

Sat. Mar 25, 2023

K205

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

[K205-4am] 05. Physical Chemistry -Chemical**Kinetics and Dynamics-**

Chair: Kenichi Okutsu, Shinji Nonose

9:00 AM - 11:10 AM K205 (K205, Lecture Hall Bldg. [2F])

[K205-4am-01] Investigation of the reaction mechanism of inhibition of HFO-1123

disproportionation by addition of iodine inhibitor using GC-MS

○Karin Domoto¹, Sae Fujita¹, Hiroyuki Aoyama¹, Hikaru Murakami², Hirotaka Kitagawa², Takahiko Hashimoto², Yukio Nakano¹ (1. Tokyo Gakugei University, 2. Panasonic Corp.)

9:00 AM - 9:20 AM

[K205-4am-02] Hypervalent Carbon and Iodine

Compounds Investigated by Cryogenic Gas-Phase Spectroscopy

○Satoru Muramatsu¹, Akihito Matsuyama¹, Daiki Iwanaga¹, Keiji Ohshimo², Motoki Kida¹, Yuan Shi¹, Rong Shang, Yohsuke Yamamoto¹, Fuminori Misaizu², Yoshiya Inokuchi¹ (1. Hiroshima Univ., 2. Tohoku Univ.)

9:20 AM - 9:40 AM

[K205-4am-03] Temperature Dependence of Proton Transfer in Protonated Aminobenzoic Acid Studied by Cryogenic Ion Trap and Ion Mobility– Mass Spectrometry○Keiji Ohshimo¹, Yuya Takasaki², Kengo Tsunoda¹, Ryosuke Ito¹, Fuminori Misaizu¹ (1. Graduate School of Science, Tohoku University, 2. Faculty of Science, Tohoku University)

9:40 AM - 10:00 AM

[K205-4am-04] Proton Transfer Reactions of Bimolecular Ions in Gas Phase on OPIG-DC Voltage○Shinji Nonose¹, Hiroto Ohta¹, Satofumi Tago¹, Soju Tomiyama¹ (1. Yokohama City University)

10:10 AM - 10:30 AM

[K205-4am-05] Elucidating electronic structure of excimer-like species formed from a luminescent diradical○Ryota Matsuoka¹, Yusuke Yoneda¹,Hikaru Kuramochi¹, Tomoaki Miura², Tadaaki Ikoma², Masaki Saigo³, Takumi Ehara³, Kiyoshi Miyata³, Ken Onda³, Tetsuro Kusamoto^{1,4} (1. IMS, 2. Niigata Univ., 3. Kyushu Univ., 4. JST-PRESTO)

10:30 AM - 10:50 AM

[K205-4am-06] Single-molecule magnetoluminescence from a carbazole-based luminescent diradical○Asato Mizuno¹, Ryota Matsuoka¹, Shojiro Kimura², Tetsuro Kusamoto^{1,3} (1. Institute for Molecular Science, 2. Tohoku University, 3. JST-PRESTO)

10:50 AM - 11:10 AM

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

[K205-4pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-

Chair: Tetsuro Katayama, Yo-ichi Yamamoto

1:00 PM - 2:50 PM K205 (K205, Lecture Hall Bldg. [2F])

[K205-4pm-01] Cycloreversion reaction of diarylethene nanocolloids induced by intense pulse laser excitationShintaro Matsumoto¹, ○Yukihide Ishibashi¹, Daichi Kitagawa², Seiya Kobatake², Tsuyoshi Asahi¹ (1. Ehime University, 2. Osaka Metropolitan University)

1:00 PM - 1:20 PM

[K205-4pm-02] Observation of carrier dynamics in single and few layers of WSe₂ by femtosecond transient absorption microscopy and its interlayer angle dependence○Tetsuro Katayama¹, Akira Yamamoto¹, Naohiko Endo², Yasumitsu Miyata², Akihiro Furube¹ (1. Tokushima University, 2. Tokyo Metropolitan University)

1:20 PM - 1:40 PM

[K205-4pm-03] Ultrafast nonradiative deactivation and tautomerization of the solvatochromic dye, phenol blue○Yutaka Nagasawa¹, Takemoto Tanaka¹, Tsubasa Hidaka¹, Akifumi Matsumoto¹, Chikashi Ota¹, Takahiro Teramoto² (1. Ritsumeikan University, 2. Osaka University)

1:40 PM - 2:00 PM

[K205-4pm-04] Ultrafast Photoemission Spectroscopy of

Solvated Electrons and Development of Spectral Retrieval Method

○Yo-ichi Yamamoto¹, Toshinori Suzuki¹ (1. Kyoto University)

2:10 PM - 2:30 PM

[K205-4pm-05] Formation of petal-like concentric precipitation patterns by continuous injection of dye solution into filter paper associated with solvent evaporation

○Amiko Aizawa¹, Taisuke Banno¹, Kouichi Asakura^{1,2} (1. Faculty of Science and Technology, Keio University, 2. Meiji Institute for Advanced Study of Mathematical)

2:30 PM - 2:50 PM

K305

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

[K305-4am] 08. Catalysts and Catalysis

Chair: Hiroki Miura, Takafumi Yatabe

9:00 AM - 11:30 AM K305 (K305, Lecture Hall Bldg. [3F])

[K305-4am-01] Decarbonylation and Metathesis via C–S Bond Scission by Ni or Pd-Based Catalysts

○Takehiro Matsuyama¹, Takafumi Yatabe¹, Tomohiro Yabe¹, Kazuya Yamaguchi¹ (1. The University of Tokyo)

9:00 AM - 9:20 AM

[K305-4am-02] Au nanoparticles-catalyzed regioselective aerobic oxidation of tertiary amines: mechanism elucidation and application to enaminone synthesis

○Takafumi Yatabe^{1,2}, Syunsuke Kanamoto¹, Yuta Funami¹, Kazuya Yamaguchi¹ (1. The University of Tokyo, School of Engineering, Department of Applied Chemistry, 2. JST, PRESTO)

9:20 AM - 9:40 AM

[K305-4am-03] Remarkably Efficient Hydrogenolysis of Esters to Alkanes by A Multifunctional Pt/WO₃–ZrO₂ Catalyst

○Yukari Yamazaki¹, Kang Yuan¹, Xiongjie Jin¹, Kyoko Nozaki¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[K305-4am-04] Emergence of Hydrosilylation Catalysis of Cyclic Carbonate by Immobilization on Silica Surface

○Shingo Hasegawa¹, Kousuke Soga¹, Keisuke Nakamura², Kei Usui², Yuichi Manaka^{2,3}, Ken Motokura^{1,2} (1. Yokohama National University, 2. Tokyo Institute of Technology, 3. National Institute of Advanced Industrial Science and Technology)

10:00 AM - 10:20 AM

[K305-4am-05] Synthesis of Ni nanoparticles using hydrosilanes and their catalytic activity

○Yusuke Kita¹, Shun Takeuchi¹, Takaaki Oyoshi¹, Keigo Kamata¹, Michikazu Hara¹ (1. Tokyo Tech.)

10:30 AM - 10:50 AM

[K305-4am-06] Selective Hydrogenation of CO₂ to MeOH using Sterically Confined Ir Complexes

○Bendik Groemer¹, Susumu Saito^{1,2} (1. Graduate School of Science, Nagoya University (Grad. Sch. Sci., Nagoya Univ.), 2. Integrated Research Consortium on Chemical Sciences, Nagoya University (IRCCS, Nagoya Univ.))

10:50 AM - 11:10 AM

[K305-4am-07] Bimetallic Subnanoparticles Enable Thermally-driven CO₂ Hydrogenation from Room Temperature

○Augie Atqa¹, Masataka Yoshida¹, Masanori Wakizaka³, Wang-Jae Chun⁴, Akira Oda⁵, Takane Imaoka^{1,2}, Kimihisa Yamamoto^{1,2} (1. Tokyo Institute of Technology, 2. JST ERATO Yamamoto Atom Hybrid Project, 3. Tohoku University, 4. International Christian University, 5. Nagoya University)

11:10 AM - 11:30 AM

K505

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

[K505-4am] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Akitaka Ito, Yoshihiro Sekine

9:00 AM - 11:30 AM K505 (K505, Lecture Hall Bldg. [5F])

[K505-4am-01] Magnetic Properties of Organic-Inorganic Perovskites with Ferroelasticity

○Naoto Tsuchiya¹, Ishinuki Tatsuya¹, Saya Aoki¹, Yuki Nakayama¹, Goulven Cosquer², Sadafumi Nishihara^{1,2,3}, Katsuya Inoue^{1,2,4} (1. Graduate School of Advanced Science and

Engineering, Hiroshima Univ., 2. Chirality Research Center, Hiroshima Univ., 3. JST, PRESTO, 4. International Institute for Sustainability with Knotted Chiral Meta Matter, Hiroshima Univ.)

9:00 AM - 9:20 AM

[K505-4am-02] Multifunctional Spin Crossover Compounds with Chiral Anions

○Hikaru Zenno¹, Yoshihiro Sekine¹, Shinya Hayami¹ (1. Kumamoto University)

9:20 AM - 9:40 AM

[K505-4am-03] Luminescence from Terbium(III) Species upon Sensitization using Ionic Nanosphere

○Nikita Madhukar¹, Taizo Misato¹, Akitaka Ito¹ (1. Kochi Univ. of Tech.)

9:40 AM - 10:00 AM

[K505-4am-04] Energy-Transfer Quenching of [Ru(bpy)₃]²⁺ in Ionic Nanosphere

○Taizo Misato¹, Akitaka Ito¹ (1. Kochi Univ. of Tech.)

10:00 AM - 10:20 AM

[K505-4am-05] Symmetry-breaking Assembly of a Supramolecular Ir Complex within a Hydrogen-bonded Host

○Shinnosuke Horiuchi^{1,2}, Eri Sakuda², Yasuhiro Arikawa², Shuichi Hiraoka¹, Keisuke Umakoshi² (1. The Univ. of Tokyo, 2. Nagasaki Univ.)

10:30 AM - 10:50 AM

[K505-4am-06] Control of Molecular Arrangement and Polarity in Vapochromic Crystals

○Fumiya Kobayashi¹, Misato Gemba¹, Makoto Tadokoro¹ (1. Tokyo Univ. of Sci.)

10:50 AM - 11:10 AM

[K505-4am-07] Latest progress on halogen-bridged metal complex chemistry

○Masanori Wakizaka¹, Shinya Takaishi¹, Masahiro Yamashita¹ (1. Tohoku Univ.)

11:10 AM - 11:30 AM

K606

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

[K606-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kentaro Suzuki, Tomohisa Sawada

9:00 AM - 11:10 AM K606 (K606, Lecture Hall Bldg. [6F])

[K606-4am-01] Effect of substrate curvature and relative humidity on branched shape of hollow crystals for vapor phase crystal growth of photochromic diarylethene

○Mami Isobe¹, Daichi Kitagawa^{1,2}, Seiya Kobatake^{1,2} (1. Grad. Sch. of Eng., Osaka Metropolitan Univ., 2. Grad. Sch. of Eng., Osaka City Univ.)

9:00 AM - 9:20 AM

[K606-4am-02] X-ray observation of steric zipper interactions in metal-induced peptide cross- β nanostructures

○Eisuke Tsunekawa¹, Tomohisa Sawada^{2,3}, Makoto Fujita^{1,4} (1. Grad. School of Engineering, The university of Tokyo, 2. Lab. for Chem. &Life Sci., Tokyo Tech, 3. JST PRESTO, 4. IMS)

9:20 AM - 9:40 AM

[K606-4am-03] Syntheses and Emission Properties of Rotaxane-type Fluorophores Encapsulating Pyridinium-conjugated Molecules

○Kohei Nishioki¹, Yuki Ohishi¹, Junya Chiba¹, Masahiko Inouye¹ (1. University of Toyama)

9:40 AM - 10:00 AM

[K606-4am-04] Phototriggered supramolecular polymerization with anthracene diketone precursors

○Mitsuaki Yamauchi¹, Hidenori Nakanishi¹, Hironobu Hayashi¹, Hiroko Yamada¹ (1. Nara Institute of Science and Technology)

10:10 AM - 10:30 AM

[K606-4am-05] Charge-Segregated Stacking Structure Comprising Charged NIR-Dye

○Kazuhisa Yamasumi¹, Kentaro Ueda¹, Yohei Haketa¹, Hiromitsu Maeda¹ (1. Ritsumeikan University)

10:30 AM - 10:50 AM

[K606-4am-06] Reversible Photocontrol over Hydrogen-bond-directed Supramolecular Polymorphism

○Kenta Tamaki¹, Shiki Yagai² (1. Grad. Sch. of Sci. and Eng., Chiba Univ., 2. IAAR, Chiba Univ.)

10:50 AM - 11:10 AM

K705

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

[K705-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Masaki Nishijima, Shinichiro Fuse

9:00 AM - 10:20 AM K705 (K705, Lecture Hall Bldg. [7F])

[K705-4am-01] Multistep-flow Syntheses of APIs Utilizing

Continuous-flow C–N Bonds Forming Reactions with Heterogeneous Catalysts

○Ken Nishizawa¹, Yuki Saito¹, Shu Kobayashi¹

(1. The university of Tokyo)

9:00 AM - 9:20 AM

[K705-4am-02] Development of Flow Microwave Reactor

Using CSTR and Rapid Synthesis of Organic Compounds

○Takeko Matsumura¹, Akiyoshi Ono¹, Isao

Kotani², Kentaro Kotani², Nobuyuki Nakayama²,

Mitsuyoshi Kishihara³, Yoshihito Mori⁴ (1.

MINERVA LIGHT LAB., 2. Mac engineering Co.

Ltd., 3. Okayama Prefectural University, 4.

Ochanomizu University)

9:20 AM - 9:40 AM

[K705-4am-03] Oil/water-biphasic dynamic kinetic

resolution in a Pickering emulsion

○Kyohei Kanomata¹, Jihoon Moon¹, Takusho

Kin¹, Karin Mizuno¹, Shuji Akai¹ (1. Osaka

University)

9:40 AM - 10:00 AM

[K705-4am-04] Photosensitized Singlet Oxygen-

supported Alcohol Oxidation Mediated by Nitroxyl Radical Catalyst

○Masaki Nishijima¹, Shota Nagasawa¹, Yusuke

Sasano¹, Yasuyuki Araki¹, Yoshiharu Iwabuchi¹,

Takehiko Wada¹ (1. Tohoku University)

10:00 AM - 10:20 AM

E1661

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

[E1661-4am] 17. Biofunctional Chemistry, Biotechnology

Chair: Nobuhiko Hosono, Takashi Matsuo

9:00 AM - 11:10 AM E1661 (1611, Bldg. 16 [1F])

[E1661-4am-01] Screening of decoy molecules for

propane hydroxylation using intracellular Cytochrome P450BM3

○Yuki Sugai¹, Masayuki Karasawa¹, Yusaku

Kadama¹, Kai Yanemura¹, Shinya Ariyasu¹,

Yuichiro Aiba¹, Osami Shoji¹ (1. Graduate

School of Science, Nagoya University)

9:00 AM - 9:20 AM

[E1661-4am-02] Dimerization of Artificial Hemoprotein

Containing a Tetraphenylporphyrin

Derivative Based on Metal Coordination

○Hiroaki Inaba¹, Yuma Shisaka¹, Garyo Ueda¹,

Erika Sakakibara¹, Shinya Ariyasu¹, Yuichiro

Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1.

Graduate school of Science, Nagoya

University, 2. RIKEN SPring-8)

9:20 AM - 9:40 AM

[E1661-4am-03] Whole-Cell Biocatalysts Harboring P450s

Triggered by External Additives for

Microbial Degradation of Environmental Pollutants

○Fumiya Ito¹, Shinya Ariyasu¹, Masayuki

Karasawa¹, Chie Kasai¹, Yuichiro Aiba¹, Osami

Shoji¹ (1. Graduate School of Science,

Nagoya University)

9:40 AM - 10:00 AM

[E1661-4am-04] Catalytic Hydroxylation of Non-native

Substrates by Cytochrome P450BM3

Mutants with Expanded Structural

Availability of Decoy Molecules by

Directed Evolution

○Yuya Yokoyama¹, Shinya Ariyasu¹, Masayuki

Karasawa¹, Kai Yonemura¹, Yuichiro Aiba¹,

Hiroshi Sugimoto², Osami Shoji¹ (1. School

of Science, Nagoya University, 2. RIKEN

SPring-8)

10:10 AM - 10:30 AM

[E1661-4am-05] Chemical modification of

peptides/proteins using specific affinity

of transition metal for alkene

Asuki Okada¹, Tsubasa Kinugawa¹, Shun

Hirota¹, ○Takashi Matsuo¹ (1. Nara Inst. Sci.

Tech.)

10:30 AM - 10:50 AM

[E1661-4am-06] Selective Removal of Denatured Proteins

by Metal-Organic Frameworks

○Hiroataka Taketomi¹, Nobuhiko Hosono¹,
Takashi Uemura¹ (1. Grad. Sch. of Eng., The
Univ. of Tokyo)
10:50 AM - 11:10 AM

B445

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

[B445-4am] 19. Colloid and Interface Chemistry

Chair: Hiroyuki Arafune, Takeshi Kawai

9:00 AM - 11:10 AM B445 (445, Bldg. 4 [4F])

[B445-4am-01] Odd-even effect in two-dimensional self-assembly of curcumin derivatives at the solid/liquid interface

○Suyi Liu^{1,2}, Yoshihiro Kikkawa², Yasuo
Norikane^{1,2} (1. University of Tsukuba, 2.
National Institute of Advanced Industrial
Science and Technology (AIST))
9:00 AM - 9:20 AM

[B445-4am-02] Structural model of a large spherical colloidal cluster with icosahedral symmetry

○Ryosuke Ohnuki¹, Yukikazu Takeoka², Shinya
Yoshioka¹ (1. Tokyo University of Science, 2.
Nagoya University)
9:20 AM - 9:40 AM

[B445-4am-03] Fabrication of perovskite/carbonaceous nanocomposite and its evaluation toward electrochemical detection of amino acids

○Jeevika Alagan¹, Ryosuke Yambe¹, Yuna Kim¹,
Ken-ichi Iimura¹ (1. Utsunomiya University)
9:40 AM - 10:00 AM

[B445-4am-04] Catalytic Reduction of Methylene Blue by Gallium-Based Liquid Metals

○Nichayanan Manyuan¹, Hideya Kawasaki¹ (1.
Kansai University)
10:10 AM - 10:30 AM

[B445-4am-05] New cleaning mechanism by dynamic wetting using nonionic surfactant oil solution

○Yuko Nagasaki¹, Mariko Kagaya¹, Chihiro
Ueyama¹, Hitoshi Tajima¹ (1. Kao
corporation)
10:30 AM - 10:50 AM

[B445-4am-06] Characterization of friction-induced molecular orientation change in

fluoropolymer thin film using MAIRS

○Motohiro Kasuya¹, Touma Nagata¹, Miyuki
Matsushita¹, Nobutaka Shioya², Takahfumi
Shimoaka², Akihito Hibara³, Takeshi
Hasegawa² (1. Komatsu University, 2. Kyoto
University, 3. Tohoku University)
10:50 AM - 11:10 AM

K206

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

[K206-4am] 20. Materials Chemistry -Basic and Application-

Chair: Kazuki Sada, Koki Sano

9:00 AM - 10:20 AM K206 (K206, Lecture Hall Bldg. [2F])

[K206-4am-01] Diarylethene crystal showing unusual mechanofluorochromism

○Ryo Nishimura¹, Yuka Kobayashi¹, Masakazu
Morimoto¹ (1. Rikkyo University)
9:00 AM - 9:20 AM

[K206-4am-02] Self-assembling and stimuli-responsive behaviors of donor-acceptor type fluorenone derivatives

○Atsushi Seki^{1,2}, Mao Suzuki², Shota Yamada¹,
Soun Doi¹, Ken'ichi Aoki^{1,2} (1. Tokyo Univ. of
Science, 2. Grad. School of Science, Tokyo
Univ. of Science)
9:20 AM - 9:40 AM

[K206-4am-03] Evaluation of Atomic Oxygen Resistance of POSS film

○Kazuki Yukumatsu¹, Aki Goto¹, Soichi
Yokoyama², Yutaka Ie², Yugo Kimoto¹ (1.
Japan Aerospace Exploration Agency, 2. Osaka
University)
9:40 AM - 10:00 AM

[K206-4am-04] Ambient-condition methane storage in carbon nanopores with with temperature-triggered locking/unlocking

○Shuwen Wang¹, Katsumi Kaneko¹ (1.
Research Initiative for Supra-Materials, Shinshu
University)
10:00 AM - 10:20 AM

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

[K206-4pm] 20. Materials Chemistry -Basic and

Application-

Chair: Ken'Ichi Aoki, Masakazu Morimoto

1:00 PM - 2:40 PM K206 (K206, Lecture Hall Bldg. [2F])

Graduate School of Env. Science)

2:20 PM - 2:40 PM

[K206-4pm-01] Temperature and solvent dependence of polybenzimidazole adsorption on carbon materials

○Islam A B M Nazmul¹, Nana Kayo¹, Mai Akamine¹, Naoki Tanaka^{1,2}, Tsuyohiko Fujigaya^{1,2,3} (1. Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 2. WPI-I2CNER, Kyushu University, 3. Centre for Molecular System, Kyushu University)

1:00 PM - 1:20 PM

[K206-4pm-02] Sol-gel reaction of linear oligosiloxanes and their derivation to silicates

○Yohei Sato¹, Asahi Sugimoto¹, Ryohei Hayami¹, Kazuki Yamamoto¹, Takahiro Gunji¹ (1. Tokyo University of Science)

1:20 PM - 1:40 PM

[K206-4pm-03] Hybridization of cellulose and hydroxyapatite applicable to tough biomass materials

○Kohei Okuda¹, Tadashi Mizutani¹ (1. Doshisha university graduate school)

1:40 PM - 2:00 PM

[K206-4pm-04] Preparation and physical properties of hydrogels based on coordination between DNA and various metal ions

○Arisa Fukatsu¹, Sari Kurisu², Nanami Kuramoto², Waka Yoshida², Ibuki Yasui², Tadashi Inoue³, Kenji Okada^{1,4}, Masahide Takahashi¹ (1. Osaka Metropolitan University, 2. Osaka Prefecture University, 3. Osaka University, 4. JST-PRESTO)

2:00 PM - 2:20 PM

[K206-4pm-05] CO₂ gas separation properites of composite membranes consisting of organic polymer and metal-organic framework thin films

○Xin Zheng¹, Roman Selyanchyn^{2,3,4}, Shigenori Fujikawa^{2,3}, Shin-ichiro Noro^{1,5} (1. Hokkaido University, Faculty of Env. Earth Science, 2. Kyushu University, I²CNER, 3. Kyushu University, K-NETs, 4. Kyushu University, Q-PIT, 5. Hokkaido University,

Academic Program [Oral B] | 05. Physical Chemistry -Chemical Kinetics and Dynamics- | Oral B**[K205-4am] 05. Physical Chemistry -Chemical Kinetics and Dynamics-**

Chair: Kenichi Okutsu, Shinji Nonose

Sat. Mar 25, 2023 9:00 AM - 11:10 AM K205 (K205, Lecture Hall Bldg. [2F])

[K205-4am-01] Investigation of the reaction mechanism of inhibition of HFO-1123 disproportionation by addition of iodine inhibitor using GC-MS[○]Karin Domoto¹, Sae Fujita¹, Hiroyuki Aoyama¹, Hikaru Murakami², Hirotaka Kitagawa², Takahiko Hashimoto², Yukio Nakano¹ (1. Tokyo Gakugei University, 2. Panasonic Corp.)

9:00 AM - 9:20 AM

[K205-4am-02] Hypervalent Carbon and Iodine Compounds Investigated by Cryogenic Gas-Phase Spectroscopy[○]Satoru Muramatsu¹, Akihito Matsuyama¹, Daiki Iwanaga¹, Keiji Ohshimo², Motoki Kida¹, Yuan Shi¹, Rong Shang, Yohsuke Yamamoto¹, Fuminori Misaizu², Yoshiya Inokuchi¹ (1. Hiroshima Univ., 2. Tohoku Univ.)

9:20 AM - 9:40 AM

[K205-4am-03] Temperature Dependence of Proton Transfer in Protonated Aminobenzoic Acid Studied by Cryogenic Ion Trap and Ion Mobility– Mass Spectrometry[○]Keiji Ohshimo¹, Yuya Takasaki², Kengo Tsunoda¹, Ryosuke Ito¹, Fuminori Misaizu¹ (1. Graduate School of Science, Tohoku University, 2. Faculty of Science, Tohoku University)

9:40 AM - 10:00 AM

[K205-4am-04] Proton Transfer Reactions of Bimolecular Ions in Gas Phase on OPIG-DC Voltage[○]Shinji Nonose¹, Hiroto Ohta¹, Satofumi Tago¹, Soju Tomiyama¹ (1. Yokohama City University)

10:10 AM - 10:30 AM

[K205-4am-05] Elucidating electronic structure of excimer-like species formed from a luminescent diradical[○]Ryota Matsuoka¹, Yusuke Yoneda¹, Hikaru Kuramochi¹, Tomoaki Miura², Tadaaki Ikoma², Masaki Saigo³, Takumi Ehara³, Kiyoshi Miyata³, Ken Onda³, Tetsuro Kusamoto^{1,4} (1. IMS, 2. Niigata Univ., 3. Kyushu Univ., 4. JST-PRESTO)

10:30 AM - 10:50 AM

[K205-4am-06] Single-molecule magnetoluminescence from a carbazole-based luminescent diradical[○]Asato Mizuno¹, Ryota Matsuoka¹, Shojiro Kimura², Tetsuro Kusamoto^{1,3} (1. Institute for Molecular Science, 2. Tohoku University, 3. JST-PRESTO)

10:50 AM - 11:10 AM

GC-MS を用いたヨウ素系抑制剤添加による HFO-1123 不均化反応抑制の反応機構の検討

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

Investigation of the reaction mechanism of inhibition of HFO-1123 disproportionation by addition of iodine inhibitor using GC-MS (¹Tokyo Gakugei University, ²Panasonic Corporation) ○Karin Domoto¹, Sae Fujita¹, Hiroyuki Aoyama¹, 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. To practical use of HFO-1123 as refrigerant, it is necessary to understand the disproportionation reaction and then suppress it. 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 of the emission during the reaction and chemical kinetics simulation. We had found the disproportionation reaction can be suppressed by adding a small amount of iodine compounds (iodine inhibitors) to HFO-1123. However, the mechanism of the suppression of the disproportionation reaction by iodine inhibitors is not obtained. Therefore, we investigated of the reaction mechanism of suppression of HFO-1123 disproportionation by addition of iodine inhibitors using GC-MS in this study.

Keywords : Refrigerant, HFO-1123, Inhibitor, Disproportionation reaction, Reaction mechanism

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。我々はこれまでにこの不均化反応を実験室規模で再現することに成功し、不均化反応後の生成物分析、反応中の発光の分光測定、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起こることを報告した。また、HFO-1123 にヨードフルオロメタン (CF₂HI) をはじめとするヨウ素化合物を微量添加することにより不均化反応が抑制できることを報告した¹⁾。しかし、ヨウ素化合物による不均化反応の抑制メカニズムに関する知見は得られていなかった。そこで、本研究では抑制反応後の生成物の GC-MS 測定結果を用いてヨウ素系反応抑制剤添加による不均化反応の反応機構の検討を行った。

1) H. Murakami et al., The 102nd CSJ annual meeting, F102-1pm-02(2022).

Hypervalent Carbon and Iodine Compounds Investigated by Cryogenic Gas-Phase Spectroscopy

(¹Graduate School of Advanced Science and Engineering, Hiroshima University, ²Graduate School of Science, Tohoku University) ○ Satoru Muramatsu¹, Akihito Matsuyama¹, Daiki Iwanaga¹, Keijiro Ohshimo², Motoki Kida¹, Yuan Shi¹, Rong Shang¹, Yohsuke Yamamoto¹, Fuminori Misaizu², Yoshiya Inokuchi¹

Keywords: Hypervalent compound; Gas-phase spectroscopy; Cryogenic; Photodissociation spectroscopy; Ion mobility-mass spectrometry

Hypervalent compounds possess a main group element that formally has more than eight valence electrons, apparently exceeding the Lewis octet rule. Their characteristic electronic states that realize the “hypervalent state” have been intensively studied from a viewpoint of theoretical chemistry [1], while few attempts were made toward their spectroscopic identification. In this talk, we present our recent achievements in experimentally characterizing electronic states and bonding natures of following hypervalent carbon [2] and iodine [3] compounds, by using our spectroscopic techniques under cryogenic gas-phase conditions.

(1) Carbon compound [4] Yamamoto and co-workers have recently synthesized hypervalent pentacoordinate carbon compounds bearing a flexible 7-6-7 membered ring (Figure 1a) [2]. It was revealed that their bonding nature, penta-coordinate (hypervalent) *versus* tetra-coordinate (normal-valent) of the central carbon atom, is dependent on electron donating ability of substituent on ligands, X (Figure 1a). However, the structure of a compound with moderately electron donating one, X = SMe, remained ambiguous. Herein, our combined study of photodissociation spectroscopy (PDS), ion mobility-mass spectrometry, and density functional theory calculations demonstrated the coexistence of penta- and tetra-coordinate forms as isomers in solution and gas phase. It is in sharp contrast to the exclusive presence of the latter one in crystal, highlighting the effects of environment on stability of the hypervalency.

(2) Iodine compound We extend our study to an iodine compound, which has a colinear “N–I–N” moiety: [(C₅H₅N)₂I]⁺ (Figure 1b) [3]. PDS of the cryogenically (~10 K) cooled [(C₅H₅N)₂I]⁺ ion identified well-resolved vibronic bands, where N–I symmetrical stretching mode was observed at 168 cm^{−1}. It corresponds to an effective spring constant of 132 N·m^{−1} for the N–I bond in the electronically excited state. This study provides a clue toward quantitative understanding of the hypervalency.

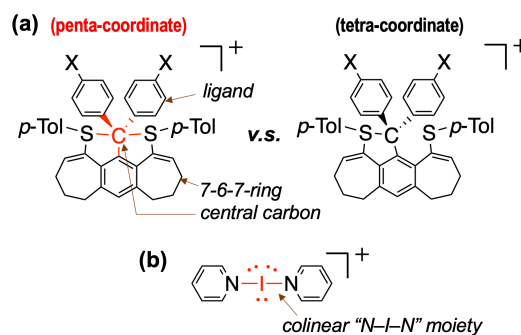


Fig. 1 Hypervalent (a) carbon and (b) iodine compounds used in this study.

[1] Braïda, B.; *et al. Nat. Chem.* **2013**, 5, 417. [2] Yamamoto, Y.; *et al. Chem. Eur. J.* accepted. [3] Carlsson, A. C. C.; *et al. Chem. Commun.* **2012**, 17, 1458. [4] Muramatsu, S.; *et al. Chem. Eur. J.* accepted.

低温イオントラップとイオン移動度質量分析を用いたプロトン付加アミノ安息香酸におけるプロトン移動の温度依存性の研究

(東北大院理¹・東北大理²)

○大下 慶次郎¹・高崎 佑也²・角田 健吾¹・伊藤 亮佑¹・美齊津 文典¹

Temperature Dependence of Proton Transfer in Protonated Aminobenzoic Acid Studied by Cryogenic Ion Trap and Ion Mobility–Mass Spectrometry

(¹Graduate School of Science, Tohoku University, ²Faculty of Science, Tohoku University)

○Keijiro Ohshimo,¹ Yuya Takasaki,² Kengo Tsunoda,¹ Ryosuke Ito¹, Fuminori Misaizu¹

Protonated aminobenzoic acid formed in the gas phase by electrospray ionization was accumulated in an ion trap, and isomers were separated by cryogenic ion mobility-mass spectrometry. In addition, ammonia was introduced into the ion trap to induce a proton transfer reaction. When the ion trap was cooled by liquid nitrogen, a complex ion of protonated aminobenzoic acid with ammonia was observed. On the other hand, this complex was hardly observed when the ion trap was kept at room temperature. The structure of this complex ion, an intermediate in the proton transfer reaction, was assigned from the measurement of collision cross section. **Keywords:** Proton Transfer, Aminobenzoic Acid, Protonated Molecule, Ion Mobility-Mass Spectrometry

エレクトロスプレーイオン化により気相に生成したプロトン付加 *p*-アミノ安息香酸 ($\text{H}_2\text{NC}_6\text{H}_4\text{COOH}\cdot\text{H}^+$, $\text{PABA}\cdot\text{H}^+$) をイオントラップで蓄積した後、低温イオン移動度質量分析 (IM-MS) を用いて構造同定した。溶媒に $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$ を用いた場合、 PABA の NH_2 基にプロトンが付加した $\text{PABA}\cdot\text{H}^+$ の N-protomer のみが観測された。次にイオントラップへ 0.005% NH_3/He を 10 sccm の流量で導入すると、 $\text{C}=\text{O}$ 基にプロトンが付加した O-protomer が N-protomer とともに観測された。さらにイオントラップを液体窒素で冷却したところ、 $\text{PABA}\cdot\text{H}^+$ に NH_3 が付加した錯体 ($\text{PABA}\cdot\text{H}^+\cdot\text{NH}_3$) が観測された (図 1)。図 1 の $\text{PABA}\cdot\text{H}^+\cdot\text{NH}_3$ の到達時間から、この錯体の He との衝突断面積は 97.6 \AA^2 と決定され、O-protomer に NH_3 が結合した錯体に帰属された。一方、イオントラップが室温の場合、この錯体はほとんど観測されなかった。この実験と反応経路探索計算から、この錯体は N-protomer と NH_3 とのイオン分子反応により O-protomer を生成するプロトン移動反応の反応中間体であると結論した。この反応は、 $\text{PABA}\cdot\text{H}^+$ と類似した構造をもつプロトン付加ベンゾカインで観測されたのと同様のビークル機構¹⁾により進行すると考えられる。

1) K. Ohshimo, S. Miyazaki, K. Hattori, F. Misaizu, *Phys. Chem. Chem. Phys.* **2020**, 22, 8164.

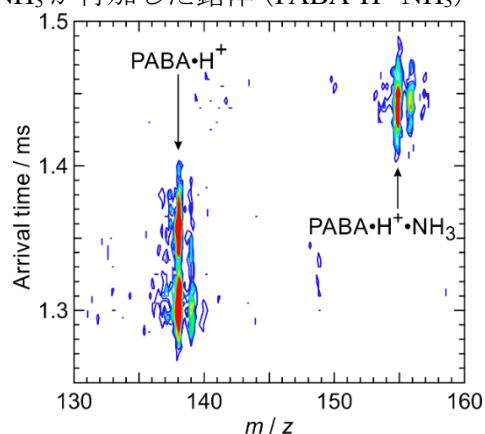


図 1. 低温 IM-MS で得られた到達時間–質量 2 次元プロット

気相生体分子イオンのプロトン移動反応の OPIG-DC 電圧依存性

(横浜市立大学生命ナノ¹) ○野々瀬真司¹・太田寛人¹・田子智郁¹・豊見山蒼樹¹

Proton Transfer Reactions of Biomolecular Ions in Gas Phase on OPIG-DC Voltage

(¹Graduate School of Nanobioscience, Yokohama City University)

○Shinji Nonose,¹ Hiroto Ota,¹ Satofumi Tago,¹ Soju Tomiyama¹

Time-, temperature-, and OPIG-DC voltage-resolved proton transfer reactions of multiply-protonated biomolecular ions to 1,5-pentanediamine (Peda) were examined in the gas phase. Absolute reaction rate constants for proton transfer were determined from intensities of precursor and product ions in the mass spectra. With changes of direct current (DC) voltage to put octapole ion guide (OPIG) in the collision cell, V_{DC} , remarkable change was observed for distribution of the ions and reaction rate constants of proton transfer. The results indicate that conformation changes on ions at OPIG-DC voltage range, which relate with complex formation. An issue that is attracting considerable attention is their conformations might resemble structural evolution that originated from internal energy in the gas phase.

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

気相中で生体分子の多電荷イオンと 1,5-pentanediamine (Peda) とのプロトン移動反応に関して研究した。プロトン移動の反応速度を指標として、反応温度、反応時間、およびオクタポールイオンガイド (OPIG) の直流電圧 (OPIG-DC) である V_{DC} を変化させることによって、イオンの立体構造と反応に関して検討した。図 1 に lysozyme イオン、 $[M + 7H]^{7+}$ と Peda とのプロトン移動反応の V_{DC} 依存性に関する質量スペクトルを示す。(A) は ESI によってイオンを生成した場合、(B) は $[M + 7H]^{7+}$ のみを選別した場合、(C) ~ (G) は衝突反応セルに Peda を導入して、プロトン移動反応を誘起した場合をそれぞれ表す。(C) から (G) への順で V_{DC} が増加している。 V_{DC} の値が 0~90V では V_{DC} の増加に伴って、 $[M + 7H]^{7+}$ の割合が減少し $[M + 6H]^{6+}$ の割合が増加した。ところが、 V_{DC} の値が 100V 付近では $[M + 6H]^{6+}$ の割合が減少し $[M + 7H]^{7+}$ の割合が増加した。

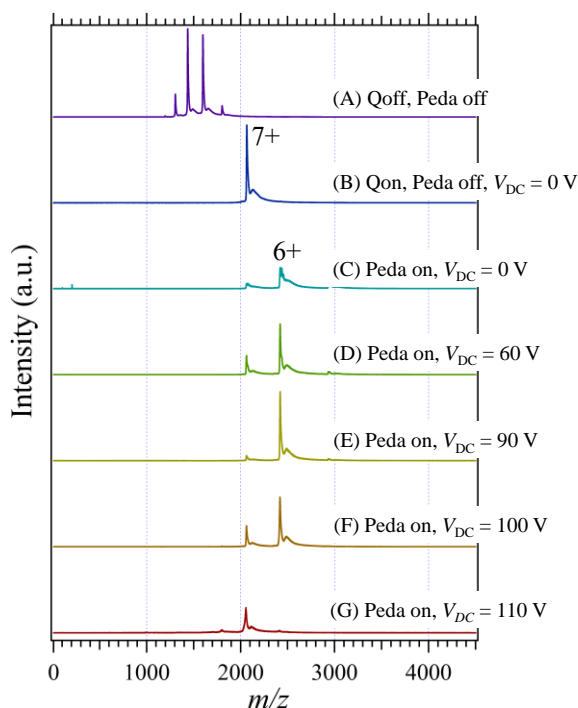


Figure 1. Mass spectra of lysozyme ion, $[M + 7H]^{7+}$, reacted with Peda in various V_{DC} .

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

発光性ジラジカルが形成するエキシマー的励起種の電子状態解明

(分子研¹・新潟大²・九州大³・JST さきがけ⁴) ○松岡亮太¹・米田勇祐¹・倉持光¹・三浦智明²・生駒忠昭²・西郷将生³・江原巧³・宮田潔志³・恩田健³・草本哲郎^{1,4}

Elucidating electronic structure of excimer-like species formed from a luminescent diradical (¹IMS, ²Niigata Univ., ³Kyushu Univ., ⁴JST-PRESTO) ○Ryota Matsuoka,¹ Yusuke Yoneda,¹ Hikaru Kuramochi,¹ Tomoaki Miura,² Tadaaki Ikoma,² Masaki Saigo,³ Takumi Ehara,³ Kiyoshi Miyata,³ Ken Onda,³ Tetsuro Kusamoto^{1,4}

Luminescent organic radicals often show a red-shifted, broad and structureless emission band when doped at moderate to high concentrations in host matrices.¹⁾ This emission has been attributed to “excimers” formed from a radical dimer or multimer in the solid matrices based on absorption and excitation spectroscopic measurements. However, their concrete electronic structures have not been clarified. We have recently prepared a spatially confined luminescent radical dimer (diradical **1**) and observed its intramolecular excimer-like photoluminescence in poly(methyl methacrylate).²⁾ In this study, we investigated the formation process and electronic structure of the excimer-like state of **1** by various spectroscopic techniques, including transient absorption spectroscopy.

Keywords : Radical; Luminescence; Excimer; Transient Absorption Spectroscopy

発光性有機ラジカルをホスト物質中に中～高濃度でドーピングすると、ブロードで振動構造のない発光帯が長波長域に現れる¹⁾。これは吸収および励起スペクトルの特徴からラジカル二量体あるいは多量体が形成する「エキシマー」からの発光と帰属されてきた。しかしながら、その具体的な電子状態は実験的に明らかにされてこなかった。近年我々は安定発光ラジカルユニットを剛直なリンカーで近接固定化したジラジカル分子 **1** (Figure 1) を合成し、これがポリ(メタクリル酸メチル)中、単分子状態で分子内エキシマー的種に由来した発光を示すことを明らかにした²⁾。本研究ではこのジラジカル **1** を対象とし、過渡吸収分光をはじめとする各種分光測定によって、これまでラジカル「エキシマー」と呼ばれてきた励起種の形成過程および電子状態を調べた。

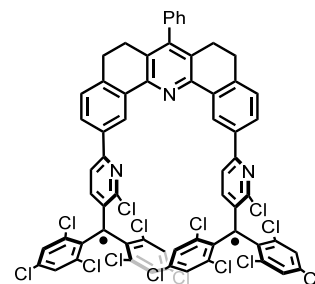


Figure 1. Chemical structure of luminescent diradical **1**.

- 1) (a) D. Blasi, D. M. Nikolaidou, F. Terenziani, I. Ratera, J. Veciana, *Phys. Chem. Chem. Phys.* **2017**, *19*, 9313–9319; (b) S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki, H. Nishihara, *Angew. Chem. Int. Ed.* **2018**, *57*, 12711–12715; (c) S. Kimura, S. Kimura, H. Nishihara, T. Kusamoto, *Chem. Commun.* **2020**, *56*, 11195–11198; (d) R. Matsuoka, S. Kimura, T. Kusamoto, *ChemPhotoChem* **2021**, *5*, 669–673.
- 2) R. Matsuoka, S. Kimura, T. Miura, T. Ikoma, T. Kusamoto, *ChemRxiv* **2021**, DOI: 10.26434/chemrxiv-2022-1wscq.

カルバゾール骨格を有する発光性ジラジカルにおける単分子マグネトルミネッセンス

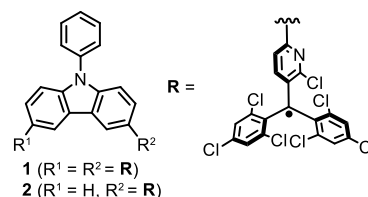
(分子研¹・東北大²・JST さきがけ³)

○水野 麻人¹・松岡 亮太¹・木村 尚次郎²・草本 哲郎^{1,3}

Single-molecule magnetoluminescence from a carbazole-based luminescent diradical (¹*Institute for Molecular Science*, ²*Tohoku University*, ³*JST-PRESTO*)

○Asato Mizuno,¹ Ryota Matsuoka,¹ Shojiro Kimura,² Tetsuro Kusamoto^{1,3}

Luminescent radicals have been intensively studied in recent years as a new class of materials exhibiting novel photofunctions unique to open-shell systems.¹ One of the intriguing photofunctions is magnetoluminescence (ML), which emerges when luminescent radicals are doped in host matrices at concentrations around 10 wt%^{2a} or embedded in coordination polymers.^{2b} Our recent study has been unveiling the detailed mechanism of the ML through single-molecule-ML behavior from a diradical emitter dispersed in poly(methyl methacrylate) (PMMA).^{2c} In the present research, we prepared a novel carbazole-based diradical emitter **1**, and investigated its luminescence properties in solution and in PMMA. We found that PMMA-dispersed samples of **1** exhibited ML at 4.2 K and a unique temperature-dependent luminescence, i.e., a decrease in the emission intensities upon cooling below ca. 50 K. In this presentation, the magnetic-field and thermal effects on the luminescence properties of the diradical **1** will be discussed, in comparison with those of a monoradical **2**.



Keywords : Radical; Luminescence; Magnetic-field effect

発光性ラジカルは開殻電子系ならではの光機能を示す新しい物質群として近年精力的に研究されており¹、ホストマトリクス中に 10 wt%程度ドープされた状態^{2a}や配位高分子中に埋め込まれた状態^{2b}において発光の磁場効果(マグネトルミネッセンス、以下 ML)を発現する。近年、当グループでは、ポリ(メタクリル酸メチル) (PMMA)中に分散した発光性ジラジカルの単分子 ML 挙動から、その詳細な発現機構を明らかにしてきた^{2c}。本研究では、カルバゾール骨格を有する新規発光性ジラジカル **1** を合成し、その溶液中及び PMMA 中での発光特性を調べた。我々は **1** の PMMA 分散試料が発光の磁場効果(at 4.2 K)並びに特異な発光の温度依存性(約 50 K 以下に降温すると発光強度が減少)を示すことを見出している。当日は、ジラジカル **1** の発光の磁場・温度効果についてモノラジカル **2** の発光特性と比較しながら、詳細に議論する。

1) Z. Cui, A. Abdurahman, X. Ai, Feng Li, *CCS Chem.* **2020**, 2, 1129; R. Matsuoka, A. Mizuno, T. Mibu, T. Kusamoto, *Coord. Chem. Rev.* **2022**, 467, 214616.

2) a) S. Kimura, T. Kusamoto, S. Kimura, K. Kato, T. Yoshio, H. Nishihara, *Angew. Chem. Int. Ed.* **2018**, 57, 12711. b) S. Kimura, R. Matsuoka, S. Kimura, H. Nishihara, T. Kusamoto, *J. Am. Chem. Soc.* **2021**, 143, 5610. c) R. Matsuoka, S. Kimura, T. Miura, T. Ikoma, T. Kusamoto, (DOI: 10.26434/chemrxiv-2022-1wscq).

Academic Program [Oral B] | 05. Physical Chemistry -Chemical Kinetics and Dynamics- | Oral B**[K205-4pm] 05. Physical Chemistry -Chemical Kinetics and Dynamics-**

Chair: Tetsuro Katayama, Yo-ichi Yamamoto

Sat. Mar 25, 2023 1:00 PM - 2:50 PM K205 (K205, Lecture Hall Bldg. [2F])

[K205-4pm-01] Cycloreversion reaction of diarylethene nanocolloids induced by intense pulse laser excitationShintaro Matsumoto¹, [○]Yukihide Ishibashi¹, Daichi Kitagawa², Seiya Kobatake², Tsuyoshi Asahi¹ (1. Ehime University, 2. Osaka Metropolitan University)

1:00 PM - 1:20 PM

[K205-4pm-02] Observation of carrier dynamics in single and few layers of WSe₂ by femtosecond transient absorption microscopy and its interlayer angle dependence[○]Tetsuro Katayama¹, Akira Yamamoto¹, Naohiko Endo², Yasumitsu Miyata², Akihiro Furube¹ (1. Tokushima University, 2. Tokyo Metropolitan University)

1:20 PM - 1:40 PM

[K205-4pm-03] Ultrafast nonradiative deactivation and tautomerization of the solvatochromic dye, phenol blue[○]Yutaka Nagasawa¹, Takemoto Tanaka¹, Tsubasa Hidaka¹, Akifumi Matsumoto¹, Chikashi Ota¹, Takahiro Teramoto² (1. Ritsumeikan University, 2. Osaka University)

1:40 PM - 2:00 PM

[K205-4pm-04] Ultrafast Photoemission Spectroscopy of Solvated Electrons and Development of Spectral Retrieval Method[○]Yo-ichi Yamamoto¹, Toshinori Suzuki¹ (1. Kyoto University)

2:10 PM - 2:30 PM

[K205-4pm-05] Formation of petal-like concentric precipitation patterns by continuous injection of dye solution into filter paper associated with solvent evaporation[○]Amiko Aizawa¹, Taisuke Banno¹, Kouichi Asakura^{1,2} (1. Faculty of Science and Technology, Keio University, 2. Meiji Institute for Advanced Study of Mathematical)

2:30 PM - 2:50 PM

高強度パルスレーザー励起によるジアリールエテンナノ粒子コロイドの開環反応

(愛媛大院工¹・阪公大院工²) 松本慎太郎¹、○石橋千英¹、北川大地²、小畠誠也²、朝日 剛¹

Cycloreversion Reaction of Diarylethene Nanocolloids Induced by Intense Pulse Laser Excitation (¹Graduate School of Science and Engineering, Ehime University, ²Graduate School of Engineering, Osaka Metropolitan University) Shintaro Matsumoto¹, ○Yukihide Ishibashi¹, Daichi Kitagawa², Seiya Kobatake², Tsuyoshi Asahi¹

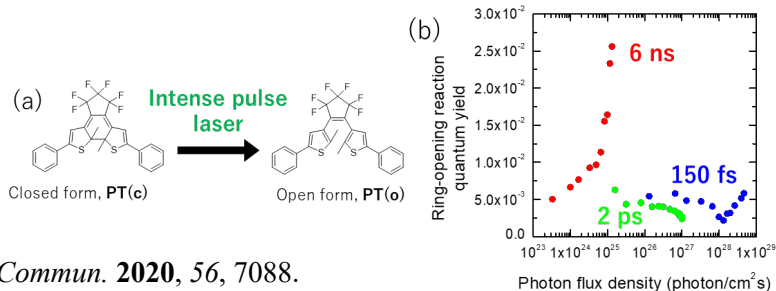
Nanosecond laser pulse excitation to photochromic diarylethene nanocolloids induced the increase of the cycloreversion reaction yield nonlinearly to the excitation intensity, while femtosecond laser pulse exposure led to the decrease because the reactive excited molecules decreased via the bimolecular annihilation process. These results indicated that the increased reaction yield was not affected by the photon flux density but by the laser heating, by which the temperature of nanoparticles transiently and rapidly rose. We will discuss the mechanisms from the viewpoint of the temperature elevation of the nanoparticles at the presentation.

Keywords : Intense Pulse Laser Excitation; Photosynergetic Interaction; Diarylethene Nanocolloids; Laser Heating

これまでに、我々はフォトクロミズムを示すジアリールエテン (Figure 1(a)、PT) の閉環体ナノ粒子にナノ秒 532 nm パルスレーザーを照射すると、開環反応量子収率が励起光強度に対して2次の傾きをもって増大することを見出した。この増大メカニズムとしては、1つのパルス内でナノ粒子の温度が高くなり (レーザー加熱)、その状態で同じパルス内の光子を吸収することで高効率に反応が進行する過程を提案した[1]。このような非線形反応には励起光の光子束密度 (photons cm⁻²s⁻¹) が重要な因子であると考え、本研究ではPT閉環体ナノ粒子に対してパルス幅の異なるパルスレーザーを照射し、開環反応収率の励起パルス幅効果を検討した。Figure 1(b)に、その結果を示す。パルス幅が150 fs および 2 ps の場合 (共に励起波長は400 nm)、開環反応収率は定常光照射による一光子開環反応収率よりも低い値を示した。この反応収率の低下は、現段階では、励起分子による2分子消滅過程により反応に関与する励起分子数が減少したためであると考えられる。これらの結果から、反応収率を増大させるためには、単に光子束密度を高くすればよいのではなく、数十ピコ秒からナノ秒といったパルス幅を持つレーザー光による過渡的な過熱が重要であることが示唆された。

Figure 1.

(a) Cycloreversion reaction of PT. (b) Pulse duration effect of the cycloreversion reaction yield in PT(c) nanocolloids.



1) Y. Ishibashi et al, *Chem. Commun.* **2020**, 56, 7088.

フェムト秒顕微過渡吸収分光法による WSe₂ 単層および数層のキャリアダイナミクス観測とその層間角度依存性

(徳大 pLED¹、徳大院理工²、JST 創発、東京都立大学) ○片山哲郎^{1,2,3}、山本 輝²、遠藤 尚彦⁴、宮田 耕充^{3,4}、古部 昭広^{1,2}

Observation of Carrier Dynamics in Single and Few Layers of WSe₂ by Femtosecond Transient Absorption Microscopy and Its Interlayer Angle Dependence

(¹Institute of post-LED Photonics, ²Graduated school of Science and Technology, Tokushima University, ³JST FOREST, ⁴Department of Physics, Tokyo Metropolitan University)

○Tetsuro Katayama^{1,2,3}, Akira Yamamoto², Naohiko Endo⁴, Yasumitsu Miyata^{3,4}, Akihiro Furube^{1,2}

Recently, many reports have focused on the novel conductivity and luminescence properties of transition metal dichalcogenides, which are layered materials and adsorbed on substrates after exfoliation into a monolayer. The transient absorption measurements of monolayer and few-layer WSe₂ fabricated by CVD have shown change in three transition-induced bleach bands and an induced emission band, revealing different relaxation processes with different time constants. We will discuss the carrier dynamics of the transition states at K- and Q-points with several interlayer angles.

Keywords : Transition Metal Dichalcogenide; Transient Absorption Microscopy; Carrier transfer dynamics

近年、層状物質である遷移金属ジカルコゲナイドを単層に剥離し基板に吸着させることで、新奇な導電性や発光特性を示すことが多く報告されており注目を集めている¹⁾。特に異なる二次元材料を重ねたヘテロ層においてモアレ励起子の発現が報告されて以降、同一の二次元材料を重ねた二層の研究も進められ、積層した時の角度によりバンド構造が変化するという報告もされている。これら二層膜の研究は積層状態により異なる物性を示すため単層膜の研究と比べて測定や解析が複雑となっている。そのため二層膜表面の電子と正孔の挙動を観測するためには高度な時・空間分解計測が必要である。そこで時・空間分解能を持つ過渡吸収分光法を用いて WSe₂ 単層および数層におけるキャリア挙動の観測を行った。一例として単層の過渡吸収スペクトルを Fig.1 に示す。本発表では単層及び 0°、30°、60° の角度で重なった複数層における過渡吸収スペクトル、過渡吸光度イメージングの結果からバンド図内の K 点と Q 点のキャリア緩和過程を層数ごとに考察する。

1) S. Gupta, F. Rortais, R. Ohshima, Y. Ando, T. Endo, Y. Miyata, M. Shiraishi, *Sci. Rep.* **2019**, 9, 17032.

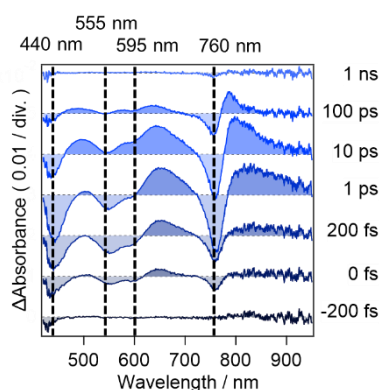


Fig.1 Transient absorption spectra of WSe₂ monolayer excited by femtosecond pulse at 400 nm

ソルバトクロミズムを示す色素フェノールブルーの超高速無輻射失活過程と互変異性化

(立命館生命科学¹・阪大 IRS²) ○長澤 裕¹・田中 丈朝¹・日高 翼¹・松本 誠史¹・太田 周志¹・寺本 高啓²

Ultrafast nonradiative deactivation and tautomerization of the solvatochromic dye, phenol blue (¹*Life Sciences, Ritsumeikan*, ²*IRS, Osaka University*) ○ Yutaka Nagasawa,¹ Takemoto Tanaka,¹ Tsubasa Hidaka,¹ Akifumi Matsumoto,¹ Chikashi Ota,¹ Takahiro Teramoto²

Phenol blue (PhB) is a non-fluorescent dye that exhibits solvatochromism. We have carried out femtosecond time-resolved transient absorption spectroscopy by exciting the ethanol solution at shorter and longer wavelength sides of the visible absorption band of PhB [1]. Non-radiative deactivation occurs in the sub-picosecond range, and a vibrationally excited hot ground state is generated followed by thermal diffusion in the picosecond range. Subsequently, the hydrogen bond (H-bond) with the solvent molecule is broken and a tautomer that absorbs at shorter wavelengths is generated, which causes the ground state bleach (GSB) to shift to the longer wavelengths. Presumably, tautomerization proceeds by the twisting of the benzoquinone-imine moiety of PhB due to the breaking of the H-bond (Fig. 1). Recombination of the H-bond occurs with a time constant of ~30 ps, and finally the system returns to the original thermal equilibrium state. In addition, the GSB shift was also modulated by a low-frequency coherent nuclear wavepacket motion.

Keywords : *Ultrafast spectroscopy; Solvatochromism; Nonradiative decay; Tautomerization*

フェノールブルー(PhB)はソルバトクロミズムを示す無蛍光性の色素である。我々は PhB のエタノール溶液について、可視吸収帯の短波長側と長波長側の2つの波長で励起することにより、フェムト秒の時間分解能で過渡吸収スペクトル測定を行い、超高速の無輻射失活と、それに続く基底状態でのスペクトル変化を観察した[1]。無輻射失活はサブピコ秒領域で起こり、励起状態が超高速で減衰すると、振動励起されたホットな基底状態が生成し、数ピコ秒程度で熱拡散が起こる。その際、溶媒分子との水素結合が切断され、短波長に吸収帯を有する互変異性体が生成し、基底状態の吸収ブリーチ (GSB) の長波長シフトが引き起こされる。おそらく、図1のように水素結合の切断によって PhB のベンゾキノニイミン部分がねじれることにより、互変異性化が進行すると考えられる。その後、30 ps 程度の時定数で水素結合の再結合が起こり、最終的に系は元の熱平衡状態に戻る。また、GSB のシフトには低波数コヒーレント核波束運動による変調も観察された。

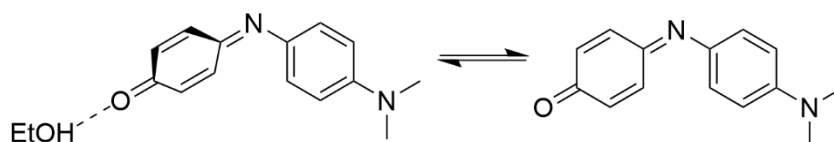


Figure 1. Molecular structure of PhB and its tautomerization.

[1] C. Ota, et al., *J. Phys. Chem. B*, **125**(38), 10832–10842 (2021).

溶媒和電子の超高速光電子分光とスペクトル回復法の開発

(京大院理) ○山本遥一・鈴木俊法

Ultrafast Photoemission Spectroscopy of Solvated Electrons and Development of Spectral Retrieval Method (*Graduate School of Science, Kyoto University*) ○Yo-ichi Yamamoto, Toshinori Suzuki

Time-resolved photoemission spectroscopy (TRPES) of liquids is in the process of development as a new method for studying solution chemistry, which allows direct observation of the electronic states governing reactions and real-time tracing of reaction pathways. However, one of the problems is that the photoelectrons generated inside the solution are subject to scattering by the solvent molecules before emission from the liquid surface into the vacuum. In this study, we developed the Spectral Retrieval method to solve this problem. To develop this method, we specified the change in spectra before and after the scattering as a first-order transformation using the known spectra of solvated electron, which enables us to back-transform any spectrum into those before scattering.

In this talk, we will explain the principle and discuss its application to several reactive systems. In addition, the high accuracy of the Spectral Retrieval method will be demonstrated by comparing the photoelectron spectra obtained by removing the effect of scattering in this way with those measured using extreme ultraviolet light, in which the effect of scattering is negligible.

Keywords : solvated electrons; photoemission spectroscopy; spectral retrieval method

溶液の時間分解光電子分光法(TRPES)は、溶液化学を研究する新手法として発展途上にある。従来の過渡吸収分光法等と異なり、TRPES は反応を司る電子状態を直接観測することができ、反応経路をリアルタイムに追跡することができる。ただし、溶液内部で発生する光電子は、液面から真空中に放出されるまでの間に溶媒による散乱を受けることが問題であった。本研究では、この問題を解決する Spectral Retrieval 法を開発した。その開発のために、溶媒和電子の光電子スペクトルを利用した。溶媒和電子の電子束縛エネルギーは既に決定済みであり、各々の紫外 probe 光子エネルギーに対して期待される光電子スペクトルは容易に予測できる。実測のスペクトルは、電子の非弾性散乱の影響でこの予測から偏移するため、この偏移を具に検討することで、各運動エネルギーの電子が如何に溶媒によって散乱され、その分布が変化するかを明らかにした。この変化を一次変換として規定することで、任意の実測のスペクトルから散乱前の電子エネルギーに逆変換することが可能となった。このような方法論の開発は初めてである。

本講演では、その原理を解説すると共に、幾つかの反応系に対する応用例について述べる。また、このようにして散乱の影響を除去した光電子スペクトルと、散乱の影響が現れないような極端紫外光を用いて測定したスペクトルを比較し、Spectral Retrieval 法の高い精度を証明する。

Formation of petal-like concentric precipitation patterns by continuous injection of dye solution into filter paper associated with solvent evaporation

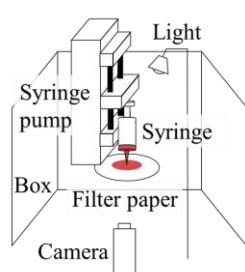
(¹Faculty of Science and Technology, Keio University, ²Meiji Institute for Advanced Study of Mathematical Sciences, Meiji University) ○ Amiko Aizawa,¹ Taisuke Banno,¹ Kouichi Asakura^{1,2}

Keywords: Precipitation Pattern; Petal-like Pattern; Concentric Pattern; Permeation Associated with Evaporation; Supersaturation Theory

Temporal, spatial, and spatio-temporal patterns are spontaneously generated in far-from-equilibrium system, and they are called dissipative structure.¹ Liesegang ring, a concentric precipitation pattern, has been studied as the example of dissipative structure since its discovery about 150 years ago.² In the present study, attempts were made to generate similar concentric precipitation pattern by different mechanisms.

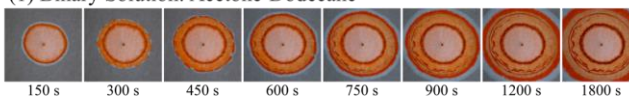
The system we have employed was continuous injection of mixed solvent solution of dye into filter paper associated with solvent evaporation from its surface. Red dye, Sudan III, was dissolved in binary solution of acetone and dodecane and ternary solution of hexane, ethanol, and decane. These solutions were injected into the circular filter paper from its center at a constant flow rate. Since the experiments were conducted in an open environment, the dye concentration in the solution increased with the solvents evaporation to lead to the precipitation.

In both cases, concentric precipitation patterns similar to the Liesegang ring were found to be generated. A theoretical model was proposed for reproducing the precipitation pattern based on the supersaturation theory for the Liesegang ring and Richards' equation for the unsaturated permeation. The model explained that the concentric precipitation pattern was generated by the repetition of intermittent precipitation. The concentric precipitation rings were radially segmented to form petal-like patterns. Protuberance of liquid droplets were found to be generated at the periphery of the liquid permeated into the filter paper, and the droplet formation was due to Marangoni contraction.³ The formation of the petal-like structure was found to be associated with the continuous formation and collapsing of the droplets.

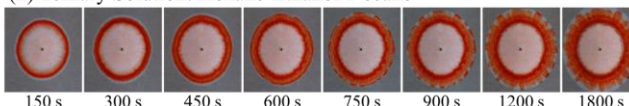


Formation of Petal-like Concentric Precipitation Patterns

(1) Binary Solution: Acetone-Dodecane



(2) Ternary Solution: Hexane-Ethanol-Decane



1) I. R. Epstein, J. A. Pojman, O. Steinbock, *Chaos* **2006**, *16*, 037101. 2) H. Nabika, M. Itatani, I. Lagzi, *Langmuir* **2020**, *36*, 481-497. 3) S. Karpitschka, F. Liebig, H. Riegler, *Langmuir* **2017**, *33*, 4682-4687.

[K305-4am] 08. Catalysts and Catalysis

Chair: Hiroki Miura, Takafumi Yatabe

Sat. Mar 25, 2023 9:00 AM - 11:30 AM K305 (K305, Lecture Hall Bldg. [3F])

[K305-4am-01] Decarbonylation and Metathesis via C–S Bond Scission by Ni or Pd-Based Catalysts○Takehiro Matsuyama¹, Takafumi Yatabe¹, Tomohiro Yabe¹, Kazuya Yamaguchi¹ (1. The University of Tokyo)

9:00 AM - 9:20 AM

[K305-4am-02] Au nanoparticles-catalyzed regioselective aerobic oxidation of tertiary amines: mechanism elucidation and application to enaminone synthesis○Takafumi Yatabe^{1,2}, Syunsuke Kanamoto¹, Yuta Funami¹, Kazuya Yamaguchi¹ (1. The University of Tokyo, School of Engineering, Department of Applied Chemistry, 2. JST, PRESTO)

9:20 AM - 9:40 AM

[K305-4am-03] Remarkably Efficient Hydrogenolysis of Esters to Alkanes by A Multifunctional Pt/WO₃–ZrO₂ Catalyst○Yukari Yamazaki¹, Kang Yuan¹, Xiongjie Jin¹, Kyoko Nozaki¹ (1. The University of Tokyo)

9:40 AM - 10:00 AM

[K305-4am-04] Emergence of Hydrosilylation Catalysis of Cyclic Carbonate by Immobilization on Silica Surface○Shingo Hasegawa¹, Kousuke Soga¹, Keisuke Nakamura², Kei Usui², Yuichi Manaka^{2,3}, Ken Motokura^{1,2} (1. Yokohama National University, 2. Tokyo Institute of Technology, 3. National Institute of Advanced Industrial Science and Technology)

10:00 AM - 10:20 AM

[K305-4am-05] Synthesis of Ni nanoparticles using hydrosilanes and their catalytic activity○Yusuke Kita¹, Shun Takeuchi¹, Takaaki Oyoshi¹, Keigo Kamata¹, Michikazu Hara¹ (1. Tokyo Tech.)

10:30 AM - 10:50 AM

[K305-4am-06] Selective Hydrogenation of CO₂ to MeOH using Sterically Confined Ir Complexes○Bendik Groemer¹, Susumu Saito^{1,2} (1. Graduate School of Science, Nagoya University (Grad. Sch. Sci., Nagoya Univ.), 2. Integrated Research Consortium on Chemical Sciences, Nagoya University (IRCCS, Nagoya Univ.))

10:50 AM - 11:10 AM

[K305-4am-07] Bimetallic Subnanoparticles Enable Thermally-driven CO₂ Hydrogenation from Room Temperature○Augie Atqa¹, Masataka Yoshida¹, Masanori Wakizaka³, Wang-Jae Chun⁴, Akira Oda⁵, Takane Imaoka^{1,2}, Kimihisa Yamamoto^{1,2} (1. Tokyo Institute of Technology, 2. JST ERATO Yamamoto Atom Hybrid Project, 3. Tohoku University, 4. International Christian University, 5. Nagoya University)

11:10 AM - 11:30 AM

Ni あるいは Pd 触媒を用いた C-S 結合切断を伴う脱カルボニル反応およびメタセシス反応

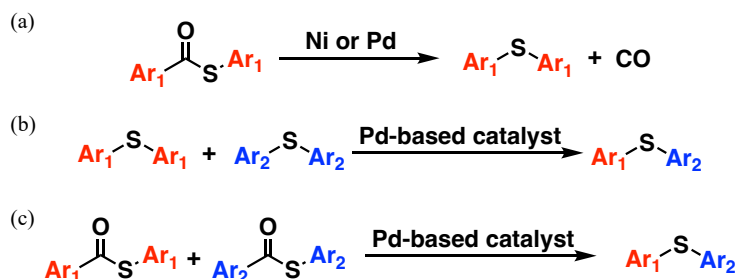
(東大院工¹⁾) ○松山 剛大¹・谷田部 孝文¹・矢部 智宏¹・山口 和也¹

Decarbonylation and Metathesis via C-S Bond Scission by Ni or Pd-based catalysts (¹*School of Engineering, The University of Tokyo*) ○Takehiro Matsuyama, Takafumi Yatabe, Tomohiro Yabe, Kazuya Yamaguchi

Molecular transformations via C-S bond activation have attracted increasing attention as an alternative to conventional halogen-based synthetic methods. In this study, we have developed heterogeneously catalyzed decarbonylation of thioesters using supported Ni and Pd nanoparticle catalysts. This system exhibited wide substrate scope and functional group tolerance, affording various symmetrically substituted sulfides from symmetrically substituted thioesters via decarbonylation (Scheme 1(a)). In addition, C-S bond metathesis of diaryl sulfides successfully proceeded in the presence of homogeneous Pd catalysts with phosphine ligands (Scheme 1(b)). Then, based on the findings about the homogeneous Pd catalyst, we have designed the heterogeneous catalyst for efficient C-S bond metathesis of diaryl sulfides. This catalytic system was also applicable to a tandem reaction starting from two kinds of symmetrically substituted thioesters to afford unsymmetrically substituted sulfides through decarbonylation and C-S bond metathesis (Scheme 1(c)).

Keywords : C-S Bond metathesis; Decarbonylation; Sulfides; Thioesters

C-S 結合の活性化を伴う反応は、ハロゲン化物を用いない新たな合成手法として期待されている¹⁾。本研究では、担持 Ni および Pd ナノ粒子触媒を用いたチオエステルの脱カルボニル反応を開発した (Scheme 1(a))。本反応は幅広い基質適用性、官能基耐性を示し、対称チオエステルから対応する対称スルフィドを高収率で得ることができた。また、ホスフィン配位子を有する均一系 Pd 触媒を用いることでジアリールスルフィドの C-S 結合メタセシス反応が良好に進行することを見出した (Scheme 1(b))。さらに、この知見をもとに担持ナノ粒子触媒の設計を行い、不均一系 Pd 触媒を用いてジアリールスルフィドの C-S 結合メタセシス反応を高効率に進行させることに成功した。本触媒は 2 種の対称チオエステルを出発物質として脱カルボニル、C-S 結合メタセシスによる非対称スルフィド合成への適用も可能であった (Scheme 1(c))。



Scheme 1. (a) チオエステルの脱カルボニル反応. (b) ジアリールスルフィドの C-S 結合メタセシス. (c) 対称チオエステルを出発物質としたタンデム反応による非対称スルフィド合成.

1) J. Hou, Q. Wang, P. Wu, H. Wang, Y.-G. Zhou, Z. Yu, *Chem. Soc. Rev.* **2020**, *49*, 4307.

Au ナノ粒子触媒による位置選択的第三級アミン酸素酸化の反応機構とエナミノン合成への応用

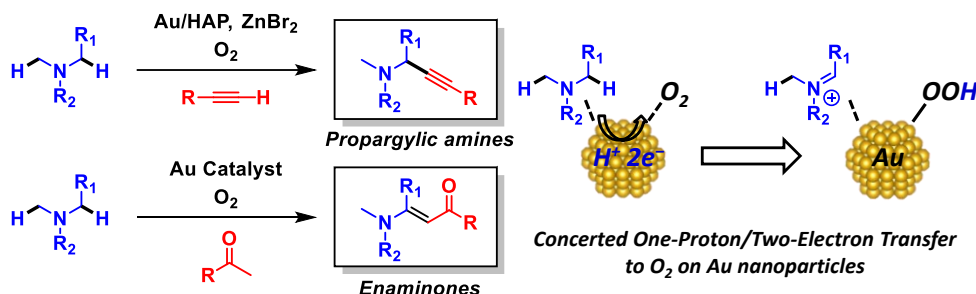
(東大院工¹・JST さきがけ²) ○谷田部 孝文^{1,2}・金元 俊輔¹・舩見 悠太¹・山口 和也¹

Au Nanoparticles-Catalyzed Regioselective Aerobic Oxidation of Tertiary Amines: Mechanism Elucidation and Application to Enaminone Synthesis (¹*School of Engineering, The University of Tokyo*, ²*JST, PRESTO*) ○Takafumi Yatabe,^{1,2} Syunsuke Kanamoto,¹ Yuta Funami,¹ Kazuya Yamaguchi¹

Oxidative α -C-H bond functionalization of tertiary amines is important for efficient synthesis of useful molecules such as novel medicines; however, previously reported selective tertiary amine oxidation systems are generally limited to α -methyl oxidative functionalization due to the quite difficult regioselectivity control. In this study, based on our previous work on aerobic α -oxygenation of secondary and tertiary amines, we found supported Au nanoparticles-catalyzed α -methylene regioselective aerobic oxidation of tertiary amines. From various control experiments by utilizing α -alkynylation of tertiary amines, we revealed that the unique regioselectivity is derived from a concerted one-proton/two-electron transfer from tertiary amines to molecular oxygen on Au nanoparticles. In addition, we have successfully developed unprecedented enaminone synthesis via tandem oxidation from tertiary amines and ketones.

Keywords : Au Nanoparticles; Tertiary Amines; Regioselectivity; Aerobic Oxidation; Enaminones

第三級アミンの酸化的 α 位 C-H 結合官能基化は新薬等の効率的合成のために注目されているが、アミン酸化の位置選択性制御がきわめて困難であり、これまでの手法では α -メチル基選択的官能基化に限られていた。本研究では、第二級および第三級アミンの α -酸素化反応における知見をもとに¹⁾、担持 Au ナノ粒子触媒の α -メチレン基特異的な第三級アミン酸素酸化能を見出し、 α -アルキニル化反応を利用した種々の対照実験等から、Au ナノ粒子上における第三級アミンから酸素分子への協奏的二電子一プロトン移動がその特異な位置選択性の起源であることを明らかにした²⁾。さらに、担持 Au ナノ粒子触媒の特異な第三級アミン酸化能および酸化的脱水素能を組み合わせ、ケトンを求核剤としたエナミノンへの未踏のタンデム酸化も開発した。



- 1) X. Jin, K. Kataoka, T. Yatabe, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2016**, 55, 7212.
- 2) T. Yatabe, K. Yamaguchi, *Nat. Commun.* **2022**, 13, 6505.

Remarkably Efficient Hydrogenolysis of Esters to Alkanes by A Multifunctional Pt/WO₃–ZrO₂ Catalyst

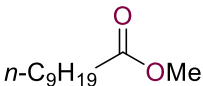
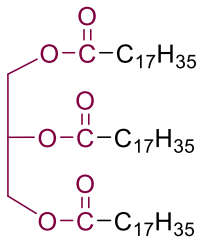
(¹Graduate School of Engineering, The University of Tokyo) ○Yukari Yamazaki,¹ Kang Yuan,¹ Xiongjie Jin,¹ Kyoko Nozaki¹

Keywords: Hydrogenolysis; Esters; Alkanes; WO₃–ZrO₂ support; Platinum

Hydrogenolysis of plant oils or fats to diesel-range hydrocarbons has received considerable attention in recent decades. Because plant oils or fats are primarily composed of triglycerides, which are esters derived from fatty acids and glycerol, the hydrogenolysis of esters to hydrocarbons is a key protocol for conversion to fuels. Thus far, various heterogeneous catalysts have been developed for the hydrogenolysis of esters to hydrocarbons. Most of the reported catalyst systems require harsh conditions such as high temperatures (>250 °C) or H₂ pressures (>1 MPa) to achieve high conversion and selectivity. Therefore, the development of catalysts for efficient hydrogenolysis of esters under mild conditions is highly desirable.

In this study, we developed a tungsten and zirconium oxide-supported platinum catalyst (Pt/WO₃–ZrO₂) for the hydrogenolysis of esters to alkanes at low temperatures and under ambient pressure (1 atm) of H₂. When Pt(0.25)/WO₃–ZrO₂ (0.25 wt% of Pt deposited on the support) was used as the catalyst, the hydrogenolysis of methyl decanoate in dodecane at 130 °C and under 1 atm of H₂ gave decane as the sole product in 96% yield (Table 1, entry 1). In addition, the heterogeneous nature of the catalyst system permits multiple reuse of the catalyst without any significant loss of its high activity and selectivity. Moreover, hydrogenolysis of tristearin by Pt(0.25)/WO₃–ZrO₂ at 130 °C and under 1 atm of H₂ gave 96% yield of octadecane (Table 1, entry 2). Therefore, our catalyst system is expected to be broadly applicable to the energy-efficient and economical conversion of plant oils and fats to hydrocarbon fuels.¹

Table 1 Hydrogenolysis of esters to alkanes using Pt(0.25)/WO₃–ZrO₂ catalysts.

Entry	Substrate	Catalyst	Product	<i>T</i> (°C), <i>t</i> (h)	Yield (%)
1		Pt(0.25)/WO ₃ –ZrO ₂ (Pt:1.5 mol%)	<i>n</i> -C ₉ H ₁₉ –CH ₃	130, 24	96
2		Pt(0.25)/WO ₃ –ZrO ₂ (Pt: 2.5 mol%)	<i>n</i> -C ₁₈ H ₃₈ <i>n</i> -C ₁₇ H ₃₆	130, 48	96 3

1) K. Yuan, Y. Yamazaki, X. Jin, K. Nozaki, *J. Am. Chem. Soc.* in press.

Emergence of Hydrosilylation Catalysis of Cyclic Carbonate by Immobilization on Silica Surface

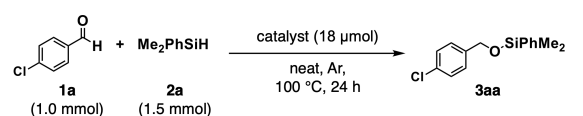
(¹*Yokohama National University*, ²*Tokyo Institute of Technology*, ³*National Institute of Advanced Industrial Science and Technology*) ○Shingo Hasegawa,¹ Kousuke Soga,¹ Keisuke Nakamura,² Kei Usui,² Yuichi Manaka,^{2,3} Ken Motokura^{1,2}

Keywords: Organocatalyst; Surface Immobilization; Cyclic Carbonate; Silica; Hydrosilylation

Organocatalyst has recently attracted great interest as an essential component for environmentally benign and efficient synthesis of fine chemicals, leading to the growing demand for the exploration of the novel catalysis of organic molecules. Cyclic carbonates are an important group of compounds; they are easily synthesized from CO₂ and extensively used as aprotic polar solvents and electrolytes for batteries. These characteristics imply the potential of cyclic carbonates as Lewis base organocatalysts, although the catalytic application has not been reported. In this study, we employed the surface immobilization as a method to create the novel catalysis¹⁾ of cyclic carbonates and found that the immobilization of cyclic carbonates on silica with specific methylene linker length led to the emergence of hydrosilylation catalysis. Novel carbonate catalysts supported on nonporous silica (SiO₂/carbonate(*Cn*)) and mesoporous silica (MS(*x*)/carbonate(*Cn*)) with different linker length (*Cn*) and pore size (*x* Å) were systematically prepared to investigate the effects of the structural parameters on catalysis.

Hydrosilylation of 4-chlorobenzaldehyde (**1a**) by dimethylphenylsilane (**2a**) was performed with prepared catalysts (**Table 1**). Only the carbonate catalysts immobilized on SiO₂ and MS(23) afforded the silyl ether (**3aa**) in high yield (91% and 81%, respectively). In contrast, free propylene carbonate, silica supports, and their physical mixture did not show the catalytic activity. These results clearly indicate that the immobilization on silica surface is critical for the novel hydrosilylation catalysis of cyclic carbonate. When the surface silanol of SiO₂ was capped with methyl group, SiO₂/carbonate(C4) was completely deactivated, suggesting that the surface silanol takes a pivotal role for the activation of aldehyde. Furthermore, we demonstrated that the linker length and pore size largely affected the catalysis; the highest catalytic activity was obtained when *Cn* = C4 and *x* = 23 Å. Based on the correlation between structures and catalysis and results of infrared spectroscopy, we proposed that the aldehyde and silane are concertedly activated by silanol and carbonate, respectively, and undergo efficient hydride transfer followed by silyl ether formation. This reaction mechanism was supported by the results of density functional theory (DFT) calculations.

Table 1. Emergence of hydrosilylation catalysis of cyclic carbonates by immobilization on silica

	
Catalyst	Yield of 3aa (%)
SiO ₂ /carbonate(C4)	91
SiO ₂ + propylene carbonate	<1
SiO ₂	7
Propylene carbonate	5
MS(23)/carbonate(C4)	81
MS(23) + propylene carbonate	7
MS(23)	19

1) K. Motokura, M. Tada, Y. Iwasawa, *J. Am. Chem. Soc.* **2007**, 129, 9540.

ヒドロシランを用いたニッケルナノ粒子の合成とその触媒作用

(東工大フロンティア研) ○喜多 祐介・竹内 舜・大吉 孝明・鎌田 慶吾・原 亨和
 Synthesis of Ni Nanoparticles Using Hydrosilanes and their Catalytic Activity (*Institute of Innovative Research, Tokyo Institute of Technology*) ○Yusuke Kita, Shun Takeuchi, Takaaki Oyoshi, Keigo Kamata, Michikazu Hara

Synthetic method for nickel nanoparticles has been actively investigated due to their high catalytic activity for various transformations. Among them the liquid-phase reduction method is widely used because it does not require a special apparatus and the size of nanoparticles can be controlled by adjusting the preparation conditions; however, the addition of a protective agent is essential for synthesizing particles of several nanometers, and the protective agent often decrease in catalytic activity by covering the nanoparticles. In study, we synthesized nickel nanoparticles by using hydrosilane as a reducing agent. The prepared nickel nanoparticles exhibited high catalytic activity for hydrogenation of various unsaturated compounds. The organosilicon compounds acted as modifying groups of nanoparticles, promoting catalytic reactions and imparting air stability.

Keywords : Hydrosilane; Nanoparticle; Nickel; Hydrogenation

ニッケルは地殻中に豊富に存在し、種々の変換反応に対して高い触媒活性を示すことから、ナノ粒子合成法の開発が盛んに行われている。中でも液相還元法は、特殊な装置を必要としない点や調製条件によりナノ粒子のサイズ制御が可能な点から広く用いられている。しかしながら、数ナノメートルの粒子を合成するには保護剤の添加が必須であり、使用した保護剤がナノ粒子を覆い触媒活性の低下を招くことが多い。本研究では、ヒドロシランを還元剤として用いることで、ケイ素上置換基の効果により粒子径制御が可能なだけでなく、還元で使用された後の有機ケイ素化合物がナノ粒子の修飾基としても作用し、触媒反応の促進および大気安定性の付与を行うことを明らかにした。本手法は担持触媒の調製にも利用することが可能であり、調製した触媒はアルコールの直接アミノ化反応に対して、一般的な水素還元で調製した触媒よりも高い活性を示した(Table 1)。

Table 1. Synthesis of BAMF from HMF

Entry	Catalyst	Conv. (%)	Yield (%)	
			BAMF	HMFA
1	Ni-Si/TiO ₂	>99	88	-
2	Ni/TiO ₂	>99	-	99

Selective Hydrogenation of CO₂ to MeOH using Sterically Confined Ir Complexes

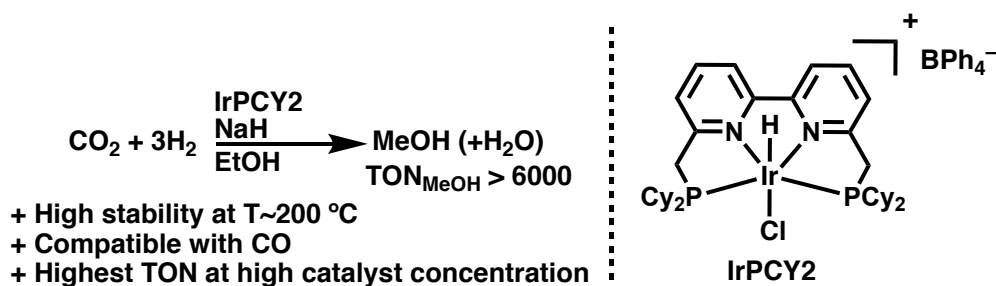
(¹Graduate School of Science, Nagoya University (Grad. Sch. Sci., Nagoya Univ.),
²Integrated Research Consortium on Chemical Sciences, Nagoya University (IRCCS, Nagoya Univ.))

○Bendik Groemer¹, Susumu Saito^{1,2}

Keywords: CO₂ Hydrogenation, Iridium Catalyst, Base Additive

Due to the ever-pressing issues related to global warming, the discovery of new methods to utilize CO₂ has become an attractive research field. Among CO₂ utilization, the development of direct hydrogenation of CO₂ to MeOH represents one of the most promising fields, in relationship with the proposed MeOH economy¹. However, the field of hydrogenation of CO₂ to MeOH using homogeneous catalysts is still in its infancy. Although great achievements have been made in the field in the past decade, there is still much left to be desired when considering the thus far reported systems. In particular, the reported systems struggle with catalyst deactivation at elevated temperatures and in the presence of side product CO²⁻⁴, thus limiting the possible reactivity, and necessitating the utilization of very high pressure for achieving high reactivity.

Our group has in the past years been developing a highly stable Ir(PNNP)-type catalyst, which has shown great activity for selective hydrogenation of mono- and dicarboxylic acids either through lactone- or ester-intermediates^{5,6}. Due to the high rigidity and stability of the PNNP framework, the catalysts were compatible with harsh reaction conditions in regard to both temperature and pressure, without significantly observed deactivation. In this work, we demonstrate that by utilizing the same Ir(PNNP) catalyst, selective hydrogenation of CO₂ to MeOH is realized. Importantly, our system is compatible with high reaction temperatures, and also shows stability in presence of CO. Through mechanistic studies, the necessity and plausible role of catalytic amounts of base additive was demonstrated, and through reaction optimization, we were able to achieve higher turnover numbers than any other reported homogeneous system at relevant catalyst concentrations.



1) Olah, G. A. *Angew. Chem. Int. Ed.*, **2005**, 44, 2636–2639. 2) Klankermayer, Leitner et. al. *Angew. Chem. Int. Ed.*, **2012**, 51, 7499–7502. 3) Klankermayer et. al. *ACS Catal.*, **2020**, 10, 3890–3894. 4) Beller et. al. *Adv. Synth. Catal.*, **2018**, 361, 374–379. 5) Yoshioka, S.; Nimura, S.; Naruto, M.; Saito, S. *Sci. Adv.* **2020**, 6, eabc0274. 6) Grømer, B.; Yoshioka, S.; Saito, S. *ACS Catal.* **2022**, 12, 1957–1964.

Bimetallic Subnanoparticles Enable Thermally-driven CO₂ Hydrogenation from Room Temperature

(¹Tokyo Institute of Technology, ²JST ERATO Yamamoto Atom Hybrid Project, ³Tohoku University, ⁴International Christian University, ⁵Nagoya University) ○ Augie Atqa,¹ Masataka Yoshida,¹ Masanori Wakizaka,³ Wang-Jae Chun,⁴ Akira Oda,⁵ Takane Imaoka,^{1,2} Kimihisa Yamamoto^{1,2}

Keywords: Subnanoparticles; Molybdenum; Platinum; Carbon Dioxide Hydrogenation

CO₂ hydrogenation is a promising strategy for achieving a carbon-neutral society.¹ For example, CO₂ hydrogenation can produce carbon monoxide (CO) as the raw material for fuel production via Fischer-Tropsch (FT) reaction.² However, this reaction is generally feasible only at high temperatures (>200 °C) due to its high activation barrier, which is unachievable at low temperatures. Here, we present a partially-oxidized bimetallic Mo-Pt subnanoparticle (Mo₄Pt₈O_x) exhibiting excellent catalytic activity on the thermally-driven CO₂ hydrogenation starting from room temperature. It shows high catalytic activity compared to monometallic Mo₁₂O_x and Pt₁₂ subnanoparticles. A mechanistic study and DFT calculations revealed that Mo species activate CO₂ even at room temperature and weaken the catalyst-CO binding energy, resulting in excellent CO₂ hydrogenation activity at low temperatures.



1) R.P. Ye, *Nat. Commun.* **2019**, *10*, 5698. 2) X. Chen, *Front. Chem.* **2020**, *8*, 709.

Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry | Oral B**[K505-4am] 09. Coordination Chemistry, Organometallic Chemistry**

Chair: Akitaka Ito, Yoshihiro Sekine

Sat. Mar 25, 2023 9:00 AM - 11:30 AM K505 (K505, Lecture Hall Bldg. [5F])

[K505-4am-01] Magnetic Properties of Organic-Inorganic Perovskites with Ferroelasticity

○Naoto Tsuchiya¹, Ishinuki Tatsuya¹, Saya Aoki¹, Yuki Nakayama¹, Goulven Cosquer², Sadafumi Nishihara^{1,2,3}, Katsuya Inoue^{1,2,4} (1. Graduate School of Advanced Science and Engineering, Hiroshima Univ., 2. Chirality Research Center, Hiroshima Univ., 3. JST, PRESTO, 4. International Institute for Sustainability with Knotted Chiral Meta Matter, Hiroshima Univ.)

9:00 AM - 9:20 AM

[K505-4am-02] Multifunctional Spin Crossover Compounds with Chiral Anions

○Hikaru Zenno¹, Yoshihiro Sekine¹, Shinya Hayami¹ (1. Kumamoto University)

9:20 AM - 9:40 AM

[K505-4am-03] Luminescence from Terbium(III) Species upon Sensitization using Ionic Nanosphere

○Nikita Madhukar¹, Taizo Misato¹, Akitaka Ito¹ (1. Kochi Univ. of Tech.)

9:40 AM - 10:00 AM

[K505-4am-04] Energy-Transfer Quenching of [Ru(bpy)₃]²⁺ in Ionic Nanosphere

○Taizo Misato¹, Akitaka Ito¹ (1. Kochi Univ. of Tech.)

10:00 AM - 10:20 AM

[K505-4am-05] Symmetry-breaking Assembly of a Supramolecular Ir Complex within a Hydrogen-bonded Host

○Shinnosuke Horiuchi^{1,2}, Eri Sakuda², Yasuhiro Arikawa², Shuichi Hiraoka¹, Keisuke Umakoshi² (1. The Univ. of Tokyo, 2. Nagasaki Univ.)

10:30 AM - 10:50 AM

[K505-4am-06] Control of Molecular Arrangement and Polarity in Vapochromic Crystals

○Fumiya Kobayashi¹, Misato Gemba¹, Makoto Tadokoro¹ (1. Tokyo Univ. of Sci.)

10:50 AM - 11:10 AM

[K505-4am-07] Latest progress on halogen-bridged metal complex chemistry

○Masanori Wakizaka¹, Shinya Takaishi¹, Masahiro Yamashita¹ (1. Tohoku Univ.)

11:10 AM - 11:30 AM

Magnetic Properties of Organic-Inorganic Perovskites with Ferroelasticity

(¹Graduate School of Advanced Science and Engineering, Hiroshima University, ²Chirality Research Center (CResCent), Hiroshima University, ³PRESTO, JST, ⁴International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM²), Hiroshima University)
 ○Naoto Tsuchiya,¹ Tatsuya Ishinuki,¹ Saya Aoki,¹ Yuki Nakayama,¹ Goulven Cosquer,^{1,2} Sadafumi Nishihara,^{1,2,3} Katsuya Inoue^{1,2,4}

Keywords: Magnetic Properties; Ferroelasticity; Multiferroics; Organic-Inorganic Perovskites;

Ferroc orders including ferromagnetism, ferroelectricity and ferroelasticity exhibit spontaneous magnetization, polarization and strain, respectively. Multiferroic properties, coupling of two or more ferroic orders, have been attracting recent interest. Especially, multiferroic materials in which ferromagnetism and ferroelectricity are coupled, showing electrically induced magnetism and magnetically induced electric polarization,¹ have been studied extensively. On the other hand, there are fewer studies about the coupling between ferromagnetism and ferroelasticity. We reported the organic-inorganic (C₆H₅C_nH_{2n}NH₃)₂FeCl₄ perovskites, which exhibit ferroelasticity and canted antiferromagnetism.²

Herein, we synthesized (C₆H₅C_nH_{2n}NH₃)₂FeCl₄ (n = 1, 2, 3) (Fig. 1) to investigate the coupling of ferroelasticity and magnetic ordering. Field dependence of magnetization of n = 2 shown the hysteresis displacements only after cooling in a magnetic field (Fig. 2). Single crystal X-ray structure analysis revealed that n = 1, 2 and 3 have perovskite-like structures. Magnetic and DSC measurements suggested there is canted antiferromagnetic phase transition at 75K (Fig. 3) but no structural phase transitions in n = 1. In this presentation, we will discuss the presence or absence of ferroelasticity and magnetic properties in detail.

1) T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, *Nature*. **2003**, 426, 55–58. 2) Y. Nakayama, S. Nishihara, K. Inoue, T. Suzuki and M. Kurmoo, *Angew. Chem. Int. Ed.* **2017**, 56, 9367–9370.

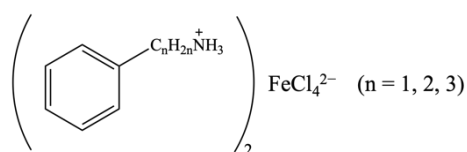


Fig. 1. Crystal formula of salts.

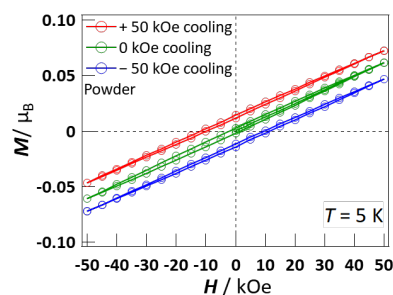


Fig. 2. Field-dependence magnetization of n = 2 for powder after zero-field cooling (ZFC) and field-cooling (FC).

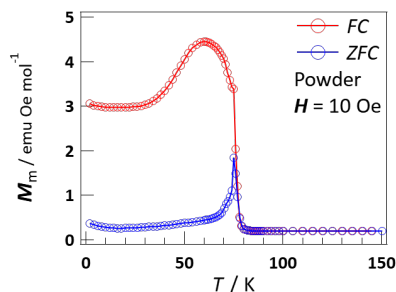


Fig. 3. Temperature-dependence magnetization of n = 1 for powder after ZFC and FC.

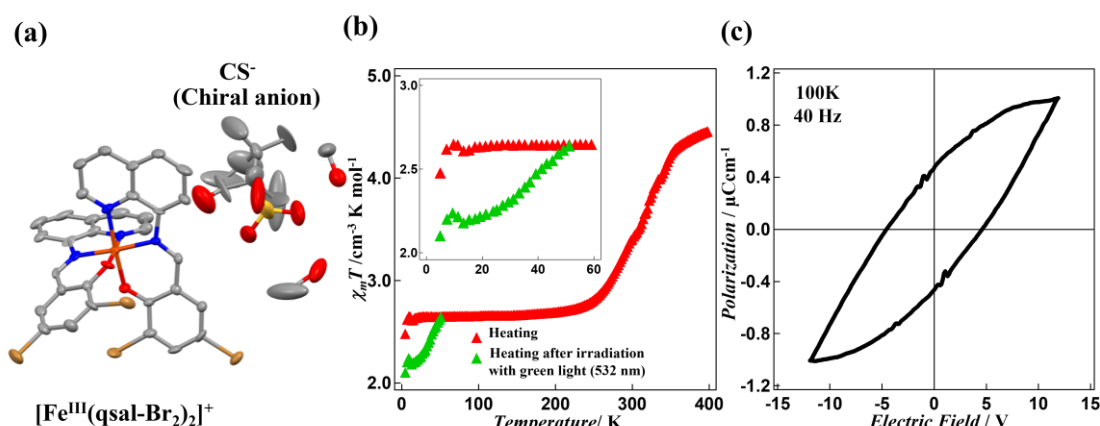
Multifunctional Spin Crossover Compounds with Chiral Anions

(¹Graduate School of Science and Technology, Kumamoto University) ○ Hikaru Zenno,¹ Yoshihiro Sekine,¹ Shinya Hayami¹

Keywords: Multifunctional material, Spin crossover behaviour, Ferroelectricity, Iron(III) complexes, light induced excited spin state trapping

Multifunctional molecular materials exhibiting synergistic coexistence of two or more properties, have attracted a great deal of attention over recent years not only for their fundamental aspects but also because of their potential applications including information storage, sensors, spintronics and electro-optic devices. Spin crossover (SCO) compounds exhibiting switching between two different spin states are used as multifunctional molecular materials because of the ability to combine various properties such as luminescence and conduction properties.¹ Molecular functional materials exhibiting both SCO behavior and ferroelectric property might show magnetoelectric (ME) effect that ferroelectricity can be controlled by magnetic field.² However, to the best of our knowledge, there is a general lack of reports concerned with the synthesis and investigation of such ferroelectric SCO compounds.

Herein, we aimed to construct a new ferroelectric SCO compound whose ferroelectric properties originated from the chiral anions. we synthesized an iron(III) complex, [Fe^{III}(qsal-Br₂)₂](CS)·2MeOH (**1**·2MeOH; qsal-Br₂= 4,6-dibromo-2-(8quinolylimino)methylphenolate, CS=camphor-10-sulfonate)(Figure (a)). **1**·2MeOH assembles in the solid state *via* π - π interactions and halogen bond involving adjacent ligands to form 2D layered domains. **1**·2MeOH exhibited the SCO phenomenon of transitions between mixture spin states with a 6:4 ratio of high spin to high spin and low spin states, and at low temperatures exhibited the reverse light induced excited spin state trapping (LIESST) phenomenon after irradiation with green light (Figure (b)). In addition, the compounds showed PE curve with hysteresis loop (Figure (c)).



1) a) J. Tao, *et. al.*, *Angew. Chem. Int. Ed.* **2015**, 54, 1574-1577. b) K. Takahashi, *et. al.*, *J. Am. Chem. Soc., Int. Ed.* **2008**, 130, 6688-6689. 2) G. G. Morgan, *J. Am. Chem. Soc.* **2022**, 144, 195-211.

Luminescence from Terbium(III) Species upon Sensitization Using Ionic Nanosphere

(¹Graduate School of Engineering, Kochi University of Technology) ○Nikita Madhukar,¹ Taizo Misato,¹ Akitaka Ito,¹

Keywords: Sensitization; Terbium; Luminescence; Ionic Nanosphere;

Terbium(III) species have been used in a variety of applications, including sensing, photovoltaics, phosphor, display devices, bioimaging and others,¹ owing to their color purity of luminescence whose bands are narrow. In contrast to such applicability, their luminescence is typically weak since both excitation and luminescence processes are Laporte-forbidden. Therefore, a number of terbium(III) systems with strong luminescence have been hitherto developed on the basis of enhancement and acceleration of these processes. In this study, we successfully sensitized the luminescence from terbium(III) species by doping in the ionic nanosphere, which can accommodate various ions in its spherical space with a diameter of <300 nm by the electrostatic interaction,² via the energy transfer from the $\pi\pi^*$ excited state of the copolymerized styrene–divinylbenzene backbone.

Terbium(III) ion was doped in the nanospheres (5–300 nmol/mg) by soaking the ionic nanosphere in an aqueous solution of TbCl₃. In the luminescence spectra of the terbium(III)-ion-doped ionic nanospheres (excitation wavelength: 260 nm, Fig. 1), several luminescence bands were observed at 488, 544, 583 and 620 nm in addition to fluorescence from the ionic nanosphere at around 330 nm. The new bands resemble to the 4f–4f luminescence originating in the $^5D_4 \rightarrow ^7F_J$ ($J = 3-6$) transitions in terbium(III) species. It is worth emphasizing that there was no luminescence observed for the aqueous TbCl₃ solution with the comparable concentration and that the excitation spectra monitored at 544 nm were similar to the absorption spectrum of the ionic nanosphere. Therefore, the luminescence from terbium(III) species was obtained by the light absorption of the ionic nanosphere, followed by the energy transfer to the terbium(III) ion.

1) D. Sarkar, S. Ganguli, T. Samanta, V. Mahalingam, *Langmuir* **2019**, 35, 6211. 2) H. Yamamoto, M. Taomoto, A. Ito, D. Kosumi, *J. Photochem. Photobiol. A: Chem.* **2020**, 401, 11277.

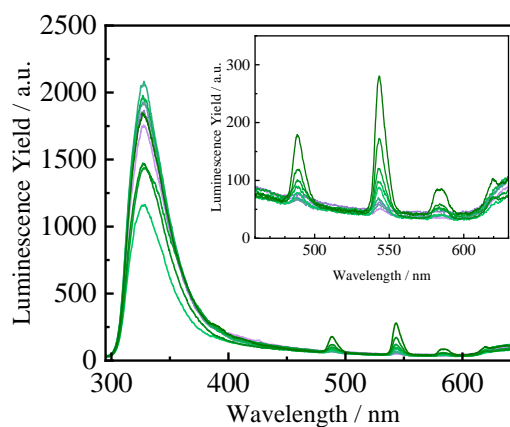


Fig. 1 Luminescence spectra of terbium(III)-ion-doped ionic nanospheres (5–300 nmol/mg, purple → green, $\lambda_{\text{ex}} = 260$ nm).

Energy-Transfer Quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Ionic Nanosphere

(¹Graduate School of Engineering, Kochi University of Technology) ○Taizo Misato,¹ Akitaka Ito¹

Keywords: Metal Complex; Excited-State Energy Transfer; Ionic Polymer; Solid-State Medium

Photoinduced energy- and electron-transfer reactions are primary processes in the solar-energy conversion system such as artificial photosynthesis and solar photovoltaics. Therefore, constructing an efficient photoinduced-reaction system is one of the most important research topics. In this study, we demonstrated energy-transfer quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by a 9,10-diphenylanthracene derivative ($[\text{DPA-N}_2]^{2+}$) by codoping in ionic nanospheres,¹ a class of cationic exchange resins with a diameter of <300 nm.

$[\text{Ru}(\text{bpy})_3]^{2+}/[\text{DPA-N}_2]^{2+}$ -codoped nanospheres ($[\text{Ru}(\text{bpy})_3]^{2+}$: 50 nmol/mg, $[\text{DPA-N}_2]^{2+}$: 0–10 nmol/mg) were prepared by soaking the ionic nanosphere with a poly(styrenesulfonate-*co*-divinylbenzene) structure in aqueous solutions of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and $[\text{DPA-N}_2]\text{Cl}_2$ at room temperature. $[\text{Ru}(\text{bpy})_3]^{2+}$ doped in the nanosphere exhibited emission from the triplet metal-to-ligand charge transfer excited state with a quantum yield (Φ_{em}) being 0.105, which was higher than that of the aqueous solution ($\Phi_{\text{em}} = 0.063$). The emission quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$ decreased even by codoping 10-nmol/mg $[\text{DPA-N}_2]^{2+}$ and, furthermore, an excitation band similar to the absorption band of $[\text{DPA-N}_2]^{2+}$ was observed by monitoring at 620 nm. These results are explainable by the excited-state energy transfer between $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{DPA-N}_2]^{2+}$. The emission from the $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{DPA-N}_2]^{2+}$ -codoped nanosphere was responsive to the presence of the molecular oxygen as shown in Fig. 1. Upon an increase in an oxygen concentration, the emission from $[\text{Ru}(\text{bpy})_3]^{2+}$ was reduced. Since the emission lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ was also shortened ($\langle\tau_{\text{em}}\rangle = 910, 770$ and 560 ns under argon, air and oxygen atmospheres, respectively), energy-transfer quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by oxygen occurred by a dynamic process.

1) H. Yamamoto, M. Taomoto, A. Ito, D. Kosumi, *J. Photochem. Photobiol. A: Chem.* **2020**, 401, 112771.

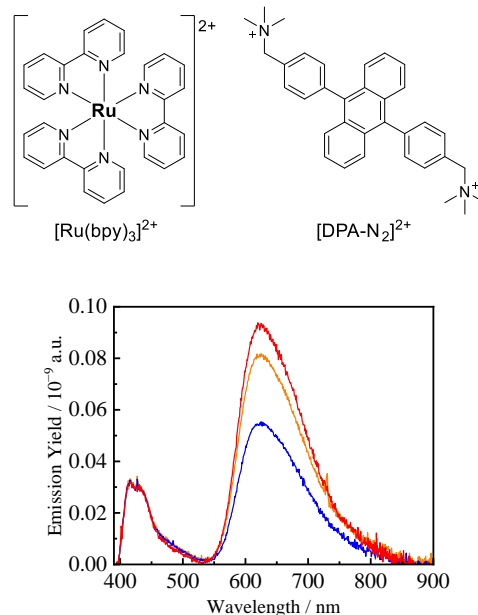


Fig. 1: Emission spectra of the ionic nanosphere containing 50-nmol/mg $[\text{Ru}(\text{bpy})_3]^{2+}$ and 10-nmol/mg $[\text{DPA-N}_2]^{2+}$ ($\lambda_{\text{ex}} = 375$ nm) under argon (red), air (orange) and oxygen atmospheres (blue).

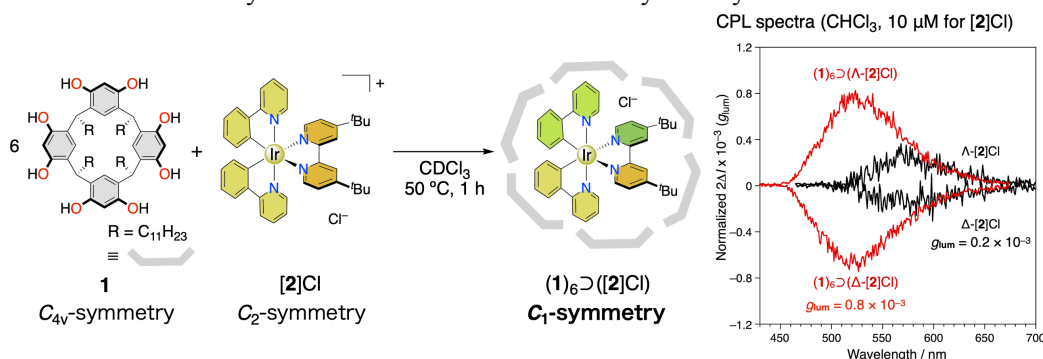
Symmetry-breaking Assembly of a Supramolecular Ir Complex within a Hydrogen-bonded Host

(¹Graduate School of Arts and Sciences, The University of Tokyo, ²Graduate School of Engineering, Nagasaki University) ○ Shinnosuke Horiuchi,^{1,2} Eri Sakuda,² Yasuhiro Arikawa,² Shuichi Hiraoka,¹ Keisuke Umakoshi²

Keywords: Host–guest Chemistry; Inclusion compound; Ir Complex; Circularly polarized luminescence; Symmetry-breaking

Molecular self-assembly is invaluable to create well-defined giant structures from small molecular components. Owing to a large entropy loss in the self-assembly process, highly symmetric architectures are typically obtained as thermodynamic products while formation of a low symmetric structure is still challenging. In contrast to the artificial molecular system, large biomolecules can form low-symmetric and information-rich structures via self-assembly by a synergistic effect of weak interactions. Herein we show the symmetry-breaking assembly forming from a C_2 -symmetric luminescent coordination complex and C_{4v} -symmetric organic hosts. Similar to the natural system, weak binding forces among the components concertedly work to overcome the large entropic disadvantage, achieving a formation of the C_1 -symmetric supramolecular structure.¹

When a 6:1 mixture of organic host **1** and Ir complex salt **[2]Cl** was heated in $CDCl_3$ at 50 °C for 1 h, the 1H NMR spectrum showed severely splitting signals assigned to the host–guest complex. The 1H - ^{13}C HSQC spectrum of the host–guest complex revealed that all signals of the organic hosts and the guest were observed inequivalently on NMR timescale, indicating formation of a defined C_1 -symmetric host–guest complex. The circularly polarized luminescence properties of the Δ - and Λ -configured complex guest **[2]Cl** were modulated by the symmetry-breaking effect. The dissymmetry factors g_{lum} were increased from 0.2×10^{-3} to 0.8×10^{-3} upon the formation of the host–guest complex, suggesting that the vectors of the transition electric and magnetic dipole moments in the photo luminescent process were altered by the reduction of the molecular symmetry.



1) S. Horiuchi, T. Yamaguchi, J. Tessarolo, H. Tanaka, E. Sakuda, Y. Arikawa, E. Meggers, G. H. Clever, K. Umakoshi, *Nat. Commun.*, **2023**, DOI:10.1038/s41467-023-35850-4.

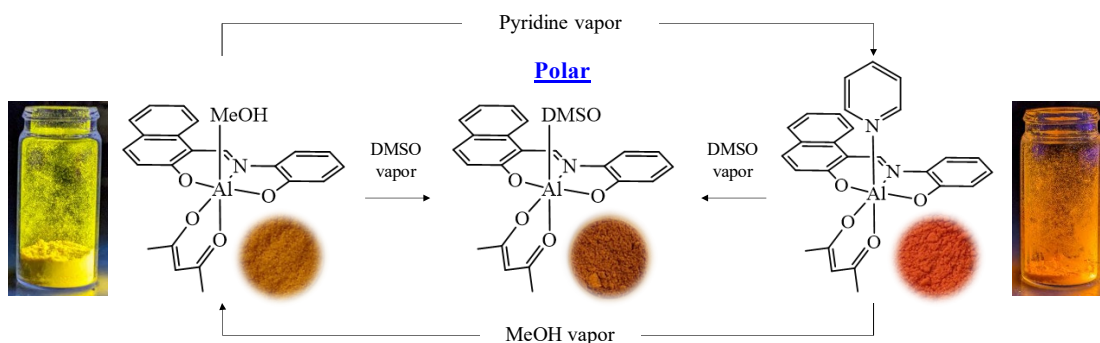
Control of Molecular Arrangement and Polarity in Vapochromic Crystals

(Department of Chemistry, Faculty of Science, Tokyo University of Science) ○Fumiya Kobayashi, Misato Gemba, Makoto Tadokoro

Keywords: Vapochromic; Polarity; Dielectric Property; Second Harmonic Generation (SHG)

The development of molecule-based multifunctional materials that are responsive to external stimuli is gaining significant attention recently owing to their advantages for application in novel functional devices, such as memory devices and sensors. In particular, vapor-induced functional switching systems, which exhibit facile structural transformations in response to specific vapor stimuli, have been reported; such transformations include changes in magnetic properties and luminescence properties. However, reports on materials that experience switching of dielectric properties and polarity, such as ferroelectric properties and nonlinear optical effects, are extremely limited.

In our previous study, we demonstrated that mononuclear complexes of type $[M(\text{sap})(\text{acac})(\text{solvent})]$ ($M = \text{Fe}^{\text{III}}, \text{Al}^{\text{III}}$; $\text{H}_2\text{sap} = 2\text{-salicylideneaminophenol}$; $\text{acac} = \text{acetylacetonate}$), incorporating a substitution-prone coordination site, could switch dielectric behavior and polarity, which was attributed to the structural transformations triggered by exposure to solvent vapor.^{1,2)} The study provided a novel example of vapor-induced polarity switching systems, wherein coordinated solvent substitution was the ‘trigger’ for the corresponding structural rearrangements. Thus, expanding the scope of application of the above system to other type compounds is highly desirable for the development of multifunctional molecular materials. Herein, we report the first achievement of solvent vapor-induced polarity switching in vapochromic crystals of the type $[\text{Al}(\text{nap})(\text{acac})(\text{sol})]$ ($\text{H}_2\text{nap} = N\text{-(2-hydroxyphenyl)-2-hydroxy-1-naphthylaldimine}$; $\text{sol} = \text{MeOH}$ (**1**), DMSO (**2**), pyridine (**3**)).



1) F. Kobayashi, R. Akiyoshi, D. Kosumi, M. Nakamura, L. F. Lindoy, S. Hayami, *Chem. Commun.*, **2020**, 56, 10509–10512. 2) F. Kobayashi, M. Gemba, S. Hoshino, K. Tsukiyama, M. Shiotsuka, T. Nakajima, M. Tadokoro, **2023**, *submitted*.

ハロゲン架橋金属錯体化学の最近の進展

(東北大院理¹) ○脇坂 聖憲¹・高石 慎也¹・山下 正廣¹

Latest progress on halogen-bridged metal complex chemistry

(¹Graduate School of Science, Tohoku University) ○Masanori Wakizaka,¹ Shinya Takaishi,¹ Masahiro Yamashita¹

Halogen-bridged metal complexes (MX-Chains) are molecular chains having the one-dimensional (1D) electronic system.^[1] They have been researched for more than 100 years and several hundred kinds of compounds have been synthesized. Their 1D electronic systems are unique; namely, electron-electron repulsion energy and electron-phonon interaction energy competes to afford semiconductive Mott insulators or Peierls insulators. Recently, the heterostructure composed from the Mott insulator of Ni–Br chains and the Peierls insulator of Pd–Br chains was reported.^[2] Additionally, the orthogonal grade-separated structure of the Pt MX-Chain was reported.^[3] These structures would be well models of 1D heterojunctions and 1D nanowiring.

Keywords : *Halogen-bridged metal complexes, Mott insulator, Peierls insulator, Heterostructure, Orthogonal chains*

ハロゲン架橋金属錯体 (MX) は、金属イオンとハロゲン化物イオンが交互に並んだ分子鎖化合物である^[1]。金属の d_z^2 軌道とハロゲンの p_z 軌道が連結することで一次元電子系をつくる。Ni の MX は電子相関が強いため、平均原子価 Ni(III) のモット・ハバード (MH) 状態をとる。一方、Pd や Pt の MX は電子格子相互作用がより強く働くため、混合原子価 M(II)/M(IV) の電荷密度波 (CDW) 状態をとる。

近年、MH 状態の Ni の MX と CDW 状態の Pd の MX を電気化学的エピタキシャル法によって接合することに成功した^[2]。STM により、二種類の分子鎖が原子レベルで繋がっていることを明らかにした。マクロスケール及び原子スケールにおける一次元ヘテロ接合を解明した例はこれまでなく、その概念を実証した。

一方、CDW 状態の Pt の MX が、対アニオンに三方両錐型の $[\text{Fe}^{\text{III}}\text{Cl}_5]^{2-}$ を持つことで、三次元的な水素結合ネットワークによって直交鎖構造をつくることを明らかにした^[3]。通常の鎖化合物は、鎖が平行に並ぶ結晶構造をとるため、直交鎖構造は非常に珍しい。錬金術師の金と呼ばれる化合物である $\text{Hg}_{3-x}\text{AsF}_6$ は、よく知られた直交鎖であり、MX の直交鎖とは同じ空間群および同じトポロジーであることが分かった。単分子鎖の直交構造はこれまで報告例がなく、その合成に初めて成功した。

[1] M. Yamashita, *Bull. Chem. Soc. Jpn.* **2021**, 94, 209–264.

[2] M. Wakizaka, S. Kumagai, H. Wu, T. Sonobe, H. Iguchi, T. Yoshida, M. Yamashita, S. Takaishi, *Nat. Commun.* **2022**, 13, 1188.

[3] H. Nakajima, H. Iguchi, S. Takaishi, T. Sato, B. K. Breedlove, R. Ishikawa, S. Kawata, Q. Wan, M. Wakizaka, M. Yamashita, *Chem. Mater.* **2023**, 35, 116–122.

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

[K606-4am] 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-

Chair: Kentaro Suzuki, Tomohisa Sawada

Sat. Mar 25, 2023 9:00 AM - 11:10 AM K606 (K606, Lecture Hall Bldg. [6F])

[K606-4am-01] Effect of substrate curvature and relative humidity on branched shape of hollow crystals for vapor phase crystal growth of photochromic diarylethene

○Mami Isobe¹, Daichi Kitagawa^{1,2}, Seiya Kobatake^{1,2} (1. Grad. Sch. of Eng., Osaka Metropolitan Univ., 2. Grad. Sch. of Eng., Osaka City Univ.)

9:00 AM - 9:20 AM

[K606-4am-02] X-ray observation of steric zipper interactions in metal-induced peptide cross- β nanostructures

○Eisuke Tsunekawa¹, Tomohisa Sawada^{2,3}, Makoto Fujita^{1,4} (1. Grad. School of Engineering, The university of Tokyo, 2. Lab. for Chem. &Life Sci., Tokyo Tech, 3. JST PRESTO, 4. IMS)

9:20 AM - 9:40 AM

[K606-4am-03] Syntheses and Emission Properties of Rotaxane-type Fluorophores Encapsulating Pyridinium-conjugated Molecules

○Kohei Nishioki¹, Yuki Ohishi¹, Junya Chiba¹, Masahiko Inouye¹ (1. University of Toyama)

9:40 AM - 10:00 AM

[K606-4am-04] Phototriggered supramolecular polymerization with anthracene diketone precursors

○Mitsuaki Yamauchi¹, Hidenori Nakanishi¹, Hironobu Hayashi¹, Hiroko Yamada¹ (1. Nara Institute of Science and Technology)

10:10 AM - 10:30 AM

[K606-4am-05] Charge-Segregated Stacking Structure Comprising Charged NIR-Dye

○Kazuhisa Yamasumi¹, Kentaro Ueda¹, Yohei Haketa¹, Hiromitsu Maeda¹ (1. Ritsumeikan University)

10:30 AM - 10:50 AM

[K606-4am-06] Reversible Photocontrol over Hydrogen-bond-directed Supramolecular Polymorphism

○Kenta Tamaki¹, Shiki Yagai² (1. Grad. Sch. of Sci. and Eng., Chiba Univ., 2. IAAR, Chiba Univ.)

10:50 AM - 11:10 AM

Effect of Substrate Curvature and Relative Humidity on Branched Shape of Hollow Crystals for Vapor Phase Crystal Growth of Photochromic Diarylethene

(¹Graduate School of Engineering, Osaka Metropolitan University, ²Graduate School of Engineering, Osaka City University)

○Mami Isobe,¹ Daichi Kitagawa,^{1,2} Seiya Kobatake^{1,2}

Keywords: Diarylethene; Vapor Phase Crystal Growth; Hyperbranched Hollow Crystal

In sublimation of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) on the flat glass substrates, the hollow and feather-like crystals are produced separately on each surface of them with the different wettability by adjusting the relative humidity at the early stage of the sublimation¹⁾. The hollow and feather-like crystals are generated on the polycrystalline thin films formed with micro-crystals having the uniform shape and size packed tightly (*A*) and with micro-crystals having the non-uniform shape and size packed loosely (*B*), respectively. In this work, to prepare the hyperbranched hollow crystals densely on substrate surfaces, we have investigated the effects of the relative humidity and substrate curvature for the crystal growth process on a concave surface of the spherical glass substrate.

When sublimating **1a** on a hydrophilic concave surface of the spherical glass substrates (height of spherical cap: 8 mm, inner radius of curvature: 24 mm) with hydrophilic surface by heating 15 mg of the powder crystals of **1a** to 100 °C (Figure 2), the hyperbranched hollow crystals were produced more densely on the substrate surface by the high relative humidity than by the low relative humidity. The mechanism of the formation of the hyperbranched hollow crystals is as follows. After the sublimation for 2 h, the polycrystalline thin films consisting of two domains, *A* and *B*, were spread entirely on the substrate surface. *Domains A* and *B* were located around the edge and in the center of the substrate surface, respectively (Figure 3a). After the sublimation for 4 h, *Domain A* expanded in the entire area of the substrate surface and *Domain B* was present in the remainder area sparsely distributed across the center of it (Figure 3b). The micro-crystals in *Domain A* have the more uniform shape and size and are packed more tightly than those in *Domain B*. Moreover, after the sublimation for 6 h, the hyperbranched hollow and feather-like crystals were generated in *Domains A* and *B*, respectively. In summary, the hyperbranched hollow crystals, which are never generated on a hydrophilic surface of the flat substrate, were produced densely in *Domain A* formed on a hydrophilic concave surface of the spherical substrate.

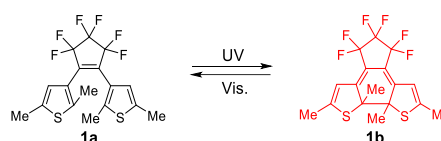


Figure 1. Photochromic reaction of **1a**.

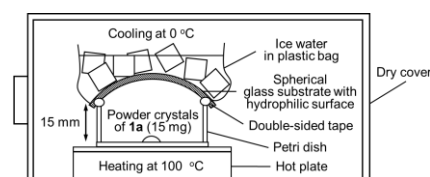


Figure 2. Setup for the sublimation of **1a** for a concave surface of a spherical glass substrate.

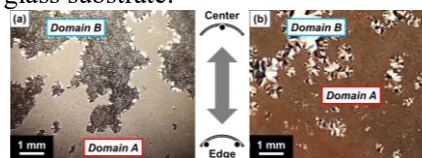


Figure 3. Distribution of thin film domains formed on spherical substrate surfaces after sublimation for 2 h (a) and 4 h (b), as observed by polarizing microscope under crossed Nicols.

1) M. Isobe, D. Kitagawa, S. Kobatake, *Cryst. Growth Des.* **2022**, 22, 5489.

配位結合を用いたクロスβ性ペプチドナノ構造におけるβシート積層相互作用のX線観察

(東大院工¹・東工大化生研²・JST さきがけ³・分子研⁴) ○恒川英介¹・澤田 知久^{2,3}・藤田 誠⁴

X-ray observation of steric zipper interactions in metal-induced peptide cross-β nanostructures (¹Grad. School of Engineering, The University of Tokyo, ²Lab. for Chem. & Life Sci., Tokyo Tech, ³JST PRESTO, ⁴IMS) ○Eisuke Tsunekawa,¹ Tomohisa Sawada,^{2,3} Makoto Fujita^{1,4}

The molecular structure of amyloid fibrils is characterized by a cross-β structure, in which two-layers of β-sheets are aggregated in the same direction. The layers are stabilized by a hydrophobic packing of peptide side chains called as a steric zipper.¹⁾ In this work, to achieve the de novo construction of cross-β nanostructures, we designed various alternating tetrapeptide sequences of coordinating/hydrophobic residues, and examined their folding and assembly through metal complexation (Fig. 1a). From peptide **1**, having Ala, a crystalline nanotube was obtained in a high yield through the complexation with Zn(NCS)₂. In the crystal structure, a steric zipper of an interdigitation type was observed among nanotubes (Fig. 1b, left). In contrast, with a combination of Val and Leu (**2**), a similar nanotube was formed, but the steric zipper changed to a hydrophobic contact type (Fig. 1b, right). Moreover, from the peptide with a hydrophilic residue, construction of a novel pattern of the steric zipper was also achieved, which was clearly observed by crystallographic study.²⁾

Keywords: Peptide; Parallel β-sheet; Self-assembly; Cross-β structure; Metal coordination

アミロイド線維の分子構造は、二層のβシートが向きを揃えて積層したクロスβ構造とよばれ、その層間はペプチド側鎖同士の疎水的なパッキング構造¹⁾ (Steric zipper) によって安定化されている。本研究では、そのような高次ペプチド構造のデノボ構築を目指し、金属配位性のアミノ酸残基と疎水性残基を交互に配列させたテトラペプチドと、金属イオンとのフォールディング集合を検討した (図 1a)。疎水性残基に Ala を用いたペプチド **1** と Zn(NCS)₂ の錯形成からは、単結晶性のナノチューブが高収率で生成し、そのチューブ間には噛み合い型の Steric zipper の生成が確認された (図 1b 左)。疎水性残基に Val と Leu を用いた場合には、同様にナノチューブが生成し、疎水性コンタクト型の Steric zipper が観測された (図 1b 右)。さらに、本手法をさまざまな配列へ適用したところ、親水性側鎖を持つ配列から、観測例の無い様式の Steric zipper の生成が確認され、その詳細な X 線観察に成功した²⁾。

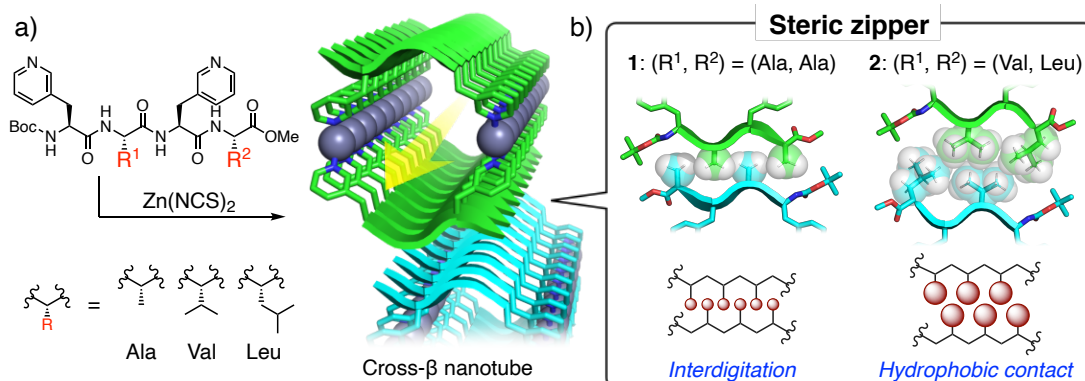


図 1. (a) クロスβ性ナノチューブ構造の合成スキームと (b) 観察された Steric zipper.

1) D. Eisenberg, *et al.*, *Nature* **2005**, 435, 7644. 2) E. Tsunekawa, *et al.*, *in revision*.

Syntheses and Emission Properties of Rotaxane-type Fluorophores Encapsulating Pyridinium-conjugated Molecules

(Graduate School of Pharmaceutical sciences, University of Toyama) ○Kohei Nishioki, Yuki Ohishi, Junya Chiba, Masahiko Inouye

Keywords: Cyclodextrin; Cucurbit[6]uril; Rotaxane; Fluorophore; Conjugated Molecule

Encapsulating fluorescence dyes with macrocyclic molecules can improve emission efficiency, photostability, and solubility of the dyes. Recently, we reported [3]rotaxane-type fluorescence dyes, in which a fluorescent core is irreversibly encapsulated by cyclodextrins (CDs). These dyes showed high quantum efficiency of blue emission and extremely high photostability. Herein, we aimed to apply this rotaxane strategy to various fluorescent cores emitting longer wavelength lights. We newly designed [5]rotaxane-type fluorescent dyes, in which a pyridinium-conjugated core is encapsulated by CDs and cucurbit[6]urils (CB6) (Fig. 1). Because donor-acceptor conjugated dyes are known to emit longer wavelength light, we expected these new rotaxanes emitting green to red light.

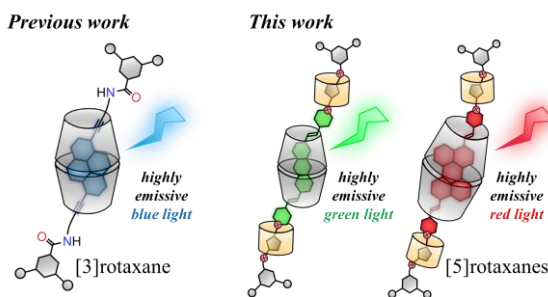


Fig. 1 Structures of [3]rotaxane and [5]rotaxanes.

The pyridinium-conjugated anthracene axis **1** was applied to “template-directed click reaction” known as a high-yield rotaxane synthesis method (Fig. 2). We succeeded in synthesizing a [5]rotaxane **2** in high yield, and **2** showed higher emission efficiency ($\Phi_{\text{FL}} \approx 1.00$, in water) compared to **1** ($\Phi_{\text{FL}} = 0.01$). Unexpectedly, the emitting-color light of the rotaxane **2** differed from that of **1**. This finding suggests that CDs and CB6 should affect the excited fluorescence core. In this presentation, we will also report other [5]rotaxane-type fluorescence dyes.

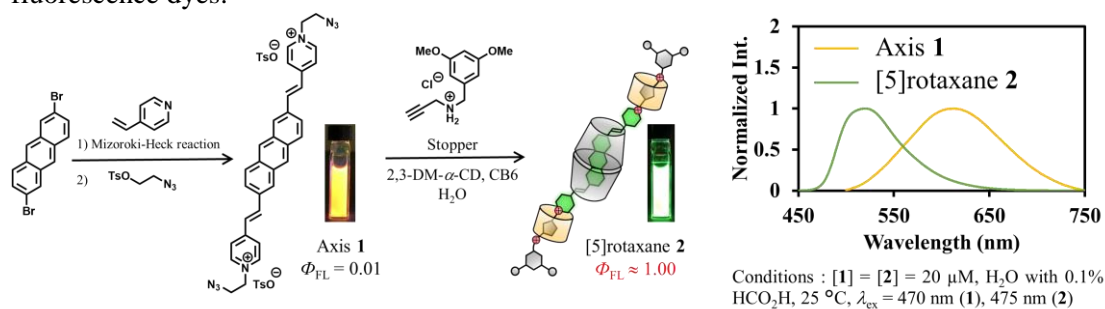


Fig. 2 Syntheses and emission spectrum of axis **1** and [5]rotaxane **2**.

1) M. Inouye, A. Yoshizawa, M. Shibata, Y. Yonenaga, K. Fujimoto, T. Sakata, S. Matsumoto, M. Shiro, *Org. Lett.* **2016**, 18, 1960. 2) X. Hou, C. Ke, J. F. Stoddart, *Chem. Soc. Rev.* **2016**, 45, 3766.

アントラセンジケトン前駆体を用いた光誘起超分子重合

(奈良先端大先端科技) ○山内 光陽・中西 秀徳・林 宏暢・山田 容子

Phototriggered supramolecular polymerization with anthracene diketone precursors (*Graduate School of Science and Technology, Nara Institute of Science and Technology*)

○Mitsuaki Yamauchi, Hidenori Nakanishi, Hironobu Hayashi, Hiroko Yamada

Precious control of molecular assembly structures based on supramolecular chemistry is required to improve the performance of organic semiconductor devices because the performance depends on the supramolecular assembly structures. Therefore, pre-organization of defect-free supramolecular assembly via intermolecular interactions in solution is of importance. Previously, our group has reported a quantitative synthesis of acene derivatives in solution by using α -diketone-type acene-based photoprecursors with good solubility¹⁾. Here, we designed and synthesized a new anthracene-based diketone photoprecursor possessing amide groups as a directional hydrogen bond moiety, and revealed a phototriggered supramolecular polymerization. The analysis of absorption spectra revealed that the photoirradiation to monomeric **1** in solution resulted in the formation of an anthracene derivative **2**, followed by self-assembly.

Keywords : Photoprecursor; Self-assembly; Supramolecular Polymerization; Anthracene; Organic Semiconductor

有機半導体デバイスの性能は、有機分子の超分子集合構造に依存するため、高性能化を達成するためには超分子化学に立脚した精密な構造制御が求められる。そのため、溶液中で働く分子間相互作用を利用して、欠陥の無い超分子集合体を事前に構築する“事前組織化”が重要となる。

当研究グループはこれまで、難溶性のアセン類の定量的合成アプローチとして、光変換可能な可溶性ジケトン前駆体から目的アセン類への光変換反応を報告している¹⁾。本研究では、ジケトン前駆体に指向性の高い水素結合部位としてアミド結合を導入した新規分子 (**1**, Fig. 1) を設計・合成し、光照射によって誘起された超分子重合を明らかにした。吸収スペクトル解析により、**1** のモノマー溶液へ可視光照射すると、アントラセン **2** の形成に伴い集合体が形成されることが示唆された。

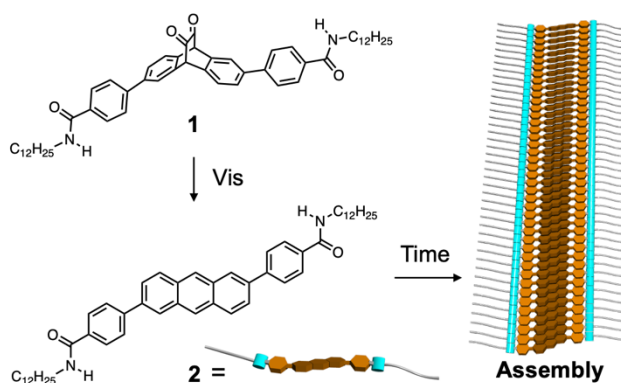


Fig. 1 Schematic representation of phototriggered self-assembly.

- 1) M. Suzuki, T. Aotake, Y. Yamaguchi, N. Noguchi, H. Nakano, K.-i. Nakayama, H. Yamada, *J. Photochem. Photobiol. C: Photochem. Rev.*, **2014**, 18, 50–70.

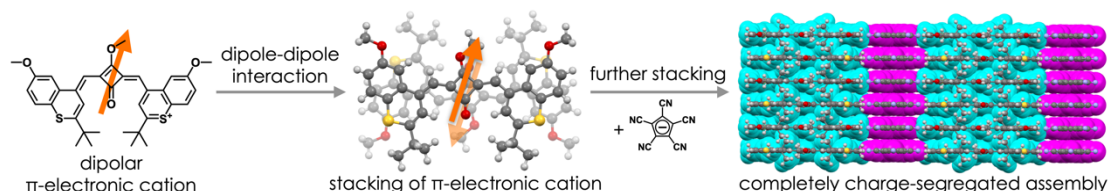
荷電近赤外色素から形成される電荷種分離配置型集合体

(立命館大生命科学) ○山角 和久・上田 健太郎・羽毛田 洋平・前田 大光
 Charge-Segregated Stacking Structure Comprising Charged NIR Dye (*College of Life Sciences, Ritsumeikan University*) ○Kazuhisa Yamasumi, Kentaro Ueda, Yohei Haketa, Hiromitsu Maeda

Squarylium-based π -electronic cation with an augmented dipole was synthesized to induce stacking of identically charged species. The cation formed various ion pairs in combination with anions, and the ion pairs exhibited distinct photophysical properties in the dispersed state, ascribed to the formation of J- and H-aggregates. The ion pairs provided solid-state assemblies based on cation stacking. It is noteworthy that the cations and the anions were completely segregated in a pseudo-polymorph of the ion pair with pentacyanocyclopentadienide as a π -electronic anion, resulting in anisotropic electric conductivity derived from cation stacking. The charge-segregated mode and fascinating properties were ascribed to the reduced electrostatic repulsion between adjacent antiparallelly oriented π -electronic cations via dipole-dipole interactions.

Keywords : charged π -electronic systems; ion-pairing assemblies; near-infrared dyes; chiroptical properties; electric conductivity

π 電子系は特徴的な吸光・発光特性や酸化還元能から有機エレクトロニクスをはじめとして多様な分野での応用が期待されている。とくに、同種の荷電 π 電子系を積層させることで、電子豊富・電子不足といった特徴的な電子状態に起因して半導体への応用が期待される。¹⁾ しかし、各荷電 π 電子系（カチオン・アニオン）が独立して積層したカラム構造からなる電荷種分離配置型集合体は報告されていない。今回、同種電荷種の積層を指向して、スクアリリウム骨格を基盤とした双極子を有する π 電子系カチオンを構成ユニットとしたイオンペアの形成・集合化挙動を検証した。貧溶媒中・結晶中でカチオンの積層に基づいた集合体を形成し、対アニオンに応じた集合化形態に依存した近赤外吸光・発光特性の変調が観測された。とくに π 電子系アニオンとのイオンペアは結晶中で電荷種分離配置型集合体を形成し、半導体性を示すことも明らかにした。エネルギー分割解析から、直接積層したカチオン間での静電反発の低下、すなわち双極子-双極子相互作用の寄与が示唆された。²⁾



1) Review: Haketa, Y.; Urakawa, K.; Maeda, H. *Mol. Syst. Des. Eng.* **2020**, 5, 757.

2) Yamasumi, K.; Ueda, K.; Haketa, Y.; Hattori, Y.; Suda, M.; Seki, S.; Sakai, H.; Hasobe, T.; Ikemura, R.; Imai, Y.; Ishibashi, Y.; Asahi, T.; Nakamura, K.; Maeda, H. *Angew. Chem. Int. Ed.* **2023**, 62, in press (DOI: 10.1002/anie.202216013).

Reversible Photocontrol over Hydrogen-bond-directed Supramolecular Polymorphism

(¹Graduate School of Science and Engineering, Chiba University, ²Institute for Advanced Academic Research, Chiba University) ○Kenta Tamaki,¹ Shiki Yagai²

Keywords: Hydrogen bond; Supramolecular polymorphism; Sheet; Supramolecular polymer; Azobenzene

Controlling polymorphism, an occurrence of more than one phase with different molecular packing arrangements, is of great importance because it crucially affects physical and chemical properties of the molecules.¹ The polymorphic phenomenon exhibited by supramolecularly engineered molecules is called “supramolecular polymorphism”, which is typically controlled by complicated multistep processing.² If the transitions between the polymorphs can be achieved by one simple and facile step and are reversible, it will be applied to smart functional materials with stimuli-responsive properties.

Our research group has investigated that barbituric acid-functionalized π -conjugated molecules can form polymeric tape-like hydrogen-bonding patterns (tapes)³ and discrete cyclically hexameric ones (rosettes),⁴ which can hierarchically self-assemble to afford insoluble sheet-like aggregates and soluble supramolecular polymers, respectively. Herein, we demonstrate reversible photocontrol of the above hydrogen-bond-directed supramolecular polymorphisms by using *trans*–*cis* photoisomerization of a novel azobenzene-incorporated molecule **1** (Figure 1a). *Trans*-isomers of **1** (**1_{trans}**) afforded insoluble tape-derived crystalline sheets in nonpolar solvent (Figure 1b). Upon UV-irradiation, the photo-generated sterically bulky *cis*-isomers (**1_{cis}**) reduced the crystallinity of tapes, causing a structural transition into the rosette-derived soluble supramolecular polymers (Figure 1c). Insoluble sheets were reproduced by *cis*–*trans* reverse isomerization of the azobenzene unit (Figure 1d).

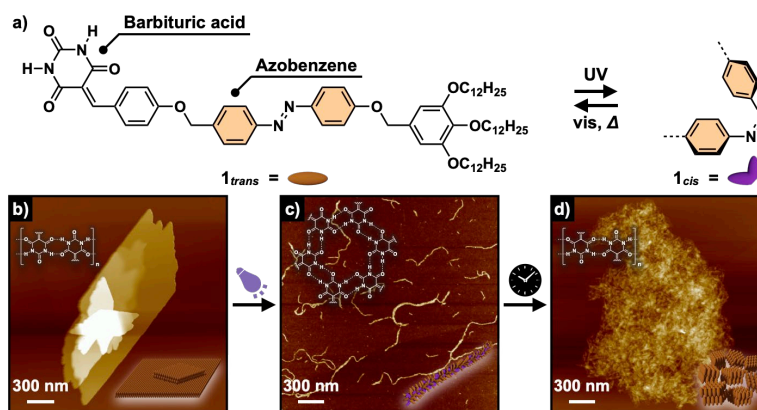


Figure 1. a) Chemical structure of molecule **1** (**1_{trans}** and **1_{cis}**). b–d) AFM images of molecular assemblies of **1** in methylcyclohexane (MCH) b) before and c) after UV-irradiation and d) 2-days aged after UV-irradiation.

1) B. Moulton and M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629. 2) M. Wehner, F. Würthner et al., *J. Am. Chem. Soc.* **2019**, *141*, 6092. 3) M. Kawaura, S. Yagai et al., *Chem. Sci.* **2022**, *13*, 1281. 4) S. Yagai et al., *Acc. Chem. Res.* **2019**, *52*, 1325; *Acc. Mater. Res.* **2022**, *3*, 259.

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

[K705-4am] 15. Organic Chemistry -Aliphatic and Alicyclic Compounds, and New Synthetic Technology-

Chair: Masaki Nishijima, Shinichiro Fuse

Sat. Mar 25, 2023 9:00 AM - 10:20 AM K705 (K705, Lecture Hall Bldg. [7F])

[K705-4am-01] Multistep-flow Syntheses of APIs Utilizing Continuous-flow C– N Bonds Forming Reactions with Heterogeneous Catalysts

○Ken Nishizawa¹, Yuki Saito¹, Shu Kobayashi¹ (1. The university of Tokyo)

9:00 AM - 9:20 AM

[K705-4am-02] Development of Flow Microwave Reactor Using CSTR and Rapid Synthesis of Organic Compounds

○Takeko Matsumura¹, Akiyoshi Ono¹, Isao Kotani², Kentaro Kotani², Nobuyuki Nakayama², Mitsuyoshi Kishihara³, Yoshihito Mori⁴ (1. MINERVA LIGHT LAB., 2. Mac engineering Co. Ltd., 3. Okayama Prefectural University, 4. Ochanomizu University)

9:20 AM - 9:40 AM

[K705-4am-03] Oil/water-biphasic dynamic kinetic resolution in a Pickering emulsion

○Kyohei Kanomata¹, Jihoon Moon¹, Takusho Kin¹, Karin Mizuno¹, Shuji Akai¹ (1. Osaka University)

9:40 AM - 10:00 AM

[K705-4am-04] Photosensitized Singlet Oxygen-supported Alcohol Oxidation Mediated by Nitroxyl Radical Catalyst

○Masaki Nishijima¹, Shota Nagasawa¹, Yusuke Sasano¹, Yasuyuki Araki¹, Yoshiharu Iwabuchi¹, Takehiko Wada¹ (1. Tohoku University)

10:00 AM - 10:20 AM

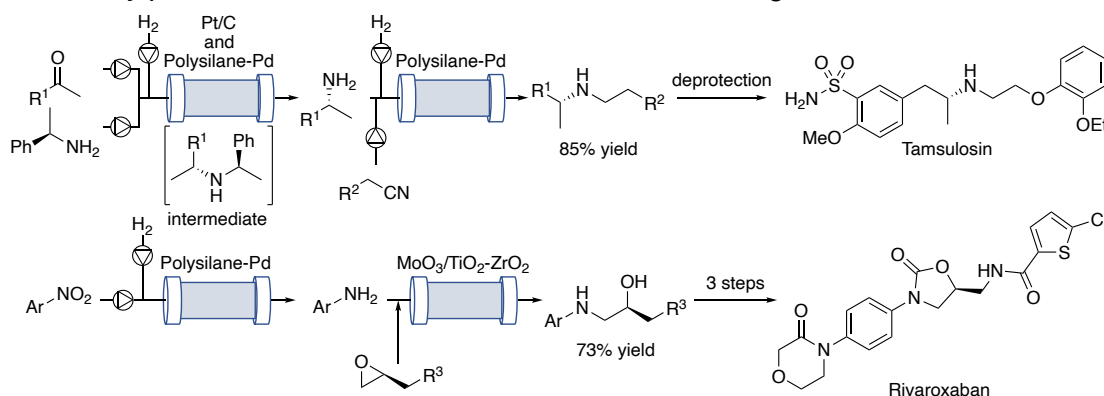
Multistep-flow Syntheses of APIs Utilizing Continuous-flow C–N Bonds Forming Reactions with Heterogeneous Catalysts

(School of Science, The Univ. of Tokyo) ○ Ken NISHIZAWA, Yuki SAITO, Shū KOBAYASHI

Keywords: Heterogeneous catalyst; Solid acid catalyst; Pd catalyst; Sequential-flow synthesis; APIs synthesis

Multistep-flow synthesis is an efficient synthetic method to access complex structures such as active pharmaceutical ingredients (APIs). However, it's still challenging because byproduct formation disturbs consecutive reactions. C–N bond is one of the most abundant structures in fine chemicals, and most of the APIs have at least one C–N bond in their structures. Therefore, to achieve the multistep-flow synthesis of APIs, the development of continuous-flow C–N bond forming reactions with minimal amounts of byproducts is crucial. In this work, we investigated multistep-flow synthesis of APIs utilizing two types of continuous-flow C–N bond forming reactions with heterogeneous catalysts.

First, a Tamsulosin intermediate was synthesized via three-step sequential-flow reaction utilizing three different hydrogenation reactions. Of these, two types of polysilane-Pd catalysts were developed independently and used in the second and the third steps. An activated carbon- $\text{Ca}_3(\text{PO}_4)_2$ -supported Pd catalyst and a silica-supported catalysts showed high activity and durability in reductive amination of a nitrile and hydrogenolysis of phenethyl group, respectively, and the overall yield was reached to 85%^[1]. Second, a Rivaroxaban intermediate was synthesized in 73% yield via two-step reaction involving aminolysis of epoxide. In the aminolysis reaction, TiO_2 - ZrO_2 supported molybdenum oxide catalyst exhibited high catalyst activity. Catalyst characterization revealed that acid density of the catalyst is one of important factors for the high activity. Both of the target compounds could be synthesized without any purification of intermediates and solvent exchange.



1) Y. Saito, K. Nishiawa, B. Laroche, H. Ishitani, S. Kobayashi, *Angew. Chem. Int. Ed.* **2022**, *61*, e2022115643.

CSTR 連続攪拌槽マイクロ波反応装置の開発と有機合成反応への適用 (ミネルバライトラボ)¹ (株) マックエンジニアリング² 岡山県立大学³ お茶の水女子大学⁴・○松村竹子¹・小野晃義¹・小谷功²・小谷研太郎²・中山伸行²・岸原充佳³・森義仁⁴

Development of Flow Microwave Reactor Using CSTR and Rapid Synthesis of Organic Compounds

(¹Minerva Light Laboratory L.L.D.,²Mac engineering Co. Ltd., ³Okayama Prefectural University, ⁴Ochanomizu University,

Microwave chemistry have developed various speedy synthetic processes in chemical synthesis since the development of home microwave oven in 1945. However, the application methods are limited mainly magnetron as a power supply. We developed various microwave reactors with solid state semiconductors as microwave power supply. In this time CSTR flow microwave reactor is developed to in which a continuous stirring tank reactor (CSTR) is settled to the mixing of sample solutions. This system is applied to esterification reactions. Reaction time was shortened with good yield under small electric power.

Keywords : CSTR microwave reactor; Flow microwave methods, Solid state microwave power supply

【緒言】

マイクロ波加熱法は家庭用電子レンジに代表されるような迅速急速加熱法であることはよく知られている。現在、省エネルギー生産プロセスの開発は SDGs の立場から強く求められている。マイクロ波加熱法による迅速加熱法が、種々の工業生産に用いられるとその省エネルギー効果は著しいと考えられる、これまでのマイクロ波加熱装置に用いられてきた電源はマグネトロンが大勢を占めていたため、装置設計などに制約があった。演者らは種々の半導体電源を用いたマイクロ波装置を作製し、その活用

今回、複数の反応槽を溶液が通る際に攪拌、混合され、反応が連続的に進むという原理に基づく CSTR 装置と半導体電源同軸マイクロ波反応器が結合した新しいフローマイクロ波反応装置を開発し、エステル化反応などの有機反応の迅速化を試みた。今回の実験で反応時間の短縮、反応収率の増加、使用電力の著しい軽減が認められた。さらに種々のフロー反応法への適用について検討した結果を報告する。

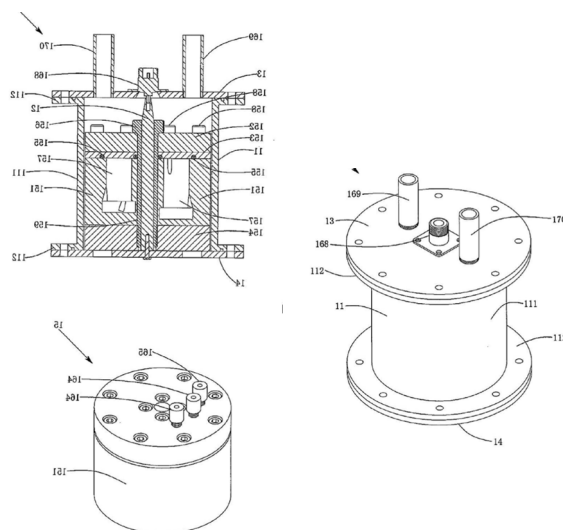


図 1. 同軸キャビティ (全体図) と CSTR 装置

Pickering エマルションを反応場とする油水二相系での動的速度論的光学分割

(阪大院薬¹) ○鹿又 喬平¹・文 志勲¹・金 澤昇¹・水野 花鈴¹・赤井 周司¹
 Oil/water-biphasic dynamic kinetic resolution in a Pickering emulsion (¹*Graduate School of Pharmaceutical Sciences, Osaka University*) ○Kyohei Kanomata,¹ Jihoon Moon,¹ Takusho Kin,¹ Karin Mizuno,¹ Shuji Akai¹

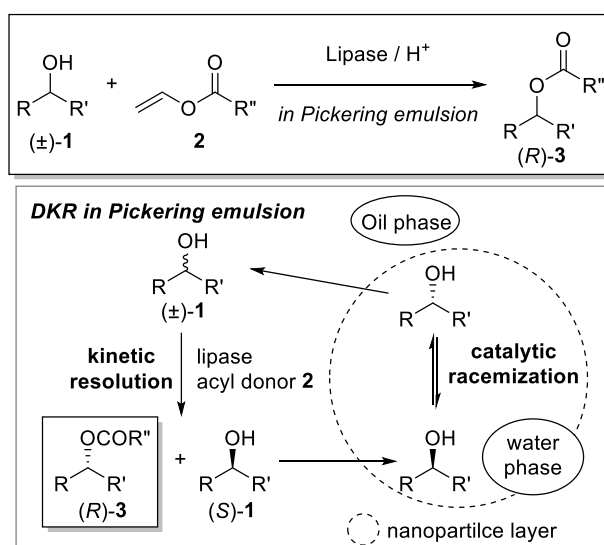
A new strategy of dynamic kinetic resolution (DKR) using a Pickering emulsion is reported. A water-in-oil emulsion was prepared from octane, 1.0 M H₂SO₄, and amphiphilic silica nanoparticles. A lipase-catalyzed DKR of (±)-1-phenylethanol was investigated using vinyl decanoate as an acyl donor, in which acid-catalyzed alcohol racemization proceeded inside the emulsion droplets and lipase-catalyzed kinetic resolution proceeded outside. The reaction gave the desired ester with 91% yield in an optically pure form.

Keywords : *Pickering emulsion; Dynamic Kinetic Resolution; Lipase; Asymmetric Synthesis; Alcohol*

速度論的光学分割 (KR) とラセミ化反応を同一系内で行う動的速度論的光学分割 (DKR) は、高い収率かつ光学純度で光学活性化合物を合成する優れた手法である。しかしラセミ化に伴う副反応や、KR とラセミ化それぞれの触媒の共存性に課題を抱えている。当研究室では、細孔径 4 nm のメソポーラスシリカ担持オキソバナジウムをアルコールのラセミ化触媒として独自に開発し、多孔質構造によりラセミ化と KR の反応場を分離した DKR を報告している。¹ しかしラセミ化に伴う副反応が依然として課題となっていた。今回演者らは、両親媒性ナノ粒子が形成する Pickering エマルションを利用し、触媒の共存性や副反応などの諸課題を解決する研究に取り組んだ。

疎水化処理したシリカナノ粒子を乳化剤とし、オクタンと 1 M 硫酸から water-in-oil エマルションを調製した。エマルション外部にリパーゼを加えることで、エマルション外部でリパーゼによる KR、内部で酸触媒によるラセミ化が進行するアルコールの DKR を達成した。基質に(±)-1-phenylethanol、アシル化剤にデカン酸ビニルを用いた場合、収率 91% (>99%ee) で目的のエステルが得られた。Pickering エマルションを形成することで、リパーゼと硫酸という本来は共存し得ない組み合わせを同一系内で用いることが可能となった。

1) Sugiyama, K.; Akai, S. et al., *Catal. Sci. Technol.* **2016**, 6, 5023–5030.



光増感一重項酸素を活用したニトロキシラジカル触媒によるアルコール酸化

(東北大多元研¹・東北大院薬²) ○西嶋 政樹¹・長澤 翔太²・笹野 裕介²・荒木 保幸¹・岩渕 好治²・和田 健彦¹

Photosensitized Singlet Oxygen-supported Alcohol Oxidation Mediated by Nitroxyl Radical Catalyst (¹IMRAM and ²Graduate School of Pharmaceutical Sciences, Tohoku University)

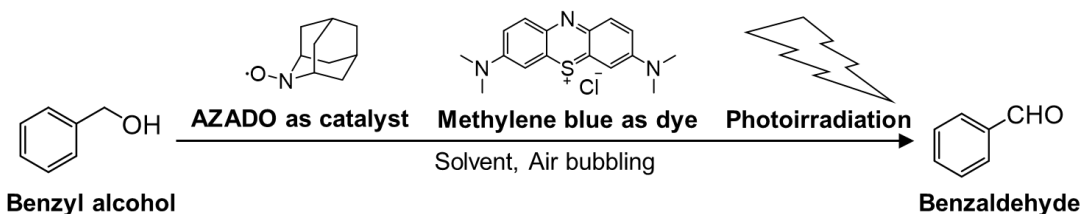
○Masaki Nishijima,¹ Shota Nagasawa,² Yusuke Sasano,² Yasuyuki Araki,¹ Yoshiharu Iwabuchi,² Takehiko Wada¹

An aerobic oxidation of alcohols with organic radical catalysts has attracted much attention. 2-Azaadamantane *N*-oxyl (AZADO) is becoming as an excellent radical catalyst that achieves higher activity than the well-known TEMPO for the alcohol oxidation. However, generally, the addition of transition metal salt or excess amount of unstable oxidant as additive reagent or co-oxidant, respectively, is needed to the system. In contrast, singlet oxygen, which is readily generated by photoirradiation to dye under air condition, can strongly oxidize organic compounds. In this study, we try to utilize the photosensitized singlet oxygen as a co-oxidant to construct a metal-free nitroxyl radical-catalyzed alcohol oxidation. The plausible reaction mechanism and the optimization of this oxidation will also be discussed.

Keywords : Singlet Oxygen; Radical Catalyst; Nitroxyl Radical; Aerobic Alcohol Oxidation; Co-oxidant

有機ラジカル触媒を用いたアルコール酸化は、空気を酸素源に用いることから、持続可能な手法として着目されている。従来の有機ラジカル触媒に TEMPO が知られているが、より優れた触媒開発を目指し、我々はアダマンタン骨格を有する 2-azaadamantane *N*-oxyl (AZADO) の開発により、2 級アルコールのみならず低活性アルコールに対する高効率・高選択的酸化反応の構築に成功した¹⁾。しかしながら本触媒系は重金属塩の添加剤や、化学量論量以上の不安定酸化剤を必要とする。一方、溶液中色素に可視光照射すると、溶存酸素が励起され、一重項酸素 (¹O₂) が発生する。¹O₂ は強力な酸化剤であるが、触媒プロセスへの適応は限られていた。

本研究では、光化学的に発生させた一重項酸素のアルコール酸化触媒系における共酸化剤への適応可能性について検討し、反応副生成物フリーなアルコール酸化を構築した(スキーム)。併せて、反応機構および最適化条件探索結果についても報告する。



Scheme. Photosensitized singlet oxygen-supported alcohol oxidation mediated by radical catalyst.

1) Y. Iwabuchi, *Chem. Pharm. Bull.* **2013**, *61*, 1197.

Academic Program [Oral B] | 17. Biofunctional Chemistry, Biotechnology | Oral B**[E1661-4am] 17. Biofunctional Chemistry, Biotechnology**

Chair: Nobuhiko Hosono, Takashi Matsuo

Sat. Mar 25, 2023 9:00 AM - 11:10 AM E1661 (1611, Bldg. 16 [1F])

[E1661-4am-01] Screening of decoy molecules for propane hydroxylation using intracellular Cytochrome P450BM3[○]Yuki Sugai¹, Masayuki Karasawa¹, Yusaku Kadama¹, Kai Yanemura¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Osami Shoji¹ (1. Graduate School of Science, Nagoya University)

9:00 AM - 9:20 AM

[E1661-4am-02] Dimerization of Artificial Hemoprotein Containing a Tetraphenylporphyrin Derivative Based on Metal Coordination[○]Hiroaki Inaba¹, Yuma Shisaka¹, Garyo Ueda¹, Erika Sakakibara¹, Shinya Ariyasu¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1. Graduate school of Science, Nagoya University, 2. RIKEN SPring-8)

9:20 AM - 9:40 AM

[E1661-4am-03] Whole-Cell Biocatalysts Harboring P450s Triggered by External Additives for Microbial Degradation of Environmental Pollutants[○]Fumiya Ito¹, Shinya Ariyasu¹, Masayuki Karasawa¹, Chie Kasai¹, Yuichiro Aiba¹, Osami Shoji¹ (1. Graduate School of Science, Nagoya University)

9:40 AM - 10:00 AM

[E1661-4am-04] Catalytic Hydroxylation of Non-native Substrates by Cytochrome P450BM3 Mutants with Expanded Structural Availability of Decoy Molecules by Directed Evolution[○]Yuya Yokoyama¹, Shinya Ariyasu¹, Masayuki Karasawa¹, Kai Yonemura¹, Yuichiro Aiba¹, Hiroshi Sugimoto², Osami Shoji¹ (1. School of Science, Nagoya University, 2. RIKEN SPring-8)

10:10 AM - 10:30 AM

[E1661-4am-05] Chemical modification of peptides/proteins using specific affinity of transition metal for alkeneAsuki Okada¹, Tsubasa Kinugawa¹, Shun Hirota¹, [○]Takashi Matsuo¹ (1. Nara Inst. Sci. Tech.)

10:30 AM - 10:50 AM

[E1661-4am-06] Selective Removal of Denatured Proteins by Metal-Organic Frameworks[○]Hiroataka Taketomi¹, Nobuhiko Hosono¹, Takashi Uemura¹ (1. Grad. Sch. of Eng., The Univ. of Tokyo)

10:50 AM - 11:10 AM

菌体内のシトクロム P450BM3 によるプロパン水酸化を促進する デコイ分子のスクリーニング

(名大院理¹) ○須貝 友紀¹・唐澤 昌之¹・児玉 侑朔¹・米村 開¹・有安 真也¹・愛
場 雄一郎¹・荘司 長三¹

Screening of decoy molecules for propane hydroxylation using intracellular Cytochrome
P450BM3 (¹*Graduate School of Science, Nagoya University*) ○Yuki Sugai,¹ Masayuki
Karasawa,¹ Yusaku Kodama,¹ Kai Yonemura,¹ Shinya Ariyasu,¹ Yuichiro Aiba,¹ Osami Shoji¹

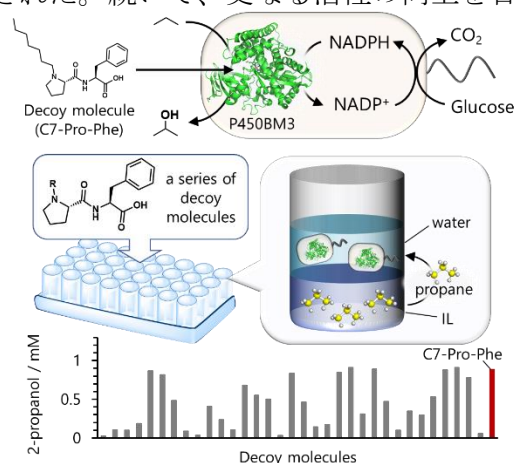
We have demonstrated that amino acid derivatives called decoy molecules facilitate the hydroxylation of non-native substrates by Cytochrome P450BM3 (P450BM3), a heme enzyme which catalyzes hydroxylation of long chain fatty acids. We have also succeeded in hydroxylation of benzene derivatives by P450BM3 overexpressed in *E. coli* in the presence of decoy molecules. This whole-cell catalyst enables the regeneration of NADPH, an expensive cofactor, via bacterial metabolism. In this research, we adapted this whole-cell catalyst to hydroxylation of propane. First, propane hydroxylation reaction in *E. coli* was performed in the presence of the decoy molecule, C7-Pro-Phe, and the formation of 2-propanol was successfully observed. For further improvement of activity, we performed screening of decoy molecules in microplates. Propane dissolved in an ionic liquid (IL) was used for high throughput screening and we discovered the structural features of decoy molecules with high activity in propane hydroxylation in *E. coli*.

Keywords : P450 Enzymes; Biotransformation; Ionic liquid; Screening;

当研究室では、デコイ分子と名付けたアミノ酸誘導体の添加により、長鎖脂肪酸の水酸化を触媒するヘム酵素であるシトクロム P450BM3 (P450BM3) を用いた非天然基質の水酸化を可能にした¹⁾。また、P450BM3 を発現させた大腸菌にデコイ分子を取り込ませ、代謝によって再生される NADPH を用いた菌体内でのベンゼン誘導体の水酸化にも成功している²⁾。本研究では、この菌体内反応を利用したプロパン水酸化に取り組んだ。反応容器内をプロパンで置換して反応を行うと、デコイ分子である C7-Pro-Phe 存在下でプロパノールの生成が観測された。続いて、更なる活性の向上を目指し、デコイ分子のスクリーニングを行った。この際、操作を簡便化するためにプロパンを溶解させたイオン液体を利用し、マイクロプレート中で反応を行った。スクリーニングによって C7-Pro-Phe に匹敵する効果を持つデコイ分子が複数得られており、今後、デコイ分子の構造による反応への影響について詳細に分析していく予定である。

1) K. Yonemura *et al.*, *ACS Catal.*, **2020**, *10*, 9136

2) M. Karasawa *et al.*, *Angew. Chem. Int. Ed.*, **2018**, *57*, 12264



Dimerization of Artificial Hemoprotein Containing a Tetraphenylporphyrin Derivative Based on Metal Coordination

(¹Graduate School of Science, Nagoya University, ²RIKEN SPring-8) ○Hiroaki Inaba,¹ Yuma Shisaka,¹ Garyo Ueda,¹ Erika Sakakibara,¹ Shinya Ariyasu,¹ Yuichiro Aiba,¹ Hiroshi Sugimoto,² Osami Shoji¹

Keywords: Hemoprotein; Porphyrin; Supramolecular chemistry

In the past decade, artificial protein assemblies have been rapidly developed, which is expected to result in the creation of functional materials. Alternatively, in the field of supramolecular chemistry using small molecules, the tetraphenylporphyrin (TPP) skeleton is widely used due to its ease of modification and symmetric structure. Recently, we reported the first example of complexation between a metalloTPP and a protein using heme acquisition system protein A (HasA) secreted by *Pseudomonas aeruginosa* (HasAp).¹ We expect HasA to be a stepping stone that makes TPP-based supramolecular designs available for artificial protein assemblies. In this study, we have attempted to form a HasA dimer using a TPP derivative bearing a metal coordination site, which would be a unit of artificial HasA assemblies.²

We designed Fe-TPP-phen having a phenanthroline which is a well-known bidentate ligand in coordination-driven self-assembly (Fig. b). However, HasAp with Fe-TPP had the stability problem of easily decomposing in neutral buffers,¹ and was not optimal for utilizing metal coordination. As a new scaffold, we focused on HasA derived from *Pseudomonas fluorescens* PF-5 (HasApf5) which has 77 % sequence homology with HasAp. Interestingly, HasApf5 can incorporate Fe-TPP like HasAp (Fig. a) but keep the binding form even in neutral buffers. As expected, UV/Vis spectroscopy and ESI-TOF-MS indicated that HasApf5 successfully incorporated the bulky Fe-TPP-phen like Fe-TPP. We investigated the effects of various metal ions on HasApf5 with Fe-TPP-phen in order to dimerize HasApf5. The results of size-exclusion chromatography (SEC) suggest formation of a HasApf5 dimer in the presence of Ni²⁺ ions (Fig. b, c). Now, we are trying to identify the resulting dimer.

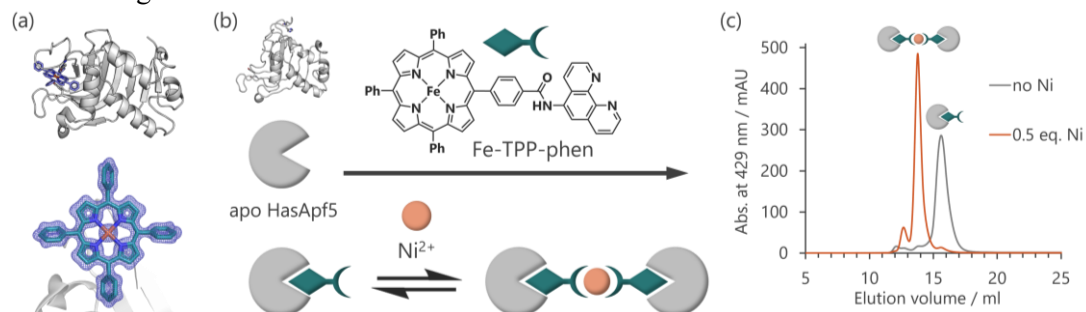


Fig. (a) Crystal structure of Fe-TPP HasApf5 (b) Preparation of Fe-TPP-phen HasApf5 and its dimerization based on metal coordination (c) SEC charts of before and after adding Ni²⁺ ions

1) Y. Shisaka *et al.*, *ChemBioChem* **2022**, 23, e202200095. 2) H. Inaba *et al.*, *manuscript in preparation*.

外部添加剤をトリガーとする P450 発現菌体内物質変換技術の環境汚染浄化への展開

(名大院理) ○伊藤 史哉・有安 真也・唐澤 昌之・笠井 千枝・愛場 雄一郎・荘司 長三

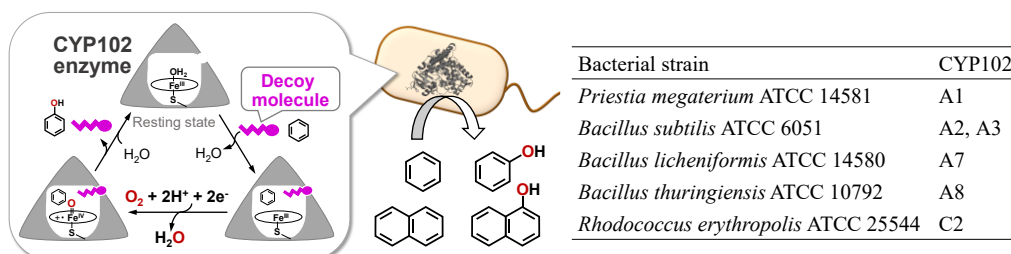
Whole-cell Biocatalysts Harboring P450s Triggered by External Additives for Microbial Degradation of Environmental Pollutants (*Graduate School of Science, Nagoya University*)

○Fumiya Ito, Shinya Ariyasu, Masayuki Karasawa, Chie Kasai, Yuichiro Aiba, Osami Shoji

Decoy molecules, mimics of fatty acids, trigger non-native reactions including benzene hydroxylation catalyzed by P450BM3 isolated from *Priestia megaterium* and its homologs by forming small space on the active sites.¹ By using *E. coli* cells expressing P450BM3, those reactions were also achieved in vivo.² We screened bacterial species which naturally express P450BM3 and its homologs and investigated their catalytic activities towards hydroxylation of benzene in order to apply this methodology to bioremediation, which is the use of microorganisms for degradation of contaminants. Not only *P. megaterium* but also some species including *Bacillus subtilis* functioned as biocatalysts without genetic recombination. We also tried optimization of reaction conditions, enzyme identification, and examination of substrate scope of the non-native reactions. Optimal reaction conditions differed depending on the species, and various substrates known as pollutants were hydroxylated by these systems.

Keywords : P450; Environmental pollutant; Whole-cell biocatalyst; *Bacillus subtilis*; Decoy molecule

Priestia megaterium 由来の長鎖脂肪酸水酸化酵素 P450BM3 (CYP102A1) やその近縁酵素は、脂肪酸を模倣した偽物の基質（デコイ分子）の添加により通常進行しないベンゼン等の小分子水酸化反応を引き起こす¹。酵素内に小さな反応空間を形成することで起こると考えられる本反応は P450BM3 発現大腸菌等を用いた in vivo 反応も達成している²。本研究では本技術を微生物の浄化能を利用するバイオレメディエーションへ展開するため、P450BM3 を含む CYP102 酵素を天然にて発現する種々の細菌でデコイ分子添加をトリガーとした非天然基質水酸化活性を評価した。ベンゼン水酸化活性を指標としたスクリーニングにより *P. megaterium* だけでなく、*Bacillus subtilis* などの細菌が遺伝子組み換えすることなく水酸化反応の微生物触媒として機能した。最適反応条件探索や酵素同定、基質範囲を調査したところ、菌種による最適条件の違いや汚染物質として知られる種々の化合物に対する水酸化活性が得られた。



1) O. Shoji *et al.*, *ACIE* **2013**, 52, 6606-6610. 2) M. Karasawa *et al.*, *ACIE* **2018**, 57, 12264-12269.

Catalytic Hydroxylation of Non-native Substrates by Cytochrome P450BM3 Mutants with Expanded Structural Availability of Decoy Molecules by Directed Evolution

(¹Graduate School of Science, Nagoya University, ²RIKEN, SPring-8) ○Yuya Yokoyama,¹ Shinya Ariyasu,¹ Masayuki Karasawa,¹ Kai Yonemura,¹ Yuichiro Aiba,¹ Hiroshi Sugimoto,² Osami Shoji¹

Keywords: Cytochrome P450; Decoy Molecules; Directed Evolution; *N*-Acyl Homoserine Lactones; Hydroxylation Reaction

Cytochrome P450BM3 (P450BM3) is a heme enzyme that catalyzes the hydroxylation of long-chain fatty acids at their sub-terminal positions. While P450BM3 shows the highest catalytic activity toward its natural substrates, it hardly hydroxylates non-native substrates such as benzene and propane. Our research group has reported the hydroxylation of inactivated C–H bonds of non-native substrates by wild-type (WT) P450BM3 in the presence of chemically synthesized substrate mimics “decoy molecules”.¹ However, the structural diversity of developed decoy molecules remains limited in a few scaffolds such as perfluorinated carboxylic acid, *N*-acyl amino acids, and *N*-substituted dipeptides.^{2,3}

In this study, we employed *N*-acyl homoserine lactones (AHLs) having different structural scaffold from existing decoy molecules to expand their structural diversity. AHLs are produced by some gram-negative bacteria and its permeability through cell membrane is high, which motivated us to use them for decoy molecules. However, AHLs hardly induce hydroxylation reaction of non-native substrates by WT P450BM3. Therefore, we developed P450BM3 mutants efficiently hydroxylating benzene in the presence of C10-AHL, by directed evolution (Figure 1). As the result of fifth-round evolution, the evolved mutant showed significant turnover rate of benzene hydroxylation with C10-AHL. Interestingly, the evolved mutant responds not only C10-AHL but also existing decoy molecules, indicating that the availability of decoy molecules has expanded. Moreover, X-ray crystal structure reveals that the evolved mutant tightly binds C10-AHL with hydrogen bonds between homoserine lactone (HSL) group and the amino acids of the mutant. To improve more catalytic activity of the evolved mutant and application to whole-cell reaction, we attempt to optimize the structure of decoy molecules having HSL substructure.



Figure 1. Concept of this study. Engineered mutants by directed evolution hydroxylates benzene to phenol in the presence of C10-AHL unlike the WT enzyme.

1) N. Kawakami, O. Shoji, Y. Watanabe, *Angew. Chem. Int. Ed.* **2011**, 50, 5315. 2) O. Shoji, *et. al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 5315. 3) K. Yonemura, O. Shoji, *et. al.*, *ACS Catal.* **2020**, 10, 9136.

遷移金属のアルケンに対する親和性を用いたペプチドおよびタンパク質の化学修飾

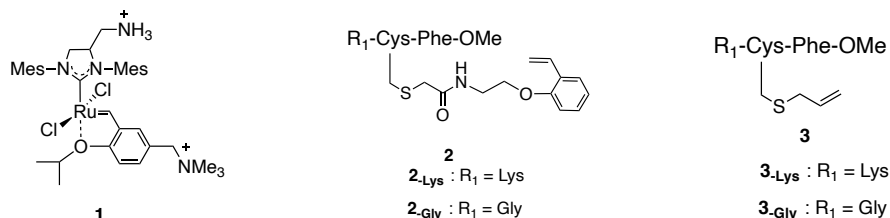
(奈良先端大・物質創成¹⁾ 岡田 明日輝¹、衣川 翼¹、廣田 俊¹、○松尾 貴史¹
 Chemical Modification of Peptides/proteins Using Specific Affinity of Transition Metal for Alkene (¹*Division of Materials Science, Nara Institute of Science and Technology*) Asuki Okada, Tsubasa Kinugawa,¹ Shun Hirota,¹ ○Takashi Matsuo¹

Transition metal-alkene interaction, a driving force of olefin metathesis, is expected as a tool of biomolecule modification because of its high functional group specificity. However, the hydrophobicity of transition metal complexes and reactivity reduction in water should be overcome for the application. Accordingly, we investigated the availability of the transition metal-alkene interaction in aqueous media using cationic Hoveyda-Grubbs-type complex **1** and tripeptide with an olefin moiety **2**, where we observed the ruthenium complex transfer from **1** to **2**. As a result, the reaction proceeded with 60% yield although both reactants are cationic, proving that ruthenium-alkene interaction occurs on the peptide in water. Further, the modification of proteins using the ruthenium complex transfer was found to be possible.

Keywords : Transition Metal, Alkene, Chemical Modification, Hoveyda-Grubbs Complex

オレフィンメタセシスの遷移金属-オレフィン相互作用は、高い官能基選択性を示すことから、多様な官能基を有する生体分子の修飾への応用が期待できる。しかし、多くの遷移金属錯体は疎水性が高く、水系での反応性低下が懸念される。

そこで、ホベイダグラブス型錯体 **1** を用いて、オレフィン部位を側鎖に有するトリペプチド **2** との配位子交換によるルテニウム錯体移動反応を水中で観測し、遷移金属-オレフィン相互作用が水中でも機能するかを検証した。カチオン性である錯体およびトリペプチドの間での電荷反発が想定されたが、錯体移動反応は 60% の反応率で進行し、NHC ルテニウム錯体で修飾されたペプチドが得られた^{1,2)}。また、Cys 残基にオレフィンを導入したアデニル酸キナーゼ三変異体 (A55C/C77S/V16C) 上でも同様の反応を観測でき、遷移金属-オレフィン相互作用に基づく化学修飾はタンパク質にも適用可能であることがわかった。一方、ペプチド同士のセルフメタセシス反応では、ジカチオン性のペプチド **3_{Lys}** では収率 5% 程度、モノカチオン性のペプチド **3_{Gly}** で収率 13% と電荷の影響を受けることが明らかとなり、生体分子同士の連結反応においては、反応点と帯電部位を遠ざけることが重要であることが示唆された。



1) Matsuo, T. et al. *Chem. Lett.* **2020**, *49*, 1490. 2) Matsuo, T. *Catalysts* **2021**, *11*, 359.

MOF を用いた変性タンパク質の選択的除去

(東大院工¹) ○武富 大空¹・細野 暢彦¹・植村 卓史¹

Selective Removal of Denatured Proteins by Metal-Organic Frameworks (¹*Graduate School of Engineering, The University of Tokyo*) ○Hiroataka Taketomi,¹ Nobuhiko Hosono,¹ Takashi Uemura¹

Proteins are denatured with significant loss of their three-dimensional folding structures when they are exposed to external stress (e.g. heat, pH change, chemical denaturant). Once proteins are denatured, they often form insoluble aggregates that prohibit the original function of native proteins, which may cause serious diseases. Therefore, effective method to remove denatured proteins without affecting native ones has been demanded. In this study, we have developed a method for removing denatured protein from a mixture of native (folded)/denatured (unfolded) proteins using metal-organic frameworks (MOFs) as a nanoporous adsorbent. Due to the steric reason, folded proteins cannot enter the MOF nanopores. On the other hand, unfolded proteins can enter the nanopores and strongly adsorbed in the MOF since the thickness of polypeptide chain is smaller than the pore window (**Figure 1**). Investigation of protein types and presence/absence of disulfide bonds in the structure revealed that the MOF only accepts denatured proteins in random coil, single-stranded state.

Keywords : *Metal-Organic Frameworks; Denatured Protein; Adsorptive Separation; Lysozyme*

タンパク質は熱や pH 変化などの外部ストレスにより変性し、本来の三次元的折り畳み構造を失う。変性タンパク質は天然タンパク質の機能を阻害し、重篤な疾患を引き起こすことが知られていることから、効率的な除去技術の開発が求められてきた。本研究では多孔性金属錯体 (MOF) が有するナノサイズの細孔を利用して、天然/変性タンパク質混合溶液から変性体のみを認識し、選択的に MOF 内へ吸着させることで取り除く技術の開発に成功した(**Figure 1**)。天然構造のタンパク質は MOF の細孔窓よりも大きいため立体障害により吸着しない一方で、一本鎖状態に変性したポリペプチド鎖は MOF の細孔窓よりも細いため、MOF 細孔内へ浸入し吸着する。さらにタンパク質の種類、S-S 結合の有無の状態を検討することで、random coil かつ 1 本鎖状態の変性タンパク質のみ MOF 細孔内へと浸入することを見出した。本技術により天然/変性体混合物から天然体の活性を落とさずに変性体のみを取り除くことに成功した。

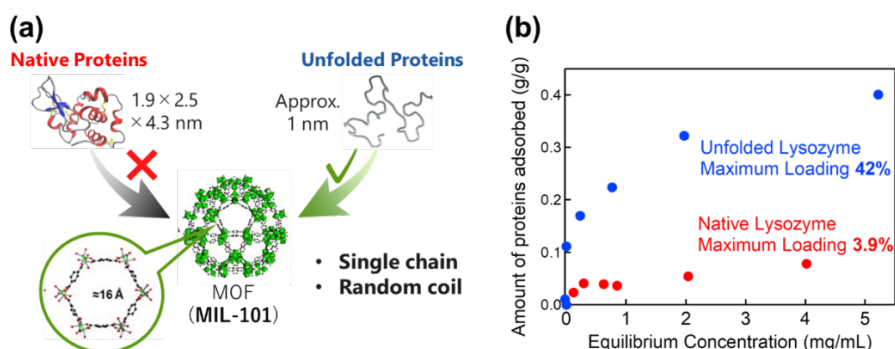


Figure 1. (a) Schematic illustration of the protein adsorption in the MOF. (b) Adsorption isotherms of native and unfolded lysozyme, measured in (Native) Tris-HCl (pH 8.5), (Unfolded) 3M GdmCl/Tris-HCl (pH 8.5).

Academic Program [Oral B] | 19. Colloid and Interface Chemistry | Oral B**[B445-4am] 19. Colloid and Interface Chemistry**

Chair: Hiroyuki Arafune, Takeshi Kawai

Sat. Mar 25, 2023 9:00 AM - 11:10 AM B445 (445, Bldg. 4 [4F])

[B445-4am-01] Odd-even effect in two-dimensional self-assembly of curcumin derivatives at the solid/liquid interface○Suyi Liu^{1,2}, Yoshihiro Kikkawa², Yasuo Norikane^{1,2} (1. University of Tsukuba, 2. National Institute of Advanced Industrial Science and Technology (AIST))

9:00 AM - 9:20 AM

[B445-4am-02] Structural model of a large spherical colloidal cluster with icosahedral symmetry○Ryosuke Ohnuki¹, Yukikazu Takeoka², Shinya Yoshioka¹ (1. Tokyo University of Science, 2. Nagoya University)

9:20 AM - 9:40 AM

[B445-4am-03] Fabrication of perovskite/carbonaceous nanocomposite and its evaluation toward electrochemical detection of amino acids○Jeevika Alagan¹, Ryosuke Yambe¹, Yuna Kim¹, Ken-ichi Iimura¹ (1. Utsunomiya University)

9:40 AM - 10:00 AM

[B445-4am-04] Catalytic Reduction of Methylene Blue by Gallium-Based Liquid Metals○Nichayanan Manyuan¹, Hideya Kawasaki¹ (1. Kansai University)

10:10 AM - 10:30 AM

[B445-4am-05] New cleaning mechanism by dynamic wetting using nonionic surfactant oil solution○Yuko Nagasaki¹, Mariko Kagaya¹, Chihiro Ueyama¹, Hitoshi Tajima¹ (1. Kao corporation)

10:30 AM - 10:50 AM

[B445-4am-06] Characterization of friction-induced molecular orientation change in fluoropolymer thin film using MAIRS○Motohiro Kasuya¹, Touma Nagata¹, Miyuki Matsushita¹, Nobutaka Shioya², Takahfumi Shimoaka², Akihito Hibara³, Takeshi Hasegawa² (1. Komatsu University, 2. Kyoto University, 3. Tohoku University)

10:50 AM - 11:10 AM

Odd-even Effect in Two-Dimensional Self-Assembly of Curcumin Derivatives at the Solid/Liquid Interface

(¹Graduate School of Science and Technology, University of Tsukuba, ²National Institute of Advanced Industrial Science and Technology (AIST)) ○Suyi Liu^{1,2}, Yoshihiro Kikkawa², Yasuo Norikane^{2,1}

Keywords: Self-assembly; Scanning tunneling microscopy; Solid/liquid interface; Curcumin; Odd-even effect

Self-assembly on surfaces has been an effective strategy to fabricate functional nanomaterials.¹ Various two-dimensional (2D) structures could be constructed via non-covalent interactions such as hydrogen bonding, metal coordination, and dispersion force. Scanning tunneling microscopy (STM) is a powerful tool for the direct visualization of 2D structures at atomic scale.² Odd-even effect, afforded by the number of alkyl units, has periodic influences on chemical and physical properties,³ and controlling the 2D structures by this effect is attractive. Although curcumin has been widely studied in biomedical fields⁴, its self-assembly behaviors on surfaces are unclear. In this contribution, we report the 2D structures of curcumin derivatives with different alkoxy substitutions, and discuss the factors affecting the emergence of odd-even effect.

Curcumin derivatives with alkoxy groups (various chain lengths) at different positions were prepared (**BC**, **CR**, **TC**, Figure 1a), and their 2D structures before and after Cu(II) coordination were revealed by STM at the solid/liquid interface. **BC** compounds before and after the metal coordination individually showed periodic change in 2D structures, indicating the existence of odd-even effect (Figure 1b). However, in curcumin derivatives with methoxy groups (**CR**) or longer alkoxy chains (**TC**), 2D structures almost unchanged by the alkyl chain length, suggesting the disappearance of odd-even effect. These results indicate that tuning the appearance of odd-even effect is available by modulating the alkoxy substitutions. This work will contribute to develop the controlling method of 2D molecular patterns on surfaces.

1) J.V. Barth, G. Costantini, K. Kern, *Nature*, **2005**, 437, 671. 2) S. De Feyter, F. C. De Schryver, *J. Phys. Chem. B*, **2005**, 109, 4290. 3) F. Tao, S. L. Bernasek, *Chem. Rev.*, **2007**, 107, 1408. 4) M. Zhu, J. Liu, L. Gan, M. Long, *Eur. Polym. J.*, **2020**, 129, 109651.

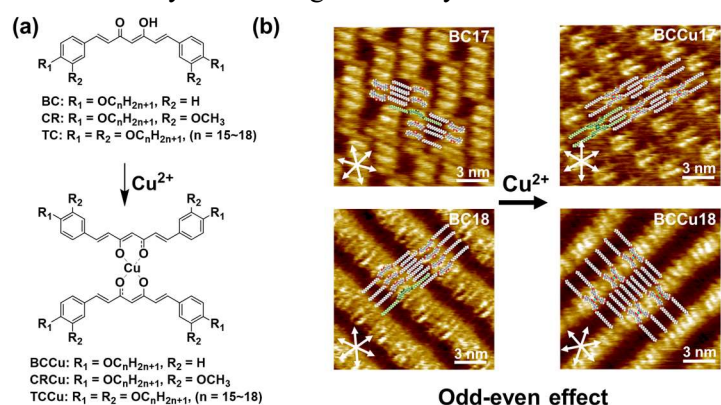


Figure 1 (a) Chemical structures of curcumin derivatives before and after Cu(II) coordination, (b) Representative STM images of **BC** compounds ($n = 17, 18$) and their complexes at the highly oriented pyrolytic graphite/1,2,4-trichlorobenzene interface.

Structural model of a large spherical colloidal cluster with icosahedral symmetry

(¹Graduate School of Science and Technology, Tokyo University of Science, ²Graduate School of Engineering, Nagoya University) ○ Ryosuke Ohnuki¹, Yukikazu Takeoka², Shinya Yoshioka¹

Keywords: Cluster; Icosahedral Symmetry; Colloidal Crystal; Structural Color; Self-assembly;

Colloidal clusters with a spherical shape can be easily produced from water-in-oil-type emulsions by evaporating water. Because the clusters produce brilliant structural colors, colloidal clusters have been widely applied in optical materials, such as colorimetric sensors and pigments. It was recently discovered that spherical colloidal clusters have particle arrangements with icosahedral symmetry

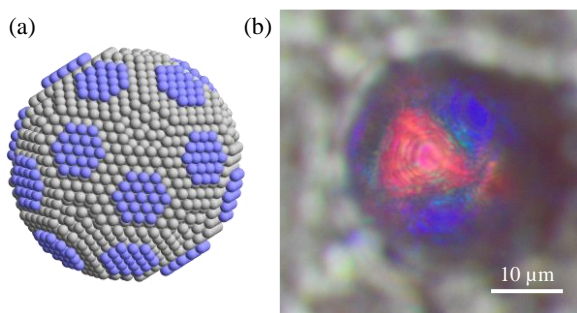


Figure. (a) structural model and (b) optical micrograph of a spherical colloidal cluster with icosahedral symmetry.

(Figure (a)) when the shrinkage speed of the droplet during evaporation is slow and the number of constituent particles of the cluster is less than 10,000^{1,2}. Optical investigations of clusters with icosahedral symmetry have only been performed using microscopy, and unique triangular reflections have been reported¹. However, among the clusters we prepared, we found a very large cluster with icosahedral symmetry and nearly 500,000 particles. Because of this large size, it exhibits a more distinct triangular reflection than a previous study¹ (Figure (b)), allowing us to perform detailed optical characterizations.

In this study, we performed a more detailed optical investigation of a large icosahedral colloidal cluster. The peak position of the reflectance spectra was consistent with the wavelength calculated from the structural model of clusters with icosahedral symmetry³. Measurements of the reflectance spectra of various small regions within the triangle showed a tendency for the peak wavelength to be longer at the center of the triangle. This fact cannot be explained by the structural model assumed in previous studies. Thus, we propose a modified structural model that is consistent with the experimental results⁴. Although this modified model is still in the hypothesis stage, it is expected to be a clue to understand the formation process of clusters.

1) J. Wang *et al.*, *Adv. Funct. Mater.*, **2020**, 30, 1907730.

2) J. Wang *et al.*, *Nat. Commun.*, **2018**, 9, 5259.

3) R. Ohnuki *et al.*, *Part. Part. Syst. Charact.*, **2022**, 39, 2100257.

4) R. Ohnuki *et al.*, *Materials Science Forum*, in press.

Fabrication of perovskite/carbonaceous nanocomposite and its evaluation toward electrochemical detection of amino acids

(¹Center for Innovation Support, Institute for Social Innovation and Cooperation, Utsunomiya University, ²Faculty of Engineering, Utsunomiya University) ○Alagan Jeevika,¹ Ryosuke Yambe,² Yuna Kim,² Ken-ichi Iimura²

Keywords: Perovskite; Amino acids; Electrochemical sensor; Bimetal-based nanocomposite; Co-precipitation method

Tryptophan (Trp) is one of the eight fundamental amino acids, it is useful for human's everyday action, and hence the detection of Trp levels in the food samples is necessary [1]. In this study, a $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ perovskite was synthesized and used for decoration of F-Multi walled carbon nanotube ($\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}$) electrocatalyst which was utilized as an electrochemical sensor for determination of Trp. $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ and $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}$ nanocomposite were prepared by co-precipitation and ultrasonication methods, respectively. The products were confirmed by various analytical techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometry (XRD), and Field emission scanning electron microscopy (FE-SEM). FT-IR results show that polar functional groups are successfully introduced onto the surface of the MWCNT, aided by binding the surface of the $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. FE-SEM results show flake-like $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ particles with the highly uniform arrangement. XRD results confirmed that produced $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ are highly crystalline in a monoclinic system with a space group $\text{P}2_1/\text{c}$ [2]. The electrochemical performance of Trp was investigated by cyclic voltammetry (CV) using bare platinum electrode (PE), F-MWCNT/PE, $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{PE}$ and $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}/\text{PE}$ in a 100 μM Trp solution containing 0.1 M phosphate buffer (pH 6.0) at 50 mV s^{-1} under N_2 atmosphere. The $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}/\text{PE}$ exhibited the highest irreversible oxidation peak potential at +0.81 V, compared to other electrodes. CV response of pH displays the oxidation peak current increases in the existence of Trp from pH 3.0 to 11.0, and the maximum peak current was observed at pH 6.0, signifying that the electrochemical activity of Trp was pH-dependent. As increase the scan rate, the observed anodic peak shifted toward more positive potential due to the formation of a complex between Trp and $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}$. These results suggest that $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}$ may be employed as robust electrochemical sensors toward Trp in food samples in the future.

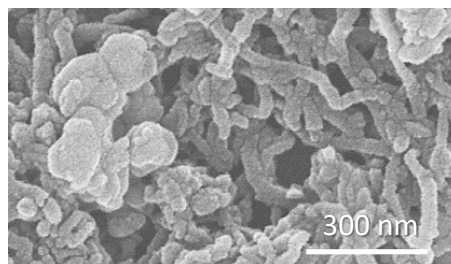


Fig.1 A SEM image of $\text{Sr}_7\text{Mn}_4\text{O}_{15}/\text{F-MWCNT}$ nanocomposite.

Acknowledgment: This work is supported by 3C fund of Utsunomiya University.

[1] E. Murugan, K Kumar, *Anal. Chem.* **2019**, 91, 5667. [2] J. F. Vente, *Phys. Rev. B.* **2001**, 64, 214403.

Catalytic Reduction of Methylene Blue by Gallium-Based Liquid Metals

(Graduate School of Science and Engineering, Kansai University) ○Nichayanan Manyuan, Hideya Kawasaki

Keywords: Gallium-based liquid metals; Methylene blue reduction; Pt loading

Liquid metals (LMs) such as Ga and Ga-based liquid metal alloys have received significant attention because of their unique properties that combine fluidic and metallic properties at room temperature. More recently, LMs have been considered a new class of composite materials for catalytic applications, such as converting methane to pure hydrogen and CO₂ decomposition [1]. Platinum (Pt) loading in LMs is expected to enhance catalytic performance in various reaction systems. Nonetheless, the Pt loading methods into Ga-based LMs have not yet been apparent to improve the catalytic performance and the Pt utilization efficiency in the Pt-LMs. This study utilized two Pt loading methods : (i) Pt deposition by sputtering deposition (EGaIn/Pt deposition) and (ii) Pt black by simple mixing (EGaIn/Pt blacks). We investigated their catalytic activities based on a model reaction: methylene blue (MB) reduction via the realtime-monitoring by UV-vis spectroscopy.

Fig. 1 shows MB reduction in an acidic aqueous solution (0.1M HCl) in the presence of EGaIn and EGaIn/Pt. We observed no MB reduction in EGaIn (no Pt) presence, but Pt loading (~0.7 wt%) in LMs significantly enhanced the MB reduction rate. Compared to EGaIn/Pt blacks, the EGaIn/Pt deposition showed a higher MB reduction rate of 0.0075 min⁻¹. The TEM images showed Pt layers obtained by the sputtering deposition on LM surfaces, consisting of tiny Pt nanoparticles (NPs)-assembly with sizes of a few nm (for TEM grids). The SEM images demonstrated well-dispersed Pt NPs in EGaIn/Pt deposition, in contrast to the significant aggregation of Pt NPs in EGaIn/Pt black. The catalytic active Pt NPs on the LM surface were found to be richer in EGaIn/Pt deposition than in EGaIn/Pt black, as suggested by the higher H₂ production rate. In addition, we found Ga–Pt alloying in EGaIn/Pt deposition using XPS analysis, and Ga–Pt alloy is a highly efficient catalyst [2]. The Pt liquid metal catalyst prepared by Pt sputtering deposition guarantees the high dispersion of Pt NPs, the active Pt sites, and Ga–Pt alloying, which explains the high catalytic activity in Pt/EGaIn catalysts.

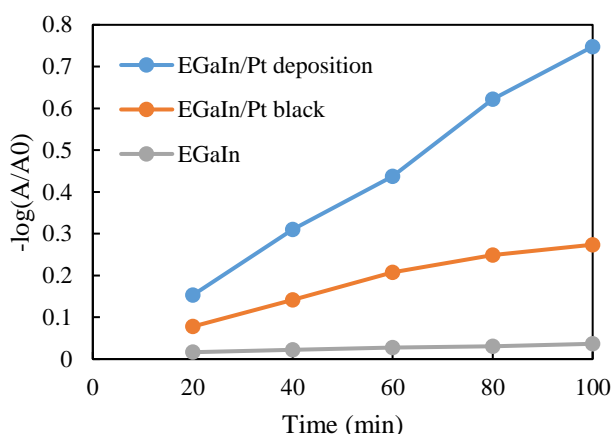


Fig. 1 MB reduction in the presence of EGaIn or EGaIn/Pt

- 1) Sun et al., Recent Progress of Ga-based Liquid Metals in Catalysis, *RSC Adv.*, 2022, 12, 24946.
- 2) Zhang et al., Subsurface-Regulated PtGa Nanoparticles Confined in Silicalite-1 for Propane Dehydrogenation, *ACS Appl. Mater. Interfaces*, 2021, 13, 16259.

非イオン性界面活性剤油溶液を用いた動的な濡れによる新たな洗浄機構

(花王株式会社) ○長崎 裕子・加賀谷 真理子・上山 千紘・田島 準

New cleansing mechanism by dynamic wetting using nonionic surfactant oil solution (*Kao Corporation*) ○Yuko Nagasaki, Mariko Kagaya, Chihiro Ueyama, Hitoshi Tajima

Makeup is a mixture of hydrophobic powder and oil, etc., and is known as a stain that is difficult to remove. Therefore, an oil agent may be used as a cleansing base. In the cleansing process, after applying the cleansing agent to the makeup, it is necessary to disperse and mix the makeup adhering to the skin with a cleansing agent by physical force, as in other cleansing. After that, that mixture is emulsified and dispersed in rinse water to remove it. This time, we found a new cleansing mechanism that can remove makeup without this physical force by using the nonionic surfactant alkyl ethoxylate ($C_{12}EO_3$) oil solution.

As a result of observing the cleansing process using a solid substrate, it was found that water entered between the solid substrate and the oil (cleansing agent + makeup), and the makeup was removed. It is presumed that the solid-oil interface was hydrophilized from the three-phase contact point of oil/water/solid, and at the same time as the adhesion between the makeup and the solid substrate decreased, wetting by water occurred. It is considered to be a new mechanism that removes stain by weakening the adhesion between the stain and the substrate by the action of surfactants on the substrate, unlike the conventional one in which the surfactant acts directly on the stain.

Keywords : nonionic surfactant; dynamic wetting; oil stains; cleansing mechanism; oil solution

メイクは疎水性粉体と油等の混合物であり、落としにくい汚れとして知られている。そのため、洗浄力の高い油剤を洗浄基剤として用いることがある。その洗浄過程においては、洗浄剤をメイクに塗布後、肌に付着したメイクを洗浄剤に分散・混合させるために、他の洗浄と同様、物理力を加えることが必要である。その後、この混合物をすすぎ水に乳化・分散させることで除去される。今回、非イオン性界面活性剤アルキルエトキシレート ($C_{12}EO_3$) の油溶液を用いることで、物理力を加えることなくメイクを除去できる新たな洗浄機構を見出した。

固体基板を用いて洗浄過程を観察した結果、すすぎ時に固体基板と油（洗浄剤＋メイク）の間に水が入り込み、メイクが除去されることが分かった。油／水／固体の三相接触点から固油界面が親水化され、固体基板とメイクの付着力の低下と同時に、水による濡れが発現したと推察される。この機構は、界面活性剤の働き方という点で非常に興味深い。つまり、界面活性剤を汚れに直接作用させる従来とは異なり、基板に作用して汚れとの付着力を弱めることで汚れを落とす、新たな機構と考えられる。

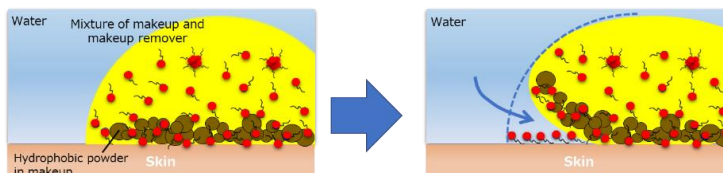


Fig.1 Image of a new cleansing mechanism that removes stain by wetting the substrate with water by surfactants.

フッ素樹脂薄膜における摩擦誘起分子配向変化の MAIRS 法による定量的解析

(小松大生産システム¹・京大化研²・東北大多元研³) ○粕谷 素洋¹・長田 透真¹・
松下 美幸¹・塩谷 暢貴²・下赤 卓史²・火原 彰秀³・長谷川 健²

Characterization of friction-induced molecular orientation change in fluoropolymer thin film using MAIRS (¹*Faculty of Production Systems Engineering and Sciences, Komatsu University*, ²*ICR, Kyoto University*, ³*IMRAM, Tohoku University*) ○Motohiro Kasuya¹, Touma Nagata¹, Miyuki Matsushita¹, Nobutaka Shioya², Takahfumi Shimoaka², Akihide Hibara³, Takeshi Hasegawa²

Fluoropolymers are used as low-friction materials in the sliding parts of many machines. Reducing wear of the fluoropolymer is important for their application. In this study, we observe the friction-induced change in molecular orientation of fluoropolymer thin films using multiple-angle incidence-resolved infrared spectroscopy, which enables quantitative evaluation of the orientation of each substituent group of the polymer molecules. Based on the obtained spectrum, the molecular mechanism of friction and wear can be elucidated.

Keywords : *fluoropolymer, multiple-Angle Incidence Resolution Spectrometry¹⁾, infrared spectroscopy, friction, wear, stratified dipole-array theory (SDA theory)²⁾*

フッ素樹脂は優れた自己潤滑性を示すため、固体潤滑剤として自動車エンジンや空調調機圧縮機の摺動部等の多様な機械に用いられる一方、耐摩耗が課題である。しかしながら、材料特性の改善に重要なフッ素樹脂の摩擦・摩耗時における高分子鎖の挙動は分子レベルでは十分に理解されていない。本研究では分子の各置換基の配向が定量的に評価可能な多角入射分解赤外分光(MAIRS 法)¹⁾を用いて、フッ素樹脂薄膜における摩擦に伴う分子配向変化を調べた結果を報告する。

シリコンウェハにスピコート法により成膜したポリ(フルオロアルキルアクリレート)薄膜をもう一枚のシリコン基板と接触・せん断させ、前後でのIR-MAIRS スペクトル変化を比較した結果を右図に示す。1300 cm⁻¹周辺のCF₂伸縮振動に由来するピークには面内/面外の比率に変化がないのに対して、1200 cm⁻¹周辺のフォノンバンドには大きな変化が観測された。これはパーフルオロアルキル鎖の配向は変化せず、集合構造は変化することを示している。当日は有機フッ素化合物の特性を決める SDA 理論²⁾で重要なフッ化アルキル基の長さの影響についても報告予定である。

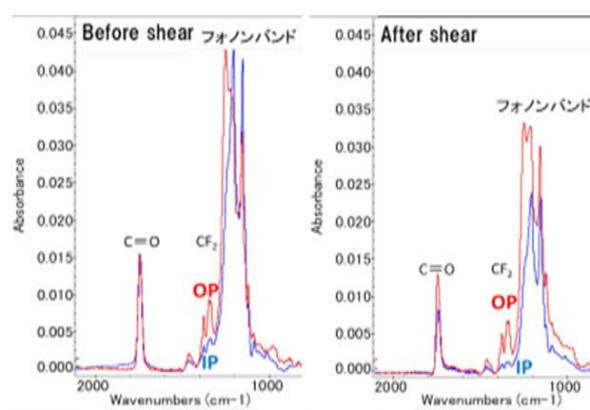


図 フッ素樹脂薄膜の摩擦に伴う面内および面外の赤外スペクトル変化

1) T. Hasegawa, MAIRS: Innovation of Molecular Orientation Analysis in a Thin Film *Bull. Chem. Soc. Jpn.* **2020**, 93, 1127–1138. 2) T. Hasegawa, Physicochemical Nature of Perfluoroalkyl Compounds Induced by Fluorine *Chem. Rec.* **2017**, 10, 903.

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

[K206-4am] 20. Materials Chemistry -Basic and Application-

Chair: Kazuki Sada, Koki Sano

Sat. Mar 25, 2023 9:00 AM - 10:20 AM K206 (K206, Lecture Hall Bldg. [2F])

[K206-4am-01] Diarylethene crystal showing unusual mechanofluorochromism

○Ryo Nishimura¹, Yuka Kobayashi¹, Masakazu Morimoto¹ (1. Rikkyo University)

9:00 AM - 9:20 AM

[K206-4am-02] Self-assembling and stimuli-responsive behaviors of donor-acceptor type fluorenone derivatives

○Atsushi Seki^{1,2}, Mao Suzuki², Shota Yamada¹, Soun Doi¹, Ken'ichi Aoki^{1,2} (1. Tokyo Univ. of Science, 2. Grad. School of Science, Tokyo Univ. of Science)

9:20 AM - 9:40 AM

[K206-4am-03] Evaluation of Atomic Oxygen Resistance of POSS film

○Kazuki Yukumatsu¹, Aki Goto¹, Soichi Yokoyama², Yutaka Ie², Yugo Kimoto¹ (1. Japan Aerospace Exploration Agency, 2. Osaka University)

9:40 AM - 10:00 AM

[K206-4am-04] Ambient-condition methane storage in carbon nanopores with with temperature-triggered locking/unlocking

○Shuwen Wang¹, Katsumi Kaneko¹ (1. Research Initiative for Supra-Materials, Shinshu University)

10:00 AM - 10:20 AM

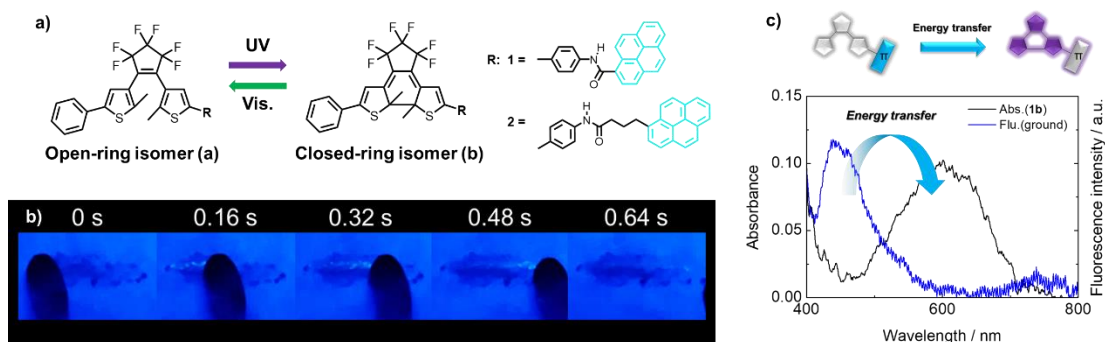
新奇なメカノフルオロクロミズムを示すジアリールエテン結晶

(立教大理¹) ○西村 涼¹・小林 優加¹・森本 正和¹

Diarylethene crystal showing unusual mechanofluorochromism (¹ Department of Chemistry, Rikkyo University)○Ryo Nishimura¹ Yuka Kobayashi,¹ Masakazu Morimoto¹

Mechanofluorochromism, which is caused by mechanical force to the crystalline fluorescence materials, is one of the candidates for stress sensing materials. Here, we report the dynamic stress sensing luminescent solid material of photochromic diarylethene, which emitted cyan-colored transient emission when the stress was applying to the crystals. This mechanical induced luminescent phenomenon was reversibly repeated by combination of light irradiation (UV and visible light) and the other external stimuli (organic solvent vapor and/or heat). By the spectroscopic analysis, this mechanofluorochromism originated from the excimer emission from the pyrene moiety caused by the crystal-to-amorphous phase transition by grinding the crystal.

Keywords : Photochromism; Diarylethene; Mechanofluorochromism; Organic crystal



メカノフルオロクロミズムは機械的刺激により発光色が変化する現象であり、応力を検知するセンサー材料としての応用が期待されている¹⁾。一方、応力発光は、機械的刺激が加わった瞬間だけ発光し、すぐに消光する現象であり、こちらは、リアルタイムでの応力センシングが可能である²⁾。本発表では、完全に有機物のみからなるフォトクロミック分子であるジアリールエテン誘導体の結晶に対して、機械的刺激を加えて結晶を崩壊させると、その瞬間のみ発光する現象を見出したので報告する。

合成したジアリールエテン誘導体 **1a** は溶液中、単結晶中で可逆的なフォトクロミズムを示した。**1a** の単結晶を紫外光 ($\lambda = 313 \text{ nm}$) 照射下でスパチュラで擦ると、擦った瞬間のみ水色に発光し、1秒以内に消光した。種々の測定により、この現象は応力発光ではなく、ピレン部位からのエキシマー発光に由来するメカノフルオロクロミズムであり、その発光が励起光によって生成した **1b** へのエネルギー移動によって消光していることが明らかとなった。また、溶媒蒸気暴露による再生、発光時間の励起波長依存性についても検討した。

1) M. Ikeya, G. Katada, S. Ito, *Chem. Commun.* **2019**, 55, 12296–12299.

2) Y. Hirai, T. Nakanishi, Y. Kitagawa, K. Fushimi, T. Seki, H. Ito, Y. Hasegawa, *Angew. Chem. Int. Ed.* **2017**, 56, 7171–7175.

ドナー・アクセプター連結型フルオレノン誘導体の自己組織化挙動と刺激応答性

(東理大理二¹・東理大院理²) ○関 淳志^{1,2}・鈴木 真緒²・山田 翔太¹・土井 早雲¹・青木 健一^{1,2}

Self-assembling and stimuli-responsive behaviors of donor-acceptor type fluorenone derivatives (¹*Faculty of Science Division II, Tokyo University of Science*, ²*Graduate School of Science, Tokyo University of Science*) ○Atsushi Seki,^{1,2} Mao Suzuki,² Shota Yamada,¹ Soun Doi,¹ Ken'ichi Aoki^{1,2}

Electron donor-acceptor (D-A) type dye molecules exhibit intramolecular charge transfer (ICT), which leads to characteristic absorption and emission bands in the visible light region. As the ICT transitions are sensitive to the environment around the molecules, D-A type dyes exhibit stimuli-responsive color change in solution state. In this study, we studied the self-assembling and stimuli-responsive behaviors of several D-A type fluorenone derivatives. Several fluorenone-based D-A-D triads exhibited liquid-crystalline properties. In addition, the fluorenone derivatives bearing hydrogen-bonding urethane units formed supramolecular gels in appropriate solvents. These compounds showed characteristic absorption and emission behaviors derived from ICT transition. Stimuli-responsive behaviors in solution states as well as bulk states were evaluated. We found that aggregation behaviors and fluorescent properties in the bulk state of some fluorenone derivatives were changed in response to the chemical stimuli.

Keywords : *Intramolecular Charge Transfer; Stimuli-Responsive Materials; Supramolecular Gels; Liquid Crystals*

電子ドナー-アクセプター (D-A) 連結型色素は、分子内電荷移動 (ICT) を生じ、可視光領域に特徴的な吸収帯・発光帯があらわれる。この ICT 遷移は、色素分子の周囲環境に敏感であり、溶液状態において、外部刺激に応答した色調変化をもたらす。本研究では、数種類の D-A 連結型フルオレノン誘導体 (Figure 1) を合成し、各化合物の自己組織化挙動、および、刺激応答性について検討した。

フルオレノン誘導体 **FL-1**, **FL-2**, **FL-3** は、いずれも液晶性を示し、スメクチック相を発現した。また、水素結合性ウレタンユニットを有する **FL-1**, **FL-2** は、適当な溶媒中で超分子ゲルを形成した。これらの化合物は、ICT 遷移に由来する特徴的な吸収・発光挙動を示した。溶液状態およびバルク状態での外部刺激応答性を評価したところ、**FL-1**, **FL-2** は、ゲル状態で化学的刺激に応答し、凝集挙動や蛍光特性に変化が認められた。詳細については、当日、報告する。

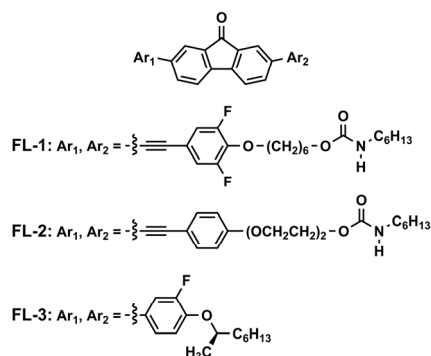


Figure 1. Chemical structures of D-A type fluorenone derivatives **FL-1**, **FL-2** and **FL-3**.

シルセスキオキサン薄膜の耐原子状酸素特性評価

(宇宙航空研究開発機構¹・阪大産研²) ○行松 和輝¹・後藤 亜希¹・横山 創一²・
家 裕隆²・木本 雄吾¹

Evaluation of Atomic Oxygen Resistance of POSS film

(¹Japan Aerospace Exploration Agency, ²SANKEN, Osaka University) ○Kazuki Yukumatsu,¹
Aki Goto,¹ Soichi Yokoyama,² Yutaka Ie,² Yugo Kimoto¹

Atomic oxygen (AO), which exists at low Earth orbit, erodes polymeric materials used on the external surface of spacecraft. Silsesquioxane (POSS), an organic-inorganic hybrid molecule, is known as one of the candidates for AO resistant materials. POSS molecules modified with fluoroalkyl groups might have higher AO resistance because fluoropolymers tend not to be eroded by AO. However, the AO resistance of fluoroalkyl-POSS has not been understood yet.

This study aimed to clarify the effects of modifying with fluoroalkyl groups for POSS on AO resistance. The fluoroalkyl-POSS ($R = -(\text{CH}_2)_2\text{CF}_3$ or $-(\text{CH}_2)_2(\text{CF}_2)_3\text{CF}_3$) and the alkyl-POSS ($R = -(\text{CH}_2)_7\text{CH}_3$) were synthesized and deposited thinly on Si substrates. The changes of mass losses and the silica layer thicknesses were investigated after AO irradiation (3×10^{19} - 1.5×10^{20} atoms/cm², Kobe Univ.). The mass losses and the silica thicknesses of the fluoroalkyl-POSS were larger than those of the alkyl-POSS. These results will be discussed based on the spatial configurations of the POSS inorganic frames, obtained by X-ray diffraction.

Keywords : Atomic Oxygen; Polyhedral Oligomeric Silsesquioxane

地球周回低軌道に存在する原子状酸素 (AO) は、宇宙機と約 8 km/s の速度で衝突することで、宇宙機最外層に用いられる高分子材料を浸食する。有機無機ハイブリッド分子であるシルセスキオキサン (POSS、 $\text{RSiO}_{1.5}$) は、耐 AO 性材料の候補として知られている。AO に対して浸食を受けにくいフルオロアルキル構造を官能基として導入することで、より高い耐 AO 性の POSS 材料となる可能性がある。しかしフルオロアルキル POSS の耐 AO 性は明らかになっていなかった。

本研究では、フルオロアルキル構造の POSS への導入が、AO との相互作用に与える影響の理解を目的とした。フルオロアルキル基 ($R = -(\text{CH}_2)_2\text{CF}_3$ または $-(\text{CH}_2)_2(\text{CF}_2)_3\text{CF}_3$) とアルキル基 ($R = -(\text{CH}_2)_7\text{CH}_3$) をそれぞれ修飾した POSS を合成し (Fig.1)、Si 基板に成膜した上で、AO 照射に伴う質量損失と、反応で生じる酸化層の形成厚さを調べた。AO を照射した結果 (3×10^{19} - 1.5×10^{20} atoms/cm²、神戸大学装置)、フルオロアルキル POSS がアルキル POSS に比べて、質量損失が大きく、酸化層が厚く形成された。その要因について、合成した POSS の空間配置を X 線回折で評価した結果を基に議論する。

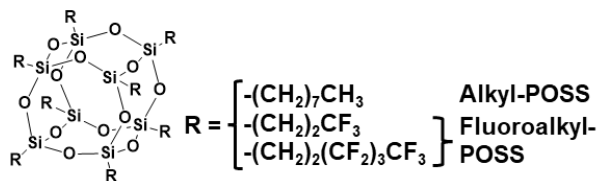


Figure 1. The chemical structures of modified POSS

謝辞：本研究は JSPS 科研費 (JP21K04494) の助成を受けたものである。

Ambient-condition storage of highly pressurized methane in carbon nanopores with graphene-mediated locking/unlocking

○ Shuwen Wang¹, Fernando Vallejos-Burgos², Ayumi Furuse¹, Juan P. Marco-Lozar³, Miu Nagae¹, Hideki Tanaka¹, Hirofumi Kanoh⁴, Joaquín Silvestre-Albero⁵, Takuya Hayashi⁶, Katsumi Kaneko¹ (1. Research Initiative for Supra-Materials, Shinshu University. 2. Morgan Advanced Materials, State College, USA. 3. G2MTech, Alicante, Spain. 4. Graduate School of Science, Chiba University. 5. Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, Spain. 6. Department of Water Environment and Civil Engineering, Shinshu University)

The world is facing an urgent issue on global warming due to its serious influences on the weather pattern and ecosystems. Natural gas is considered to have a significant role in smoothing the transition from fossil fuels to renewable sources. This is because the adsorbed natural gas (ANG) can offer a safer and potentially more cost-effective method for storing methane. Department of Energy of U.S. gave the target performance of methane adsorption amount at 3.5 MPa for application. However, the methane of 3.5 MPa employed in ANG is still classified as a compressed gas, which requires storage vessel with a high-pressure rating and special safety precautions for operation. In addition, the physisorption of methane exhibits a strong dependence on temperature. Consequently, we need a new type of nanoporous materials which can store compressed methane stably at ambient conditions for utilization of the ANG.

In current study, an entrance-wrapped pore structure with temperature triggered locking/unlocking is prepared for ambient-condition methane storage. The graphene wrapping can be installed on the entrance of carbon pore by graphene planting through a CVD method. The entrance-wrapped pores which are inaccessible to methane molecules under ambient condition becomes accessible by heating about 473 K due to the enhanced vibrational motion of graphene. Methane can be encapsulated in the entrance-wrapped carbon pores at 473 K and stored ambiently irrespective of the temperature fluctuation. The low heating temperature required for triggering the unlocking of entrance-wrapped pores can be achieved by using the low-quality waste heat from industry or vehicles. This novel ambient pressure storage method for pressurized methane can deliver the largest amount of methane compared to any other adsorbent at 3.5 MPa and 298 K. Special safety precautions for compressed gases are not necessary for methane stored at ambient conditions, enabling its convenient operation. The container for methane storage can be designed into a flexible shape rather than cylindrical or spherical to achieve the maximum space utilization.

Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application- | Oral B**[K206-4pm] 20. Materials Chemistry -Basic and Application-**

Chair: Ken'ichi Aoki, Masakazu Morimoto

Sat. Mar 25, 2023 1:00 PM - 2:40 PM K206 (K206, Lecture Hall Bldg. [2F])

[K206-4pm-01] Temperature and solvent dependence of polybenzimidazole adsorption on carbon materials

○Islam A B M Nazmul¹, Nana Kayo¹, Mai Akamine¹, Naoki Tanaka^{1,2}, Tsuyohiko Fujigaya^{1,2,3} (1. Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 2. WPI-I2CNER, Kyushu University, 3. Centre for Molecular System, Kyushu University)

1:00 PM - 1:20 PM

[K206-4pm-02] Sol-gel reaction of linear oligosiloxanes and their derivation to silicates

○Yohei Sato¹, Asahi Sugimoto¹, Ryohei Hayami¹, Kazuki Yamamoto¹, Takahiro Gunji¹ (1. Tokyo University of Science)

1:20 PM - 1:40 PM

[K206-4pm-03] Hybridization of cellulose and hydroxyapatite applicable to tough biomass materials

○Kohei Okuda¹, Tadashi Mizutani¹ (1. Doshisha university graduate school)

1:40 PM - 2:00 PM

[K206-4pm-04] Preparation and physical properties of hydrogels based on coordination between DNA and various metal ions

○Arisa Fukatsu¹, Sari Kurisu², Nanami Kuramoto², Waka Yoshida², Ibuki Yasui², Tadashi Inoue³, Kenji Okada^{1,4}, Masahide Takahashi¹ (1. Osaka Metropolitan University, 2. Osaka Prefecture University, 3. Osaka University, 4. JST-PRESTO)

2:00 PM - 2:20 PM

[K206-4pm-05] CO₂ gas separation properites of composite membranes consisting of organic polymer and metal-organic framework thin films

○Xin Zheng¹, Roman Selyanchyn^{2,3,4}, Shigenori Fujikawa^{2,3}, Shin-ichiro Noro^{1,5} (1. Hokkaido University, Faculty of Env. Earth Science, 2. Kyushu University, I²CNER, 3. Kyushu University, K-NETs, 4. Kyushu University, Q-PIT, 5. Hokkaido University, Graduate School of Env. Science)

2:20 PM - 2:40 PM

Temperature and solvent dependence of polybenzimidazole adsorption on carbon materials

(¹ Department of Applied Chemistry, Graduate School of Engineering, Kyushu University,

²WPI-PCNER, Kyushu University, ³Centre for Molecular System (CMS), Kyushu University)

○Islam A B M Nazmul,¹ Nana Kayo,¹ Mai Akamine,¹ Naoki Tanaka,^{1,2} Tsuyohiko Fujigaya^{1,2,3}

Email: fujigaya.tsuyohiko.948@m.kyushu-u.ac.jp

Keywords: Polybenzimidazole; Carbon black; Adsorption isotherm; Langmuir model; Thermodynamic parameter

Polymer coating on the solid surface by physical modification is a fascinating technique to improve the surface charge, wettability, and dispersibility in solvents [1]. We have reported that polymer coating on carbon materials improves homogeneity of metal loading that is useful for electrocatalyst applications [2]. Especially, as a coating polymer, polybenzimidazole (PBI) have been used due to their excellent adsorption efficiency on the carbon materials. However, solvents dependency on their adsorption behavior have not been studied. In this study, the adsorption behavior of PBI onto carbon surface in different solvents was investigated based on adsorption isotherm measurements.

Adsorption isotherm of PBI was measured for Vulcan at 0, 25, 50, and 75 °C in *N,N*-dimethylacetamide (DMAc), *N*-methyl pyrrolidone (NMP), and dimethyl sulfoxide (DMSO). Langmuir constant (K_L) and maximum adsorption amount (Γ_{\max}) were calculated by fitting the adsorption isotherm by Langmuir model. Thermodynamic parameters (ΔG , ΔH , ΔS) were calculated based on vant' Hoff equation.

Figure 1 shows the adsorption isotherms of PBI on Vulcan for different temperature in NMP and Γ_{\max} increased as temperature increased. Γ_{\max} were increased as increase the temperature, indicating that adsorption reaction of PBI to carbon materials is entropy-driven. The positive values of ΔS attributed for the affinity to Vulcan and the increasing randomness at the solid-solution interface whereas the negative ΔG indicated the spontaneous nature of adsorption (Table 1). The ΔH and K_L value suggested that the interaction of solvent with PBI during adsorption among the solvents, where higher polymer-solvent interaction impede the physical adsorption on carbon surface. Finally, from this adsorption isothermal study, we got the higher PBI adsorption onto carbon surface at high temperature due to increased kinetic energy of PBI, and the diverse interactions among investigated solvents and PBI, which confirmed the trend of solvent affinity.

1) J. A. Prithi, *et.al.*, *Int. J. Hydrogen Energy*. **2021**, 46, 17871. 2) T. Fujigaya, *et al.*, *Adv. Mater.*, **2013**, 25, 1666.

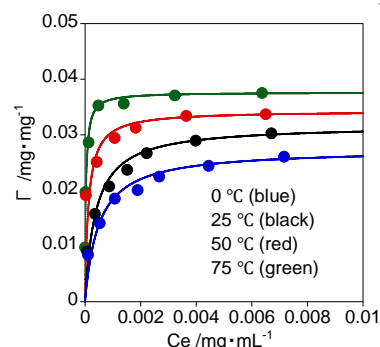


Figure 1. Adsorption isotherm of PBI onto Vulcan in NMP at different temperature

Table 1. Thermodynamic parameters and Langmuir constant for PBI onto Vulcan

	NMP	DMAc	DMSO
$\Delta H(\text{kJ/mol})$	38.2	23.0	6.35
$\Delta S(\text{kJ/mol} \cdot \text{K})$	0.197	0.142	0.089
$\Delta G (75^\circ\text{C})$	-28.5	-24.9	-23.3
$K_L (75^\circ\text{C})$	29.9×10^3	8.17×10^3	4.53×10^3

Sol-gel reaction of linear oligosiloxanes and their derivation to silicates

(Graduate School of Science and Technology, Tokyo University of Science) ○ Yohei Sato,¹ Asahi Sugimoto,¹ Ryohei Hayami,¹ Kazuki Yamamoto,¹ Takahiro Gunji¹

Keywords: Polysiloxane, Alkoxysilane, Sol-gel reaction, Oligosiloxane, Silicone

Sol-gel method is one of the most representative methods of the synthesis of silica materials. In the initial stage of the sol-gel reaction of tetraethoxysilane (TEOS), the formation of linear ethoxyoligosiloxanes was confirmed by GC-MS. Because the selective synthesis of linear ethoxyoligosiloxanes is difficult by the sol-gel reaction of TEOS due to its polyfunctionality, we could find only a few reports on the reaction and properties of these compounds. In this study, the reactivity of these compounds was monitored by MS of silylates and ²⁹Si NMR. In addition, the properties of silicates derived from these compounds were also investigated.

After linear ethoxyoligosiloxanes were hydrolyzed at ice bath temperature, trimethylsilyl derivatives of the hydrolyzates (HP) were analyzed by MS. Major products using TEOS, hexaethoxydisiloxane (HEDS), and octaethoxytrisiloxane (OETS) were linear and cyclic trimer to hexamer, linear oligomers having even numbered silicon atoms and linear trimer and tetramer, respectively. A mixture, which was formed by aging at r. t. after the hydrolysis at ice bath temperature, was monitored by ²⁹Si NMR. The results suggested that TEOS generates network-type polymers having cyclic siloxanes (Fig. 1a), HEDS generates polymers having four-membered cyclic siloxanes in the main chain (Fig. 1b), and OETS generates polymers having various membered cyclic siloxanes in the main chain (Fig. 1c).

Silica gels as noted G_{TEOS}, G_{HEDS}, and G_{OETS} were obtained by hydrolysis of linear ethoxyoligosiloxanes followed by heating at 100, 300, 500, 700, and 900 °C. G_{OETS} just showed micropore at 100 °C. The specific surface area of the gels at 300 °C was decreased in the order G_{TEOS} > G_{OETS} > G_{HEDS}. The pore structures of all gels were disappeared at 500 °C. These pore structures were found to be related to network structures; the difference of these structures was indicated by IR spectra.

These results were considered the appearance of differences in raw materials.

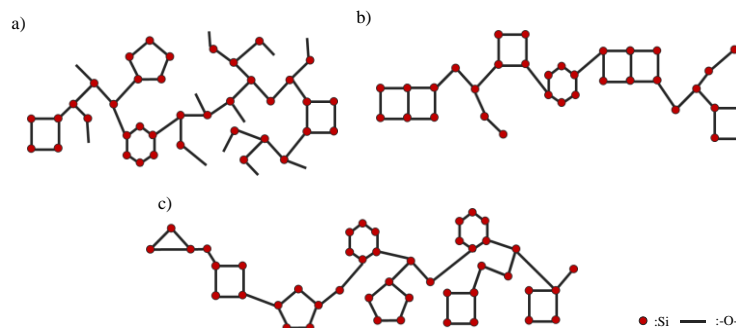


Fig. 2 Estimated polymer structure

高靱性バイオマス材料の開発を目指したセルロースとヒドロキシアパタイトの複合化

(同志社院理工) ○奥田 耕平、水谷 義

Hybridization of cellulose and hydroxyapatite applicable to tough biomass materials (*Graduate School of Science and Engineering, Doshisha University*) ○Kohei Okuda, Tadashi Mizutani

Cellulose microfibrils (CMF) and hydroxyapatite (HAP) were hybridized by coprecipitation with the aim of developing new tough biomass materials by imitating bone. Three-point-bending test revealed that at each coprecipitation temperature, the composites obtained with the feed inorganic contents (IC_{feed}) of 70 wt% had higher bending strengths than those obtained with IC_{feed} of 96 wt% (Fig. 1). Furthermore, their elastic moduli were above 9.0 GPa. As shown in Fig. 2, when the IC_{feed} of the composites was 70 wt%, the amount of HAP not interacting with CMF was small, and HAP crystals were dispersed uniformly in the composites, so the bending strengths were improved than those of 96 wt%. Although CMF and HAP are obtained from abundant forests and mineral resources on earth and the composites were synthesized at room temperature, the bending strengths of the composites were comparable to that of acrylonitrile-butadiene-styrene copolymer and the elastic moduli to that of glass fiber reinforced polybutylene terephthalate. These composites are expected to be used as new tough biomass materials to replace petroleum-derived plastics.

Keywords : Cellulose; Hydroxyapatite; Composite; Biomass; Mechanical property

骨の模倣による高靱性バイオマス材料の開発を目指し、セルロースマイクロファイバー (CMF) とヒドロキシアパタイト (HAP) を共沈複合化¹⁾した。三点曲げ試験の結果、Fig. 1 のとおり、各共沈温度において、仕込み無機重量分率 (IC_{feed}) が 70 wt% で得られた複合体の方が、96 wt% のものよりも高い曲げ強度を示した。また、その弾性率は 9.0 GPa 以上であった。Fig. 2 のように、 IC_{feed} : 70 wt% のときに最も CMF と相互作用していない余分な HAP が少なく、均一に HAP が分散しているため、 IC_{feed} : 96 wt% のものよりも機械的性質が向上したものと考えられる。CMF・HAP は地球上に豊富に存在する森林・鉱物資源から得られ、かつ、室温という穏やかな共沈温度で得られたにも関わらず、アクリロニトリル-ブタジエンスチレン共重合樹脂の曲げ強度とガラス繊維強化ポリブチレンテレフタレート²⁾の弾性率に匹敵したことから、石油由来プラスチックに代わる新規の高靱性バイオマス材料としての利用が期待できる²⁾。

- 1) S. I. Stupp *et al.* *J. Biomed. Mater. Res.* 26, 169 (1992).
- 2) Purasuchikku Dokuhon 22nd ed. 2019 (PLASTICS AGE Co. Ltd.)

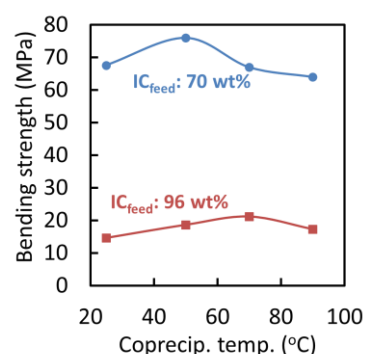


Fig. 1. Effects of coprecipitation temperature and feed inorganic contents on the bending strengths of the composites.

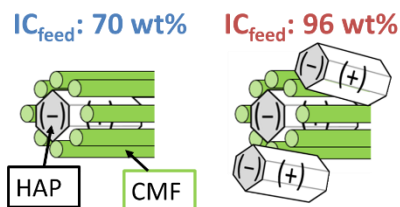


Fig. 2. Schematic representation of crystal growth of HAP on CMF.

DNA と各種金属イオンの配位結合を利用したハイドロゲルの作製と物性評価

(阪公大院工¹・阪府大院工²・阪大院理³・JST さきがけ⁴) ○深津 亜里紗¹・栗栖 沙理²・倉本 七夏海²・吉田 和加²・安井 伊吹²・井上 正志³・岡田 健司^{1,4}・高橋 雅英¹

Preparation and Physical Properties of Hydrogels Based on Coordination between DNA and Various Metal Ions (¹Graduate School of Engineering, Osaka Metropolitan University, ²Graduate School of Engineering, Osaka Prefecture University, ³Graduate School of Science, Osaka University, ⁴JST-PRESTO) ○Arisa Fukatsu,¹ Sari Kurisu,² Nanami Kuramoto,² Waka Yoshida,² Ibuki Yasui,² Tadashi Inoue,³ Kenji Okada,^{1,4} Masahide Takahashi¹

DNA has attracted attention as an eco-friendly bio-based material in terms of both resource supply and environmental impact of waste, and as a polymer with a multi-functional double helical structure. Inspired by the specific interaction between DNA and metal ions, in this study, DNA-based hydrogels were prepared by mixing DNA, which can be extracted from biomass such as fish waste, with various metal salts. The rheological measurement indicated that the hydrogels were elastic materials. The various physical properties of the hydrogels depending on the metal ions were also investigated.

Keywords : DNA; Hydrogel; Biomass; Organic-Inorganic Hybrid; Coordination Bond

DNA は資源の供給と廃棄物の環境負荷の両面で環境親和性が高い生体由来材料であるとともに、高度に構造が規定された二重らせん構造を有し、周囲の温度・pH・イオン濃度等による環境応答性を示す高分子材料として近年注目されている。また、DNA は種々のヘテロ原子（窒素、酸素、リン）を含む様々な官能基から構成されており、様々な金属イオンと特異的に配位結合等の相互作用を示すことが知られている。そこで本研究では、海洋生物の残渣などの天然資源から獲得可能な DNA と種々の金属との相互作用を利用した DNA ハイドロゲル (Fig. 1) を作製し、物性評価を行った。

DNA ハイドロゲルは、DNA の水溶液と、第 3 族から第 13 族までの金属元素を含む各種金属塩水溶液を混合することにより作製した。レオロジー測定により、作製したハイドロゲルは弾性体であることが示された。また、構成金属イオンに応じて、高い伸縮応答性や自己修復性、分解性など多様な物性を示すことが明らかとなった。この主な要因としては、金属種により DNA との相互作用する箇所や配位活性が異なることが考えられる。種々の金属塩を用いて作製した各種 DNA ハイドロゲルの詳細な物性については、当日議論する予定である。

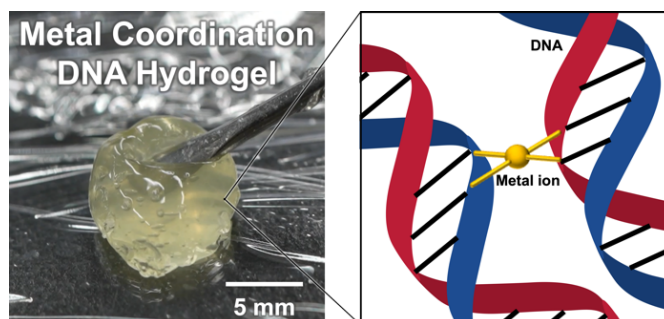


Fig. 1. Photographic image (left) and schematic illustration (right) of the DNA hydrogel.

CO₂ gas separation properties of composite membranes consisting of organic polymer and metal-organic framework thin films

(¹Faculty of Env. Earth Science, Hokkaido University, ²ICNER, Kyushu University, ³K-NETs, Kyushu University, ⁴Q-PIT, Kyushu University) ○ Xin Zheng,¹ Roman Selyanchyn,^{2,3,4} Shigenori Fujikawa,^{2,3} Shin-ichiro Noro¹

Keywords: Composite membrane; Metal-organic framework; CO₂ capture

To reach net-zero carbon dioxide (CO₂) emissions by the middle of this century, we must develop energy-efficient CO₂ capture systems to replace current high-energy demanding amine-based CO₂ chemical scrubbing technology. Direct air capture systems using membranes have recently attracted much attention due to their potential for lower energy consumption and deployment options.¹ Although single-component organic polymer membranes have the advantage of lower cost and easier processability, their permeability-selectivity trade-off limit hinders their practical use.² In this work, we fabricated the composite membranes consisting of a metal-organic framework thin film as the CO₂ selective layer and a polydimethylsiloxane (PDMS) thin film as the gutter layer³ to overcome the trade-off.

Using a simple dip-coating method, the MOF thin film of [Cu₃(1,3,5-benzenetricarboxylate)₂] (HKUST-1) with ca. 100 nm thickness was successfully prepared on the PDMS thin film with ca. 800 nm thickness as shown in Fig. 1a.⁴ The composite membrane showed higher CO₂/O₂ selectivity compared to a pure PDMS membrane and had balanced separation properties (CO₂/O₂ selectivity and CO₂ permeance) when compared to reported organic polymer membranes (Fig. 1b).

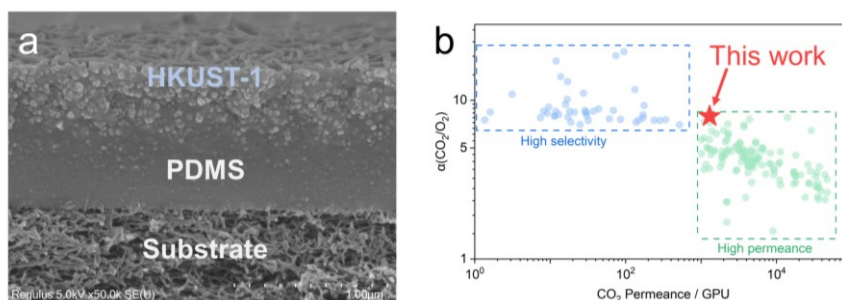


Fig. 1 (a) SEM image of the cross-sectional view of HKUST-1/PDMS composite membrane. (b) CO₂/O₂ selectivity versus CO₂ permeance plot for the HKUST-1/PDMS composite membrane and reported organic polymer membranes (assuming the membrane thicknesses of 1 μm).

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