

Symposium | Special Program : Lectureship Award MBLA 20th Anniversary Special Lectures

📅 Tue. Mar 19, 2024 1:00 PM - 3:40 PM JST | Tue. Mar 19, 2024 4:00 AM - 6:40 AM UTC 🏠 G01(Room [L], Auditorium)

[G01-2pm] Lectureship Award MBLA 20th Anniversary Special Lectures

Lectureship Award MBLA 設立20 年を機に講演会を開催する。本講演会では、直近のMBLA 受賞者の最先端研究に加えて各人の研究マインドやビジョンを、また特別講演として山本尚先生からイノベーションを生む研究についてお話いただく計画である。MBLA 受賞者は、独創的で卓越した研究成果を次々に挙げているだけでなく、欧米の一流研究機関を巡る講演ツアーを経験し、国際性においても大変優れた資質を兼ね備え、まさに次世代研究者の目標となる存在である。山本尚先生の高い視座からのメッセージとともに、日本化学会に集う若手研究者がこれらの講演の聴講によって、この上ない刺激を受けることは間違いないであろう。本会は国際競争力のある高度人材養成の方向性を再確認する絶好の機会であり、日本の有機化学分野の発展並びに人材育成に大きな貢献をもたらすことを確信している。

📌 English

1:00 PM - 1:15 PM JST | 4:00 AM - 4:15 AM UTC

[G01-2pm-01]

A Catalyst for Epigenome Sensing and Regulation

○Kenzo Yamatsugu¹ (1. Chiba University)

📌 English

1:15 PM - 1:30 PM JST | 4:15 AM - 4:30 AM UTC

[G01-2pm-02]

Radical-based Transformations through Reductive Carbon–Sulfonyl Bond Activation

○Masakazu Nambo¹ (1. Nagoya University)

📌 English

1:30 PM - 1:45 PM JST | 4:30 AM - 4:45 AM UTC

[G01-2pm-03]

Photocatalytic Reactivity of Zwitterions

○Kohsuke Ohmatsu¹ (1. Nagoya University)

📌 English

1:45 PM - 2:00 PM JST | 4:45 AM - 5:00 AM UTC

[G01-2pm-04]

Extended Umpolung: Aromatic, Nitrogen, Phosphorus, and Beyond

○Koji Hirano¹ (1. Graduate School of Engineering, Osaka University)

📌 English

2:00 PM - 2:15 PM JST | 5:00 AM - 5:15 AM UTC

[G01-2pm-05]

Exploring Novel Nonbenzenoid Hydrocarbons toward Unusual Yet Stable Optoelectronic Materials

○Aiko Fukazawa¹ (1. Kyoto University)

2:15 PM - 2:25 PM JST | 5:15 AM - 5:25 AM UTC

Break

📌 English

2:25 PM - 2:40 PM JST | 5:25 AM - 5:40 AM UTC

[G01-2pm-06]

New Research Playground after MBLA

○Naoya Kumagai¹ (1. Keio University)

◆ English

2:40 PM - 2:55 PM JST | 5:40 AM - 5:55 AM UTC

[G01-2pm-07]

Supramolecular Assemblies and Systems Based on Pillar-Shaped Macrocyclic Compounds
"Pillar[n]arenes"

○Tomoki Ogoshi^{1,2} (1. Grad. Sch. Eng., Kyoto Univ., 2. WPI-NanoLSI, Kanazawa Univ.)

◆ English

2:55 PM - 3:10 PM JST | 5:55 AM - 6:10 AM UTC

[G01-2pm-08]

Reactivity prediction based on quantum chemical calculations

○Satoshi Maeda¹ (1. Hokkaido University)

◆ English

3:10 PM - 3:25 PM JST | 6:10 AM - 6:25 AM UTC

[G01-2pm-09]

Exploration of New Molecular Catalysis and Reactivity

○Jun Takaya¹ (1. Tokyo Institute of Technology)

◆ Japanese

3:25 PM - 3:40 PM JST | 6:25 AM - 6:40 AM UTC

[G01-2pm-10]

Disruptive Innovation

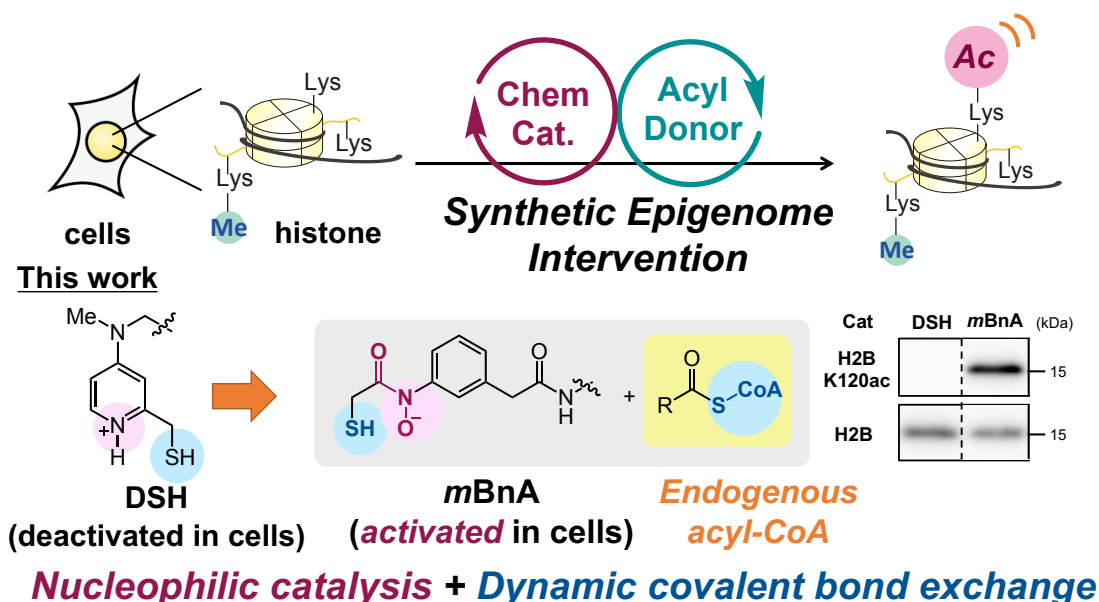
○Hisashi Yamamoto¹ (1. Chubu University)

A Catalyst for Epigenome Sensing and Regulation

(¹Graduate School of Pharmaceutical Sciences, Chiba University) ○Kenzo Yamatsugu¹

Keywords: Catalyst; Epigenome; Histone; Acylation; acetyl-CoA

Life emerges from biomolecules and a network of chemical reactions among them. Post-translational modifications of histone proteins are the representative. They regulate gene transcription and thus form the basis of epigenome. We have been developing chemical catalysts that acylate histone proteins in living cells to synthetically regulate the epigenome.¹ If successful, it will be a new way to regulate life and will also serve as a useful cell biology tool. In this talk, I will discuss a catalyst enabling in-cell histone lysine acylation with endogenous acyl-CoA as the sole acyl donor.² Its application to sense in-cell acyl-CoA concentration under various environmental stimuli will also be disclosed.



1) a) Y. Amamoto, Y. Aoi, N. Nagashima, H. Suto, D. Yoshidome, Y. Arimura, A. Osakabe, D. Kato, H. Kurumizaka, S. A. Kawashima, K. Yamatsugu, M. Kanai, *J. Am. Chem. Soc.* **2017**, *139*, 7568. b) Y. Fujiwara, Y. Yamanashi, A. Fujimura, Y. Sato, T. Kujirai, H. Kurumizaka, H. Kimura, K. Yamatsugu, S. A. Kawashima, M. Kanai, *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2019554118. c) C. Adamson, H. Kajino, S. A. Kawashima, K. Yamatsugu, M. Kanai, *J. Am. Chem. Soc.* **2021**, *143*, 14976. d) K. Yamatsugu, S. A. Kawashima, M. Kanai, *Curr. Opin. Chem. Biol.* **2018**, *46*, 10. 2) M. Habazaki, S. Mizumoto, H. Kajino, T. Kujirai, H. Kurumizaka, S. A. Kawashima, K. Yamatsugu, M. Kanai *Nat. Commun.* **2023**, *14*, 5790.

Radical-based Transformations through Reductive Carbon–Sulfonyl Bond Activation

(¹*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University*)

○ Masakazu Nambo¹

Keywords: Sulfone; Radical; C–SO₂ bond activation; Photoredox catalysis; Alkylation

Organosulfones are versatile intermediates in organic synthesis because of the ease with which they permit facile structural modification through α -functionalization or conjugate addition.¹ Due to the inherent stability of sulfonyl groups, strong reducing agents such as Na amalgam and Mg are generally required for their removal. Recently, organosulfones have attracted considerable attention in cross-coupling reactions as a new class of electrophiles.² Our group and others have developed several transition-metal catalyzed cross-coupling reactions of functionalized aromatic and benzylic sulfones via carbon–sulfonyl (C–SO₂) bond activation.^{2c} Substituents on the sulfonyl group were found to provide a powerful new avenue for controlling reactivity. Building on these reports, next we envisioned that a controlled single electron reduction of sulfones would have the potential to establish a new method for the generation of carbon radicals in organic synthesis and expand the utility of sulfones. In this presentation, we will present a radical-based transformations through reductive C–SO₂ bond activation of sulfones.

1. Giese reaction via reductive desulfonylation of alkylsulfones

We have developed a simple method for the conversion of tertiary alkylsulfones to tertiary alkyl radicals, and their alkylation to generate quaternary carbon centers.³ The Giese reaction proceeds efficiently using readily available Zn powder with 1,10-phenanthroline (phen) as a new single electron reducing agent. The tetrazolyl group on the sulfonyl group was found to be an effective substituent for radical generation. A variety of quaternary products could be synthesized from tertiary alkylsulfones and electron-deficient olefins. And substrates in which the olefin moieties were introduced by α -alkylation of secondary sulfones can be employed in an intramolecular Giese reaction, giving interesting spiro compounds. The radical generation process involving a single electron transfer and subsequent fragmentation of sulfone radical was investigated by control experiments and theoretical calculations.

2. Desulfonylative transformations by visible-light photoredox catalysis

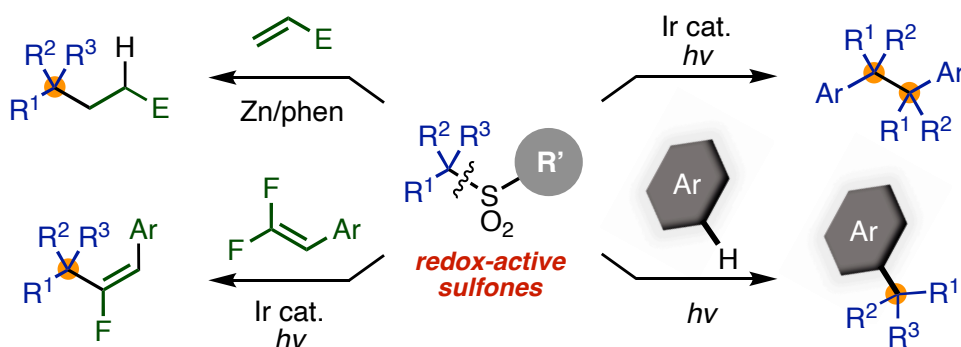
Building on our previous work with regards to the application of sulfones in catalysis, we found that visible-light photoredox catalysts can be employed to promote the reductive desulfonylation of tertiary alkylsulfones and their reaction with *gem*-difluoroalkenes.⁴ Notably, this method produces thermodynamically unfavorable *E*-fluoroalkenes as the major products in one-pot, compounds that are difficult to synthesize by traditional routes. Investigation of the origin of stereoselectivity indicates that the Ir catalyst also promotes photocatalytic *Z/E*

isomerization of initially generated *Z*-isomers to give the observed *E*-isomers.

When benzylic sulfones were used instead of alkyl sulfones, the desulfonylative homocoupling proceeded smoothly.⁵ This method enables the facile synthesis of a variety of multiply-arylated ethanes, including those functionalized with deuterium or fluorine at the benzylic position prior to cross-coupling, which provides interesting motifs in medicinal chemistry.

3. Visible-light-induced direct C–H alkylation of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are fragments of graphene that have attracted considerable attention as a new class of carbon-based materials. The functionalization of edge positions in PAHs is important to enable the modulation of physical and chemical properties essential for various applications. However, straightforward methods that combine functional group tolerance and regioselectivity remain sought after. We have developed a photochemical approach for the direct alkylation of carbon–hydrogen bonds in PAHs that takes place in a regiospecific manner, an outcome that has never been achieved in the related thermal reactions.⁶ A reaction mechanism involving a single electron transfer process from photo-excited PAHs to sulfones, and a rationale for the origin of regioselectivity are proposed on the basis of spectroscopic analyses and theoretical calculations.



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- 4) a) M. Nambo, K. Ghosh, J. C.-H. Yim, Y. Tahara, N. Inai, T. Yanai, C. M. Crudden, *ACS Catal.* **2022**, *12*, 9526. b) Y. Tahara, K. Ghosh, M. Nambo, *Can. J. Chem.* **2023**, *101*, 491.
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- 6) Manuscript in preparation.

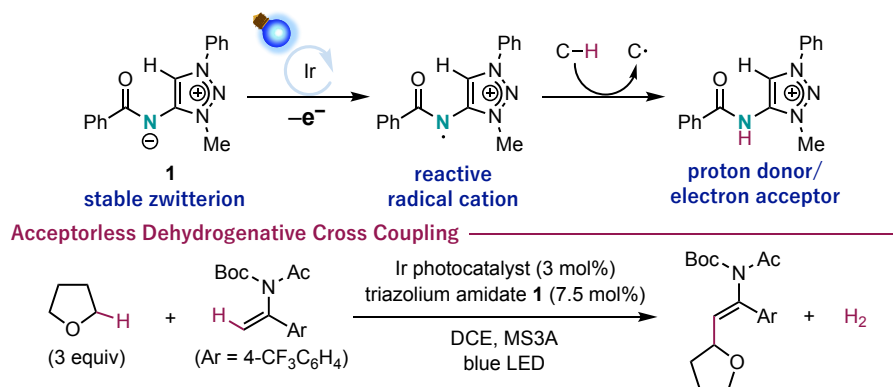
Photocatalytic Reactivity of Zwitterions

(¹*Institute of Transformative Bio-Molecules (ITbM) and Graduate School of Engineering, Nagoya University*) ○Kohsuke Ohmatsu¹

Keywords: Radical, Photoredox Catalysis, Zwitterion, C–H Functionalization

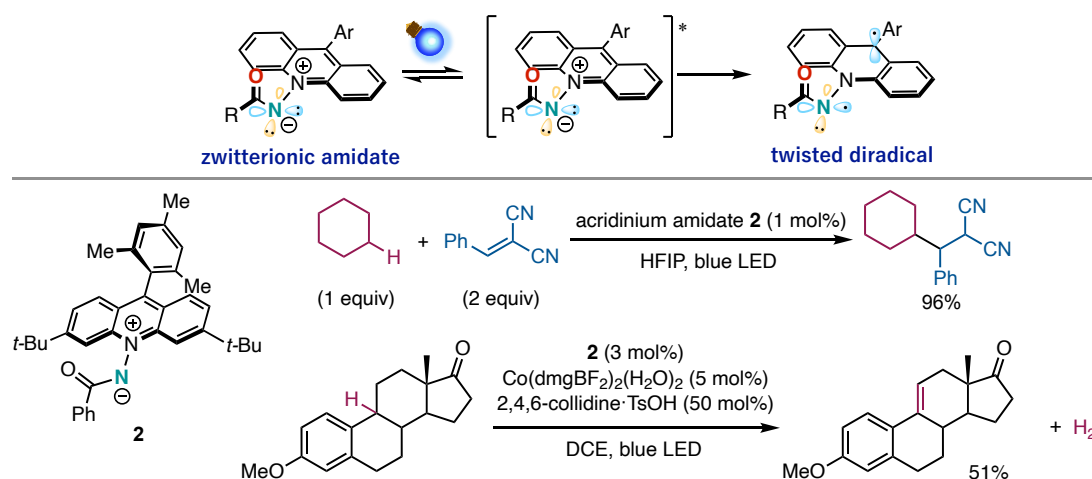
Zwitterions, which have both positive and negative charges in a single molecular framework, often exhibit unique properties such as large polarization, high crystallizability, and strong ionic interaction. These properties enable the application of zwitterions in a various field of chemical sciences. Another important aspect is their stability. Compared to typical cations and anions, zwitterions are generally easy to generate and often isolable owing to the stabilization by the inductive and resonance effects. From the viewpoint of synthetic chemistry, such stable species are usually unsuitable for the use as catalysts and reagents because they do not show notable reactivity. However, since highly polarized zwitterions efficiently undergo single electron transfer (SET) processes to generate the reactive radical ion species, zwitterions can be regarded as the easy-to-handle precursors of highly active intermediates. In light of this consideration and our research program on the design of ionic organic molecular catalysts,¹ we have been interested in the characteristic features of zwitterions, particularly in their potential reactivity exerted via photocatalytic activation.

One of our recent studies is the catalyst and reaction development by harnessing the reactivity of electron-deficient radical cations generated from the stable zwitterions through photocatalytic SET. For instance, we have devised a bench-stable, zwitterionic 1,2,3-triazolium amidate **1** and achieved catalytic hydrogen-atom transfer (HAT) reactions based on the generation of the amidyl radical via intermolecular SET with a photocatalyst. Furthermore, the discovery that the conjugate acid of the triazolium amidate, 1,2,3-triazolium amide, behaves as a one-electron acceptor and oxidatively regenerates photocatalysts with dehydrogenation has led to the development of acceptorless dehydrogenative cross-coupling (ADC) reactions.²



While triazolium amidate is effective for photoinduced HAT with a range of aliphatic C–H bonds, its intrinsic reactivity has yet to be fully elicited because the actual concentration of amidyl radicals generated in the intermolecular SET is extremely low. To overcome this problem, we have pursued an approach toward more efficient HAT directly triggered by the photoexcitation of zwitterions.

Photoinduced direct hydrogen atom transfer, termed d-HAT, has been regarded as an ideal strategy owing to its high catalyst economy and broad applicability.³ The existing catalysts capable of undergoing d-HAT uniformly rely on molecular entities containing oxo groups (Z=O), such as aromatic ketones, xanthene dyes, and inorganic metal oxo complexes, thus being constrained to oxygen-centered radicals. This restriction poses inherent difficulty in enhancing the reactivity of the d-HAT catalysts owing to the limited possibility of structural modification around the oxo-groups. On the other hand, unlike oxo-containing molecules, their nitrogen analogs lack an ability to exert d-HAT catalysis, and no reliable strategy has been available to endow them with pertinent photocatalytic reactivity to promote HAT reactions. Under these circumstances, we have developed zwitterionic acridinium amidates as photoreactive amidyl radical precursors, which exert prominent reactivity as d-HAT catalysts. The key to our catalyst design was the perpendicular orientation of the acridinium 2p orbitals and lone pair in the 2p orbital of the amidate nitrogen. This enabled the generation of a twisted diradical consisting of reactive amidyl radicals and stable acridinyl radicals as HAT-active species via photoexcitation and intramolecular charge transfer.⁴



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- 4) L.-M. Entgelmeier, S. Mori, S. Sendo, R. Yamaguchi, R. Suzuki, T. Yanai, O. García Mancheño, K. Ohmatsu, T. Ooi, *ChemRxiv* **2023**, doi: 10.26434/chemrxiv-2023-pj884

Extended Umpolung: Aromatic, Nitrogen, Phosphorus, and Beyond

(Graduate School of Engineering, Osaka University) ○Koji Hirano

Keywords: organic synthetic chemistry; bond formation; umpolung; heteroatoms; direct C-H coupling

The development of new bond forming strategies is the most fundamental but the most important research subject in synthetic organic chemistry. In general, chemists understand the polarity of two organic fragments and successfully connect one to the other. Namely, one is a negatively polarized nucleophile, and the other is a positively polarized electrophile. Such nucleophilic or electrophilic character is fundamentally dependent on the inherent polarity of functional groups or elements themselves. However, if the inherent polarity is inverted, highly challenging bond-forming reactions can be achieved. This polarity inversion concept is known as *umpolung* and was originally proposed by Corey and Seebach, where the inherently electrophilic aldehyde was inverted to the nucleophilic acyl fragment via dithioacetalization/deprotonative electrophilic substitution/deprotonation sequence.¹

Our research group focused on the conceptual extension of *umpolung* and successfully developed several new bond forming reactions based on the concept of *extended umpolung*: i) copper-promoted oxidative aromatic C–H coupling via aromatic *umpolung*,² ii) highly selective copper-catalyzed electrophilic amination reactions via nitrogen *umpolung*,³ and iii) electrophilic phosphination reactions via Tf₂O-mediated phosphorus *umpolung*.⁴

Here, recent advances, particularly, highly chemo- and stereoselective alkoxylation reactions based on oxygen *umpolung* will be presented.

1) a) D. Seebach, E. J. Corey, *J. Org. Chem.* **1975**, *40*, 231. b) D. Seebach, *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

2) Accounts and reviews: a) K. Hirano, M. Miura, *Chem. Commun.* **2012**, *48*, 10704. b) K. Hirano, M. Miura, *Top. Catal.* **2014**, *57*, 878. c) K. Hirano, M. Miura, *Chem. Lett.* **2015**, *44*, 868.

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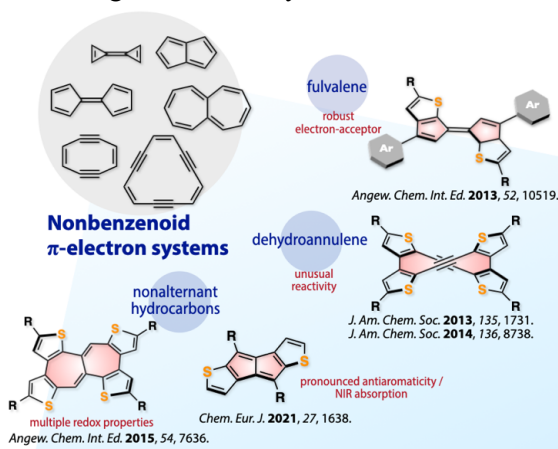
Exploring Novel Nonbenzenoid Hydrocarbons toward Unusual Yet Stable Optoelectronic Materials

(¹WPI-iCeMS, Kyoto University) ○Aiko Fukazawa¹

Keywords: π -Conjugation; Nonbenzenoid hydrocarbons; Aromaticity; Antiaromaticity; Redox properties

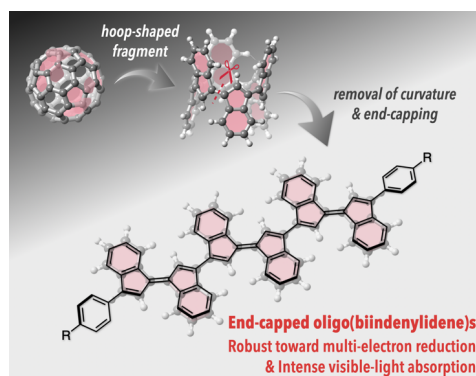
Advancements made to date in organic optoelectronic materials are primarily attributed to aromatic hydrocarbons and their heteroaromatic analogs. These classes of compounds are highly valued for their high thermal and chemical stability as well as the desirable properties, and have stimulated the development of various synthetic methodologies, resulting in a wide variety of molecular materials. However, to achieve properties and functionalities beyond the capabilities of existing organic materials, innovative molecular designs and exploration into uncharted chemical spaces are crucial. In this context, nonbenzenoid hydrocarbons and related cross-conjugated π -electron systems are an attractive class of compounds due to their characteristic properties such as long-wavelength absorption, multistep redox properties, and distinctive behaviors in excited states, most of which are difficult to attain with benzenoid π -electron systems of comparable molecular weight. Despite their potential, nonbenzenoid π -electron systems remained unexplored as optoelectronic materials due to the difficulty in their synthesis, high reactivity, and a lack of guiding principles for molecular aimed at material applications. Our motivation is to explore the potential of nonbenzenoid π -electron systems as game-changing building blocks for next-generation functional materials, tackling the longstanding issues from three perspectives: to ensure stability without bulky substituents, to develop efficient synthetic methods, and to provide molecular design guidelines to harness their characteristic properties. This presentation will provide an overview of our strategies and some of the recent research along two major topics as follows:

1. Strategy for the stabilization of labile nonbenzenoid π -conjugated systems without using bulky substituents. To address the first challenge in a stability issue, we have been focusing on the molecular design based on the annulation of weakly aromatic rings such as thiophene and phenanthrene on the nonbenzenoid hydrocarbons in a ring-fused manner. Based on this strategy, we have so far succeeded in synthesizing stable yet unusual π -conjugated systems including dehydroannulenes,¹ a nonaromatic² and antiaromatic nonalternant hydrocarbons,^{3,4} and fulvalene.⁵ Notably, the annulation of thiophene rings rendered these nonbenzenoid



π -electron systems high thermal stability even without bulky substituents, while maintaining the inherent characteristics of the parent π -systems. This molecular design thereby allowed us to access thermochromic behavior in near-infrared region based on exciton interactions even in solution,^{3a} as well as the dense packing in the solid state.^{3b} It should be also noted that most of these ring-fused nonbenzenoid π -electron systems cannot be synthesized by known methods, and we explored several new reactions and synthetic strategies for their synthesis.^{1,2,4,5}

2. Novel molecular design concepts. A significant challenge lies in translating the diverse structures and properties of nonbenzenoid π -electron systems into the molecular designs for groundbreaking materials. In this context, we have recently designed and synthesized the oligo(biindenylidene)s, π -conjugated hydrocarbons that are composed of flattened one-dimensional fragments of fullerene C₆₀. Notably, the oligo(biindenylidene)s exhibit high electron affinity and the robustness against multi-electron reduction comparable to fullerenes only based on hydrocarbon scaffolds.⁶ This molecular design is complementary to the conventional design of electron-accepting π -electron systems, by introducing many electron-withdrawing groups into an inherently electron-donating π -electron system. Given their potential for further structural diversification, our molecular design concepts described above would be new fundamentals in the chemistry of electron acceptors. In this presentation, I will also describe some of our recent studies based on this strategy.⁷⁻⁹



References

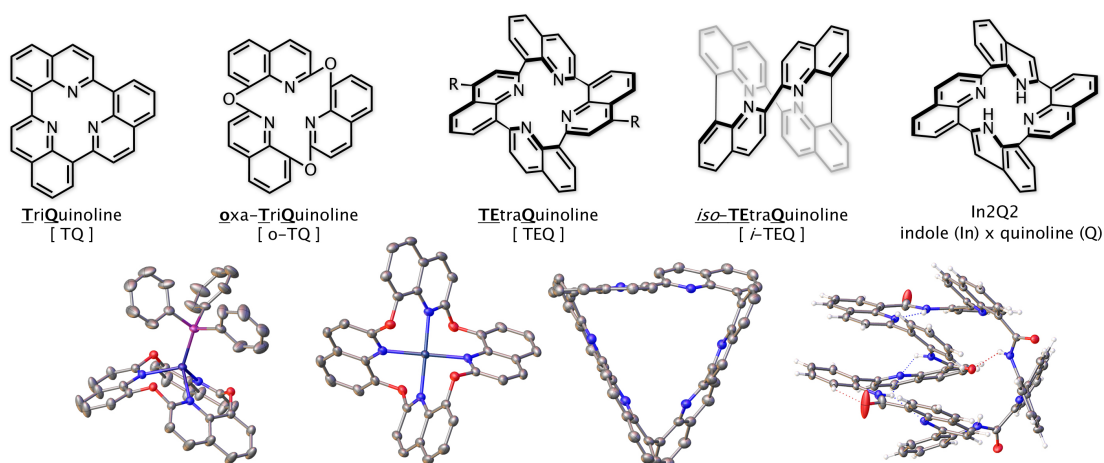
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New Research Playground After MBLA

(¹Graduate School of Pharmaceutical Sciences, Keio University, ²Institute of Microbial Chemistry) ○Naoya Kumagai^{1,2}

Keywords: quinoline; multidentate; macrocycles; fluorescence; supramolecular chemistry

MBLA is a perfect opportunity to change the direction of main research field for young chemists. After ca. 20 years of exploration in asymmetric catalysis, our group is now motivated to design and synthesize quinoline-based cyclic oligomers to develop a new family of functional small molecules. The simplest cyclic trimer, TriQuinoline (TQ), tightly captures proton at the center of the molecule and the resulting cationic aromatic material renders supramolecular complexation via π - π /CH- π interactions in polar media. Embedding oxygen atoms between quinoline units allows TQ to acquire a non-flat architecture, and the thus-formed oxa-TriQuinoline (o-TQ) serves as a bowl-shaped tridentate ligand to Cu(I), exhibiting catalysis, supramolecular complexation, and aggregation-induced emission.¹ Simple incrementation of a quinoline unit gave rise to a saddle-shaped rigid tetramer, TEtraQuinoline (TEQ), which is regarded as a chiral C_2 -symmetric porphyrin-like material.² A distinct quinoline tetramer with alternative ring connectivity, *iso*-TEQ, and an indole and quinoline hybrid molecule, In2Q2, are also presented. Other unpublished fun molecules are also discussed with their unique X-ray structures and functions.



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Supramolecular Assemblies and Systems Based on Pillar-Shaped Macrocyclic Compounds “Pillar[*n*]arenes”

(¹Graduate School of Engineering, Kyoto University, ²WPI-NanoLSI, Kanazawa University)

○Tomoki Ogoshi^{1,2}

Keywords: Pillar[*n*]arenes; Host–guest property; Functionalization; Supramolecules

Pillar[*n*]arenes have become one of the important key players in supramolecular chemistry. In this study, organic reactions based on molecular recognition in crystalline pillar[*n*]arenes are introduced. First, complexation of linear polymer chains using crystalline state pillar[*n*]arenes is discussed. Using the complexation in crystalline state, ring-opening polymerization of cyclic monomers is also discussed. Second, formation of planar-chiral inter-locked molecules resulting from supramolecular structures in solid state is discussed.

Complexation of linear polymers using crystalline pillar[5]arenes: Pillar[5]arenes have a π -electron-rich space enclosed by π -planes. Consequently, multiple C–H/ π interactions work with guest molecules with C–H groups. Almost all organic compounds and polymers contain C–H groups, thus pillar[5]arenes can encapsulate nearly all organic compounds and polymers with suitable size for their cavity. However, C–H/ π interactions are inherently weak in normal solvent system. For instance, polyethylene oxide (PEO) has a thickness of approximately 3.7 Å, which fits within the pore size of pillar[5]arene (approximately 4.7 Å). However, pillar[5]arene **1** cannot form complex with PEO in solvent system. In the solvent system, solvation inhibited the complexation due to the weak nature of C–H/ π interactions. On the other hand, when polyethylene oxide (PEO) was melted and directly immersed in crystalline pillar[5]arene **1**, crystalline pillar[5]arene **1** took up PEO. In this system, weak multiple C–H/ π interactions work for the complexation due to no solvation. Interestingly,

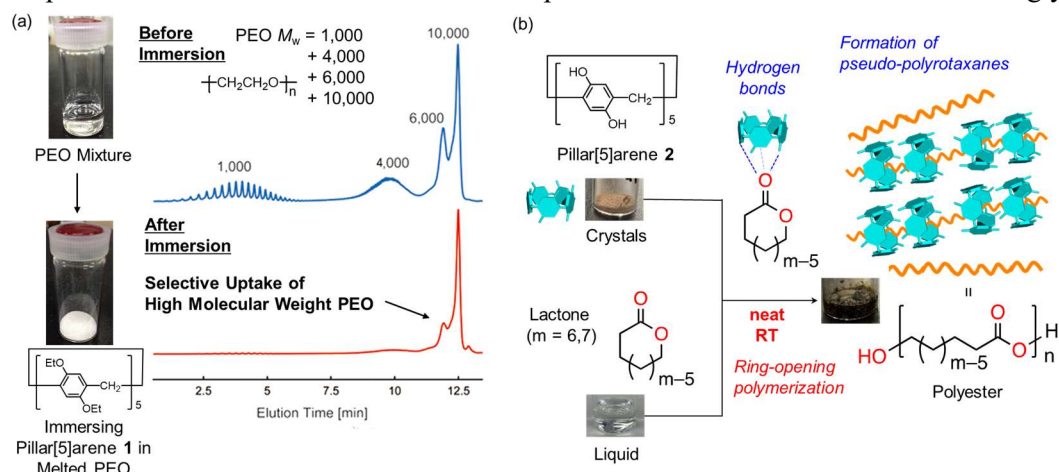


Figure 1 (a) High mass fractionation by crystalline pillar[5]arene **1**. Liquid chromatography traces of an equal-weight mixture of PEOs (upper) and host–guest complex crystals after the immersion in the mixture (lower). (b) Ring-opening polymerization of lactones with crystalline pillar[5]arene **2** and formation of pseudo-polyrotaxanes.

when PEO containing various molecular weights was immersed, crystalline pillar[5]arene **1** selectively took up high-molecular-weight PEO.¹⁾ The complexation with linear polymer can be used for initiation of polymerization. When lactone monomers were directly immersed in crystalline pillar[5]arene with phenolic groups **2**, ring-opening polymerization occurred (Figure 1b), while the polymerization did not occur with solvent. The results were obtained because the phenolic hydroxy groups have catalytic activity via hydrogen bonds and the pillar[5]arene cavities prefer linear guests. After the reaction, pillar[5]arenes **2** and polyesters formed pseudo-polyrotaxanes.²⁾

Planar-chiral inter-locked molecules from supramolecular structures in solid states:

Pillar[*n*]arenes exhibit planar chirality i.e., *pS* and *pR* forms, due to the position of the alkoxy groups. Pillar[5]arene with (*S*)-2-methylbutoxy groups in the side chains **3** (Figure 2) exhibits diastereomeric relationships referred to as (*S*, *pR*)-**3** and (*S*, *pS*)-**3**, and two diastereomers can interconvert in solution via the rotation of benzene units (stereodynamic). As a result, an energy difference is generated between *pR* and *pS* forms and the *pR/pS* ratio can be changed by inversion between the (*S*, *pR*) and (*S*, *pS*) forms. However, in our previous work, pillar[5]arene **3** with high *pR/pS* ratios could not be generated even in various solvents. This is because the energy difference between (*S*, *pR*)-**3** and (*S*, *pS*)-**3** is too small in solution to show diastereoselectivity. However, when crystallization of **3** was conducted in the presence of long axis C16 with amino groups at both ends, a [3]pseudorotaxane was obtained, where two (*S*, *pS*)-**3** rings penetrated one axle. [3]Pseudorotaxanes consisting of either two (*S*, *pS*)-**3**, two (*S*, *pR*)-**3**, or (*S*, *pS*)-**3** and (*S*, *pR*)-**3** wheels are the three possible supramolecular diastereomers. By the co-crystallization, the [3]pseudorotaxane consisting of two (*S*, *pS*)-**3** wheels diastereoselectively formed in the solid state because higher effective molarity worked in the solid state with aid by packing effects to form the [3]pseudorotaxane, and the [3]pseudorotaxane consisting of two (*S*, *pS*)-**3** wheels was most stable among the three [3]pseudorotaxane diastereomers. Subsequent end-capping reactions of the polycrystalline [3]pseudorotaxane with high *de* in solvent-free conditions successfully yielded rotaxanes while maintaining the high *de* generated by the co-crystallization.³⁾

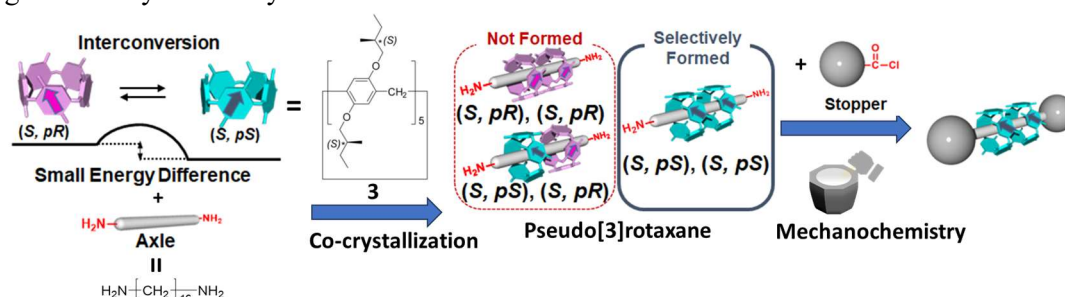


Figure 2 Selective formation of the [3]pseudorotaxane with two (*S*, *pS*)-**3** wheels by the co-crystallization and chiral [3]rotaxane formation by the mechanochemical reaction in the solid state.

1) *Nature Commun.* **2019**, 10, 479. 2) *Angew Chem. Int. Ed.* **2022**, 61, e202212874. 3) *J. Am. Chem. Soc.* **2023**, 145, 15324.

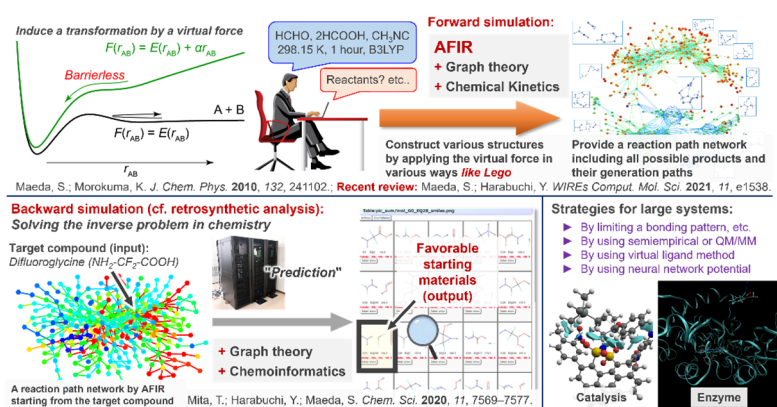
Reactivity Prediction Based on Quantum Chemical Calculations

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Keywords: Quantum Chemistry; Reaction Path; Reaction Design and Discovery

The motion of atoms during a chemical reaction, hereafter referred to as the reaction path, can in principle be elucidated by repeated quantum chemical calculations in all energetically feasible atomic configurations. However, the number of possible atomic arrangements involved in a reaction path can be enormous. Previous studies have therefore relied on assumptions, i.e., human input, about the atomic configurations along the reaction path under consideration. To address this problem, we have developed an automated reaction path search method called artificial force induced reaction (AFIR) [1]. AFIR automatically explores possible reaction paths by systematically inducing geometric transformations in a molecule using a virtual force, providing a network of reaction paths.

When AFIR is combined with a chemical kinetics method called rate constant matrix contraction (RCMC) [2], on-the-fly kinetic simulation can be performed [3]. Both forward and backward modes are available in on-the-fly kinetic simulations [3]. The forward mode starts the search from a given reactant and proceeds towards possible products. On the other hand, the backward mode starts the search from a given product towards possible reactants that give the product with high yields. Finally, the forward mode predicts all possible products along with their reaction yields and the backward mode predicts all possible reactants along with the yields of the input product in reactions from these reactants. In my talk, I will discuss the forward and backward on-the-fly kinetic simulations [3] shown in Figure 2 and their applications to real reaction discovery [4].



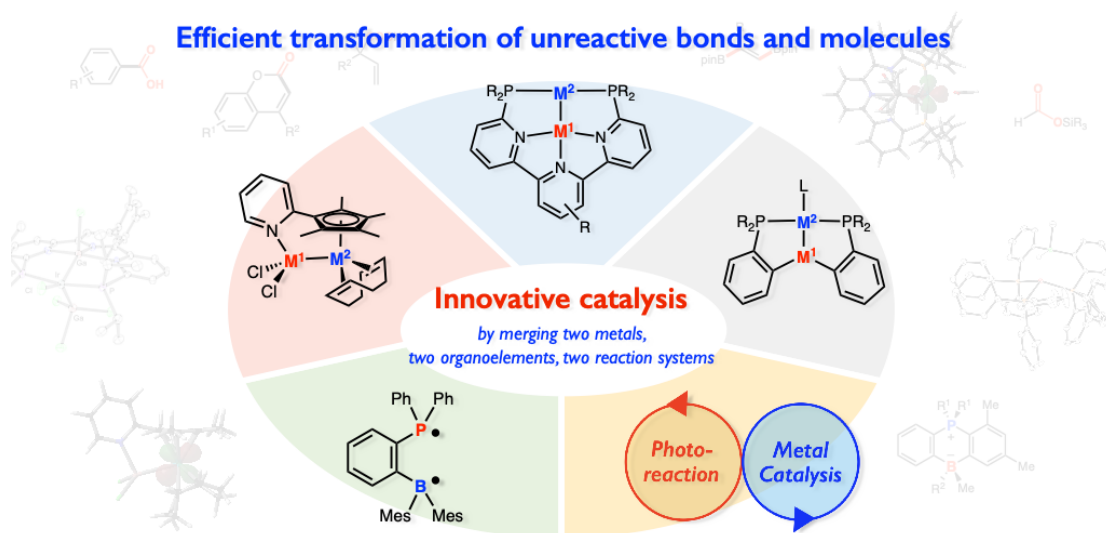
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Exploration of New Molecular Catalysis and Reactivity

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Keywords: Bimetallic Complexes; Ambiphilic Compounds; Photoexcitation; Cooperation;

Creation of innovative catalysts and reactive species that enable efficient transformation of unreactive bonds and molecules has been a formidable challenge in synthetic chemistry and catalysis science. We have been working on design, synthesis, and utilization of heterobimetallic transition metal catalysts having metal-metal bonds supported by precisely designed organic scaffolds, which enable efficient transformation of carbon dioxide and other organic molecules.¹ One of successful examples was demonstrated in hydrosilylation of carbon dioxide, where an Al–Pd bimetallic complex exhibited the highest catalytic activity ever reported.² We also achieved an unprecedented C–C σ -bond cleavage reaction of ambiphilic phosphine-borane compounds under photoirradiation conditions enabled by transiently generated excited Frustrated Lewis Pairs.^{3,4} Furthermore, we have demonstrated that the new cooperative catalysis merging photochemistry and transition metal catalysis enables unprecedented C–C σ -bond cleavage and functionalization of arylketones.⁵ In this presentation, recent progresses on these chemistry focusing on transformation of carbon dioxide and unreactive C–C σ -bonds will be discussed.



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破壊的イノベーション

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Disruptive innovations (¹ Peptide Research Center, Chubu University) ○Hisashi Yamamoto¹

To solve 30-years problem of Japan, several difficult problems should be solved. The most important key is to start destructive innovation as soon as possible. Unfortunately, government and companies in our country have sustainable innovation but not destructive innovation. Real innovation, that is destructive innovation can revive Japan. I would like to discuss how to introduce destruction innovation during my presentation.

Keywords : Destructive Innovation; Sustainable Innovation.

1980年代から続いた我が国の景気の悪い時代は、米国のグローバリゼーションなどの政策がその始まりを作ったと言われている。この状況を改善するには、我が国で破壊的イノベーションをできるだけ多く始める他ない。しかし、我が国の政府や産業界はリスクの多い破壊的イノベーションには極めて消極的である。基本的には持続的イノベーションで十分だと考えているが、これは大きな間違いである。持続的イノベーションだけでは、米国の統計では企業は数十年で倒産すると言われているからだ。一方、破壊的イノベーションが好景気を呼び込むのに、非常に効果的であることも実証されている。

MABL の受賞者のプロジェクトを見て、すぐにわかることは、一つ一つがしっかりとした本当の破壊的イノベーションを目指していることである。このスタンスを化学会の研究者が取り入れることができれば、我が国の将来は明るいものになるだろう。さらに強調したいことは、研究の目標を立てることが極めて重要であるが、目標は研究用語を使わずに縦書き 1 行で表現してほしい。目標は数週間で考えたものではなく、数ヶ月から数年かけて考えて欲しい。これに成功すれば、研究の成功は約束される。

1) イノベーションのジレンマ、技術革新が巨大企業を滅ぼすとき、クレイトン・クリステンセン、玉田俊平太監修・伊豆原弓訳