Institute for Molecular Science

annual review

2022

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URL: https://www.ims.ac.jp/en/

Editorial Committee 2022

The Institute for Molecular Science (IMS) is one of the world's core research facilities for molecular science and is also a center for inter-university joint research in Japan. It sets an extremely wide range of research goals, from understanding the behavior of individual molecules to that of collective molecular systems. These molecular systems have close relation to scientific understanding of biology, engineering and space sciences. Currently, IMS is engaged in six (four plus two) areas of research: Theoretical and computational molecular science, Photo-molecular science, Materials molecular science, and Life and coordination-complex molecular science. Research Center of Integrative Molecular Systems (CIMoS) has started from April 2013 to develop the highly functional molecular systems such as molecular rhythms, sensing and response, and even self-repair. Starting from April 2017, Center for Mesoscopic Sciences (CMS) is launched to develop innovative methodology of studying mesoscopic molecular systems, covering from theoretical methods to leading-edge measurement methods. Division of Advanced Molecular Science is launched to promote outstanding research example of Molecular Science from April 2018. From April 2019, Division of Research Innovation and Collaboration is launched to strengthen the tie between the social activities. In addition to these research divisions, IMS has three research facilities; UVSOR Synchrotron Facility, Instrument Center facilitated with various molecular detectors, and Equipment Development Center. IMS also operates the Research Center for Computational Science, jointly with National Institute for Physiological Sciences and National Institute for Basic Biology in the same campus. From April 2018, Exploratory Research Center on Life and Living Systems (ExCELLS) is launched directly under the National Institutes of Natural Sciences to advance the activity of Okazaki Institute for Integrative Bioscience (OIIB).

Annual Review 2022 is a summary of research activities performed in IMS during October 2021–September 2022. Individual research groups at IMS are making steady progress in basic research on molecular structures, reactions and functions demonstrating "novel molecular capabilities," as reported in this Review. In addition to these individual activities, IMS conducts the six special programs in the institute basis: (i) Development of cold-atom based quantum simulators and their applications to quantum computing within the framework of Japan's flagship program on quantum sciences and technologies "Q-LEAP" by MEXT and "PRISM" by the Cabinet Office of Japan (2018–2028); (ii) Nano science project, called Nanotechnology Platform (ended in March 2022); (iii) Advanced Research Infrastructure for Materials and Nanotechnology in Japan; (iv) Inter-University Network for Common Utilization of Research Equipments; (v) Project on trans-hierarchical studies of materials and biological systems with molecular observations, as a joint program of NINS (ended in March 2022), Promotion of Frontier Research on Multi-Hierarchical Systems of Molecular Materials and Brain Circulation, from April 2022; (vi) IMS runs several international collaboration programs and also owns an internship program for young scientists: The Institute for Molecular Science International Internship Program (IMS-IIP). IMS-IIP provides the opportunity of internship for young researchers (e.g., master's and doctoral students, postdoctoral researchers and young faculty members of MOU partners) from overseas to stay in IMS laboratories.

Our life in Okazaki has changed since April 2021 due to the pandemic of COVID19. Utilization of WEB meeting has become standard for most of academic meetings and thus the opportunity to meet and discuss with our colleague all around the world has become easier than ever. Unexpected discoveries that come from meeting people face to face are no longer a reality in everyday life. Accepting Post-Docs and students from outside Japan is extremely difficult. Experimental collaboration based on practical exchange of personal has been restricted, while some new idea to perform the experiment by accepting samples from the users has started this year. From the administration point of view, acceleration of reforming our work style such as work from home has been realized, accompanied with paperless meeting and digitalization of office documents.

IMS will continue to contribute to lead the Molecular Science together with many young promising and well-established senior scientists. This institute has been most benefited with your constant support and we do expect your further support and advice for creating this new era of molecular science.

August, 2022

WATANABE, Yoshihito
Director General, Institute for Molecular Science

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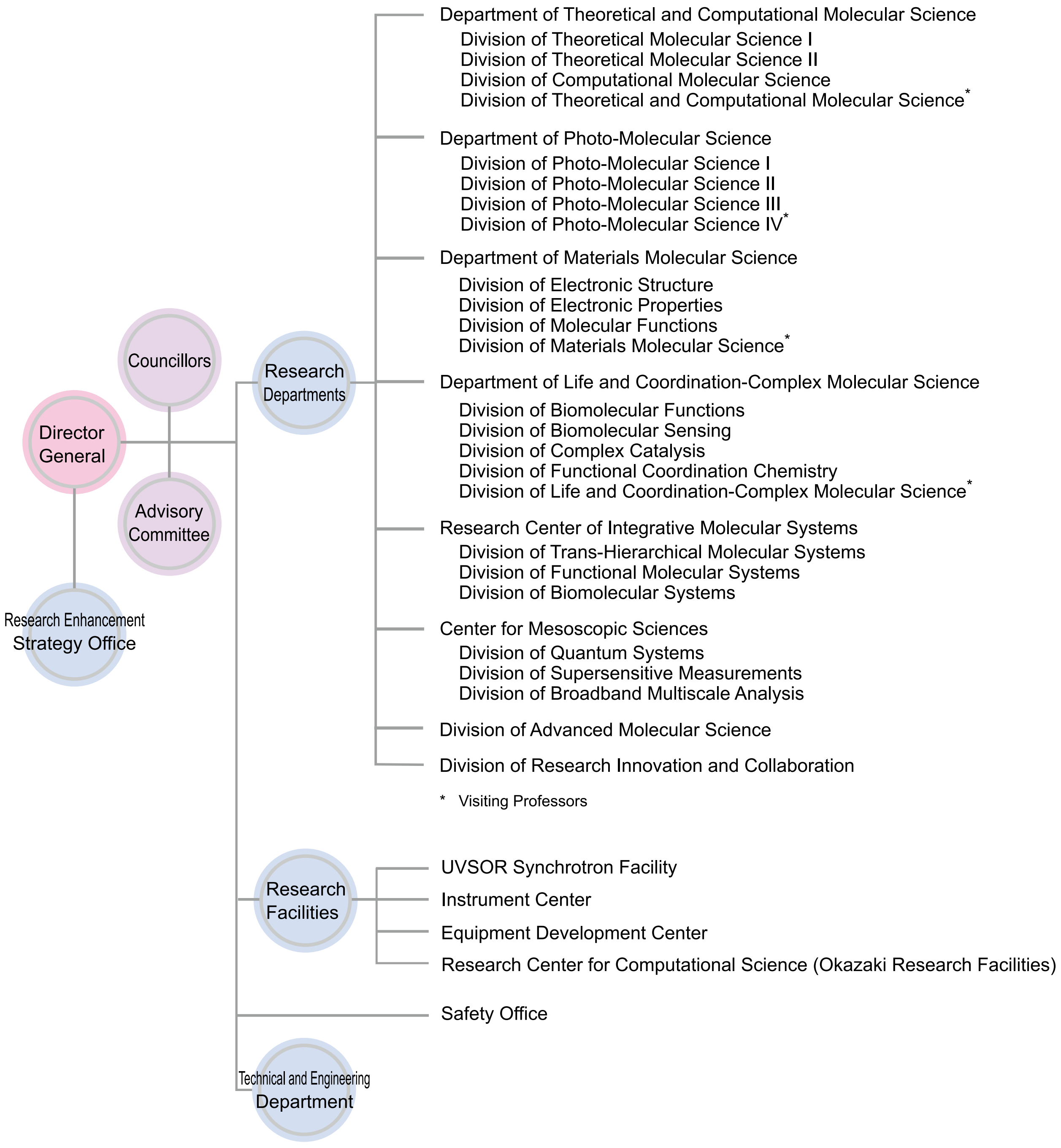
ORGANIZATION



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  - Councillors
  - Advisory Committee
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      - Division of Theoretical Molecular Science I
      - Division of Theoretical Molecular Science II
      - Division of Computational Molecular Science
      - Division of Theoretical and Computational Molecular Science*
    - Department of Photo-Molecular Science
      - Division of Photo-Molecular Science I
      - Division of Photo-Molecular Science II
      - Division of Photo-Molecular Science III
      - Division of Photo-Molecular Science IV*
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      - Division of Electronic Properties
      - Division of Molecular Functions
      - Division of Materials Molecular Science*
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      - Division of Biomolecular Sensing
      - Division of Complex Catalysis
      - Division of Functional Coordination Chemistry
      - Division of Life and Coordination-Complex Molecular Science*
    - Research Center of Integrative Molecular Systems
      - Division of Trans-Hierarchical Molecular Systems
      - Division of Functional Molecular Systems
      - Division of Biomolecular Systems
    - Center for Mesoscopic Sciences
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      - Division of Broadband Multiscale Analysis
    - Division of Advanced Molecular Science
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    - Instrument Center
    - Equipment Development Center
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* Visiting Professors

COUNCIL

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The Council is the advisory board for the Director General.
* Two of the councillors are selected among distinguished foreign scientists.

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OHMINE, Iwao	Professor Emeritus, Institute for Molecular Science, The Graduate University for Advanced Studies

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UOZUMI, Yasuhiro	Professor, Institute for Molecular Science
YAMAMOTO, Hiroshi	Professor, Institute for Molecular Science
YOKOYAMA, Toshihiko	Professor, Institute for Molecular Science

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NAKAMURA, Hiroki	Professor Emeritus, The Graduate University for Advanced Studies
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YAKUSHI, Kyuya	Professor Emeritus, The Graduate University for Advanced Studies
URISU, Tsuneo	President, NANORUS Co., Ltd.
NAGASE, Shigeru	Professor Emeritus, The Graduate University for Advanced Studies
HIRATA, Fumio	Professor Emeritus, The Graduate University for Advanced Studies
TANAKA, Koji	Specially Appointed Professor, Institute for Integrated Cell-Material Sciences, Kyoto University
KUWAJIMA, Kunihiro	Professor Emeritus, The Graduate University for Advanced Studies and The University of Tokyo
OHMINE, Iwao	Professor Emeritus, The Graduate University for Advanced Studies
KOSUGI, Nobuhiro	Director, Institute of Materials Structure Science, High Energy Accelerator Research Organization
WATANABE, Yoshihito	Executive Director, The Graduate University for Advanced Studies, Director General, Institute for Molecular Science
OKAZAKI, Susumu	Specially Appointed Professor, The University of Tokyo

GROUP LEADERS

Theoretical and Computational Molecular Science

SAITO, Shinji
Professor
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MINAMITANI, Emi
Associate Professor
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ISHIZAKI, Akihito
Professor
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EHARA, Masahiro
Professor
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OKUMURA, Hisashi
Associate Professor
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OKAZAKI, Kei-ichi
Associate Professor
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Photo-Molecular Science

OHMORI, Kenji
Professor
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KERA, Satoshi
Professor
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KATOH, Masahiro
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TAIRA, Yoshitaka
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OHIGASHI, Takuji
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(Cross Appointment)
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MATSUI, Fumihiko
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TANAKA, Kiyohisa
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Materials Molecular Science

YOKOYAMA, Toshihiko
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SUGIMOTO, Toshiki
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HIRAMOTO, Masahiro
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NISHIMURA, Katsuyuki
Associate Professor
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KOBAYASHI, Genki
Associate Professor
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Life and Coordination-Complex Molecular Science


AONO, Shigetoshi
Professor
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KATO, Koichi
Professor
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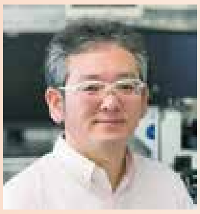
IINO, Ryota
Professor
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UOZUMI, Yasuhiro
Professor
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MOMIYAMA, Norie
Associate Professor
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KUSAMOTO, Tetsuro
Associate Professor
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SEGAWA, Yasutomo
Associate Professor
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Research Center of Integrative Molecular Systems


AKIYAMA, Shuji
Professor
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KOGA, Nobuyasu
Associate Professor
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KURAMOCHI, Hikaru
Associate Professor
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YAMAMOTO, Hiroshi
Professor
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Center for Mesoscopic Sciences


OKAMOTO, Hiromi
Professor
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KUMAGAI, Takashi
Associate Professor
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Division of Research Innovation and Collaboration


TAIRA, Takunori
Project Professor
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Division of Advanced Molecular Science


FUJITA, Makoto
Distinguished Professor
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KIMURA, Shin-ichi
Professor
(Cross Appointment)
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ONISHI, Hiroshi
Professor
(Cross Appointment)
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TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
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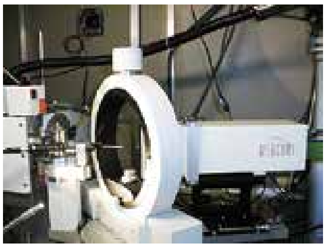
RESEARCH FACILITIES

UVSOR Synchrotron Facility p. 104

KERA, Satoshi
Director

Instrument Center p. 106

YOKOYAMA, Toshihiko
Director



Equipment Development Center p. 107

YAMAMOTO, Hiroshi
Director

Research Center for Computational Science (Okazaki Research Facilities) p. 108

EHARA, Masahiro
Director

VISITING PROFESSORS

Theoretical and Computational Molecular Science p. 24

SATO, Hirofumi
Visiting Professor
(Kyoto University)

YOSHIDA, Norio
Visiting Professor
(Nagoya University)

NOGUCHI, Hiroshi
Visiting Associate Professor
(University of Tokyo)

Photo-Molecular Science p. 41

MASE, Kazuhiko
Visiting Professor
(High Energy Accelerator
Research Organization)

FUKUHARA, Takeshi
Visiting Associate Professor
(RIKEN)

NAKAYAMA, Yasuo
Visiting Associate Professor
(Tokyo University of Science)

Materials Molecular Science p. 55

TANAKA, Koichiro
Visiting Professor
(Kyoto University)

OSAKA, Itaru
Visiting Professor
(Hiroshima University)

AKIMOTO, Ikuko
Visiting Associate Professor
(Wakayama University)

Life and Coordination-Complex Molecular Science p. 72

FUKAZAWA, Aiko
Visiting Professor
(Kyoto University)

UEDA, Akira
Visiting Associate Professor
(Kumamoto University)

KAMIYA, Yukiko
Visiting Associate Professor
(Nagoya University)

PERSONNEL CHANGES

Moving In

Nov. 1, 2021	Dr. ONISHI, Hiroshi joined IMS as a Prof. (Cross Appointment) in the Division of Advanced Molecular Science
Nov. 16, 2021	Senior Researcher MATSUI, Fumihiko joined IMS as a Prof. in the UVSOR Synchrotron Facility
Dec. 1, 2021	Res. Assist. Prof. MIWA, Kuniyuki joined IMS as an Assist. Prof. in the Department of Theoretical and Computational Molecular Science
Feb. 1, 2022	Dr. OHIGASHI, Takuji joined IMS as an Assoc. Prof. (Cross Appointment) in the UVSOR Synchrotron Facility
Feb. 16, 2022	Dr. OHNUKI, Jun joined IMS as an Assist. Prof. in the Department of Theoretical and Computational Molecular Science
Apr. 1, 2022	Prof. WATANABE, Yoshihito appointed Director General of IMS
Apr. 1, 2022	Dr. TANG, Zhiye joined IMS as an Assist. Prof. in the Department of Theoretical and Computational Molecular Science
Aug. 1, 2022	Dr. NAKAMURA, Akihiko joined IMS as an Assoc. Prof. (Cross Appointment) in the Division of Advanced Molecular Science

Moving Out

Jan. 31, 2022	Assist. Prof. OHIGASHI, Takuji (UVSOR Synchrotron Facility) moved out as an Assoc. Prof. of High Energy Accelerator Research Organization (KEK)
Feb. 28, 2022	Assoc. Prof. (Cross Appointment) TAKAYA, Hikaru (Division of Advanced Molecular Science) resigned from his post
Mar. 31, 2022	Director General KAWAI, Maki moved out as the President of National Institutes of Natural Sciences
Mar. 31, 2022	Assist. Prof. FUJIMOTO, Masaki (UVSOR Synchrotron Facility) moved out to Nagoya University
Mar. 31, 2022	Assist. Prof. YAGI, Maho (Department of Life and Coordination-Complex Molecular Science) moved out to Nagoya City University
Mar. 31, 2022	Assist. Prof. HIROBE, Daichi (Research Center of Integrative Molecular Systems) moved out to Shizuoka University
Mar. 31, 2022	Assist. Prof. NARUSHIMA, Tetsuya (Center for Mesoscopic Sciences) moved out to Ministry of Education, Culture, Sports, Science and Technology
May 31, 2022	Assoc. Prof. KOBAYASHI, Genki (Department of Materials Molecular Science) moved out as a Chief Scientist of RIKEN
Jul. 31, 2022	Assist. Prof. KOITAYA, Takanori (Department of Materials Molecular Science) moved out as an Assoc. Prof. of Kyoto University
Aug. 31, 2022	Assoc. Prof. MINAMITANI, Emi (Department of Theoretical and Computational Molecular Science) moved out as a Prof. of Osaka University
Aug. 31, 2022	Assist. Prof. MURAKI, Norifumi (Department of Life and Coodination-Complex Molecular Science) moved out as an Assoc. Prof. of Keio University
Aug. 31, 2022	Assist. Prof. YANAKA, Saeko (Department of Life and Coodination-Complex Molecular Science) moved out to Kyushu University
Sep. 30, 2022	Assoc. Prof. KOGA, Nobuyasu (Research Center of Integrative Molecular Systems) moved out as a Prof. of Osaka University

Graduate Programs

IMS is one of the leading national research institutes in natural science. For graduate education, IMS has two departments in Graduate School of Physical Sciences, SOKENDAI (The Graduate University for Advanced Studies): Department of Structural Molecular Science and Department of Functional Molecular Science. One year is divided into two terms, the first semester (April-to-September) and the second semester (October-to-March). The graduate education at IMS focuses on the molecular sciences. Each graduate student can study molecular science under guidance of the IMS faculty members in the following areas: Photomolecular science, materials molecular science, biomolecular and coordination molecular science, and theoretical and computational molecular science. In the 1st and 2nd years of the 5-year doctoral course, the programs emphasize the scientific education related to the expertises of IMS laboratories. By providing such opportunities, the program seeks to help students develop extensive knowledge on physical sciences and high degree of professional quality as well as to help them prepare for the education in their 3rd to 5th years of the 5-year doctoral course. Young scientists and graduate students from abroad are also encouraged to visit IMS through several opportunities such as the IMS Open Campus and Lecture in June, Summer Training Program in August, and Asian Winter School in addition to IMS International Internship Program as shown below.

In 2022, SOKENDAI has started planning the transition to a 20-program system at the Graduate Institute for Advanced Studies in April 2023. Thus, in order to develop human resources for researchers who can tackle complex and interdisciplinary issues based on the ever-changing trends in academic fields and the demands of society, it is necessary to build a system that can flexibly utilize highly specialized educational resources across disciplines.

International Collaboration and Exchange Programs

Many foreign researchers and students stay for 1–12 months in IMS to collaborate with us in the field of molecular science, or stay for 1–2 weeks to use various kinds of research equipments in our research facilities such as the UVSOR Synchrotron Facility, Instrument Center, and Equipment Development Center. IMS has own budget to carry out these international exchange and collaboration programs, and covers part of research expenses and travel expenses for visitors from abroad. They can use our guest houses, Mishima Lodge and Myodaiji Lodge.

Exchange/Collaboration program		Duration of Stay	Eligibility
IMS visiting faculty program	Long-term	3–12 months	Professors, Associate Professors and other corresponding positions
	Short-term*	1–3 months	
IMS International Internship Program (IMS-IIP)	Long-term	>6 months	Ph.D. students and PostDoc.
	Short-term*	1–6 months	
IMS facility user program		1–2 weeks	Professors, Researchers, and Ph.D. students

* We preferentially invite researchers and students from MOU partnership institutions

International Symposia

We organize several kinds of international symposia based on screening of submitted proposals. In addition, we have international collaborative symposia with MOU partners at IMS or at MOU partner's country as listed in Collaboration Programs.

Program		Purpose
International Symposia and Workshop	Okazaki Conference	An international conference with distinguished foreign researchers by focusing on an emerging field as a fundamental issue in the field of molecular science and related research area
	Mini-International Workshop	A small international workshop on a specific field
	Asia/Oceania IMS Workshop	Workshop with Asian and Oceanian researchers and students
IMS Workshop	IMS Workshop (General)	Workshop on timely topics in molecular science, organized as a collaborative effort between outside and IMS researchers
	IMS Workshop in cooperation with a specified research community	
	IMS Workshop in cooperation with graduate students	Workshop and other related activities planned by graduate students

RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

The goal of the Department is understanding and prediction of static and dynamic properties, reactions, and functions in condensed phase including biomolecular and heterogeneous catalytic systems by developing novel theories and computational methodologies based on theories in quantum mechanics, statistical mechanics, and solid state physics. The Department collaborates with Research Center for Computational Science on researches.

Theoretical Studies on Reactions, Functions, and Fluctuations in Many-Body Molecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

SAITO, Shinji
Professor
[shinji@ims.ac.jp]

Education

1988	B.S. Keio University
1990	M.E. Kyoto University
1995	Ph.D. The Graduate University for Advanced Studies

Professional Employment

1990	Technical staff, Institute for Molecular Science
1994	Research Associate, Nagoya University
1998	Associate Professor, Nagoya University
2005	Professor, Institute for Molecular Science
2006	Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
KODA, Shin-ichi
TANG, Zhiye
JSPS Post-Doctoral Fellow
MATSUMURA, Yoshihiro
Post-Doctoral Fellow
KOIZUMI, Ai
Graduazte Student
ZHU, Zhe
Secretary
CHIBA, Fumika

Keywords Reactions, Functions, Fluctuations

Many-body molecular systems, such as (supercooled) liquids and biomolecules, exhibit complex fluctuations. Furthermore, in these systems, various physical properties and biological functions are created and chemical reactions proceed under the fluctuations. We aim to elucidate the properties, functions, and reactions by investigating fluctuations and dynamics of the many-body molecular systems.

We have investigated fluctuations and dynamics of liquids by developing computational method for multi-dimensional nonlinear spectroscopy that can reveal detailed dynamical infomation not available from conventional linear spectroscopy. Consequently, we revealed the molecular origins of the ultrafast energy relaxation and time evolution of inhomogeneous fluctuations in liquid water. In supercooled liquids, rare and non-uniform structural changes, called dynamic heterogeneity, are induced by fluctuations. We elucidated the relationship between the lifetime of the dynamic heterogeneity and the fragility using the three-time correlation function of density fluctuations.

We study the molecular origin of anomalous properties of liquid water. We revealed that the anomalies of liquid water are related to the structural and dynamical instabilities hidden in the experimentally inaccessible region and the physical reason of the low glass transition of liquid water. Now we investigate how rare but persistent structural relaxations proceed at low temperatures towards the glass transition temperature.

Complex conformational fluctuations and changes are also found in biomolecular systems. In addition, conformational dynamics are considered to be essential for biological functions. We examine the relationship between fluctuation and biomolecular function found in the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. We investigate the dynamic effects of enzymatic reactions and find the importance of prearranged states for the rare but persistent enzymatic reactions. Furthermore, we examine dynamic disorder in conformational changes of proteins at the molecular level.

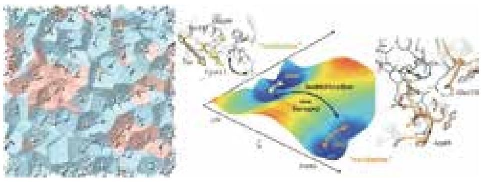


Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013). T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys. (Perspective)* **150**, 100901 (17 pages) (2019), C. R. Baiz *et al.*, *Chem. Rev.* **120**, 7152–7218 (2020).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018), S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019).
- T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).
- S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).

1. Multimeric Structure Enables the Acceleration of KaiB-KaiC Complex Formation Induced by ADP/ATP Exchange Inhibition[1)]

Circadian clocks tick a rhythm with a nearly 24-hour period in a variety of organisms. In the clock proteins of cyanobacteria, KaiA, KaiB, and KaiC, known as a minimum circadian clock, the slow KaiB-KaiC complex formation is essential in determining the clock period. This complex formation, occurring when the C1 domain of KaiC hexamer binds ADP molecules produced by the ATPase activity of C1, is considered to be promoted by accumulating ADP molecules in C1 through inhibiting the ADP/ATP exchange (ADP release) rather than activating the ATP hydrolysis (ADP production). Significantly, this ADP/ATP exchange inhibition accelerates the complex formation together with its promotion, implying a potential role in the period robustness under environmental perturbations. However, the molecular mechanism of this simultaneous promotion and acceleration remains elusive because inhibition of a backward process generally slows down the whole process. In this article, to investigate the mechanism, we build several reaction models of the complex formation with the pre-binding process concerning the ATPase activity. In these models, six KaiB monomers cooperatively and rapidly bind to C1 when C1 binds ADP molecules more than a given threshold while stabilizing the binding-competent conformation of C1. Through comparison among the models proposed here, we then extract three requirements for the simultaneous promotion and acceleration: The stabilization of the binding-competent C1 by KaiB binding, slow ADP/ATP exchange in the binding-competent C1, and relatively fast ADP/ATP exchange occurring in the binding-incompetent C1 in the presence of KaiB. The last two requirements oblige KaiC to form a multimer. Moreover, as a natural consequence, the present models can also explain why the binding of KaiB to C1 reduces the ATPase activity of C1.

2. Vectorial Insertion of a β-Helical Peptide into Membrane: A Theoretical Study on Polytheonamide B[2)]

Spontaneous unidirectional, or vectorial, insertion of transmembrane peptides is a fundamental biophysical process for toxin and viral actions. Polytheonamide B (pTB) is a potent cytotoxic peptide with a $\beta^{6.3}$-helical structure. Previous experimental studies revealed that the pTB inserts into the membrane in a vectorial fashion and forms a channel with its single molecular length long enough to span the membrane. Also, molecular dynamics simulation studies demonstrated that the pTB is prefolded in aqueous solution. These are unique features of pTB because most of the peptide toxins form channels through oligomerization of transmembrane helices. Here, we performed all-atom molecular dynamics simulations to examine the dynamic mechanism of the vectorial insertion of pTB, providing underlying elementary processes of the membrane insertion of a prefolded single transmembrane peptide. We find that the insertion of pTB proceeds with only the local lateral compression of the membrane in three successive phases: "Landing," "penetration," and "equilibration" phases. The free energy calculations using the replica-exchange umbrella sampling simulations present an energy cost of ~4 kcal/mol at the membrane surface for the membrane insertion of pTB from bulk water. The trajectories of membrane insertion revealed that the insertion process can occur in two possible pathways, namely "trapped" and "untrapped" insertions; in some cases, pTB is trapped in the upper leaflet during the penetration phase. Our simulations demonstrated the importance of membrane anchoring by the hydrophobic N-terminal blocking group in the landing phase, leading to subsequent vectorial insertion.

3. Excited States of Chlorophyll *a* and *b* in Solution by Time-Dependent Density Functional Theory[3)]

The ground state and excited state electronic properties of chlorophyll (Chl) *a* and Chl *b* in diethyl ether, acetone, and ethanol solutions are investigated using quantum mechanical and molecular mechanical calculations with density functional theory (DFT) and time-dependent DFT (TDDFT). Although the DFT/TDDFT methods are widely used, the electronic structures of molecules, especially large molecules, calculated with these methods are known to be strongly dependent on the functionals and the parameters used in the functionals. Here, we optimize the range-separated parameter, μ, of the CAM-B3LYP functional of Chl *a* and Chl *b* to reproduce the experimental excitation energy differences of these Chl molecules in solution. The optimal values of μ for Chl *a* and Chl *b* are smaller than the default value of μ and that for bacteriochlorophyll *a*, indicating the change in the electronic distribution, *i.e.*, an increase in electron delocalization, within the molecule. We find that the electronic distribution of Chl *b* with an extra formyl group is different from that of Chl *a*. We also find that the polarity of the solution and hydrogen bond cause the decrease in the excitation energies and the increase in the widths of excitation energy distributions of Chl *a* and Chl *b*. The present results are expected to be useful for understanding the electronic properties of each pigment molecule in a local heterogeneous environment, which will play an important role in the excitation energy transfer in light-harvesting complex II.

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Theoretical Studies on Novel Physical Properties Arising from Many-Body Interaction

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

MINAMITANI, Emi
Associate Professor
(–August, 2022)
[eminamitani@ims.ac.jp]

Education

2005	B.S. Osaka University
2010	Ph.D. Osaka University

Professional Employment

2010	Postdoctoral Fellow, Osaka University
2011	Special Postdoctral Researcher, RIKEN
2013	Assistant Professor, The University of Tokyo
2015	Lecturer, The University of Tokyo
2019	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2022	Professor, Osaka University

Awards

2008	L'Oréal–UNESCO Japan National Fellowships for Women in Science
2011	Best Poster Award in ISSS-6 Internal Symposium on Surface Science
2017	Young Scientist Award of the Physical Society of Japan
2019	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2020	The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science
2021	The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan

Member

Assistant Professor
SHITADE, Atsuo

IMS Research Assistant Professor
MIWA, Kuniyuki

Secretary
AKABA, Atsuko

Keywords Quantum Many-Body Interaction, Density Functional Theory, Quantum Field Theory

Quantum many-body interaction is a source of novel physical properties in condensed matters. In our group, we develop theoretical methods by combining quantum field theory and density functional theory, and carry out collaborative research with experimental groups. As specific targets, we focus on magnetism in nanostructure and energy dissipation.

For magnetism in nanostructure, we are interested in the Kondo effect and spin–orbit interaction. The Kondo effect arises from the interaction between the localized spin and conduction electrons, which forms a characteristic many-body state so-called the Kondo singlet state. The spin–orbit interaction originating from the relativistic effect constrains the magnetic moment direction to a specific direction. We investigate the possibility of novel physical phenomena induced by these interactions in the nanostructure and molecules on surfaces.

For energy dissipation, we focus on the effect of electron–phonon interaction. The electron–phonon interaction is one of the most fundamental interactions in the condensed matter physics, and the quantitative evaluation in realistic materials is highly demanding. We adopt the ab-initio calculation to analyze the signal of electron–phonon coupling in surface spectroscopy and thermal properties in various kind of solids.

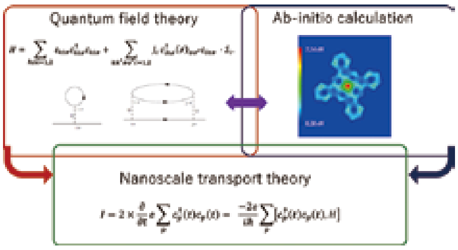

Figure 1. Schematic image of the theoretical method developed in our group.

Selected Publications

- E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi and M. Kawai, "Symmetry-Driven Novel Kondo Effect in a Molecule," *Phys. Rev. Lett.* **109**, 086602 (2012).
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- R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai and N. Takagi, "Single-Molecule Quantum Dot as a Kondo Simulator," *Nat. Commun.* **8**, 16012 (2017).
- E. Minamitani, M. Ogura and S. Watanabe, "Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential," *Appl. Phys. Express* **12**, 095001 (2019).
- E. Minamitani, "Ab Initio Analysis for the Initial Process of Joule Heating in Semiconductors," *Phys. Rev. B* **104**, 085202 (2021).
- E. Minamitani, T. Shiga, M. Kashiwagi and I. Obayashi "Topological Descriptor of Thermal Conductivity in Amorphous Si," *J. Chem. Phys.* **156**, 244502 (2022).

1. Topology and Machine Learning Reveal a Hidden Relationship between Thermal Conductivity and Amorphous Structure

The structure of amorphous materials is characterized by the absence of long-range order (LRO) and the presence of some medium-range order (MRO) beyond the short-range order (SRO). Revealing the quantitative correlation between the structural and physical properties of amorphous materials remains a challenging task. Thermal conductivity is a fundamental physical property that shows unique behavior in amorphous materials owing to the strong interaction between lattice vibrations and disorders. The lack of LRO reduces the lattice thermal conductivity by several orders than that of a crystal with the same stoichiometry. The heat carriers, vibrational modes, in amorphous materials are generally classified into propagating and non-propagating modes. The former is exhibited in the low-frequency range and has characteristics similar to those of phonons in the crystal. In contrast, the latter carries heat in a diffusive manner rather than propagating energy as phonons do in the crystal. It is expected that the MRO affects the propagation and diffusion of these vibrational modes, and thus the thermal conductivity.

Previous studies indicated that determination of the atomic structure corresponding to the MRO and extraction of the correlation between the MRO and the lattice thermal conductivity is essential to precisely control the thermal properties of amorphous Si. However, these tasks remain challenging because determining the essential features of MRO from the traditional structural analysis is difficult, such as the pair distribution function and bond-orientation order analysis.

Recently, persistent homology, an emerging technique in the field of topological data analysis, has been employed to describe the atomic structures corresponding to MRO in SiO_2 glass, metallic glass, and amorphous ice. The advantage of persistent homology is that multiscale topological information can be extracted from complicated structures. For the analysis of persistent homology, we considered a growing sequence of network structures for given data points with different scale lengths defined by the filtration procedure. A schematic of the filtration procedure is shown in Figure 2. As can be seen, we considered spheres centered at the respective data points. Subsequently, the radius of each sphere gradually increases. The sequence of increases in radius is often referred to as "time." At some radius, the spheres start to intersect with each other, and we set an edge between the centers of the spheres. When the edges form a closed ring, this corresponds to a topological feature called a "cycle." As the radius further increases, the ring gets fully covered by circles. This is interpreted as the cycle converting into another class of topological features called a "boundary." The topology of the data is represented by the pairs of birth and death times at which the cycle appears and is converted into a boundary. The two-dimensional visualization of birth and death time pairs is called a persistence diagram (PD).

In this study, using persistent homology, we constructed reliable descriptors for lattice thermal conductivity, reflecting the topological features of the MRO in amorphous Si.

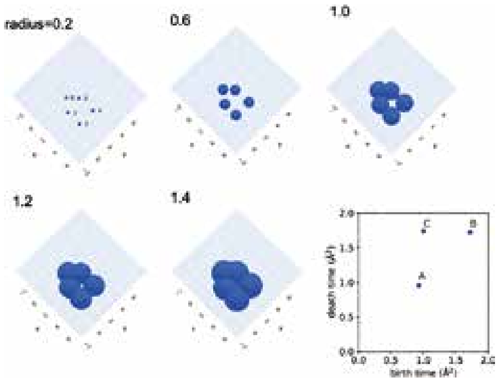

Figure 2. Schematic of the filtration procedure used to obtain a PD from data points.

A structural model of amorphous Si was generated via the melt–quench method using classical molecular dynamics (MD), where the system temperature was increased above the melting temperature and then gradually cooled to room temperature. The difference in structural characteristics was introduced by changing the cooling rate in the MD simulation from 10^{14} to 10^{11} K/s. We selected 570 snapshots from the equilibrated MD simulation after the melt–quench procedure, and the thermal conductivity mediated by non-propagating modes and the PD were evaluated for each structure.

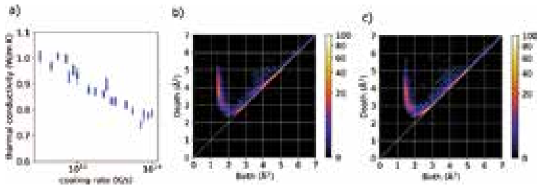

Figure 3. a) and b) Persistent diagrams for amorphous structure generate by the cooling rate of 10^{14} and 10^{11} K/s, respectively.

As shown in Figure 3, both thermal conductivity and PD depend on the cooling rates. Therefore, we constructed a descriptor of the topological features using the persistent image of the PD. We demonstrated that supervised training for the dataset of these descriptors and lattice thermal conductivities could achieve accurate predictions. In addition, from the inverse analysis by volume-optimal cycle, we determined the typical ring features correlated with the thermal conductivity and MRO.[1] Our study demonstrates that the physical properties of amorphous Si can be predicted based on topological features. In addition, our results illustrate the hidden relationship between MRO and the physical properties of amorphous Si. This study could open an avenue for controlling material characteristics through the topology of nanostructures.

2. Other Ongoing Projects:

- Mechanical Properties in Amorphous Solids

Reference

1) E. Minamitani, T. Shiga, M. Kashiwagi and I. Obayashi, *J. Chem. Phys.* **156**, 244502 (2022).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science II

ISHIZAKI, Akihito
Professor
[ishizaki@ims.ac.jp]

Education

2001	B.S. Kyoto University
2005	M.S. Kyoto University
2008	D.S. Kyoto University

Professional Employment

2006	JSPS Research Fellow, Kyoto University
2008	JSPS Postdoctoral Fellow for Research Abroad, University of California, Berkeley
2010	Postdoctoral Fellow, Lawrence Berkeley National Laboratory
2012	Research Associate Professor, Institute for Molecular Science
2013	Fellow 2012–2013, Wissenschaftskolleg zu Berlin
2016	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting professor, Nagoya University

Awards

2015	10th Condensed-Matter Science Prize, Japan
2016	10th Young Scientist Award of the Physical Society of Japan
2016	18th Sir Martin Wood Prize
2017	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2020	JSPS Prize
2020	Japan Academy Medal

Member
Assistant Professor
MIWA, Kuniyuki
IMS Research Assistant Professor
FUNO, Ken
Post-Doctoral Fellow
SAKAMOTO, Souichi
JO, Ju-Yeon
YAN, Yaming
Secretary
AKABA, Atsuko

Keywords Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

Essentially, any quantum systems can never be regarded as "isolated systems." Quantum systems are always in contact with "the outside world," and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spectroscopic signals. Therefore, theoretical tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

(1) Developments of condensed phase quantum dynamic theories
(2) Quantum theories to describe dynamical and transport processes in materials and biological systems
(3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

Selected Publications

- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, "Using Coherence to Enhance Function in Chemical and Biophysical Systems," *Nature* **543**, 647–656 (2017).
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- A. Kato and A. Ishizaki, "Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases," *Phys. Rev. Lett.* **121**, 647 (2018).
- Y. Fujihashi, R. Shimizu and A. Ishizaki, "Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules," *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, "Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy," *J. Chem. Phys.* **153**, 051102 (2020). [Editor's Pick]

1. Probing Exciton Dynamics with Spectral Selectivity through the Use of Quantum Entangled Photons

Quantum light, such as entangled photons, are promising resources for the development of new spectroscopic techniques. For example, non-classical correlations between entangled photons can be potentially exploited to enhance the precision of optical measurements beyond classical techniques or to extract matter information with simpler optical systems compared to conventional schemes. In this respect, the entangled photons may open new avenues for unambiguously extracting information about dynamic processes in complex molecules such as photosynthetic light-harvesting systems, in which multiple electronic states are present within a narrow energy range, from the congested spectra. However, to date, only a few theoretical studies have been reported on the application of entangled photons to time-resolved spectroscopic measurements. Hence, there is no comprehensive understanding of what non-classical states of light are suitable for implementing real-time observation of dynamical processes in condensed phases.

Here, we propose a novel time-resolved spectroscopy technique that selectively enhances specific signal contributions by harnessing the non-classical correlations between entangled photons generated via parametric down-conversion (PDC) pumped with a monochromatic laser. The key feature in the proposed technique is that the entanglement time, which is the hallmark of the non-classical photon correlations, works as a spectral filter in signal processing to selectively resolve a specific region of spectra, while it simultaneously offers a knob for controlling the accessible time region of dynamics in molecules. For demonstration purposes, we apply the proposed spectroscopic scheme to the Fenna-Matthews-Olson (FMO) pigment-protein complex from the photosynthetic green sulfur bacterium. The results show that the phase-matching functions of the PDC in the nonlinear crystals such as periodically poled $KTiOPO_4$ (PPKTP) crystal and β-BaB_2O_4 (BBO) crystal allow one to separately measure specific peaks of spectra in the FMO complex by tuning the entanglement time and the central frequencies of the entangled photons. It is also found that the spectral filtering can be implemented in the range of currently available entangled photon sources. Moreover, the results indicate that the spectral filter effects can be easily adjusted by changing nonlinear crystals and/or their properties because the spectral distribution of the phase-matching function strongly depends on the properties of the nonlinear crystal. Since, in addition to the BBO and PPKTP crystals considered in this study, there is a wide range of nonlinear crystals that have been used for PDC in the near-infrared and visible regions, the proposed technique is expected to be applicable not only to the FMO complex but also to other light-harvesting systems by finding an appropriate nonlinear crystal corresponding to the spectral range of the molecular system of interest. We thus anticipate that the proposed technique can be a useful tool for monitoring step-by-step energy transfer pathway in the light-harvesting systems by selectively extracting desired signal contributions from the congested spectra.[1)]

2. Benefit of Coexistence of Chlorophyll *a* and *b* in Antenna of Photosystem II

Chlorophylls (Chls) in the photosystem II (PSII) play essential parts in the initial process of oxygenic photosynthesis, *i.e.*, the solar light is collected by Chls embedded in the light-harvesting complexes termed antenna, and then the excitation energy is transferred to Chls in the reaction center, where the charge separation takes place. The antenna includes two distinct types of Chls, Chls *a* and *b*, whereas the reaction center possesses a single type Chl *a*. As the transition energy of Chl *b* is higher than that of Chl *a*, the excitation energy flows from Chl *b* to Chl *a*. Hence, if all the pigments in the antenna are composed of Chl *b*, higher efficiency of the excitation energy transfer to the reaction center could be expected [H. Kim, *et al.*, *arXiv*:2101.04848 (2021)]. Even though such an 'all-*b*' system would offer an advantage in photosynthesis, the naturally occurring antenna binds both Chls *a* and *b* throughout the green plants. The reason why the mixed Chl system is adopted in the antenna found in nature has yet to be understood clearly.

In this work, we investigated the role of Chl *a* existed in the antenna during the excitation energy transfer (EET). The rate constants of the EET within and between domains, each of which comprises strongly coupled Chls forming delocalized excited states, were calculated with the aid of the Redfield and generalized Förster theory. To discuss how the ratio κ of Chl *b* to *a* in the antenna affects the time evolution of the excitation energy distribution, we considered the hypothetical models of the PSII where κ was equal to or different from that in the natural PSII. The results show the quantum yield of the EET to the reaction center is improved with increasing κ, as expected. Moreover, it is found that in the case of the natural PSII, the excitation energy was localized at particular pigment-protein complexes in the antenna, termed CP26 and CP29, where the occurrence of non-photochemical quenching during the photoprotection was suggested in the previous study [T. K. Ahn, *et al.*, *Science* **320**, 794 (2008)]. The results indicate the natural PSII possesses the optimal structure not only for collecting the light energy into the reaction center but also for balancing the EET and the other processes, such as photoprotection.

3. Dynamics of the Coupled System Composed of Electrons and Anharmonic Lattice Vibrations in Solid

Anharmonicity of lattice vibrations is responsible for a large quantity of phenomena including thermal conductivity, structural phase transition, and so forth. Moreover, recent studies suggested lattice anharmonicity would have a dominant role in the carrier dynamics of some sort of soft semiconductors, *e.g.*, lead-based halide perovskites which exhibit novel optoelectronic properties. Here, we theoretically investigate the dynamics of the coupled systems composed of electrons and anharmonic lattice vibrations. We highlight the importance of the timescale difference between electron and lattice dynamics in determining the materials properties.

Reference

1) Y. Fujihashi *et al.*, to be submitted.

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

Department of Theoretical and Computational Molecular Science Division of Computational Molecular Science

EHARA, Masahiro
Professor
[ehara@ims.ac.jp]

Education

1988 B.E. Kyoto University
1990 M.E. Kyoto University
1993 Ph.D. Kyoto University

Professional Employment

1993 Postdoctral Fellow, Institute for Fundamental Chemistry
1994 JSPS Postdoctoral Fellow
1994 Visiting Researcher, Heidelberg University (–1995)
1995 Assistant Professor, Kyoto University
2002 Associate Professor, Kyoto University
2006 Theoretical Research Division Supervisor, Kyoto University (–2008)
2008 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2012 Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009 APATCC Pople Medal
2009 QSCP Prize CMOA

Member

IMS Research Assistant Professor
ZHAO, Pei
Post-Doctoral Fellow
KANAZAWA, Yuki
INAI, Naoto
Graduate Student
HATORI, Atsuya
Secretary
SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, “SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution,” *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, “Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser,” *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, “CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions,” *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, “Cooperative H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study,” *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Aggregation-Induced Phosphorescence of Platinum(II) Complexes: The Role of the Metal–Metal Interactions on Emission Decay in the Crystalline State[1)]

Discerning the origins of the phosphorescent aggregation-induced emission (AIE) from Pt(II) complexes is crucial for developing the broader range of photo-functional materials. In this work, we describe phosphorescence and deactivation processes of four class of AIE active Pt(II) complexes in the crystalline state based on experimental and theoretical investigation. These complexes show metal-to-ligand and/or metal–metal-to-ligand charge transfer emission in crystalline state with different heat resistance against thermal emission quenching. The calculated energy profiles including the minimum energy crossing point (MECP) between S_0 and T_1 states were consistent with the heat resistant properties, which provided the mechanism for AIE expression. Furthermore, we have clarified the role of metal–metal interaction in AIE by comparing two computational models.

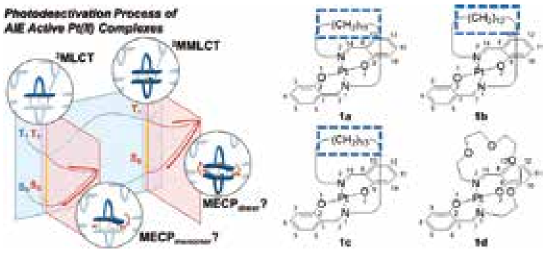

Figure 1. The mechanism of phosphorescent AIE by estimating the MECP of four Pt(II) complexes in crystalline state, along with an investigation of the role of metal–metal interaction on AIE.

2. Asymmetric Twisting of C-Centered Octahedral Gold(I) Clusters by Chiral *N*-Heterocyclic Carbene Ligation[2)]

Asymmetric induction of metal clusters by ligation of chiral ligands is intriguing in terms of the mechanism of chirality transfer and the stability of the resulting chiral structure. In this work, we report the asymmetric induction of *C*-centered hexanuclear $\mathrm{CAu^I_6}$ clusters into an asymmetrically twisted structure through monodentate, chiral benzimidazolylidene-based *N*-heterocyclic carbene (NHC) ligands. X-ray diffraction analysis revealed that the NHC-ligated $\mathrm{CAu^I_6}$ cluster was diastereoselectively twisted with directionally-selective, bond length expansion and contraction of the Au–Au contacts, and that the original cluster with high symmetry was transformed into an optically pure, asymmetric $\mathrm{CAu^I_6}$ cluster with C_1 symmetry. The circular dichroism (CD) spectroscopy confirmed that the asymmetrically twisted $\mathrm{CAu^I_6}$ structure was maintained even in solution. The TD-DFT calculations provided the detailed assignments of the CD spectrum and clarified the origin of the chiroptical properties of this cluster. Such asymmetric induction of configurationally stable metal clusters would greatly expand the molecular design possibilities of asymmetric catalysts and chiroptical materials by utilizing library chiral NHC ligands.

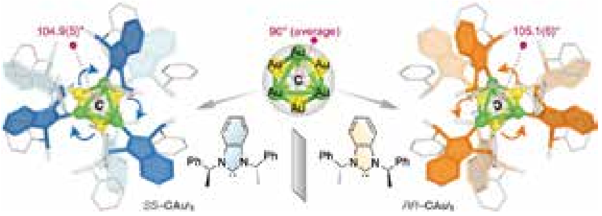

Figure 2. *C*-centered octahedral gold(I) clusters ($\mathrm{CAu^I_6}$) mono-ligated by *N*-heterocyclic carbene (NHC) ligands. Asymmetrically twisted $\mathrm{CAu^I_6}$ core structures were induced by NHC ligands.

3. Enhanced Oxygen Reduction Activity of Size-Selected Platinum Subnanocluster Catalysts: Pt_n (n = 3–9)[3)]

Nanoclusters (NCs) are promising candidates to improve catalytic activity despite of the controversial size specificity, because the atomicity is a crucial parameter that determines the activity of platinum (Pt) NCs. In this work, we show the enhanced catalytic activity based on the charge redistribution in Pt sub-NCs containing three to nine Pt atoms (Pt_n; n = 3–9) on a glassy carbon substrate. The sub-NCs show 1.6–2.2 times higher activity than the standard Pt/C catalysts with a Pt crystallite diameter of 2 nm. The geometric structures are identified using structure analyses by X-ray absorption fine structure spectroscopy and density functional theory, and the activity origin within the supported Pt sub-NCs is theoretically discussed from viewpoints of energetics for reaction intermediates in the electrochemical processes. It should be possible to use sub-NCs in future fuel cell technologies as an active catalyst with a high atomic efficiency.

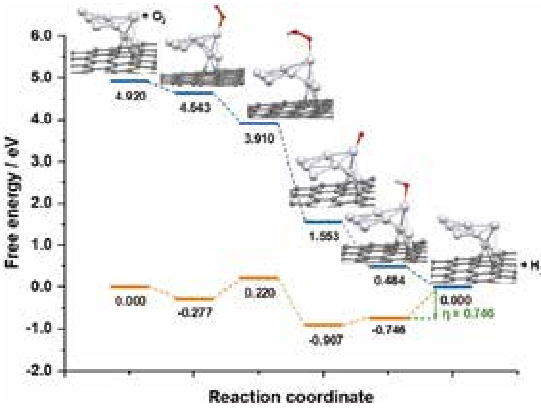

Figure 3. Oxygen reduction reaction (ORR) free energy diagrams for sequential reactions of $\mathrm{Pt_8/Gr}$ isomer between O_2 reactants and H_2O products with applied potentials of 0 V (blue) and 1.23 V (orange).

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2) X.-L. Pei, P. Zhao, H. Ube, Z. Lei, K. Nagata, M. Ehara and M. Shionoya, *J. Am. Chem. Soc.* **144**, 2156–2163 (2022).

3) A. Ohnuma, K. Takahashi, H. Tsunoyama, T. Inoue, P. Zhao, A. Velloth, M. Ehara, N. Ichikuni, M. Tabuchi and A. Nakajima, *Catal. Sci. Technol.* **12**, 1400–1407 (2022).

Molecular Dynamics Simulations of Disease-Related Biomolecules

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

OKUMURA, Hisashi
Associate Professor
[hokumura@ims.ac.jp]

Education

1998	B.S. Keio University
2002	Ph.D. Keio University

Professional Employment

2002	Postdoctoral Fellow, The University of Tokyo
2002	Research Associate, Institute for Molecular Science
2004	Research Associate, The Graduate University for Advanced Studies
2006	Research Lecturer, Nagoya University
2008	Research Assistant, Rutgers University
2009	Assistant Research Professor, Rutgers University
2009	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2018	Associate Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Award

2014	Academic Award of the Molecular Simulation Society of Japan

Member

Assistant Professor
ITOH, Satoru G.

Post-Doctoral Fellow
TANIMOTO, Shoichi

Graduate Student
MIYAZAWA, Kazuhisa
FUKUHARA, Daiki
OTAWA, Masaki

Secretary
KAWAGUCHI, Ritsuko

Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. The conventional canonical-ensemble molecular dynamics (MD) simulations tend to get trapped in a few of the local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as the replica-permutation method. We apply these methods to proteins and peptides and try to predict the native structures of proteins, as in Figure 1.

We are also interested in disease-related biomolecules. For example, protein aggregates such as spherical substances called oligomers and acicular substances called amyloid fibrils (Figure 2) cause more than 30 kinds of diseases. Alzheimer's disease is thought to be caused by aggregated amyloid-β (Aβ) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of Aβ peptides. We perform such MD simulations of oligomers and amyloid fibrils.

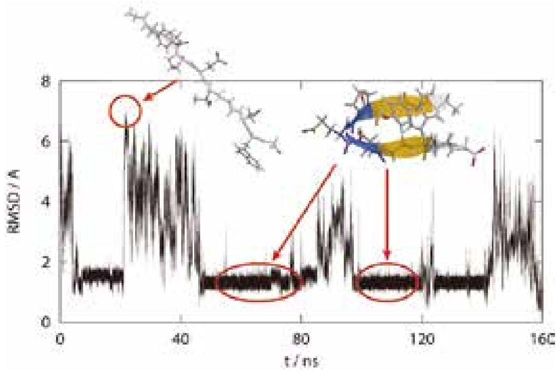

Figure 1. Time series of protein folding simulation.

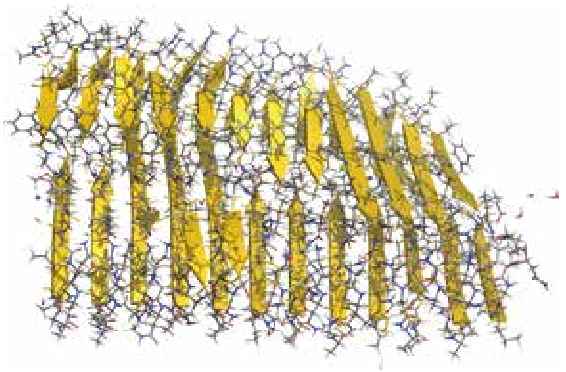

Figure 2. Snapshot of an Aβ amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- S. G. Itoh and H. Okumura, "Oligomer Formation of Amyloid-β(29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* **120**, 6555–6561 (2016).
- H. Okumura, S. G. Itoh, K. Nakamura and T. Kawasaki, "Role of Water Molecules in the Laser-Induced Disruption of Amyloid Fibrils Observed by Nonequilibrium Molecular Dynamics Simulations," *J. Phys. Chem. B* **125**, 4964–4976 (2021).
- S. Tanimoto, S. G. Itoh and H. Okumura, ""Bucket Brigade" Using Lysine Residues in RNA-Dependent RNA Polymerase of SARS-CoV-2," *Biophys. J.* **120**, 3615–3627 (2021).

1. Replica Permutation with Solute Tempering for Molecular Dynamics Simulation and Its Application to the Dimerization of Amyloid-β Fragments

We proposed the replica permutation with solute tempering (RPST)[1] by combining the replica-permutation method (RPM) and the replica exchange with solute tempering (REST), as in Figure 3. Temperature permutations are performed among more than two replicas in RPM, whereas temperature exchanges are performed between two replicas in the replica-exchange method (REM). The temperature transition in RPM occurs more efficiently than in REM. In REST, only the temperatures of the solute region, the solute temperatures, are exchanged to reduce the number of replicas compared to REM. Therefore, RPST is expected to be an improved method taking advantage of these methods. For comparison, we applied RPST, REST, RPM, and REM to two amyloid-β(16–22) peptides in explicit water. We calculated the transition ratio and number of tunneling events in the temperature space, and the number of dimerization events of amyloid-β(16–22) peptides. The results indicate that in RPST, the number of replicas necessary for frequent random walks in the temperature and conformational spaces is reduced compared to the other three methods. Additionally, we focused on the dimerization process of amyloid-β(16–22) peptides. The RPST simulation with a relatively small number of replicas shows that the two amyloid-β(16–22) peptides form the intermolecular antiparallel β-bridges due to the hydrophilic side-chain contact between Lys and Glu and hydrophobic side-chain contact between Leu, Val, and Phe, which stabilizes the dimer of the peptides.

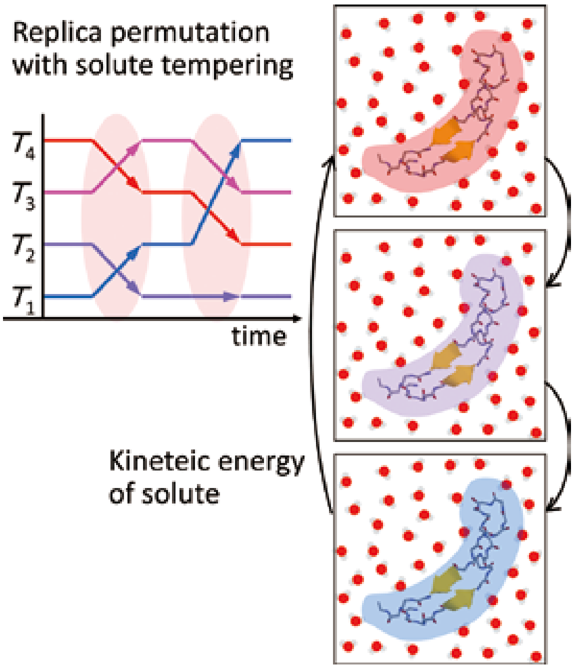

Figure 3. Schematic illustration of replica permutation with solute tempering. Temperatures in the solute region are permutated among more than two replicas.

2. Implementations of Replica-Permutation and Replica Sub-Permutation Methods into LAMMPS

The replica-permutation method (RPM) and the replica sub-permutation method (RSPM) have been proposed as improved alternatives to the replica-exchange method (REM). We implemented the RPM and RSPM in the canonical and isothermal-isobaric ensembles into an open-source classical molecular dynamics package, LAMMPS.[2] We applied the RPM and RSPM to a polyethylene chain in a vacuum and an alanine dipeptide in explicit water to test the implemented codes. We demonstrated that the RPM and RSPM by our codes achieved higher transition ratios of temperatures and faster convergence of physical quantities than the REM. We also validated that the RPM and RSPM generate statistical ensembles correctly.

3. Dimerization of α-Synuclein Fragments Studied by Isothermal-Isobaric Replica-Permutation Molecular Dynamics Simulation

Aggregates and fibrils of intrinsically disordered α-synuclein are associated with Parkinson's disease. Within a non-amyloid β component (NAC) spanning from 61st to 95th residues of α-synuclein, an 11-residue segment called NACore is an essential region for both fibril formation and cytotoxicity. Although NACore peptides alone are known to form aggregates and amyloid fibrils, the mechanisms of the aggregation and fibrillation remain unknown. We investigated the dimerization process of NACore peptides as the initial stage of the aggregation and fibrillation process by isothermal-isobaric replica-permutation molecular dynamics simulation.[3] The simulation succeeded in sampling a variety of dimer structures. An analysis of secondary structure revealed that most of NACore dimer forms intermolecular β-bridges. In particular, more antiparallel β-bridges were observed than parallel β-bridges. We also found that intramolecular secondary structures such as α-helix and antiparallel β-bridge are stabilized in the pre-dimer state. However, we identified that the intermolecular β-bridges tend to form directly with no specific structure because the NACore peptides have a low propensity to form the intramolecular secondary structures.

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2) M. Yamauchi, G. La Penna, S. G. Itoh and H. Okumura, *Comput. Phys. Commun.* **276**, 108362 (12 pages) (2022).

3) M. Yamauchi and H. Okumura, *J. Chem. Inf. Model.* **61**, 1307–1321 (2021).

Dynamics of Biomolecular Machines in Function Revealed by Theoretical Methods

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

OKAZAKI, Kei-ichi
Associate Professor
[keokazaki@ims.ac.jp]

Education

2004	B.S. Kyoto University
2006	M.S. Kobe University
2009	Ph.D. Kobe University

Professional Employment

2007	JSPS Research Fellow (DC2), Kobe University
2009	JSPS Postdoctoral Fellow (PD), Waseda University
2010	Part-time Lecturer, Waseda University
2012	JSPS Postdoctoral Fellow for Research Abroad, National Institutes of Health, U.S.A.
2014	Postdoctoral Fellow, Max Planck Institute of Biophysics, Germany
2016	Research Associate Professor, Institute for Molecular Science
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

2014	Early Career Award in Biophysics, Biophysical Society of Japan

Member
Assistant Professor
OHNUKI, Jun
JSPS Post-Doctoral Fellow
KOBAYASHI, Ryohei
Post-Doctoral Fellow
MAHMOOD, Md Iqbal
Secretary
CHIBA, Fumika

Keywords Theoretical Biophysics, Biomolecular Machines, Molecular Simulation

Biomolecular machines, such as molecular motors and transporters in the cell, are known to change their structure when they function. For example, ATP synthase, which synthesizes ATP in mitochondria, is a molecular motor that uses chemical energy to rotate unidirectionally. Transporters, which transport substrate molecules across the cell membrane, perform substrate transport by changing their structure between an inwardly and outwardly open structure relative to the membrane. Our goal is to elucidate the mechanism of these elaborate and dynamic nanomachines created by nature at the atomic and molecular level, and to control their functions based on our findings.

We would like to understand the mechanism of biomolecular machines by "seeing" the motion of biomolecular machines at the moment they function at the molecular level, on a computer. However, this is not an easy task, because biomolecular machines are huge molecules, and their functioning time scale is slow (for a molecular scale) at milliseconds or longer. Conventional atomistic molecular dynamics (MD) simulations cannot cover millisecond-long functional dynamics, especially for a large system like typical biomolecular machines. Therefore, we have developed and applied methods such as coarse-grained modeling, enhanced sampling and importance sampling to capture the motion at the moment of function.

We have been working on biomolecular motors such as ATP synthase. ATP synthase is a rotary motor that produces most of ATP required in the cell. It is composed of two rotary motors: F_o and F_1. F_o motor is embedded in the membrane and driven by proton gradient, while F_1 motor is driven by ATP hydrolysis reaction. We clarified how the rotation of F_1 motor is driven by a key chemical step, P_i release after ATP hydrolysis reaction, by accelerating atomistic MD simulations with external forces.

Transporters are membrane proteins that transport their substrates across the membrane. We have studied Na^+/H^+ antiporter, which exchanges sodium ions and protons inside and outside the cell. The ion transport process by the Na^+/H^+ antiporter was simulated in atomic detail with transition path sampling technique to capture the moment of the ion transports. The simulations predicted the mutation that can speed up the ion transport. The mutation was tested in experiments and shown to speed up the ion transport twice faster than the wild type. Therefore, we succeeded in controlling the function of the transporter based on mechanism obtained from simulations.

Selected Publications

- K. Okazaki and G. Hummer, "Phosphate Release Coupled to Rotary Motion of F_1-ATPase," *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).
- K. Okazaki and G. Hummer, "Elasticity, Friction, and Pathway of γ-Subunit Rotation in F_oF_1-ATP Synthase," *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, "Mechanism of the Electroneutral Sodium/Proton Antiporter PaNhaP from Transition-Path Shooting," *Nat. Commun.* **10**, 1742 (2019).

1. Mechanism of Na$^+$/H$^+$ Antiporter and Engineering of a Faster Transporter

Na$^+$/H$^+$ antiporters control pH and Na$^+$ concentration in the cell by exchanging sodium ions and protons across lipid membranes. They belong to the cation/proton antiporter (CPA) superfamily, and prevail in all domains of life. The archaeal Na$^+$/H$^+$ antiporters PaNhaP and MjNhaP1 as well as human NHE1, which is linked to a wide spectrum of diseases from heart failure to autism and has no structure solved yet, are electroneutral antiporters of the CPA1 family, exchanging one proton against one sodium ion. As a model system in mechanistic studies of electroneutral Na$^+$/H$^+$ exchange, we studied the transport mechanism of PaNhaP.$^{1)}$

Na$^+$/H$^+$ antiporters use the gradient of either sodium ion or proton to drive the uphill transport of the other ion (Figure 1A). The conformational transition of the transporter makes the ion-binding site accessible from either side of the membrane in the alternating manner. For PaNhaP, the inward-open conformation was obtained by X-ray crystallography, while the outward-open conformation is not known experimentally. We modelled the outward-open conformation by MDFF flexible fitting to the low-resolution outward-open structure of the homologous MjNhaP1 from cryo-EM, followed by the long equilibrium MD simulations. It was shown that the transporter domain moves ~3.5 Å in the direction normal to the membrane to take the outward-open state.

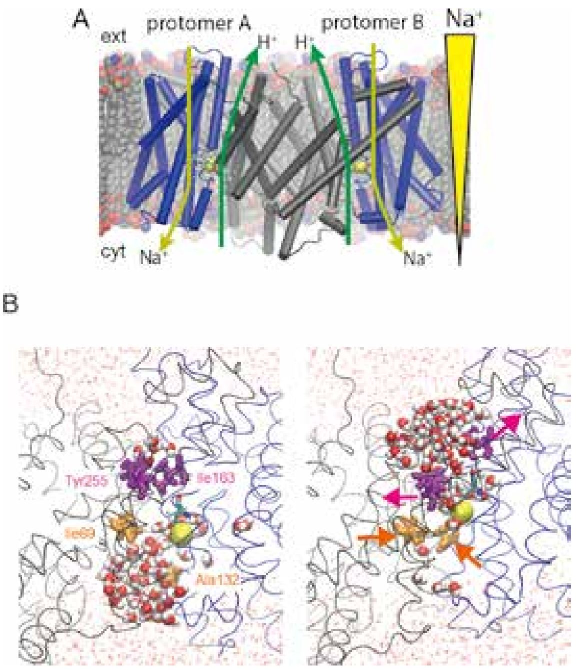

Figure 1. (A) PaNhaP dimer structure. (B) The outside (purple) and inside (orange) gates found in the transition path simulations.

By applying the transition path sampling technique, we sampled unbiased transition paths between the inward- and outward-open states. In analysis of the transition paths, we found hydrophobic gates above and below the ion-binding site, which open and close in response to the domain motions (Figure 1B). From the reaction coordinate analysis, it was shown that open-close motion of the outside gate (Ile163-Tyr255) is a rate-limiting step of the alternating-access conformational change. Based on this result, we weakened the outside gate by mutating the residues to both alanine. It was expected that this mutation lowers the barrier and makes the ion transport faster. It was confirmed by experiments that the ion-transport speed of the mutant is indeed twice faster than the wild-type transporter.

2. Machine Learning of Reaction Coordinates

It is a challenging task to identify reaction coordinates for biomolecular systems with many degrees of freedom. Unlike order parameters or collective variables, a reaction coordinate should describe progress of a reaction between two metastable states. We have developed a machine learning method to identify reaction coordinates based on the committor function. Assuming a linear combination of many collective variables, reaction coordinates are optimized via likelihood maximization or cross-entropy minimization.$^{2)}$ From coefficients of the optimized reaction coordinates, we can also identify rate-limiting variables, which play an important role in transition state area. We have also applied a deep neural network and Explainable Artificial Intelligence (XAI) for this problem.$^{3)}$

3. Mechanism of Membrane Remodeling by F-BAR Protein Pacsin1

F-Bin/Amphiphysin/Rvs (F-BAR) domain proteins play essential roles in biological processes that involve membrane remodelling, such as endocytosis and exocytosis. Notably, Pacsin1 from the Pacsin/Syndapin subfamily has the ability to transform the membrane into various morphologies: Striated tubes, featureless wide and thin tubes, and pearling vesicles. We clarified the membrane curvature induction and sensing characteristics of Pacsin1 by combining all-atom (AA) and coarse-grained (CG) MD simulations.$^{4)}$ By matching structural fluctuations between AA and CG simulations, a CG protein model called "Gō-MARTINI" was developed and optimized.$^{5)}$ The model should prove useful for describing protein dynamics that are involved in membrane remodeling processes.

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3) T. Kikutsuji, Y. Mori, K. Okazaki, T. Mori, K. Kim, and N. Matubayasi, *J. Chem. Phys.* **156**, 154108 (2022).
4) M. I. Mahmood, H. Noguchi and K. Okazaki, *Sci. Rep.* **9**, 14557 (2019).
5) M. I. Mahmood, A. B. Poma and K. Okazaki, *Front. Mol. Biosci.* **8**, 619381 (2021).

Visiting Professors

Visiting Professor
SATO, Hirofumi *(from Kyoto University)*

Theoretical Study of Electronic Structure and Statistical Mechanics for Molecular Systems

Our research focuses on developing new theories in quantum chemistry and statistical mechanics and on analysing chemical phenomena in condensed matter systems consisting of polyatomic molecules.

(1) Based on biorthogonal second quantisation, we proposed a method to extract the resonance structures embedded in molecular orbital computations and the local spin structures. (2) The statistical mechanics of molecular liquids is an analytical and systematic approach to understanding liquids' structure and thermodynamic properties. In addition to hybrid methods with quantum chemistry, we have developed many novel methods, including density functional theory and diffusion equations for polyatomic molecular systems. Recently, we proposed an ab initio theory for NMR chemical shifts based on the RISM-SCF-SEDD method. (3) The mechanisms of various chemical reactions and phenomena have been clarified at the molecular level. For example, the self-assembly process of the transition metal complex system was clarified. The phenomena at the electrode interface were systematised based on molecular dynamics simulation.

Visiting Professor
YOSHIDA, Norio *(from Nagoya University)*

Theoretical Study of Chemical and Biological Processes in Solution

We are interested in the chemical and biological processes in solution with a particular focus on the role of solvents in these processes. Our group is studying the role of solvents in these processes based on the integral equation theory of molecular liquids. Recently, we have developed an accurate pKa prediction method for molecules in solution based on a hybrid method of integral equation theory and quantum chemical methods. Related to the method, in collaboration with the Institute for Molecular Science, we are developing an efficient structural sampling method for the pH-dependent protonation state of dissociative amino acid residues in proteins. We are also developing a novel integral equation theory that takes into account the electronic polarization of the solvent and applies it to electron-transfer reactions in solution.

Visiting Associate Professor
NOGUCHI, Hiroshi *(from University of Tokyo)*

Theoretical Study on Soft Matter and Biophysics

We study soft-matter physics and biophysics using theory and simulations. Our main targets are the structure formation of biomembrane and the dynamics of complex fluids under various conditions. This year, we investigated the shape transformation of membrane induced by curvature-inducing proteins using mean-field theory and coarse-grained membrane simulations. We clarified the difference between laterally anisotropic and isotropic proteins in the curvature sensing and generation. In particular, the sensing curvature of the anisotropic proteins depends on the protein density, whereas that of the isotropic proteins is constant. Traveling waves of chemical reactions containing curvature-inducing proteins change the membrane shapes and vice versa. Moreover, we investigated cavitation and bubble oscillation in sound-wave propagation using massively parallel simulations.

RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction of atoms and molecules with optical fields with its possible applications to active control of atomic and molecular functionality and reactivity. We also develop novel light sources to promote those studies. Two research facilities, the Center for Mesoscopic Sciences and the UVSOR Synchrotron Facility, closely collaborate with the Department.

The core topics of the Department include attosecond coherent control for the development of ultrafast quantum computers and simulators, high-resolution optical microscopy applied to nanomaterials, synchrotron-based spectroscopy of core-excited molecules and solid-state materials, vacuum-UV photochemistry, and the development of novel laser- and synchrotron-radiation sources.

Ultrafast Quantum Simulator and Computer

Department of Photo-Molecular Science
Division of Photo-Molecular Science II

OHMORI, Kenji
Professor
[ohmori@ims.ac.jp]

Education

1987	B. E. The University of Tokyo
1992	Ph.D. The University of Tokyo

Professional Employment

1992	Research Associate, Tohoku University
2001	Associate Professor, Tohoku University
2003	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2004	Visiting Professor, Tohoku University (–2005)
2007	Visiting Professor, Tokyo Institute of Technology (–2008)
2009	Visiting Professor, The University of Tokyo (–2011)
2012	Visiting Professor (Humboldt Awardee), University of Heidelberg
2014	Visiting Professor, University of Strasbourg (–2016)

Awards

1998	Award by Research Foundation for Opto-Science and Technology
2007	JSPS Prize
2007	Japan Academy Medal
2008	Norman Hascoe Distinguished Lecturer, University of Connecticut, USA
2009	Fellow of the American Physical Society
2012	Humboldt Research Award
2017	Hiroshi Takuma Memorial Prize of Matsuo Foundation
2018	Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan
2021	Medal with Purple Ribbon (by His Majesty the Emperor of Japan)

Member

Assistant Professor
  SUGAWA, Seiji
  DE LÉSÉLEUC, Sylvain

IMS Research Assistant Professor
  TOMITA, Takafumi

Post-Doctoral Fellow
  BHARTI, Vineet
  KUNIMI, Masaya
  CHAUHAN, Vikas

Visiting Scientist
  MATSUBARA, Takuya*
  MORLA AL YAHYA, Joa*
  DENECKER, Tom*
  KOCIK, Robin*
  BARRE, Maxence*
  MARTHOURET, Hugo*
  DELABRE, Antoine*

Graduate Student
  CHEW TORII, Yuki
  TIRUMALASETTY PANDURANGA, Mahesh
  VILLELA, Rene

Secretary
  KAWAMOTO, Minako
  TANAKA, Ryo

Keywords Quantum Simulation, Quantum Computing, Attosecond

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.1) This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as "collapse" in quantum theory, is often accepted as a discontinuous change, but a basic question arises: When and how the delocalized wave function becomes localized? Our objective is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this objective in mind, we have developed coherent control with precisions on the picometer spatial and attosecond temporal scales. Now we apply this ultrafast and ultrahigh-precision coherent control to delocalized wave functions of macroscopic many-particle systems of an array of ultracold rubidium (Rb) Rydberg atoms, as depicted schematically in Figure 1 and named "ultrafast quantum simulator," envisaging the quantum-classical boundary connected smoothly.

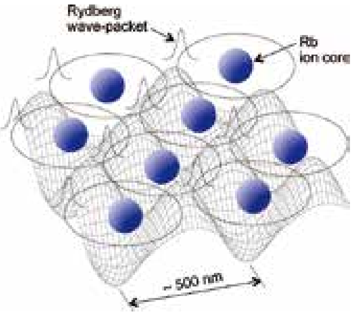

Figure 1. Metal-like quantum gas. A schematic of the many-body quantum simulator with ultracold Rydberg atoms, named "ultrafast quantum simulator," where electronic wave functions spatially overlap between neighboring atoms.[2,7]

Selected Publications

- H. Katsuki *et al.*, "Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference," *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, "Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales," *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, "Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule," *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, "Strong-Laser-Induced Quantum Interference," *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, "All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth," *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, "Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas," *Nat. Commun.* **7**, 13449 (2016).
- C. Liu *et al.*, "Attosecond Control of Restoration of Electronic Structure Symmetry," *Phys. Rev. Lett.* **121**, 173201 (2018).
- M. Mizoguchi *et al.*, "Ultrafast Creation of Overlapping Rydberg Electrons in an Atomic BEC and Mott-Insulator Lattice," *Phys. Rev. Lett.* **124**, 253201 (2020).
- Y. Chew *et al.*, "Ultrafast Energy Exchange between Two Single Rydberg Atoms on a Nanosecond Timescale," *Nat. Photonics* **16**, 724 (2022).

1. Development of an “Ultrafast Quantum Simulator” by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales[3–10]

Quantum many-body problems are at the heart of a variety of physical functionalities including superconductivity and magnetism in solid materials. It is extremely hard, however, to solve such quantum many-body problems. In solving the Hubbard model with 1000 particles, for example, the diagonalization would take 10 to the power of 573 years even with the world’s fastest supercomputers. In this project, we develop a novel quantum simulator that can simulate quantum many-body dynamics for more than 1000 particles within one nanosecond, combining our two unique experimental resources: “coherent control with attosecond precision”[8] and “a strongly-correlated ultracold Rydberg gas.”[7,9,10]

We have completed a standard hardware of this ultrafast quantum simulator composed of an array of ultracold Rb atoms trapped in an optical lattice and excited to Rydberg levels with a coherent picosecond (ps) laser pulse, as schematically illustrated in Figure 2.[3,4,6,7,10] The broad bandwidth of the ps laser pulse has allowed us to excite the atoms in the neighboring lattice sites to Rydberg levels simultaneously for the first time. With this standard hardware, we have succeeded in creating an exotic electronic state with spatially overlapping wave-functions as shown schematically in Figures 1 and 2.[2,7,10] The degree of spatial overlap is actively tuned with ~50 nanometer precision. This exotic metal-like quantum gas under exquisite control opens up a completely new regime of many-body physics for simulating ultrafast many-body electron dynamics dominated by Coulomb interactions.[7,10]

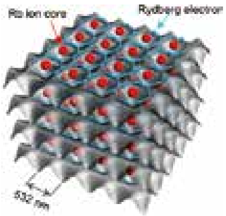

Figure 2. Schematic of the standard hardware of the ultrafast quantum simulator.[3,4,6,7,10]

We have also completed a read-out interface of our ultrafast quantum simulator, which is the time domain Ramsey interferometry of ultracold Rydberg atoms with attosecond precision, whose contrast is almost 100%.[5] The phase and visibility of this Ramsey interferogram are highly sensitive to the nature and strength of many-body interactions among the Rydberg atoms.

2. Development of an Ultrafast Quantum Computer[3,10,12]

So far we have developed arbitrary two dimensional optical trap arrays for cold atoms, which are necessary for quantum computing, in tight collaborations with Hamamatsu Photonics K.K.[3] Their examples are shown in Figure 3, the world’s smallest arbitrary trap arrays whose nearest neighbor distance is only ~1 micron, which used to be typically ~4 micron in previous works.[11]

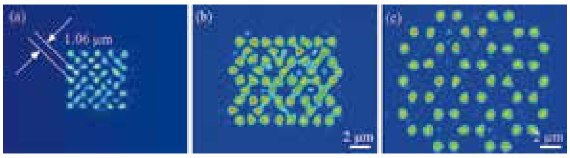

Figure 3. Examples of the world’s smallest arbitrary arrays of optical traps. (a) Square lattice; (b) Kagome Lattice; (c) Hexagonal (Honeycomb) lattice.[10]

We have succeeded in loading a single atom into each trap of those arbitrary arrays, and reassembling those atoms with a movable optical tweezers. Such an array of cold atoms has been manipulated with an ultrafast laser for the first time, leading to a completely new quantum computer we refer to as an “ultrafast quantum computer.” With this ultrafast quantum computer, we have recently succeeded in executing a controlled-Z gate in just 6.5 ns, as depicted schematically in Figure 4.[12] This is the world’s fastest controlled gate, which is the most important two-qubit gate (a fundamental arithmetic element essential for quantum computing). This high-impact result was highlighted on the front cover of the Oct 2022 Issue of Nature Photonics,[12] and by more than 200 news articles worldwide, such as in Japan, US, Europe, China, *etc*.

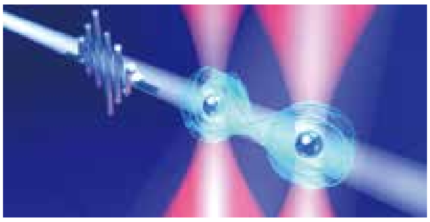

Figure 4. Conceptual diagram of the world’s fastest controlled gate for ultrafast quantum computing. Two single atoms captured in optical tweezers (red light) with a separation of a micrometer are entangled by an ultrafast laser pulse (blue light) shone for only 10 picoseconds.[12] Image source: Dr. Takafumi Tomita (IMS)

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4) White Paper 2018 on Manufacturing Industries published by Ministry of Economy Trade and Industry, JAPAN.
5) C. Liu *et al.*, *Phys. Rev. Lett.* **121**, 173201 (2018).
6) Highlighted in “Quantum-Technology Innovation Strategy” by the Cabinet Office of Japan, January 2020.
7) M. Mizoguchi *et al.*, *Phys. Rev. Lett.* **124**, 253201 (2020).
8) H. Katsuki *et al.*, *Acc. Chem. Res.* **51**, 1174–1184 (2018).
9) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).
10) S. Sugawa *et al.*, *Solid State Physics* **56**, 243 (2021). (Invited Paper/Cover-Page Highlight)
11) D. Barredo *et al.*, *Science* **354**, 1021 (2016).
12) Y. Chew *et al.*, *Nat. Photonics* **16**, 724 (2022). (Cover-Page Highlight)

Award

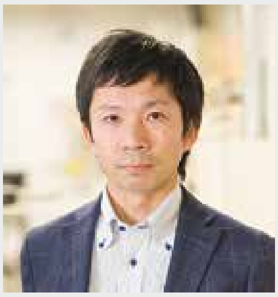
OHMORI, Kenji; National Medal with Purple Ribbon by His Majesty the Emperor of Japan (2021).

---

* IMS International Internship Program

Electronic Property of Functional Organic Materials

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



KERA, Satoshi
Professor
[kera@ims.ac.jp]

Education

1996	B.E. Chiba University
1998	M.E. Chiba University
2001	Ph.D. Chiba University

Professional Employment

1998	JSPS Research Fellow
2001	Research Associate, Chiba University
2003	Research Associate, Institute for Molecular Science
2003	Postdoctoral Fellow, Wuerzburg University
2004	Assistant Professor, Chiba University
2007	Associate Professor, Chiba University
2009	Visiting Associate Professor, Institute for Molecular Science
2013	Adjunct Lecturer, The Open University of Japan
2013	Visiting Associate Professor, Soochow University
2014	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting Professor, Chiba University
2019	Visiting Professor, Kyoto University, Hiroshima University
2020	Visiting Professor, Tohoku University

Member

Assistant Professor
FUKUTANI, Keisuke

Graduate Student
NISHINO, Fumi
PALASSERY ITHIKKAL, Jaseela
KANAZAWA, Shingo*
MIYATA, Takeshi†
YAMAUCHI, Saki‡
SEMA, Ryota‡

Secretary
HAGIWARA, Hisayo
KAMIYA, Miho

Keywords Photoelectron Spectroscopy, Molecular Assemble, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However, the mechanisms and the origin of various device characteristics are still under debate. Scientific discussions have been redundant because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is essential to investigate precisely the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the electronic states is very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

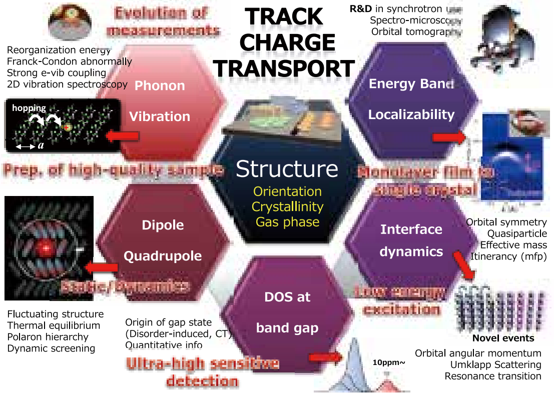


Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- Y. Nakayama, S. Kera and N. Ueno, *J. Mater. Chem. C* **8**, 9090–9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
- S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Photoemission Tomography of One Dimensional Row Structure of Flat-Lying Picene Multilayer on Ag(110)[1)]

Photoemission tomography (PT) is a powerful technique for the detailed analysis of the shape and the energy of molecular orbitals from the photoelectron momentum distribution. In the case of planar-conjugated molecules with light atoms, the momentum map of the photoelectrons from frontier orbitals can be seen as the Fourier transform (FT) of the corresponding molecular orbital, by assuming the plane-wave final state in the photoemission process. Thus, PT is able to determine the shape of the molecular orbitals in the sample if the molecular arrangement in the sample is known, while it can also be utilized for the determination of the molecular arrangement in the specimen if the molecular orbital of the sample molecule is known.

We applied PT to a unique one-dimensional row structure of a picene multilayer realized on an anisotropic Ag(110) surface. The clearly deconvoluted experimental momentum maps were compared to the FT simulation of the molecular orbitals of picene in detail, enabling not only the evaluation of the electronic structure of the picene in the multilayer but also the quantitative determination of the molecular orientation in the multilayer within a few degrees. In addition, the PT results indicated the orientation of the molecules in all layers to be flat-lying. The successful demonstration of PT of the multilayer molecular film marks an important step toward the wide-range utilization of the PT technique.

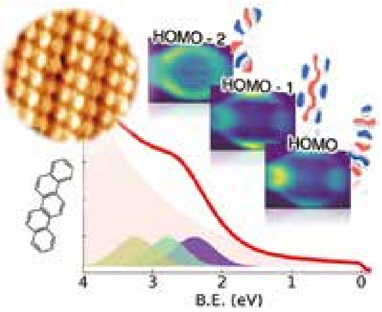


Figure 2. Scheme of photoelectron spectrum of the picene film, STM molecular arrangement, and PT images for top three molecular orbitals. The figure is after ref 1).

2. Sample-Shape Dependent Energy Levels in Organic Semiconductors[2)]

Most of the tuning of the ionization energy and electron affinity was done by changing the constituent molecules in the device. This is because the organic solids consist of organic molecules bound by weak vdW interactions, hence intermolecular interaction is considered to play a minor role. The contribution of the intermolecular interaction to the energy levels of organic solids is represented by the difference in the energy levels between the gas and solid phases.

Recent studies, however, have revealed that the energy levels can be altered as much as 1 eV by the molecular orientation in the film or the molecular mixing ratio in the binary film, owing to the intermolecular electrostatic interaction. Because of the long-range nature of Coulomb interaction, theory predicts that the electrostatic energy should depend on the sample shape. In this study, we examined the coverage-dependent energy levels of zinc phthalocyanine (ZnPc) and per-fluorinated ZnPc (F_{16}ZnPc) in the monolayer region with ultraviolet photoelectron spectroscopy and low-energy inverse photoelectron spectroscopy. Using the procedure we reported previously, we separately evaluated the electronic polarization energy and electrostatic energy as a function of coverage. Unlike the electronic polarization, which contributes only as much as 10 meV, the electrostatic energy contributes as much as 120 meV to the coverage-dependent energy shift. We concluded that the shift in energy levels by changing the coverage is attributed to the sample shape-dependent energy level, owing to the long-range nature of the charge–permanent quadrupole interaction.

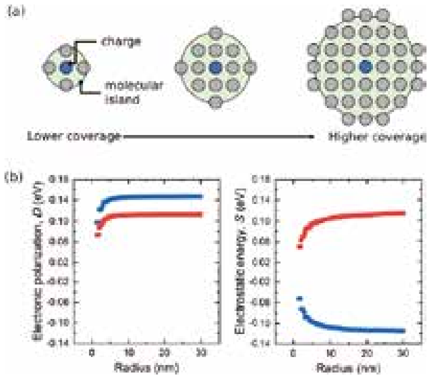


Figure 3. (a) Disk model for the growing island without a changing lattice constant. (b) Clculated polarization energy and electrostatic energy for ZnPc and F_{16}ZnPc are indicated with blue circles and red squares. The figure is after ref 2).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope are developing at BL6U.[3,4)]

References

1) M. Iwasawa, S. Kobayashi, M. Sasaki, Y. Hasegawa, H. Ishii, F. Matsui, S. Kera and Y. Yamada, *J. Phys. Chem. Lett.* **13**, 1512–1518 (2022).

2) S. A. Abd-Rahman, T. Yamaguchi, S. Kera and H. Yoshida, *Phys. Rev. B* **106**, 075303 (8 pages) (2022).

3) Y. Hasegawa, F. Matsui and S. Kera, *e-J. Surf. Sci. Nanotechnol.* **20**, 174–179 (2022).

4) F. Matsui, Y. Okano, H. Matsuda, T. Yano, E. Nakamura, S. Kera and S. Suga, *J. Phys. Soc. Jpn.* **91**, 094703 (6 pages) (2022).

* carrying out graduate research on Cooperative Education Program of IMS with Chiba University

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

‡ carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Light Source Developments by Using Relativistic Electron Beams

UVSOR Synchrotron Facility
Division of Advanced Accelerator Research

KATOH, Masahiro
Project Professor
[mkatoh@ims.ac.jp]

Education
1982 B.S. Tohoku University
1997 Ph.D. Tohoku University

Professional Employment
1986 Reseach Associate, National Laboratory for High Energy Physics
2000 Associate Professor, Institute for Molecular Science
2004 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2019 Professor, Hiroshima University
Project Professor, Institute for Molecular Science

Member
Assistant Professor
FUJIMOTO, Masaki*

Keywords Accelerator, Beam Physics, Synchrotron Radiation

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz waves to the soft X-rays. Although it was constructed nearly 40 years ago, its performance is still in the world top level particularly among the low energy synchrotron light sources. This is the result of the continuous efforts on improving the machine. Our research group has been developing and introducing new accelerator technologies toward producing brighter synchrotron light with high stability, such as low emittance electron beam optics, novel insertion devices or state-of-the-art beam injection scheme. We have been developing novel light source technologies, such as free electron laser, coherent synchrotron radiation, optical vortices and laser Compton gamma-rays. We have been investigating beam physics which would be the basis of the future developments of the facility.

Figure 1. UVSOR-III Electron Storage Ring and Synchrotron Radiation Beamlines.

Selected Publications

- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, "Tunable Narrowband Terahertz Emission from Mastered Laser–Eelectron Beam Interaction," *Nat. Phys.* **4**, 390–393 (2008).
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- T. Kaneyasu, Y. Hikosaka, M. Fujimoto, H. Iwayama and M. Katoh, "Electron Wave Packet Interference in Atomic Inner-Shell Excitation," *Phys. Rev. Lett.* **126**, 1132202 (2021).
- T. Kaneyasu, M. Hosaka, A. Mano, Y.Takashima, M. Fujimoto, E. Salehi, H. Iwayama, Y. Hikosaka and M. Katoh, "Double-Pulsed Wave Packets in Spontaneous Radiation from a Tandem Undulator," *Sci. Rep.* **12**, 9682 (2022).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have been developing light source technologies at the UVSOR-III electron storage ring using a dedicated experimental station BL1U, which was constructed under the support of Quantum Beam Technology Program of JST/MEXT aiming to develope novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beamline consisting of mirrors and a monochromator whose arrangement can be flexibly changed according to the types of the experiments.

In collaboration with Hiroshima Univ. and Nagoya Univ., we have succeeded in producing spatially structured synchrotron radiation such as vortex beam and vector beam, and we are exploring their applications. In these years, we are focusing on exploring the possibility utilizing the temporal structure of undulator radiation, in collaboration with Saga Light Source and Toyama Univ. We have succeeded in the coherent controls of atoms and in observing ultrafast change of an electronic state of an atom by using radiation from two undulators arranged in tandem. We have started developing state-of-the-art technology to observe ultrafast properties of synchrotron radiation, in collaboration with Toyota Technological Institute.

We have been developing a laser Compton scattering gamma-ray source at BL1U, which is capable of producing monochromatic and energy-tunable gamma-rays. Currently we are interested in controlling the wave properties of gamma-ray photons. Theoretically we have shown that vortex photons carrying orbital angular momentum can be produced by nonlinear Compton scattering of circularly polarized photons. We are challenging its experimental demonstration.

We continue experimental studies on the origin of the homochirality of biomolecules using intense circularly polarized undulator radiation at BL1U, in collaboration with Yokohama National Univ. and Hiroshima Univ. Recently we have started a new project on this subject, which includes specialist of plasma physics from NIFS.

Figure 2. Twin Polarization-variable Undulators/Optical Klystron at UVSOR-III.

2. Accelerator Technology Developments for Electron Synchrotrons

We carried out several upgrade plans on UVSOR electron synchrotron since 2000. We designed a special beam optics intended to higher brightness. We developed necessary accelerator components, reconstructed the accelerator and commissioned it. We have constructed and commissioned six undulators successfully. Moreover, we have been continuously introducing new accelerator technologies such as the top-up operation in which the electron beam intensity is kept quasi-constant at a high beam current, 300mA, and the novel beam injection scheme with a pulsed sextupole magnet. As the result of all these efforts, now, the machine is one the brightest synchrotron light sources among the low energy machines below 1GeV in the world.

Currently, the storage ring is stably operated for many of the users, however, the requirements from the users for the stability is getting higher and higher. As a near-term upgrade plan, we are considering replacing some of the undulators to fit the changes of the users' requirements on the wavelength. Also, we are seeking a possibility to reduce the emittance with the present magnet configuration. So far, we have found a few beam optics which would give lower emittance around 10 nm. Although they are not compatible with the operation of the narrow gap undulators, they may be used for special experiments which requires lower emittance. For a long-term plan, we continue the design study on a new light source facility. We have been investigating various accelerator systems such as a diffraction-limited synchrotron, an energy recovery linear accelerator and so on. Currently we are focusing on designing a synchrotron with the electron energy of 1 GeV and the circumference of around 70 m. We have designed a synchrotron which would give low emittance of around 5 nm under the achromatic condition.

We are collaborating with Nagoya Univ. and developing new technologies for the future plan. Accelerator magnets based on permanent magnets are being developed, which would contribute to the power consumption saving. New pulsed multipole magnet is also being developed to realize a novel beam injection scheme.

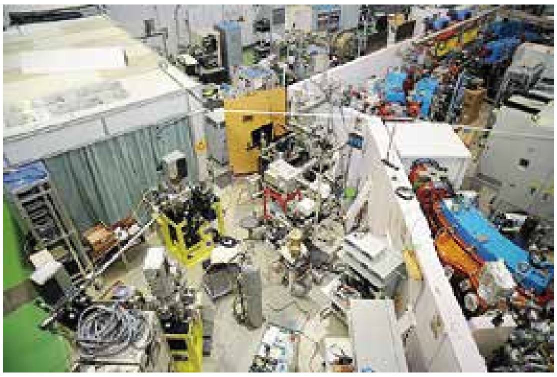

Figure 3. UVSOR BL1U experimental station for source development studies.

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* Present Address; Nagoya University

Development and Utilization of Novel Quantum Beam Sources Using a High Energy Electron Beam

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

TAIRA, Yoshitaka
Associate Professor
[yostaira@ims.ac.jp]

Education

2007	B.S. Nagoya University
2009	M.S. Nagoya University
2012	Ph.D. Nagoya University

Professional Employment

2011	JSPS Research Fellow
2012	Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST)
2018	Senior Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST)
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2010	Young Researcher Best Presentation Award, The 53rd Annual Meeting of the Japanese Society of Radiation Chemistry
2011	Nagoya University Outstanding Graduate Student Award
2012	Oral Presentation Award, The 9th Annual Meeting of Particle Accelerator Society of Japan
2012	Young Researcher Best Poster Award, 12th International Symposium on Radiation Physics
2013	Young Scientist Award of the Physical Society of Japan
2015	Young Researcher Best Presentation Award, Beam Physics Workshop 2015
2021	Outstanding Presentation Award, 64th Annual Meeting of the Japanese Society of Radiation Chemistry

Member
Assistant Professor
SUGITA, Kento
Post-Doctoral Fellow
SALEHI, Elham
Graduate Student
KOYAMA, Kazuki*
YAMAMOTO, Ryohei*
GOTO, Keita*
TANABE, Keigo*

Keywords Electron Beams, Synchrotron Radiation, Gamma-Rays

Our group develop new electromagnetic wave sources using a high energy electron beam. In the UVSOR-III electron storage ring at the Institute for Molecular Science, a 750-MeV electron beam can be generated. Electromagnetic waves in a wide frequency range from ultraviolet waves to gamma-rays are emitted by interacting the electron beam with magnetic fileds and lasers.

Inverse Thomson (Compton) scattering is a method to generate a high energy gamma-ray by the interaction between a high energy electron and a laser. We have developed ultra-short pulsed gamma-rays with the pulse width of sub-ps to ps range by using 90-degree inverse Thomson scattering (Figure 1). This ultra-short pulsed gamma-rays were applied to gamma induced positron annihilation pectroscopy (GiPAS). A positron is an excellent probe of atomic scale defects in solids and of free volumes in polymers at the sub-nm to nm scale. GiPAS enables defect analysis of a thick material in a few cm because positrons are generated throughout a bulk material via pair production. Our group is conducting research on improving the properties of the material by using GiPAS.

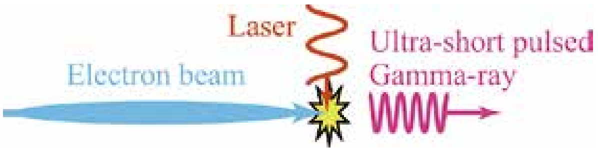

Figure 1. Schematic illustration of 90-degree inverse Thomson scattering.

Selected Publications

- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultra-Short-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696 (2011).
- Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, "Photon-Induced Positron Annihilation Lifetime Spectroscopy Using Ultrashort Laser-Compton-Scattered Gamma-Ray Pulses," *Rev. Sci. Instrum.* **84**, 053305 (2013).
- Y. Taira, T. Hayakawa and M. Katoh, "Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light," *Sci. Rep.* **7**, 5018 (2017).
- Y. Taira and M. Katoh, "Gamma-Ray Vortices Emitted from Nonlinear Inverse Thomson Scattering of a Two-Wavelength Laser Beam," *Phys. Rev. A* **98**, 052130 (2018).
- Y. Taira, M. Fujimoto, S. Ri, M. Hosaka and M. Katoh, "Measurement of the Phase Structure of Elliptically Polarized Undulator Radiation," *New J. Phys.* **22**, 093061 (2020).

1. Gamma Ray-Induced Positron Annihilation Spectroscopy (GiPAS)

In Gamma ray-induced positron annihilation lifetime spectroscopy (GiPALS), positron lifetime spectrum is calculated by measuring the time difference between a reference signal and a detector output for the annihilation gamma-rays, which is emitted when a positron annihilates with an electron inside material. A reference signal is the output of a photodiode located near the injection position of a laser. A BaF_2 scintillator and a photomultiplier tube is utilized to detect the annihilation gamma-rays. Two detectors are arranged at 180 degrees because two annihilation gamma-rays are generated at 180-degree direction.

A digital oscilloscope is used to store the waveforms of the photodiode and the BaF_2 detector, and calculate the time difference distribution. One digital oscilloscope for four BaF_2 detectors is used as a pair of detection systems. The annihilation gamma-rays are generated to whole solid angle. Therefore array detectors are effective to increase the count rate of the annihilation gamma-rays and to reduce the measurement time. A detection system with eight detectors and two digital oscilloscopes was constructed (Figure 2). Time resolution is 140 ps in full width at half maximum, which is high despite the use of a 52-mm thick BaF_2 scintillator. The count rate is 20 cps.

Users can currently utilize GiPALS at BL1U in UVSOR-III. A result of defect analysis for a $Lu_3Al_5O_{12}$ scintillator was published in 2022.[1)]

Figure 2. Positron annihilation lifetime measurement system using eight detectors and two digital oscilloscope.

Positron age-momentum correlation (AMOC) is an approach for measuring the time resolved momentum distribution of an electron, which provides different information about defects compared to positron annihilation lifetime. Gamma ray-induced AMOC has been developed by using a BaF_2 detector, a germanium detector, and a 12-bit digital oscilloscope. Typically, a multichannel analyzer is used to measure the energy spectrum of gamma rays. However, a 12-bit digital oscilloscope is employed in this experiment; thus, high-energy resolution can be obtained with the digital oscilloscope alone. The results of multiple sample measurements are summarized in the paper.

We are planning to develop other measurement technique for the annihilation gamma-rays, such as coincidence Doppler broadening and spin polarized positrons generated from circularly polarized gamma-rays.

2. Gamma-Ray Vortices

An optical vortex is an electromagnetic wave with a helical phase structure. When an optical vortex beam is viewed in a plane transverse to the direction of propagation, an annular intensity profile is observed due to the phase singularity at the center axis. An important consequence of the optical vortex is that it carries orbital angular momentum (OAM) due to the helical phase structure.

While fundamental and applied research on optical vortices using visible wavelength lasers is widely studied, much less has been done in ultraviolet, X-rays, and gamma-rays energy ranges. We have proposed for the first time a method to generate a gamma-ray vortex using nonlinear inverse Thomson scattering of a high energy electron and an intense circularly polarized laser. In our method, the circularly polarized laser is important because the helical phase structure arises from the transverse helical motion of the electron inside the circularly polarized laser field. When peak power of a laser achieves terawatt class, high harmonic gamma-rays are generated. Only gamma-rays more than the first harmonic carry OAM. High harmonic gamma-rays show the annular intensity distribution due to this characteristic.

There are few facilities in the world which can carry out the experiment for the nonlinear inverse Thomson scattering using an intense circularly polarized laser in terawatt class. We carried out the experiment at Kansai Photon Science Institute in Japan, where a 150 MeV microtron and a petawatt laser are available. We were not able to achieve the measurement of an annular intensity distribution of high harmonic gamma-rays.

UVSOR-III also has a laser with a pulse energy of 50 mJ and has completed start-up work on the laser. Experiments on nonlinear inverse Thomson scattering will be performed after October 2022 to measure the spatial distribution of high harmonic gamma rays.

Reference

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Award

SALEHI, Elham; 4th International School on Beam Dynamics and Accelerator Tehnology, ISBA Gold award (2022).

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* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Application of X-Ray Microscopy

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

OHIGASHI, Takuji
Associate Professor
(Cross Appointment)
[ohigashi@ims.ac.jp]

Education

1998	B.E. University of Tsukuba
2003	Ph.D. (Engineering) University of Tsukuba

Professional Employment

2003	Lecturer, University of Tsukuba
2004	Research Fellow, Tohoku University
2005	Research Fellow, Japan Synchrotron Radiation Research Institute (JASRI)
2008	Postdoctoral Fellow, Ritsumeikan University
2011	Assistant Professor, Institute for Molecular Science
2022	Associate Professor, KEK
2022	Associate Professor (Cross Appointment), Institute for Molecular Science

Member
Secretary
ISHIHARA, Mayumi
KAMO, Kyoko

Keywords X-Ray Microscopy, In-Situ Technique, X-Ray Absorption Spectroscopy

A synchrotron-based scanning transmission X-ray microscope (STXM) is a technique to perform 2-dimensional (2-D) X-ray absorption spectroscopy with high spatial resolution up to 30 nm. By noticing the X-ray absorption edge of the specific element, 2-D chemical state of a sample can be obtained. Since characteristics of UVSOR is suitable for using extreme ultra-violet and soft X-ray region, the STXM in UVSOR is suitable to analyze soft materials and organic materials. The unique features of STXM, such as high transmittance of X-ray and relatively wide working distance, gain flexibility of the sample and its environment. Therefore, we have been developing special observation/analytical techniques mainly by designing sample cells for STXM. Especially, nowadays, an in-situ/operando analysis is attracting more attentions of researchers because that is an important technique to understand intrinsic state of the samples. For example, heating and cooling of the sample, humidity control system and electrochemistry, 2-D orientation of molecules, 3-D chemical state mapping, a sample transfer system without exposing to air and microscopic analysis of chemical state of lithium have been developed to explore a new filed of science. These techniques are difficult to perform by using the other microscopic techniques.

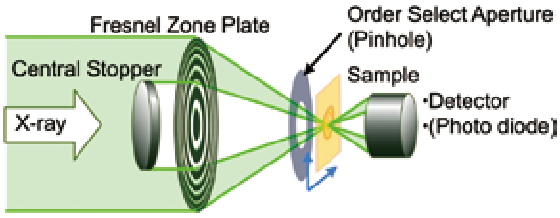

Figure 1. Schematic optical system of STXM.

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- T. Ohigashi, M. Nagasaka, T. Horigome, N. Kosugi, S. M. Rosendahl and A. P. Hitchcock, "Development of In-Situ Sample Cells for Scanning Tranmission X-Ray Microscopy," *AIP Conf. Proc.* **1741**, 050002 (2016).
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- J.-J. V. Véles, Y.-Y. Chin, M.-H. Tsai, O. J. Burton, R. Wang, S. Hofmann, W.-H. Hsu, T. Ohigashi, W.-F. Pong and C.-H. Chuang, "Evidence of Synergistic Elecrocatalysis at a Cobalt Oxide-Graphene Interface through Nanochemical Mapping of Scanning Transmission X-Ray Microscopy," *Chin. J. Phys.* **76**, 135–144 (2022).

1. Analysis of Organic Materials in Returned Samples from the Asteroid *Ryugu* by STXM

In 2014, a small spacecraft Hayabusa2 was launched to an asteroid 1999 JU3, named Ryugu, 280,000,000 km away from the earth. Hayabusa2 accumulates 5.4 g of pebbles and sands from surface (stored in a chamber A) and subsurface (in a chamber C) of Ryugu and the sample chambers came back to the earth in the end of 2020.1) Compared to ordinally meteorites, those samples from Ryugu are expected to retain pristine information of the asteroid since they did not suffer from heating by the atmosphere and contamination by terrestrial materials. Moreover, the samples in the chamber C are likely to have less space weathering than those of the chamber A. Therefore, the samples in the chamber C could be one of the standards of nature of extraterrestrial material. Our team, Phase2 curation Kochi team (collaborative team among JAXA, JAMSTEC, NIPR, SPring-8 and IMS), has developed "a linkage analytical system" to analyze the sample by using various apparatus, such as synchrotron-based X-ray diffraction (XRD), computed tomography (CT), focused-ion-beam (FIB) process, transmission electron microscopy (TEM), NanoSIMS and STXM, without exposing to the air through whole process and a protocol for analysis with minimum destructive process and damages.2) Ryugu is primarily considered as a carbonaceous asteroid so that abundant of organic material is expected. Main concerns of Phase2 Kochi team are water and organic materials. Therefore, the STXM at BL4U in UVSOR is a promising tool to analyze localized organic materials with high spatial resolution around 30 nm. In BL4U, a sample transfer system, a special sample cell, an FIB grid (namely Kochi grid), and a container to transfer between facilities, which enable to transfer the sample from a glovebox to a main chamber of the STXM without exposing to air, have been developed for the analysis of the Ryugu samples.

First of all, 3-dimensional structure and crystallography of a grain C0068 in the chamber C were confirmed by CT and XRD in SPring-8 to determine a region of interest (ROI) without any destructive process. The ROI was roughly cut out by using a diamond saw and was finished as an ultra-thin section sample by using FIB process in JAMSTEC as dimension of 25×25×0.1 (thick) µm^3 on the Kochi-grid.2) That ultra-thin section sample is used for high spatial resolution analyses by TEM, NanoSIMS and STXM. The procedures including the sample preparation, measurement and transportation between research institutes were performed under grade 1 nitrogen gas condition.

Figure 2(a) shows representative NEXAFS spectra of aromatic (C=C)-rich (plotted in red), C–H bonding-rich regions (green), matrix (blue) of the sample C0068,25 and Murchison meteorite (gray) around C K-edge. From this comparison, the peak at 287.5 eV, assigned as C–H bonding including aliphatic, is remarkable feature of the Ryugu samples. Their distributions are depicted in Figure 2(c) as RGB-color composite mapping. In regard to the distributions, the aromatic-rich region (shown in red) is less than the other components. Figure 2(b) shows spatial distribution of carbon-related materials. Then, the dark area has no (or much less) carbon-related component. Detailed analyses of dashed line squares in Figures 2(b) and 2(c) were performed by using TEM (shown in Figures 2(d) and 2(e)). The corresponding dark spot areas are confirmed as pyrrhotite and pentlandite. A large nanoglobule is consisted of amorphous silicate as a core and aromatic-rich organic materials around that.

Further analysis of the Ryugu samples is in progress. As one of the topics, we notice a potential relationship between space weathering and evolution of organic materials.

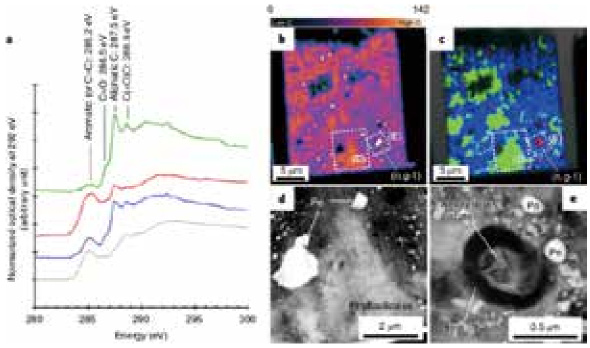

Figure 2.3) (a) NEXAFS spectra around C K-edge normalized to 292 eV of aromatic (C=C)-rich regions (red), C–H bonding-rich regions (green) and matrix (blue). The grey line is a spectrum of Murchison insoluble organic matter. (b) An STXM image dominated by carbon. (c) An RGB mapping with aromatic-rich (C=C) areas (red), C–H bonding-rich areas (green) and matrix (blue). (d) C–H bonding-rich organics concentrated in coarse-grained phyllosilicates in an area enlarged from the white dashed boxes in (b) and (c). (e) A large nanoglobule extracted from the dashed white boxes in (b) and (c) where Po and Pn are pyrrhotite and pentlandite, respectively.

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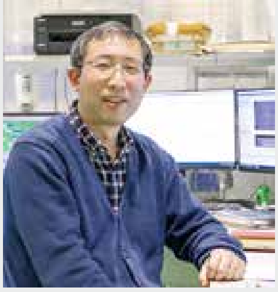
3) M. Ito *et al.*, *Nat. Astron.* **6**, 1163–1171 (2022).

Establishing Advanced Photoemission Methodologies for Novel Spin Materials Science

UVSOR Synchrotron Facility
Division of Advanced Solid State Physics



MATSUI, Fumihiko
Professor
[matui@ims.ac.jp]

Education

1995	B.S. The University of Tokyo
1997	M.S. The University of Tokyo
2000	Ph.D. The University of Tokyo

Professional Employment

2000	Assistant Professor, Nara Institute of Science and Technology
2011	Guest Professor, Physik Insitut, Universität Zürich, Switzerland (–2012)
2013	Associate Professor, Nara Institute of Science and Technology
2018	Senior Researcher, Institute for Molecular Science
2021	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Awards

2007	NAIST Award (NAIST foundation)
2008	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Awards for Science and technology (Research Category)
2009	Young Scientist Award of the Physical Society of Japan
2021	The NAGAI Foundation for Science & Technology Encouragement Award

Member
Secretary
ISHIHARA, Mayumi
KAMO, Kyoko

Keywords Photoelectron Spectroscopy, Momentum Microscope, Electronic Spin Structure

Electrons in material are excited by photons and emitted into the vacuum as photoelectrons. Interestingly, the angular distribution of these photoelectrons reveals a truly beautiful holographic pattern derived from the motion of valence electrons and the arrangement of atoms in the material. Analyzing "art" based on physical laws can lead to discoveries that connect the world of atoms with practical technology and applications, and this is what makes us so excited.

We have constructed an advanced photoelectron momentum microscope (PMM) experimental station at the UVSOR Synchrotron Facility of IMS. The PMM is a novel concept analyzer for imaging photoelectron holograms and Fermi surface patterns from the selected μm-sized area. The combination of domain-resolved photoelectron microscopy and μm-scale momentum-resolved photoelectron spectroscopy techniques is essential for the investigation of fragile radiation sensitive materials and complicated phase-separated systems.

Electron spins, which we pay particular attention to, are the source of various physical properties and functions such as magnetism, superconductivity, and topology. We are developing a unique 3D spin vector imaging system and element-selective resonant photoelectron diffraction and spectroscopy technique for the complete photoelectron analysis. We aim to pioneer cutting-edge spin materials science through comprehensive and detailed characterization of electrons.

Figure 1. Photoelectron momentum microscope at BL6U of UVSOR synchrotron facility together with valence photoelectron holograms and dispersions of TaS_2 and Bi_2Se_3. Charge density wave phase transition and topological nature can be directly studies in detail.

Selected Publications

- F. Matsui, Y. Okano, H. Matsuda, T. Yano, E. Nakamura, S. Kera and S. Suga, "Domain-Resolved Photoelectron Microscopy and μm-Scale Momentum-Resolved Photoelectron Spectroscopy of Graphite Armchair Edge Facet," *J. Phys. Soc. Jpn.* **91**, 094703 (2022).
- F. Matsui and S. Suga, "Coupling of k_z-Dispersing π Band with Surface Localized States in Graphite," *Phys. Rev. B* **105**, 23526 (2022).
- F. Matsui, S. Makita, H. Matsuda, E. Nakamura, Y. Okano, T. Yano, S. Kera and S. Suga, "Valence Band Dispersion Embedded in Resonant Auger Electrons," *J. Phys. Soc. Jpn.* **90**, 124710 (2021).
- F. Matsui and H. Matsuda, "Projection-Type Electron Spectroscopy Collimator Analyzer for Charged Particles and X-Ray Detections," *Rev. Sci. Instrum.* **92**, 073301 (2021).
- F. Matsui, S. Makita, H. Matsuda, T. Yano, E. Nakamura, K. Tanaka, S. Suga and S. Kera, "Photoelectron Momentum Microscope at BL6U of UVSOR-III synchrotron," *Jpn. J. Appl. Phys.* **59**, 067001 (2020).
- F. Matsui, H. Nishikawa, H. Daimon, M. Muntwiler, M. Takizawa, H. Namba, and T. Greber, "The 4π k_z Periodicity in Photoemission from Graphite," *Phys. Rev. B* **97**, 045430 (2018).

1. Single Graphite Step Visualized

Graphite is an incredibly important, versatile mineral, with uses spanning industries. Graphite is an essential component of many batteries, including lithium-ion batteries, and demand is only increasing as new technology is developed. Even though graphite has been thoroughly researched for decades, there is still more to be uncovered. Surprisingly, no photoelectron spectroscopic studies have so far accurately measured the electronic states of the surface and the edge of graphite from a microscopic point of view. It has been "common knowledge" that the electronic structure of graphite is six-fold symmetric, but local observations using microscopy capabilities[1] have revealed the existence of two three-fold symmetric domains that are mirror symmetric by the termination of the alternating stacking structure at the topmost surface (Figure 2).[2] Whereas conventional measurements look at the sum of both, photoelectron momentum microscopy reveals a step-edge structure at the boundary of two terraces of monoatomic layers of graphite with mirror symmetry with respect to each other.

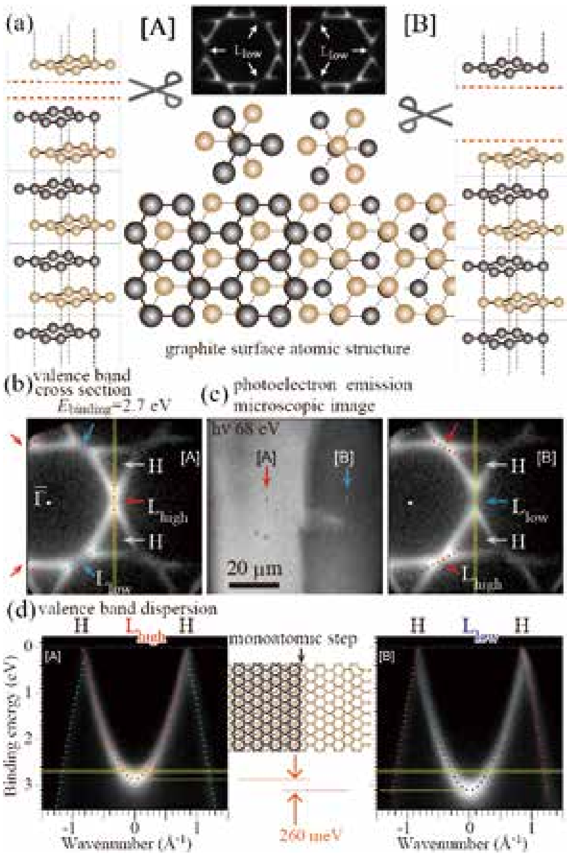


Figure 2. (a) Atomic structure of the cleaved graphite surface. (b) Iso-energy cross section of the graphite surface π band. (c) Graphite single atomic layer step was imaged with different contrast owing to the difference in the π band binding energies in two different terraces as shown in (d).[2]

2. Embed Valence Band in Auger Electrons

Resonant photoelectron spectroscopy highlights certain elemental components of the valence band by adjusting the photon energy to a core-level excitation threshold. However, most of the investigations to date has focused on angle-integrated spectral analysis for elucidating the element-specific density of states. Thus, we explored the condition for the transition of the valence band dispersion information to the Auger electrons by momentum-resolved measurements with a wide-range and high-resolution and realized a new photoelectron spectroscopy with the specificity of elemental and atomic orbitals in band structure analysis.

We performed momentum-resolved resonant photoelectron spectroscopy measurements of graphite crystals using soft X-ray. We identified four different types of resonant pathways at the C K-shell absorption threshold (Figure 3).[3] Fano-resonance-like behavior was confirmed for photoelectron emission from the π band dispersion. The π band dispersion disappeared just below the absorption threshold, and was strongly enhanced at the π* absorption resonance peak photon energy. In addition, two types of resonant Auger electron emission involving the Dirac cone shake-up process were observed. Furthermore, we discovered a peculiar dispersion structure embedded in the normal Auger electron energy region. This phenomenon has also been confirmed with monolayer graphene and adsorbed aromatic molecular species.[4] This resonant valence excitation technique provides a versatile means for characterizing valence band and molecular orbital with element specification.

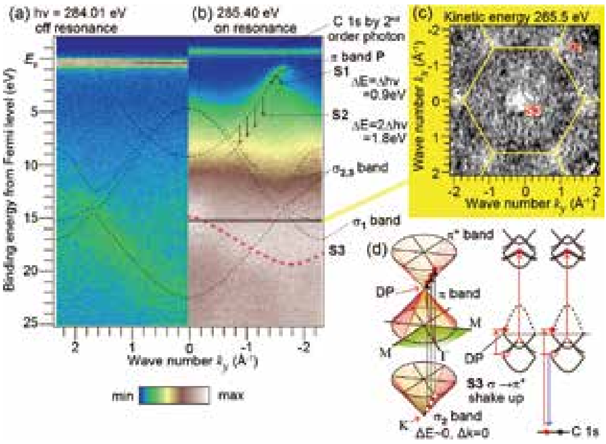


Figure 3. Momentum-resolved valence photoelectron and Auger electron spectra along the direction excited at the photon energy of (a) 284.01 eV and (b) 285.40 eV. Black and red dotted lines indicate the valence band and Auger electron dispersions, respectively. (c) Iso-energy momentum-resolved Auger electron intensity distribution at the kinetic energy of 266.5 eV. (d) Schematic of resonant Auger-electron emission for the pathway S3.[3]

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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

UVSOR Synchrotron Facility
Division of Advanced Solid State Physics

TANAKA, Kiyohisa
Associate Professor
[k-tanaka@ims.ac.jp]

Education

2000	B.S. The University of Tokyo
2005	Ph.D. The University of Tokyo

Professional Employment

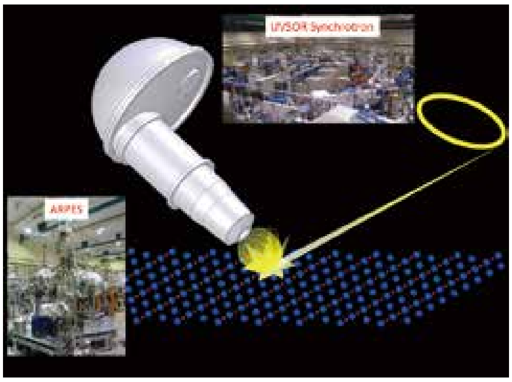
2005	Postdoctoral Fellow, Stanford University and Lawrence Berkeley National Laboratory
2008	Assistant Professor, Osaka University
2013	Associate Professor, Osaka University
2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Member
Graduate Student
HOSHINA, Takumi*
SUGIMOTO, Takafumi*

Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials have attracted more attentions in the last few decades because of their unusual and fascinating properties such as high-T_c superconductivity, giant magnetoresistance, heavy fermion and so on. Those unique properties can offer a route toward the next-generation devices. We investigate the mechanism of the physical properties as well as the electronic structure of those materials by using angle-resolved photoemission spectroscopy (ARPES). ARPES is a powerful experimental technique, directly measuring the energy (E) and momentum (k) relation, namely the band structure of solids. In the last quarter of a century, the energy resolution and angular resolution of ARPES have improved almost three order of magnitude better, which makes us possible to address the fine structure of the electronic structure near the Fermi level: Superconducting gap, kink structure and so on. The main target materials of our group is high-T_c superconductors, such as cuprates and iron pnictides and use UVSOR-III as a strong light source.

Our group is also developing high-efficiency spin-resolved ARPES system. Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin-resolved ARPES is one of the most powerful experimental techniques to investigate the magnetic properties of such materials.



Selected Publications

- K. Tanaka *et al.*, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- K. Tanaka *et al.*, "Quantitative Comparison between Electronic Raman Scattering and Angle-Resolved Photoemission Spectra in $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductors: Doping Dependence of Nodal and Antinodal Superconducting Gaps," *J. Phys. Soc. Jpn.* **88**, 044710 (2019).
- S. Ideta, K. Tanaka *et al.*, "Experimental Investigation of the Suppressed Superconducting Gap and Double-Resonance Mode in $Ba_{1-x}K_xFe_2As_2$," *Phys. Rev. B* **100**, 235135 (7 pages) (2019).
- S. Ideta, K. Tanaka *et al.*, "Hybridization of Bogoliubov Quasiparticles between Adjacent CuO_2 Layers in the Triple-Layer Cuprate $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ Studied by Angle-Resolved Photoemission Spectroscopy," *Phys. Rev. Lett.* **127**, 217004 (6 pages) (2021).

1. Hybridization of Bogoliubov Quasiparticles between Adjacent CuO_2 Layers in the Triple-Layer Cuprate $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ 1)

It has been known that one of the most efficient ways to increase the critical temperature (T_c) of high-T_c cuprate superconductors (HTSCs) is to increase the number of neighboring CuO_2 planes (n). T_c generally increases from single-layer (n = 1), double-layer (n = 2), to triple-layer (n = 3) and then decreases for $n \geq 4$. Although several mechanisms have been proposed to explain the n dependence of T_c, it is still not clear because of the lack of detailed knowledge about the electronic structure of the multi-layer ($n \geq 3$) cuprates. In this study, we performed ARPES of optimally doped triple-layer $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223, T_c = 110 K) in the superconducting states at UVSOR BL7U.1)

Figures 1(a)–(h) show hybridization of Bogoliubov quasiparticles (BQPs) between the outer CuO_2 plane (OP) and the inner CuO_2 plane (IP). The OP and IP are hybridized with each other and open a gap at the crossing point (an anticrossing gap between the two BQP bands) as shown in Figure 1(i). We noticed that the magnitude of the gap ($\Delta_{t\perp}(k)$) gradually increases as one goes away from the node toward the antinode and the momentum dependence of $\Delta_{t\perp}(k)$ can be reproduced by assuming the interlayer single-particle hopping parameter $t\perp \sim 56$ meV using the tight-binding model for coupled CuO_2 planes. In order to reproduce the high energy kinks for the OP and IP bands of the measured ARPES spectra, we have performed model calculation including the coupling to several oxygen-derived phonons. Taking into account the contribution of acoustic phonons, the flatness of the top of the IP band seen in the experiment is reproduced to some extent.

The most intriguing and important question relevant to the present study is how much the interlayer single-particle hopping and the obtained $\Delta_{t\perp}(k)$ contribute to the enhancement of T_c in Bi2223. In order to discuss a possible mechanism for the T_c enhancement in triple-layer cuprates, a simple four-well model calculation is performed assuming contributions from four bosonic modes, namely, the acoustic phonon, the c-axis buckling phonon, the in-plane breathing phonon, and spin fluctuations. The present model calculation suggests that the electron–phonon coupling alone may not be sufficient to cause the observed T_c in the triple-layer cuprate, and the combination of spin fluctuations and phonons is essential (not shown).

As another candidate of the anticrossing gap, the effect of interlayer Cooper-pair hopping could not be isolated from the present data, but might be important to increase the T_c of Bi2223. To answer the question of how interlayer interactions, *i.e.*, single-particle hopping versus Cooper-pair hopping, contribute to the enhancement of superconductivity, further systematic studies are needed both experimentally and theoretically. The momentum-dependent hybridization gap, which is proportional to the square of the SC order parameter, would be a key piece of information to solve the T_c-enhancement mechanism of the multilayer cuprates.

2. Development of Spin-Resolved ARPES with Image-Spin Detection

Our group is developing a new high-efficient spin-resolved ARPES system with multi-channel detection (we call “image-spin” detection) in beamline BL5U at UVSOR. We successfully obtained spin-resolved signal of Au(111) surface and achieved 100 times better efficiency and several times better momentum resolution than the current synchrotron-based spin-resolved ARPES systems in the world. In 2021, we installed a spin-manipulator lens system, where the direction of the spin can be changed to any directions. The calibration of the lens parameters will be done in 2022.

Reference

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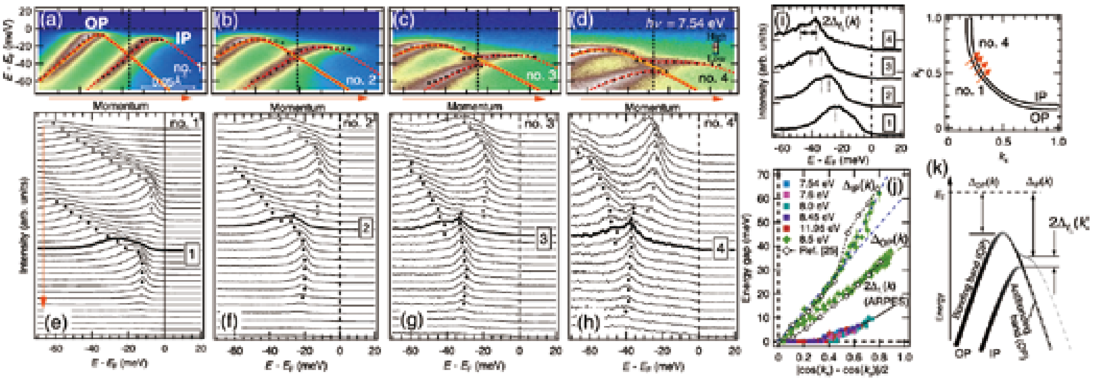

Figure 1. ARPES spectra of the OP and IP bands in Bi2223. (a)–(d): E-k plots near E_F. (e)–(h): Energy-distribution curves (EDCs) corresponding to (a)–(d). (i): EDCs at momenta where the OP band and the IP band cross extracted from panels (e)–(h). (j): Momentum dependence of $\Delta_{t\perp}(k)$ plotted against the d-wave order parameter. (k): Schematic illustration of the hybridization between the OP and IP BQP bands in the off-nodal region.

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* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Soft X-Ray Absorption Spectroscopy for Observing Chemical Processes in Solution

Department of Photo-Molecular Science
Division of Photo-Molecular Science III

NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) observes local structures of liquids with different light elements. We have developed liquid cells and devices with precise absorbance control and observed several chemical processes in solution by using *operando* XAS.[1,2] In this year, we have investigated the process of hydrophobic cluster formation in aqueous ethanol solutions by using XAS.[3]

1. Hydrophobic Cluster Formation in Aqueous Ethanol Solutions

Hydrophobic cluster structures in aqueous ethanol solutions at different concentrations have been investigated by XAS.[3] In the O K-edge XAS, we have found that hydrogen bond structures among water molecules are enhanced in the middle concentration region by the hydrophobic interaction of the ethyl groups in ethanol. On the other hand, in the C K-edge XAS, the lower energy features arise from a transition from the terminal methyl C 1s electron to an unoccupied orbital of 3s Rydberg character and show characteristic four concentration regions. From the comparison of C K-edge XAS with the inner-shell calculations, we have revealed the intermolecular interactions of ethanol with water at different concentration regions and found that ethanol clusters are easily formed in the middle concentration region due to the hydrophobic interaction of the ethyl group in ethanol, resulting in the enhancement of the hydrogen bond structures among water molecules.

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3) M. Nagasaka, M. Bouvier, H. Yuzawa and N. Kosugi, *J. Phys. Chem. B* **126**, 4948–4955 (2022).

Twisted Structure Analysis of Soft Matters by Resonant Soft X-Ray Scattering

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

IWAYAMA, Hiroshi
Assistant Professor

Soft matters exhibit their intriguing properties due to mesoscopic physical structures by self-organizations. To understand properties of soft matters, we need to investigate their structure in the mesoscopic scale. We developed a new resonant soft x-ray scattering method which has various kind of selectivities such as elements, groups and molecular alignments.[1)]

1. Twisted Structure of Helical-Nanofilament

Twisted structure can be often observed in soft matter. However, since electron density modulations resulting from the twisted structures are weak, conventional small angle x-ray scattering method is difficult to observe it. The resonant soft x-ray scattering measurements can probe twisted structures and obtain pitch of twisted structure. This is because a resonant process strongly depends on an angle between molecule and polarization vector of incident soft x-ray. In this year, we performed resonant soft x-ray scattering experiments at UVSOR BL3U for a helical-nanofilament of liquid-crystal matter.

We successfully obtained diffraction images at the wavelength of 4.34 nm (285 eV), which correspond to C 1s-to-π* core excitations. From the analysis of images, we found a resonant enhancement of diffractions corresponding to a twist pitch of 80 nm. We also found that twist pitch depends on the sample compositions and its temperatures.

Reference

1) B. A. Collins and E. Gann, *J. Polym. Sci.* **60**, 1199 (2022).

Visiting Professors

Visiting Professor

MASE, Kazuhiko *(from High Energy Accelerator Research Organization)*

Development of New Nonevaporable Getter (NEG) with a Low Activation Temperature

Nonevaporable getter (NEG) is a functional material that evacuates residual gases at room temperature (RT) by forming an active surface when heated in ultra-high vacuum (UHV). When NEG is deposited on the inner wall of a vacuum vessel, the vacuum vessel will evacuate the residual gases just by baking, and UHV can be maintained without electric power for long time. Therefore, the development of NEG will contribute to CO_2 emission reduction and Sustainable Development Goals (SDGs). However, the activation temperature of NEG (the temperature required to create an active surface by heating in UHV) needs to be lowered if NEG is to be widely used in various vacuum-related industries. Recently we have developed a new NEG, Pd overcoated on Ti thin film with a purity higher than 99.95% (oxygen-free Pd/Ti hereafter), which evacuates H_2 and CO at RT after baking at 133 °C for 12 hours. NEG pumps using oxygen-free Pd/Ti deposition has been commercialized in 2019 and are widely used in synchrotron radiation facilities such as SPring-8, UVSOR, and Photon Factory.

Visiting Associate Professor

FUKUHARA, Takeshi *(from RIKEN)*

Single-Atom-Resolved Imaging of Quantum Gases in Optical Lattices

Ultracold quantum gases in optical lattices provide a clean and controllable platform for studying quantum many-body systems; especially they enable us to emulate various fundamental models in solid-state physics. Key technologies for this research are the detection and manipulation of such gases at the single-atom level. We have prepared quantum gases in triangular optical lattices for the study of frustration physics and successfully realized single-atom-resolved detection using fluorescence imaging. Raman sideband cooling has been utilized for the detection because the sample of ultracold atoms is heated and destroyed due to photon scattering. Several parameters, such as intensities and frequencies of the cooling lasers, are required to be tuned for successful imaging. We automatically adjusted the parameters using Bayesian optimization, which is a machine learning method. Now we are improving the scheme for the optimization method to enhance the imaging fidelity.

Visiting Associate Professor

NAKAYAMA, Yasuo *(from Tokyo University of Science)*

Epitaxially-Grown Single-Crystalline Organic Molecular Semiconductors

While epitaxial growth of single-crystalline (inorganic) semiconductor materials is one of the most essential technologies for modern electronic applications, current organic semiconductor electronics are mostly built on heterojunctions composed of polycrystalline or amorphous molecular solids. On the other hand, single-crystalline organic semiconductor materials exhibiting “band transport” realize considerably high charge carrier mobility of over 10 $cm^2V^{-1}s^{-1}$ and have potential applications as flexible and efficient electronic devices. Our group has been working on single-crystalline heterojunctions of organic molecular semiconductors by epitaxial growth techniques. Recently, we discovered as a collaborative work with IMS groups that a methyl- and trifluoromethyl-substituted derivative of rubrene forms high-quality single-crystalline junctions on the single-crystal surface of (unsubstituted) rubrene in a “quasi-homoepitaxial” manner. Electronic band measurements on this quasi-homoepitaxial molecular junction by means of angle-resolved photoelectron spectroscopy are one of our next targets.

RESEARCH ACTIVITIES
Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

YOKOYAMA, Toshihiko
Professor
[yokoyama@ims.ac.jp]

Education

1983	B.S. The University of Tokyo
1985	M.S. The University of Tokyo
1990	Ph.D. The University of Tokyo

Professional Employment

1987	Research Associate, Hiroshima University
1993	Research Associate, The University of Tokyo
1994	Lecturer, The University of Tokyo
1996	Associate Professor, The University of Tokyo
2002	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
KOITAYA, Takanori*
YAMAMOTO, Kohei
Visiting Scientist
BUTTEINS, Thomas†
Graduate Student
KOBAYASHI, Akito‡
Secretary
ISHIKAWA, Azusa
KURITA, Yoshiko

Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard and Soft X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage. Recently, assistant professor Kohei Yamamoto is developing the reflectance soft x-ray magnetic circular dichroism system for the clarification of depth resolved magnetism of magnetic thin films with the atomic layer resolution scale.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although photoelectron spectroscopic measurement is usually done under high vacuum, recent material science often requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time in the world using Beamline 36XU of SPring-8. Moreover, we designed and constructed the subsecond time resolved AP-HAXPES measurement system, and successfully investigated electrochemical reaction dynamics for the cathode Pt oxidation/reduction and the S^2-adsorption/desorption processes upon an abrupt step of the cathode-anode bias voltages. These works were supported by the NEDO Fuel Cell project. More recently, assistant professor, Takanori Koitaya, has been investigating various kinds of surface chemical reactions such as methane activation and CO_2 hydrogenation using the AP-HAXPES system combined with the near ambient pressure soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8.

The third subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using the x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Moreover, conventional temperature dependent extended x-ray absorption fine structure (EXAFS) spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of alloy systems.

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- T. Nakamura *et al.*, *J. Phys. Chem. C* **124**, 17520 (2020).
- S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866 (2021).

1. *Operando* Characterization of Copper-Zinc-Alumina Catalyst for Methanol Synthesis from CO_2 and H_2 by AP-HAXPES1)

Operando spectroscopy is a very powerful tool for the characterization of heterogeneous catalysts under working conditions. In this study, an AP-HAXPES investigation of an industrial copper-zinc-alumina methanol synthesis catalyst was performed using our AP-HAXPES system shown in Figure 1(a) to reveal surface chemical states of the catalyst and adsorbed intermediates during the catalytic reaction. The reaction activity of the present catalyst is quite important because of the significance of the CO_2 circulation. *In-situ* formation of metallic Cu-Zn particles was detected during the reduction process of the catalyst under hydrogen atmosphere. More interestingly, a significant amount of Al atoms was found to be incorporated into ZnO during H_2 reduction and also CO_2 hydrogenation chemical reaction as seen in Figures 1(b) and 1(c).

In this study, we also installed a quadrupole mass spectrometer installed in the differentially pumped electron lens chamber to observe the reaction products in the presence of near ambient-pressure CO_2 and H_2 gases. The formation of CO and methanol was actually observed very clearly. Temperature dependence was found to differ between rWGS (reverse water-gas shift to form CO) reaction and methanol synthesis; the reaction products of rWGS monotonically increased as a function of the sample temperature between 420 K and 593 K, whereas the rate of the methanol synthesis reached a local maximum at 480 K, and decreased at 593 K. The observed temperature-dependence of methanol synthesis correlates well with the dynamic changes in the chemical states of the catalyst and adsorption intermediates during the reaction observed in the AP-HAXPES.

Figure 2 shows the C 1s and O 1s HAXPES during the CO_2 hydrogenation reaction. The total environmental pressure amounts 53 kPa. Although the C 1s spectra measurement was rather difficult due to the small C 1s photoionization cross section, important reaction intermediate species such as CO_3(a), HCOO(a), CH_3O(a) were observed. The present AP-HAXPES measurements clearly show the importance of *operando* characterization of the dynamic nature of heterogeneous catalysts.

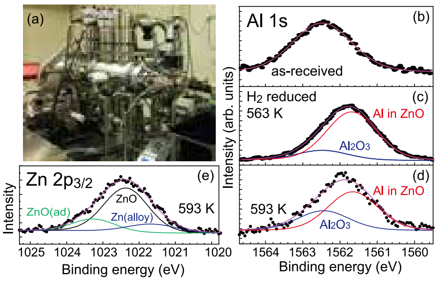

Figure 1. (a) Our AP-HAXPES system installed at BL36XU in SPring-8, (b–d) Al 1s HAXPES ($h\nu$ = 7.94 keV) from the CuZn/Al_2O_3 catalyst: (b) as-received, (c) during H_2 reduction at 563 K, and (d) in the 36 kPa H_2 and 17 kPa CO_2 atmosphere at 593 K, together with (e) Zn $2p_{3/2}$ HAXPES in the same condition as (d). The Al atoms are found to be incorporated in ZnO in CO_2 hydrogenation reaction, which is a key role for the catalytic activity in this system.

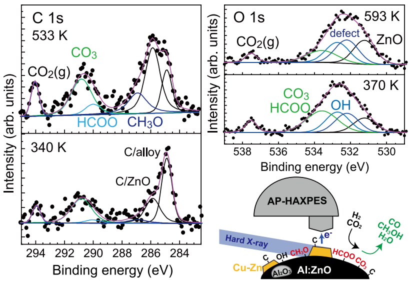

Figure 2. (left) C 1s HAXPES during the CO_2 hydrogenation reaction (8 kPa H_2 and 5 kPa CO_2 at 340 and 533 K) and (right) O 1s HAXPES during the reaction (36 kPa H_2 and 17 kPa CO_2 at 370 and 593 K). Reaction intermediate species as CO_3(a), HCOO(a), and CH_3O(a) are seen, implying successful direct observation in the present catalytic reaction. Schematic surface reaction model is also shown in the figure.

2. Exploitation of Reflectance Soft X-Ray Magnetic Circular Dichroism System for the Clarification of Layer-Resolved Magnetic Structures

Magnetic thin films/multilayers with complex depth structures exhibit a wide variety of magnetic phenomena due to the interactions between layers. Furthermore, multilayer structures have been used to realize useful properties in recording media, which is an important application of magnetic materials. Direct observation of the magnetic distribution in the depth direction of such magnetic multilayers has been used to elucidate the mechanism of evolution of magnetic structures in thin films. We installed an experimental setup for reflectance x-ray magnetic circular dichroism (XMCD) method in the soft X-ray regime at UVSOR BL4B and experiments were performed on test samples. The sample was CoFeB and an oscillating structure was observed due to the interference of the cap layer and the underlying layers. We observed the difference corresponding to XMCD by changing the direction of magnetic field, which is consistent with the simulation results. We also conducted spectroscopic measurements and obtained photon energy and reflection angle dependence to analyze the depth-resolved magnetization information. We will test the silicon drift detector for getting information of higher angle regions and eliminating the fluorescence effect with energy selectivity.

Reference

1) T. Koitaya K. Yamamoto, T. Uruga and T. Yokoyama, submitted.

* Present Address; Kyoto University

† IMS International Internship Program

‡ carrying out graduate research on Cooperative Education Program of IMS with Nagoya Institute of Technology

Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

Department of Materials Molecular Science
Division of Electronic Structure

SUGIMOTO, Toshiki
Associate Professor
[toshiki-sugimoto@ims.ac.jp]

Education

2007	B.S. Kyoto University
2011	Ph.D. The University of Tokyo

Professional Employment

2012	Assistant Professor, Kyoto University
2016	JST-PRESTO Researcher [Innovative Catalysts] (–2019)
2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2019	JST-PRESTO Researcher [Innovative optics and photonics]
2021	Senior Scientific Research Specialist, Ministry of Education, Culture, Sports, Science and Technology

Awards

2014	Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014	39th Vacuum Science Paper Award
2018	PCCP Prize 2018
2018	CSJ Presentation Award 2018
2018	Encouragement Award, The Spectroscopic Society of Japan
2018	Morino Foundation for Molecular Science
2019	12th Young Scientist Awards of the Japan Society for Molecular Science
2019	14th Young Scientist Award of the Physical Society of Japan

Member

Assistant Professor
SAKURAI, Atsunori

Post-Doctoral Fellow
SAITO, Hikaru
ICHII, Tomoaki
TAKAHASHI, Shota

Graduate Student
SATO, Hiromasa
LIN, Zhongqiu
NOGUCHI, Naoki
MOCHIZUKI, Tatsuto
JIN, ChengXiang
YOSHIZAWA, Ryu

Technical Fellow
TSURUOKA, Kazuyuki

Secretary
SHIMURA, Maki

Keywords Surface & Interface Science, Nonlinear Optical Spectroscopy, Water Molecules

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning prove microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that Im$\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected Im$\chi^{(2)}$ SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

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- T. Sugimoto *et al.*, "Emergent High-T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film," *Nat. Phys.* **12**, 1063–1068 (2016).
- K. Shirai *et al.*, "Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO_2 Photocatalyst," *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- T. Sugimoto *et al.*, "Topologically Disordered Mesophase at Topmost Surface of Crystalline Ice Between 120 and 200 K," *Phys. Rev. B* **99**, 121402(R) (2019).
- F. Kato *et al.*, "Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice," *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
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- H. Sato *et al.*, "*Operando* FT-IR Spectroscopy of Steam-Methane-Reforming Photocatalyst under Irradiation of Intensity Modulated UV Ligh," *Vac. Surf. Sci.* **63**, 476–481 (2020).

1. Critical Impacts of Interfacial Water on the Photocatalytic C–H Conversion of Methane[1)]

On-site and on-demand photocatalytic methane conversion under ambient conditions is one of the urgent global challenges for the sustainable use of ubiquitous methane resources. However, the lack of microscopic knowledge on its reaction mechanism prevents the development of engineering strategies for methane photocatalysis. Combining real-time mass spectrometry and *operando* infrared absorption spectroscopy with *ab initio* molecular dynamics simulations, here we report key molecular-level insights into photocatalytic green utilization of methane. Activation of the robust C–H bond of methane is hardly induced by the direct interaction with photogenerated holes trapped at the surface of photocatalyst; instead, the C–H activation is significantly promoted by the photoactivated interfacial water species (Figure 1). The interfacial water hydrates and properly stabilizes hydrocarbon radical intermediates, thereby suppressing their overstabilization. Owing to these water-assisted effects, the photocatalytic conversion rates of methane under wet conditions are dramatically improved by typically more than 30 times at ambient temperatures (~300 K) and pressures (~1 atm) in comparison to those under dry conditions. This study sheds new light on the role of interfacial water and provides a firm basis for design strategies for non-thermal heterogeneous catalysis of methane under ambient conditions.

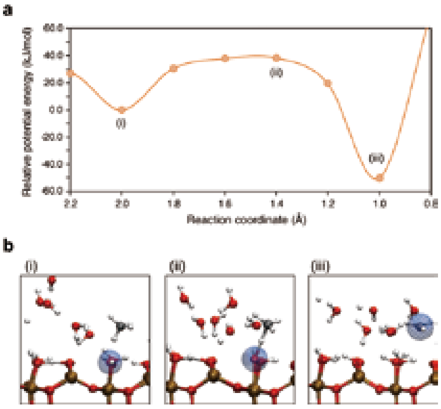

Figure 2. (a) Potential energy curve and (b) snapshots for methane activation under wet conditions on β-Ga_2O_3 surfaces.

2. Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water[2,3)]

Environmentally sustainable and selective conversion of methane to valuable chemicals under ambient conditions is pivotal for the development of next-generation photocatalytic technology. However, due to the lack of microscopic knowledge about the non-thermal methane conversion, controlling and modulating photocatalytic oxidation processes driven by photogenerated holes remain a challenge. Here, we report novel function of metal cocatalysts to accept photogenerated holes and dominate the oxidation selectivity of methane (Figure 2), which is clearly beyond the conventional concept in photocatalysis that the metal cocatalysts loaded on the surfaces of semiconductor photocatalysts mostly capture photogenerated electrons and dominate reduction reactions exclusively. The novel photocatalytic role of metal cocatalysts was verified by *operando* molecular spectroscopy combined with real-time mass spectrometry for metal-loaded Ga_2O_3 model photocatalysts under methane gas and water vapor at ambient temperature and pressure. Our concept of metal cocatalysts that modulate photocatalytic oxidation as well as reduction opens a new avenue for controlling photocatalytic redox reactions by metal-cocatalyst engineering.

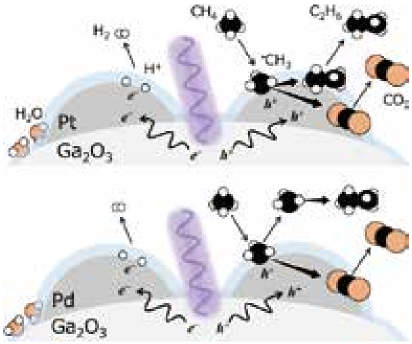

Figure 3. Schematic illustration of the role of metallic cocatalysts on the photocatalytic methane oxidation.

3. Monolayer-Sensitive Coherent Raman Spectroscopy for Molecular Systems on Conductive Surfaces[4)]

Highly sensitive and versatile spectroscopy for molecular systems on conductive surfaces, relating with electrochemistry, corrosion processes, and catalytic reactions is crucial in many scientific and technological fields. However, conventional spectroscopy based on spontaneous Raman scattering requires some specific electronic/plasmonic enhancements due to its weak signal, imposing serious restriction on the system to which it is applied. Here, we introduce a monolayer-sensitive and versatile stimulated Raman spectroscopy without using any electronic/plasmonic enhancements. This spectroscopy innovation is achieved by coherent anti-stokes Raman scattering (CARS) with dramatical improvement of signal-to-noise ratio based on an optimally shaped time-delayed pulse; our stimulated and time-resolved Raman observation scheme not only enhance the vibrational signal but also significantly suppress the huge background from conductive surfaces, which is demonstrated by focusing on well-defined self-assembled monolayers on flat gold substrates.

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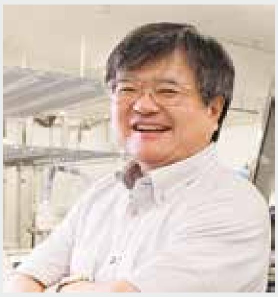
4) T. Ichii, A. Sakurai and T. Sugimoto, in preparation.

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



HIRAMOTO, Masahiro
Professor
[hiramoto@ims.ac.jp]

Education

1984	B.E. Osaka University
1986	Ph.D (Engineering) Osaka University

Professional Employment

1984	Technical Associate, Institute for Molecular Science
1988	Research Associate, Osaka University
1997	Associate Professor, Osaka University
2008	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Awards

2021	Outstanding Achievement Award, Molecular Electronics & Bioelectronics Division, Japan Society of Applied Physics
2017	Fellow Award of Japan Society of Applied Physics
2006	Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
2006	Research and Education Award, Osaka University
2004	Editor Award, Japanese Journal of Applied Physics

Member

Assistant Professor
IZAWA, Seiichiro

Post-Doctoral Fellow
LEE, Jihyun

Research Fellow
YABARA, Yusuke
ADACHI, Kazuhiro

Graduate Student
PALASSERY ITHIKKAL, Jaseela

Secretary
NAKAMURA, Yuka
OGURA, Yasuko

Keywords Organic Semiconductors, Up-Conversion, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc*. Followings are our recent results. (1) Photon up-conversion (UC) from near infrared (NIR) to visible yellow (Figure 1) by utilizing charge transfer (CT) states at donor/acceptor (D/A) interface of organic solar cells. (2) A novel concept of the structure of organic solar cell, namely, a lateral junction in which the photogenerated holes and electrons are laterally transported and extracted to the respective electrodes. Even 1.8 cm-length lateral cells (Figure 2) showed clear photovoltaic behavior. (3) The reduction of open-circuit voltage (V_{oc}) loss due to non-radiative recombination in organic solar cells by using high-mobility organic semiconductors. The V_{oc} reaching to thermodynamic (Shockley-Queisser) limit was observed. (4) The ppm-level doping effects in organic semiconductor films and organic single crystals for organic solar cells. So far, we have reported complete *pn*-control, doping sensitization, and the ppm-level doping effects using an ultra-slow deposition technique reaching 10^{-9} nm s^{-1} (Figure 3) in organic rubrene single crystals measured by the Hall effect, which shows a doping efficiency of 82% comparable to the B in Si. These results can be regarded as a foundation for the construction of highly efficient organic solar cells.

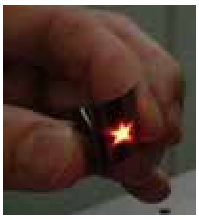


Figure 1. Up-converted (UC) yellow emission by star-shaped near infrared irradiation.

Figure 2. Picture of a 1.8 cm-length lateral cell.

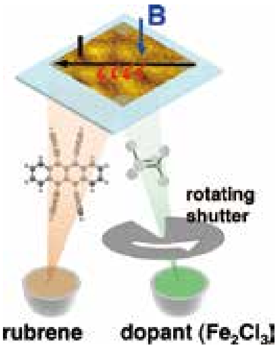


Figure 3. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

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- S. Izawa and M. Hiramoto, "Efficient Solid-State Photon Upconversion by Spin Inversion at Organic Semiconductor Interface," *Nat. Photonics* **15**, 895–900 (2021).
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- S. Izawa, N. Shintaku, M. Kikuchi and M. Hiramoto, "Importance of Interfacial Crystallinity to Reduce Open-Circuit Voltage Loss in Organic Solar Cells," *Appl. Phys Lett.* **115**, 153301 (2019).
- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* **30**, 1801236 (15 pages) (2018).
- *Organic Solar Cells—Energetic and Nanostructural Design*, M. Hiramoto and S. Izawa, Eds., Springer Nature Singapore Pte Ltd. (2021).

1. Efficient Interfacial Up-Conversion Enabling Bright Emission with Extremely Low Driving Voltage in Organic Light-Emitting Diodes1)

We reported the photon up-conversion (UC) from near infrared (NIR) to visible yellow (Figure 1).2) The UC emission occurs by the combination of organic solar cell process and up-conversion (UC) process (Figure 4(b)). Double layer consists of rubrene donor (D) and non-fullerene acceptor (A) was used. In the solar cell process, the free charges are generated at D/A interface by near-infrared (NIR) excitation. In the UC process, the charge recombination at the D/A interface takes place and triplet states (T_1) are formed in the rubrene film through the CT states. Finally, the UC emission occurs by the T–T annihilation.

The UC process can also occur by the injected electrons and holes from the electrodes. So, we could fabricate the up-converted organic EL device. Red EL of 2.0 eV could be emitted by applied voltage of half energy of 1.0 V by utilizing up-conversion (Figure 4(a)). 100 cd/m^2 at 1.5 V and 1000 cd/m^2 at 2.5 V were obtained. A battery of 1.5 V was enough for EL operation. This is the world lowest operating voltage reported so far. Thus, the CT state, which is an essence of organic solar cell process, can be also utilized for up-converted organic EL.

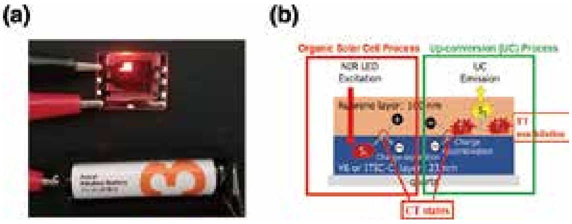

Figure 4. (a) Up-converted EL operated by a battery of 1.5 V. (b) Up-conversion (UC) mechanism.

2. Monolayer-Digitized Band Mapping for Doped Rubrene Single Crystals3)

The band mapping for doped rubrene single crystals by using Atomic/Kelvin force microscopy (AFM/KFM) was performed. The ppm-level doping technique using an ultra-slow deposition (Figure 3) was used. Doped rubrene single crystal was obtained by the homoepitaxial growth on rubrene single crystal substrate. Mo_3O_9 (1,000 ppm) was used as an acceptor dopant. Thicknesses of doped homoepitaxial layers were varied from 0 to 20 nm.

Morphological and potential images of doped homoepitaxial rubrene are shown in Figures 5(a) and 5(b). The island image (AFM) (Figure 5(a)) and the simultaneously obtained potential image (KFM) (Figure 5(b)) are roughly coincided. The average work functions of 3 and 4 rubrene monolayers were determined to 4.18 and 4.22 eV, respectively. Thus, we could plot the relationship between work function and number of rubrene monolayer (Figure 5(c), blue dots).

For Mo_3O_9 (1,000 ppm) doped rubrene single crystal, the number of negatively ionized acceptors of 2.0×10^{18} cm^{-3} and the doping efficiency of 3.3% were calculated by the band mapping. Specific values of work function observed for each number of rubrene monolayer suggests that the built-in potentials are monolayer-digitized.

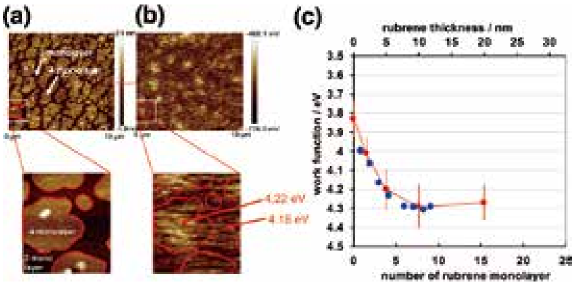

Figure 5. (a) Morphological image of Mo_3O_9 (1,000 ppm) doped homoepitaxial rubrene having the thickness of 5 nm. (b) Simultaneously obtained potential image. Magnified image (lower) of white rectangle area (upper) are also shown. Island shapes emphasized by red curves are overlayed in the potential image. (c) Monolayer-digitized band mapping.

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2) S. Izawa and M. Hiramoto, *Nat. Photonics* **15**, 895–900 (2021).
3) M. Hiramoto, Y. Yabara, T. Minato and S. Izawa, *68th Spring meeting of Japan Society of Applied Physics*, 17p-Z23-2 (2021).

Awards

IZAWA, Seiichiro; NF Foundation R&D Encouragement Award (2021).
IZAWA, Seiichiro; The 11th Young Scientist Award of National Institutes of Natural Sciences (2022).
IZAWA, Seiichiro; The Morino Foundation for Molecular Science (2022).

Solid-State NMR for Molecular Science

Department of Materials Molecular Science
Division of Molecular Functions

NISHIMURA, Katsuyuki
Associate Professor
[nishimur@ims.ac.jp]

Education
1994 B.S. Himeji Institute of Technology (University of Hyogo)
1999 Ph.D. Himeji Institute of Technology (University of Hyogo)

Professional Employment
1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
2001 Assistant Professor, Yokohama National University
2006 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Award
2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

Member
Secretary
YOKOTA, Mitsuyo

Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

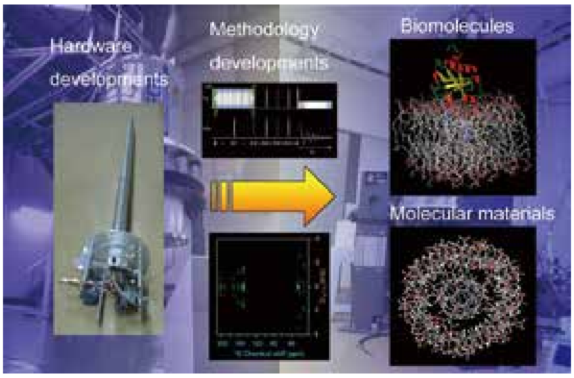

Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, “Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1,” *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
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- M. Yagi-Utsumi, K. Kato and K. Nishimura, “Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure,” *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, “‘Helix-in-Helix’ Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity,” *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).

1. Structural Characterization of Protein Using Solid-State NMR

Water bear possess extreme tolerance for environments. So far, the molecular mechanisms to protect their cells in such environments have not been clarified yet. Especially, under extremely dry environment, water bear takes torpor, then recovers under wet environment. It has been reported that several specific proteins have been expressed in water bear before torpor. Secretary abundant heat soluble protein (SAHS) is one of those proteins, and its biological functions have not been clarified yet. However, it has been considered that SAHS plays important roles to conserve their tissues, thus cells of water bear during torpor. The molecular structure of SAHS under hydrated state has been characterized precisely. In contrast, their structural information is limited under dry state. Therefore, we have been attempted to clarify the SAHS structure at dry state using solid-state NMR spectroscopy. This is collaboration project with Prof. Kato group in IMS and Prof. Yagi group in Nagoya city university.

Any proteins under dry condition may be expected to exhibit inhomogeneous structure. In order to investigate local structural and those homogeneity of SAHS at dry state, 2D dipolar assisted rotational resonance (DARR) ^{13}C-homonuclear correlation solid-state NMR measurements were carried out for the dry-state SAHS protein which only isoleucine residues are isotopically enriched by ^{13}C and ^{15}N. Those samples were newly prepared by improved procedures. Together with solid-state NMR analyses for several mutants for SAHS, signal assignments were successfully achieved. Then local secondary structures were identified through investigations of obtained ^{13}C chemical shifts of individual sites. Consequently, the result suggests that essentially most of secondary structure of SAHS are conserved even under dry state.

2. Developments of Spectral Editing Solid-State NMR Techniques

For the characterization of molecules using NMR, signal assignment is the first important step. Especially for biomolecules, such as proteins, ^{13}C and ^{15}N uniform isotope enrichments of samples is common and essential approach. Those isotope enrichments of samples enable to detect homo-, and heteronuclear correlation peaks among ^{13}C and ^{15}N nuclei at reasonable sensitivities. Those analyses enable structural characterizations of molecules. However, those isotope enrichments are not generally applicable, such as natural products and synthetic molecules via complicated processes. For such unlabeled samples, the efficient approach is quite limited due to the difficulties of observation of ^{13}C and ^{15}N correlation signals among natural abundant nuclei. Therefore, totally different approaches must be applied for their characterizations.

We have been working on developments of efficient spectral editing techniques to support accurate signal assignments for such unlabeled organic samples in solid-state NMR spectroscopy under both rigid and mobile sample conditions. The applicability of the developed technique has been verified for reference samples and their applications are under study.

3. Development of Solid-State NMR Probes

We have been working on developments of totally original solid-state NMR probes during a couple of years. In those probes, only spinning module and spinning counting module are remained as commercial parts. In order to replace those remained commercial parts to our original ones, we have been working on developments of original sample spinning modules for magic angle spinning (MAS) solid-state NMR probes which are fully compatible with currently using Bruker spectrometer and commercial sample tubes. As an initial stage, we started the design of a spinning module for standard 4.0 mm sample tube for Bruker. After two times of version up, our original spinning module reached to the spinning performance of commercial one from Bruker. The experimental performance of developed spinning module was evaluated by installing the module to the originally developed bench spinner system. By using Bruker automated spinning controller using standard parameters of drive- and bearing gas pressures for commercial 4.0 mm sample tube, our spinning modules achieved maximum sample spinning rate of 15 kHz for Bruker commercial sample tube. In addition, by using originally built manual spinning controller system with original drive-, and bearing-gas pressures, our spinning module achieved higher spinning rate over maximum spinning rate for Bruker commercial spinning module. Currently, a shrink version of the spinning module is under development in order to enable installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.

Study on Hydride Ion Conductive Materials for Novel Electrochemical Devices

Department of Materials Molecular Science
Division of Molecular Functions

KOBAYASHI, Genki
Associate Professor
(–May, 2022)
[gkobayashi@ims.ac.jp]

Education

2006	B.E. Kanazawa University
2010	D.S. Tokyo Institute of Technology

Professional Employment

2010	Postdoctoral Fellow, Tokyo Institute of Technology
2011	Assistant Professor, Kanagawa University
2012	JST-PRESTO Researcher (Additional post)
2013	Research Associate Professor, Institute for Molecular Science
2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2022	Chief Scientist, RIKEN

Awards

2011	Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018	The 39th Honda Memorial Young Researcher Award, The Honda Memorial Fundation
2018	The 7th Ishida Award, Nagoya University
2019	Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan
2019	Morino Foundation for Molecular Science
2022	Academic Award, The NAGAI Foundation for Science & Technology

Member

Assistant Professor
TAKEIRI, Fumitaka

Graduate Student
OKAMOTO, Kei
UCHIMURA, Tasuku
IZUMI, Yoshiki
KUSUMOTO, Keiko

Technical Fellow
IMAI, Yumiko
KUBOTA, Akiko

Secretary
KAMIYA, Miho

Keywords Solid State Ionics, H^- Conductor, Battery

Hydrogen has a charge flexibility and can take various charge states such as proton (H^+), atomic hydrogen (H^0), and hydride (H^-) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H^0, H^+ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H^- is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H^- has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties ($E^o(H^-/H_2) = -2.35$ V vs. SHE), its electrochemical applications have not been considered. Against this background, we developed a series of H^- conductive oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$, in 2016 and found its function as an H^- solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H^- conductors and the development of novel electrochemical devices utilizing H^-conduction phenomena.

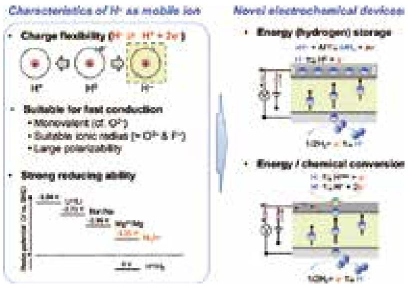

Figure 1. Our research concept toward realization of electrochemical devices utilizing hydrogen charge flexibility.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85(2)**, 88–92 (2017).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- H. Nawaz, F. Takeiri, A. Kuwabara and M. Yonemura and G. Kobayashi, *Chem. Commun.* **56**, 10373–10376 (2020).
- T. Uchimura, F. Takeiri, K. Okamoto, T. Saito, T. Kamiyama and G. Kobayashi, *J. Mater. Chem. A* **9**, 20371–20374 (2021).
- F. Takeiri, A. Watanabe, K. Okamoto, D. Bresser, S. Lyonnard, B. Frick, M. Yonemura, T. Saito, K. Ikeda, T. Otomo, T. Kamiyama, R. Kanno and G. Kobayuashi, *Nat. Mater.* **21**, 325–330 (2022).

1. Study on H^- Conductive Oxyhydrides[1–4]

In 2016, we synthesized a series of K_2NiF_4-type oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of H^-, O^{2-}, and vacancies (Figure 2 upper) and demonstrated pure H^- conduction properties in the oxyhydrides.[1] The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH_2 cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H^- conduction phenomena.

Based on elemental substitutions to LSLHO, we have been exploring hydride ion conducting oxyhydrides. As shown in Figure 2, we have found that the H^- and O^{2-} arrangement in the K_2NiF_4-type structure can be controlled by tuning the valence (electrostatic valence rule) and size balance of the cation species (tolerance factor). More recently, we reported a new H^- conductive oxyhydride, $Ba_{1.75}LiH_{2.7}O_{0.9}$ (BLHO), containing a high amount of barium and hydrogen vacancies and exhibiting long-range ordering at room temperature. Increasing the temperature above 315 °C disorders the long-range ordering, triggering superionic conduction with a high H^- conductivity of over 0.01 $S \cdot cm^{-1}$ nearly independent of the temperature. The finding of the H^- superionic conductor operating intermediate temperature range, which might open up possibilities for new electrochemical device.

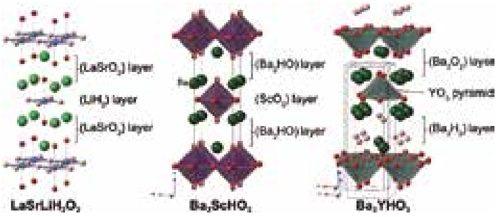

Figure 2. Comparison of the crystal structures of H^- conductive oxyhydrides $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0, y = 0, 1, 2$) and Ba_2MHO_3 (M = Sc, Y).

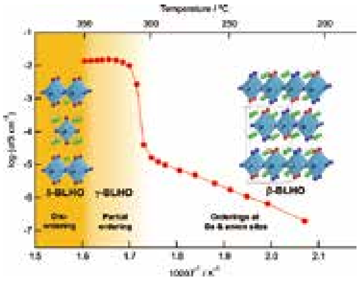

Figure 3. The temperature dependence of H^- conductivity for BLHO. After the β-γ transition, the conductivity drastically enhances, and its value is nearly independent of temperature.

2. Materials Processing of Oxyhydrides for Electrochemical Applications[5–7]

Synthesizing oxyhydrides usually requires unique methods such as high-pressure reactions, and topochemical reactions using CaH_2 reductant. Since the former method is a sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an O^{2-}/H^-exchange reaction and is useful for preparing metastable phases. However, the high-pressure method and the topochemical reaction have each problem of low synthesis volume and low reproducibility, respectively. To expand the research on hydride ionic conductors to the development of electrochemical devices, it is necessary to establish a simple and large volume synthesis process for the constituent materials. We have been trying to establish a suitable synthesis method for oxyhydrides to resolve the above problems.

For the K_2NiF_4-type oxyhydrides, we have successfully established the solid-state reaction method under ambient-pressure.[4,5] Furthermore, we have succeeded in direct synthesis of barium titanium oxyhydride $BaTiO_{3-x}H_x$ by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of transition metal oxyhydrides. We also confirmed that the prepared polycrystalline $BaTiO_{3-x}H_x$ worked as a hydrogen-permeable electrode. This result suggests that H^-/e^- mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices (Figure 4).

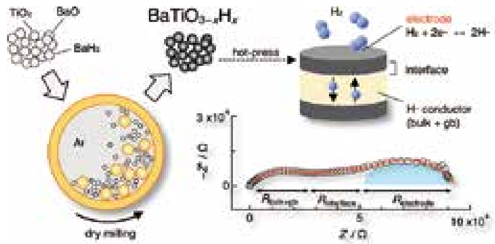

Figure 4. $BaTiO_{3-x}H_x$ synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

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2) F. Takeiri, G. Kobayashi* *et al.*, *Inorg. Chem.* **58**, 4431–4436 (2019).
3) H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* **56**, 10373–10376 (2020).
4) F. Takeiri, G. Kobayashi* *et al.*, *Nat. Mater.* **21**, 325–330 (2022).
5) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85(2)**, 88–92 (2017).
6) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
7) T. Uchimura, G. Kobayashi* *et al.*, *J. Mater. Chem. A* **9**, 20371–20374 (2021).

Awards

KOBAYASHI, Genki; The NAGAI Foundation for Science & Technology Academic Award (2022).
OKAMOTO, KEI; Student Presentation Award, The Electrochemical Society of Japan (2021).

Nanoscale Mechanical Properties at Electrode/Electrolyte Interface during Energy Conversion Process Analyzed by Scanning Probe Microscopy

Instrument Center

MINATO, Taketoshi
Senior Researcher

Physical properties and elementary processes at the interface between electrode and electrolyte are strongly related to the performance of energy devices.[1,2] Traditionally, the physical properties and elementary processes have been indirectly discussed based on the changes of the device performances. Developments of the techniques of spectroscopic measurements have analyzed the physical properties and elementary processes at the interface. In addition to the spectroscopic analysis, direct imaging and nano/atomic-scale analysis by microscopic measurements of the interface will reveal the real nature of the interface.

Historically, scanning probe microscopy (SPM) have been developed as the experimental technique to analyze the physical properties and elementary process in nano/atomic-scale in ideal conditions such as ultra-high vacuum and low temperature for single crystal samples. We have constructed SPM systems to analyze the physical properties and elementary process at electrode/electrolyte interface (Figure 1).

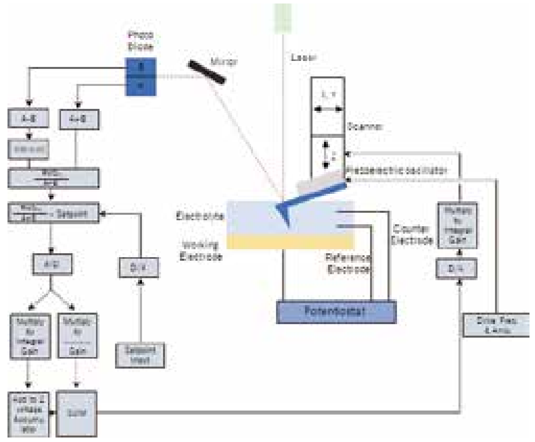

Figure 1. A schematic illustration of the electrochemical SPM systems to analyze the mechanical properties at the electrode/electrolyte interface.

At the interface between electrode and electrolyte of rechargeable battery during the charge and discharge reactions, solvent molecules, carrier ions and additives congregate and form specific states.[1–3] The properties of interface phases are related to the battery performances (capacity, cyclability, rate performance etc.), however, much is unknown at the interface.[4–6] We have investigated the mechanical properties at the interface. Figure 2 shows force curves obtained by the SPM with changing the electrode potential in an electrolyte for rechargeable battery. At open circuit potential (OCP), the adhesion force (negative force in the force curve) was negligible value. By changing the potential to −1.25 V (*vs*. Pt), the adhesion force was increased to ~60 nN. Further sweep of the potential to −2.0 V, the adhesion force was returned to negligible value. These changes of the mechanical properties are caused by the changes of the interface phases by applied electric fields that relate to the battery perforamance.

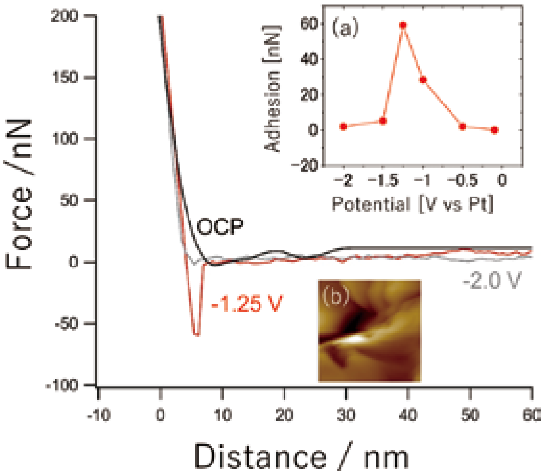

Figure 2. Force curves obtained by the electrochemical SPM systems at the interface between an electrolyte for rechargeable battery and the electrode with changing the sample potential. The black, red and gray curves were obtained at open circuit potential (OCP) = ~−0.1 V, −1.25 and −2.0 V, respectively. Inset (a); the change of the adhesion force obtained by the SPM by changing the potential. Inset (b); an SPM image at −1.25 V (300 nm × 300 nm in *xy* scales and 0 ~ 180 nm in *z* scale). All potential is defined from the difference from Pt.

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6) Y. Takabayashi, K. Kimura, H. Konishi, T. Minato, R. Takekawa, T. Nakatani, S. Fujinami, T. Abe and K. Hayashi, *Adv. Energy Sustainability Res.* **3**, 2200020 (2022).

Visiting Professors

Visiting Professor

TANAKA, Koichiro *(from Kyoto University)*

Ultrafast Laser Spectroscopy and Terahertz Optical Sciences

In recent years, the technology of ultra-short lasers and terahertz light has made remarkable progress, revealing unprecedented ultra-non-equilibrium physics and order formation of solid materials under high-intensity light irradiation. We make full use of such state-of-the-art optical technology to study the excited state dynamics of semiconductors, single-layer materials, photonic crystals, and metamaterials, as well as "non-equilibrium physics under high-intensity light fields." We are also looking for ways to bring out new physical properties by utilizing the interaction between light and matter. Specific research topics include (1) elucidation of non-equilibrium physical properties of solids in high-intensity light fields, (2) research on ultrafast nonlinear phenomena using ultrashort pulse lasers, and (3) new spectroscopy using terahertz light, (4) optical properties of monoatomic layer materials, (5) research on exciter quantum effects in semiconductors, *etc*.

Visiting Professor

OSAKA, Itaru *(from Hiroshima University)*

π-Conjugated Polymers for High-Efficiency Organic Photovoltaics

Organic photovoltaics (OPVs) have been attracting much attention due to lightweight, flexible, low-cost and low-energy solution-processability. Improving the power conversion efficiency is one of the important issues in OPVs. We designed and synthesized a series of π-conjugated polymers based on an extended fused ring, named dithienonaphthobisthiadiazole. The polymers had rigid and coplanar backbone structure, which resulted in high-crystalline structure in the thin film. The efficiency of the photovoltaic cells was as high as 12% when one of the polymers was combined with a fullerene acceptor, which was among the highest values for polymer/fullerene cells. Importantly, extremely high fill factors of over 0.8 were obtained, which was likely ascribed to the high charge carrier mobility. In addition, when another dithienonaphtobisthiadiazole-based polymer was combined with a nonfullerene acceptor, it showed high efficiencies of over 16%. Moreover, the polymer showed high photocurrent generation even with very small driving force energy. These results would be important guidelines for the development of high-performance polymers.

Visiting Associate Professor

AKIMOTO, Ikuko *(from Wakayama University)*

Pulsed EPR Spectroscopy of Electron and Hole Spins in Semiconductor Crystals

The coexistence of electrons and holes in semiconductors provides the functionality of optoelectronic devices, such as photo sensors, solar cells, and organic light emitting diodes (OLEDs). A microscopic understanding of the underlying physics of electron–hole interaction is essential for further development of devices. The pulsed electron–electron double resonance (DEER or PELDOR) technique, a pump–probe measurement of two-spin interactions, has been established to analyze the distance between separated spin labels in a molecule. However, it is challenging to apply this technique to the randomly distributed spin systems that are typically realized in optoelectronic devices. We have investigated the spin interactions between randomly distributed electron and hole traps created by optical excitation in a semiconductor by the DEER technique using arbitrary-waveform pulses of Gaussian and chirped rectangular microwave pulses. Adiabatic excitation of the spin system extracted widely distributed interacting distances of 3–4 Å, indicating reasonable values before tunneling recombination, from the vast background interactions.

RESEARCH ACTIVITIES
Life and Coordination-Complex Molecular Science

Department of Life and Coordination-Complex Molecular Science is composed of two divisions of biomolecular science, two divisions of coordination-complex molecular science, and one adjunct division. Biomolecular science divisions cover the studies on functions, dynamic structures, and mechanisms for various biomolecules such as sensor proteins, metalloproteins, biological-clock proteins, glycoconjugates, antibodies, and motor proteins. Coordination-complex divisions aim to develop molecular catalysts and functional metal complexes for transformation of organic molecules, and molecular materials with photonic-electronic-magnetic functions and three-dimensional complex structures. Interdisciplinary alliances in this department aim to create new basic concepts for the molecular and energy conversion through the fundamental science conducted at each division.

Bioinorganic Chemistry of Metalloproteins Responsible for Metal Homeostasis and Signal Sensing

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions

AONO, Shigetoshi
Professor
[aono@ims.ac.jp]

Education
1982 B.S. Tokyo Institute of Technology
1987 Ph.D. Tokyo Institute of Technology

Professional Employment
1988 Postdoctoral Fellow, Georgia University
1989 Assistant Professor, Tokyo Institute of Technology
1994 Associate Professor, Japan Advanced Institute of Science and Technology
2002 Professor, Institute for Molecular Science
Professor, Okazaki Institute for Integrative Bioscience (–2018)
Professor, The Graduate University for Advanced Studies
2018 Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Member
Assistant Professor
MURAKI, Norifumi*
Post-Doctoral Fellow
NAM, Dayeon
TOHDA, Rei
Secretary
NAKANE, Kaori

Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

Transition metal ions and metalloproteins play crucial roles in meeting the energy demands of the cell by playing roles in intermediary metabolism and in signal transduction processes. Although they are essential for biological function, metal ion bioavailability must be maintained within a certain range in cells due to the inherent toxicity of all metals above a threshold. This threshold varies for individual metal ions. Homeostasis of metal ions requires a balance between the processes of uptake, utilization, storage, and efflux and is achieved by the coordinated activities of a variety of proteins including extracytoplasmic metal carriers, ion channels/pumps/transporters, metal-regulated transcription and translation proteins, and enzymes involved in the biogenesis of metal-containing cofactors/metalloproteins. In order to understand the processes underlying this complex metal homeostasis network, the study of the molecular processes that determine the protein-metal ion recognition, as well as how this event is transduced into a functional output, is required. My research interests are focused on the elucidation of the structure and function relationships of metalloproteins responsible for the regulation of biological homeostasis.

I am also working on gas sensor proteins. Gas molecules such as O_2, NO, CO and ethylene are present in the environment and are endogenously (enzymatically) produced to act as signaling molecules in biological systems. Sensing these gas molecules is the first step in their acting as signaling molecules. Sensor proteins are usually required. Input signals generated by gas sensing have to transduce to output signals that regulate biological functions. This is achieved by biological signal-transduction systems. Recognition of the cognate gas molecules is a general mechanism of functional regulation for gas sensor proteins. This induces conformational changes in proteins that controls their activities for following signal transductions. Interaction between gas molecules and sensor proteins is essential for recognition of gas molecules. Metal-containing prosthetic groups are widely used. In my research group, our research focuses on transition metal-based gas-sensor proteins and the signaling systems working with them.

Selected Publications

- D. Matsui, N. Muraki, K. Chen, T. Mori, A. A. Ingram, K. Oike, H. Gröger, S. Aono and Y. Asano, "Crystal Structural Analysis of Aldoxime Dehydratase from *Bacillus sp.* OxB-1: Importance of Surface Residues in the Optimization for Crystallization," *J. Inorg. Biochem.* **230**, 111770–111779 (2022).
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- N. Muraki, K. Ishii, S. Uchiyama, S. G. Itoh, H. Okumura and S. Aono, "Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase," *Commun. Biol.* **2**, 385 (12 pages) (2019).

1. Structural Characterization of Aldoxime Dehydratase OxdB That Catalyzes Dehydration Reaction of Aldoximes to Form Nitriles

Nitrile compounds are important intermediates in some industrial processes to produce nylon and acrylic fibers, insecticides, and pharmaceuticals. Though one of the most useful methods for nitrile production is dehydration of aldoxime, the chemical dehydration of aldoxime used in the industrial process requires harsh conditions. Therefore, a more environmentally benign process of aldoxime dehydration is expected to be established, for which a biological dehydration of aldoxime is a possible candidate. In nature, some microbes have “aldoxime-nitrile pathway,” where aldoximes are metabolized to the corresponding carboxylic acids through nitriles formed by dehydration of aldoximes with aldoxime dehydratase (Oxd; EC4.99.1.-). There are two pathways for the conversion of nitriles to carboxylic acids. One is hydrolysis of nitriles by nitrilase, and the other is the combination of the reactions catalyzed by nitrile hydratase and amidase. Nitriles are the important intermediate not only in some industrial processes but also in this biological system. The detail characterization of such a biological process to produce nitriles will give some useful information to develop an environmentally benign process for the production of nitriles in industrial field.

The crystal structures of OxdRE from *Rhodococcus sp.* N-771 and OxdA from *Pseudomonas chlororaphis* have been reported. Based on the biochemical characteristics of Oxds and the crystal structure of its Michaelis complex, a mechanism for the dehydration of aldoxime to the corresponding nitrile has been proposed. The active site of Oxds includes heme b as a cofactor and a catalytic triad, which consists of, for example, OxdA, arginine, histidine, and serine. The Fe^{2+} ion is additionally coordinated to another histidine. When the substrate enters the active site, it becomes N-coordinated to Fe^{2+}. The hydroxyl moiety of aldoxime also forms hydrogen bonds with serine and histidine. Oxds share a common architecture to achieve this reaction, but show varying substrate selectivities. In particular, OxdB (Oxd from *Bacillus sp.* OxB-1) shows different enantioselectivities from those of OxdRE and OxdA when bulky compounds, such as racemic E/Z-2-methyl-3-(3,4-methylenedioxyphenyl)-propanal oxime, are used as substrates. The structural features of OxdB are considered to be responsible for the difference in substrate selectivity between OxdRE and OxdB. However, the structure of this broadly applicable biocatalyst has not yet been determined due to the challenges associated with its crystallization. Thus, it is difficult to discuss the relationship between protein structure and substrate selectivity.

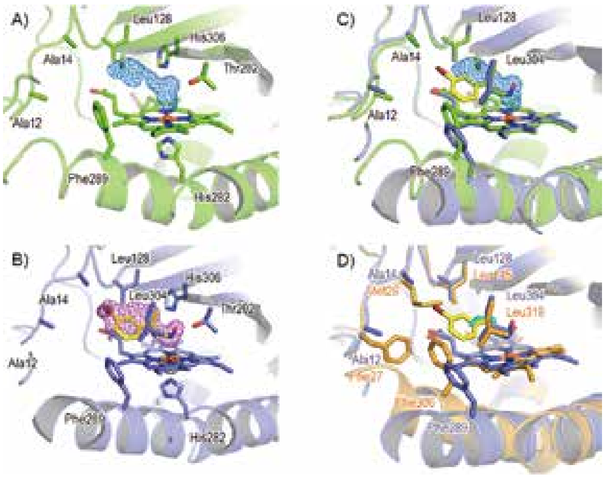

Figure 1. Structure of active site in OxdB-E85A. (A) OxdB-E85A (Substrate-free) is shown in green. *Fo-Fc* map (4σ) in active site is shown in blue mesh. (B) OxdB-E85A and Z-2-(3-bromo-phenyl)-propanal oxime (**1**) complex is shown in slate color. **1** is shown in yellow stick model. Anomalous Fourier map (4σ) in active site is shown in black mesh. Polder map (4σ) of **1** is shown in magenta mesh. (C) Superposition of substrate-free form and substrate-bound form is shown in green and slate color, respectively. *Fo-Fc* map (4σ) of substrate-free form is shown in blue mesh. (D) Superposition of OxdB-E85A and **1** complex, and OxdRE in complex with butyraldoxime. OxdRE is shown in orange. Butyraldoxime is shown in cyan stick model.

In this work, we have determined the crystal structure of OxdB by adding a site-specific mutation to Glu85 located on the surface of the protein, we succeeded in crystallizing OxdB without reducing the enzyme activity. (Figure 1) The catalytic triad essential for Oxd activity were structurally conserved in OxdB. The catalytic triad were conserved in the structure of OxdB. Based on the crystal structure of OxdB, the molecular mechanism of the aldoxime dehydration in OxdB is as follows. When the substrate is bound to heme in OxdB, Thr202 forms a hydrogen bond with the hydroxyl group of the substrate. Dehydration of the substrate proceeds as a result of the proton supply by His306. His306 receives a proton from Glu126 or Arg159. The imidazole ring of His282 in OxdB was more perpendicular to heme than that of His299 in OxdRE and OxdA. This fact suggests that His282 in OxdB is highly nucleophilic toward heme iron. The experiments with mutagenesis on axial histidine and exogenous imidazole derivatives in OxdB have shown that the enzyme activity increases under conditions of high nucleophilicity by the axial ligand. In this context, the activity of OxdB is expected to be higher than that of OxdRE and OxdA.

In addition, the crystal structure of the Michaelis complex of OxdB and the diastereomerically pure substrate Z-2-(3-bromophenyl)-propanal oxime implied the importance of several hydrophobic residues for substrate selectivity. Mutational analysis implicated Ala12 and Ala14 in the E/Z selectivity of bulky compounds. The N-terminal region of OxdB was shown to be shorter than those of OxdA and OxdRE, and have high flexibility. These structural differences possibly result in distinct preferences for aldoxime substrates based on factors such as substrate size.

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* Present Address; Keio University

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions

KATO, Koichi
Professor
[kkatonmr@ims.ac.jp]

Education

1986	B.S. The University of Tokyo
1991	Ph.D. The University of Tokyo

Professional Employment

1991	Assistant Professor, The University of Tokyo
1997	Lecturer, The University of Tokyo
2000	Professor, Nagoya City University
2008	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies
2006	Visiting Professor, Ochanomizu University
2013	Project Leader, JSPS Grant in Aid for Scientific Research on Innovative Areas “Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions”
2018	Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Awards

2000	The Pharmaceutical Society of Japan Award for Young Scientists
2011	The Pharmaceutical Society of Japan Award for Divisional Scientific Promotions
2011	The 48th Baelz Prize

Member

Assistant Professor
- YAGI-UTSUMI, Maho*
- YANAKA, Saeko†

Post-Doctoral Fellow
- NISHI, Emiko

Visiting Scientist
- MOUTAKANNI, Alix‡

Graduate Student
- SEKIGUCHI, Taichiro
- SAITO, Taiki§
- UMEZAWA, Fumiko§
- YAMADA, Rino§
- NISHIMURA, Seiji§
- SHEN, Jiana§
- YAMAMOTO, Shiori§

Technical Fellow
- ISONO, Yukiko
- HIRAMINE, Rina

Secretary
- FUKUTOMI, Yukiyo

Keywords Biomolecule Organization, NMR

Living systems are characterized as dynamic processes of assembly and disassembly of various biomolecules that are self-organized, interacting with the external environment. The omics-based approaches developed in recent decades have provided comprehensive information regarding biomolecules as parts of living organisms. However, fundamental questions still remain unsolved as to how these biomolecules are ordered autonomously to form flexible and robust systems (Figure 1). Biomolecules with complicated, flexible structures are self-organized through weak interactions giving rise to supramolecular complexes that adopt their own dynamic, asymmetric architectures. These processes are coupled with expression of integrated functions in the biomolecular systems.

Toward an integrative understanding of the principles behind the biomolecular ordering processes, we conduct multidisciplinary approaches based on detailed analyses of dynamic structures and interactions of biomolecules at atomic level, in conjunction with the methodologies of molecular and cellular biology along with synthetic and computational technique.

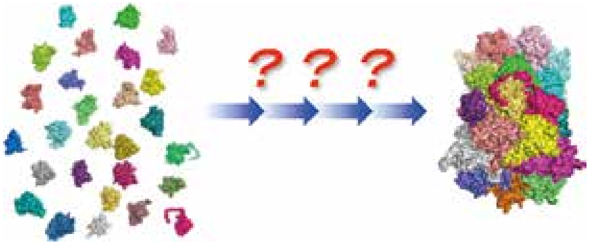

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- M. Yagi-Utsumi and K. Kato, “Conformational Variability of Amyloid-β and the Morphological Diversity of Its Aggregates,” *Molecules* **27**, 4787 (2022).
- K. Kato, T. Yamaguchi and M. Yagi-Utsumi, “Experimental and Computational Characterization of Dynamic Biomolecular Interaction Systems Involving Glycolipid Glycans,” *Glycoconjugate J.* **39**, 219–228 (2022).
- H. Yagi, S. Yanaka and K. Kato, “Structural and Functional Roles of the *N*-Glycans in Therapeutic Antibodies,” in *Comprehensive Glycoscience, 2nd edition*, J. Barchi, Ed., Elsevier; Oxford, **vol. 5**, pp. 534–542 (2021).
- S. Yanaka, R. Yogo and K. Kato, “Biophysical Characterization of Dynamic Structures of Immunoglobulin G,” *Biophys. Rev.* **12**, 637–645 (2020).
- T. Satoh and K. Kato, “Structural Aspects of ER Glycoprotein Quality-Control System Mediated by Glucose Tagging,” in *Glycobiophysics*, Y. Yamaguchi and K. Kato, Eds., Springer Nature; Singapore, pp. 149–169 (2018).
- K. Kato and T. Satoh, “Structural Insights on the Dynamics of Proteasome Formation,” *Biophys. Rev.* **10**, 597–604 (2018).

1. Elucidation of Molecular Mechanisms of Regulation of Protein Glycosylation

Our research on protein glycosylation has made significant progresses over the past year. First, we identified a molecular code embedded in protein for regulating its glycosylation. Many proteins in nature exist as glycoproteins, which are molecules comprised of protein (polypeptide chain) and glycan (sugar chain). While the protein structure is determined on the basis of its genetic blueprint, the information on glycans is not directly encoded by the genome. We recently found a specific 29-amino-acid sequence in the glycoprotein LAMP-1 that promotes a specific glycan structure called Lewis X.1) This sequence induces Lewis X modification when fused to other proteins such as erythropoietin (Figure 2). These findings on a regulatory code of protein glycosylation are expected to pave the way for controlling glycosylation of biopharmaceuticals, which is critical for their efficacy and safety.

Protein glycosylation also has implications in disease. We previously discovered the presence of a novel post-translational modification, in which glycerol phosphate (GroP) caps the core part of matriglycan, thereby blocking its elongation. We recently found that the GroP modification is mediated by PCYT2, a CDP-Gro synthase in humans, and disrupts glycan-mediated cell adhesion, thereby promoting the migration of cancer cells.2,3) These findings can contribute to the development of cancer therapies targeting this modification.

Furthermore, we are continuously developing methodologies for structural analyses of glycoproteins, which include updating the web application GALAXY for HPLC/MS-based glycosylation profiling4) and improving the stable isotope labeling protocol for NMR spectroscopy.5) These methodological developments have led to the promotion of new collaborative researches as exemplified by identification of distinct N-glycosylation patterns on extracellular vesicles from small-cell and non-small-cell lung cancer cells.6)

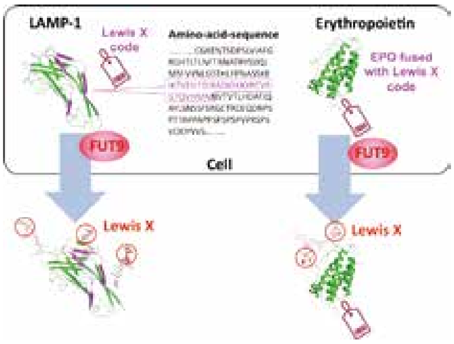

Figure 2. Specific 29-amino-acid sequence from the glycoprotein LAMP-1 serves as a "Lewis X code," which is deciphered by the fucosyltransferase FUT9, and it can be embedded into erythropoietin to evoke Lewis X modification.

2. Characterization of Biomacromolecules that Function in Extreme Environments

Our research also aims to understand the mechanisms of adaptation of life to the environments through analysis of the structure, dynamics, and function of biomacromolecules working in extreme environments. In FY2021, through collaboration with the ExCELLS groups lead by Dr. Uchihashi, Dr. Murata, and Dr. Arakawa, we published several papers on the molecular mechanisms of tardigrade unhydrobiosis. Our integrative spectroscopic and microscopic data demonstrate that CAHS1 (cytosolic-abundant heat-soluble protein 1), an abundant protein in *Ramazzottius varieornatus*, self-assembles into fibrous condensates under desiccation-mimicking conditions in a reversible manner7) (Figure 3). This dynamic protein organization suggests multistep anhydrobiotic mechanisms, including the reversible formation of protective compartments for desiccation-sensitive biomolecules, water-holding gelation, and maintenance of the integrity of biomolecular complexes under extremely dry conditions. We also characterized structures of g12777 protein, a novel Mn-dependent peroxidase, from *R. varieornatus*,8) and EtAHS, a novel abundant heat-soluble protein from *Echinisicus testudo*.9) Our findings illustrate adaptation strategies of organisms to extreme environments without water.

Moreover, we applied the integrative biophysical approach to characterize the overall structure of cyanobacterial circadian clock protein complex10) and single-molecular interactions between the complement component C1 and antibodies.11)

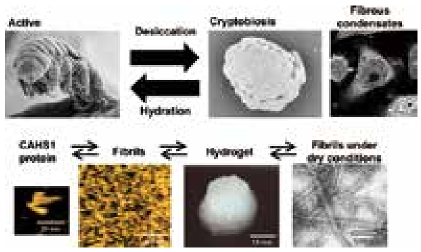

Figure 3. Spontaneous assembling of CAHS1 proteins into fibrous condensates under desiccation-mimicking conditions.

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2) F. Umezawa *et al.*, *Int. J. Mol. Sci.* **23**, 6662 (2022).
3) F. Yamasaki *et al.*, *Biochem. Biophys. Res. Commun.* **579**, 8–14 (2021).
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8) Y. Yoshida *et al.*, *BMC Genomics* **23**, 405 (2022).
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11) S. Yanaka *et al.*, *Int. J. Mol. Sci.* **23**, 2090 (2022).

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* Present Address; Nagoya City University

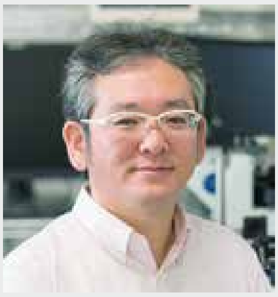
† Present Address; Kyushu University

‡ IMS International Internship Program

§ carrying out graduate research on Cooperative Education Program of IMS with Nagoya City University

Operation and Design Principles of Biological Molecular Machines

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions



IINO, Ryota
Professor
[iino@ims.ac.jp]

Education

1995	B.E. Kyoto University
1997	M.E. Kyoto University
2003	Ph.D. Nagoya University

Professional Employment

2000	Research Associate, Japan Science and Technology Cooperation
2002	Research Associate, Japan Science and Technology Agency
2005	Specially-Appointed Assistant Professor, Osaka University
2006	Assistant Professor, Osaka University
2011	Lecturer, The University of Tokyo
2013	Associate Professor, The University of Tokyo
2014	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies

Award

2012	Emerging Investigator. Lab on a Chip., The Royal Society of Chemistry, U.K.

Member

Assistant Professor
OTOMO, Akihiro

Post-Doctoral Fellow
KIM, Ju-Young
KEYA, Jakia Jannat
HARASHIMA, Takanori
MATSUMOTO, Kohsuke

Visiting Scientist
YU, Yan

Technical Fellow
OKUNI, Yasuko
KON, Yayoi

Secretary
NAKANE, Kaori

Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by various molecular machines made of proteins. Protein molecular machines are tiny, but show very high performance, and are superior to man-made machines in many aspects. One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces and torques that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane. We unveil operation principles of molecular motors with advanced single-molecule functional analysis. With the help of site-saturation mutagenesis and robot-based automation, we also engineer non-natural molecular motors to understand their design principles.

Figure 1. Protein molecular machines. (Left) A linear molecular motor chitinase A. (Center and Right) Rotary molecular motors F_1-ATPase and V_1-ATPase, respectively.

Selected Publications

- A. Nakamura, N. Kobayashi, N. Koga and R. Iino, “Positive Charge Introduction on the Surface of Thermostabilized PET Hydrolase Facilitates PET Binding and Degradation,” *ACS Catal.* **11**, 8550–8564 (2021).
- A. Visootsat, A. Nakamura, P. Vignon, H. Watanabe, T. Uchihashi and R. Iino, “Single-Molecule Imaging Analysis Reveals the Mechanism of a High-Catalytic-Activity Mutant of Chitinase A from *Serratia marcescens*,” *J. Biol. Chem.* **295**, 1915–1925 (2020).
- J. Ando, T. Shima, R. Kanazawa, R. Shimo-Kon, A. Nakamura, M. Yamamoto, T. Kon and R. Iino, “Small Stepping Motion of Processive Dynein Revealed by Load-Free High-Speed Single-Particle Tracking,” *Sci. Rep.* **10**, 1080 (2020).
- J. Ando, A. Nakamura, M. Yamamoto, C. Song, K. Murata and R. Iino, “Multicolor High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles,” *ACS Photonics* **6**, 2870–2883 (2019).
- T. Iida, Y. Minagawa, H. Ueno, F. Kawai, T. Murata and R. Iino, “Single-Molecule Analysis Reveals Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V_1-ATPase,” *J. Biol. Chem.* **294**, 17017–17030 (2019).
- J. Ando, A. Nakamura, A. Visootsat, M. Yamamoto, C. Song, K. Murata and R. Iino, “Single-Nanoparticle Tracking with Angstrom Localization Precision and Microsecond Time Resolution,” *Biophys. J.* **115**, 2413–2427 (2018).
- A. Nakamura, K. Okazaki, T. Furuta, M. Sakurai and R. Iino, “Processive Chitinase is Brownian Monorail Operated by Fast Catalysis after Peeling Rail from Crystalline Chitin,” *Nat. Commun.* **9**, 3814 (2018).
- A. Nakamura, T. Tasaki, Y. Okuni, C. Song, K. Murata, T. Kozai, M. Hara, H. Sugimoto, K. Suzuki, T. Watanabe, T. Uchihashi, H. Noji and R. Iino, “Rate Constants, Processivity, and Productive Binding Ratio of Chitinase A Revealed by Single-Molecule Analysis,” *Phys. Chem. Chem. Phys.* **20**, 3010–3018 (2018).

1. Direct Observation of Stepping Rotation of V-ATPase Reveals Rigid Component in Coupling between V_o and V_1 Motors[1)]

V-ATPases are rotary motor proteins that convert the chemical energy of ATP into the electrochemical potential of ions across cell membranes (Figure 2). V-ATPases consist of two rotary motors, V_o and V_1, and *Enterococcus hirae* V-ATPase (EhV_oV_1) actively transports Na^+ in V_o (EhV_o) by using torque generated by ATP hydrolysis in V_1 (EhV_1). Here, we observed ATP-driven stepping rotation of detergent-solubilized EhV_oV_1 wild-type, aE634A, and BR350K mutants under various Na^+ and ATP concentrations ([Na^+] and [ATP], respectively) by using a 40-nm gold nanoparticle as a low-load probe. When [Na^+] was low and [ATP] was high, under the condition that only Na^+ binding to EhV_o is rate-limiting, wild-type and aE634A exhibited 10-pausing positions reflecting 10-fold symmetry of the EhV_o rotor and almost no backward steps. Duration time before the forward steps was inversely proportional to [Na^+], confirming that Na^+ binding triggers the steps. When both [ATP] and [Na^+] were low, under the condition that both Na^+ and ATP bindings are rate-limiting, aE634A exhibited 13-pausing positions reflecting 10- and 3-fold symmetries of EhV_o and EhV_1, respectively (Figure 3). The distribution of duration time before the forward step was fitted well by the sum of two exponential decay functions with distinct time constants. Furthermore, occasional backward steps smaller than 36° were observed. Small backward steps were also observed during three long ATP cleavage pauses of BR350K. These results indicate that EhV_o and EhV_1 do not share pausing positions, Na^+ and ATP bindings occur at different angles, and the coupling between EhV_o and EhV_1 has a rigid component (Figure 4).

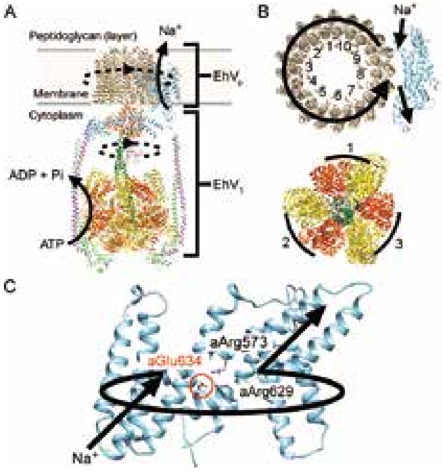


Figure 2. (A) Overall architecture of EhV_oV_1. The dotted circular arcs represent the rotation direction driven by ATP hydrolysis. (B) (top) Top view of a-subunit (cyan) and c_{10}-ring (brown) of EhV_o and (bottom) A- (yellow), B- (orange), D- (green), and F-subunits (pink) of EhV_1. The black arrow at the top indicates the path of Na^+ movement during ATP-driven rotation. The arcs at the bottom represent the catalytic AB pairs. (C) Side view of a-subunit viewed from the c-subunit. The mutated residue, aGlu634, is located on the surface of the entry half-channel of the a-subunit as highlighted in red letters and a circle.

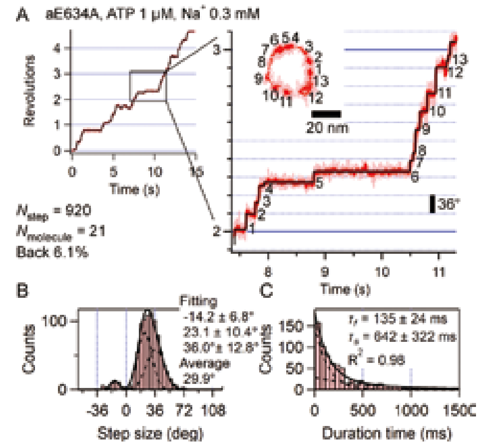


Figure 3. (A) Typical trajectory of rotation at 1 μM ATP and 0.3 mM Na^+ recorded at 1,000 fps. Enlarged view of one revolution (360°) is shown on the right. Pink, red, and black traces represent raw, median-filtered (current ± 7 frames), and fitted trajectories, respectively. The inset shows the corresponding *x*-*y* trajectory. Pink lines and red dots represent the raw and median-filtered (current ± 7 frames) coordinates, respectively. (B) Distribution of the step size fitted with the sum of three Gaussians: One peak in backward (minus) direction and two peaks in forward (plus) direction, one of which was fixed at 36°, assuming that it was the step of EhV_o. (C) Distribution of the duration time before the forward step fitted with the sum of two exponential decay functions.

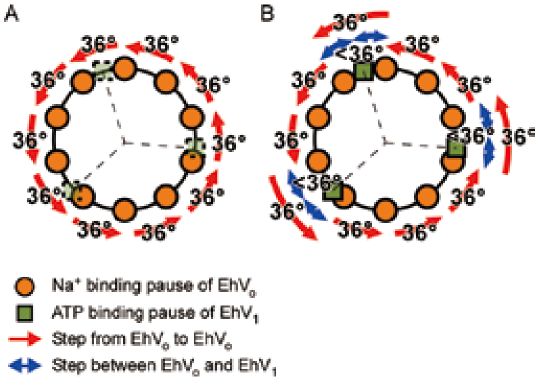


Figure 4. Schematic models of the stepping rotation and rigid coupling of EhV_oV_1. The orange circles and dark green squares indicate the pausing positions waiting for Na^+ binding to EhV_o and ATP binding to EhV_1, respectively. The red arrows indicate the 36° steps between adjacent pausing positions for the EhV_o. The blue arrows indicate the backward and forward steps smaller than 36° between adjacent pausing positions for EhV_o and EhV_1. (A) Condition in which only Na^+ binding to EhV_o is rate-limiting. In this condition, the pauses waiting for ATP binding to EhV_1 are too short to be detected, and EhV_oV_1 rotates unidirectionally without backward steps. (B) Condition in which both Na^+ and ATP bindings are rate-limiting. The pausing positions waiting for ATP binding are visualized, and then 13-pausing positions are detected per single turn. Because no torque is generated during the pauses waiting for ATP binding to EhV_1, EhV_oV_1 rotates to the backward and forward pausing positions of EhV_o driven by Brownian motion.

Reference

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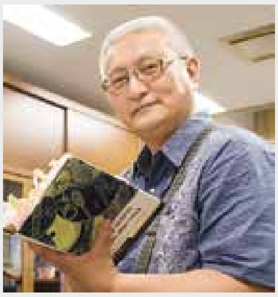
Development of Novel Catalytic Organic Transformations

Department of Life and Coordination-Complex Molecular Science
Division of Complex Catalysis



UOZUMI, Yasuhiro
Professor
[uo@ims.ac.jp]

Education

1984	B.S. Hokkaido University
1990	Ph.D. Hokkaido University

Professional Employment

1988	JSPS Research Fellow
1988	Research Associate, Hokkaido University
1990	Assistant Professor, Hokkaido University
1994	Research Associate, Columbia University
1995	Lecturer, Kyoto University
1997	Professor, Nagoya City University
2000	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2007	Research team leader, RIKEN
2014	Distinguished Professor, Three George University
2003	Research Project Leader, JST CREST Project (–2008)
2008	Research Project Leader, NEDO Project (–2012)
2011	Deputy Research Project Leader, JST CREST (–2016)
2014	Research Project Leader, JST ACCEL Project (–2019)

Awards

1991	Eisai Award, Synthetic Organic Chemistry
1998	The Pharmaceutical Society of Japan Award for Young Scientist
2007	The Chemical Society of Japan (CSJ) Award for Creative Work
2007	MEXT Ministerial Award for Green Sustainable Chemistry
2010	Inoue Prize for Science
2014	The Commendation for Science and Technology by the Minister of MEXT (Research Category)

Member

Assistant Professor
OKUMURA, Shintaro

Graduate Student
TAKAHASHI, Teruki
ZHANG, Kaili
HATTORI, Shusuke

Technical Fellow
TORII, Kaoru
TAZAWA, Aya
NIIMI, Ryoko

Secretary
SASAKI, Tokiyo
TANIWAKE, Mayuko

Keywords Transition Metal Catalysis, Green Chemistry, Photocatalysis

Our research interests lie in the development of catalytic reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, development of a wide variety of the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels, have been achieved. Furthermore, we have recently been developing a novel photocatalysis where, for example, the electrophilic substitution of carbonyl groups took place under visible-light irradiation (Figure 1).

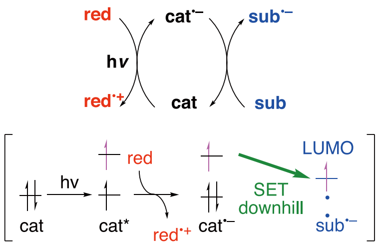


Figure 1. The outlined concept of photocatalytic reductive activation of substrate (*e.g.* carbonyls).

Selected Publications

- G. Hamasaka, D. Roy, A. Tazawa and Y. Uozumi, "Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate," *ACS Catal.* **9**, 11640–11646 (2019).
- R. David and Y. Uozumi, "Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review)," *Adv. Synth. Catal.* **360**, 602–625 (2018).
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1. Photocatalytic Carbinol Cation/Anion Umpolung: Direct Addition of Aromatic Aldehydes and Ketones to Carbon Dioxide[1]

We have developed a new photocatalytic umpolung reaction of carbonyl compounds to generate anionic carbinol synthons. Aromatic aldehydes or ketones reacted with carbon dioxide in the presence of an iridium photocatalyst and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole (DMBI) as a reductant under visible-light irradiation to furnish the corresponding α-hydroxycarboxylic acids through nucleophilic addition of the resulting carbinol anions to electrophilic carbon dioxide.

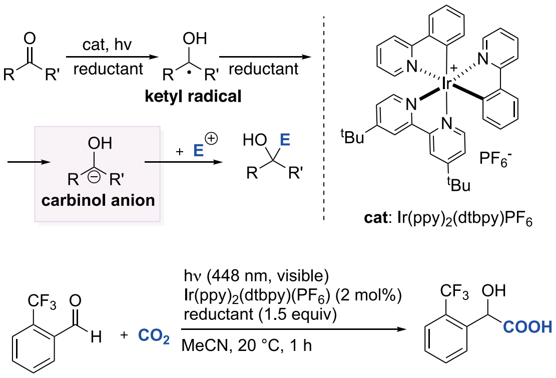

Figure 2. Photocatalytic Eelectrophilic Substitution of Carbonyls with Carbon Dioxide via Carbinol Anion Species.

2. Palladium-Catalyzed Aminocarbonylation of Aryl Halides with *N*,*N*-Dialkylformamide Acetals[2]

We developed a protocol for the palladium-catalyzed aminocarbonylation of aryl halides using less-toxic formamide acetals as bench-stable aminocarbonyl sources under neutral conditions. Various aryl (including heteroaryl) halides reacted with *N*,*N*-dialkylformamide acetals in the presence of a catalytic amount of $Pd_2(dba)_3$ and xantphos to give the corresponding aromatic carboxamides at 90–140 °C without any activating agents or bases in up to quantitative chemical yield. This protocol was applied to aryl bromides, aryl iodides, and trifluoromethanesulfonic acid, as well as to relatively less-reactive aryl chlorides. A wide range of functionalities on the aromatic ring of the substrates were tolerated under the aminocarbonylation conditions. The catalytic aminocarbonylation was used to prepare the insect repellent *N*,*N*-diethyl-3-methylbenzamide as well as a synthetic intermediate of the dihydrofolate reductase inhibitor triazinate.

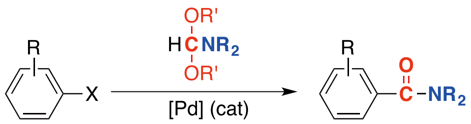

Figure 3. Palladium-Catalyzed Aminocarbonylation with *N*,*N*-Dialkylformamide Diacetals.

3. Cyanide-Free Cyanation of Aryl Iodides with Nitromethane by Using an Amphiphilic Polymer-Supported Palladium Catalyst[3]

A cyanide-free aromatic cyanation was developed using nitromethane as a cyanide source in water with an amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin-supported palladium catalyst and an alkyl halide (*i.e.*, 1-iodobutane). The cyanation proceeded through the palladium-catalyzed cross-coupling of aryl halides and nitromethane, followed by transformation of the resultant nitromethylarene intermediates into nitriles by 1-iodobutane.

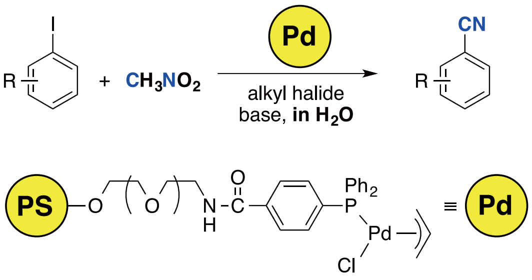

Figure 4. Cyanation of Aryl Iodides with Nitromethane by Using an Amphiphilic PS-PEG resin-Supported Palladium Catalyst in Water.

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Award

OKUMURA, Shintaro; The Society of Synthetic Organic Chemistry, Fujifilm Research Proposal Award (2021).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

Department of Life and Coordination-Complex Molecular Science Division of Complex Catalysis

MOMIYAMA, Norie
Associate Professor
[momiyama@ims.ac.jp]

Education
2000 B.S. Nagoya University
2005 Ph.D. The University of Chicago

Professional Employment
2005 Postdoctoral Fellow, Harvard University
2006 Assistant Professor, Tohoku University
2014 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards
2003 The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
2004 Abbott Laboratories Graduate Fellowship
2005 Damon Runyon Cancer Research Foundation Post Doctoral Research Fellowship
2008 Thieme Chemistry Journals Award
2014 The 17th Morita Science Research Award
Central Glass Co., Ltd. Award in Organic Chemistry, Japan

Member
Assistant Professor
OHTSUKA, Naoya
Graduate Student
HORI, Tatsuaki
OISHI, Shunya
KATO, Masayuki
Technical Fellow
NISHIOKA, Yukina
HARADA, Kuniko
KAKINUMA, Shuya
Secretary
USHIDA, Hinano

Keywords Synthetic Chemistry, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, "metal" has been frequently used as the activation center, and conformationally rigid catalyst framework has been preferably components for the catalyst design. To develop new type of molecular catalysis, we have focused on the use of hydrogen and halogen atom as activation unit, and have utilized non-covalent interactions as organizing forces of catalyst framework in the molecular design of catalyst, which had not received much attention until recently. We hope that our approach will open the new frontier in chiral organic molecules from chiral molecular chemistry to chiral molecular science.

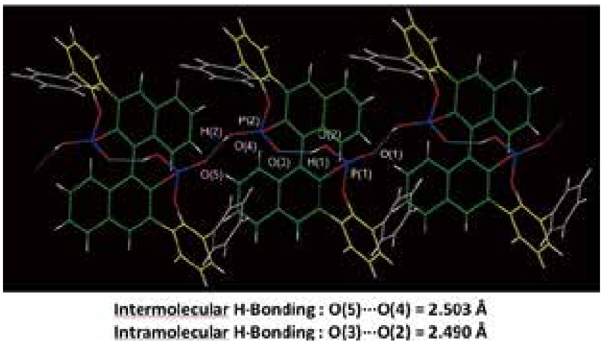

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

Selected Publications

- T. P. Yoon and E. N. Jacobsen, *Science* **299**, 1691–1693 (2003).
- N. Momiyama and H. Yamamoto, "Brønsted Acid Catalysis of Achiral Enamine for Regio- and Enantioselective Nitroso Aldol Synthesis," *J. Am. Chem. Soc.* **127**, 1080–1081 (2005).
- N. Momiyama, H. Tabuse and M. Terada, "Chiral Phosphoric Acid-Governed Anti-Diastereoselective and Enantioselective Hetero-Diels–Alder Reaction of Glyoxylate," *J. Am. Chem. Soc.* **131**, 12882–12883 (2009).
- N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, "Design of Chiral Bis-Phosphoric Acid Catalyst Derived from (*R*)-3,3'-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels–Alder Reaction of α,β-Unsaturated Aldehydes with Amidodienes," *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
- N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, "Molecular Design of a Chiral Brønsted Acid with Two Different Acidic Sites: Regio-, Diastereo-, and Enantioselective Hetero-Diels–Alder Reaction of Azopyridinecarboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid–Monophosphoric Acid," *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).

1. Design of Hydrogen Bond-Based Molecular Catalysts

Allylation of imines with allylic metal reagents has been one of the most valuable tools to synthesize enantioenriched homoallylic amines. Due to the inherent nature of allylic metal reagent, however, regioselectivity has been a long-standing subject in this area. To develop the synthetic reaction for enantioenriched linear homoallylic amines, we discovered chirality transferred formal 1,3-rearrangement of ene-aldimines in the presence of Brønsted acid, and developed it as synthetic method for variety of enantioenriched linear homoallylic amines.1) Furthermore, we studied details of reaction mechanism and succeeded catalytic asymmetric version of this rearrangement.2) On the basis of our discovery, catalytic asymmetric version of this reaction was developed.3) To the best our knowledge, our discovery is the first example of catalytic asymmetric methylene migration.

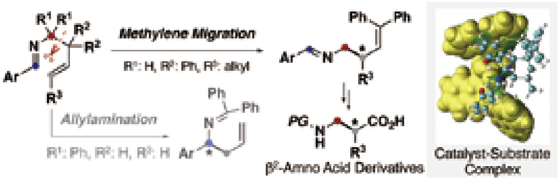

Figure 2. Asymmetric counteranion-directed catalysis *via* OH···O, CH···O, CH···π, π···π interactions.

Perfluorinated aryls have emerged as an exquisite class of motifs in the design of molecular catalysts, and their electronic and steric alterations lead to notable changes in the chemical yields and the stereoselectivities. We developed the perfluoaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deliver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino–ene reaction using aldehydes and $FmocNH_2$.4)

We have developed (*R*)-3,3'-di(2-hydroxy- 3-arylphenyl) binaphthol derived chiral bis-phosphoric acid which efficiently catalyzed enantioselective Diels–Alder reaction of acroleins with amidodienes.5,6) We demonstrated that two phosphoric acid groups with individually different acidities can play distinct roles in catalyst behavior through hydrogen bonding interactions. Therefore, we developed a Brønsted acid with two different acidic sites, aryl phosphinic acid-phosphoric acid.7) Furthermore, molecular design of a chiral Brønsted acid with two different acidic sites, chiral carboxylic acid–cyclic mono-phosphoric acid, was identified as a new and effective concept in asymmetric hetero-Diels–Alder reaction of 2-azopyridinoester with amidodienes.8)

2. Design of Halogen Bond-Based Molecular Catalysts

Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of the type R—X (X = Cl, Br, I) and Lewis bases LBs. It has been known that strong halogen bonds are realized when "R" is highly electronegative substituents such as perfluorinated alkyl or aryl substituents. On the basis of electrophilic feature for halogen atom, we have examined it to develop catalysis with halogen bond for carbon–carbon bond forming reactions.9,10)

We found that perfluorinated iodoaryls are able to catalyze the allylation reaction to *N*-activated heteroaromatics. On the basis of this discovery, a quantitative approach was studied using 4-substituted perfluorinated iodobenzene.11) Examination of the electrostatic potential surfaces showed that substituent R groups significantly affected the charge density of iodine, fluorine, and carbon on the benzene ring. ^{19}F NMR titrations were used to determine the binding constants *K* for chloride, and their catalytic activities were evaluated in the allylation reaction. We revealed that the log *K* and product yields were linearly correlated, and that they were dependent on the Hammett substituent parameter, σ_{meta}. This linear correlation provided a quantitative predictive model for both the binding constant and the reaction yield. Concomitantly, this efficiently permitted the development of a highly active anion-binding catalyst, namely 4-CNC_6F_4I. The catalytic activity of 4-CNC_6F_4I was established in the allylation and crotylation of silatrane reagents to *N*-activated isoquinolines.

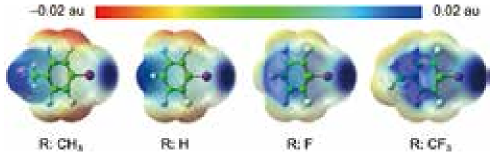

Figure 3. Molecular electrostatic potential surfaces of 4-RC_6F_4I (R: CH_3, H, F, and CF_3) at the M06-2X-D3/6-311+G(d,p)-SDD level of theory.

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Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry

KUSAMOTO, Tetsuro
Associate Professor
[kusamoto@ims.ac.jp]

Education

2003	B.S. The University of Tokyo
2010	Ph.D. The University of Tokyo

Professional Employment

2005	Sony Corporation
2010	Postdoctoral Fellow, RIKEN
2012	Project Assistant Professor, The University of Tokyo
2013	Assistant Professor, The University of Tokyo
2019	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2019	Research Encouragement Award, Japan Society of Coordination Chemistry
2010	Research Award, Graduate School of Science, the University of Tokyo
2008	BCSJ Award, The Chemical Society of Japan

Member

Assistant Professor
MATSUOKA, Ryota
Post-Doctral Fellow
MIZUNO, Asato
Technical Fellow
NAKAGAI, Kozue
MIBU, Takuto
Secretary
KAWAGUCHI, Ritsuko

Keywords Radical, Open-Shell Electronic States, Photonic-Electronic-Magnetic Properties

The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of their rarity and low chemical (photo-)stability. We have developed highly photostable luminescent organic radicals, PyBTM and its analogues, and investigated photofunctions attributed to their open-shell electronic states. We have discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence at RT with φ_{em} = 89%, which is exceptionally high in radicals, (ii) radical-doped crystals and radical-based coordination polymers exhibit drastic changes in the emission spectra by applying a magnetic field. These are the first demonstrations of magnetoluminescence in radicals, and are attributed to interplay between the spin and the luminescence. Our studies provide novel and unique concepts in molecular photonics, electronics, and spintronics, and also bring innovative ideas in the development of light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

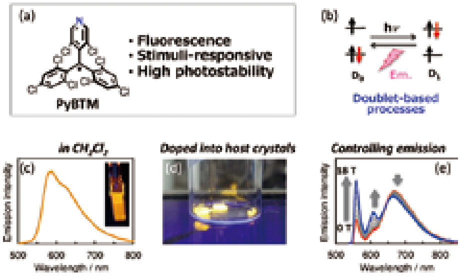

Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, "An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice and Triangular Organic Radical," *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).
- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).

1. A Novel Organic Quantum Spin Liquid Material with a Triangular Lattice

Quantum spin liquid (QSL) is a novel quantum state of matter, in which charges are localized while spins are highly fluctuating. In general, interacting spins with antiferromagnetic (AFM) exchange couplings result in long-range ordered magnetic ground state at low temperatures, with vanishing the spin entropy. On the other hand, spins in QSL that are entangled strongly remain highly fluctuating with high entropy even at very low temperatures. In QSL materials, geometrical frustrations, in addition to quantum fluctuations, are suggested to play a critical role. Among them, organic crystalline solids with triangular lattices have attracted much attention because of their intriguing properties at low temperatures. So far, organic QSL materials are rarely reported, which limits in-depth investigation for elucidating the fundamental characteristics of the QSL. In this study, we prepared a novel triangular-lattice organic QSL material (Et-4IT)[Ni(mnt)$_2$]$_2$, and the structure and physical properties were investigated (Figure 2a).1) The Ni(mnt)$_2$ anions constructed *k*-type molecular arrangement in the crystal. The two crystallographically independent anion layers both realized Mott insulating states, showing that (Et-4IT)[Ni(mnt)$_2$]$_2$ is a novel bilayer Mott system. The magnetic susceptibility and magnetic torque measurements and low-temperature heat capacity measurements confirmed the absence of the long-range magnetic ordering down to 25 mK with an appreciably significant γ value of 94 ± 7 mJ K^{-2} mol^{-1}. The AFM interaction ($J/k_B \sim -24$ K) detected between the spins was much smaller than that in the other organic QSLs, while χ_0 and γ values were larger. We found significant relationships, χ_0, $\gamma \propto 1/J$, for all the organic QSLs (Figure 2b). These results suggest the presence of the spinon Fermi surface in the QSLs.

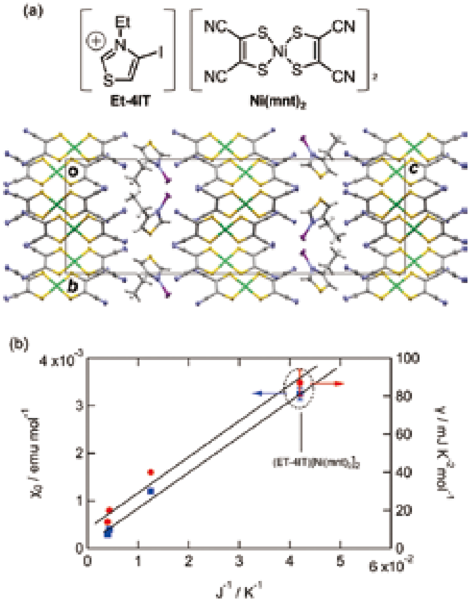

Figure 2. (a) Chemical and crystal structures of (Et-4IT)[Ni(mnt)$_2$]$_2$. (b) γ-J^{-1} and χ_0-J^{-1} plots for organic QSLs.

2. Development of Two-Dimensional Kagome-Honeycomb Lattice Coordination Polymer Based on Triangular Radical

Two-dimensional (2D) open-shell coordination polymers (CPs) with honeycomb, Kagome, and Kagome-honeycomb hybrid lattices have attracted growing interest because of the exotic electronic structures and physical properties attributed to the structural topology. Employing organic radicals as building blocks is a promising approach to producing open-shell CPs, where structural topology and efficient electronic and magnetic interaction between the radical ligands and the metal ions enable peculiar electrical, magnetic, and photonic properties. Recently, we have prepared a highly-crystalline 2D honeycomb lattice CP, trisZn, via coordination of a triangular-shaped organic radical tris(3,5-dichloro-4-pyridyl)methyl radical (trisPyM) to Zn ions.2) The coordination structure of trisZn was stable under evacuation at 60 °C. trisZn exhibited photoluminescence below 79 K at λ_{em} = 695 nm. Importantly, trisZn demonstrated magnetoluminescence below 20 K.3) This is the first example showing magnetoluminescence of pure (*i.e.*, non-doped) radical compounds. trisPyM can be a promising building block in constructing a new class of 2D CPs with spin-correlated novel photofunctions. In this study, we aimed to create a Kagome-honeycomb hybrid lattice CP with magnetic functions by employing a magnetic ion Cu^{II} instead of the nonmagnetic Zn^{II}. The synthesized 2D CP, trisCu, was isostructural to trisZn, where the Cu^{II} ions constructed a Kagome lattice while trisPyMs formed a honeycomb lattice. In this situation, efficient magnetic couplings between the Cu^{II} ions and the radicals extended onto two dimensions were expected to induce strong magnetic anisotropy.

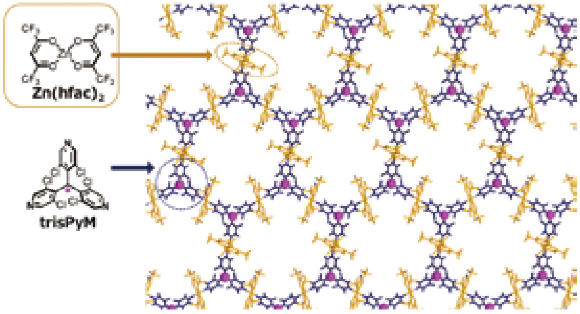

Figure 3. Crystal structure of trisZn and the chemical structure of the components.

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3) S. Kimura, R. Matsuoka, S. Kimura, H. Nishihara and T. Kusamoto, *J. Am. Chem. Soc.* **143**, 5610–5615 (2021).

Design and Synthesis of Three-Dimensional Organic Structures

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry

SEGAWA, Yasutomo
Associate Professor
[segawa@ims.ac.jp]

Education

2005	B.S. The University of Tokyo
2007	M.S. The University of Tokyo
2009	Ph.D. The University of Tokyo

Professional Employment

2009	Assistant Professor, Nagoya University
2013	Designated Associate Professor, Nagoya University
2013	Group Leader and Project Coordinator, JST ERATO Itami Molecular Nanocarbon Project (until 2020)
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

2013	RSC PCCP Prize
2014	Akasaki Award
2017	Chemical Society of Japan Award for Young Chemists
2018	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2019	Nozoe Memorial Award for Young Organic Chemists
2021	Chemist Award BCA

Member
Assistant Professor
SUGIYAMA, Haruki
Graduate Student
NAGASE, Mai
HIROTA, Soshi
WATANABE, Kosuke
YOSHIDA, Ryu
Technical Fellow
NAKANO, Sachiko
Secretary
TANIWAKE, Mayuko

Keywords π-Conjugated Molecules, Molecular Topology, 3D Network Polymer

Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights.

To achieve our purpose, this group will start electron-diffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultra-small crystals (1 µm or less). There are many fields such as covalent organic crystals with a three-dimensional structure and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

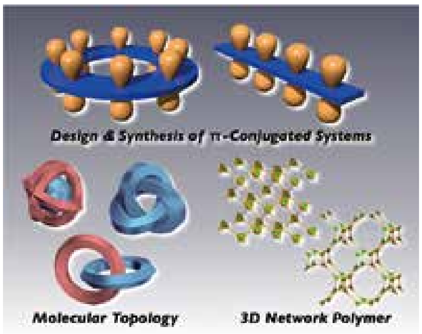

Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- Y. Segawa, T. Watanabe, K. Yamanoue, M. Kuwayama, K. Watanabe, J. Pirillo, Y. Hijikata and K. Itami, "Synthesis of a Möbius Carbon Nanobelt," *Nat. Synth.* **1**, 535–541 (2022).DOI: 10.1038/s44160-022-00075-8
- K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, "Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes," *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).
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- Y. Segawa, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," *Acc. Chem. Res.* **52**, 2760–2767 (2019).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).

1. Möbius Carbon Nanobelt

Technologies for the creation of topological carbon nanostructures have greatly advanced synthetic organic chemistry and materials science. Although simple molecular nanocarbons with a belt topology have been constructed, analogous carbon nanobelts with a twist—more specifically, Möbius carbon nanobelts (MCNBs), have not yet been synthesized owing to their high intrinsic strain. Herein, we report the synthesis, isolation and characterization of a MCNB. Calculations of strain energies suggest that large MCNBs are synthetically accessible. Designing a macrocyclic precursor with an odd number of repeat units led to a successful synthetic route via *Z*-selective Wittig reactions and nickel-mediated intramolecular homocoupling reactions, which yielded (25,25) MCNB over 14 steps (Figure 2a). NMR spectroscopy and theoretical calculations reveal that the twist moiety of the Möbius band moves quickly around the MCNB molecule in solution (Figure 2b,c). The topological chirality originating from the Möbius structure was confirmed experimentally using chiral HPLC separation and CD spectroscopy.

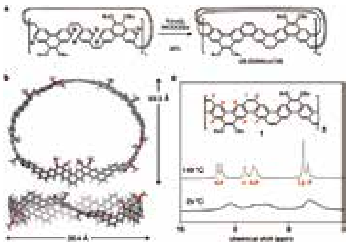


Figure 2. (a) Synthesis of (25,25)MCNB. (b) Structure of (25,25) MCNB. (c) ^{1}H NMR spectra of (25,25)MCNB.

2. Perfluorocycloparaphenylene

Perfluorinated aromatic compounds, the so-called *perfluoroarenes*, are widely used in materials science owing to their high electron affinity and characteristic intermolecular interactions. However, methods to synthesize highly strained perfluoroarenes are limited, which greatly limits their structural diversity. Herein, we report the synthesis and isolation of perfluorocycloparaphenylenes (PFCPPs) as a class of ring-shaped perfluoroarenes. Using macrocyclic nickel complexes, we succeeded in synthesizing PF[*n*]CPPs (*n* = 10, 12, 14, 16) in one-pot without noble metals (Figure 3a). The molecular structures of PF[*n*]CPPs (*n* = 10, 12, 14) were determined by X-ray crystallography to confirm their tubular alignment (Figure 3b,c). Photophysical and electrochemical measurements revealed that PF[*n*]CPPs (*n* = 10, 12, 14) exhibit wide HOMO–LUMO gaps, high reduction potentials, and strong phosphorescence at low temperature. PFCPPs are not only useful as electron-accepting organic materials but can also be used for accelerating the creation of topologically unique molecular nanocarbon materials.

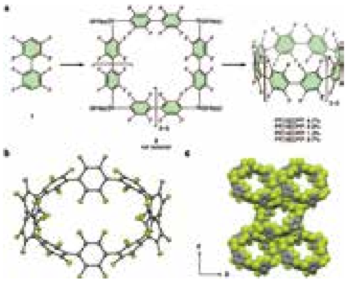


Figure 3. (a) Synthesis of PFCPPs. (b) ORTEP of PF[10]CPP. (c) Packing structure of PF[10]CPP.

3. A Photochromic Carbazolyl-Imidazolyl Radical Complex

Optical phenomena which occur on a timescale of microseconds to milliseconds are instantaneous or invisible for human visions, whereas they can be easily detected by conventional photodetectors. Therefore, fast photoswitching materials that work in these time ranges have received considerable attention for the applications to bioimaging, anticounterfeiting, and dynamic holographic materials. Here we report the synthesis of carbazole-incorporated photochromic radical complex.3) The molecular structure of **CIC-tBuPh** was determined by X-ray crystallography (Figure 4a). The long-wavelength photosensitivity of the photochromic reaction of the molecule is enhanced up to ~580 nm by substituting a triphenyl amine group to the 3-position of the carbazole moiety. These photochromic reactions are investigated by subpicosecond-to-microsecond transient absorption measurements (Figure 4b).

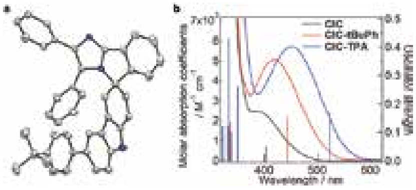


Figure 4. (a) ORTEP representation of **CIC-tBuPh** with thermal ellipsoids (50% probability), where the nitrogen atom is highlighted in blue. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Steady-state absorption spectra of **CIC**, **CIC-tBuPh** and **CIC-TPA** in benzene at room temperature. Vertical lines indicate the theoretical spectra of each molecule.

References

1) Y. Segawa, T. Watanabe, K. Yamanoue, M. Kuwayama, K. Watanabe, J. Pirillo, Y. Hijikata and K. Itami, *Nat. Synth.* **1**, 535–541 (2022).
2) H. Shudo, M. Kuwayama, M. Shimasaki, T. Nishihara, Y. Takeda, N. Mitoma, T. Kuwabara, A. Yagi, Y. Segawa and K. Itami, *Nat. Commun.* **13**, 3713 (2022).
3) Y. Kawanishi, Y. Segawa, K. Mutoh, J. Abe and Y. Kobayashi, *Chem. Commun.* **58**, 4997–5000 (2022).

Awards

SEGAWA, Yasutomo; Chemist Award BCA 2021 (2021).
SEGAWA, Yasutomo; Thieme Chemistry Journals Award 2022 (2022).
SEGAWA, Yasutomo; 62nd Academic Encouragement Award from the Ube Industries Foundation (2022).

Visiting Professors

Visiting Professor

FUKAZAWA, Aiko *(from Kyoto University)*

Renaissance of Nonbenzenoid π-Conjugated Systems toward Functional Materials

The work of our group has focused on exploring functional organic compounds with unusual superb optical and/or electronic properties, based on the molecular designs of novel π-conjugated scaffolds as well as unusual functional groups. In particular, we have recently proposed a rational design of stable yet unusual π-conjugated systems based on the characteristics of nonbenzenoid hydrocarbons such as dehydroannulenes and non-alternant hydrocarbons by annulation of weakly aromatic (hetero)arenes. This year, we have succeeded in synthesizing several thiophene-fused antiaromatic π-systems that exhibit high thermal stability even without bearing bulky substituents while retaining pronounced antiaromatic character. Moreover, we have recently succeeded in synthesizing the fulvalene-based π-conjugated oligomers that exhibit exceptional electron-accepting character as well as robustness toward multi-electron reduction.

Visiting Associate Professor

UEDA, Akira *(from Kumamoto University)*

Development of Neutral Radical Molecular Conductors with Intramolecular Charge Degrees of Freedom

Design and synthesis of novel molecular materials have been a central issue for the development of molecular science. In this work, we have successfully developed a new type of neutral radical molecular conductor crystals with intramolecular charge degrees of freedom. Measurements of X-ray diffraction, electrical resistivity, and magnetic susceptibility have revealed that this new type of charge degrees of freedom is coupled to the intermolecular charge degrees of freedom, leading to unique strongly correlated electron phenomena and properties in molecular materials. In particular, we emphasize that the successful formation of a 3/4-filled electron band in this system is an unprecedented event in neutral molecular solids, which allows not only the realization of an ambient-pressure metallic state but also the emergence of exotic Mott insulating states relevant to the charge degrees of freedom. These results offer new possibilities of neutral radical solids as a molecular strongly correlated electron system.

Visiting Associate Professor

KAMIYA, Yukiko *(from Nagoya University)*

Expand the Artificial Nucleic Acid World Based on the Studies of Molecular Science

Nucleic acids (DNA and RNA) are essential biopolymers that carry genetic information in all living organisms. On the other hand, various artificial nucleic acids (XNAs) having ribose-modified or non-ribose type backbone and nucleic acid recognition ability have been developed. One of the motivation of XNA study is development of nucleic acid drugs. Another big motivation is addressing the fundamental question why nature selected ribose as backbone of genetic materials. Our group has focused on amino acid-type artificial nucleic acids and we are studying on characterization of their molecular recognition properties, design of unique structures, and development of molecular tools and drugs that target RNA as applications. The unique feature of the XNAs is that they form highly stable homo-duplex than XNA/RNA hetero duplex. In the recent study we have developed the methodology that can control the hybridization of XNA/XNA and XNA/RNA by designing the nucleobase structures.

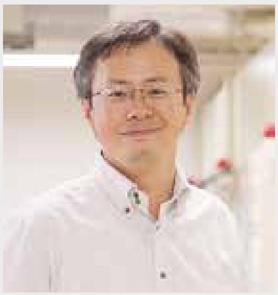
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

The mission of CIMoS is to analyze molecular systems in nature to find the logic behind the sharing and control of information between the different spatiotemporal hierarchies, with the ultimate goal of creating novel molecular systems on the basis of these findings.

Biological Rhythm and Dynamics through Chemistry

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems



AKIYAMA, Shuji
Professor
[akiyamas@ims.ac.jp]

Education

1997	B.E. Kyoto University
1999	M.E. Kyoto University
2002	Ph.D. Kyoto University

Professional Employment

2001	JSPS Research Fellow
2002	JSPS Postdoctoral Fellow
2003	RIKEN Special Postdoctoral Researcher
2005	JST-PRESTO Researcher
2008	Junior Associate Professor, Nagoya University
2011	Associate Professor, Nagoya University
2012	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Awards

2022	NAGASE Research Promotion Award
2016	The 13th (FY2016) JSPS PRIZE
2008	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2007	Young Scientist Prize, The Biophysical Society of Japan
2006	SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
2002	The Protein Society Annual Poster Board Award

Member
Assistant Professor
MUKAIYAMA, Atsushi
FURUIKE, Yoshihiko
Visiting Scientist
DUBERN, Lucie*
LEDOIGT, Magali*
Graduate Student
SIMON, Damien
Technical Fellow
WASHIO, Midori
SUGISAKA, Kanae
WADA, Kotoe
TANIURA, Aiko
OHARA, Satomi
Secretary
SUZUKI, Hiroko

Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

Living organisms on Earth evolved over time to adapt to daily environmental alterations, and eventually acquired endogenous time-measuring (biological clock) systems. Various daily activities that we perform subconsciously are controlled by the biological clock systems sharing three characteristics. First, the autonomic rhythm repeats with an approximately 24-hour (circadian) cycle (self-sustainment). Second, the period is unaffected by temperature (temperature compensation). Third, the phase of the clock is synchronized with that of the outer world in response to external stimuli (synchronization). We seek to explain these three characteristics, and consider the biological clock system of cyanobacteria to be an ideal experimental model.

The major reason that cyanobacteria are considered to be the ideal experimental model is that the core oscillator that possesses the three characteristics of the clock can be easily reconstructed within a test tube. When mixing the three clock proteins KaiA, KaiB, and KaiC with ATP, the structure and enzyme activity of KaiC change rhythmically during a circadian cycle. Taking advantage of this test tube experiment, we used an approach combining biology, chemistry, and physics to elucidate the means by which the clock system extends from the cellular to atomic levels.

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC revelas the rhythm of autophosphorylation and dephosphorylation; however, the cycle of this rhythm depends on the ATPase activity of KaiC independent of KaiA or KaiB. For example, when the ATPase activity of KaiC doubles as a result of amino acid mutations, the frequencies of both the *in vitro* oscillator and the intracellular rhythm also double (the cycle period is reduced to half). This mysterious characteristic is called a transmural hierarchy, in which the cycle (frequency) and even the temperature compensation both *in vitro* and *in vivo* are greatly affected (controlled) by the function and structure of KaiC.

How are the circadian activities and temperature compensation features encoded in KaiC and then decoded from it to propagate rhythms at the cellular level? We are committed to better understanding biological clocks and other dynamic systems through the chemistry of circadian ***rhythm***, ***structure***, and evolutionary ***diversity***.

Selected Publications

- Y. Furuike, A. Mukaiyama, S. Koda, D. Simon, D. Ouyang, K. Ito-Miwa, S. Saito, E. Yamashita, T. Nishiwaki, K. Terauchi, T. Kondo and S. Akiyama, *Proc. Natl. Acad. Sci. U. S. A.* **119**, e2119627119 (2022).
- Y. Furuike, A. Mukaiyama, D. Ouyang, K. Ito-Miwa, D. Simon, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Adv.* **8**, eabm8990 (2022).
- Y. Furuike, D. Ouyang, T. Tominaga, T. Matsuo, A. Mukaiyama, Y. Kawakita, S. Fujiwara and S. Akiyama, *Commun. Phys.* **8**, 75 (2022).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. *Structure*: Reasons for Seeking Structure and Dynamics of Circadian Clock Components in Cyanobacteria[1–4]

A great deal of effort has been devoted to characterizing structural changes in the clock proteins along the circadian reaction coordinate. However, little is known about the mechanism driving the circadian cycle, even for the simple cyanobacterial protein KaiC that has ATPase and dual phosphorylation sites in its N-terminal C1 and C-terminal C2 domains, respectively. Nearly all KaiC structures reported to date share a nearly identical structure, and they do not appear to be suggestive enough to explain the determinants of circadian period length and its temperature compensation. We are studying the structural and dynamical origins in KaiC using high-resolution x-ray crystallography,[1,2] real-time fluorescence detection,[3] and quasielastic neutron scattering.[4]

2. *Rhythm*: Cross-Scale Analysis of Cyanobacterial Circadian Clock System[4–6]

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations and also it is temperature compensated. This unique property has inspired us to develop an ATPase-based screening[5] for KaiC clock mutants giving short, long, and/or temperature-dependent periods.[6] A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 1). Using the developed device, we are screening a number of temperature-dependent mutants of KaiC.[4,5]

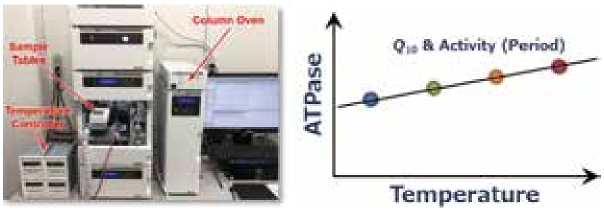


Figure 1. Development of a quick ATPase assay system.

3. beyond Evolutionary *Diversity*[7]

In the presence of KaiA and KaiB, the ATPase activity of KaiC oscillates on a 24-hour cycle. KaiC is not capable of maintaining a stable rhythm on its own, but its activity was observed to fluctuate with reduced amplitude over time (Figure 2A). We have identified a signal component that is similar to damped oscillation, and propose that it encodes the specific frequency, equivalent to a 24-hour cycle.

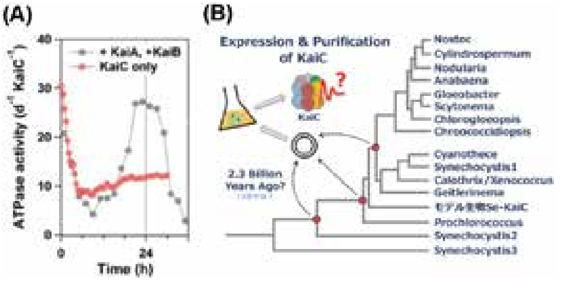


Figure 2. Damped oscillation of KaiC ATPase activity (**A**) and evolutionary diversity of cyanobacteria (**B**).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.[7] Furthermore, some KaiA and KaiB genes are missing in several strains of cyanobacteria. This is understandable to some extent if KaiC possesses the specific frequency. Given this assumption, *what specific frequencies are possessed by KaiC homologues in other species and ancestral cyanobacteria?* (Figure 2B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS[8]

We have supported SAXS users so that they can complete experiments smoothly and publish their results.[8]

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1) Y. Furuike, A. Mukaiyama, D. Ouyang, K. Ito-Miwa, D. Simon, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Adv.* **8**, eabm8990 (2022).
2) Y. Furuike, A. Mukaiyama, S. Koda, D. Simon, D. Ouyang, K. Ito-Miwa, S. Saito, E. Yamashita, T. Nishiwaki-Ohkawa, K. Terauchi, T. Kondo and S. Akiyama, *Proc. Natl. Acad. Sci. U. S. A.* **119**, e2119627119 (2022).
3) A. Mukaiyama, Y. Furuike, E. Yamashita and S. Akiyama, *Biochem. J.* **479**, 1505–1515 (2022).
4) Y. Furuike, D. Ouyang, T. Tominaga, T. Matsuo, A. Mukaiyama, Y. Kawakita, S. Fujiwara and S. Akiyama, *Commun. Phys.* **5**, 75 (2022).
5) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019)
6) D. Simon, A. Mukaiyama, Y. Furuike and S. Akiyama, *Biophys. Physicobiol.* **19**, e190008 (2022)..
7) A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
8) M. Okumura, S. Kanemura, M. Matsusaki, Y. H. Lee, S. Akiyama and K. Inaba, *Structure* **29**, 1–14 (2021).

Awards

AKIYAMA, Shuji; NAGASE Research Promotion Award (2022).
FURUIKE, Yoshihiko; The Early Career Award in Biophysics (2022).
FURUIKE, Yoshihiko; SPRUC 2022 Young Scientist Award (2022).

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* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems

KOGA, Nobuyasu
Associate Professor
(–September, 2022)
[nkoga@ims.ac.jp]

Education

2001	B.S. Kobe University
2006	Ph.D. Kobe University

Professional Employment

2003	JSPS Research Fellow
2006	Postdoctoral Fellow, Kobe University
2007	Postdoctoral Fellow, Kyoto Universtiy
2007	JSPS Postdoctoral Fellow for Research Abroad
2009	Postdoctoral Fellow, University of Washington
2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2014	JST-PRESTO Researcher (additional post) (–2017)
2018	Associate Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)
2022	Professor, Osaka University

Awards

2013	Young Scientist Award, The 13th Annual Meeting of the Protein Science Society of Japan
2013	Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan
2018	Morino Foundation for Molecular Science

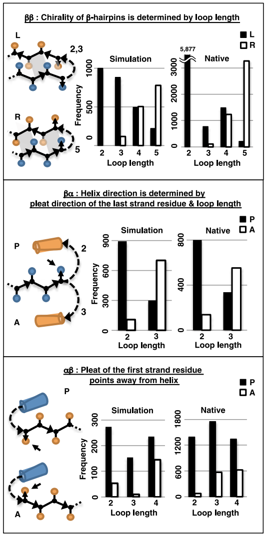
Member
Assistant Professor
KOSUGI, Takahiro
Post-Doctoral Fellow
KOGA, Rie
Research Fellow
MINAMI, Shintaro
Graduate Student
MITSUMOTO, Masaya
KAIDA, Shingo
Secretary
SUZUKI, Hiroko

Keywords Protein Design for Structure and Function, Protein Folding, Structural Biology

Protein molecules spontaneously fold into unique three-dimensional structures specified by their amino acid sequences from random coils to carry out their functions. Many of protein studies have been performed by analyzing naturally occurring proteins. However, it is difficult to reach fundamental working principles of protein molecules only by analyzing naturally occurring proteins, since they evolved in their particular environments spending billions of years. In our lab, we explore the principles by computationally designing protein molecules completely from scratch and experimentally assessing how they behave.

Protein design holds promise for applications ranging from catalysis to therapeutics. There has been considerable recent progress in computationally designing new proteins. Many of protein design studies have been conducted using naturally occurring protein structures as design scaffolds. However, since naturally occurring proteins have evolutionally optimized their structures for their functions, implementing new functions into the structures of naturally occurring proteins is difficult for most of cases. Rational methods for building any arbitrary protein structures completely from scratch provide us opportunities for creating new functional proteins. In our lab, we tackle to establish theories and technologies for designing any arbitrary protein structures precisely from scratch. The established methods will open up an avenue of rational design for novel functional proteins that will contribute to industry and therapeutics.

Rules relating local backbone structures to tertiary structures



Selected Publications

- R. Koga*, M. Yamamoto, T. Kosugi, N. Kobayashi, T. Sugiki, T. Fujiwara and N. Koga*, "Robust Folding of a De Novo Designed Ideal Protein Even with Most of the Core Mutated to Valine," *Proc. Natl. Acad. Sci. U. S. A.* **117(49)**, 31149–31156 (2020).
- N. Koga*, R. Koga, G. Liu, J. Castellanos, G. T. Montelione and D. Baker*, "Role of Backbone Strain in De Novo Design of Complex α/β Protein Structures," *Nat. Commun.* **12**, 3921 (12 pages) (2021).

1. State-Targeting Stabilization of Adenosine A$_{2A}$ Receptor by Fusing a Custom-Made De Novo Designed α-Helical Protein

G-protein coupled receptors (GPCRs) are known for their low stability and large conformational changes upon transitions between multiple states. A widely used method for stabilizing these receptors is to make chimeric receptors by fusing soluble proteins (*i.e.*, fusion partner proteins) into the intracellular loop 3 (ICL3) connecting the transmembrane helices 5 and 6 (TM5 and TM6). However, this fusion approach requires experimental trial and error to identify appropriate soluble proteins, residue positions, and linker lengths for making the fusion. Moreover, this approach has not provided state-targeting stabilization of GPCRs.

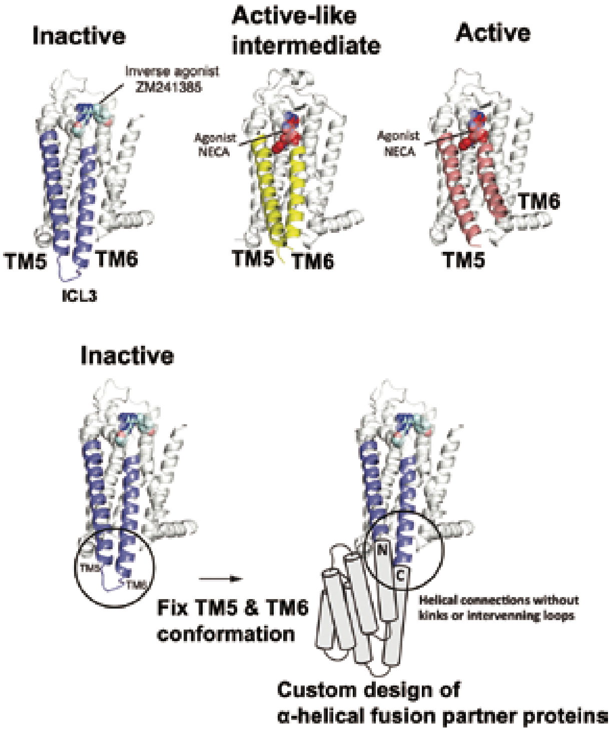


Figure 1. Strategy for state-targeting stabilization of GPCR, using de novo designed fusion partner proteins.

We designed fusion partner proteins customized for stabilizing one of the class A GPCRs, adenosine A$_{2A}$ receptor (A$_{2A}$R), in an inactive state. Class A GPCRs are the largest subfamily of GPCRs, and the receptors in the class have been suggested to undergo large conformational changes in TM6 associated with TM5 upon the state transitions. We assumed that the TM5 and TM6 conformation could be fixed in a specific state through straight helical connections between a fusion partner protein and A$_{2A}$R. Therefore, we sought to design α-helical protein structures de novo, of which the N- and C-terminal helices are, respectively, connected to TM5 and TM6 of an inactive state A$_{2A}$R structure without any kinks or intervening loops.

The chimeric A$_{2A}$R fused with one of the designs (FiX1) exhibited increased thermal stability. We studied the stability of A$_{2A}$R–FiX1 by measuring the apparent melting temperatures in the clear-native polyacrylamide gel electrophoresis (CN–PAGE) method. The melting temperature was found to be significantly increased. For comparison, the melting temperature for A$_{2A}$R–BRIL (BRIL is one of the major fusion partner proteins) was also measured; the value was comparable to those of A$_{2A}$R–FiX1. Moreover, compared with the wild type, the binding affinity of the chimera against the agonist NECA was significantly decreased, whereas that against the inverse agonist ZM241385 was similar, indicating that the inactive state was selectively stabilized. Our strategy contributes to the rational state-targeting stabilization of GPCRs.

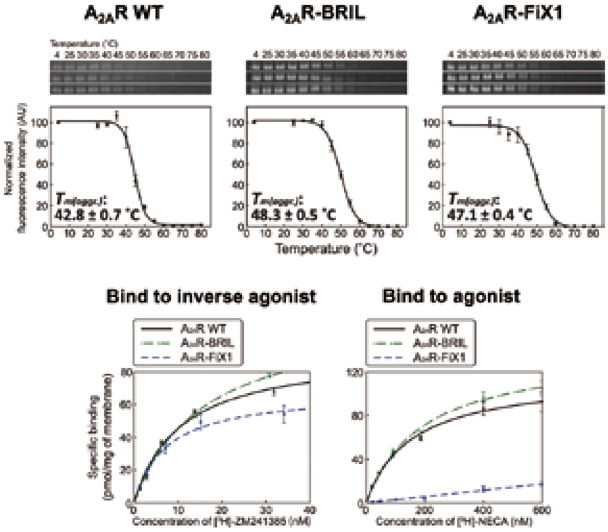


Figure 2. Experimental characteristics of A$_{2A}$R fused with or without fusion partner proteins.

Reference

1) M. Mitsumoto, K. Sugaya, K. Kazama, R. Nakano, T. Kosugi, T. Murata and N. Koga*, *Int. J. Mol. Sci.* **22**, 12906, 13 pages (2022).

Awards

MITSUMOTO, Masaya; The Student Presentation Award of Biophysical Society of Japan (BSJ) (2021).
KAIDA, Shingo; The Student Presentation Award of Biophysical Society of Japan (BSJ) (2021).
MITSUMOTO, Masaya; The SOKENDAI Award from Dean of School of Physical Sciences (2022).
KAIDA, Shingo; The Chemical Society of Japan Tokai Branch Award (2022).

Elucidation of Function, Structure, and Dynamics of Condensed-Phase Molecular Systems by Advanced Ultrafast Laser Spectroscopy

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems

KURAMOCHI, Hikaru
Associate Professor
[hkuramochi@ims.ac.jp]

Education

2007	B.S. Tokyo Institute of Technology
2013	Ph.D. Tokyo Institute of Technology

Professional Employment

2013	Special Postdoctoral Researcher, RIKEN
2016	Research Scientist, RIKEN
2017	JST-PRESTO Researcher
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2017	The 8th Research Incentive Award of RIKEN
2017	The Spectroscopical Society of Japan Award for Young Scientists
2019	RSC PCCP Prize
2020	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
2020	Morino Foundation for Molecular Science
2020	The 13th Young Scientist Awards of the Japan Society for Molecular Science
2021	The 13th Inoue Science Research Award

Member
Assistant Professor
YONEDA, Yusuke
Secretary
ITO, Atsuko

Keywords Ultrafast Spectroscopy, Nonlinear Spectroscopy, Chemical Reaction Dynamics

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study the chemical reaction dynamics of the condensed-phase molecules. In particular, we focus on exploiting unique methodologies based on few-cycle ultrashort pulses (*e.g.*, time-domain impulsive vibrational spectroscopy and multidimensional spectroscopy) and tracking molecular dynamics from electronic and structural viewpoints throughout the chemical reaction with exquisite temporal resolution. We also develop a novel methodology and light source to probe ultrafast dynamics of single molecules in the condensed phase at room temperature, with the aim to understand chemical reaction dynamics at the single-molecule level. Our particular interest rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our advanced spectroscopic approaches, we aim to establish a new avenue for the study of chemical reaction dynamics.

Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi and T. Tahara, "Tracking Ultrafast Structural Dynamics by Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).
- H. Kuramochi, S. Takeuchi, H. Kamikubo, M. Kataoka and T. Tahara, "Fifth-Order Time-Domain Raman Spectroscopy of Photoactive Yellow Protein for Visualizing Vibrational Coupling in Its Excited State," *Sci. Adv.* **5**, eaau4490 (2019).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photoreception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
- T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, "Role of Coherent Low-Frequency Motion in Excited-State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy," *J. Am. Chem. Soc.* **138**, 3942–3945 (2016).
- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* **87**, 043107 (2016).

1. Towards Sub-10-fs Time-Resolved Spectroscopy of Single Molecules at Room Temperature

In complex biological molecular systems, the slow (μs–ms), large-amplitude structural fluctuation significantly modulates the molecular environment inside/outside the molecule, affecting the reactivity at the relevant local sites. Elucidating how such a fluctuation modulates and regulates particular "fast" local chemical reaction dynamics is vital to interrogating the sophisticated molecular mechanisms behind the functions. Nevertheless, the relevant information cannot be accessed by conventional time-resolved spectroscopy because it only provides statistically averaged information about the ensemble. Unraveling how the slow spontaneous fluctuation regulates the chemical reaction inevitably requires observation of the dynamics at the single-molecule level. To this end, we have been developing ultrafast spectroscopy that can track the reaction dynamics of single molecules at room temperature with a temporal resolution as high as <10 fs. Recently, we constructed a confocal microscope as a platform to perform single-molecule ultrafast spectroscopy, and successfully verified that we could detect single molecules. Using a newly developed high-repetition-rate ultrashort laser, ultrafast spectroscopy with single-molecule sensitivity is now underway.

2. Generation of Wavelength-Tunable Sub-10-fs Pulses at a Multi-MHz Repetition Rate

Time-resolved spectroscopy at the single-molecule level inevitably requires extremely high sensitivity, so the light source having high stability and repetition rate is essential. Typically, an optical parametric oscillator (OPO) or a supercontinuum laser is employed as a light source, which offers stable, tunable outputs with a >MHz repetition rate. However, measurements using OPO have a limitation in the temporal resolution (~200 fs) and lack spectral information of detected transients due to the narrow bandwidth. Supercontinuum laser offers broad bandwidth, but its pulse duration is limited to a few ps due to nontrivial phase structure. To realize ultrafast spectroscopy of various complex molecules with single-molecule sensitivity, we need a light source having wavelength tunability, high repetition rate, ultrashort pulse duration, and high stability. We developed a light source for generating sub-10-fs pulses at a multi-MHz repetition rate. Using a ytterbium fiber chirped-pulse-amplification system, we generated pulses tunable from 500–950 nm with broad bandwidths. The outputs were dispersion-compensated,[1)] and the typical pulse duration of the compressed output was <10 fs, as shown in Figure 2. Shot-to-shot and long-term (>hours) fluctuations were evaluated to be <0.3% rms. This high stability holds promise for the application to single-molecule spectroscopy. We will use this high repetition-rate ultrashort light source for ultrafast spectroscopy of single molecules under the microscope and aim to investigate primary events in photoactive proteins with single-molecule sensitivity.

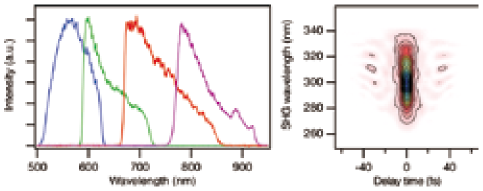


Figure 2. (Left) Typical spectra of the broadband pulses that support Fourier transform limit pulse duration of <10 fs. (Right) Typical FROG trace of the broadband pulse. The pulse duration was evaluated as 6.8 fs.

3. Development of Ultrabroadband Two-Dimensional Electronic Spectrometer

Two-dimensional electronic spectroscopy (2D-ES) is a powerful tool for studying the dynamics and structure of molecules having multiple chromophores with high temporal and frequency resolution. 2D-ES disentangles and visualizes how the optical transitions of each chromophore are coupled and how the excitation energy transfers among them. The technique has been successfully utilized to elucidate the primary energy transfer dynamics in photosynthetic systems and various other biological and materials systems. When the technique is applied to the transients, it is even possible to visualize the migration of wavepackets and/or dynamic heterogeneity. While its success, the spectral range of most of the previous 2D-ES measurements has been limited to <100 nm, hampering us from gaining full insights into the intricate electronic dynamics of condensed-phase complex molecular systems. Aiming to broaden the spectral coverage of 2D-ES and enable investigating electronic and nuclear dynamics comprehensively, we constructed an ultrabroadband 2D-ES setup covering >200 nm for the excitation axis and >400 nm for the detection axis. As shown in Figure 3, the typical data measured for a molecular thin film fully resolve auto- and cross-correlations of the electronic transitions of the ground and excited states over the broad spectral region.

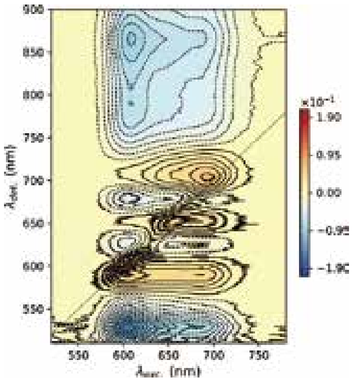


Figure 3. Ultrabroadband two-dimensional electronic spectrum of a molecular thin film measured with <8-fs pulses.

Reference

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Awards

YONEDA, Yusuke; Best Presentation Award at The 15th Annual Meeting of Japan Society for Molecular Science (2021).
YONEDA, Yusuke; The Early Career Award in Biophysics (2022).

Open up Future Electronics by Organic Molecules

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems

YAMAMOTO, Hiroshi
Professor
[yhiroshi@ims.ac.jp]

Education
1993 B.S. The University of Tokyo
1998 Ph.D. The University of Tokyo

Professional Employment
1998 Research Associate, Gakushuin University
1999 Special Postdoctral Fellow, RIKEN
2000 Research Scientist, RIKEN
2007 Senior Research Scientist, RIKEN
2012 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards
2009 RSC Publishing CrystEngComm Prize
2009 Young Scientist Awards, Japan Society for Molecular Science
2010 RIKEN-ASI Award for the Young Scientist
2019 The CSJ Award for Creative Work
2020 NAGAI Foundation for Science & Technology Academic Award

Member
Assistant Professor
HIROBE, Daichi*
SATO, Takuro
Visiting Scientist
PACHARIYANGKUN, Anna
KUMSAMPAO, Jakkapan†
CHAIWAI, Chaiyon†
Graduate Student
AIZAWA, Hiroki
NABEI, Yoji
NAKAJIMA, Ryota
URBAN, Adrian
MALATONG, Ruttapol
Technical Fellow
MURATA, Ryosuke
Secretary
SUZUKI, Ai
ISHIKAWA, Yuko

Keywords Organic Spintronics, Chirality, Organic Superconductor

Spintronics is a new indegredient of electronics in which a magentic moment of an electron is utilized as an information carrier together with its charge. Spin-polized current is one of the most important resources in spintronics, because it can drive devices such as ferromagnetic memory with spin angular momentum. In convetional spintronics, such a spin-polarized current is generated by passing a charge current through ferromagnetic metals. However, recently, researchers are finding other ways of spin-polarized current gentertion by using topological insulators and non-collinear antiferromagnets, which can sometimes be more efficient than those with ferromagnets.

Chiral molecules are attracting recent attention as a new source of spin-polarized current. Chirality-Induced Spin Selectivity (CISS) effect generates spin polarization parallel to or antiparallel to the electron's velocity depending on the handedness of the chiral molecule that is being passed through by a tunneling electron (Figure 1). Although the mechanism of CISS effect is still under debate, it seems to create spin-polarization higher than those of ferromagnets, which is suprisingly large when the small spin–orbit coupling energy of organic molecules is considered. In order to rationalize such a large effect, some microscopic hyptheses are proposed based on experimental results, whose proofs are being waited for. Our group is trying to unveil such mechanisms that drive CISS effect by using chiral crystalline materials.

The use of crystalline materials has serveral advantages. For example, one can employ theoretical framework with well-difined wave number of electrons. Another advantage is the size of the chiral material which allows direct attachment of detection electrodes in different positions. With these merits in mind, we are fabricating spintronic devices suitable for the CISS investigations.

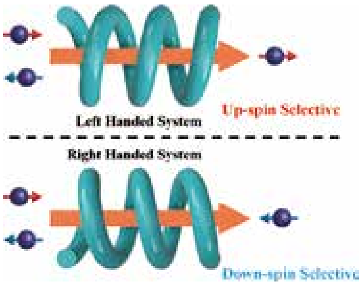

Figure 1. Conceptual schematic for CISS effect. P-helix molecule (lower panel) can transmit more electrons with spins antiparallel to the velocity (negative helicity electrons) than the other, while M-helix molecule (upper panel) favors transmission of electrons with parallel spin (positive helicity electrons).

Selected Publications

- Y. Nabei, D. Hirobe, Y. Shimamoto, K. Shiota, A. Inui, Y. Kousaka, Y. Togawa and H. M. Yamamoto, *Appl. Phys. Lett.* **117**, 052408 (2020).
- A. Inui, R. Aoki, Y. Nishiue, K. Shiota, Y. Kousaka, H. Shishido, D. Hirobe, M. Suda, J.-i. Ohe, J.-i. Kishine, H. M. Yamamoto and Y. Togawa, *Phys. Rev. Lett.* **124**, 166602 (2020).
- M. Suda, Y. Thathong, V. Promarak, H. Kojima, M. Nakamura, T. Shiraogawa, M. Ehara and H. M. Yamamoto, "Light-Driven Molecular Switch for Reconfigurable Spin Filters," *Nat. Commun.* **10**, 2455 (7 pages) (2019).
- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).

1. Spin Current Generation in a Chiral Organic Superconductor

Although *s*- and *d*-wave superconductors are in a spin singlet state at its ground state, a superconductor with broken mirror symmetry is expected to show spin triplet state when supercurrent is flowing, according to a theory developed by Edelstien.[1] This means spin polarization can be generated by applying supercurrent in a chiral superconductor. The magnetization direction that depends on the lattice symmetry has been recently calculated by group theory.[2] We have tested this idea by employing κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (hereafter, κ-NCS) which is an organic superconductor with chiral and polar crystal lattice. The space group of this crystal is $P2_1$, and its handedness is defined by the relative arrangement between the anionic Cu(NCS)$_2$ and cationic BEDT-TTF. This handedness can be experimentally determined by X-ray diffraction or circular dichroism (CD).

After confirming pure enantiomeric lattice system with CD microscope, a thin crystal of κ-NCS has been laminated onto a resin substrate with prepatterned gold and nickel electrodes. At temperature lower than superconducting T_c, an a.c. electrical excitation was applied to induce spin polarization (Figure 2). The spin polarization accumulated at the interface between κ-NCS and the magnetic electrode was detected as a built-up voltage that is dependent on the relative angle between the accumulated and ferromagnetic spins. We have compared the observed voltage with theoretical estimation and found that it exceeds the value predicted by Edelstein effect more than 1000 times. This surprising result suggests that there is a spin enhancement effect other than Edelstein effect, implying existence of an effect analogous to CISS for a chiral superconductor.

By measuring the angle dependency of this magneto–voltaic signal, the direction of accumulated spin could be determined. The observed spin polarization direction was dependent on the location of the detection electrode inside the crystal, and its arrangement was consistent with a magnetic monopole structure which has been hypothesized in a chiral molecule under non-equilibrium state with CISS effect. More specifically, the spin accumulation was forming an antiparallel pair on the upper and lower sides of the κ-NCS crystal. With a right-handed crystal, the accumulated spins showed outward spin pairs.

To our surprise, this spin accumulation could be observed in nonlocal measurements where the excitation and detection electrodes are separated by 600 µm. We have also fabricated a nonlocal detection device with a crystal possessing two chirality domains where right- and left-handed crystal structures are spatially separated. By exciting this crystal at two different positions with opposite handednesses, we have observed a switching of spin pairing mode from outward to inward. This corresponds to the sign reversal of magnetic monopole in the language of multipole expression.[3] An interesting point here is that the sign of magnetic monopole, which shows time-reversal-odd (*T*-odd) characteristics, is connected to the chirality of underlying crystal lattice so that representing *T*-odd chirality. Although this *T*-odd chirality is a metastable state and disappears at ground state, its relevance to the enantio-separation experiments in CISS effect is directly implied in this experiment. If one accepts the fact that a sign of such a metastable magnetic monopole at excitation can represent the sign of chirality (electric toroidal monopole) at ground state lattice, both the large enhancement of spin polarization and the enantio-separation of chiral molecules at non-equilibrium state observed in CISS experiments can be naturally understood, because such a monopole can interact with magnetic substrate in a handedness-specific manner. In this sense, this experiment provides the first direct observation of spin pair (or magnetic monopole) formation from coherent chiral system and provides proof of concept for microscopic CISS mechanism. Although the Hamiltonians describing the chiral superconductor and chiral molecules are quite different, there are many common features such as singlet ground state, chiral lattice and quantum coherence over the entire body. Therefore, we believe the present result provides a lot of stimulating insights for microscopic understanding of CISS. Since the conversion from *T*-even spin current to *T*-odd spin accumulation requires time integration with an existence of spin reservoir, the spin carriers in chiral molecules and superconductors should be identified in future studies. We also expect emergence of superconducting spintronics once a sourcing of spin-polarized current in superconductor is established by chiral superconductors.

(BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene)

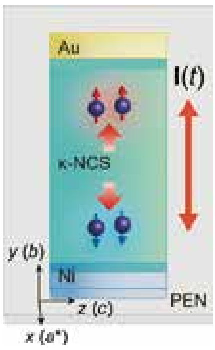

Figure 2. Device schematic for the detection of spin polarization in a chiral superconductor κ-NCS. By applying electrical current, electron spins are polarized along the current direction by CISS-like effect which can be detected as voltage across the κ-NCS/Ni interface. The amplitude of the signal is proportional to the accumulated spins at the interface.

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* Present Address; Shizuoka University

† IMS International Internship Program

RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

In the past few decades, great progress in experimental and theoretical methods to analyze structures, dynamics, and properties of single-component (or single hierarchical) molecules and nanomaterials has been made. Now we should also direct our attention to properties and functions of multi-hierarchical molecular systems. We develop innovative methods of measurements and analysis for molecular and materials systems to elucidate the processes that trigger the functions and reactions of the systems in the mesoscopic regime, that is the regime where micro and macroscopic properties influence each other.

Nano-Optical Imaging and Application to Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

OKAMOTO, Hiromi
Professor
[aho@ims.ac.jp]

Education
1983 B.S. The University of Tokyo
1991 Ph.D. The University of Tokyo

Professional Employment
1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Award
2012 The Chemical Society of Japan (CSJ) Award for Creative Work
2020 The Commendation for Science and Technology by the MEXT Awards for Science and Technology Research Category

Member
Assistant Professor
NARUSHIMA, Tetsuya
YOSHIZAWA, Daichi
IMS Research Assistant Professor
YAMANISHI, Junsuke
Project Assistant Professor (NINS)
AHN, Hyo-Yong
Technical Fellow
ISHIKAWA, Akiko
Secretary
NOMURA, Emiko

Keywords Nano Optics, Plasmons, Chirality

Studies of local optical properties of molecular assemblies and materials are the keys to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Nano-optical methods, such as scanning near-field optical microscopy (SNOM), enable optical imaging with spatial resolution beyond the diffraction limit of light. Combination of nano-optical techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterial systems. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies. In the past several years, we succeeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

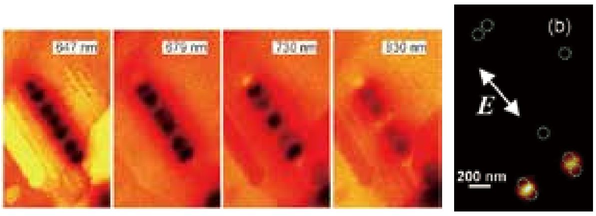

Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20\ \text{nm}^D \times 510\ \text{nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates the incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

1. Optical Trapping of Chiral Metal Nanoparticles[1)]

Micro- to nano-scale particle can be trapped by tightly focused laser beam at the focal point of the beam. This is due to the interaction between the incident optical field and induced polarization on the particle. The force exerted on the particle is in the direction of the gradient of the optical intensity (gradient force), and the particle is stabilized at the most intense position, *i.e.*, the focal point, of the optical beam. The strength of the gradient force has been considered to be determined by the real part of the refractive index of the particle.

When a chiral nanoparticle is optically trapped using a circularly polarized laser beam, a circular polarization (CP)-dependent gradient force can be induced on the particle. We investigated the CP-dependent gradient force exerted on three-dimensional chiral nanoparticles.[2)] The experimental results showed that the gradient force depended on the handedness of the CP of the trapping light as well as the particle chirality. The analysis revealed that the spectral features of the CP-handedness-dependent gradient force are not simply influenced by the real part of the refractive index but also by the electromagnetic field perturbed by the chiral particle resonant with the incident light. This is in sharp contrast to the well-known behavior of the gradient force, which is governed by the real part of the refractive index. The extended aspect of the chiral optical force obtained here can provide novel methodologies on chirality sensing, manipulation, separation, enantio-selective biological reactions, and other fields.

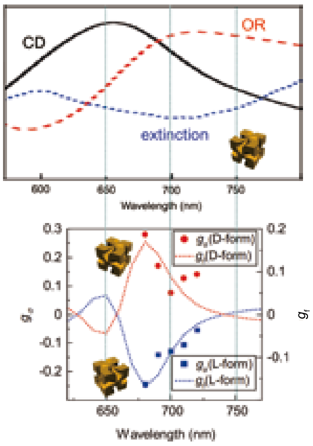

Figure 2. (Top panel) Circular dichroism (CD), optical rotation (OR), and extinction spectra of the colloidal solution of chiral gold nanoparticles. (Bottom panel) Dissymmetry factors (*g*-values: $|g| \leq 2$) of the gradient forces exerted on the chiral nanoparticles by circularly polarized light, experimentally observed (dots) and simulated (dashed curves). The dissymmetry factor follows the CD spectrum of the colloidal solution of the particle rather than OR. This observation gives a new insight into the mechanism of chirality-dependent gradient forces.

2. Development of High-Precision Circular Dichroism Microscopy[3)]

Circular dichroism (CD) is a general and powerful method widely used to detect chirality of materials. However, signal is in general weak and difficult to detect, and interference from linear dichroism signal is sometimes serious for inhomogeneous anisotropic samples. For this reason, only very few microscopic measurements of CD have been reported until now. Some years ago, we developed a novel CD imaging method that is in principle free from linear dichroism and achieved high-precision CD imaging of micro- to nano-scale samples.[4)] Presently, we improved this method by introducing a new mechanism of detection, and achieved higher sensitivity and shorter measurement time compared to the previous apparatus. The detection sensitivity at the present stage is ≈0.06 mOD (≈2 mdeg in ellipticity) with a reasonable measurement time. We are now trying to achieve further rapid measurement time and extension of the wavelength range.

3. Circularly Polarized Luminescence from Chiral Plasmons

A number of studies to develop materials yielding circularly polarized luminescence have been reported. One of the ways to achieve the circularly polarized luminescence is synthesizing luminescent molecules with chiral structure. However, in most cases, the dissymmetry factor of the circular polarization (*g*-value: $|g| = 2$ for completely circularly polarized luminescence) was found to be small (typically of the order of 10^{-5} to 10^{-3}), with a few exceptions of rare-earth complexes and chiral assemblies of molecules. In contrast, chiral plasmons have potentials to provide highly circularly polarized luminescence. Based on this idea, we previously reported generation of circularly polarized luminescence from the chiral plasmonic material combined with achiral fluorescent molecules. We are now pursuing the possibility to further improve the characteristics of the circularly polarized luminescence.

4. Chiral Nanostructure Creation with Plasmonic Chemical Reaction Field

Chiral plasmons can be generated by illuminating metal nanostructure with circularly polarized light, even if the material is achiral. Chiral nanostructure formation is expected by chemical reactions induced by the chiral plasmonic excitations on achiral metal nanostructures. In this case, the handedness of the product is determined by that of the circularly polarized light. We have found a unique chiral structure formation based on this idea, and the detailed study on it is now under way.

References

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2) H.-E. Lee, H.-Y. Ahn, J. Mun, Y. Y. Lee, M. Kim, N. H. Cho, K. Chang, W. S. Kim, J. Rho and K. T. Nam, *Nature* **556**, 360 (2018).
3) H. Okamoto and T. Narushima, PAT. P. (PCT).
4) T. Narushima and H. Okamoto, *Sci. Rep.* **6**, 35731 (2016).

Atomic-Scale Optical Spectroscopy

Center for Mesoscopic Sciences
Division of Broadband Multiscale Analysis

KUMAGAI, Takashi
Associate Professor
[kuma@ims.ac.jp]

Education

2006	B.S. Ritsumeikan University
2008	M.S. Kyoto University
2011	Ph.D. Kyoto University

Professional Employment

2008	JSPS Research Fellow, Kyoto University
2011	JSPS Research Fellow, Fritz-Haber Institute
2013	Group Leader, Fritz-Haber Institute
2021	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2020	Guest Professor, Hokkaido University
2022	Guest Professor, Kyoto University

Awards

2013	Inoue Research Award for Young Scientists
2014	Morino Award for Molecular Science
2016	Gerhard Ertl Young Investigator Award
2020	Gaede Prize (German Physical Society)
2020	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
2020	Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science)

Member
Assistant Professor
NISHIDA, Jun
JSPS Post-Doctral Fellow
LIU, Shuyi
Secretary
ITO, Atsuko

Keywords Atomic-Scale Optical Spectroscopy, Scanning Probe Microscopy, Nanoscale Science

Optical imaging and spectroscopy at atomic resolution is an overarching goal in modern nanoscale science and technology, allowing us to directly access atomic-scale structures and dynamics in real space and real time. Atomic-scale crystal imperfections, defects and inhomogeneities indeed play a crucial role in physicochemical properties and functions of solid catalysts and semiconductor optoelectronic devices. We have challenged to attain atomic-scale optical spectroscopy by combining advanced low-temperature scanning tunneling microscopy, laser spectroscopy and nanoplasmonics.

Electromagnetic fields can be confined to nanoscale through excitation of localized surface plasmon resonances of metallic nanostructures. Plasmonics is a mature research field, enabling precise control of nanoscale light. Accordingly, nanoscale optical imaging and spectroscopy well below the diffraction limit has become a more routine technique. However, the typical spatial resolution remains a few tens of nanometers, which is still far from the atomistic length scale. More recently, state-of-the-art experiments and theories demonstrated that atomic-scale confinement of electromagnetic fields occurs at atomistic asperities existing on metallic nanostructures. However, it is an outstanding challenge to precisely manipulate atomically confined light. We have developed advanced experimental techniques to manipulate extremely confined, strong plasmonic fields in scanning tunneling microscope junctions and implemented ultrasensitive and ultrahigh resolution optical spectroscopy. We also investigate intriguing atomic-scale strong light–matter interactions in an atomically well-defined environment.

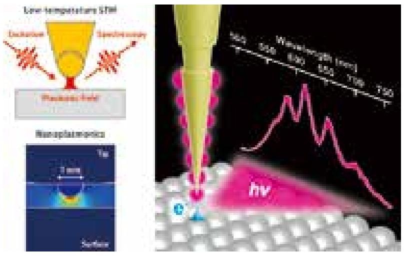

Figure 1. Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

Selected Publications

- H. Böckmann, S. Liu *et al.*, "Near-Field Manipulation in a Scanning Tunneling Microscope Junction with Plasmonic Fabry-Pérot Tips," *Nano Lett.* **19**, 3597–3602 (2019).
- S. Liu *et al.*, "Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation," *Nano Lett.* **20**, 5879–5884 (2020).
- S. Liu *et al.*, "Atomic Point Contact Raman Spectroscopy of a Si(111)-7×7 Surface," *Nano Lett.* **21**, 4057–4061 (2021).
- S. Liu *et al.*, "Anti-Stokes Light Scattering Mediated by Electron Transfer Across a Biased Plasmonic Nanojunction," *ACS Photonics* **8**, 2610–2617 (2021).
- B. Cirera *et al.*, "Charge Transfer-Mediated Dramatic Enhancement of Raman Scattering upon Molecular Point Contact Formation," *Nano Lett.* **22**, 2170–2176 (2022).
- S. Liu *et al.*, "Nanoscale Heating of an Ultrathin Oxide Film Studied by Tip-Enhanced Raman Spectroscopy," *Phys. Rev. Lett.* **128**, 206803 (2022).

1. Inelastic Light Scattering by a Plasmonic Nanogap

Light scattering from plasmonic nanojunctions is routinely used to assess their optical properties. However, the microscopic mechanism remains imperfectly understood, and an accurate description requires the experiment in a well-defined environment with a highly precise control of the nanojunction. We investigated inelastic light scattering (ILS) in a plasmonic STM junction at cryogenic temperature and found that a broad continuum occurs in the anti-Stokes regime when the bias voltage is applied (Figure 2).1) The underlying mechanism was examined by recording the ILS spectra concurrently with STM luminescence. We proposed that electronic Raman scattering is dominant when the excitation wavelength matches the gap-mode plasmon, whereas photoluminescence mainly contributes under off-resonance conditions. The results provide an in-depth understanding of ILS by electrically biased plasmonic nanojunctions and demonstrate nonthermal origin of the anti-Stokes scattering.

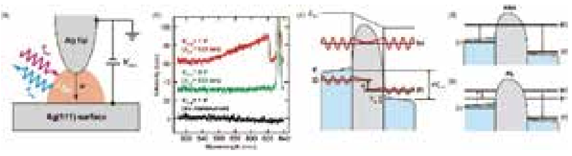

Figure 2. (a) Schematic of the experiment. (b) ILS spectra in the anti-Stokes regime measured for the Ag tip–vacuum–Ag(111) junction at a different bias voltage and in the presence/absence of the illumination. (c–e) Anti-Stokes scattering mechanism in an electrically-biased STM junction. (d) Electronic Raman scattering. (e) Photoluminescence.

2. Atomic-Point Contact Raman Spectroscopy

Tip-enhanced Raman spectroscopy (TERS) is a powerful tool for ultrasensitive chemical analysis at surfaces. Although the enhancement mechanism underlying TERS has been intensively studied, it remains to be elucidated, particularly in sub-nanometer plasmonic gaps. We investigated TERS at atomic-point contacts (APCs) in plasmonic STM junctions and found that large enhancement can be obtained when APCs are formed. Figure 3 shows an example of APC-TERS for an ultrathin ZnO film epitaxially grown on the Ag(111) surface.2) The TERS spectra are recorded as a function of the tip–surface distance including two distinct regimes, namely the tunneling and APC regimes. The remarkable enhancement can be observed at the distance of the APC formation. We suggest that the enhancement is explained by chemical effects resulting from hybridization between the tip apex and surface atoms of the ZnO film.

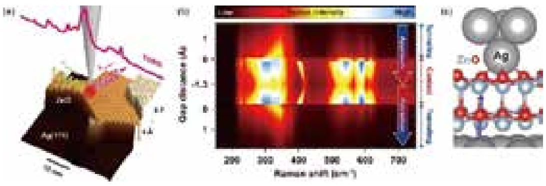

Figure 3. (a) Schematic of the experiment. (b) Waterfall plot of the gap-distance-dependent TER spectra recorded over 2-ML ZnO. The tip approaches and retracts toward and backward from the ZnO from the tunneling to the APC regime. (c) Structure at the APC determined by the DFT calculation.

3. Nanoscale Heating of an Ultrathin Oxide Film

Heating is one of the most basic physical processes. Rapid advances of nanofabrication techniques raise a fundamental issue regarding thermal management at nanoscale. TERS thermometry provides a unique opportunity to study local heating. We investigated the nanoscale heating mechanism of an ultrathin ZnO film using TERS (Figure 4).3) The exceptional sensitivity of TERS allowed to observe Stokes and anti-Stokes scattering of the ZnO film and to perform nanoscale thermometry. It was revealed that the local heating originates mainly from inelastic electron tunneling through the electronic resonance when the bias voltage exceeds the conduction band edge of the 2-monolayer (ML) ZnO. When the bias voltage is lower than the conduction band edge, the local heating arises from two different contributions, namely direct optical excitation between the interface state and the conduction band of 2-ML ZnO or injection of photoexcited electrons from an Ag tip into the conduction band. Simultaneous mapping of tip-enhanced Raman spectroscopy and scanning tunneling spectroscopy for 2-ML ZnO including an atomic-scale defect demonstrates visualizing a correlation between the heating efficiency and the local density of states, which further allows us to analyze the local electron-phonon coupling strength with ~2 nm spatial resolution.

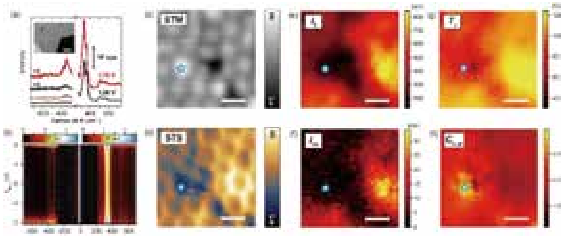

Figure 4. (a) TERS spectra of 2-monolayer ZnO/Ag(111) including the Stokes and anti-Stokes regimes. (b) Waterfall TERS plot as a function of the applied bias voltage. (c) and (d) STS image of 2-monolayer ZnO film including an atomic-scale defect and the corresponding STS mapping. (e–g) Mapping of the Stokes and anti-Stokes intensity and the effective temperature recorded in the same area with (c–d). (f) Mapping of the relative electron–phonon coupling strength.

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1) S. Liu *et al.*, *ACS Photonics* **8**, 2610–2617 (2021).
2) S. Liu *et al.*, *Nano Lett.* **20**, 5879–5884 (2020).
3) S. Liu *et al.*, *Phys. Rev. Lett.* **128**, 206803 (2022).

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
2020	Clarivate Citation Laureates (Chemistry)
2020	“Major Results” of Nanotechnology Platform, MEXT

Member

IMS Research Assistant Professor
MITSUHASHI, Takaaki

Research Fellow
CHEN, Jiazhuo

Visiting Scientist
TAKATA, Yusuke
GONDO, Keisuke

Graduate Student
JUNG, Youngcheol*

Secretary
MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

Our research is based on the design of new self-assembled molecular systems using coordination chemistry. We not only create the new self-assembled molecular systems but also try to utilize the created system for various purpose. One example is a molecular system called crystalline sponge (CS).

The CS is a porous crystal of a coordination network, into which various kinds of small molecules could be introduced. Notably, we can know structures of the small molecules accommodated in the pore of the CS by X-ray crystallography, because the CS has the accommodated small molecules periodically aligned. Thus, the CS can be utilized for the structure analysis, and this technique is called the CS method. This method has some advantages; i) only nanogram to microgram scale of analytes is required, ii) the absolute stereochemistry can be determined, iii) even oily substances can be analyzed by X-ray crystallography. Because of these fascinating features, the CS method attracts the interests of many people not only in academia but also in industry.

Currently, we are improving the CS method in various ways. At the same time, we also try to apply the CS method to other field of science. For example, we use the CS method for the studies on natural product chemistry.

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).

Here, we show our recent attempts to improve the performance of the CS method and deepen understanding of this method. These studies would broaden the range of compounds, which can be analyzed by the CS method, and provide information helpful for people who want to try this method. We hope these studies encourage many people who needs to analyze the structure of small molecules to use the CS method for their own works and studies.

1. Solvent Effect in the Crystallin Sponge Method[1)]

Recently, we found that a choice of a solvent used in the CS method is important, especially when we want to heighten the quality of data obtained by this method. Before the analytes are introduced into the CS, the pore of the CS is filled with solvents. When the analytes come into the CS, the solvents go out, but a part of the solvents still remain in the pore. Previously, non-polar solvents are frequently used in the CS method, because the non-polar solvents exhibit only limited interactions with the CS, and are easily replaced with analytes. However, in this study, we tried to use various kinds of polar solvents. As a result, we found that the polar solvents are sometimes better than the non-polar solvents. Since the polar solvents remained in the pore show stronger interactions with both analyte and the CS, it can mediate the interaction between the analytes and the CS (Figure 1). It would result in an inhibition of disorder of analyte in the pore of the CS and an improvement of the quality of data.

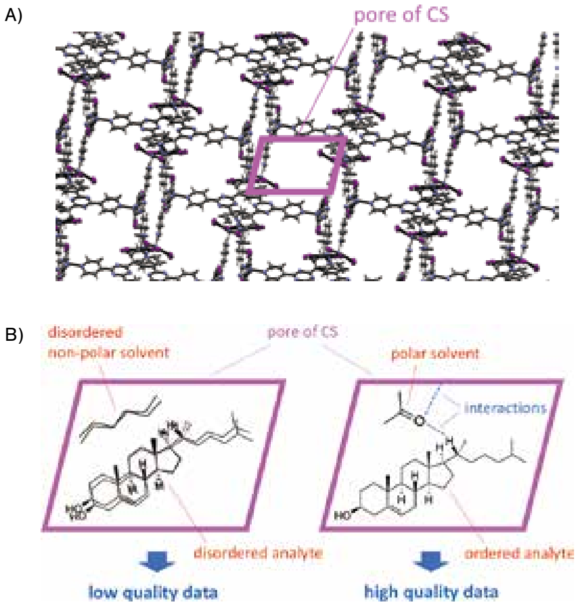

Figure 1. A) Structure of the CS. B) Image of the solvent effect in the CS method.

2. Crystalline Sponge Method Is Suitable for the Structure Analysis of Halogenated Compounds[2)]

The CS method could be used for the structure analysis of a broad range of small molecules. However, it is worth knowing which kinds of analytes is suitable for the analysis using the CS method. We recently found that the halogenated compounds are easily analyzed by the CS method in many cases. For example, we successfully analyzed a series of halogenated compounds classified as persistent organic pollutants (POPs), which are important compounds from the point view of environmental problem. The analysis of the POPs using the CS method revealed that halogen atoms of the analytes effectively interact with the CS (Figure 2). We consider that these interactions help the alignment of the halogenated compounds inside the pore of the CS.

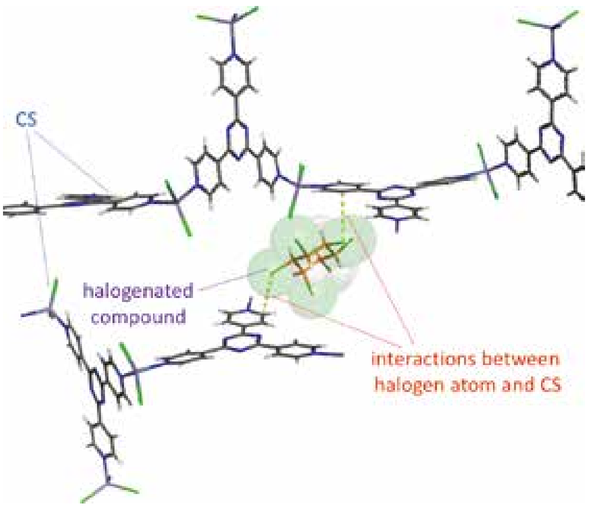

Figure 2. One example of interaction between the CS and a halogenated compound.

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2) J. Chen, T. Kikuchi, K. Takagi, H. Kiyota, K. Adachi, T. Mitsuhashi and M. Fujita, *Chem. Lett.* **51**, 85–87 (2022).

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* 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
KURITA, Yoshiko

Keywords Condensed Matter, Electronic Structure, Synchrotron Radiation

Physical and chemical properties of solids, such as conductivity, magnetism, superconductivity and chemical reactions originate from microscopic electronic structure, lattice/molecular vibrations, and molecular movements based on quantum mechanics in materials and their interactions. By revealing the microscopic states, we can learn about the origin of physical and chemical properties and hidden functionalities. Also, the microscopic information is helpful for the creation of novel functional properties. To visualize hidden microscopic information, we develop novel spectroscopic techniques using synchrotron radiation, high brilliant electron beams, and other so-called quantum beams. We are now developing a new electron spectroscopy technique, Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS), with bulk-sensitive primary energies of 0.3–1.5 keV, as shown in Figure 1, in order to detect spin-selective element-specific bulk plasmons. Based on the obtained information of electronic structures, we aim to develop novel physical properties of new materials.

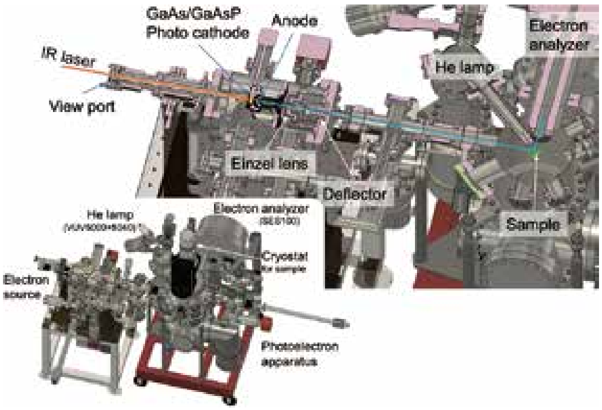

Figure 1. Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

Selected Publications

- 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, "Non-Trivial Surface States of Samarium Hexaboride at the (111) Surface," *Nat. Commun.* **10**, 2298 (7 pages) (2019).
- 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).
- 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]
- 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).

1. Optical Study of the Electronic Structure of Locally Noncentrosymmetric $CeRh_2As_2$[1]

The electronic structures of the heavy-fermion superconductor $CeRh_2As_2$ with local inversion symmetry breaking and the reference material $LaRh_2As_2$ have been investigated using experimental optical conductivity [$\sigma_1(\omega)$] spectra and first-principles density functional theory calculations. The low-temperature $\sigma_1(\omega)$ spectra of $LaRh_2As_2$ revealed a broad peak at ~0.1 eV and a sharp peak at ~0.5 eV after subtracting the Drude contribution of free carriers. The peak features and the background intensity were nicely reproduced in calculated $\sigma_1(\omega)$ spectra from DFT calculations, implying a conventional metallic nature. In $CeRh_2As_2$, two mid-IR peaks at about 0.12 and 0.4 eV corresponding to the unoccupied Ce $4f_{5/2}$ and $4f_{7/2}$ states, respectively, were strongly developed with decreasing temperature as shown in Figure 2, which suggests the emergence of hybridization states between the conduction and 4*f* electrons. We compared the temperature dependence of the mid-IR peaks of $CeRh_2As_2$ with corresponding data from $CeCu_2Si_2$ and $CeNi_2Ge_2$ in a $ThCr_2Si_2$-type structure to examine the possible impact of local inversion symmetry breaking on electronic structures. We also clarify the local and itinerant character in the electronic structure by investigating the temperature dependence in the $\sigma_1(\omega)$ spectra of various Ce and Yb compounds with a tetragonal $ThCr_2Si_2$-type crystal structure.[2] The temperature variation in the $\sigma_1(\omega)$ spectrum is still present in the more localized case, even though the Kondo effect is strongly suppressed.

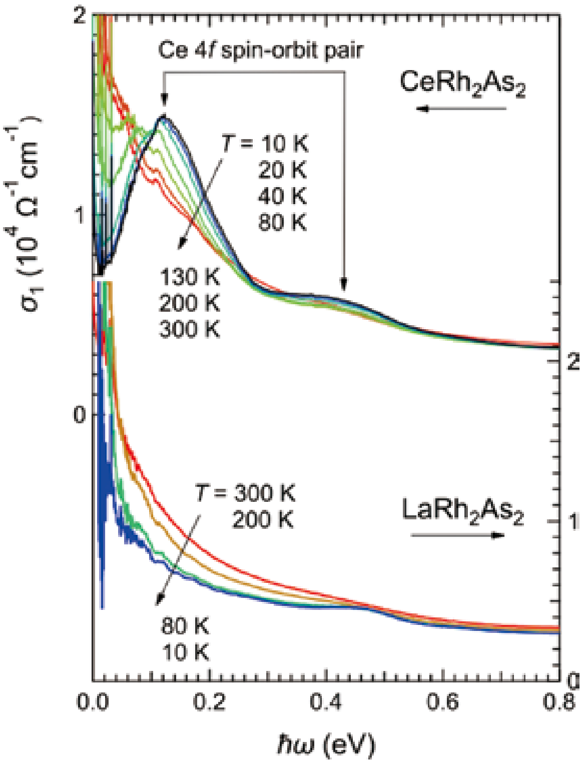

Figure 2. Temperature-dependent optical conductivity [$\sigma_1(\omega)$] spectra of $CeRh_2As_2$ and $LaRh_2As_2$.

2. Bulk-Sensitive Spin-Resolved Resonant Electron Energy-Loss Spectroscopy (SR-rEELS): Observation of Element- and Spin-Selective Bulk Plasmons[3]

We have developed spin-resolved resonant electron energy-loss spectroscopy (SR-rEELS) with the primary energy of 0.3–1.5 keV, which corresponds to the core excitations of 2*p*–3*d* absorption of transition metals and 3*d*–4*f* absorption of rare-earths, with the energy resolution of about 100 meV using a spin-polarized electron source as a GaAs/GaAsP strained superlattice photocathode. Element- and spin-selective carrier and valence plasmons can be observed using the resonance enhancement of core absorptions and electron spin polarization. The Ni 2*p*–3*d* rEELS of nickel monoxide NiO as an example is shown in Figure 3. Furthermore, bulk-sensitive electron energy-loss spectroscopy spectra can be obtained because the primary energy corresponds to the mean free path of 1–10 nm. The methodology is expected to provide us with novel information about elementary excitations by resonant inelastic x-ray scattering and resonant photoelectron spectroscopy.

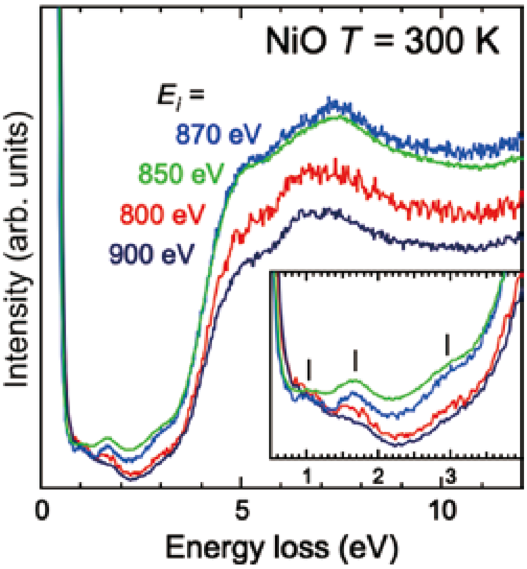

Figure 3. Resonant EELS spectra of nickel monoxide NiO with the primary energies (E_i) of 800–900 eV. The overall spectral intensity is enhanced at E_i = 850 and 870 eV near the Ni 2*d*–3*d* absorption edge. (Inset) Enlarged view of the Ni *d*–*d* excitations (indicated by vertical lines) below the lowest charge transfer excitation energy of about 4 eV.

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2) S. Kimura, Y. S. Kwon, C. Krellner and J. Sichelschmidt, *Electron. Struct.* **3**, 024007 (8 pages) (2021).

3) S. Kimura, T. Kawabata, H. Matsumoto, Y. Ohta, A. Yoshizumi, Y. Yoshida, T. Yamashita, H. Watanabe, Y. Ohtsubo, N. Yamamoto and X. Jin, *Rev. Sci. Instrum.* **92**, 093103 (8 pages) (2021).

Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

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

ONISHI, Hiroshi
Professor
(Cross Appointment)
[oni@ims.ac.jp]

Education
1985 B.S. The University of Tokyo
1993 Ph.D. The University of Tokyo

Professional Employment
1989 Assistant Professor, The University of Tokyo
1997 Associate Professor, The University of Tokyo
1999 Project Leader, Kanagawa Academy of Science and Technology
2004 Professor, Kobe University
2021 Professor (Cross Appointment), Institute for Molecular Science

Awards
2001 Young Scientist Award , Catalysis Society of Japan
2002 Nano-Probe Technology Award, Nano-Probe Technology Committee, JSPS
2003 Technical Award, Surface Science Society of Japan
2004 Yazaki Award, Yazaki Foundation
2019 Society Award, Japan Society of Vacuum and Surface Science

Member
Secretary
ISHIKAWA, Azusa
KURITA, Yoshiko

Keywords Reactions at Interfaces, Catalysis, Energy-Related Chemistry

We are proud of our international-compatible studies of liquid–solid interfaces, *e.g.* photocatalysts for artificial photosynthesis and lubricants for smooth tribology. Characterization with frequency-modulation AFM, time-resolved ATR-IR spectroscopy, soft X-ray absorption, and microelectrode-based amperometry are being developed. We are pleased to collaborate with researchers in academic and industrial organizations to reveal science behind material conversion and energy dissipation at liquid–solid interfaces.

A new era of molecular science should be revealed in liquid–solid interfaces of finite thickness (Figure 1). The molecular interface is the place of reaction where molecules of interest collide with or interact with other molecules. We need to observe individual molecules there. On the other hand, the molecular interface is connected to liquid and solid. Materials and energy come from/to the two condensed phases, since functional interfaces are always open to the environment. In addition, operando characterization is definitely required for investigating the interface in its working state.

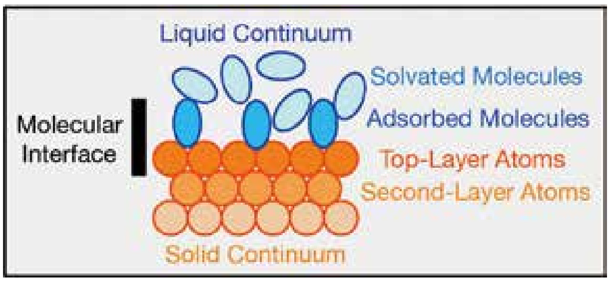


Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- T. Kosaka, Y. Teduka, T. Ogura, Y. Zhou, T. Hisatomi, H. Nishiyama, K. Domen, Y. Takahashi and H. Onishi, "Transient Kinetics of O_2 Evolution in Photocatalytic Water-Splitting Reaction," *ACS Catal.* **10**, 13159–13164 (2020).
- S. Xue, A. Sasahara and H. Onishi, "Atom-Scale Imaging of TiO_2(110) Surface in Water by Frequency-Modulation Atomic Force Microscopy," *J. Chem. Phys.* **152**, 054703 (7 pages) (2020).
- T. Fujiwara, A. Sasahara, N. Happo, K. Kimura, K. Hayashi and H. Onishi, "Single-Crystal Model of Highly Efficient Water-Splitting Photocatalysts: A $KTaO_3$ Wafer Doped with Calcium Cations," *Chem. Mater.* **32**, 439–1447 (2020).
- S. Moriguchi, T. Tsujimoto, A. Sasahara, R. Kokawa and H. Onishi, "Nanometer-Scale Distribution of Lubricant Modifier on Iron Films: A Frequency-Modulation Atomic Force Microscopy Study Combined with Friction Test," *ACS Omega* **4**, 17593–17599 (2019).
- H. Onishi, "Sodium Tantalate Photocatalysts Doped with Metal Cations: Why Are They Active for Water Splitting?" *ChemSusChem* **12**, 1825–1834 (2019).
- H. Imada, K. Kimura and H. Onishi, "Water and 2-Propanol Structured on Calcite (104) Probed by Frequency-Modulation Atomic Force Microscopy," *Langmuir* **29**, 10744–10751 (2013).

1. Microelectrode-Based Transient Amperometry of O_2 Adsorption and Desorption on a $SrTiO_3$ Photocatalyst Excited under Water

Oxygen evolution at water–solid interfaces is a key reaction for sustainable energy production. Although some intermediate states have been detected in transient absorption spectroscopy, the O_2 evolution kinetics after the multi-step, four-electron oxidation of water remain unknown. In this study,[1)] transient amperometry with a microelectrode was applied to *operando* O_2 detection over Al-doped $SrTiO_3$ particles doubly loaded with $RhCrO_x$ and CoO_y cocatalysts, an efficient photocatalyst for the overall water-splitting reaction. A platinum electrode (radius: 10 μm) was moved close to the particles in an electrolyte solution. Molecular oxygen was released on the particles, diffused across the electrode–particle gap, and converted to a current on the electrode (Figure 2).

Electrochemical O_2 detection at intervals of 0.1 s, which was thereby achieved, unexpectedly indicated instantaneous O_2 adsorption and desorption in addition to steady, photocatalytic O_2 evolution on the photocatalyst modified under intense light irradiation. We hypothesized that electrons excited in the conduction band were transferred to O_2 in water thorough Ti cations neighboring an oxygen anion vacancy on the modified Al-doped $SrTiO_3$. The negatively charged O_2 was then bound to the Ti cations. It was neutralized and released when shaded through electron back-transfer to the conduction band. The hypothesized mechanism for O_2 adsorption and desorption was compared with the photoinduced O_2 desorption known to occur on anion vacancies of TiO_2(110). The microelectrode-based transient amperometry demonstrated here will be applied to many other phenomena at liquid–solid interfaces.

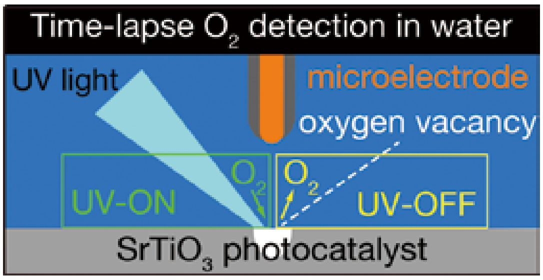


Figure 2. Transient amperometry for detection of molecular oxygen released into water.

2. Long-Life Electrons in Metal-Doped Alkali-Metal Tantalate Photocatalysts Excited under Water

Conversion of materials for artificial photosynthesis is completed in milliseconds or seconds by assembling atoms over semiconductor photocatalysts. Bandgap-excited electrons and holes reactive on this time scale are key for efficient atom assembly to yield the desired products. In this study,[2)] attenuated total reflection of infrared (IR) light was applied to characterize the electronic absorption of long-life charge carriers excited under water. This was a difficult task since water absorbs IR light for probing, while excitation light is absorbed by photocatalyst particles. An attenuated total reflection (ATR) assembly with a diamond prism is key for guiding the excitation light to the volume probed by IR light (Figure 3).

Under excitation, $NaTaO_3$ and $KTaO_3$ photocatalyst particles doped with Sr or La cations absorbed IR light. A broad absorption band appeared with a maximum at 1400 cm^{-1}, which was enhanced by the addition of hole scavengers (*e.g.*, methanol and Na_2SO_3) and disappeared in the presence of electron scavengers (*e.g.*, $FeCl_3$, $NaIO_3$, and H_2O_2). This absorption corresponded to the electronic transition of bandgap-excited electrons accommodated in mid-gap states. In anaerobic *n*-decane, the electron absorption was enhanced by the excitation light power, P, with absorbance being proportional to $P^{1/2}$. The observed 1/2-order power law suggested de-excitation via recombination of electrons and holes. When the excitation light was stopped, the absorbance decreased as a function of time with a second-order rate law, as expected in the case of recombinative de-excitation. In addition, the 1/2-order power law and second-order decay rate law were observed in anaerobic water, with an accelerated decay rate, which was possibly due to a water-related electron-consuming reaction. This study demonstrated that long-life electrons contribute to surface redox reactions over semiconductor photocatalysts for artificial photosynthesis.

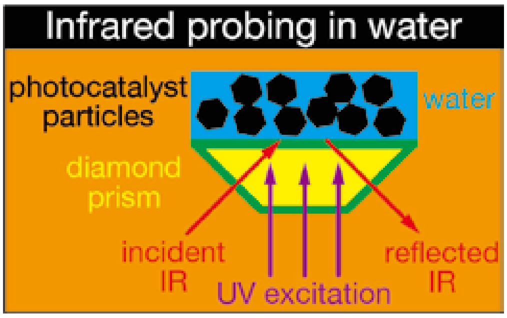


Figure 3. An attenuated total reflection assembly with a diamond prism for guiding ultraviolet light to the volume probed by IR light.

References

1) T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, *Phys. Chem. Chem. Phys.* **23**, 19386–19393 (2021).

2) Z. Fu, T. Hirai and H. Onishi, *J. Phys. Chem. C* **125**, 26398–26405 (2021).

Award

ONISHI, Hiroshi; 2021 HOT PCCP article [T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, *Physical Chemistry Chemical Physics* **23**, 19386–19393 (2021)] (2021).

Innovative Catalysis Development Based on Radiant Light Spectroscopy

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

TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
(–February, 2022)
[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
2022	Professor, Teikyo University of 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.

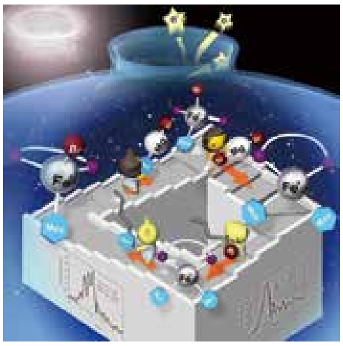


Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

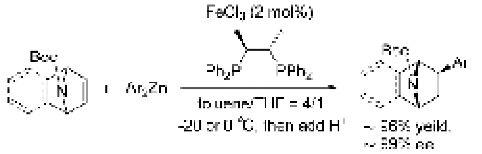
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada–Tamao–Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).
- 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).
- Y. Kanazawa, T. Mitsudome*, H. Takaya* and M. Hirano*, "Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate: Synchrotron Radiation Sheds Light on the Cu Cycle Mechanism," *ACS Catal.* **10**, 5909–5919 (2020).
- L. Adak, M. Jin, S. Saito, T. Kawabata, T. Itoh, S. Ito, A. K. Sharma, N. J. Gower, P. Cogswell, J. Geldsetzer, H. Takaya, K. Isozaki and M. Nakamura*, "Iron-Catalysed Enantioselective Carbometalation of Azabicycloalkenes," *Chem. Commun.* **57**, 6975–6978 (2021).

1. DFT-XAS-Based Mechanistic Investigation of Transition-Metal-Catalyzed Reaction in Homogeneous Phase[1,2]

Mechanistic study on transition-metal complex-catalyzed reaction in homogeneous phase mostly carried out by means of solution-phase NMR analysis. However, studies on base metal catalysts being essential for SDGs achievement often suffer from difficulties due to their paramagnetic property which provide unusual large paramagnetic shifts with significant peak broadening. To solve the problems in mechanistic study of base metal-catalyzed reaction, we performed XAS measurement which enables element specific analysis to determine the oxidation state and the geometry of catalytic species without interference from the paramagnetic property.

Recently, we have successfully elucidated the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate where the oxidation states and the local coordination geometries of catalytic intermediates were determined under the stoichiometric conditions of each reaction path.[1] DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is the 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 paramagnetic transition-metal complex-catalyzed reactions being difficult by means of the conventional solution-phase NMR analysis.

Effectiveness of the DFT-XAS-based mechanistic study on paramagnetic transition-metal complex-catalyzed reaction was clearly demonstrated in iron-catalyzed enantioselective carbometallation of azabicylcoalkenes (eq. 1).[2] In this study, formation of diphosphine ligand-coordinated tetrahedral iron species, which is a key species for chiral recognition of substrate, was successfully identified with the molecular structure in the reaction mixture.



(1)

2. XAFS-Based Structural Study on Flexible Organometallic Systems[3–6]

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal bearing 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.[3]

Another successful application was achieved in the structure determination of double-decker type iron porpyrin/phtalocyanine dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials or iron-oxo linkage.[4] 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.

Another successful example of the DFT-XAS-based structural study was demonstrated by the molecular strucutre detertmination of an anionic homoleptic organo–transition metal complex of $[Li(12\text{-}crown\text{-}4)_2][MPh_6\{Li(thf)\}_2]$ (M = Rh and Ir) in THF solution which are the first examples of hexaaryl complexes of d6 metals with a partially contacted ion pair structure of Ir^{2-}-Li^+ in solution-phase.[5]

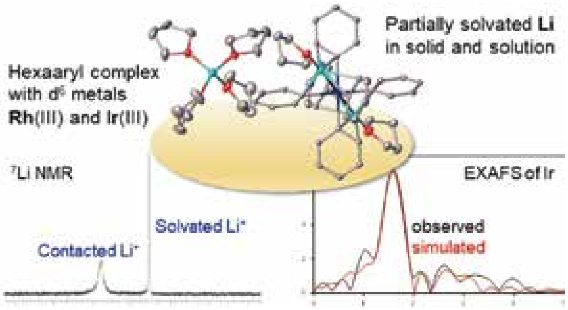


Figure 2. The molecular structure determination of $[Li(12\text{-}crown\text{-}4)_2][MPh_6\{Li(thf)\}_2]$.

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RESEARCH ACTIVITIES

Division of Research Innovation and Collaboration

As the open innovation hub managed by IMS and companies, we conduct the research projects in collaboration with Academia, Industry and Government.

Micro Solid-State Photonics

Division of Research Innovation and Collaboration

TAIRA, Takunori
Project Professor
[taira@ims.ac.jp]

Education

1983	B.A. Fukui University
1985	M.S. Fukui University
1996	Ph.D. Tohoku University

Professional Employment

1985	Researcher, Mitsubishi Electric Corp.
1989	Research Associate, Fukui University
1993	Visiting Researcher, Stanford University (–1994)
1998	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2018	Group Director, RIKEN SPring-8 Center
2019	Project Professor, Institute for Molecular Science

Awards

2004	Persons of Scientific and Technological Research Merits, Commendation by Minister of Education, Culture, Sports, Science and Technology, Japan
2010	OSA Fellow Award, The Optical Society (OSA)
2012	SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014	IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)
2018	IAPLE (The International Academy of Photonics and Laser Engineering) Fellow
2019	LSJ (The Laser Society of Japan) Fellow

Member
Program Manager
- SANO, Yuji
- TAKIGAMI, Hiroyuki*

Associate Program Manager
- SUMIYA, Rie
- SUZUKI, Masayo
- UEGURI, Atsushi
- YOSHIOKA, Takashi

Visiting Professor
- KAWASE, Kodo

Visiting Associate Professor
- YOSHIDA, Mitsuhiro

Post-Doctoral Fellow
- TAKEYA, Kei
- ISHIZUKI, Hideki
- SATO, Yoichi
- YAHIA, Vincent
- LIM, Hwanhong
- TSUJI, Akihiro
- ICHII, Tomoaki
- MURATE, Kosuke

Research Fellow
- KAUSAS, Arvydas

Visiting Scientist
- MOREIRA, Joel†

Technical Fellow
- MATSUDA, Miho*
- KOBAYASHI, Jun
- MIZUSHIMA, Kazuhiko
- IBUKI, Takeshi*
- JUNG, Heeseob*

Secretary
- ONO, Yoko
- INAGAKI, Yayoi
- OKUHARA, Norie*

Keywords Solid-State Lasers, Nonlinear Optics, Micro Solid-State Photonics

"Micro Solid-State Photonics" based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro ceramic and single-crystal, solid-state lasers can provide excellent spatial mode quality and narrow linewidths with enough power. High-brightness nature of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion: The world first laser ignited car, highly efficiency broad frequency conversions from the wavelength of 118nm VUV until 300µm–1mm THz waves, and so on. In addition, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. Lately, we propose a new architecture to realize a monolithic multi-disk laser by the surface activated bonding (SAB). This multiple thin-disk or chip gain medium for distributed face cooling (DFC) structure can manage the high-power and high-field laser with high-gain compact system. Besides, QPM-structured crystal quartz constructed by multi-plate stacking could be promising as a high-power and reliable VUV frequency conversion devices. These downsized and modularized **tiny integrated lasers** (TILA) promise the extremely high-brightness lasers to open up the new science, such as laser driven electron accelerator toward table-top XFEL, and innovation by the compact power laser (Figure 1).

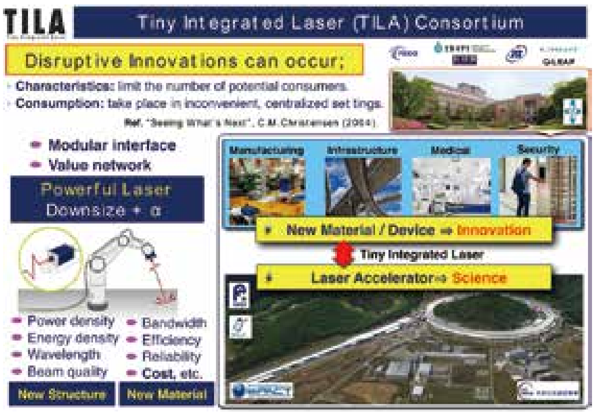

Figure 1. TILA consortium toward "Laser Science and Innovation" by micro solid-state photonics.

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- T. Taira *et al.*, *IEEE J. Sel. Top. Quantum Electron.* **3**, 100 (1997).
- T. Taira, *IEEE J. Sel. Top. Quantum Electron.* **13**, 798 (2007).
- T. Taira, *Opt. Mater. Express* **1**, 1040 (2011).
- Y. Sato *et al.*, *Sci. Rep.* **7**, 10732 (2017).
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- S.W. Jolly *et al.*, *Nat. Commun.* **10**, 1 (2019).

1. Laser-Induced Damage Study of Bonded Material for a High-Brightness Laser System[1)]

We evaluated the laser-induced damage threshold (LIDT) of the interface between two identical YAG crystals, bonded by an inter-layer assisted surface activated bonding (il-SAB) method. The experimental results indicate slight damage threshold degradation for both single- and polycrystalline trivalent rear-earth (RE^{3+})-ion-doped YAG gain media in the sub-nanosecond pulse regime. Moreover, crystal annealing prior to damage testing could provide additional improvement for the laser damage threshold of the bulk and bonded interface.

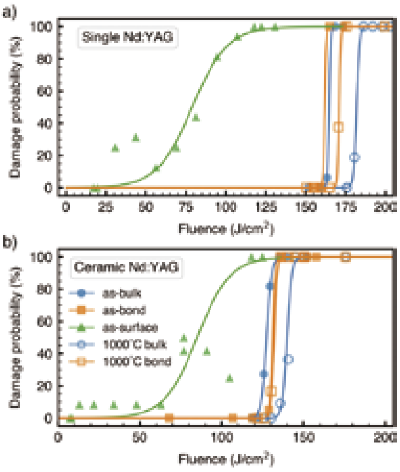

Figure 2. LIDT data for (a) single crystal and (b) ceramic Nd:YAG materials. Both experimental data (points) and fitting (lines) for surface (green), bulk (blue), and bonded interface (orange) are shown. Each data point on the graph represents 16 and 12 measurements for the single crystal and ceramic Nd:YAG, respectively.

2. Development of a Portable Laser Peening Device and Its Effect on the Fatigue Properties of HT780 Butt-Welded Joints[2)]

Laser peening (LP) is a well-established technique for introducing compressive residual stress (RS) near the surface of metal components, to improve their high-cycle fatigue properties. The authors have developed a compact LP device with a thumb-sized Nd:YAG microchip laser mounted on a collaborative robot arm. The device was applied to 9-mm-thick HT780 high-strength steel plate samples with irradiated pulse energies of 7.5–8.0 mJ, spot sizes of 0.42–0.58 mm and pulse densities of 100–1,600 pulses/mm^2. X-ray diffraction showed that the maximum compressive RS was over 500 MPa near the surface, and the LP effect reached a depth of approximately 0.1 mm from the surface. Butt-welded HT780 samples were laser-peened with a pulse energy of 7.7 mJ, spot size of 0.49 mm and pulse density of 800 pulses/mm^2. Then, the samples were subjected to a uniaxial fatigue test with a stress ratio of 0.1. The results showed that the fatigue strength at 107 cycles was improved by at least 50 MPa, comparable to the improvement attained by LP in a previous study with a pulse energy of 200 mJ from a conventional Nd:YAG laser.

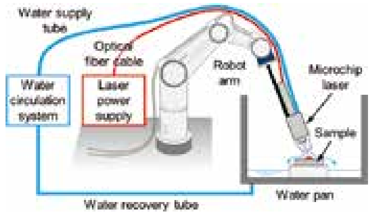

Figure 3. Configuration of the portable laser peening device with an Nd:YAG microchip laser.

3. >50 MW Peak Power, High Brightness Nd:YAG/Cr^{4+}:YAG Microchip Laser with Unstable Resonator[3)]

We demonstrated a flat-convex unstable cavity Nd:YAG/Cr^{4+}:YAG ceramic air-cooled microchip laser (MCL) generating a record 37.6 and 59.2 MW peak power pulses with an energy of 17.0 and 24.1 mJ and a width of 452 and 407 ps at 20 Hz by using a uniform power square and hexagon pump, respectively. For hexagon pump, the near field hexagon donut beam was changed in to a Bessel-like beam in far field, whose beam quality was estimated as 2nd moment M^2 of 7.67. The brightness scale of unstable resonator MCL was achieved up to 88.9 TW/(sr·cm^2) in contrast with flat-flat cavity MCL. However, the high intense center part of Bessel-like beam increased its brightness effectively more than 8 times, up to 736 TW/(sr·cm^2).

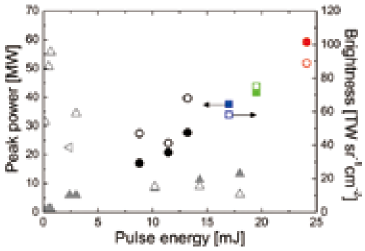

Figure 4. New record peak powers of 37.6, 41.7, and 52.9 MW of Nd:YAG/Cr^{4+}:YAG microchip laser (MCL) using uniform power pump. Successful brightness scale of unstable cavity MCL up to 88.9 TW/(sr·cm^2) in contrast to flat-flat cavity, promising further brightness scale up.

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* RIKEN SPring-8 Center
† IMS International Internship Program

RESEARCH FACILITIES

The Institute includes four research facilities, UVSOR Synchrotron Facility, Instrument Center, Equipment Development Center, and Research Center for Computational Science (Okazaki Research Facilities).

UVSOR Synchrotron Facility

KERA, Satoshi	Director, Professor
MATSUI, Fumihiko	Professor
KATOH, Masahiro	Project Professor
TANAKA, Kiyohisa	Associate Professor
TAIRA, Yoshitaka	Associate Professor
OHIGASHI, Takuji	Associate Professor (Cross Appt.)
KANEYASU, Tatsuo	Associate Professor (SAGA-LS)
IWAYAMA, Hiroshi	Assistant Professor
SUGITA, Kento	Assistant Professor
FUJIMOTO, Masaki	Assistant Professor (Nagoya Univ.)
MATSUDA, Hiroyuki	Post-Doctoral Fellow
SALEHI, Elham	Post-Doctoral Fellow
HAYASHI, Kenji	Engineer (Unit Leader)
NAKAMURA, Eiken	Chief Engineer
MAKITA,Seiji	Engineer
YAMAZAKI, Jun-ichiro	Chief Technician
SAKAI, Masahiro	Chief Technician
YANO, Takayuki	Chief Technician
OKANO, Yasuaki	Chief Technician
TESHIMA, Fumitsuna	Technician
KONDO, Naonori	Technician
YUZAWA, Hayato	Technician
OTA, Hiroshi	Technician
HORIGOME, Toshio	Technical Fellow
MINAKUCHI, Aki	Technical Fellow
MIZUKAWA, Tetsunori	Technical Fellow
SUGIMOTO, Yasunobu	Technical Fellow
ISHIHARA, Mayumi	Secretary
KAMO, Kyoko	Secretary

Outline of the UVSOR Synchrotron Facility

Since the first light in 1983, the UVSOR Synchrotron Facility has been successfully operated as one of the major synchrotron light sources in Japan. After the major upgrade of accelerators in 2003, UVSOR Synchrotron was renamed to UVSOR-II Synchrotron and became one of the world's brightest low energy synchrotron light sources. In 2012, it was upgraded again and has been renamed to be UVSOR-III Synchrotron. The brightness of the electron beam was increased further. Today, six undulators are installed in total, and the storage ring, that is *ca.* 53 meters in circumference, is regularly operated in the top-up mode, irrespective of multi bunches or single bunch.

The UVSOR accelerator complex consists of a 15 MeV injector LINAC, a 0.75 GeV booster synchrotron, and a 0.75 GeV storage ring. The magnet lattice of the storage ring consists of four extended double-bend cells with distributed dispersion function. The single bunch top-up operation (176 ns, 5.6 MHz) for time-resolved measurements or low current measurements is also conducted for two weeks per year.

Six undulators and eight bending magnets provide synchrotron radiation (SR). The bending magnet, its radius of 2.2 m, produces SR with the critical energy of 425 eV. There are eight bending magnet beamlines (Table. 1). Three of the six undulators are in-vacuum soft X-ray (SX) linear-polarized undulators (BL3U, BL4U, and BL6U) and the other three are vacuum/extreme ultraviolet (VUV/XUV or EUV) circular-polarized undulators (BL1U, BL5U, and BL7U). Two beamlines, BL1U and BL6U, are so-called "in-house beamlines," which are dedicated to strategic projects conducted by internal IMS groups in tight collaboration with domestic and foreign scientists. The BL1U can produce pulsed γ-ray radiation by laser Compton scattering technique. In 2022, it was developed by constructing a laser transport system to generate high-intense γ-ray beams. Other twelve beamlines are so-called "public beamlines," which are open to scientists from universities, governmental research institutes, public and private enterprises, and also to overseas scientists. After each development, the in-house beamline will be opened for use as a public beamline.

From the viewpoint of photon energies, we have one SX station equipped with a double-crystal monochromator, seven SX stations with a grazing incidence monochromator, three VUV stations with a normal incidence monochromator, two IR/THz stations equipped with Fourier transform interferometers and one beamline for light source development without any monochromators.

Table 1. List of beamlines at UVSOR-III Synchrotron.

Beamline	Optics	Energy Range	Targets	Techniques
BL1B	Martin-Puplett FT-FIR	0.5-30 meV	Solid	Reflection/Absorption
BL6B	Michelson FT-IR	4 meV-2.5 eV	Solid	Reflection/Absorption
BL7B	3-m normal incidence	1.2-25 eV	Solid	Reflection/Absorption
BL3B	2.5-m off-plane Eagle	1.7-31 eV	Solid	Reflection/Absorption
BL5B	Plane grating	6-600 eV	Solid	Calibration/Absorption
BL2B	18-m spherical grating (Dragon)	23-205 eV	Solid	Photoionization Photodissociation
BL4B	Varied-line-spacing plane grating (Monk-Gillieson)	25 eV-1 keV	Gas, Liq. Solid	Photoionization, XAS Photodissociation, XMCD
BL2A	Double crystal	585 eV-4 keV	Solid	Reflection/XAFS
BL1U	Tandem undulators/ Free electron laser	1.6-13.9 eV	Gas Solid	Laser Compton Scattering Orbital Momentum Light
BL7U	10-m normal incidence (modified Wadsworth)	6-40 eV	Solid	Photoemission
BL5U	Varied-line-spacing plane grating (Monk-Gillieson)	20-200 eV	Solid	ARPES Spin-resolved ARPES
BL6U	Variable-included-angle varied- line-spacing plane grating	40-700 eV	Solid	ARPES XAFS / XPD
BL4U	Varied-line-spacing plane grating (Monk-Gillieson)	50-700 eV	Gas, Liq. Solid	XAFS Microscopy (STXM)
BL3U	Varied-line-spacing plane grating (Monk-Gillieson)	60-800 eV	Gas, Liq. Solid	XAFS / Photoemission Photon-emission

Inter-University and International Collaboration Programs

A variety of molecular science and related subjects have been carried out at UVSOR Synchrotron Facility by IMS and external/overseas researchers. The cumulative total number of visiting researchers (person-days) per year tops > 4000, who come from > 60 different institutes. International collaborations are also pursued actively, and the number of visiting foreign researchers reaches ~70. UVSOR-III Synchrotron invites new/continuing research proposals twice a year. The proposals both for academic and public research (charge-free) and for private enterprises (charged) are acceptable. COVID-19 issue has a serious impact on user activity, the overseas activity was almost dropped especially. The fruits of the research activities using UVSOR-III Synchrotron are published as the UVSOR ACTIVITY REPORT annually.

Recent Developments

The UVSOR accelerators have been operated for 39 years. We have been upgrading and replacing the machine components, such as magnet power supplies or RF power amplifiers, to continue the stable operation. In these years, troubles occurred on some core components, such as the vacuum chambers and the magnets. We are carefully planning their replacements with short shutdown periods and under the limitation of the facility budget.

UVSOR has several ARPES undulator beamlines and users can choose proper beamline according to their purpose. We are putting effort into setting up state-of-the-art experimental stations that take advantage of our unique beamline performance. BL5U is an angle-resolved photoemission spectroscopy (ARPES) beamline with micro-focused beam (23×40 μm). By combining the ARPES analyzer with the super quick deflector scan mode, users can perform ARPES measurements on small samples or inhomogeneous samples without changing the sample position. At BL7U, high-energy resolution ARPES is available with extremely low energy of photons (6 eV~) using low-temperature 6-axis manipulator with sample temperature 4 K. In 2021, the latest version of ARPES analyzer has been installed so that users can easily perform a quick Fermi surface mapping. In BL6U, "photoelectron momentum microscope (PMM)" has been installed in February 2020.[1,2] PMM is a new concept device based on photoelectron spectroscopy and photoelectron microscopy techniques to visualize electronic states in real and reciprocal lattice space in selected small regions. It was upgraded to a double hemispherical analyzer with spin filter and spin rotator in May 2022.

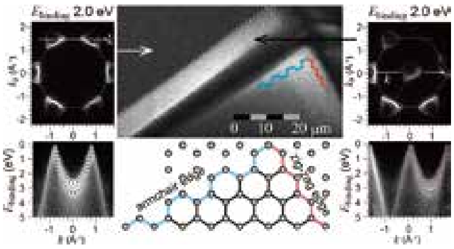

Figure 1. μm-photoelectron spectroscopy of graphite edge facet by PMM.

Reserch Highlights

At BL1U, new light sources such as coherent synchrotron radiation, free electron lasers, high-order harmonic generation, optical vortex and vector beams, and ultrashort pulsed gamma rays have been developed. As the energy of ultrashort pulsed gamma rays is 6.6 MeV, positrons are generated inside materials when they are irradiated. Positron annihilation spectroscopy is a powerful analytical tool for nondestructive measurement of atomic-scale defects. Positron annihilation spectroscopy using ultrashort pulsed gamma rays is available at BL1U.[3] In positron annihilation spectroscopy, the annihilation gamma rays produced when a positron annihilates are measured numerous times to determine the positron lifetime and the energy spread of the positron annihilation. Therefore, it is important to increase the counting rate of annihilation gamma rays in order to complete the measurement in a short time. To increase the counting rate of annihilation gamma rays, the intensity of ultrashort pulsed gamma rays should be increased. The intensity of gamma rays can be increased by colliding the electron beam and the laser in a focused state.

Until March 2021, gamma ray was generated using an optical window that allowed the laser to be injected from the vertical direction. The laser size at this time was 1 mm. The other side of the incident window is not a window but stainless steel, which generates gas when the laser hits it. The laser size could not be focused to a smaller size because of the problem of background bremsstrahlung gamma rays due to the increased gas generation when the laser is focused.

In April 2021, a new vacuum chamber for laser injection, shown in Figure 2, was installed in the electron storage ring. This vacuum chamber has optical windows at each end of the horizontal and vertical directions, which allows the laser to collide with the electron beam in a focused state. The intensity of the gamma rays can be improved as the laser can be injected from the horizontal direction. During installation of the vacuum chamber, 1/4 circumference of the electron storage ring was opened to the atmosphere.

The laser size at the electron beam interaction point with the new vacuum chamber is 15 μm at full width at half maximum. The gamma-ray intensity was increased by a factor of 40 due to the smaller laser size and the horizontal injection of the laser. Using this ultrashort pulse gamma-ray source, experiments such as analysis of atomic-scale defects in scintillators and photocatalysts, in-situ measurement of defect formation in iron-based materials under stress loading, and magnetic Compton scattering are underway.

Figure 2. A new vacuum chamber for laser injection installed in the electron storage ring.

References

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Instrument Center

YOKOYAMA, Toshihiko	Director, Professor
SUZUKI, Toshiyasu	Team Leader
NAKAMURA, Toshikazu	Team Leader
MINATO, Taketoshi	Senior Researcher
TAKAYAMA, Takashi	Engineer
FUJIWARA, Motoyasu	Chief Technician
OKANO, Yoshinori	Technician
UEDA, Tadashi	Technician
ASADA, Mizue	Technician
URUICHI, Mikio	Technician
MIYAJIMA, Mizuki	Technician
ISHIYAMA, Osamu	Project Manager
NAKAMOTO, Keiichi	Project Manager
OTA, Yasuhito	Project Manager
KAKU, Mie	Project Manager
OHARA, Mika	Research Fellow
IKI, Shinako	Technical Fellow
NAGAO, Haruyo	Technical Fellow
FUJIKAWA, Kiyoe	Technical Fellow
TOYAMA, Aya	Technical Fellow
FUNAKI, Yumiko	Secretary
HYODO, Yumiko	Secretary
ISHIKAWA, Azusa	Secretary
UCHIDA, Mariko	Secretary
KURITA, Yoshiko	Secretary

Instrument Center was organized in April of 2007 by integrating the general-purpose and state-of-the-art facilities of Research Center for Molecular Scale Nanoscience and Laser Research Center for Molecular Science. The mission of Instrument Center is to support the in-house and external researchers in the field of molecular science, who intend to conduct their researches by utilizing general-purpose and state-of-the-art instruments. The staffs of Instrument Center maintain the best conditions of the measurement apparatuses, and provide consultation for how to use them.

The main instruments the Center now maintains in Yamate campus are: Nuclear magnetic resonance (NMR) spectrometers (JNM-ECA 600 for solutions, JNM-ECS400 for solutions and Bruker AVANCE800 Cryoprobe for solutions), matrix assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometer (microflex LRF, Bruker Daltonics), powder X-ray diffractometer (Rigaku RINT-Ultima III), molecular structure analysis using crystalline sponge method (Rigaku SuperNova), circular dichroism (CD) spectrometer (JASCO J-1500), differential scanning calorimeter (MicroCal VP-DSC), isothermal titration calorimeter (MicroCal PEAQ-iTC & iTC200), solid-state calorimeter (Rigaku DSC8231/TG-DTA8122), scanning electron microscope (SEM; JEOL JSM-6700F), and elemental analyzer (J-Science Lab Micro Corder JM10).

In the Myodaiji campus, the following instruments are installed: Electron spin resonance (ESR) spectrometers (Bruker E580 installed in 2022, E680, E500, EMX Plus, ns pulsed laser for time resolved experiments), NMR spectrometer (Bruker AVANCE600 for solids), superconducting quantum interference devices (SQUID; Quantum Design MPMS-7 and MPMS-XL7), solution X-ray diffractometer (Rigaku NANO-Viewer), single-crystal X-ray diffractometers (Rigaku Mercury CCD-1, CCD-2, RAXIS IV, and Rigaku HyPix-AFC), *operando* multipurpose x-ray diffraction for powder and thin films (Panalytical Empyrean), thermal analysis instruments (Rigaku DSC8231/TG-DTA8122), fluorescence spectrometer (SPEX Fluorolog), UV-VIS-NIR spectrometer (Shimadzu UV- 3600Plus), Absolute PL quantum yield measurement (Hamamatsu Photonics Quantaurus-QY C11347-01), Raman microscope (Renishaw INVIA REFLEX 532), picosecond tunable laser system (Spectra Physics Tsunami/Quantronix Titan/Light Conversion TOPAS), low vacuum analytical SEM (Hitachi SU6600), field emission transmission electron microscope (JEOL JEM-2100F), angle resolved ultraviolet photoelectron spectroscopy (ARUPS) for functional band structures (Scienta-Omicron DA30), and FTIR spectrometer (Bruker IFS 66v/S), two sets of *operando* scanning probe microscopes (Bruker Dimension XR Icon Nanoelectrical & Nanoelectrochemical), and electron spectrometers for chemical analysis (ESCA) equipment (Scienta-Omicron, R4000L1).

In the fiscal year of 2021, Instrument Center accepted 98 applications from outside and the total user time amounted 2,563 days for outside and 1,974 days for in-house with 31 equipments. Instrument Center also maintains helium liquefiers in the both campus and provides liquid helium to users (43,765 L/year). Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute (37,294 L/year).

Instrument Center also organizes the Inter-University Network for Common Utilization of Research Equipments, the Molecule and Material Synthesis Platform in the Nanotechnology Platform Program (FY2012–2021), and the ARIM (Advanced Research Infrastructure for Materials and Nanotechnology in Japan) Program (FY2021–2030) supported by Ministry of Education, Culture, Sports, Science and Technology. These special programs are described in the other chapter of the booklet.

Equipment Development Center

YAMAMOTO, Hiroshi	Director
KONDO, Takuhiko	Chief Engineer (Unit Leader)
TOYODA, Tomonori	Engineer
MATSUO, Junichi	Chief Technician
TAKADA, Noriko	Technician
KIMURA, Sachiyo	Technician
KIKUCHI, Takuro	Technician
KIMURA, Kazunori	Technician
SAWADA, Toshihiro	Technical Fellow
ISHIKAWA, Akiko	Technical Fellow
MIZUTANI, Nobuo	Technical Fellow
SUGANUMA, Kouji	Technical Fellow
INAGAKI, Itsuko	Secretary

Research and development of novel instruments demanded in the forefront of molecular science, including their design and fabrication, are the missions of this center. Technical staffs in the three work sections, mechanics, electronics and lithography ones, are engaged in developing state-of-the-art experimental instruments in collaboration with scientists. We expanded our service to other universities and research institutes since 2005, to contribute to the molecular science community and to improve the technology level of the center staffs. A few selected examples of our recent developments are described below.

Machining with High Accuracy

Researchers need new equipment to realize advanced experimental setups designed for their novel scientific achievements. We, the Equipment Development Center (EDC), receive various requests from researchers. For example, there is a plastic pipe shaped as shown in Figure1. This product was made by a precision lathe owned by the EDC shown in Figure 2, the process of which is full of ingenuity by the staffs with the knowledge on the materials properties. (Figure 3)

The pipe is designed to connect to a custom-made equipment as a gas tube adapter. A commercial product cannot be connected to the equipment due to a limitation in space. Furthermore, tolerance is very strict and needs to be less than 5/1000mm, because a high-pressure gas may blow the tube away from the equipment.

Such strict requirements are difficult to be handled by outsourcing. Even if it is possible, the cost is unreasonably high, or the product may not be available on schedule. We respond to such request from researchers with quick delivery, meticulous work, and less costs in order to contribute to their experiments which will lead to scientific advancements.

Figure 1. Plastic Pipe.

Figure 2. Precision Lathe.

Figure 3. Machining a pipe.

Fabrication of a Signal Splitter

In order to synchronize an AFM system with lock-in amplifier, it is necessary to amplify the system signal whose frequency and amplitude are in the range from 200 kHz to 250 kHz and about 100 mVp-p, respectively, by about 10 times. In addition, when the input signal to the lock-in amplifier has jitter, synchronization cannot be achieved. Thus it is required to remove unnecessary frequency components and amplify the signal with high precision. It is also required to split the signal into two circuits before the amplification for the sake of simultaneous topographic observation. Moreover, an current output which can drive the 50Ω input impedance of the measurement system is mandatory.

We have developed a Signal Splitter shown in Figure 4; it buffers the signal detected by AFM with high input impedance by JFET type operational amplifier (Analog Devices AD825ARZ), and cuts unnecessary frequency components off by active high-pass filter with a cutoff frequency of 100 kHz. Then the signal is amplified by 6 times with another operational amplifier (Analog Devices AD8639ARZ), which allows driving of 50Ω impedance with the help of current feedback operational amplifier (Texas Instruments THS3001CD).

This instrument has enabled vibrational spectroscopy of single proteins and ultrafast nano-spectroscopy.

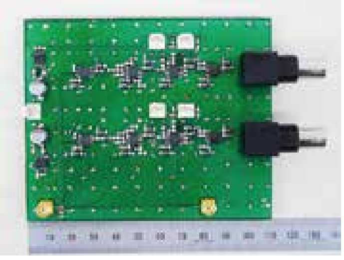


Figure 4. The Circuit Board of the Signal Splitter.

Award

TOYODA, Tomonori; The Chemical Society of Japan Award for Technical Achievements for 2021 (2022).

Research Center for Computational Science (Okazaki Research Facilities)

EHARA, Masahiro	Director, Professor
SAITO, Shinji	Professor
OKUMURA, Hisashi	Associate Professor
OKAZAKI, Kei-ichi	Associate Professor
OONO, Hitoshi	Associate Professor
UCHIYAMA, Ikuo	Associate Professor
OHNUKI, Jun	Assistant Professor
ISHIDA, Tateki	Research Assistant
IWAHASHI, Kensuke	Chief Engineer (Unit Leader)
MIZUTANI, Fumiyasu	Engineer
NAITO, Shigeki	Chief Technician
KAMIYA, Motoshi	Chief Technician
SAWA, Masataka	Technician
NAGAYA, Takakazu	Technician
KINOSHITA, Takamasa	Technician
YAZAKI, Toshiko	Technical Fellow
UNO, Akiko	Technical Fellow
KONDO, Noriko	Secretary
URANO, Hiroko	Secretary

Research Center for Computational Science provides state-of-the-art computational resources to academic researchers in molecular science and related fields, *e.g.* solid state physics, biophysics, basic biology, and physiology. Our systems consist of NEC LX (406Rh-2, 110-Rh1, 108Th-4G; since Oct. 2017). The NEC LX 406Rh-2 and 110-Rh1 combined system, named “Molecular Simulator,” is ranked 448th position in the TOP500 supercomputer list in June 2022. These massive computer resources have been used for various kinds of large-scale calculations, for example accurate electronic structure calculations of molecular systems and conformation searches using non-Boltzmann ensemble methods. We also provide about 30 application programs to the users: Gaussian, GAMESS, Molpro, AMBER, Gromacs, and so on. In particular, we have implemented some original programs developed by researchers in Japan to provide them to the users. The supercomputer systems had been used by 1,175 researchers from 278 groups in fiscal year 2021. Some of the computational resources are provided to the following projects: Program for Promoting Research on the Supercomputer Fugaku, Professional development Consortium for Computational Materials Scientists (PCoMS), and Elementary Strategy Initiative to Form a Core Research Center.

For fostering young generation, we organize the schools of quantum chemistry and molecular dynamics simulation every year. In the fiscal year 2021, the numbers of registered attendants of these schools were 482 and 377, respectively. We also organize the RCCS supercomputer workshop focusing on the new trends of computational chemistry for the purpose of the research exchange and human resource development. In the fiscal year 2021, we organized the workshop under the title, “Computational science of structure, function and design of biomolecules.”

In cooperation with Institute for Materials Research, Tohoku University, Institute for Solid State Physics, University of Tokyo, and Nanoscience Design Center, Osaka University, we established the Computational Materials Science Forum (CMSF) to promote the cutting-edge computational materials science technology of Japan, to create world-class results, and to realize the social implementation of simulation technology and materials information science technology.

We also offer Quantum Chemistry Literature Database (QCLDB; http://qcldb2.ims.ac.jp/), Force Constant Database (FCDB; http://fcdb.ims.ac.jp/), and Segmented Gaussian Basis Set (SGBS; http://sapporo.center.ims.ac.jp/sapporo/) services. The latest release, QCLDB II Release 2016, containing 139,657 data of quantum chemical studies is available for the registered users. FCDB provides force constants of molecules collected from literature. SGBS service provides basis sets for atoms which efficiently incorporate valence and core electron correlations (also known as Sapporo basis sets) in various quantum chemistry package formats. Further details about the hardware, software, and the other services are available on our website (English: https://ccportal.ims.ac.jp/en/, Japanese: https://ccportal.ims.ac.jp/).

The center is jointly managed with National Institute for Physiological Sciences and National Institute for Basic Biology (both in the same campus).

Figure 1. NEC LX.

Safety Office

TANAKA, Shoji	Director
TOMURA, Masaaki	Research Assistant
SHIGEMASA, Eiji	Technical Associate
UEDA, Tadashi	Technical Associate
TAKAYAMA, Takashi	Technical Associate
SAKAI, Masahiro	Technical Associate
MAKITA, Seiji	Technical Associate
MATSUO, Junichi	Technical Associate
KIKUCHI, Takuro	Technical Associate
TSURUTA, Yumiko	Secretary
ASAKURA, Yukiko	Secretary

The Safety Office was established in April 2004. The mission of the Office is to play a principal role in the institute to secure the safety and health of the staffs by achieving a comfortable workplace environment, and improvement of the working conditions. In concrete terms, it carries out planning, work instructions, fact-findings, and other services for safety and health in the institute. The Office is composed of the following staffs: The Director of the Office, Safety-and-Health Administrators, Safety Office Personnel, Operational Chiefs and other staff members appointed by the Director General.

The Safety-and-Health Administrators patrol the laboratories in the institute once every week, and check whether the laboratory condition is kept sufficiently safe and comfortable to conduct researches. The Office also edits the safety manuals and gives safety training courses, for Japanese and foreign researchers.

SUPPORTING STAFF

Research Enhancement Strategy Office

OKAMOTO, Hiromi	Head
YAMAMOTO, Hiroshi	Professor (in charge of Foreign Affairs)
AKIYAMA, Shuji	Professor (in charge of Personnel Affairs)
IINO, Ryota	Professor (in charge of Public Affairs)
ISHIZAKI, Akihito	Professor (in charge of Facilities/Buildings and Foreign Affairs)
KATAYANAGI, Hideki	Research Assistant (in charge of Public Affairs)
SHIGEMASA, Eiji	Technical Associate (in charge of General Affairs)
NAKAMURA, Toshikazu	Team Leader, Instrument Center
FUKUI, Yutaka	URA (Administrative Associate, Assistant to Head)
FUJITA, Hiromasa	URA (Administrative Associate, Assistant to Head)
HARADA, Miyuki	URA (Technical Associate)
KAMETAKA, Ai	URA (Administrative Associate)
NAGASONO, Hisayo	URA (Administrative Associate)
MASE, Toshiaki	Senior Specialist
NAKAMURA, Rie	Technical Fellow
OHTA, Minori	Secretary
SUZUKI, Satomi	Secretary
SUGIYAMA, Kayoko	Secretary
SHIMODE, Ayako	Secretary
YOKOTA, Mitsuyo	Secretary

In 2013, Research Enhancement Strategy Office was established in each research institute in NINS by support of the MEXT University Research Enhancement Project of 10 years 2013 to 2023. In this office, university research administrators (URA) and supporting staff members realize several strategic plans for the enhancement of international and inter-university collaborations, public relations, and research activities of young, female, and foreign scientists in collaboration with Head Office in NINS.

Technical and Engineering Department

SHIGEMASA, Eiji	Head of Department
UCHIYAMA, Koichi	Chief Technician
TANAKA, Kei	Secretary

Secretary for Director General

NOGAWA, Kyoko	Secretary

Information Office

TSURUTA, Yumiko	Secretary
ASAKURA, Yukiko	Secretary

All technical staff at IMS belong to the Technical and Engineering Department (TED). IMS offers collaborators a unique array of support services. A group of engineers and technicians technically support not only scientists outside from IMS but also inhouse scientists.

The technical division of IMS (TD-IMS) was initially organized in 1975 as the first organization of technical staff in Japan to support both in-house and outside scientists technically. Over time, the number of personnel with high levels of technical skills in TD-IMS increased dramatically, and the division outgrew its organization system. Consequently, the TD-IMS has been reorganized as the “Technical and Engineering Department” since April 1st 2021.

The TED operates directly under the director general of IMS, and consists of four Units (Optical Engineering Unit, Computing and Information Technology Unit, Equipment Development Unit, and Instrumental Analysis Unit), as well as staff members taking charge of safety, facilities, and publicity activities. Each unit has a unit leader, who manages the unit staff.

In addition, several members belonging to the TED support administrative activities in IMS by managing the Safety Office, the Public Affairs Office, the Archives, and the Information Office.

The annual meeting for technical staff of research institutes and universities in Japan, was organized in 1975 and since then it has been regularly held every year. We aim toward higher technology and knowledge exchange concerning various technical subjects related to our technology and engineering. Our best endeavors have been, and will be made, to promote the advanced research of IMS.

Special Research Projects

IMS has special research projects supported by national funds. Four projects in progress are:

(a) MEXT Nanotechnology Platform Program
Platform of Molecule and Material Synthesis
(b) Inter-University Network for Common Utilization of Research Equipments
(c) MEXT Program Advanced Research Infrastructure for Materials and Nanotechnology in Japan:
Spoke Organization in Advanced Material Circulation Techniques
(d) MEXT Project for Promoting Public Utilization of Advanced Research Infrastructure (support for formation of advanced research platforms): NMR PLATFORM

These four projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

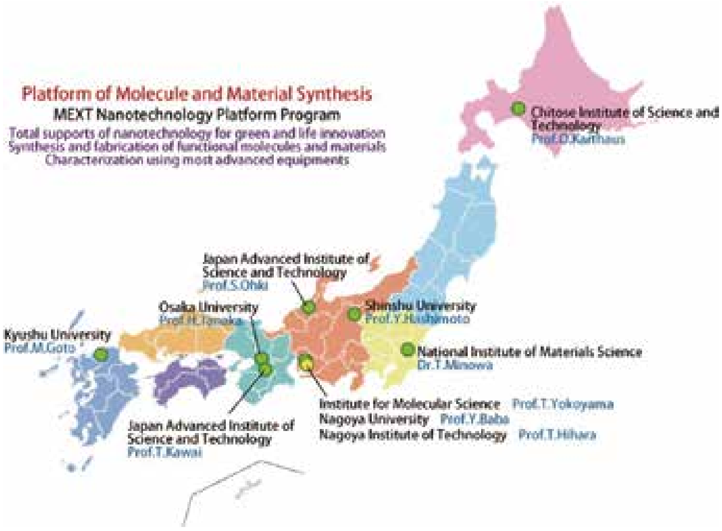
(a) MEXT Nanotechnology Platform Program Platform of Molecule and Material Synthesis

Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT) was conducted from July 2012 to March 2022 in order to promote public usage of various nanotechnology facilities. This program consisted of three platforms of nanostructure analysis, nanoprocessing, and molecule and material synthesis, together with the management center of the platforms. About ten organizations from all over Japan took part in each platform. IMS conducted a representative core organization of the Molecule and Material Synthesis Platform. All the organizations in this platform are shown in Figure. In this platform, to promote green and life innovation researches using nanotechnology related techniques not only for universities and government institutes but also for private companies, we opened various kinds of our facilities with total supports including molecular synthesis, materials fabrications, characterization, data analysis and scientific discussion. We encouraged applications not only to each element, but to combined usage of several supporting elements for biotechnology and green chemistry. In IMS, the number of accepted proposals in FY2021 amounted 125 (116 non-proprietary and 9 proprietary proposals, excluding inhouse applications from IMS) and the total number of days used for the supports is 2,969 (2,720 days for non-proprietary proposals and 38 days for proprietary ones).

List of Supports in IMS (FY2021)

Supporting Element		Responsible Persons	Charging Persons
Platform Management		T. Yokoyama	M. Ohara, K. Nakamoto
Organization Management in IMS			Y. Hyodo, Y. Funaki
UVSOR Synchrotron Radiation	X-Ray Magnetic Circular Dichroism	T. Yokoyama	T. Koitaya, K. Yamamoto, O. Ishiyama
Microstructure Fabrication	Maskless Lithography with Step Gauge	H. Yamamoto	T. Kondo, N. Takada, S. Kimura, T. Kikuchi, N. Mizutani, A. Ishikawa
	3D Optical Surface Profiler		
Equipment Development	Machine Shop		T. Kondo, T. Toyota, J. Mathuo
Electron Microscopy	Field Emission Scanning Electron Microscopy	T. Yokoyama	O. Ishiyama, A. Toyama, T. Ueda
	Low Vacuum Analytical Scanning Electron Microscopy		
	Field Emission Transmission Electron Microscope		S. Iki, T. Ueda, M. Uruichi
Scanning Probe Microscope	Scanning Probe Microscope		T. Minato, T. Ueda, T. Sugimoto
X-rays	Single Crystal X-Ray Diffractometer		Y. Okano
	Low Temperature Single Crystal X-Ray Diffractometer for Microcrystals		
	Molecular Structure Analysis using Crystalline Sponge Method		M. Fujita, T. Mitsuhashi
	Powder X-Ray Diffractometer		M. Fujiwara, M. Miyajima
	Operando Multi-Purpose X-Ray Diffraction		G. Kobayashi, F. Takeiri, M. Fujiwara, M. Miyajima
	Small Angle X-Ray Scattering for Solutions	S. Akiyama	A. Mukaiyama

Electron Spectroscopy	Angle Resolved Ultraviolet Photoelectron Spectroscopy for Functional Band Structures	S. Kera, K. Tanaka	
	X-Ray Photoelectron Spectroscopy	T. Yokoyama	T. Koitaya, K. Yamamoto, O. Ishiyama
Electron Spin Resonance	Pulsed High Field ESR	T. Yokoyama, T. Nakamura	M. Asada, M. Fujiwara, S. Iki, T. Ueda, M. Miyajima
	X-Band CW ESR		
	X, Q-Band CW ESR		
SQUID	Superconducting Quantum Interference Device		M. Asada, M. Fujiwara, S. Iki, M. Miyajima
Thermal Analysis	Differential Scanning Calorimeter (Solutions)	T. Yokoyama	M. Uruichi, H. Nagao
	Isothermal Titration Calorimeter (Solutions)		
	Calorimeter for solids		M. Fujiwara, M. Miyajima
Mass Spectrometer	Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer		M. Uruichi, K. Fujikawa
Spectroscopy	Microscopic Raman Spectroscopy		M. Uruichi
	Fourier Transform Far Infrared Spectroscopy		
	Fluorescence Spectroscopy		T. Ueda
	Ultraviolet & Visible Absorption Spectroscopy		
	Absolute PL Quantum Yield Measurement		
	Circular Dichroism		M. Uruichi, K. Fujikawa
Lasers	Picosecond Laser		T. Ueda
High Field NMR	800 MHz Solutions, Cryostat Probe	K. Kato	M. Yagi, S. Yanaka, Y. Isono
	600 MHz Solids	K. Nishimura	
	600 MHz Solutions	T. Yokoyama	M. Uruichi, H. Nagao
Functional Molecular Synthesis and Molecular Device Fabrication	Organic Thin Film Solar Cells	M. Hiramoto	S. Izawa
	Organic Field Effect Transistors	H. Yamamoto	D. Hirobe, T. Sato
	Functional Organic Synthesis	N. Momiyama, T. Suzuki	N. Ohtsuka, T. Fujinami
	Large Scale Quantum Mechanical Calculations	M. Ehara	
	Magnetic Thin Films	T. Yokoyama	T. Koitaya, K.Yamamoto
	Metal Complexes	T. Kusamoto	R. Matsuoka
	Inorganic Materials	G. Kobayashi	F. Takeiri
	Biomolecule System	S. Akiyama	A. Mukaiyama, Y. Furuike
	Supplementary Apparatus in Instrument Center	T. Yokoyama	



(b) Inter-University Network for Common Utilization of Research Equipments

It is highly important to improve instrumental supporting environments for research and education in the field of science and engineering. Nowadays, advanced research instruments are indispensable for conducting researches and educations with high standard quality. To install such sophisticated instruments, tremendous amount of budgets would be necessary. In 2007, for constructing a national-wide network to provide easy accesses to high-level equipments to researchers and students in universities all over Japan, the five-year project "Functioning of Inter-University Network for Efficient Utilization of Chemical Research Equipments" was launched. The network maintains an internet machine-time reservation and charging system by the help of equipment managers and accounting sections in each university. 72 national universities as well as Institute for Molecular Science (total 73 organizations) all over Japan have been participating in the network. From 2009, the registered equipments are open to the researchers and students of all the public (prefectural *etc.*) and private universities and private companies. Since 2010, the project has been renamed "Inter-University Network for Common Utilization of Research Equipments" still keeping the original strategy and stable functioning. Since 2018, the institutions that provide research facilities are open to public and private universities. Currently, the network is organized by 78 organizations. The number of registered users amounts to 16,000 in 550 universities/institutions/companies covering over 4,300 laboratories in Japan (July, 2022). Network usage reaches about 170,000 times a year, and the number continues to grow. Moreover, we have actively provided various opportunities where technical staffs and users can improve their technical skills and frankly communicate with each other.

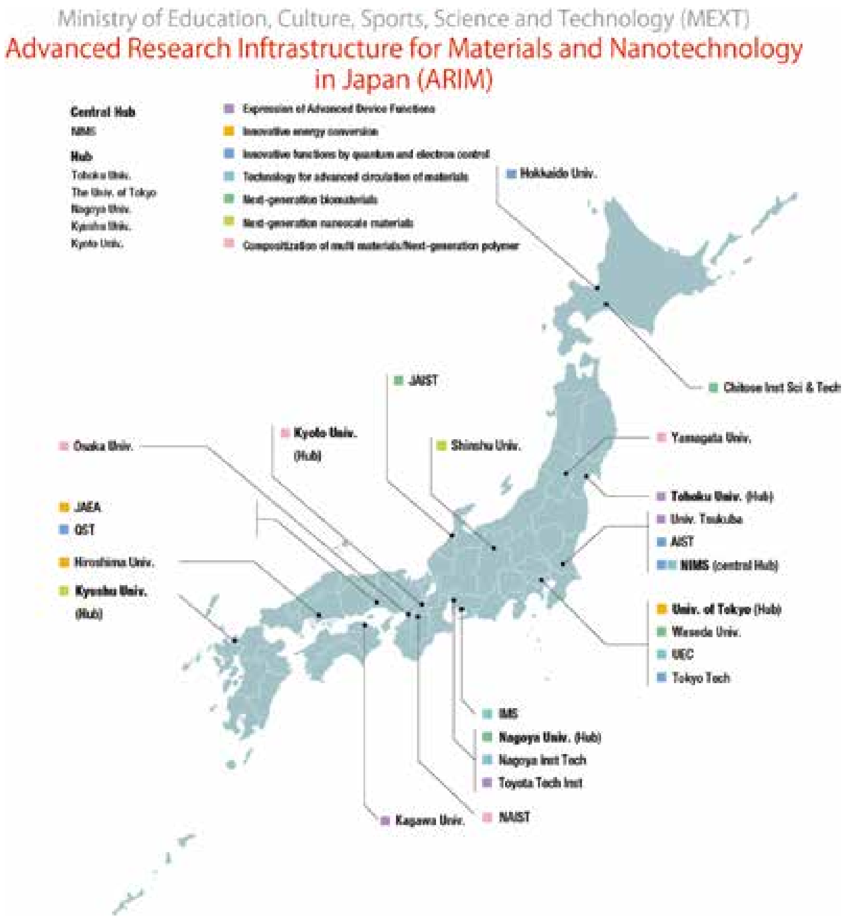
(c) MEXT Program Advanced Research Infrastructure for Materials and Nanotechnology in Japan: Spoke Organization in Advanced Material Circulation Techniques

Since 2021, ARIM (Advanced Research Infrastructure for Materials and Nanotechnology in Japan) program supported by MEXT (Ministry of Education, Culture, Sports, Science and Technology) has been conducted, succeeding to MEXT Nanotechnology Platform program that was completed in March, 2022. In this new program, seven "key technology domains" are set. Each key technology domain team consist of one hub organization and several spoke organizations, with the center hub of National Institute of Materials Science (NIMS). The hub & spoke networks for collecting, accumulating, and structuring research data that are created from observation, measurement, synthesis and fabrication equipment and facilities, were launched in order to strengthen AI-driven materials & device R&D using informatics techniques. IMS belongs to one of the key technology domains of "Technology for advanced circulation of materials" lead by the NIMS hub, together with the spoke organizations of Nagoya Institute of Technology and The University of Electro-Communications. Domestic and international equipment sharing is the most important purpose in this program, as in the Nanotechnology Platform program. Moreover, users and staffs are requested to provide experimentally obtained data to the Data Platform Center (DPC) that are being constructed in NIMS. Accumulated structured data will be shared through the NIMS DPC. In addition, we will contribute to strengthening material innovation force by building a "Material DX Platform" in collaboration with the Materials Data Creation and Utilization R&D Project. In this program, three areas of shared methodology are set to promote cooperation across the seven key technology domains. IMS also acts as a representative organization for the cross-sectional technological area concerning the material synthesis process to promote technological cooperation among all the participating organizations. Human resource development is also an important aim in this program and IMS regularly conducts training sessions with "EQ-NET" to upskilling of the technical staffs engaged in this program. In IMS, the mission for the ARIM program is mainly organized by Instrument Center, supported by Research Center for Computational Science in data storage and transfer to NIMS DPC. Because in 2021 equipment sharing was conducted through the Nanotechnology Platform program, this year FY2022 is the first year in this program, and equipment sharing is being conducted as previously, while the data accumulation mission is progressively in preparation. Through this program, a new electron spin resonance (ESR) system was installed in IMS last year, and also a new superconducting quantum interference device (SQUID) magnetometer will be introduced at the end of FY2022. We hope that this program will successfully be performed and equipment sharing and data sharing will be accelerated.

List of Equipment Supports in IMS Spoke (FY2022)

Supporting Element	Responsible Persons	Charging Persons
Organization Management in IMS Spoke	T. Yokoyama	T. Nakamura, M. Ehara, K. Iwahashi, T. Suzuki, K. Nakamoto, Y. Ota, M. Kaku, Y. Funaki, Y. Hyodo
Organization Management in Cross-Sectional Technological Area of Material Synthesis	T. Yokoyama	Y. Ota, K. Nakamoto, M. Kaku, Y. Kurita, A. Ishikawa

UVSOR Synchrotron Radiation	X-Ray Magnetic Circular Dichroism	T. Yokoyama	T. Koitaya, K. Yamamoto, O. Ishiyama
Microstructure Fabrication	Maskless Lithography with Step Gauge	H. Yamamoto	T. Kondo, T. Kikuchi, S. Kimura, N. Takada, A. Ishikawa
	3D Optical Surface Profiler		
	Electron Beam Lithgraphy		
Electron Microscopy	Field Emission Scanning Electron Microscopy	T. Yokoyama	O. Ishiyama
	Low Vacuum Analytical Scanning Electron Microscopy		
	Field Emission Transmission Electron Microscope		S. Iki, T. Ueda, M. Uruichi
X-rays	Single Crystal X-Ray Diffractometer		Y. Okano
	Low Temperature Single Crystal X-Ray Diffractometer for Microcrystals		
	Powder X-Ray Diffractometer		M. Fujiwara, M. Miyajima
	Operando Multi-Purpose X-Ray Diffraction		G. Kobayashi, F. Takeiri, M. Fujiwara, M. Miyajima
	Small Angle X-Ray Scattering for Solutions	S. Akiyama	A. Mukaiyama, Y. Furuike
	Molecular Structure Analysis using Crystalline Sponge Method	M. Fujita	T. Mitsuhashi, T. Yokoyama
Electron Spectroscopy	X-Ray Photoelectron Spectroscopy	T. Yokoyama	T. Koitaya, S. Iki, K. Yamamoto, O. Ishiyama
	Angle Resolved Ultraviolet Photoelectron Spectroscopy for Functional Band Structures	S. Kera, K. Tanaka	K. Fukutani
Electron Spin Resonance	Pulsed High Field ESR	T. Yokoyama, T. Nakamura	M. Asada, M. Fujiwara, M. Miyajima, S. Iki, T. Ueda
	X-Band CW ESR		
	X, Q-Band CW ESR		
	Pulsed ESR		
SQUID	Superconducting Quantum Interference Device		M. Asada, M. Fujiwara, M. Miyajima, S. Iki
Thermal Analysis	Differential Scanning Calorimeter (Solutions)	T. Yokoyama	H. Nagao, M. Uruichi
	Isothermal Titration Calorimeter (Solutions)		
	Calorimeter for solids		M. Fujiwara, M. Miyajima
Mass Spectrometer	Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer		M. Uruichi, K. Fujikawa
Spectroscopy	Microscopic Raman Spectroscopy		M. Uruichi, K. Fujikawa
	Fourier Transform Far Infrared Spectroscopy		
	Fluorescence Spectroscopy		T. Ueda
	Ultraviolet & Visible Absorption Spectroscopy		
	Absolute Photoluminescence Quantum Yield Spectrometer		
	Circular Dichroism		T. Mizukawa, M. Uruichi, K. Fujikawa
Lasers	Picosecond Laser		T. Ueda
High Field NMR	600 MHz Solids	K. Nishimura	
	600 MHz Solutions	T. Yokoyama	T. Mizukawa, M. Uruichi, H. Nagao
Functional Molecular Synthesis and Molecular Device Fabrication	Organic Field Effect Transistors	H. Yamamoto	T. Sato
	Organic Synthesis DX	T. Suzuki	N. Momiyama, N. Ohtsuka
	Large Scale Quantum Mechanical Calculations	M. Ehara	Y. Kanazawa
	Magnetic Thin Films	T. Yokoyama	T. Koitaya, K.Yamamoto
	Metal Complexes	T. Kusamoto	R. Matsuoka
	Supplementary Apparatus in Instrument Center	T. Yokoyama	



(d) MEXT Project for Promoting Public Utilization of Advanced Research Infrastructure (support for formation of advanced research platforms): NMR PLATFORM

MEXT has been working on "Project for Promoting Public Utilization of Advanced Research Infrastructure (support for formation of advanced research platforms)" to maintain and advance the world's leading R&D infrastructure by forming platforms for shared use to construct a network of research facilities/equipment. The objective is to contribute to the sustainable maintenance and improvement of R&D infrastructures in Japan by forming a nationwide advanced research platforms for all researchers.

In this context, the NMR PLATFORM is based on a network of advanced NMR facilities that can be shared by industry, academia, and government. Under this platform, research institutions that have cutting-edge NMR research facilities and knowledge work closely to provide opportunities for researchers from diverse disciplines and organizations around the nation to use their facilities. Furthermore, the objective is to establish a system that contributes to the promotion of R&D and the creation of innovation throughout Japan. The NMR PLATFORM is conducted by RIKEN, the representative organization, eight universities or research institutes, all of which have established an advanced NMR research infrastructure, and four manufacturers of related NMR technologies and products.

IMS began participating in NMR PLATFORM in FY2021, aiming to enhance overall scientific and technological activities by providing an 800-MHz solution NMR spectrometer for a wide range of uses in industry and academia. In addition, the project is developing initiatives to support researchers in various fields at universities and research institutes through the shared use of NMR equipment. ExCELLS has been participating in this project on behalf of IMS since FY2022.

Joint Studies Programs

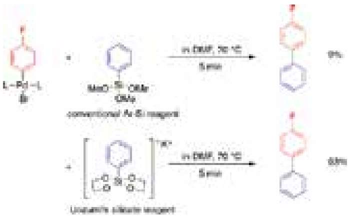
As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

(a) *Operando* Structural Studies on the Reacting Species of the Cross-Coupling Catalysis

FUJIKAWA, Shigenori (*Kyushu Univ.*)
TAKAYA, Hikaru (*Teikyo Univ. Sci. and IMS (concurrent)*)
NAGASAKA, Masanari (*IMS*)
OKUMURA, Shintaro (*IMS*)
UOZUMI, Yasuhiro (*IMS*)

The palladium-catalyzed cross-coupling reactions have been recognized as the most powerful synthetic means of carbon–carbon bond formation. Coupling of aryl halides and organosilicon reagents, the so-called Hiyama coupling, is one of the representatives. Recently, Uozumi at IMS developed aryl silicate reagents which exhibited remarkably high reactivity toward the Hiyama coupling with aryl halides (Scheme 1). These observations prompted us to the joint project that examines the *operando* structural studies on the aryl silicates as well as conventional aryl silyl reagents under the actual coupling reaction conditions by *in situ* NEXAFS measurements. Figure 1 shows the carbon K-edge NEXAFS spectrum of 100 mM trimethoxy(phenyl)silane (Ph-Si(OMe)$_3$) in tetrahydrofuran (THF) measured at BL3U of UVSOR-III Synchrotron (by Okumura, Nagasaka, Uozumi). The C=C π* peak of phenyl groups in Ph-Si(OMe)$_3$ is observed even in organic solvent containing carbon atoms since the peaks of THF exist at the higher energy side. We have investigated the C–Si bond length of several organosilicon compounds by C K-edge NEXAFS experiments and inner-shell quantum chemical calculations and have discussed the relation of the reaction mechanism of Hiyama coupling reaction. This project also aims to achieve the Si L-edge NEXAFS measurements of organosilicon compounds under the actual reaction conditions by the combination of (1) a new coupling reaction (by Uozumi, Okumura) and (2) an ultrathin liquid cell that achieves the 2.6 mm optical length of argon gas (by Nagasaka, Takaya) including novel Si-free nanomembranes developed by Fujikawa (Figure 2). In the present status, we have tested the ultrathin liquid cell including Si-free nanomembranes by using a conventional FT-IR system (by Nagasaka) and will apply the Si L-edge NEXAFS measurements at BL3U of UVSOR-III in this year.



Scheme 1. The Hiyama Coupling Reactions with Uozumi's Aryl Silicate.

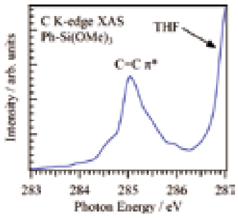


Figure 1. C K-edge NEXAFS spectrum of 100 mM Ph-Si(OMe)$_3$ in THF.

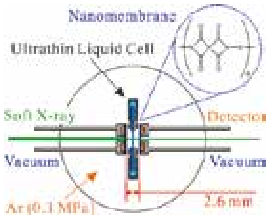


Figure 2. The schematic of an ultrathin liquid cell including Si-free nanomembranes.

(b) Analysis and Elucidation of Deactivation Mechanism for High Durability of Metal Complex-Carbon Electrodes for Electroreduction of CO$_2$ in Water

SAITO, Susumu (*Nagoya Univ.*)
SATO, Shyunsuke (*Toyota Central R&D Labs., Inc.*)
SUGIMOTO, Toshiki (*IMS*)

In order to investigate the cause of the performance degradation of the cathode electrode during the ongoing electroreduction of CO$_2$ in water using a complex-carbon electrode,[1] *in-situ* observations of the cathode electrode are performed using third-order nonlinear vibrational spectroscopy. We have jointly constructed an electrolysis cell for spectroscopy equipped with an anhydrous quartz window, which is the most suitable material for measurement. Using this spectroscopic cell, we first optimized the optical system for third-order nonlinear spectroscopic measurement for the complex-carbon electrode installed in the reaction cell. As the next step, we are going to conduct third-order nonlinear vibrational spectroscopy to identify the cause of the deterioration of the electrode performance, while systematically changing the reaction conditions such as the temperature, pH, applied voltage, and CO$_2$ concentration of the aqueous solution.

Reference

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(2) Research Symposia

(From Oct. 2021 to Sep. 2022)

Dates	Theme	Chair
Feb. 28–Mar. 1, 2022	Current Status and Future Prospects for Attosecond Laser Facility (ALFA)	**YAMANOUCHI, Kaoru** **OKAMOTO, Hiromi**
Mar. 8, 2022	Frontiers in Energy Science: Towards Cross-Hierarchical Understanding	**NAKAMURA, Toshikazu** **YAMAMOTO, Hiroshi**
Sep. 7, 9, Nov. 8–17, 2021	Study of Spin Transport Unique to Chiral Materials	**SUZUKI, Yuta** **YAMAMOTO, Hiroshi**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2021–Mar. 2022			Apr. 2022–Sep. 2022		Total			
		Regular	NanoPlat	NMRPlat	Regular	ARIM	Regular	NanoPlat/ ARIM	NMRPlat	Sum
Special Projects		1			1		2			2
Research Symposia		2			3		5			5
Research Symposia for Young Researchers		0			1		1			1
Cooperative Research		27	36	1	22	14	49	50	1	100
Use of Facility	Instrument Center		78			59		137		137
	Equipment Development Center	0	4		0	4	0	8		8
	UVSOR	110	2		103	2	213	4		217
Use of Facility Program of the Computer Center							278*			278*

* from April 2021 to March 2022

Collaboration Programs

(1) MOU Partnership Institutions

IMS has concluded academic exchange agreements with overseas institutions.

The agreements encourage

- Exchange of researchers
- Internship of students and postdoctoral fellows
- Joint research workshops
- Joint research laboratories

Institution	Period	Accept*	Send*
The Korean Chemical Society, Physical Chemistry Division [Korea]	2006.12–2026.10	0	0
Institute of Atomic and Molecular Sciences (IAMS) [Taiwan]	2005. 1–2023. 1	0	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2009.10–2024.10	7	1
Freie Universität Berlin (FUB) [Germany]	2013. 6–2025. 6	1	0
National Nanotechnology Center, National Science and Technology Development Agency (NANOTEC/NSTDA) [Thailand]	2017.10–2027.10	0	1
Sungkyunkwan University, Department of Chemistry (SKKU) [Korea]	2018. 4–2026. 3	0	0
University of Oulu [Finland]	2021. 5–2024. 5	2	0
National Yang Ming Chiao Tung University [Taiwan]	2018. 6–2023. 5	0	0
Peter Grünberg Institute, Forschungszentrum Jülich GmbH (FZJ) [Germany]	2018.10–2023. 9	0	0
State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University) [China]	2019.12–2024.12	0	0
Indian Institute of Technology Kanpur [India]	2020. 4–2025. 3	1	0
Fritz-Haber-Institut der Max-Planck-Gesellschaft [Germany]	2021. 4–2023. 3	0	2

* No. of researchers during the period from Oct. 2021 to Sep. 2022

Academic Exchange Agreement with Overseas Universities/Institutes (SOKENDAI) as follows ;

Institution	Period	Accept*	Send*
Kasetsart University, Faculty of Science [Thailand]	2011. 3–2026. 3	0	0
University of Malaya, Faculty of Science [Malaysia]	2014. 3–2024.11	0	0
Vidyasirimedhi Institute of Science and Technology [Thailand]	2018. 9–2023. 9	1	1
Friedrich Schiller University Jena [Germany]	2020. 7–2023. 7	1	0
Chulalongkon University [Thailand]	2010. 4–2027. 9	0	1

* No. of researchers during the period from Oct. 2021 to Sep. 2022

(2) IMS International Internship Program

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (IMS-IIP)	13*	–

* from Oct. 2021 to Sep. 2022

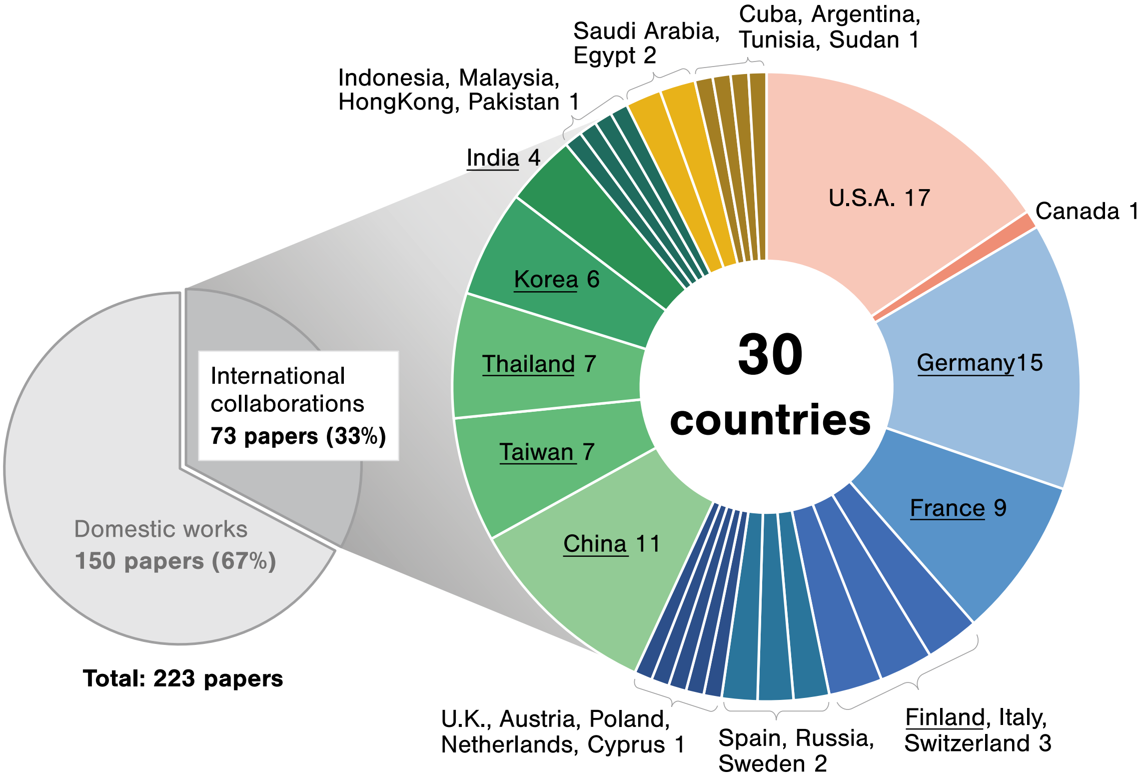
(3) IMS International Collaboration (Including online meetings)

Category	Number of People
International Joint Research Programs	79
International Use of Facilities Programs	14

from Oct. 2021 to Sep. 2022

Internationally Collaborated Publications

Articles and reviews published in 2021



Underlined countries include MOU Partnership Institutions
Scopus dataset, Oct. 2022

KAWAI, Maki Former Director General	Person of Cultural Merit in 2021 Former Director General Maki Kawai was honored by the Minister of Education, Culture, Sports, Science and Technology as a Person of Cultural Merit in 2021 for her outstanding contributions to research on molecules on surfaces. The highest honor for cultural figures is the Order of Cultural Merit, but since the Constitution of Japan stipulates that the Order of Cultural Merit does not entail any privileges, the Person of Cultural Merit system was established to reward contributors to culture by providing them with pensions. The Person of Cultural Merit is an honor equivalent to the Order of Cultural Merit. Former Director General Maki Kawai has led the world in the field of research on molecules on surfaces. She has realized single-molecule chemical reactions using scanning tunneling microscope (STM). She also realized single-molecule vibrational spectroscopy by “action spectroscopy” using STM, which opened a new way for the study of the dynamics of molecules on surface. We hope that Former Director General Maki Kawai will continue to lead not only the surface science but also all the natural sciences in Japan.
OHMORI, Kenji Photo-Molecular Science	National Medal with Purple Ribbon “For His Achievements on Quantum Physics” Professor Kenji Ohmori is awarded a national honor, the Medal with Purple Ribbon, by His Majesty the Emperor of Japan for his achievements on quantum physics. The Medal with Purple Ribbon is awarded for inventions and discoveries in science and technology, and for outstanding achievements in the fields of science, sports, art and culture. Professor Ohmori, in the field of quantum physics, has developed a revolutionary method in which the relative oscillation timing of two laser electric fields is controlled with attosecond precision, and imprinted on the wave functions of matter to control their interference almost perfectly. He has applied this method to various phases of matter including atoms, molecules, solids and artificial crystal of ultracold atoms cooled down to temperatures close to absolute zero, making significant contributions to the advancement of the relevant fields of science. These achievements have been highly appreciated, leading to the nation’s Medal with Purple Ribbon this time. Professor Ohmori is currently leading large-scale/long-term national projects on the development of ultrafast quantum computers and simulators, expected as one of the top runners in the quantum technologies to further promote its progress.
KOBAYASHI, Genki Materials Molecular Science	NAGAI Foundation for Science & Technology Academic Award “Development of Elemental Technologies for Pioneering Hydride Ion Conductive Materials and Creating Novel Electrochemical Devices”
SEGAWA, Yasutomo Life and Coordination-Complex Molecular Science	Thieme Chemistry Journals Award 2022 “Chemical Synthesis, Catalysis, and Related Areas of Organic Chemistry” Chemist Award BCA 2021 “Synthesis and Properties of Nonplanar Aromatic Hydrocarbons” 62nd Academic Encouragement Award from the Ube Industries Foundation “Development of Crystalline Organic Semiconducting Materials by the Topological Control of Three-Dimensional Structures”
MINATO, Taketoshi Instrument Center	RIEC Award “Development of the Design Principles of Rechargeable Batteries as Mobile Power by Controlling Electrode/Electrolyte Interface”
IZAWA, Seiichiro Materials Molecular Science	NF Foundation R&D Encouragement Award “Photon Upconversion at an Organic Semiconductor Interface” The 11th Young Scientist Award of National Institutes of Natural Sciences “Novel Photon Up-Conversion for Low Energy Light Utilization” Morino Foundation for Molecular Science “Exploring Efficient Photoconversion System at Organic Semiconductor Interface”
OKUMURA, Shintaro Life and Coordination-Complex Molecular Science	The Society of Synthetic Organic Chemistry, Fujifilm Research Proposal Award, 2021 “Photocatalytic Umpolung of Carbonyl Compounds by Activation with Carbon Dioxide”
FURUIKE, Yoshihiko Research Center of Integrative Molecular Systems	The Early Career Award in Biophysics “Visualizing a Day of Circadian Clock at Atomic Resolution” SPRUC 2022 Young Scientist Award “Elucidation of Master Allostery Essential for Circadian Clock Oscillation in Cyanobacteria”

AWARDS

YONEDA, Yusuke Research Center of Integrative Molecular Systems	The Early Career Award in Biophysics “Exciton-Charge Transfer Mixing Drives Oxygenic Photosynthesis”
TOYODA, Tomonori Equipment Development Center	The Chemical Society of Japan Award for Technical Achievements for 2021 “Development of Arithmetic Instruments in Photo-Induced Force Microscope and Control Systems for Promoting Molecular Science”

LIST OF VISITING FOREIGN SCHOLARS

Visitors from abroad are always welcome at IMS and they have always played an important role in the research activities of the Institute. The foreign scientists who visited IMS during the past year (October 2021–September 2022) are listed below.

(1) JSPS Invited Fellow			
Prof. CHANDRA, Amalendu	Indian Institute of Technology, Kanpur	India	May ’22–Jul. ’22
Prof. YU, Yan	Indiana University	U.S.A.	Jun. ’22–Jul. ’22
(2) IMS Visiting Scientist			
Ms. LEDOIGT, Magali	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Ms. DUBERN, Lucie	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Ms. MOLA AL YAHYA, Joa	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Mr. MOREIRA, Joel	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Mr. BUTTIENS, Thomas	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Mr. CABRIERES, Marc	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Mr. MOUTAKANNI, Alix	École Nationale Supérieure de Chimie de Paris (ENSCP)	France	Apr. ’22–Aug. ’22
Mr. KOCIK, Robin	University Paris Saclay	France	Apr. ’22–Aug. ’22
Mr. DENECKER, Tom	Ecole NormaleSupérieure Paris-Saclay	France	Apr. ’22–Sep. ’22
Prof. MANNA, Sujit	Indian Institute of Technology	India	Jul. ’22
Prof. PATANEN, Minna	University of Oulu	Finland	Jul. ’22
Dr. MANSIKKALA, Leo	University of Oulu	Finland	Jul. ’22
Mr. DELABRE, Antoine	Lycée Faidherbe	France	Jul. ’22–Aug. ’22
Mr. BARRE, Maxence	Lycée Faidherbe	France	Jul. ’22–Aug. ’22
Mr. MARTHOURET, Hugo	Lycée Faidherbe	France	Jul. ’22–Aug. ’22
Dr. SILLY, Mathieu	Synchrotron Soleil	France	Aug. ’22
Dr. CEOLIN, Denis	Synchrotron Soleil	France	Aug. ’22
Dr. SAISOPA, Thanit	Rajamangala University of Technology Isan	Thailand	Aug. ’22
Dr. RATTANACHAI, Yuttakarn	Rajamangala University of Technology Isan	Thailand	Aug. ’22
Mr. ESCUSA DOS SANTOS, Luis Filipe	University of Gothenburg	Sweden	Aug. ’22
Dr. MAHRT, Fabian	Paul Scherrer Institute	Switzerland	Aug. ’22
Dr. KONG, Xiangrui	University of Gothenburg	Sweden	Aug. ’22
Ms. LI, Linjie	University of Gothenburg	Sweden	Aug. ’22
Dr. ALPERT, Peter	Paul Scherrer Institute	Switzerland	Aug. ’22
Prof. CHUANG, Cheng-Hao	Tamkang University	Taiwan	Sep. ’22
Dr. HUANG, Wun-Cin	Tamkang University	Taiwan	Sep. ’22
Dr. RODRIGUEZ, Jan Sebastian Dominic	Tamkang University	Taiwan	Sep. ’22
Prof. RÜHL, Eckart	Free University of Berlin	Germany	Sep. ’22
(3) Visitor to IMS			
Prof. ANDERSON, Dana	ColdQuanta, Inc.	U.S.A.	Jun. ’22
Prof. SIVAK, David	Simon Fraser University	Canada	Aug. ’22

Scientists who would like to visit IMS under program (1) are invited to make contact with IMS staff in their relevant field.

LIST OF PUBLICATIONS

Theoretical and Computational Molecular Science

Y. FURUIKE, A. MUKAIYAMA, S.-I. KODA, D. SIMON, D. OUYANG, K. ITO-MIWA, S. SAITO, E. YAMASHITA, T. NISHIWAKI-OHKAWA, K. TERAUCHI, T. KONDO and S. AKIYAMA, "Regulation Mechanisms of the Dual ATPase in KaiC," *bioRxiv* 2021. 10.28.466029 (2021). DOI: 10.1101/2021.10.28.466029

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E. MINAMITANI, T. SHIGA, M. KASHIWAGI and I. OBAYASHI, "Relationship between Local Coordinates and Thermal Conductivity in Amorphous Carbon," *J. Vac. Sci. Technol., A* **40(3)**, 33408 (2022). DOI: 10.1116/6.0001744

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H. NARITA, J. ISHIZUKA, R. KAWARAZAKI, D. KAN, Y. SHIOTA, T. MORIYAMA, Y. SHIMAKAWA, A. V. OGNEV, A. S. SAMARDAK, Y. YANASE and T. ONO, "Field-Free Superconducting Diode Effect in Noncentrosymmetric Superconductor/Ferromagnet Multilayers," *Nat. Nanotechnol.* **17(8)**, 823–828 (2022). DOI: 10.1038/s41565-022-01159-4

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Photo-Molecular Science

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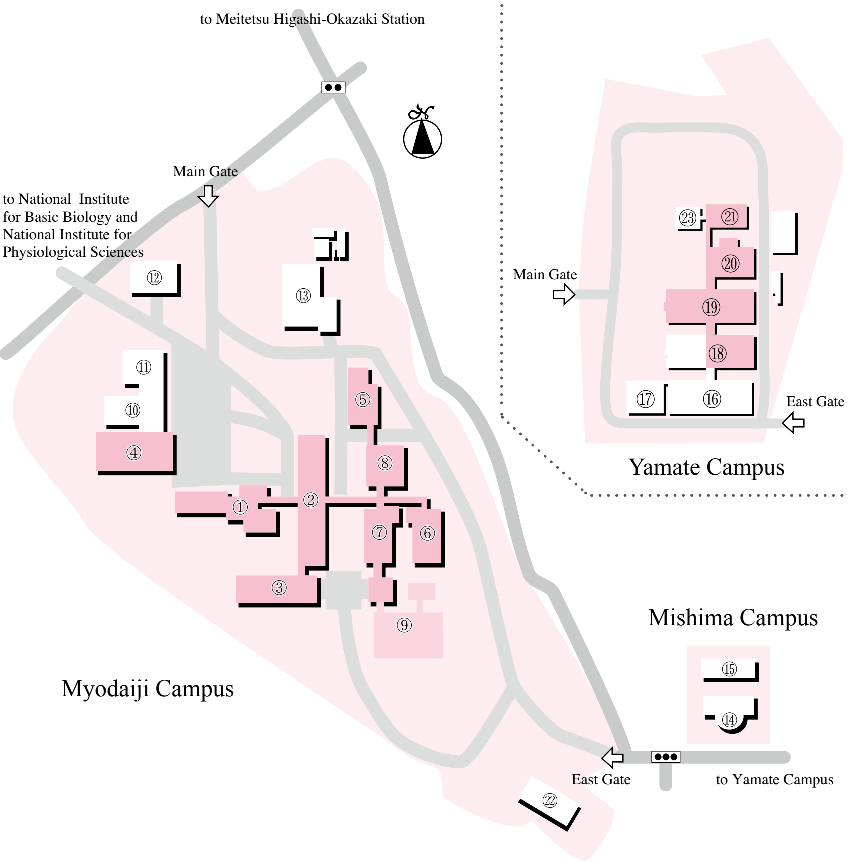

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6. Joint Research Bldg. D
7. Joint Research Bldg. C
8. Joint Research Bldg. B
9. Joint Research Bldg. UVSOR
10. Administration Bureau
11. Library
12. Faculty Club & Coop
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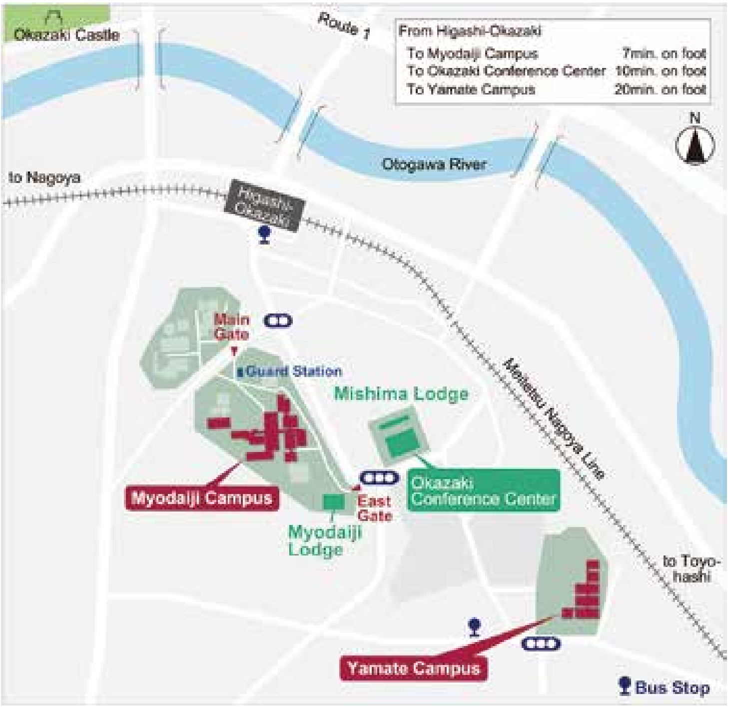

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