RESEARCH ACTIVITIES

Division of Advanced Molecular Science

The division consists of two sections. In the first one, scientists of the first water are invited as "distinguished professors," and the environment, in which they can devote themselves to their own research, is provided. The research in this section should be the last word in the field of molecular science.

In the second section, we invite researchers in the universities performing unique researches in the field of molecular science as cross-appointment faculty members, and provide the research environment to enable research activity with advanced facilities in IMS.

Self-Assembling Molecular Systems Based on Coordination Chemistry

Division of Advanced Molecular Science

FUJITA, Makoto
Distinguished Professor
[mfujita@ims.ac.jp]

Education

1980	B.S. Chiba University
1982	M.S. Chiba University
1987	Ph.D. Tokyo Institute of Technology

Professional Employment

1982	Researcher, Sagami Chemical Research Center
1988	Assistant Professor to Associate Professor, Chiba University
1997	Associate Professor, Institute for Molecular Science
1999	Professor, Nagoya University
2002	Professor, The University of Tokyo
2018	Distinguished Professor, Institute for Molecular Science
2019	Distinguished Professor, The University of Tokyo

Awards

1994	Progress Award in Synthetic Organic Chemistry, Japan
2000	Division Award of Chemical Society of Japan (Organic Chemistry)
2001	Tokyo Techno Forum 21 Gold Medal
2001	Japan IBM Award
2003	Nagoya Silver Medal
2004	Izatt-Christensen Award
2006	G. W. Wheland Award (Chicago University Lectureship Award)
2010	The Reona Esaki Award
2010	The JSCC Award
2011	3M Lectureship Award (University of British Columbia)
2012	Thomson Reuters Research Front Award 2012
2013	The Chemical Society of Japan (CSJ) Award
2013	Arthur C. Cope Scholar Award (ACS National Award)
2013	Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)
2014	ISNSCE 2014 Nanoprize
2014	Medal with Purple Ribbon
2014	Fred Basolo Medal (Northwestern University)
2018	Wolf Prize in Chemistry
2019	The Imperial Prize and the Japan Academy Prize
2020	The 73rd Chunichi Cultural Award

Member
IMS Research Assistant Professor
MITSUHASHI, Takaaki
Post-Doctoral Fellow
CHAN, Kwun Wa
Graduate Student
ALBERTSMA, Jelco*
CHEN, Jiazhuo†
KAGEYAMA, Ko†
YOUNGCHEOL, Jung†
YU, Zhengsu†
WADA, Naoki†
ZHOU, Boyu†
Secretary
MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

We are designing new self-assembled molecular systems based on coordination chemistry, and apply the molecular system to various research fields. One of these examples is a molecular system called “crystalline sponge (CS).” The CS is a porous crystal, which can accommodate various kinds of small molecules, and align the accommodated molecules neatly in its inner space. Actually, we can observe the structure of the small molecules neatly aligned in the CS by the X-ray crystallography (Figure 1). Therefore, we can use the CS for the structure elucidation of the small molecules. This technique developed by us is called “CS method.” The CS method has a potential to accelerate the various kinds of researches, in which the structure elucidation of novel compounds is required.

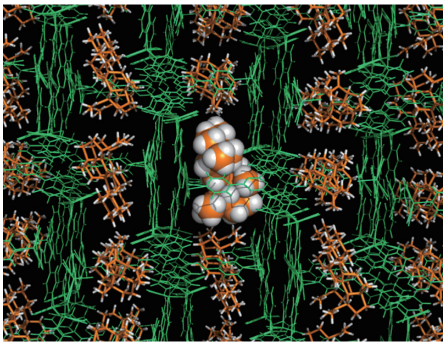

Figure 1. One example of the crystalline sponge method analysis result. Orange molecules are accommodated molecules, and green one is a framework of the crystalline sponge.

Selected Publications

- Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, “X-Ray Analysis on the Nanogram to Microgram Scale Using Porous Complexes,” *Nature* **495**, 461–466 (2013).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, “Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components,” *Nature* **540**, 563–566 (2016).

1. The CS Method Accelerates an Attempt to Create Artificial Natural Products

The natural products, compounds isolated from nature, exhibit great structural diversity and complexity. Such diversity and complexity of the natural products are generated by enzymatic reactions in organisms such as plants and bacteria. The enzymes can convert simple substrates into complex natural products. The natural products can be utilized for many kinds of purposes, such as medicines, industrial materials, and so on. Therefore, it can be said that the natural products are attractive resource for the exploration into useful compounds. However, recently, it becomes difficult to obtain new natural products with novel structures, because almost all types of natural products, which can be easily isolated, are considered to be already found through long history of natural product chemistry.

One way to solve this problem is a chemo-enzymatic approach. In this approach, we prepare unnatural synthetic substrates. Then, the substrates are converted into complex artificial molecules by enzymes, which is involved in the biosynthesis of natural products. In this way, we can expand the diversity of small molecules, using the biosynthetic mechanism of the natural products. One of the bottle-necks of this approach is the structural elucidation of the enzyme products, because the products often possess complex and unexpected structures. We consider that the CS method can solve this problem, since this method enables rapid structural elucidation of small molecules.

2. The CS Method Analysis of Artificial Indole-Containing Compound[1)]

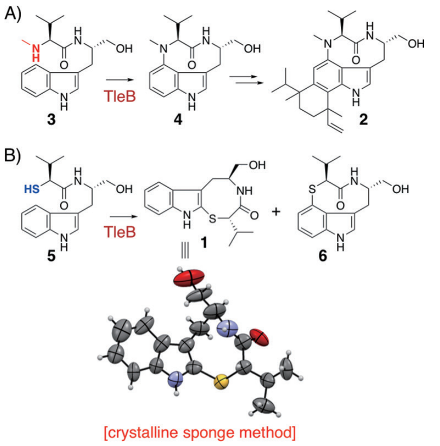

Figure 2. A) Reaction catalyzed by TleB in nature. B) Enzyme reaction to produce **1** and **6** from unnatural substrate **5**.

We elucidated a structure of a compound **1** generated by reaction using a biosynthetic enzyme, TleB, which is involved in a biosynthesis of **2** (Figure 2). In nature, TleB accepts **3** as a substrate and produce **4** (Figure 2A). However, it was found that unnatural substrate **5** could also be accepted by TleB, and **1** and **6** were generated (Figure 2B). Even though the structure elucidation of **6** could be accomplished by the NMR, MS, and single-crystal X-ray diffraction study, that of **1** could not be determined by the conventional methods. Therefore, we subjected **1** to the CS method, and succeeded in the structure elucidation.

3. The CS Method Analysis of Artificial Natural Products Produced by Enzymatic Cyclization Reaction[2)]

One of the important reactions to form basic skeletons of the natural products is a cyclization reaction. When a chemically synthesized unnatural substrate **7** was converted by an enzymatic cyclization reaction, **8** was generated (Figure 3). **8** has a novel structure, but its structure could not be determined by the NMR analysis. Thus, the structure of **8** was revealed by the CS method.

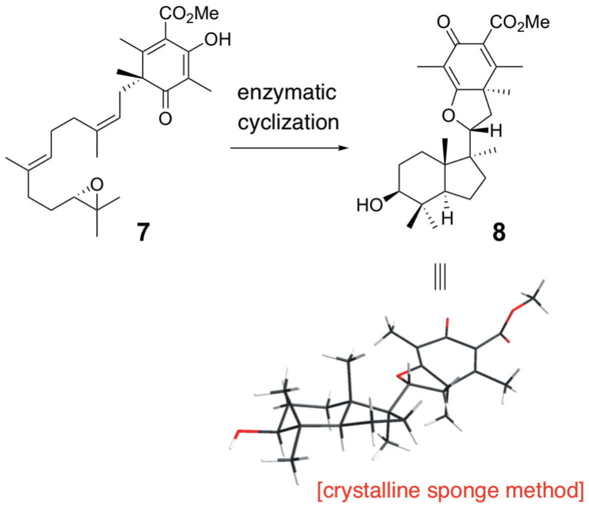

Figure 3. Enzyme reaction to produce **8** from **7**.

References

1) I. Morita, T. Mori, T. Mitsuhashi, S. Hoshino, Y. Taniguchi, T. Kikuchi, K. Nagae, N. Nasu, M. Fujita, T. Ohwada and I. Abe, *Angew. Chem., Int. Ed.* **59**, 3988–3993 (2020).

2) T. Mitsuhashi, L. Barra, Z. Powers, V. Kojasoy, A. Cheng, F. Yang, Y. Taniguchi, T. Kikuchi, M. Fujita, D. J. Tantillo, J. A. Porco and I. Abe, *Angew. Chem., Int. Ed.* **59**, in press (2020).

Award

FUJITA, Makoto; The 73rd Chunichi Cultural Award (2020).

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* from the University of Twente

† carrying out graduate research on Cooperative Education Program of IMS with the University of Tokyo

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

Division of Advanced Molecular Science
(Department of Materials Molecular Science, Electronic Structure)

KIMURA, Shin-ichi
Professor
(Cross Appointment)
[kimura@ims.ac.jp]

Education

1988	B.S. Tohoku University
1990	M.S. Tohoku University
1991	Ph.D. Tohoku University

Professional Employment

1991	JSPS Postdoctoral Fellow, Tohoku University
1993	Research Associate, Kobe University
1993	Research Associate, Institute for Molecular Science
1998	Associate Professor, Kobe University
2002	Associate Professor, Institute for Molecular Science
2013	Professor, Osaka University
2020	Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	Young Incentive Award, Japanese Society for Synchrotron Radiation Research
2008	The Commendation for Science and Technology by MEXT, Japan Science and Technology Prize (Research Field)
2008	Morita Memorial Prize

Member
Secretary
ISHIKAWA, Azusa

Keywords Condensed Matter, Biological Materials, Optical Property

Physical and chemical properties of solids, such as conductivity, magnetism, superconductivity and chemical reactions, and also life phenomena, such as redox and photosynthesis, originate from microscopic electronic and molecular vibrations and/or molecular movements based on quantum mechanics in materials and their interactions. To clarify the microscopic states provides us not only the knowledge of the origins of the physical properties and life phenomena but also the clarification of hidden functionalities. The information is useful for the creation of novel functional properties. To visualize the microscopic state, we also develop novel spectroscopic techniques using synchrotron radiation, high brilliant electron beams, and other so-called quantum beams. Recently, we have successfully developed a novel electron spectroscopy, namely resonant electron-energy-loss spectroscopy, as shown in Figure 1, to detect element-specific plasmons. Based on the obtained information of electronic structures, we are aiming to develop novel physical properties of new materials.

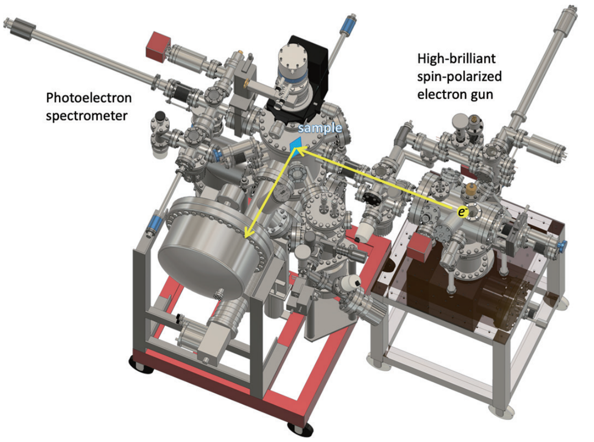


Figure 1. Resonant electron-energy-loss spectroscopy (rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

Selected Publications

- S. Kimura, T. Ito, M. Sakai, E. Nakamura, N. Kondo, K. Hayashi, T. Horigome, M. Hosaka, M. Katoh, T. Goto, T. Ejima and K. Soda, "SAMRAI: A Variably Polarized Angle-Resolved Photoemission Beamline in the VUV Region at UVSOR-II," *Rev. Sci. Instrum.* **81**, 053104 (7 pages) (2010).
- S. Kimura, T. Iizuka, H. Miyazaki, A. Irizawa, Y. Muro and T. Takabatake, "Electronic-Structure-Driven Magnetic Ordering in a Kondo Semiconductor $CeOs_2Al_{10}$," *Phys. Rev. Lett.* **106**, 056404 (4 pages) (2011).
- S. Kimura and H. Okamura, "Infrared and Terahertz Spectroscopy of Strongly Correlated Electron Systems under Extreme Conditions," *J. Phys. Soc. Jpn.* **82**, 021004 (28 pages) (2013). [review]
- K. Hagiwara, Y. Ohtsubo, M. Matsunami, S. Ideta, K. Tanaka, H. Miyazaki, J. E. Rault, P. Le Fèvre, F. Bertran, A. Taleb-Ibrahimi, R. Yukawa, M. Kobayashi, K. Horiba, H. Kumigashira, K. Sumida, T. Okuda, F. Iga and S. Kimura, "Surface Kondo Effect and Non-Trivial Metallic State of the Kondo Insulator YbB_{12}," *Nat. Commun.* **7**, 12690 (7 pages) (2016).

1. Non-Trivial Surface States of Samarium Hexaboride at the (111) Surface[1)]

The peculiar metallic electronic states observed in the Kondo insulator, samarium hexaboride (SmB_6), has stimulated considerable attention among those studying non-trivial electronic phenomena. However, experimental studies of these states have led to controversial conclusions mainly to the difficulty and inhomogeneity of the SmB_6 crystal surface.

In this work, the detailed electronic structure of SmB_6 is revealed by angle-resolved photoelectron spectroscopy measurements of the three-fold (111) surface, where only two inequivalent time-reversal-invariant momenta (TRIM) exists. We observe the metallic two-dimensional state was dispersed across the bulk Kondo gap. Its helical in-plane spin polarization around the surface TRIM indicates that SmB_6 is topologically non-trivial, according to the topological classification theory for weakly correlated systems. Based on these results, we propose a simple picture of the controversial topological classification of SmB_6.

We expect that this discovery could provide a new, fertile playground for the following researches about the concert effect between electron correlation and topology. It would also be applicable for future spintronic technologies.

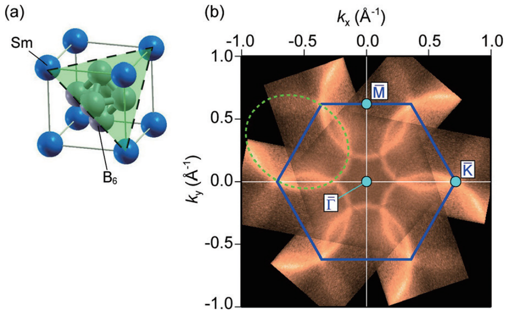


Figure 2. (a) Crystal structure of SmB_6. A shaded area is the (111) surface studied in the current work. (b) Surface electronic structure of SmB_6 obtained by angle-resolved photoelectron spectroscopy. Bright area represents the electrons with corresponding wavenumber (Fermi surface). A solid hexagon is the zone boundary determined from surface periodicity.

2. Relaxation Dynamics of $[Re(CO)_2(bpy)\{P(OEt)_3\}_2](PF_6)$ in TEOA Solvent Measured by Time-Resolved Attenuated Total Reflection Terahertz Spectroscopy[2)]

To reveal highly efficient photocatalytic properties of an artificial photosynthesis material $[Re(CO)_2(bpy)\{P(OEt)_3\}_2](PF_6)$, we have directly observed the photo-induced relaxation dynamics and reductive quenching process of the photo-excited state on a photosynthesis material in Triethanolamine (TEOA) solvent as an electron donor by time-resolved attenuated total reflection spectroscopy in the terahertz (THz) region. The spectrum of the complex in TEOA has an intermolecular vibrational mode between the complex and TEOA molecules, which reflects the precursor of the reductive quenching process. The intermolecular vibrational mode has three-step relaxation process in a picosecond timescale after photo-excitation, where firstly the triplet metal-to-ligand charge transfer excited state is vibrationally cooled down, secondly the distance between Re and TEOA is reduced by the rotation of TEOA molecules due to dipole–dipole interaction accelerated by heat transfer, and finally electrons transfer from TEOA to Re. These observations provide us the detailed information of the electron transfer process of photocatalytic properties of $[Re(CO)_2(bpy)\{P(OEt)_3\}_2](PF_6)$ in TEOA solvent.

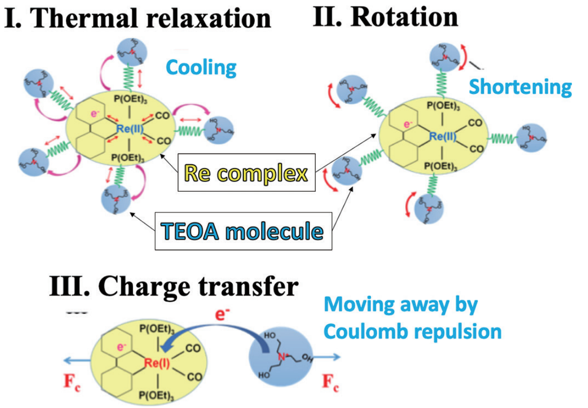


Figure 3. The schematic figures of the temporal evolution from I to III of the interaction between photocatalyst $[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+$ as a photocatalyst and TEOA molecules as reductants.

References

1) Y. Ohtsubo, Y. Yamashita, K. Hagiwara, S. Ideta, K. Tanaka, R. Yukawa, K. Horiba, H. Kumigashira, K. Miyamoto, T. Okuda, W. Hirano, F. Iga and S. Kimura, *Nat. Commun.* **10**, 2298 (7 pages) (2019).

2) P. N. Nguyen, H. Watanabe, Y. Tamaki, O. Ishitani and S. Kimura, *Sci. Rep.* **9**, 11772 (7 pages) (2019).

Innovative Catalysis Development Based on Radiant Right Spectroscopy

Division of Advanced Molecular Science (Department of Photo-Molecular Science, Photo-Molecular Science III)

TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
[takaya@ims.ac.jp]

Education
1993 B.S. Osaka University
1995 M.S. Osaka University
1998 Ph.D. Osaka University

Professional Employment
1995 JSPS Research Fellow
1998 Assistant Professor, Osaka University
2002 Guest Scientist, Scripps Research
2008 Associate Professor, Kyoto University
2019 Associate Professor (Cross Appointment), Institute for Molecular Science

Awards
2001 N.E. CHEMCAT Award in Synthetic Organic Chemistry, Japan
2008 The 22nd Special Young Lecturer in the 88th CSJ Annual Meeting
2012 Theme Chemistry Journal Award
2015 BCSJ Award, The Chemical Society of Japan
2019 BCSJ Award, The Chemical Society of Japan

Member
Secretary
HAGIWARA, Hisayo

Keywords Organometallic Catalyst, Peptide-Based Material, X-Ray Spectroscopy

For future sustainable development, we promote research development of advanced catalysts based on element strategy criteria. Non-precious metal such as iron, nickel, cobalt, and cupper catalysts are investigated for synthetic transformation of various organic molecules related to pharmaceutical and photoelectronic materials. To elucidate the precise catalytic properties and mechanism, X-ray absorption spectroscopy (XAS) and various radiant right spectroscopies provided at UVSOR are used, where development of a solution-phase in situ XAS spectroscopic techniques and system will be intensively conducted for the study of homogeneous organometallic catalysts. Multidisciplinary research covered on DFT and XAS spectroscopy is also conducted to achieve an efficient structural determination technique being never accessible by the conventional XAS-based structural analysis. Using these cutting-edge spectroscopic technologies, we aim to promote innovative catalyst research which enable us highly efficient transformation of extremely unreactive organic molecules such as simple aromatic compounds, CO_2, and biomass into valuable functional materials.

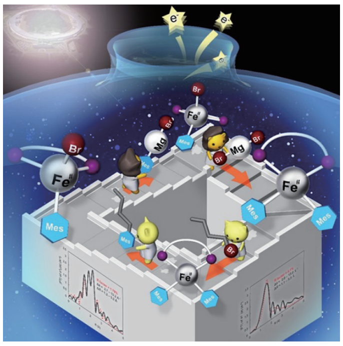


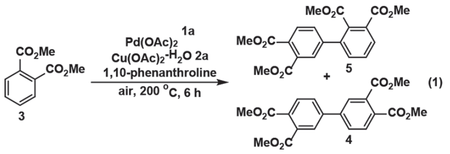
Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

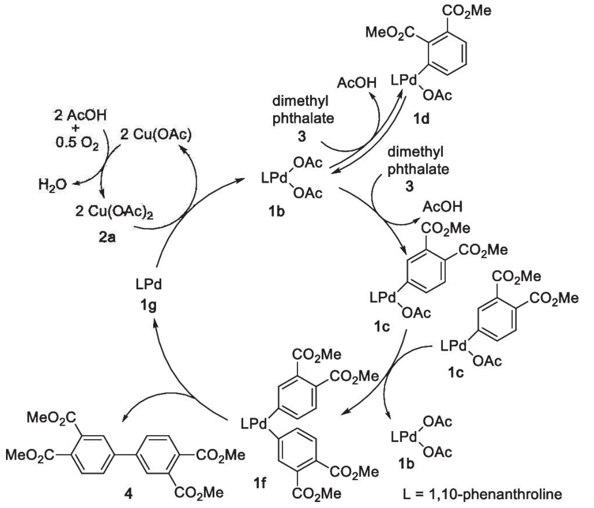
Selected Publications

- R. N. Dhital, A. Sen, T. Sato, H. Hu, R. Ishii, D. Hashizume, H. Takaya, Y. Uozumi* and Y. M. A. Yamada, "Activator-Promoted Aryl Halide-Dependent Chemoselective Buchwald-Hartwig and Suzuki-Miyaura Type Cross-Coupling Reactions," *Org. Lett.* **22**, 4797–4801 (2020).
- L. O. Benjamin, H. Takaya and T. Uemura, "Polymer Guest Directing the Solid-State Conversion of a Metal-Organic Framework," *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
- R. Agata, H. Takaya, T. Iwamoto, T. Hatakeyama, K. Takeuchi, N. Nakatani and M. Nakamura, "Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and Fe^{II}/Fe^{IV} Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations," *Bull. Chem. Soc. Jpn.* **92**, 381–390 (2019).
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada–Tamao–Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).

1. DFT-XAS-Based Mechanistic Investigation of Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate[1,2]

Pd-catalyzed oxidative coupling reaction of phthalate esters is a well-known industrial process for the production of biphenyl compounds which can be readily converted into biphenyl tetracarboxylic dianhydride (BPDA), being an important monomer of polyimides. Equation 1 shows a typical procedure of the oxidative coupling, where dimethyl phthalate **3** readily couples in the presence of catalytic amounts of $Pd(OAc)_2$ **1a** and $Cu(OAc)_2$ **2a** to afford the corresponding biphenyls **4** and **5**. Despite the widespread use of this process, the precise reaction mechanism had still remained unclear due to the severe reaction condition and the complex Pd/Cu heterobimetallic catalyst system including paramagnetic Cu(II) species, both which hamper the conventional analysis based on solution-phase NMR. To solve such problems in mechanistic study of homogeneous catalysis, we conducted to use XAS which enables element specific analysis to determine the oxidation state and the geometry of catalytic species.[3,4] Recently, we have succeeded to elucidate the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate as shown in Scheme 1. The oxidation states and the local coordination geometries of catalytic intermediates **1d**, **1c**, and **2a** were determined under the stoichiometric conditions of each reaction path. DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is first to provide a clear answer to the long-term debate on the reaction mechanism in the last three decades and demonstrated that XAS is the powerful tool for the mechanistic study on homogeneous transition-metal-catalyzed reactions, being difficult by means of the conventional solution-phase NMR analysis.





Scheme 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAFS analysis.

2. XAFS-Based Structural Study on Flexible Organometallic Systems[5–7]

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal with sufficient size and quality for X-ray crystallography. We conducted DFT-XAS-based structural analysis of such flexible molecule. Recently, Prof. Uemura and Benjamin found a flexible MOF prepared from $[Zn_2(BDC)_2(DABCO)]_n$ and polystyrene which has a polymer-threaded multi-layered structure after removing the DABCO pillar ligand. The polymer-threaded extremely flexible molecular scaffolds showed no clear diffraction pattern except for a broad peak. To determine the molecular structure of this flexible MOF system, we carried out Zn K-edge and O K-edge XAS. A DFT-based simulation of both XAS spectra clearly demonstrated that $[Zn_2(BDC)_2]_n$-monolayer was preserved well in the turbostratic phase without DABCO pillar.

Another successful application was achieved in the structure determination of rotaxane-linked iron porpyrin dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials. Fe K-edge XAS-based structural analysis supproted with DFT-MD-based simulation succefully provides the precise local coordionation geometry of iron centers in highly flexible supramolecular system.

References

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2) Y. Kanazawa, T. Mitsudome, H. Takaya and M. Hirano, *ACS Catal.* **10**, 5909–5919 (2020).
3) Y. Aoki, T. Toyota, H. Kawasaki, H. Takaya, A. K. Sharma, K. Morokuma and M. Nakamura, *Asian J. Org. Chem.* **8**, 1–6 (2019).
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5) L. O. Benjamin, H. Takaya and T. Uemura, *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
6) N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, K. Igawa, K. Tomooka, H. Fujii and K. Tanaka, *Chem. –Eur. J.* **25**, 3369–3375 (2019).
7) N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, S. Aoyama, K. Igawa, K. Tomooka and, K. Tanaka, *Chem. –Eur. J.* **23**, 7508–7514 (2017).