



広島大学

ABSTRACT



國立臺灣大學
National Taiwan University

Hiroshima University & National Taiwan University Joint Symposium on Chemistry

Saturday, March 19, 2022

from 8:50 to 16:50 (TWN time); 9:50 to 17:50 (JPN time)

via ZOOM in English

<https://zoom.us/j/97038632019?pwd=MW9mSzRZR1FudUdaQmcrM2Nnb012UT09>

Meeting ID: 970 3863 2019

Passcode: 610394



Hiroshima University & National Taiwan University

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Program and Schedule

8:50 – 9:00 TWN time (9:50 – 10:00) (JPN time)	Opening Address	Prof. Manabu Abe (HU) Prof. Jye-Shane Yang (NTU)
The 1st Session	Speaker. Title	Moderator
09:00 – 09:30 (10:00 – 10:30)	Dr. Takeharu Haino Edge-Functionalized Graphene Materials	Dr. Manabu Abe
09:30 – 10:00 (10:30 – 11:00)	Dr. Yi-Tsu. Chan 2D Porous Arrays Assembled from Giant Metallo-Supramolecular Cages	Dr. Jye-Shane Yang
10:00 – 10:30 (11:00 – 11:30)	Dr. Hiroto Yoshida Synthetic Chemistry with Lewis Acidity-Diminished Organoboron Compounds	Dr. Manabu Abe
10:30 – 11:00 (11:30 – 12:00)	Dr. Jeffery Farrell Warped and Boron-Doped sp ² -Hybridized Carbon Scaffolds via Electrophilic C-H Borylations	Dr. Jye-Shane Yang
The 2nd Session	Moderator	
12:30 – 13:00 (13:30 – 14:00)	Dr. Rong Shang Developments of Main-group Ligands for Transition Metal Complexes: a Journey of Unexpected Reactivity	Dr. Manabu Abe
13:00 – 13:30 (14:00 – 14:30)	Dr. Ching-Wen Chiu Group 13 Cations in Catalysis	Dr. Jye-Shane Yang
13:30 – 14:00 (14:30 – 15:00)	Dr. Shoko Kume Organic Layer Assembly on Cu Electrode toward Selective CO ₂ Electrolysis	Dr. Manabu Abe
14:00 – 14:30 (15:00 – 15:30)	Dr. Hao Ming Chen Potential-driven Dynamic Structures of Electrocatalysts	Dr. Jye-Shane Yang
The 3rd Session	Moderator	
14:40 – 15:10 (15:40 – 16:10)	Dr. Minori Abe Theoretical study of uranium isotope fractionation for 64 U compounds	Dr. Manabu Abe
15:10 – 15:40 (16:10 – 16:40)	Dr. Yuan-Chung Cheng Theoretical Simulations of Excitonic Dynamics in Molecular Systems: From Photosynthesis to Organic Materials	Dr. Jye-Shane Yang
15:40 – 16:10 (16:40 – 17:10)	Dr. Yoshiya Inokuchi Crown Ether Complexes with Ion Guests Studied by Cold, Gas-Phase Spectroscopy	Dr. Manabu Abe
16:10 – 16:40 (17:10 – 17:40)	Dr. Jerry Chun Chung Chan Phase Transformation and Structural Characterization of Amorphous Calcium Carbonate	Dr. Jye-Shane Yang
16:40 – 16:50	Closing Address	Prof. Jye-Shane Yang (NTU) Prof. Manabu Abe (HU)



Moderators



Manabu Abe (安倍 学) was born in Osaka, Japan. He received his Ph.D. from the Kyoto Institute of Technology with Professor Akira Oku, in 1995. In 1995, he became a faculty staff at Osaka University (Prof. Masatomo Nojima's group). From 1997–1998, he was an Alexander-von-Humboldt fellow with Professor Dr. Waldemar Adam at the Universität Würzburg. He was also a visiting researcher at the LMU München (Professor Dr. Herbert Mayr) in 2007. He moved to Hiroshima and became a full-time professor of Organic Chemistry at the Department of Chemistry, Hiroshima University in 2007. Associate Editor of Journal of Physical Organic Chemistry. His research focuses on reactive intermediates chemistry, especially on diradicals.



Jye-Shane Yang (楊 吉水), National Taiwan University (B.S. 1988; M.S. 1990), Northwestern University, USA (Ph.D. 1997), MIT (postdoct. 1998), Assistant Prof. (1998) and Associate Prof. (2002) of National Central University, Taiwan, Associated Prof. (2005) and Prof. (2007) of National Taiwan University (NTU). Chair (2013-2016) of the Chemistry Department of NTU. Visiting Prof. of Kyushu University (2012) and Kyoto University (2017). Editor-in-Chief (2021-present) of Journal of the Chinese Chemical Society (JCCS). Research Interest: light- and voltage-gated molecular machinery systems, photoluminescent organic and organometallic molecules, and electronic properties of π -conjugated oligomers and polymers.

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Edge-Functionalized Graphene Materials

Takeharu Haino

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Oxidatively exfoliated nano-size graphene is named as nanographene with a diameter of approximately 20 nm. There are oxygen functionalities such as carboxylic acid, carbonyl, phenol, etc. at the edge of nanographene, which can be converted to various functional groups. The edge-functionalization of the nanographene is a great method to modify their electronic properties. Our group has been continuously studying the chemical modification of nanographene.¹ White-light emission² and near-IR emission³ were established through the edge functionalization of nanographene. The basal plane of the nanographene was chirally twisted by the introduction of chiral auxiliaries to result in the circular dichroism in absorption.⁴ The introduction of hydrogen bonding groups at the edge resulted in supramolecular graphene gel.⁵ Supramolecular graphene polymers were fabricated through the self-assembly of functional nanographene.⁶ Recently, the triphenylamine groups were installed at the edge of nanographene, which showed electrochromic property that covered NIR region over 200 nm.⁷ This presentation will describe our recent progress in the post-synthetic modification of nanographene..

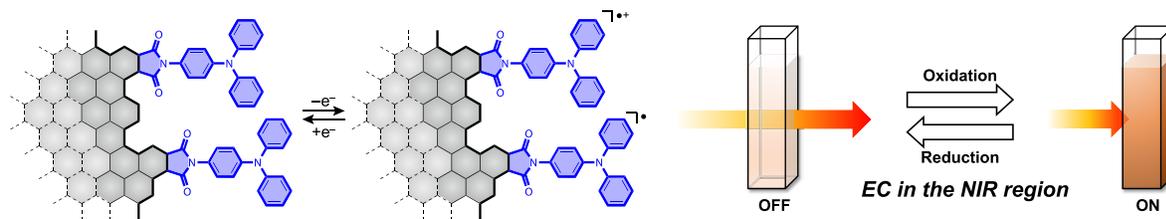


Figure 1. Electronic structures of nanographene upon oxidation and reduction, and schematic picture of electrochromic property.⁷ Reprinted and adapted from Ref. 7. Copyright 2022, Wiley-VCH, Weinheim.

- (1) Sekiya, R.; Haino, T. *Chem. Eur. J.* **2021**, *27*, 187-199.
- (2) Sekiya, R.; Uemura, Y.; Murakami, H.; Haino, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 5619-5623.
- (3) Yamato, K.; Sekiya, R.; Suzuki, K.; Haino, T. *Angew. Chem. Int. Ed.* **2019**, *58*, 9022-9026.
- (4) Nishitani, S.; Sekiya, R.; Haino, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 669-673.
- (5) Uemura, Y.; Yamato, K.; Sekiya, R.; Haino, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 4960-4964.
- (6) Matsumoto, I.; Sekiya, R.; Haino, T. *Angew. Chem. Int. Ed.* **2021**, *60*, 12706-12711.
- (7) Matsumoto, I.; Sekiya, R.; Fukui, H.; Sun, R.-D.; Haino, T. *Angew. Chem. Int. Ed.* **2022**, *61*, doi: anie.202200291.



Takeharu Haino (灰野岳晴)

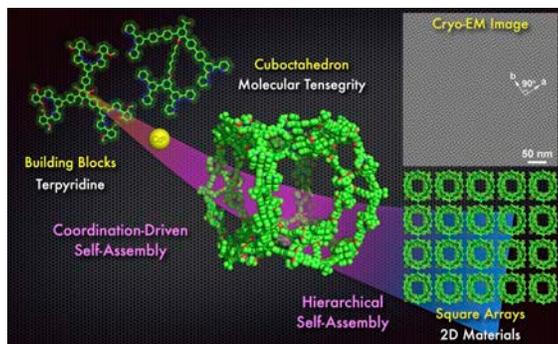
Distinguished Professor, Department of Chemistry, Hiroshima University (2021-) Hiroshima University (BS, 1987), Hiroshima University (Ph.D. 1992). Sagami Chemical Research Center (Post Doctorial Fellow, 1992-93), Assistant Professor, Department of Chemistry, Hiroshima University (1993-2000), The Scripps Research Institute (Post Doctorial Fellow, 1999-2000), Associate Professor (2000-2007), Full Professor (2007-). Research Interests: Supramolecular Chemistry, Polymer Chemistry, and Graphene Chemistry.

2D Porous Arrays Assembled from Giant Metallo-Supramolecular Cages

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Surface layers (S-layers) are commonly seen in prokaryotic organisms and play an important role in cell protection and surface interactions. These layers are composed of identical proteinaceous subunits that can self-assemble into ordered porous 2D arrays of 5-15 nm thickness and unit cell sizes in the range of 3-30 nm. To explore how protein motifs can be tiled into 2D crystalline materials, we researched porous layers assembled from artificially synthesized molecules of similar dimensions to explore the construction of giant well-defined building units. Inspired by Buckminster Fuller's concept of tensegrity (tensional integrity), we developed precise coordination-driven self-assembly methodologies¹ for the rational construction of a molecular cuboctahedron with a circumscribed sphere diameter of over 10 nm. The result not only marks a significant breakthrough in the area of chemical mimicry of S-layer self-assembly but is also the largest synthetic cuboctahedron reported to date.² The cuboctahedron is assembled from 76 subcomponents and has a double-layered structure, resembling a tensegrity architectural structure. It is worth mentioning that the high stability of the cuboctahedral complex enables small-angle X-ray scattering (SAXS) measurements under dilute conditions, providing crucial structural evidence. Moreover, we collaborated with the Academia Sinica Cryo-EM Center (ASCEM) to conduct cryo-EM experiments on the S-layer-like square arrays of the giant cuboctahedra in vitrified acetonitrile solution with a lattice constant of 7.9 nm. Through this experiment, such local packing defects as dislocations and grain boundaries in the 2D arrays were analyzed and elucidated. The general self-assembly methodology and the serendipitous observation of S-layer-like square arrays presented in this study not only exemplify scientific discovery but also lay the foundation for developing bottom-up techniques for the construction of 2D porous supramolecular materials.



[1] (a) J.-H. Fu, Y.-H. Lee, Y.-J. He, Y.-T. Chan, *Angew. Chem., Int. Ed.* **2015**, *54*, 6231–6235. (b) S.-Y. Wang, J.-H. Fu, Y.-P. Liang, Y.-J. He, Y.-S. Chen, Y.-T. Chan, *J. Am. Chem. Soc.* **2016**, *138*, 3651–3654. (c) J.-H. Fu, S.-Y. Wang, Y.-S. Chen, S. Prusty, Y.-T. Chan, *J. Am. Chem. Soc.* **2019**, *141*, 16217–16221. (d) S.-C. Wang, K.-Y. Cheng, J.-H. Fu, Y.-C. Cheng, Y.-T. Chan, *J. Am. Chem. Soc.* **2020**, *142*, 16661–16667. [2] L. He, H.-K. Hsu, L. Li, L.-T. Lin, T.-H. Tu, T.-G. Ong, G.-G. Liou, Yi-Tsu Chan, *Chem* **2022**, *8*, 494–507.



Yi-Tsu Chan (詹益慈)

The University of Akron, USA (Ph.D. 2010, Professor George R. Newkome). JSPS Research Fellow, Department of Chemistry and Biotechnology, The University of Tokyo (Professor Takuzo Aida). Assistant Professor, Associate Professor, Professor (since 2021), Department of Chemistry, National Taiwan University (NTU). Research Interests: Supramolecular Coordination Chemistry and Polymer Chemistry

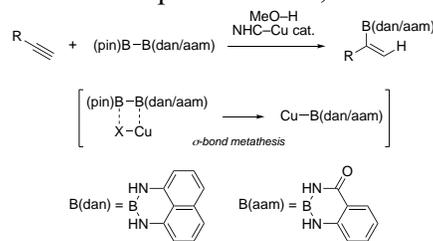
Synthetic Chemistry with Lewis Acidity-Diminished Organoboron Compounds

Hiroto Yoshida

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Organoboron compounds have been regarded as indispensable organometallic reagents in modern synthetic organic chemistry for constructing carbon–carbon and carbon–heteroatom bonds, owing to their easiness to handle, high availability, low toxicity, high functional group-compatibility, etc. Therefore, development of new borylation reactions that leads to direct and potent access to diverse organoboron compounds endowed with controlled stereochemistry and high functionalities has continued to be a key challenge in synthetic organic chemistry. In particular, our attention has been directed toward diminishing the inherent Lewis acidity of boron moieties to be installed by employing naphthalene-1,8-diaminato (dan) or anthranilamidato (aam) as a substituent on boron centers.¹ In view of the boron Lewis acidity, which strongly impacts reactivity and regio/stereoselectivity in borylation reactions, we envisaged that the use of B(dan)- or B(aam)-based reagents with diminished boron-Lewis acidity could bring about a drastic change in behavior in the borylation reactions, and properties of organoboranes obtained therefrom.

We demonstrated that unsymmetrical diborons such as (pin)B–B(dan) and (pin)B–B(aam) could be activated by a copper(I) catalyst to generate Lewis acidity-diminished borylcopper species, Cu–B(dan/aam) via chemoselective σ -bond metathesis through selective interaction between the Lewis acidic B(pin) moiety and a Lewis basic counter anion on the copper. The resulting borylcopper species served as a key catalytic intermediate for B(dan/aam)-installing three-component hydroboration of terminal alkynes with methanol as a proton source; it should be noted that the boron moiety is selectively connected to the internal carbons by use of a bulky NHC ligand to afford branched alkenylboron compounds in high yields,² which is in sharp contrast to the *anti*-Markovnikov regioselectivity observed in the usual hydroborations. Direct cross-coupling of R–B(dan) will also be presented.³



[1] (a) Yoshida, H. *Chem. Rec.* **2021**, *21*, 3483. (b) Kamio, S.; Yoshida, H. *Adv. Synth. Catal.* **2021**, *363*, 2310. (c) Li, J.; Yoshida, H. *Heterocycles* **2021**, *102*, 1478. [2] (a) Yoshida, H.; Takemoto, Y.; Takaki, K. *Chem. Commun.* **2014**, *50*, 8299. (b) Tsushima, T.; Tanaka, H.; Nakanishi, K.; Nakamoto, M.; Yoshida, H. *ACS Catal.* **2021**, *11*, 14381. [3] Yoshida, H.; Seki, M.; Kamio, S.; Tanaka, H.; Izumi, Y.; Li, J.; Osaka, I.; Abe, M.; Andoh, H.; Yajima, T.; Tani, T.; Tsuchimoto, T. *ACS Catal.* **2020**, *10*, 346.



Hiroto Yoshida (吉田 拓人)

Kyoto University (Ph.D. 2001, Professor Tamejiro Hiyama). Assistant Professor, Associate Professor, Department of Applied Chemistry, Hiroshima University (2001–2020). Since 2020, Professor, Department of Chemistry, Hiroshima University (HU). Research Interests: Synthetic Organic Chemistry and Organometallic Chemistry

Warped and Boron-Doped sp^2 -Hybridized Carbon Scaffolds via Electrophilic C-H Borylations

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Polycyclic sp^2 -hybridized carbon structures are a cornerstone of organic electronics and possess fascinating structural, (opto-)electronic, and magnetic properties. The inclusion of heteroatoms or non-six-membered rings in these structures is a powerful means to manipulate important properties. Specifically, modifications to sp^2 -hybridized carbon scaffolds by boron doping or heptagonal ring inclusion are intriguing, yet synthetically challenging, endeavors. Herein a one-pot electrophilic C-H borylation protocol^[1] is described that provides facile access to a wide array of emissive, low-LUMO boron-containing polycyclic aromatic hydrocarbons (PAHs) with tunable optoelectronic properties (Figure 1).^[1-3] Boron-doped PAHs prepared in this way can also serve as precursors for warped heptagon-containing sp^2 carbon scaffolds through multifold C-C coupling reactions.^[4]

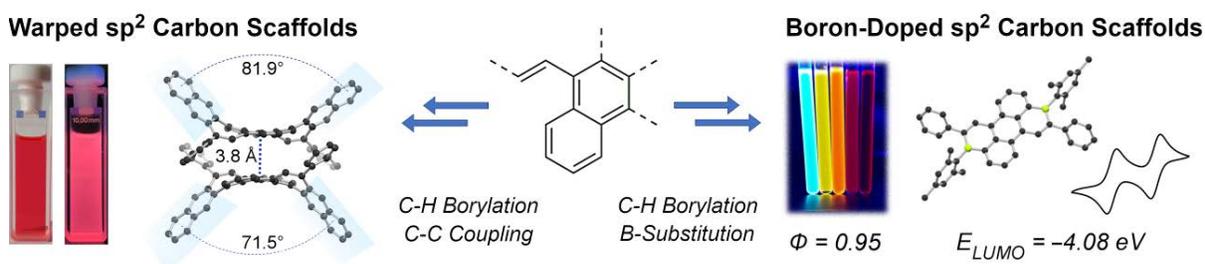


Figure 1: Generalized transformations of vinylnaphthyl moieties to furnish warped or boron-doped sp^2 -hybridized carbon scaffolds via C-H borylations.

[1] Farrell, J. M.; Schmidt, D.; Grande, V.; Würthner, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 11846-11850. [2] Farrell, J. M.; Mützel, C.; Bialas, D.; Rudolf, M.; Menekse, K.; Krause, A.-M.; Stolte, M.; Würthner, F. *J. Am. Chem. Soc.* **2019**, *141*, 9096-9104. [3] Mützel, C.; Farrell, J. M.; Shoyama, K.; Würthner, F. *Angew. Chem. Int. Ed.* **2022**, *61*, DOI: 10.1002/anie.202115746. [4] Farrell, J. M.; Grande, V.; Schmidt, D.; Würthner, F. *Angew. Chem. Int. Ed.* **2019**, *58*, 16504-16507.



Jeffrey M. Farrell (方韻睿)

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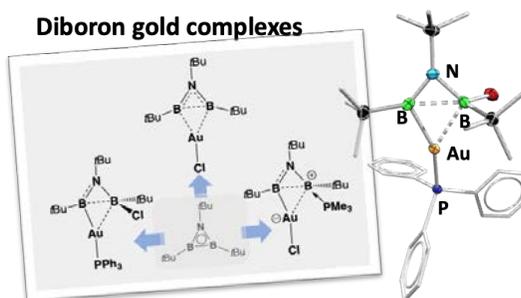
Developments of main-group ligands for transition metal complexes: a journey of unexpected reactivity

Rong SHANG

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The ability of main-group ligands to cooperate with the metal ion offers opportunities for rational control and tuning of transition metal (T.M.) reactivity and properties. In contrast to Group 14-17 elements, the only non-metal group 13 element, boron, was not an obvious candidate for stabilizing T.M. cations owing to its electron-deficient and electropositive nature. However, its Lewis acidity towards electron-rich metal centres has been used as a $2e^-$ σ -acceptor (Z-type ligand), as well as a strong σ -donor, which can be chemically active in reactions with organic substrates.^[1] Our research has centred on design, synthesis, and reactivity of diboron-containing ligands for novel reactivity and properties. We envisioned that more than one reactive boron centre would permit more metal, ligand and substrate interplay during reactions. In addition to boron's role of σ -accepter, we are systematically exploring boron's electronic effect on chemo-selectivity of the metal complex as a strong σ -donor and π acceptor through boryl and borane ligands.

This presentation will showcase gold(I) complexation chemistry by diboron ligand precursors, which offered a higher level of complexity in controlling chemo-selectivity and the structure of the resulting complex. Both metal-borane (Z-type) and metal-boryl (X-type) interactions can be used in bond cleavage/formation processes.^[2] In addition, through conjugated π systems, the diverse valences and electronegativity of Group 13-15 elements (B, C, N) shows potential in tuning redox properties of T.M. complexes through orbital interactions as redox-active non-innocent ligands.



[1] a) Parshall, G. W.; *J. Am. Chem. Soc.* **1964**, 86, 361-364. b) Brand, J.; Braunschweig, H.; Sen, S. S.; *Acc. Chem. Res.* **2014**, 47, 180-191. c) Bouhadir, G.; Bourissou, D.; *Chem. Soc. Rev.* **2016**, 45, 1065-1079.

[2] a) Shang, R.; Saito, S.; Jimenez-Halla, J. O. C.; Yamamoto, Y., *Dalton Trans.* **2018**, 47, 5181-5188. b) Oishi, T.; Lugo-Fuentes, L. I.; Jing, Y.; Jimenez-Halla, J. O. C.; Barroso-Flores, J.; Nakamoto, M.; Yamamoto, Y.; Tsunoji, N.; Shang, R., *Chem. Sci.* **2021**, 15603-15608.



Dr. Rong SHANG (商 融)

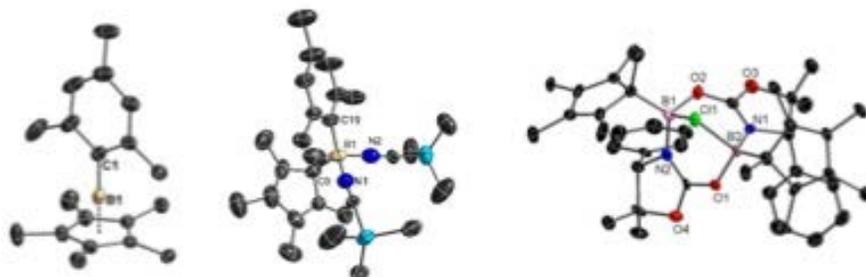
Australian National University (Ph.D. 2012, Professor Anthony F. Hill); Julius-Maximilians-Universität Würzburg (Post-Doc, 2011-2015); Assistant Professor, Department of Chemistry, Hiroshima University (HU, 2015-). Research Interests: Organo-main group chemistry, Organometallic complexes, Small molecule activation, and Structural and bonding.

Group 13 Cations in Catalysis

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Group 13 complexes are prototypical Lewis acids that have found numerous applications in organic synthesis. As the library of halogenated neutral group 13 catalyst continues to expand, the application of cationic group 13 complexes in catalysis has also emerged in the past few years. During our study of Cp*-substituted boron cations, we came to discover that the central hypercoordinate boron atom remains highly acidic.¹ [Cp*B-R]⁺ cation can be viewed as a masked potent Lewis acid that serves as an efficient catalyst for hydrosilylation of carbonyl, imine, and nitrile compounds. In addition to an achiral aryl substituent, we have also introduced a chiral oxazolidinone group to the system. The presence of a basic carbonyl group in oxazolidinone leads to the isolation of a series of [B-Cl-B]⁺ diboron cations, whose enantioselectivity can be further enhanced by coordinating the bridging chloride with SnCl₄.² In addition to the Cp*-substituted boron cations, we have also examined the catalytic application of an amino-aryl borinium ion, [TMP-B-Mes]⁺. The incorporation of an amino group significantly reduced the instability of the borinium ion, rendering it an active catalyst for hydrosilylation of ketones and aldehydes. Interestingly, when the TMP group is replaced by HMDS, an intramolecular methyl migration occurs to afford a silylium ion that is stabilized by intramolecular arene coordination.³ To extend the chemistry of boron cation, we have also prepared a tetra-coordinate chiral aluminum cation that features two chiral prolinol-derived ligands in C₂-symmetry.⁴ Through a competition experiment and fluoride ion affinity calculation, we have confirmed that this prolinol-coordinated aluminum cation is considerably more Lewis acidic than B(C₆F₅)₃.



- (1) Tseng, H.-C.; Shen, C.-T.; Matsumoto, K.; Shih, D.-N.; Liu, Y.-H.; Peng, S.-M.; Yamaguchi, S.; Lin, Y.-F.; Chiu, C.-W.* *Organometallics* **2019**, *38*, 4516.
- (2) Shih, D.-N.; Ramalingam, B.; Liu, Y.-H.; Chein, R.-J.;* Chiu, C.-W.* *Inorg. Chem.*, **2021**, *60*, 16266-16272
- (3) Chen, P.-H.; Hsu, C.-P.; Tseng, H.-C.; Liu, Y.-H.; Chiu, C.-W.* *Chem. Commun.*, **2021**, *57*, 13732-13735
- (4) Hsu, C.-P.; Liu, Y.-H.; Ramalingam, B.; Chein, R.-J.;* Chiu, C.-W.* *Organometallics* **2021**, *40*, 1244.



Ching-Wen Chiu (邱靜雯)

Texas A&M University (Ph.D. 2003, Professor François P. Gabbaï). Assistant Professor, Department of Chemistry, National Taiwan University (2010-2015). Since 2016, Associate Professor, Department of Chemistry, National Taiwan University (NTU). Research Interests: low-coordinate group 13 and 14 complexes, Lewis acid catalysts, stable p-block radicals.

Organic Layer Assembly on Cu Electrode toward Selective CO₂ Electrolysis

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Electrocatalytic activity of metallic copper reducing CO₂ to viable hydrocarbons has been focused since its first report,[1] and the interest is currently burgeoning in response to global warming. Processed Cu materials such as nanomaterials and alloys has been reported to show excellent performance.[2] Adsorption of organic molecules on a metal surface tends to deactivate its catalytic activity, but recent studies have shown that organic groups can cooperate to afford effective and selective catalytic CO₂ conversion.

We have developed a new modification method, exploiting catalytic activity of oxidized Cu surface itself to grow hardly soluble organic polymers onto the surface via copper(I)-catalyzed azide alkyne cycloaddition (CuAAC). Cu metal electrode is anodically activated in an electrolyte solution containing CuAAC monomers, which readily forms organic-metallic contact surface.(Figure(a)) The CO₂ reduction performance of the on-surface modified copper cathode exhibited improved CO₂ reduction over undesired H₂ evolution, while the traditional cast modification of triazole derivative led to dominant H₂ evolution. [3] The present method also enables us to introduce various organic moieties, and the product distribution strongly suggested that CO₂ reduction is biased by proton transport ability of the introduced organic moiety.[4] CuAAC modification also proceeded on Cu₂O nanocrystalline surface, and the layer growth was plateaued to give a flat modified surface with thickness of ca. 3 nm.(Figure(b)) The suppression of hydrogen evolution was even greater(Figure(c)) in CO₂ electrolysis for these modified cubes, and the selection is strongly related to the quality of growth uniformity. It is suggested that the organic layer tunes relative permeation of CO₂ and H₂O onto exposed Cu atom, leading to high selectivity.

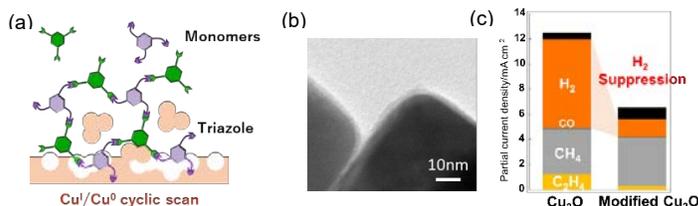


Figure (a) On-surface CuAAC modification by Cu anodization (b) modified Cu₂O cubes (c) CO₂ reduction selectivity for Cu₂O cubes

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Potential-driven dynamic structures of electrocatalysts

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Electrochemical reduction of CO₂ is heavily pursued as a potential solution of CO₂ recycling and realizes the high-density renewable energy storage. Among numerous types of catalysts, copper-based catalysts have been shown to perform interesting nature toward hydrocarbon products. Nevertheless, achieving practical CO₂ reduction reaction (CO₂RR) selectivity toward desired products on the state-of-the-art copper-based catalysts is still facing great challenges. The great challenge for promoting the CO₂RR selectivity may arise to a fact that this electrochemical process is a multiple proton-electron-transfer step and highly surface-sensitive, implying that the surface state of electrocatalyst may be dynamic and unpredictable under practical situations. By employing the comprehensive in-situ techniques we developed during past few years, we have demonstrated the first empirical demonstration to track the dynamic structural reconstruction/transformation in a model bimetallic system, which establishes a good understanding of the correlation between catalyst surface structure and catalytic selectivity. Furthermore, we also realized a very important achievement to develop an operando seconds-resolved X-ray absorption spectroscopy to uncover the chemical state evolution of working catalysts. It's well-known that a chemical reaction driven by applied potential is extremely fast, which is difficult to track the electrochemistry with acceptable temporal-resolution. This work is able to offer scientific insights into the roles metal states serve in chemical reaction in electrolyte.

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Theoretical study of uranium isotope fractionation for 64 U compounds

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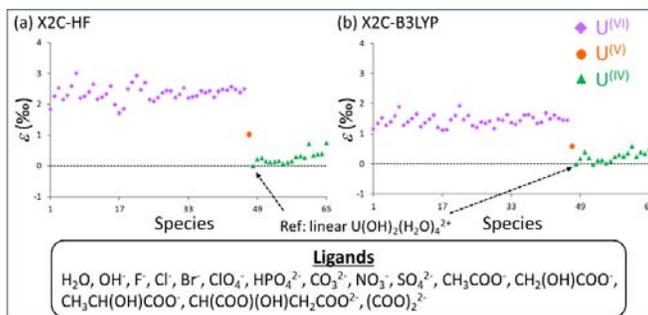
Uranium has two major isotopes (²³⁵U and ²³⁸U) and the variation of their ratio, ²³⁵U/²³⁸U, is widely used for dating and paleoclimate studies in geochemistry. An isotope fractionation coefficient ϵ between hexavalent and tetravalent uranium is defined as $(^{238}\text{U}^{(\text{VI})}/^{235}\text{U}^{(\text{VI})}) - (^{238}\text{U}^{(\text{IV})}/^{235}\text{U}^{(\text{IV})})$, and a single value approximately 1.3‰ is conventionally used as the equilibrium ϵ , without considering the coordination environment of uranium.^{1,2} However, uranium forms compounds with various anion ligands such as CO₃²⁻, CH₃COO⁻, and Cl⁻, and such environment can change the value of ϵ . Therefore, we determined the isotope fractionation coefficients for 64 uranium compounds with various ligands from quantum chemical calculations. ϵ can be theoretically calculated as a sum of electronic term (namely, nuclear volume term, $\ln K_{\text{nv}}$) and vibrational term (namely, nuclear mass term, $\ln K_{\text{nm}}$).³ Because $\ln K_{\text{nv}}$ is heavily affected by relativistic effects,^{4,5} we used an accurate relativistic approach called exact two-component method (X2C) for Hartree-Fock and DFT with B3LYP functional calculations.

Right figure shows the ϵ values of 64 kinds of uranium compounds. The magnitude of ϵ is approximately U^(VI) > U^(V) > U^(IV). The ϵ values between U^(VI)-U^(IV) were obtained in the range of 0.96~3.00‰ for X2C-HF and 0.53~1.94‰ for X2C-B3LYP; thus, the results between HF and DFT are different. The equilibrium ϵ between U^(VI)-U^(IV) in hydrochloric acid was estimated as 1.70‰ from X2C-HF and 0.92‰ from X2C-B3LYP, while the experimental counterpart was reported as 1.64‰.⁶

Therefore, the X2C-HF method seems to be more reliable for the ϵ calculation between U^(VI)-U^(IV). From projection analysis, the occupation number of 5f orbital in U^(IV) compounds was larger than that of U^(VI) in the X2C-HF results, while both values were unchanged in the X2C-B3LYP results unexpectedly. Hence, the results of X2C-B3LYP seems to be converged to wrong electronic states especially in U^(IV), which leads to underestimation of ϵ between U^(VI)-U^(IV). X2C-HF results show a wide range of ϵ values, indicating a strong dependence on species; thus, coordination environment is important for geochemical discussions.

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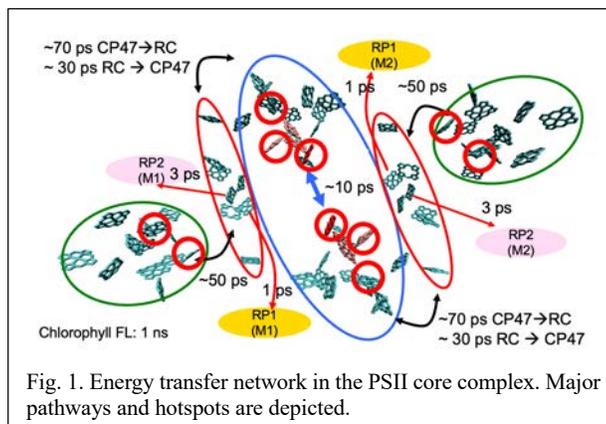
Theoretical Simulations of Excitonic Dynamics in Molecular Systems: From Photosynthesis to Organic Materials

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Excitonic phenomena in molecular systems play crucial roles in a broad array of optoelectronic materials, and my research group has been focused on the developments of theoretical tools for the accurate simulations of excitonic dynamics in molecular systems. In this talk, I will present our theoretical study on excitation energy transfer (EET) in photosynthetic systems as well as organic materials.

In particular, I will present a first-principle multiscale approach that combines quantum chemistry calculations and quantum dynamics theories to model EET processes in molecular systems, and several applications of this framework will also be discussed. We demonstrate that with careful parameterization, our model yields EET dynamics in excellent agreement with experimental 2D spectra, leading to details of light-harvesting processes in the photosynthetic systems. The approach enables us to describe EET in the photosystem II core complex, which is a crucial photosynthetic system with ~ 70 chlorophylls (Fig. 1). More importantly, the results allowed us to reveal several key elements that play important roles in the speedup and robustness of energy trapping in photosynthesis. We also show that the ultrafast EET in a donor-acceptor oligomer system can be described by our theory to unravel the role of quantum coherence in the non-Förster EET mechanism and how it could be utilized towards making more efficient materials. In summary, we have developed an effective theoretical approach for describing spectra and coherent energy transfer dynamics in molecular aggregates, and this framework is applicable to general molecular systems and useful for the design of efficient light-harvesting materials.



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Crown Ether Complexes with Ion Guests Studied by Cold, Gas-Phase Spectroscopy

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After the discovery of crown ethers (CEs) by Pedersen, considerable effort was made to understand their guest selectivity [1]. The selectivity has been explained mainly in terms of size matching between CEs and guest ions. However, the relation between the selectivity and encapsulation structure was not fully elucidated so far; X-ray diffraction analysis, which could have been only method for conformational determination, was not applicable to all CE complexes due to the limitation of crystallization. In the last decade, we have been studying CE complexes with ion guests by cold, gas-phase spectroscopy [2]. It enables us to determine the electronic and vibrational energy levels of the CE complexes with high accuracy ($< 1 \text{ cm}^{-1}$), providing information on the encapsulation structure. One of our goals is to understand the origin of functions characteristic of CEs from microscopic and spectroscopic viewpoints.

Figure 1 shows a schematic drawing of our home-built mass spectrometer for UV photodissociation (UVPD) spectroscopy under cold gas-phase conditions [3]. Ion complexes are produced by an electrospray ion source and introduced into a Paul-type quadrupole ion trap. The trap is cooled to $\sim 4 \text{ K}$ by a He cryostat, and the ion complexes are cooled to $\sim 10 \text{ K}$ with cold He buffer gas in the trap. The ion complexes are irradiated by an output of a UV laser, and resulting fragment ions are mass-analyzed by a time-of-flight mass spectrometer. UVPD action spectra of the ion complexes are obtained by plotting the yield of the fragment ions as a function of UV wavenumber. It is possible to observe conformer-specific UV and IR spectra with UV-UV and IR-UV double-resonance techniques. In this talk, we will present our recent spectroscopic results of CE complexes with metal and molecular ions.

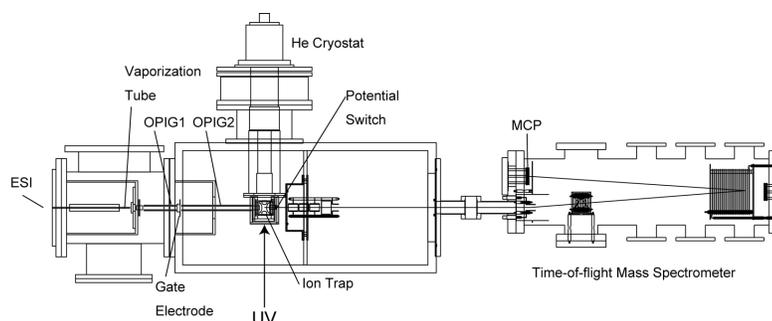


Fig. 1. Schematic drawing of a mass spectrometer for UVPD spectroscopy.

The trap is cooled to $\sim 4 \text{ K}$ by a He cryostat, and the ion complexes are cooled to $\sim 10 \text{ K}$ with cold He buffer gas in the trap. The ion complexes are irradiated by an output of a UV laser, and resulting fragment ions are mass-analyzed by a time-of-flight mass spectrometer. UVPD action spectra of the ion complexes are obtained by plotting the yield of the fragment ions as a function of UV wavenumber. It is possible to observe conformer-specific UV and IR spectra with UV-UV and IR-UV double-resonance techniques. In this talk, we will present our recent spectroscopic results of CE complexes with metal and molecular ions.

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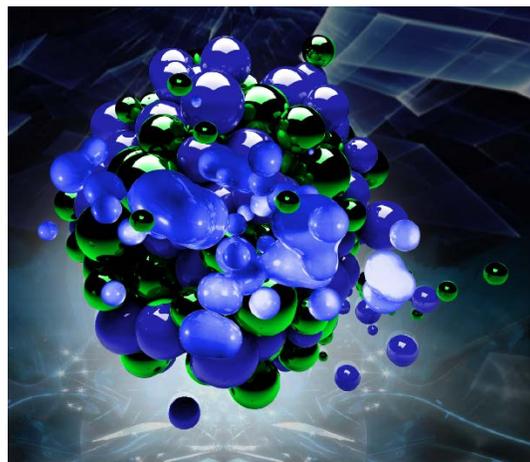
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Phase Transformation and Structural Characterization of Amorphous Calcium Carbonate

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Biomineralization is a process describing the formation of composite materials in organisms such as teeth, bone, and shell. It is a particularly challenging research area because biomaterials usually comprise organic and inorganic components. Biogenic amorphous calcium carbonate ACCs play a crucial role in the mineralization process of calcareous tissue. We carried out in-vitro experiments to show that Mg-stabilized ACC could transform to meso-crystallites of Mg-calcite.¹ Various physical techniques, with particular emphasis on electron microscopy had been exploited to unravel the phase transformation pathway.² It is very interesting to find that nano-magnesite could be found in the spicule-like morphology of calcitic species upon phase transformation.³ Most biogenic ACCs contain Mg ions but the coordination environment of Mg, which may influence the kinetics of the phase transformation of an ACC, remains poorly understood. Solid-state NMR spectroscopy, being applicable to crystalline or amorphous systems, is well suited to study the structures of biominerals at the molecular level.⁴ We will demonstrate how we could characterize the structural order of Mg-ACC by advanced NMR techniques.^{5,6}



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