

The 4th IRCCS International Symposium: "Multidimensional control over material structure and function"

**Thematic Session on
"Asymmetry in materials and properties"**

March 15, 2021 Online

Integrated Research Consortium on Chemical Sciences (IRCCS)

**The 4th IRCCS International
Symposium:
"Multidimensional control over
material structure and function"**

**Thematic Session,
"Asymmetry in materials and properties"**

March 15, 2021 Online

The 4th IRCCS International Symposium:

"Multidimensional control over material structure and function"

With a Thematic Session, "Asymmetry in materials and properties"

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13:00-13:05 Opening remarks

Jun-ya Hasegawa (Hokkaido Univ.)

Chair: Atsushi Fukuoka

13:05-13:30 Senior talk 1 Kunio Awaga (Nagoya Univ.) **Thematic Session**

"Development of Molecular Mimics of Carbon Allotropes"

13:30-13:50 Younger scientist talk 1 Ewa Kowalska (Hokkaido Univ.) **Thematic Session**

"Morphology design in heterogeneous photocatalysis: Symmetry vs asymmetry"

Chair: Tamaki Nakano

13:50-14:10 Younger scientist talk 2 Masato Goto (Kyoto Univ.)

"Structural and magnetic properties of B-site-ordered double perovskites $\text{Ln}_2\text{LiFeO}_6$ (Ln: lanthanoid elements) with unusually high valence Fe^{5+} ion"

14:10-14:45 Keynote Lecture Xinhua Wan (Peking Univ.) **Thematic Session**

"From Pasteur Resolution to Controlled Preparation of Chiral Organic Crystals"

14:45-15:50 Poster Session

Chair: Daisuke Uraguchi

15:50-16:15 Senior talk 2 Katsuhiko Tomoomka (Kyushu Univ.) **Thematic Session**

"New Aspects of Asymmetric Preparation of Chiral Molecules"

16:15-16:35 Younger scientist talk 3 Akiko Yagi (Nagoya Univ.)

"Programmable Synthesis of Multiply Arylated Cubanes through C–H Metalation and Arylation"

16:35-16:55 Younger scientist talk 4 Shu-Qi Wu (Kyushu Univ.)

"Macroscopic Polarization Change via Electron Transfer in a Valence Tautomeric Cobalt Complex"

16:55-17:00 Short Break

Chair: Jun-ya Hasegawa

17:00-17:30 Emerging Scientist Lecture Adriana Pietropaolo (Univ. Catanzaro) **Thematic Session**

"Molecular asymmetry from chiral free-energy approaches"

Chair: Tamaki Nakano

17:30-18:15 Plenary Lecture Ron Naaman (Weizmann Institute of Science) ***Thematic Session***
“The electron spin and chiral systems-Merging that results in novel properties “

18:15-18:35 Committee members’ comments

18:35-18:40 Closing remarks
Shigehiro Yamaguchi (Nagoya Univ.)

18:40-20:00 Open Baquet in breakout rooms

Poster Presentations

- P-01 Spontaneous Deposition of Pt on Au(111)
○Bing Hu, Daiki Kido, Kaiyue Dong, Md. Harun Al Rashid, Hiroko Ariga-Miwa, Satoru Takakusagi, Kiyotaka Asakura (Hokkaido Univ.)
- P-02 Electric-assisted propane dehydrogenation at low temperature: far beyond the equilibrium conversion
○Jianshuo Zhang, Ruoyun Ma, Ken-ichi Shimizu, Shinya Furukawa (Hokkaido Univ.)
- P-03 Exploring the Mechanism of Novel Bifunctional Al^{III} Porphyrin Catalyzed Copolymerization of CO₂ and Cyclohexene Oxide: A DFT Study
○Manussada Ratanasak, Jingyuan Deng, Hideki Tokuda, Chihiro Maeda, Tadashi Ema, Kyoko Nozaki, Jun-ya Hasegawa (Hokkaido Univ.)
- P-04 Mechanistic Study on the Selective Catalytic Reduction of NO_x Catalyzed by Fe/SO₄²⁻/CeO₂ with NH₃
○Kai Oshiro, Min Gao, Jun-ya Hasegawa (Hokkaido Univ.)
- P-05 Asymmetric Hyperbranched and Linear Fluorene-vinylene Polymers ***Thematic Poster***
○Pengfei Wu, Zhiyi Song, Masayoshi Bando, and Tamaki Nakano (Hokkaido Univ.)
- P-06 Doping of Rh in In₂O₃ promotes methanol formation during CO₂ hydrogenation
○Nazmul Hasan MD Dostagir, Coogan Thompson, Hirokazu Kobayashi, Ayman M. Karim, Atsushi Fukuoka and Abhijit Shrotri (Hokkaido Univ.)
- P-07 The Variation of Surface/Bulk Structure and Activity of Titania Photocatalyst Particles by Milling
○Chen, G.; Takashima, M.; Ohtani, B. (Hokkaido Univ.)
- P-08 Interparticle Charge-transfer Excitation at Adjoined Anatase and Rutile Interface Proved by Reversed Double-beam Photoacoustic Spectroscopy
○Shen, Y.; Nitta, A.; Takashima, M.; Ohtani, B. (Hokkaido Univ.)
- P-09 Titania Inverse-opal with a Gold Nanoparticle Incorporated per Void Space for Photoabsorption Amplification
○Raja-Mogan, T.; Kowalska, E.; Takashima, M.; Lehoux, A.; Ohtani, B. (Hokkaido Univ.)
- P-10 Solid State Fabrication of Polythiénylenevinylene Thin Films via Cis-to-trans Thermal Isomerization
○Masayuki Wakioka, Natsumi Yamashita, Hiroki Mori, Richard Murdey, Atsushi Wakamiya, Yasushi Nishihara, Fumiyuki Ozawa (Kyoto Univ.)

- P-11 Isolation of Organophosphorus Zwitterions
○Yoshifumi Hashikawa, Shu Okamoto, Yasujiro Murata (Kyoto Univ.)
- P-12 Comparative investigation of quadruple perovskite structures $AA'_3B_4O_{12}$ containing divalent manganese, iron, cobalt and nickel square-planar centers at the A' sites
○Midori AMANO, Fabio Denis Romero, Masato Goto, Yuichi Shimakawa (Kyoto Univ.)
- P-13 Stabilisation and characterisation of the polymorphs of $BaRhO_3$ between 7 and 22 Gpa
○Sean INJAC, Romero, Denis. F, Xu Yuanhui, Shimakawa Yuichi (Kyoto Univ.)
- P-14 Near-Ultraviolet Transparent Organic Hole-Transporting Materials Containing Partially Oxygen-Bridged Triphenylamine Skeletons for Efficient Perovskite Solar Cells
○TRUONG Minh Anh, Hayoon Lee, Ai Shimazaki, Richard Murdey, Atsushi Wakamiya (Kyoto Univ.)
- P-15 Asymmetric Synthesis of Chiral Silicon Molecules *Thematic Poster*
○Kazunobu Igawa, Katsuhiko Tomooka (Kyushu Univ.)
- P-16 Synthesis and Transformation of Silylalkene
○Yuuya Kawasaki, Kazunobu Igawa, Katsuhiko Tomooka (Kyushu Univ.)
- P-17 Electronic Pyroelectricities of Heterometallic Dinuclear Complexes
○Shinji Kanegawa, SadhuKhan Pritam, Jeremy Ian Long and Osamu Sato (Kyushu Univ.)
- P-18 Water-orientated reversible magnetic anisotropy transition
○Shengqun Su, Shuqi Wu, Shinji Kanegawa and Osamu Sato (Kyushu Univ.)
- P-19 Observation of Proton Transfer Coupled Spin Transition in Fe(II) Complexes
○Takumi Nakanishi and Osamu Sato (Kyushu Univ.)
- P-20 Effect of Urea Additives in the Iridium-Catalyzed C-H Borylation of Aromatic Compounds
○Takeru Torigoe, Jie Wang, Yadong Pang, Koji Kubota, Hajime Ito, Yoichiro Kuninobu (Kyushu Univ.)
- P-21 Novel Access to Silacyclic Compounds
○Kohei Sekine, Yafang Dong, Kazuto Fuji, Masashiko Sakai, Yoichiro Kuninobu (Kyushu Univ.)
- P-22 Contactless mass transfer between alternating droplets
○Shusaku Asano, Yu takahashi, Taisuke Maki, Yosuke Muranaka, Nikolay Cherkasov, Kazuhiro Mae (Kyushu Univ.)
- P-23 Synthesis of macrocyclic compounds using 1,8,13-substituted triptycenes as a foundation
○Takayuki Iwata, Yusuke Maehata, Tatsuro Yoshinaga, Mitsuru Shindo (Kyushu Univ.)

- P-24 Multiple droplets formation by a simple mixing method with microfabricated channel and their mass-transport mechanism
○Kenta Goto, Kyoka Nakanishi, Fumito Tani (Kyushu Univ.)
- P-25 Ink-Jet Printable Thermally-Activated Delayed Fluorescence Dendrimers
○Ken Albrecht, Kenichi Matsuoka, Amruth C., Beata Luszczynska, Jacek Ulanski, Katsuhiko Fujita, Kimihisa Yamamoto (Kyushu Univ.)
- P-26 Syntheses of donor- π -acceptor (D- π -A) conjugated enamines
○Atsushi Tahara, Ikumi Kitahara, Hideo Nagashima (Kyushu Univ.)
- P-27 Investigating the Nonradiative Decay Pathway in the Excited State of Silepin Derivatives: A Study with Second-Order Multireference Perturbation Wavefunction Theory
○Naoto Inai, Daisuke Yokogawa, Takeshi Yanai (Nagoya Univ.)
- P-28 Analytical Nuclear Gradients for the State-Averaged Density Matrix Renormalization Group Complete-Active-Space Self-Consistent-Field Method
○Tsubasa Iino, Toru Shiozaki, Takeshi Yanai (Nagoya Univ.)
- P-29 Enzymatic Hydroxylation of Small Alkanes by P450BM3 with Decoy Molecules under High Pressure
○Shinya Ariyasu, Yusaku Kodama, Kai Yonemura, Chie Kasai, Joshua Kyle Stanfield, Yuma Shisaka, Yuichiro Aiba, Yoshihito Watanabe, Osami Shoji (Nagoya Univ.)
- P-30 The Building of Rigid Heme Protein Multimers Based on Metal Coordination
○Hiroaki Inaba, Yuma Shisaka, Garyo Ueda, Kazuto Suzuki, Shinya Ariyasu, Yuichiro Aiba, Hiroshi Sugimoto, Osami Shoji (Nagoya Univ.)
- P-31 Directed Evolution of Cytochrome P450BM3 for Responding to Decoy Molecule Produced by Bacteria
○Yuya Yokoyama, Masayuki Karasawa, Shinya Ariyasu, Yuichiro Aiba, Osami Shoji (Nagoya Univ.)
- P-32 Synthesis of zigzag carbon nanobelt
○Kosuke Watanabe, Kwan Yin Cheung, Yasutomo Segawa, Kenichiro Itami (Nagoya Univ.)
- P-33 Photoredox-catalyzed decarboxylative direct aminomethylation towards aryl bromides: Straightforward synthesis of primary benzylamine
○Jaehyun Jung, Yota Sakakibara, Kei Murakami, Kenichiro Itami (Nagoya Univ.)

- P-34 Synthesis and Properties of Non-alternant Aromatic Belts
 ○Hideya Kono, Yuanming Li, Yasutomo Segawa, Akiko Yagi, Kenichiro Itami (Nagoya Univ.)
- P-35 Phosphorus-Based Organocatalysis for Dehydrative Cyclization of N-(2-Hydroxyethyl)amides into 2-Oxazolines
 ○Farzaneh Soleymani Movahed, Siong Wan Foo, Saeko Ogawa, Susumu Saito (Nagoya Univ.)
- P-36 C–O bond formation between aryl halides and carboxylic acids using titanium dioxide photocatalyst and a nickel complex
 ○Riku Hashimoto, Hiroya Tada, Shogo Mori, Jieun Jung, Susumu Saito (Nagoya Univ.)
- P-37 Photoreduction of CO₂ using molybdenum complexes bearing PNNP-type tetradentate ligands
 ○Hiroaki Shibayama, Hiroko Okuwa, Kenji Kamada, Jieun Jung, Susumu Saito (Nagoya Univ.)
- P-38 Crystal structures and physical properties of a triptycene derivative annulated with electron donating thianthrene moieties
 ○Takuma Yoshiyuki, Yoshiaki Shuku, Kunio Awaga (Nagoya Univ.)
- P-39 A metallomacrocyclic tethering eight corannulenes and the host–guest interaction with C₆₀
 ○Yuta Kobayashi, Shin-ichiro Kawano, Kentaro Tanaka (Nagoya Univ.)
- P-40 Template-independent RNA sequential synthesis using modified nucleic acid as substrate
 ○Kato Shunichi, Nakamoto Kosuke, Murase Hirotaka, Inagaki Masahito, Hashiya Fumitaka, Kimura Yasuaki, Abe Hiroshi (Nagoya Univ.)
- P-41 Development of post-cleaving PCR primers for genome-scale DNA synthesis
 ○Kase Mikiya, Inagaki Masahito, Hiraoka Haruka, Abe Naoko, Hashiya Fumitaka, Kimura Yasuaki, Abe Hiroshi (Nagoya Univ.)
- P-42 Tunneling ionization of molecular hydrogen by using a high-repetition-rate pulse laser
 ○Shinnosuke Inaba, Daimu Ikeya, Hikaru Fujise, and Akiyoshi Hishikawa (Nagoya Univ.)
- P-43 Development of momentum imaging apparatus for intense-field dynamics of molecular ions
 ○M. Yamada, H. Hasegawa, A. Matsuda, M. Fushitani and A. Hishikawa (Nagoya Univ.)
- P-44 Association reaction of gaseous C₆H₁₄ in femtosecond laser filament studied by product mass spectrometry
 ○Y. Okumura, A. Matsuda, and A. Hishikawa (Nagoya Univ.)

- P-45 Cross-linking gelation of isomaltodextrin for the chromatographic separation of semiconducting carbon nanotubes
○Yuki Matsunaga, Jun Hirotsu, Yutaka Ohno and Haruka Omachi (Nagoya Univ.)
- P-46 Catalytic NO Reduction Performances of Cr and Rh-incorporated Ceria
○Satoru Ikemoto, Satoshi Muratsugu, Mizuki Tada (Nagoya Univ.)
- P-47 Preparation and Catalytic Performances of Copper and Ruthenium Incorporated Ceria
○Chaoqi Chen, Satoru Ikemoto, Satoshi Muratsugu, Mizuki Tada (Nagoya Univ.)
- P-48 Preparation and Luminescent Properties of Surface-Attached Chiral Tb Complexes
Thematic Poster
○Sora Shirai, Satoshi Muratsugu, Hidetaka Nakai, Mizuki Tada (Nagoya Univ.)

Lectures

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Education:

1983 B.S., Univ. of Tokyo
1985 M.S. Univ. of Tokyo
1988 D.S., Univ. of Tokyo
Received a PhD (Supervisor: Prof. Minoru Kinoshita)

Professional Career:

1988 Assistant Professor, Institute of Molecular Science
1992 Associate Professor, School of Ars and Sciences, University of Tokyo
2001 Professor, School of Science, Nagoya University
2004-13 Professor, Research Center for Materials Science, Nagoya University
2014- present Professor, School of Science, Nagoya University

2013-17 Director, Professor, Research Center for Materials Science, Nagoya University
2019- Dean, School of Science, Nagoya University.

Research Interests:

- 1) Topological materials
- 2) Organic electronics
- 3) Solid-state electrochemistry

Honors:

1993 Chemical Society of Japan (CSJ) Award for Young Chemists Fellowship
2001 Morino Foundation Award
2003 IBM Japan Prize for Science
2012 Chemical Society of Japan (CSJ) Award for Creative Work
2020 Japan Society of Molecular Science Award

O-1

Development of Molecular Mimics of Carbon Allotropes

Kunio Awaga

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Isostructure and isoelectronicity are crucial concepts in chemistry for understanding the chemical and physical properties of atoms, ions, molecules and even solid-state materials. They are also useful in materials research to reproduce and improve the properties and functions of existing materials. As model systems for material design, carbon allotropes are extremely interesting; the electronic structure of graphene has conical bands, so-called Dirac cones. K_4 carbon, which is a theoretically-predicted carbon allotrope consisting of sp^2 carbons, is also predicted to possess the $S=1$ Dirac cones, and the valence band of diamond has characteristic nodal lines. It is thus clear that these carbon allotropes possess unique band structures due to their highly symmetrical structures. From this perspective, isostructure of the carbon allotropes are promising structures, particularly electron systems of which were delocalized. Although it is difficult to reproduce such structures by using simple non-carbon elements, it is highly possible to realize molecule-based carbon-allotrope structures by means of supramolecular chemistry.

In this presentation, we discuss the rational synthesis of the molecule-based K_4 and honeycomb structures, using polyhedral π -conjugated molecules. It is found that a chiral molecule, (-)-NDI- Δ , forms a K_4 lattice in the crystal structure of $(TBA)_{1.5}[(-)\text{-NDI-}\Delta]$, by an intermolecular π - π overlap between the NDI moieties [1,2]. The spin lattice in this salt is identical to the hyper-kagome lattice of $S=1/2$ Mott dimers, and the low-temperature magnetic and thermal measurements reveal the presence of a gap-less spin liquid state [3]. We also report molecule-based honeycomb lattices, formed the triptycene analogs [4,5].

- [1] A. Mizuno, Y. Shuku, K. Awaga, *Bull. Chem. Soc. Japan*, **92**, 1068 (2019).
- [2] A. Mizuno, Y. Shuku, R. Suizu, M.M. Matsushita, M. Tsuchiizu, D.R. Maneru, F. Illas, V. Robert, K. Awaga, *J. Am. Chem. Soc.*, **137**, 7612 (2015).
- [3] A. Mizuno, Y. Shuku, M.M. Matsushita, M. Tsuchiizu, Y. Hara, N. Wada, Y. Shimizu, K. Awaga, *Phys. Rev. Lett.*, **119**, 057201 (2017).
- [4] Y. Shuku, A. Mizuno, R. Ushiroguchi, C. S. Hyun, Y.J. Ryu, B.K. An, J.E. Kwon, S.Y. Park, M. Tsuchiizu, K. Awaga, *Chem. Commun.*, **54**, 3815 (2018).
- [5] R. Ushiroguchi, Y. Shuku, R. Suizu, K. Awaga, *Cryst. Growth Des.* **20**, 7593 (2020).

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Education:

1992–1998 (B.Sc./M.Sc. Eng.) Faculty of Chemistry,
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1998–2004 Faculty of Chemistry, GUT, Poland
Received a PhD (Supervisor: Prof. Jan Hupka)

Professional Career:

2002–2003 Marie Skłodowska-Curie Fellow at Paris-sud University, France

2004–2009 postdoctoral researcher at GUT, Poland

2005–2007 JSPS postdoctoral fellow at Hokkaido University

2007–2009 GCOE fellow at Hokkaido University

2009–2012 Marie Skłodowska-Curie Fellow at FAU/Ulm University, Germany

2012–present Associate Professor at Hokkaido University

Research Interests:

- 1) Heterogenous photocatalysis
- 2) Environmental protection
- 3) Plasmonic photocatalysis
- 4) Multi-functional (nano)materials
- 5) Antimicrobial properties

Honors:

since 2020 Deputy Editor-in-Chief for Micro & Nano Letters (MNL), IET/Wiley

2019 Hokkaido University President's Award for Excellence in Research and Education

2014 Global Networking Award, WinGS Project, Hokkaido University

2012 Brigitte Schlieben-Lange-Programme stipend from Ministry of Science, Research and the Arts of Baden-Württemberg, Germany

2005 Award in STEF-NANO-ACC contest for the best PhD thesis in the field of nanotechnology, nanoscience and multifunctional materials under the European Commission Sixth Framework Programme

2004 Doctoral dissertation with distinction

O-2

Morphology design in heterogeneous photocatalysis: Symmetry vs asymmetry

Ewa Kowalska

Institute for Catalysis (ICAT), Hokkaido University, Sapporo 001-0021, Japan

Heterogeneous photocatalysis has been considered as the future for humanity, especially solar photocatalysis (under natural sunlight), solving environmental and energy problems. However, there are two main problems facing heterogeneous photocatalysis, i.e., charge carriers' recombination and low efficiency of light harvesting as the most active photocatalysts are usually active under UV irradiation only. Accordingly, the proper design of photocatalytic materials has been broadly investigated to achieve better photocatalytic performance. Although, it is well known that all surface properties, e.g., specific surface area, crystallinity and crystal/particle sizes, have crucial impact on the overall photocatalytic activity, the recent studies have indicated that the morphology of photocatalysts, including also symmetry and asymmetry aspects, has governed the photocatalytic performance.

It is thought that symmetry and asymmetry of photocatalysts is highly important for different photocatalytic reaction. Indeed, our studies on the design of photocatalysts have confirmed that slight change in the photocatalyst morphology might result in significant change of photocatalytic activity.¹ For example, the polydispersity in gold deposits on titania surface is highly recommended for activity under visible-light irradiation (plasmonic photocatalysis) due to enhanced light harvesting efficiency.² Moreover, even slight increase in the crystallite size of gold results in an increase in photocatalytic efficiency because of significant enhancement of plasmonic field.³ The deposition of noble metals on anatase facets with different morphology, resulting in high or low photocatalytic activity,⁴⁻⁵ will be also discussed during this presentation to underline the importance of morphology.

(1) Wei, Z.; Janczarek, M.; Zheng, S.; Wang, K.; Kowalska, E. *Catalysts* **2020**, *10*, 1070.

(2) Kowalska, E.; Abe, R.; Ohtani, B. *Chem. Commun.* **2009**, *2*, 241.

(3) Wei, Z.; Rosa, L.; Wang, K.; Endo, M.; Juodkazis, S.; Ohtani, B.; Kowalska, E. *Appl. Catal. B-Environ.* **2017**, *206*, 393.

(4) Wei, Z.; Endo, M.; Wang, K.; Charbit, E.; Markowska-Szczupak, A.; Ohtani, B.; Kowalska, E. *Chem. Eng. J.* **2017**, *318*, 121.

(5) Wei, Z.; Janczarek, M.; Endo, M.; Balčytis, A.; Nitta, A.; Mendez Medrano, M. G.; Colbeau-Justin, C.; Juodkazis, S.; Ohtani, B.; Kowalska, E. *Appl. Catal. B-Environ.* **2018**, *237*, 574.

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Education:

2008–2012 Kyoto University
2012–2014 Graduate School of Science, Kyoto University
2014–2017 Graduate School of Science, Kyoto University
Received a PhD (Supervisor: Prof. Kazuyoshi Yoshimura)

Professional Career:

2017–2019 Postdoctoral researcher at Kyoto University
2019–present Assistant Professor at Kyoto University

Research Interests:

- 6) Solid State Chemistry
- 7) Condensed Matter
- 8) Magnetism

Honors:

2018 Inoue Research Award for Young Scientists
2014 Papers of JPSJ Editors' Choice

O-3

Structural and magnetic properties of *B*-site-ordered double perovskites Ln_2LiFeO_6 (Ln : lanthanoid elements) with unusually high valence Fe^{5+} ion

Masato Goto

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Geometrically frustrated magnets have attracted much attention owing to their exotic magnetic properties originating from the suppression of antiferromagnetic ordering. We focus on *B*-site-rock-salt-ordered double perovskites $A_2BB'O_6$, which belong to one of famous frustrated systems. In this work, we succeeded in synthesizing double perovskites Ln_2LiFeO_6 ($Ln = Nd, Sm, Eu$) with a frustrated f.c.c. lattice of unusually high valence Fe^{5+} ions by using a high pressure and high temperature condition, and then investigated their structural and magnetic properties.

The ^{57}Fe Mossbauer spectra (Figure 1) showed that Ln_2LiFeO_6 ($Ln = Nd, Sm, Eu$) had a highly negative isomer shift (-0.4 mm/s), confirming unusually high valence Fe^{5+} state. Ln_2LiFeO_6 ($Ln = Nd, Sm, Eu$) were found to adopt a monoclinic structure (Figure 2) at room temperature and show magnetic transitions at low temperatures. Interestingly, each magnetic transition temperature is much lower than the absolute value of Weiss temperature, which could be due to geometrical spin frustration. Detailed structural and physical properties of the obtained compounds will be presented and the effects of lanthanoid ions at the A site will be discussed.

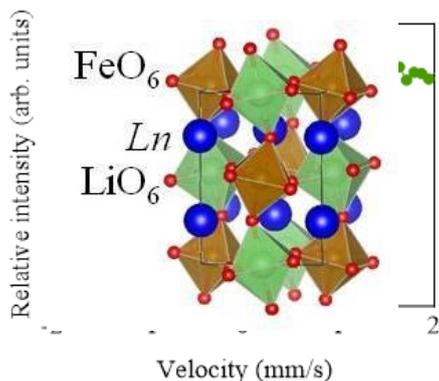


Figure 1. Mossbauer spectra of Ln_2LiFeO_6 ($Ln = Nd, Sm, Eu$) at room temperature.

Figure 2. Crystal structure of Ln_2LiFeO_6 ($Ln = Nd, Sm, Eu$).

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Education:

1981–1985 Hefei University of Technology
1985–1988 Department of Chemical Fiber Engineering, China Textile
University
1988–1991 Department of Chemical Fiber Engineering, China Textile
University
Received a PhD (Supervisor: Prof. Tong Sun)

Professional Career:

1991–1993 Postdoctor at Peking University
1993–1997 Associate Professor at Peking University
1995–1996 Visiting Scholar at the Hong Kong University of Science &
Technology
1997–present Professor at Peking University
2001–2001 Senior Visiting Scholar at the University of Akron
2004–2005 Senior Visiting Scholar at Harvard University

Research Interests:

9) Helical polymers, chiral resolution, circularly polarized luminescence, chiroptical switches;
10) Liquid crystalline polymers, high performance polymers;
11) Living/controlled polymerization, helix-sense-selective polymerization;
12) Self-assembly of polymers, organic/inorganic hybrid assembly.

Honors:

1997 The National Award for Natural Science, Tier III, the Ministry of Science &
Technology of China
1999 Trans-Century Training Programme Foundation for the Talents by the
Ministry of Education of China
2003 National Outstanding Young Investigator Found by Natural Science
Foundation of China
2010 Changjiang Professorship by the Ministry of Education of China
2017 Polymer science innovation award of Chinese Chemical Society

O-4

From Pasteur Resolution to Controlled Preparation of Chiral Organic Crystals

Xinhua Wan

Beijing National Laboratory for Molecular Sciences, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China

Since Louis Pasteur separated sodium ammonium tartrate crystals into two sets of crystals with mirror images of each other in 1848, selective crystallization has become one of the most economical and convenient techniques to provide large-scale enantiomerically pure chiral compounds. Usually, only one enantiomer can be obtained at a low yield in a single operation. In the past several years, we have been searching for an efficient method to meet such a challenge. First, we design and prepare a novel polymer aggregates that act as the additives of crystallization to inhibit, enrich, and promote the crystallization of one enantiomer. By the aid of these “nano-splitters”, the precipitation of second enantiomer is directly read out from the crystal color and the completely isolation of the crystallization processes of two enantiomers is realized. Second, we endow the “nano-splitters” with magnetism. The magnetic “nano-splitters” are selectively wrapped into the crystals of the second enantiomer. As a result of efficient separation under magnetic field, high purity chiral compounds (99.2 ee% for *R*-crystals and 95.0 ee% for *S*-crystals) can be obtained in a simple one-step crystallization process, with an extremely high separation yield (95.1%). Moreover, the nano-splitters show expandability and excellent recyclability. Herein, we describe a strategy that enables the preferred formation of one enantiomorph directly from racemic solutions as well as their in-situ oriented attachment to fabricate macroscopic chiral crystal aggregates, only aided by the “tailor-made” polymeric additives with various molar masses. When a *L*-polymer with a medium molar mass is used, Plus (P)-type fan-shaped crystal aggregates of *D*-*p*-hydroxyphenylglycine *p*-toluenesulfonate (*D*-*p*HpgpTs) are obtained. Changing the molar mass of the polymer can switch the chirality of the hierarchically ordered structures thus formed on both molecular and supramolecular levels. The financial support of the National Natural Science Foundation of China (No. 51833001) is greatly appreciated.

- (1) Li, N., Wang, H., Zhang, J., Wan, X. H. *Polym. Chem.* **2014**, *5*, 1702.
- (2) Ye, X. C., Zhang, J., Cui, J. X., Wan, X. H. *Chem. Commun.* **2018**, *54*, 2785.
- (3) Ye, X. C., Cui, J. X., Li, B. W., Li, N., Zhang, J., Wan, X. H. *Angew. Chem. Int. Ed.* **2018**, *57*, 8120.
- (4) Ye, X. C., Cui, J. X., Li, B. W., Li, N., Wang, R., Yan, Z. J., Tan, J. Y., Zhang, J., Wan, X. H. *Nat. Commun.* **2019**, *10*, 1964.

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Education:

1983 Bachelor of Engineering, Keio University

1985 Master of Engineering, Keio University

1988 Doctorate of Science, Keio University

(SV: Prof. G.-i. Tsuchihashi and Prof. K. Suzuki)

Professional Career:

1988–1998 Assistant Professor at Tokyo Institute of Technology (Prof. T. Nakai group)

1991–1993 Postdoctoral Research Associate at Stanford University (SV: Prof. P. A. Wender)

1998–2006 Associate Professor at Tokyo Institute of Technology

2007–present Professor at Kyushu University

Research Interests:

1) Development of synthetic methods

2) Synthetic and structural chemistry of natural and unnatural chiral molecules

Honors:

1988 The 5th Inoue Research Award for Young Scientists

1996 Eisai Award in Synthetic Organic Chemistry

1996 Incentive Award in Synthetic Organic Chemistry

2001 Thieme Journal Award

2009, 2010, 2014, 2015 and 2016

Asian Core Program Lectureship Award [Korea], [Singapore], [Hong Kong], [China], [Taiwan]

2010 SSOCJ Astellas Award for Organic Chemistry in Life Science

2010 The Chemical Society of Japan Award for Creative Work

2012 Nagase Foundation Award

2019 Synthetic Organic Chemistry Award

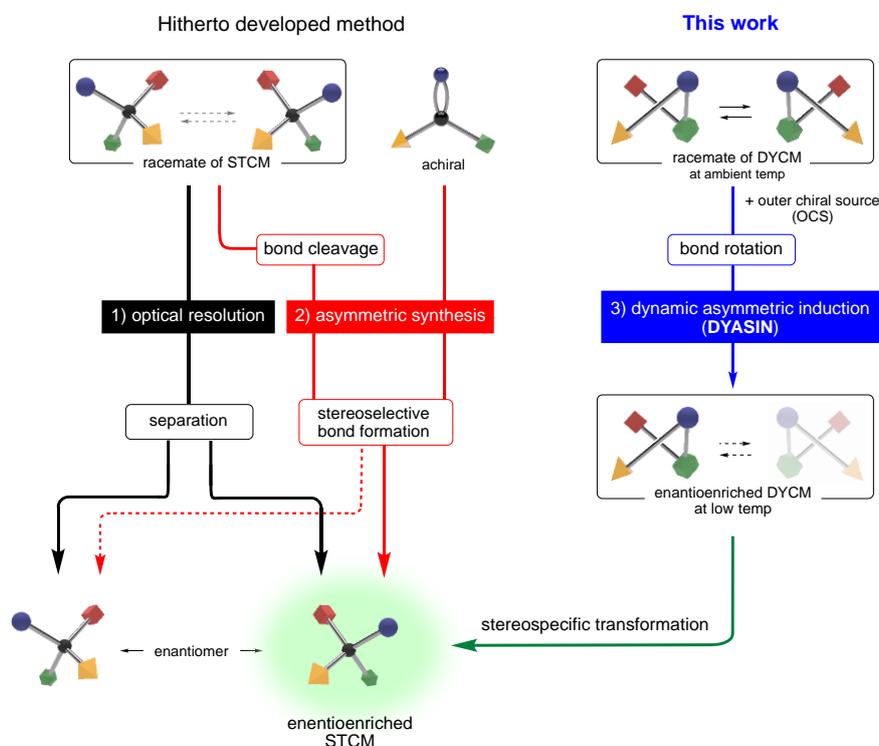
O-5

New Aspects of Asymmetric Preparation of Chiral Molecules

Katsuhiko Tomooka

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In modern organic chemistry, chemists have put forth considerable efforts in order to obtain desired enantiomers selectively. Chiral molecules with configurational isomerism of an asymmetric carbon represent a principal motif in this field, because most biologically relevant chiral molecules fall under such category. In general, the chirality of an asymmetric carbon is thermally stable, and hence it can be called “static chirality”. Developed approaches towards enantioenriched static chiral molecules (STCMs) are generally classified by **optical resolution** and **asymmetric synthesis**. On the other hand, it is well known that molecular chirality can also be caused by conformational isomerism and many examples are dynamic, i.e., enantiomers are capable of interconversion via bond rotation, in sharp contrast to STCMs. Dynamic chiral molecules (DYCMs) have a potential advantage in that the enantioenriched forms can be prepared in a very different way from STCMs. In this regard, recently we have developed a new approach termed **dynamic asymmetric induction (DYASIN)** for the preparation of enantioenriched chiral molecules based on the stereocontrol of DYCMs using an outer chiral source (OCS). DYASIN makes it possible to obtain the enantioenriched form of dynamic chiral molecules from their racemic form without bond cleavage or bond formation.



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Education:

2007–2011 Nagoya University
2011–2013 Graduate School of Science, Nagoya University
2013–2016 Graduate School of Science, Nagoya University
Received a PhD (Supervisor: Prof. Kenichiro Itami)

Professional Career:

2013–2016 JSPS Fellow at Nagoya University
2016–2017 Postdoctoral Fellow (JSPS Overseas Research Fellowship)
Department of Chemistry, The Scripps Research Institute, USA
(Prof. Ryan A. Shenvi)
2017–2020 Assistant Professor at Nagoya University
2021–present Designated Associate Professor at Nagoya University

Research Interests:

- 1) Nanocarbons
- 2) Synthetic Chemistry
- 3) Structural Chemistry

Honors:

2019 The KANTO Chemical Co. Award in Synthetic Organic Chemistry
2017 The 33th Inoue Research Award for Young Scientist
2016 The 6th Otsu Award Fellow
2014 The 9th L'OREAL–UNESCO for Women in Science Japan Fellowships

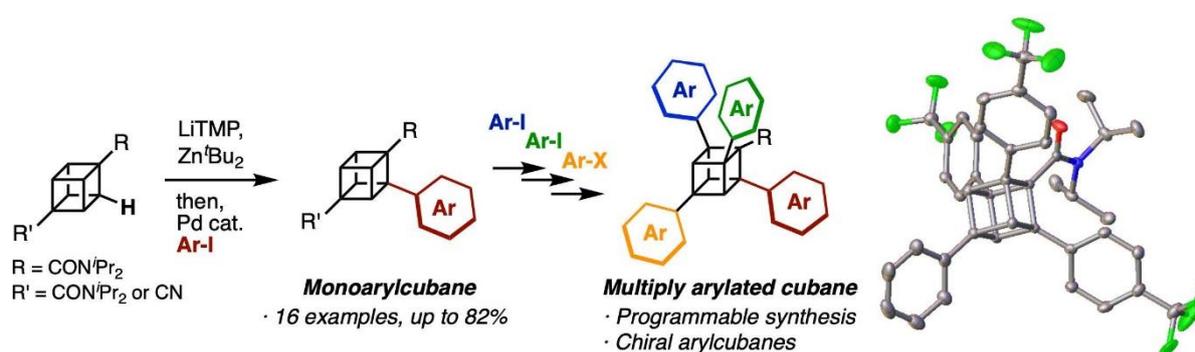
O-6

Programmable Synthesis of Multiply Arylated Cubanes through C–H Metalation and Arylation

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Structurally unique molecules have always fascinated scientists, which has driven investigations into their synthesis, functionalization, and applications. Cubane, which is a cubic alkane represented by C_8H_8 , has particularly attracted attention over the ages^[1]. Despite the high demand as an unique 3D carbon framework, the synthesis of cubane derivatives has been a very difficult task. Most of the reported derivatives have substituents on their 1- and 4-positions because these molecules are easily accessible from commercially available 1,4-cubanedicarboxylic acid. In order to utilize the cubane scaffold widely in science and technology, a powerful method for synthesizing diverse cubane derivatives is required. Herein, we present the synthesis of mono-, di-, tri-, and tetraarylated cubanes^[2]. Directed *ortho*-metalation with lithium base/alkyl zinc and subsequent palladium-catalyzed arylation enabled C–H metalation and arylation of cubane. This reaction allows the late-stage and regioselective installation of a wide range of aryl groups, realizing the first programmable synthesis of diverse multiply arylated cubanes. Furthermore, we have recently developed the direct catalytic arylation or halogenation of bicyclo[1.1.1]pentane, which is also a polycyclic hydrocarbon promising as a 3D carbon scaffold, by applying the method for the arylation of cubane.



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Education:

2007. Sept.–2011. Jul.	Tsinghua University
2011. Sept.–2014. Jul.	Department of Chemistry, Tsinghua University
2014. Oct.–2018. Mar.	Department of Chemistry, Kyushu University
	Received a Ph. D. (Supervisor: Prof. Osamu Sato)

Professional Career:

2018. Apr.–2021. Jan.	Researcher at Kyushu University
2021. Feb.–present	Assistant Professor at Kyushu University

Research Interests:

- 13) Molecular Magnetism;
- 14) Electronic Dynamics in Molecular Crystals;
- 15) Magnetoelectric Coupling in Molecular Crystals.

O-7

Macroscopic Polarization Change via Electron Transfer in a Valence Tautomeric Cobalt Complex

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Polarization of materials characterizes the degree of co-alignment of permanent molecular dipole moments. Switching polarization by different external stimuli provides an efficient way for energy conversion. Herein, we report electronic pyroelectricity in the single crystal of a mononuclear cobalt complex, $[\text{Co}(\text{phendiox})(\text{rac-cth})](\text{ClO}_4) \cdot 0.5\text{EtOH}$ ($\text{H}_2\text{phendiox}$ = 9, 10-dihydroxyphenanthrene, rac-cth = racemic 5, 5, 7, 12, 12, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane) crystallized in the polar $P2_1$ space group¹. The complex exhibits a two-step valence tautomerism (VT), and the co-alignment of the complex motifs amplify the change of the molecular dipole moment during the VT process to a macroscopic level, giving two pyroelectric peak currents in the same temperature domain of the VT transition. Different from common ferroelectric materials, no pre-polarization process is needed to obtain the optimized pyroelectric coefficient. The photo-induced metastable state could be trapped at low temperature, meaning that the Co compound exhibits a photo-tunable polarization bistability.

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Education:

1999–2004	Università di Catania and Scuola Superiore di Catania
2005–2007	Alma Mater Studiorum, Università di Bologna
2008	PhD (Supervisor: Prof. Claudio Zannoni)

Professional Career:

2008–2010	Research Fellow at ETH-Zürich
2010–2020	Assistant Professor at Università di Catanzaro
2011	Visiting Scientist at Forschungszentrum Jülich
2012/2013	Visiting Scientist at Hokkaido University
2021 at present	Associate Professor at Università di Catanzaro

Research Interests:

- 16) Simulations of chiral molecular systems and of the related spectroscopic signatures.
- 17) Development of free-energy methods for simulating excited state molecular rearrangements.
- 18) Free-energy predictions of molecular asymmetry and its implication on luminescent properties.

Honors:

- 2021: Member of Italian Research Evaluation for the chemistry area (GEV03).
2015: “Raffaele Piria” Prize for Chemistry.

O-8

Molecular asymmetry from chiral free-energy approaches

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Widespread motions in functional nanostructures stem from transforming chemical energy into a functional activity.^{1,2} Owing to continuous observations at how nature works and functions, chemists moved from a static molecular design to the synthesis of molecular frameworks capable of displaying stimuli-based motions.^{3,4} Light irradiation is a source of induction of these collective functional movements that in turn can cause a symmetry breaking in the molecular structure,^{5,6} originating inherent stimuli-based chiral switches that can work away from the global free-energy minimum.^{7,8}

The realization of *à la carte* molecules with tunable optical properties can be speeded up nowadays thanks to the incredible computational resources facing the exascale computing.

In this vein, we recently developed several simulation frameworks⁷⁻¹⁰ to reconstruct and predict the free-energetics of the ground and the excited states⁹ of chiral systems.

A perspective of nanoscale simulations of photoactive chiral transitions will be presented.

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- (3) Yashima, E; Ousaka, N; Taura, D; Shimomura, K; Ikai, T; Maeda, K. *Chem. Rev.* **2016**, 116, 22, 13752–13990
- (4) Gon, M; Tanaka, K; Chujo Y. *Angew. Chem. Int. Ed.* **2018**, 57, 6546.
- (5) Sakamoto T, Fukuda Y, Sato S, Nakano T. *Angew. Chem. Int. Ed.* **2009**, 48, 9308.
- (6) Wang Y, Sakamoto T, Nakano T. *Chem. Commun.* **2012**, 48, 1871.
- (7) Pietropaolo, A; Nakano, T. *J. Am. Chem. Soc.* **2013**, 135, 5509.
- (8) Pietropaolo, A; Wang, Y; Nakano, T. *Angew. Chem. Int. Edit.* **2015**, 54, 2688.
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- (10) Cozza, C; Raymo, F; Pietropaolo, A. *Mol. Sys. Des. Eng.* **2021**
doi.org/10.1039/D0ME00164C.

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Education:

1970–1973 BSc, Ben Gurion University, Beer Sheba, Israel
1973–1978 PhD, Weizmann Institute, Rehovot, Israel

Professional Career:

1978–1979 Postdoctoral Fellow, Stanford University, USA
1980 Research Associate and Lecturer, Harvard University, USA
1981–1986 Senior Scientist at the Weizmann Institute
1987–1992 Associate Professor at the Weizmann Institute
1993–2019 Professor at the Weizmann Institute
2019- Professor Emeritus

Research Interests:

- 19) Interaction of electrons and their spins with molecules and chiral molecules
- 20) Organic-inorganic interfaces

Honors:

Fellow of the American Physical Society
2007- Recipient of the "Lectureship Award of the Division of Colloid and Surface Chemistry"
authorized by The Chemical Society of Japan.
2010 Lectureship of the Chemical Society, Taiwan.
2013-The prize of the Israel Vacuum Society
2014 Kolthof award from the Technion Israel.
2018 Israel Chemical Society Prize for Excellent Scientist
2019 Recipient of the Humboldt-Meitner award.

O-9

The electron spin and chiral systems- Merging that results in novel properties

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Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we found that chiral molecules act as spin filters for photoelectrons transmission, in electron transfer, and in electron transport.

The new effect, termed Chiral Induced Spin Selectivity (CISS),ⁱ was found, among others, in bio-molecules and in bio-systems. It has interesting implications for the production of new types of spintronics devices,ⁱⁱ in controlling magnetization,ⁱⁱⁱ and on electron transfer and conduction. Recently we also found that charge polarization in chiral molecules is accompanied by spin polarization. This finding shed new light on spin dependent interaction between chiral molecules and between them and magnetic surfaces^{iv} and on the ability to control chemical reactions by controlling the spin polarization.^v

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Poster Presentations

P-01

Spontaneous Deposition of Pt on Au(111)

Bing Hu, Daiki Kido, Kaiyue Dong, Md. Harun Al Rashid, Hiroko Ariga-Miwa, Satoru Takakusagi, Kiyotaka Asakura

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Abstract Pt-skin electrocatalyst or Pt monolayer catalyst is one major breakthroughs in hydrogen fuel cell research in recent years, as it has the potential to afford >100% Pt atom economy due to the complete exposure of Pt atoms to fuel cell catalysis and the enhanced activity as well as stability compared to Pt metal alone^[1,2]. Meanwhile, the structural investigation of this kind of vital top-layer atoms on heterogeneous solid catalyst has long remained a challenge^[3]. In this work, we explore the phenomenon of spontaneous deposition of monolayer Pt species onto Au(111). We have applied the technique of polarization-dependent total reflection fluorescent X-ray absorption fine structure (PTRF-XAFS) to study the surface deposited species. It was found that the Pt L3 XANES and EXAFS spectra of the species both show dependence to the polarization direction of the X-ray and show enhanced signals when the polarization is parallel to the Au surface, from which planar structure parallel to Au(111) can be inferred. The EXAFS spectra were rationalized by nearest Cl neighbors at 2.27 Å. From XPS, we also confirmed surface Pt and Cl after spontaneous deposition. The XANES simulation corroborates the proposal of PtCl₄²⁻ species. From these evidences, we conclude that the spontaneous deposition of Pt on Au(111) produces PtCl₄²⁻ sticking parallel to Au(111) single crystal surface. The mechanism for the reduction of PtCl₆²⁻ into Pt(II) species is also discussed. The current work not only provides new insight for the preparation of Pt-skin electrocatalysts, but also serves as the pilot research for further in situ study of Pt stability and dynamic structural variation under electrochemical conditions.

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P-02

Electric-assisted propane dehydrogenation at low temperature: far beyond the equilibrium conversion

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Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan

The propane dehydrogenation proceeded at low temperature (300°C), where the equilibrium conversion is only 0.7%, by using an electric field and Pt-In intermetallic compounds (IMCs) supported on TiO₂. HAADF-STEM, XAFS revealed the formation of Pt₃In IMCs, in which Pt atoms became electron-rich by In atoms. Pt-In/TiO₂ showed much higher propylene yield compared with Pt/TiO₂ (2.5%→6.9%, with 2.0 W of electric power). Electric field plays an essential role on the propane dehydrogenation at low temperature. Kinetic analysis suggested that the electric field enabled the proton hopping on TiO₂ surface and its collision to propane at the Pt-TiO₂ interface was accelerated by the electric field. This electro-assisted unique mechanism allowed to break the equilibrium limitation of propane conversion at low temperature.

P-03

Exploring the Mechanism of Novel Bifunctional Al^{III} Porphyrin Catalyzed Copolymerization of CO₂ and Cyclohexene Oxide: A DFT Study

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Kyoko Nozaki², Jun-ya Hasegawa^{1*}

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²*Graduate School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan*

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Abstract: A detailed study on the mechanism for the copolymerization of CO₂ and cyclohexene oxide (CHO) catalyzed by novel bifunctional Al^{III} porphyrins with quaternary ammonium (QA) bromide was performed by using DFT calculations. To the best of our knowledge, our catalyst is the highest TOF (TOF=10,000 h⁻¹) among monometallic catalysts reported so far for the CHO/CO₂ copolymerization. Moreover, the carbonate-linkage selectivity >99%. DFT calculation results clearly indicated that the high polymerization activity and high selectivity of the Al^{III} catalyst originate from the cooperative actions of the metal center and the QA cation, both of which facilitate the epoxide-ring opening by the nucleophilic carbonate anion in the key transition state to form the carbonate linkages.

Deng, J.; Ratanasak, M.; Sako, Y.; Tokuda, H.; Maeda, C.; Hasegawa, J.; Nozaki, K.; Ema, T., Aluminum porphyrins with quaternary ammonium halides as catalysts for copolymerization of cyclohexene oxide and CO₂: metal–ligand cooperative catalysis. *Chem. Sci.* **2020**, 11, 5669-5675.

P-04

Mechanistic Study on the Selective Catalytic Reduction of NO_x Catalyzed by Fe/SO₄²⁻/CeO₂ with NH₃

Kai Oshiro¹, Min Gao², Jun-ya Hasegawa²

¹*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan*

²*Institute for Catalysis, Hokkaido University, Japan*

Selective catalytic reduction (SCR) is one of most efficient method for removing nitrogen oxides (NO_x) in exhaust gases released from factories and power plants. However, alkali metals in the exhaust gases disturb the adsorption of NH₃ which is the reducing agent in SCR, and therefore deactivate the catalyst. Recently, Zhang *et al.* reported the Fe-decorated SO₄²⁻-modified CeO₂ (Fe/SO₄²⁻/CeO₂) catalyst with alkali poisoning resistance.¹ The purpose of this study is to clarify the effect of Fe and SO₄²⁻ on the NH₃-SCR reaction by *ab initio* calculations. The influence of H₂SO₄ and Fe on the properties of CeO₂ adsorbed molecules were investigated. The results suggest that Fe works as a Lewis acid site to promote the adsorption of NH₃, while H₂SO₄ is contributed to the increase in surface acidity.

(1) M. N. Khan, L. Han, P. Wang, D. Zhang, *j. iScience.*, **2020**, 23, 101173

P-05

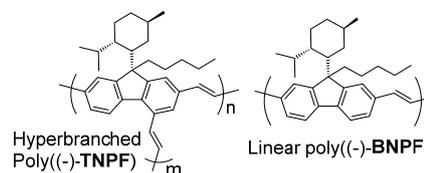
Asymmetric Hyperbranched and Linear Fluorene-vinylene Polymers

Pengfei Wu, Zhiyi Song, Masayoshi Bando, and Tamaki Nakano

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Circularly polarized light (CPL) is expected to find a variety of application including advanced display devices, and agricultural technologies. While CPL can be created by modulating non-polarized light (NPL) using proper optics, organic light-emitting diodes (OLED's) emitting efficient CPL without the need of modulation would bring benefits.

In this context, we have been developing light-emitting polymers and molecules with chiral structures,^[1-4] and in this work, we synthesized optically active poly(fluorenevinylene) derivatives having neomenthyl group as the source of chirality with hyperbranched and linear chain structures (poly(**TNPF**) and poly(**BNPF**)).



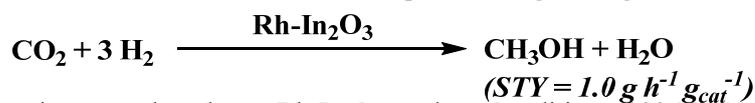
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P-06

Doping of Rh in In₂O₃ Promotes Methanol Formation During CO₂ Hydrogenation

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CO₂ hydrogenation to methanol is important because of the versatile use of methanol in chemical industry. Current industrial catalyst, Cu-ZnO/Al₂O₃, deactivates during the reaction and is unable to handle CO₂ rich feedstocks.^[1] Recently, In₂O₃ with oxygen vacancies on the surface was reported as a selective and stable catalyst.^[2] However, space time yield (STY) of methanol was low due to poor CO₂ conversion. To overcome this issue, promotion with a secondary metal such as Pd is required.^[3] Herein, we use Rh doped In₂O₃ catalyst where the Rh atoms are atomically dispersed in the In₂O₃ matrix. Catalyst with a 0.96 wt% Rh loading showed the best activity with a methanol STY of 1.0 g h⁻¹ g_{cat}⁻¹ (Scheme 1), one of the highest reported so far. Characterization suggested the formation of Rh single atom which were stable under reaction condition. During reaction, Rh atoms were reduced to create oxygen vacancy. Rh atoms helped in strong CO₂ chemisorption and promoted formate formation with the help of the neighboring In atoms.



Scheme 1: CO₂ hydrogenation to methanol over Rh-In₂O₃ catalyst. Conditions: 300 °C, 5 MPa, SV = 60,000 mL h⁻¹ g_{cat}⁻¹, H₂/CO₂ = 4.

References: [1] J. Wu *et al. Appl. Catal. A Gen.* **2001**, *218*, 235–240. [2] O. Martin *et al. Angew. Chemie - Int. Ed.* **2016**, *55*, 6261–6265. [3] M. S. Frei *et al. Nat. Commun.* **2019**, *10*, 1–11.

P-07

The Variation of Surface/Bulk Structure and Activity of Titania Photocatalyst Particles by Milling

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Solids are sometimes not crystalline, that is, an amorphous part might be included. Surface structures are indescribable since there is no systematic nomenclature method for solid surfaces except for single crystals exposing only one type of facet. Amorphous structures are entirely indescribable; therefore, they are called amorphous. In the majority of material science studies, discussions without the description of surface and amorphous structures were put forward even if those structures are included in them. Recently, we have developed a novel technique, reversed double-beam photoacoustic spectroscopy (RDB-PAS), which enables characterization of semiconducting metal oxides, to obtain the energy-resolved distribution of electron traps (ERDT), predominantly located on the surface of samples [1,2]. In this study, amorphous titania samples were prepared by braying rutile titania powder in an automatic agate mortar and post calcination in air at 773 K. Those samples were characterized by RDB-PAS measurement to elucidate the surface/bulk structure changes by the above-mentioned treatment.

[1] *Chem. Commun.* **2016**, 52, 12096-12099. [2] *Electrochim. Acta*, **2018**, 264, 83.

P-08

Interparticle Charge-transfer Excitation at Adjoined Anatase and Rutile Interface Proved by Reversed Double-beam Photoacoustic Spectroscopy

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¹*Graduate School of Environmental Science and Institute for Catalysis, Hokkaido University*

Herein, we obtain experimental evidence of interparticle spatial overlapping of orbitals to result in interparticle charge-transfer excitation (ICTE) at an anatase-rutile interface measured by reversed double-beam photoacoustic spectroscopy (RDB-PAS). The detailed energy-resolved distribution of electron traps (ERDT) analyses of various anatase-rutile mixtures revealed that all of the photoexcitation occurred from a high-density part of states (h-DOS) in valence band of rutile in a thoroughly mixed sample, and h-DOS of rutile was located ca. 0.2-eV higher than that of anatase. This is the first experimental results of practical h-DOS, which enable to cause photoabsorption, of materials. In addition, the ICTE analysis suggested a new concept, hetero-contact degree, which could be quantitatively evaluated by comparison of ERDT patterns of mixture sample to simulation patterns with thoroughly adjoined mixture particles and non-contacted particles.

[1] A. Nitta et al. *Chem. Commun.* **2016**, 52, 12096–12099. [2] A. Nitta et al. *Electrochim. Acta*, **2018**, 264, 83–90. [3] Y. Shen et al. *Chem. Lett.* **2021**, 50, 80-83.

P-09

Titania Inverse-opal with a Gold Nanoparticle Incorporated per Void Space for Photoabsorption Amplification

Tharishinny Raja Mogan,¹ Ewa Kowalska,^{1,2} Mai Takashima,^{1,2} Anais Lehoux,²
and Bunsho Ohtani^{1,2}

Graduate School of Environmental Science¹ and Institute for Catalysis,² Hokkaido University

Photochemical reactions are initiated by photoabsorption and proceeded by chemical reactions by utilizing the photoexcited charge carriers, thus the overall efficiency of the reactions could be defined as a product of photoabsorption efficiency and quantum efficiency. Till date, almost all the studies related to photoreactions have focused only to improve the chemical reactions occurring after photoexcitation of charge carriers, i.e., quantum efficiency rather than photoabsorption efficiency as it is difficult to alter the photoabsorption coefficient of any photoabsorbing materials. Inverse opal (IO) photonic crystals (PCs) are known as periodic nanostructures that could exhibit photonic band gap (PBG), resulting in photons with reduced group velocity, namely as slow photons which could be utilized by photoabsorbing materials. In this regard, a novel photocatalyst design, TiO₂ IO PC incorporated with a gold nanoparticle (Au NP) per void space (Au-NP@TiO₂ IO) has been developed as a strategy to amplify the photoabsorption efficiency. Several Au-NP@TiO₂ IO photocatalysts have been prepared in a similar way except in the variance of nanovoid diameter to study on the slow photons' effect. The precise wavelengths overlapping of slow photons arising in TiO₂-IO structure, surface plasmon peak from Au NPs and monochromatic irradiation source exhibited an amplified photocatalytic activity, i.e., enhanced photoabsorption has been evident by the photoabsorbing material (Au NPs).

P-10

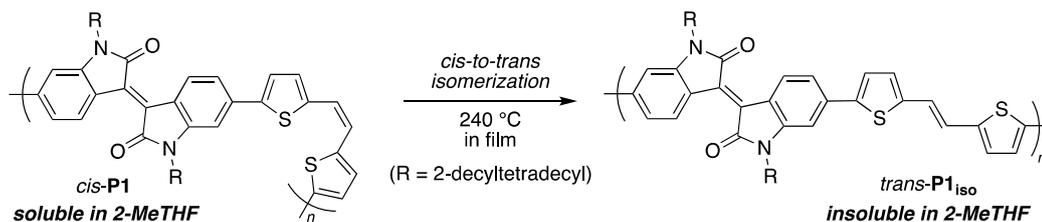
Solid State Fabrication of Polythienylenevinylene Thin Films via Cis-to-trans Thermal Isomerization

Masayuki Wakioka,¹ Natsumi Yamashita,¹ Hiroki Mori,² Richard Murdey,¹ Atsushi Wakamiya,¹
Yasushi Nishihara,² and Fumiyuki Ozawa¹

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Although *trans*-polythienylenevinylenes (PTVs) are desirable organic semiconductors, their limited solubility necessitates the use of toxic halogenated solvents to process the polymers into thin films. In this work, we demonstrate the efficient thermal conversion of thin film of *cis*-PTV (*cis*-P1), which is readily fabricated from environmentally friendly 2-MeTHF solution, to thin films of the *trans*-polymer (*trans*-P1_{iso}). In organic field effect transistors (OFETs), the *trans*-P1_{iso} films prepared by isomerization are shown to have comparable hole mobility as films prepared from CHCl₃ solutions of the *trans*-polymer.



P-11

Isolation of Organophosphorus Zwitterions

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Organophosphorus zwitterions are one of the most important but elusive intermediates for carbon–carbon bond formation in synthetic chemistry and biology. However, a lack of isolated examples due to their lability has hampered in-depth understanding of structures and their reaction mechanisms. In this study, we crystallographically revealed the solid-state structure of a phosha-Michael adduct engaged in a cage-opened C₆₀

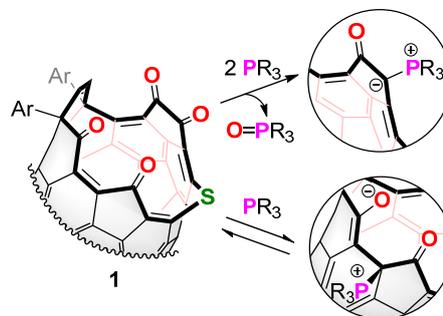


Figure 1. Synthesis of zwitterions

skeleton, which was formed as a kinetic product. From the 1,2-dicarbonyl moiety on the conjugated orifice, β -oxo-phosphorus ylide was obtained as a thermodynamic product. The reaction mechanism that has long been disputed was examined by experimental and theoretical studies, showing a pathway which includes an S_N2 reaction as a key step instead of hitherto considered carbene pathway.

(1) Hashikawa, Y.; Okamoto, S.; Murata, Y. *Commun. Chem.* **2020**, *3*, 90.

P-12

Comparative investigation of quadruple perovskite structures AA'₃B₄O₁₂ containing divalent manganese, iron, cobalt and nickel square-planar centers at the A' sites

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The A-site-ordered quadruple perovskite structure of general formula AA'₃B₄O₁₂ can accommodate transition metal cations at the square-planar A' site. When A and B are non-magnetic, the complex interactions between the spins at the A'-sites can provide exotic magnetic orders.¹ We recently found that CaA'₃Ti₄O₁₂ with A'-site Fe²⁺ centers, adopts an unusual multi-*k* antiferromagnetic spin ordering which responds to applied magnetic fields. To further understand the non-trivial A'-site magnetism in this structural class, we focused on the synthesis of the series A' = Mn²⁺, Co²⁺, Ni²⁺. Here we present some insights on the challenging preparation and the results from characterization of these materials.

(1) Y. Shimakawa and T. Saito, *Phys. Status Solidi Basic Res.* **2012**, *249*, 423.

P-13

Stabilisation and characterisation of the polymorphs of BaRhO₃ between 7 and 22 GPa

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We report the synthesis and characterisation of two phases of BaRhO₃ stabilised under high pressure, high temperature (HPHT) synthesis conditions. Synthesis at pressures of 4 to 7 GPa resulted in stabilisation of the 4H perovskite polymorph.¹ Synthesis at higher pressures of 14 to 22 GPa stabilised a novel 6H phase of BaRhO₃.

Physical property measurements were carried out for both compounds. The magnetic susceptibilities include large temperature-independent terms. Metallic conductivity is observed for the 4H polymorph, while resistivity measurements

indicate the 6H polymorph is a semiconductor due to grain boundary effects. High Wilson ratios of approximately $R_w \approx 2$ indicate both polymorphs are strongly electron correlated systems. Magnetic ground state and density of state calculations were carried out for both compounds. These electronic structure calculations give metallic ground states for both structures. All these results indicate Pauli paramagnetic ground states for both polymorphs.

(1) B. L. Chamberland and J. B. Anderson, *J. Solid State Chem.* **1981**, 39(1), 114-119.

P-14

Near-Ultraviolet Transparent Organic Hole-Transporting Materials Containing Partially Oxygen-Bridged Triphenylamine Skeletons for Efficient Perovskite Solar Cells

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In this study, three transparent organic semiconducting materials were designed and synthesized. The combination of strong donor oxygen-bridged triphenylamine and weaker electron-donating group at the head position suppresses the π - π^* transition, leading to weak absorption in the NUV

region (Fig. 1).^{1,2} All of three materials were successfully applied as hole-transporting materials in both conventional and bifacial semitransparent perovskite solar cells.

(1) A. Wakamiya, Y. Murata, H. Kaji, et al. *Angew. Chem., Int. Ed.* **2014**, 53, 5800.

(2) M. A. Truong, Y. Kanemitsu, A. Wakamiya, et al. *ACS Appl. Energy Mater.* **2021**, in press.

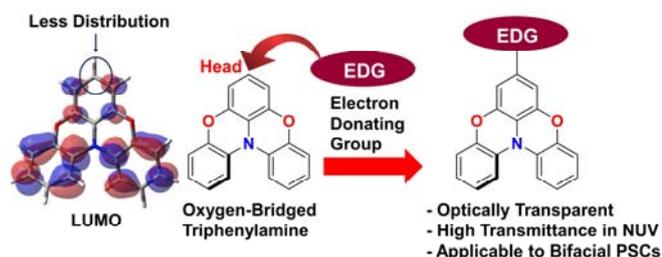


Fig. 1. The molecular design for transparent organic hole-transporting materials.

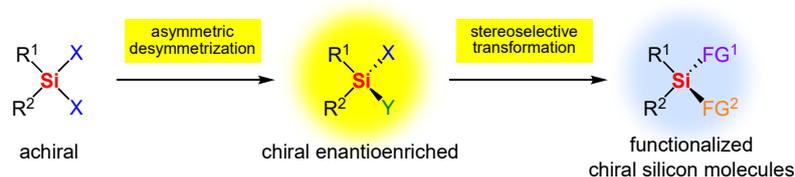
P-15

Asymmetric Synthesis of Chiral Silicon Molecules

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Chiral silicon molecules having asymmetric silicon are non-existence in nature, which have quite different chiral functionality from chiral carbon molecules owing to the structural and electrical features of silicon. To open up a novel chiral technology with chiral silicon molecules, we have developed asymmetric synthetic methods to obtain functionalized ones based on the asymmetric desymmetrization of prochiral silicon molecules¹⁻³⁾ and further stereoselective transformations.⁴⁻⁶⁾ The detail of this chemistry will be presented.



(1) *J. Amer. Chem. Soc.* **2008**, *130*, 16132. (2) *Angew. Chem. Int. Ed.* **2012**, *51*, 12745. (3) *Angew. Chem. Int. Ed.* **2016**, *55*, 5814. (4) *Angew. Chem. Int. Ed.* **2010**, *49*, 728. (5) *Synlett* **2017**, *28*, 2445. (6) *J. Org. Chem.* **2020**, *85*, 4165.

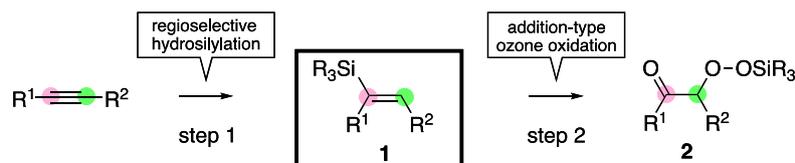
P-16

Synthesis and Transformation of Silylalkene

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Silylalkene **1** is a versatile synthetic precursor for a variety of functional molecules (eg. tri-substituted alkenes, ketones, acyloin, etc.). For the efficient synthesis and further transformation of silylalkene **1**, we have developed highly regioselective hydrosilylation of unsymmetric alkyne (step 1),¹ and addition-type ozone oxidation of silylalkene **1**, which provides α -silylperoxy carbonyl compounds **2** (step 2).³⁻⁴ The detail of the reactions and further transformation of **2** will be presented.



(1) *J. Am. Chem. Soc.* **2011**, *133*, 20712. (2) *Chemistry Letters* **2011**, *40*, 233. (3) *Chem. Eur. J.* **2014**, *20*, 9255. (4) *J. Org. Chem.* **2020**, *85*, 4065.

P-17

Electronic Pyroelectricities of Heterometallic Dinuclear Complexes

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Pyroelectricity and ferroelectricity are macroscopic physical properties caused by charge asymmetry in matter. Classically, these phenomena have been understood by changes in the position and arrangement of molecules and/or ions throughout the matter. This time, we focused on the intramolecular electron transfer phenomenon that occurs in one molecule and the resulting dynamic and microscopic permanent dipole moment, and discovered a pyroelectric phenomenon based on a new mechanism.

The directional intramolecular electron transfer in the polar structure was confirmed by magnetic measurement and crystal structure analysis of various heteronuclear dinuclear complexes containing 3d metal elements obtained by using chirality. By measuring the pyroelectricity of these heteronuclear complex single crystals, the relationship between intramolecular electron transfer and pyroelectric current was investigated.

P-18

Water-orientated reversible magnetic anisotropy transition

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Magnetic anisotropy greatly affects the hysteresis in ferromagnets, the blocking temperature in single-molecule magnets, and the operation temperature of quantum computing. However, the manipulation of magnetic anisotropy remains, especially the effect of subtle structural variation. Here, we observed a two-step reversible magnetic anisotropy transition depending on the orientation of the coordinated water in a cobalt(II) complex. The water molecule rotated ca. 24° in total around the Co-O bond and the magnetic susceptibility changed ca. 30% along the a-axis after a two-step phase transition. The angular-resolved magnetometry studies reveal that this complex possesses easy plane anisotropy and the direction of the magnetic hard axis changed after structural transition. Theoretical calculations further indicated that the orientation of the coordinated water molecule is the main effect on the magnetic anisotropy. This complex can be used as a magnetic switch and the discovery of the effect of water orientation will be useful in the magnetic devices and MRI.

P-19

Observation of Proton Transfer Coupled Spin Transition in Fe(II) Complexes

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Proton transfer phenomenon occurring with electron transfer or the change of electronic state plays an important role in biological reactions, catalytic reactions, and solid state materials. In this presentation, we will report Fe(II) hydrazone complexes, where two kinds of protonation state can be switched via the photo- and thermally-induced spin transition in crystalline system (Fig. 1).

(1) T. Nakanishi et al., *Angew. Chem. Int. Ed.*, **2020**, *132*, 14891-14897.

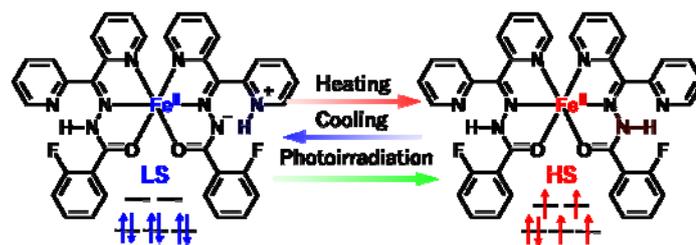


Figure 1. Proton transfer coupled spin transition.

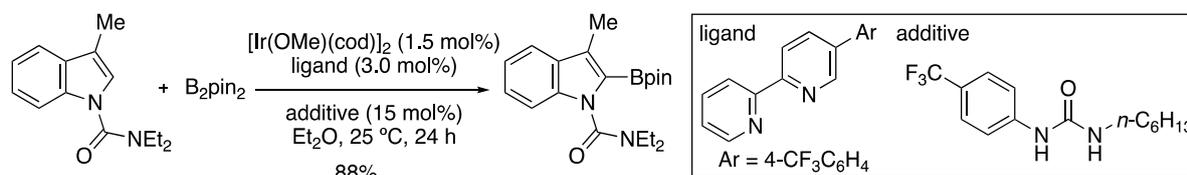
P-20

Effect of Urea Additives in the Iridium-Catalyzed C–H Borylation of Aromatic Compounds

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¹*Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580, Japan,* ²*Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan,* ³*Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo 060-8628, Japan,* ⁴*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

We found iridium-catalyzed 2-position-selective C–H borylation of 1,3-disubstituted indoles by modifying the structure of a bipyridine-type ligand and the yield could be improved by addition of urea additives. The results of solid-state reactions, in which the interactions between substrates and urea additives can be strong, will also be shown.



P-21

Novel Access to Silacyclic Compounds

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²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*

Five- or six-membered silacycles are attractive for applications as organic electronic materials. Their common synthetic method is the reaction of dichlorosilanes with dilithiated intermediates prepared from dihalogenated biaryl or diaryl substrates. However, efficient and versatile synthetic methods based on atom and step economy are desirable.

Herein, we report a simple and efficient synthetic method of multi-substituted silafluorene and phenoxasilin derivatives by double sila-Friedel–Crafts reaction of dihydrosilanes with amino group-substituted biphenyls, or diaryl ethers.¹ A synthesis of other silacycles will be discussed.

(1) (a) Takata, Y.; Yoshigoe, Y.; Sekine, K.; Kuninobu, Y. *Chem. Commun.* **2019**, 55, 13303. (b) Dong, Y.; Sakai, M.; Fuji, K.; Sekine, K.; Kuninobu, Y. *Beilstein J. Org. Chem.* **2020**, 16, 409.

P-22

Contactless mass transfer between alternating droplets

○Shusaku Asano¹, Yu takahashi², Taisuke Maki, Yosuke Muranaka, Nikolay Cherkasov,

Kazuhiro Mae

1. *Kyushu University, Japan.* 2. *Kyoto University, Japan.* 3. *University of Warwick, UK*

This study¹ demonstrates the possibility of mass transfer between two aqueous slugs (droplets) separated by an oil slug in Taylor flow inside milli-channels. Separation of the alternating aqueous slugs at the outlet was performed by switching a couple of solenoid valves at branched outlets according to signals obtained by an optical sensor at the branch. Transfer of bromothymol blue (BTB) from acidic to basic aqueous slugs was performed for demonstration. Almost complete (93%) transfer of BTB was achieved within a short residence time of several minutes under optimized conditions. The presented system opens a way for advanced separation using minimum amounts of the oil phase and allows concentrating the solute by altering relative lengths of the sender and receiver slugs.

(1) Asano, S.; Takahashi, Y.; Maki, T.; Muranaka, Y.; Cherkasov, N.; Mae, K. *Sci. Rep.* **2020**, 10 (1), 7685.

P-23

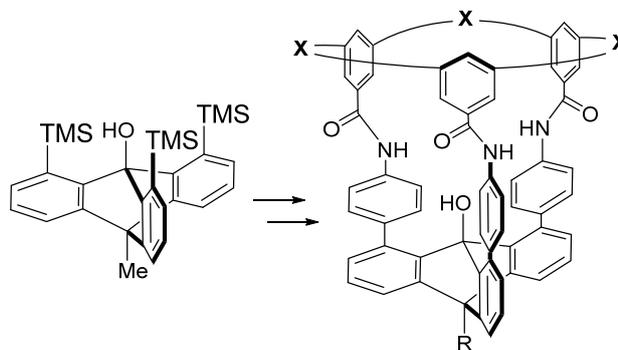
Synthesis of macrocyclic compounds using 1,8,13-substituted triptycenes as a foundation

○Takayuki Iwata,¹ Yusuke Maehata,² Tatsuro Yoshinaga,² Mitsuru Shindo¹

¹*Institute for Materials Chemistry and Engineering, Kyushu University, Japan*

²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Japan*

Triptycenes, which have fixed three benzene rings, have been utilized in material sciences and so on. We have recently developed a novel regioselective synthesis of 1,8,13-substituted triptycenes using ynolates and 3-methoxy-¹ or silylbenzynes.² In this presentation, our recent study on synthesis of macrocyclic compounds using 1,8,13-substituted triptycenes as a foundation will be shown.



(1) T. Iwata, M. Shindo, et al., *Angew. Chem. Int. Ed.*, **2017**, 56, 1298. (2) T. Iwata, M. Shindo, et al., *Chem. Eur. J.*, **2019**, 25, 13855.

P-24

Multiple droplets formation by a simple mixing method with microfabricated channel and their mass-transport mechanism

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Multiple droplets and/or emulsions are defined as dispersed droplets including tiny droplets in immiscible liquid phases. A couple of methods are present for formation of multiple droplets. Among them, multiple droplets obtained from phase separation show an attractive phenomenon including pattern dynamics and mass-transport. On the other hand, fabricated micro channel is a promising candidate for droplet formation. We developed multiple droplets formation by a simple mixing method with microfabricated channel in the diethyl phthalate (DEP)-ethanol-water system in the presence of a polymer surfactant, Pluronic F-127. Formation and mass-transport mechanism on phased-separated multiple droplets will be discussed.

P-25

Ink-Jet Printable Thermally-Activated Delayed Fluorescence Dendrimers

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Katsuhiko Fujita¹, Kimihisa Yamamoto³

¹ Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen
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² Department of Molecular Physics, Lodz University of Technology, 90924, Lodz, Poland

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The development of emitting materials for OLEDs has started with fluorescence, moved to phosphorescence, and recently reached thermally-activated delayed-fluorescence (TADF). The important design principle of a TADF material is to spatially separate the HOMO and LUMO because this reduces the difference in the singlet and triplet energy level. Carbazole dendrimers have the LUMO at the inner layer and the HOMO at the outer-layer. Attachment of an acceptor can further separate the HOMO and LUMO and this molecule showed efficient TADF¹. These TADF dendrimers can be used as efficient solution-processable emitting-layer for printed OLEDs².

(1) K. Albrecht & K. Matsuoka *et al. Chem. Commun.* **2017**, 53, 2439.

(2) Amruth C *et al. Org. Electron.* **2019**, 74, 218.

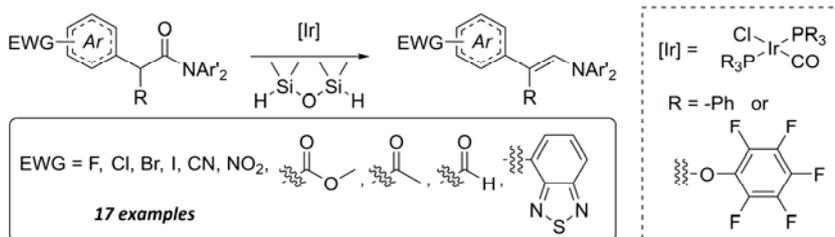
P-26

Syntheses of donor- π -acceptor (D- π -A) conjugated enamines

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Hydrosilane reduction of *N,N*-diaryl-2-arylacetamides bearing various electron-withdrawing groups (**2**) with 1,1,3,3-tetramethyldisiloxane (TMDS) was catalyzed by Vaska-type iridium complexes *trans*-IrCl(CO)(PR₃)₂ (**1X**; R = Ph, **1Y**; R = OC₆F₅) to afford donor- π -acceptor (D- π -A) conjugated enamines (**4**). Various types electron- withdrawing groups such as halogen, carbonyl, cyano, nitro, and 2,1,3-benzothiazol-4-yl (BTD) group were selected as an acceptor. Some D- π -A conjugated enamines showed photo luminescence properties.¹



(1) Tahara, A.; Kitahara, I.;

Sakata, D.; Kuninobu, Y.; Nagashima H. *J. Org. Chem.* **2019**, 84(23), 15236.

P-27

Investigating the Nonradiative Decay Pathway in the Excited State of Silepin Derivatives: A Study with Second-Order Multireference Perturbation Wavefunction Theory

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Computational estimation of the nonradiative decay rate constant has become an attractive task. Since rate constant of thermally activated decay via conical intersection (CI) is sensitive to the activation energy to reach CI geometry, the accuracy of the excited-state potential energies is critical. In this study, we employed a second-order multireference perturbation theory (MRPT) for studying decay via conical intersection of silepin derivatives. MRPT-level geometry optimization of the transition state in the pathway triggered by the central C–C bond twisting resulted in a reasonable estimation of the activation energy.

(1) N. Inai, D. Yokogawa and T. Yanai, *J. Phys. Chem. A* **2021**, *125*, 559.

P-28

Analytical Nuclear Gradients for State-Averaged Density Matrix Renormalization Group Complete-Active-Space Self-Consistent-Field Method

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The SA-DMRG-CASSCF method¹ is a class of multiconfigurational quantum chemical theory, which has been widely-recognized as an efficient approach to describe ground and excited states simultaneously with a qualitatively reliable accuracy, for large systems. However, this method cannot be used for molecular geometric search on top of the potential energy surface calculated at this level of theory because its analytical nuclear gradient method has not been established so far. To break through the current situation, we present a formalism of the gradient method and its implementation by combining Lagrangian approach for SA-CASSCF² with DMRG linear response theory.^{3,4} The illustrative performance of its application to acenes will be shown. (1) D. Ghosh *et al.*, *J. Chem. Phys.* **2008**, *128*, 144117. (2) P. Celani and H.-J. Werner, *J. Chem. Phys.* **2003** *119*, 5044. (3) J. J. Dorando *et al.*, *J. Chem. Phys.* **2009** *130*, 184111. (4) N. Nakatani *et al.*, *J. Chem. Phys.* **2014** *140*, 024108.

P-29

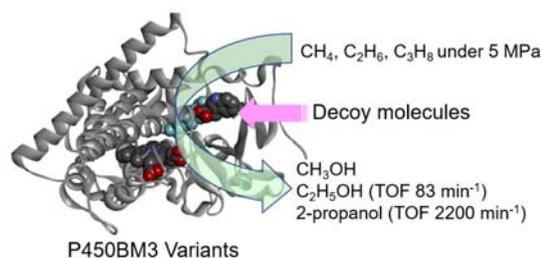
Enzymatic Hydroxylation of Small Alkanes by P450BM3 with Decoy Molecules under High Pressure

○Shinya Ariyasu, Yusaku Kodama, Kai Yonemura, Chie Kasai, Joshua Kyle Stanfield,

Yuma Shisaka, Yuichiro Aiba, Yoshihito Watanabe, Osami Shoji

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P450BM3 exhibits promising catalytic hydroxylation activity against long fatty acids. We have previously achieved the hydroxylation of non-native substrates such as propane by utilizing decoy molecules. However, its turnover frequencies were not as high as for natural substrate hydroxylation. Recently we have developed a new type of high-pressure reactor¹ and succeeded in drastic improvement of hydroxylation efficiencies of not only propane but also ethane in the presence of chemically evolved decoy molecules.²



(1) S. Ariyasu, Y. Kodama et al. *ChemCatChem*, **2019**, *11*, 4709, (2) K. Yonemura, S. Ariyasu et al. *ACS Catal.*, **2020**, *10*, 9136

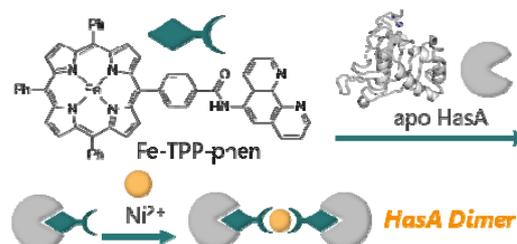
P-30

The Building of Rigid Heme Protein Multimers Based on Metal Coordination

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Supramolecular heme protein assemblies undergo great developments in recent years, but it is not so easy to control defined architectures because reported systems have flexible scaffolds. On the other hand, when using synthetic small molecules, self-assembled metal complexes such as MOF achieve control of highly defined architectures by metal coordination. Based on this knowledge, we have attempted to build rigid heme protein multimers based on metal coordination for units of rigid supramolecular heme protein assemblies. Thus, we incorporated Fe-TPP-phen into heme acquisition system protein A (HasA) and obtained HasA dimer by adding Ni²⁺ to the solution of Fe-TPP-phen HasA monomer (Figure). Currently, we are investigating this dimer for the detail and other metal ions are also under consideration.



P-31

Directed Evolution of Cytochrome P450BM3 for Responding to Decoy Molecule Produced by Bacteria

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Cytochrome P450BM3 (P450BM3) is a heme enzyme that catalyzes the efficient hydroxylation of long-chain fatty acids. We demonstrated that addition of synthesized dummy substrates called “Decoy Molecules” enabled hydroxylation of non-native substrates such as benzene.¹ In this research, we attempt to develop the reaction system without synthesis and addition of decoy molecules using C10-acyl homoserine lactone (C10-AHL), produced by a kind of bacteria, as a decoy molecule (Fig. 1). Herein, we engineered P450BM3 mutants responding C10-AHL by directed evolution to improve their catalytic efficiencies. We introduced random mutagenesis to P450BM3 heme domain and obtained a 1.5-fold active mutant from >1600 mutants screening through benzene hydroxylation in the presence of C10-AHL. The obtained mutant contains mutagenesis points which are far from heme. Thus, we hypothesize that these residues are essential and examine detail effects of these residues by saturation mutagenesis.

(1) O. Shoji, *et. al.*, *Angew Chem. Int. Ed.* **2017**, *56*, 10324-10329.

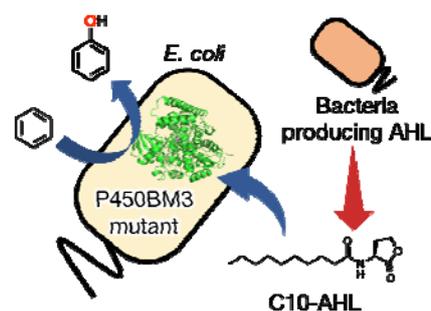


Fig. 1 Whole-cell reaction using bacteria producing C10-AHL.

P-32

Synthesis of a zigzag carbon nanobelt

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Herein we report the synthesis and isolation of a zigzag carbon nanobelt.¹ The synthesis involves an iterative Diels–Alder reaction sequence followed by reductive aromatization of oxygen-bridged moieties. The structure of the zigzag carbon nanobelt was fully characterized by X-ray crystallography, and its wide energy gap with blue fluorescence properties were revealed by photophysical measurement. As predicted by theoretical calculations, the carbon nanobelt was isolated as a stable compound.

1) Cheung, K. Y.; Watanabe, K.; Segawa, Y.; Itami, K. *Nat. Chem.* **2021**, DOI: 10.1038/s41557-020-00627-5

P-33

Photoredox-catalyzed decarboxylative direct aminomethylation towards aryl bromides: Straightforward synthesis of primary benzylamine

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Primary benzylamines are not only highly important building blocks in pharmaceutical chemistry, but also useful in the construction of electrophilic fragment libraries such as chloroacetamide, acrylamide, and cyanide for fragment-based drug discovery in covalent drugs.^[1] Recently, the synthesis of benzylamine derivatives by photoredox-catalyzed aminoalkylation toward aryl halide has been developed by several groups.^[2] However, a straightforward synthesis of primary benzylamines through the direct introduction of aminomethyl group is limited. Herein, we report the development of photoredox/nickel-catalyzed direct aminomethylation of aryl bromides. This reaction exploits glycine derivative as aminomethyl source via carbon radical species generated in a decarboxylative process under blue light irradiation. The wide range of aryl bromides, including heteroarenes, polycyclic aromatic hydrocarbons (PAHs) as well as drug precursors could be applied to our procedure.

(1) Keeley, A.; Petri, L.; Ábrányi-Balogh, P.; Keserü, G. M. *Drug Discovery Today* **2020**, *6*, 983. (2) (a) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J.A.; Doyle, A. G.; MacMillan, D. W. C. *Science* **2014**, *345*, 437. (b) Luo, J.; Zhang, J. *ACS Catal.* **2016**, *6*, 873.

P-34

Synthesis and properties of non-alternant aromatic belts

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Herein we report the synthesis of a methylene-bridged [6]cycloparaphenylene ([6]MCP), a non-alternant aromatic belt.¹ [6]MCP was obtained in 18% isolated yield by the aryl-aryl intramolecular coupling reaction using nickel complexes with pillar[6]arene derivatives. Compared with [6]CPP, the methylene bridges co-planarize neighboring paraphenylene units and enhance the degree of π -conjugation, resulting in a significant decrease in energy gap. Moreover, the incorporation of small molecules in the defined pocket of [6]MCP makes it an attractive supramolecular architecture.

(1) Li, Y.; Segawa, Y.; Yagi, A.; Itami, K. *J. Am. Chem. Soc.* **2020**, *142*, 12850.

P-35

Phosphorus-Based Organocatalysis for Dehydrative Cyclization of *N*-(2-Hydroxyethyl)amides into 2-Oxazolines

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2-Oxazolines possess an extensive range of applications,^{1,2} and due to the vital potential of the heterocyclic units in natural products and pharmaceuticals, practical and cost-efficient synthetic approaches have yet to be developed. In this work, our biomimetic catalytic protocol features the minimum employment of the catalyst and a broad substrate scope (up to 99% yield), along with high chemoselectivity toward 2-oxazolines; furthermore, it can be utilized as a gram-scale (4 g) synthetic pathway with high efficiency.

(1) Van Steenberge, P. H. M.; Sedlacek, O.; Hernandez-Ortiz, J. C.; Verbraeken, B.; Reyniers, M.-F.; Hoogenboom, R.; D'hooge, D. R. *Nat. Commun.* **2019**, *10*, 3641. (2) Yang, G.; Zhang, W. *Chem. Soc. Rev.* **2018**, *47*, 1783.

P-36

C–O bond formation between aryl halides and carboxylic acids using titanium dioxide photocatalyst and a nickel complex

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Carboxylic acids are important carbon resources since they are abundant in nature and they can be synthesized from carbon dioxide. Recently, C–O bond formation between aryl halides and carboxylic acids has been achieved using photocatalyst/Ni complex systems under mild conditions for the purpose of effective utilization of carboxylic acids.¹ Our group has also developed this transformation using a cheap, safe, reusable and heterogeneous photocatalyst, titanium dioxide (TiO₂). TiO₂ can activate carboxylic acids to carboxyl radicals (RCOO[•]), most of which are too unstable to undergo rapid decarboxylation into carbon-centered radicals (R[•]).² In our TiO₂/Ni complex system, RCOO[•] may be immediately intercepted by the nickel complex upon their formation on/near the TiO₂ surface, which resulted in the selective and rapid C–O bond formation.

(1) (a) Welin, E. R.; Le, C.; Arias-Rotond, D. M.; McCusker, J. K.; MacMillan, D. W. C. *Science* **2017**, *355*, 380–385. (b) Pieber, B.; Malik, J. A.; Cavedon, C.; Gisbertz, S.; Savateev, A.; Cruz, D.; Heil, T.; Zhang, G.; Seeberger, P. H. *Angew. Chem. Int. Ed.* **2019**, *58*, 9575–9580.

(2) Manley, D. W.; McBurney, R. T.; Miller, P.; Howe, R. F.; Rhydderch, S.; Walton, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 13580–13583.

P-37

Photoreduction of CO₂ using molybdenum complexes bearing PNNP-type tetradentate ligands

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Photocatalytic CO₂ reduction has attracted extensive interest since the photocatalytic conversion of CO₂ to energy-enriched compounds could potentially be achieved under mild conditions. Herein, we report new molybdenum (Mo) complexes bearing PNNP-type tetradentate ligands, which has been shown to prevent catalyst deterioration and promote CO₂ reduction,¹ acting as mononuclear photocatalysts for CO₂ photoreduction. These non-precious metal complexes show selective catalytic activities in photocatalytic conversion of CO₂ to HCO₂H under visible light irradiation. Nanosecond transient absorption spectrophotometer measurements and EPR measurements were performed to investigate their reaction mechanisms.

(1) Kamada, K.; Jung, J.; Wakabayashi, T.; Sekizawa, K.; Sato, S.; Morikawa, T.; Fukuzumi, S.; Saito, S. *J. Am. Chem. Soc.* **2020**, *142*, 10261–10266.

P-38

Crystal structures and physical properties of a triptycene derivative annulated with electron donating thianthrene moieties.

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Graphene with a honeycomb structure is in the spotlight due to its unique physical properties derived from the band structure called Dirac cone. To constructing molecule based honeycomb structure, we focused on triptycene derivatives, which are paddle-wheel shaped molecules having a three-fold rotational symmetry. Previously, we have reported a honeycomb crystal structure of triptycene derivative (*p*-TT) and its unique band structure, namely Dirac cone and flat band.¹⁾ However, the pore size of the honeycomb structure was too small to insert ions on the band filling control. Therefore, we focused on the thianthrene skeleton as an extended and electron donating π conjugated system. It is known that the radical cation of thianthrene molecules often form a dimer by their strong π - π interaction. We designed and synthesized a triptycene derivative having thianthrene moieties and prepared its radical cation salts by chemical oxidation. The details of the crystal structures and physical properties will be discussed.

(1) Y. Shuku, *et al. Chem. Commun.* **2018**, *54*, 3815-3818.

P-39

A metallomacrocyclic tethering eight corannulenes and its host–guest interaction with C₆₀

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Recently, we reported Schiff-base containing macrocycles composed of dibenzothiophene and metal-salen complexes with a nanometer-sized inner cavity.¹ In this paper, we discuss the macrocycle containing four Co(III) complexes at the salen units with aminomethylcorannulenes as the axial ligands. The metallomacrocyclic with eight corannulene moieties could be a fullerene receptor, because of high affinity between corannulene and fullerene. Single crystallographic analysis of the conjugate of the Co-macrocyclic and C₆₀ revealed that the receptor molecule captured four C₆₀, in which each four pair of corannulenes sandwiches a single C₆₀ through concave-convex interaction.

(1) S. Kawano, T. Hamazaki, A. Suzuki, K. Kurahashi, K. Tanaka, *Chem. Eur. J.*, **2016**, *22*, 15674.

P-40

Template-independent RNA sequential synthesis using modified nucleic acid as substrate

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In recent years, oligonucleotide therapeutics including antisense oligonucleotides and short interfering RNA (siRNA) has attracted a great deal of attention as a new type of drug, following small molecule drugs and antibody therapeutics. These oligonucleotides are prepared by solid-phase synthesis with phosphoramidite-based chemistry and are widely applied to medicine. On the other hand, the chemical synthesis of long RNA that can be applied for mRNA therapeutics has not been achieved. In general, mRNA is synthesized by in vitro transcription (IVT) using T7 RNA polymerase. However, since the IVT method cannot introduce the modified nucleoside analog site specifically, it is not suitable to prepare modified mRNA which is highly stable in vivo and efficiently translated for pharmaceutical applications.

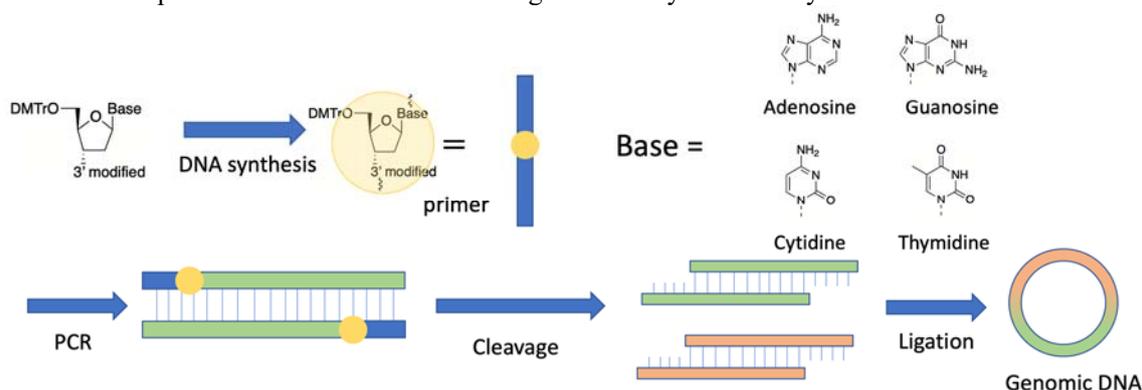
In the present work, we have attempted the enzymatic synthesis of long RNA strands using modified nucleic acid. In general, RNA ligation by ligase proceeds in a three-step reaction. First, RNA ligase and ATP form an enzyme-AMP complex. Next, the complex transfers AMP to the phosphate group located on a terminal of RNA to form adenylated RNA. Finally, the adenylated RNA and the hydroxyl group of another RNA strand react to complete ligation. The formation of adenylated RNA in the second step is a reversible reaction, and it seems to be the rate-determining step of ligation reactions. Therefore, we chemically prepared adenylated RNA and developed a new RNA ligation reaction that circumvents the rate-determining step.

P-41

Development of post-cleaving PCR primers for genome-scale DNA synthesis

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In order to synthesize genome-scale long DNA strands, DNA assembly techniques are essential to connect DNA fragments via sticky ends. Since conventional restriction enzyme-based methods such as golden gate assembly limit the length of sticky end to 4 nt, our group has developed cleavable primer that can generate site-specific DNA strand cleavage by introducing modified nucleic acids to prepare any length and sequence sticky ends. In this study, we have developed a new method to create arbitrary 3' overhang sticky ends. This method uses the principle of chemical reactive cleavage of DNA with 3' modification. So first, we needed to synthesize each nucleoside derivative containing modification at 3'. We have completed the synthesis and optimization of reaction conditions of cytidine, adenosine and thymidine derivatives, and currently working on the synthesis of guanosine derivatives. We plan to synthesize PCR primers and measure the cleavage efficiency after the synthesis.



P-42

Tunneling ionization of molecular hydrogen by using a high-repetition-rate pulse laser

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Rates of laser tunneling ionization in intense laser fields ($\sim 10^{14}$ W/cm²) reflect electron distributions in a molecule. Therefore, the molecular frame angular distribution of photoelectrons (MFPAD) can be used to visualize molecular orbitals and electron dynamics in reaction processes (1). Electron-ion coincidence momentum imaging technique is powerful in measuring MFPAD, as it allows us to determine the orientation of the molecular axis from the momenta of fragment ions. However, it requires a long accumulation time to obtain a sufficient amount of data, because the event rate per laser shot should be kept low (≤ 0.1) to suppress accidental coincidences. In this work, we use a high-repetition-rate Yb:KGW pulsed laser (<100 kHz, 190 fs) to reduce the time required for the electron-ion coincidence measurements. We constructed a pulse compression system to generate ultrashort pulses for tunneling ionization imaging, and investigated the field intensity dependence of MFPAD of molecular hydrogen.

(1) A. Staudte *et al.*, *Phys. Rev. Lett.* **2009**, *102*, 033004.

P-43

Development of momentum imaging apparatus for intense-field dynamics of molecular ions

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Molecules in intense fields show a variety of exotic processes such as Coulomb explosion and tunneling ionization, which provide unique methods for investigating ultrafast molecular and electronic dynamics in chemical reactions. So far, studies on intense field processes have mostly focused on neutral molecules. Molecular ions have different geometrical and electronic structures from neutral molecules, and are therefore interesting targets for a deeper understanding of intense field dynamics (1). In this study, we developed a three-dimensional momentum imaging apparatus equipped with a pulsed ion source for generation of molecular ions. Two different ionizers can be used depending on desired ion species. The design of the apparatus and the characteristics are presented.

(1) B. Jochim *et al.*, *J. Phys. Chem. Lett.* **2019**, *10*, 2320-2327.

P-44

Association reaction of gaseous C₆H₁₄ in femtosecond laser filament studied by product mass spectrometry

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Many-body reactions using femtosecond laser filaments has recently attracted attention. For example, formation of short polyynes, C₆H₂, C₈H₂, from gaseous C₆H₁₄ in a laser filament has been confirmed by UV absorption spectroscopy of products recovered by condensation(1). In this study, we investigate the products from a laser filament of C₆H₁₄ by mass-spectrometry, where the reaction gas cell is connected directly to a time-of-flight mass spectrometer via a differential pumping stage. In addition to C₆H₂ and C₈H₂ observed by the previous UV spectroscopy, we have identified other hydrocarbons, such as C₄H_{2n}, C₆H_{2n} (n=1,2,3···), which could be considered as reaction intermediates in polyne formation.

(1)N. Takizawa *et al.*, *Carbon.* **2019**, *152*, 372-375.

P-45

Cross-linking gelation of isomaltodextrin for the chromatographic separation of semiconducting carbon nanotubes

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We report the cross-linking gelation of a cost-efficient polysaccharide isomaltodextrin (IMD) for the high-purity separation of semiconducting single-wall carbon nanotubes (SWCNTs) by column chromatography¹). The cross-linking reaction with epichlorohydrin under precisely controlled basic conditions gave the sub-micrometer porous IMD gels, which was important for achieving gel chromatographic SWCNT separation. Furthermore, the thin-film transistors prepared from the separated s-SWCNTs exhibited excellent on/off ratios.

(1) Y. Matsunaga, J. Hirotsu, Y. Ohno, H. Omachi, *Appl. Phys. Express.* **2021**, *14*, 017001.

P-46

Catalytic NO Reduction Performances of Cr and Rh-incorporated Ceria

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Cr and Rh-incorporated ceria catalysts (denoted as $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_x$) with low-temperature redox activity¹ exhibited superior NO reduction performances over $\text{Cr}_{0.17}\text{CeO}_x$ and $\text{Rh}_{0.04}\text{CeO}_x$ incorporated with only Cr or Rh, and CeO_2 without Cr and Rh; quantitative NO conversion with 100% selectivity to N_2 at 473 K using CO as a reductant (Figure 1). Changes in adsorbed species on the surface of $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_x$ from *in situ* FT-IR and changes in the oxidation states of each metal species from *in situ* XAFS analyses suggested that the NO reduction performance on $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_x$ was enhanced by the co-involvement of CrO_x species as an efficient O mediator from NO to CO with Rh species as both NO and CO adsorption and activation sites.

(1) Ikemoto, S. *et al. Phys. Chem. Chem. Phys.* **2019**, *21*, 20868-20877.

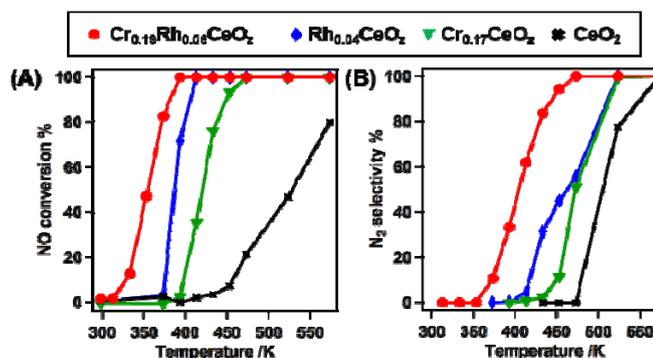


Figure 1. (A) NO conversion and (B) N_2 selectivity for NO reduction with CO on $\text{Cr}_{0.19}\text{Rh}_{0.06}\text{CeO}_x$, $\text{Rh}_{0.04}\text{CeO}_x$, $\text{Cr}_{0.17}\text{CeO}_x$, and CeO_2 .

P-47

Preparation and Catalytic Performances of Copper and Ruthenium Incorporated Ceria

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We prepared a Cu and Ru-incorporated ceria catalyst (denoted as $\text{Cu}_{0.17}\text{Ru}_{0.05}\text{CeO}_z$) which maintained the fluorite structure of CeO_2 from XRD and TEM. $\text{Cu}_{0.17}\text{Ru}_{0.05}\text{CeO}_z$ exhibited highest catalytic activities on ammoxidation of benzyl alcohol over $\text{Cu}_{0.18}\text{CeO}_z$ and $\text{Ru}_{0.04}\text{CeO}_z$ incorporated with only Cu or Ru, and CeO_2 without Cu and Ru. It showed not only the highest yield for benzonitrile (90 %, 24 h) 423 K by using O_2 (1 MPa) as an oxidant and aqueous NH_3 as a nitrogen source. The recycling test of $\text{Cu}_{0.17}\text{Ru}_{0.05}\text{CeO}_z$ showed stable catalytic activity.

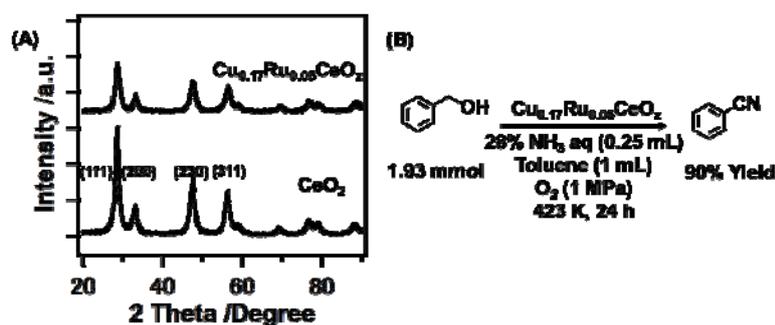


Figure 1 (A) XRD peak pattern of $\text{Cu}_{0.17}\text{Ru}_{0.05}\text{CeO}_z$. (B) Catalytic performances for ammoxidation of benzyl alcohol on $\text{Cu}_{0.17}\text{Ru}_{0.05}\text{CeO}_z$.

Thematic Poster

P-48

Preparation and Luminescent Properties of Surface-Attached Chiral Tb Complexes

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We investigated a new preparation method of surface-attached chiral metal complex and the inducement of solid-state circularly polarized luminescence (CPL) by using luminescent achiral terbium (Tb) complex and chiral ligand attached on silica surface. A new chiral benzyl alcohol ligand was synthesized and successfully attached on silica surface. Then, achiral Tb complex (1_{Tb})⁽¹⁾ was grafted on the prepared surface-attached chiral ligand (L(R/S)/SiO_2), and the coordination of the Tb complex to the chiral ligand moiety was confirmed with UV-vis spectra and quantification of eliminated ligand. Luminescent properties of the surface-attached Tb complexes ($1_{\text{Tb}}/\text{L(R/S)/SiO}_2$) were evaluated with solid-state CPL spectra.

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

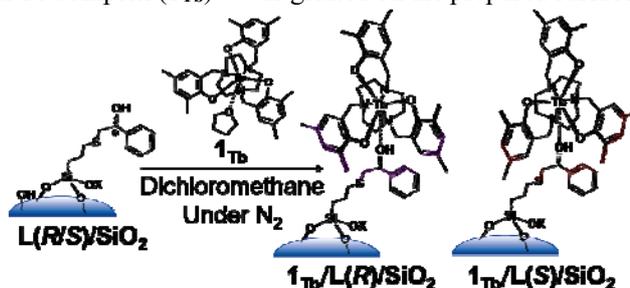


Figure 1. Preparation scheme of surface-attached chiral Tb complex ($1_{\text{Tb}}/\text{L(R/S)/SiO}_2$) by the coordination of 1_{Tb} to L(R/S)/SiO_2 .



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