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Institute for Molecular Science

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Editorial Committee 2023

Institute for Molecular Science (IMS) is one of the world's leading core research facilities in 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 are closely related to scientific understanding in biology, engineering and space sciences. Currently, IMS is engaged in four major research areas and two interdisciplinary research fields: theoretical and computational molecular science, photo-molecular science, materials molecular science, and life and coordination-complex molecular science. Since April 2013, Research Center of Integrative Molecular Systems (CIMoS) has been working to develop highly functional molecular systems, including molecular rhythms, sensing and response, and even self-repair. In April 2017, Center for Mesoscopic Sciences (CMS) was launched to develop innovative methodologies to study mesoscopic molecular systems, ranging from theoretical methods to state-of-the-art measurement techniques. A year later, IMS also established Advanced Molecular Science Research Division, which showcases outstanding examples of research in molecular science. Division of Research Innovation and Collaboration started in April 2019, working to strengthen collaboration with social activities. Other than 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 Research Center for Computational Science, jointly with National Institute for Physiological Sciences and National Institute for Basic Biology located on the same campus. In April 2018, Okazaki Institute for Integrative Bioscience (OIIB) was reorganized into Exploratory Center for Life and Living Systems (ExCELLS) directly under National Institutes of Natural Sciences (NINS) to advance its activities.

Annual Review 2023 is a summary of the research activities by all individual research groups conducted at IMS during October 2022–September 2023 on molecular structures, reactions and functions demonstrating "novel molecular possibilities." In addition to these individual activities, IMS conducts many special programs in the institute basis such as (i) Large-scale and high-coherence fault-tolerant quantum computer with dynamical atom arrays supported by a JST program "MOONSHOT Goal 6: Realization of a fault-tolerant universal quantum computer that will revolutionize economy, industry, and security by 2050," (ii) 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), (iii) Advanced Research Infrastructure for Materials and Nanotechnology in Japan, and (iv) Inter-University Network for Common Utilization of Research Equipments. In addition to these national projects, IMS runs several international collaboration programs and also owns an internship program for young scientists: Institute for Molecular Science International Internship Program (IMS-IIP). IMS-IIP provides internship opportunities for young overseas researchers (master's and doctoral students, post-doctoral fellows, young faculty members of MOU partners, *etc*) to stay in IMS laboratories.

With the COVID19 pandemic, the use of web conferencing became the standard for most conferences, making the opportunity to meet and discuss with colleagues around the world easier than ever before. After the recovery from CORVID19, we are now able to take advantage of the benefits of web conferencing while also taking advantage of the opportunity to meet face-to-face, the so-called hybrid conferencing. Apparently, IMS has to be flexible its style in conducting international collaboration as well as sharing new findings and ideas by utilizing these benefits. The rapid development of digital transformation technologies in recent years has made it challenging for us to facilitate remote operation of research facilities.

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

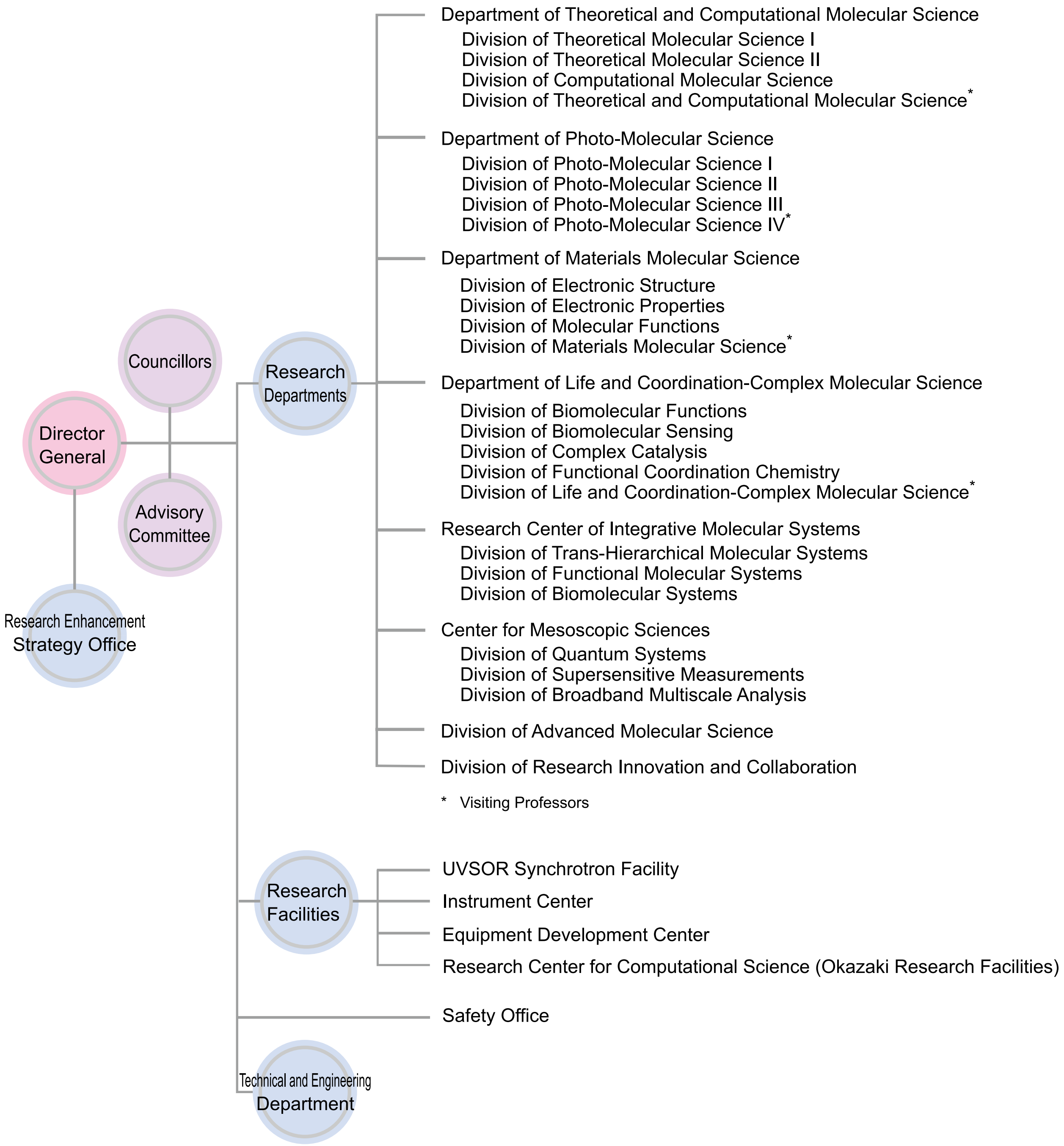
August, 2023

WATANABE, Yoshihito

Y. Watanabe

Director General, Institute for Molecular Science

ORGANIZATION



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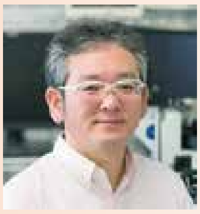

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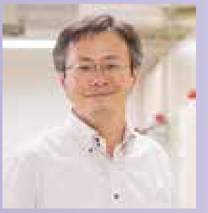

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KERA, Satoshi
Director

Instrument Center p. 100

YOKOYAMA, Toshihiko
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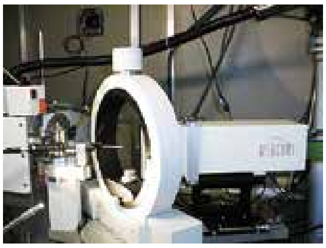

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YAMAMOTO, Hiroshi
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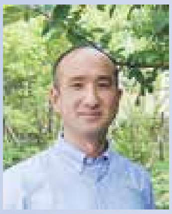
EHARA, Masahiro
Director

Theoretical and Computational Molecular Science p. 22

SATO, Hirofumi
Visiting Professor
(Kyoto University)



YOSHIDA, Norio
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(Nagoya University)

NOGUCHI, Hiroshi
Visiting Associate Professor
(University of Tokyo)

Photo-Molecular Science p. 40

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Visiting Professor
(High Energy Accelerator
Research Organization)

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(RIKEN)

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Visiting Professor
(Hiroshima University)

AKIMOTO, Ikuko
Visiting Associate Professor
(Wakayama University)

Life and Coordination-Complex Molecular Science p. 68

KAMIYA, Yukiko
Visiting Professor
(Nagoya University)

SATO, Sota
Visiting Professor
(Kumamoto University)

TOYABE, Shoichi
Visiting Professor
(Kyoto University)

PERSONNEL CHANGES

Moving In

Dec. 1, 2022	Dr. KANDA, Tomoya joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Dec. 16, 2022	Dr. HARASHIMA, Takanori joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Jan. 1, 2023	Dr. ARAKI, Tohru joined IMS as a Senior Researcher in UVSOR Synchrotron Facility
Jun. 1, 2023	Dr. TOMITA, Takafumi joined IMS as an Assist. Prof. in the Department of Photo-Molecular Science
Jul. 1, 2023	Dr. SHIRAOGAWA, Takafumi joined IMS as an Assist. Prof. in the Department of Theoretical and Computational Molecular Science

Moving Out

Dec. 31, 2022	Assist. Prof. IZAWA, Seiichiro (Department of Materials Molecular Science) moved out as an Assoc. Prof. of Tokyo Institute of Technology
Feb. 28, 2023	Assist. Prof. SUGITA, Kento (UVSOR Synchrotron Facility) moved out to Ex-Fusion
Feb. 28, 2023	Assist. Prof. SHITADE, Atsuo (Department of Theoretical and Computational Molecular Science) moved out to Osaka University
Mar. 31, 2023	Prof. HIRAMOTO, Masahiro (Department of Materials Molecular Science) retired from IMS
Mar. 31, 2023	Assoc. Prof. KUSAMOTO, Tetsuro (Department of Life and Coodination-Complex Molecular Science) moved out as a Prof. of Osaka University
Mar. 31, 2023	Assist. Prof. SUGAWA, Seiji (Department of Photo-Molecular Science) moved out as an Assoc. Prof. of The University of Tokyo
Mar. 31, 2023	Assist. Prof. SUGIYAMA, Haruki (Department of Life and Coodination-Complex Molecular Science) moved out to CROSS
Mar. 31, 2023	Assist. Prof. TAKEIRI, Fumitaka (Department of Materials Molecular Science) moved out to RIKEN
Mar. 31, 2023	Assist. Prof. MUKAIYAMA, Atsushi (Research Center of Integrative Molecular Systems) moved out as an Assoc. Prof. of Fukui Prefectural University
Mar. 31, 2023	Assist. Prof. YAMAMOTO, Kohei (Department of Materials Molecular Science) moved out to National Institutes for Quantum Science and Technology
Mar. 31, 2023	Assist. Prof. YOSHIZAWA, Daichi (Center for Mesoscopic Sciences) moved out
Mar. 31, 2023	Assoc. Prof. (Cross Appointment) OHIGASHI, Takuji (UVSOR Synchrotron Facility) resigned from his post
Jul. 31, 2023	Assist. Prof. MATSUOKA, Ryota (Department of Life and Coodination-Complex Molecular Science) moved out to Osaka University

Graduate Programs

For graduate education, IMS has the Molecular Science Program, Graduate Institute for Advanced Studies, SOKENDAI. In April 2023, SOKENDAI has started new 20-program system at the Graduate Institute for Advanced Studies which can flexibly utilize highly specialized educational resources across disciplines, 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. 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: Theoretical and computational molecular science, Photo-molecular science, Materials molecular science, and Life and coordination-complex molecular science. One year is divided into two terms, the first semester (April-to-September) and the second semester (October-to-March). 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 Online Open Campus, Training Program, and Asian Winter School in addition to IMS International Internship Program as shown below.

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 Condensed Molecular Systems

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

SAITO, Shinji
Professor
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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
Post-Doctoral Fellow
KOIZUMI, Ai
Graduazte Student
ZHU, Zhe
Secretary
CHIBA, Fumika

Keywords Reactions, Functions, Fluctuations

Our research focuses on the intricate fluctuations in condensed molecular systems, including liquids and biomolecules. In these systems, fluctuations affect various properties and biological functions, and reactions occur under fluctuations.

We investigate fluctuations and dynamics in these molecular systems to elucidate the molecular origins of the physical properties, functions, and reactions. To this end, we have developed advanced computational methods for multi-dimensional nonlinear spectroscopy, which allow us to extract detailed dynamical information that conventional linear spectroscopy cannot provide. Our investigations have successfully revealed the molecular origins of ultrafast energy relaxation and the time evolution of inhomogeneous fluctuations in liquid water. Additionally, we have explored the phenomenon of dynamic heterogeneity in supercooled liquids, characterized by slow and non-uniform structural changes induced by fluctuations. Using three-time correlation functions, we have also shed light on dynamic couplings of conformational fluctuations with different timescales in a protein.

Our work extends to the study of anomalous properties of liquid water, uncovering the connections between these anomalies and hidden structural and dynamical properties. Additionally, we have investigated the origin behind the low glass transition of water. We are also investigating the origin of rare but persistent structural change dynamics at low temperatures based on theories of stochastic processes and reaction rates.

In biomolecular systems, conformational fluctuations and changes are essential for function. Our investigations have explored the intricate interplay between fluctuations and biomolecular functions, exemplified by the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. Our work on enzymatic reactions has highlighted the importance of prepared conformational states with specific structures that facilitate reactions. We have also studied the molecular origin of dynamic disorder in the conformational dynamics of proteins at the molecular level, unraveling the intricacies of this phenomenon.

As seen in these studies, we aim to deepen our understanding of structural dynamics, reactions, and functions in condensed molecular systems based on theoretical and computational methods.

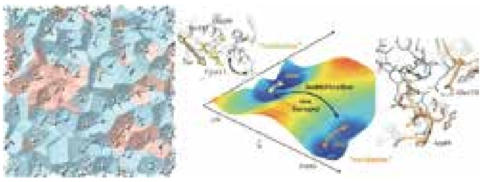

Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

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. Anisotropic and Finite Effects on Intermolecular Vibration and Relaxation Dynamics: Low-Frequency Raman Spectroscopy of Water Film and Droplet on Graphene by Molecular Dynamics Simulations[1)]

The structural and dynamical properties of water can be greatly altered by the anisotropic interfacial environment. Here, we study the intermolecular vibration and relaxation dynamics of a water film and a water droplet on a graphene surface based on low-frequency Raman spectra calculated from molecular dynamics simulations. The calculated Raman spectra of the interfacial water systems show a weakened libration peak and an enhanced intermolecular hydrogen bond (HB) stretching peak compared to the spectrum of bulk water, which are attributed to softened orientation motion. We also find that the collective polarizability relaxation in the droplet is much slower than that in the film and bulk, which is completely different from the collective dipole relaxation. The slow relaxation is due to a positive correlation between the induced polarizabilities of distinct molecules caused by the global and anisotropic structural fluctuations of the water droplet. Furthermore, we find that the two-dimensional HB network by the orientation-ordered interfacial water molecules leads to different intermolecular vibration dynamics between the parallel and perpendicular components. The present theoretical study demonstrates that low-frequency Raman spectroscopy can reveal the anisotropic and finite effects on the intermolecular dynamics of the water film and droplet.

2. Conformational Dynamics in Proteins: Entangled Slow Fluctuations and Nonequilibrium Reaction Events[2)]

Proteins exhibit conformational fluctuations and changes over various timescales, ranging from rapid picosecond-scale local atomic motions to slower microsecond-scale global conformational transformations. In the presence of these fluctuations, chemical reactions occur and functions emerge. These conformational fluctuations of proteins are not merely stochastic random motions but possess distinct spatiotemporal characteristics. Moreover, chemical reactions do not always proceed along a single reaction coordinate in a quasi-equilibrium manner. Therefore, it is essential to understand spatiotemporal conformational fluctuations of proteins and conformational change processes associated with reactions. In this Perspective, we shed light on the complex dynamics of proteins and their role in enzyme catalysis by presenting recent results regarding dynamic couplings and disorder in the conformational dynamics of proteins and rare but rapid enzymatic reaction events obtained from molecular dynamics simulations.

3. Molecular Insights into the Intrinsic Dynamics and Their Roles During Catalysis in Pin1 Peptidyl-prolyl Isomerase[3)]

Proteins are intrinsically dynamic and change conformations over a wide range of time scales. While the conformational dynamics have been realized to be important for protein functions, *e.g.*, in activity–stability trade-offs, how they play a role during enzyme catalysis has been of debate over decades. By studying Pin1 peptidyl-prolyl isomerase using extensive molecular dynamics simulations, here we discuss how the slow intrinsic dynamics of Pin1 observed in the NMR relaxation dispersion experiment occur and couple to isomerization reactions in molecular detail. In particular, we analyze the angular correlation functions of the backbone N–H bonds and find that slow conformational transitions occur around the 3_{10} helix in the apo state. These events at the helical region further affect the residues around the ligand binding site. Unfolding of this helix leads to a tight hydrogen bond between the helical region and the ligand binding loop, thus forming a stable coiled structure. The helical and coiled structures are found to be characteristic of the Pin1–ligand complex with the ligand in the *trans* and *cis* states, respectively. These results indicate that the changes in the slow dynamics of Pin1 by the isomerization reaction occur via the shift in populations of the helical and coiled states, where the balance is dependent on the ligand isomerization states.

4. Excited States of Chlorophyll *a* and *b* in Solution by Time-Dependent Density Functional Theory[4)]

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.

References

1) T. Inagaki, M. Hatanaka and S. Saito, *J. Phys. Chem. B* **127**, 5869–5880 (2023).

2) J. Ono, Y. Matsumura, T. Mori and S. Saito, *J. Phys. Chem. B (Perspective)*, accepted.

3) T. Mori and S. Saito, *J. Phys. Chem. B* **126**, 5185–5193 (2022).

4) Z. Zhu, M. Higashi and S. Saito, *J. Chem. Phys. (Special topic on Photosynthetic Light-Harvesting and Energy Conversion)* **156**, 124111 (13 pages) (2022).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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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

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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).
- T. P. Nguyen and A. Ishizaki, "Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering," *J. Phys. Chem. Lett.* **9**, 1243 (2018).
- 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. Control and Enhancement of Single-Molecule Electroluminescence through Strong Light-Matter Coupling

The energetic positions of molecular electronic states at molecule/electrode interfaces are crucial factors for determining the transport and optoelectronic properties of molecular junctions. Strong light-matter coupling offers a potential for manipulating these factors, enabling to boost in the efficiency and versatility of these junctions. Here, we investigated electroluminescence from single-molecule junctions in which the molecule is strongly coupled with the vacuum electromagnetic field in a plasmonic nanocavity. We demonstrated an improvement in the electroluminescence efficiency by employing the strong light-matter coupling in conjunction with the characteristic feature of single-molecule junctions to selectively control the formation of the lowest-energy excited state. The mechanism of efficiency improvement was discussed based on the energetic position and composition of the formed polaritonic states. Our findings indicated the possibility to manipulate optoelectronic conversion in molecular junctions by strong light-matter coupling.$^{1)}$

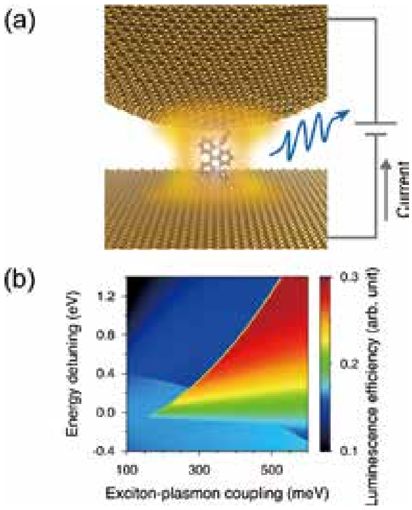

Figure 1. (a) Schematic illustration of electroluminescence from a dye molecule in a plasmonic nanocavity. (b) Two-dimensional plot of the electroluminescence efficiency as a function of the exciton–plasmon coupling strength and energy detuning.

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

Quantum light is increasingly recognized as a promising resource for developing optical measurement techniques. Particular attention has been paid to enhancing the precision of the measurements beyond classical techniques by using nonclassical correlations between quantum entangled photons. Recent advances in quantum optics technology have made it possible to manipulate the spectral and temporal properties of entangled photons, and the photon correlations can facilitate the extraction of matter information with relatively simple optical systems compared to conventional schemes. In these respects, the applications of entangled photons to time-resolved spectroscopy can open new avenues for unambiguously extracting information on dynamical processes in complex molecular and materials systems. Here, we proposed time-resolved spectroscopy in which specific signal contributions are selectively enhanced by harnessing the nonclassical correlations of entangled photons. The entanglement time characterizes the mutual delay between an entangled twin and determines the spectral distribution of the photon correlations. This characteristic allows us to filter out specific frequency regions of spectra while temporally resolving the state-to-state dynamics in the time region longer than half of the entanglement time. Therefore, the entanglement time plays a dual role as the knob for controlling the accessible time region of dynamical processes and the degrees of spectral selectivity. The results demonstrated that the application of quantum entangled photons to time-resolved spectroscopy leads to monitoring dynamical processes in complex molecular and materials systems by selectively extracting desired signal contributions from congested spectra. We anticipated that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.$^{2)}$

3. Network Analysis with Quantum Dynamics Clarifies Why Photosystem II Exploits both Chlorophyll *a* and *b*

In land plants, chlorophyll-a and chlorophyll-*b* in light-harvesting proteins are responsible for absorbing solar energy. While the individual characteristics of these pigments are well-understood, the advantages of their coexistence have not been fully elucidated. Here, we presented a principled framework based on complex network analysis and quantum dynamics to investigate and quantify the features of this coexistence during excitation energy transfer in a photosystem II supercomplex. By using model networks with diverse chlorophyll compositions, our analysis revealed that the excited energy preferentially flows through specific domains, where excessive energy can be controlled, solely in those supercomplexes with a natural chlorophyll-*a*/*b* ratio, resulting in a moderate charge separation yield. Our findings suggested that light-harvesting proteins with the natural chlorophyll-*a*/*b* ratio are optimized to safely and efficiently capture light energy across various light intensities. By leveraging our framework, we could gain valuable insights into the mechanisms by which light-harvesting proteins harvest light energy and adapt to changing environmental conditions.$^{3)}$

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3) E. Kim, D. Lee, S. Sakamoto, J.-Y. Jo, M. Vargas, A. Ishizaki, J. Minagawa and H. Kim, submitted.

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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2008 Professor, Institute for Molecular Science
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SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photochemistry, Heterogeneous Catalysis

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

(1) Inverse design and theory for complex electronic states

We are interested in improving the various functions of molecular systems. Inverse design approach can optimize the functions in the "functional space." Recently, we adopted the inverse design approach and succeeded in maximizing various photofunctions of the molecular aggregates and molecule-nanoparticle systems. We also work on developing electronic structure theories for complex electronic states such as CAP/SAC-CI method for locating metastable resonance states.

(2) Nanocluster and heterogeneous catalysts

We proceeded the national project of Element Strategy Initiatives for Catalysts and Batteries (ESICB) where we focused on the developments of the platinum-group metal (PGM) reduced or PGM-free catalysts. We elucidated the mechanism of various three-way catalysts like PGM-free tandem catalyst. We also investigated the nanocluster and heterogeneous catalysts for the fuel cells and fine chemicals like Pt sub-nanoclusters for oxygen reduce reaction (ORR), Pd-Au alloy nanoparticle for hydrosilylation, Niobium oxide surface for direct synthesis of various amides and imides.

(3) Functions of *C*-centered Au(I) based clusters

We theoretically investigate the various functions of metal nanoclusters. In the recent project, we worked on *C*-centered Au(I) based clusters such as chiral induction of $C\mathrm{Au}^{\mathrm{I}}_{6}$ cluster with monodentate *N*-heterolytic carbene (NHC) ligands, intense photoluminescence (PL) of $C\mathrm{Au}^{\mathrm{I}}_{6}\mathrm{Ag}^{\mathrm{I}}_{n}$ (n = 2–4) clusters and its biological application, vapochromism of $C\mathrm{Au}^{\mathrm{I}}_{6}$ cluster, and the generation of $C\mathrm{Au}^{\mathrm{I}}_{5}$ cluster and its red-shifted PL as well as catalytic activity.

(4) Photoluminescence of modified single-walled carbon nanotubes (SWNTs)

In the series of works, we have investigated the selective photoluminescence (PL) from photofunctional molecular systems. Introducing the quantum defects into single-walled carbon nanotubes (SWNTs) enhances their PLs with red-shifted peaks. Previously, we proposed the substitution rule using Clar-sextet theory. Recently, we have achieved the control of near-IR PL by the stepwise chemical functionalization, the selective E** PL (~1,200 nm) by tether alkyl functionalization, and the PL in telecommunication wavelength (>1,300 nm) by perfluoroalkyl functionalization.

Selected Publications

- T. Shiraogawa, G. Dall'Osto, R. Cammi, M. Ehara and S. Corni, "Inverse Design of Molecule-Metal Nanoparticle Systems Interacting with light for the Desired Photophysical Properties," *Phys. Chem. Chem. Phys.* **24**, 22768 (2022).
- P. Hirunsit, T. Toyao, S. M. A. H. Siddiki, K. Shimizu and M. Ehara, "Origin of $\mathrm{Nb_2O_5}$ Lewis Acid Catalysis for Activation of Carboxylic Acids in the Presence of a Hard Base," *ChemPhysChem* **19**, 2848 (2018).
- Z. Lei, M. Endo, H. Ube, T. Shiraogawa, P. Zhao, K. Nagata, X.-L. Pei, T. Eguchi, T. Kamachi, M. Ehara, T. Ozawa and M. Shionoya, "*N*-Heterocyclic Carbene-Based C-Centered Au(I)-Ag(I) Clusters with Intense Phosphorescence and the Organelle-selective Translocation in Cells," *Nat. Commun.* **13**, 4288 (2022).
- Y. Maeda, R. Morooka, P. Zhao, D. Uchida, Y. Konno, M. Yamada and M. Ehara, "Controlling Near-Infrared Photoluminescence Properties of Single-Walled Carbon Nanotubes by Substituent Effect in the Stepwise Chemical Functionalization," *J. Phys. Chem. C* **127**, 2360 (2023).

1. Inverse Design of Molecule–Metal Nanoparticle Systems Interacting with Light for the Desired Photophysical Properties[1)]

Molecules close to a metal nanoparticle (NP) have different photophysical properties from those of the isolated one. To harness the potential of molecule–NP system, appropriate design guidelines are expected. In this work, we propose an inverse design method of the optimal molecule–NP systems and incident electric field for desired photophysical properties. It is based on a gradient-based optimization search within the time-dependent quantum chemical description for the molecule and the continuum model for the metal NP. We designed the optimal molecule, relative molecule–NP spatial conformation, and incident electric field of a molecule–NP system to maximize the population transfer to the target electronic state of the molecule. The present method is promising as the basis for designing molecule–NP systems and incident fields and accelerates discoveries of efficient molecular plasmonics systems.

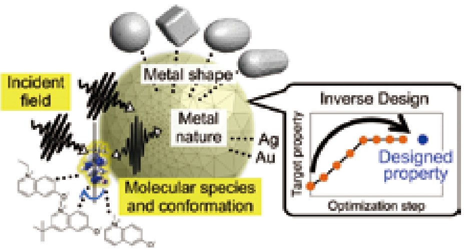

Figure 1. Inverse design of the photophysical properties of molecule–nanoparticle system.

2. *N*-Heterocyclic Carbene-Based *C*-Centered Au(I)-Ag(I) Clusters with Intense Phosphorescence and Organelle-Selective Translocation in Cells[2)]

Luminescent metal nanoclusters are expected to exhibit unique physical properties in the cluster structure depending on the ligand structure, metal type, number of nuclei and arrangement. In this study, carbon-centered gold-silver (CAu_6Ag_2) clusters with *N*-heterocyclic carbene (NHC) ligands were designed and synthesized, and it was found that these clusters emit strong phosphorescence in solution, and the contribution of NHC ligands to phosphorescence emission was revealed by theoretical calculation. The luminescence rate constant was calculated by an analysis including spin–orbit interactions, and the quantum yield was discussed in terms of the energy barrier to the minimum energy crossing point. Furthermore, the phosphorescent gold-silver clusters with long luminescence lifetime were used for cellular imaging, which revealed the pathway of uptake into the cell and selective localization to specific organelles, confirming their superior functionality, which is different from the non-selective uptake of conventional phosphine ligands.

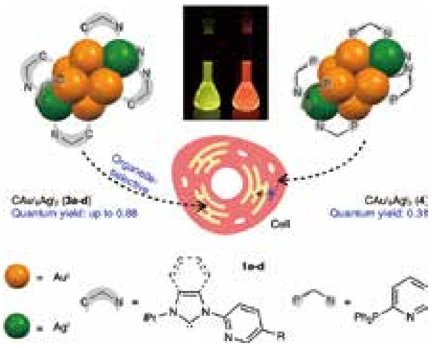

Figure 2. Schematic diagram of Carbon(*C*)-centered Au(I)-Ag(I) clusters with *N*-heterocyclic carbene (NHC) ligands with intense phosphorescence and their ligand-specific, organelle-selective translocation in cells.

3. Controlling Near-Infrared Luminescence of Single-Walled Carbon Nanotubes by Substituent Effect in Stepwise Chemical Functionalization[3)]

Introducing the quantum defects into single-walled carbon nanotubes (SWNTs) enhances their photoluminescence (PL) with red-shifted peaks. In this work, the stepwise chemical functionalization of SWNTs was shown to be useful for controlling site-specific functionalization and PL. Dialkylated and hydroalkylated SWNTs were selectively synthesized. The ^{n}Bu-SWNTs-^{n}Bu and ^{n}Bu-SWNTs-H adducts of the (6,4), (6,5), (8,3), and (7,5) SWNTs that were separated using gel chromatography showed dominant E_{11}^{**} PL and E_{11}^{*} PL, respectively. The systematic assignments of the PL were performed based on the thermodynamic stability and transition energy of 1,2- and 1,4-adducts of SWNTs using DFT and TD-DFT calculations. It was shown that the steric hindrance of the added group and the *R* value, *i.e.*, mod(*n*-*m*, 3) in an (*n*,*m*) chiral nanotube are key factors that control the addition site and the magnitude of the local bandgap.

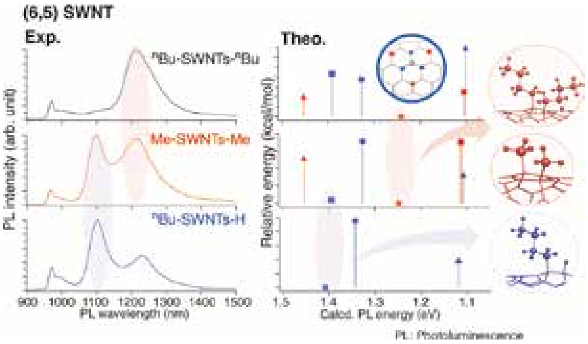

Figure 3. Control of near-IR photoluminescence (PL) of substituted SWNTs regarding E_{11}^{**} PL, and E_{11}^{*} PL.

References

1) T. Shiraogawa, G. Dall'Osto, R. Cammi, M. Ehara and S. Corni, *Phys. Chem. Chem. Phys.* **24**, 22768–22777 (2022).

2) Z. Lei, M. Endo, H. Ube, T. Shiraogawa, P. Zhao, K. Nagata, X.-L. Pei, T. Eguchi, T. Kamachi, M. Ehara, T. Ozawa and M. Shionoya, *Nat. Commun.* **13**, 4288 (2022).

3) Y. Maeda, R. Morooka, P. Zhao, D. Uchida, Y. Konno, M. Yamada and M. Ehara, *J. Phys. Chem. C* **127**, 2360–2370 (2023).

Molecular Dynamics Simulations of Disease-Related Biomolecules

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Education

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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
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Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have a 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.

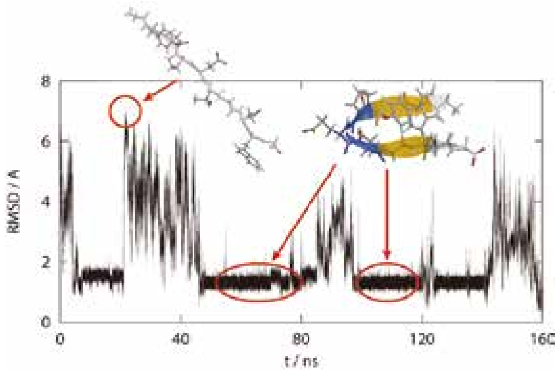

Figure 1. Time series of protein folding simulation.

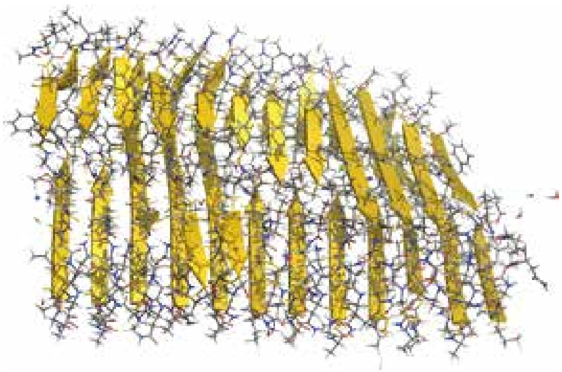

Figure 2. Snapshot of an Aβ amyloid fibril.

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. Key Residue for Aggregation of Amyloid-β Peptides

Aβ mainly has two isoforms, Aβ40 and Aβ42. Although the difference between Aβ40 and Aβ42 is only two additional C-terminal residues, Aβ42 aggregates much faster than Aβ40. It is not known what role the C-terminal two residues play in accelerating aggregation. Since Aβ42 is more toxic, its oligomerization process needs to be clarified. Moreover, clarifying the differences between the oligomerization processes of Aβ40 and Aβ42 is essential to elucidate the key factors of oligomerization. To investigate the dimerization process, which is the early process of the oligomerization, Hamiltonian replica-permutation molecular dynamics simulations were performed for Aβ40 and Aβ42.[1] We identified the key residue, Arg5, for the Aβ42 dimerization, as shown in Figure 3. The two additional residues in Aβ42 allow the C-terminus to form a contact with Arg5, and this contact stabilizes β-hairpin. This β-hairpin promotes dimer formation with formation of intermolecular β-bridges. To approve this theoretical prediction, experiments on Aβ aggregations were also conducted. We confirmed that the aggregation of Aβ42 is remarkably suppressed by a mutation of Arg5. Moreover, mutation of Arg5 also suppresses the Aβ40 aggregation. It was found by analyzing the simulations that Arg5 is important for Aβ40 to form the intermolecular contacts. Thus, it was clarified that the role of Arg5 in the oligomerization process is changed by the two additional C-terminal residues.

The fact that we could predict the experimental results from the simulation results means that the differences seen in the formation of dimers make a difference in the formation of much larger aggregates, such as amyloid fibrils observed in experiments. Thus, it is essential to elucidate the process of small oligomer formation to fully understand the Aβ aggregation.

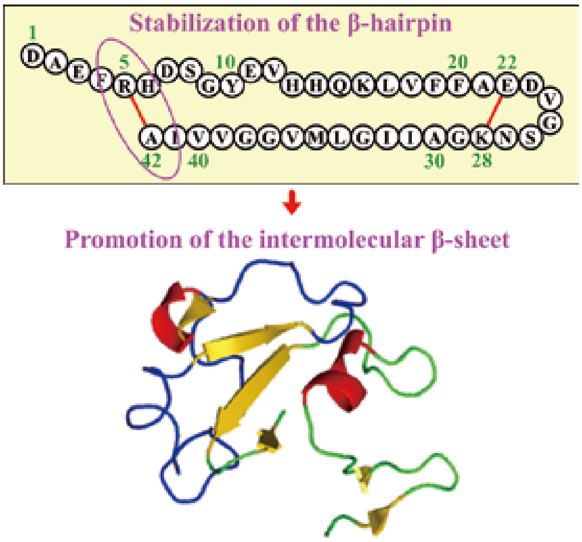

Figure 3. The key residue for the aggregation of amyloid-β peptides is Arg5, which stabilizes the β-hairpin structure and promotes the intermolecular β-sheet.

2. Ingenuity in Performing Replica Permutation: How to Order the State Labels for Improving Sampling Efficiency

Replica-exchange method (REM) is one of the generalized ensemble algorithms and is widely used for systems with many local minima, such as biomolecules. In this method, copies of the systems, call replicas, are prepared. The temperatures are excahnged between two replicas, as shown in Figure 4. As an advanced alternative to REM, the replica-permutation method (RPM) has been developed. In this method, all combinations of replicas and parameters are considered for parameter permutation, and a list of all the combinations is prepared. We reported that the temperature transition probability depends on how the list is created, especially in replica permutation with solute tempering (RPST).[2] We found that the transition probabilities decrease at large replica indices when the combinations are sequentially assigned to the state labels as in the originally proposed list. To solve this problem, we propose to modify the list by randomly assigning the combinations to the state labels. We performed molecular dynamics simulations of amyloid-β(16–22) peptides using RPST with the "randomly assigned" list (RPST-RA) and RPST with the "sequentially assigned" list (RPST-SA). The results show the decreases in the transition probabilities in RPST-SA are eliminated, and the sampling efficiency is improved in RPST-RA.

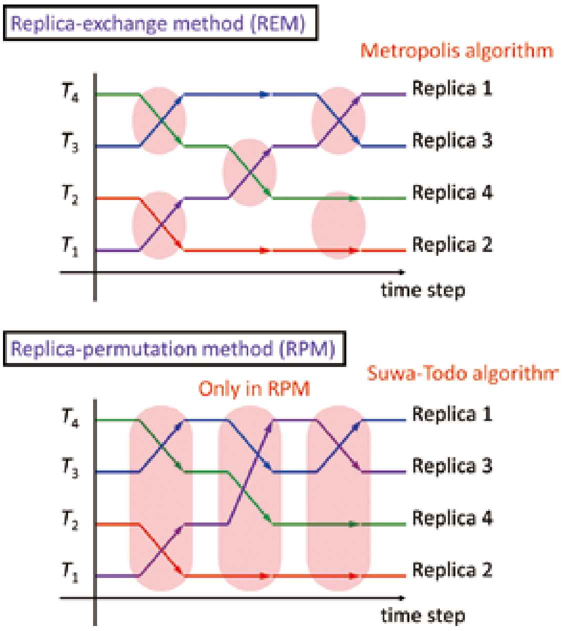

Figure 4. Schematic illustration of replica-exchange method (REM) and replica permutation method (RPM).

References

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2) D. Fukuhara, M. Yamauchi, S. G. Itoh and H. Okumura, *J. Comput. Chem.* **44**, 534–545 (2023).

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Dynamics of Biomolecular Machines in Function Revealed by Theoretical Methods

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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.1)

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.2)

Selected Publications

- 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).
- R. Kobayashi, H. Ueno, K. Okazaki and H. Noji, "Molecular Mechanism on Forcible Ejection of ATPase Inhibitory Factor 1 from Mitochondrial ATP Synthase," *Nat. Commun.* **14**, 1682 (2023).

1. Mechanism of Oxalate Transporter

Oxalate is contained in our daily food such as spinach and nuts. Excess oxalate forms insoluble salts with calcium ions, causing kidney stone disease. *Oxalobacter formigenes*, an oxalate-degrading bacterium that lives in the intestine, absorbs oxalate as its sole carbon source and excretes formate, a metabolic degradation product. As a result, *Oxalobacter formigenes* contributes to reducing the risk of kidney stone disease by lowering the oxalate level. The oxalate transporter (OxlT), which exists in the membrane of the bacterium, is responsible for oxalate uptake into and formate efflux out of the bacterium. The crystal structures of the two different conformations taken by OxlT during its transport cycle have been determined by our collaborators.3) One structure is in the outward-open conformation, while the other structure is in the occluded conformation with the bound oxalate.

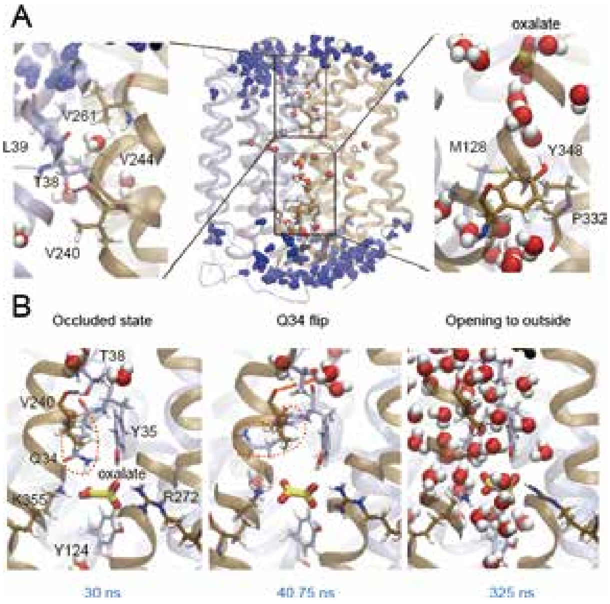

Figure 1. (A) The determined periplasmic and cytoplasmic gates. (B) The conformational transition from the occluded to the outward-open state.3)

The atomistic MD simulation from the occluded conformation of OxlT and analysis of the water molecule density revealed the presence of gates above and below the substrate binding pocket that control the influx of water and substrate molecules.3) The periplasmic gate consists of a hydrogen bond between Thr38-Val240 and a hydrophobic structure around it (Figure 1A left). The cytoplasmic gate consists of a hydrophobic structure composed of Met128, Pro332, and Tyr348 (Figure 1A right). Furthermore, in microsecond-scale simulations, OxlT undergoes a conformational change from the occluded conformation to the outward-open conformation.3) The overall conformational change was preceded by a localized change in the flip of the Gln34 side chain at the oxalate binding site and the dissociation of the Thr38-Val240 hydrogen bond mentioned above, followed a few hundred nanoseconds later by the opening of the periplasmic gate to the open conformation (Figure 2B). Thus, the Gln34 side chain and the Thr38-Val240 hydrogen bond are considered to be "latches" for the periplasmic gate.

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.4) 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.5)

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.6) By matching structural fluctuations between AA and CG simulations, a CG protein model called "Gō-MARTINI" was developed and optimized.7) This model should prove useful for describing protein dynamics that are involved in membrane remodeling processes.

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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 quantum chemistry and statistical mechanics theories and 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 and the local spin structures. A geminal theory for a molecule's electronic structure is also proposed based on generalised electron pairing. (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.

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, based on a multiscale hybrid method of integral equation theory and quantum chemical methods, we have elucidated the mechanism of pKa shift due to molecular recognition in solution. In addition, using a hybrid Monte Carlo framework, we developed a method for structural sampling of biomolecules in solution that satisfies the Hamiltonian based on integral equation theory.

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. We estimated the anisotropic bending rigidity and spontaneous curvature of crescent curvature-inducing proteins from tethered-vesicle experimental data using a mean-field theory. Our coarse-grained simulations revealed that reaction waves of curvature-inducing proteins can induce large shape transformations, such as membrane budding and necking, that erase or divide the wave. Moreover, we demonstrated that the occasional disappearance of the waves can alter the pathway of wave propagation on a membrane network.

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

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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 (Germany)
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	National Medal with Purple Ribbon (by His Majesty the Emperor of Japan)

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- DE LÉSÉLEUC, Sylvain
- TOMITA, Takafumi

IMS Research Assistant Professor
- CHEW TORII, Yuki
- MATSUBARA, Takuya
- TAMURA, Hikaru

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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.

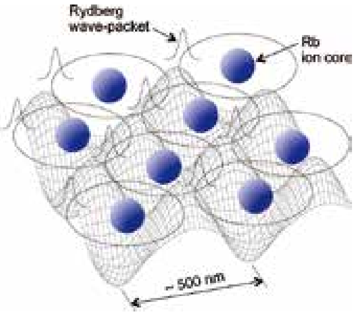

Figure 1. Metal-like quantum gas. A schematic of the many-body quantum simulator with ultracold Rydberg atoms, named "ultrafast quantum simulator," where electronic wave functions spatially overlap between neighboring atoms.2)

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," *Nature Physics* **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," *Nature Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, "Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas," *Nature 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," *Nature Photonics* **16**, 724 (2022).
- V. Bharti, S. Sugawa *et al.*, "Picosecond-Scale Ultrafast Many-Body Dynamics in an Ultracold Rydberg-Excited Atomic Mott Insulator," *Phys. Rev. Lett.* **131**, 123201 (2023).

1. Development of an "Ultrafast Quantum Simulator" by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales(6)

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"(3) and "a strongly correlated ultracold Rydberg gas."(4–6)

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.(5,6) 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.

Very recently in 2023, quantum magnetism has successfully been simulated with this standard hardware assembled with ~30,000 Rb atoms.(6) Our novel scheme above completes the simulation in just several hundreds of picoseconds, accelerating the simulation speed by three orders of magnitude compared to any other quantum simulators of magnetism so far. This innovative acceleration solves the issue with external noise on the timescale of ~1 microsecond or slower in general, which has been one of the biggest concerns for quantum simulation. Moreover, we have succeeded in simulating the formation dynamics of "quantum entanglement," which is difficult to measure in actual magnetic materials, on the fastest timescale of several hundred picoseconds, as schematically depicted in Figure 2.

We continue upgrading this ultrafast quantum simulators, generously supported by the Q-LEAP program of the MEXT of Japan.

2. Development of an Ultrafast Quantum Computer with Cold Atoms(7)

We have developed arbitrary two dimensional optical trap arrays for cold atoms with optical tweezers, which are necessary for quantum computing.

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,(7) accelerating a two-qubit gate (a fundamental arithmetic element essential for quantum computing) of cold-atom quantum computers by two orders of magnitude. It is also two orders of magnitude faster than the noise from the external environment and operating lasers, whose timescale is in general 1 microsecond or slower, and thus can be safely isolated from the noise. Moreover, the speed of this two-qubit gate is faster than that of the fast two-qubit gate demonstrated recently by "Google AI Quantum" with superconducting qubits.(8) We continue upgrading this ultrafast quantum computers, generously supported by the Moonshot program of the Cabinet Office of Japan.

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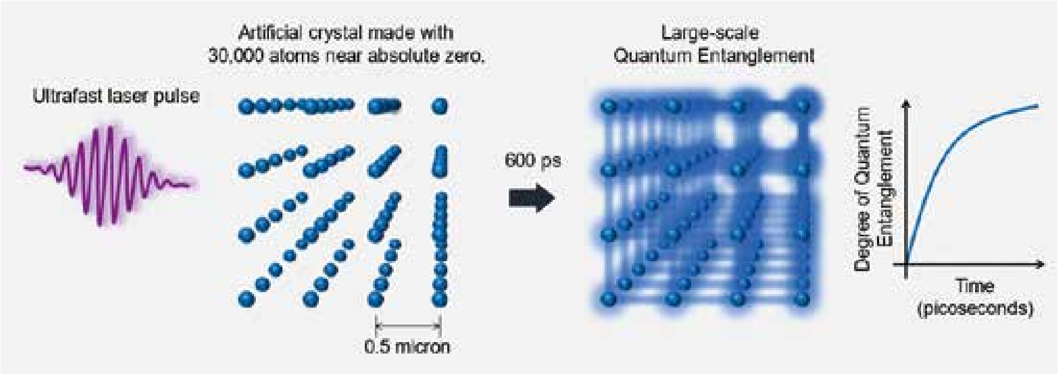

Figure 2. Conceptual diagram of ultrafast quantum simulation of magnetic material.(6) A large-scale array of 30,000 atoms, with a spacing of 0.5 micron, is controlled with a ~10 picosecond ultrafast laser pulse. After irradiating an ultrafast laser pulse, large-scale "quantum entanglement" is formed in only ~600 picoseconds. Image source: Prof. Seiji Sugawa (U. Tokyo).

Award

DE LÉSÉLEUC, Sylvain; The 12th Young Scientist Award of National Institutes of Natural Sciences (2023).

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Electronic Property of Functional Organic Materials

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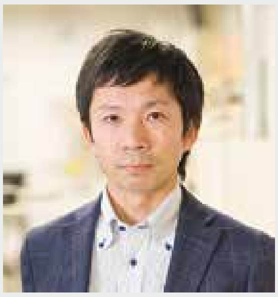
Division of Photo-Molecular Science III



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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

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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.

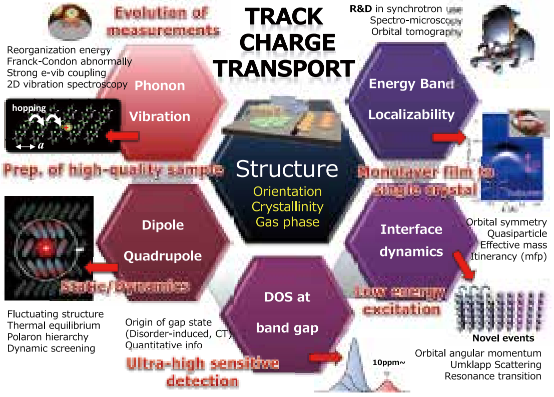

Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

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. Surface Characterization of Covalent Organic Frameworks[1)]

Covalent organic frameworks (COFs), as a large class of porous organic materials, have attracted intense research in the past few decades due to the great potential for applications. Substituting carbon with silicon in organic molecules and materials has been an attractive way to modify their electronic structure and properties. Silicon-doped graphene-based materials are known to exhibit exotic properties, yet conjugated organic materials with atomically precise Si substitution have remained difficult to prepare. We present the on-surface synthesis of one- and two-dimensional covalent organic frameworks whose backbones contain 1,4-disilabenzene (C_4Si_2) linkers. Silicon atoms were first deposited on a Au(111) surface, forming a $AuSi_x$ film on annealing. The subsequent deposition and annealing of a bromo-substituted polyaromatic hydrocarbon precursor on this surface led to the formation of the C_4Si_2-bridged networks, which were characterized by a combination of high-resolution scanning tunnelling microscopy and X-ray photoelectron spectroscopy taken at BL2B of UVSOR supported by density functional theory (DFT) calculations. Each Si in a hexagonal C_4Si_2 ring was found to be covalently linked to one terminal Br atom. For the linear structure obtained with the pyrene-based precursor, the C_4Si_2 rings were converted into C_4Si pentagonal siloles by further annealing.

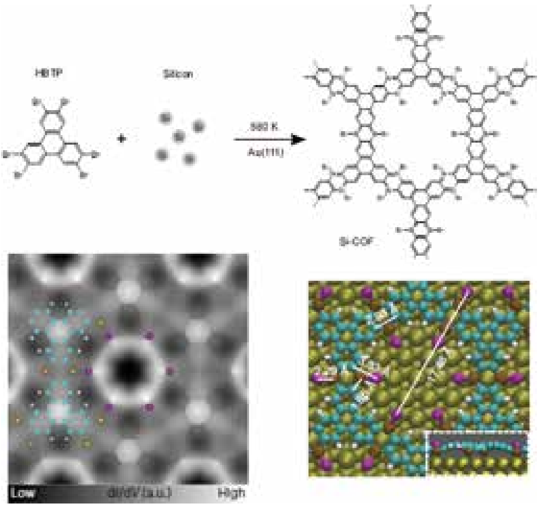

Figure 2. Top: Scheme of on-surface reaction for the aryl–Si coupling reaction on Au(111). Bottom: High-resolution constant height *dI*/*dV* map of the COF taken with a CO tip and the top and side views of DFT simulation. The figure is after ref 1).

2. Photoemission Tomography of Br-Doped Perylene Monolayer[2)]

Energy level alignment at the organic–metal interface is an important issue in the field of organic electronics to understand the efficiency of charge injection and fundamental conduction mechanisms. The spectroscopic data of organic cations seem slightly insufficient, comparing to that of organic anions using strong molecular acceptor and alkali metal doping. Halogens are fundamental elements and have been widely used as hole dopants for organic electronics since the very early stages of research. Perylene doped with bromine exhibit a dramatic increase in conductivity. In this study, we observed the geometric and electronic structures of a monolayer of perylene molecules on the surfaces of Au(110) and Au(111). The effect of bromine doping was studied using C-K NEXAFS, angle-resolved photoemission spectroscopy (ARPES), and X-ray photoelectron spectroscopy (XPS). C-K NEXAFS can be used to observe vacant states, particularly a hole state, which is essential for p-type organic semiconductors. Moreover, the inclined molecular orientation is analyzed by measuring the polarization dependence. ARPES and 2D momentum map using a photoelectron momentum microscope at BL6U of UVSOR is a powerful technique for discussing the changes in the molecular orbital character upon the doping.

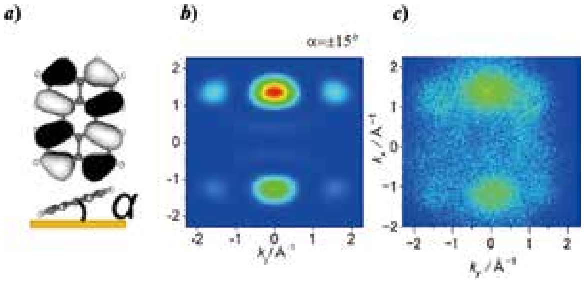

Figure 3. (a) HOMO distribution of a perylene molecule. (b) Simulated photoemission momentum maps of HOMO. (c) Experimental momentum map at binding energy of 1.5 eV. The figure is after ref 2).

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.[2,3)] The perspectives required for future light-source facility have been discussed with communities.[4)]

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4) H. Ota *et al.*, *J. Phys.: Conf. Ser.* **2380**, 012003 (5 pages) (2022).

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Light Source Developments by Using Relativistic Electron Beams

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2000 Associate Professor, Institute for Molecular Science
2004 Professor, Institute for Molecular Science
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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. Fuji, T. Kaneyasu, M. Fujimoto, Y. Okano, E. Salehi, M. Hosaka, Y. Takashima, A. Mano, Y. Hikosaka, S. Wada and M. Katoh, "Spectral Phase Interferometry for Direct Electric-Field Reconstruction of Synchrotron Radiation," *Optica* **10(2)**, 302–302 (2023).

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., Hiroshima Univ. and KEK Photon Factory and are 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.

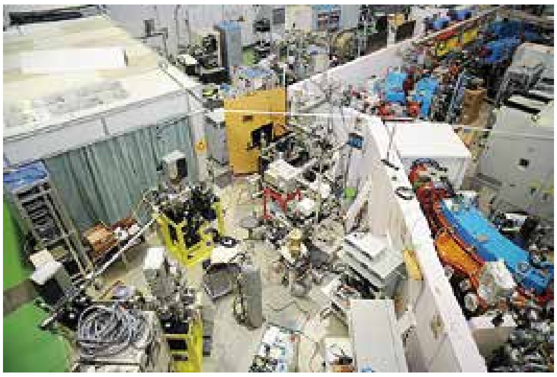

Figure 3. UVSOR BL1U experimental station for source development studies.

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

UVSOR Synchrotron Facility
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Education

2007	B.S. Nagoya University
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Professional Employment

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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

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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-ray-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.

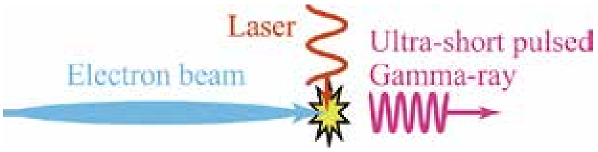

Figure 1. Schematic illustration of 90-degree inverse Thomson scattering.

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- 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).
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- Y. Taira, R. Yamamoto, K. Sugita, Y. Okano, T. Hirade, S. Namizaki, T. Ogawa and Y. Adachi, "Development of Gamma-Ray-Induced Positron Age-Momentum Correlation Measurement," *Rev. Sci. Instrum.* **93**, 113304 (2022).
- Y. Taira *et al.*, "Measurement of the Spatial Polarization Distribution of Circularly Polarized Gamma Rays Produced by Inverse Compton Scattering," *Phys. Rev. A* **107**, 063503 (2023).

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.

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

User applications are currently underway at BL1U in UVSOR-III, including measurements of bulk materials and in situ measurements of defect formation under stress loading.

Meanwhile, we are also developing gamma-ray-induced spin-polarized positron annihilation spectroscopy using circularly polarized gamma rays. If the electron spins of a sample are ordered in a particular direction and the positrons are also spin-polarized, the Doppler broadening spectra of annihilation gamma rays and the positron lifetime will change. The spin-polarized positrons are generated from the circularly polarized gamma rays inside a sample. From this change, it is possible to obtain information about the electron spins around defects in magnetic materials. To demonstrate the principle of circularly polarized gamma-ray-induced spin-polarized positron annihilation spectroscopy, a pure iron sample is mounted between permanent magnets and the positron lifetime and Doppler broadening are measured.

Inverse Compton scattering of a polarized laser by energetic electrons is an excellent method to generate polarized gamma rays. A 100% polarized laser can generate 100% polarized gamma rays, but polarization varies depending on the scattering angle of the gamma rays. We have experimentally measured the spatial polarization distribution of circularly polarized gamma rays using magnetic Compton scattering that can measure the circular polarization of MeV gamma rays. Measurements of the asymmetry of gamma-ray transmission relative to the magnetized iron at each scattering angle clearly show that gamma rays are circularly polarized near the central axis, and they change from circular to linear polarization as the scattering angle increases.[1)]

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.

As there is a laser with a pulse energy of 50 mJ and a pulse width of 130 fs (FWHM) in UVSOR-III, the laser strength parameter is 0.4 if the beam size can be focused to 3 μm (rms). Nonlinear inverse Thomson scattering experiments were performed in 2022, but no higher harmonic gamma-ray generation was observed. Concentric fringes were observed in the laser focusing pattern, suggesting that the laser energy was dispersed and the laser strength parameter was reduced. Further improvements will be made and re-experiment is planned in the future.

Reference

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

Application of X-Ray Microscopy

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Keywords X-Ray Microscopy, Computer Tomography, Soft X-Ray Absorption Spectroscopy

A synchrotron-based scanning transmission X-ray microscope (STXM) is a technique to perform 2-dimensional (2D) X-ray absorption spectroscopy with high spatial resolution. The schematic image is shown in Figure 1. A monochromatic X-ray is focused by an X-ray focusing lens, a Fresnel zone plate, on a sample as a diameter around 30 nm through an order select aperture and the transmitted X-ray is detected. By scanning the sample 2-dimensionally, an X-ray absorption image is obtained. Then, by noticing the near edge X-ray absorption fine structure (NEXAFS) of the specific element, 2D chemical state of the sample can be obtained. Since characteristics of UVSOR is suitable for using extreme ultra-violet and soft X-ray region, the STXM in UVSOR, BL12, is suitable to analyze soft materials and organic materials. The X-ray range from 55 to 770 eV is a unique feature of BL12 and enables to approach lithium K-edge (55 eV~) with spatial resolution at 72 nm.[1] The advantages 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.[2] Especially, nowadays, an in-situ/operando analytical technique is attracting more attentions of researchers because that is an important technique to understand intrinsic state of the samples. Recently, heating and cooling of the sample, humidity control system and electrochemistry, 2D orientation of molecules, 3D 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.[3] These techniques are difficult to perform by using the other microscopic techniques, such as an electron microscope.

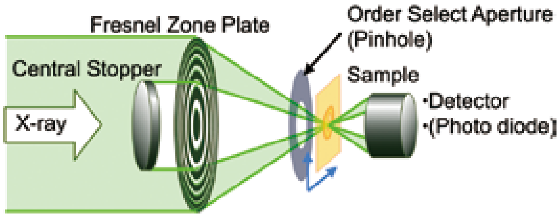

Figure 1. Schematic optical system of STXM.

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- D. Asakura, E. Hosono, M. Kitamura, K. Horiba, E. Magome, H. Setoyama, E. Kobayashi, H. Yuzawa, T. Ohigashi, T. Sakai, R. Kanega, T. Funaki, Y. Sato and A. Ohira, *Chem. –Asian J.* **18**, e202201047 (2023).
- Y.-C. Huang, Y. Li, K. T. Arul, T. Ohigashi, T. T. T. Nga, Y.-R. Lu, C.-L. Chen, J.-L. Chen, S. Shen, W.-F. Pong, C.-L. Dong and W.-C. *Chou, ACS Sustainable Chem. Eng.* **11**, 5390–5399 (2023).

1. 3-Dimensional near Edge X-Ray Absorption Fine Structure of an Isolated Cell Nucleus

Computer tomography (CT) is an arithmetic method to reconstruct a 3D structure from serial tilted 2D X-ray absorption images without any destructive process. Reconstructed images of CT with full-rotation (or 180° rotation) data acquisition have quantitative values of X-ray line absorption coefficient. Therefore, by changing the X-ray energies around the absorption edge, 3D nano-NEXAFS can be performed. CT is typically performed by using full-field imaging X-ray microscopy because of shorter acquisition time of 2D X-ray transmission images. On the other hand, in regard to the radiation dose, STXM-CT is one order less than by the full-field imaging CT. This advantage is preferable to analyze 3D nano-NEXAFS of organic and bio samples with complicated structures, such as a cell nucleus. To establish STXM-CT, we have designed a rotating sample cell.4,5)

An isolated cell nucleus of a HeLa S3 cell was chemically fixed with glutaraldehyde. After the critical point drying, the cell nucleus was glued on a tip of a tungsten needle (TP-001, Micro Support co., ltd.) by a crystal bond. 50 energy stacks around O K-edge (530 ~ 538 eV) dataset, $f(x,y,\theta,E)$, were obtained with tilting the sample 3.6° each, in total 180° rotation. In the energy stack, X-ray absorption images were acquired by scanning 8×8 μm^2 area of the sample with 160 nm pitch. Then, the dwell time was 1 ms per pixel. In total, the whole measurement process took ~12 hours. As pre-reconstruction process, the X-ray absorption images in all the energy stacks were grouped according to the X-ray energy. The 2D cross sectional images were reconstructed from each group and the 3D image was obtained by stacking those images. Finally, a 3D NEXAFS mapping dataset, $F(x,y,z,E)$, was obtained by sorting the reconstructed 3D images by the X-ray energy. For example, a 3D volume projection image is shown in Figure 2(a). A reconstructed cross sectional image in the plane shown in Figure 2(a) by a red dashed line and its local XAS spectra are shown in Figure 2(b) and 2(c), respectively. O K-edge spectra were extracted from structures of cell nucleolus (red and green areas) and cytoskeleton (yellow and blue areas) in Figure 2(b). Figure 2(d) shows RGB color distribution of these chemical components by performing SVD fitting to the 2D NEXFAS by using aXis2000 software. The colors of the plots and of the RGB map are coincident with those of the area in Figure 2(b) except for the yellow plot. In Figure 2(d), the distribution of the green color is not only at the cell nucleolus but also slightly at the cytoskeleton. In the case of the measurement of biological samples, the measurement under cryo condition is necessary to keep samples from radiation damage.

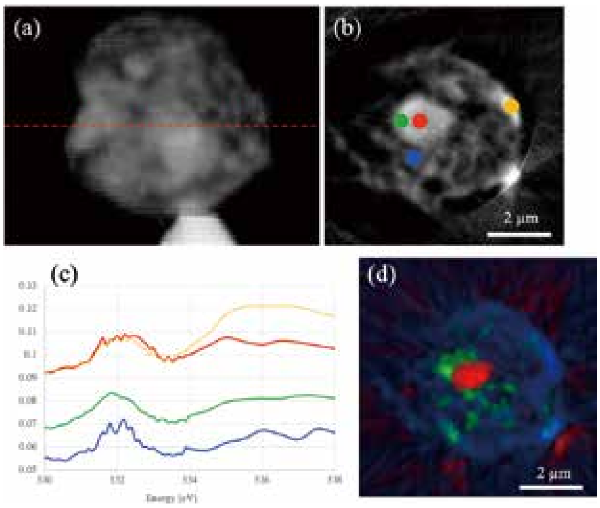

Figure 2.3) (a) A 3D volume projection image of an isolated cell nucleus of HeLa S3 cell, (b) a reconstructed cross sectional image of the cell nucleus at a red dashed line, (c) X-ray absorption spectra extracted from 2(b) and (d) a RGB color distribution of the spectra. Colors of the plots and the RGB color distribution are coincident with those of areas in (b).

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4) T. Ohigashi, Y. Inagaki, A. Ito, K. Shinohara and N. Kosugi, *J. Phys.: Conf. Ser.* **849**, 4 (2017).

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Novel Spin and Chiral Materials Science by Advanced Photoemission Methodologies

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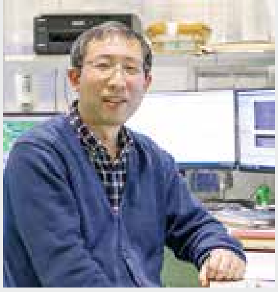
Division of Advanced Solid State Physics



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2018 Senior Researcher, Institute for Molecular Science
2021 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards
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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

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Keywords Photoelectron Spectroscopy, Momentum Microscope, Electronic Spin Structure

When electrons in a material are excited by photons, they are emitted into the vacuum as photoelectrons. Interestingly, the angular distribution of these photoelectrons shows 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 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/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 station at UVSOR synchrotron facility. Soft X-rays from BL6U for k_z dispersion and core-level excitations and vacuum ultraviolet light from BL7U at normal incidence for atomic orbital analysis make this station unique.

Selected Publications

- F. Matsui *et al.*, "Soft X-Ray Photoelectron Momentum Microscope for Multimodal Valence Band Stereography," *Rev. Sci. Instrum.* **94**, 083701 (2023).
- F. Matsui *et al.*, "Domain-Resolved Photoelectron Microscopy and µm-scale Momentum-resolved Photoelectron Spectroscopy of Graphite Armchair Edge Facet," *J. Phys. Soc. Jpn.* **91**, 094703 (2022).
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- 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).

1. Chiral Charge Density Wave Revisited

1T-TaS$_2$ has fascinated researchers for half a century as a system that undergoes a phase transition with three structural changes from high to low temperatures. In the lowest temperature phase, a chiral charge density wave (CDW) structure ($\sqrt{13}\times\sqrt{13}$)-R±13.90° (Figure 2(a) and (b)) is observed by electron diffraction and scanning probe microscopy. Regarding the electronic structure, the first paper on two-dimensional ARPES, which observed the average of both chiral structures,$^{1)}$ had a strong impact, and it greatly influenced subsequent papers. Only recently has the nesting vector, which is the basis of charge density waves, begun to be accurately discussed in measurements using chiral single domains. In a single layer, unpaired electron spins are isolated in a 13-Ta-atom units, commonly known as the Star of David (six pointed star). Isolated spins are stabilized by interlayer interactions. Recently, STM revealed coexistence of Mott-insulator and band-insulator domains on the cleaved surface,$^{2)}$ which has attracted attention as a great opportunity to elucidate the CDW mechanism (Figure 2(c) and (d)). Here, spin-resolved micro-ARPES using PMM will be a decisive tool to clariify the physics behind this complex CDW phenomena.

Figures 2(e) and 2(f) shows the constant energy countour and band dispersion of 1T-TaS$_2$, respectively, measured by UVSOR-PMM$^{3)}$ at 30 K.$^{4)}$ The ellipsoidal electron pockets around the M points are modified and exhibit the so-called “windmill” rotational symmetry modulation around the Γ point due to the CDW formation. The microscopic field-of-view enabled selective observation of one of the two types of twinned CDW domains. Although we have expected the formation of a sharp gap on the band dispersion due to CDW, noticeable intensity remained even around the region of $E_{\mathrm{binding}} = 1$ eV and $|k| = 1$ Å^{-1} (Figure 2(f)). This result may be due to the observed mixture of multiple electronic states in the Mott insulator and band insulator at different surface terminations, which was pointed out in STM.$^{2)}$ Further detailed PMM works will be described elsewhere.

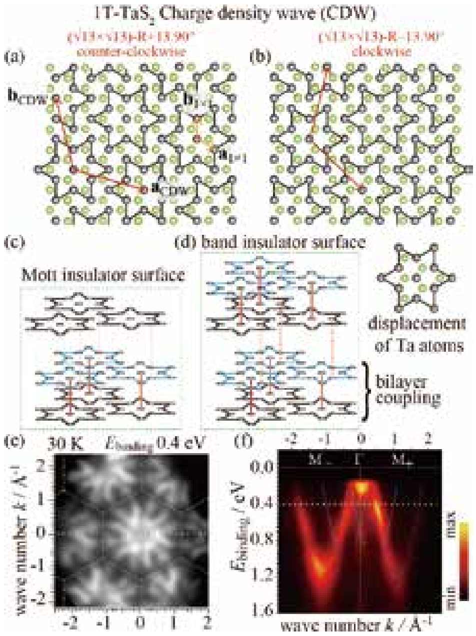

Figure 2. (a) and (b) Lateral atomic structure models of 1T-TaS$_2$ in the CDW phase. (c) and (d) Structure models of different surface terminations. (e) Constant energy contour at the binding energy of 0.4 eV. (f) Valence band dispersion along the MΓM axis.

2. Original Analyzer for 3D-Atomic Structure Imaging and 3D-Spin Vector Analysis

Photoelectron holography is an element specific 3D atomic imaging technique. Local atomic arrangements of dopant atoms can be characterized. Compositional crossover of multiple-site Ag doping in Bi$_2$Se$_3$ from substitution to intercalation was revealed (Figure 3).$^{5)}$

We are aiming at highly efficient and comprehensive measurement of atomic structure and spin distribution. Omnidirectional photoelectron acceptance lens (OPAL)$^{6)}$ together with Projection-type electron spectroscopy collimator analyzer (PESCATORA)$^{7)}$ enables photoelectron holography measurement of the full hemisphere. Moreover, we invented Right angle deflection imaging analyzer (RADIAN)$^{8)}$ for spin vector analysis with *k*/*r*-space resolution. We are expanding the MM system based on our original inventions.

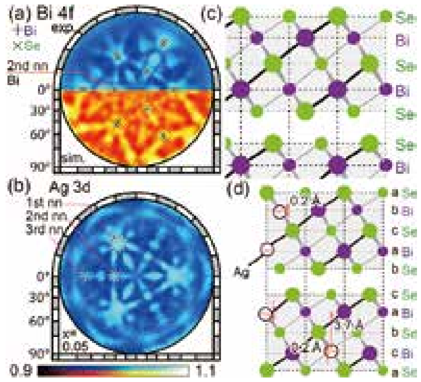

Figure 3. (a) Bi4f and (b) Ag3d photoelectron holograms of Ag-doped Bi$_2$Se$_3$. Atomic structure models of (c) pristine and (d) Ag-doped Bi$_2$Se$_3$ deduced by holography analysis.

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4) F. Matsui *et al.*, *Rev. Sci. Instrum.* **94**, 083701 (2023). [Editor’s pick]
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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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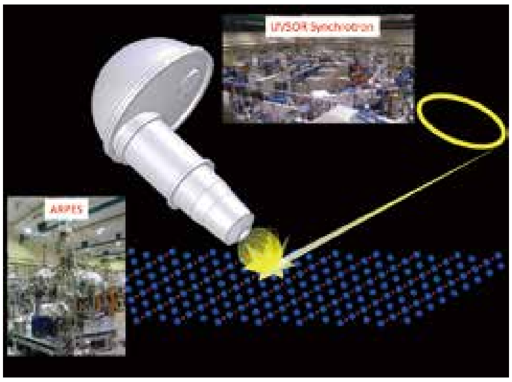
Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

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, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* **450**, 81–84 (2007).
- K. Tanaka, N. Hieu, G. Vincini, T. Masui, S. Miyasaka, S. Tajima and T. Sasagawa, "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, N. Murai, M. Nakajima, R. Kajimto and K. Tanaka, "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).

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

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- and angle-resolved photoemission spectroscopy (spin-resolved ARPES) is one of the most powerful experimental techniques to investigate the magnetic properties of such materials, where one can know the "complete" information of the electronic states of materials; energy, momentum, and spin direction. Recent development of high energy and angle resolved photoelectron analyzer as well as the contemporary light sources such as third generation synchrotron radiation make it possible for the photoemission spectroscopy to investigate not only band structures but many body interactions of electrons in solids. However, appending the spin resolution to photoemission spectroscopy is quite difficult because of an extremely low efficiency (10^{-4}) of Mott-type spin detections. Recently, very-low-energy-electron-diffraction (VLEED-type) spin detector with 100 times higher efficiency than that of conventional Mott-type has been developed and spin-resolved ARPES has been started to be realized. So far, most of the spin-resolved ARPES systems in the world are using the single-channel detector and efficiency is still a problem.

Beamline BL5U at UVSOR has been totally reconstructed by our group, and opened for users as high photon flux and high energy resolution ARPES beamline since 2017. As a new function for this beamline, we have started high-efficient spin-resolved ARPES project with multi-channel detection (we call "image-spin" detection). The goal of this project is to realize the 100 times better efficiency and the 10 times better momentum resolution than the current spin-resolved ARPES system in the world, which can be a breakthrough in this field.

In 2020, we set up the spin detection apparatus shown in Figure 1(a) and finished tuning the electron lens parameters of the spin detection section. With this apparatus, we succeeded in obtaining a spin-resolved signal on the Au(111) surface as shown in Figure 2(c). According to rough estimates, the efficiency of spin-resolved ARPES was 100 times higher than that of the single-channel detection systems currently used in the world. However, the spin-resolved ARPES bands were broad compared to the normal ARPES ones shown in Figure 2(b), meaning that the momentum resolution was not so good. With this apparatus, the instrument required two VLEED detection chambers and a high-quality spin target of the same quality to detect spin information in the *x*, *y*, and *z* directions of the sample. In addition, the spin targets had to be magnetized frequently during the measurement.

To overcome these problems, we have introduced a new "spin manipulator" that can change the spin direction of the passing electrons in any direction. The new setup shown in Figure 1(b) requires only one VLEED detection chamber and the users do not need to magnetize the spin target during the measurement. The installation of the spin manipulator and optimization of the spin target deposition conditions have greatly improved the spin-resolved images, and in 2022, we were able to obtain spin-resolved images with momentum resolution comparable to that of normal ARPES, as shown in Figure 2 (d). We are currently optimizing the lens parameters of the spin manipulator to obtain spin information in the remaining two axial directions.

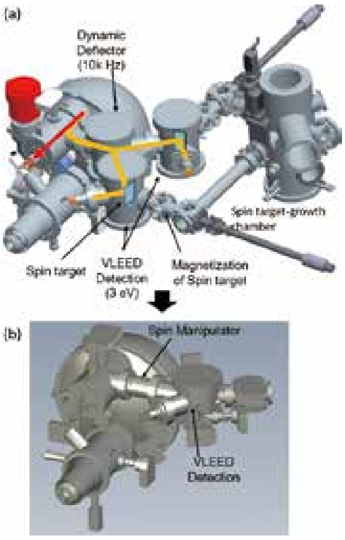


Figure 1. Previous (a) and current (b) setup of image-spin ARPES.

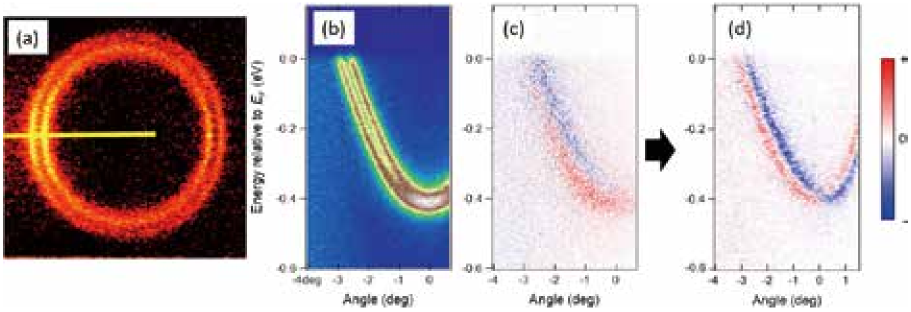


Figure 2. a) Fermi surface of Rashba spin splitting in Au(111) surface states and (b) image plot of normal ARPES along the yellow bar in (a). Spin-resolved ARPES data showing the spin polarization (blue–red scale) with the previous experimental setup (c) and the current setup (d).

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Soft X-Ray Spectro-Microscopy and Spectro-Scattering for Life Science Research

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Senior Researcher

Scanning Transmission X-ray Microscopy: STXM is a mainstream of Soft X-ray Spectromicroscopy techniques due to that versatility since it is a photon-in & photon-out technique, which allow us to have some freedom of the sample specimen environments, like under magnetic field or wet condition. STXM utilizes the NEXAFS: Near Edge X-ray Absorption Fine Structure as the image contrast mechanism. When we study the soft materials ex. polymers, which consist of Carbon, Nitrogen, and Oxygen as a main element, through the NEXAFS spectral features we can obtain the chemical bonding/functional group information about the samples. Combined with the focused soft x-ray beam, about several tens of nanometer, we can achieve the chemical component mapping of the samples. If we look at the phase-separated polymer blend, we can speciate each domain with such high spatial resolution. Figure 1 shows an example of the chemical component map; blend of PS: Polystyrene, PMMA: Polymethylmethacrylate, and PVC: Polyvinylchloride mixed with nano-clays. The thin-section sample was prepared by a ultramicrotome (~100 nm thick).

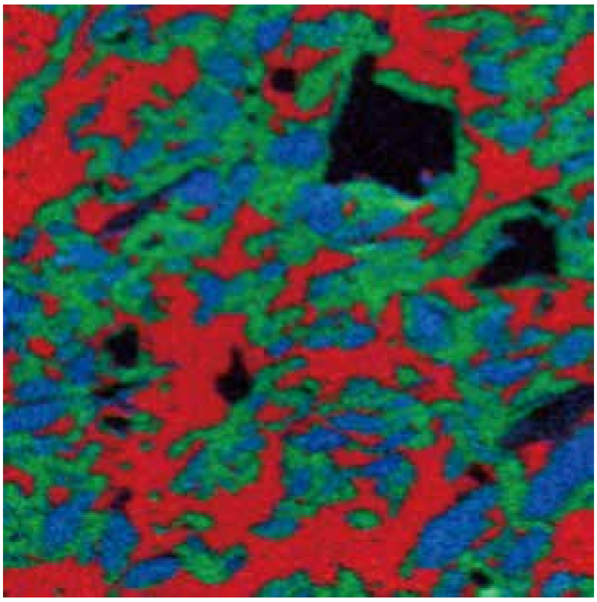

Figure 1. STXM chemical component map of the Polymer-Nano Clay Blend. R:PS, G: PMMA, B: PVC. The image size is 20 µm by 20 µm.

Before joined the IMS, at the Diamond Light Source in the UK, I had worked with my collaborators to study many environmental science cases to understand the interaction between minerals and organics including bacteria with using STXM in the Soft and Tender X-ray regimes.[2,3]

Since January 2023 I have been responsible to operate the BL4U STXM beamline at the UVSOR to maintain the user program including the industrial research, especially for the soft materials research like the radiation sensitive rubbery materials, which is difficult to study by the electron microscopy.

Another important mission is to plan the future UVSOR project,[1] which will be under the Research Center for Autonomous Functions by Tailor-made Photon Science. Toward the new approach using the combination of the low energy range photon from infrared to soft/tender x-rays, currently I am working with many scientists in the Life Science field to start the feasibility/trial studies using STXM and other soft x-ray techniques such as RSoXS: Resonant Soft X-ray Scattering, counterpart of STXM in reciprocal space. Figure 2 illustrates my concept to study the soft materials including biological samples using the three types of x-ray technique based on the NEXAFS spectroscopy.

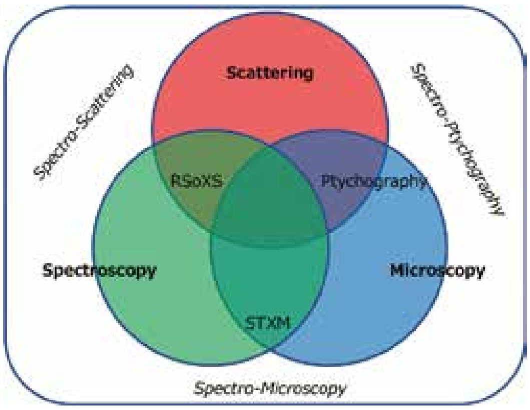

Figure 2. Concept of the NEXAFS based submicron chemical speciation methods.

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

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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 developed time-resolved XAS of photochemical reactions by synchronizing soft X-ray probe pulses with the laser pump pulses.[3]

1. Time-Resolved XAS of Photochemical Reactions in Solutions

The time-resolved XAS system has been developed at the soft X-ray beamline BL-13A of the Photon Factory, KEK.[3] The laser pump pulses (515 nm, 290 fs) were almost coaxially introduced to the liquid cell with the soft X-ray probe pulses. A trigger clock system and a frequency synchronization module were used for the synchronization of the laser pulses with soft X-ray pulses.

By using this measurement system, we have measured the time-resolved N K-edge XAS spectra of iron phenanthroline $[Fe(phen)_3]^{2+}$ aqueous solutions during the photoexcitation process with the time resolution of 45 ps. The C=N π* peaks of the ligands in the photoexcited (high spin) state of $[Fe(phen)_3]^{2+}$ are shifted to the lower photon energy compared to those in the ground (low spin) state. The temporal evolution of the peak intensity difference as a function of the delay time of the soft X-ray pulses with the laser pulses has determined that the time constant of the relaxation process from the high spin state to the low spin state is 550 ± 12 ps.

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Mesoscopic Structural Analysis of Polymer Materials

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Polymer composites, made by mixing multiple materials, have become increasingly important in developing polymer materials with higher functionality. Structural analysis is required for each constituent material (chemical species). However, with conventional small-angle X-ray and neutron scattering methods (SAXS/SANS), it is not easy to analyze the structure of each constituent material because the overall structural information is obtained simultaneously.

1. Resonant Soft X-Ray Scattering for Polymer Materials

Recently, we have developed resonant soft X-ray scattering (RSoXS) method. RSoXS has element, molecule and molecular orientation selectivity, making it possible to observe specific mesoscopic structures that cannot be observed with conventional SAXS. In particular, soft X-rays have the advantage of being able to selectively observe light elements such as carbon, nitrogen, and oxygen. Last year, we succeeded in analyzing the twisted structure of self-assembled liquid-crystal helical nanofilaments without electron density modulation.[1]

This year, we started researching polymers. In order to understand the performance of epoxy resins, it is necessary to analyze the crosslinked structure, which is usually composed of light elements and cannot be observed by conventional SAXS. Therefore, by using our resonant soft X-ray scattering method, we focused on the elements peculiar to crosslinked molecules and started to analyze the crosslinked structures of polymers by utilizing the resonance scattering of these elements.

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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 by forming an active surface when heated in ultra-high vacuum (UHV). Recently we have developed a new NEG thin film that was prepared by the following simple procedure, sublimation of high-purity Ti under UHV in the range of 10^{-7} to 10^{-8} Pa, followed by N_2 introduction (partially nitrided high-purity Ti). We confirmed that partially nitrided high-purity Ti deposited on inner surfaces of a vacuum vessel pumps H_2, H_2O, O_2, and CO gases even after 30 cycles of pumping, baking at 185 °C for 6 hours, cooling down to room temperature, introduction of high-purity N_2, and exposure to air. We applied surface-partially nitrided high-purity Ti deposition to the inner surface of the vacuum ducts in the upstream section of BL-12C in the Photon Factory 2.5 GeV ring and baked them at 250 °C. Pressure in the section reached 2.2×10^{-8} Pa without ion pumps after isolation from a turbomolecular pump with a gate valve. Partially nitrided high-purity Ti deposition is also applicable to UVSOR beamlines.

Visiting Professor

FUKUHARA, Takeshi *(from RIKEN)*

Quantum Gas Microscopy of a Frustrated XY Model in Triangular 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 a variety of fundamental models in solid-state physics. We have prepared Bose-Einstein condensates (BECs) in triangular optical lattices for the study of frustration physics, and implemented quantum gas microscope, which makes it possible to observe such quantum gases at the single atom level. By regarding the phase of BECs as a spin and by implementing antiferromagnetic spin–spin couplings via a lattice shaking technique, we have realized frustrated XY spin model. The frustration leads to two-fold ground states corresponding to two chiral modes. We have investigated the relaxation dynamics from the ferromagnetic phase to the spiral phases with the chiral modes by dynamically changing the spin–spin coupling. The domain formation of the chiral modes has been observed though high-spatial-resolution time-of-flight measurements.

Visiting Associate Professor

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

Epitaxially-Grown Single-Crystalline Organic Molecular Semiconductors

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. However, current organic semiconductor electronics are mostly built on heterojunctions composed of polycrystalline or amorphous molecular solids, in contrast to the inorganic semiconductor cases where epitaxial growth of single-crystalline is one of the most essential technologies for modern electronic applications. Our group has been working on single-crystalline heterojunctions of organic molecular semiconductors by “molecular beam epitaxy” techniques. Recently, we have published that on the single-crystal surface on phthalocyanine-copper (CuPc), which is one of the most well-studied organic semiconductors, perfluorinated CuPc exhibits epitaxial growth. As this is an analogical finding to our previous collaborative achievement with IMS for epitaxial perfluorinated pentacene on the single-crystal pentacene, further studies on its electronic properties will be 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

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Education

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

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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

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Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, 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 (UVMCD) 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.

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. These works were supported by the NEDO Fuel Cell project. More recently, more general chemical reactions on heterogeneous catalyst surfaces such as CO_2 hydrogenation using the AP-HAXPES system have been investigating on typical conditions of $\sim 5\times10^4$ Pa and ~600 K.

The third subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using 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 EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional materials as negative thermal expansion alloys.

Selected Publications

- T. Nakagawa and T. Yokoyama, "Magnetic Circular Dichroism near the Fermi Level," *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, "Anharmonicity and Quantum Effects in Thermal Expansion of an Invar Alloy," *Phys. Rev. Lett.* **107**, 065901 (2011).
- Y. Uemura *et al.*, "Dynamics of Photoelectrons and Structural Changes of Tungsten Trioxide Observed by Femtosecond Transient XAFS," *Angew. Chem., Int. Ed.* **55**, 1364–1367 (2016).
- Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, "X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions," *Appl. Phys. Express* **10**, 076603 (2017).
- T. Koitaya, K. Yamamoto, T. Uruga and T. Yokoyama, "*Operando* Characterization of Copper–Zinc–Alumina Catalyst for Methanol Synthesis from Carbon Dioxide and Hydrogen by Ambient-Pressure Hard X-Ray Photoelectron Spectroscopy," *J. Phys. Chem. C* **127**, 13044–13054 (2023).

1. Metallic Bonds and Thermal Vibration in Brass[1)]

Nature of the metallic bond and thermal vibration in brass alloy is investigated from the local structural and thermodynamical points of view by the temperature-dependent Cu and Zn K-edge EXAFS spectroscopy and the path-integral effective classical potential (PIECP) theoretical simulation. It is unexpectedly found that the thermal vibrational amplitude around Zn is a little but meaningfully smaller than that around Cu, although it is usually believed that Zn is a much softer metal than Cu in terms of various thermodynamical physical quantities of elemental metals. Moreover, it is found that the nearest neighbor distance around Zn is almost equivalent to that around Cu (only ~0.01 Å difference), although the metallic radius of Zn commonly used is considerably larger than that of Cu (~0.06–0.09 Å difference). These peculiar findings can be interpreted as a result of confinement of Zn atoms in a smaller space than usual and a significantly larger repulsive potential of Zn than Cu.

Figure 1 shows the mean square relative displacements C_2 for the first-nearest neighbor (NN) shells obtained by the EXAFS experiment and the PIECP simulation. The EXAFS results show slightly smaller temperature dependence around Zn than around Cu, this yielding the Debye temperatures of $\Theta_D(Cu)$ = 295 K and $\Theta_D(Zn)$ = 302 K. The PIECP results agree with the EXAFS finding qualitatively [$\Theta_D(Cu)$ = 329 K and $\Theta_D(Zn)$ = 348 K]. This consequence is surprising since it seems to be essentially contradictory to the simple prediction based on the potential stiffness (Cu should be stiffer than Zn). The reason for a smaller thermal vibration and thus a larger force constant in Zn–Zn atom pair is probably ascribed to a steeper repulsive potential at a shorter distance side in the Zn–Zn pair. When the system is really diatomic, the Zn–Zn distance is hardly contracted due to the steep repulsive potential and is easily elongated, resulting in large anharmonic vibrational amplitude in the diatomic Zn_2 molecule. On the contrary, in a closed packed solid like *fcc*, the Zn–Zn distance is hardly elongated due to the existence of other atoms at the opposite side, leading to confinement of the Zn atom. This indicates that the Zn atoms in brass are likely to be confined in a space that is a little too small for Zn and are hardly movable.

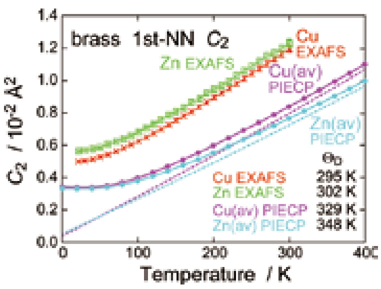

Figure 1. Mean square relative displacements C_2 for the first-nearest neighbor pairs obtained by the EXAFS analysis (with error bars; Cu: Red; Zn: Green) and the PIECP simulations (average Cu: Magenta; average Zn: Light blue; solid line: Quantum; dashed line: Classical), respectively. The corresponding Debye temperatures are also given in the figure.

2. Metastable Structure of Photoexcited WO_3 Determined by the Pump–Probe EXAFS Spectroscopy[2)]

Photocatalysts have drawn much attention with respect to harvesting sunlight to split water into H_2 and O_2. Usually, the process is understood using the energy band model. In the energy band model, the positions of Fermi level, minimum of the conduction band, and maximum of the valence band are important with respect to the reduction and oxidation potentials for H_2/H_2O and O_2/H_2O. The local structure and electronic state of the photoexcited state need to be elucidated to understand the photocatalysis of water splitting and to improve the performance of water-splitting photocatalysts. In this work, we report the PP-EXAFS results for the structure of the metastable (MS) WO_3 state to clarify the local structure change and to attempt to explain the long formation time for the MS WO_3.

The WO_3 aqueous solution jet was supplied to the cross point of the laser used for photoexcitation (mode-lock Ti-sapphire laser with a 1 ps pulse width, 945 Hz repetition rate, and 400 nm wavelength) and the X-ray beam emitted from the Photon Factory Advanced Ring (single bunch operation with pulse width of 100 ps, and pulse interval of 1.26 µs). The fluorescence X-rays were monitored using a scintillation counter with a Cu filter to attenuate the elastic X rays. The local structure of WO_3 photocatalyst in the photoexcited MS state created 150 ps after laser irradiation as well as the ground state (GS) one has been determined by pump–probe EXAFS and constrained thorough search EXAFS analysis. As shown in Figure 2, a highly distorted octahedral local structure was found, especially one of the shortest W–O was further shortened. We have discussed some contradiction with theoretical calculation and propose a possible structure for the metastable state.

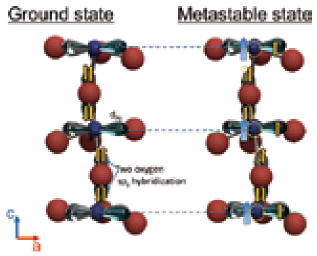

Figure 2. The local structure change in the ground state (GS) WO_3 and the metastable (MS) WO_3. Large red and small blue circles represent O and W atoms, respectively. Yellow broken circles indicate the position of W in GS. Thick blue arrows show the movement of W atoms in the MS WO_3. W atoms along the *c*-axis move in the direction corresponding to W=O contraction. Orange filled and empty arrows in the orbitals correspond to electrons with spin and holes, respectively. Grey filled circles indicate holes. The unpaired electron spins are all parallel in the polaron cluster.

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Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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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 The 14th Young Scientist Award of the Physical Society of Japan

Member
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Post-Doctoral Fellow
SAITO, Hikaru
TAKAHASHI, Shota
SATO, Hiromasa
OYAMADA, Nobuaki
Graduate Student
LIN, Zhongqiu
MOCHIZUKI, Tatsuto
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YOSHIZAWA, Ryu
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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.

Selected Publications

- 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).
- T. Sugimoto *et al.*, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).
- H. Sato *et al.*, "Critical Impacts of Interfacial Water on C–H Activation in Photocatalytic Methane Conversion," *Commun. Chem.* **6**, 8 (2023).
- H. Sato *et al.*, "Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water," *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
- S. Takahashi *et al.*, "Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity," *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).

1. Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity$^{1)}$

Squeezing light beyond the diffraction limit and controlling the optical processes caused by the nano-confined light are central issues of nanophotonics. In particular, localized and enhanced light at the plasmonic nanogaps in scanning probe microscopes provides us unique platform for obtaining site-specific optical information at the molecular/atomic scale. Very recently, not only linear but also nonlinear optics have been applied to such tip-enhanced nanoscopy to gain higher sensitivity and spatial resolution. In this context, understanding the intrinsic nonlinear optical properties of plasmonic nanocavities is of growing importance to control the nanosized nonlinear optics more precisely. Recently, we have directly tackled this issue by focusing on second harmonics of wide range of infrared light enhanced in the tip-substrate plasmonic nanogaps. Combining a wavelength-tunable femtosecond pulse laser system with a scanning tunnelling microscope, we for the first time report unexpectedly broad tip-enhanced nonlinear optical response in a plasmonic nanocavity.

We demonstrated that the strong tip-enhancement of second harmonic generation (SHG) is maintained over the visible to infrared wavelength range. The prominent geometrical effects of plasmonic tips dominating this broadband enhancement ability were also verified; while the micrometer-scale tip shafts extend the spectral range of the field enhancement to the near- and mid-infrared region, the nanometer-scale tip apexes mainly contribute to boosting the visible/near-infrared light. This indicates that the nanometer-scale tip apexes and micrometer-scale tip shafts jointly enable the simultaneous enhancement of both infrared excitation and visible/infrared radiation processes, realizing the strongly enhanced SHG over the visible to infrared broadband region. Indeed, we have also succeeded in demonstrating both experimentally and theoretically that the broadband tip-enhanced SHG properties can be significantly altered in response to the micro- and macro-scale tip structures.

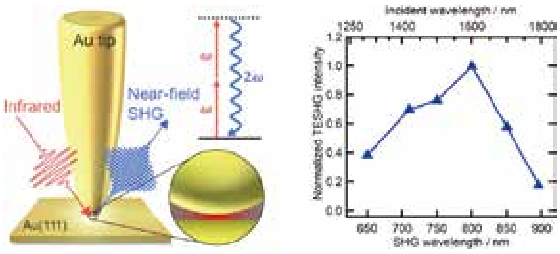

Figure 2. Tip-enhanced second harmonic generation.

2. Critical Impacts of Interfacial Water on the Photocatalytic C–H Conversion of Methane$^{2,3)}$

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. 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.

3. Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water$^{4)}$

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, 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.

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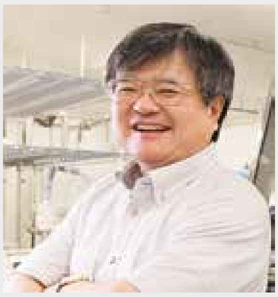
3) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).

4) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



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Professional Employment
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1988 Research Associate, Osaka University
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2008 Professor, Institute for Molecular Science
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Awards
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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

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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.

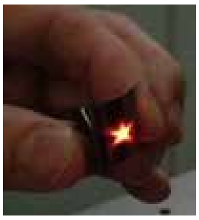

Figure 1. Up-converted (UC) yellow emission by star-shaped near infrared irradiation.

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

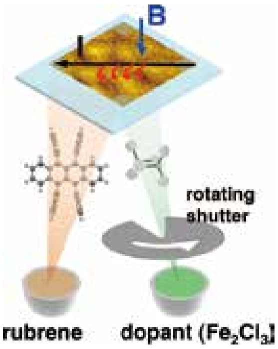

Figure 3. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

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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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- *Organic Solar Cells—Energetic and Nanostructural Design*, M. Hiramoto and S. Izawa, Eds., Springer Nature Singapore Pte Ltd. (2021).
- M. Hiramoto, "Organic Photocurrent Multiplication," in *the Series of Electronic Materials: Science & Technology*, Springer Nature Singapore Pte Ltd. (2023).

1. Blue Organic Light-Emitting Diode with a Turn-On Voltage at 1.47 V[1)]

Blue light is vital for light-emitting devices, lighting applications, as well as smartphone screens and large screen displays. However, it is challenging to develop efficient blue organic light-emitting diodes (OLEDs) owing to the high applied voltage required for their function. Conventional blue OLEDs typically require around 4 V for a luminance of 100 cd/m^2; this is higher than the industrial target of 3.7 V—the voltage of lithium-ion batteries commonly used in smartphones. Therefore, there is an urgent need to develop novel blue OLEDs that can operate at lower voltages.

We reported a novel OLED device with a remarkable ultralow turn-on voltage of 1.47 V for blue emission and a peak wavelength at 462 nm (2.68 eV) (Figure 4).[1)] This OLED operates via a mechanism called upconversion (UC). Herein, holes and electrons are injected into donor (emitter) and acceptor (electron transport) layers, respectively. They recombine at the donor/acceptor (D/A) interface to form a charge transfer (CT) state. Subsequently, the energy of the CT state is selectively transferred to the low-energy first triplet excited states of the emitter, which results in blue light emission through the formation of a high-energy first singlet excited state by triplet–triplet annihilation (TTA). As the energy of the CT state is much lower than the emitter's bandgap energy, the UC mechanism with TTA significantly decreases the applied voltage required for exciting the emitter. As a result, this UC-OLED reaches a luminance of 100 cd/m^2, equivalent to that of a commercial display, at just 1.97 V.

Figure 4. Lighting up a blue organic LED with a single 1.5 V battery.

2. Exciton-Free Carrier Generation in Doped Rubrene Single Crystals[2)]

We combined the rubrene organic single crystal growth technique with our original ultra-slow deposition technique of 10^{-9} nm s^{-1} and have succeeded in producing the 1 ppm doped organic single crystal and in detecting the Hall effect signal (Figure 3).

Doping efficiencies of 82 and 60% for hole creation were observed for the rubrene single crystal by doping with the organic acceptors F4-TCNQ and HAT-CN, respectively. Corresponding activation energies (ΔE_A) are 9 and 26 meV (Figure 5), which are smaller than the thermal energy of room temperature, So, the organic acceptor doping can be regarded as exciton-free carrier generation. The organic dopants also observed a slight decrease in Hall mobility. An interstitial doping model is proposed to avoid hole scattering and disturbance of hole delocalization. On the other hand, less efficient doping efficiencies of 37 and 8% by doping inorganic acceptors of Mo_3O_9 and Fe_2Cl_6 were observed. Corresponding ΔE_A are 51 and 144 meV (Figure 5). This can be regarded as carrier generation through the Wannier excitons. A significant decrease in Hall mobility was observed for the inorganic dopants. A substitutional doping model that considers both hole scattering and the disturbance of hole delocalization is proposed.

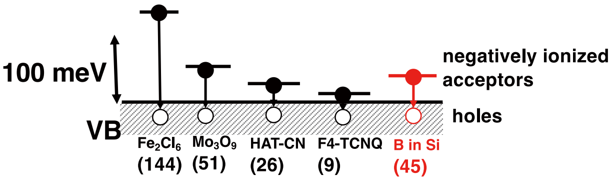

Figure 5. Energetic diagram of acceptor levels for Mo_3O_9, Fe_2Cl_6, F4-TCNQ, and HAT-CN in rubrene single crystal. That for B in Si is also shown for comparison. Numericals in the parentheses are activation energies in meV.

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1) S. Izawa, M. Morimoto, K. Fujimoto, K. Banno, Y. Majima, M. Takahashi, S. Naka and M. Hiramoto, *Nat. Commun.* **14**, 5494 (2023).

2) M. Hiramoto, "Carrier generation in high-mobility organic semiconductors," Keynote lecture in 13th International Conference on Nano-Molecular Electronics, Tokyo Institute of Technology, Japan, 13, Dec. 2022.

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Solid-State NMR for Molecular Science

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Education

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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

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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 characterizations 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.

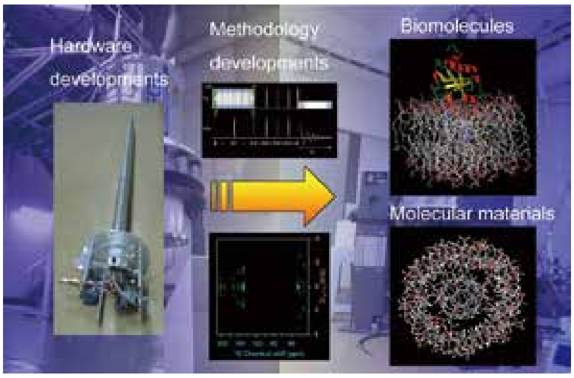

Figure 1. Outline of our studies.

Selected Publications

- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- T. Asakura, T. Ohata, S. Kametani, K. Okushita, K. Yazawa, Y. Nishiyama, K. Nishimura, A. Aoki, F. Suzuki, H. Kaji, A. Ulrich and M. Williamson, "Intermolecular Packing in B. Mori Silk Fibroin: Multinuclear NMR Study of the Model Peptide (Ala-Gly)15 Defines a Heterogeneous Antiparallel Antipolar Mode of Assembly in the Silk II Form," *Macromolecules* **48**, 28–36 (2015).
- 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. Huang, L. Zhai, D. E. Coupry, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine and D. Jiang, "Multi-Component Covalent Organic Frameworks," *Nat. Comm.* **7**, 12325 (12 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).
- M. Yagi-Utsumi, S. G. Itoh, H. Okumura, K. Yanagisawa, K. Kato and K. Nishimura, "The Double-Layered Structure of Amyloid-β Assemblage on GM1-Containing Membranes Catalytically Promotes Fibrillization," *ACS Chem. Neurosci.* **14**, 2648–2657 (2023).

1. Structural Determination of Amyloid-β Protein Oligomer Promoted on Model Neuronal Cell Membranes Using State NMR1)

Amyloid β (Aβ) protein is disordered in solutions under diluted conditions, however it conforms insoluble amyloid fibrils, which are found in senile plaque as a hallmark of Alzheimer's disease. Although molecular structures of amyloid fibrils have been determined, its molecular process for fibrillation in vivo has not been clarified yet. However, accumulated evidences suggest that the fibrillation process may be promoted on neuronal cell membrane. Especially, it has been reported that Aβ specifically interacts with ganglioside GM1 which is one of the key lipids in lipid raft. Therefore, GM1 embedded into lipid bilayers composed of neutral lipid DMPC may be considered to be the most simplified model neuronal cell membrane. In order to clarify the role of GM1 in the fibrillation process, first, we have successfully determined the oligomeric structure of Aβ(1-40) induced on DMPC bilayers based on solid-state NMR.2) We have been collaborated with Prof. Kato group and Prof. Okumura group for those Aβ studies.

In the current study, the molecular structure of Aβ(1-40) oligomer induced on model neuronal cell membranes consisting of GM1 and DMPC have been determined together with their intermolecular packing using solid-state NMR. Based on information of intra- and intermolecular distances and torsion angles of backborn obtained from solid-state NMR analyses, precise molecular structure of Aβ oligomer was determined from restrained molecular dynamics simulations. In addition, the location of C-terminal segment of Aβ(1-40) on the lipid bilayers has been clarified by solid-state NMR experiment in addition to biochemical experiments.

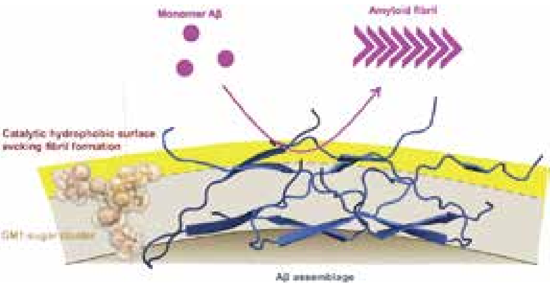

Figure 2. Schematic drawing of Aβ assemblage on GM1-containing membrane which catalytically promotes amyloid fibrillization.

The determined Aβ structure conforms disordered N-terminus followed by center and C-terminus β-sheets. Aβ takes intermolecular configuration of antiparallel β-sheet among adjacent molecules, in which different from Aβ fibrils prepared in solution and also Aβ oligomer induced on DMPC bilayers.2) Those suggest specific roles of GM1 for the formation of Aβ oligomers. Based on those experimental evidences, finally we have proposed the model process that Aβ assemblage on GM1-containing membrane catalytically promotes amyloid fibrillization as shown in Figure 1. We expect the significant contribution of our determined Aβ oligomer structure to reveal the molecular mechanism of Aβ fibrils on neuronal cell membranes, and thus understanding of Alzheimer's disease.

2. Developments of Core Technologies for Solid-State NMR Probes

We have been working on developments of totally original solid-state NMR probes during a couple of years. The probe has been built using originally designed parts except for spinning module. Then, 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. We started the design of a spinning module for standard 4.0 mm sample tube for Bruker. After 3 times of version up, our original spinning module over the spinning performance of commercial one from Bruker. In order to improve spinning performance further for our original spinning module, the development of original sample tube may be essential due to the lack of strength of commercial sample tube.

Currently, final version of the spinning module is under development in order to realize installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.

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1) M. Yagi-Utsumi, S. G. Itoh, H. Okumura, K. Yanagisawa, K. Kato and K. Nishimura, *ACS Chem. Neurosci.* **14**, 2648–2657 (2023).
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Clarification of Physical Properties and Reaction Mechanisms at Surfaces and Interfaces by Scanning Probe Microscopy

Instrument Center

MINATO, Taketoshi
Senior Researcher

Surfaces and interfaces are fascinating fields for physical, chemical and biological phenomena. While these phenomena are well known, the mechanisms underlying them remain poorly understood in many cases. Scanning probe microscopy (SPM) is a superior method for analyzing the mechanism. We have established the advanced system to clarify these mechanisms at surface and interface in nano/atomic scales (Figure 1).

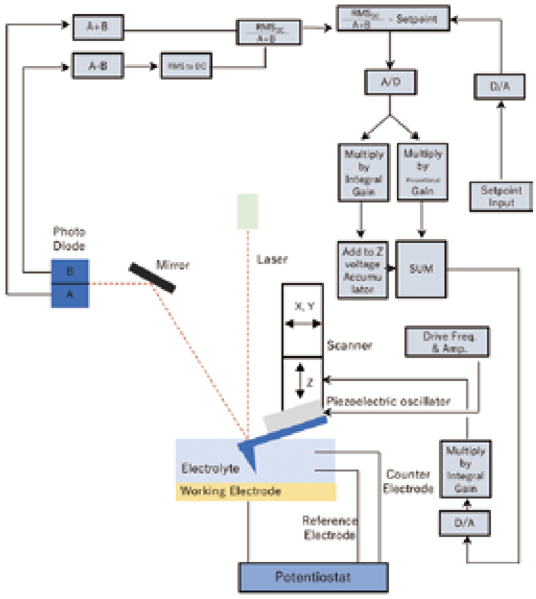

Figure 1. SPM system used in the analysis of physical properties and reaction mechanism at the surface and interface.

Recently, our focus has been on analyzing the electrode/electrolyte interface in electrochemical reactions.[1,2] Figure 2 shows the changes of the surface structure of gold electrode during the electrochemical dissolution in aqueous electrolyte. This dissolution reaction proceeds through the reactions of halogen ions with gold atoms. However, the elemental process driving this reaction remain unsolved. Through high resolved image and mechanical properties analysis of the surface by SPM, we have found the reactions are triggered by the distortion of the surface structure.

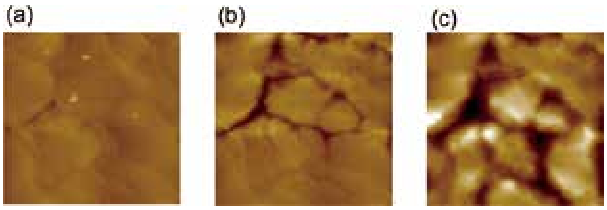

Figure 2. SPM images (1 µm × 1 µm) of the dissolution of gold surface obtained in aqueous electrolyte after (a) 0 min, (b) 5 min and (c) 9 min from starting dissolution.

In addition to above analysis, we reported several significant achievements in understanding the physical properties and reaction mechanisms by SPM. It is reported that when the electron transfers within chiral molecules, the conductivities exhibit spin-selectivity. By employing molecules capable of undergoing chiral transformations through photon and thermal excitation, stable switching of the spin selectivity within a molecule was demonstrated.[3] Also, it was reported that the spin-selectivity are not limited to only micro-scale chirality but can be applied to macro-scale chirality.[4] These reports are based on the collaborative works with the research group of Prof. Hiroshi Yamamoto at IMS. Further, we reported on investigations into the wettability and surface tension of ionic liquids with pentyl, ethoxyethyl, and ethylthioethyl groups.[5] This achievement is a collaborative work with the research group of Prof. Hideaki Shirota at Chiba University. These studies demonstrated that SPM can unravel the mechanism underlying surfaces and interfaces.

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3) R. Malatong, T. Sato, J. Kumsampao, T. Minato, M. Suda, V. Promarak and H. M. Yamamoto, *Small* **19**, 2302714 (2023).
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5) M. Ando, M. Ando, M. Koyakkat, T. Ueda, T. Minato and H. Shirota, *Langmuir* **39**, 12090–12098 (2023).

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)*

Time-Resolved Cyclotron Resonance of Optically Injected Free Carriers in Semiconductor Crystals

Momentum and spin are degrees of freedom for free carriers other than charge, which have recently attracted attention as valleytronics and spintronics. Silicon, a semiconductor commonly used in electronics, is also a strong candidate for valleytronics due to the multi-valley structures in its conduction band. Maintaining and transporting valley polarization is key to device design. Time-resolved cyclotron resonance (TRCR) can measure valley polarization by distinguishing electrons with different effective masses under a magnetic field. We performed TRCR measurements of optically injected electrons in a highly pure silicon crystal at cryogenic temperatures using a time-resolved electron spin resonator by applying an additional DC-electric field. Analysis of the evolution of the TRCR spectra after a laser pulse elucidates how the optically induced valley polarization is dispersed by intra-valley and inter-valley electron scattering under an operando DC-electric field. The results provide basic physical parameters for designing future devices.

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

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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).
- Y. Ikenoue, Y. Tahara, M. Miyata, T. Nishioka, S. Aono and H. Nakajima, "Use of a Ferritin L134P Mutant for the Facile Conjugation of Prussian Blue in the Apoferritin Cavity," *Inorg. Chem.* **60**, 4693–4704 (2021).
- M. Nishinaga, H. Sugimoto, Y. Nishitani, S. Nagai, S. Nagatoishi, N. Muraki, T. Tosha, K. Tsumoto, S. Aono, Y. Shiro and H. Sawai, "Heme Controls the Structural Rearrangement of Its Sensor Protein Mediating Bacterial Survival," *Commun. Biol.* **4**, 467 (12 pages) (2021).
- N. Muraki, K. Takeda, D. Nam, M. Muraki and S. Aono, "Structural Characterization of Thermoglobin from a Hyperthermophilic Bacterium *Aquifex aeolicus*," *Chem. Lett.* **50**, 603–606 (2021).
- N. Muraki, C. Kitatsuji, Y. Okamoto, T. Uchida, K. Ishimori and S. Aono, "Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria," *Chem. Commun.* **55**, 13864–13867 (2019).
- 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. Complex Formation between [NiFe] Hydrogenase Maturation Factors Responsible for $Fe(CN)_2CO$ Biosynthesis

[NiFe] hydrogenase is a metalloenzyme that catalyzes the oxidation of hydrogen and the reduction of protons reversibly. As its name implies, the metal cluster of [NiFe] hydrogenase is composed of nickel and iron. In the active center of [NiFe] hydrogenase, nickel is ligated by the three cysteine side chains of the protein, while iron is coordinated with two cyanide ions and one carbon monoxide in addition to the cysteine side chains. This intricate metal complex is not spontaneously formed, but is biosynthesized step-by-step in coordination with multiple proteins. The cyanide ions and carbon monoxide are also biosynthesized to form $Fe(CN)_2CO$ complex, which is then incorporated into hydrogenase. We have reported the crystallographic analysis of HypX, which is an enzyme responsible for carbon monoxide biosynthesis during [NiFe] hydrogenase maturation. Additionally, we have showed that the HypC-HypD complex, which acts as a scaffold protein for $Fe(CN)_2CO$ biosynthesis, forms a complex with HypX.

Recently, we have determined the crystal structures of *A. aeolicus* HypC, HypD, and HypE, which are involved in cyanide ion transport (Figure 1 (A), (B), (C)). The crystal structures of these maturation factors show high structural similarity to previously reported structures of corresponding proteins from Archaea. Based on these structure, we propose that the HypCDXE complex will be transiently formed to assemble $Fe(CN)_2CO$ unit (Figure 1 (D)).

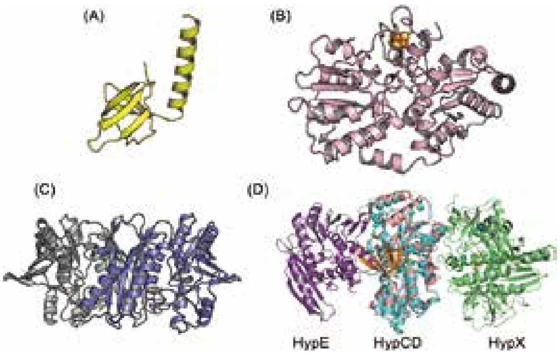

Figure 1. X-ray crystal structures of (A) HypC, (B) HypD, and (C) HypE from *Aquifex aeolicus*, and (D) proposed model of HypCDEX complex.

2. Structural Analysis of Heme-Based Oxygen Sensor Protein HemAT

Recently, it has been reported that gas molecules, including oxygen and nitric oxide, have a role as “signal molecules,” and they regulate various physiological functions. In these systems, the regulation of physiological functions is performed when some signal transduction proteins that selectively recognize gas molecules sense external signals. Therefore, signal sensing and signal transduction proteins are essential for regulating physiological functions in response to gas molecules.

O_2 acts as a signal molecule in the bacterial chemotaxis regulating system, in which the heme-containing signal transducer protein HemAT (Heme Aerotaxis Transducer protein) works as an oxygen sensor protein. HemAT is mainly composed of two domains, sensor and siganaling domain. Sensor domain and signaling domain of HemAT is homologous to globin structures and the chemotaxis receptor Methyl-accepting Chemotaxis Protein (MCP), respectively.

HemAT forms a complex with the histidine kinase CheA and the conjugation protein CheW. Signal transduction proceeds in the HemAT/CheA/CheW complex upon O_2 sensing by HemAT, which results in the activation of CheA kinase activity. However, the molecular mechanisms of O_2-dependent signal transduction in the HemAT/CheA/CheW complex remain to be elucidated because of a lack of the structural information of HemAT and the HemAT/CheA/CheW complex. To understand the sensing mechanism and signaling mechanism of the HemAT and HemAT/CheA/CheW complex, we tried to solve the structures of HemAT and HemAT/CheA/CheW complex by X-ray crystallography and cryo-electron microscopy (Cryo-EM), respectively. In this year, we have determined the crystal structure of the sensor domain of HemAT from *Bacillus smithii* (Figure 2).

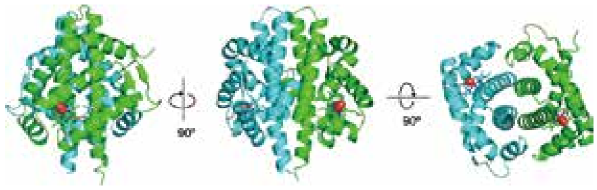

Figure 2. X-ray crystal structure of the sensor domain of HemAT from *Bacillus smithii*.

3. Iron Sensing by Sensor Kinase, VgrS, Responsible for Intracellular Iron Homeostasis

Iron is an essential trace element for all organisms. While it is essential, excess intracellular iron can generate reactive oxygen species, leading to oxidative stress and cellular damage. Therefore, iron homeostasis is essential for cells. In *Xanthomonas campestris*, the two-component system, VgrS/VgrR, plays an important role for the regulation of iron homeostasis. The periplasmic sensor domain of histidine kinase VgrS senses extracellular iron ions. However, detailed mechanism for regulating iron homeostasis by VgrS/VgrR has not yet been elucidated. In this work, we examined the structure-function relationships of VgrS.

To determine the stoichiometry of metal ion binding to VgrS sensor domain, ICP analyses was carried out, which revealed that VgrS sensor domain bound 2.5 equivalents Fe(III) or 1 equivalents Mn(II) or Co(II), respectively. The ExxE motif in VgrS seems to be a metal binding site at which Fe(III) binds. To determine the structure of VgrS, we prepared three constructs of the sensor domain of VgrS composed of Met1-Thr100, Met1-Met87, and Met27-Met87, respectively. The single crystal was obtained for the truncated sensor domain composed of Met27-Met87 while two other samples were not crystalized. X-ray crystallographic analysis of this construct is now in progress.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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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.

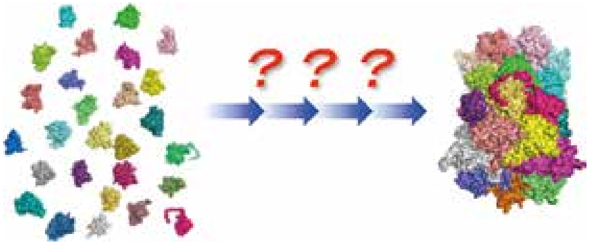

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- K. Kato and H. Yagi, "Current Status and Challenges in Structural Glycobiology," *Trends Carbohydr. Res.* **15**, 38–46 (2023).
- K. Kato, H. Yagi and S. Yanaka, "Four-Dimensional Structures and Molecular Designs of Glycans," *Trends Glycosci. Glycotechnol.* **34**, E85–E90 (2022).
- 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).

1. Exploring Dynamic Biomolecular Organization: Insights from Amyloid β Assembly and Protein Folding Analyses

Utilizing our structural analysis techniques, we enhanced and developed our collaborative research network both within and outside IMS to investigate the mechanisms governing the dynamic organization of biomolecules. Specifically, our focus was on exploring the dimerization process during the early stages of amyloid β (Aβ) protein oligomerization, a process implicated in the onset of Alzheimer's disease. Through molecular dynamics (MD) simulations and in vitro assays, we uncovered that intramolecular electrostatic interactions between the Arg5 side chain and the carboxyl terminal play a pivotal role in the dimerization of Aβ42 (in partnership with the Okumura group).1) The Aβ protein is recognized for its interaction with GM1 ganglioside, a glycolipid abundant in neuronal cell membranes, and its role in promoting the formation of amyloid fibrils. Our investigation encompassed a comprehensive three-dimensional structural analysis of the GM1-Aβ complex using solid-state NMR and MD simulations, revealing a distinctive assembly characterized by a double-layered antiparallel β structure.2) Furthermore, our findings indicate that this specific Aβ assembly does not undergo a transition into amyloid fibrils directly. Instead, it facilitates the conversion of Aβ monomers into amyloid fibrils by presenting a hydrophobic surface composed of β sheets on the GM1 glycan (in collaboration with the Nishimura and Okumura groups).

We also pursued an analysis of protein folding processes using NMR techniques. Using hydrogen/deuterium exchange NMR spectroscopy, we captured residual structural information in proteins denatured by 6 M guanidinium chloride (in collaboration with Dr. Kunihiro Kuwajima of the University of Tokyo),3) and by capturing proteins within the cavity of spherical self-assembling complexes, we were able to observe hysteresis behavior in the folding and refolding processes of proteins (in collaboration with Dr. Makoto Fujita of the University of Tokyo and IMS).4)

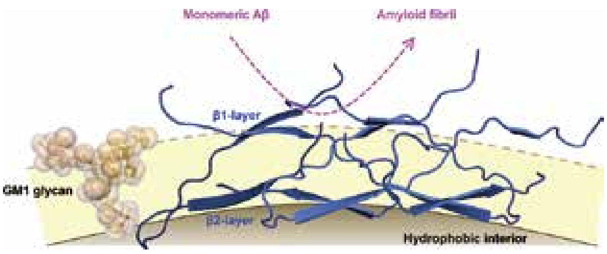

Figure 2. Schematic drawing of Aβ assemblage on GM1-containing membrane which catalytically promotes amyloid fibrillization. The distance between β1- and β2-layers of the assemblage is almost the same as the GM1 glycan dimension. The β1-layer provides a catalytic hydrophobic surface evoking fibril formation in GM1-sugar clusters.

2. Exploration, Design, and Control of Higher-Order Functions Arising from Multidomain Proteins

Multidomain proteins can manifest intricate functions through cooperative interactions and allosteric regulation, achieved by spatial rearrangements of their constituent domains. Our study delved into the potential of utilizing multidomain proteins as a foundation for Förster resonance energy transfer (FRET) biosensors, with a specific focus on protein disulfide isomerase (PDI) and Lys48-linked ubiquitin (Ub) chains as model cases.

The substrate-recognition domains of PDI undergoes redox-dependent conformational changes. Both experimental and computational approaches were employed to characterize FRET efficiency across various redox states of these domains fused with fluorescent proteins as the FRET acceptor and donor. In vitro and in vivo assessments revealed heightened FRET efficiency of this biosensor in the oxidized form of PDI, underscoring domain reorganization and its responsiveness to intracellular redox environments.5)

On a different note, the conformational flexibility of Lys48-linked diUb presented a distinctive framework for engineering Ub-based biosensors, enabling the detection of environmental conditions like temperature and pH, as well as the recognition of binding molecules. The present findings emphasized the sensitivity of the open-closed conformational equilibrium of diUb to modifications at position 48 of the distal Ub unit, offering a means to manipulate its conformational distribution.6)

Furthermore, our investigation into the impact of serum proteins on the functionality of therapeutic antibodies revealed that the human serum albumin (HSA) and the Fab region of serum immunoglobulin G (IgG) non-competitively inhibit antibody-dependent cellular cytotoxicity mediated by the interaction of Fcγ receptor III (FcγRIII) with rituximab, an anti-CD20 mouse/human-chimeric IgG1.7) Stable-isotope- assisted NMR data demonstrated the interaction of HSA with the Fab and Fc regions of rituximab, as well as the extracellular domain of FcγRIII. These findings suggest the significance of considering interactions with serum proteins in the design and application of therapeutic antibodies.

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1) S. G. Itoh *et al.*, *ACS Chem. Neurosci.* **22**, 3139–3151 (2022).
2) M. Yagi-Utsumi *et al.*, *ACS Chem. Neurosci.* **14**, 2648–2657 (2023).
3) S. Yanaka *et al.*, *Protein Sci.* **32**, e4569 (2023).
4) T. Nakama *et al.*, *Chem. Sci.* **14**, 2910–2914 (2023).
5) M. Yagi-Utsumi *et al.*, *Int. J. Mol. Sci.* **24**, 12865 (2023).
6) M. Hiranyakorn *et al.*, *Int. J. Mol. Sci.* **24**, 6075 (2023).
7) S. Yanaka *et al.*, *Front. Immunol.* **14**, 1090898 (2023).

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Operation and Design Principles of Biological Molecular Machines

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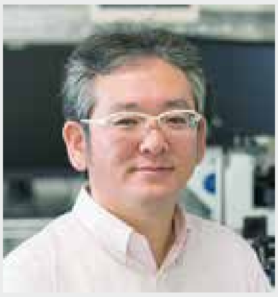

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Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

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 the mechanical forces that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane. We unveil operational 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

- T. Kosugi, T. Iida, M. Tanabe, R. Iino and N. Koga, "Design of Allosteric Sites into Rotary Motor V_1-ATPase by Restoring Lost Function of Pseudo-Active Sites," *Nat. Chem.* (2023). DOI: 10.1038/s41557-023-01256-4
- A. Otomo, T. Iida, Y. Okuni, H. Ueno, T. Murata and R. Iino, "Direct Observation of Stepping Rotation of V-ATPase Reveals Rigid Component in Coupling between V_o and V_1 Motors," *Proc. Natl. Acad. Sci. U. S. A.* **119**, e2210204119 (2022).
- 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, 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).

1. Six States of *Enterococcus hirae* V-Type ATPase Reveals Non-Uniform Rotor Rotation during Turnover[1)]

The vacuolar-type ATPase from *Enterococcus hirae* (EhV-ATPase) is a thus-far unique adaptation of V-ATPases, as it performs Na^+ transport and demonstrates an off-axis rotor assembly (Figure 2). Recent single molecule studies of the isolated V_1 domain have indicated that there are subpauses within the three major states of the pseudo three-fold symmetric rotary enzyme. However, there was no structural evidence for these. Herein we activate the EhV-ATPase complex with ATP and identified multiple structures consisting of a total of six states of this complex by using cryo-electron microscopy. The orientations of the rotor complex during turnover, especially in the intermediates, are not as perfectly uniform as expected (Figure 3 and 4). The densities in the nucleotide binding pockets in the V_1 domain indicate the different catalytic conditions for the six conformations. The off-axis rotor and its' interactions with the stator a-subunit during rotation suggests that this non-uniform rotor rotation is performed through the entire complex.

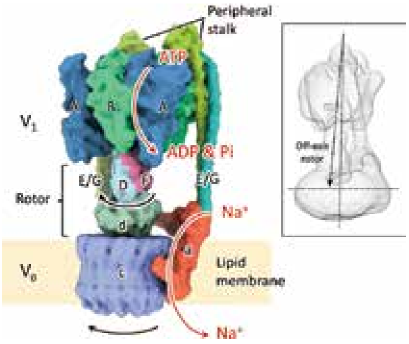

Figure 2. Schematic drawing of the EhV-ATPase. A-, B-, D-, E-, F-, G- and d-subunits form the V_1 domain, while a- and c-subunits form the V_o domain. The a-subunit and c-ring are embedded in lipid membrane. The rotation of the D/F/d rotor shaft and c-ring proceeds clockwise when viewed from V_1 to V_o domains, as indicated. Turnover is driven by the entry of ATP into a binding pocket at the interface of each A/B dimer, the hydrolysis reaction drives conformational changes which cause the rotation of the rotor. Inset shows the off-axis rotor.

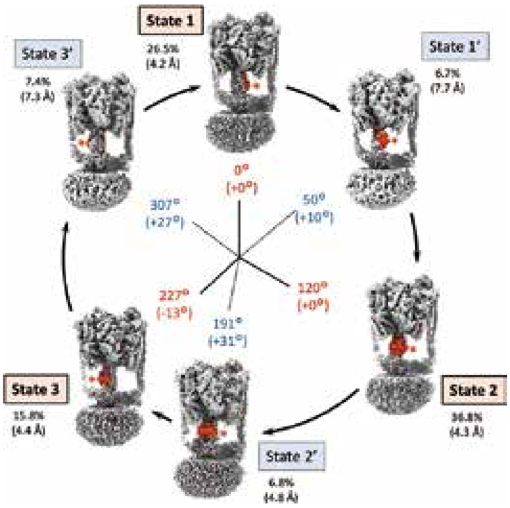

Figure 3 (top right). The six state structures of EhV-ATPase isolated. The F-subunit position is highlighted in red for easier identification of orientation of the rotor. Starting in State 1 at "12 o'clock" on the circle and proceeding clockwise when turnover is viewed from the V_1 to V_o domains. The six state structures are defined as State 1, State 1', State 2, State 2', State 3, and State 3' with comparisons to the other V-ATPases. Total rotation of the rotor at F subunit is labelled in red for the major states and blue for the intermediate states internally of the circle. The gaps from the orientations based on the single-molecule imaging studies (120° major pauses, and 40/80° subpauses in the major pauses) are in brackets. Relative percentages of the total final particles used and their resolutions (brackets) for each reconstruction are indicated externally of the circle. The cryo-EM maps of EhV-ATPase are aligned according to the orientation of the F-subunit.

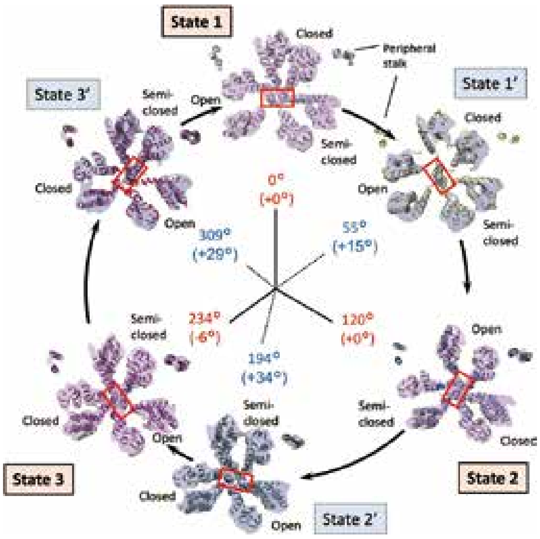

Figure 4. V_1 domain cross-section view of the six states. The figure is laid out as shown in Figure 3 viewed from the V_1 to V_o domains. The rotor D subunit is boxed in red, demonstrating the positions of a pair of the longest helices. The catalytic conformations of the A/B subunit in V_1 domain are indicated with "Open," "Closed," and "Semi-closed." The positions of peripheral stalk are labelled.

Reference

1) R. N. Burton-Smith, C. Song, H. Ueno, T. Murata, R. Iino and K. Murata, *Commun. Biol.* **6**, 755 (2023).

Award

HARASHIMA, Takanori; Best Presentation Award, 2022 Annual Meeting of the Biophysical Society of Japan Chubu Branch (2023).

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* IMS International Internship Program

Development of Novel Catalytic Organic Transformations

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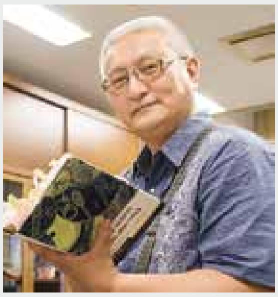

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Awards

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
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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 carbonyl groups underwent two successive one-electron reduction to generate carbinol anion species achieving electrophilic carbonyl substitution.

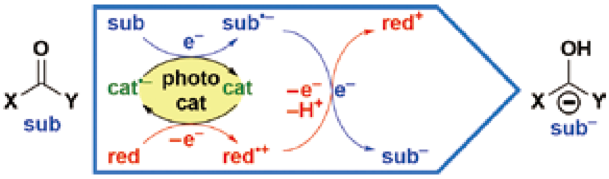

Figure 1. The outlined concept of photocatalytic reductive activation of substrate through two successive one-electron transfer process (*e.g.* carbonyl reduction to carbinol anion).

Selected Publications

- S. Okumura and Y. Uozumi, "Photocatalytic Carbinol Cation/Anion Umpolung: Direct Addition of Aromatic Aldehydes and Ketones to Carbon Dioxide," *Org. Lett.* **23**, 7194–7198 (2021).
- 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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- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).

1. Umpoled Carbonyl Chemistry

Carbonyl chemistry is dominated by nucleophilic additions in which a carbonyl compound (an aldehyde or ketone) serves as an electrophilic carbinol cation synthon to form a secondary or tertiary alcohol product [Figure 2(a)]. In contrast to the well-investigated conventional chemistry of carbonyl compounds, their umpoled nucleophilic reactivity has been less-well explored [Figure 2(b)]. Symmetrization of the carbonyl reactivity, which would permit carbonyl compounds to react as nucleophilic carbinol anions (i.e., carbinol cation/anion umpolung), could open a new avenue in synthetic organic chemistry.

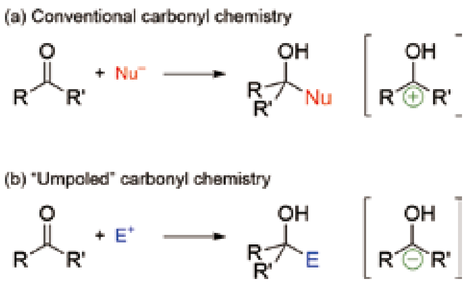

Figure 2. Carbonyl Reactivity: Conventional *vs*. Umpoled.

In previous report, we have developed a novel photocatalytic carboxylation of aromatic aldehydes and ketones to give mandelic acid derivatives [Figure 3(a)]. In this reaction, nucleophilic carbinol anion species were generated under visible light that subsequently reacted with carbon dioxide. Here, in 2023, we developed photocatalytic cross-pinacol coupling between two different carbonyl compounds to afford the unsymmetric 1,2-diols, where the resulting carbinol anions reacted with second carbonyl compounds [Figure 3(b)]. We also achieved the photocatalytic 1,4-addition of carbonyl compounds with electron-deficient olefins to give the corresponding γ-substituted alcohols [Figure 3(c)].

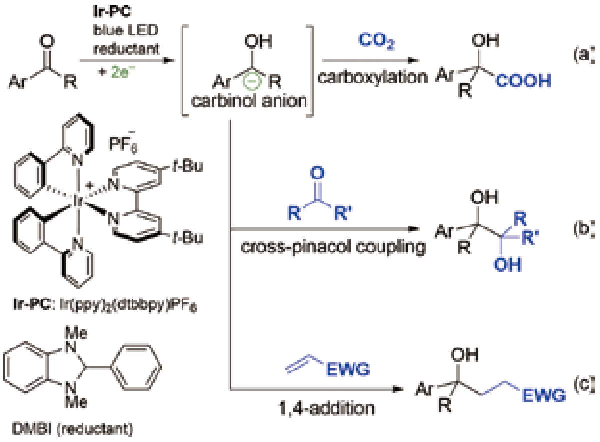

Figure 3. Photocatalytic Eelectrophilic Substitution of Carbonyls: (a) carboxylation, (b) cross-pinacol coupling, (c) 1,4-addition.

1-1. Cross-Pinacol Coupling[1)]

We have developed the first photocatalytic cross-pinacol coupling between two different carbonyl compounds, promoted by a CO_2 additive. The cross-pinacol coupling took place with a various combination of two aldehydes, two ketones, or an aldehyde and a ketone 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 afford the corresponding unsymmetric vicinal 1,2-diols in up to 91% yield [Figure 3(b)]. In the coupling reaction, an umpoled carbinol anions are generated in situ through successive one-electron reduction and the resulting anions attack the more-electron-rich carbonyl compounds serving as electrophiles. CV and DFT calculations revealed that the CO_2 additive plays a key role in the second reduction to suppress undesired dimerization.

1-2. Conjugate Addition of Carbonyls to Electron-Deficient Olefins[2)]

A 1,4-addition reaction of aromatic aldehydes and ketones to electron-deficient olefins was achieved under photocatalytic conditions [Figure 3(c)]. In the reaction, an umpoled carbinol anion generated in situ through two successive one-electron reductions of the carbonyl compound reacted nucleophilically with the electron-deficient olefin. Various electron-deficient aromatic aldehydes and ketones successfully underwent the reaction to afford the corresponding γ-functionalized alcohols.

2. Transition Metal Catalysis Forming C–H, C–C, C–N, C–S Bonds[3,4)]

We have developed transition metal-catalyzed C–H, C–C, C–N, C–S bond forming reactions. A phenylboronic ester-activated aryl iodide-selective Buchwald−Hartwig-type C–N bond forming reaction using $Ni(acac)_2$ catalyst was developed. This reaction does not proceed in the absence of phenylboronic ester.[3)] C–S bond formation was achieved in the reaction of 2,2'-dithiobis(benzenamine)s with various aldehydes in the presence of CuOAc catalyst under air without any additives to afford the corresponding benzothiazoles.[4)] We recently developed in-water C–H bond forming catalysis with PS-PEG supported palladium nanoparticles using tetrahydroxydiboron ($B_2(OH)_4$) as a water-compatible reducing agent.

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4) K. Minami, M. Minakawa and Y. Uozumi, *Asian J. Org. Chem.* **11**, e202200211 (2022). DOI: 10.1002/ajoc.202200211

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* IMS International Internship Program

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Awards
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Keywords Synthetic Chemistry, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research for realizing efficient and new transformations in the synthesis of functional molecules. The design of 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, "metals" have been frequently used as the activation centers, and conformationally rigid catalyst frameworks have been preferably components for the catalyst design. To develop a new type of molecular catalysis, we have focused on the use of non-metal elements as activation centers and have incorporated non-covalent interactions as organizing forces in the molecular design of catalysts. This approach had not received much attention until recently. We hope that our approach will open a new frontier in chiral organic molecules to chiral molecular science from chiral molecular chemistry.

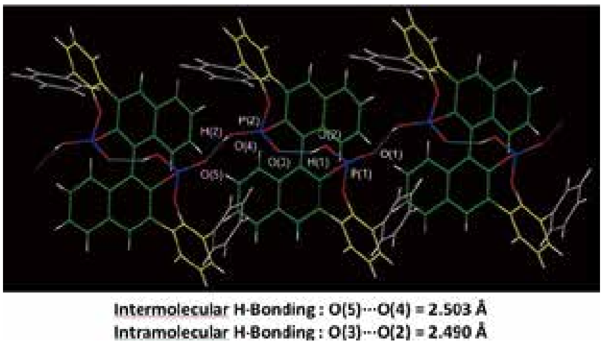

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

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, 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).
- S. Oishi, T. Fujinami, Y. Masui, T. Suuki, M. Kato, N. Ohtsuka and N. Momiyama, "Three-Center-Four-Electron Halogen Bond Enables Non-Metallic Complex Catalysis for Mukaiyama-Mannich-Type Reaction," *iScience* **25**, 105220 (2022).

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.

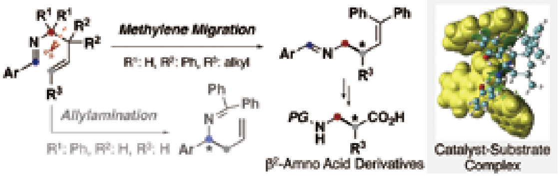

Figure 2. Asymmetric counteranion-directed catalysis *via* OH···O, CH···O, CH···π, π···π interactions.

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.9,10,11)

We found that the three-center-four-electron halogen bond become a new driving force for catalysis.9) By integrating halogen(I) (X^+: I^+ or Br^+), the bis-pyridyl ligand *NN*, and a non-nucleophilic counter anion Y, we developed non-metallic complex catalysts, [*N*···X···*N*]Ys, that exhibited outstanding activity and facilitated the Mukaiyama–Mannich-type reaction of *N*-heteroaromatics with parts-per-million-level catalyst loading. NMR titration experiments, CSI-MS, computations, and UV-vis spectroscopic studies suggest that the robust catalytic activity of [*N*···X···*N*]Y can be attributed to the unique ability of the 3c4e X-bond for binding chloride: i) the covalent nature transforms the [*N*···X···*N*]$^+$ complexation to sp^2 CH as a hydrogen-bonding donor site, and ii) the noncovalent property allows for the dissociation of [*N*···X···*N*]$^+$ for the formation of [Cl···X···Cl]$^-$. This study introduces the application of 3c4e X-bonds in catalysis *via* halogen(I) complexes.

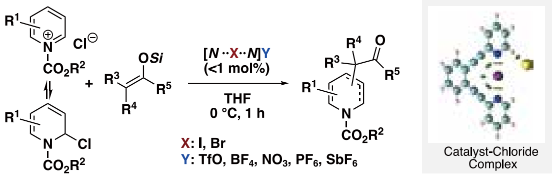

Figure 3. Three-center-four-electron halogen bond enables non-metallic complex catalysis for Mukaiyama–Mannich-type reaction.

References

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3) N. Momiyama, A. C. Jongwohan, N. Ohtsuka, P. Chaibuth, T. Fujinami, K. Adachi and T. Suzuki, *J. Org. Chem.* **87**, 9399–9407 (2022).
4) N. Momiyama, H. Okamoto, J. Kikuchi, T. Korenaga and M. Terada, *ACS Catal.* **6**, 1198–1204 (2016).
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8) 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, *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).
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Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

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2010	Postdoctoral Fellow, RIKEN
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2019	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
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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.

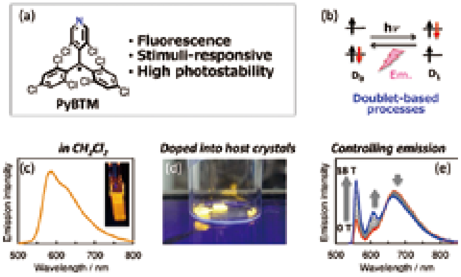

Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

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. 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 (Figure 2).1) TrisZn demonstrated magnetoluminescence (MagLum) below 20 K.2) This is the first example showing MagLum of pure (*i.e.*, non-doped) radical compounds.

Employing magnetic ions such as $\mathrm{Cu^{II}}$ (S = 1/2) and $\mathrm{Ni^{II}}$ (S = 1) instead of the nonmagnetic $\mathrm{Zn^{II}}$ is expected to enable Kagome-honeycomb hybrid lattices, where the magnetic ions and trisPyMs construct Kagome and honeycomb lattices, respectively. We prepared $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$ Kagome-honeycomb hybrid lattices. Magnetic investigations indicated the emergence of long-range magnetic order and metamagnet-like behavior at low temperatures in these materials. Efficient magnetic couplings between the magnetic ions and the radicals extended onto two dimensions were expected to induce strong magnetic anisotropy.

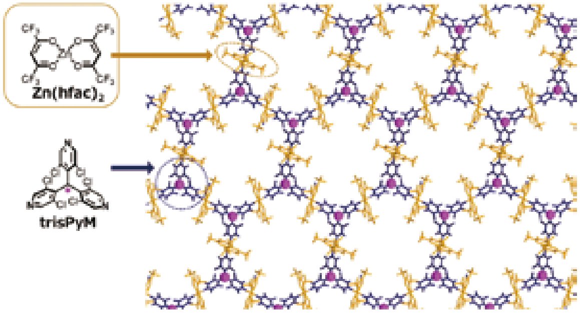

Figure 2. Crystal structure of trisZn and the chemical structure of the components.

2. Single-Molecule Magnetoluminescence from a Luminescent Diradical

Luminescent radicals attract increasing interest as a new class of materials that enable unique photofunctions not found in conventional closed-shell molecules due to their open-shell electronic structure. Particularly promising are photofunctions resulting from the correlation between the radical's spin and luminescence, such as MagLum, in which an external magnetic field reversibly controls the luminescence. Developing such photofunctions and elucidating their mechanisms would establish fundamental understandings that could be a basis for future spin-photonics and photo-spintronics. However, previous observations of MagLum in radicals have been limited to systems where radicals are randomly doped in host crystals or periodically arranged within the crystal lattices of the coordination polymer through metal complexation. This study shows that a diradical with covalently-linked two radical units within a single molecular skeleton can exhibit MagLum as a single-molecular property (Figure 3).3) This enables the detailed elucidation of the requirements for and mechanisms of MagLum in assembled radicals and can aid the rational design of MagLum-active radicals based on synthetic chemistry.

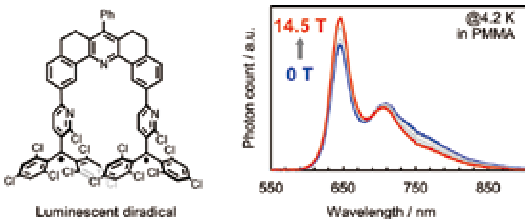

Figure 3. Chemical structure and magnetoluminescence at 4.2 K of a luminescent diradical.

References

1) S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).

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

3) R. Matsuoka, S. Kimura, T. Miura, T. Ikoma and T. Kusamoto, *J. Am. Chem. Soc.* **145**, 13615–13622 (2023).

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Design and Synthesis of Three-Dimensional Organic Structures

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Award

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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

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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.

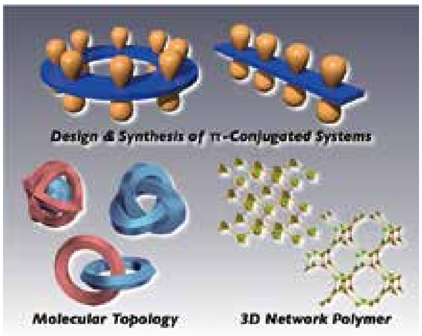

Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- M. Nagase, S. Nakano and Y. Segawa, "Synthesis of Penta- and Hexa(3,4-thienylene): Size-Dependent Structural Properties of Cyclic Oligothiophenes," *Chem. Commun.* **59**, 11129–11132 (2023).
- Y. Segawa, "Nonplanar Aromatic Hydrocarbons: Design and Synthesis of Highly Strained Structures," *Bull. Chem. Soc. Jpn.* **95**, 1600–1610 (2022).
- 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).
- 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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- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).

1. Synthesis of Cyclic ß-Thiophenes

Macrocyclic polyaromatic molecules are interesting materials that exhibit a wide variety of electronic and optical properties derived from their structures, but they are often synthetically challenging because of the ring strain associated with their macrocyclic structures. In this study, we have succeeded in synthesizing 3,4-pentathienylene (**5T**) and 3,4-hexathienylene (**6T**), in which all five and six thiophenes are linked at the 3,4-positions (β-positions), using Ni-catalyzed borylation, Pd-catalyzed cross-coupling and Ni-mediated homocoupling reactions (Figure 2).[1)]

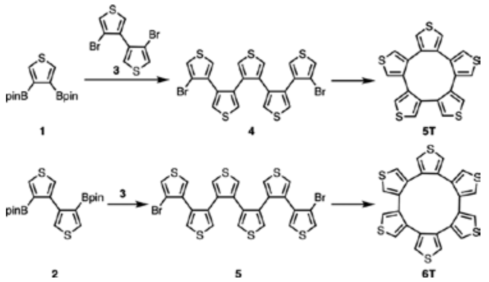


Figure 2. Synthesis of penta(3,4-thienylene) (**5T**) and hexa(3,4-thienylene) (**6T**).

X-ray crystallographic analysis confirmed the C_2 and D_2 symmetries of **5T** and **6T**, respectively (Figure 3). Interestingly, the ^{1}H NMR spectra of the two molecules were very different: **5T** had a single singlet, whereas three different signals were observed for **6T**, and these remained unchanged at both low and high temperatures (Figure 3).

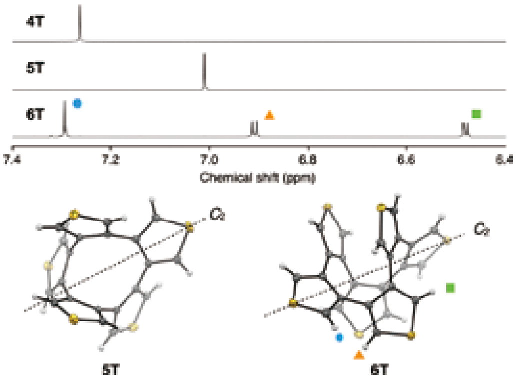


Figure 3. ^{1}H NMR spectra of **4T**–**6T** in CD_2Cl_2, and X-ray structures of **5T** and **6T** with thermal ellipsoids at 50% probability.

The isomerization barriers of **5T** and **6T** calculated by DFT method were 5.0 kcal/mol and 26.5 kcal/mol, respectively, and the difference in isomerization rate was the reason for the difference in NMR spectra (Figure 4). The synthesized **5T** and **6T** are useful as a platform for the synthesis of novel polycyclic π-conjugated compounds utilizing the macrocyclic nonplanar structures and the active α-positions.

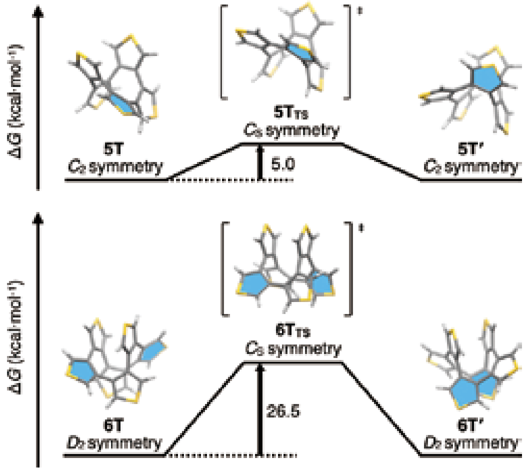
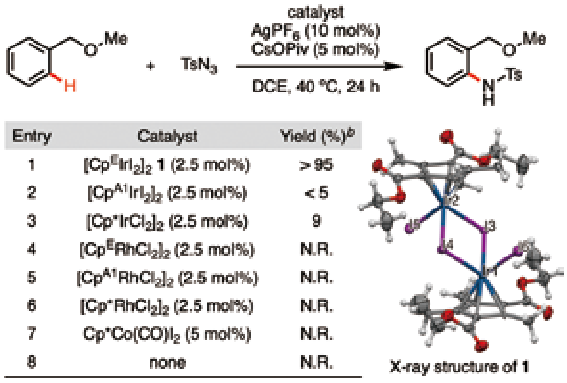


Figure 4. Energy diagrams for the enantiomerization of **5T** and **6T**.

2. An Electron-Deficient Cp^E Iridium(III) Catalyst for Ether-Directed C–H Amidation

The synthesis, characterization, and catalytic performance of an iridium(III) catalyst with an electron-deficient cyclopentadienyl ligand ($[CpEIrI_2]_2$) are reported.[2)] The $[CpEIrI_2]_2$ catalyst was synthesized by the complexation of a precursor of the CpE ligand with $[Ir(cod)OAc]_2$ followed by oxidation, desilylation, and removal of the COD ligand. The electron-deficient $[CpEIrI_2]_2$ enabled C–H amidation reactions assisted by a weakly coordinating ether directing group. Experimental mechanistic studies and DFT calculations suggested that the high catalytic performance of $[CpEIrI_2]_2$ is due to its electron-deficient nature, which accelerates both C–H activation and Ir(V)-nitrenoid formation.



Entry	Catalyst	Yield (%)^b
1	$[Cp^EIrI_2]_2$ 1 (2.5 mol%)	> 95
2	$[Cp^{A1}IrI_2]_2$ (2.5 mol%)	< 5
3	$[Cp^*IrCl_2]_2$ (2.5 mol%)	9
4	$[Cp^ERhCl_2]_2$ (2.5 mol%)	N.R.
5	$[Cp^{A1}RhCl_2]_2$ (2.5 mol%)	N.R.
6	$[Cp^*RhCl_2]_2$ (2.5 mol%)	N.R.
7	$Cp^*Co(CO)I_2$ (5 mol%)	N.R.
8	none	N.R.

Figure 5. Optimized reaction conditions and control experiments for the Ir-catalyzed ether-directed C–H amidation reaction.

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Visiting Professors

Visiting Professor
KAMIYA, Yukiko *(from Kobe Pharmaceutical 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) such as ribose-modified or non-ribose type nucleic acids having nucleic acid recognition ability have been developed. One of our 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. In recent study we successfully established a preparation scheme for full-XNA oligonucleotides possessing artificial nucleobases. The artificial oligonucleotides are currently being applied in in vitro and in vivo study to test whether they function in the biological system.

Visiting Professor
SATO, Sota *(from The University of Tokyo)*

Integrated Molecular Structure Analysis Through Industry-Academia Collaboration

Elucidating molecular structures is crucial in various fields of molecular science, regardless of academia or industry. In addition to NMR and mass spectrometry, X-ray/electron diffraction is a powerful analytical technique that can directly determine atomic positions, enabling clear determination of three-dimensional structures. We are actively pursuing the “crystalline sponge method” as one of core technologies, which eliminates the need for the crystallization process and completes sample preparation by simply soaking the target molecules into crystalline sponge, allowing structural analysis even with minute sample amounts. Furthermore, we are extensively deriving technological advancements and building collaborative relationships with numerous companies and institutions to promote research aimed at creating new industries. Recently, we have been dedicated to fostering future talent who will support the scientific community in Japan and the world. We organized mock lectures and research experiences for high school students in collaboration with corporate researchers, aiming to nurture the next generation of scientists.

Visiting Professor
TOYABE, Shoichi *(from Tohoku University)*

Optimal Control of Biological Molecular Motors—What Is the Most Efficient Way to Control Motors?

ATP synthase plays a central role in cellular energetics by synthesizing most of the ATP molecules required by cells. ATP synthase consists of two coupled motors, F_1 and F_o. F_1 has the ATP-synthesizing activity and catalyzes ATP synthesis using the mechanical driving force rovided by F_o. We assume that nature has optimized F_o and F_1 to rotate F_1 efficiently. However, we do not know in detail how F_o rotates F_1. Instead, we should be able to know what is the most efficient way to rotate F_1 based on physical theory. We use optimal transport theory to find the optimal way to rotate F_1 with the least amount of work, and practice the obtained optimal protocol by single molecule experiments. We have not found the optimal protocol. However, we have at least found that rotation by trapping torque at constant speed requires less work than rotation by constant torque at the same speed.

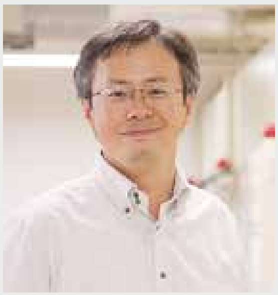
RESEARCH ACTIVITIES

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



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Education

1997	B.E. Kyoto University
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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
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- BOUDRIAH, Nihad[†]

Technical Fellow
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- SUGISAKA, Kanae
- WADA, Kotoe
- TANIURA, Aiko
- YAMAMOTO, Yurika
- 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).
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- 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 Cyanobacteria1–4)

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,1–4) real-time fluorescence detection,5) and quasielastic neutron scattering.6)

2. *Rhythm*: Cross-Scale Analysis of Cyanobacterial Circadian Clock System6–8)

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 screening7) for KaiC clock mutants giving short, long, and/or temperature-dependent periods.8) 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.6,7)

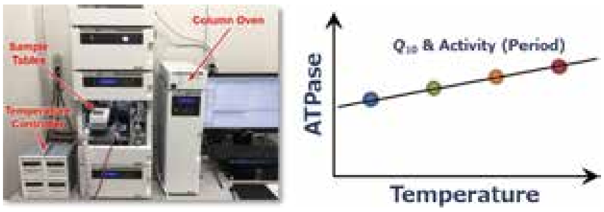

Figure 1. Development of a quick ATPase assay system.

3. beyond Evolutionary *Diversity*9)

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.

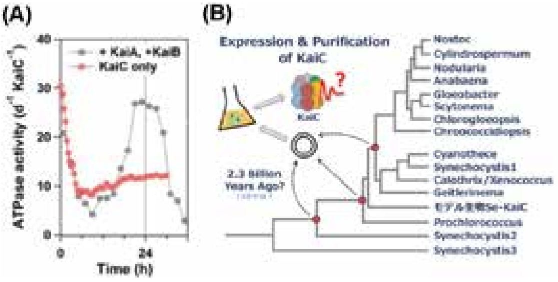

Figure 2. Damped oscillation of KaiC ATPase activity (**A**) and evolutionary diversity of cyanobacteria (**B**).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.9) 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 IMS10)

We have supported SAXS users so that they can complete experiments smoothly and publish their results.10)

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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).
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3) Y. Furuike and S. Akiyama *et al.*, Submitted (2023).
4) Y. Furuike, T. Mori, S. Saito, S. Akiyama *et al.*, Submitted (2023).
5) A. Mukaiyama, Y. Furuike, E. Yamashita and S. Akiyama, *Biochem. J.* **479**, 1505–1515 (2022).
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9) A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
10) M. Okumura, S. Kanemura, M. Matsusaki, Y. H. Lee, S. Akiyama and K. Inaba, *Structure* **29**, 1–14 (2021).

Award

FURUIKE, Yoshihiko; The Progress Award of the Crystallographic Society of Japan (2022).

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† IMS International Internship Program

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
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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

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YONEDA, Yusuke

Visiting Scientist
BADARAU, Adrian*

Graduate Student
OCHIAI, Keisuke

Secretary
KAMIYA, Miho

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

- Y. Yoneda, and H. Kuramochi, "Rapid-Scan Resonant Two-Dimensional Impulsive Stimulated Raman Spectroscopy of Excited States," *J. Phys. Chem. A* **127**, 5276–5286 (2023).
- 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).

1. Rapid-Scan Resonant Two-Dimensional Impulsive Stimulated Raman Spectroscopy of Excited States

Photochemical reactions occur in the electronically excited state, which is effectively represented by a multi-dimensional potential energy surface (PES) with a vast degree of freedom of nuclear coordinates. The elucidation of the intricate shape of the PES constitutes an important topic in the field of photochemistry and has long been studied both experimentally and theoretically. Recently, fully time-domain resonant two-dimensional Raman spectroscopy has emerged as a potentially powerful tool to provide unique information about the coupling between vibrational manifolds in the excited state.[1,2) However, the wide application of this technique has been significantly hampered by the technical difficulties associated with experimental implementation and remains challenging. We demonstrated fully time-domain resonant two-dimensional impulsive stimulated Raman spectroscopy (2D-ISRS) of excited states using sub-10-fs pulses based on the rapid scan of the time delay, which facilitates the efficient collection of time-domain signals with high sensitivity. As a proof-of-principle experiment, we performed 2D-ISRS of TIPS-pentacene in solution. Through 2D Fourier transformation of the high-quality time–time oscillatory signal, we obtained a 2D frequency–frequency correlation map of excited-state TIPS-pentacene in the broad frequency window of 0–2000 cm^{-1}. The data clearly resolve a number of cross peaks that signify the correlations among excited-stated vibrational manifolds. The high capability of the rapid-scan-based 2D-ISRS spectrometer presented in this study enables the systematic investigation of various photochemical reaction systems, thereby further promoting the understanding and applications of this new multi-dimensional spectroscopy.3)

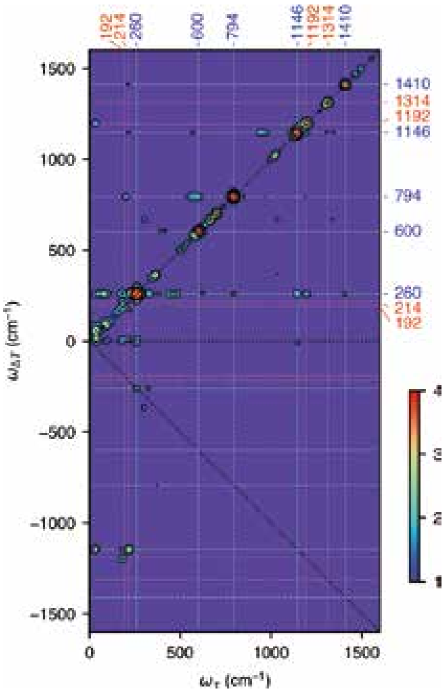

Figure 2. Two-dimensional frequency-frequency correlation map of excited-state TIPS-pentacene in chloroform.

2. Fourier Transform Excitation-Emission Spectroscopy with Phase-Locked Pulse Pairs

Polyatomic molecules in condensed phases undergo constant fluctuations in molecular structure and solvent environment. These fluctuations can lead to variations in the physical properties, reactivities, and functionalities. However, conventional ensemble measurements only provide statistically averaged information, making it challenging to observe the properties of individual molecules and transitions between subensembles. In order to overcome this limitation, we aim to develop new single-molecule spectroscopic techniques capable of observing the fluctuations of electronic and vibrational transitions and reaction dynamics. Recently, we developed Fourier transform excitation-emission spectroscopy in a room-temperature solution. We send a phase-locked pulse pair of broadband pulses to a home-built confocal microscope and detect the fluorescence with time-correlated single photon counting. Fourier transform of the fluorescence interferogram obtained by scanning the interpulse delay provides a fluorescence excitation spectrum, which shows an identical spectral shape to the bulk absorption spectrum. We aim to achieve single-molecule sensitivity in this experiment and interrogate how the excitation energy of chromophores fluctuates with large amplitude spontaneous fluctuation of photoresponsive proteins.

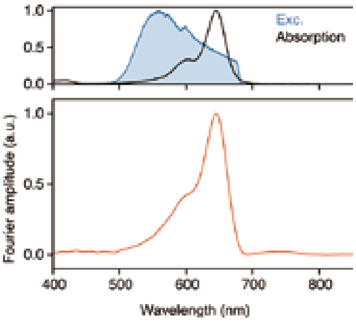

Figure 3. Fluorescence excitation spectrum of ATTO647N aqueous solution measured with broadband pulses. The excitation spectrum and bulk absorption spectrum are shown at the top.

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2) G. Fumero, C. Schnedermann, G. Batignani, T. Wende, M. Liebel, G. Bassolino, C. Ferrante, S. Mukamel, P. Kukura and T. Scopigno, *Phys. Rev. X* **10**, 011051 (2020).
3 Y. Yoneda, H. Kuramochi, S. Takeuchi and T. Tahara, *J. Phys. Chem. A* **127**, 5276–5286 (2023).

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Open up Future Electronics by Organic Molecules

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems

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Education

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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

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URBAN, Adrian
MALATONG, Ruttapol

Technical Fellow
MURATA, Ryosuke

Secretary
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 genertation 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.

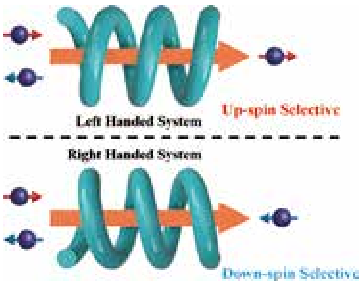

Figure 1. Conceptual schematic for CISS effect. P-helix molecule (lower panel) can transmit more electrons with spins antiparallel to the velocity (negative helicity electrons) than the other, while M-helix molecule (upper panel) favors transmission of electrons with parallel spin (positive helicity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

Selected Publications

- R. Nakajima, D. Hirobe, G. Kawaguchi1, Y. Nabei1, T. Sato, T. Narushima, H. Okamoto and H. M. Yamamoto, *Nature* **613**, 479 (2023).
- 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).

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)

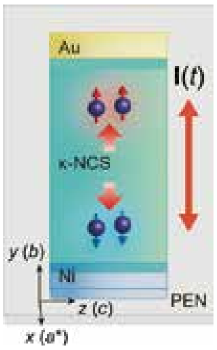

Figure 2. Device schematic for the detection of spin polarization in a chiral superconductor κ-NCS. By applying electrical current, electron spins are polarized along the current direction by CISS-like effect which can be detected as voltage across the κ-NCS/Ni interface. The amplitude of the signal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

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2) W.-Y. He and K. T. Law, *Phys. Rev. Res.* **2**, 012073(R) (2020).
3) J. Kishine, H. Kusunose and H. M. Yamamoto, *Isr. J. Chem.* **62**, e202200049 (2022).

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* IMS International Internship Program

Design of Protein Functions Using Computational and Experimental Approaches

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

KOSUGI, Takahiro
Assistant Professor

Our research is to design a variety of protein functions using computational and experimental approaches. We try to (1) design enzymes from scratch and reveal the origin of the enzymatic activity, (2) control concerted functions by rationally engineering protein complexes and understand their mechanisms and (3) uncover roles of protein complexes in cells and control cellar functions by creating several customized proteins or protein complexes.

1. Design of Allosteric Sites into a Rotary Molecular Motor by Restoring Lost Function of Pseudo-Active Sites

We have succeeded in designing artificial allosteric sites (where by binding an effector molecule, activity at the distal active site is regulated) into a rotary molecular motor, *Enterococcus hirae* V_1-ATPase.1) The allosteric sites were created by restoring lost functions of pseudo-active sites in a pseudo enzyme, of which function is predicted to have been lost during the evolution. Single-molecule experiments together with X-ray crystallography analyses revealed that the rotational rate of the designed V_1-ATPase, which was restored the lost ATP binding ability at the pseudo-active sites, is allosterically accelerated. In principle, our strategy enables us to create allosteric sites into various kinds of protein complexes and to artificially control the concerted functions.

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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 Chiral Light-Matter Interaction in Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

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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	YOSHIZAWA, Daichi
IMS Research Assistant Professor	YAMANISHI, Junsuke
Project Assistant Professor (NINS)	AHN, Hyo-Yong
Post-Doctoral Fellow	CHAKRABORTY, Ipsita
Visiting Scientist	NARUSHIMA, Tetsuya
Technical Fellow	ISHIKAWA, Akiko
Secretary	NOMURA, Emiko ITO, Atsuko

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. Optical microscopic methods, in particular nano-optical methods, such as scanning near-field optical microscopy (SNOM) which enables resolution beyond the diffraction limit of light, reveals essential characteristics of the materials and develop novel properties of them. Combination of microscopic techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. 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 polarization dependence and nonlinear/time-resolved measurements. The developed apparatuses achieved 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, plasmon wave packet propagation dynamics, 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 is also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

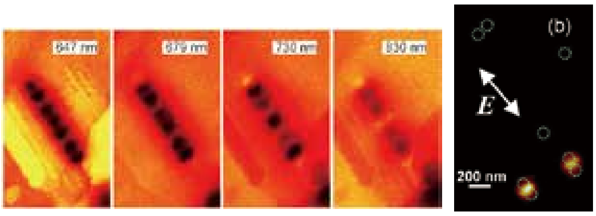

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) 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. Development of Nanoscopic Observation Method of Chiral Optical Fields by Optical Force Measurement[1)]

Nanoscopic observation of chiro-optical phenomena is essential in wide scientific areas but the measurement is sometimes not straightforward. To obtain a full understanding of the physics of chiro-optical systems and derive the full potentials, it is essential to perform in situ observation of the chiro-optical effect from the individual parts because the macroscopic chiro-optical effect cannot be translated directly into microscopic effects. One of the methods to overcome difficulties in direct access to nanoscopic chiro-optical characteristics is the use of near-field optical microscopy. In the present study, we develop an alternative method to access to near-field chiro-optical responses with optical force measurements. We achieved that at the nanoscale level by detecting the chiro-optical forces, which were generated by illumination of the material/probe system with left- and right-circularly polarized light. The induced optical force was dependent on the handedness of the incident circularly polarized light.

The measured differential image between left- and right-circularly polarized light illuminations was well correlated to the difference in the electric-field intensity near the nanostructure simulated with electromagnetic theory. Our results facilitate the clarification of chiro-optical phenomena at the nanoscale level and could innovate chiro-optical nanotechnologies. The present optical measurement method based on chiral photoinduced force microscopy is anticipated to be applied to chemical, biological, and pharmaceutical sciences, where the chirality of molecules plays an essential role.

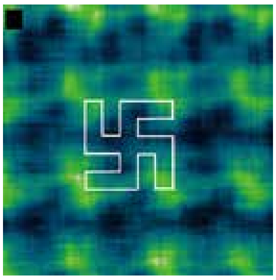

Figure 2. Chiro-optical force image of a gammadion-shaped gold nanostructure fabricated with electron beam lithography lift-off method. The base length of the gammadion is 460 nm.

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

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.[3)] 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. In contrast, chiral plasmons have potentials to provide highly circularly polarized luminescence. We are now pursuing the possibility to obtain highly circularly polarized luminescence with chiral plasmonic systems.

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.

5. Fundamental Characteristics of Chiro-Optical Properties of Pseudo Two-Dimensional Chiral Nanostructures

Based on the electromagnetic theory, it is expected that (ideal) two-dimensional chiral structures with 1- or 2-fold rotational symmetry exhibit chiro-optical effects, while those with 3-fold or higher rotational symmetry do not. However, for the pseudo two-dimensional gammadion-type metal nanostructures with 4-fold rotational symmetry in reality fabricated by electron beam lithography, they exhibit strong chiro-optical effects. In the present study, we experimentally confirmed that difference in rotational symmetry of the pseudo two-dimensional nanostructure gives totally different chiro-optical characteristics. We also obtain information on the origin of chiro-optical effects in pseudo two-dimensional 4-fold symmetry systems.

References

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2) H. Okamoto and T. Narushima, PAT. P. (PCT).

3) T. Narushima and H. Okamoto, *Sci. Rep.* **6**, 35731 (2016).

Nano- and Atomic-Scale Spectroscopy

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Education

2006	B.S. Ritsumeikan University
2008	M.S. Kyoto University
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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)

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Assistant Professor
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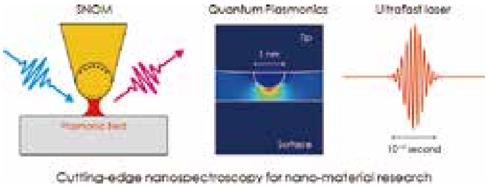
JSPS Post-Doctral Fellow
LIU, Shuyi

Secretary
ITO, Atsuko

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

Optical spectroscopy is a potent method to study material structures and properties through light–matter interactions. As nanoscience and nanotechnology have advanced, the significance of spectroscopy at the nanoscale, and even at the atomic scale, has grown immensely. Achieving optical imaging and spectroscopy at atomic resolution stands at the forefront of nanoscience and nanotechnology, allowing for the direct investigation of atomic-scale structures, properties and dynamics in real space and real time. Using near-field optics, electromagnetic fields can be confined at the nano- and atomic-scale. In particular, the localized surface plasmons of metallic nanostructures enable exceptionally sensitive optical spectroscopy due to their significant field enhancement. To achieve nano- and atomic-scale optical spectroscopy, we integrate advanced technologies such as low-temperature scanning tunneling microscopy (STM), laser spectroscopy, and quantum plasmonics. Specifically, the use of low-temperature STM allows us to directly observe atomic-level structures and to precisely manipulate individual atoms and molecules, whereas laser spectroscopy not only facilitates precise optical measurements but also traces ultrafast dynamics using ultrashort laser pulses. Consequently, the combination of these techniques offers a promising avenue for optical spectroscopy with ultrahigh spatiotemporal resolution.

In this review, I provide a concise summary of our recent advancements in nano- and atomic-scale spectroscopy.



Selected Publications

- 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).
- B. Cirera *et al.*, "Joule Heating in Single-Molecule Point Contacts Studied by Tip-Enhanced Raman Spectroscopy," *ACS Nano* **16**, 16443 (2022).
- S. Liu *et al.*, "Nanoscale Coherent Phonon Spectroscopy," *Sci. Adv.* **8**, eabq5682 (2022).
- S. Liu *et al.*, "Inelastic Light Scattering in the Vicinity of a Single-Atom Quantum Point Contact in a Plasmonic Picocavity," *ACS Nano* **17**, 10172 (2023).
- K. Nishikawa, J. Nishida *et al.*, "Metastability in the Insulator Metal Transition for Individual Vanadium Dioxide Nanoparticles," *J. Phys. Chem. C* **127**, 16485–16495 (2023).

1. Atomic-Scale Optical Spectroscopy

Recent studies have demonstrated that sub-nanometer confinement of near fields arises in the presence of atomic-scale protrusions on metallic nanostructures, and extremely strong light–matter interactions occur in “picocavity.” However, the specific impact of atomic-level structures on plasmonic properties still remains to be elucidated. This requires precise experiments using atomically well-defined model systems. We investigated inelastic light scattering of a single Ag atom adsorbed onto the Ag(111) surface using low-temperature tip-enhanced Raman spectroscopy (TERS), as shown in Figure 1. We discovered that the vibration mode localized at the adatom can be observed in the TERS spectrum. Furthermore, we trace how the TERS spectrum evolves as a function of the gap distance. The exceptional stability provided by the low-temperature STM enabled us to clearly examine the different electron transport regimes of the picocavity, specifically in both the tunneling and quantum point contact (QPC) regimes. Our measurements highlight a distinct vibration mode localized at the adatom. Moreover, its TERS intensity undergoes a pronounced shift upon the QPC formation. This observation underscores that the atomic-level structure has a crucial impact on the plasmonic properties. To gain microscopic insights into the intricate of picocavity optomechanics, we meticulously analyzed the structure and plasmonic field within the STM junction, employing time-dependent density functional theory. These simulations unveiled that atomic-scale structural relaxations at the single-atom QPC lead to discernible variations in the plasmonic field’s strength, volume, distribution, as well as the vibration mode localized at the individual atom.

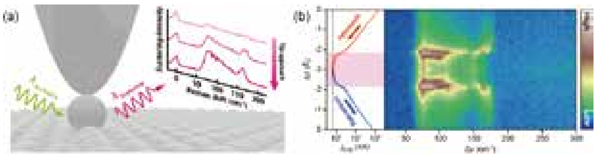


Figure 1. Inelastic light scattering spectroscopy for a single Ag adatom on the Ag(111) surface. (a) Schematic of the experiment. (b) ILS spectra measured as a function of the tip–adatom distance.

2. Nanoscale Coherent Phonon Spectroscopy

Coherent phonon spectroscopy offers microscopic insights into ultrafast lattice dynamics, especially when considering its interaction with other degrees of freedom in nonequilibrium conditions. While ultrafast optical spectroscopy is an established method for studying coherent phonons, the restrictions imposed by the diffraction limit have made direct observations of their nanoscale dynamics elusive. We successfully showcased nanoscale coherent phonon spectroscopy using an ultrafast laser-induced STM within a plasmonic junction (Figure 2). Coherent phonons are locally excited in ultrathin zinc oxide films by the highly confined plasmonic field and are probed via the photoinduced tunneling current through an electronic resonance of the zinc oxide film. Using concurrently performed TERS, we revealed the specific phonon modes involved. Unlike the Raman spectra, the phonon dynamics detected in coherent phonon spectroscopy display pronounced nanoscale spatial variations. These variations correlate with the distribution of the electronic local density of states, as discerned by scanning tunneling spectroscopy..

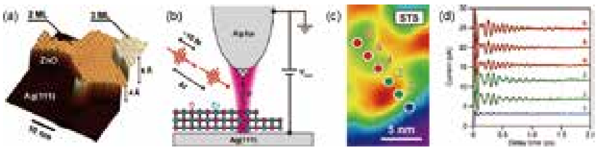


Figure 2. Nanoscale coherent phonon spectroscopy. (a) STM image of the ZnO ultrathin film expitaxially grown on the Ag(111) surface. (b) Schematic of the experiment. (c) Scanning tunneling spectroscopy image of the ZnO ultrathin film. (d) Interferometric autocorrelation of the tunneling current recorded over the ZnO ultrathin film.

3. Nanoscale Infrared Imaging of Nanomaterials

We have also developed advanced mid-infrared (MIR) spectroscopy and imaging techniques based on scattering-type scanning near-field optical microscopy (s-SNOM). We have successfully set up s-SNOM equipped with a MIR tunable broadband laser for investigation of nanomaterials. Figure 3 presents a direct observation of the insulator–metal transition in individual vanadium dioxide (VO_2) nanoparticles. Using temperature-dependent mid-IR nanoimaging, we were able to discern the phase transition of these individual VO_2 nanoparticles. Particles of smaller volumes generally transition to metal at elevated temperatures. This is attributed to fewer nucleation sites within each particle. Using mid-IR nanoimaging, we observed that the phase transition displays a stochastic behavior: The same particle shows varying transition temperatures across different heating cycles. Our findings suggest that the phase transition in VO_2 nanoparticles is prone to superheating and supercooling, and these transitions are limited by nucleation.

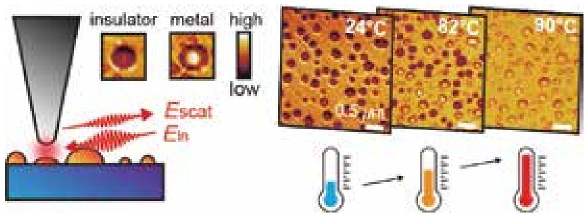


Figure 3. Nanoscale MIR imaging of VO_2 nanoparticles at different temperatures.

References

1) S. Liu *et al.*, *ACS Nano* **17**, 10172 (2023).
2) S. Liu *et al.*, *Sci. Adv.* **8**, eabq5682 (2022).
3) K. Nishikawa, J. Nishida *et al.*, *J. Phys. Chem. C* **127**, 16485 (2023).

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

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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
2022	Le Grand Prix 2022 de la Fondation de la Maison de la Chimie
2023	Asahi Prize

Member
IMS Research Assistant Professor
MITSUHASHI, Takaaki
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 research the application of them.

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 accommodated small molecules periodically aligned in the CS. 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.

Besides structure analysis by the CS method, we also use the self-assembled molecular systems for various purpose, and try opening up new research field.

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 progress. In the first case, we used the self-assembled molecular system for chemical reaction. In the second case, we applied the self-assembled molecular system to protein science.

1. Tetradehydro-Diels–Alder Reactions of Flexible Arylalkynes via Folding Inside the Self-Assembled Molecular Cage[1]

The tetradehydro-Diels–Alder reaction is useful, but not so straightforward, requiring careful substrate design and harsh reaction consition. Recently, we found that efficient and site-selective tetradehydro-Diels–Alder reaction can be achieved by using a kind of self-assembled molecular system, called a Pd_6L_4 cage. The Pd_6L_4 cage has a cavity, into which broad range of compound can be introduced.

In the reaction we found, the substrate was captured inside the Pd_6L_4 cage, and the conformation of the substrate was fixed. The control of the substrate conformation results in the efficient and site-selective reaction (Figure 1).

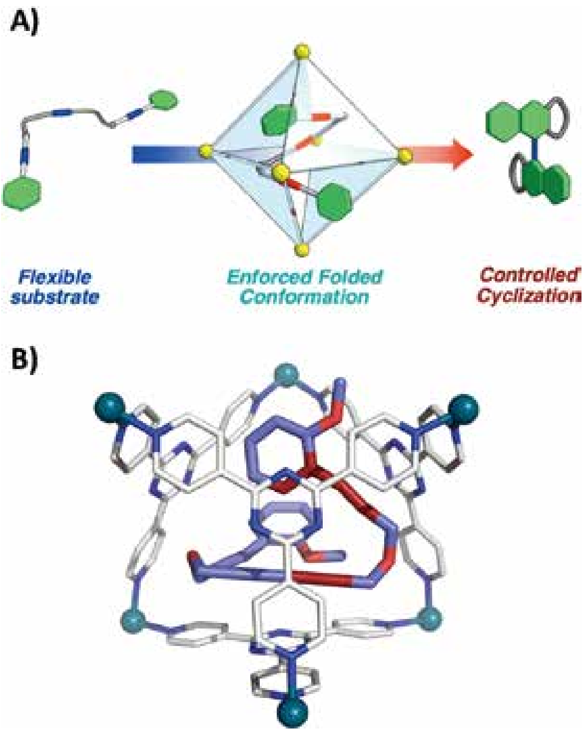

Figure 1. A) Concept of this study. B) Crystal structure of the substrate-Pd_6L_4 cage complex.

2. Hysteresis Behavior in the Unfolding/Refolding Processes of a Protein Trapped in the Self-Assembled Molecular Cage[2]

The $M_{12}L_{24}$ self-assembled cage possesses a cavity large enough to accommodate proteins (Figure 2A).

Recently, we use this cage to analyze unfolding/refolding processes of a protein. When the concentration of organic solvent is increased in protein solution, the protein would be denatured. Then, the protein would be aggregated and precipitated normally. However, when the protein is captured in the self-assemble cage, the precipitation is prevented, because only single protein exists inside the cage. Thus, we can carry out the protein transient structure analysis, using this cage.

Concretely, we increase and decrease the concentration of acetonitrile of the protein solution, and the protein conformation was monitored by NMR analysis. As a result, it was revealed that the protein folding/unfolding process exhibited hysteresis behavior (Figure 2B).

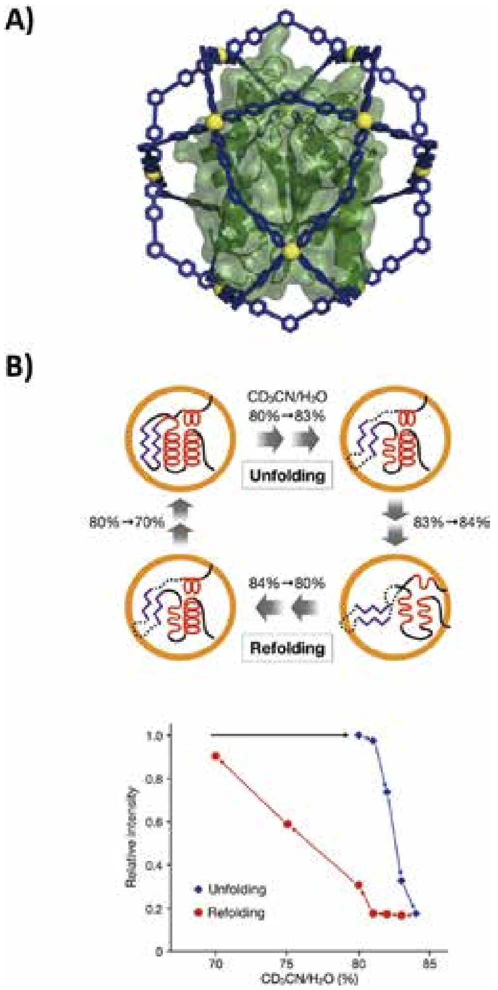

Figure 2. A) Molecular modeling of protein in the $M_{12}L_{24}$ self-assembled cage. B) Protein folding/unfolding process exhibited hysteresis behavior.

Award

FUJITA, Makoto; The Asahi Prize 2022 (2023).

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2) T. Nakama, A. Rossen, R. Ebihara, M. Yagi-Utsumi, D. Fujita, K. Kato, S. Sato and M. Fujita, *Chem. Sci.* **14**, 2910–2914 (2023).

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

Division of Advanced Molecular Science
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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
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 and their evolution, 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 have started a novel electron spectroscopy technique, Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS), with bulk-sensitive primary energies of 0.3–1.5 keV. At present, we combine it with a time- and angle-resolved technique, shown in Figure 1, to simultaneously observe both the changing electronic structure and collective excitations and the lattice and magnetic structure relaxation. Based on the obtained information on electronic structures, we aim to develop novel physical properties of new materials.

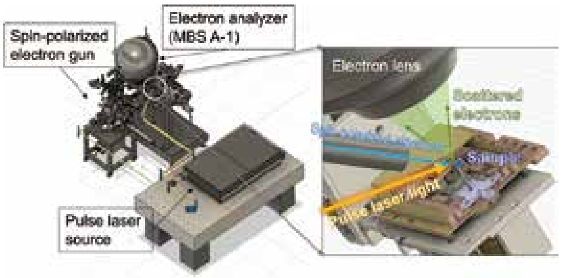

Figure 1. Time-, Spin-, and Angle-Resolved resonant Electron-Energy-Loss Spectroscopy (tSAR-rEELS) apparatus, which our group is now developing. The apparatus comprises a high-brilliant spin-polarized electron gun, a photoelectron spectrometer, and a femtosecond pulse laser with an optical parametric amplifier.

Selected Publications

- Y. Ohtsubo, T. Nakaya, T. Nakamura, P. Le Fèrve, F. Bertran, F. Iga and S. Kimura, “Breakdown of Bulk-Projected Isotropy in Surface Electronic States of Topological Kondo Insulator SmB_6(001),” *Nat. Commun.* **13**, 5600 (7 pages) (2022).
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- 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]

1. Breakdown of Bulk-Projected Isotropy in Surface Electronic States of Topological Kondo Insulator SmB$_6$(001)1)

The topology and spin-orbital polarization of two-dimensional (2D) surface electronic states have been extensively studied in this decade. One major interest in them is their close relationship with the parities of the bulk (3D) electronic states. In this context, the surface is often regarded as a simple truncation of the bulk crystal. Here we show a breakdown of the bulk-related in-plane rotation symmetry in the topological surface states (TSSs) of the Kondo insulator SmB$_6$.2) Angle-resolved photoelectron spectroscopy (ARPES) performed on the vicinal SmB$_6$(001)-*p*(2×2) surface showed that TSSs are anisotropic and that the Fermi contour lacks the fourfold rotation symmetry maintained in the bulk. This result emphasizes the important role of the surface atomic structure even in TSSs. Moreover, it suggests that the engineering of surface atomic structure could provide a new pathway to tailor various properties among TSSs, such as anisotropic surface conductivity, nesting of surface Fermi contours, or the number and position of van Hove singularities in 2D reciprocal space.

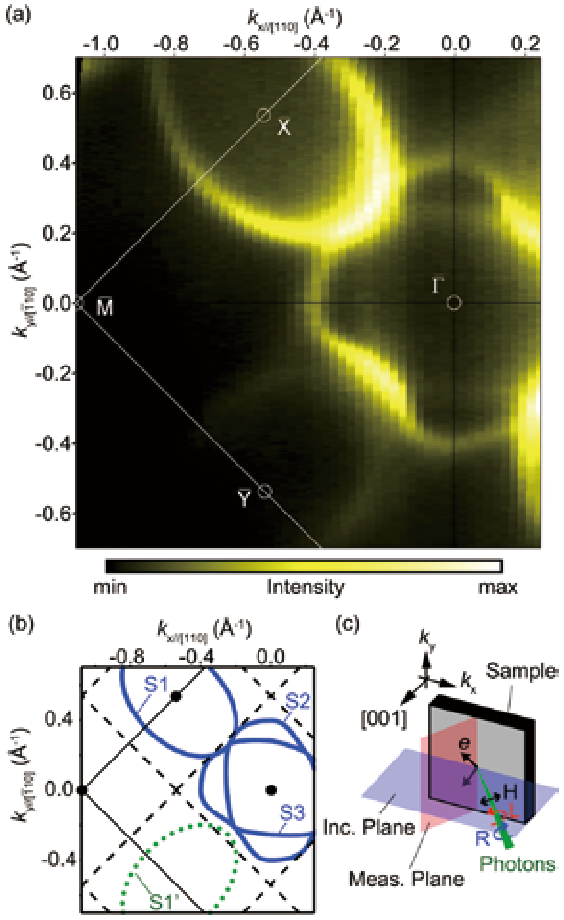

Figure 2. (a) ARPES Fermi contours (FCs) taken at the photon-incident plane of ($\bar{1}$10) at 13 K. (b) Schematic drawing of the observed FCs together with the border of surface Brillouin zones; solid lines for bulk-truncated (1×1) and dashed for (2×2). (c) Experimental geometry and definition of the in-plane wavevectors k_x and k_y. k_x and k_y are always in the photon-incident and photoelectron detection planes, respectively.

2. Fluctuating Spin-Orbital Texture of Rashba-Split Surface States in Real and Reciprocal Space3)

Spin–orbit interaction in low-dimensional systems, namely, Rashba systems and the edge states of topological materials, has been extensively studied in this decade as a promising source to realize various fascinating spintronic phenomena, such as the source of the spin current and spin-mediated energy conversion. Here, we show the odd fluctuation in the spin-orbital texture in a surface Rashba system on Bi/InAs(110)-(2×1) by spin- and angle-resolved photoelectron spectroscopy and a numerical simulation based on a density-functional theory (DFT) calculation. The surface state shows a paired parabolic dispersion with the spin degeneracy lifted by the Rashba effect. Although its spin polarization should be fixed in a particular direction based on the Rashba model, the observed spin polarization varies greatly. It even reverses its sign depending on the wave number. DFT calculations also reveal that the spin directions of two inequivalent Bi chains on the surface change from nearly parallel (canted parallel) to antiparallel in real space in the corresponding wave vector region. These results indicate an oversimplification of the nature of spin in Rashba and Dirac systems and provide more freedom than expected for spin manipulation of photoelectrons.

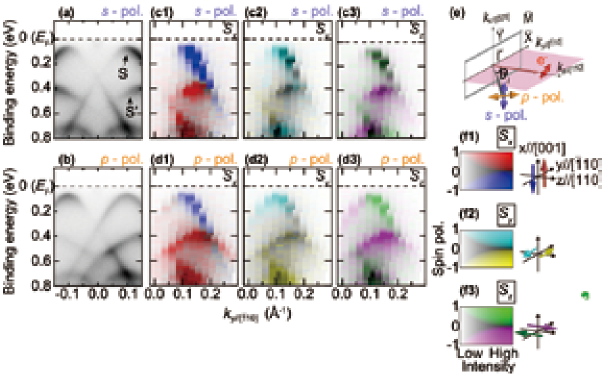

Figure 3. Spin-polarized surface band structures measured by spin- and angle-resolved photoelectron spectroscopy (SARPES) (a) and (b) ARPES and (c) and (d) SARPES 2D plots measured with s-polarized (top) and p-polarized (bottom) photons along $\bar{\Gamma}$–$\bar{X}$ (parallel to the Bi chains). (a) and (b) Spin-integrated ARPES intensity maps. SARPES maps polarized to (c1) and (d1) S_x, (c2) and (d2) S_y, and (c3) and (d3) S_z. The spin orientations are defined in (f). (e) Experimental geometry of the SARPES measurements and definitions of the coordinates. The (2×1) surface Brillouin zone and the common plane of the photon incidence and photoelectron detection are superposed simultaneously. (f) Definitions of the spin directions of the photoelectrons.

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3) T. Nakamura, Y. Ohtsubo, A. Harasawa, K. Yaji, S. Shin, F. Komori and S. Kimura, *Phys. Rev. B* **105**, 235141 (7 pages) (2022).

Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

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

ONISHI, Hiroshi
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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
KURITA, Yoshiko

Keywords Reactions at Interfaces, Catalysis, Energy-Related Chemistry

We are proud of our internationally 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 look forward to collaborating with researchers in academic and industrial organizations to unravel the science behind material conversion and energy dissipation at liquid-solid interfaces.

A new era of molecular science will be revealed at liquid-solid interfaces of finite thickness (Figure 1). The molecular interface is the site of reaction where molecules of interest collide or interact with other molecules. We need to observe individual molecules there. On the other hand, the molecular interface is connected to the liquid and solid. Materials and energy come from/to the two condensed phases, since functional interfaces are always open to the environment. Operando characterization is absolutely necessary to study the interface in its working state.

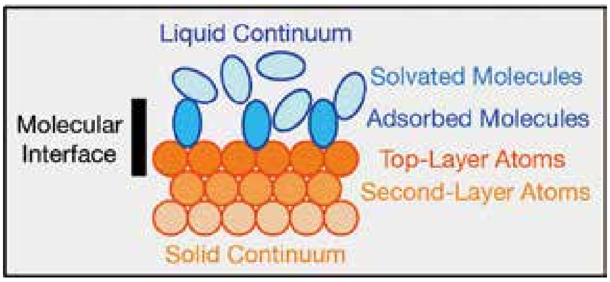

Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- Z. Fu, T. Hirai and H. Onishi, "Long-Life Electrons in Metal-Doped Alkali-Metal Tantalate Photocatalysts Excited under Water," *J. Phys. Chem. C* **125**, 26398–26405 (2021).
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- 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).
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- 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).

1. Infrared and Near-Infrared Spectrometry of Anatase and Rutile Particles Bandgap Excited in Liquid

The chemical transformation of materials is accomplished in milliseconds or seconds by assembling atoms over semiconductor photocatalysts. Bandgap-excited electrons and holes, which are reactive on this time scale, are key to the efficient assembly of atoms to yield the desired products. In this study,1) attenuated total reflection of infrared and near-infrared light was used to characterize and quantify the electronic absorption of TiO_2 photocatalysts excited under liquid. Nanoparticles of rutile or anatase were placed on a diamond prism, covered with liquid, and irradiated with continuous UV light through the prism. Electrons excited in rutile particles (JRC-TIO-6) formed small polarons characterized by a symmetric absorption band spread over 10000–700 cm^{-1} with a maximum at 6000 cm^{-1} (Figure 2). Electrons in anatase particles (JRC-TIO-7) formed large polarons and produced an asymmetric absorption band that gradually strengthened at wave numbers below 5000 cm^{-1} and weakened sharply at 1000 cm^{-1}. The absorption spectrum of large electron polarons in TIO-7 was compared with the absorption reported in a Sr-doped $NaTaO_3$ photocatalyst, and it was suggested that excited electrons were accommodated as large polarons in $NaTaO_3$ photocatalysts efficient for artificial photosynthesis. The UV light power dependence of the absorption bands was observed in N_2-exposed decane liquid to derive the electron–hole recombination kinetics. At light power densities P greater than 200 W m^{-2} (TIO-6) and 2000 W m^{-2} (TIO-7), the polaron absorptions were enhanced with the absorbance proportional to $P^{1/2}$. The observed 1/2 power law suggested recombination of multiple electrons and holes moving randomly in each particle. Upon excitation with smaller P, the power law order increased to unity. The unity-order power law was interpreted as the recombination of an electron and a hole excited by the same photon. Furthermore, an average lifetime of 1 ms was estimated for electron polarons in TIO-6 when weakly excited at P = 20 W m^{-2} to simulate solar light irradiation.

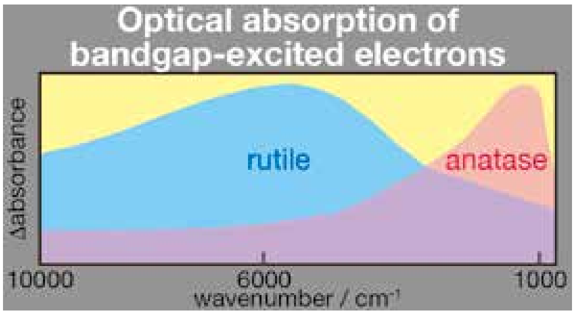

Figure 2. Optical absorption of electrons photoexcited in rutile and anatase TiO_2.

2. Three Dimensional Atom Imaging in $KTaO_3$ Photocatalysts Doped with Metal Cations

Potassium tantalate, $KTaO_3$, is a highly efficient semiconductor photocatalyst for the overall water splitting reaction. Doping a semiconductor photocatalyst with foreign metal cations typically increases the apparent quantum yield of the splitting reaction. In this study,2) we constructed a single-crystal model of cation-doped photocatalysts that would be suitable for future investigation using advanced surface-sensitive methods. Centimeter-sized (001)-oriented $KTaO_3$ wafers were doped with Sr or La cations in KCl flux. X-ray diffraction revealed Sr- and La-containing perovskite-structured layers epitaxially covering the bulk $KTaO_3$. On the Sr-doped wafer, the surface layer lattice was expanded by 2% relative to the bulk lattice. X-ray fluorescence holography was used to determine the three-dimensional short-range ordered structure around the K and Sr cations (Figure 3). Holograms obtained with Sr Kα fluorescence confirmed the simultaneous placement of Sr cations in the A and B sites. The placement of the Sr cations in the B sites was supported by the TaO_6 breathing vibration observed in Raman scattering. These experimental results suggest that a $KTaO_3$-$Sr(Sr_{1/3}Ta_{2/3})O_3$ solid solution is generated by doping. Two La-containing phases, one with a 2% lattice contraction and the other with a 0.4% expansion, were detected on the La-doped wafer. La Lα fluorescence holograms indicated a complex type of doping. The obtained atom distribution around La cations was interpreted by the simultaneous La cation occupancy at the A site, B site and an interstitial site. Local lattice deformation was quantitatively deduced around the La cations occupying the interstitial site. Elemental composition determined by X-ray photoelectron spectroscopy revealed the enrichment of dopant elements on the wafer surface. Nanometer-scale topography observed by atomic force microscopy suggested that doping concentrations should be optimized to obtain flat, crystalline surfaces.

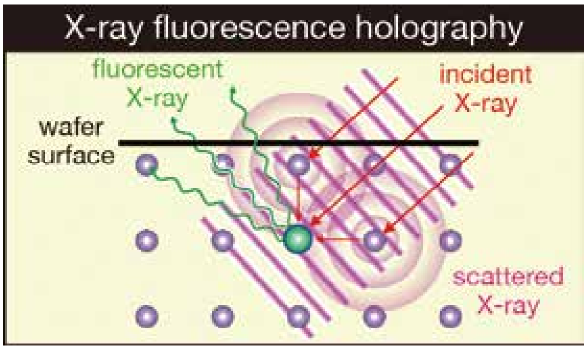

Figure 3. X-ray fluorescence holography.

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2) A. Sasahara, K. Kimura, H. Sudrajat, N. Happo, K. Hayashi and H. Onishi, *J. Phys. Chem. C* **126**, 19745–19755 (2022).

Engineering of PET Hydrolase for Plastic Recycling and Environmental Remediation, and Engineering of Plastic Binding Domains for Detection and Quantification of Particles

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

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Education

2009	B.S. The University of Tokyo
2014	Ph.D. The University of Tokyo

Professional Employment

1995	Postdoctoral Fellow, The University of Tokyo
2015	Assistant Professor, Okazaki Institute for Integrative Bioscience
2018	Assistant Professor, Institute for Molecular Science
2020	Tenure-track Associate Professor, Shizuoka University
2022	Associate Professor (Cross Appointment), Institute for Molecular Science

Awards

2015	HAMMON President Choice
2019	ATI Research Encouragement Award
2019	Early Career Award in Biophysics
2021	8th Biophysics and Physicobiology Editors' Choice Award

Member
Secretary
NAKANE, Kaori
NOMURA, Junko

Keywords Solid-Liquid Interfacial Reaction, Protein-Engineering, Single-Molecule Observation

Plastic is an indispensable material in our daily lives. It is used in a wide variety of products because it is low-cost, mass-producible, and easy to mold and process. However, due to its convenience, the amounts of plastic used and disposed are increasing every year, raising concerns about its environmental impact and sustainability. Therefore, there is a need to develop efficient and environmentally friendly recycling methods, as well as simple and rapid methods to detect plastics that have leaked into the environment.

We are attempting to obtain more active mutants by exhaustively mutating amino acid residues on the enzyme surface and screening their activity using a dispensing robot. We are also attempting to create plastic adsorption domains by modifying the amino acids constituting the adsorption surface of the carbohydrate binding domain and using a phage display method.

These studies will promote the recycling of used plastics by enzymatic degradation and promote more sustainable use of plastics. In addition, by creating a protein that detects and stains plastics, we will contribute to the protection of the natural environment by monitoring runoff into the environment (Figure 1).

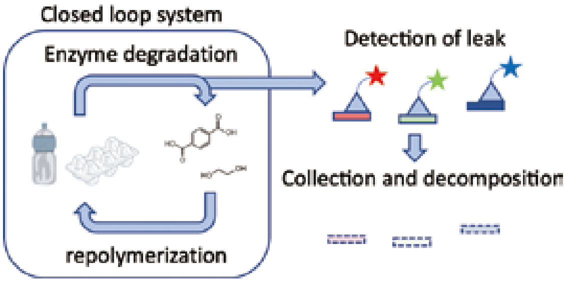

Figure 1. Scheme of plastic recycling and detection system.

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).
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- 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. Ishida, K. Kusaka, T. Yamada, S. Fushinobu, I. Tanaka, S. Kaneko, K. Ohta, H. Tanaka, K. Inaka, Y. Higuchi, N. Niimura, M. Samejima and K. Igarashi, "'Newton's Cradle' Proton Relay with Amide-Imidic Acid Tautomerization in Inverting Cellulase Visualized by Neutron Crystallography," *Sci. Adv.* **1**, e1500263 (2015).

1. High Throughput Screening Method of PET Hydrolase Activity

Mutations were introduced into PET hydrolytic enzyme PET2 derived from a metagenomic library to create a mutant with improved thermostability and PET degrading activity.[1] In this study, the improvement was achieved with a combination of single mutations, but a saturation mutation, for example, in which a combination of all amino acids is tested in two locations, we need to test a library of 399 candidate mutants. Since it is difficult to purify and measure the activity of each mutant individually, a method was created to evaluate the activity without purification of the enzyme and without the use of HPLC.

We artificially prepared PET particulate suspensions by dissolving PET in Hexafluoro-2-propanol (HFIP) and regenerating it in water. Since the concentration of the suspension correlates with the intensity of light scattering at 595 nm, we attempted to measure PET degradation activity using turbidity as an indicator.

When the temporal changes in degradation rate and turbidity were analyzed by changing the concentration of PET degrading enzyme, it was observed that the turbidity decreased over time, and it was found that the high degradation activity could be evaluated from the rate of decrease in turbidity (Figure 2). Therefore, we created a library in which saturation mutations were introduced at two substrate recognition sites of the PET2 mutant and performed selection. colonies were cultured in 96-well plates, and after one night of enzyme induction, the culture medium was collected and mixed with the PET suspension. The rate of decrease in turbidity was analyzed in the culture medium of approximately 800 colonies, and 13 enzymes were found to be more than twice as active as the PET2 mutant that used as the template.

To further verify thermostability, activity measurements were performed using heat-treated enzymes. The use of 384 wells for activity measurement enabled analysis of many enzymes at one time and efficient screening. The best three mutants were produced and purified at large scare cultivation and the activities against PET film are under comparison

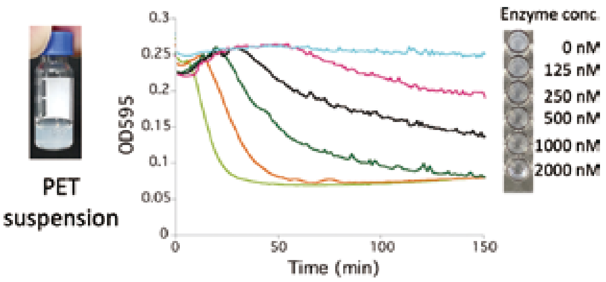

Figure 2. Results of PET degrading enzyme activity measurement using turbidity as an indicator.

2. Artificial Evolution of Carbohydrate Binding Domain to PET Binding Domain

To develop a method for detecting plastics in samples using plastic binding proteins, we first developed a protein targeting PET. The template enzyme was a thermostable domain that adsorbs on chitin, which has a hydrophobic plane similar to PET.

Saturation mutations were introduced at four amino acid residues oriented on the adsorption surface and involved in chitin recognition. Since the number of candidate mutants is about 160,000 and it is difficult to verify them one by one, we created a library of phage vectors with adsorption domain mutant genes inserted into, which were then used to create a library of M13 phage presenting adsorption domain mutants on their surface. The M13 phage library was incubated with PET film, unbound phage were washed away, and phage bound on PET were recovered by trypsin digestion and re-amplified by infection with *E. coli*. The reproduced first-generation phage library was again mixed with PET and the number of washes was increased to 10 before PET adsorbed phage were collected and infected with *E. coli*. After the second-generation phage library was produced, the phage vectors were purified from *E. coli*, and the mutated portions were analyzed using a next-generation sequencer. In the pre-screening library, the percentage of amino acids that appeared for the four mutations was almost the same, but in the second-generation library, a large difference was observed in the probability of occurrence of different amino acids depending on the position of the mutation. This was thought to be the result of selection of amino acids structurally important for PET recognition. In order to select mutants with strong binding and high thermal stability, a third-generation screening was conducted with binding and washing temperatures set at 60 °C. As a result, 29 colonies were obtained, 27 of which were the same mutant. The mutant enzyme was conjugated with RFP, and when mixed with PET powder, the mutant complex stained the PET powder red, whereas the template enzyme did not (Figure 3). Currently, we are introducing further mutations into the mutant to improve the specificity of binding on PET.

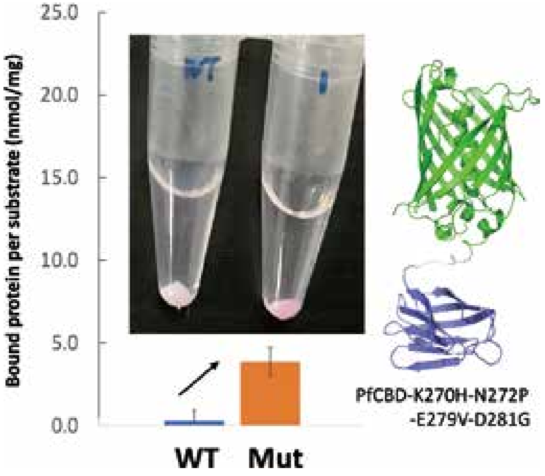

Figure 3. Binding measurement results using PET binding domain and RFP complex.

Reference

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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
2023	Invited Professor, National Institute for Fusion Science
2023	Director, The Amada Foundation

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
Associate Program Manager
SUMIYA, Rie
SUZUKI, Masayo
UEGURI, Atsushi
YOSHIOKA, Takashi
TAMURA, Akiyoshi
Visiting Professor
KAWASE, Kodo
Visiting Associate Professor
YOSHIDA, Mitsuhiro
Post-Doctoral Fellow
TAKEYA, Kei
YAHIA, Vincent
LIM, Hwanhong
ICHII, Tomoaki
CASSOURET, Florent
BRUNETEAU, Baptiste
Research Fellow
KAUSAS, Arvydas*
Visiting Scientist
TAKIGAMI, Hiroyuki*
ISHIZUKI, Hideki*
SATO, Yoichi*
TSUJI, Akihiro*
MURATE, Kosuke
ODAKA, Hideho*
FLAMENT, Aliénor†
Technical Fellow
MATSUDA, Miho*
KOBAYASHI, Jun*
MIZUSHIMA, Kazuhiko*
IBUKI, Takeshi*
JUNG, Heeseob*
Secretary
ONO, Yoko
INAGAKI, Yayoi
OKUHARA, Norie*
YAMASAKI, Misuzu

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. With the engineered materials of micro ceramic and single-crystal, solid-state lasers can provide excellent spatial mode quality and narrow linewidths with enough power. The high brightness of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion: The world first laser-ignited car, high efficiency broad frequency conversions from the wavelength of 118nm VUV to 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 and is a foundational technology for, *e.g.*, attosecond pulse generation (https://www.nobelprize.org/prizes/physics/2023/krausz/prize-presentation/). 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.

Selected Publications

- T. Taira *et al.*, *Opt. Lett.* **16**, 1955 (1991).
- 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).
- H. Sakai *et al.*, *Opt. Express* **16**, 19891 (2008).
- M. Tsunekane *et al.*, *IEEE J. Quantum Electron.* **46**, 277 (2010).
- F. Krausz *et al.*, *Opt. Lett.* **37**, 4973 (2012).
- T. Taira *et al.*, *The 1st Laser Ignition Conference ’13, OPIC ’13, Yokohama, April 23-26*, LIC3-1 (2013).
- R. Bhandari *et al.*, *Opt. Express* **21**, 28849 (2013).
- S. Hayashi *et al.*, *Sci. Rep.* **4**, 5045 (2014).
- L. Zheng *et al.*, *Opt. Mater. Express* **7**, 3214 (2017).
- H. Ishizuki *et al.*, *Opt. Mater. Express* **8**, 1259 (2018).
- S.W. Jolly *et al.*, *Nat. Commun.* **10**, 1 (2019).
- K. Tamura *et al.*, *J. Nucl. Sci. Technol.* **58**, 405 (2020).
- Y. Sano *et al.*, *Forces in Mechanics* **7**, 100080 (2022).

1. Widely Tunable Near-Infrared Optical Parametric Oscillator Based on a 5%MgO:PPLN Partial Cylinder Pumped at 1064 nm by a 1-kHz Sub-Nanosecond Microchip Laser[1)]

We report the implementation of a singly resonant optical parametric oscillator using a 5%MgO:PPLN (periodically poled Mg-doped $LiNbO_3$) partial cylinder pumped by a sub-nanosecond microchip laser emitting 1064 nm at a repetition rate of 1 kHz. It is continuously tunable from 1410 nm up to 4330 nm by rotating the cylinder and a total energy of several microjoules is emitted with a beam quality factor M^2 lower than 3.

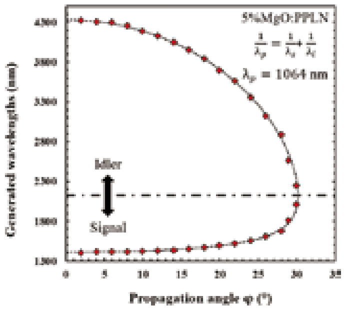

Figure 2. Angular quasi-phase-matching tuning curve of the PPMgLN cylindrical OPO. The horizontal line at 2128 nm stands for degeneracy.

2. Recovery of the Laser-Induced Breakdown Spectroscopy System Using a Ceramic Microchip Deteriorated by Radiation for the Remote Elemental Analysis[2)]

The radiation-induced deterioration of ceramic microchip laser properties limits the applications of laser-induced breakdown spectroscopy (LIBS) systems. The deteriorated properties were recovered through thermal treatment of ceramics as derived by the spectroscopic comparison of ceramics and single crystals (SCs). The absorption in spectra was increased by gamma rays irradiation, which was higher for the ceramics than for the SCs in the infrared radiation region. Although the amount of absorption decreased by heating and increased via cooling ceramics, no significant thermal effects were observed for the SCs. The effects of irradiation on the laser properties of ceramics were examined, and the laser pulse energy loss was well recovered via heating. Although heating reduced the number of generated pulses and affected the burst-mode measurement, the reduction was recovered by increasing the pump laser power. Because the radiation-induced deterioration of the LIBS signal for single-pulse and multiburst mode measurements was well recovered, the procedures are considered effective for the application of LIBS systems using radiation-sensitive ceramics, particularly in harsh radiation environments.

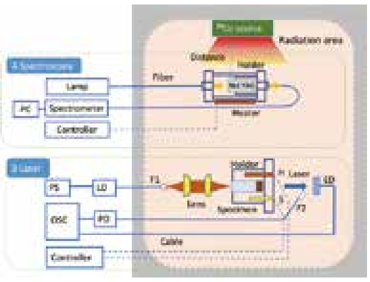

Figure 3. Experimental setup for spectroscopy (A: Spectroscopy), and laser properties measurement (B: Laser). Controller: temperature controller; ED: energy detector; H, Heater: heater; Holder: specimen holder; OSC: oscilloscope; PD 1,2: photodiode; PS: power supply; and S: temperature sensor.

3. >70 MW Peak Power/100 Hz Unstable Cavity Microchip Laser[3)]

We have 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 M^2 of 7.67. The brightness scale of unstable resonator MCL was up to 88.9 TW/(sr·cm^2) in contrast with flat–flat cavity MCL. However, the intense central part of Bessel-like beam increased its brightness effectively more than 8 times, up to 736 TW/(sr·cm^2).

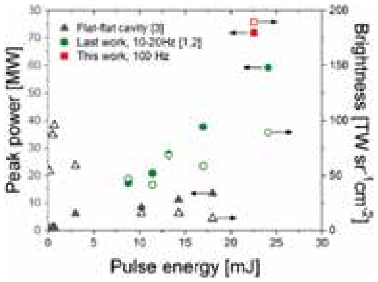

Figure 4. Measured peak power and brightness as a function of pulse energy. The recent results (square) were compared with last results using unstable cavity (circle) [1,2] and flat-flat cavity (triangle) [3]. ([1] *Opt. Express* **27**, 31307 (2019), [2] *Opt. Express* **30**, 5151 (2022), [3] Reference 14–19 of [2])

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1) B. Bruneteau, P. Segonds, H. Ishizuki, T. Taira, B. Boulanger *et. al.*, *Opt. Lett.* **48**, 3669 (2023).
2) K. Tamura, R. Nakanishi, H. Ohba, T. Taira and I. Wakaida, *J. Nucl. Sci. Technol.* **60**, 175–184 (2023).
3) H. H. Lim and T. Taira, *The 25th Congress of the International Commission for Optics (ICO-25), Technische Universität Dresden, Dresden, Germany, September 5-9*, TS 1-7-04 (2022). (Post-Deadline Paper)

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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 (Hiroshima Univ.)
TANAKA, Kiyohisa	Associate Professor
TAIRA, Yoshitaka	Associate Professor
OHIGASHI, Takuji	Associate Professor (Cross Appt.)
KANEYASU, Tatsuo	Associate Professor (SAGA-LS)
ARAKI, Tohru	Senior Researcher
IWAYAMA, Hiroshi	Assistant Professor
SUGITA, Kento	Assistant Professor
KATAYANAGI, Hideki	Research Associate
HAGIWARA, Kenta	IMS Fellow
MATSUDA, Hiroyuki	Post-Doctoral Fellow
SALEHI, Elham	Post-Doctoral Fellow
HAYASHI, Kenji	Engineer (Unit Leader)
NAKAMURA, Eiken	Chief Engineer
MAKITA,Seiji	Engineer
SAKAI, Masahiro	Chief Technician
YANO, Takayuki	Chief Technician
OKANO, Yasuaki	Chief Technician
TESHIMA, Fumitsuna	Chief Technician
KONDO, Naonori	Chief Technician
YUZAWA, Hayato	Chief Technician
OTA, Hiroshi	Technician
SHIMIZU, Kohei	Technician
HORIGOME, Toshio	Technical Fellow
MINAKUCHI, Aki	Technical Fellow
MIZUKAWA, Tetsunori	Technical Fellow
SUGIMOTO, Yasunobu	Technical Fellow
YAMAZAKI, Jun-ichiro	Technical Fellow
ISHIHARA, Mayumi	Secretary
KAMO, Kyoko	Secretary
YOKOTA, Mitsuyo	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. 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 > 5000, 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. The fruits of the research activities using UVSOR-III Synchrotron are published as the UVSOR ACTIVITY REPORT annually.

Recent Developments

UVSOR has several angle-resolved photoemission spectroscopy (ARPES) beamlines and users can choose proper beamline according to their purpose. At BL7U, users can perform high-energy resolution measurements with extremely low energy of photons (6 eV~) using low-temperature 6-axis manipulator with sample temperature 4 K.

For a long time, when changing photon energies in this beamline, users themselves had to optimize the beamline by using motors to adjust the mirror angle of the beamline to maximize the photon flux at the endstation. This was due to the lack of reproducibility of the position and angle of the mirrors by the motors. Recently, we performed ray-trace simulations and found that the mirror angle at which the photon flux is maximized is optically using the edge of the diffraction grating, which does not yield the correct photon energy. In fact, for some users, there was a difference of up to 500 meV between the actual photon energy and the set photon energy. This was a major problem for a high-energy-resolution beamline discussing a 1 meV superconducting gap, and made it difficult to perform automatic photon energy dependent ARPES measurements.

Therefore, we reviewed the mechanics of mirror position and angle control and introduced new motor control settings accordingly, and succeeded in precise control of photon energy with excellent reproducibility. As a result, we succeeded in setting the optically correct mirror angle, which enabled us to provide users with the correct photon energy within ±3 meV over the entire photon energy range available at BL7U ($h\nu$ = 6–40 eV). Users no longer need to adjust the mirror angle themselves. It should be noted that while many synchrotron radiation facilities have problems with photon energy reproducibility and energy drift with time at the endstations due to cooling problems of mirrors and changes in the electron trajectory of the accelerator and so on, BL7U is a normal-incident beamline, which is less susceptible to these problems. This is another reason why we were able to control photon energy so precisely. Having achieved accurate photon energy control, we plan to introduce various automated ARPES measurements in the future, including automatic photon energy dependent measurements.

Figure 1. Schematic view of beamlines BL7U and BL6U. The low-energy photon of BL7U will be introduced to BL6U for multi-modal experiments.

Reserch Highlights

We started to develop resonant soft X-ray scattering (RSoXS) at BL3U. RSoXS can be used similarly to small angle X-ray scattering (SAXS) and can provide information on samples' mesoscopic structure (1 ~ 100 nm). Due to the resonance process, RSoXS have selectivities of elements, functional groups, and molecular orientations. In particular, since SX regions include K-edge energies of light elements such as carbon, nitrogen, and oxygen, RSoXS will be a powerful tool to investigate soft matter such as liquid-crystal and polymer materials, mainly consisting of light element atoms. Wang group in ALS recently applied the carbon K-edge RSoXS method to investigate polymer blends, block copolymers, organic bulk heterojunction solar cells, and polymeric transistors, as all of which the complex refractive indices of the different components have distinct energy and polarization dependences for X-ray energies near the edge.

As a first experiment, RSoXS was applied to the helical filamentary phase of liquid-crystals, a twist-bend liquid-crystal phase. As shown in Figure 2(a), the structure has spatial periodicity without electron density modulation. The sample is sandwiched with SiN and isolated from the vacuum. In addition, the sample temperature was controlled from 0 to 150 °C, and the structure was analyzed in various phases.

Figure 2(b) shows typical scattering RSoXS images at carbon K edge for helical nanofilaments.[1] Photon energies were 285 and 270 eV, corresponding to carbon K-edge resonance and non-resonance energies. Diffraction rings derived from a clear periodic structure were observed at the resonant energy. For the resonant RSoXS image, the scattering angle 2θ is approximately 3°, corresponding to 80 nm. This pitch corresponds to the half pitch of the helical structure. Conventional SAXS cannot unravel helical structures due to no electron density modulation. Thus, by observing the molecular orientation order, we succeeded in characterizing the helix pitch of self-assembled liquid-crystal materials in situ.

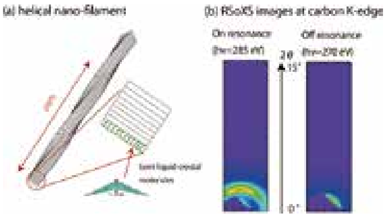


Figure 2. (a)Self assembled helical nanofilament of bent liquid-crystal molecules. (b) RSoXS images of helical nanofilaments at photon energies of 285 eV (resonance) and 270 eV (non-resonance).

Reference

1) Y. Takanishi *et al.*, *RSC Adv.* **12**, 29346 (2022).

Award

NAKAMURA, Eiken; The 10th Japan Society for Synchrotron Radiation Research (JSSRR) Achievement Award (2023).

Instrument Center

YOKOYAMA, Toshihiko	Director, Professor
SUZUKI, Toshiyasu	Team Leader
NAKAMURA, Toshikazu	Team Leader
MINATO, Taketoshi	Senior Researcher
SHIGEMASA, Eiji	Unit Leader
TAKAYAMA, Takashi	Chief Engineer
FUJIWARA, Motoyasu	Chief Technician
UEDA, Tadashi	Chief Technician
ASADA, Mizue	Chief Technician
OKANO, Yoshinori	Technician
URUICHI, Mikio	Technician
MIYAJIMA, Mizuki	Technician
NAGAO, Haruyo	Technician
HIRANO, Kaho	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
FUJIKAWA, Kiyoe	Technical Fellow
KUBOTA, Akiko	Technical Fellow
IMAI, Yumiko	Technical Fellow
FUNAKI, Yumiko	Secretary
HYODO, Yumiko	Secretary
ISHIKAWA, Azusa	Secretary
UCHIDA, Mariko	Secretary
KURITA, Yoshiko	Secretary
TOYAMA, Yu	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 repaired in 2022–2023 and JNM-ECZL 600 installed in 2023 for solutions, and JNM-ECS400 for solutions), matrix assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometer (microflex LRF, Bruker Daltonics), ESI-TOF mass spectrometer (Bruker Daltonics, maXis), 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), scanning electron microscope (SEM; JEOL JSM-6700F), elemental analyzer (J-Science Lab Micro Corder JM10), and ICP atomic emission spectroscopy (Agilent 5110 ICP-OES).

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, MPMS-XL7, and MPMS-3 installed in 2022), solid-state calorimeter (Rigaku DSC8231/TG-DTA8122), solution X-ray diffractometer (Rigaku NANO-Viewer), single crystal X-ray diffractometers (Rigaku Mercury CCD-1, CCD2, 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 and 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), 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 2022, Instrument Center accepted 101 applications from outside and the total user time amounted 1,615 days for outside and 1,276 days for in-house. Instrument Center also maintains helium liquefiers in the both campus and provides liquid helium to users (51,198 L/year). Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute (41,816 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	Chief Engineer
MATSUO, Junichi	Chief Technician
TAKADA, Noriko	Chief Technician
KIMURA, Sachiyo	Technician
KIKUCHI, Takuro	Technician
KIMURA, Kazunori	Technician
MIYAZAKI, Yoshino	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, mechatronics, electronics and lithography 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.

Development of 12-bit A/D Conversion Module with Contact Output

It would be useful to have a module that monitors the input analog voltage and reacts when the input voltage exceeds a threshold value. For example, it could be used to monitor abnormalities in the output voltage of laboratory equipment. For such purpose, it is enough to work in the low frequency range input of DC ~ a few kHz. We have developed such a module with a very simple configuration (Figure 1).

The input voltage range is from 0 to 5 V and threshold voltage can be adjusted using variable resistors. If the input voltage crosses the threshold, the contact output is shorted. A comparator (LM2903M by Texas Instruments) with hysteresis characteristics is provided in the front stage of the contact output to suppress the unexpected output due to slight fluctuations in input voltage near the threshold. Insulated BNC receptacle connector is used for both input and output. It works standalone by supplying 9V from the DC jack. It is also equipped with a Pmod interface for SPI communication. This interface can be used to supply power as well as to communicate with the built-in 12-bit A/D converter (MCP3221 by Microchip Technology) that can provide read input voltage values. In addition, despite the small size (45×90×25 mm) of the housing, the distance between the input and output BNC connectors is designed so as not to interfere with cable insertion and removal.

Figure 1. Module overview.

Molecular Modeling with Transparent Materials

We accept requests for making models of molecules and proteins. Scientists use these models to imagine their responses and behaviors in nanoscale. Models are also used to explain the research results in a lucid way.

3D printers are indispensable for making models. Since we introduced a full-color plastic 3D printer 3DUJ-2207 (Mimaki Engineering, Nagano, Japan) last year, we are now able to provide models with transparent resins. By using this, we can embed a full-color ribbon model in a transparent surface model (Figure 2), for example. When the ribbon model is placed in water, transparency of the ribbon model increases (Figure 3). In addition, we have made crystal models with transparent or semi-transparent crystal facets (Figure 4).

We would like to continue to contribute to the research activities of the Institute for Molecular Science by upgrading our technologies and skills.

Figure 2. Clear surface & ribbon model.

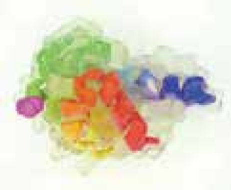


Figure 3. Underwater visibility of a model shown in Figure 2.

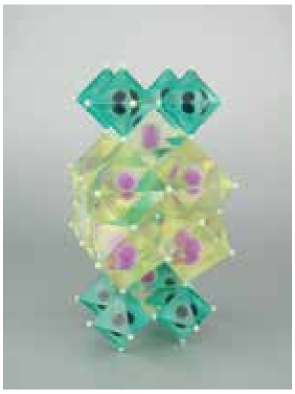


Figure 4. Crystal model with crystal facets.

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
SHIRAOGAWA, Takafumi	Assistant Professor
ISHIDA, Tateki	Research Associate
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
SUZUKI, Kazuma	Technician
KANESHIRO, Ikuma	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 HPE Apollo 2000 and Apollo 6500 (since Feb. 2023). The combined system, named "Molecular Simulator," is ranked 196th position in the TOP500 supercomputer list in June 2023. 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 1,242 researchers from 298 groups in fiscal year 2022. 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 2022, the numbers of registered attendants of these schools were 360 and 414, 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 2022, we organized the workshop under the title, "Theoretical and Computational Science for Complex Electronic States."

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. HPE Apollo 2000 and Apollo 6500.

Safety Office

TANAKA, Shoji	Director
TOMURA, Masaaki	Research Associate
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

YAMAMOTO, Hiroshi	Head
OKAMOTO, Hiromi	Professor
AKIYAMA, Shuji	Professor
IINO, Ryota	Professor (in charge of Public Affairs)
ISHIZAKI, Akihito	Professor (in charge of Facilities/Buildings and Foreign Affairs)
SHIGEMASA, Eiji	Technical Associate (in charge of General Affairs)
NAKAMURA, Toshikazu	Team Leader, Instrument Center
FUJITA, Hiromasa	URA (Administrative Associate, Assistant to Head)
HARADA, Miyuki	URA (Technical Associate)
NAGASONO, Hisayo	URA (Administrative Associate)
OHTA, Minori	Administrative Associate
KAWAJIRI, Toshitaka	Administrative Associate
IKENAGA, Yumiko	Administrative Associate
NOGAWA, Kyoko	Administrative Associate
NAKAMURA, Rie	Technical Fellow
NOMURA, Emiko	Secretary (for Director General)
SUZUKI, Satomi	Secretary
SUGIYAMA, Kayoko	Secretary
OGURA, Yasuko	Secretary
TACHIKAWA, Mari	Secretary
TSURUTA, Yumiko	Secretary
ASAKURA, Yukiko	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

Information Office

TSURUTA, Yumiko	Secretary
ASAKURA, Yukiko	Secretary
NOGAWA, Kyoko	Administrative Associate

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) Inter-University Network for Common Utilization of Research Equipments
(b) MEXT Program Advanced Research Infrastructure for Materials and Nanotechnology in Japan:
    Spoke Organization in Advanced Materials Recycling Technologies and Representative Organization in Cross Sectional Technical Domain of Materials Synthesis Process
(c) "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)
(d) "Large-Scale and High-Coherence Fault-Tolerant Quantum Computer with Dynamical Atom Arrays" Supported by the Cabinet Office/JST Program "Moonshot Goal 6": Realization of a Fault-Tolerant Universal Quantum Computer That Will Revolutionize Economy, Industry, and Security by 2050

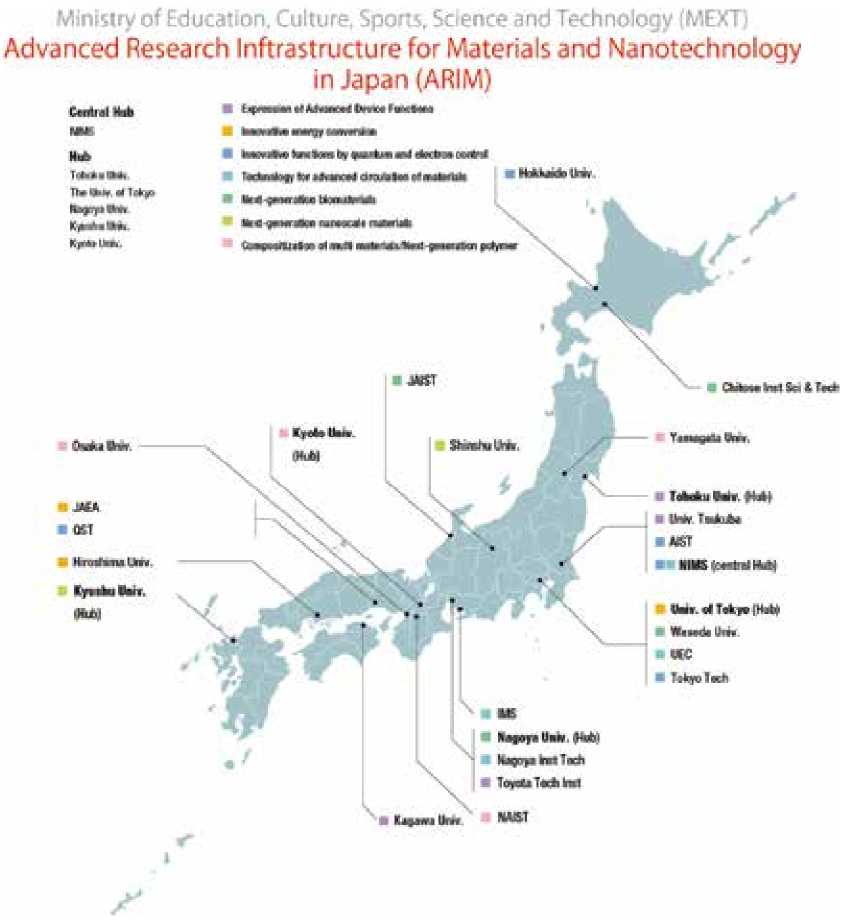
These four projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

(a) 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 17,000 in ~600 universities/institutions/companies (as of March, 2023). Network usage reaches more than 170,000 times a year, in which external usage amounts to 3,800 times, and these numbers continue 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.

(b) MEXT Program Advanced Research Infrastructure for Materials and Nanotechnology in Japan: Spoke Organization in Advanced Materials Recycling Technologies and Representative Organization in Cross Sectional Technical Domain of Materials Synthesis Process

Since 2021, ARIM (Advanced Research Infrstructure for Materials and Nanotechnology in Japan) program supported by MEXT (Ministry of Education, Cultre, Sports, Science and Technology) has been conducted, succeeding to MEXT Nanotechnology Platform progrm that was completed in March, 2022. In this new program, seven "key technology domains" are set. Each key technlogy domain team consist of one hub organization and several spoke organizations, with the center hub of NationalInstitute of Materials Science (NIMS). The hub & spoke networks for collecting, accumulating, and structuring reseach data that are created from observation, measurement, synthesis and fabrication equipment and facilities, were launhed in order to strengthen AI-driven materials & device R&D using informatics techniques. IMS belongs to one ofthe key technology domains of "Advanced materials recycling technologies" led by the NIMS hub, together with the spoke organizations of Nagoya Institute of Technology and The University of Electro-Communications. Domesic and international equipment sharing is the most important purpose in this program, as in the Nanotechnology Plaform program. Moreover, users and staffs are requested to provide experimentally obtained data to the Data Platfor Center (DPC) that are being constructed in NIMS. Accumulated structured data will be shared through the NIS DPC. In addition, we will contribute to strengthening material innovation force by building a "Material D Platform" in collaboration with the Data creation/utilization type material research and development project. In ths program, three areas of shared methodology are set to promote cooperation across the seven key technology domins. IMS also acts as a representative organization for the cross-sectional technological area concerning the maerial synthesis process to promote technological cooperation among all the participating organizations. Human resouce development is also an important aim in this program and IMS regularly conducts training sessions with "EQ-NT" to upskilling of the technical staffs engaged in this program. In IMS, the mission for the ARIM program is mainly rganized by Instrument Center, supported by Research Center for Computational Science in data storage and transfer t NIMS DPC. Because in 2021 equipment sharing was conducted through the Nanotechnology Platform program, FY2022 is the first year for equipment sharing in this program, while the data accumulation mission is in pogress. Through this program, a new electron spin resonance (ESR) system and a new superconducting quantum inteference device (SQUID) magnetometer were installed in IMS in 2021 and 2022, and a high-throughput low-temperatur single-crystal x-ray diffractometer and an automatic organic synthesis system will be introduced at the end of FY2023 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	T. Yokoyama	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	

(c) "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)

Quantum science and technology, such as quantum computers, quantum simulators, and quantum sensors, are qualitatively new technologies that take advantage of the "wave nature" of electrons and atoms. Since quantum science and technology can revolutionize functional materials, drug design, information security, artificial intelligence, *etc*., huge investments are being made in the science and technology policies of various countries around the world. In Japan, the "Committee on Quantum Science and Technology" was established in June 2015 by the Ministry of Education, Culture, Sports, Science and Technology to discuss policy issues related to quantum science and technology, and a new national project, the "MEXT-Quantum Leap Flagship Program (MEXT Q-LEAP)" was launched in 2018 based on the discussions held in the committee. This program is a research and development program that aims for discontinuous solutions (Quantum leap) to important economic and social issues by making full use of quantum science and technology (https://www.jst.go.jp/stpp/q-leap/en/index.html). The program consists of three technological areas: (1) Quantum information technology (Quantum simulator, Quantum computer), (2) Quantum metrology & sensing, and (3) Next generation laser.

In the ongoing research project "Development of cold-atom based quantum simulators by optical control with precisions on the attosecond temporal and nanometer spatial scales and their applications to quantum computing," which has been adopted as a Large-Scale Basic Foundation Research project in the Q-LEAP "Quantum information technology" area, the project aims to develop a completely new quantum simulator / quantum computer with core competences, which will cut deeply and sharply into fundamental problems of quantum mechanics, in close collaboration with Hamamatsu Photonics Central Research Laboratory, Kyoto University, Okayama University, Kindai University, University of Oxford, Heidelberg University, University of Strasbourg, University of Innsbruck, and others.

(d) "Large-Scale and High-Coherence Fault-Tolerant Quantum Computer with Dynamical Atom Arrays" Supported by the Cabinet Office / JST Program "Moonshot Goal 6": Realization of a Fault-Tolerant Universal Quantum Computer That Will Revolutionize Economy, Industry, and Security by 2050

The "Moonshot R&D Program" is a large-scale national research program led by the Cabinet Office, aiming to create disruptive innovations originating in Japan to address important social issues such as the super-aging society and global warming, and to promote the realization of ambitious goals "Moon Shots." (Cabinet Office/JST Moonshot R&D Program: https://www.jst.go.jp/moonshot/en/)

Goal 6, "Realization of a fault-tolerant universal quantum computer that will revolutionize economy, industry, and security by 2050," aims to develop a quantum computer that can meet the exploding demand for information processing, while conventional computers are reaching their limits in terms of progress. The key to solving diverse, complex, and large-scale real-world problems with quantum computers is the realization of a fault-tolerant universal quantum computer that can correct quantum errors during computations.

In the R&D program "Large-scale and high-coherence fault-tolerant quantum computer with dynamical atom arrays" under Goal 6, we are developing the implementation of dynamic qubit arrays in which each of the cooled atomic qubits arranged in a large array of optical tweezers is freely and rapidly moved, and gate operations, error detection and correction are carried out, as well as the implementation of a quantum computer with a quantum error-correction functionality. The goal is to realize a fault-tolerant quantum computer by achieving high stability and usability through integration and packaging of the components under the collaboration of industry and academia.

Joint Studies Programs

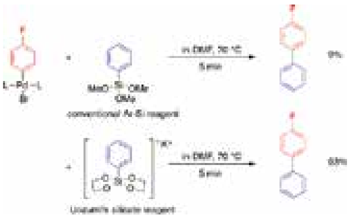
As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and 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. In the last year, we have measured the carbon K-edge NEXAFS spectrum of 100 mM trimethoxy(phenyl)silane (Ph-Si(OMe)$_3$) in tetrahydrofuran (THF) at BL3U of UVSOR-III Synchrotron, and the C–Si bond length of several organosilicon compounds were related to the reaction mechanism of Hiyama coupling reaction (by Okumura, Nagasaka, Uozumi). In this year, we have developed 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 1). Figure 2 shows the soft X-ray transmission of the developed polymer film in the soft X-ray region from 50 eV to 560 eV. Since the polymer film includes the C=C and C=N groups, the sharp absorption peaks are observed at the C and N K-edges. Since the polymer film includes no Si atoms, there is no peaks at the Si L-edge (100 eV). Soft X-ray transmission of the polymer film shows a still high value below 200 eV, indicating the developed polymer film is suitable to measure XAS of liquid in the low-energy region. By using this measurement system, we 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.

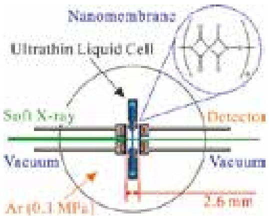


Figure 1. The schematic of an ultrathin liquid cell including Si-free nanomembranes.

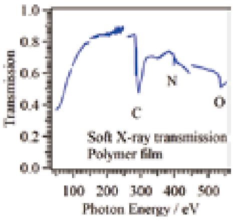


Figure 2. Soft X-ray transmission of the polymer film.

(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 by nonlinear optical spectroscopy. In particular, we conducted *operando* measurement of second-harmonic generation (SHG) and third-harmonic generation (THG) using the home-made electrochemical spectroscopic cells and systems. Then, we found that the SHG signal is highly sensitive to microscopic structural changes and degradation of the electrode surfaces in response to the applied bias voltage, whereas the electronic non-resonant THG signal is almost unaffected by structural changes on the electrode surfaces. Using SHG, we succeeded in investigating not only the oxidation process of electrode, but also the adsorption of ion and the subsequent rearrangement of interfacial water molecules. Moreover, we have succeeded in newly developing highly sensitive coherent Raman spectroscopy technique. We are also applying this new method to the observation of working electrode surfaces under reaction conditions.

Reference

1) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).

(2) Research Symposia

(From Oct. 2022 to Sep. 2023)

Dates	Theme	Chair
Nov. 8, 2022	Resonant Soft X-Ray Scattering and Reflectivity: Nano/Mesoscale Structural Analysis of Soft Materials and Soft Matter	**ARAKI, Tohru** **KERA, Satoshi**
Nov. 28, 2022	Conference on Generation and Advanced Applications of Various Quantum Beams in UVSOR-III	**TAIRA, Yoshitaka**
Mar. 29–30, 2023	Understanding and Design of Biomolecular Machinery: Next Challenges of Molecular Engine	**UENO, Takafumi** **IINO, Ryota**
Jun. 14–15, 2023	Industry-Academia-Government-Citizens Collaboration for a Sustainable Society with Examples from Chemistry, Engineering, and Environmental Studies	**TOKORO, Chiaru** **OKAMOTO, Hiromi**
Jul. 29–30, 2023	Seeds and Needs for Tomorrow’s Synchrotron Radiation Photoelectron Spectroscopy Research	**MATSUI, Fumihiko**
Aug. 31, 2023	Morino Discussion	**MUNAKATA, Toshiaki** **KURAMOCHI, Hikaru**
Sep. 13–14, 2023	Toward the Development of Ionic Liquid Informatics	**KITADA, Atsushi** **KERA, Satoshi**
Sep. 29, 2023	UVSOR–SPring8 Infrared Beamline Joint Users Meeting	**TANAKA, Kiyohisa**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2022–Mar. 2023		Apr. 2023–Sep. 2023		Total		
		Regular	ARIM	Regular	ARIM	Regular	ARIM	Sum
Special Projects		2		1		3		3
Research Symposia		3		5		8		8
Research Symposia for Young Researchers		0		0		0		0
Cooperative Research		25	25	17	22	42	47	89
Use of Facility	Instrument Center		75		70		145	145
	Equipment Development Center	0	7	0	5	0	12	12
	UVSOR	105	3	104	1	209	4	213
Use of Facility Program of the Computer Center						298*		298*

* from April 2022 to March 2023

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. 1–2026. 1	6	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2009.10–2024.10	8	0
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	1	0
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. 6–2028. 5	1	1
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	2	1
Fritz-Haber-Institut der Max-Planck-Gesellschaft [Germany]	2021. 4–2023. 3	0	0
China Scholarship Council [China]	2023. 1–2028. 1	0	0

* No. of researchers during the period from Oct. 2022 to Sep. 2023

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	3	1
Vidyasirimedhi Institute of Science and Technology [Thailand]	2018. 9–2023. 9	0	0
Friedrich Schiller University Jena [Germany]	2020. 7–2023. 7	0	2
Chulalongkon University [Thailand]	2010. 4–2027. 9	1	2

* No. of researchers during the period from Oct. 2022 to Sep. 2023

(2) IMS International Internship Program

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (IMS-IIP)	32*	–

* from Oct. 2022 to Sep. 2023

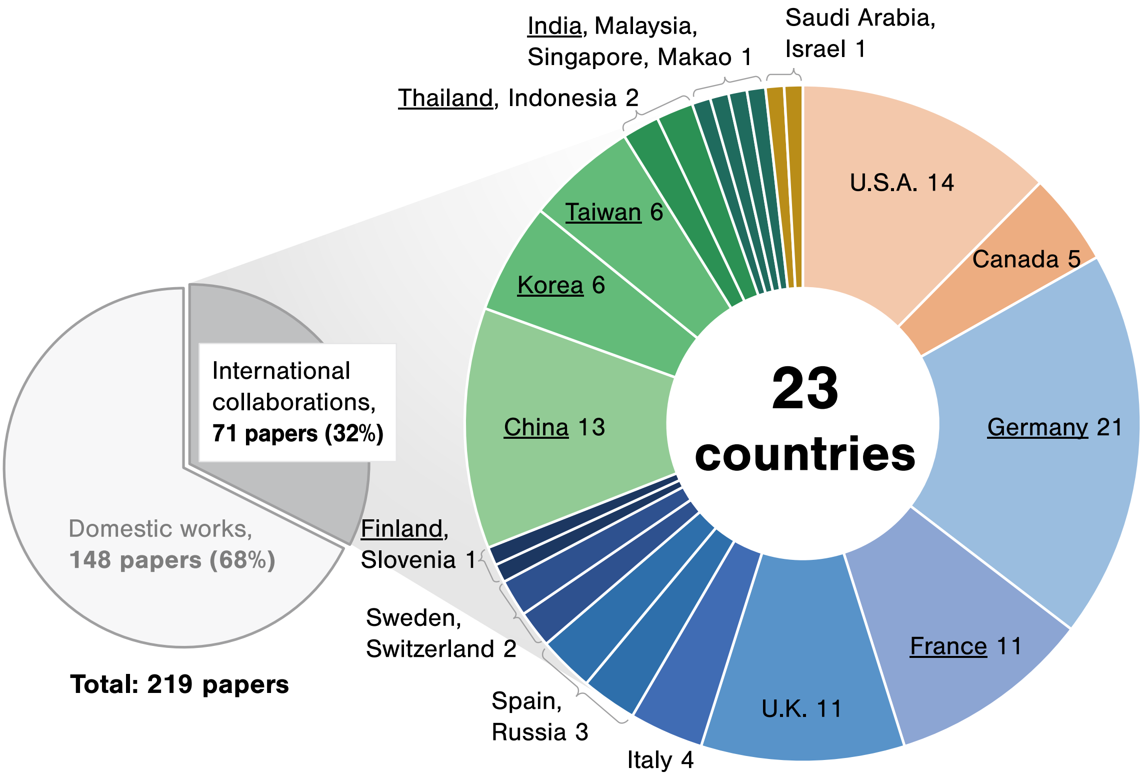
(3) IMS International Collaboration (Including online meetings)

Category	Number of People
International Joint Research Programs	82
International Use of Facilities Programs	31

from Oct. 2022 to Sep. 2023

Internationally Collaborated Publications

Articles and reviews published in 2022



Underlined countries include MOU Partnership Institutions
Scopus dataset, Oct. 2023

AWARDS

NAKAMURA, Hiroki Former Director General	The Order of the Sacred Treasure, Gold Rays with Neck Ribbon Former Director General Hiroki Nakamura received the Order of the Sacred Treasure, Gold Rays with Neck Ribbon for his many years of distinguished contributions to education and research. His pioneering research includes the development of semiclassical molecular dynamics methods, the establishment of fundamental theories for the control of chemical kinetics, and the development of molecular functions based on the non-adiabatic transition theory. In addition, he made significant contributions to the elucidation of various chemical kinetic processes, including chemical reactions. As Director General of the Institute for Molecular Science, Vice President, and Executive Director of the National Institutes of Natural Sciences, he has devoted himself to the management of not only the Institute for Molecular Science but also the National Institutes of Natural Sciences. In addition, he has made significant contributions to education and research as a professor, a dean, a chair, and a Councilor at the Graduate University for Advanced Studies. He was awarded this prize in recognition of his many years of dedication and significant contributions to the enrichment and development of research and education in chemical physics, theoretical chemistry, and molecular science, both in Japan and abroad.
FUJITA, Makoto Division of Advanced Molecular Science	The Asahi Prize 2022 “Creating Self-Assembling Molecular Systems in Nano-Space and Pursuing Applications for Such Systems”
DE LÉSÉLEUC, Sylvain Photo-Molecular Science	The 12th Young Scientist Award of National Institutes of Natural Sciences “Realization of Quantum Devices Built Atom-by-Atom”
FURUIKE, Yoshihiko Research Center of Integrative Molecular Systems	The Progress Award of the Crystallographic Society of Japan “Elucidation of Allosteric Regulation Mechanism in Clock Protein KaiC Orchestrating Circadian Rhythms”
NAKAMURA, Eiken UVSOR Synchrotron Facility	The 10th Japan Society for Synchrotron Radiation Research (JSSRR) Achievement Award “Significant Contribution to Support for Synchrotron Radiation Research and Technology”

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 2022–September 2023) are listed below.

(1) IMS Councillor

Prof. LEIGH, David A.	Univ. of Manchester	U.K.	Mar. ’23
Prof. WEIDEMÜLLER, Matthias	Heidelberg Univ.	Germany	Mar. ’23
Prof. LISY, James	Univ. of Illinois Urbana-Champaign	U.S.A.	May ’23

(2) IMS Visiting Professor or Associate Professor from Abroad

Prof. AVARVARI, Narcis	Univ. d’Angers	France	Nov. ’22–Dec. ’22 Mar. ’23–Apr. ’23

(3) IMS Visiting Scientist

Mr. MALIK, Ravi	Indian Inst. of Tech., Kanpur	India	Oct. ’22–Jan. ’23
Mr. CHANDRA, Abhilash	Indian Inst. of Tech., Kanpur	India	Oct. ’22–Jan. ’23
Mr. MOHD ARIS, Muhammad Zhafran Bin	Univ. Malaya	Malaysia	Oct. ’22–Mar. ’23
Dr. BOODSARIN, Sawatlon	Chulalongkorn Univ.	Thailand	Dec. ’22–Jan. ’23
Prof. DONG, Chung-Li	Tamkang Univ.	Taiwan	Dec. ’22
Ms. TA THỊ THÚY NGA	Natl. Yang Ming Chiao Tung Univ.	Taiwan	Dec. ’22
Mr. PAN, Chien-Lin	Tamkang Univ.	Taiwan	Dec. ’22
Dr. MANNU, Pandian	Tamkang Univ.	Taiwan	Dec. ’22
Mr. HUANG, Hou-Yi	Tamkang Univ.	Taiwan	Dec. ’22
Ms. HAO, Yuxin	Northwest Univ., China	China	Feb. ’23–Mar. ’23 Aug. ’23–Sep. ’23
Dr. KONG, Xiangrui	Univ. of Gothenburg	Sweden	Feb. ’23–Mar. ’23 Aug. ’23–Sep. ’23
Mr. FAURE, Nicolas	Univ. of Gothenburg	Sweden	Feb. ’23–Mar. ’23
Dr. CHEN, Jie	ETH	Switzerland	Feb. ’23–Mar. ’23
Prof. RÜHL, Eckart	Free Univ. of Berlin	Germany	Mar. ’23
Mr. TETTEKPOE, Jean-Samuel	ENSCP	France	Mar. ’23–Aug. ’23
Mr. POITRINAL, Martin	ENSCP	France	Mar. ’23–Aug. ’23
Mr. MARTIN, Romain	ENSCP	France	Mar. ’23–Aug. ’23
Mr. DENECKER, Tom	ENSCP	France	Apr. ’23–Aug. ’23
Ms. PRAVONGVIENGKHAM, Metkham	Paris Saclay Univ.	France	Apr. ’23–Aug. ’23
Ms. FANG, Lisa	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Ms. ABDULLA, Farida	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Ms. BOUDRIAH, Nihad	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Mr. GUYOT, Constantin	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Ms. DORESSOUNDIRAM, Elodie	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Ms. ZHU, Lucy	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Ms. FLAMENT, Aliénor	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Mr. BADARAU, Adrian	Chimie ParisTech	France	Apr. ’23–Sep. ’23
Ms. GUILLEMANT, Oscar	Sorbonne Univ.	France	May ’23–Jun. ’23
Prof. PATANEN, Minna	Univ. of Oulu	Finland	May ’23–Jun. ’23
Dr. MANSIKKALA, Tuomas	Univ. of Oulu	Finland	May ’23–Jun. ’23
Prof. U. DEVA, Priyakumar	IIIT-H	India	May ’23–Jul. ’23
Mr. CHAUHAN, Anjali	Inst. of Sci. Banaras Hindu	India	Jun. ’23
Mr. DUBON HERNANDEZ, Joaquin Ernesto	MIT	U.S.A.	Jun. ’23–Aug. ’23
Prof. HE, Ruihua	Westlake Univ.	China	Jul. ’23
Mr. HONG, Caiyun	Westlake Univ.	China	Jul. ’23
Ms. JIANG, Congying	Westlake Univ.	China	Jul. ’23
Dr. SHIU, Hung Wei	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Jul. ’23
Dr. CHEN, Wan-Ting	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Jul. ’23
Dr. LAI, Yu-Ling	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Jul. ’23
Dr. HSU, Yao-Jane	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Jul. ’23
Prof. ZHAO, Xiang	Xi’an Jiaotong Univ.	China	Jul. ’23–Sep. ’23
Prof. CHUANG, Cheng-Hao	Tamkang Univ.	Taiwan	Aug. ’23
Mr. LU, Hsin-Chan	Tamkang Univ.	Taiwan	Aug. ’23

Mr. Jan Sebastian Dominic Rodriguez	Tamkang Univ.	Taiwan	Aug. ’23
Mr. Carl Osby M. Mariano	Tamkang Univ.	Taiwan	Aug. ’23
Dr. THANIT, Saisopa	Rajamangala Univ. of Tech. Isan	Thailand	Aug. ’23
Dr. ATTANACHAI, Yuttakarn	Rajamangala Univ. of Tech. Isan	Thailand	Aug. ’23
Dr. SAILUAM, Wutthigrai	Rajamangala Univ. of Tech. Isan	Thailand	Aug. ’23
Dr. CÉOLIN, Denis	Synchrotron SOLEIL	France	Aug. ’23
Dr. STEINER, Lea-Marina	Eberhard Karls Univ. Tübingen	Germany	Aug. ’23–Sep. ’23
Ms. WEDOWSKI, Roxana	Eberhard Karls Univ. Tübingen	Germany	Aug. ’23–Sep. ’23

(4) Visitor to IMS

Prof. KIM, Hyung J.	Carnegie Mellon Univ.	U.S.A.	Oct. ’22
Prof. FLEMING, Graham	Univ. of California, Berkeley	U.S.A.	Oct. ’22
Prof. PETEK, Hrvoje	Univ. of Pittsburgh	U.S.A.	Oct. ’22
Prof. MAZUMDAR, Shyamalava	TIFR	India	Nov. ’22
Prof. GABRIELA, Schlau-Cohen	MIT	U.S.A.	Nov. ’22
Dr. JELÍNEK, P.	Czech Academy of Sci.	Czech	Nov. ’22
Ms. Binti Mohd Rashid Hasratul Nadiah	Univ. Malaya	Malaysia	Dec. ’22
Mr. TANG, Liang Wei	Univ. Malaya	Malaysia	Dec. ’22
Mr. PAUL, Lipman	Quantum Computing at ColdQuanta, Inc.	U.S.A.	Feb. ’23
Prof. DANA, Anderson	Quantum Computing at ColdQuanta, Inc.	U.S.A.	Feb. ’23
Mr. JASON, Hyland	Quantum Computing at ColdQuanta, Inc.	U.S.A.	Feb. ’23
Prof. MITRA, Rajib Kumar	S. N. Bose Natl. Cent. for Basic Sci.	India	Feb. ’23
Prof. LEO, Karl	Dresden Univ. of Tech.	Germany	Mar. ’23
Prof. EBBESEN, Thomas	Univ. of Strasbourg	France	Apr. ’23
Dr. DE VIDO, Mariastefania	STFC Rutherford Appleton Laboratory	U.K.	Apr. ’23
Dr. PAVEL, Nicolaie	Natl. Inst. for Laser, Plasma and Radiation Physics	Roumania	Apr. ’23
Dr. MATLIS, Nicholas	Deutsches Elektronen-Synchrotron, DESY	Germany	Apr. ’23
Prof. PERAKIS, Foivos	Stockholm Univ.	Sweden	Jun. ’23
Prof. MISCHA, Bonn	Max Planck Inst. for Polymer Res.	Germany	Jun. ’23
Prof. BERNIEN, Hannes	Univ. of Chicago	U.S.A.	Jul. ’23
Prof. HUMMER, Gerhard	Max Planck Inst. of Biophysics	Germany	Aug. ’23
Dr. TSOU, Pei-Kang	IAMS	Taiwan	Sep. ’23
Dr. HUANG, Qian-Rui	IAMS	Taiwan	Sep. ’23
Ms. LIN, Yen-hsiu	IAMS	Taiwan	Sep. ’23
Dr. KUO, Jer-lai	IAMS	Taiwan	Sep. ’23
Dr. LIN, Jim	IAMS	Taiwan	Sep. ’23
Dr. TAKAHASHI, Kaito	IAMS	Taiwan	Sep. ’23
Prof. MILLER, Dwayne	Univ. of Toronto	Canada	Sep. ’23
Prof. CAMPBELL, Wesley C.	Univ. of California, Los Angeles	U.S.A.	Sep. ’23

Scientists who would like to visit IMS under program (2) are invited to make contact with IMS staff in their relevant field.

Theoretical and Computational Molecular Science

T. INAGAKI, M. HATANAKA and S. SAITO, “Anisotropic and Finite Effects on Intermolecular Vibration and Relaxation Dynamics: Low-Frequency Raman Spectroscopy of Water Film and Droplet on Graphene by Molecular Dynamics Simulations,” *J. Phys. Chem. B* **127**, 5869–5880 (2023). DOI: 10.1021/acs.jpcb.3c02109

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M. YAGI-UTSUMI, H. MIURA, C. GANSER, H. WATANABE, M. HIRANYAKORN, T. SATOH, T. UCHIHASHI, K. KATO, K. OKAZAKI and K. AOKI, “Molecular Design of FRET Probes Based on Domain Rearrangement of Protein Disulfide Isomerase for Monitoring Intracellular Redox Status,” *Int. J. Mol. Sci.* **24(16)**, 12865 (2023). DOI: 10.3390/ijms241612865

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W. HIGEMOTO, M. YOKOYAMA, T. U. ITO, T. SUZUKI, S. RAYMOND and Y. YANASE, "Direct Measurement of the Evolution of Magnetism and Superconductivity toward the Quantum Critical Point," *Proc. Natl. Acad. Sci. U. S. A.* **119(49)**, e2209549119 (2022). DOI: 10.1073/pnas.2209549119

M. MATSUBARA, T. KOBAYASHI, H. WATANABE, Y. YANASE, S. IWATA and T. KATO, "Polarization-Controlled Tunable Directional Spin-Driven Photocurrents in a Magnetic Metamaterial with Threefold Rotational Symmetry," *Nat. Commun.* **13(1)**, 6708 (2022). DOI: 10.1038/s41467-022-34374-7

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Photo-Molecular Science

V. BHARTI, S. SUGAWA, M. MIZOGUCHI, M. KUNIMI, Y. ZHANG, S. DE LÉSÉLEUC, T. TOMITA, T. FRANZ, M. WEIDEMÜLLER and K. OHMORI, "Picosecond-Scale Ultrafast Many-Body Dynamics in an Ultracold Rydberg-Excited Atomic Mott Insulator," *Phys. Rev. Lett.* **131**, 123201 (12 pages) (2023). DOI: 10.1103/PhysRevLett.131.123201

F. MATSUI, K. HAGIWARA, E. NAKAMURA, T. YANO, H. MATSUDA, Y. OKANO, S. KERA, E. HASHIMOTO, S. KOH, K. UENO, T. KOBAYASHI, E. IWAMOTO, K. SAKAMOTO, S. TANAKA and S. SUGA, "Soft X-Ray Photoelectron Momentum Microscope for Multimodal Valence Band Stereography," *Rev. Sci. Instrum.* **94(8)**, 083701 (2023). DOI: 10.1063/5.0154156

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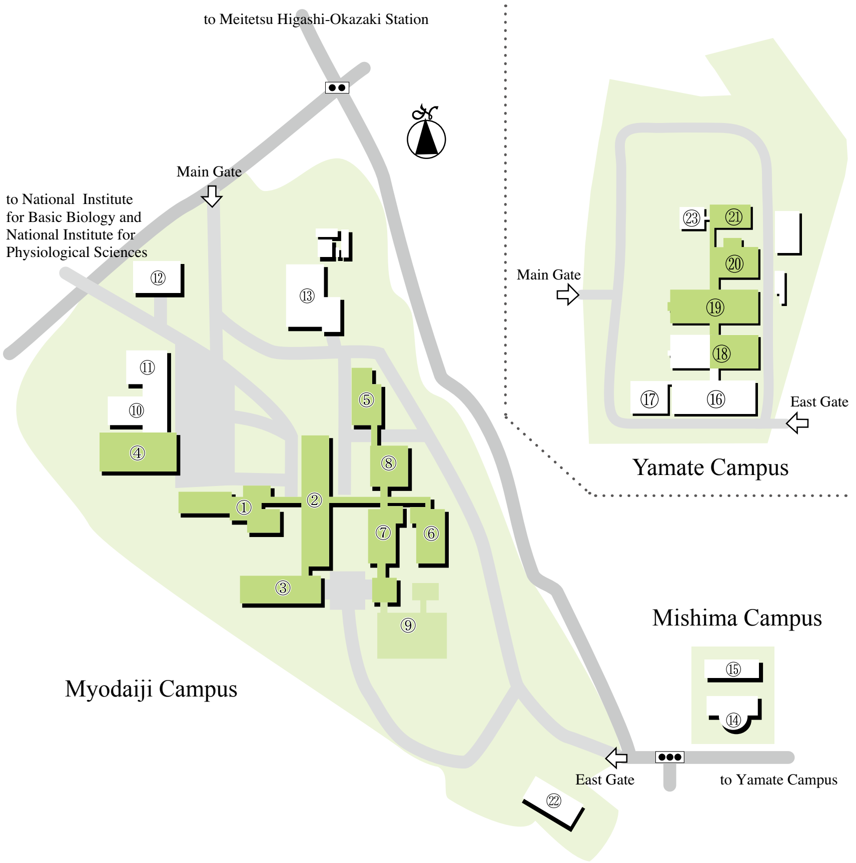

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4. Computer Center Bldg.
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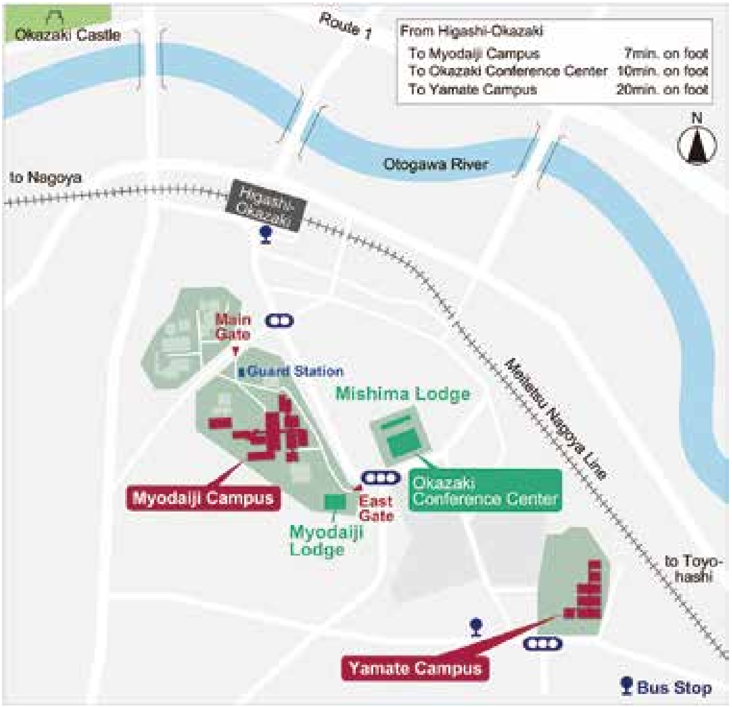

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