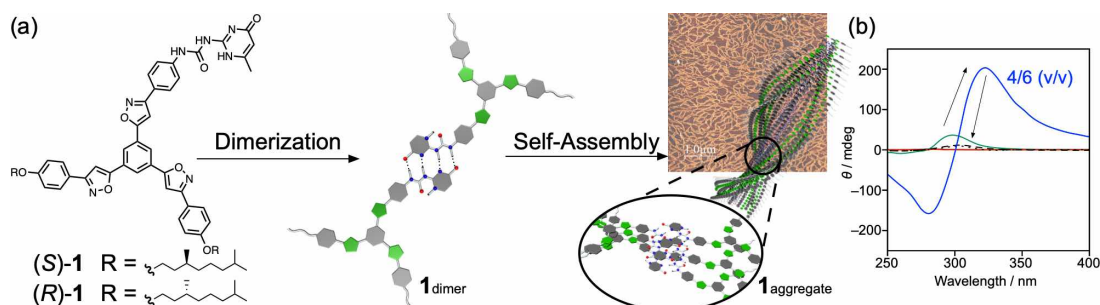


Figure 1. (a) Cartoon representation of the formation of helically twisted supramolecular polymer consisting of **1**. Inserted AFM image was spin-coated film of (*S*)-**1** on mica prepared from its CHCl_3 solution. (b) CD spectra of (*S*)-**1** in CHCl_3 /MCH. The red, black, green, blue, dotted, and broken lines denote the spectra of (*S*)-**1** recorded in CHCl_3 /MCH (v/v) = 10/0, 8/2, 6/4, 4/6, 2/8, and 0/10, respectively. $[(S)\text{-}\mathbf{1}] = 1.0 \times 10^{-4} \text{ mol L}^{-1}$.

The CD spectra were measured when varying the enantiomeric excesses (*ee*) for (*S*)- and (*R*)-**1** mixtures in CHCl_3 /MCH (4/6, v/v). The plot of the net helicity against the *ee* showed negative non-linear dependence at the concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ (Figure 2). We will give a presentation about the detailed discussion on the self-assembly behavior and negative non-linear dependence of (*S*)- and (*R*)-**1** mixtures.

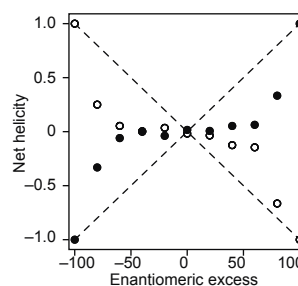


Figure 2. Plot of the net helicity at (closed circle) 280 nm and (open circle) 320 nm against the *ee* of mixed monomer of (*S*)- and (*R*)-**1**.

- 1) F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer, *J. Am. Chem. Soc.*, **1998**, *120*, 6761-6769.
- 2) M. Tanaka, T. Ikeda, J. Mack, N. Kobayashi, T. Haino, *J. Org. Chem.*, **2011**, *76*, 5082-5091.

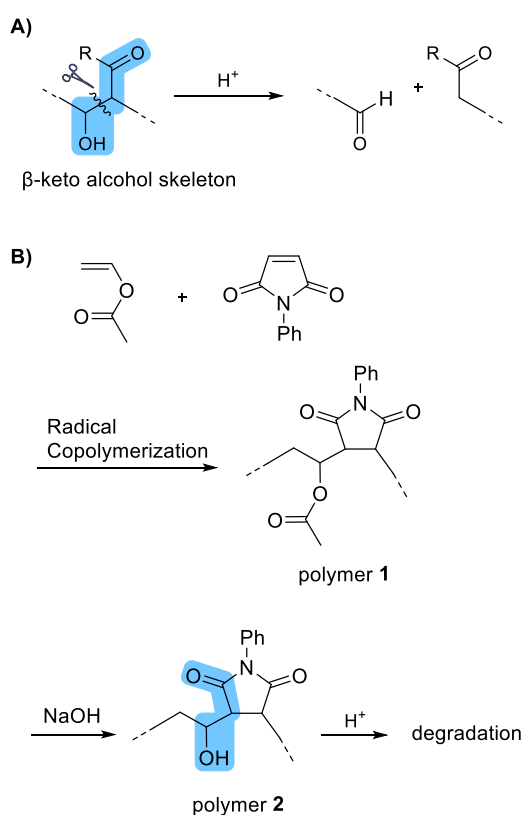
Vinyl polymers degradable through main chain scission by retro-aldol reaction over the backbone and pendants

(¹Faculty of Textile Science and Technology, Shinshu University, ²Research Initiative for Supra-Materials (RISM), Shinshu University, ³Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology) ○ Akane Kazama,¹ Patrick Théato,³ Yasuhiro Kohsaka^{1,2}

Keywords: retro-aldol reaction, vinyl acetate, *N*-phenyl maleimide, main chain scission, β -keto alcohol

Retro-aldol reaction (**Scheme A**), proceeding in a β -keto alcohol skeletons (highlighted by light blue), is known as a common tool for the cleavage of carbon-carbon bond in organic synthetic chemistry. We have envisioned that the reaction is also effective for the degradation of vinyl polymers through main chain scission.

In order to incorporate β -keto alcohol skeletons covering over polymer backbone and pendants, the radical copolymerization of an equimolar mixture of vinyl acetate (VAc) and *N*-phenyl maleimide (PMI), a pair of electron-rich and electron poor monomer for the alternative sequence, was conducted (**Scheme B**). The polymer **1** had a number-averaged molar mass (M_n) and dispersity of molar mass (\mathcal{D}) of 5200 and 1.76, respectively, and the composition was [VAc]/[PMI]=30/70. Thus, **1** was not an ideal alternating copolymer. The hydrolysis of **1** with NaOH was conducted; the degree of saponification of VAc units was 87%, while the M_n was decreased to 1900 (\mathcal{D} = 1.08). The obtained **2** was then treated with 3 equivmolar of hydrochloride in a cosolvent of water and dimethyl sulfoxide. The M_n s of the polymer were gradually decreased and reached 620 after 5 days, suggesting a possibility of the main chain scission by retro-aldol reaction. Additional experiments to confirm the reaction mechanism is in progress.



Scheme A) Retro-aldol reaction under acid condition. **B)** Copolymerization of vinyl acetate and *N*-phenyl maleimide.

Synthesis of π -Conjugated Organometallic Polymers Containing Fused Titanacycle and Thiophene Units

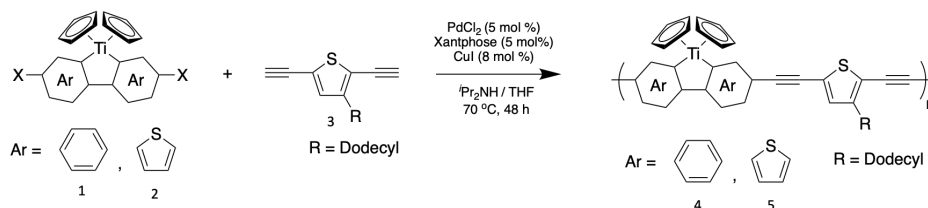
(¹Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology)

○Alvin Tanudjaja,¹ Ryoyu Hifumi,¹ Shinsuke Inagi,¹ and Ikuyoshi Tomita¹

Keywords: π -conjugated polymers, fused ring, titanacycle, thiophene

π -Conjugated polymers possessing heteroles of transition metals would be potentially attractive materials for optoelectronic applications on the basis of the d-electrons of the transition metals. We have been working on the synthesis of titanacyclopentadiene-containing polymers by the reaction of aromatic diynes and a low-valent titanium complex, which serve as useful synthetic precursors for π -conjugated polymers containing heteroatoms.¹ Based on the advantages of fused heterole systems, we have also reported the synthesis of π -conjugated polymers containing titanafluorene² and dithienotitanacyclopentadiene moieties.³ Herein we describe the synthesis of polymers containing both thiophene and fused titanacycles so as to obtain polymers with advanced optoelectronic performances.

As monomers for the polycondensation processes, a 4,4'-dibromotitanafluorene derivative (**1**) was prepared by the lithiation of 4,4'-dibromo-2,2'-diiodobiphenyl using *n*-BuLi followed by the reaction with titanocene dichloride, while 5,5'-diido-bithiophene (**2**) was prepared by the reaction of dithienotitanacyclopentadiene with *N*-iodosuccinimide. The arylene dihalides possessing titanacycle moieties thus obtained (**1** and **2**) were subjected to the Sonogashira-Hagihara polycondensation using 3-dodecyl-2,5-diethynylthiophene (**3**) in the presence of a palladium catalyst to produce the corresponding polymers (**4** and **5**). Unique optical and electronic properties of the resulting polymers will also be described.



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- 2) A. Tanudjaja, S. Inagi, F. Kitamura, T. Takata, I. Tomita, *Dalton Trans.* **2021**, *50*, 3037-3043.
- 3) A. Tanudjaja, R. Hifumi, S. Inagi, I. Tomita, *Polymer* **2022**, *241*, 124511.

Improvement of Hydrolysis Resistance for PET by Copper Catalyzed Decarboxylation of Terminal Carboxylic Acid

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Keywords: polyester; copper catalyst; acid value; terminal carboxylic acid; hydrolysis

Polyester resin such as polyethylene terephthalate (PET) has high mechanical properties, a high chemical stability and a high transparency, and also has a high cost performance. Accordingly, the polyester resin is most widely used for fibers, bottles, films, sheets and containers.

However, polyester resin has a fundamental issue for hydrolysis of an ester bonding. Furthermore, a terminal acidic carboxyl group accelerates the hydrolysis of the ester bonding because it acts as a catalyst.

Herein, we will report improvement of hydrolysis resistance for PET by copper catalyzed decarboxylation of terminal carboxylic acid.

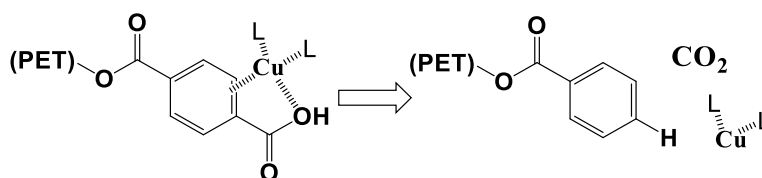


Fig.1

Copper Catalyzed Decarboxylation of Terminal Carboxylic Acid.

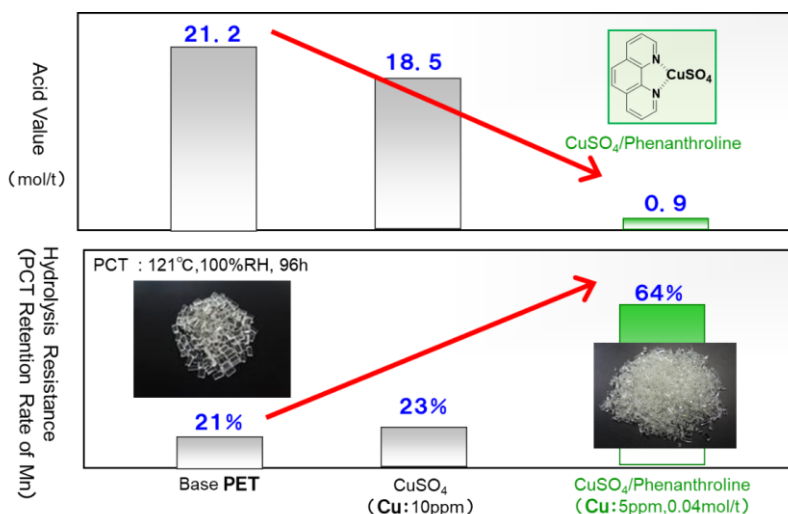


Fig.2

Improvement of Hydrolysis Resistance by using Copper Catalyzed Decarboxylation

水素結合や配位結合を用いた超分子硫黄ポリマーの合成

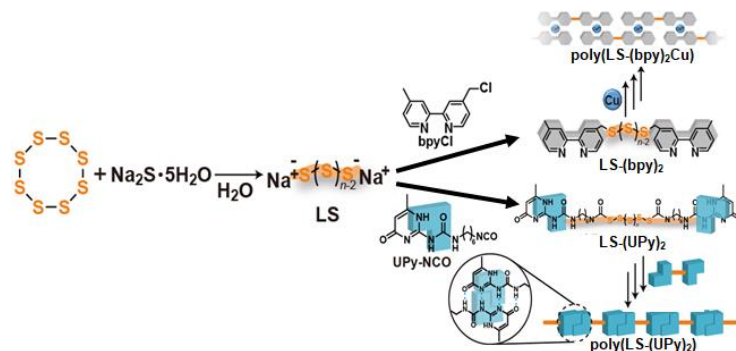
(阪大院理¹・ICS-OTRI²) ○小林 裕一郎¹・山岸 佑輝¹・堀口 顕義¹・北野 大輝¹・山口 浩靖^{1,2}

Synthesis of supramolecular polysulfide polymers using hydrogen bonds and coordination bonds (¹Graduate School of Science, Osaka University, ²Innovative Catalysis Science Division-Institute for Open and Transdisciplinary Research Initiatives, Osaka University)○ Yuichiro Kobayashi¹, Yuki Yamagishi¹, Akiyoshi Horiguchi¹, Daiki Kitano¹, Hiroyasu Yamaguchi^{1,2}

Establishing a method for synthesizing polymers from waste sulfur is highly desirable in order to create a sustainable society because it leads to the development of alternative polymer materials made from petroleum. In this paper, we report the preparation of a supramolecular polysulfide polymer using hydrogen bonds and metal-ligand interactions. The supramolecular polysulfide polymer was prepared by introducing 2-ureido-4[1H]pyrimidinone (UPy) or bipyridine unit at both ends of linear sulfur and linking the UPys or bipyridine with Cu(II), respectively. The molecular weight of the supramolecular polysulfide polymer was higher than polysulfide polymer obtained from conventional polymerization. In the case of metal-ligand interactions, the addition of chelating agents and Cu(II) controlled the decomposition and re-formation of the supramolecular polysulfide polymer.

Keywords : Hydrogen bonds; Sulfur; Coordination bonds; Supramolecules; Polysulfide polymer

硫黄は年間 700 万トン地上廃棄されており、有効活用が求められている。その一つの方法としてポリマー材料の開発が行われている。これまでの硫黄ポリマーは硫黄を加熱することで生じるラジカルを用いてビニルモノマーと共重合する手法と、硫黄を開環し、直鎖硫黄とした後にジハロゲン化合物と重縮合する手法によって合成されてきた。本研究ではこれまでのような共重合や重縮合のような共有結合による硫黄ポリマーを合成するという高分子化学からのアプローチとは異なり、超分子化学のアプローチから硫黄ポリマーを合成する手法を開発したので報告する。具体的には線状硫黄の両端に水素結合可能な 2-ureido-4[1H]pyrimidinone や、金属と配位結合可能なビピリジンを導入してモノマーとし(LS-(UPy)₂、LS-(bpy)₂)、このモノマーを非共有結合で連結することで超分子硫黄ポリマーを合成した(poly(LS-(UPy)₂)、poly(LS-(bpy)₂)Cu)。



Academic Program [Oral B] | 18. Polymer | Oral B**[C203-1pm] 18. Polymer**

Chair: Kenichi Kato, Yoshinori Takashima

Wed. Mar 23, 2022 1:20 PM - 3:40 PM C203 (Online Meeting)

[C203-1pm-01] Carboxyl-substituted Poly(quinoxaline-2,3-diyl) for Quantification of a Small Enantiomeric Imbalance of Chiral Amines by CD Spectroscopy in Water○Tomonori Yamawaki¹, Takuma Kuroda¹, Yuuya Nagata¹, Michinori Suginome¹ (1. Kyoto Univ.)

1:20 PM - 1:40 PM

[C203-1pm-02] Construction of Donor-Acceptor Type Conjugated Polymers Based on Pilar[5]arene Units○Keisuke Wada¹, Shunsuke Ohtani¹, Kenichi Kato¹, Shixin Fa¹, Tomoki Ogoshi^{1,2} (1. Grad. Sch. of Eng., Kyoto Univ., 2. Kanazawa University WPI-NanoLSI)

1:40 PM - 2:00 PM

[C203-1pm-03] Synthesis of boratrane-pendant polymers and their specific properties changes through side chain reactions○Akira Takahashi¹, Masahiro Yamanishi¹, Atsushi Kameyama¹ (1. Kanagawa Univ.)

2:00 PM - 2:20 PM

[C203-1pm-04] Increasing the strength of temperature-responsive polymer gels○Kazunari Yoshida¹, Naofumi Fujiwara¹ (1. Yamagata Univ.)

2:20 PM - 2:40 PM

[C203-1pm-05] Low-voltage-driven hydrogel actuator using hydrophobic interaction between poly(ethylene glycol) and iodine○Hongyao Zhou¹, Teppei Yamada¹ (1. The Univ. of Tokyo)

2:40 PM - 3:00 PM

[C203-1pm-06] Functional design of polymeric materials based on movable cross-links and application for strain-sensor○Ryohei Ikura¹, Shunsuke Murayama³, Junsu Park¹, Yuka Ikemoto⁴, Motofumi Osaki^{1,5}, Hiroyasu Yamaguchi^{1,6}, Akira Harada⁷, Go Matsuba³, Yoshinori Takashima^{1,2,5,6} (1. Grad. Sch. of Sci., Osaka Univ., 2. Inst. for Advanced Co-Creation Studies, Osaka Univ., 3. Grad. Sch. of Org. Mater. Eng., Yamagata Univ., 4. JASRI, 5. PRC, Osaka Univ., 6. OTRI, Osaka Univ., 7. ISIR, Osaka Univ.)

3:00 PM - 3:20 PM

[C203-1pm-07] Novel Reticular Polymeric Nanomembranes Formed within Unconventional Electric Double Layer: Synthesis and Functions○Yoshimitsu Itoh^{1,2}, Tengfei FU¹, Pier-Luc CHAMPAGNE¹, Takuzo AIDA^{1,3} (1. Graduate School of Engineering, The University of Tokyo, 2. JST PRESTO, 3. RIKEN CEMS)

3:20 PM - 3:40 PM

Carboxyl-substituted Poly(quinoxaline-2,3-diyl) for Quantification of a Small Enantiomeric Imbalance of Chiral Amines by CD Spectroscopy in Water

(Graduate School of Engineering, Kyoto University) ○Tomonori Yamawaki, Takuma Kuroda, Yuuya Nagata, Michinori Suginome

Keywords: Helical Chirality; Asymmetric Amplification; Chiral Discrimination; CD Spectroscopy; Acid-base Interaction

Quantification of enantiomeric ratio of chiral compounds is an important basis in the development of chiral science. Chromatography using a chiral stationary phase and NMR measurement using a chiral shift reagent are widely employed as useful chiral quantification methods. However, since these methods rely on quantification of the peak integration ratios of enantiomer signals, it is difficult to evaluate small enantiomeric imbalance. To overcome this problem, induced CD method using dynamic helical polymers has attracted much attention since a small enantiomeric imbalance of chiral compounds can be detected as amplified CD signals of polymers. Nevertheless, only limited helical polymers have been applied for the highly sensitive chirality detection. Poly(quinoxaline-2,3-diyl)s (PQXs) are known as helical polymers with long persistence length, which facilitates quantitative evaluation of the chiral amplification effect.^{1,2} In this study, we investigated helical chirality induction of achiral **P(100)** bearing carboxyl side chains, which leads to the quantification of a small enantiomeric imbalance of chiral amines through acid-base interaction.

The helical chirality induction of achiral **P(100)** using (*S*)-1-phenylethylamine (**PEA**) with varied ee (10 mM) was investigated by CD measurements in water (Fig. 1a). Kuhn dissymmetry factor g_{abs} ($\Delta\epsilon/\epsilon$) at 370.5 nm is plotted against the ee of (*S*)-**PEA** (Fig. 1b). The g_{abs} values of **P(100)** increased nonlinearly with the increase of the ee of **PEA**, enabling the detection of extremely low optical purity (down to 0.1% ee). Notably, the observed g_{abs} values against **PEA** with low optical purity ($\leq 1\%$ ee) can be approximated to a linear relationship (Fig. 1b, inset). The CD spectrum of **P(100)** in aqueous solution of purchased racemic **PEA** showed the induction of a left-handed helical structure (Fig. 1c). This result suggests that the purchased lot of racemic **PEA** has a slight enantiomeric imbalance (0.6% ee (*S*)).

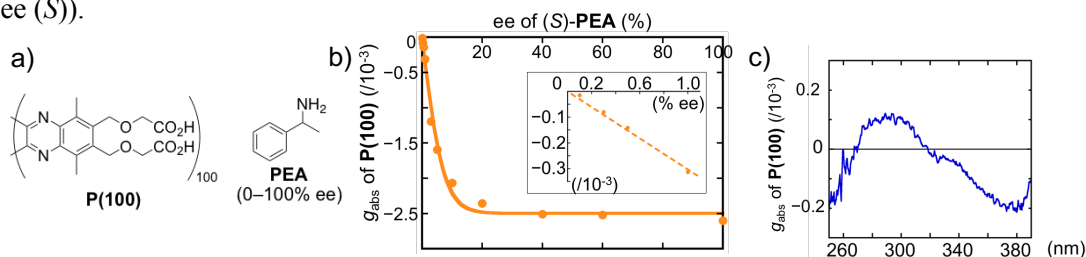


Fig. 1. a) The structure of **P(100)** and **PEA**. b) The relationship between ee of **PEA** and g_{abs} of **P(100)** at 370.5 nm. The inset shows linear approximation between ee and g_{abs} at the low ee range. c) The CD spectrum of **P(100)** in aqueous solution of purchased racemic **PEA**. **P(100)**; 0.09 mM as monomer unit, **PEA**; 10 mM.

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- 2) Nagata, Y.; Takeda, R.; Suginome, M. *ACS Cent. Sci.* **2019**, *5*, 1235–1240.

Construction of Donor-Acceptor Type Conjugated Polymers Based on Pillar[5]arene Units

(¹Grad. Sch. of Eng., Kyoto Univ., ²Kanazawa Univ., WPI-NanoLSI)

○Keisuke Wada,¹ Shunsuke Ohtani,¹ Kenichi Kato,¹ Shixin Fa,¹ Tomoki Ogoshi^{1,2}

Keywords: Pillar[n]arene; Donor-Acceptor Type; Conjugated Polymers; Molecular Recognition

Pillar[5]arenes are highly symmetrical macrocyclic molecules and can take up linear guest molecules because of the formation of multiple CH/π interactions between C–H moieties and electron-rich pillar[5]arene cavity (**Fig. 1a**). Besides, functional groups can be easily introduced into pillar[n]arenes. Especially, only one unit of pillar[5]arenes can be selectively functionalized. In Previous our studies, we synthesized conjugated polymers with pillar[5]arenes as building blocks by coupling reactions. However they hardly responded to guest molecules in optical properties.¹⁾

In this study, we constructed new conjugated polymers, **Bn-Polymer** and **Bt-polymer** (**Fig. 1b**). From the solvatochromism of emission bands and subsequently Lippert–Mataga plots, it was revealed that **Bn-Polymer** has two emission modes, which are derived from local excitation (LE fluorescence) and charge transfer fluorescence (CT fluorescence). These polymers showed response to guest molecules due to inclusion of the guest molecules in the pillar[5]arene cavities. In case of **Bt-Polymer**, fluorescence intensity was only increased without large peak shift upon addition of 1,2-dicyanoethane. On the other hands, **Bn-Polymer** showed mainly CT fluorescence before addition of 1,2-dicyanoethane. However, after the addition of 1,2-dicyanoethane, CT derived emission decreased and LE derived emission increased, resulting in color change upon the addition of guest molecules (**Fig. 1c**).

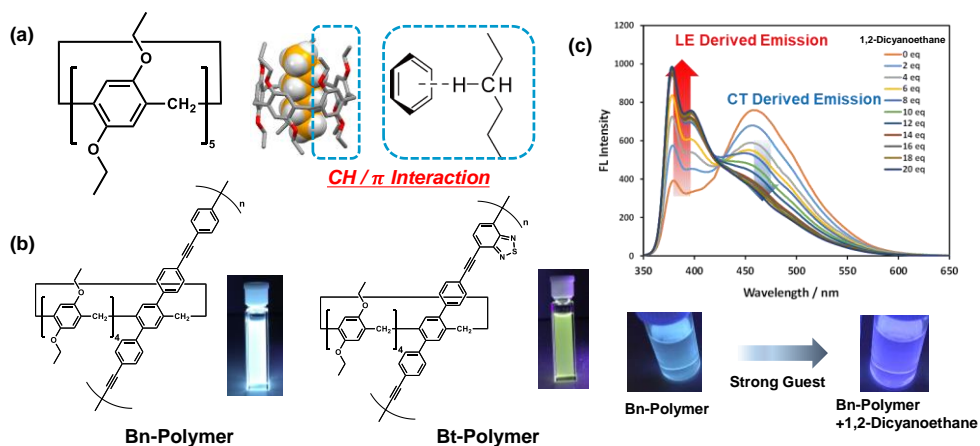


Fig. 1. (a) Chemical structures of pillar[5]arenes and their host-guest properties. (b) Chemical structures of **Bn-Polymer** and **Bt-Polymer**. (c) Fluorescence spectra of **Bn-Polymer** before (orange line) after (blue line) addition of 1,2-dicyanoethane in CHCl_3 (0.01 mM, $\lambda_{\text{ex}} = 330$ nm)

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側鎖ボラトラン含有高分子の合成とその側鎖反応に伴う特異的物性変化

(神奈川大工¹) ○高橋 明¹・山西 雅大¹・亀山 敦¹

Synthesis of boratrane-pendant polymers and their specific properties changes through side chain reactions (¹*Faculty of Engineering, Kanagawa University*) ○ Akira Takahashi,¹ Masahiro Yamanishi,¹ Atsushi Kameyama¹

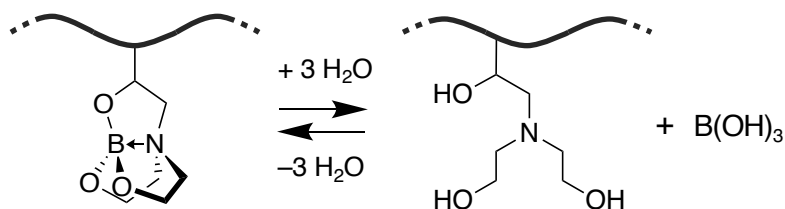
Side chain topology is an important factor for polymer properties. Triethanolamine borate (TEAB) is a boratrane compound possessing a tricyclic cage structure with an internal N–B dative bond. TEAB is formed by borylation of triethanolamine (TEA) and recovers TEA by the hydrolysis. While such huge structural conversion between TEAB and TEA is a promising molecular tool for post-polymerization regulation of polymer properties, boratrane-containing polymers have yet been explored over half century since its finding.^{1,2)}

To reveal the basic properties of boratrane-containing polymers and their changes along with the structural conversion, we synthesized polymers bearing TEAB group as a representative boratrane unit at the side chain. Several synthetic approaches to the targeted polymers were examined, and some basic properties and reactivities of the obtained polymers with TEAB and/or TEA at the side chains were investigated.³⁾

Keywords : Boratrane, Triethanolamine borate ester, Hydrolysis

高分子側鎖の立体構造は高分子物性を支配する要素の1つである。橋頭位の N–B 間が配位した三環式ホウ酸エステル (ボラトラン) であるトリエタノールアミンボレート (TEAB) は、トリエタノールアミン (TEA) のホウ酸エステル化により選択的に生成し、また加水分解により TEA を再生する。TEAB の剛直なカゴ構造と TEA の柔軟な分岐アルキル構造との劇的かつ選択的な立体構造変換は重合後の高分子改質に有用と考えられるが、TEAB の発見以降^{1,2)} そのような研究例は全く無い。

本研究では、TEAB 含有高分子が示す物性、および TEAB–TEA 分子変換を高分子側鎖で起こした際に誘起される物性変化について明らかにすべく、TEAB および TEA を側鎖に持つポリマーの合成を行った。本発表ではポリマーの複数経路による合成、得られたポリマーの基礎物性、側鎖における TEAB/TEA の反応性、およびその反応に伴うポリマーの物性変化を検討した結果について報告する³⁾。



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温度変化応答性高分子ゲルの高強度化

(山形大院理工¹⁾) ○吉田 一也¹・藤原 尚史¹

Increasing the Strength of Temperature-Responsive Polymer Gels (¹*Graduate School of Science and Engineering, Yamagata University*) ○Kazunari Yoshida,¹ Naofumi Fujiwara¹

Functional hydrogels have been widely studied, too date. Volume phase transition of hydrogels has, in particular, been paid attention¹⁾. Poly(*N*-isopropylacrylamide) (PNIPAm) gel was found to undergo a volume phase transition with temperature change, because the PNIPAm polymer have a lower critical solution temperature (LCST)²⁾. However, the PNIPAm gel is brittle and has a possibility to change into microplastics. Hence, we focused on the high-strength double network structure³⁾ and the eco-friendly and temperature-responsive cellulose derivative having LCST.

In this study, we developed the temperature-responsive hydrogels composed of hydroxypropyl cellulose (HPC) and *N,N*-Dimethylacrylamide (DMAAm). The compression test showed that the maximum pressures of HPC/DMAAm double-network gels and HPC single gels were 0.4 and 0.1 MPa, respectively. Furthermore, the weight of HPC/DMAAm hydrogel was reduced from 1 (initial weight) to 0.7 with an increase in temperature from room temperature to 76 °C. We obtained volume changeable and high-strength hydrogel.

This work was partly supported by Z mechanism Technology Institute Co., Ltd. and JST A-STEP Tryout JPMJTM20BB.

Keywords : *Polymer Hydrogel; Soft Matter; Soft Actuator; Polysaccharide*

機能性高分子ヒドロゲルはこれまでに広く研究がなされている。特に、体積相転移を引き起こすゲルは注目されている¹⁾。ポリ(*N*-イソプロピルアクリルアミド) (PNIPAm)高分子は下限臨界溶液温度(LCST)を示すため、PNIPAm ゲルは温度変化に伴い体積相転移を引き起こすことが見いだされた²⁾。しかし、PNIPAm ゲルはもろく、マイクロプラスチックの原因となる可能性がある。それゆえ、我々は高強度のダブルネットワーク構造と、低環境負荷で LCST を持つ温度応答性のセルロース誘導体に着目した。

本研究において、我々は、ヒドロキシプロピルセルロース(HPC)と *N,N*-ジメチルアクリルアミド(DMAAm)から構成される温度応答性のヒドロゲルを開発した。圧縮試験により、HPC/DMAAm ダブルネットワークゲルの最大圧縮応力が 0.4 MPa で、HPC 単一ネットワークのゲルは 0.1 MPa であった。さらに、室温から 76 °C への温度変化により、HPC/DMAAm の重量は初期値を 1 とした場合、0.7 程度まで減少した。本研究により、体積が可変で高強度なゲルを得た。

本研究の一部は、Z メカニズム技研株式会社と JST A-STEP トライアウト JPMJTM20BB から支援を受けたものである。

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3) J. P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, *Adv. Mater.* **2003**, 15, 1155-1158.

Low-voltage-driven hydrogel actuator using hydrophobic interaction between poly(ethylene glycol) and iodine

(¹Graduate School of Science, Department of Chemistry, The University of Tokyo)

○Hongyao Zhou,¹ Teppei Yamada¹

Keywords: hydrogel, soft actuator, supramolecular complex, redox reaction

Biological muscle responds to the electric stimuli emitted from the nerve cells, and the voltage across the cell membrane is generated by opening/closing of numerous ion channels. Here we present a supramolecular hydrogel actuator which can reversibly swell and shrink in response to external voltage and electrochemical production of redox-active ions. The hydrogel is composed of crosslinked polyethylene glycol (PEG), which selectively captures triiodide anion (I_3^-).^{1,2} When PEG hydrogel adsorbs I_3^- , the hydrogel shrinks because of formation of the hydrophobic PEG–iodine complex, and water is released from the hydrogel (**Figure 1a**).

The hydrophobicity/hydrophilicity of the I_3^-/I^- redox pair can be reversibly switched by applying a small external voltage (< 1 V). The volume and rheology of the hydrogel can be controlled by applying an external current *in situ* (**Figure 1b**). The storage modulus of the gel decreased when I_3^- was reduced to I^- anion (a softer gel), and the value increased again when I^- was oxidized back to I_3^- anion (a harder gel). Further, a force was produced from the hydrogel when the hydrogel swells. PEG–iodine hydrogel actuator only requires a small voltage (0.5 V), and the applications into biomimetic soft robots are highly anticipated.

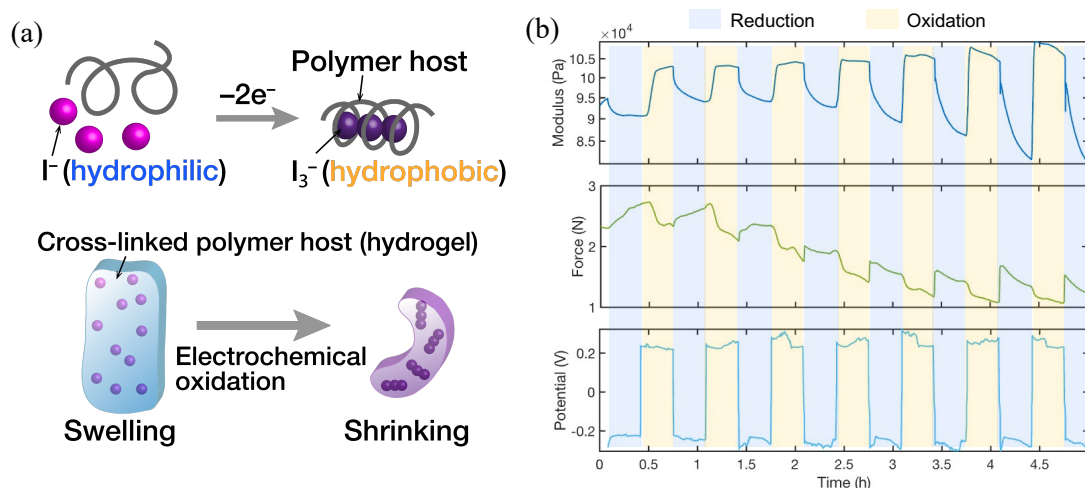


Figure 1. (a) Swelling/shrinking mechanism of PEG–iodine hydrogel actuator (b) In-situ measurement of rheology of the hydrogel under electrochemical cycles at a constant current (0.5 mA cm^{-2}). A force normal to the electrode was generated at the reduction (swelling) step.

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Functional design of polymeric materials based on movable cross-links and application for strain-sensor

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Keywords: Cyclodextrin; Supramolecular elastomer; Host-guest interaction; Movable cross-links; Polymer blending

[Introduction] A design of cross-links affects mechanical properties of polymeric materials. The movable cross-links were found to be formed by the bulk polymerization between cyclodextrin (CD) monomer and main chain monomer^{1,2}. Herein, we designed the materials where movable cross-links connect between dissimilar polymers.

[Result] Movable cross-linked materials knitting dissimilar polymers (PS-CD(20,1)⊃PEA(79)) were obtained by the bulk polymerization of ethyl acrylate (EA) in presence of peracetylated γ CD modified polystyrene. In tensile tests, the polymer blend materials (PS(20)/PEA(80): comparison) exhibited low toughness and heterogeneous domains on the order of 0.1 mm due to low miscibility (**Fig. 1**). PS-CD(20,1)⊃PEA(79) showed a 170 ± 30 times increase in toughness and 1.6 ± 0.3 times increase in the Young's modulus of PS(20)/PEA(80). PS-CD(20,1)⊃PEA(79) were white elastomers without heterogeneous domains on the order of 0.1 mm.

DSC measurements reveals three-phase structure: PEA, PS and a mixed phase (**Fig. 2**). The PEA phase contributes to effective stress dispersion by the movable cross-links on account of its low T_g and high mobility. The PS phase contributes to a high Young's modulus as a hard domain with a high T_g (~ 100 °C). The movable cross-links connect the two phases and result in a mixed phase, enabling each phase to work together. In addition, compositing Ketjenblack EC600JD[®] (carbon-filler) achieved high electrical conductivity (7.5 ± 0.3 S/m) and high strain-sensitivity (gauge factor at 100% strain = 120), enabling application for strain-sensor (**Fig. 3**).

1) R. Ikura, A. Harada, Y. Takashima, et. at. *Macromolecules* **2019**, 52, 6953-6962.

2) R. Ikura, A. Harada, Y. Takashima, et. at. *Polymer* **2020**, 196, 122465.

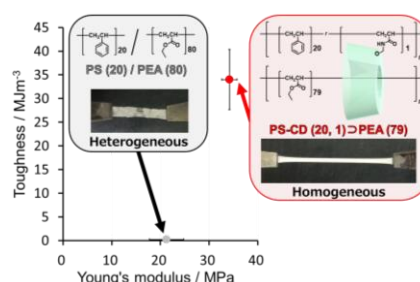


Fig. 1. Photographs and plots of Toughness vs Young's modulus for PS-CD(20,1)⊃PEA(79) and PS(20)/PEA(80).

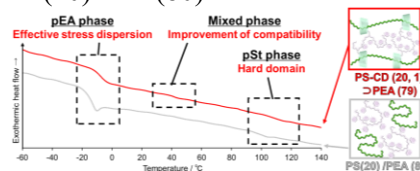


Fig. 2. DSC curves of PS-CD(20,1)⊃PEA(79) and PS(20)/PEA(80).

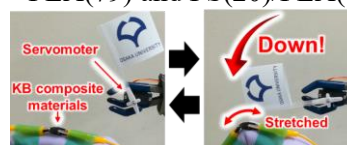


Fig. 3. Photographs of strain-sensor

Synthesis and Functions of Novel Reticular Polymeric Nanomembranes Formed within Unconventional Electric Double Layer

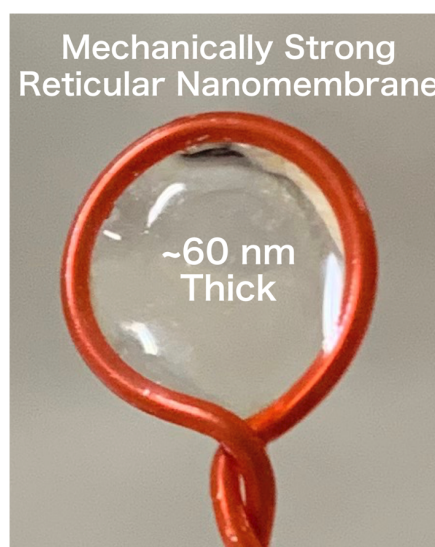
(¹Graduate School of Engineering, The University of Tokyo, ²JST PRESTO, ³RIKEN CEMS)
○Yoshimitsu ITOH,^{1,2} Tengfei FU,¹ Pier-Luc CHAMPAGNE,¹ Takuzo AIDA^{1,3}

Keywords: Nanomembrane; Reticular structure; Electric double layer; Separation membrane

An ultrathin free-standing sheets (<100 nm) known as nanomembranes (NMs) have a large potential to carry extraordinary properties in optical, electronic, and separation applications, which are inaccessible using bulk materials.^{1,2} However, despite the development of fabrication approaches such as mechanical or chemical exfoliation of 2D crystals, layer-by-layer assembly, and interfacial methods, challenges remain in the development of improved synthetic methods allowing efficient and low-cost access to NMs of precise dimensions and high quality.

Here we report a new environmentally friendly polymerization method of exceptional efficiency to prepare large, smooth, and defect-free NMs of tailorable thickness, which is inspired by our previous study on a self-assembled monolayer which responds to a local pH gradient generated by an applied potential on the electrode surface.² It simply requires applying an external potential to an electrochemical cell containing monomers and water alone for as little as 1 minute. The NM formed on the electrode surface was immediately released upon its submersion in pure water, which is difficult to achieve for a NM formed by conventional electropolymerization methods. The resulting polymers possess interconnected voids fostering a reticular framework with the highest Young's Modulus reported thus far for polymeric NMs. This porosity and unrivaled mechanical robustness were brought to bear in the preparation of thin-film composite (TFC) membranes which permitted the characterization of the porous structures by means of nanofiltration, revealing pH-responsive effective pores of ~1 nm capable of separating small organic molecules based on charge and size.³

- 1) Jakšić, Z.; Matovic, J. *Materials* **2010**, *3*, 165.
- 2) Watanabe, H.; Vendamme, R.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 433.
- 3) *Submitted*.



[A202-1pm] 19. Colloid and Interface Chemistry

Chair: Hideyuki Mitomo, Hiroyasu Nishi

Wed. Mar 23, 2022 1:00 PM - 3:40 PM A202 (Online Meeting)

[A202-1pm-01] Room-Temperature Coalescence of Metal Nanoparticles by Ligand Exchange with Tri-*n*-Octylphosphine Oxide and Subsequent Dipping into an Organic Solvent Containing a Sintering Agent

○Soichiro Okada¹, Yoshio Nakahara¹, Mitsuru Watanabe², Toshiyuki Tamai², Yasuyuki Kobayashi², Setsuko Yajima¹ (1. Faculty of Systems Engineering, Wakayama University, 2. Osaka Research Institute of Industrial Science and Technology)

1:00 PM - 1:20 PM

[A202-1pm-02] Platinum-Group-Metal High-Entropy-Alloy Nanoparticles

○DONGSHUANG WU¹, Kohei Kusada¹, Hiroshi Kitagawa¹ (1. Kyoto university)

1:20 PM - 1:40 PM

[A202-1pm-03] The effects of Hofmeister series of salts for the aggregation of polyion complex particles composed of polysaccharides

○Makoto Yamazaki¹, Makoto Yabe², Kazutoshi Iijima¹ (1. Yokohama National Univ., 2. Mol Processing)

1:40 PM - 2:00 PM

[A202-1pm-04] Generation of Hydroxyl radical by Ultrasound-Excited Titanium Dioxide Nanoparticles - Gold Nanocluster Loading Effect-

○Hideya Kawasaki¹, Atsuya Ikeda³, Ken Yamamoto² (1. Kansai University, 2. Kansai University, 3. Kansai University)

2:00 PM - 2:20 PM

[A202-1pm-05] Preparation of smart core-shell gel particles having hydrophilic core and temperature-responsive shell

○Akifumi Kawamura^{1,2}, Mitsuhide Sasaoka¹, Takashi Miyata^{1,2} (1. Fac. Chem. Mater. Bioeng., Kansai University, 2. ORDIST, Kansai University)

2:20 PM - 2:40 PM

[A202-1pm-06] Role of Surface Ligand Structure in the Colloidal Stability of TiO₂ Nanoparticles

○Shohei Yamashita¹, Hidehiro Kamiya¹, Yohei Okada² (1. Tokyo University of Agriculture and Technology, 2. Tokyo University of Agriculture and Technology)

2:40 PM - 3:00 PM

[A202-1pm-07] Acid-controlled reactivities of ligand-protected gold nanoclusters

○Wataru Suzuki¹, Ryo Takahata¹, Toshiharu Teranishi¹ (1. Institute for Chemical Research, Kyoto University)

3:00 PM - 3:20 PM

[A202-1pm-08] Type I collagen-stabilized gold nanoparticles produced by pulsed laser ablation in liquids and γ -ray irradiation

○Nazgul Assan¹, Tomoyuki Suezawa, Satoshi Seino¹, Yuta Uetake^{1,2}, Michiya Matsusaki^{1,2}, Hidehiro Sakurai^{1,2} (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

3:20 PM - 3:40 PM

Room-temperature Coalescence of Metal Nanoparticles by Ligand Exchange with Tri-*n*-Octylphosphine Oxide and Subsequent Dipping into an Organic Solvent Containing a Sintering Agent

(¹Faculty of Systems Engineering, Wakayama University, ²Osaka Research Institute of Industrial Science and Technology) ○ Soichiro Okada,¹ Yoshio Nakahara,¹ Mitsuru Watanabe,² Toshiyuki Tamai,² Yasuyuki Kobayashi,² Setsuko Yajima¹

Keywords: Metal Nanoparticle; Room-temperature Coalescence; Electrical Resistivity; Catalytic Activity; Tri-*n*-octylphosphine Oxide

Room-temperature (RT) coalescence of metal nanoparticles (NPs) is the remarkable technology in various fields such as flexible electronics and heterogeneous catalysts. In the RT coalescence of NPs, the metal surface is normally capped by ligands with a long alkyl chain to avoid their aggregation but the ligands must be effectively removed after the immobilization of NPs on the substrate. In this study, the RT coalescence of metal (Ag, Pd) NPs (diameter: ~6 nm) prepared by ligand exchange with tri-*n*-octylphosphine oxide (TOPO) was conducted using sintering agents, which promote the desorption of ligands from the metal surface.

The TOPO paste of Ag NPs was cast on the substrate (PET and glass) and they coalesced at RT by dipping into methanol containing cetyltrimethylammonium chloride (CTAC) as a sintering agent (Figure 1a). The resistivity of the obtained Ag thin film was $3.8 \times 10^{-5} \Omega \text{ m}$. The SEM image of the Ag thin film indicated that most of Ag NPs coalesced after the RT sintering (Figure 1b). In addition, porous Pd structures were obtained from the TOPO paste of Pd NPs by dipping into methanol containing KOH as a sintering agent. Their catalytic activities in the Suzuki coupling reaction increased with the increase of the KOH concentration in the sintering process (Figure 2).

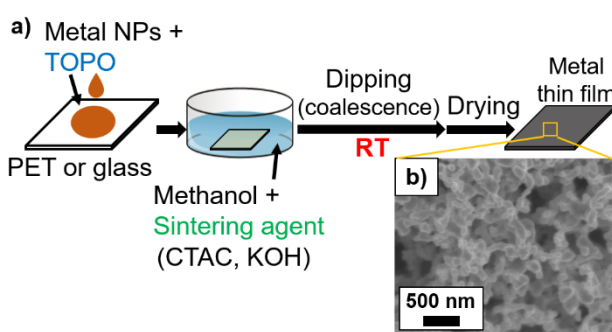


Figure 1. a) General procedure of RT coalescence and b) SEM image of the Ag thin film obtained by dipping into methanol containing CTAC.

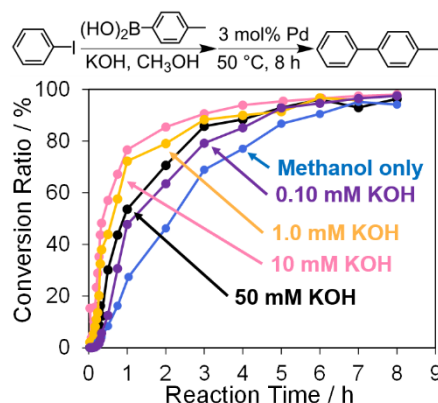


Figure 2. Conversion ratio against reaction time in the Suzuki reaction in the absence and presence of porous Pd structures prepared by various KOH concentrations.

Platinum-Group-Metal High-Entropy-Alloy Nanoparticles

(¹Graduate School of Science, Kyoto University) ○Dongshuang Wu,¹ Kohei Kusada,¹ Hiroshi Kitagawa¹

Keywords: *High-entropy alloy; platinum-group metals; nanoparticles; electrochemistry; catalysis*

The platinum group metals (PGMs) are six neighboring elements, i.e., ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt), in the periodic table of the elements, which are crucial to our daily lives, from household items to industrial catalysis. One in four of the goods manufactured today either contain PGMs or are produced through processes promoted by PGM catalysts.¹ Each PGM can efficiently promote unique reactions, and therefore, alloying PGMs would create ideal catalysts for complex or multi-step reactions that involve several reactants and intermediates.

High-entropy alloys (HEAs), which are defined as at least five elements in near-equiatomic concentrations (recently reported as 5–35 at.% for each constituent),² boost the discovery of new materials and phenomena, especially in structural bulk materials. However, the development of HEA nanoparticles (NPs) is limited by the synthetic method, which mainly require special experimental apparatuses.³ Here, we report the first example of HEA NPs of all six PGMs (denoted as **PGM-HEA NPs**) using a facile wet chemical synthesis (**Figure A**) and demonstrate that PGM-HEA NPs efficiently promote the ethanol oxidation reaction (EOR) with complex 12-electron/proton transfer processes. **PGM-HEA NPs** shows higher activity than the commercial catalysts. Remarkably, **PGM-HEA NPs** record more than 1.5 times higher mass activity than the most active catalyst to date. The valence band spectrum of HEA NPs is featureless, which suggests a great variety of adsorption sites on their surfaces. Our findings pave the way for promoting complex or multi-step reactions that are seldom realized by mono- or bi-metallic catalysts.

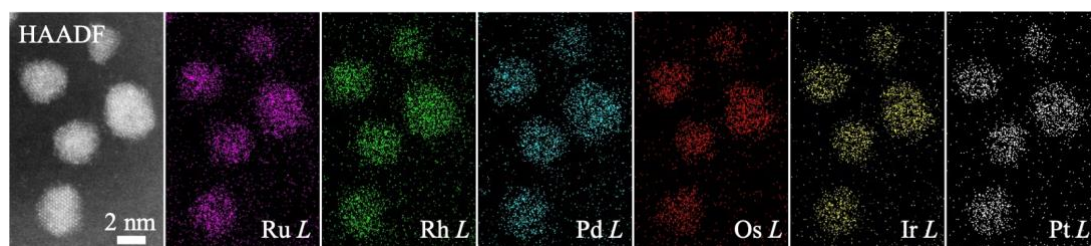


Figure A. HAADF-STEM image of the **PGM-HEA NPs** and the corresponding EDX maps using the *L*-line characteristic X-ray from each element.

1) Thermofisher homepage. <https://www.thermofisher.com/blog/metals/platinum-group-metals-at-work-industrial-applications/>. 2) a) J. Yeh et al., *Metall. Mater. Trans. A*, **2004**, *35*, 2533. b) E. George et al., *Nat. Rev. Mater.*, **2019**, *4*, 515. 3) Y. Yao et al., *Science* **2018**, *359*, 1489.

ホフマイスター系列が多糖ポリイオンコンプレックス粒子の凝集に与える影響の解析

(横国大院¹・モルプロセッシング²) ○山崎 誠¹・矢部 誠²・飯島 一智¹

The effects of Hofmeister series for the aggregation of polyion complex particles composed of polysaccharides (¹*Yokohama National University*, ²*Mol processing*) ○Makoto Yamazaki,¹ Makoto Yabe,² Kazutoshi Iijima¹

Polysaccharide polyion complex (PIC) particles aggregated in salts solution. In this study, the effects of the Hofmeister series, which is an ionic permutation of the precipitation-inducing ability of polymers, on the aggregation behavior of PIC particles were investigated (Fig. 1). By adding solutions of six kinds of salts (NaCl, NaBr, NaNO₃, NaI, NaClO₄, and NaSCN) to PIC particle dispersions composed of chitosan (CHI) and chondroitin sulfate C (CS), PIC particles were aggregated in a concentration-dependent manner. In particular, the chaotropic anion promoted the aggregation of PIC particles. Dynamic light scattering and zeta potential measurements indicated that salts decrease the surface charge of PIC particles and increase their particle diameter, suggesting that the neutralization effect of salts contributes to the aggregation of PIC particles. The shielding effects caused by ions were also observed between sugar chains by using molecular dynamics simulation with oligosaccharides.

Keywords : Polysaccharides; Polyion complexes; Colloidal particles; Hofmeister series; Molecular dynamics

多糖のポリイオンコンプレックス (PIC) 粒子はリン酸緩衝生理食塩水などの塩存在下で凝集する。本研究では、塩による PIC 粒子の凝集挙動の解明に向け、高分子の沈殿誘起能力のイオン順列 (ホフマイスター系列) が PIC 粒子の凝集に与える影響を解析した (Fig. 1)。

キトサン (CHI) およびコンドロイチン硫酸 C (CS) から構成される PIC 粒子分散液に、6 種の塩溶液 (NaCl, NaBr, NaNO₃, NaI, NaClO₄, NaSCN) をそれぞれ加えた結果、塩濃度依存的に PIC 粒子が凝集することが確認された。特に、カオトロピック性の高いアニオンは PIC 粒子の凝集を促進することが示された。動的光散乱法およびゼータ電位測定より、塩を加えることで PIC 粒子の表面電荷が低下し、粒径が増加した。このことから、塩が PIC 粒子の表面電荷を中和することで、凝集を誘起することが示された。さらに、オリゴ糖を用いた分子動力学シミュレーションから、イオンによる遮蔽効果が糖鎖間に生じることが確認された。

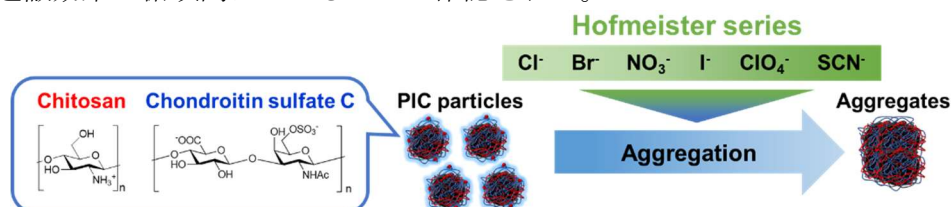


Fig. 1 The schematic illustration of the concept of this research.

超音波励起された酸化チタンナノ粒子によるヒドロラジカル生成 ～金ナノクラスター担持効果～

(関大化学生命工¹・関大システム理工²) ○川崎 英也¹・池田 篤哉¹・山本 健²
Generation of Hydroxyl radical by Ultrasound-Excited Titanium Dioxide Nanoparticles - Gold Nanocluster Loading Effect- (¹*Faculty of Chemistry, Materials and Bioengineering, Kansai University*, ²*Faculty of Engineering Science, Kansai University*) ○Hideya Kawasaki,¹ Atsuya Ikeda,¹ Ken Yamamoto²

In this study, we first investigated the sonocatalytic activity of TiO₂-supported Au nanoclusters (NCs) (Au NCs/TiO₂) by monitoring the production of hydroxyl radicals (•OH) under ultrasonication conditions. The deposition of Au₁₄₄ NCs on TiO₂ NPs was found to enhance sonocatalytic activity for •OH production by approximately a factor of 2. Electron-hole recombination in ultrasonically excited TiO₂ NPs is suppressed by Au₁₄₄ NCs acting as an electron trap; this charge separation resulted in enhanced •OH production. The sonocatalytic action that forms electron-hole pairs on the Au₁₄₄/TiO₂ catalyst is suggested to be due to both heat and sonoluminescence from the implosive collapse of cavitation bubbles.

Keywords : Gold nanoclusters; Titanium dioxide; Sono-Catalysis; reactive oxygen species

金ナノクラスター (Au NCs) とは、粒径 1-2 nm の数個から数百個の金原子集合体である。Au NCs は金属錯体や粒径 3 nm 以上の金ナノ粒子とは異なるユニークな物理化学的特性 (光学, 電子, 磁気, 触媒作用) を示す。その中で Au NCs 触媒は, その高い活性, 選択性, 安定性から有望な金属触媒として注目されている。Au NCs はその高い比表面積と離散化した電子エネルギー準位から, 様々な化学反応に対して高い触媒活性を示すことが報告されている。我々は Au NCs の光増感作用 (光励起) 及び音増感作用 (超音波励起) を見出し, Au NCs の Photodynamic (PDT) や Sonodynamic Therapy (SDT) への展開を進めている [1]。他方, 光触媒として知られている二酸化チタン (TiO₂) は強い酸化力特性から PDT や SDT を含む様々な分野で利用されており, TiO₂ に超音波を照射するとヒドロキシルラジカル (•OH) の生成が促進されることが知られている。この •OH 生成増大には, TiO₂ 内で生成する励起電子と正孔の再結合を抑制し電荷分離を促進することが有効である。そこで本研究では AuNCs を担持した TiO₂ ナノ粒子 (Au NCs/TiO₂ NPs) において, 超音波照射下での •OH 生成に関する AuNCs 担持効果を検討した。その結果, AuNCs を TiO₂ NPs へ担持することで •OH 生成量が増大し, その促進効果は AuNCs の構成原子数 (金 144 量体 (Au₁₄₄ NCs) と金 25 量体 (Au₂₅ NCs) の違い) に強く依存することを見出した [2]

- 1) T. Kawawaki, Y. Negishi, H. Kawasaki, Photo/electrocatalysis and photosensitization using metal nanoclusters for green energy and medical applications, *Nanoscale Advances*, 2,17(2020).
- 2) K. Kawamura, A. Ikeda, A. Inui, K. Yamamoto, H. Kawasaki, TiO₂-supported Au₁₄₄ nanoclusters for enhanced sonocatalytic performance, *Journal of Chemical Physics*, 155, 124702(2021).

親水性コアと温度応答性シェルからなるスマートコア-シェルゲル微粒子の調製

(¹関西大化学生命工・²関西大 ORDIST) ○河村 暁文^{1,2}・笹岡 洸秀¹・宮田 隆志^{1,2}
Preparation of Smart Core-shell Gel Particles Having Hydrophilic Core and Temperature-responsive Shell (¹*Faculty of Chemistry, Materials and Bioengineering and* ²*ORDIST, Kansai University*) ○Akifumi Kawamura,^{1,2} Mitsuhide Sasaoka,¹ Takashi Miyata,^{1,2}

The block copolymer composed of poly[oligo(ethylene glycol) methacrylate-*co*-2-(2'-methoxyethoxy) ethyl methacrylate] and poly(2-methacryloxyethyl phosphorylcholine) blocks was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization. Submicron-scale water-in-oil (W/O) emulsions were formed in the presence of resulting P(OEGMA-*co*-MEO₂MA)-*b*-PMPC in water-chloroform two phase system. The inverse miniemulsion RAFT copolymerization of MPC and *N,N'*-methylenebisacrylamide proceeded from P(OEGMA-*co*-MEO₂MA)-*b*-PMPC to obtain core-shell type gel particles composed of PMPC core and P(OEGMA-*co*-MEO₂MA) shell. The transmittance of the gel particle dispersion decreased drastically above 40 °C owing to the phase transition of P(OEGMA-*co*-MEO₂MA) shell.

Keywords : Core-shell gel particle; Temperature-responsiveness; W/O emulsion; RAFT polymerization; Block copolymer

pH や温度などの外部刺激に応答して表面特性が変化する刺激応答性コア-シェルゲル微粒子は、塗料や接着、医療などへの応用が検討されている。本研究では、従来のシード乳化重合などとは異なり、poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) ブロックと poly[oligo(ethylene glycol) methacrylate-*co*-2-(2'-methoxyethoxy) ethyl methacrylate] (P(OEGMA-*co*-MEO₂MA)) ブロックとを有する水溶性ブロック共重合体により安定化された Water-in-Oil (W/O) エマルションを用いた逆ミニエマルション可逆的付加開裂連鎖移動 (RAFT) 重合により、MPC と *N,N'*-methylenebisacrylamide とを共重合することにより温度応答性コア-シェルゲル微粒子を調製した。得られたゲル微粒子の粒径は約 270 nm であった。また、濁度測定によりゲル微粒子分散液の温度応答挙動を評価したところ、ゲル微粒子分散液の透過率は 40 °C 付近を境に大きく減少した (Fig. 1)。したがって、得られたゲル微粒子はコアに PMPC、シェルに P(OEGMA-*co*-MEO₂MA) を有するコア-シェル構造であることが示唆された。

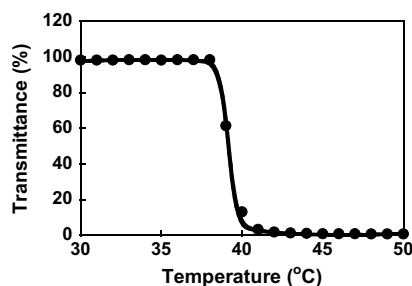


Fig. 1. Change in transmittance (650 nm) of the PMPC gel particle dispersion as a function of temperature.

TiO₂ ナノ粒子の表面リガンド構造がコロイド安定性に与える影響

(東農工大) ○山下 翔平・神谷 秀博・岡田 洋平

Role of Surface Ligand Structure in the Colloidal Stability of TiO₂ Nanoparticles (*Tokyo University of Agriculture and Technology*) ○Shohei Yamashita, Hidehiro Kamiya, Yohei Okada

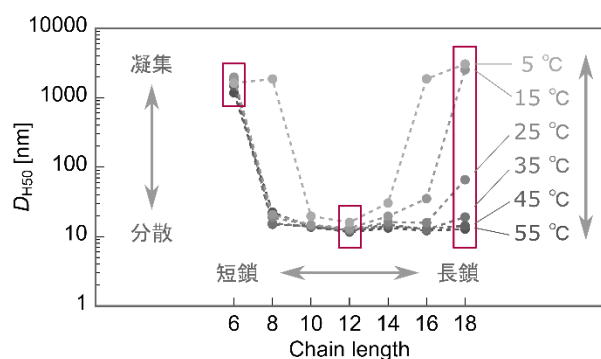
Nanoparticle-ligand complexes, which are nanoparticles coated with organic molecules, are expected to be applied in various fields because of their processability and size-dependent properties. One of the roles of ligands is to ensure colloidal stability in solvents, but the length of the *n*-alkyl chain of the ligand required to enhance colloidal stability has been a subject of controversy, because experimental facts inconsistent with classical colloid theory have been reported in recent years.¹

In this study, sub-10 nm TiO₂ nanoparticles capped with *n*-alkylphosphonates having various chain lengths are synthesized by the solvothermal method² and their dispersibility in organic solvents are evaluated. The figure describes the results of hydrodynamic diameter measurements in toluene. The highest dispersibility was obtained in the case of carbon 12, and the hydrodynamic diameter varied with solution temperature.

Keywords : Nanoparticle, Colloidal stability, Organic ligands

ナノ粒子を有機分子で被覆したナノ粒子ーリガンド複合体は、処理加工性とサイズ依存的な特性によって多くの分野への応用が期待されている。リガンドの役割のひとつに溶媒中でのコロイド安定性の確保があるが、コロイド安定性を高めるために求められるリガンドの *n*-アルキル鎖の長さについては、古典的なコロイド理論と一致しない実験事実が近年報告されており、議論の的となっている。¹

本研究では、ソルボサーマル法²を用いて合成したシングルナノサイズの酸化チタンナノ粒子に様々な鎖長を持つ *n*-アルキルホスホン酸を修飾し、各粒子の有機溶媒中での分散性を評価した。図にトルエン中での流体力学的径の測定結果を示す。炭素数 12 の場合に最も高い分散性が得られたことに加え、溶液温度によっても流体力学的径が大きく変化することがわかった。



(1) Kraus, T. *et al. ACS Nano* **2018**, *12*, 5969–5977.

(2) Do, T.-O. *et al. ACS Nano* **2009**, *3*, 3737–3743.

酸による配位子保護金クラスターの反応性制御

(京大化研) ○鈴木 航・高畑 遼・寺西 利治

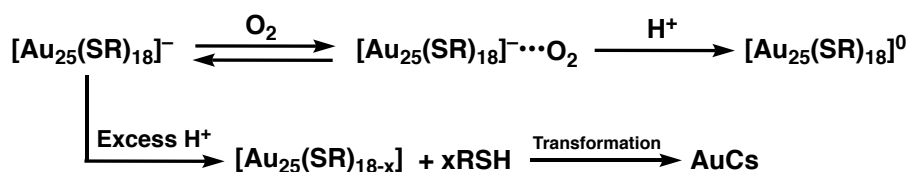
Acid-controlled reactivities of ligand-protected gold nanoclusters (*Institute for Chemical Research, Kyoto University*) ○Wataru Suzuki, Ryo Takahata, Toshiharu Teranishi

It is well known that thiolate-protected Au₂₅ cluster anions ([Au₂₅(SR)₁₈][−]) have attracted attention due to their unique reactivities and catalytic activities. In this work, we investigated the reactivities of [Au₂₅(SR)₁₈][−] in the presence of protons. Air-oxidation of [Au₂₅(SR)₁₈][−] to form neutral Au₂₅ clusters ([Au₂₅(SR)₁₈]⁰) were accelerated by addition of a proton source like trifluoroacetic acid in THF. Kinetic analysis revealed the pre-equilibrium of the interaction between [Au₂₅(SR)₁₈][−] and O₂ before air-oxidation. Thiolate ligands (SR[−]) on [Au₂₅(SR)₁₈][−] controlled the redox potential of the Au₂₅ cluster anions, which was the main controlling factor on the above reactivity. Moreover, in non-polar solvent like toluene, increasing the amount of protons caused protonation-induced elimination of a thiolate ligand in [Au₂₅(SR)₁₈][−].

Keywords : Gold nanocluster, Oxygen reduction reaction, Protecting ligands, Protonation

配位子保護金クラスターは、金属錯体やナノ粒子とは異なる特異な反応性を示すことから興味を持たれている¹⁾。しかしながら、基質との反応が起こるクラスター表面・界面での化学現象に対する知見は乏しく、特に反応機構は未解明な点が多い。本研究では、チオラート保護 Au₂₅ クラスターアニオン ([Au₂₅(SR)₁₈][−]) をモデルとして酸性条件下における反応性を検討し、反応メカニズムの解明を目指した。

酸素存在下 THF 中において、酸としてトリフルオロ酢酸 (TFA) を添加したところ、[Au₂₅(SR)₁₈][−] は空気酸化され、1 電子酸化体 ([Au₂₅(SR)₁₈]⁰) が生成した。この反応の見かけの速度定数が、酸素濃度に対して飽和挙動を示したことから、[Au₂₅(SR)₁₈][−] と酸素分子間の前平衡過程の存在が示唆された (Scheme 1)。また、この酸化反応の速度は保護配位子によって異なり、配位子の種類に依存した [Au₂₅(SR)₁₈][−] の酸化還元電位の違いが、反応性を決める主支配因子であることがわかった。一方、より極性の低いトルエンを溶媒とした場合、[Au₂₅(SR)₁₈][−] の空気酸化反応と競合して、TFA によるチオラート配位子のプロトン化に起因した配位子脱離反応が起こり、不可逆的に別のクラスター (AuCs) へと変換されることがわかった (Scheme 1)。この結果より、酸化反応では、保護配位子が脱離することなく [Au₂₅(SR)₁₈][−] と酸素分子が相互作用していることが示唆された。



Scheme 1. [Au₂₅(SR)₁₈][−] の空気酸化反応の推定反応スキーム

1) R. Jin and co-workers, *Chem. Rev.* **2021**, 121, 567. T. Tsukuda and co-workers, *Acc. Chem. Res.* **2014**, 47, 816.

Type I collagen-stabilized gold nanoparticles produced by pulsed laser ablation in liquids and γ -ray irradiation

(¹Grad. Sch. Eng., Osaka Univ., ²ICS-OTRI, Osaka Univ.) ○ Nazgul Assan¹, Tomoyuki Suezawa¹, Satoshi Seino¹, Yuta Uetake^{1,2}, Michiya Matsusaki¹, Hidehiro Sakurai^{1,2}

Keywords: Gold nanoparticle; type I collagen; pulsed laser ablation in liquids; γ -ray irradiation; microchip laser

Peptides and/or gelatin have attracted considerable attention as unique matrices to stabilize metal nanoparticles (NPs). These metal NPs excel in their colloidal stability and enhanced biocompatibility¹. In this study, we focused on type I collagen (Col^{T1}) as a unique stabilizing matrix, since it has distinctive chemical structure; triple helix structure and exceptional physical property as thermal sensitivity^{2,3}.

AuNPs stabilized by Col^{T1} (Au:Col^{T1}) with the particle size of 2.2 ± 1.3 nm were successfully prepared in 1xPBS by ablating target bulk Au (pulsed laser ablation in liquids-PLAL) within 1 h using a microchip laser (1064 nm, Nd:YAG, 160 mW) (Figure 1A).⁴ The triple-helix structure of Col^{T1} was maintained after laser irradiation by circular dichroism spectroscopy. Likewise, HAuCl₄·3H₂O was added to Col^{T1} in 1xPBS to form metal cross-linked gel, which was later irradiated by γ -ray (20 kGy) and produced uniformly distributed AuNPs with the particle size of 4.3 ± 1.3 nm (Figure 1B). In

addition, the thus-obtained gel from HAuCl₄, showed improved viscoelasticity compared with the pristine metal cross-linked collagen gels. SEM images of the irradiated sample showed that the morphology of collagen changed after γ -ray irradiation.

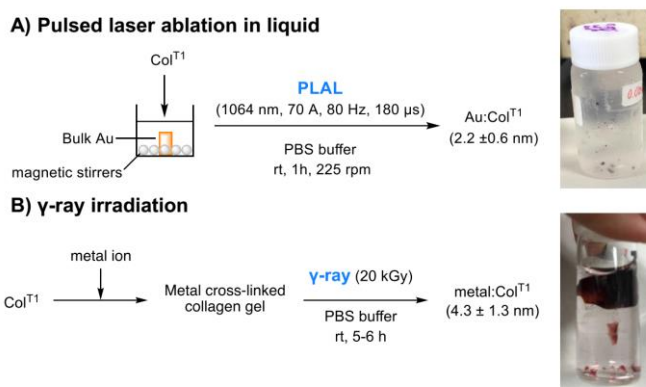


Figure 1 Preparation of Au:ColT1 by (A) PLAL and (B) γ -ray irradiation.

1) J.-J. Zhang, M.-M. Gu, T.-T. Zheng, J.-J. Zhu, *Anal. Chem.* **2009**, *81*, 6641. 2) N. J. Greenfield, *Nature Protoc.* **2006**, *1*, 2891. 3) J. R. Macdonald, H. P. Bächinger, *J. Biol. Chem.* **2001**, *276*, 25399. 4) H. H. Lim, T. Taira, *Opt. Express.* **2017**, *25*, 6302.

[A202-1vn] 19. Colloid and Interface Chemistry

Chair: Yuta Uetake, Masashi Mizukami

Wed. Mar 23, 2022 4:10 PM - 6:50 PM A202 (Online Meeting)

[A202-1vn-01] Solvent effects on pulsed laser ablation in liquids (PLAL) using microchip laser for preparation of gold nanoparticles

○Barana Sandakelum Hettiarachchi¹, Yuta Uetake^{1,2}, Yumi Yakiyama^{1,2}, Hidehiro Sakurai^{1,2} (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

4:10 PM - 4:30 PM

[A202-1vn-02] Site-Selective Introduction of Metal Oxide Co-catalysts through Plasmon-Induced Charge Separation and Galvanic Replacement

○Hiroyasu Nishi¹, Kangseok Kim¹, Tetsu Tatsuma¹ (1. The University of Tokyo)

4:30 PM - 4:50 PM

[A202-1vn-03] Liquid-Crystalline Organic-Inorganic Hybrid Dendron-Modified Fe₃O₄ Nanoparticles: Characterization of the Self-organized Structure

○Takehiro Yachi¹, Masaki Matsubara^{1,2}, Xiangbing Zeng³, Goran Ungar³, Atsushi Muramatsu¹, Kanie Kiyoshi¹ (1. Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, 2. National Institute of Technology, Sendai College, 3. The University of Sheffield)

4:50 PM - 5:10 PM

[A202-1vn-04] Construction of Ultra-thin Pt Layers on Ni Substrates for Highly Efficient Oxygen Reduction Reaction Catalysts

○Dilnigeer Dilixiati¹, Yuka Araki¹, Toshihiro Kondo¹ (1. Ochanomizu University)

5:10 PM - 5:30 PM

[A202-1vn-05] Validation of a quantitative analysis for intramolecular vibrations of electrolytes in the heterophase system by the near-infrared spectroscopy

○Jingchao Xu¹, Hideshi MAKI¹, Minoru MIZUHATA^{1,2} (1. Kobe University, 2. Jagiellonian University)

5:30 PM - 5:50 PM

[A202-1vn-06] Synthesis and characterization of porous boron nitride having specific gas adsorption properties

○Takahiro Ohkubo¹, Jun Kimura¹, Kai Egami¹, Masato Yamashita¹, Yasushige Kuroda¹ (1. Okayama Univ.)

5:50 PM - 6:10 PM

[A202-1vn-07] Direct Determination of Structure of Concentrated Polymer Brushes by Surface Forces Measurement

○Yutaka Takahashi¹, Masashi Mizukami¹, Yoshinobu Tsujii², Kazue Kurihara¹ (1. Tohoku University, 2. Kyoto University)

6:10 PM - 6:30 PM

[A202-1vn-08] Development of a long-term stabilization method of chlorosilane in air and its application to superhydrophobic materials with self-

healing ability by the reconstruction of surface morphologies

○Satoshi Nakamura¹, Atsushi Hozumi¹ (1. AIST)

6:30 PM - 6:50 PM

Solvent effects on pulsed laser ablation in liquid (PLAL) using microchip laser for preparation of gold nanoparticles

(¹Grad. Sch. Eng., Osaka Univ., ²ICS-OTRI, Osaka Univ.)

○Hettiarachchi Barana Sandakelum,¹ Yuta Uetake,^{1,2} Yumi Yakiyama,^{1,2} Hidehiro Sakurai^{1,2}

Keywords: Pulsed Laser Ablation in Liquids; Microchip Laser; Gold Nanoparticles; Solvent Effect; Graphitic Carbon

Pulsed laser ablation in liquids (PLAL) is one of the promising techniques in the field of metal nanoparticles (NPs) synthesis. It is based on the use of a liquid-phase synthesis route of NPs with the assistance of the pulsed laser ablation process. So far, attempts to prepare polymer-stabilized gold nanoparticle by PLAL have been investigated using conventional large laser system. The cutting-edge discovery of microchip laser system by Taira et al. introduced the new era to utilize the laser technique in more convenient manner.¹ While it is well known that gold nanoparticles can be ablated from bulk gold in large laser systems, laser ablation using low-power microchip laser systems has not been explored.

In this study, we report gold nanoparticles (AuNPs) stabilized by polymers, such as poly(*N*-vinyl-2-pyrrolidone) (PVP) and polystyrene, are prepared by PLAL method using microchip laser. By increasing PVP concentration diminishes the ablation rate due to the increase in solution viscosity (Fig. 1). The average size of the AuNPs stabilized by polystyrene highly depends on the solvent. It is attributed to the aromatic solvents decomposition such as toluene occur under the laser irradiation and makes graphitic carbon (GC) mentioned by Meneghetti's previous approach.² GC layer thickness could be reduced by optimizing the laser power and polymer concentration. In which high polymer concentration absorb heat from the generated NPs thereby reduce the solvents decomposition and GC layer thickness.

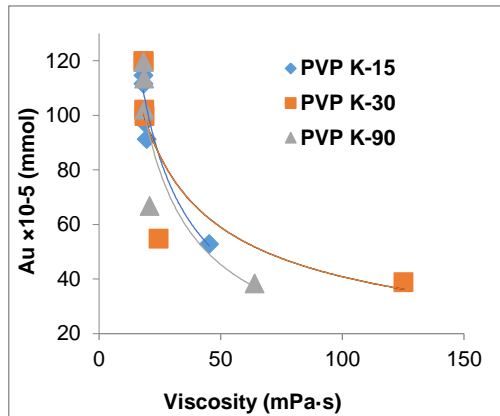


Fig 1. Viscosity effect on Au NP ablation efficiency.

1) H. Lim, T. Taira, *Opt. Express.* **2017**, 25, 6302.

2) V. Amendola, G. A. Rizzi, S. Polizzi, M. Meneghetti, *J. Phys. Chem. B* **2005**, 109, 23125.

プラズモン誘起電荷分離とガルバニック置換による金属酸化物助触媒の部位選択的導入

(東大生研) ○西 弘泰・キム カンソク・立間 徹

Site-Selective Introduction of Metal Oxide Co-catalysts through Plasmon-Induced Charge Separation and Galvanic Replacement (*Institute of Industrial Science, The University of Tokyo*)

○Hiroyasu Nishi, Kangseok Kim, Tetsu Tatsuma

PbO₂ was introduced site-selectively onto the top face of Au nanocubes (AuNCs), the interfacial region between the AuNCs and TiO₂, or the entire AuNC surface via plasmon-induced charge separation (PICS), and was replaced with MnO₂ as a co-catalyst on the basis of galvanic replacement. Their PICS efficiencies depending on the reaction site were investigated. **Keywords** : Plasmonic Photocatalyst; Plasmon-Induced Charge Separation; Gold Nanocube; Galvanic Replacement; MnO₂ Co-catalyst

当研究室では、プラズモン誘起電荷分離 (PICS)¹ によって金ナノ粒子上で駆動される PbO₂ の酸化析出反応が、局在電場の強い部分で部位選択的に起こることを利用し、様々なナノ構造を作製してきた²。しかしながら、現状では部位選択的に導入できる物質は PbO₂ にほぼ限られている³、本研究では、PICS に基づいて部位選択的に導入した PbO₂ を、助触媒としての効果が期待できる MnO₂ にガルバニック置換反応によって変換する手法を確立するとともに、助触媒の導入部位と光電気化学特性との関係を調べた

既報⁴と同様に、TiO₂ 電極上に担持した金ナノキューブ (AuNC) の上面付近、TiO₂ と AuNC の界面付近、AuNC の表面全体に PbO₂ を導入した 3 種類の構造を作製した (図 1a-c)。これらの電極を Mn²⁺ イオンを含む水溶液に浸漬すると、析出物の形態が変化した (図 1d-f)。X 線光電子分光などの結果から、PbO₂ の大部分が MnO₂ に置換されていることが示された。MnO₂ を導入した電極の PICS に基づく短絡光電流応答を測定したところ、AuNC の上面付近に MnO₂ を導入した電極 (図 1d) では、助触媒効果による内部量子収率の向上が見られた。

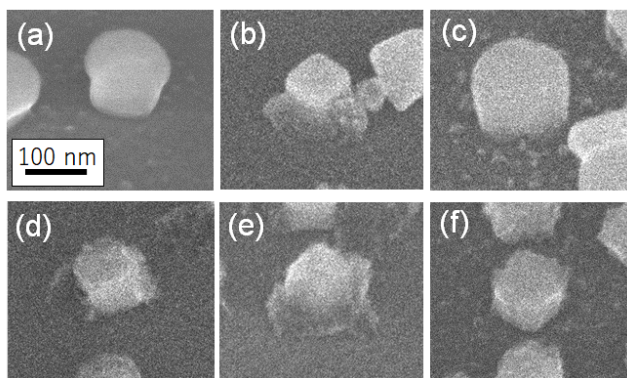


Figure 1. (a-c) PbO₂ を部位選択的に導入した AuNC と (d-f) MnO₂ に置換後の走査型電子顕微鏡像。

1) Y. Tian, T. Tatsuma, *J. Am. Chem. Soc.* **2005**, *127*, 7632. 2) T. Tatsuma, H. Nishi, *Nanoscale Horiz.* **2020**, *5*, 597. 3) R. Ogata, H. Nishi, T. Ishida, T. Tatsuma, *Nanoscale* **2021**, *13*, 681. 4) H. Nishi, M. Sakamoto, T. Tatsuma, *Chem. Commun.* **2018**, *54*, 11741.

Liquid-Crystalline Organic-Inorganic Hybrid Dendron-Modified Fe₃O₄ Nanoparticles: Characterization of the Self-organized Structure

(¹*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,*

²*Department of general Engineering, National Institute of Technology, Sendai College,*

³*Department of Materials Science and Engineering, The University of Sheffield)*

○ Takehiro Yachi,¹ Masaki Matsubara,^{1,2} Xiangbing Zeng,³ Goran Ungar,³ Atsushi Muramatsu,¹ Kiyoshi Kanie¹

Keywords: self-organization; magnetic nanoparticle; liquid-crystalline; organic-inorganic hybrid

Magnetic nanoparticles (NPs) exhibit the interparticle-dependent magnetic properties because of strong magnetic interactions from adjacent particles. Therefore, a dynamic control of the magnetic nanoparticles-based array structure is one of the promising techniques that allows us to control the magnetic properties. However, it is still a challenging problem due to strong magnetic interaction between particles. In our previous studies, we have demonstrated that surface modification with liquid-crystalline dendron molecule is a powerful tool to control NP-based structure, since it allows us to introduce the dynamic property of dendrons to inorganic NPs.^{1,2)}

In the present study, the dendron-modified Fe₃O₄ NPs have been developed to control the array structure based on magnetic NPs. A typical synthetic procedure is as follows: Firstly, COOH-modified Fe₃O₄ NPs were prepared by a ligand exchange reaction with a terminal COOH-substituted phosphonic acid.³⁾ Then, dendron modification was carried out by an amidation reaction between the COOH group on the particle surface and an amino-substituted dendron molecule. The structural analysis was performed by grazing-incidence small angle X-ray scattering (SAXS) for resulting particles. The temperature-dependent SAXS profiles of the dendron-modified Fe₃O₄ NPs in **Figure 1** revealed that array structure was changed dynamically due to thermal phase transition and the structure formed at 170 °C could be assigned as BCC structure. The result indicated that dendron modification enables us to control the array structure based on magnetic NPs.

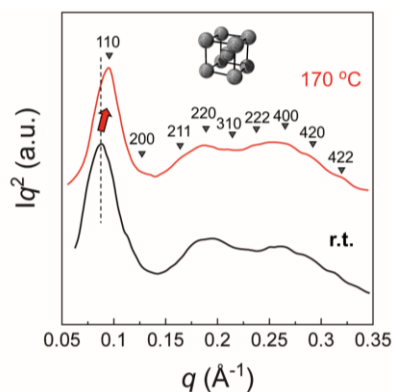


Figure 1. SAXS profiles of dendron-modified Fe₃O₄ NPs at different temperatures.

1) K. Kanie, M. Matsubara, X. Zheng, F. Liu, G. Ungar, H. Nakamura, A. Muramatsu, *J. Am. Chem. Soc.*, **2012**, 134, 808. 2) M. Matsubara, W. Stevenson, J. Yabuki, X. Zeng, H. Dong, A. Muramatsu, G. Ungar, K. Kanie, *Chem*, **2017**, 2, 86. 3) T. Yachi, M. Matsubara, C. Shen, S. Asami, N. B. Milbrandt, M. Ju, S. Wickramasinghe, A. C. S. Samia, A. Muramatsu, K. Kanie, *ACS Appl. Nano Mater.* **2021**, 4, 7395.

Construction of Ultra-thin Pt Layers on Ni Substrate for Highly Efficient Oxygen Reduction Reaction Catalysts

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Keywords: Electrocatalyst for Oxygen Reduction Reaction; Ultra-thin Pt Layers on Ni; Self-termination

In order to construct highly efficient and low-cost electrocatalysts for oxygen reduction reaction (ORR), ultra-thin Pt layers prepared on the Ni substrate is expected as one of the best electrocatalysts for ORR, because of the surface electronic energy effect and also because of using cheaper Ni as a substrate. However, it is difficult to electrochemically deposit Pt, which is a noble metal, on Ni which is a base metal. In this study, using self-termination phenomenon of Pt,^{1,2} we constructed ultra-thin Pt layers on the Ni substrate in the pH-controlled electrolyte solution, evaluated their thickness by x-ray photoelectron spectroscopy (XPS), and then discussed the relationship between thickness of Pt layers and electrocatalytic activity for ORR.

After the surface oxide-free Ni polycrystalline substrates were prepared by mechanically polishing and electrochemically etching, ultra-thin Pt layers were constructed on them by using self-termination of Pt, *i.e.*, by dipping them at -0.60 V (vs. Ag/AgCl) ~ -0.64 V for several hundreds seconds in the 1 M NaCl electrolyte solution with pH = 8.0.¹⁻³ After washing them with ultra-pure water, the electrochemical characteristics and surface analyses of the samples were evaluated by the electrochemical and XPS measurements, respectively.

The more positive the electrodeposition potential of Pt and the longer the electrodeposition period, the more Pt was electrodeposited on Ni. However, the smaller the amount of the electrodeposited Pt, that is, the thinner the Pt layer on Ni, the higher the electrocatalytic activity for ORR. Therefore, the present results suggested that the thinner the Pt layer on Ni, the greater the effect of the surface electric energy and then the higher the electrocatalytic activity. However, if the Pt layer was too thin, the electrocatalytic activity would decrease during the experiments. This indicates that the underlying Ni seemed to electrochemically dissolve into the electrolyte solution. Therefore, it was found that it is necessary to construct the Pt layers, which have an optimum thickness so that the electrocatalytic activity is high and Ni does not dissolve.

1) Y. Liu, D. Gokcen, U. Bertocci, T. P. Moffat, *Science* **2012**, 338, 1327. 2) Y. Liu, C. M. Hangarter, D. Garcia, T. P. Moffat, *Surf. Sci.* **2015**, 631, 141. 3) G. D. Moon, S. Ko, Y. Min, J. Zeng, Y. Xia, U. Jeong, *Nano Today* **2011**, 6, 186.

Validation of a quantitative analysis for intramolecular vibrations of electrolytes in the heterophase system by the near-infrared (NIR) spectroscopy

(¹Graduate School of Engineering, Kobe University, ²Faculty of Chemistry, Jagiellonian University) ○Jingchao Xu,¹ Hideshi Maki,¹ Minoru Mizuhata^{1,2}

Keywords: Ion-solvent interaction; Quantitative near-infrared spectroscopy; Solid-liquid coexistence system

Ionic-solvent interactions reflecting the solvation structure of electrolyte solutions are often discussed by infrared and Raman spectroscopy, but the extremely strong infrared absorption and poor quantitative Raman spectroscopy are not suitable for their quantitative analysis very much. In particular, for electrolytes coexisting with solids, where the influence of the interface is reflected, an analytical method with quantitative capability that takes into account the volume fraction of the liquid is necessary. Near-infrared (NIR) spectroscopy can be measured with an ordinary optical cell and has excellent quantitative properties.¹ In this study, the quantitative properties of various aqueous electrolyte solutions and its coexisting system with fumed silica were discussed.

NIR spectra of aqueous chloride solutions containing Li⁺, Na⁺, K⁺, and Ca²⁺ were measured in the wavelength range of 1200-1800 nm using a JASCO V7200 with a 1-mm optical path length cell. Each water occupied volume is calculated from the value of each weight ratio and density. The NIR spectra of liquids coexisting with solids were measured by mixing them with fumed silica to obtain an arbitrary solid phase fraction at the same method. Each intensity of absorption bands assigned to the dissolving species is calculated was calculated from the area intensity based on the spectral shape with the wavenumber as the horizontal axis as shown Fig.1.

Variations of detected absorption intensity of $\nu_1+\nu_3$ at ca 6300cm⁻¹ with water occupied volume in each solution are shown in Fig.2. In all electrolyte systems, the absorbance was lower than the theoretical value expected based on the number of solvent molecules present in the system, whereas the absorbance decreases in proportion to the volume ratio of the water coexisting with fumed silica. This is thought to be due to a decrease in the dielectric constant of the dissolved molecules and a decrease in the absorption coefficient. The difference between the measured and theoretical values in aqueous cationic solutions with different charge densities shows different trends with concentration, which, in combination with the variation of the absorption peaks of water at each concentration, offers the possibility of quantitatively studying the changes in the network structure of water. The relationship between NIR intensity and occupied volume will be discussed in the presentation.

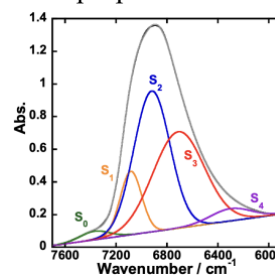


Fig. 1. OH combination band $\nu_1+\nu_3$ of H₂O at ca. 6800 cm⁻¹.

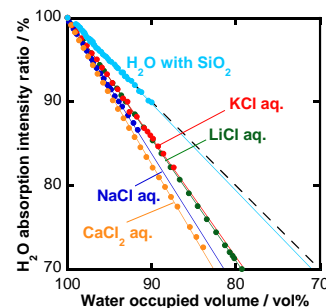


Fig. 2. Absorption intensity ratio of $\nu_1+\nu_3$ of H₂O to occupied volume of water for various circumstance.

Ref. 1) D. H. Dagade et al., *ChemPhysChem.* **2016**, *17*, 902.

Synthesis and Characterization of Porous Boron Nitride Having Specific Gas Adsorption Properties

(¹Graduate School of Natural Science and Technology and ²Faculty of Science, Okayama University) ○Takahiro Ohkubo,¹ Jun Kimura,¹ Kai Egami,¹ Masato Yamashita,² Yasushige Kuroda¹

Keywords: Porous Material; Gas adsorption; Ceramics

Boron nitride (BN) is a fine ceramic material used in a wide variety of fields. From chemical and physical points of view, BN is an isoelectronic compound with carbon and crystalline structure of hexagonal BN (h-BN) is quite similar to that of graphite, but it is an insulator and forms atomically heterogeneous basal plane. Recent progress in synthetic methods has been able to provide nanoporous BN (p-BN) materials with high specific surface area constructed by fine crystallites of h-BN.¹ Lately, we have succeeded in revealing gas adsorption properties of p-BN that interact with N₂ molecules stronger than that of activated carbons.² Although the results indicate that p-BN will be a practical material for gas adsorption and separation, there is a crucial issue; p-BN needs development of the method to control pore size or surface chemistry. In our presentation, we first introduce the gas adsorption properties of p-BN and subsequently discuss possibilities to actively control its pore structure and surface properties through optimization of synthetic methods.

Regarding the typical synthesis route¹, we examined the effect of a gas atmosphere during the calcination process. A result is shown in **Figure** suggesting the effect of the gas species used in the calcination process. Interestingly, when we choose CO₂ as a flow gas, the specific surface area of micropore of p-BN (p-BN-CO₂) were about 1/10 of p-BN synthesized under the N₂- or Ar-flow conditions (p-BN-N₂ and p-BN-Ar) at the same temperature (*i.e.* 1473 K), but its mesopore structure has remained almost intact. The result supports that we can control the pore structure of p-BN by the synthetic conditions even for a thermally durable BN material. Dependences of other conceivable conditions like precursor species and calcination temperature will be also discussed in the presentation.

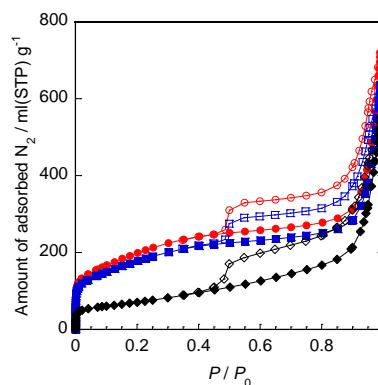


Figure Adsorption-desorption isotherms of N₂ on p-BN-N₂ (red), p-BN-Ar (blue), and p-BN-CO₂ (black) at 77 K.

1) S. Marchesini, C. M. McGilvery, J. Bailey, C. Petit, *ACS Nano*, **2017**, *11*, 10003. 2) J. Kimura, T. Ohkubo, Y. Nishina, K. Urita, Y. Kuroda, *RSC Adv.* **2021**, *11*, 838.

表面力測定による濃厚ポリマーブラシの構造の精密評価

(東北大 NICHe¹・京大化研²)

○高橋 裕¹・水上雅史¹・辻井敬亘²・栗原和枝¹

Direct Determination of Structure of Concentrated Polymer Brushes by Surface Forces Measurement (¹New Industry Creation Hatchery Center, Tohoku University, ²Institute for Chemical Research, Kyoto University) ○Yutaka Takahashi,¹ Masashi Mizukami,¹ Yoshinobu Tsujii,² Kazue Kurihara¹

Concentrated poly(methyl methacrylate) (PMMA) brushes exhibit superior lubrication properties in a good solvent (toluene). In order to understand the lubrication mechanism, we studied their properties by surface forces and resonance shear measurements. In this presentation, the composition (structure) of concentrated PMMA brush layers was investigated based on changes in the refractive index measured by fringes of equal chromatic order. The changes in their properties under the applying load and shear were discussed.

Keywords : Surface Forces Measurement; Resonance Shear Measurement; Polymer Brushes; Fringes of Equal Chromatic Order

濃厚ポリマーブラシ (CPB) は優れた潤滑性を示すことが知られている。これまでに、シリカ表面上の濃厚 PMMA ブラシ層 (膨潤膜厚: 530 nm, グラフト密度: 0.83 鎖/nm²) の粘弾性を表面力および共振ずり測定によって検討した¹⁾。荷重およびせん断振動を与えることで、膨潤したブラシ層は高分子鎖が相互貫入し、さらにより大きなせん断下では相互貫入が解消された。CPB を潤滑剤として応用するために、この挙動を理解することは重要である。そこで本研究では、等色次数干渉縞 (FECO) を用いた屈折率測定によって、荷重およびせん断下における表面間での濃厚 PMMA ブラシ層の組成からその構造および相互貫入について評価した。

FECO 法での屈折率測定には、ブラシ層の厚さが測定に用いる光の波長より十分に薄い必要があるため、より薄い PMMA ブラシ層 (膨潤膜厚: 95 nm, グラフト密度: 0.71 鎖/nm²) を合成した。この薄膜 PMMA ブラシ層の粘弾性を評価したところ、膨潤膜厚が 530 nm のそれと同様の挙動を示すことが分かった。

さらに、屈折率の詳細な解析から膨潤した PMMA ブラシ層の厚み方向に対する体積分率分布を検討したところ、ブラシ層の表面 (膨潤膜厚の約 20%) に低密度層が観測された (**Fig. 1**)。この低密度層の割合は PMMA ブラシ全体の約 10% だった。圧縮およびせん断振動下における濃厚 PMMA ブラシ層の相互貫入は、この低密度層によるものであると考えられる。また、せん断振幅に対する屈折率の変化は、相互貫入した高分子鎖が引き抜かれることも支持した。

[1] M. Mizukami, M. Gen, S.-Y. Hsu, Y. Tsujii, and K. Kurihara: *Soft Mater*, **15**, 7765 (2019).

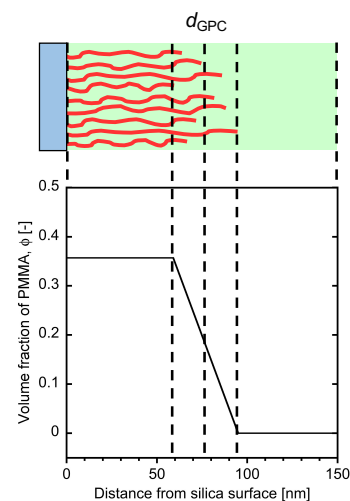


Fig. 1 Density distribution of PMMA brush layer between the silica surfaces against the distance from silica surface. d_{GPC} : the extended chain length calculated from M_w analyzed by the GPC.

クロロシランの大気中での長期安定保存法の開発：表面微細構造の再構築により自己修復する超撥水性材料への応用

(産総研¹) ○中村 聡¹・穂積 篤¹

Development of a long-term stabilization method of chlorosilane in air and its biomimetic application to self-healing superhydrophobic surfaces through the reconstruction of surface morphologies (¹*National Institute of Advanced Industrial Science and Technology*) ○Satoshi Nakamura¹・Atsushi Hozumi¹

Chlorosilanes have recently attracted much attention as silane compounds that form unique micro/nanostructures with superhydrophobicity through a combination of hydrolysis/polycondensation reactions. On the other hand, chlorosilanes are known to be extremely reactive and immediately react with moisture in air, significantly reducing their reactivity after a relatively short time. In order to solve this trade-off, the authors have developed a simple method to stably store chlorosilane in air for a long period using paraffin wax. Specifically, by simply mixing methyltrichlorosilane (MTCS) with paraffin wax, it was possible to stably store MTCS in air for one month without decreasing its reactivity. The resulting surface of the MTCS/paraffin wax mixture not only exhibited superhydrophobicity, but also showed self-healing ability for one month by reconstructing its microstructures even after severe physical damages (Figure 1). This clearly indicates that MTCS effectively worked stably as a repair agent for superhydrophobic surfaces.

Keywords : Self-healing; Superhydrophobicity; Methyltrichlorosilane; Hydrolysis/polycondensation; Paraffin wax

クロロシランは加水分解/縮重合反応により、超撥水性を示す特異な微細構造を形成するシラン化合物として最近、注目されている。一方で、クロロシランは反応性が極めて高く、大気中の水分と直ちに反応するため、短期間で反応性が著しく低下する。演者らは、このトレードオフの関係を解消するため、パラフィンを用いてクロロシランを大気中で長期間、安定に保存する手法の開発を実施した。具体的には、メチルトリクロロシラン(MTCS)をパラフィンワックスと混合するだけで、MTCSの反応性を損なうことなく、大気中で一ヶ月間、安定に保存できることがわかった。また、このMTCS/パラフィンワックス混合物の表面は超撥水性を示すだけでなく、物理的ダメージを与えた後も、微細構造の再構築により超撥水性が1ヶ月に渡り自己修復したことから(図1)、MTCSが超撥水性表面の補修剤として長期間、有効に機能することも明らかとなった。

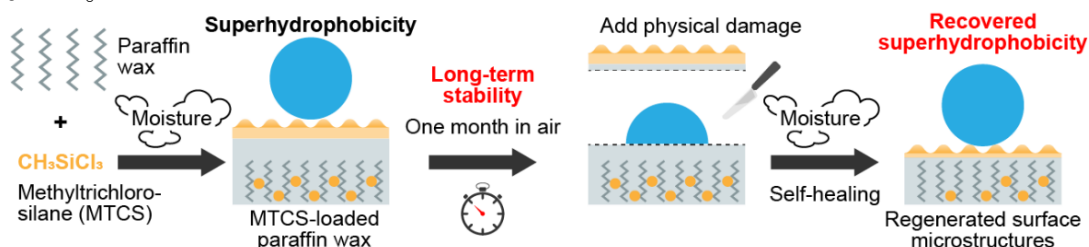


Figure 1. Conceptual scheme of this study.

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

[C205-1pm] 20. Materials Chemistry -Basic and Application-

Chair: Masahiko Nakamoto, Shun-ichi Tamaru

Wed. Mar 23, 2022 1:40 PM - 3:40 PM C205 (Online Meeting)

[C205-1pm-01] Polypeptide Responsive Out-of-Equilibrium Volume Change of Hydrogel-Enzyme Hybrid

○Masahiko Nakamoto¹, Shiro Kitano^{1,2}, Michiya Matsusaki¹ (1. Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2. Technical Research Institute, TOPPAN INC.)

1:40 PM - 2:00 PM

[C205-1pm-02] Production of a hybrid hydrogel consisting of synthetic polymers and artificial protein nanocages

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

2:00 PM - 2:20 PM

[C205-1pm-03] Programmed Porous Nanostructures with Biomolecular Machines and Nanoparticles

○Kiyoshi Morishita¹, P. K. Hashim¹, Haruaki Yanagisawa¹, Masahide Kikkawa¹, Tatsuya Niwa², Hideki Taguchi², Takuzo Aida^{1,3} (1. The University of Tokyo, 2. Tokyo Institute of Technology, 3. RIKEN Center for Emergent Matter Science)

2:20 PM - 2:40 PM

[C205-1pm-05] Screw Dislocation-Induced Mirror Symmetry-Breaking in Bulk Metal-Organic Crystals

○Gangfeng CHEN^{1,2} (1. The University of Tokyo, 2. RIKEN Centre for Emergent Matter Science)

3:00 PM - 3:20 PM

[C205-1pm-06] Formation of novel concave surface structures by patterned photopolymerization induced molecular diffusion

○Sayuri Hashimoto¹, Norihisa Akamatsu¹, Shoichi Kubo¹, Atsushi Shishido¹ (1. Tokyo Institute of Technology)

3:20 PM - 3:40 PM

標的ポリペプチドに応答して動的な体積変化を生じる ハイドロゲル-酵素複合材料の開発

(阪大院工¹) ○仲本 正彦¹・松崎 典弥¹

Polypeptide Responsive Out-of-Equilibrium Volume Change of Hydrogel-Enzyme Hybrid
(¹Graduate School of Engineering, Osaka University) ○Masahiko Nakamoto,¹ Michiya Matsusaki¹

The dissipative nature of the living system plays a crucial role for diverse biological functions from molecular to cellular level. Recently, the engineering of the artificial dissipative system is of great interest to realize a man-made material with the dynamic function. However, to the best of our knowledge, there is no report on the bio-macromolecule responsive hydrogel showing the transient and macroscopic volume change. Taking inspiration from the nutrient intake, metabolism and waste excretion processes in the living system, we report the engineering of the metabolic cycle-inspired hydrogel showing target peptide-responsive transient volume change. The transient secretion of a model payload driven by the volume change will also be reported in the presentation.

Keywords : Artificial dissipative system; Biomacromolecule responsive hydrogel; Hydrogel-enzyme hybrid; Bio-inspired hydrogel

近年、生体のようにダイナミックに機能する材料設計を目指した人工散逸システムの構築が注目を集めている⁽¹⁾。しかしながらこれまでに、生体高分子に応答した散逸サイクルに駆動されて、巨視的かつ動的な体積変動を生じるハイドロゲルの報告例はない。我々は生体における代謝プロセスに着想を得て、標的生体高分子の摂取、代謝、排出により動的体積変動を生じる Metabolic cycle-inspired hydrogel (MC ゲル) を開発した。MC ゲルは標的ペプチドである α -ポリ-L-リジンに応答した動的な収縮および自発的な再膨潤を生じた (Figure 1A)。MC ゲルは多点的な静電相互作用によりポリリジンを摂取し、ポリマーネットワーク内に静電的架橋構造を構築 (同化) することで収縮挙動を示したと示唆される。次いで、ゲル内での酵素分解による静電的架橋構造の崩壊 (異化) と、分解物の排出によりゲルが再膨潤したと考えられる (Figure 1B)。本発表では動的体積変動に伴う物質徐放についても報告する。本研究はダイナミックに生物学的プロセスを制御する革新的バイオマテリアルの開発のための重要な知見となる。

1) Boekhoven, J.; Hendriksen, W. E.; Koper, G. J. M.; Eelkema, R.; van Esch, J. H. *Science* 2015, 349, 1075–1079.

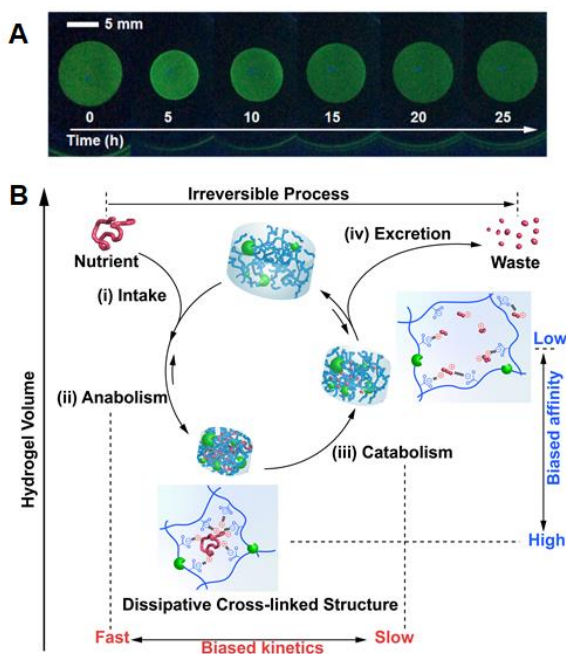


Figure 1. (A) Transient volume change of MC gel in response to poly-lysine. (B) Supposed mechanism of the transient volume change of the

人工タンパク質ナノケージを用いたタンパク質-ポリマーハイドロゲルの構築

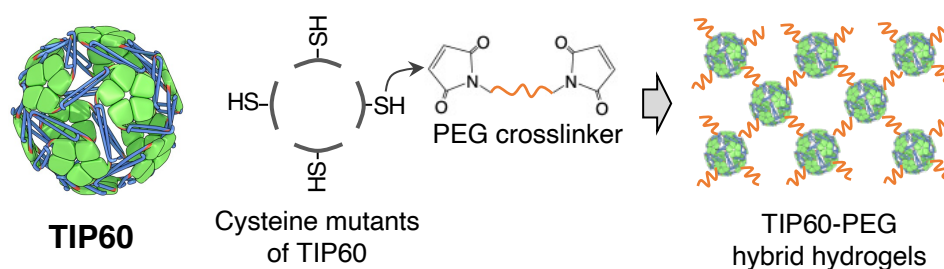
(慶大理工) ○那須 英里圭・川上 了史・宮本 憲二

Production of a hybrid hydrogel consisting of synthetic polymers and artificial protein nanocages (*Department of Biosciences and Informatics, Keio University*) ○Erika Nasu, Norifumi Kawakami, Kenji Miyamoto

Proteins are of interest as biocompatible components of functional hydrogels. In this study, we attempted to produce protein-polymer hybrid hydrogels containing artificial protein nanocages TIP60 as junctions of network structure. The TIP60 is a 60-mer spherical protein. The cysteine residues can be introduced on the exterior surface of TIP60 by mutation. These cysteine residues can be used for chemical modifications. Thus, we connected the mutant TIP60 by the chemical modification using polyethylene glycol (PEG) with maleimide groups at both ends. As a result, the hydrogel cross-linking of the mutant TIP60 by PEG was obtained.

Keywords : Artificial protein nanocages; Supramolecule; Hydrogel

生体適合性や多様な構造・機能を持つタンパク質は、ハイドロゲルの構成要素として注目されている。当研究室が設計した人工タンパク質ナノ粒子 TIP60 は、60 分子のモノマーが会合してできるサッカーボール型の中空な粒子である^{1,2)}。TIP60 の内外表面には変異導入により選択的にシステインを導入することが可能であり、化学修飾の標的として利用することができる³⁾。本研究では、TIP60 をポリマー分子で架橋することによる TIP60-ポリマーハイドロゲルの構築を検討した。具体的には、TIP60 の外側にシステインを導入した変異体を、両端にシステインと特異的に反応するマレイミド基を有するポリエチレングリコール (PEG) で修飾した。TIP60 の濃度や PEG の鎖長などの条件を検討し、TIP60 の PEG 架橋によるゲルの形成を確認した。本ゲルは、多量体タンパク質である TIP60 が PEG ネットワークの架橋点となる設計であり、TIP60 の構造がゲルの性質に強く影響すると考えられる。実際に、これを反映したと期待されるゲルの性質として、タンパク質の変性剤である SDS の添加によるゲルの分解と熱による素早いゾル-ゲル転移を観察した。



1) N. Kawakami *et al.*, *Angew. Chem. Int. Ed.*, 2018, 57, 12400

2) J. Obata *et al.*, *Chem. Commun.*, 2021, 57, 10226

3) E. Nasu *et al.*, *ACS Appl. Nano Mater.* 2021, 4, 2434

Programmed Porous Nanostructures with Biomolecular Machines and Nanoparticles

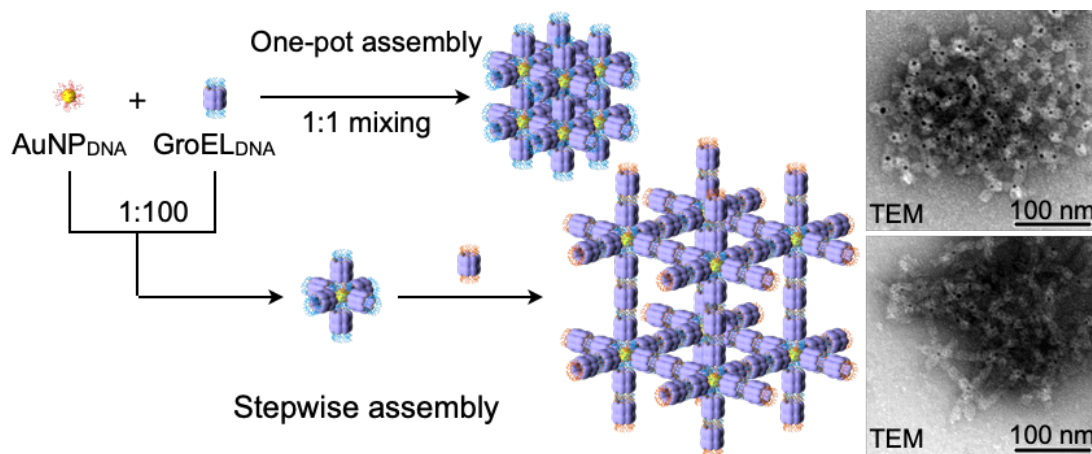
(¹The University of Tokyo, ²Tokyo Institute of Technology, ³RIKEN Center for Emergent Matter Science) ○Kiyoshi Morishita,¹ P.K. Hashim,¹ Haruaki Yanagisawa,¹ Masahide Kikkawa,¹ Tatsuya Niwa,² Hideki Taguchi,² Takuzo Aida^{1,3}

Keywords: Supramolecular Chemistry; GroEL; DNA Nanotechnology; Porous Materials

We report a class of supramolecular architectures, analogous to metal organic frameworks but with ultra-large pore sizes on the order of several tens of nanometers, consisting of gold nanoparticles (AuNPs) and the biomolecular machine GroEL.

In nature, the chaperonin protein GroEL assists in protein refolding by capturing denatured proteins within its hydrophobic cavities and releasing them with ATP-induced conformational motions.¹ GroEL (ca. 800 kDa) adopts a barrel-shaped structure, with height of 14.6 nm and outer/inner diameters of 13.7 nm/4.5 nm. We have previously used this biomolecular machine to form supramolecular structures² and demonstrated ATP-responsive guest release where GroEL mechanical motions alter the assembled structure morphology.³

Inspired by the self-assembled structures of metal organic frameworks (MOFs), we constructed analogous frameworks formed by AuNPs as nodes and GroEL as linkers. The use of DNA to link these components allowed for programming of the assembly. The real-time growth of clusters and manipulation thereof was tracked by dynamic light scattering. Distinct assembly pathways led to porous clusters having 1 or 3 GroEL units linking AuNPs, as characterized by cryoEM tomography. The porous clusters retained their ATPase activity and were able to load ultra-large macromolecular guests.



- 1) H. Taguchi, *J. Biochem.* **2005**, *137*, 543. 2) a) S. Biswas, et al., *J. Am. Chem. Soc.* **2009**, *131*, 7556. b) D. Kashiwagi, et al., *J. Am. Chem. Soc.* **2018**, *140*, 26. c) D. Kashiwagi, et al., *J. Am. Chem. Soc.* **2020**, *142*, 13310. 3) S. Biswas, et al., *Nat. Chem.* **2013**, *5*, 613.

Screw Dislocation-Induced Mirror-Symmetry Breaking in Bulk Metal-Organic Crystals

(¹Graduate School of Engineering, The University of Tokyo, ²RIKEN Center for Emergent Matter Science) ○Gangfeng Chen,^{1,2} Hubiao Huang,² Hiroshi Sato,² Takuzo Aida^{1,2}

Keywords: Screw Dislocation; Metal-Organic Crystals; Symmetry Breaking; Helical Structure; Chiral

Mirror-symmetry breaking in crystals largely relies on arrangement of building units into either a specific chiral space group or a chiral morphology.¹ However, screw dislocation—a type of topological defects—can furnish certain nanocrystals with helical growth spirals without the use of any chiral building units or additives.² Although these helical structures have been frequently observed by using atomic force microscopy or electron microscopy,² the chirality of crystals are rarely identified due to the difficulty in characterizing both sides of crystals. Moreover, as the crystal size increases from nanoscale to microscale, the number of screw dislocations increases drastically, where helical spirals with either same or opposite handedness interact with each other, which may result in the disappearance of helicity.³

Here we report mirror-symmetry breaking in a bulk layer-structured metal-organic crystal (^LCryst) induced by a single screw dislocation. A growth spiral with either clockwise (CW) or counterclockwise (CCW) direction develops consecutively from the geometric center of ^LCryst to its peripheral edge, forming a spiral pyramid on the crystal surface. This indicates that bulky ^LCryst bearing a single screw dislocation, though crystallographically achiral, is morphologically chiral due to screw dislocation-induced mirror-symmetry breaking.

- 1) T. Buhse *et al.* *Chem. Rev.* **2021**, *121*, 2147. 2) S. Jin *et al.* *Acc. Chem. Res.* **2013**, *46*, 1616.
3) M. P. Attfield *et al.* *Chem. Eur. J.* **2012**, *18*, 15406.

Formation of novel concave surface structures by patterned photopolymerization induced molecular diffusion

(Laboratory for Chemistry and Life Science, Tokyo Institute of Technology) ○ Sayuri Hashimoto, Norihisa Akamatsu, Shoichi Kubo, Atsushi Shishido

Keywords: Liquid Crystal; Photopolymerization; Surface Structure

The precise control of the surface topology has drawn great attention for the fabrication of functional devices widely applicable to wettability and adhesion control, modulation of optical properties, and so on. Lithography processes have been widely used to fabricate surface structures, especially in the industrial field. Alternatively, the photoinduced formation of surface relief gratings (SRGs) using liquid crystals (LCs) has been developed to give anisotropic functions^{1,2}. The surface structures formed on LCs have advantage of reversible changes in molecular alignment in response to external stimuli such as light, electricity, and heat. Recently, we presented the formation of surface relief structures accompanied with molecular alignment in LC polymer films by patterned photopolymerization, based on a concept of molecular diffusion³⁻⁵. However, the height of the relief structures is limited to several hundred nanometers. Fabrication of surface structures with a depth of micrometers still remains a challenge.

In this study, we report on the formation of novel surface concave structures in the LC films by simple patterned photopolymerization (Fig. 1). We revealed that the surface relief structures were formed by the molecular diffusion, and the period of the surface structures depended on the width of light pattern. Interestingly, concave structures with depths of several micrometers were formed on LC polymer films when the light pattern was changed in terms of the ratio of the irradiation width to the dark width. Moreover, we successfully designed the spatial arrangement of the concave structures, i.e. canals and holes, by controlling the irradiation patterns and photopolymerization conditions. The formation mechanism of the concave structures will be discussed.

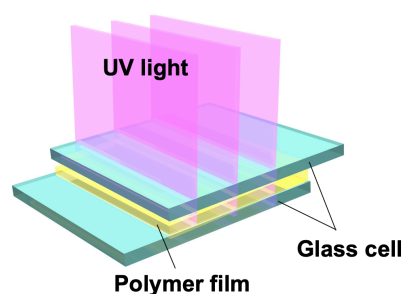


Fig. 1. Schematic illustration of patterned irradiation.

1) A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139. 2) T. Seki, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1026. 3) K. Hisano, Y. Kurata, M. Aizawa, M. Ishizu, T. Sasaki, A. Shishido, *Appl. Phys. Express* **2016**, *9*, 072601. 4) K. Hisano, M. Aizawa, M. Ishizu, Y. Kurata, W. Nakano, N. Akamatsu, C. J. Barrett, A. Shishido, *Sci. Adv.* **2017**, *3*, e1701610. 5) S. Hashimoto, M. Aizawa, N. Akamatsu, T. Sasaki, A. Shishido, *Liq. Cryst.* **2019**, *46*, 1995.

Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B**[C204-1pm] 20. Materials Chemistry -Basic and Application-**

Chair: Takeshi Maeda, Osamu Tsutsumi

Wed. Mar 23, 2022 1:40 PM - 3:40 PM C204 (Online Meeting)

[C204-1pm-01] Triboluminescence of luminophores in blended polymers: Simple preparation method for triboluminescent films○ayumu karimata¹, Robert R Fayzullin², Julia R Khusnutdinova¹ (1. OIST, 2. Arbuzov Institute)

1:40 PM - 2:00 PM

[C204-1pm-02] Synthesis and Near-Infrared Photoluminescence Properties of Novel D- π -A-Type Pyridinium Betaine Dyes Based on Thiophene-Derived π -Skeleton○Ami Morimoto¹, Mao Saikusa¹, Naoya Suzuki¹, Takeshi Maeda¹, Shigeyuki Yagi¹, Seiji Akiyama² (1. Osaka Prefecture University, 2. Mitsubishi Chemical Corporation)

2:00 PM - 2:20 PM

[C204-1pm-03] 3-Dimensional Control of Nanostructure of Chiral-Nematic Liquid-Crystals in Monodispersed Polymeric Microparticles○Tomoki Shigeyama¹, Kyohei Hisano¹, Osamu Tsutsumi¹ (1. Ritsumeikan Univ.)

2:20 PM - 2:40 PM

[C204-1pm-04] Aggregation-induced room-temperature phosphorescence from mesogenic gold(I) complexes○Andriani Furoida¹, Kyohei Hisano¹, Osamu Tsutsumi¹ (1. Ritsumeikan University)

2:40 PM - 3:00 PM

[C204-1pm-06] High-Speed Bending of Salicylideneaniline Crystals by Photothermal-Induced Natural Vibration○Shodai Hasebe¹, Yuki Hagiwara¹, Toru Asahi¹, Hideko Koshima¹ (1. Waseda Univ.)

3:20 PM - 3:40 PM

Triboluminescence of luminophores in blended polymers: simple preparation method for triboluminescent films

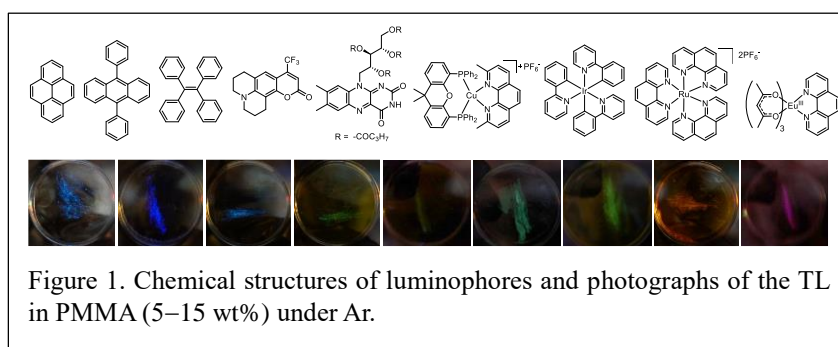
(¹Okinawa Institute of Science and Technology, ²Arbuzov Institute) ○Ayumu Karimata¹, Robert R Fayzullin², Julia R Khusnutdinova¹

Keywords: Photoluminescence, Triboluminescence, Mechanoresponsive materials, Tribology.

Triboluminescent materials, which produce emission of light by mechanical actions, are attractive components for smart materials and mechanical sensors. In order to produce triboluminescence (TL) in luminophores, piezoelectric (non-centrosymmetric) crystal structure has been proposed for a factor to generate electric field by mechanical stimuli, which leads to the excitation of luminophore. During our study on TL of a family of photoluminescent [(pyridinophane)Cu^I(NHC)]X complexes, we found that both centrosymmetric and non-centrosymmetric crystals show intense TL.¹ And TL of the Cu^I complexes was also observed even in amorphous polymers, which inspired us to establish a new concept to produce triboluminescent materials by utilizing common luminophores and polymers. To the best of our knowledge, we for the first time demonstrate that triboluminescent films can be obtained by simply blending common luminophores and polymers without crystalline formation of luminophores. Representative nine luminophores, which show fluorescence or phosphorescence, were selected and physically mixed with poly(methylmethacrylate) (PMMA) to provide amorphous films. (Figure 1) TL of the luminophores in PMMAs were observed by rubbing the surface under inert atmosphere, in spite of the TL property of the luminophores in the crystals. The photographs of TL generated by rubbing the surface of the PMMAs containing the luminophores (5–15 wt%) using glass rod under Ar are shown in Figure 1. PXRD analysis and fluorescence microscopy images confirmed the absence of crystalline form and nano/micro particles of the luminophores in the PMMAs. The TL spectra of the PMMAs (1 wt%) show photoluminescence of each luminophore and Ar gas plasma emission, which imply gas discharging by triboelectrification. TL is also observed in polystyrene, polycaprolactone, poly(vinyl chloride), and polycarbonate.

TL of the luminophores in crystal as well as influence of surrounding gas on TL will also be discussed in the presentation.

1) A. Karimata, P. H. Patil, R. R. Fayzullin, E. Khaskin, S. Lapointe, J. R. Khusnutdinova, *Chem. Sci.* **2020**, *11*, 10814.



Synthesis and Near-Infrared Photoluminescence Properties of Novel D- π -A-Type Pyridinium Betaine Dyes Based on Thiophene-Derived π -Skeleton

(¹Graduate School of Engineering, Osaka Prefecture University, ²Mitsubishi Chemical Corporation) ○ Ami Morimoto,¹ Mao Saikusa,¹ Naoya Suzuki,¹ Takeshi Maeda,¹ Shigeyuki Yagi,¹ Seiji Akiyama²

Keywords: Near-infrared fluorescence; Betaine dye; Intramolecular charge transfer; Fluorescent dye; Thiophene

Near-infrared (NIR) light, which shows high transmittance to the living body and is invisible to the naked eye, has attracted much attention from the viewpoint of application in biomedical science and security technology. However, there are few examples of NIR luminescent dyes with high quantum yields (Φ_{PL}) due to facilitation of nonradiative decay according to the energy gap law. To develop novel NIR fluorescent dyes, we here focus on donor- π -acceptor (D- π -A)-type pyridinium-cyclic enolate betaines (Fig. 1). We recently reported that **PB-Th** (π -spacer: 2,5-thienylene) exhibited deep red fluorescence at 669 nm with Φ_{PL} of 0.75 in dichloromethane.¹ The *N,N*-diphenylamino donor group leads to achievement of red-shifted fluorescence through the intramolecular charge transfer character and plays an essential role in reduction of the non-radiative decay rate. Also, as demonstrated in our previous work,² the electron-deficient five-membered cyclic enolate based on maleimide promises the improvement of Φ_{PL} due to suppression of twisted intramolecular charge transfer at the pyridinium-enolate moiety upon photoexcitation. In this research, we develop D- π -A-type pyridinium-cyclic enolate betaine dyes bearing extended π -skeletons, aimed at highly efficient red-shifted photoluminescence (PL) to the NIR region. Thiophene-derived extended π -spacers were effective to achieve NIR fluorescence. For example, one of the present betaine dyes exhibited intense NIR emission at 719 nm with Φ_{PL} of 0.66 in dichloromethane. Theoretical calculations indicate that it adopts a quinoidal electronic structure at the excited state, and thus the structural relaxation upon photoexcitation should be suppressed to achieve high Φ_{PL} . In the presentation, we report the synthesis of the NIR-fluorescent pyridinium betaine dyes and discuss their PL properties in detail.

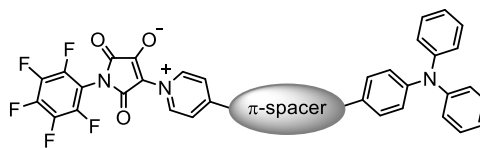


Fig. 1. General structure of D- π -A-type pyridinium-cyclic enolate betaine dyes.

1) M. Saikusa, S. Yagi, *et. al.*, 2021 Japan Society of Colour Material Annual Conference, 2A01 (online). 2) Y. Hayashi, S. Yagi, *et. al.*, *New J. Chem.*, **2021**, 45, 9770–9779.

3-Dimensional Control of Nanostructure of Chiral-Nematic Liquid-Crystals in Monodispersed Polymeric Microparticles

(Department of Applied Chemistry, Ritsumeikan University) ○Tomoki Shigeyama, Kyohei Hisano, Osamu Tsutsumi

Keywords: Chiral-nematic liquid-crystals; Dispersion polymerization; Polymeric particles

Chiral-nematic liquid-crystals (N^* LCs), which spontaneously form helical nanostructure of molecular orientation, exhibit Bragg reflection depending on the alignment of helical nanostructure. Among various application of N^* LC, the polymeric microparticles have attracted much attention as small optical elements. Recently, N^* LC polymeric particles have been produced by the polymerization of N^* LC monomer droplets. Therefore, the nanostructure that can be realized was limited. In this study, we found unique nanostructure in the N^* LC polymeric particles fabricated by dispersion polymerization. In dispersion polymerization, a large number of monodisperse microparticles can be obtained in single-step. The resulting polymer precipitates and grows to form monodisperse particles.

From the scanning electron microscopy (SEM) image (Figure 1a), the average particle size of the obtained particles was $2.6 \pm 0.1 \mu\text{m}$, indicating that monodispersed particles were obtained. In addition, transmission electron microscopy (TEM) image of the cross-section showed spiral stripe pattern from two orientation defects (Figure 1b). The nanostructure predicted by this pattern was different from that of fabricated by the conventional method. We now expect that this nanostructure was formed during the growth process of the particles during dispersion polymerization.

Next, we investigated the optical function of N^* LC particles. Figure 2 shows the characters drawn using the N^* LC particle ink. The drawn characters showed an angular-independent reflection because of their centrally symmetric nanostructures.

The monodispersed N^* LC particles developed in this study can be applied to reflective coatings and security inks utilizing the circularly polarized reflective property of N^* LC.

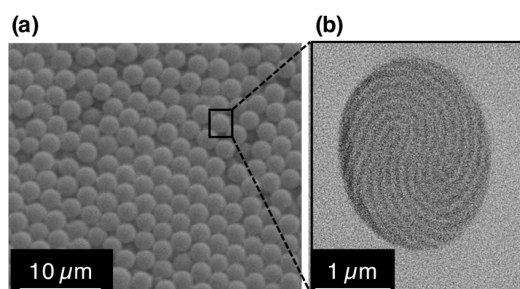


Figure 1. (a) SEM image and (b) TEM image of the N^* LC particles fabricated in this study.

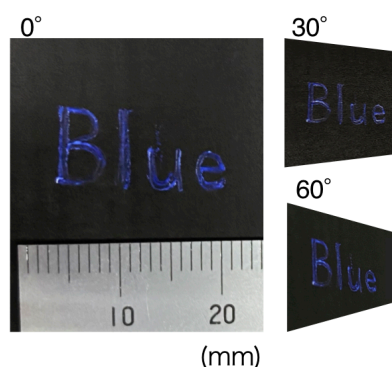


Figure 2. Reflective coating of the N^* LC particles and its reflection color observed from 0° , 30° and 60° .

Aggregation-Induced Room-Temperature Phosphorescence from Mesogenic Gold(I) Complexes

(¹Graduate School of Life Science, Ritsumeikan University) ○Andriani Furoida,¹ Kyohei Hisano,¹ Osamu Tsutsumi¹

Keywords: Aggregation-Induced Emission; Room-Temperature Phosphorescence; Gold Complexes.

Luminescent organic materials generally show efficient luminescence only in dilute solutions, and the emission is quenched by aggregation. This phenomenon is well known as the aggregation-caused quenching (ACQ), which has become the main concern for practical light-emitting applications.¹ In 2001, Tang *et al.* introduced an opposite phenomenon to ACQ, termed aggregation-induced emission (AIE), in which the aggregation of molecules significantly enhanced the emission.² Gold(I) complexes have been noticed as a type of AIEgens, as their luminescence is significantly enhanced in the solid-state. Au–Au (aurophilic) interactions in gold complexes play an important role not only in inducing efficient luminescence from aggregates, but also controlling the luminescence behaviour.

In the present study, we designed and synthesized a series of rod-like gold(I) complexes having mesogenic biphenylethynyl ligand and an isocyanide ligand. Here, we varied the length of flexible alkoxy or alkyl chains as shown in Figure 1, and investigated their AIE properties and liquid crystalline (LC) nature. All synthesized gold(I) complexes are AIE-active where, in crystal, strong room-temperature phosphorescence (RTP) with relatively high quantum yields of up to 23% was observed even in air. AIE study also revealed that such strong RTP is greatly affected by crystal quality and aggregated structure (e.g., Au–Au distance) that depends on crystal size and/or crystal growth process. Moreover, B3-5 complex with longer flexible chains showed LC phase where RTP can be observed.

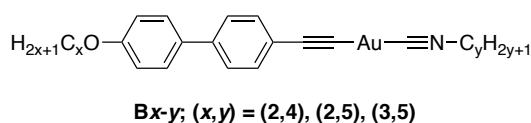


Figure 1. Molecular structures of gold complexes used in this study.

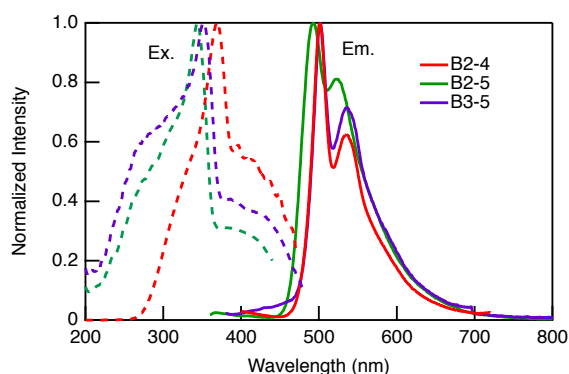


Figure 2. Emission spectra of gold complexes in the crystal

- 1) K. Zhang, J. Liu, Y. Zhang, J. Fan, C. Wang, L. Lin, *J. Phys. Chem. C.*, **2019**, 123, 24705
- 2) B.Z. Tang, X. Zhan, G. Yu, P.P. Sze Lee, Y. Liu, D. Zhu, *J. Mater. Chem.*, **2001**, 11, 2974

High-Speed Bending of Salicylideneaniline Crystals by Photothermal-Induced Natural Vibration

(¹Graduate School of Advanced Science and Engineering, Waseda University, ²Research Organization for Nano & Life Innovation, Waseda University) ○Shodai Hasebe,¹ Yuki Hagiwara,¹Toru Asahi,¹ Hideko Koshima²

Keywords: High-speed Crystal Bending; Photothermal Effect; Natural Vibration; Salicylideneaniline

Mechanically responsive organic materials have attracted much attention in both basic research and applications to smart actuators and soft robots.¹ We have developed many light-driven mechanical crystals over the past decade, mainly based on photoisomerization.^{2,3} Recently, we reported 25 Hz fast bending of a molecular crystal by a photothermal effect, a phenomenon by which heat is generated by nonradiative deactivation of the photoexcited state during a photophysical process.⁴ We then focused on a salicylideneaniline derivative with an *o*-amino substituent (enol-1, Figure 1a) and elucidated the bending mechanism that a nonsteady temperature gradient in the thickness direction triggers photothermally driven crystal actuation, ultimately achieving 500 Hz high-speed bending.⁵

Following this finding, we remeasured photothermally driven bending of another enol-1 crystal (Figure 1b) using a higher performance high-speed camera. Upon ultraviolet (UV) light irradiation for 0.1 s, the crystal bent away from the light source to reach 1.4° after 0.1 s by the photothermal effect (Figure 1c). We analyzed the bending motion in detail and discovered that the crystal oscillated while bending (Figure 1c, inset); it was revealed that this oscillation (773 Hz) is derived from natural vibration of the crystal. The crystal was then exposed to a pulsed UV light of the same frequency as its natural frequency; the bend angle was amplified to 7.2° by resonance, achieving high-speed and large bending of 773 Hz (Figure 1d). It was revealed that fast and large bending can be generated by using photothermal-induced natural vibration.

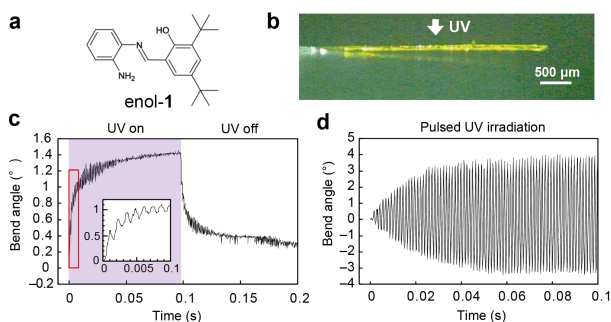


Figure 1. (a) Molecular structure of enol-1. (b) Photograph of an enol-1 crystal viewed from the side face. (c) Photothermally driven bending upon UV irradiation for 0.1 s. (d) 773-Hz high-speed bending by photothermal-induced natural vibration upon pulsed UV irradiation (773 Hz).

1) *Mechanically Responsive Materials for Soft Robotics*, ed. H. Koshima, Wiley-VCH, **2020**. 2) H. Koshima, N. Ojima, H. Uchimoto, *J. Am. Chem. Soc.*, **2009**, 131, 6890–6891. 3) H. Koshima, K. Takechi, K. Uchimoto, N. Ojima, *Chem. Commun.*, **2011**, 47, 11423–11425. 4) Y. Hagiwara, T. Taniguchi, T. Asahi, H. Koshima, *J. Mater. Chem. C* **2020**, 8, 4876–4884. 5) S. Hasebe, Y. Hagiwara, J. Komiya, M. Ryu, H. Fujisawa, J. Morikawa, T. Katayama, D. Yamanaka, A. Furube, H. Sato, T. Asahi, H. Koshima, *J. Am. Chem. Soc.* **2021**, 143, 8866–8877.

[J401-1vn] 22. Resources Utilization Chemistry, Environmental and Green Chemistry

Chair: Yoshito Ando, Takeru Ohe

Wed. Mar 23, 2022 4:10 PM - 6:10 PM J401 (Online Meeting)

[J401-1vn-01] Relationship between coloration of chrome-tanned leathers reacted by glucose oxides and their mechanical strength

○Takeru Ohe¹, Yurika Yoshimura¹ (1. Osaka Research Institute of Industrial Science and Technology)

4:10 PM - 4:30 PM

[J401-1vn-02] Removal, Separation and Recovery of Cs, Co, and Sr from the Mixed Solution Using *Arthrobacter* Cells

○Takehiko Tsuruta¹, Jun Tachibana¹, Kazuya Yokoyama¹, Takahiro Nagane¹, Yuya Koseki¹, Akira Shiga¹ (1. Hachinohe Institute of technology)

4:30 PM - 4:50 PM

[J401-1vn-03] New separation technology of Ni and Co in solution by chelating resin for resource recovery from waste lithium-ion batteries.

○Jiro Kondo^{1,2}, Aono Hiromichi², Tsugita Yasuhiro¹ (1. EGS.,co.Ltd, 2. The Univ. of Ehime)

4:50 PM - 5:10 PM

[J401-1vn-04] Design of thermoplastic materials using cellulose as a base matrix

○RUOZHU WANG¹, Yoshito Andou¹ (1. Kyushu Institute of Technology)

5:10 PM - 5:30 PM

[J401-1vn-05] Conductive Properties of Oxygen Deficient Titanium Dioxide by In-liquid Plasma Treatment

○Kai Takagi¹, Yuta Fujii², Haruo Kuriyama¹, Takenori Hayakawa¹, Izumi Serizawa¹, Naoya Ishida², Chiaki Terashima², Akira Fujishima² (1. ORC MANUFACTURING CO., LTD, 2. Tokyo University of Science)

5:30 PM - 5:50 PM

[J401-1vn-06] Complete mineralization of fluorinated ionic liquids using low-temperature superheated water

○Hisao Hori¹, Satomi Oishi¹ (1. Kanagawa Univ.)

5:50 PM - 6:10 PM

グルコース酸化物で反応したクロム鞣し革の着色と機械強度の関係

(大阪技術研) ○大江 猛・吉村 由利香

Relationship between coloration of chrome-tanned leathers reacted by glucose oxides and their mechanical strength (*Osaka Research Institute of Industrial Science and Technology*)

○Takeru Ohe, Yurika Yoshimura

We have experienced in our daily living well that foods including both reducing sugars and proteins, become yellow or brown after the heating process or long storage. These coloration reactions are called the Maillard reaction. In our laboratory, new textile coloration not using toxic synthetic dyestuffs have been investigated as application of the Maillard reactions. Our recent works also afforded interesting results that the usage of oxides of the reducing sugars, including reactive intermediates of the Maillard reaction, enhanced largely the coloration speed of the wool fibers comparably to those of synthetic dyes. Here, we investigated the relationship between coloration of chrome-tanned leathers, one of protein fibers, reacted by glucose oxides and their mechanical strength.

Keywords : Maillard Reaction; Leather; Coloration; Mechanical Strength; Glucose Oxide

当研究室では、食品のメイラード反応を利用して、有害性が問題視されている合成染料の代替技術の開発に取り組んでいる。最近の研究で、メイラード反応の中間体が含まれる還元糖の酸化物を着色剤に利用することによって、合成染料に匹敵する着色時間で羊毛などのタンパク質繊維を着色できることを明らかにした。本発表では、羊毛よりも耐熱性の低い皮革を用いて、グルコース酸化物による皮革の着色効果と機械強度への影響について調べたので報告する。

はじめに、グルコースをフェントン反応で酸化させたグルコース酸化物を利用してクロム鞣し革を着色し、その機械強度への影響について検討を行った。皮革の機械強度は、一定時間蒸留水に浸漬させた湿潤状態の皮革の引張強度の相対値を用いて評価した。着色時の条件として、着色時間、着色温度、さらに、グルコース酸化物の濃度について調べたところ、いずれの反応条件によっても、着色濃度が高い皮革ほど機械強度の低下が認められた。その原因の一つとして、フェントン反応後のグルコース酸化物の水溶液が強酸性であることが挙げられる。そこで、着色反応の前に水酸化ナトリウムで溶液の pH を制御したところ、高い pH 値ではグルコース酸化物による着色濃度が低下する反面、着色した皮革の機械強度は未加工のものよりも高い値を示した (図 1)。この結果は、着色効果との両立は難しいものの、糖質の酸化物が皮革の鞣し剤に利用できる可能性を示している。

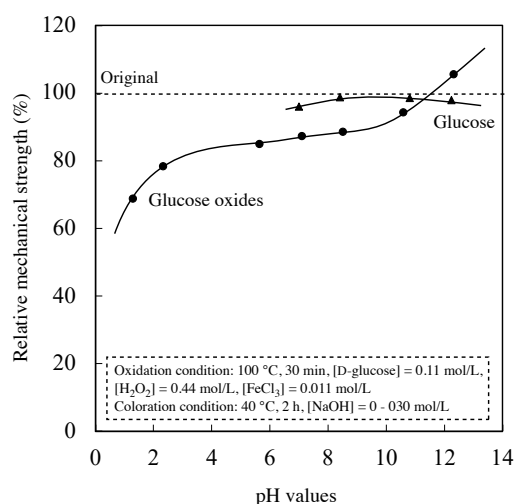


図 1 グルコース酸化物で着色した皮革の強度変化

Arthrobacter 菌体を用いた、Cs, Co, および Sr の混合溶液からの各金属の除去、分離および回収

(八戸工大工¹) ○鶴田 猛彦¹・立花 純¹・横山 和也¹・長根 貴宏¹・小関 裕也¹・志賀 晶¹

Removal, Separation and Recovery of Cs, Co, and Sr from the Mixed Solution Using *Arthrobacter* Cells (¹Faculty of Engineering, Hachinohe Institute of Technology)
○Takehiko Tsuruta¹, Jun Tachibana¹, Kazuya Yokoyama¹, Takahiro Nagane¹, Yuya Koseki¹, Akira Shiga¹

In detected metals around Fukushima Daiichi nuclear power plant, adsorption of Co, Sr, and Cs from the solution containing mixed metals using *Arthrobacter nicotianae* was examined. The amount of adsorbed each metal using microorganism was increased with increasing the pH of the solution. The amount of adsorbed each metal ($\mu\text{mol/g}$ dry wt. cells) using microorganism was also increased with increasing the metal concentration in the solution. The relative degree of metal adsorbed by *A. nicotianae* cells was observed to be Co, Sr > Cs. The amount of total adsorbed each metal (%) was increased with increasing the cell amounts. Co and Sr were removed quantitatively using enough amount of microbial cells, however, Cs was not removed perfectly using microbial cells by batch system. Quantitative Co, Sr, and Cs by immobilized *A. nicotianae* cell was next examined. All of the ions were removed by passing through the column. Most of the adsorbed Cs could be desorbed separately, however, Co and Sr couldn't be separated. To separate these metal ions, Sr was removed batch treatment at pH 2. As the amount of Sr removed was about in this method was about 60 %, this treatment was continued three times. After removed Sr, remained Co and Cs solution was passed through the immobilized microbial column. All of the Co and Cs adsorbed was desorbed by diluted nitric acid and separated perfectly.

Keywords : Co, Cs, Sr Removal; Co, Cs, Sr separation; Co, Cs, Sr recovery; *Arthrobacter nicotianae* Cells

福島第一原発の周りで検出された金属の中から Cs、Co、Sr の混合溶液からの *Arthrobacter nicotianae* 菌体を用いた吸着除去を検討した。微生物を用いた各金属の除去量は pH 1~5 の範囲で pH の上昇とともに増加した。各金属の除去量(乾燥菌体 1g 当り) はまた溶液中の金属量の上昇とともに増加した。各金属の除去量の相対的な比は Co, Sr > Cs であった。各金属の全除去量は菌体量の増加とともに増加した。バッチ処理における Co と Sr の除去量は十分量の菌体を使用することにより完全に除去されたが Cs は完全には除去できなかった。固定化菌体を使用したカラム法による Co, Sr および Cs の完全な除去が可能であった。Cs の大部分はカラム中での脱着により分離可能であったが Co と Sr の分離は困難であった。これらの金属イオンを分離するために種々の検討をした結果、Sr のみが pH 2 でバッチ処理を行ったことにより除去できた。この方法での Sr の除去量は約 60% であった。この処理を 3 回行うことによりほとんどの Sr を除去できた。Sr の除去後、Co と Cs の溶液を固定化微生物カラムに通すことにより吸着された Co と Cs は希硝酸により別々に分離されて脱着された。

廃リチウムイオン電池からの資源回収を目的としたキレート樹脂による溶液中の Ni および Co の新規分離技術

(愛媛大学¹・株式会社イージーエス²) ○近藤 治郎^{1,2}・青野 宏通¹・次田 泰裕²
New Separation Technology of Ni and Co in Solution by Chelating Resin for Resource Recovery from Waste Lithium-ion Batteries (¹*Graduate School of Science and Engineering, Ehime University*, ²*EGS, Co., Ltd.*) ○Jiro Kondo,^{1,2} Hiromichi Aono,¹ Yasuhiro Tsugita²

Among the rare metals contained in waste lithium-ion batteries (Spent-LIBs), Ni and Co are important elements as functional materials for lithium-ion batteries (LIBs), but they are extremely difficult to separate. For example, both Ni and Co in solution are adsorbed by chelating resin. In this study, the separation of Ni and Co was achieved by the action of metal complexes formed by inorganic salts such as citric acid and ammonia with the metals.

In fact, in the column test on chelating resin (iminodiacetic acid), the adsorption of both Ni and Co was unstable in citric acid only, and more than 90 % of both Ni and Co were adsorbed in ammonia only. On the other hand, when the pH was adjusted to 10 or more in the presence of citric acid and ammonia, the adsorption rates of Ni and Co were more than 90 % and less than 10%, respectively. We have found that this new technology makes it possible to separate easily Ni and Co.

In addition to Ni and Co, Li, Mn, Fe, and Al are contained in the recovered liquid obtained by calcination, pulverization, and dissolution of Spent-LIB, and the problems in their separation are also discussed in this paper. Tanaka and Kunimune also present related research at this conference.

Keywords : *lithium-ion battery; Ni; Co; Inorganic salt; Chelating resin*

廃リチウムイオン電池 (Spent-LIB) に含まれるレアメタルの中でも Ni および Co はリチウムイオン電池 (LIB) の機能材料として重要な元素であるが、きわめて分離が困難である。例えばキレート樹脂による溶液の吸着特性として Ni と Co の両方が吸着されてしまう。そこで本研究では、クエン酸およびアンモニア等の無機塩類と金属とで形成される金属錯体を作用させることによって Ni と Co の分離を達成した。

実際に、キレート樹脂 (イミノジ酢酸) へのカラム試験において、クエン酸のみでは Ni および Co の双方の吸着が不安定であり、アンモニアのみでは Ni および Co 共に 90%以上が吸着された。一方、クエン酸とアンモニアの存在下で pH を 10 以上に調整したところ Ni の吸着率が 90%以上、Co の吸着率が 10%以下の結果が得られ、この新規技術により Ni および Co の分離が容易に行えることを見出した。

さらに本報では、Spent-LIB の焼成・粉砕・溶解で得られる回収液には Ni、Co の他、Li、Mn、Fe、Al などが含まれ、これら分離における課題についても考察した。本大会において、田中および國宗も関連研究の発表を行う。

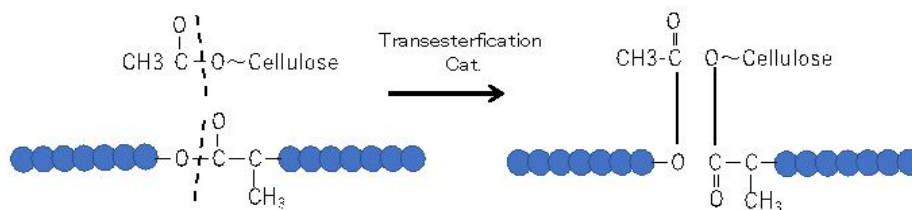
Design of thermoplastic materials using cellulose as a base matrix

(¹ *Kyushu Institute of Technology*) ○Ruozhu Wang,¹ Yoshito Andou ²

Keywords: Cellulose acetate; Polylactic acid; Thermoplastic; Melt-kneading

In recent years, pollution such as marine plastics and climate change are considered important global issues due to environmental aspects. Various measures to solve the environmental problem are being considered. As a countermeasure, the development of biodegradable plastics which has the potential to replace petroleum-based plastics such as polyethylene and polypropylene has attracted particular attention. Cellulose is one of the most abundant biodegradable polymer available in nature and exhibits excellent mechanical properties. However, cellulose does not have the thermoplasticity of general-purpose resins, which limits its utilization.

In this study, transesterification reaction by melt-kneading method was utilized to produce thermoplastic composite with commercialized cellulose acetate (CA) and polylactic acid (PLA). In general, CA has a high melting point of 250-300°C, and will be carbonized after melting. It's low thermoplasticity makes it difficult to use as a resin. PLA which is versatile biodegradable resin, a polyesters, and the transesterification reactions between molecular chains have been reported ¹⁾. Here-in, we focused on the transesterification reaction between the acetyl group of CA and polyester (Scheme 1). As shown in Fig.1, unlike PLA, the composite resin obtained by melt-kneading CA and PLA was incompatible, and no thermoplasticity was obtained. However, when 2-Ethylhexanoic Acid Tin(II) was added as a catalyst, a composite material showing thermoplasticity between CA and PLA was obtained under certain kneading conditions. Characterization results confirmed that PLA successfully grafted onto CA backbone.



Scheme 1. Transesterification reaction between the molecular chains of CA and PLA



Fig. 1. Sample after melt kneading

1) J. Yang et al. *Polymer* 83(2016)230-238.

液中プラズマ還元による酸化チタンの酸素欠損化と導電性の付与

(オーク製作所¹・東理大院理工²・東理大総研³) ○高木 海¹・藤井 悠太^{2,3}・栗山 晴男¹・早川 壮則¹・芹澤 和泉¹・石田 直哉³・寺島 千晶^{2,3}・藤嶋 昭³

Conductive Properties of Oxygen Deficient Titanium Dioxide by In-liquid Plasma Treatment (¹ORC MANUFACTURING CO., LTD., ²Graduate School of Science and Technology, Tokyo University of Science, ³Research Institute for Science and Technology, Tokyo University of Science) ○ Kai Takagi¹, Yuta Fujii^{2,3}, Haruo Kuriyama¹, Takenori Hayakawa¹, Izumi Serizawa¹, Naoya Ishida³, Chiaki Terashima^{2,3}, Akira Fujishima³

In recently years, the recycling of carbon dioxide using electroreduction has been studied. It is known that carbon dioxide can be selectively reduced by loading conductive carbon with an auxiliary catalyst such as gold, lead, etc¹⁾. However, the carbon is degraded by redox reactions, resulting in decreased long-term stability and selectivity. In this study, we aimed to improve the inexpensive and chemically resistant anatase as a high electrical conductivity material by using in-liquid plasma method. Resistivity at different voltage pulse width of pulse power supply and XPS spectra of O1s before and after in-liquid plasma treatment ($\tau = 0.26 \mu\text{s}$) are shown in Fig. 1 and Fig. 2, respectively. The resistivity decreased as the pulse width increased. It can be considered that the increase in electronic conductivity due to the increase in oxygen vacancies results in a decrease in resistance. On that day, we will report on the carbon dioxide electroreduction properties of gold-loaded anatase.

Keywords : In-liquid Plasma; Oxygen-deficient Titanium Dioxide; Electrode; Conducive Aid; Carbon dioxide reduction

近年、電解還元を用いた二酸化炭素の再利用化が研究されている。二酸化炭素は、導電性カーボンに金や鉛等の助触媒を担持することで選択的に還元される¹⁾。しかし、カーボンが酸化還元反応により劣化し、長期的安定性や選択性が低下する問題がある。そこで本研究では、液中プラズマ法を用いて、安価で耐薬品性があるアナターゼを導電性が高い助触媒担持体として適用することを目的とした。パルス電源の電圧パルス幅を変化させた際の抵抗率と、液中プラズマ処理前後 ($\tau = 0.26 \mu\text{s}$) の O1s の XPS スペクトルをそれぞれ図 1、図 2 に示す。パルス幅が大きくなると抵抗率が減少した。酸素欠損の増加による電子伝導度の上昇により、抵抗値が低下していると考察できる。当日は、金を担持したアナターゼの二酸化炭素電解還元特性について報告する。

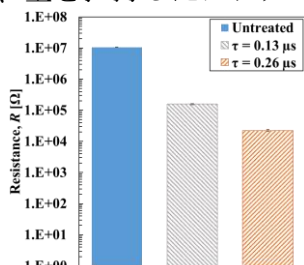


Fig. 1 液中プラズマ処理前後の抵抗率

1) L. Jin et. al., *Nanoscale*, 10, 14678 (2018).

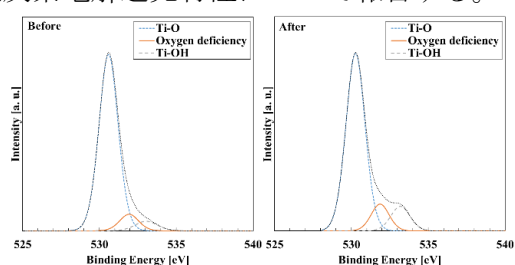


Fig. 2 O1s の XPS スペクトル ($\tau = 0.26 \mu\text{s}$)

Complete Mineralization of Fluorinated Ionic Liquids Using Low-Temperature Superheated Water

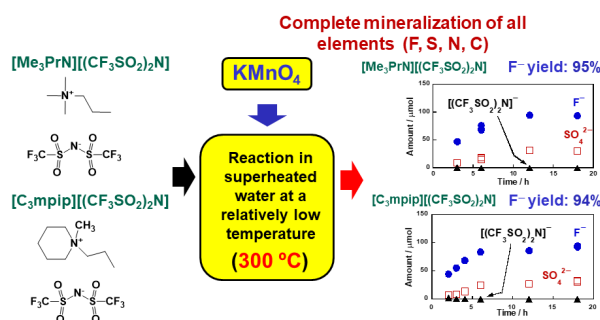
(Faculty of Science, Kanagawa University) ○Hisao Hori, Satomi Oishi

Keywords: Ionic Liquid; Superheated Water; Decomposition; Fluorine

Ionic liquids (ILs) are cutting-edge materials for green chemistry applications because they have unique characteristics such as negligible vapor pressure, high thermal and chemical stability, and high solvation ability, and they are non-flammable. Among them, fluorinated ILs, which are combinations of an organic cation and a perfluorinated organic anion, are used as electrolytic media for energy-related applications in batteries, dye-sensitized solar cells, supercapacitors, and actuators, because they not only have the common characteristics of ILs but they also fulfill crucial requirements for electrochemical devices.

The increasing number of industrial usages of fluorinated ILs has led to increased examination of their aquatic toxicity. Several ILs are reported to be biodegradable; however, their biodegradation is limited mostly in the organic cation moiety and does not result in complete mineralization of the IL. Furthermore, the perfluorinated anion moiety, bis(trifluoromethanesulfonyl)imide, $[(CF_3SO_2)_2N]^-$, the most common anion used in fluorinated ILs, has been shown to not biodegrade. Under these circumstances, waste treatment technologies that allow complete mineralization of fluorinated ILs are needed.

We report herein an effective method that allows almost complete mineralization of two fluorinated ILs— $[Me_3PrN][[(CF_3SO_2)_2N]]$ and 1-methyl-1-propylpiperidium bis(trifluoromethanesulfonyl)imide, $[C_3mpip][[(CF_3SO_2)_2N]]$ —in superheated water (often referred to subcritical water or pressurized hot water) at a relatively low temperature (300 °C) by using $KMnO_4$ as an oxidizing agent. $KMnO_4$ is a safe oxidizing agent that is currently used at drinking water treatment plants to remove iron component and to control the formation of trihalomethanes and other disinfection byproducts.



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