ANNUAL REVIEW 2024

Institute for Molecular Science

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Editorial Committee 2024

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.

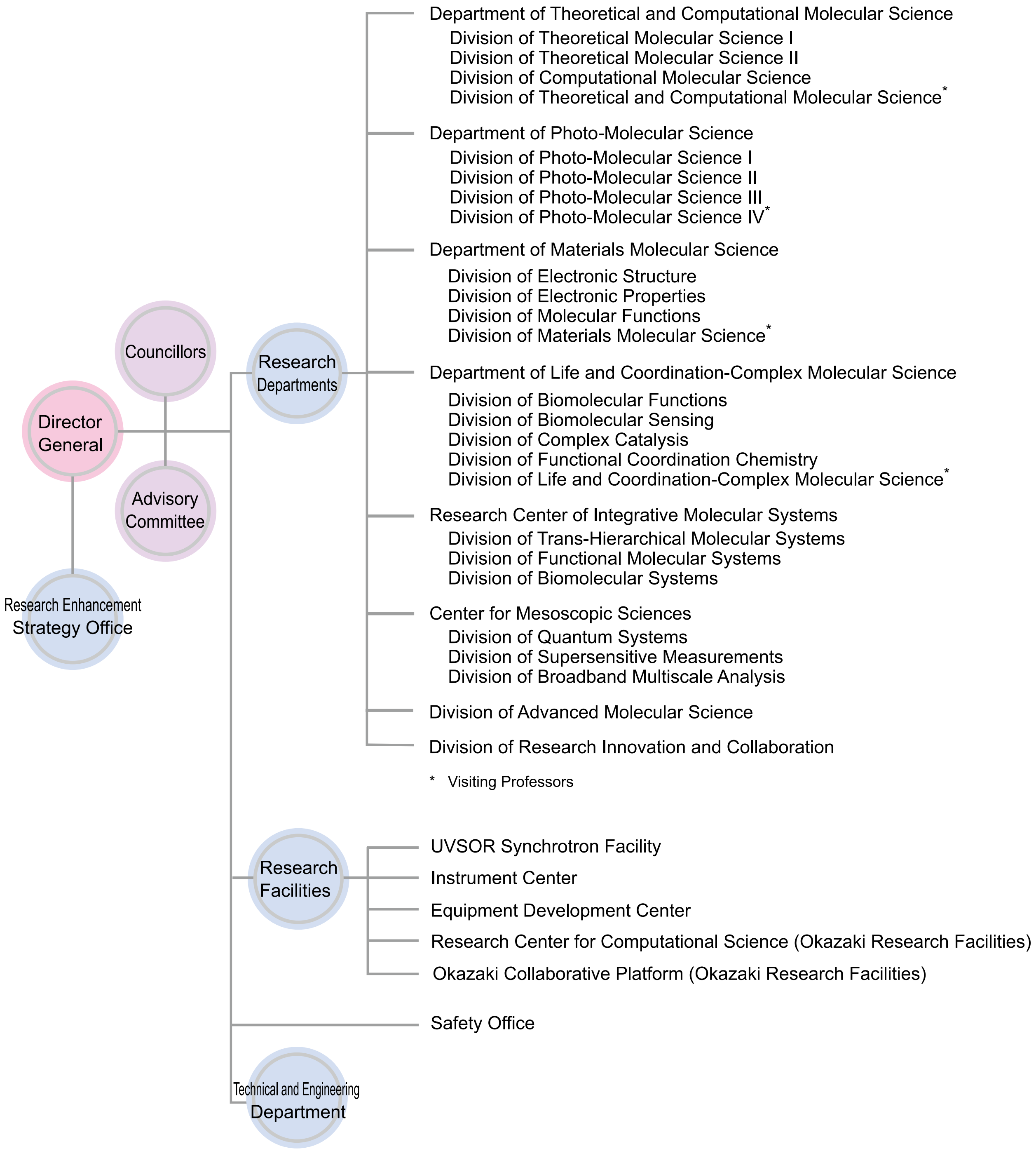
Annual Review 2024 is a summary of the research activities by all individual research groups conducted at IMS during October 2023–September 2024 on molecular structures, reactions and functions demonstrating “novel molecular possibilities.” In addition to these individual activities, IMS conducts many 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) in 2024, IMS, National Institute for Physiological Sciences (NIPS), and ExCELLS have jointly launched “the Core for Spin Life Sciences.” In this project, a wide range of life science and physiological science research will be promoted under one roof, covering technological development at the molecular level and life phenomena at the individual level, such as novel magnetic resonance (MR) imaging of individual molecules targeted by new MR molecular probes. As a complementary collaboration with the Core for Spin Life Sciences, the project was adopted by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) as part of the “Coalition of Universities for Research Excellence Program (CURE)” program, and collaboration with related universities has been initiated. IMS also conducts (iv) Advanced Research Infrastructure for Materials and Nanotechnology in Japan, and (v) 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.

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, 2024

WATANABE, Yoshihito
Director General, Institute for Molecular Science

ORGANIZATION



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KATOH, Masahiro	Project Professor, Institute for Molecular Science and Professor Emeritus, The Graduate University for Advanced Studies
FUJII, Masaaki	Professor Emeritus, The Graduate University for Advanced Studies

GROUP LEADERS

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Photo-Molecular Science


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MATSUI, Fumihiko
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Life and Coordination-Complex Molecular Science

AONO, Shigetoshi
Professor
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KATO, Koichi
Professor
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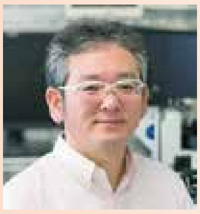

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Division of Research Innovation and Collaboration

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RESEARCH FACILITIES

UVSOR Synchrotron Facility

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KERA, Satoshi
Director

Instrument Center

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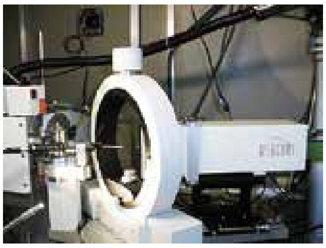
YOKOYAMA, Toshihiko
Director



Equipment Development Center

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YAMAMOTO, Hiroshi
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EHARA, Masahiro
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VISITING PROFESSORS

Theoretical and Computational Molecular Science

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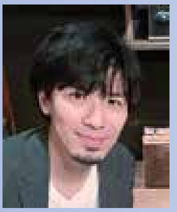

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Life and Coordination-Complex Molecular Science

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(Kobe Pharmaceutical University)

SATO, Sota
Visiting Professor
(The University of Tokyo)

TOYABE, Shoichi
Visiting Professor
(Tohoku University)

PERSONNEL CHANGES

Moving In

Oct. 1, 2023	Dr. HORIUCHI, Kota joined IMS as an Assist. Prof. in the Research Center of Integrative Molecular Systems
Mar. 1, 2024	Dr. KANAI, Tsuneto joined IMS as a Research Lecturer in the Department of Materials Molecular Science
Apr. 1, 2024	Dr. SAWAI, Hitomi joined IMS as an Assoc. Prof. (Cross Appointment) in the Division of Advanced Molecular Science
Apr. 1, 2024	Dr. HARIMOTO, Takashi joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Apr. 1, 2024	Dr. SATO, Yusuke joined IMS as an Assist. Prof. in the UVSOR Synchrotron Facility
Jun. 1, 2024	Dr. HATANAKA, Miho joined IMS as an Assoc. Prof. (Cross Appointment) in the Division of Advanced Molecular Science
Aug. 1, 2024	Dr. OKAMOTO, Yasunori joined IMS as an Assoc. Prof. in the Research Center of Integrative Molecular Systems
Sep. 1, 2024	Dr. IZUMI, Yudai joined IMS as a Research Lecturer in the UVSOR Synchrotron Facility

Moving Out

Jan. 7, 2024	Assist. Prof. KANDA, Tomoya (Department of Life and Coordination-Complex Molecular Science) moved out
Mar. 31, 2024	Assist. Prof. OKUMURA, Shintaro (Department of Life and Coordination-Complex Molecular Science) moved out to Kyoto University
Sep. 30, 2024	Prof. ISHIZAKI, Akihito (Department of Theoretical and Computational Molecular Science) moved out as a Prof. of The University of Tokyo

Graduate Programs

For graduate education, IMS has the Molecular Science Program, Graduate Institute for Advanced Studies, SOKENDAI. Since April 2023, SOKENDAI has been providing 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-Phase Systems

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

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

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

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

Member
Assistant Professor
KODA, Shin-ichi
TANG, Zhiye
Graduazte Student
ZHU, Zhe
Secretary
CHIBA, Fumika

Keywords Reactions, Functions, Fluctuations

Our research centers on complex fluctuations in condensed systems, including supercooled liquids and biomolecules. These fluctuations significantly influence various properties, functions, and reactions. By investigating the dynamics and fluctuations in these molecular systems, we aim to uncover the molecular origins of these properties, functions, and reactions.

We have pioneered advanced computational methods for multi-dimensional nonlinear spectroscopy, enabling us to elucidate the molecular basis of ultrafast energy relaxation and the temporal evolution of nonuniform fluctuations in liquid water that conventional linear spectroscopy has not revealed. Additionally, we have delved into the dynamical heterogeneity of supercooled liquids, characterized by slow, inhomogeneous structural changes driven by fluctuations. Using a three-time correlation function, we unveiled the dynamic coupling of structural fluctuations across different time scales in proteins.

Our research has also focused on the anomalous properties of water, establishing a link between these anomalies and previously hidden structural and dynamical characteristics. Recently, we developed a novel analytical method for studying dynamical disorder based on stochastic process theory, elucidating the mechanisms behind slowing structural changes as systems approach the glass transition.

In the realm of biomolecular systems, structural fluctuations and conformational changes are crucial for functions. Our studies on enzymatic reactions underscore the importance of specific prepared conformational states that facilitate these reactions. Furthermore, we have probed the molecular origins of dynamic disorder within protein conformational dynamics, revealing the complexity of these processes. Our investigations also extend to the molecular mechanisms underlying efficient excitation energy transfer in photosynthetic systems.

Through these efforts, we are engaged in a broad spectrum of theoretical and computational studies to unravel the dynamical phenomena that govern condensed-phase systems.

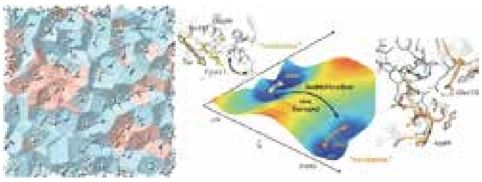

Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

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), S. Saito, *J. Chem. Phys.* **160**, 194506 (13 pages) (2024).
- J. Ono, Y. Matsumura, T. Mori and S. Saito, *J. Phys. Chem. B (Perspective)* **128**, 20–32 (2024).
- S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).

1. Conformational Dynamics in Proteins: Entangled Slow Fluctuations and Nonequilibrium Reaction Events[1]

Proteins exhibit conformational fluctuations and changes over various time scales, ranging from rapid picosecond-scale local atomic motions to slower microsecond-scale global conformational transformations. In the presence of these intricate 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 the 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.

2. Locating Transition States by a Variational Reaction Path Optimization with an Energy-Derivative-Free Objective Function[2]

Locating transition states is essential for understanding molecular reactions. We propose a double-ended transition state search method by revisiting a variational reaction path optimization method known as the MaxFlux method. Although its original purpose is to add temperature effects to reaction paths, we conversely let the temperature approaches zero to obtain an asymptotically exact minimum energy path and its corresponding transition state in variational formalism with an energy-derivative-free objective function. Using several numerical techniques to directly optimize the objective function, the present method reliably finds transition states with low computational cost. In particular, only three force evaluations per iteration are sufficient. This is confirmed in a variety of molecular reactions where the nudged elastic band method often fails.

3. Unraveling the Dynamic Slowdown in Supercooled Water: The Role of Dynamic Disorder in Jump Motions[3]

When a liquid is rapidly cooled below its melting point without inducing crystallization, its dynamics slow down significantly without noticeable structural changes. Elucidating the origin of this slowdown has been a long-standing challenge. Here, we report a theoretical investigation into the mechanism of the dynamic slowdown in supercooled water, a ubiquitous yet extraordinary substance characterized by various anomalous properties arising from local density fluctuations. Using molecular dynamics simulations, we found that the jump dynamics, which are elementary structural change processes, deviate from Poisson statistics with decreasing temperature. This deviation is attributed to slow variables competing with the jump motions, *i.e.*, dynamic disorder. The present analysis of the dynamic disorder showed that the primary slow variable is the displacement of the fourth nearest oxygen atom of a jumping molecule, which occurs in an environment created by the fluctuations of molecules outside the first hydration shell. As the temperature decreases, the jump dynamics become slow and intermittent. These intermittent dynamics are attributed to the prolonged trapping of jumping molecules within extended and stable low-density domains. As the temperature continues to decrease, the number of slow variables increases due to the increased cooperative motions. Consequently, the jump dynamics proceed in a higher-dimensional space consisting of multiple slow variables, becoming slower and more intermittent. It is then conceivable that with further decreasing temperature, the slowing and intermittency of the jump dynamics intensify, eventually culminating in a glass transition.

4. Effect of Counterions on the Structure and Dynamics of Water near a Negatively Charged Surfactant: A Theoretical Vibrational Sum Frequency Generation Study[4]

Charged aqueous interfaces are of paramount importance in electrochemical, biological, and environmental sciences. The properties of aqueous interfaces with ionic surfactants can be influenced by the presence of counterions. Earlier experiments involving vibrational sum frequency generation (VSFG) spectroscopy of aqueous interfaces with negatively charged sodium dodecyl sulfate (Na^+DS^- or SDS) surfactants revealed that the hydrogen bonding strength of the interfacial water molecules follows a certain order when salts of monovalent and divalent cations are added. It is known that cations do not directly participate in hydrogen bonding with water molecules, rather they only influence the hydrogen-bonded network through their electrostatic fields. In the current work, we have simulated the aqueous interfacial systems of sodium dodecyl sulfate in the presence of chloride salts of mono and divalent countercations. The electronic polarization effects on the ions are considered at a mean-field level within the electronic continuum correction model. Our calculations of the VSFG spectra show a blue shift in the presence of added countercations whose origin is traced to different relative contributions of water molecules from the solvation shells of the surfactant headgroups and the remaining water molecules in the presence of countercations. Furthermore, the cations shield the electric fields of the surfactant headgroups, which in turn influences the contributions of water molecules to the total VSFG spectrum. This shielding effect becomes more significant when divalent countercations are present. The dynamics of water molecules are slower at the interface than the bulk. The interfacial depth dependence of various dynamical quantities shows that the interface is structurally and dynamically more heterogeneous at the microscopic level.

References

1) J. Ono, Y. Matsumura, T. Mori and S. Saito, *J. Phys. Chem. B (Perspective)* **128**, 20–32 (2024).
2) S.-i. Koda and S. Saito, *J. Chem. Theory Comput.* **20**, 2798–2811 (2024).
3) S. Saito, *J. Chem. Phys.* **160**, 194506 (13 pages) (2024).
4) R. Malik, S. Saito and A. Chandra, *Phys. Chem. Chem. Phys.* **26**, 17065–17074 (2024).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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

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Education

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

Professional Employment

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

Awards

2015	10th Condensed-Matter Science Prize, Japan
2015	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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Research Assistant Professor
FUNO, Ken
Post-Doctoral Fellow
SAKAMOTO, Souichi
Secretary
MASUDA, Michiko

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. Dynamics of a Quantum System Interacting with White Non-Gaussian Baths: Poisson Noise Master Equation

Quantum systems are unavoidably open to their surrounding degrees of freedom. The theory of open quantum systems is thus crucial to understanding the fluctuations, dissipation, and decoherence of a quantum system of interest. Typically, the bath is modeled as an ensemble of harmonic oscillators, which yields Gaussian statistics of the bath influence on the quantum systems. However, there are also phenomena in which the bath consists of two-state systems, spins, or anharmonic oscillators; therefore, the non-Gaussian properties of the bath become important. Nevertheless, a theoretical framework to describe quantum systems under the influence of such non-Gaussian baths is not well established. Here, we develop a theory to describe quantum dissipative systems affected by Poisson noise properties of the bath, because the Lévi-Itô decomposition theorem asserts that Poisson noise is fundamental in describing arbitrary white noise beyond Gaussian properties. We introduce a quantum bath model that allows for the consistent description of dissipative quantum systems. The obtained master equation reveals non-Gaussian bath effects in the white noise regime, and provides an essential step toward describing open quantum dynamics under the influence of generic baths.1)

2. Pathway Selectivity in Time-Resolved Spectroscopy Using Two-Photon Coincidence Counting with Quantum Entangled Photons

Ultrafast optical spectroscopy is a powerful technique for studying the dynamic processes of molecular systems in condensed phases. However, in molecular systems containing many dye molecules, the spectra can become crowded and difficult to interpret owing to the presence of multiple nonlinear optical contributions. In this work, we theoretically propose time-resolved spectroscopy based on the coincidence counting of two entangled photons generated via parametric down-conversion with a monochromatic laser. We demonstrate that the use of two-photon counting detection of entangled photon pairs enables the selective elimination of the excited-state absorption signal. This selective elimination cannot be realized with classical coherent light. We anticipate that the proposed spectroscopy will help simplify the spectral interpretation of complex molecular and material systems comprising multiple molecules.2)

3. A Coarse-Grained Description of Anharmonic Lattice Environments Affecting the Quantum Dynamics of Charge Carriers

Lattice softness has a significant impact on charge carrier dynamics in condensed matter systems. Examples include the remarkable carrier lifetimes and defect tolerances of hybrid organic-inorganic perovskites. Recent studies suggest the contribution of quartic anharmonicity of the lattice vibrations. The quartic anharmonicity can be discussed with a double-well potential, and the transition between the two minima can be coarse-grained as a two-state jump stochastic process. Such a stochastic approach is typically employed to describe fluctuations introduced into a system by two-state transitions in the surroundings. To investigate charge transport in materials, however, it is crucial to describe not only the fluctuations but also the dynamic lattice distortion associated with charge transport. Therefore, there is a need for a theory to describe the charge carrier dynamics proceeding alongside the lattice distortion dynamics. In this study, we present a theory that describes quantum dynamics under the influence of an environment with two stable states, termed a bistable environment. The theory describes the effects of fluctuations and dissipation induced from the bistable environment in a reasonable manner, and the effects exhibit a different temperature dependence than the widely employed Gaussian environment. The physical implication of this temperature dependence is provided in terms of the environmental dynamics. The results of this study are expected to provide a step forward in describing charge carrier dynamics in materials with lattice softness and pronounced lattice anharmonicity.3)

4. 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.4)

References

1) K. Funo and A. Ishizaki, *Phys. Rev. Lett.* **132**, 170402 (2024).
2) Y. Fujihashi, A. Ishizaki and R. Shimizu, *J. Chem. Phys.* **160**, 104201 (2024).
3) K. Miwa, S. Sakamoto, K. Funo and A. Ishizaki, submitted.
4) 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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1994	Visiting Researcher, Heidelberg University (–1995)
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2002	Associate Professor, Kyoto University
2006	Theoretical Research Division Supervisor, Kyoto University (–2008)
2008	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

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2009	QSCP Prize CMOA

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Keywords Quantum Chemistry, Photochemistry, Heterogeneous Catalysis

We develop the useful electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, we focus on the 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 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, Y. Suzuki, Y. Konno, P. Zhao, N. Kikuchi, M. Yamada, M. Mitsuishi, A. T. H. Dao, H. Kasai and M. Ehara, “Selective Emergence of Photoluminescence at Telecommunication Wavelengths from Cyclic Perfluoroalkylated Carbon Nanotubes,” *Commun. Chem.* **6**, 159 (10 peges) (2023).

1. Elucidating Electronic Structure of Anion-Templated Silver Nanoclusters by Optical Absorption Spectroscopy and Theoretical Calculations[1]

Electronic structures of anion-templated silver nanoclusters (Ag NCs) have not been well understood compared with conventional template-free Ag NCs. In this work, we developed three new anion-templated Ag NCs, that is $[S@Ag_{17}L_{15}(PPh_3)_5]^0$, $[S@Ag_{18}L_{16}(PPh_3)_8]^0$, and $[Cl@Ag_{18}L_{16}(PPh_3)_8][PPh_4]$, where L = 4-chlorobenzene methanethiolate for which single-crystal X-ray crystallography revealed that they have $S@Ag_6$, $S@Ag_{10}$, and $Cl@Ag_{10}$ cores, respectively. Investigation of their electronic structures by optical spectroscopy and theoretical calculations elucidated the following unique features; (1) their electronic structures are different from those of template-free Ag NCs described by the superatomic concept; (2) optical absorption in the range of 550–400 nm for S^{2-}-templated Ag NCs is attributed to the charge transitions from S^{2-}-templated Ag-cage orbitals to the s-shaped orbital in the S^{2-} moiety; (3) the Cl^--templated Ag NCs can be viewed as $[Cl@Ag_{18}L_{16}(PPh_3)_8]^0[PPh_4]^0$ rather than the ion pair $[Cl@Ag_{18}L_{16}(PPh_3)_8]^-[PPh_4]^+$; and (4) the singlet-coupled singly occupied orbitals are involved in the optical absorption of the Cl^--templated Ag NC.

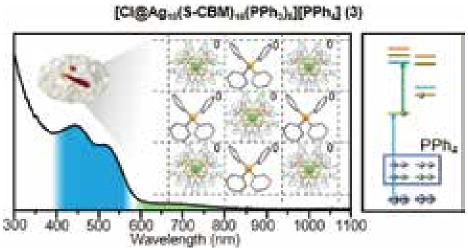

Figure 1. Photophysical properties and electronic states of $[Cl@Ag_{18}L_{16}(PPh_3)_8][PPh_4]$.

2. Single-Gold Etching at the Hypercarbon Atom of *C*-Centred Hexagold(I) Clusters[2]

Etching is an excellent top-down synthesis method for controlling the structures and chemical and physical properties of nanomaterials. Chemical etching at the atomic level is a particularly challenging task for the precise synthesis of nanosized metal clusters. The synthesis of metal clusters containing smaller metal nuclei and potential surface vacancies will further elucidate the details of structure–function relationships and facilitate future materials design. In this work, we report the successful single-gold etching at a hypercarbon centre in gold(I) clusters. Specifically, *C*-centred hexagold(I) clusters protected by chiral *N*-heterocyclic carbenes were etched with bisphosphine to yield *C*-centred pentagold(I) (CAu^I_5) clusters. The CAu^I_5 clusters exhibit an unusually large bathochromic shift in luminescence, which is reproduced theoretically. The etching mechanism was experimentally and theoretically suggested to be a tandem dissociation-association-elimination pathway. Furthermore, the vacant site of the central carbon of the CAu^I_5 cluster can accommodate AuCl, allowing for post-functionalisation of the *C*-centred gold(I) clusters.

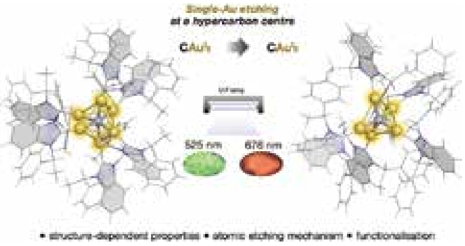

Figure 2. Schematic diagram of single-Au etching at a hypercarbon center.

3. Optimization of Metal-Support Cooperation for Boosting the Performance of Supported Gold Catalysts for the Borylation of C–O and C–N Bonds[3]

Supported metal catalysts have interfacial sites between metal nanoparticles and their supports, where multiple catalytic elements can work in cooperation to efficiently promote intermolecular reactions. In this work, we performed kinetic and theoretical studies to elucidate the effect of metal-support cooperation for the borylation of C–O bonds by supported gold catalysts and revealed that the Lewis acid density of the supports determined the number of active sites at which metal nanoparticles (NPs) and Lewis acid at the surface of the supports work in cooperation. DFT calculations revealed that strong adsorption of diborons at the interface between Au NPs and supports and lowering the LUMO level of adsorbed diboron were responsible for efficient C–O bond borylation. Supported Au catalysts with the optimized metal–metal oxide cooperation sites, namely Au/α-Fe_2O_3 catalyst, showed excellent activity for C–O bond borylation, and also enabled the synthesis of organoboron compounds by using continuous flow reactions. Furthermore, Au/α-Fe_2O_3 showed high activity for direct C–N bond borylation without the transformation of amino groups to ammonium cations. The results described herein suggest that the optimization of metal–metal oxide cooperation is beneficial for taking full advantage of the potential performance of supported metal catalysts for intermolecular reactions.

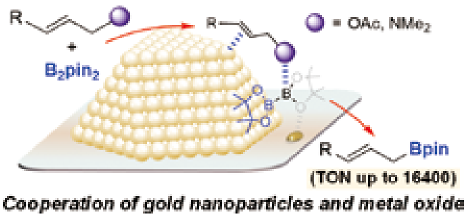

Figure 3. Borylation of C–O and C–N bonds on the supported gold catalysts: Optimization of metal-support interaction.

References

1) Y. Horita, S. Hossain, M. Ishimi, P. Zhao, M. Sera, T. Kawawaki, S. Takano, Y. Niihori, T. Nakamura, T. Tsukuda, M. Ehara and Y. Negishi, *J. Am. Chem. Soc.* **145**, 23533–23540 (2023).

2) X.-L. Pei, P. Zhao, H. Ube, Z. Lei, M. Ehara and M. Shionoya, *Nat. Commun.* **15**, 5024 (2024).

3) H. Miura, K. Imoto, H. Nishio, A. Junkaew, Y. Tsunesada, Y. Fukata, M. Ehara and T. Shishido, *J. Am. Chem. Soc.* **146**, 27528–27541 (2024).

Molecular Dynamics Simulations of Disease-Related Biomolecules

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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.

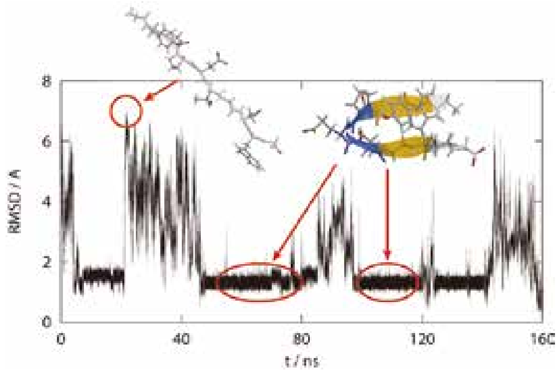

Figure 1. Time series of protein folding simulation.

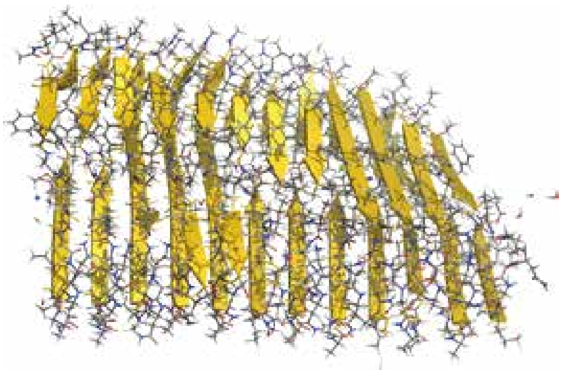

Figure 2. Snapshot of an Aβ amyloid fibril.

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).
- 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).
- S. G. Itoh, M. Yagi-Utsumi, K. Kato and H. Okumura: "Key Residue for Aggregation of Amyloid-β Peptides," *ACS Chem. Neurosci.* **13**, 3139–3151 (2022).

1. Why Is Arginine the Only Amino Acid that Inhibits Polyglutamine Monomers from Taking on Toxic Conformations?

Polyglutamine (polyQ) diseases are devastating neurodegenerative disorders characterized by abnormal expansion of glutamine repeats within specific proteins. The aggregation of polyQ proteins is a critical pathological hallmark of these diseases. Arginine was identified as a promising inhibitory compound because it prevents polyQ-protein monomers from forming intra- and intermolecular β-sheet structures and hinders polyQ proteins from aggregating to form oligomers. Furthermore, such an aggregation inhibitory effect was not observed in other amino acids. However, the underlying molecular mechanism of the aggregation inhibition and the factors that differentiate arginine from other amino acids, in terms of the inhibition of the polyQ-protein aggregation, remain poorly understood. We performed replica-permutation MD simulations to elucidate the molecular mechanism by which arginine inhibits the formation of the intramolecular β-sheet structure of a polyQ monomer.[1] We found that the intramolecular β-sheet structure with more than four β-bridges of the polyQ monomer with arginine is more unstable than without any ligand and with lysine. We also found that arginine has 1.6–2.1 times more contact with polyQ than lysine. In addition, we revealed that arginine forms more hydrogen bonds with the main chain of the polyQ monomer than lysine. More hydrogen bonds formed between arginine and polyQ inhibit polyQ from forming the long intramolecular β-sheet structure. It is known that intramolecular β-sheet structure enhances intermolecular β-sheet structure between proteins. These effects are thought to be the reason for the inhibition of polyQ aggregation. This study provides insights into the molecular events underlying arginine's inhibition of polyQ-protein aggregation.

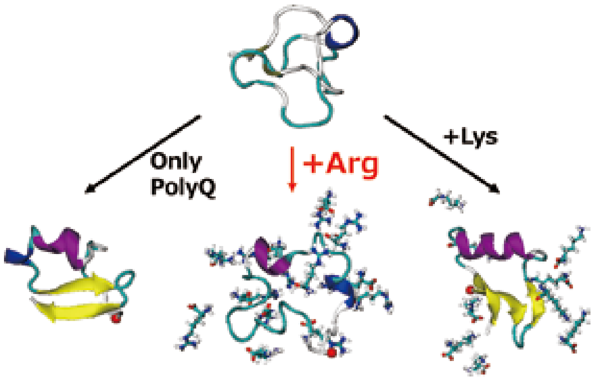

Figure 3. Arginine inhibits polyQ-proteins from forming intra- and intermolecular β-sheet structures. However, lysine, which also has a positive charge, does not have such an effect.

2. Dissociation Process of Polyalanine Aggregates by Free Electron Laser Irradiation

Polyalanine (polyA) disease-causative proteins with an expansion of alanine repeats can be aggregated. Although curative treatments for polyA diseases have not been explored, the dissociation of polyA aggregates likely reduces the cytotoxicity of polyA. Mid-infrared free electron laser (FEL) successfully dissociated multiple aggregates. However, whether the FEL dissociates polyA aggregates like other aggregates has not been tested. We applied MD simulation to follow the dissociation process by FEL.[2] We successfully observed how the intermolecular β-sheet of polyA aggregates was dissociated and separated into monomers with helix structures upon FEL irradiation. After the dissociation by FEL, water molecules inhibited the reformation of polyA aggregates. We recently verified the same dissociation process using FEL-treated amyloid-β aggregates. Thus, a common mechanism underlies the dissociation of different protein aggregates that cause different diseases, polyA disease and Alzheimer's disease. However, MD simulation indicated that polyA aggregates are less easily dissociated than amyloid-β aggregates and require longer laser irradiation due to hydrophobic alanine repeats.

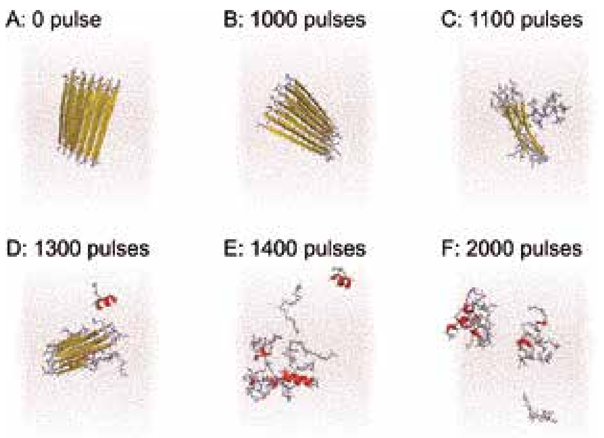
A: 0 pulse
B: 1000 pulses
C: 1100 pulses
D: 1300 pulses
E: 1400 pulses
F: 2000 pulses

Figure 4. Snapshots of polyA amyloid fibril during a nonequilibrium MD simulation. Snapshots (A) before FEL irradiation, (B) after 1000 pulses, (C) after 1100 pulses, (D) after 1300 pulses, (E) after 1400 pulses, and (F) after 2000 pulses.

References

1) S. Tanimoto and H. Okumura, *ACS Chem. Neurosci.* **15**, 2925–2935 (2024).
2) H. Okumura, S. G. Itoh, H. Zen and K. Nakamura, *PLoS One* **18**, e0291093 (2023).

Award

TANIMOTO, Shoichi, ITOH, Satoru G. and OKUMURA, Hisashi; Best Author Award, Japan Society for Simulation Technology (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 inward-open and outward-open states relative to the membrane. We aim to elucidate the mechanisms of these elaborate and dynamic nanomachines created by nature at the atomic and molecular levels and to control their functions based on our findings.

We would like to understand the mechanisms 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 dynamics, especially for a large system like typical biomolecular machines. Therefore, we have developed and applied methods such as coarse-grained modeling and enhanced 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 the ATP required in the cell. It is composed of two rotary motors: F_o and F_1. The F_o motor is embedded in the membrane and driven by a proton gradient, while the F_1 motor is driven by the ATP hydrolysis reaction. We clarified how the rotation of the F_1 motor is driven by a key chemical step, Pi release after the 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 a 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 a transition path sampling technique to capture the moment of the ion transport. The simulations predicted the mutation that could speed up 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 the mechanism obtained from simulations by creating the faster transporter.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 amounts of oxalate form 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) in the bacterium's membrane is responsible for oxalate uptake and formate efflux. 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 is in the occluded conformation with the bound oxalate.

We have identified the inward and outward gates of OxlT using MD simulations from the experimental structures.[3] An unresolved inward-open conformation was obtained by performing accelerated MD simulations, in which boost potential was applied to residues around the inward gate (Figure 1A). The obtained inward-open conformation was validated by an additional simulation observing the substrate formate binding from the inside of the membrane (Figure 1B). The contact analysis was performed to identify key interactions that change during the conformational change (Figure 1C). The residues that break contacts include D280 at the cytoplasmic side. The S162 and T258 formed a contact at the periplasmic side.

Then, we used the state-of-the-art structural prediction AI AlphaFold2 to see how mutations of the identified residues affect AlphaFold prediction (Figure 1D). While AlphaFold predicted only the outward-open conformations with the wild-type sequence, the mutation D280L or S162C/T258C made AlphaFold also predict the inward-open conformation. These mutations likely stabilize the inward-open conformation.

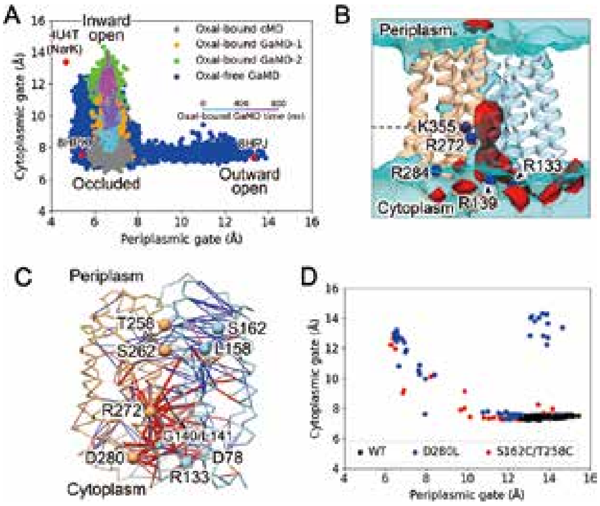

Figure 1. (A) Accelerated MD simulations discover an inward-open conformation. (B) Formate density in the inward-open state. (C) Contact analysis to identify important residue pairs. (D) AlphaFold structures for wild type and mutants.[4]

2. Integration of AlphaFold with MD Simulation

The computational cost of all-atom MD simulations for biomolecular machines is so high that direct simulation of the functional motions is impossible. We introduce a method that integrates AlphaFold with MD simulation to overcome this difficulty.[5] This method first generates broad structures by AlphaFold with reduced MSA depth, including multiple stable conformations and intermediates. Then, MD simulations are conducted from these structures to cover the broad conformational space that is involved with the function. The method was tested with the transporter protein NarK. It successfully uncovers a missing conformational state and transition dynamics between stable states.

3. 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 the progress of a reaction between two metastable states. We have developed a machine learning method to identify reaction coordinates based on the committor function.[2,6] We have applied a deep neural network and Explainable Artificial Intelligence (XAI) for this problem.[6]

References

1) K. Okazaki and G. Hummer, *Proc. Natl. Acad. Sci. U. S. A.* **110**, 16468–16473 (2013).
2) K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, *Nat. Commun.* **10**, 1742 (2019).
3) T. Jaunet-Lahary *et al.*, *Nat. Commun.* **14**, 1730 (2023).
4) J. Ohnuki, T. Jaunet-Lahary, A. Yamashita and K. Okazaki, *J. Phys. Chem. Lett.* **15**, 725–732 (2024).
5) J. Ohnuki and K. Okazaki, *J. Phys. Chem. B* **128**, 7530–7537 (2024).
6) T. Kikutsuji, Y. Mori, K. Okazaki, T. Mori, K. Kim and N. Matubayasi, *J. Chem. Phys.* **156**, 154108 (2022).

Awards

OHNUKI, Jun; Young Scientist Excellence Award of the Protein Science Society of Japan (2024).
KOBAYASHI, Ryohei; Early Career Award, The Biophysical Society of Japan (2023).

Visiting Professors

Visiting Professor

TSUCHIMOCHI, Takashi *(from Shibaura Institute of Technology)*

Theoretical and Computational Chemistry for Degenerate Electronic Structures

Our research focuses on quantum chemistry to compute the electronic structure of materials. We are particularly interested in chemical systems where electrons are strongly correlated with each other, making them notoriously difficult to compute with traditional approaches due to either the inappropriate treatment of quantum entanglement or prohibitively large computational costs. To tackle this conundrum, we have proposed several methodologies based on symmetry-breaking of the underlying wave function as well as its restoration by means of symmetry-projection. While these methods primarily fall within the realm of wave function theory, we are integrating these concepts into the more affordable density functional theory. Recently, we have also been extensively exploring the potential of quantum computer to address such challenging electronic structures; we have proposed novel quantum-classical hybrid algorithms for accurately determining both ground and excited states in fermionic systems.

Visiting Professor

FUJII, Keisuke *(from Osaka University)*

Theoretical Research on the Fundamentals and Applications of Quantum Computers

Our research interests include theoretical foundations and applied research related to quantum computing. The development of quantum computer hardware has made remarkable progress in recent years. Quantum computers with 50 to over 100 qubits have already been realized and quantum computers can be used from the cloud. However, current quantum computers are known as noisy intermediate-scale quantum computers (NISQ), suffering from noise. In the future, it is hoped to realize a larger-scale quantum computer and a fault-tolerant quantum computer (FTQC) with quantum error correction. Our group is investigating how quantum computers of the scale currently realized can be used for useful tasks, such as machine learning and quantum many-body simulations, by mitigating noise. At the same time, we are also analyzing what physical systems can be used to construct a large-scale FTQC and how much resources are needed to solve problems of practical interest.

Visiting Associate Professor

ABE, Minori *(from Hiroshima University)*

We have developed relativistic quantum chemistry software to compute molecular electronic structures involving heavy atoms. The CASPT2 method is employed in our program to treat multireference electron correlation effects, and relativistic effects are accurately incorporated by connecting to the DIRAC software. Our program was used to elucidate the ground and excited electronic states of several actinide compounds, such as UO_2^{2+} and $Cm(phen)_2^{3+}$. Our calculated excitation energies agree with experimental data and previously reported theoretical results. We will make our program publicly available on GitHub.

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, chiro-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 Computer and Simulator

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Division of Photo-Molecular Science II

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Education

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1992	Ph.D. The University of Tokyo

Professional Employment

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

Awards

1998	Award by Research Foundation for Opto-Science and Technology
2007	JSPS Prize
2007	Japan Academy Medal
2008	Norman Hascoe Distinguished Lecturer, University of Connecticut, USA
2009	Fellow of the American Physical Society
2012	Humboldt Research Award (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

Member

- Research Associate Professor
  - DE LÉSÉLEUC, Sylvain
- Assistant Professor
  - TOMITA, Takafumi
- Research Assistant Professor
  - CHEW TORII, Yuki*
  - MATSUBARA, Takuya
  - TAMURA, Hikaru
- Post-Doctoral Fellow
  - BHARTI, Vineet†
  - CHAUHAN, Vikas
  - JAUNET-LAHARY, Titouan
  - LIENHARD, Vincent
- Visiting Scientist
  - TSUGAOKA, Masato‡
  - KITADE, Sota‡
  - MAITY, Arnab‡
  - GANESAN, Karthikeyan‡
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  - SIRIWORAKOONCHAI, Phatwarach‡
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  - KECIR, Omar El Farouk‡
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  - NAKAI, Airi
  - KATAOKA, Kensuke
  - TSURUTA, Shoko
- Secretary
  - FUJIKAWA, Taketoshi
  - KAWAMOTO, Minako
  - MAKINO, Akane
  - INUKAI, Kazuhisa
  - SAKAI, Shiho
  - NISHIOKA, Wakako
  - KOSHIDA, Yoko
  - YAMAGISHI, Mei
  - TAKEI, Mio
  - KUTARA, Yuriya
  - YAWATA, Naoko
  - OKADA, Mitsuya

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.

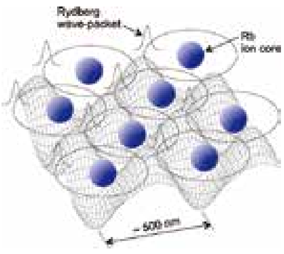

Figure 1. Metal-like quantum gas. A schematic of the many-body quantum simulator with ultracold Rydberg atoms, named "ultrafast quantum simulator," where electronic wave functions spatially overlap between neighboring atoms.2)

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 *et al.*, "Picosecond-Scale Ultrafast Many-Body Dynamics in an Ultracold Rydberg-Excited Atomic Mott Insulator," *Phys. Rev. Lett.* **131**, 123201 (2023).
- V. Bharti *et al.*, "Strong Spin-Motion Coupling in the Ultrafast Dynamics of Rydberg Atoms," *Phys. Rev. Lett.* **133**, 093405 (2024).

1. Development of an "Ultrafast Quantum Simulator" by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales[2–7]

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. Recently in 2023, quantum magnetism has successfully been simulated with this standard hardware assembled with ~30,000 Rb atoms.[6] Our novel scheme above has accelerated the simulation speed by three orders of magnitude compared to previous quantum simulators of magnetism. Moreover, we have succeeded in simulating the formation dynamics of "quantum entanglement," which is difficult to measure in actual magnetic materials, on the timescale of several hundred picoseconds.

Very recently in 2024 we have revealed the quantum entanglement between electronic and motional states in our "ultrafast quantum simulator," generated by the repulsive force due to the strong interaction between Rydberg atoms as seen in Figure 2.[7] We have also proposed a new quantum simulation method including repulsive force between particles.

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[8,10,11]

We develop a novel quantum computer with two dimensional arrays of ultracold Rb atoms trapped in optical tweezers. These atomic qubits are 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 succeeded in executing a controlled Z gate,[8] 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, and thus can be isolated from the noise. Moreover, this ultrafast two-qubit gate is faster than the fast two-qubit gate demonstrated recently by "Google AI Quantum" with superconducting qubits.[9] We are currently improving key enabling technologies for optical tweezers and operating lasers.[10,11]

We continue upgrading this ultrafast quantum computers, generously supported by the Moonshot program of the Cabinet Office of Japan.

References

1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) H. Katsuki *et al.*, *Acc. Chem. Res.* **51**, 1174–1184 (2018).
4) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).
5) M. Mizoguchi *et al.*, *Phys. Rev. Lett.* **124**, 253201 (2020).
6) V. Bharti *et al.*, *Phys. Rev. Lett.* **131**, 123201 (2023).
7) V. Bharti *et al.*, *Phys. Rev. Lett.* **133**, 093405 (2024).
8) Y. Chew *et al.*, *Nat. Photonics* **16**, 724 (2022). (Cover-Page Highlight)
9) B. Foxen *et al.*, *Phys. Rev. Lett.* **125**, 120504 (2020).
10) Y. Chew *et al.*, arXiv:2407.20699 (2024).
11) T. P. Mahesh *et al.*, arXiv:2408.02324 (2024).

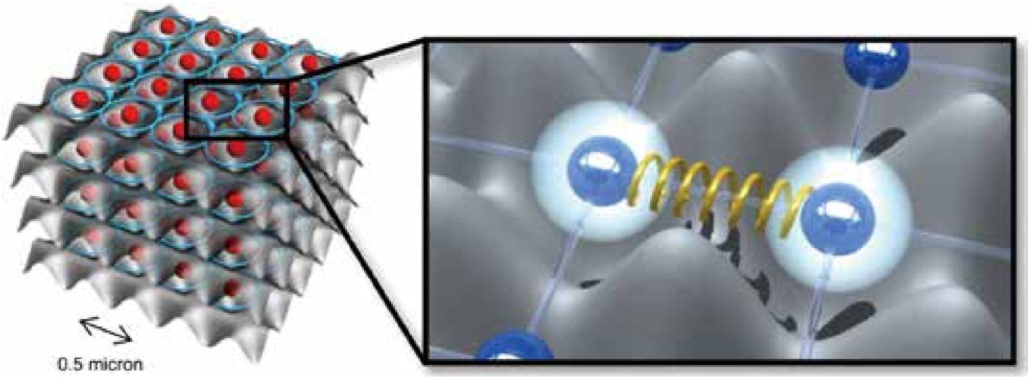

Figure 2. Conceptual diagram of the quantum entanglement between electronic and motional states in our ultrafast quantum simulation of magnetic material.[7] Atoms in the optical lattice, trapped at a distance of 0.5 micron, are excited to the Rydberg state by the ultrafast excitation technique. Interaction between close Rydberg atoms results in the repulsive force, leading to the quantum entanglement between electronic and motional states of the atoms.

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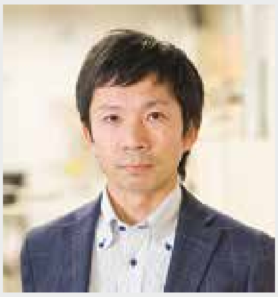
Electronic Property of Functional Organic Materials

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



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Education

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

Professional Employment

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

Member
Assistant Professor
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Research Assistant Professor
SAGEHASHI, Ryunosuke
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WANGKANYA, Ratchada*
Graduate Student
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PALASSERY ITHIKKAL, Jaseela
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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.

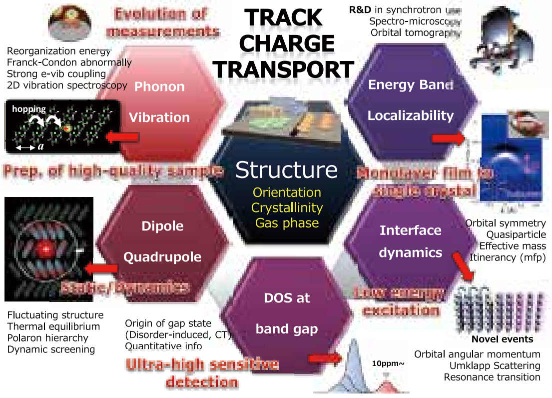

Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

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 2D Covalent Organic Frameworks[1)]

Two-dimensional (2D) covalent organic frameworks (COFs) fabricated through on-surface synthesis were investigated as a honeycomb nanopore template for the growth of 3d-transition-metal nanoclusters (NCs) with a size of 2 nm on a metallic substrate. The evolution of these NCs and their electronic characteristics were studied employing scanning tunneling microscopy/spectroscopy (STM/STS), angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), and X-ray photoelectron spectroscopy (XPS) under an ultrahigh-vacuum (UHV) condition at room temperature. The 2D COFs were synthesized on Cu(111) substrate utilizing 1,3,5-tris(4-bromophenyl) benzene (TBB) precursors, which engendered a honeycomb nanopore array of approximately 2 nm in size. In contrast to the behavior observed in the Co/Cu(111) system producing bilayer-stacking nanoclusters measuring 10–20 nm, STM imaging of Co/COFs/Cu(111) revealed the growth of Co NCs of approximately 1.5 nm within a single COF nanopore. This growth occurred without forming a monolayer film beneath the COFs, providing direct evidence that the 2D COFs on Cu(111) can effectively entrap Co atoms within the nanopore, giving rise to Co NCs (Figure 2). The spectroscopy measurements, STS, ARUPS, and XPS, confirmed the different local densities of states for Co NCs and COFs, corroborating the coexistence of Co NCs and COFs on the surface.

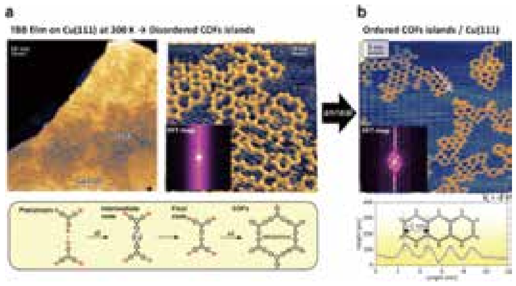

Figure 2. (a) UHV-STM topographic images obtained on the surface of TBB film grown on Cu(111) at 300 K with a schematic model of honeycomb lattice formation *via* the Ullman reaction. (b) STM topographic image of the ordered 2D-COFs islands on Cu(111) after the thermal annealing in UHV. The inset in the bottom panels denotes the FFT map. The figure is after ref 1).

2. Electronic Structure and Many-Body Interactions of Low-Mobility Carriers in Perylene Diimide Derivative[2)]

Despite the rapid progresses in the field of organic semiconductors, aided by the development of high-mobility organic materials, their high carrier mobilities are often unipolar, being sufficiently high only for either electrons or holes. Yet, the basic mechanisms underlying such significant mobility asymmetry largely remains elusive. We perform the ARUPS to reveal the occupied band structures and the many-body interactions for low-mobility hole carriers in a typical n-type semiconductor perylene diimide derivative (PTCDI-C8). The 50-nm thick PTCDI-C8 film consists of many needle-like crystallites, each of which are several hundreds of nanometres along its long axis by AFM, where the long axis of the crystallites was determined to be the crystallographic π-π stacking direction. The band dispersion is observed clearly even for random orientation of the molecular plane by thanks to large anisotropic nature of the BZ structure. The observed HOMO band by ARUPS exhibits strong renormalization to the calculated DFT results based on the single-particle electronic state (Figure 3). The analysis including many-body interactions elucidate that the significant mass enhancement can be understood in terms of strong charge–phonon coupling, leading to an important mechanism of polaron band transport of low intrinsic carrier mobility in organic semiconductor.

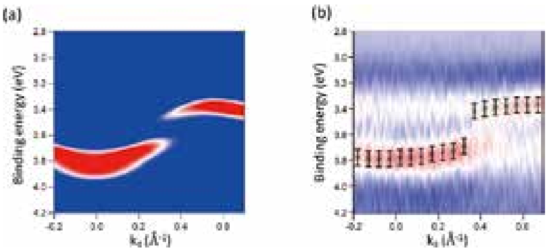

Figure 3. Second derivative plot of a simulated HOMO band dispersion with hole-intramolecular vibration coupling (a) and the observed HOMO by HeII ARUPS (b).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope are developing at BL6U.[3)] The perspectives required for future light-source facility have been discussed with communities.[4)]

References

1) T. Yamada, S. Kanazawa, K. Fukutani and S. Kera, *J. Phys. Chem. C* **128**, 1477–1486 (2024).
2) J. P. Ithikkal, K. Fukutani, F. Nishino, T. Minato, H. Ishii, S. Izawa, K. Tanaka, M. Hiramoto and S. Kera, *Appl. Phys. Lett.* **125**, 052102 (7 pages) (2024).
3) 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, *Rev. Sci. Instrum.* **97**, 083701 (10 pages) (2023).
4) S. Kera, F. Matsui, K. Tanaka, Y. Taira, T. Araki, T. Ohigashi, H. Iwayama, M. Fujimoto, H. Matsuda, E. Salehi and M. Katoh, *Electron. Struct.* **5**, 034001 (9 pages) (2023).

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* IMS International Internship Program with Kasetsart University

Light Source Developments by Using Relativistic Electron Beams

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Education

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Professional Employment

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2000	Associate Professor, Institute for Molecular Science
2004	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2019	Professor, Hiroshima University Project Professor, Institute for Molecular Science
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KAMO, Kyoko
YOKOTA, Mitsuyo

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).
- M. Shimada, M. Katoh, M. Adachi, T. Tanikawa, S. Kimura, M. Hosaka, N. Yamamoto, Y. Takashima and T. Takahashi, "Transverse-Longitudinal Coupling Effect in Laser Bunch Slicing," *Phys. Rev. Lett.* **103**, 144802 (2009).
- M. Katoh, M. Fujimoto, H. Kawaguchi, K. Tsuchiya, K. Ohmi, T. Kaneyasu, Y. Taira, M. Hosaka, A. Mochihashi and Y. Takashima, "Angular Momentum of Twisted Radiation from an Electron in Spiral Motion," *Phys. Rev. Lett.* **118**, 094801 (2017).
- Y. Hikosaka, T. Kaneyasu, M. Fujimoto, H. Iwayama and M. Katoh, "Coherent Control in the Extreme Ultraviolet and Attosecond Regime by Synchrotron Radiation," *Nat. Commun.* **10**, 4988 (2019).
- T. Kaneyasu, Y. Hikosaka, M. Fujimoto, H. Iwayama and M. Katoh, "Electron Wave Packet Interference in Atomic Inner-Shell Excitation," *Phys. Rev. Lett.* **126**, 1132202 (2021).
- T. 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 (Figure 2), 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 (Figure 3).

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.

We have been 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.

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

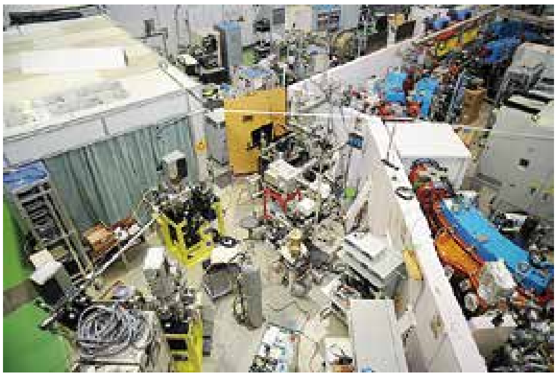

Figure 3. UVSOR BL1U experimental station for source development studies.

In these years, we are interested in the quantum nature of synchrotron radiation photons. We have established a technique to store only one electron in the synchrotron. We are working on experimental studies on photon emission from a single electron.

We have been developing a laser Compton scattering gamma-ray source at BL1U, which is capable of producing monochromatic and energy-tunable gamma-rays.

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.

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, however, the requirements from the users for the higher brightness is getting stronger, because new light sources and upgrade plans are being realized all over the world. We had seeked 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. However, they are not compatible with the operation of the narrow gap undulators. Then, we started a design study on a new light source facility. Currently we are focusing on designing a synchrotron with the electron energy of 1 GeV and the circumference of around 70 m. In parallel, we are designing a magnetic lattice which has same beam energy and circumference as the present machine but would give lower emittance.

We are collaborating with Nagoya Univ., Hiroshima Univ. and KEK Photon Factory and are developing new accelerator 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.

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

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

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Education

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

Professional Employment

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

Awards

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
2023	Young Scientist Award of the Japanese Positron Science Society

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YANG, Yuxuan†
ZHOU, Weixin†
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YOKOTA, Mitsuyo

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.

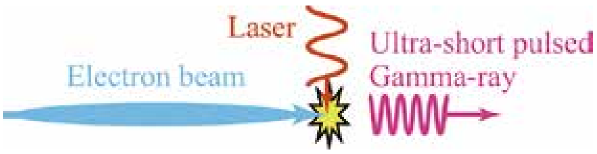

Figure 1. Schematic illustration of 90-degree inverse Thomson scattering.

Selected Publications

- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultra-Short-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696 (2011).
- Y. Taira, T. Hayakawa and M. Katoh, "Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light," *Sci. Rep.* **7**, 5018 (2017).
- Y. Taira, M. Fujimoto, S. Ri, M. Hosaka and M. Katoh, "Measurement of the Phase Structure of Elliptically Polarized Undulator Radiation," *New J. Phys.* **22**, 093061 (2020).
- 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 GiPAS, defect analysis is performed by measuring the energy spectrum and emission time distribution (positron lifetime spectrum) of annihilation gamma rays, which are generated when a positron annihilates with an electron inside material. Gamma-ray-induced positron annihilation lifetime spectroscopy (GiPALS) is a technique that measures the time difference distribution between a reference signal and a detector output of annihilation gamma rays. The reference signal is the output of a photodiode placed near the collision point between the electron beam and the laser, which detects the laser just before it generates gamma rays. 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. Gamma-ray-induced positron annihilation lifetime spectroscopy system using eight detectors and two digital oscilloscope.

Currently, user applications of GiPALS are underway at BL1U of UVSOR, and users from universities, research institutes, and private companies are using the system. Measurements of samples under special environments such as stress loading, high temperature, gas atmosphere, laser irradiation, hydrogenation, etc., which are difficult to measure with conventional methods, are being performed.

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. We have not been able to measure the difference in positron lifetime due to the helicity inversion of circularly polarized gamma rays, but we will continue our research and development.

2. Measurement of Gamma-Rays Generated by Using Polarized Lasers

Inverse Compton scattering of a polarized laser by energetic electrons is an excellent method to generate polarized gamma rays. The development and use of linearly and circularly polarized gamma rays have been conducted. The polarization state of linearly and circularly polarized lasers is homogeneous across their cross sections. However, it is possible to produce lasers with spatially variant polarization states. An example is the axially symmetric polarization state, referred to as an axially symmetric polarized laser or a cylindrical vector beam. Although the polarization characteristics of gamma rays produced by linearly or circularly polarized lasers have been theoretically clarified, that of gamma rays generated by axially symmetric polarized lasers have not. If gamma rays with novel polarization characteristics can be generated, it is possible to develop new ways to use gamma rays.

The spatial distribution of the gamma rays, which reflects the polarization characteristics, was measured with a two-dimensional CdTe imaging sensor. Gamma rays were generated through 90-degree collisional inverse Compton scattering between an electron beam and an axially symmetric polarized laser. The results showed that the spatial distribution of gamma rays generated from axially symmetric polarized lasers was changed compared to that of linearly or circularly polarized gamma rays. Comparing the linearly polarized gamma rays with those generated by the axially symmetric polarized laser, a node that appears at an outer scattering angle along the polarization axis of the linearly polarized gamma ray was absent in the gamma ray generated by the axially symmetric polarized laser. Compared to the circularly polarized gamma rays, the gamma rays generated by the axially symmetric polarized laser showed a spatial distribution that was slightly expanded in a specific direction rather than concentric, while the circularly polarized gamma rays showed a concentric spatial distribution. This was thought to be due to the relatively intense polarization component of the axially symmetric polarized laser. These results suggested that axially symmetric polarized lasers generate gamma rays with different polarization states. In the near future, a polarimeter of gamma rays will be constructed to investigate the spatial polarization distribution of gamma rays.

Award

TAIRA, Yoshitaka; Young Scientist Award of the Japanese Positron Science Society (2023).

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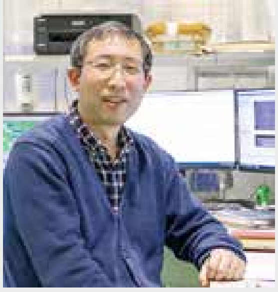
† CSC-IMS Scholarship Program

Novel Spin and Chiral Materials Science by Photoelectron Cinemato-Microspectroscopy

UVSOR Synchrotron Facility
Division of Advanced Solid State Physics



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Education

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

Professional Employment

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

Awards

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

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Keywords Photoelectron Spectroscopy, Momentum Microscope, Electronic Spin Structure

Imagine cherry blossom petals fluttering down. Under a uniform gravitational field, the slight asymmetry of the petals creates anisotropy in the airflow, causing the petals to rotate. Capturing the movement of this dynamic 3D-structure as a *cinema* is important for understanding the physics behind this.

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. Photoelectron momentum microscope (PMM) is an analyzer that can instantaneously image the behavior of electrons of material and device surfaces. PMM combines imaging-type photoelectron spectroscopy and microscopy techniques to visualize the electronic state (band dispersion, composition, and spin polarization) in reciprocal lattice space of a selected µm-sized area. We have constructed the world's first dual beamline (soft x-ray; SX and vacuum ultraviolet; VUV) PMM system at the IMS UVSOR synchrotron facility!

What we are currently very interested in is chiral phase transition phenomena, for example. The layered material TaS_2 exhibits an attractive behavior in which it undergoes a phase transition to a chiral structure at low temperatures and its electrical conductivity changes by two orders of magnitude. We succeeded in capturing a video of the hysteresis change in the valence band dispersion during this phase transition. The results serve as a benchmark experiment for *in situ* observation of material responses to various external fields.

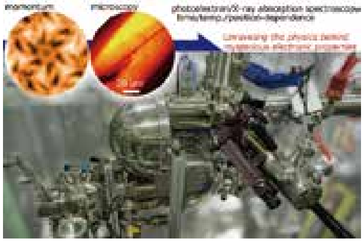

Figure 1. Photoelectron momentum microscope station at UVSOR synchrotron facility. Multimodal measurements hold the key to unlocking the mysteries of the electronic properties of materials.

Selected Publications

- K. Hagiwara, F. Matsui *et al.*, "Development of Dual-Beamline Photoelectron Momentum Microscopy for Valence Orbital Analysis," *J. Synchrotron Radiat.* **31**, 540 (2024).
- 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).
- F. Matsui and S. Suga, "Coupling of k_z-dispersing π Band with Surface Localized States in Graphite," *Phys. Rev. B* **105**, 23526 (2022).
- F. Matsui and H. Matsuda, "Projection-type Electron Spectroscopy Collimator Analyzer for Charged Particles and X-Ray Detections," *Rev. Sci. Instrum.* **92**, 073301 (2021).
- F. Matsui *et al.*, "Photoelectron Momentum Microscope at BL6U of UVSOR-III synchrotron," *Jpn. J. Appl. Phys.* **59**, 067001 (2020).

1. Visualization of Phase Transition and Phase Separation

The most distinctive advantage of PMM[1)] is its snapshot-style of measuring photoelectron constant energy intensity distribution pattern in real and reciprocal spaces. Recently, we succeeded in the development of on-the-fly scans for temperature-dependent Fermi surface and valence band measurements during phase transitions, taking advantage of the rapid acquisition (seconds to minutes) of photoelectron patterns.

1T-TaS$_2$, which exhibits various phase transitions in structural and electronic properties, has fascinated researchers for more than half a century. However, despite many angle-resolved photoelectron spectroscopy (ARPES) studies on 1T-TaS$_2$, the basic understanding of charge density wave (CDW) formation is far from a common consensus. As for the mechanism of the metal–insulator transition, the Mott insulator model, band insulator model, and one-dimensional metal model have been so far proposed.

In order to solve the mystery of CDW formation in 1T-TaS$_2$, we conducted the following photoemission measurements.[2)] (i) Band-dispersion mapping from selected µm-scale chiral CDW domains, (ii) characterization of 3D CDW nesting vectors by complete Brillouin-zone-dispersion measurements and (iii) on-the-fly observation of valence band and core-level photoelectron spectra during temperature changes.

Figure 2 shows a series of 1T-TaS$_2$ valence band cross sections scanned in 2D real space in the low-temperature CDW phase. Here, a domain boundary between two different twin domains is recognized. Typical areas of domains are tens to hundreds of µm^2. We exploited the microscopic capabilities of PMM to analyze the electronic structure of selected single domains. By measuring the valence band pattern during temperature change in real time, the hysteresis behavior of the phase transition was visualized in detail.

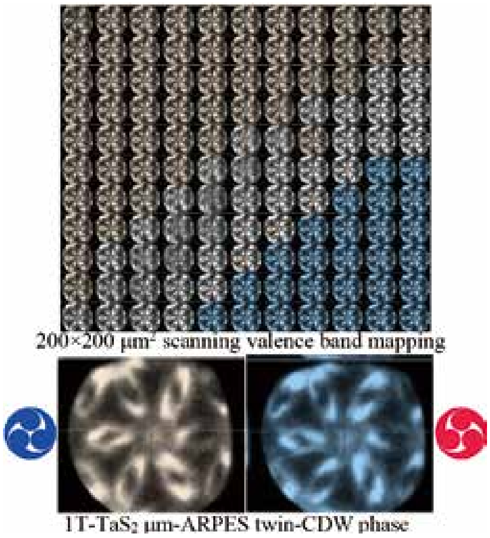

Figure 2. Valence band photoelectron patterns of 1T-TaS$_2$ surface in the low-temperature CDW phase. The field of view for the ARPES snapshot measurements was a few µm in diameter.

2. Analyzing Polarization of Atomic Orbitals and Electron Spins

The combination of PMM with synchrotron SX and VUV undulators paves the way for comprehensive characterization of atomic orbitals in the Fermi surface and valence band on the µm scale.[3)]

Figure 3 shows the 2D momentum (k_x, k_y) distribution of photoelectron intensity of the Au(111) at the Fermi level.[3)] Figures 3(a) and (b) show the 2D patterns measured using p-polarized SX light from BL6U, while s-polarized VUV light from BL7U is used in the case of Figures 3(c) and (d). In both conditions, the photoelectron pattern in the entire Brillouin Zone is covered. Shockley surface state centered at the Γ point as small circular contours (Figure 3(a)) is clearly observed with p-polarized excitation with splitting due to spin–orbit coupling (Figure 3(b)), but these features exhibit very weak intensity for normal incidence light (Figure 3(c)). The Shockley surface state mainly comprises 6s and 6p$_z$ orbitals. In the normal-incidence geometry, the transition-matrix element from the initial s and p$_z$ orbitals becomes 0 at the photoemission direction orthogonal to the excited electric vector (Figure 3(d)). The relationship between the orbital angular momentum and the effects of the transition matrix elements can be directly investigated using this normal incidence geometry.

Finally, our main goal is to employ these techniques with spin polarization sensitivity. We have just started obtaining spin-polarized valence band dispersion data for typical materials having spin polarized surface states.

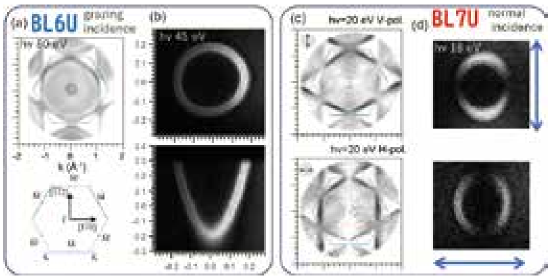

Figure 3. Fermi surface of Au(111) surface measured using grazing incident SX (a,b) and normal incident VUV (c,d) beam. (b,d) The Shockley surface state at the center is zoomed and analyzed. Parabolic band dispersion with splitting due to spin–orbit coupling, *i.e.* Rashba effect, is well resolved.

References

1) F. Matsui, S. Makita, H. Matsuda, T. Yano, E. Nakamura, K. Tanaka, S. Suga and S. Kera, *Jpn. J. Appl. Phys.* **59**, 067001 (2020).

2) 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, *Rev. Sci. Instrum.* **94**, 083701 (2023).

3) K. Hagiwara, E. Nakamura, S. Makita, S. Suga, S. Tanaka, S. Kera and F. Matsui, *J. Synchrotron Radiat.* **31**, 540 (2024).

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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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Division of Advanced Solid State Physics

Education

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

Professional Employment

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

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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 strucature 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 (Figure 1).

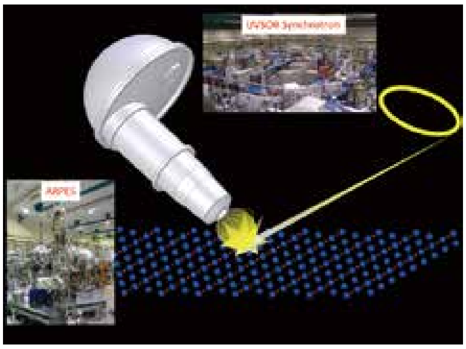

Figure 1.

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 $\mathrm{Bi_2Sr_2CaCu_2O_{8+\delta}}$ 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 $\mathrm{Ba_{1-\mathit{x}}K_\mathit{x}Fe_2As_2}$,” *Phys. Rev. B* **100**, 235135 (7 pages) (2019).

1. Evidence of Strong Violation from Fermi Arc Picture in Heavily Underdoped Bi2212

Understanding the complex nature of cuprate superconductors, especially the origin of their high superconducting transition temperature (T_c), is one of the greatest challenges in condensed matter physics. An early experimental observation in this regard is the famous Uemura plot. It shows that the T_c in the high-T_c cuprate superconductors is correlated with the muon spin relaxation rate σ_0 that is proportional to the superfluid density divided by the effective mass ($\sigma_0 \propto n_s/m^*$). This relation holds not only for all high-T_c cuprate superconductors but also for many other superconductors. While there have been various attempts at a theoretical explanation of the Uemura relation, a connection to other experimentally probed properties of cuprates is still lacking.

ARPES is a powerful experimental technique, directly measuring 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, especially the superconducting (SC) gap. Indeed, the first direct experimental evidence of *d*-wave symmetry of the SC gap has been reported by ARPES, where the SC gap follows the d-wave order parameter $\Delta(k) = \Delta_0(\cos k_x a - \cos k_y a)/2$, here a is the lattice constant. In ARPES field, T_c of cuprates has been believed to be explained by so-called "Fermi arc" picture. According to this picture, Fermi arc is a region where the SC gap closes above T_c in the momentum space and the "effective SC gap" Δ_{SC} can be defined by the gap magnitude at the edge of the Fermi arc as shown in Figure 2 (a). Since Δ_{SC} and T_c show linear correlation among different doping and even among different families of cuprates as shown in Figure 2 (d), this picture is well accepted as a phenomenological model to explain T_c in cuprates.

Recently, we have studied heavily underdoped Bi2212, whose T_c is only 30 K but still high-T_c, and found strong violation from the Fermi arc picture. In this doping, there is almost no temperature dependence of the SC gap across T_c as shown in Figure 2 (b)–(c). Therefore, Δ_{SC} should be extremely small (~1 meV) and should not be enough to explain 30 K of T_c. To understand the origin of the superconductivity in this doping, we have performed new way of ARPES analysis, where information of the spectral weight difference across T_c can be estimated. Interestingly, this new analysis shows that the doping dependence of the spectral weight along the Fermi surface quantitatively scales with the superfluid density (and T_c) for a wide range of carrier concentrations (not shown). Our new results represent the first evidence showing the close relationship between the superfluid density and T_c from ARPES. Our results also show that the whole Fermi surface contributes to superconductivity and the superfluid density can be more important than the SC gap. This is completely new idea to understand high-T_c superconductivity from ARPES.

Since it is well known that ARPES intensity strongly depends on the matrix element, which can be changed by measurement geometry, polarization, photon energy and so on, our spectral weight analysis should be affected by the measurement conditions. To make sure that our observation is universal, we have to perform many ARPES studies by changing measurement geometry, polarization and photon energy. To perform measurements with different measurement geometry, a low temperature 6-axis manipulator is necessary, since measurement geometry should be able to be changed to study the same sample surface with different geometries. We are using our home-made 6-axis manipulator which is one of the lowest temperature 6-axis manipulators in the world to complete this study.

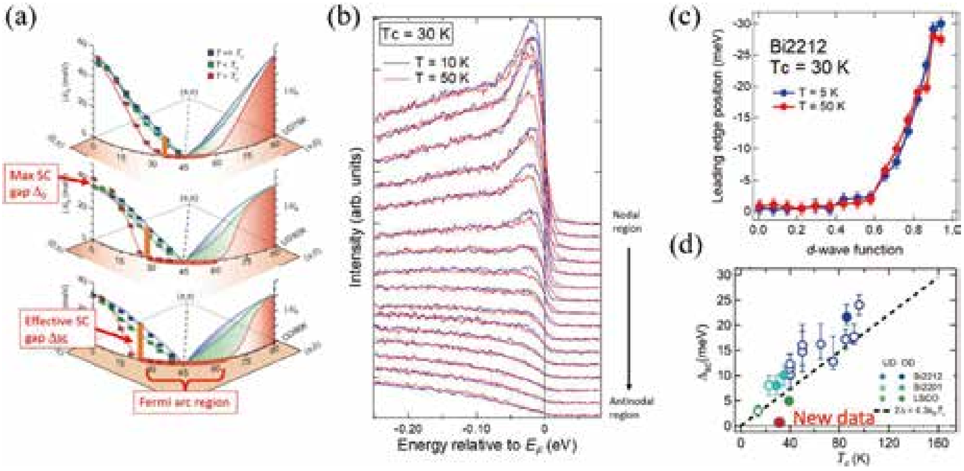

Figure 2. (a) Temperature and doping dependence of SC gap in cuprates and Fermi arc picture. (b) Temperature dependence of ARPES spectra along Fermi surface of heavily underdoped Bi2212. (c) Temperature dependence of SC gap obtained by the leading-edge position. (d) Comparison of the effective SC gap in different families of cuprates including current study.

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† carrying out graduate research on Cooperative Education Program of IMS with Southern University of Science and Technology, China

Soft X-Ray Spectro-Microscopy and Scattering for Life Science—beyond Organelle Mapping

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

ARAKI, Tohru
Senior Researcher

Beside running the user programs using the BL4U at the UVSOR, which is a STXM (Scanning Transmission X-ray Microscopy) beamline. STXM is one of the x-ray based spectro-microscopy techniques providing us a label-free chemical mapping for a wide variety of sciences like energy materials, environmental and earth science, and many in the industrial science as well. I want to push this technique applying for a life science, especially with soft x-rays, which has been studied by mainly hard x-ray regimes such as protein crystallography and small angle scattering at the synchrotron radiation facilities so far.

One of the most effective soft X-ray microscopes, the so-called soft X-ray tomography (SXT), can offer unparalleled 3D organelle mapping of entire biological cells larger than 10 micrometres. The SXT uses a fixed photon energy, just before the O K-edge absorption at 520 eV, to observe the hydrated sample using the “water window” energy region. This allows us to see the absorption contrast of the biological sample, which comes from the carbon and nitrogen content inside them. The distinctive LAC (linear absorption coefficient) at 520 eV of each organelle enables the delineation of these structures. I intend to extend this analysis by employing the full potential of the SXAS (soft X-ray absorption spectroscopy) technique, which allows for the utilisation of a range of photon energies. The utilisation of SXAS-based spectro-microscopy and spectroscopy-scattering enables the differentiation of analogous organelles and oxidation states of metal/ion within cellular structures. In order to establish this methodology, two key steps must be taken: Firstly, a basic spectral interpretation of organelles must be conducted, and secondly, the sample preparation and specimen environment must be optimised. It is of particular importance to refrain from any modifications of the samples and to maintain the native states of the cells, including the loss of metals or ions, throughout both the sample preparation and the data collection process, in order to prevent radiation damage.

In the current year, I conducted a collaborative research project on *Ramazzottius varieornatus*, a tardigrade that is renowned for its anhydrobiotic capabilities, enabling it to survive in harsh, arid environments. My colleague prepared the thin section samples embedded in resin for a comparative morphometric analysis of their microscopic anatomy using both scanning electron microscopy (SEM) and STXM. Figure 1 (a) illustrates a representative optical microscope image. In order to enhance contrast, a staining agent must be applied to the sample prior to conducting a SEM analysis. However, it offers a higher spatial resolution than other techniques. In comparison, STXM is a label-free method that provides a lower spatial resolution, yet still achieves a reasonable resolution of tens of nanometres. Figure 1 (b) depicts a STXM transmission raw image collected at the protein characteristic photon energy. Figure 1 (c) presents a RGB composite map, comprising the three STXM images acquired at distinct photon energies. The images provide insight into the structural and compositional characteristics of different organelles and biological molecules.

These results prove the STXM’s capabilities. However, there is still work to be done to fully understand the images and extract all the information they contain. One possible approach is the cryogenically vitreous ice-covered sample prepared by the plunge-freeze method. This is currently regarded as the gold standard for such sample preparation in the fields of Cryo-EM and Cryo-SXT.

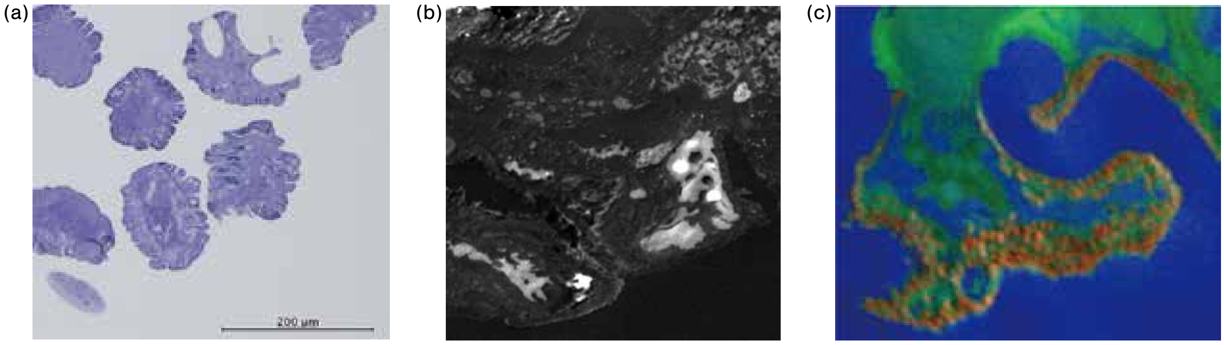

Figure 1. (a) The optical microscope images of the stained tardigrade thin section tissue samples. (b) The STXM transmission image of the tardigrade thin section tissue sample. (30 × 30 µm). (c) The RGB composite map of the tardigrade samples obtained by the STXM images at the three different photon energies. (16 × 14 µm).

Development of Resonant Soft X-Ray Scattering Spectroscopy for Soft Matter

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

IWAYAMA, Hiroshi
Senior Researcher

Soft matter, such as liquid-crystal and polymer, is essential in various technological applications. Interesting soft matter properties come from their mesoscopic structures and dynamics. Small-angle X-ray and Neutron Scattering (SAXS/SANS) are powerful tools for revealing mesoscopic structures. However, since SAXS is sensitive to modifications of electron densities, their contrast difference between similar chemical species is weak.

Resonant soft X-ray scattering (RSoXS) is an emerging characterization technique for mesoscopic structural analysis. Soft matter molecules mainly consist of light elements such as carbon, nitrogen, and oxygen, whose X-rays resonant energies are in the soft X-ray region. Resonant scattering is strongly sensitive to its element, chemical species and the molecular alignment relative to polarization vector. In particular, molecular alignment sensitivity enables us to investigate twisted structure of soft matter in mesoscopic scale.

This year, we developed a new RSoXS spectrometer. The feature of the new spectrometer is that a soft X-ray detector can be rotated along a scattering angle in vacuum. Compared to X-rays used for SAXS measurements, wavelengths of soft X-rays are much longer. Since a scattering vector, q, is proportional to $\sin(\theta)/\lambda$, where 2θ and λ are scattering angle and a wavelength of soft X-ray, a scattering angle becomes wider compared to SAXS. For examples, to analyze the structure from 5 nm to 500 nm, we need to measure the scattering angle 2θ from 0.5 to 60 degrees. To achieve this wide scattering angle measurement, we developed a new RSoXS spectrometer, where a soft X-ray detector can be rotated along the 2θ in the vacuum chamber, as shown in Figure 1.

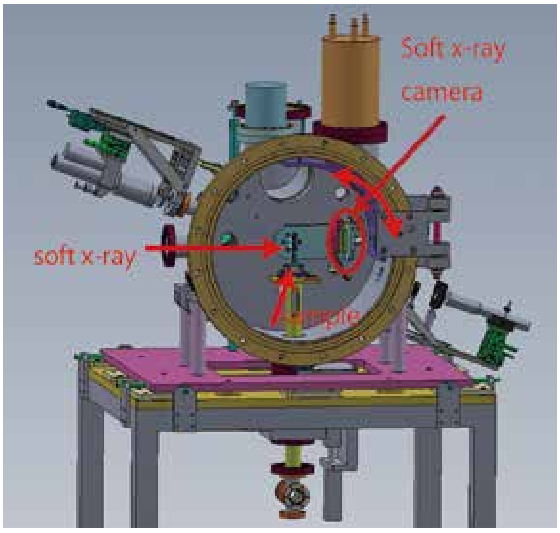

Figure 1. Schematic draw of a new RSoXS spectrometer.

For the performance evaluation, we investigated twisted bend (TB) liquid-crystal molecules with the new RSoXS spectrometer. The TB liquid-crystal phase is the newest nematic phase, only identified in 2011. There are many outstanding mysteries about the nature of its nanoscale organization and behavior. Our collaborators elucidate how the number of monomer units in a linear TB oligomer influences the structure of its nanoscale helix, an important TB phase structure–property relationship.$^{1)}$ Figures 2 show a schematic view of TB liquid-crystal molecules and a scattering image at a photon energy of 285 eV ($\lambda \sim 4.3$ nm), which is corresponding to carbon K-edge resonance. We find a sharp diffraction ring corresponding to the half-pitch periodicity of the helical filaments ($d \sim 128$ nm ($q \sim 0.005$ Å^{-1})). We also confirmed that the detector can be rotated along 2θ and we can measure scattering angles from 0 to 60 degrees. We started to analyze molecular orientation orders of liquid-crystal molecules and crosslinked structures of polymers with the spectrometer.

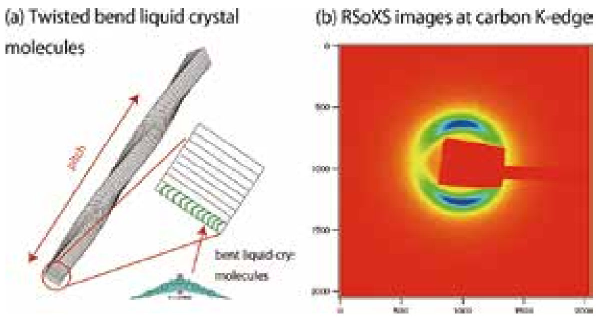

Figure 2. (a) Schematic view of twisted bend liquid crystal molecules. (b) Scattering image at a photon energy of 285 eV.

Reference

1) Y. Takanishi, F. Araoka and H. Iwayama, *RSC Adv.* **12**, 29346 (2022).

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

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

NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) observes local structures of liquids with different light elements. We have developed liquid cells and devices with precise absorbance control and observed several chemical processes in solution by using *operando* XAS.[1,2] In this year, we investigated cononsolvency mechanism of polymer solutions[3] and isolated water molecules in aqueous acetonitrile solutions.[4]

1. Mechanism of Polymer Cononsolvency Explored via Oxygen K-Edge XAS

The cononsolvency of poly(*N*-isopropylacrylamide) (PNIPAM), dissolving in pure methanol and water but being insoluble in aqueous methanol solutions, was investigate by O K-edge XAS.[3] The cononsolvency emerges from the aggregation of PNIPAM with methanol clusters, leading to the collapse of the hydrophobic hydration of PNIPAM.

2. Probing Isolated Water Molecules in Aqueous Acetonitrile Solutions

O K-edge XAS of aqueous acetonitrile solutions exhibited a sharp peak around 537 eV, which was like that of water vapor and was not observed in liquid water. The inner-shell calculations revealed that the sharp peak profiles were derived not from water clusters but from isolated water molecules surrounded by acetonitrile molecules.[4] It means that the isolated water molecules in aqueous acetonitrile solutions can be analyzed using O K-edge XAS, which separates the contributions of small water clusters.

References

1) M. Nagasaka and N. Kosugi, *Chem. Lett.* **50**, 956–964 (2021).
2) M. Nagasaka, H. Yuzawa and N. Kosugi, *Anal. Sci.* **36**, 95–105 (2020).
3) M. Nagasaka, F. Kumaki, Y. Yao, J. Adachi and K. Mochizuki, *Phys. Chem. Chem. Phys.* **26**, 13634–13638 (2024).
4) M. Nagasaka, *J. Phys. Chem. Lett.* **15**, 5165–5170 (2024).

Visiting Professors

Visiting Professor

FUKUHARA, Takeshi *(from RIKEN)*

Quantum Gas Microscope for Rb-85 Atoms with a Tunable Atom–Atom Interaction

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. An “artificial” quantum spin system described by the spin-1/2 Heisenberg model can be realized by using ultracold bosonic atoms in optical lattices. In this realization, the anisotropy of the spin–spin interaction can be controlled by changing the interatomic interaction via a Feshbach resonance. Although, for quantum gas microscope experiments, rubidium-87 atoms have been utilized, in this study we performed experiments using rubidium-85 atoms which have a Feshbach resonance at a magnetic field of $B \sim 155$ Gauss. We succeeded in observing rubidium-85 atoms in a triangular lattice at the single-atom level. We also confirmed the Feshbach resonance through atom loss spectroscopy. This system is expected to be used for a quantum simulation of frustrated magnets that follow the spin-1/2 triangular-lattice antiferromagnetic Heisenberg model.

Visiting Professor

MATSUSHITA, Tomohiro *(from Nara Institute of Science and Technology)*

Development of Analysis Methods for Photoelectron Momentum Microscope

The photoelectron momentum microscope introduced at UVSOR is a highly powerful tool for observing the composition and electronic structure of samples using photoelectron spectroscopy. This pioneering analytical apparatus enables the observation of Fermi surfaces and band structures in various systems, including surface atomic sites, thin films, interfaces, surface adsorbates, and polycrystalline materials. Currently, we are developing two methods for analyzing the data. First, the observed photoelectron intensities from valence band depend on the transition probabilities of photoelectrons, resulting in modulation of these intensities. To calculate this intensity modulation, we are developing an analysis tool based on the first-principles calculation code OpenMX. Second, we are utilizing information technology to process data and extract hidden information. Specifically, we are applying principal component analysis to the data obtained from this instrument to visualize the behavior of phase transitions.

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. Whereas current organic semiconductor electronics are mostly composed of polycrystalline or amorphous molecular solids, our group has been working on single-crystalline organic semiconductor solids and their heterojunctions formed by “molecular beam epitaxy” techniques to pursue potential applications as flexible and efficient electronic devices. Recently, we discovered as a collaborative work with an IMS group that an n-type molecule C_{60} forms well-ordered epitaxial heterojunctions on the single-crystal surface of a high-mobility p-type molecule dinaphthothienothiophene (DNTT). This work was selected as one of the “Spotlight2023” articles. In addition, our group is also engaged in exploration into the fundamental properties of molecular single-crystal materials themselves, and have published collaborative works with the UVSOR facility on vibrational properties of the single-crystals of DNTT and pentacene.

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 of molecular materials. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells, and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

YOKOYAMA, Toshihiko
Professor
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Education

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

Professional Employment

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

Member
Research Assistant Professor
KURAHASHI, Naoya
MAEJIMA, Naoyuki
Graduate Student
IZUMI, Yoshiki
Secretary
KURITA, Yoshiko

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. 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, the apparatus moved to BL46XU and is used for more general chemical reactions on heterogeneous catalysts and electrochemical cells such as CO_2 reduction.

The third subject is applications of the x-ray absorption fine structure (XAFS) spectroscopy, soft x-ray emission spectroscopy, and angle-resolved ultraviolet photoelectron spectroscopy for functional materials. These investigations include femto- and picosecond time resolved XAFS measurements using x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Conventional temperature dependent EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional alloy 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. Local Thermal Expansion of Co-Containing Invar Alloys1)

Low thermal expansion materials are quite attractive from the viewpoints of both fundamental science and industrial technology. FeNi invar alloys are quite familiar and have been applied to precision equipment as telescope, microscope, and nanodevice, and also been employed as core cables of electric high-voltage power lines to avoid sagging due to heat on high current conduction. Recently, Fujii *et al.* developed a new stainless invar alloy, which is employed for the cryogenic infrared space telescope in National Astronomical Observatory. In this work, we measured and analyzed EXAFS spectra of Co-containing invar alloys of this newly developed stainless invar, together with Kovar $Fe_{53}Co_{17}Ni_{29}X_1$ for comparison. We will focus our attention on how Co plays a role in the invar effect from the local structure viewpoint, which is often different from the macroscopic points of view.

Two stainless invar foils with 10 μm thickness were prepared and the elemental compositions are found to be $Fe_{38.8}Co_{50.1}Cr_{9.2}Ni_{1.9}$ and $Fe_{37.8}Co_{51.3}Cr_{9.0}Ni_{1.9}$ by the x-ray fluorescence spectra. Cr, Fe, Co, and Ni K-edge EXAFS spectra of commercially available Kovar (10 μm) and the stainless invar foils were recorded with the transmission mode in BL9C of Photon Factory, High Energy Accelerator Research Organization (KEK-PF) at 30–300 K using a He gas-circulating refrigerator installed at the beamline. The lattice thermal expansion coefficients of Kovar and stainless invar were measured by the laboratory dilatometer. We have also recorded Cr, Fe and Ni K-edge EXAFS of FeNi invar alloys $Fe_{64}Ni_{36}$, $Fe_{58}Ni_{42}$, and $Fe_{55}Ni_{45}$, stainless steel SUS304 ($Cr_{18.09}Fe_{71.98}Ni_{9.07}X_{0.86}$) and the Ni spanC Elinvar alloy ($Cr_{5.49}Fe_{49.66}Ni_{42.38}Ti_{2.47}$).

Temperature dependent EXAFS spectra were analyzed with the standard method including the third-order cumulant to yield thermal expansion for the first-nearest neighbor (NN) shells correctly. Since the first-NN shell includes different atom pair contributions, the analysis yields only the average distances. Nevertheless, assuming that the interatomic distance is given as a sum of the atomic radii, all the interatomic distances are evaluated as long as all the corresponding EXAFS spectra provide the average distances. Figure 1 shows the thermal expansion at 200 K thus obtained for the interatomic distances and the lattice constant as a function of corresponding distances. Since the two stainless invar alloys exhibit essentially the same results and the average values are given here. In FeNi invar, the Fe–Fe pair shows significant reduction of the interatomic distance and thermal expansion going from 42 and 45 invar to 36 invar, while the Ni–Ni one exhibits little suppression of thermal expansion and negligible distance contraction. This clearly implies that Fe exclusively contributes to the invar effect in $Fe_{64}Ni_{36}$. In stainless invar in Figure 1(b), it is found that thermal expansions of Fe–Fe, Fe–Co, and Co–Co are significantly smaller than in Kovar, associated with shortening of the corresponding interatomic distances. This implies a much more significant invar effect on Co as well as Fe in stainless invar, while the invar effect on Co is negligibly small in Kovar. The path-integral effective classical potential simulations exhibit qualitative agreement with this finding, indicating that the Co magnetization is more noticeably suppressed with a temperature rise in stainless invar, because of a smaller lattice constant and interatomic distances and also of the presence of Cr in stainless invar, both of which favor antiferromagnetic coupling. The present study clearly demonstrates importance of local structure point of view to understand detailed low thermal expansion mechanism, in which microscopic local thermal expansion noticeably differs from macroscopic lattice thermal expansion.

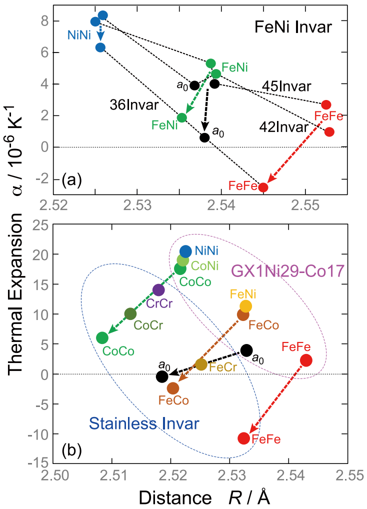

Figure 1. Thermal expansion coefficients α (10^{-6} K^{-1}) at 200 K for the first-NN interatomic distances determined by EXAFS and the lattice constant a_0 versus corresponding distances of (a) FeNi invar and (b) Kovar and stainless invar.

2. Synchrotron Radiation Based Spectroscopic Characterization of Functional Materials

In FY2023, we have been investigating following research subjects. The first one is continuous collaboration with Prof. Toshio Miyamachi in Nagoya University using high-field, low-temperature and ultrahigh-vacuum XMCD system installed at BL4B in UVSOR-III. Interesting magnetic properties such as magnetic anisotropy of ferromagnetic ultrathin films decorated organic molecules are being studied. Second, AP-HAXPES investigations are being conducted for working electrochemical cells on CO_2 reduction. This is a collaboration with Prof. T. Koitaya in Kyoto University and Dr. Y. Takagi in JASRI (both were previous assistant professors in this research group in IMS). Third, research assistant professor Dr. N. Kurahashi is studying peculiar water motion in Nafion solid electrolyte that shows abrupt phase transformation around 15°, using soft x-ray absorption and emission spectroscopy and AP-HAXPES. Fourth, research assistant professor Dr. N. Maejima is investigating a novel 2-dimensional Dirac-cone-like blue phosphorene using angle-resolved photoelectron spectroscopy and low-energy positron diffraction.

Reference

1) T. Yokoyama, H. T. Fujii, S. Matsumura, N. Sakaguchi, N. Kurahashi and N. Maejima, *Phys. Rev. Mater.* **8**, 083603 (2024).

Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

Department of Materials Molecular Science
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SUGIMOTO, Toshiki
Associate Professor
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Education

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

Professional Employment

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

Awards

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

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Technical Support Staff
SAKAKIBARA, Takayuki

Secretary
SHIMURA, Maki

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

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

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

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

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. Positive and Negative Impacts of Interfacial Hydrogen Bonds on Photocatalytic Hydrogen Evolution[1)]

Hydrogen production via photocatalytic water splitting is a sustainable solution for next-generation energy by utilizing light energy at room temperature. However, the design of innovative photocatalysts remains a challenge due to a limited molecular-level understanding of interfacial water molecules and their hydrogen bond networks. Unveiling the physicochemical properties of these interfacial water molecules is critical to optimizing photocatalytic efficiency and achieving breakthroughs in sustainable hydrogen production.[2)]

We have comprehensively investigated the impact of interfacial H-bond networks using various TiO_2 photocatalysts and uncovered a crucial role of interfacial H-bond structure/dynamics and optimal interfacial water environment for H_2 evolution. We controlled the thickness of adsorbed water from sub-monolayer to multilayers by precisely adjusting water vapor pressure. With this approach, we succeeded in directly demonstrating the correlation between H_2 formation rate and the microscopic structure of H-bond networks using real-time mass spectrometry and infrared absorption spectroscopy. Regardless of the crystalline structure of the TiO_2 photocatalyst, we observed a linear increase in H_2 formation rate with water adsorption up to three layers, indicating that reactive water molecules are present not only in the first adsorbed layer but also in several overlying layers (Figure 1). However, the H_2 formation rate turned to decrease dramatically when more than three layers of water covered the TiO_2 surface (Figure 1). In this situation, infrared spectra clearly indicated two distinct types of adsorbed water on the TiO_2 surface: Interfacial water and liquid-like water. Due to many-body interactions among adsorbed water molecules, the liquid-like water adsorbed in more than three layers led to strengthening of interfacial H-bond, which hinder interfacial proton-coupled hole transfer and drastically decreased the H_2 formation rate. Based on these microscopic insights, their study suggests that depositing three water layers in a water vapor environment is optimal for photocatalytic hydrogen evolution. These findings open new avenues for the molecular-level design and engineering of interfacial water toward the development of more innovative photocatalytic systems for next-generation renewable energy production.

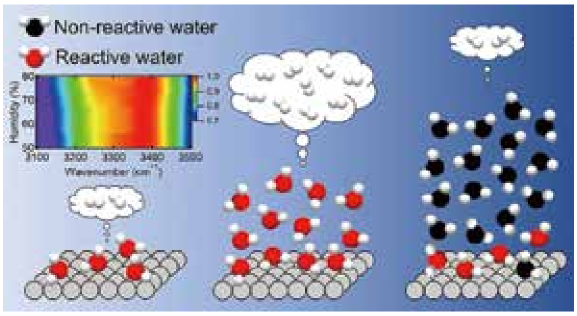

Figure 2. Identifying the reaction conditions that maximize catalytic activity in photocatalytic hydrogen evolution under water vapor atmospheres.

2. Direct Operando Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides[3)]

Understanding of reactive electron species and active reaction sites on photocatalytic reduction reaction are vital for designing and manufacturing innovative catalysts with improved evolution activity of hydrogen as sustainable energy carrier.

We succeeded in significantly suppressing the signals derived from thermally excited electrons and observing the reactive photogenerated electrons contributing to the photocatalytic hydrogen evolution. Such innovation was achieved by a new method based on synchronization of the millisecond periodic excitations of photocatalysts with a Michelson interferometer used for FT–IR spectroscopy.[4)] This demonstration was achieved for metal-loaded oxide photocatalysts under steam methane reforming and water splitting conditions. Although it has long been conventionally believed that loaded metal cocatalysts function as sinks for reactive photogenerated electrons and active sites for reduction reactions, we found that the free electron species in the metal cocatalysts were not directly involved in the photocatalytic reduction reaction. Alternatively, the electrons shallowly trapped in the in-gap states of oxides contributed to enhancing the hydrogen evolution rate upon the loading of metal cocatalysts. The electron abundance in the in-gap states, especially metal-induced semiconductor surface states, was clearly correlated to the reaction activity, suggesting that such metal-induced semiconductor surface states formed in the periphery of the metal cocatalyst play key roles in the photocatalytic hydrogen evolution. These microscopic insights shift a paradigm on the traditionally believed role of metal cocatalysts in photocatalysis and provide a fundamental basis for rational design of the metal/oxide complex interfaces.

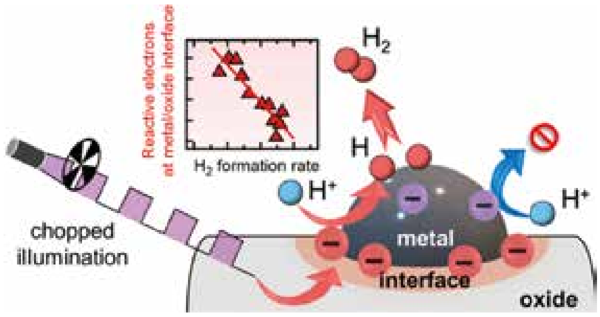

Figure 3. Unveiling actual role of metal cocatalysts. Electrons in cocatalyst periphery drive photocatalytic hydrogen evolution.

References

1) Z. Lin, H. Saito, H. Sato and T. Sugimoto, *J. Am. Chem. Soc.* **146**, 22276 (2024).
2) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
3) H. Sato and T. Sugimoto, *J. Am. Chem. Soc.* **146**, 24800 (2024).
4) H. Sato and T. Sugimoto, *Vac. Surf. Sci.* **66**, 580 (2020).

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
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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.

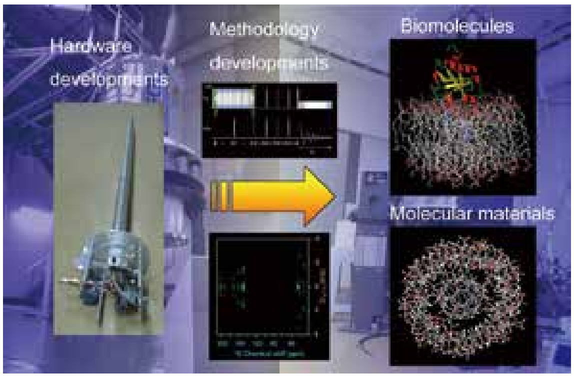

Figure 1. Outline of our studies.

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. Developments of Solid-State-NMR Techniques

Unlike solution NMR, it is not easy to achieve high resolution ^{1}H NMR spectra in solid-state NMR, since ^{1}H homonuclear dipolar couplings broaden the signals in rigid organic solids. In order to achieve ^{1}H high resolution spectra, ^{1}H homonuclear dipolar couplings must be removed by application of either sufficiently high magic angle spinning (MAS) or combination of MAS at moderate speed with multiple pulse (MP). Recent developments of fast MAS techniques enabled to remove ^{1}H homonuclear dipolar couplings efficiently with expense of sensitivity reduction. In the conventional latter approach, the MP average spin part of ^{1}H homonuclear dipolar coupling Hamiltonian at time scale shorter than MAS period. Using a high power radio frequency field, it is possible to achieve short cycle time for MP and enable combination of fast MAS without interferences between spin and spatial parts.

We have developed new MP sequences enabling us to achieve efficient ^{1}H homonuclear dipolar decoupling by removing high order correction terms. Those performances are theoretically evaluated and partly tested experimentally. The project is on the way.

In addition, we have developed new spectral editing pulse sequences which enable the selection of ^{13}C signals depending on the number of directly attached ^{1}H. The techniques are evaluated theoretically. This project is also on the way.

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

We have been working on developments of totally original solid-state NMR probes for a couple of years. The probe had been successfully built using originally designed parts except for a spinning module for 400MHz NMR. Then, we have been working on developments of original sample spinning modules for MAS solid-state NMR probes which are fully compatible with Bruker spectrometers and commercial sample tubes. We started the design of a spinning module for a standard 4.0 mm sample tube for Bruker. After 3 times of version up, our original spinning module exceeded the spinning performance of the commercial one from Bruker.

In order to achieve further improvements for our original spinning module, further developments are currently underway together with the development of original sample tubes. The spinning module is under designed in order to realize installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.

We have also started the development of the original spinning module for a 2.5 mm sample tube.

3. Characterization of Synthetic Molecules by Solid-State NMR

Solid-state NMR is one of the efficient techniques to characterize amorphous samples such as synthetic molecules. We are working on the characterization of new synthetic molecules categorized to covalent organic frameworks (COFs) which are designed by Associate Prof. Segawa group in IMS. Tentative ^{13}C solid-state NMR signal assignments had been successfully achieved. The obtained results sufficiently prove the achievement of the aimed molecular form of COFs for the sample. This project is also on the way.

Development of New Methods for Analyzing Surfaces and Interfaces Using Scanning Probe Microscopy

Instrument Center

MINATO, Taketoshi
Senior Researcher

Analytical methods based on surface and interface sciences provide crucial information for understanding physical properties and reaction mechanisms with high precision. Scanning probe microscopy (SPM) enables the analysis of geometric structures, mechanical properties, electronic properties, magnetic properties, and reaction mechanisms at surfaces and interfaces with extremely high resolution and sensitivity. We have applied SPM to energy conversion systems, such as rechargeable batteries.[1,2)]

In applying SPM to analyze surface and interface phenomena, it is essential to extract meaningful information from the data. However, the characteristics of SPM data can often be challenging to interpret. To address this, we have developed a new method to recognize specific structures and extract positional correlations in local structures from experimentally obtained SPM data. We have demonstrated that this method is applicable to mirror structures (Figure 1) and molecules adsorbed on metal surfaces, revealing specific characteristics in the positional correlations of molecular adsorption.[3)]

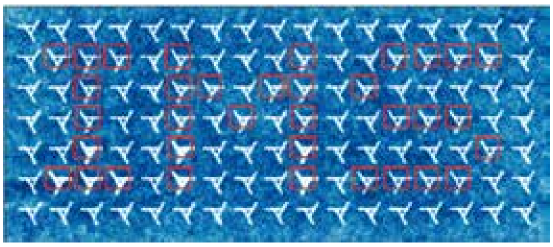

Figure 1. Recognition results for mirror structures in the scanning probe microscopy image. The red squares indicate the locations where specific structures were identified.[3)] © 2024, *Appl. Phys. Express*, CC By 4.0.

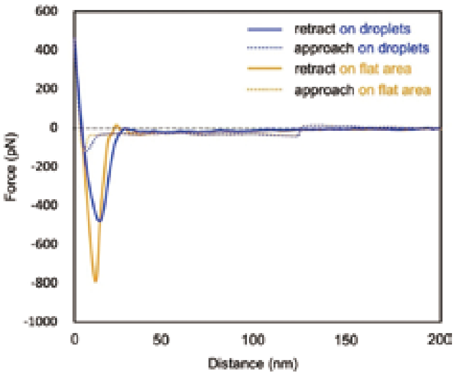

Figure 2. Force curves obtained from peak force tapping measurements at 80% humidity. The average of 10 force curves was acquired on nanometer-sized water droplets (blue) and on flat areas (orange), respectively. The dotted curves represent the approach curves, while the solid curves represent the retract curves.[4)] © 2024, *Sci. Rep.*, CC By 4.0.

We have also developed methods to analyze new physical properties of water. The wetting phenomenon of solid surfaces by water is common in everyday life, yet its detailed mechanisms remain not fully understood. Previous research suggested that as humidity increases, water molecules adsorb uniformly, leading to the formation of a water film. However, the latest studies using nonlinear spectroscopy have shown that water adsorption at low humidity is non-uniform. We have developed an experimental system that directly observes the microscopic wetting behavior on glass surfaces under different humidity levels. By using atomic force microscopy, we achieved the clarification of the change of adhesive force in nano-droplet of water.[4)]

Additionally, we have developed an experimental system to study the physical properties of ice in liquid. While detailed studies of ice surfaces under ultra-high vacuum conditions have been reported, their true nature in liquid has not been fully clarified. We successfully observed atomically flat ice surfaces in alcohol and demonstrated changes in surface structure due to reactions with the alcohols.[5)]

References

1) T. Minato and T. Abe, *Prog. Surf. Sci.* **92**, 240–280 (2017).
2) T. Minato, K.-i. Umeda, K. Kobayashi, Y. Araki, H. Konishi, Z. Ogumi, T. Abe, H. Onishi and H. Yamada, *Jpn. J. Appl. Phys. (Review)* **60**, SE0806 (2021).
3) S. Tsubokura, S. Kawano, Y. Imai, T. Ueda, K.-i. Nakamoto, H. Noma, H. Hioki and T. Minato, *Appl. Phys. Express* **17**, 035003 (2024).
4) Y. Araki, T. Minato and T. Arai, *Sci. Rep.* **14**, 10693 (2024).
5) R. Yanagisawa, T. Ueda, K.-i. Nakamoto, Z. Lu, H. Onishi and T. Minato, *J. Chem. Phys.* **161**, 024702 (2024).

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 18%. 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)*

Pulse EPR Study of Photo-Induced Paramagnetic Centers in Solid Electrolyte $BaZr_{1-x}M_xO_3$ (M = Sc, Y)

Barium zirconate $BaZrO_3$ doped with trivalent metal ions (M = Sc, Y) is a promising candidate for solid electrolytes for proton transport in fuel cells. The oxygen vacancy is noted to be a key structure for accepting hydroxyl groups and transferring protons via the Grotthus Mechanism. However, it has been challenging to investigate the local structure of oxygen vacancies using conventional methods in the ion transport field. We found that ultraviolet (UV) irradiation induces paramagnetic centers, so-called F-centers, *i.e.* electrons bound to oxygen vacancies. Then, we can apply well-established electron paramagnetic resonance (EPR) techniques to this system to elucidate the fine structure through the magnetic interactions. We performed time-domain EPR measurements under UV light irradiation at cryogenic temperatures and investigated the shape of EPR spectrum, the spin multiplicity of the signal, and the hyperfine structure buried in the broadened spectral width. Based on the results that depend on the doped ion species and hydroxyl contents, we clarify the local structure in conjunction with EPR simulations.

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 three-dimensional complex structures. Interdisciplinary alliances in this department aim to create new basic concepts for the molecular and energy conversion through the fundamental science conducted at each division.

Bioinorganic Chemistry of Metalloproteins Responsible for Metal Homeostasis and Signal Sensing

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

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1982 B.S. Tokyo Institute of Technology
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Professional Employment

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

Member
Secretary
NOMURA, Junko
KAWAGUCHI, Ritsuko

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

- H. Matsuura, N. Sakai, S. Toma-Fukai, N. Muraki, K. Hayama, H. Kamikubo, S. Aono, Y. Kawano, M. Yamamoto and K. Hirata, “Elucidating Polymorphs of Crystal Structures with Intensity-Based Hierarchical Clustering Analysis on Multiple Diffraction Datasets,” *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **79**, 909–924 (2023).
- 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, K. Ishii, S. Uchiyama, S. G. Itoh, H. Okumura and S. Aono, “Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase,” *Commun. Biol.* **2**, 385 (12 pages) (2019).

1. Structural and Functional Analysis of Heme-Based Oxygen Sensor Protein HemAT

Aerotaxis is a typical biological signal transduction system that consists of a signal transducer protein (MCP), CheA, CheY, and other Che proteins. Signal transducer proteins, sometimes called as MCPs (methyl-accepting chemotoxis proteins), bind a repellant or attractant in their sensor domain. Many chemical and physical stimuli act as a repellant or attractant, among which molecular oxygen is a typical gaseous signaling molecule. HemAT is a MCP responsible for aerotaxis control, which consists of two domains, the sensor domain and the signaling domain. Though the sensor domain of HemAT shows structural homology to myoglobin, it has a different heme environmental structure in the distal heme pocket from myoglobin. In the case of myoglobin, a distal His forms a hydrogen bond with the heme-bound oxygen to stabilize the heme-oxygen complex. However, there is no distal His in HemAT, in which a Thr is involved in the formation of a hydrogen bonding network upon oxygen binding to HemAT.

In this work, we have studied the molecular mechanisms of O_2 sensing and signal transduction of HemAT and HemAT/CheA/CheW complex based on the results of X-ray crystallography and cryo-electron microscopy (cyro-EM). We have determined the crystal structures of ferric-, ferrous (deoxy)-, and O_2-bound (oxy)-forms of the sensor domain of HemAT from Bacillus smithii (BsmHemAT) (Figure 1). We will discuss the molecular mechanisms of O_2 sensing of HemAT by comparing these structures. We have also carried out cryo-EM single particle analysis to determine the structure of HemAT/CheA/CheW complex, which revealed that BsmHemAT, CheA, and CheW formed the complex in 2:1:1 ratio.

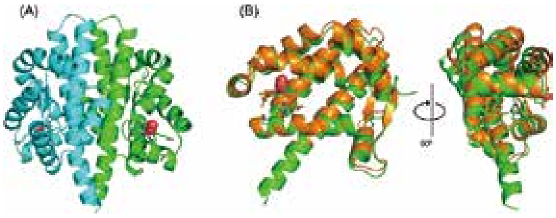

Figure 1. (A) The overall structure of the sensor domain in O_2-bound form. (B) The structural comparison of O_2-bound (green) and reduced (orange) forms of HemAT.

2. CO Biosynthesis for the Construction of the Active Site in [NiFe]-Hydrogease

Hydrogenase, an enzyme that catalyzes the oxidation of hydrogen gas and the reduction of protons, plays a central role in hydrogen metabolism in bacteria and other microorganisms. Recently, it is also expected to be utilized as a catalyst for fuel cells. There are three types of hydrogenases classified based on the structure of their active centers: [NiFe]-, [FeFe]-, and [Fe]-hydrogenases. In all cases, carbon monoxide (CO) is coordinated to the Fe in the active center. While it is known that CO is biosynthesized through enzyme reactions, the molecular mechanism of CO generation has been unclear. In this work, the crystal structure of the enzyme HypX involved in CO biosynthesis used by [NiFe]-hydrogenase was determined. It was revealed that HypX synthesizes CO through a completely novel reaction. HypX consists of two domains (N-terminal domain and C-terminal domain), and within the molecule, there is a cavity spanning across these two domains. It was also found that coenzyme A (CoA) binds to the cavity on the C-terminal domain side. Based on the obtained crystal structure, the following CO biosynthesis reaction mechanism was proposed: Two different chemical reactions occur in the N-terminal domain and the C-terminal domain of HypX. In the N-terminal domain, a formyl transfer reaction from formyl-tetrahydrofolate, which is bound in the cavity of the N-terminal domain, to CoA takes place. During this process, CoA in the cavity adopts an extended linear conformation, and the -SH group at the end of CoA is positioned adjacent to the formyl group in formyl-tetrahydrofolate. As a result of the formyl transfer reaction, formyl-CoA is generated as an intermediate. The generated formyl-CoA undergoes a significant conformational change within the cavity to position the formyl group at the end of the CoA molecule towards the enzyme active site in the C-terminal domain of HypX. In the C-terminal domain, the CO release reaction from formyl-CoA occurs, resulting in the production of CO and CoA.

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

Iron is an essential trace element for all organisms, which is used as active sites in iron proteins for electron transfer, chemical reactions, and gene regulation, *etc*. 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. Transcriptional regulators and/or iron uptake/export systems are responsible for regulating iron concentrations in cells. It is reported that several two-component systems are responsible for intracellular iron concentration in response to iron repletion/deficiency. 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 the two-component system has not yet been elucidated. In this work, we examined the structure-function relationships of *X. campestris* VgrS in detail.

To elucidate iron sensing mechanism of VgrS based on the structure, we prepared three constructs of the sensor domain of VgrS composed of Met1-Thr100, Met1-Met87, and Met27-Met87, respectively, to determine their crystal structures. The single crystal of apo and holo forms was obtained for the truncated sensor domain composed of Met27-Met87 while two other samples were not crystalized. To determine the stoichiometry of metal ion binding to VgrS M27-M87, ICP analyses was carried out, which revealed that VgrS M27-M87 bound 2 equivalents Fe(III) or 1 equivalent Mn(II), respectively. The ExxE motif in VgrS seems to be a metal binding site at which Fe(III) binds.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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Education

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Professional Employment

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

Awards

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

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- Secretary
  - FUKUTOMI, Yukiyo

Keywords Biomolecule Organization, NMR

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

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

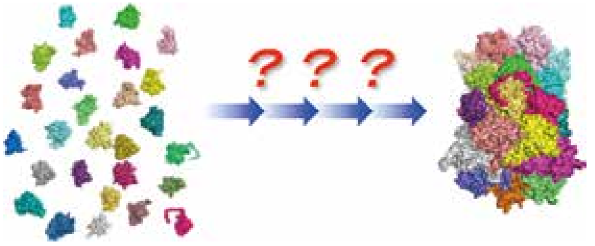

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- H. Yagi, K. Takagi and K. Kato, “Exploring Domain Architectures of Human Glycosyltransferases: Highlighting the Functional Diversity of Non-Catalytic Add-On Domains,” *Biochim. Biophys. Acta, Gen. Subj.* **1868**, 130687 (2024).
- 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. Comprehensive Multi-Scale Analysis of Protein Glycosylation: Structural, Functional, and Evolutionary Insights

Glycosylation, a diverse post-translational modification, is ubiquitous among proteins in nature. Our research group employs a multi-scale approach, from molecular to cellular levels, to elucidate the intricate mechanisms of protein glycosylation. In the Human Glycome Atlas Project, we are conducting research to obtain comprehensive and systematic information about human glycosylation.[1)] In humans, approximately 200 glycosyltransferases orchestrate the complex process of glycosylation. To gain insights into their molecular architecture, we analyzed the domain architecture of these enzymes using the AlphaFold Protein Structure Database.[2)] Our investigation particularly focused on non-catalytic add-on domains, systematically categorizing their structures and potential functions.

Concurrently, we examined the Golgi apparatus, the primary organelle of glycosylation, to unravel its spatiotemporal dynamics and glycoprotein transport pathways. We established a technical foundation for the localization analysis of glycosyltransferases within the Golgi apparatus using super-resolution microscopy.[3)] Our study of sub-Golgi distribution patterns of N-glycan diversifying enzymes revealed subtle localization differences even among enzymes presumed to coexist within the same Golgi compartment (Figure 2). Importantly, we revealed molecular codes within CTS regions as crucial determinants of their sub-Golgi localization.

We also conducted structural and functional analyses of molecular systems involved in glycoprotein folding and degradation.[4,5)] These analyses provided novel insights into the fate determination of glycoproteins within the cell through glycan recognition.

Furthermore, through collaborative research with the Deep-Sea and Deep Subsurface Life Research Group at ExCELLS, we performed glycoproteomic analysis of archaea, yielding important findings that enhance our understanding of the evolutionary dynamics of glycosylation and the molecular basis of microbial interactions in extreme environments.[6,7)]

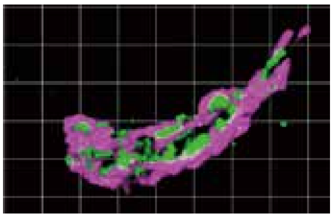

Figure 2. 3D images of two glycosyltransferases. Dual-color 3D super-resolution microscopy image of the Golgi ribbon area of an Expi293F cell expressing B3GALT6-mScarlet (magenta) and FUT9-mNeonGreen (green).

2. Biophysical Characterizations of Antibody Functions and Protein Dynamics

We also worked to elucidate the mechanisms of higher-order functional expression through the dynamics of biological molecular systems, utilizing various biophysical methods. In particular, we conducted collaborative research with the Biomolecular Dynamics Observation Group at ExCELLS, using high-speed atomic force microscopy (HS-AFM) to study interaction systems between antibodies and effector molecules central to immune defense.

While immunoglobulin G (IgG) bound to antigens forms hexamers to recruit the complement component C1q, we previously reported that a mouse IgG mutant lacking the Cγ1 domain binds to C1q and activates the complement pathway regardless of antigen presence. In this study, using HS-AFM, NMR spectroscopy, and mutation experiments, we revealed that the deletion of the Cγ1 domain enhances binding between the C_L domain and C1q through electrostatic interactions, enabling a monomeric IgG molecule to activate the complement system without forming hexamers (Figure 3).[8)]

Furthermore, quantitative analysis of the interaction between therapeutic antibodies and Fcγ receptors using HS-AFM revealed that the dwell times of antibodies on effector molecules are robust indicators of therapeutic antibody efficacy.[9)]

These studies highlight previously unknown potential binding sites for effector molecules within IgG molecules, paving the way for developing more refined therapeutic antibodies with tailored interactions.

Moreover, as part of an international collaboration at ExCELLS, we performed dynamic structural analysis of the human ATAD2 AAA+ histone chaperone to elucidate the communication mechanism between subunits.[10)] This work was a joint achievement with Dr. Ji-Joon Song from the Korea Advanced Institute of Science and Technology and the Biomolecular Dynamics Observation Group at ExCELLS.

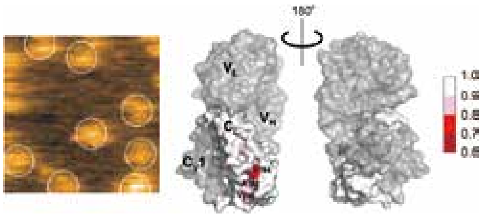

Figure 3. Characterization of interaction between the IgG C_L domain and complement component C1q using HS-AFM (left) and NMR (right) analyses.

References

1) K. F. Aoki-Kinoshita *et al.*, *Glycobiology*, in press (2024).
2) H. Yagi *et al.*, *Biochim. Biophys. Acta, Gen. Subj.* **1868**, 130687 (2024).
3) H. Yagi *et al.*, *Cell Struct. Funct.* **49**, 47–55 (2024).
4) S. Ninagawa *et al.*, *eLife* **12**, RP93117 (2023).
5) T. Satoh *et al.*, *FEBS Lett.* **598**, 2259–2268 (2024).
6) S. Nakagawa *et al.*, *BBA Adv.* **6**, 100118 (2024).
7) S. Nakagawa *et al.*, *J. Bacteriol.* **206**, e0020524 (2024).
8) S. Yanaka *et al.*, *Int. Immunol.* **36**, 405–412 (2024).
9) S. Yanaka *et al.*, *Biol. Pharm. Bull.* **47**, 334–338 (2024).
10) C. Cho *et al.*, *Commun. Biol.* **6**, 993 (2023).

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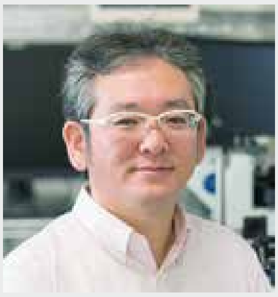
Operation and Design Principles of Biological Molecular Machines

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



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2011	Lecturer, The University of Tokyo
2013	Associate Professor, The University of Tokyo
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Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by protein molecular machines, which show higher performance than man-made machines in many aspects. One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces 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. In addition, with the help of structure-based rational design and site-saturation mutagenesis, we engineer non-natural protein molecular motors to understand their design principles. Furthermore, we challenge to engineer synthetic molecular motors.

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

- R. N. Burton-Smith, C. Song, H. Ueno, T. Murata, R. Iino and K. Murata, "Six States of *Enterococcus hirae* V-Type ATPase Reveals Non-Uniform Rotor Rotation during Turnover," *Commun. Biol.* **6**, 755 (2023).
- 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.* **15**, 1591–1598 (2023).
- 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).
- R. Iino, K. Kinbara and Z. Bryant, "Introduction: Molecular Motors," *Chem. Rev.* **120**, 1–4 (2020).
- 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).
- 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. Mechanism-Based Design of DNA-Nanoparticle Motor with High Speed and Processivity Comparable to Motor Proteins[1)]

DNA-nanoparticle motor is a burnt-bridge Brownian ratchet moving on RNA-modified surface driven by Ribonuclease H (RNase H), and one of the fastest nanoscale artificial motors. However, its speed is still much lower than those of motor proteins. Here we resolve elementary processes of motion and reveal long pauses caused by slow RNase H binding are the bottleneck (Figure 2). As RNase H concentration ([RNase H]) increases, pause lengths shorten from ~100 s to ~0.1 s, while step sizes are constant (~20 nm). At high [RNase H], speed reaches ~100 nm s^{-1}, however, processivity, run-length, and unidirectionality largely decrease. A geometry-based kinetic simulation reveals switching of bottleneck from RNase H binding to DNA/RNA hybridization at high [RNase H], and trade-off mechanism between speed and other performances. A mechanism-based newly-designed motor with 3.8-times larger DNA/RNA hybridization rate simultaneously achieves 30 nm s^{-1} speed, 200 processivity, and 3 µm run-length comparable to motor proteins.

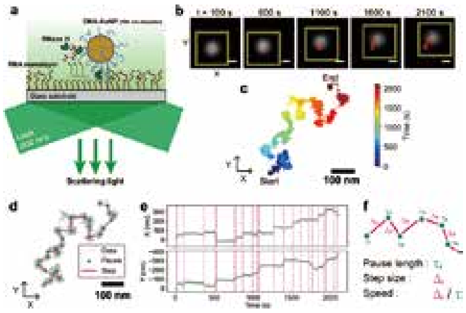

Figure 2. (a) Schematic illustration of the experimental system for high-speed/high-precision single particle tracking of DNA-AuNP motor. DNAs on the AuNP surface are hybridized with RNAs on the glass surface. RNAs that hybridized with DNAs are selectively hydrolyzed by RNase H. The motion of DNA-AuNP motor is visualized using total-internal reflection dark-field microscopy. (b) Motion of DNA-AuNP motor on RNA surface at 36 nM RNase H. Recording rate: 20 fps. Red lines indicate trajectories of the particle centroid. Dark yellow squares show the regions of interest to calculate the centroid for each frame. Scale bar: 200 nm. (c) Whole trajectory of the centroid of DNA-AuNP motor shown in (b). (d) Pauses (green dots) and steps (magenta lines) superimposed to raw trajectory shown in (c). (e) Time-course of XY-coordinates. Green solid lines are fittings to raw trajectories, and magenta dashed lines indicate positions of detected steps. (f) Schematic illustration and definitions of pause length, step size, and speed.

2. Visualizing Single V-ATPase Rotation Using Janus Nanoparticles[2)]

Understanding the function of rotary molecular motors, such as the rotary ATPases, relies on our ability to visualize the single-molecule rotation. Traditional imaging methods often involve tagging those motors with nanoparticles (NPs) and inferring their rotation from translational motion of NPs. Here, we report an approach using "two-faced" Janus NPs to directly image the rotation of single V-ATPase from *Enterococcus hirae*, an ATP-driven rotary ion pump (Figure 3 and 4). By employing a 500-nm silica/gold Janus NP, we exploit its asymmetric optical contrast—silica core with a gold cap on one hemisphere—to achieve precise imaging of the unidirectional counter-clockwise rotation of single V-ATPase motors immobilized on surfaces. Despite the added viscous load from the relatively large Janus NP probe, our approach provides accurate torque measurements of single V-ATPase. This study underscores the advantages of Janus NPs over conventional probes, establishing them as powerful tools for single-molecule analysis of rotary molecular motors.

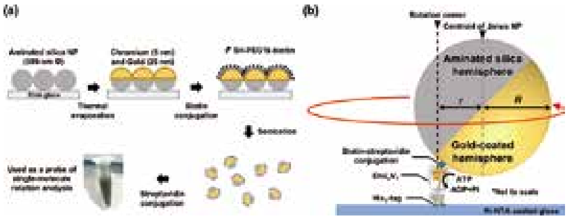

Figure 3. (a) Schematic of the Janus NP preparation process. (b) Schematic illustration of single-molecule imaging of V-ATPase rotation using a Janus NP probe. The rotor c-ring of V-ATPase is immobilized on the Ni-NTA coated coverslip via His_3-tags, while the single Janus NP is attached to the stator A-subunit of V-ATPase via biotin-streptavidin conjugation system. The black and grey dotted vertical lines indicate the rotation center and the centroid of Janus NP, respectively.

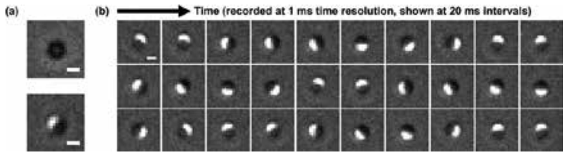

Figure 4. (a) Phase-contrast images of a single aminated silica NP (top) and a single Janus NP (bottom) non-specifically attached to the glass coverslip. (b) Time-lapse phase-contrast images demonstrating the rotational motion of a single Janus NP specifically attached to V-ATPase, driven by ATP hydrolysis. Observation was conducted at 25°C in the presence of 5 mM ATP and 300 mM NaCl. Images were recorded at 1,000 frames per second (1 ms time resolution) and are shown at 20 ms intervals. Scale bars: 500 nm.

References

1) T. Harashima, A. Otomo and R. Iino, *bioRxiv* (2024). DOI: 10.1101/2024.05.23.595615

2) A. Otomo, J. Wiemann, S. Bhattacharyya, M. Yamamoto, Y. Yu and R. Iino, *bioRxiv* (2024). DOI:10.1101/2024.08.22.609254

Awards

HARASHIMA, Takanori; Young Researcher Award at The 7th Annual Meeting of the Molecular Robotics (2024).
HARASHIMA, Takanori; Student and Early Carrier Researcher Poster Award, IUPAB2024 (2024).

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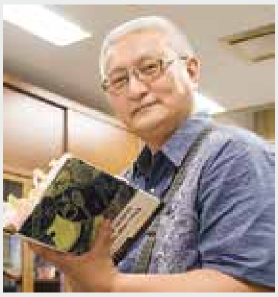
* IMS International Internship Program

Development of Novel Catalytic Organic Transformations

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



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Education

1984	B.S. Hokkaido University
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Professional Employment

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

Awards

1991	Eisai Award, Synthetic Organic Chemistry
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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. Along this line, in 2024, we have developed a series of novel diazabenzacenaphthenium photocatalysts, denoted as ***N*-BAP**s, which promoted the unprecedented 4-electron photoreduction of esters to form the corresponding alcohols with visible LED light irradiation under aqueous conditions.

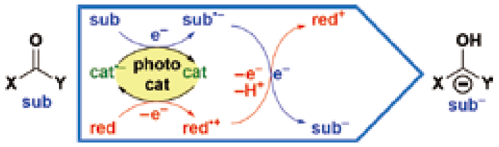


Figure 1. The outlined concept of photocatalytic reductive activation of substrate through two successive one-electron transfer process (*e.g.* carbonyl reduction to carbinol anion).

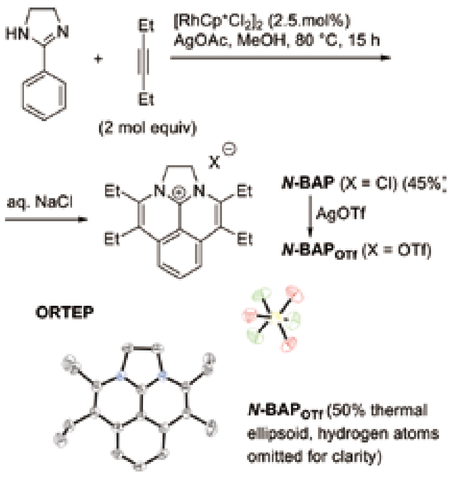
Selected Publications

- S. Okumura, K. Torii and Y. Uozumi, "Electrophilic 1,4-Addition of Carbon Dioxide and Aldehydes to Enones," *Org. Lett.* **25**, 5226–5230 (2023).
- S. Okumura, T. Takahashi, K. Torii and Y. Uozumi, *Chem. –Eur. J.* **29**, e202300840 (2023). DOI: 10.1002/chem.202300840
- 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).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, "Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin," *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels," *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Pallasium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- 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. Novel Diazabenzacenaphthenium Photocatalysts[1)]

1-1. Design and Preparation of *N*-BAP

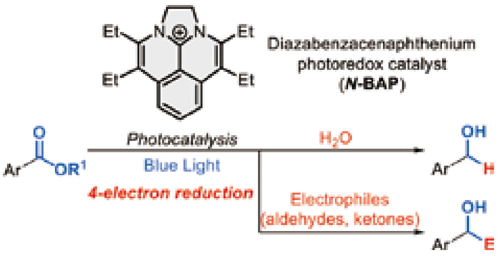
A novel diazabenzacenaphthenium photocatalyst ***N*-BAP** was designed and identified on the basis of an extensive *in silico* screening, with a view to its use as a photocatalyst under visible-light irradiation in photoinduced multielectron-transfer reactions. The photocatalyst was prepared by a rhodium-catalyzed oxidative annulation of 2-phenyl-4,5-dihydro-1*H*-imidazole with hex-3-yne in one step. Single-crystal X-ray analysis of ***N*-BAP**$_{\mathrm{OTf}}$ clearly confirmed the presence of a planar π-conjugated diazabenzacenaphthenium structure.



Scheme 1. Preparation of *N*-BAP.

1-2. Multielectron-Reduction of Esters

Under visible-light irradiation, ***N*-BAP** promoted the four-electron reduction of esters in the presence of ammonium oxalate as a “traceless reductant” to generate carbinol anion intermediates that underwent protonation with water to give the corresponding alcohols. The resulting carbinol anions also exhibited nucleophilic reactivity under the photocatalytic conditions to undergo a 1,2-addition to a second carbonyl compound, affording unsymmetric 1,2-diols.



***N*-BAP** reduces ester **I** through SET to give the acetal radical **II** and oxidized ***N*-BAP**. Oxidized ***N*-BAP** oxidizes oxalate anion to afford CO_2 and a CO_2 radical anion, with regeneration of ***N*-BAP**. The acetal radical **II** undergoes a second SET from excited ***N*-BAP** (or a CO_2 radical anion) to form the acetal carbanion **III**; this is followed by protonation with water to give the aldehyde **IV**. A second two-electron reduction of **IV** then generates the carbinol anion **V**. The four-electron-reduction process proceeds almost simultaneously to suppress radical side reactions. Lastly, the resulting carbinol anion **V** reacts with water or a carbonyl electrophile to furnish the final product **VI**.

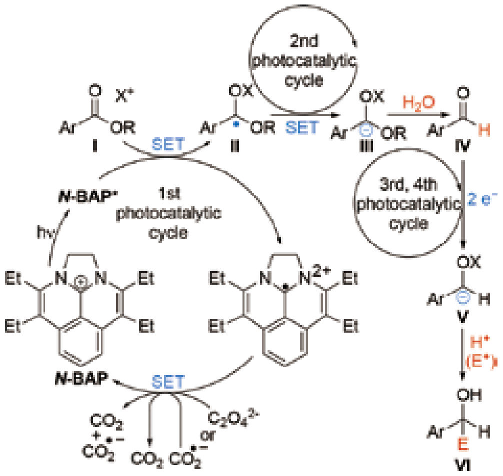


Figure 2. Proposed mechanism.

2. Tetrahydroxydiboron as a Green Reducing Agent Serving in Water[2,3)]

We have developed a transfer hydrogenation of aldehydes and ketones, as well as a transfer hydrogenolysis of O–C and N–C bonds of *O*-, and *N*-benzyl groups with $B_2(OH)_4$ as a reductant and amphiphilic resin-dispersed palladium nanoparticles as a catalyst system in an aqueous medium, where water also serves as a hydrogen donor. A variety of aldehydes and ketones, including aliphatic carbonyl compounds, reacted to give the corresponding primary and secondary alcohols, respectively. Benzyl groups of a variety of benzylic ethers, esters, carbamates, and amines, including benzyl-protected carbohydrates and amino acids, were reductively removed in high yields. The catalyst was recovered by filtration and reused nine times without a significant loss of its catalytic active.

References

1) S. Okumura, S. Hattori, L. Fang and Y. Uozumi, *J. Am. Chem. Soc.* **146**, 16990–16995 (2024). DOI: 10.1021/jacs.4c05272
2) K. Zhang, S. Okumura and Y. Uozumi, *Chem. Lett.* **53**, upae082 (2024). DOI: 10.1093/chemle/upae082
3) K. Zhang, S. Okumura and Y. Uozumi, *Eur. J. Org. Chem.* **27**, e202400322 (2024). DOI: 10.1002/ejoc.202400322

Design and Synthesis of Organic Molecules for Catalysis

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2005 Damon Runyon Cancer Research Foundation Post Doctoral Research Fellowship
2008 Thieme Chemistry Journals Award
2014 The 17th Morita Science Research Award
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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.

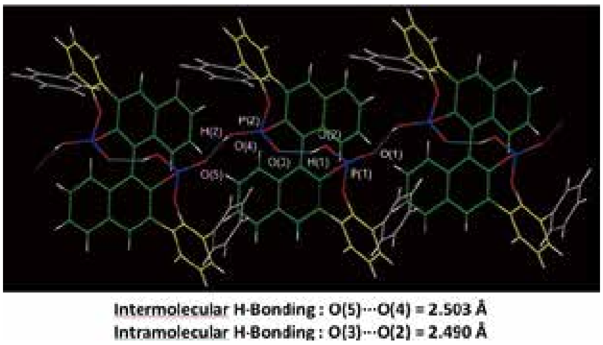

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

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 Perfluorohalogenated Arenes

Halogens form attractive non-covalent interactions between terminal halogen atoms in compounds of the type R—X (X = Cl, Br, I) and Lewis bases. This non-covalent interaction is known as either halogen bonding or σ-hole bonding, which occurs when "R" is a highly electronegative substituent, such as perfluorinated alkyl or aryl substituents. Based on the electrophilic feature of the halogen atom, we have investigated two types of perfluorohalogenated arenes in their design and synthesis: Perfluorohalogenated styrenes and naphthalenes, aimed at creating functional molecules.[1,2]

The Wittig reaction of perfluorohalobenzaldehydes was systematically studied to synthesize 2,3,5,6-tetrafluoro-4-halostyrenes (TFXSs), functional monomers bearing halogen bond donor sites.[1] The reaction proceeded efficiently in tetrahydrofuran using 1,1,3,3-tetramethylguanidine as the organic base. Correlation analysis quantitatively identified three key factors necessary for obtaining TFXS in reasonable yields. This approach not only advances the study of halogen bond-based functional molecules but also introduces digitalization as a promising strategy in small molecule synthesis.

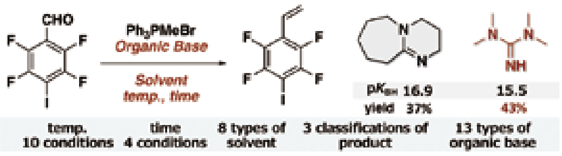

Figure 2. Synthesis of perfluoroiodinated styrenes as halogen bond donor site-introduced functional monomers.

Perfluorohalogenated naphthalenes (PFXNaPs) are unique small molecules with great potential to exhibit a new type of σ-hole and π-hole bonding, owing to the incorporation of multiple F atoms onto the naphthalene ring. We developed a synthetic protocol for PFXNaPs, conduct crystal engineering investigations, and explored the intermolecular interactions of PFXNaPs through π-hole and σ-hole bondings.[2] We successfully synthesized PFXNaPs using Mg amide-mediated halogenation reactions of electron-deficient F_7 and F_6 naphthalenes, achieving good to excellent yields. Crystal structure analyses of 3,6-I_2F_6 naphthalene unveiled intermolecular π-hole stacking between two C atoms in the naphthalene ring, in cooperation with the σ-hole bonding of two I atoms. This mode of intermolecular interaction has not been classified in previous reports. Computational studies show that the π-hole bonding in PFXNaPs is substantially enhanced compared to corresponding benzene molecules without diminishing the σ-hole bonding. The unique stacked interaction in PFXNaPs is primarily governed by electrostatic interaction and dispersion correction energies, with the contribution of C···C contacts being 10 times greater than that in benzene analogs. The results enable further applications of PFXNaPs in the fields of perfluorohalogenated arenes and organic crystalline materials.

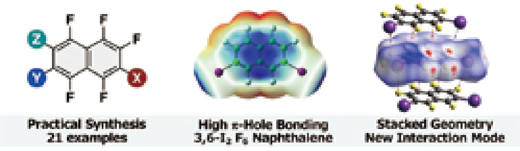

Figure 3. Synthesis and feature of perfluorohalogenated naphthalenes as potential crystalline materials.

2. Design of Halenium Complexes

In the filed of perfluorohalogenated arenes, the two-center-two-electron (2c2e) bond is a key feature. Similarly, halogen(I), generally X^+ (X = I, Br, Cl), acts as a strong halogen bond donor site. In contrast to the 2c2e halogen bond, halogen(I) simultaneously interacts with two Lewis bases. This bond is recognized as a three-center-four-electron (3c4e) halogen bond. Importantly, successful examples have consistently required the use of stoichiometric amounts of 3c4e complexes. Despite the utility of the 3c4e halogen bond in synthetic chemistry, its potential for non-metallic complex catalysis had not yet been thoroughly investigated until our report.[3,4]

We discovered that the 3c4e halogen bond can serve as a new driving force for catalysis.[3] 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 $[N\cdots X\cdots N]^+$ complexation to sp^2 CH as a hydrogen-bonding donor site, and ii) the noncovalent property allows for the dissociation of $[N\cdots X\cdots N]^+$ for the formation of $[Cl\cdots X\cdots Cl]^-$. This study introduces the application of 3c4e X-bonds in catalysis *via* halogen(I) complexes.

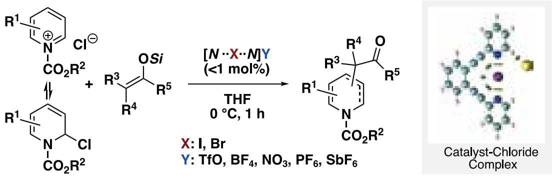

Figure 4. Halenium complex catalysis *via* three-center-four-electron halogen bond enables non-metallic complex catalysis for Mukaiyama-Mannich-type reaction.

References

1) T. Hori, S. Kakinuma, N. Ohtsuka, T. Fujinami, T. Suzuki and N. Momiyama, *Sylett* **34**, 2455–2460 (2023).
2) N. Ohtsuka, H. Ota, S. Sugiura, S. Kakinuma, H. Sugiyama, T. Suzuki and N. Momiyama, *CystEngComm* **26**, 767–772 (2024).
3) S. Oishi, T. Fujinami, Y. Masui, T. Suzuki, M. Kato, N. Ohtsuka and N. Momiyama, *iScience* **25**, 105220 (2022).
4) S. Oishi, T. Fujinami, Y. Masui, T. Suzuki, M. Kato, N. Ohtsuka and N. Momiyama, *STAR Protocols* **4**, 102140 (2023).

Design and Synthesis of Three-Dimensional Organic Structures

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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 (Figure 1).

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.

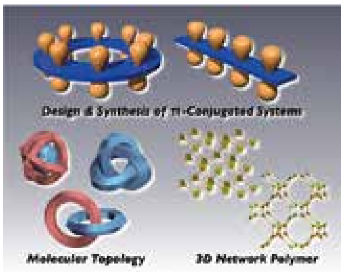


Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- R. Yoshida, H. Sugiyama and Y. Segawa, "Synthesis, Structure, and Properties of a Bay-Fluorinated Triphenylene," *Chem. Lett.* **53**, upae048 (2024).
- S. Hirota, S. Nakano, H. Sugiyama and Y. Segawa "Synthesis of Polycyclic Arenes Composed of Four-, Five-, Six-, and Eight-Membered Rings *via* an Unexpected Four-Membered Ring Formation Reaction," *Org. Lett.* **25**, 8062–8066 (2023).
- 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, "The Transannular Scholl Reaction for the Introduction of Heptagons into Aromatic Hydrocarbons," *Chem* **9**, 2725–2727 (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. Y. Cheung, K. Watanabe, Y. Segawa and K. Itami, "Synthesis of a Zigzag Carbon Nanobelt," *Nat. Chem.* **13**, 255–259 (2021).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).

1. Synthesis of Hexafluorotetraphenylene Bearing Alkoxy Chains

Triphenylene is one of the polycyclic aromatic hydrocarbons that has been extensively studied for a long time. Triphenylene is a planar π-conjugated molecule with D_{3h} symmetry, consisting of four six-membered rings. As the functionalization of triphenylenes at the peripheral positions is relatively easy, triphenylene derivatives with a variety of structural and electronic properties have been synthesized and applied in materials science.

We synthesized a bay-fluorinated triphenylene and investigated its structural and electronic properties.$^{1)}$ The synthesis of 2,3,6,7,10,11-hexaethoxy-1,4,5,8,9,12-hexafluorotriphenylene (**1**) was accomplished via a two-step one-pot reaction sequence starting from hexaethoxytriphenylene (**2**) (Figure 2). The bay-selective deprotonation of **2** was carried out using *n*-butyllithium, which was followed by an electrophilic fluorination with NFSI to generate hexafluorinated triphenylene **1**. A single-crystal X-ray diffraction analysis revealed that **1** adopts a distorted C_2 symmetric structure in the single crystal, wherein molecules of **1** arrange into one-dimensional columnar stacks. DFT calculations showed that the C_2 symmetric conformation of **1** is by 5.8 kcal·mol^{-1} more stable than the D_3 symmetric one. Due to the introduction of the fluoro groups, the absorption and fluorescence spectra of **1** showed bathochromic shifts and broadening of the spectra compared to those of **2**. DFT calculations revealed that the energy levels of the HOMOs and LUMOs change due to the introduction of the fluoro groups.

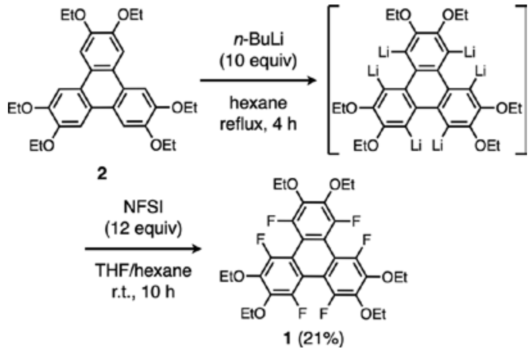


Figure 2. Synthesis of hexafluorotriphenylene **1** (NFSI: *N*-fluoro benzenesulfonimide).

2. Synthesis of Polycyclic Arenes Composed of 4-5-6-8-Membered Rings *via* an Unexpected 4-Membered-Ring Formation Reaction

Aromatic compounds having four-membered rings attract considerable interest owing to their unique structural and physical properties. Biphenylene, a simple four-membered-ring-containing arene, comprises aromatic benzene moieties fused to an antiaromatic cyclobutadiene moiety. In biphenylenes, the fused benzene rings decrease the antiaromaticity of the central four-membered ring relative to that of cyclobutadiene.

We have synthesized and characterized tricarbonylated **1**, which contains four-, five-, six-, and eight-membered rings and tetracarbonylated compound **2** *via* the carbonylation reaction of a tetraphenylene derivative.$^{2)}$ When dimethyl carbonate was used as the carbonyl source, the carbonylation of tetraphenylene yielded tricarbonylated product **1** *via* an unexpected four-membered ring formation reaction. In contrast, using dimethylcarbamoyl chloride afforded tetracarbonylated compound **2** selectively (Figure 3). The structures of the as-obtained compounds **1** and **2** were determined by X-ray crystallography, revealing one-dimensional stacking structures in the solid state in both cases. UV–vis absorption spectroscopy, CV, and DFT calculations suggested that the HOMO–LUMO gap of **1** is narrower than that of **2** (Figure 4). NICS and ACID calculations indicated that the four-membered ring of **1** and the eight-membered rings of **1** and **2** exhibit antiaromatic characteristics. The reaction reported here provides a new method for introducing a four-membered ring into polyaromatic structures at the late stage of the synthetic process.

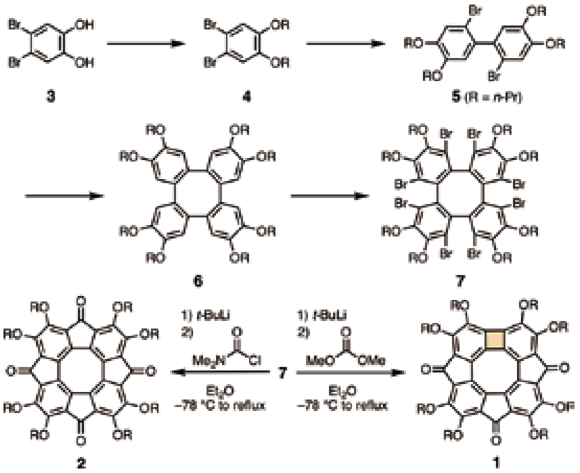


Figure 3. Synthesis of **1** and **2**.

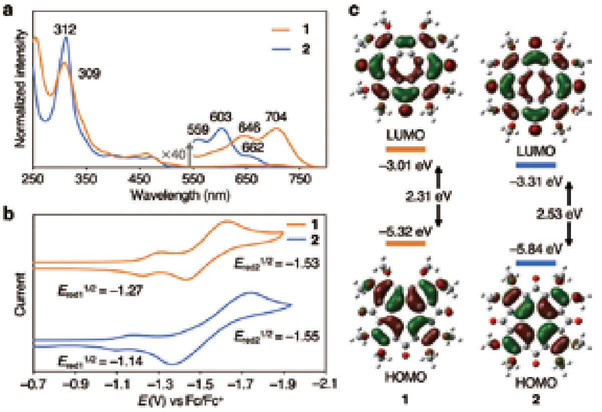


Figure 4. (a) UV–vis absorption spectra of **1** and **2**. (b) Cyclic voltammograms of **1** and **2**. (c) Frontier molecular orbitals of **1** and **2** calculated at the B3LYP/6-31G(d) level.

References

1) R. Yoshida, H. Sugiyama and Y. Segawa, *Chem. Lett.* **53**, upae048 (2024).
2) S. Hirota, S. Nakano, H. Sugiyama and Y. Segawa, *Org. Lett.* **25**, 8062–8066 (2023).

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 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 found that both SNA and L-αTNA of homopurine sequence could form unexpectedly stable triplex with XNA:RNA heteroduplex in a parallel manner, even though A*A pair had only single hydrogen bonding. This is the first report on the XNA:RNA*XNA triplex with *parallel* homopurine TFO involving single A*A *reversed* Hoogsteen pair.

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 to reduce sample amount and building collaborative relationships with numerous companies 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 in Thermally Fluctuating Systems?

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 provided by F_o. We do not know in detail how F_o rotates F_1. But, we expect that F_o and F_1 has acquired an efficient control way in thermally fluctuating environment. And, we should be able to know what is the most efficient way to rotate F_1 based on physical theory. As the first step along this purpose, we compared the external rotation of F_1 by constant torque and angle clamp. We found that rotation by angle clamp is significantly more efficient and requires much less work. Our experiments with theory and simulation revealed that the angle clamp works as a damper and reduce nonequilibrium fluctuations that produce futile dissipation.

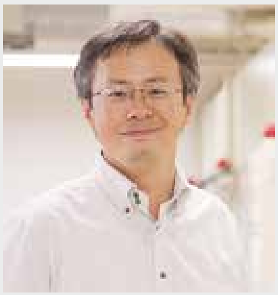
RESEARCH ACTIVITIES

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

Awards

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2016 The 13th (FY2016) JSPS PRIZE
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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

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Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

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

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

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

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

Selected Publications

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

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

A great deal of effort has been devoted to characterizing structural changes in the clock proteins along the circadian reaction coordinate. However, little is known about the mechanism driving the circadian cycle, even for the simple cyanobacterial protein KaiC that has ATPase and dual phosphorylation sites in its N-terminal C1 and C-terminal C2 domains, respectively. Nearly all KaiC structures reported to date share a nearly identical structure, and they do not appear to be suggestive enough to explain the determinants of circadian period length and its temperature compensation. We are studying the structural and dynamical origins in KaiC using high-resolution x-ray crystallography,[1–4] real-time fluorescence detection,[5] and quasielastic neutron scattering.[6]

2. *Rhythm*: Cross-Scale Analysis of Cyanobacterial Circadian Clock System[6–8]

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 screening[7] 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]

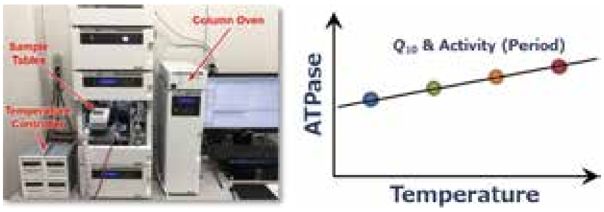

Figure 1. Development of a quick ATPase assay system.

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.

The habitats of cyanobacteria are diverse, so the space of their sequence is immense. 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) We examined the oscillation of the clock protein KaiC in modern cyanobacteria, as well as the function and structure of ancestral Kai proteins, to determine the evolutionary origin of the self-sustained Kai-protein oscillators.[9]

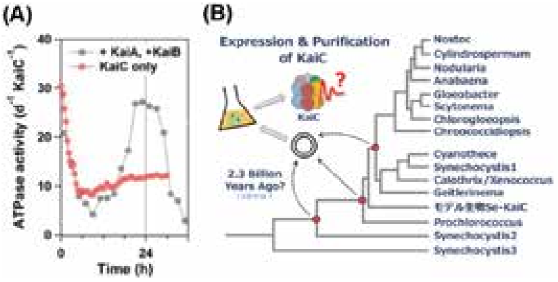

Figure 2. Damped oscillation of KaiC ATPase activity (**A**) and evolutionary diversity of cyanobacteria (**B**).

4. Bio-SAXS Activity in IMS[10]

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

References

1) Y. Furuike, A. Mukaiyama, D. Ouyang, K. Ito-Miwa, D. Simon, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Adv.* **8**, eabm8990 (2022).
2) Y. Furuike, A. Mukaiyama, S. Koda, D. Simon, D. Ouyang, K. Ito-Miwa, S. Saito, E. Yamashita, T. Nishiwaki-Ohkawa, K. Terauchi, T. Kondo and S. Akiyama, *Proc. Natl. Acad. Sci. U. S. A.* **119**, e2119627119 (2022).
3) Y. Furuike, E. Yamashita and S. Akiyama, *Biophys. Physicobiol.* **21**, e210001 (2024).
4) Y. Furuike, Y. Onoue, S. Saito, T. Mori and S. Akiyama, *BioRxiv* 10.1101/2024.03.21.584037 (2024).
5) A. Mukaiyama, Y. Furuike, E. Yamashita and S. Akiyama, *Biochem. J.* **479**, 1505–1515 (2022).
6) Y. Furuike, D. Ouyang, T. Tominaga, T. Matsuo, A. Mukaiyama, Y. Kawakita, S. Fujiwara and S. Akiyama, *Commun. Phys.* **5**, 75 (2022).
7) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019)
8) D. Simon, A. Mukaiyama, Y. Furuike and S. Akiyama, *Biophys. Physicobiol.* **19**, e190008 (2022).
9) A. Mukaiyama, Y. Furuike, K. Ito-Miwa, Y. Onoue, K. Horiuchi, E. Yamashita and S. Akiyama, *BioRxiv* 10.1101/2024.07.23.604570 (2024).
10) T. Inobe, R. Sakaguchi, T. Obita, A. Mukaiyama, S. Koike, T. Yokoyama, M. Mizuguchi and S. Akiyama, *FEBS Lett.* **598**, 2292–2305 (2024). DOI: 10.1002/1873-3468.14986

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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
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Education

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Professional Employment

2013	Special Postdoctoral Researcher, RIKEN
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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

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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.

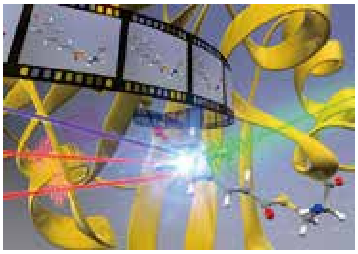

Figure 1. Schematic of the ultrafast nonlinear spectroscopy of complex molecules with few-cycle ultrashort pulses.

Selected Publications

- Y. Yoneda and H. Kuramochi, "Room-Temperature Solution Fluorescence Excitation Correlation Spectroscopy," *J. Phys. Chem. Lett.* **15**, 8533 (2024).
- 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).

1. Room-Temperature Solution Fluorescence Excitation Correlation Spectroscopy

Polyatomic molecules in condensed phases undergo constant fluctuations in molecular structure and their surrounding environment. These fluctuations lead to temporal and spatial variations in the physical properties and reactivities of the molecules, whose understanding is particularly crucial for elucidating functionalities of complex macromolecules such as proteins. Conventional ensemble measurements are insensitive to such fluctuations and resultant heterogeneity and provide only statistically averaged information, making it challenging to elucidate the properties of individual molecules and transitions between sub-ensembles. Single-molecule fluorescence spectroscopy enabled the study of the physical properties and dynamics of individual molecules. However, the long measurement time necessary for detecting intrinsically weak single-molecule fluorescence limits these studies to systems where spontaneous fluctuations are suppressed and slow, such as molecules fixed in polymer or crystalline matrices or at low temperatures, to ensure that the variations in properties of the individual molecules are not washed out during a measurement. Consequently, it remains a challenge to elucidate how properties and dynamics of individual molecules evolve in response to spontaneous fluctuation among sub-ensembles in complex and heterogeneous room-temperature solution systems, where a variety of chemical and biological processes take place. In this study, we developed fluorescence excitation correlation spectroscopy (FECS) for room-temperature solutions, which enables the study of spontaneous fluctuation of the excitation spectrum with microsecond time resolution. By employing Fourier transform spectroscopy with broadband femtosecond pulses and time-correlated single-photon counting, we achieved fluorescence excitation spectroscopy of a room-temperature solution at the single-molecule level. Based on this single-molecule measurement, we obtained an excitation wavelength-resolved fluorescence autocorrelation function in the microsecond to millisecond range, demonstrating the potential of this method to elucidate fast, spontaneous, time-dependent changes of excitation spectra in statistically equilibrium systems.[1] With further development, this method will allow the study of spectral exchange associated with transitions between sub-ensembles of solution-phase molecules with unprecedented time resolution.

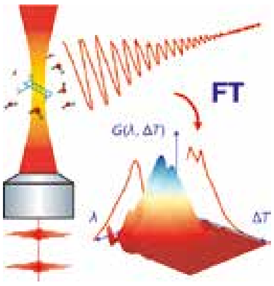

Figure 2. Schematic of fluorescence excitation correlation spectroscopy of a room temperature solution.

Award

YONEDA, Yusuke; PCCP Prize 2024 (2024).

2. Development of Sub-10-fs Time-Resolved Absorption Spectroscopy in the Short-Wave-Infrared Region

Femtosecond time-resolved absorption spectroscopy is an ideal tool for studying the ultrafast dynamics of molecules in electronically excited states. By using ultrashort optical pulses whose pulse duration is shorter than the vibrational periods of the molecule, time-resolved absorption measurements also enable one to observe coherent nuclear wavepacket motion and provide fruitful information about the excited-state molecular structure. However, due to technical difficulties, time-resolved absorption measurements with such high temporal resolution have been so far limited in the visible spectral region, leaving the dynamics in the shortwave-infrared (SWIR) region unexplored. Recently, transient species that exhibit absorption in the SWIR region have attracted much attention, such as excited singlet and triplet states of singlet fission systems. In this study, we developed a time-resolved absorption spectrometer in the SWIR region with sub-10 fs temporal resolution. In the setup, the broadband sub-10 fs pulse generated by a noncollinear optical parametric amplifier (NOPA[2]) is used as the pump, and the SWIR continuum (800–1700 nm) generated by the idler output of a newly constructed collinear OPA is used as the probe. The time-resolved absorption data of TIPS-pentacene in chloroform measured with the developed setup are shown in Figure 3. The $S_n \leftarrow S_1$ excited-state absorption band of TIPS-pentacene is observed at 1350 nm, which shows a clear temporal modulation of the spectral position caused by coherent nuclear wavepacket motion in the S_1 state. Fourier transformation of the oscillatory signal reveals the vibrational bands of the Franck–Condon state up to 1410 cm^{-1}, as well as the nonresonant solvent Raman bands up to 3000 cm^{-1}. These results demonstrate that the spectrometer has the capability to monitor the ultrafast electronic/structural dynamics in the SWIR region with high temporal resolution (< 10 fs).

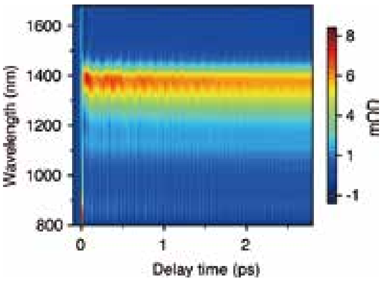

Figure 3. 2D map of the transient absorption signal recorded for TIPS-pentacene in chloroform solution upon photoexcitation with sub-10-fs visible pulse. The clear oscillatory feature represents coherent nuclear wavepacket motion launched in the S_1 state.

References

1) Y. Yoneda and H. Kuramochi, *J. Phys.Chem. Lett.* **15**, 8533 (2024).
2) Y. Yoneda and H. Kuramochi, *J. Phys. Chem. A* **127**, 5276 (2023).

Open up Future Electronics by Organic Molecules

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Keywords Organic Spintronics, Chirality, Organic Superconductor

Spintronics is a new ingredient 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 (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.

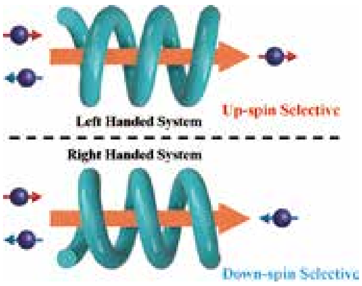

Figure 1. Conceptual schematic for CISS effect. P-helix molecule (lower panel) can transmit more electrons with spins antiparallel to the velocity (negative helicity electrons) than the other, while M-helix molecule (upper panel) favors transmission of electrons with parallel spin (positive helicity 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 antiparallel 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 magnetic monopole is also breaking the mirror symmetry, and its sign is connected to the chirality of underlying crystal lattice, although the magnetic monopole is time-reversal-odd (*T*-odd chiral). 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 (*T*-even electric toroidal monopole) in the 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. Such an interaction will also provide a large exchange energy difference for each spin. In this sense, this experiment provides the first direct observation of antiparallel spin pair formation from coherent chiral system which seems to be connected to 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. 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)

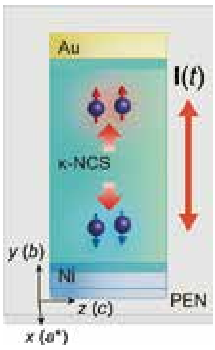

Figure 2. Device schematic for the detection of spin polarization in a chiral superconductor κ-NCS. By applying electrical current, electron spins are polarized along the current direction by CISS-like effect which can be detected as voltage across the κ-NCS/Ni interface. The amplitude of the signal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

References

1) V. M. Edelstein, *Phys. Rev. B* **72**, 172501 (2005).
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).

Award

SATO, Takuro; Young Scientist Award of the Physical Society of Japan (2024).

Design of Protein Functions Using Computational and Experimental Approaches

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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. Elucidation of Intracellular Functions Using Redesigned Protein Complex

We performed cell biological study based on new approach by rationally engineering protein complexes. Target of Rapamycin (TOR) complex, which is involved in response for their environment and in cell life span, is known to form two types of complexes with different constituent proteins, TORC1 and TORC2. Furthermore, while only one type of TORC1 is in fission yeast and mammals, budding yeast has two types of TORC1, Tor1 and Tor2 derived TORC1. It is known that eliminating only Tor1-TORC1 (deletion of the *tor1* gene) extends cell life span. However, since both TORC1 and TORC2 are essential for yeast and the *tor2* gene cannot be deleted (loss of TORC2), Tor2-TORC1 has never been studied. Nevertheless, Tor1- and Tor2-TORC1 have been thought to play the same role in the cell. Using our protein design technology, we succeeded in creating a modified Tor2 that does not produce only Tor2-TORC1, and revealed that the two TORC1s have different functions.

Reference

1) Y. Kamada, C. Umeda, Y. Mukai, H. Ohtsuka, Y. Otsubo, A. Yamashita and T. Kosugi, *J. Cell Biol.* **137**, jcs261625 (2023).

Award

KOSUGI, Takahiro; 13th National Institutes of Natural Sciences Young Researcher Award (2024).

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

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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
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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.

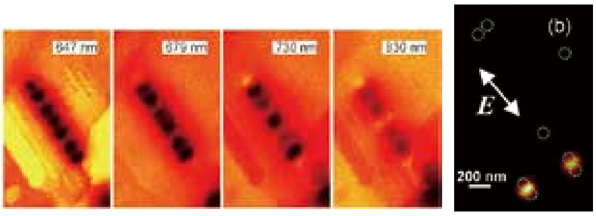

Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20\ \mathrm{nm}^D \times 510\ \mathrm{nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic 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. Highly Chiral Light Emission Using Plasmonic Helicoid Nanoparticles$^{1)}$

Materials generating circularly polarized luminescence (CPL) have received increasing interest due to their potential applications in bioimaging, sensing, etc. A chiral plasmonic nanostructure is one candidate for generating strong and highly dissymmetric CPL by coupling with the surrounding luminescent material. In this study, the generation of circularly polarized two-photon-induced photoluminescence (TPI-PL) from chiral gold nanostructures is demonstrated. Measurements of TPI-PL show that it has a strong dissymmetry factor of ≈0.7 for a single chiral Au nanoparticle. It is believed that this work provides a new route for novel CPL-generating materials with strong dissymmetry and holds promise for various applications using CPL technology.

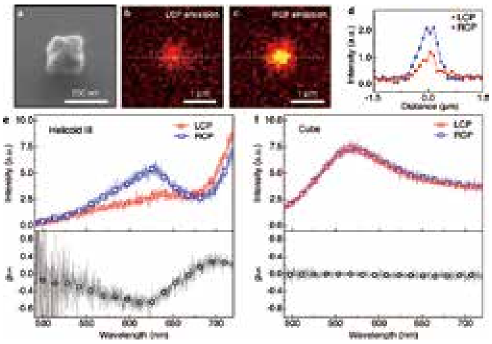

Figure 2. (a) SEM image and TPI-PL images for (b) left and (c) right circularly polarized emission of a single Au helicoid nanoparticle (NP). (d) Line profiles of the TPI-PL intensity along the dashed lines in (b) and (c). TPI-PL spectra (upper) and corresponding luminescence dissymmetry g_{lum} (lower) of (e) the Au helicoid NP and (f) the cubic NP. CC-BY-NC ©

2. Creation of a Photopolymerized Double Spiral Structure by Interference of Plasmonic Scattering and Circularly Polarized Light$^{2)}$

Chiro-optical effects of materials enable many intriguing optical phenomena in the subwavelength regime and are expanding their application in broad areas. Recently, the possibility of producing strong chiro-optical effects using achiral plasmonic nanostructures has been intensively studied. The interaction of achiral nanostructures with circularly polarized light can break the mirror symmetry. In this study, we present a method to create a novel chiral structure by using achiral plasmonic nanoparticles and circularly polarized light. The interference between the circularly polarized incident field and the plasmonic scattering field produced a double spiral pattern of the electro-magnetic fields, which was replicated via the photopolymerization reaction and resulted in chiral surface relief patterns of the polymer layer.

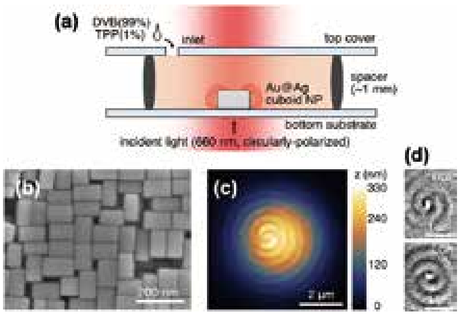

Figure 3. (a) Schematic illustration of the cell for the photopolymerization process. (b) SEM image of as-synthesized Au@Ag cuboid nanoparticles. (c) AFM images of the double spiral structures created by the irradiation of RCP light. (d) SEM images observed around the centers of the RCP and LCP light-exposed areas. CC-BY-NC-ND ©

3. Circular Dichroism of Pseudo-2-Dimensional Metal Nanostructures: Rotational Symmetry and Reciprocity$^{3)}$

Circular dichroism (CD) spectra for pseudo-two-dimensional chiral nanomaterials were systematically investigated and analyzed in relation to the rotational symmetry of the nanomaterials. For pseudo-two-dimensional chiral gold nanostructures fabricated on glass substrates using electron beam lithography, a matter with 4-fold rotational symmetry is found to be CD active, contrary to the theoretical expectation for the ideal two-dimensional case to exhibit no CD. The CD signal measured from the back side is found to be the same as that measured from the front side. The observed chiro-optical behavior arises from three-dimensional chiral characteristics of the material. For a matter that is 2- or 1-fold rotationally symmetric, the CD signal measured from the back side is not coincident with that from the front side. The observed CD spectral behavior is considered to be determined by a balance between the in-plane isotropic and anisotropic components of the chiral permittivity.

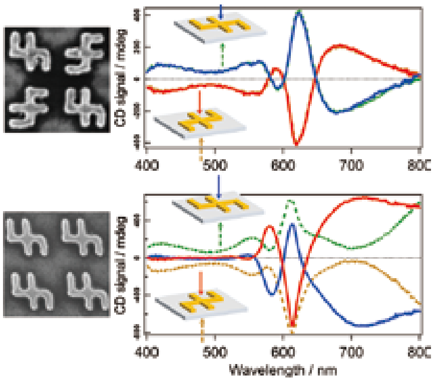

Figure 4. CD spectra obtained for (top) 4-fold rotational symmetry arrays and (bottom) translational arrays of italic f-shaped gold nanostructures. CC-BY ©

References

1) H.-Y. Ahn, K. Q. Le, T. Narushima, J. Yamanishi, R. M. Kim, K. T. Nam and H. Okamoto, *Adv. Opt. Mater.* **12**, 2400699 (2024).

2) H.-Y. Ahn, T. Narushima and H. Okamoto, *J. Phys. Chem. C* **128**, 7159 (2024).

3) K. Endo, S. Hashiyada, T. Narushima, Y. Togawa and H. Okamoto, *J. Chem. Phys.* **159**, 234706 (2023).

Nano- and Atomic-Scale Spectroscopy

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

Awards

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

Member
Assistant Professor
NISHIDA, Jun
Post-Doctoral Fellow
WANG, Yu
Secretary
ITO, Atsuko

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

An in-depth understanding of the structure and dynamics of matter at the atomic scale is crucial for designing next-generation devices and optimizing material/energy conversion processes, such as optoelectronics, solar cells, and catalysis. The rapid advancement of nanotechnology requires sophisticated measurement techniques capable of capturing phenomena with simultaneous spatiotemporal resolution at the (sub)nanometer length and pico/femtosecond time scale. Optical spectroscopy serves as a versatile tool for studying the microscopic structures, properties, and dynamics of a wide variety of materials. However, its spatial resolution is inherently limited by the diffraction limit, which restricts the ability to directly characterize nanoscale objects. Nano-spectroscopy using near-field optics offers a unique approach to overcome this physical limitation, enabling the investigation of materials at the nanoscale.

Our group has focused on the development and application of cutting-edge scanning near-field optical microscopy (SNOM) combined with various advanced spectroscopic methods, including nonlinear and ultrafast time-resolved measurements. In particular, we explore atomic-scale light–matter interactions to achieve nano-spectroscopy at the unprecedented spatiotemporal resolution. Recently, we have demonstrated the atomic-level sensitivity and spatial resolution using tip-enhanced Raman spectroscopy (TERS) based on low-temperature scanning tunneling microscopy (STM), providing novel insights into the intricate phenomena in nanoscale systems. Furthermore, by integrating ultrashort pulsed lasers, we have opened new avenues for directly observing the coherent dynamics of electrons and lattices within the STM junction. This capability is a critical step towards realizing atomic-scale ultrafast nano-spectroscopy, allowing us to probe dynamic processes that were previously inaccessible.

We are currently further pushing the boundary of nano-spectroscopy techniques with three key objectives: (1) extending the capabilities of atomic-scale spectroscopy from the visible to the infrared region to explore a broader range of materials and phenomena, (2) developing manifold nonlinear nano-spectroscopy techniques to investigate complex quantum interactions, and (3) applying these advanced methods to diverse materials, including low-dimensional materials, quantum dots, and biological molecules. These advancements will provide profound insights into the fundamental quantum properties and interactions of materials, potentially leading to the discovery of novel functionalities and the creation of innovative nanoscale devices.

Selected Publications

- 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).
- J. Nishida *et al.*, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24**, 836 (2024).

1. Atomic-Scale Optical Spectroscopy

Understanding and controlling of atomic-scale confinement of optical fields is a highly active area of research in light–matter interactions and their applications such as ultrasensitive spectroscopy and nano-optoelectronics. Recent studies have demonstrated that extreme confinement of near fields occurs in the presence of atomic-scale protrusions on metallic nanostructures, often referred to as "picocavity," formed by features as small as single atoms, resulting in unique optical phenomena. Yet, the underlying mechanisms remain to be elucidated, requiring highly precise experiments using atomically well-defined model systems. To address this, we investigated Raman scattering of a single Ag atom adsorbed onto the Ag(111) surface using low-temperature TERS,$^{1)}$ as shown in Figure 1. The experiment demonstrated that the vibration localized at the adatom is distinctly observable in the TERS spectrum. We further explored the relationship between the gap-distance dependence and Raman scattering in the different electron transport regimes of the picocavity, specifically comparing the tunneling and quantum point contact (QPC) regimes. Notably, the TERS spectra exhibited significant changes upon the formation of the QPC. These findings highlight that atomic-level structural changes can significantly influence the plasmonic properties of the system, offering new insights into how atomic-scale features modulate optical responses.

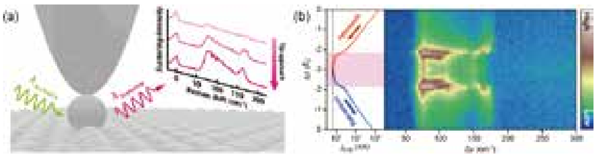

Figure 1. Inelastic light scattering spectroscopy for a single Ag adatom on the Ag(111) surface. (a) Schematic of the experiment. (b) Raman spectra measured as a function of the tip–adatom distance.

2. Nanoscale Coherent Phonon Spectroscopy

Coherent phonon spectroscopy is a valuable technique for gaining microscopic insights into ultrafast lattice dynamics, especially under nonequilibrium conditions. Understanding these dynamics is crucial for advancing our knowledge of fundamental material properties and for the development of ultrafast electronic and photonic devices. However, the conventional method cannot directly observe phonon dynamics at the nanoscale. To overcome these limitations, recently we have successfully demonstrated nanoscale coherent phonon spectroscopy using an ultrafast laser-induced STM within a plasmonic junction, as shown in Figure 2.$^{2)}$ This approach uniquely leverages the highly confined plasmonic field to locally excite coherent phonons in ultrathin zinc oxide films, which are then probed via the photoinduced tunneling current through an electronic resonance of the zinc oxide film. Unlike the Raman spectra, the phonon dynamics detected in coherent phonon spectroscopy display pronounced nanoscale spatial variations that correlate with the distribution of the electronic local density of states. We plan to further extend this technique to investigate various low-dimensional systems.

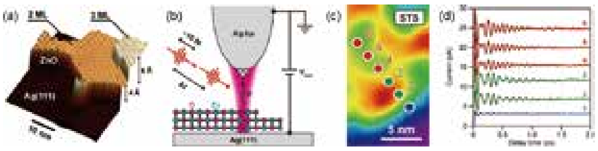

Figure 2. Nanoscale coherent phonon spectroscopy. (a) STM image of the ZnO ultrathin film grown on the Ag(111) surface. (b) Schematic of the experiment. (c) STS map of the ZnO ultrathin film. (d) Interferometric autocorrelation of the tunneling current recorded over the ZnO ultrathin film.

3. Nanoscale Infrared Nano-Spectroscopy of Nanomaterials

We have developed an advanced SNOM system based on atomic force microscopy (AFM), equipped with a wavelength-tunable pulsed laser that spans from the visible to the mid-infrared (MIR) region. This system allows us to perform nanoscale infrared (nano-IR) spectroscopy with exceptional sensitivity and resolution. The sensitivity of our nano-IR spectroscopy was demonstrated by successfully measuring the MIR response of a single protein molecule isolated on a gold (Au) surface, as shown in Figure 3.$^{3)}$ By implementing a unique detection scheme that extracts highly localized near-field MIR scattering down to a spatial resolution of just a few nanometers, we have achieved world-record sensitivity.

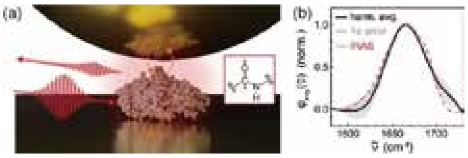

Figure 3. MIR vibrational spectroscopy of a single protein. (a) Schematic of the experiment. (b) MIR spectrum around the vibrational resonance of the amid group.

Figure 4 illustrates the application of the ultrafast visible-pump–MIR-probe nano-spectroscopy to visualize the spatially modulated many-body photo-carrier dynamics within a monolayer WS_2. By capturing these dynamics, we can directly observe how photo-carriers behave and interact in response to optical excitation, revealing intricate details of the material's electronic properties.

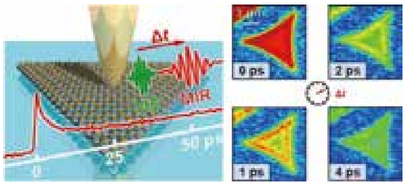

Figure 4. Ultrafast nano-imaging of spatially modulated many-body dynamics in monolayer WS_2.

References

1) S. Liu *et al.*, *ACS Nano* **17**, 10172 (2023).
2) S. Liu *et al.*, *Sci. Adv.* **8**, eabq5682 (2022).
3) J. Nishida *et al.*, *Nano Lett.* **24**, 836 (2024).

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 Prize2023
2023	2022 Natta Award (Politecnico di Milano)
2024	Van't Hoff Award

Member
Research Assistant Professor
MITSUHASHI, Takaaki
Secretary
MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

We are developing new self-assembled molecular systems using coordination chemistry and researching the application of the developed molecular systems. One representative application of the molecular system developed by us is the crystalline sponge (CS) method, which enables the rapid structure elucidation of small molecules. In this method, a porous crystal of a coordination network called CS, which was developed by us and can accommodate various kinds of small molecules, is used. 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. The CS 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.

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).

We now apply the CS method in the biological studies, especially studies on the natural product biosynthesis. Scientists in this field often obtain small molecules as products of natural product biosynthetic enzymes. However, it is often difficult to elucidate the complex structures of the enzyme products. We thus consider that the CS method, which enables the rapid structure elucidation of small molecules, is helpful, and can accelerate the studies in this field.

1. Analysis of a Terpene Synthase from a Giant Virus[1–3)]

Giant viruses are unique existence. The size of giant viruses is as large as that of bacteria, whereas normal viruses are much smaller than bacteria. Because of the unique feature of the giant viruses, many researches on the giant viruses have been reported. However, it was unknown whether the giant viruses were producers of natural products or not.

We thus investigated whether the giant viruses have the natural product biosynthetic enzymes, and noticed that a gene coding a protein relatively similar to a terpene synthase exists in the genome of a giant virus Orpheovirus IHUMI-LCC2. The terpene synthase is a kind of natural product biosynthetic enzymes, and responsible for the biosynthesis of the terpenoids, one of the largest groups of the natural products.

We named the terpene synthase from Orpheovirus IHUMI-LCC2 as OILTS (Orpheovirus IHUMI-LCC2 terpene synthase), and analyze it. As a result, we revealed that OILTS can work as the terpene synthase, and found an interesting feature of OILTS (Figure 1). Terpene synthases normally require Mg^{2+} as metal cofactor, and OILTS also requires Mg^{2+} to produce an enzyme product **1**. However, when the metal cofactor was changed to Mn^{2+}, Co^{2+}, or Ni^{2+}, the profile of the enzyme products was changed, and not only **1** but also **2** was produced. In addition, we found that **1** was relatively unstable and easily converted to four degradation products (**3**–**6**) in weakly acidic condition. Notably, the structures of **1**–**6** were successfully analyzed by the CS method.

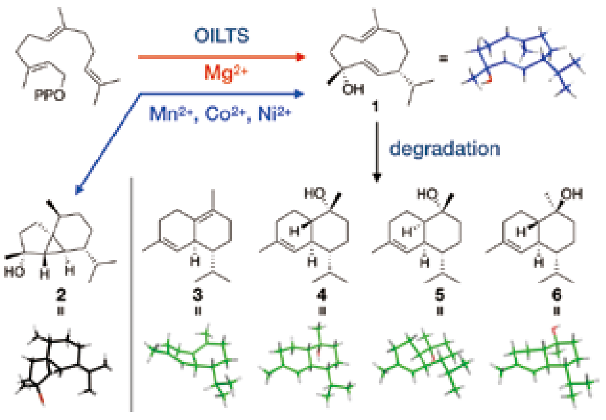

Figure 1. Reactions catalyzed by OILTS, a terpene synthase from a giant virus. Three dimensional structures of **1**–**6** were obtained by the CS method analysis.

We also performed the phylogenetic analysis, comparing terpene synthases from giant viruses and other organisms (Figure 2A). The terpene synthases from giant viruses are revealed to be phylogenetically separated from other terpene synthases. This result suggests the unique evolution of the terpene synthases from the giant viruses.

In addition, we solved the structure of OILTS by protein X-ray crystallography (Figure 2B). Whereas the structure of OILTS was similar to the structures of bacterial terpene synthases, OILTS was a little smaller than other terpene synthases whose structures have been known.

In summary, we reported the first functional analysis of the terpene synthase from the giant virus. We would like to analyze more enzymes from giant viruses in future, to more deeply understand the natural product biosynthesis in the giant viruses. In addition, the CS method could solve the structures of the enzyme products (**1** and **2**) and the degradation products (**3**–**6**) obtained in this study, showing the potential of the CS method to facilitate the studies in the field of natural product chemistry.

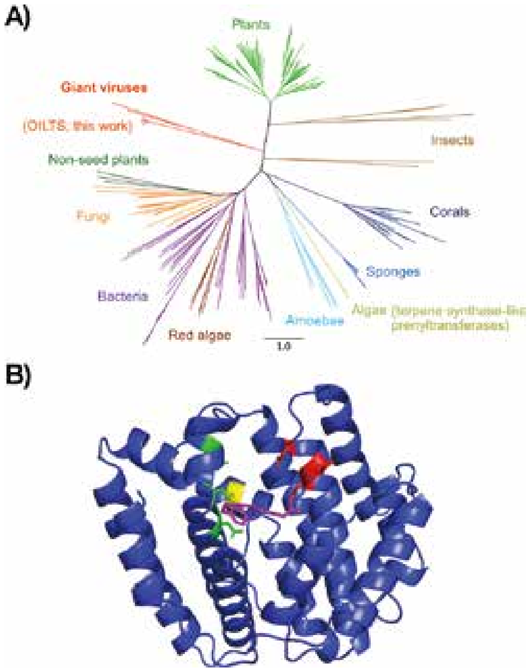

Figure 2. A) Phylogenetic analysis of the terpene synthases from giant viruses and other organisms. The figure is reprinted with permission from ref. 1). Copyright 2023 American Chemical Society. B) Structure of OILTS solved by protein X-ray crystallography.

References

1) Y. Jung, T. Mitsuhashi, S. Sato, M. Senda, T. Senda and M. Fujita, *J. Am. Chem. Soc.* **145**, 25966–25970 (2023).
2) Y. Jung, T. Mitsuhashi, T. Kikuchi and M. Fujita, *Chem. –Eur. J.* **30**, e202304317 (2024).
3) Y. Jung, T. Mitsuhashi, K. Kageyama, T. Kikuchi, S. Sato and M. Fujita, *Chem. –Eur. J.* **39**, e202400512 (2024).

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

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

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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.

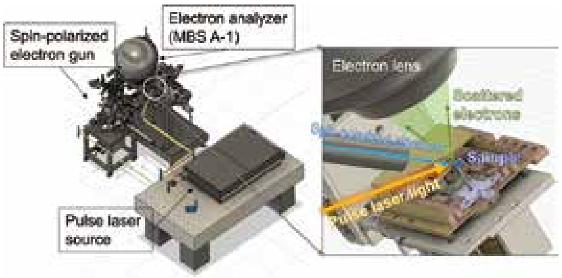

Figure 1. Time-, Spin-, and Angle-Resolved resonant Electron-Energy-Loss Spectroscopy (tSAR-rEELS) apparatus, which our group is now developing. The apparatus comprises a high-brilliant spin-polarized electron gun, a photoelectron spectrometer, and a femto-second pulse laser with an optical parametric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

Selected Publications

- T. Nakamura, H. Sugihara, Y. Chen, R. Yukawa, Y. Ohtsubo, K. Tanaka, M. Kitamura, H. Kumigashira and S. Kimura, "Two-Dimensional Heavy Fermion in Monoatomic-Layer Kondo Lattice $YbCu_2$," *Nat. Commun.* **14**, 7850 (7 pages) (2023).
- 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).
- S. Kimura, T. Kawabata, H. Matsumoto, Y. Ohta, A. Yoshizumi, Y. Yoshida, T. Yamashita, H. Watanabe, Y. Ohtsubo, N. Yamamoto and X. Jin, "Bulk-Sensitive Spin-Resolved Resonant Electron Energy-Loss Spectroscopy (SR-rEELS): Observation of Element- and Spin-Selective Bulk Plasmons," *Rev. Sci. Instrum.* **92**, 093103 (8 pages) (2021).
- K. Hagiwara, Y. Ohtsubo, M. Matsunami, S. Ideta, K. Tanaka, H. Miyazaki, J. E. Rault, P. Le Fèvre, F. Bertran, A. Taleb-Ibrahimi, R. Yukawa, M. Kobayashi, K. Horiba, H. Kumigashira, K. Sumida, T. Okuda, F. Iga and S. Kimura, "Surface Kondo Effect and Non-Trivial Metallic State of the Kondo Insulator YbB_{12}," *Nat. Commun.* **7**, 12690 (7 pages) (2016).

1. Two-Dimensional Heavy Fermion in Monoatomic-Layer Kondo Lattice $YbCu_2$[1)]

The Kondo effect between localized *f*-electrons and conductive carriers leads to exotic physical phenomena. Among them, heavy-fermion (HF) systems, in which massive effective carriers appear due to the Kondo effect, have fascinated many researchers. Dimensionality is also an important characteristic of the HF system, especially because it is strongly related to quantum criticality. However, the realization of the perfect two-dimensional (2D) HF materials is still a challenging topic. Here, we report the surface electronic structure of the monoatomic-layer Kondo lattice $YbCu_2$ on a Cu(111) surface observed by synchrotron-based angle-resolved photoemission spectroscopy. The 2D conducting band and the Yb 4*f* state are observed very close to the Fermi level. These bands are hybridized at low temperatures, forming the 2D HF state, with an evaluated coherence temperature of about 30 K. The effective mass of the 2D state is enhanced by a factor of 100 by the development of the HF state. Furthermore, clear evidence of the hybridization gap formation in the temperature dependence of the Kondo-resonance peak has been observed below the coherence temperature. Our study provides a new candidate as an ideal 2D HF material for understanding the Kondo effect at low dimensions.

2. Observation of Electronic Structure Modification in the Hidden Order Phase of CeCoSi[2)]

CeCoSi with no local inversion symmetric crystal structure (*P*4/*nmm*) exhibits a phase transition of unknown origin (Hidden Order: HO) at about 12 K (T_0) above the antiferromagnetic transition temperature (T_N = 9.4 K). The electronic structure change across T_0 was investigated with high-precision optical reflection spectroscopy. The optical spectrum changed from a typical metallic behavior above T_0 to a gap-like structure at around 15 meV below T_0. The gap-like structure was unchanged across T_N except for the narrowing of the Drude component of carriers due to the suppression of magnetic fluctuations. This result suggests a slight change from the typical metallic electronic structure above T_0 to that with an energy gap near the Fermi level in the HO phase. The change in electronic structure in the HO phase was concluded to be due to electron/valence instability.

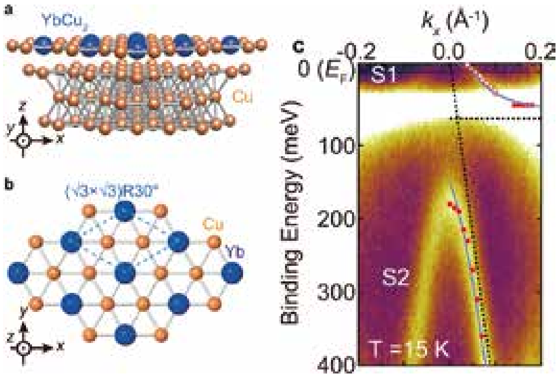

Figure 2. (a) A surface atomic structure of $YbCu_2/Cu(111)$. (b) Top view of monoatomic-layer $YbCu_2$. The dashed line indicates the unit cell of $YbCu_2$. (c) ARPES image near the center of the surface Brillouin zone taken with circularly polarized 35-eV photons at 15 K. ARPES intensities are divided by the Fermi–Dirac distribution function convolved with the instrumental resolution. The filled and break lines indicate the simulated *c-f* hybridization band dispersions with the hybridization energy of 120 meV (solid lines) and 0 meV (dashed lines) by the periodic Anderson model. The open and filled circles indicate the peak positions from energy distribution curves (EDCs) and MDCs, respectively.

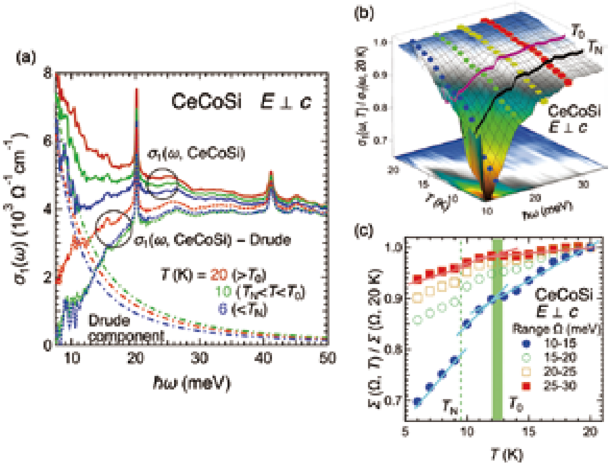

Figure 3. (a) Optical conductivity [$\sigma_1(\omega)$] spectra of CeCoSi at representative temperatures of 20 K (> T_0), 10 K ($T_N < T < T_0$), and 6 K (< T_N) (solid lines). Dot-dashed lines are Drude curves obtained from the values of electrical resistivity and the $\sigma_1(\omega)$ values at $\hbar\omega \sim 5$ meV. The interband components evaluated by subtracting the Drude components from the $\sigma_1(\omega)$ spectra are shown by dashed lines. (b) Temperature-dependent $\sigma_1(\omega)$ spectra normalized by that at 20 K of CeCoSi. The marks are the same as those in (c). (c) Temperature dependence of the spectral integrations of the range Ω of 10–15 meV (solid circle), 15–20 meV (open circle), 20–25 meV (open square), and 20–40 meV (solid square) in (b), which are representative regions of relative $\sigma_1(\omega)$ spectra in (b). The integrated intensity at each Ω is normalized by the value at T = 20 K. Solid lines are guides for the eye. T_0 and T_N are shown by vertical solid and dashed lines, respectively.

References

1) T. Nakamura, H. Sugihara, Y. Chen, R. Yukawa, Y. Ohtsubo, K. Tanaka, M. Kitamura, H. Kumigashira and S. Kimura, *Nat. Commun.* **14**, 7850 (7 pages) (2023).
2) S. Kimura, H. Watanabe, S. Tatsukawa and H. Tanida, *J. Phys. Soc. Jpn.* **92**, 043704 (5 pages) (2023).

Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

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

ONISHI, Hiroshi
Professor
(Cross Appointment)
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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 interfacess; photocatalysts for artificial photosynthesis, lubricants for smooth tribology, and ice in antifreeze liquids. Characterization with advanced 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.

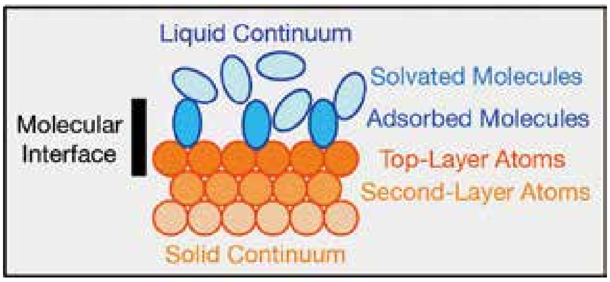

Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- Y.-H. Chew and H. Onishi, "Infrared Absorption of $Zn_{0.5}Cd_{0.5}S$ Photocatalyst Bandgap-Excited under an Aqueous Environment," *J. Phys. Chem. C* **128**, 4535–4543 (2024).
- M. Buessler, S. Maruyama, M. Zelenka, H. Onishi and E. H. G. Backus, "Unravelling the Interfacial Water Structure at the Photocatalyst Strontium Titanate by Sum Frequency Generation Spectroscopy," *Phys. Chem. Chem. Phys.* **25**, 31471–31480 (2023).
- 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).
- T. Kosaka, Y. Teduka, T. Ogura, Y. Zhou, T. Hisatomi, H. Nishiyama, K. Domen, Y. Takahashi and H. Onishi, "Transient Kinetics of O_2 Evolution in Photocatalytic Water-Splitting Reaction," *ACS Catal.* **10**, 13159–13164 (2020).
- S. Xue, A. Sasahara and H. Onishi, "Atom-Scale Imaging of TiO_2(110) Surface in Water by Frequency-Modulation Atomic Force Microscopy," *J. Chem. Phys.* **152**, 054703 (7 pages) (2020).
- 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. Ice in Antifreeze Liquids Characterized by Atomic Force Microscopy

Ice in nature is surrounded by liquid most of the time, and therefore it is key to understand how ice and liquid interact. We could now directly observe the precise shape of ice at the interface between ice and liquid, by using antifreeze and a refrigerated microscope.

Ice provides the most important crystalline molecules in our lives. Because of its critical role in science and engineering, a number of experimental studies have been conducted in bulk ice and also on ice–vacuum interfaces. On the other hand, molecular-scale knowledge of the ice–water interface is still quite limited. The problem is that an ice–water interface fluctuates in space, even when the interface is held exactly at the freezing point.

Here we performed atomic force microscopy (AFM) imaging of ice surfaces immersed in antifreeze organic solvents. Ice in contact with liquid 1-octanol, for example, is stable at temperatures lower than 0 °C and higher than the freezing point of 1-octanol (−16 °C). We expect to have a good chance of mimicking some features, hopefully important features, of the ice–water interface, even though antifreeze solvents are not equivalent to water.

We did some preliminary research in 2022 to find a way to keep the ice–liquid interface below 0 °C on a Bruker AFM (Dimension XR Icon Nano Electrochemical Microscope). The best way we found was to cool the entire microscope in a soundproof box. A liquid nitrogen vessel was pressurized to provide a steady flow of cold nitrogen vapor, and the vapor flow was introduced into the box equipped with copper pipe works cooled with antifreeze fluid (Figure 2). The temperature inside the box was controlled to a desired temperature in a range from RT to −10 °C, stable enough to record topographic images of ice under antifreeze liquids.$^{1)}$

Figure 2. The Bruker microscope at the Instrument Center devised for operation at −10 °C.

Ice films were prepared from ultrapure water. After eliminating residual gases by heating to 100 °C, 100 µl of the water was dropped onto a cleaved mica substrate on the microscope cooled in the nitrogen vapor environment. After the water was dropped on mica, the water spread on the surface. This was followed by a gradual phase change of the water from liquid to solid. After waiting about 30 minutes from the initial drop, the ice surface could be scanned using a cantilever in amplitude modulation mode. The images obtained showed that the ice surface is not atomically flat, but rather has a rough structure such as nanometer-scale frost pillars.

The imaging liquid, 1-octanol for the results shown in Figure 3, was then applied to the ice film. The thickness of the octanol layer was about 1 mm. Panel (a) in Figure 3 shows a topographic image obtained at the ice–octanol interface. Two flat terraces were separated by a straight step. A cross section was constructed along the light blue line and shown in panel (b). The height of the step was 0.10 nm, as shown in the cross section. The change of the ice surface in octanol liquid from the rough surface in N_2 vapor would be caused by the partial dissolution of the surface in octanol. A limited concentration of water dissolves in octanol (the solubility of water in 1-octanol is 2 mol l^{-1} at 25 °C in ref. 2).

Considering the various roles of ice, this study concludes that it opens up new possibilities for the study of surface and interfacial phenomena associated with ice in liquids. In addition, the microscope devised in this study is functional for imaging ice and also other materials cooled at −10 °C. It is available for use at the Instrument Center through the Advanced Research Infrastructure for Materials and Nanotechnology (ARIM).

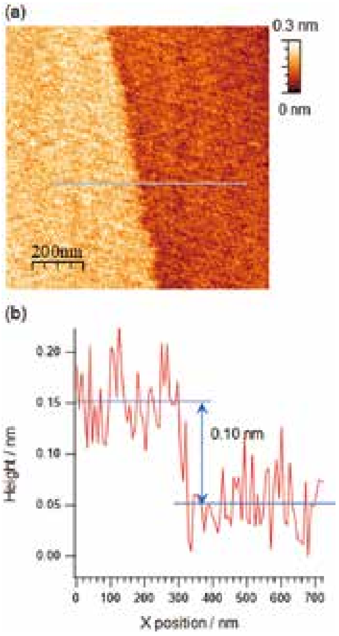

Figure 3. A topographic image of an ice film in 1-octanol liquid at −7 °C. A cross section determined along the line in panel (a) is shown in panel (b).

References

1) R. Yanagisawa, T. Ueda, K. Nakamoto, Z. Lu, H. Onishi and T. Minato, *J. Chem. Phys.* **161**, 024702 (2024).

2) I. Matsuoka, T. Naito and H. Yamada, *Bunseki-Kagaku*, **51**, 759 (2002).

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
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Education

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Professional Employment

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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

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KAWAGUCHI, Ritsuko

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 the small plastics runoff into the environment (Figure 1).

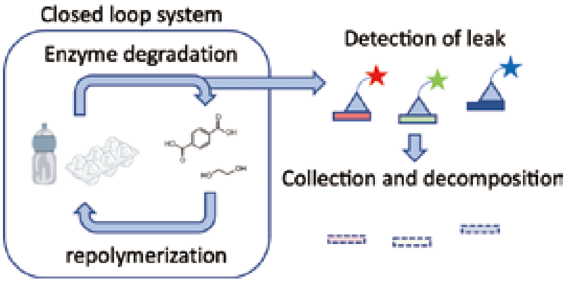

Figure 1. Scheme of plastic recycling and detection system.

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).
- A. Nakamura, D. Ishiwata, A. Visootsat, T. Uchiyama, K. Mizutani, S. Kaneko, T. Murata, K. Igarashi and R. Iino, “Domain Architecture Divergence Leads to Functional Divergence in Binding and Catalytic Domains of Bacterial and Fungal Cellobiohydrolases,” *J. Biol. Chem.* **295**, 14606–14617 (2020).
- 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, we tried to further improve the activity of PET2 with a combination of saturation mutations. For a combination of saturation mutation at two positions, we need to test 399 mutants. Since it is difficult to purify and measure the activity of each mutant individually, a screening method was created to evaluate the activity without purification of the enzyme and without the use of HPLC (Figure 2).1)

We prepared PET particulate suspensions by dissolving PET in Hexafluoro-2-propanol 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.

The correlation between the reduction of turbidity and concentration of soluble product was analyzed by HPLC. At the first stage of degradation, the two parameters showed linear correlation. 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 720 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 H229T-F233M mutant showed 3.4 times higher degradation rate against PET film than the template enzyme at the initial time. The molecular dynamics simulation implied that F233M mutation make the space for making alpha helix and H229T mutation resolved steric hindrance with Trp199. These mutations were speculated to change the angle of the Trp199 side chain of PET2 to an angle similar to that of the Trp185 of IsPETase, making it suitable for PET binding to the active center. Screening of activity using PET suspensions is compatible with robotic automation and is expected to be useful for validating computationally predicted mutations.

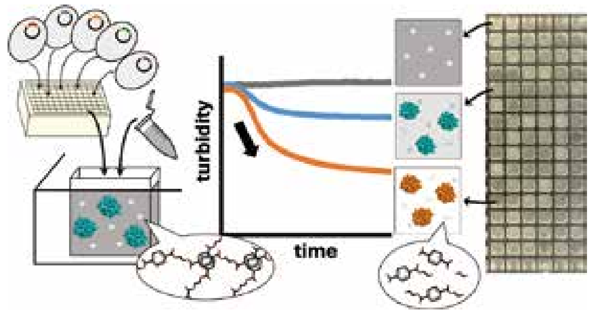

Figure 2. Scheme of PET degrading enzyme activity measurement using turbidity as an indicator.

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

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

Saturation mutations were introduced at four amino acid residues oriented on the binding surface and involved in chitin recognition. Since the number of candidates of mutants is about 160,000 and it is difficult to verify them one by one, we created a library of phage vectors with binding 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, and unbound phage were washed away. The phage bound on PET were recovered by trypsin digestion and re-amplified by infection with *E. coli*. The concentrated library of phage was further screened with more strong condition of washing.

The 3 cycles of screening of the first-generation phage library resulted in the 29 colonies of PET binding domain candidates. The 27 colonies were the PfCBD-K270H-N272P-E279V-D281G mutant (PfCBD-4M) and showed higher binding affinity to PET than WT. But the binding affinities to chitin and cellulose were remained. The other two mutant were rejected because the RFP fusion proteins were insoluble.

To improve the binding specificity, three mutations were further added to PfCBD-4M. After the 3 cycles of screening, the 425 colonies were obtained. The colonies were mixed, and the CBD genes were amplified by PCR. The CBD genes were ligated with RFP gene and the fusion proteins were produced in small scale. The solubilities of proteins were analyzed based on the RFP fluorescence signal in the solution to remove the insoluble proteins. The gens of the top 10 proteins were sequenced, and the 6 candidates were obtained. The binding amount of 2nd generation of 6 mutants, 4M and PfCBD-WT against chitin, cellulose and low and high concentrations of PET were measured. The all of 6 mutants showed almost no binding to chitin and cellulose but higher binding amount than 4M and WT (Figure 3). Therefore, we succeeded to change the binding specificity of the domain from chitin/cellulose to PET. Now we tried to make a fusion enzyme with PET hydrolase to increase the affinity to PET.

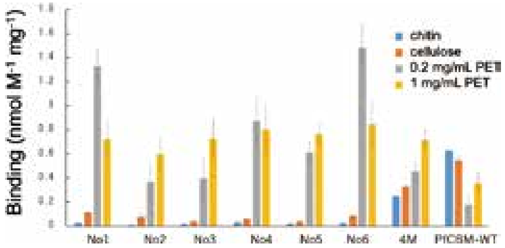

Figure 3. Binding measurement of 2nd generation of mutants against chitin, cellulose and PET.

Reference

1) Y. Ogura, Y. Hashino and A Nakamura, *ACS Omega* (2024), in press.

Molecular Science of Bio-Metal Dynamics: Understanding and Regulation of the Strategies of Metal Utilization in Living Cells

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Education

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Professional Employment

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2010	Research Assistant Professor, Okazaki Institute for Integrative Bioscience
2013	Assistant Professor, University of Hyogo
2022	Associate Professor, Nagasaki University
2024	Associate Professor (Cross Appointment), Institute for Molecular Science

Awards

2010	Yamamura Fellow, Fumi Yamamura Memorial Foundation for Female Natural Scientists, Chuo Mitsui Trust and Banking
2012	Shiseido Female Researcher Science Grant, SHISEIDO Company, Limited
2018	Excellent Research Award, The Japanese BioIron Society

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Keywords Iron Dynamics in Human Cells, Integrated Bio-Metal Sciences, Biological Inorganic Chemistry

Metals play important roles in sustaining life. Cells are mainly composed of water, proteins, and lipids, but they also contain small amounts of metals that help maintain health by being acquired from food. Those metals are used as active centers of enzymes that carry out functions essential to sustaining life, *e.g.* transport and storage of oxygen, energy production, gene synthesis, has been known for many years. However, the series of molecular mechanisms underlying metal dynamics in the body (absorption, sensing, transport, storage, and excretion of metals) (Figure1) and selectivity for individual metals remain unknown. Our group focuses on "iron," which is the most important metal among the essential metals for sustaining life of living things, focusing on various proteins that play a role in the selective absorption, sensing, and intracellular transport of iron in food. We are not only elucidating the structure of related proteins but also exploring their relationship with their functions in human cells.

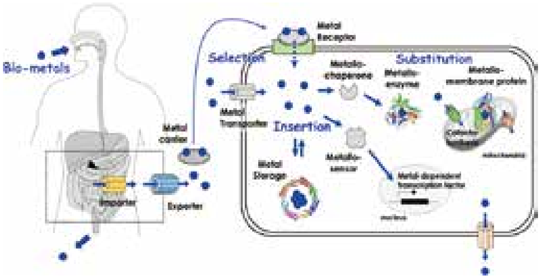

Figure 1. Our aim is to understand the uptake, trafficking, and regulation of "bio-metals" through the relay of protein–protein interactions.

Selected Publications

- M. Ganasen, H. Togashi, H. Takeda, H. Asakura, T. Tosha, K. Yamashita, K. Hirata, Y. Nariai, T. Urano, X. Yuan, I. Hamza, A. G. Mauk, Y. Shiro, H. Sugimoto and H. Sawai, "Structural Basis for Promotion of Duodenal Iron Absorption by Enteric Ferric Reductase with Ascorbate," *Commun. Biol.* **1**, 120 (2018). DOI: 10.1038/s42003-018-0121-8
- G. S. A. Wright, A. Saeki, T. Hikima, Y. Nishizono, T. Hisano, M. Kamaya, K. Nukina, H. Nishitani, H. Nakamura, M. Yamamoto, S. V. Antonyuk, S. Samar Hasnain, Y. Shiro and H. Sawai, "Architecture of the Complete Oxygen-Sensing FixL-FixJ Two-Component Signal Transduction System," *Sci. Signaling* **11**, eaaq0825 (2018). DOI: 10.1126/scisignal.aaq0825
- H. Sawai and K. Ishimori, "Integrated Bio-Metal Science: New Frontiers of Bio-Metal Science Opened with Cutting-Edge Techniques," *Biophys. Physicobiol.* **17**, 94–97 (2020).
- 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 the Hemolytic Bacterial Survival," *Commun. Biol.* **4**, 467 (2021). DOI: 10.1038/s42003-021-01987-5

1. Molecular Mechanism of Intracellular Fe^{2+} Regulation by the Iron-Delivery Chaperone PCBP

Iron is an essential “nutrient” for supporting life. In humans, iron nutrients (*e.g.*, heme iron and iron ions) ingested from food are absorbed from duodenum (upper small intestine) and after intracellular sensing, transport and storage, are eventually distributed as serum iron to organs and muscles throughout the body.[1] Iron ions can undergo redox, and although Fe^{2+} is water-soluble and easily accessible, it readily reacts with O_2 to produce reactive oxygen species, which are cytotoxic. On the other hand, Fe^{3+} is not a source of reactive oxygen species, but is less water-soluble. Therefore, the body uses a variety of proteins to avoid Fe^{2+} toxicity and strictly regulates iron homeostasis. Failure of this regulatory system to sustain iron homeostasis can lead to iron overload or deficiency. To help introduce the protein framework that dictates human iron dynamics, we focused on dietary iron dynamics via the intracellular iron-delivery chaperone, PCBP (poly rC binding protein)[2] (Figure 2).

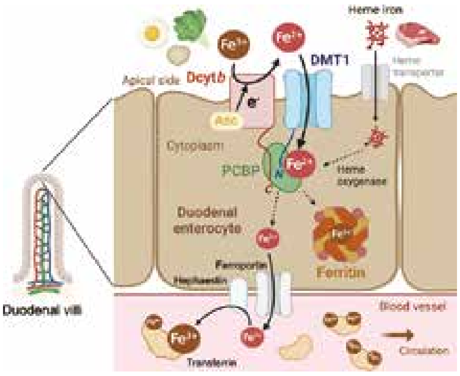

Figure 2. Dietary iron absorption in duodenum enterocyte. The first step of duodenal iron absorption is the transport of Fe^{2+} by DMT1 (divalent metal transporter 1) at the apical plasma membrane of duodenal enterocytes. Reduction of the predominant Fe^{3+} by Dcyt*b* (duodenal cytochrome *b*$_{561}$) using cytoplasmic electron doner, Asc (ascorbate), is necessary for Fe^{2+} transport by DMT1.

PCBP has been proposed to play a role in supplying iron ions to the iron storage protein ferritin,[3] but the molecular mechanism of iron trafficking from PCBP to ferritin remains elusive. To unveil these mechanisms, we prepared recombinant human PCBP and investigated its properties. Iron binding assays using apo-PCBP revealed that one molecule of apo-PCBP can bind one Fe^{2+}, while Fe^{3+} does not bind, clearly showing PCBP can only bind Fe^{2+}. The complexation of Fe^{2+}-bound PCBP and ferritin H- or L-chain were investigated by SEC-SAXS (size-exclusion chromatography integrated small-angle X-ray scattering) and mass photometry (Figures 3 and 4). Based on these results, we proposed that Fe^{2+}-bound PCBP preferentially binds the ferritin H-chain compared to the L-chain. Since the ferritin H-chain acts as a ferroxidase, converting Fe^{2+} to Fe^{3+} for the safe storage of iron in ferritin, PCBP thus mediates safe and effective iron trafficking to ferritin in the cytoplasm.

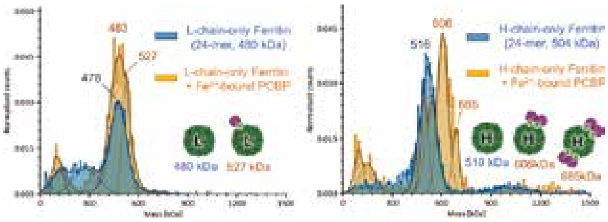

Figure 3. Mass photometry of ferritin and its mixture with Fe^{2+}-bound PCBP.

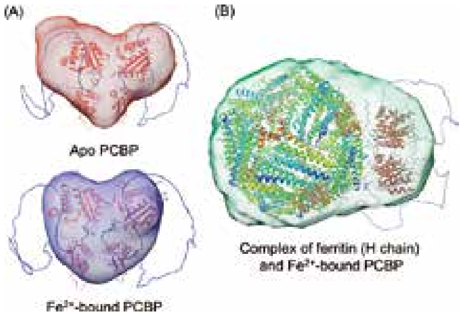

Figure 4. Space-filling models and pseudoatomic models of PCBPs (A) and its complex with H-chain only ferritin (B). Space-filling models were created based on SAXS data. Pseudoatomic models of PCBP in apo and Fe^{2+}-bound forms were predicted by AlphaFold3.

2. Cooperative Fe^{2+} Transfer between Dcyt*b* and DMT1 in the Plasma Membrane of Intestinal Living Cells

Because Fe^{2+} produced by the enzymatic reaction of Dcyt*b* is a source of reactive oxygen species, for safe and efficient trafficking of Fe^{2+}, Dcyt*b* must be close to or form a complex with DMT1 and transfer the produced Fe^{2+} to DMT1 as quickly as possible. To demonstrate that, we confirmed the localization of Dcyt*b* and DMT1 by immunofluorescence observation and proximity ligation assay between Dcyt*b* and DMT1 using Caco2-kh cells,[3] a human intestinal model cell. We further found that the *C*-terminal region of Dcyt*b* also binds to PCBP by biochemical analysis of complex formation using wild-type and deletion mutant of the *C*-terminal loop of Dcyt*b*. These data imply that not only the interaction between Dcyt*b* and DMT1 in the apical membrane of the cells, but also PCBP interacts with these membrane proteins to ensure safe and efficient Fe^{2+} transport. Therefore, it is possible that Dcyt*b*-DMT1-PCBP forms a ternary complex to play a cooperative function for the Fe^{2+} transport in the cell. Further studies at molecular and cellular levels will provide new insights into the mechanisms of ternary complex formation for dietary iron absorption in human duodenum.

References

1) N. C. Andrews, *Nat. Rev. Genet.* **1**, 208–217 (2000).
2) I. Yanatori *et al.*, *Biochim. Biophys. Acta, Gen. Subj.* **1864**, 129685 (2020).
3) H. Shi *et al.*, *Science* **320**, 1207–1210 (2008).
4) H. Fujishiro *et al.*, *J. Toxicol. Sci.* **42**, 559–567 (2017).

Integration of Quantum Chemistry and Machine Learning for a Deeper Understanding and Rational Design of Functional Materials

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Education

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Professional Employment

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2011	Fukui fellow, Kyoto University
2015	Assistant Professor, Kindai university
2015	Japan Science and Technology Agency (JST) PRESTO Researcher
2017	Associate Professor, Nara Institute of Science and Technology
2020	Associate Professor, Keio University
2024	Associate Professor (Cross Appointment), Institute for Molecular Science

Awards

2017	11th PCCP Prize
2019	12th Young Scientist Award of the Japan Society for Molecular Science
2021	The Chemical Society of Japan Award for Outstanding Young Women Chemists for 2021
2021	MEXT National Institute of Science and Technology Policy (NISTEP), NISTEP Selection (The Researchers with Nice Step) 2021

Member
Secretary
MASUDA, Michiko

Keywords Materials Informatics, Lanthanide, Computational Chemistry

We develop computational methods, apply them to elucidate mechanisms, and design materials using data science techniques such as machine learning (ML). Currently, our research focuses on the following subjects:

(1) Lanthanide Photofunctional Materials

Lanthanide (Ln) luminescence, originating from 4f–4f transitions, has been applied in various optical materials. While the 4f–4f emission wavelengths of Ln complexes are almost independent of the surroundings, the emission intensities are heavily influenced, making the design of appropriate ligand crucial. To get deeper insights into Ln luminescence, we proposed the energy shift method, which has contributed to the understanding and design of various Ln materials and has also been applied to non-Ln systems. However, it could not handle 4f–5d and charge transfer excited states, which are particularly important for cerium and europium complexes. To address this limitation, we are developing an updated method. In addition, we have constructed a database of cerium complexes containing 1.7k geometries and electronic properties. We plan to make this database public and further develop it into a platform for optical function prediction *via* ML.

(2) Transition Metal Catalysts

Transition metal (TM) complexes play a crucial role in organic synthesis, catalyzing a wide variety of chemical reactions. The catalytic abilities of TM complexes can be finely tuned by manipulating ligand-induced electronic and steric effects, which are key to controlling the reactivity and selectivity of specific reactions. In recent years, however, chemical products are being produced in smaller quantities and with greater variety, reducing the time available to study the synthesis conditions for each product. To address this challenge, we are constructing a database of TM complexes with various organophosphorus ligands, ranging from monodentate to multidentate skeletons. For descriptors applicable to different skeletons, we propose using the reaction energies of elementary reactions, such as oxidative addition and transmetallation. Our goal is to accelerate catalyst design by developing an ML model where our descriptors serve as explanatory variables and experimental catalytic activity results are used as objective variables.

Selected Publications

- S. Gocho, H. Nakamura, Q. Gao, T. Kobayashi, T. Inagaki and *M. Hatanaka, "Excited State Calculations Using Variational Quantum Eigensolver with Spin-Restricted Ansätze and Automatically-Adjusted Constraints," *npj Comput. Mater.* **9**, 13 (2023).
- X.-F. Wei, T. Wakaki, T. Itoh, H.-L. Li, T. Yoshimura, A. Miyazaki, K. Oisaki, *M. Hatanaka, *Y. Shimizu and *M. Kanai, "Catalytic Regio- and Enantioselective Proton Migration from Skipped Enynes to Allenes," *Chem* **5**, 585 (2019).
- *M. Hatanaka, Y. Hirai, Y. Kitagawa, T. Nakanishi, *Y. Hasegawa and *K. Morokuma, "Organic Linkers Control the Thermosensitivity of the Emission Intensities from Tb(III) and Eu(III) in a Chameleon Polymer," *Chem. Sci.* **8**, 423 (2017).

1. Geometry Exploration Using Bayesian Optimization

Conventional molecular geometry searches on a potential energy surface utilize energies and energy gradients from quantum chemical calculations. However, replacing energy calculations with noisy quantum computer measurements generates errors in the energies, which makes geometry optimization using the energy gradient difficult. One gradient-free optimization method that can potentially solve this problem is Bayesian optimization. To use Bayesian optimization in geometry search, a suitable acquisition function must be defined. In this study, we propose a strategy for geometry searches using Bayesian optimization and examine the appropriate acquisition functions to explore the global minimum (GM) and the most stable conical intersection (CI). The acquisition functions for the GM and CI searches were defined as the probability improvements of the energy with opposite sign and the cost function C in eq (1), respectively.

$$C(x) = -\left\{\frac{E_{S0}(x) + E_{S1}(x)}{2} + \frac{\{E_{S0}(x) - E_{S1}(x)\}^2}{\alpha}\right\} \cdots (1)$$

Here, $E_{Sn}(x)$ and α are the electronic energy of the n-the singlet state at the geometry x and the hyperparameter, respectively. We applied our strategy to two molecules, formaldehyde and ethylene, and found the GM and the most stable CI geometries with high accuracy for both molecules.

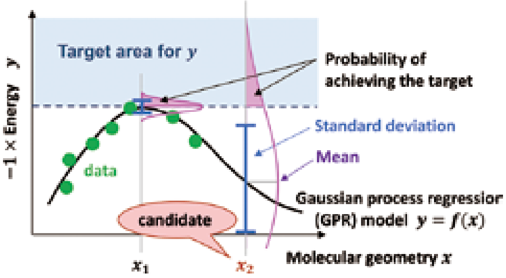

Figure 1. Schematic illustration of global minimum search using Bayesian optimization.

2. Copolymer Descriptor Database and Its Application to Machine Learning

Polymer informatics, which applies data-driven science to polymers, has attracted significant research interest. However, developing suitable descriptors for polymers, particularly copolymers, to enable machine learning models with limited data sets remains a challenge. To address this, we computed a range of parameters, including reaction energies and activation barriers of elementary reactions in the early stage of radical polymerization, for 2,500 radical–monomer pairs derived from 50 commercially available monomers. We then created an open-access database called the "Copolymer Descriptor Database (CopDDB)." Additionally, we constructed machine learning models using these descriptors as explanatory variables and various physical properties—such as the reactivity ratios, monomer conversion rates, monomer composition ratios, and molecular weights—as objective variables and achieved high predictive accuracies. We also conducted process optimization for the copolymerization of untested monomers. Typical Bayesian optimization requires an initial training set of target molecules, which entails significant experimental cost. However, our approach overcomes this challenge by using data from previously tested molecules that do not contain the target molecules for the initial training dataset. These models achieved high predictive accuracy, demonstrating the potential of our descriptors to advance polymer informatics.

3. Mechanism of Formation of Thermally Stable Cyclotrisilanyl Radicals

A halogen-substituted cyclic disilene compound, bromocyclotrisilene, $Si_3Br(Eind)_3$ (**3a**) bearing the fused-ring bulky Eind groups, was synthesized as an extraordinarily air-stable compound by our collaborators (Prof. Matsuo group at Kindai university). Even though **3a** is quite air-stable both in solutions and in the solid state, its Si–Br bond is reactive under reducing conditions. The further treatment of **3a** with Li metal leads to the formation of room-temperature thermally-stable silicon homologues of the cyclopropyl radical, *i.e.*, the cyclotrisilanyl radicals (**6a**), via intramolecular C–H bond activation in a transient silicon homologue of the cyclopropenyl radical, *i.e.*, the cyclotrisilenyl radical, $[Si_3(Eind)_3]^\bullet$ (**5a**). To elucidate the formation mechanism of **6a** from **5a**, we performed the reaction path search using the artificial force induced reaction (AFIR) method at the ONIOM (B3LYP-D3/PM6-D3) level. The reaction started from the approach of silyl radical center of **5a** to one of the H atoms in the Eind group, which afforded carbon-centered radical specie. The carbon-centered radical attacked Si_3, which induced the formation of C–Si and formed a ring-opened radical species. Then silylene center approaches the Si–H bond, which induces the formation of the Si–Si and Si–H bonds and results in the formation of the stable product **6a**. To the best of our knowledge, derivatives of the cyclopropyl radical have not yet been isolated and remained elusive. The cyclotrisilanyl radicals **6a** are the first room-temperature thermally stable homologues of the cyclopropyl radical, whose structural features and electronic properties have been experimentally and theoretically investigated.

References

1) R. Ohno, K. Ota, N. Nishimura, K. Taniguchi, S. Kurokawa, T. Wakabayashi, M. Hatanaka, A. Rosas-Sánchez, D. Hashizume and T. Matsuo, *J. Am. Chem. Soc.* **146**, 24911–24924 (2024).
2) K. Muto, M. Hatanaka, F. Kakiuchi and T. Kochi, *Organometallics* **43**, 1528–1535 (2024).
3) S. Kanno, H. Nakamura, T. Kobayashi, S. Gocho, M. Hatanaka, N. Yamamoto and Q. Gao, *npj Quantum Inf.* **10**, 56 (2024).
4) A. Wakiuchi, S. Jasial, S. Asano, R. Hashizume, M. Hatanaka, Y. Ohnishi, T. Matsubara, H. Ajiro, T. Sugawara, M. Fujii and T. Miyao, *MRS Commun.* **14**, 439–444 (2024).
5) K. Muto, M. Hatanaka, F. Kakiuchi and T. Kochi, *J. Org. Chem.* **89**, 4712–4721 (2024).
6) K. Terasaka, T. Kamoshida, T. Ichikawa, T. Yokoyama, M. Shibuta, M. Hatanaka and A. Nakajima, *J. Am. Chem. Soc.* **146**, 9605–9613 (2024).
7) T. Inoue, M. Hatanaka and A. Nakajima, *J. Am. Chem. Soc.* **145**, 23088–23097 (2023).

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

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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

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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. High-brightness nature 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. 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).

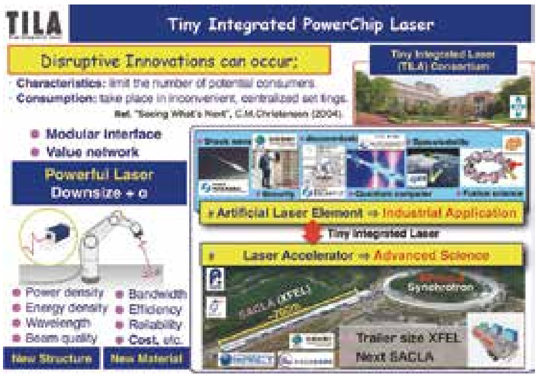

Figure 1. TILA consortium toward "Laser Science and Innovation" by micro solid-state photonics.

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).
- 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).
- Y. Sano *et al.*, *Forces in Mechanics* **7**, 100080 (2022).
- V. Yahia *et al.*, *Opt. Express* **32**, 14377 (2024).

1. Uncovering Gold Nanoparticle Synthesis Using a Microchip Laser System through Pulsed Laser Ablation in Aqueous Solution[1)]

The synthesis of gold nanoparticles (Au NPs) was carried out by utilising the pulsed laser ablation in liquids (PLAL) method with a microchip laser (MCL) system. This portable system features low power consumption and a giant-pulse laser. Aqueous solutions with and without the surfactant poly(N-vinyl-2-pyrrolidone) (PVP) were used for laser ablation of a bulk gold rod to achieve the successful formation of a colloidal solution of Au NPs. The gas bubbles formed by heating the aqueous medium around the surface of the gold target significantly reduced the efficiency of Au NP ablation. This effect was more pronounced and prolonged in high-viscosity solutions, hindering energy transfer from subsequent laser pulses to the target. Additionally, it was suggested that the chain length of PVP does not affect either the size of the Au NPs or the ablation efficiency. The relatively short pulse duration of the MCL system may contribute to the formation of NPs with consistent size, which were suppressed to grow in significantly smaller cavitation bubbles with short lifetimes.

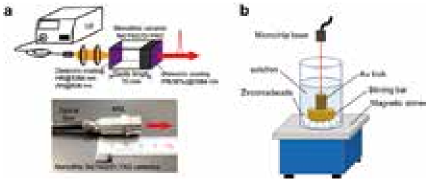

Figure 2. (a) Composition of the MCL system and the scale of the MCL laser head; (b) setup of PLAL system in the present research.

2. Joule-Class Sub-Nanosecond Pulses Produced by End-Pumped Direct Bonded Yag/Sapphire Modular Amplifier[2)]

A Joule-class room-temperature diode-pumped solid-state laser was developed. The energy scaling of the 100 mJ and 1064 nm seed pulse was realized by a series of two diode-pumped amplifiers. The gain medium consists in free combinations of Nd:YAG ceramics bonded to sapphire transparent heat sinks, to relax the thermal load induced by the 34 kW pump power. At low repetition rate, parasitic lasing was the main limitation to energy scaling. By choosing a gain module combination producing a step-like gradual doping concentration profile, mitigation of parasitic oscillations was observed, and the system delivered 2.8 J and 800 ps pulses at 2 Hz (Figure 3).

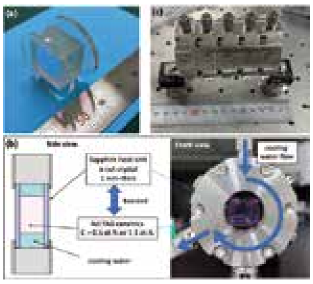

Figure 3. (a) Example of Nd:YAG ceramics with bonded sapphire end-caps that are used for the gain modules. (b) Design of a single independent gain module. (c) Modular gain medium consisting in a series of five modules.

3. Development of a Radiation Tolerant Laser-Induced Breakdown Spectroscopy System Using a Single Crystal Micro-Chip Laser for Remote Elemental Analysis[3)]

For the development of the remote elemental analysis method in a radiation environment based on the laser-induced breakdown spectroscopy (LIBS), the radiation effects on the laser oscillation properties of the single crystal (SC) Nd:YAG MCL were investigated and compared with those of ceramic Nd:YAG MCL. The laser oscillation properties were measured under gamma ray irradiation as a function of dose rate. The effects on the SC MCL properties were very small compared to those on the ceramics, indicating minimal radiation effects on the LIBS signal when using SC MCL. Pulse energy and oscillating build-up time (BUT) were measured for cumulative dose exceeding 1400 kGy. The results indicate that the effects of dose rate and cumulative dose on SC MCL laser properties are minimal. The SC MCL was then integrated into the LIBS system, and the gadolinium signal was successfully measured at a dose rate of 5 kGy/hr. These findings highlight the radiation tolerance of SC MCL for remote LIBS applications in harsh radiation environments (Figure 4).

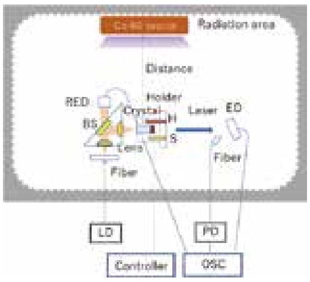

Figure 4. Experimental setup (BS: beam splitter; controller: temperature controller; crystal: YAG crystal; ED, RED: energy detector; fiber: optical fiber; H: heater; holder: specimen holder; LD: laser diode; lens: lens; OSC: oscilloscope; PD: photodiode; S: temperature sensor).

References

1) B. S. Hettiarachchi, Y. Takaoka, Y. Uetake, Y. Yakiyama, H. H. Lim, T. Taira, M. Maruyama, Y. Mori, H. Y. Yoshikawa and H. Sakurai, *Ind. Chem. Mater.* **2**, 340–347 (2024).

2) V. Yahia, A. Kausas, A. Tsuji, M. Yoshida and T. Taira, *Opt. Express* **32**, 14377–14393 (2024).

3) K. Tamura, R. Nakanishi, H. Ohbaa, T. Karino, T. Shibata, T. Taira and I. Wakaidab, *J. Nucl. Sci. Technol.* **61**, 1109–1116 (2024).

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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
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TANAKA, Kiyohisa	Associate Professor
TAIRA, Yoshitaka	Associate Professor
KANEYASU, Tatsuo	Associate Professor (SAGA-LS)
ARAKI, Tohru	Senior Researcher
IWAYAMA, Hiroshi	Senior Researcher
IZUMI, Yudai	Research Lecturer
SATO, Yusuke	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
OKANO, Yasuaki	Engineer
SAKAI, Masahiro	Chief Technician
YANO, Takayuki	Chief Technician
TESHIMA, Fumitsuna	Chief Technician
KONDO, Naonori	Chief Technician
YUZAWA, Hayato	Chief Technician
OTA, Hiroshi	Technician
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MIZUKAWA, Tetsunori	Technical Support Staff
SUGIMOTO, Yasunobu	Technical Support Staff
YAMAZAKI, Jun-ichiro	Technical Support Staff
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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/Adsorption
BL6B	Michelson FT-IR	4 meV-2.5 eV	Solid	Reflection/Adsorption
BL7B	3-m normal incidence	1.2-25 eV	Solid	Reflection/Adsorption
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

One of the unique UVSOR research activity is the discovery of the ability of synchrotron radiation to perform coherent control using the tandem undulator BL1U. Synchrotron radiation is usually considered as being of poor temporal coherence, therefore it is hardly thought that there is a hidden capability of coherent control. However, Katoh *et al.*, have demonstrated the capability of synchrotron radiation on the coherent control using the double undulator system which is capable of producing light pulses with tailored waveform.[1,2]

Wave-particle duality is one of the most fundamental concepts in quantum mechanics. The concept has previously been beautifully demonstrated by the double-slit experiment, in which particles such as electrons, atoms, molecules and neutrons passing through the double-slit exhibit interference patterns in the intensity distribution on a detection screen. To produce the temporal double-slit, a tandem-undulator system is used in which each relativistic electron in the bunch emits a pair of light wave packets that has a mutual coherence between them. A pair of light wave packets sequentially interacts with a helium atom, producing a pair of photoelectron wave packets that propagate in free space and overlap each other, leading to the appearance of the interference pattern. In order to visualize the buildup of the interference pattern, the interference in the energy domain was observed (Figure 1).

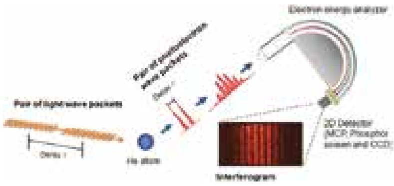

Figure 1. Time-domain double-slit experiment using a tandem-undulator system at BL1U.

Reserch Highlights

Heavy-fermion (HF) systems in rare-earth intermetallic compounds originating from the hybridization between localized *f* electrons and conduction (*c*) electrons are central topics in strongly correlated electron systems. Depending on the *c*–*f* hybridization strength at low temperatures, the ground state changes from a magnetic order to a heavy Fermi liquid. The competition between these two states makes a quantum critical point, resulting in the emergence of exotic quantum phenomena such as non-Fermi liquid and HF superconductivity. The dimensionality of the system characterizes the fundamental physical property. The combination of the HF state and low dimensionality modifies the ground state because the order parameter of these systems is much more sensitive to dimensionality. However, the monoatomic-layer Kondo-lattice showing a two-dimensional (2D) HF state has never been reported. In this study, we report the HF electronic structure of the monoatomic-layer Kondo lattice $YbCu_2$ by angle-resolved photoelectron spectroscopy (ARPES) at UVSOR-III BL5U and BL7U.[3]

Figure 2(a) shows the ARPES intensity plot around the $\bar{\Gamma}$ point at 7 K. The flat band is close to EF and highly dispersive hole bands are observed near the $\bar{\Gamma}$ point. According to the DFT calculation, the flat band and hole bands originate from the Yb^{2+} $4f_{7/2}$ and the mixing of the Yb 5*d* and Cu *sp* and *d* orbitals. The Yb^{2+} 4*f* flat band is modulated at the cross points to the conduction bands just below E_F, providing evidence of the *c*–*f* hybridization.

The temperature dependence of the quasiparticle peak just below E_F, the so-called Kondo-resonance (KR) peak, is reflected in renormalization due to the development of *c*–*f* hybridization. Figure 2(b) shows the angle-integrated (AI) photoelectron spectra as a function of temperature. The KR peak energy is shifted to the E_F with decreasing temperature, indicating the evolution of the renormalization. Figure 2(c) shows the temperature dependence of the KR peak positions. The peak position shifts with decreasing temperature and is saturated at 30 K. Such saturated temperature represents a coherence temperature (T_{coh}), at which the *c*–*f* hybridization state is fully established, resulting in a HF state.

To investigate the momentum-dependent *c*–*f* hybridization, we took the temperature-dependent peak position of the KR peak at three wavenumbers (k_x = 0.5, 0.0, −0.1 Å^{-1}) (not shown). The change of the peak position at k_x = 0.5 Å^{-1} almost follows the AI one. In contrast to the saturated feature in the AI spectrum at T = 30 K, the KR peak positions at k_x = 0.0 and −0.1 Å^{-1} are shifted to the higher-binding energy side below T_{coh}, suggesting the hybridization gap enlargement.

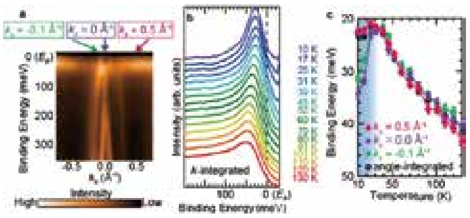

Figure 2. (a) The ARPES intensity plot around $\bar{\Gamma}$ point taken with horizontally polarized 37 eV photons at 7 K. (b) Angle-integrated photoelectron spectra as a function of temperature taken with horizontally polarized 35 eV photons. (c) Momentum dependence of the energy position of the quasiparticle peak plotted on a linear temperature scale.

References

1) Y. Hikosaka *et al.*, *Nat. Commun.* **10**, 4988 (2019); **12**, 3782 (2021).
2) T. Kaneyasu *et al.*, *Sci. Rep.* **12**, 9682 (2022).
3) T. Nakamura *et al.*, *Nat. Commun.* **14**, 7850 (2023).

Instrument Center

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SHIGEMASA, Eiji	Unit Leader
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UEDA, Tadashi	Chief Technician
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OKANO, Yoshinori	Technician
URUICHI, Mikio	Technician
MIYAJIMA, Mizuki	Technician
NAGAO, Haruyo	Technician
HIRANO, Kaho	Technician
MINAMINO, Yu	Technician
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FUJIKAWA, Kiyoe	Technical Support Staff
KUBOTA, Akiko	Technical Support Staff
IMAI, Yumiko	Technical Support Staff
UCHIDA, Mariko	Technical Support Staff
IWASE, Mahiro	Technical Support Staff
FUNAKI, Yumiko	Secretary
HYODO, Yumiko	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 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, JNM-ECZL 600, 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), field emission transmission electron microscope (JEOL JEM-2100F), elemental analyzer (J-Science Lab Micro Corder JM10), ICP atomic emission spectroscopy (Agilent 5110 ICP-OES), fluorescence spectrometer (JASCO FP-8650DS), fluorescence lifetime spectrometer (Quantaurus-Tau C16361-01), electron probe microanalyzer (EPMA, JEOL JXA-8230/SS-94000SXES), and automatic organic molecular synthesis (Cole-Parmer reaction station Integrity 10).

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), 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, Rigaku HyPix-AFC, and Rigaku XtaLAB Synergy-R/DW), operando multi-purpose 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), 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 Nano-electrical & Nanoelectrochemical), and electron spectrometers for chemical analysis (ESCA) equipment (Scienta-Omicron, R4000L1).

In the fiscal year of 2023, Instrument Center accepted 141 applications from outside and the total user time amounted 2,072 days for outside and 925 days for in-house. Instrument

Center also maintains helium liquefiers in the both campus and provides liquid helium to users (52,706 L/year). Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute (45,153 L/year).

Instrument Center also organizes the Inter-University Network for Common Utilization of Research Equipments 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.

Award

NAGAO, Haruyo; ARIM Japan The Best Technical Support Contribution Award (2024).

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
ISOGAI, Toshifumi	Technician
SAWADA, Toshihiro	Technical Support Staff
ISHIKAWA, Akiko	Technical Support Staff
SUGANUMA, Kouji	Technical Support Staff
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.

Introduction of New Lithography Equipment

Several types of lithography equipment have been installed in our clean room over the past few years.

One is a Reactive Ion Etching (RIE) machine, the "RIE-10NR" from Samco Inc. This machine can etch silicon (Si) and silicon dioxide (SiO_2) using carbon tetrafluoride gas as a process gas, and it can also etch organic materials using O_2 gas (Figure 1 left). Before this equipment was installed, we performed wet etching using corrosive solutions. With the installation of the RIE equipment, dry etching is now possible, allowing us to fabricate finer patterns that were previously unachievable with wet etching.

Another piece of equipment is the Evaporation Equipment, which was donated to us by a research group at the Institute for Molecular Science. It is a customized version of ULVAC's Compact Evaporation Equipment DEPOX Series "VTS-350M/ERH." Since the equipment was not ready for immediate use after relocation, members of the Equipment Development Center collaborated to set it up. We have successfully confirmed that gold can be deposited using this system (Figure 1 right).

We plan to use the aforementioned equipment extensively for microfabrication *via* lithography.

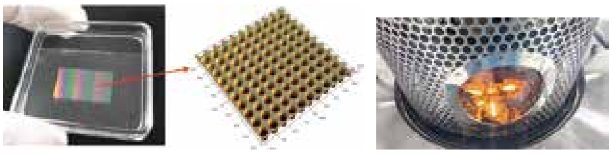


Figure 1. Examples of fabrication using O_2 gas as a process gas (left) and gold evaporation (right).

Electronics Instruments for Low-Temperature Scanning Near-Field Optical Microscopy

By utilizing near-field techniques, scientists can perform optical imaging and spectroscopy below the diffraction limit. To achieve near-field optical measurements at ultra-low temperatures and ultra-high vacuum conditions, we have developed three electronic instruments: (1) an interferometer that precisely detects and amplifies interference light generated in optical fibers; (2) an instrument that provides feedback signals based on fluctuations in the distance between the optical fiber and cantilever; (3) a driver that moves the piezo stage to fine-tune these fluctuations. Since we detect, amplify, and control weak signals, all instruments are constructed entirely with analog circuits.

The interferometer detects interference light from the optical fiber using a four-quadrant photodiode and amplifies it 250,000 times using a detection circuit built with ADA4627-1ARZ (Analog Devices). The feedback instrument smooths and holds fluctuations of less than 10 Hz, which are mixed in the interference light, using an integrating circuit with ADA4084-1ARZ (Analog Devices). The driver, constructed primarily with a high-voltage amplifier PA441DF (Apex), drives the piezo stage to fine-tune the fluctuation correction (Figure 2).

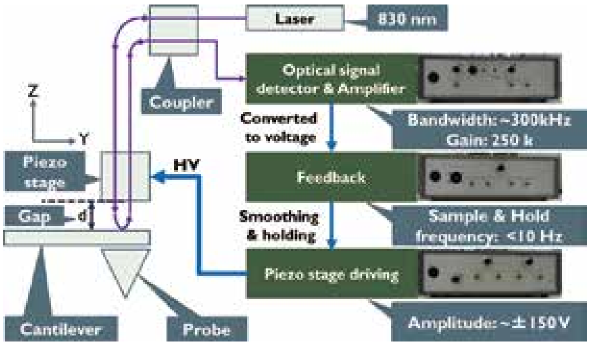


Figure 2. Schematic of electronics instruments for NCAFM (Non-Contacting Atomic Force Microscope) based on optical fiber detection.

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 Associate
UNO, Akiko	Technical Support Staff
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 1,315 researchers from 302 groups in the fiscal year 2023. 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 2023, the numbers of registered attendants of these schools were 329 and 380, 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 2023, we organized the workshop under the title, "Frontiers of Biomolecular Science based on Simulations, Informatics, and AI."

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.

SUPPORTING STAFF

Safety Office

YOKOYAMA, Toshihiko	Director
TOMURA, Masaaki	Research Associate
SHIGEMASA, Eiji	Technical Staff
UEDA, Tadashi	Technical Staff
SAKAI, Masahiro	Technical Staff
MAKITA, Seiji	Technical Staff
URUICHI, Mikio	Technical Staff
NAGAO, Haruyo	Technical Staff
ASADA, Mizue	Technical Staff
TESHIMA, Fumitsuna	Technical Staff
KIMURA, Kazunori	Technical Staff
MINAMIDA, Yu	Technical Staff
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 IMS 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 verifies the safe managements of poisonous substances and high-pressure gases, edits the safety manuals and gives safety training courses for Japanese and foreign researchers.

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 Staff (in charge of General Affairs)
NAKAMURA, Toshikazu	Team Leader, Instrument Center
FUJITA, Hiromasa	URA (Administrative Associate, Assistant to Head)
HARADA, Miyuki	URA (Technical Staff)
NAGASONO, Hisayo	URA (Administrative Associate)
OHTA, Minori	Administrative Associate
KAWAJIRI, Toshitaka	Administrative Associate
IKENAGA, Yumiko	Administrative Associate
NOGAWA, Kyoko	Administrative Associate
NAKAMURA, Rie	Technical Support Staff
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. Five 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 R&D Program "Moonshot Goal 6": Realization of a Fault-Tolerant Universal Quantum Computer That Will Revolutionize Economy, Industry, and Security by 2050

(e) MEXT Promotion of Development of a Joint Usage/Research System Project: Coalition of Universities for Research Excellence Program (CURE): Frontier of Spin Life Sciences [Spin-L]

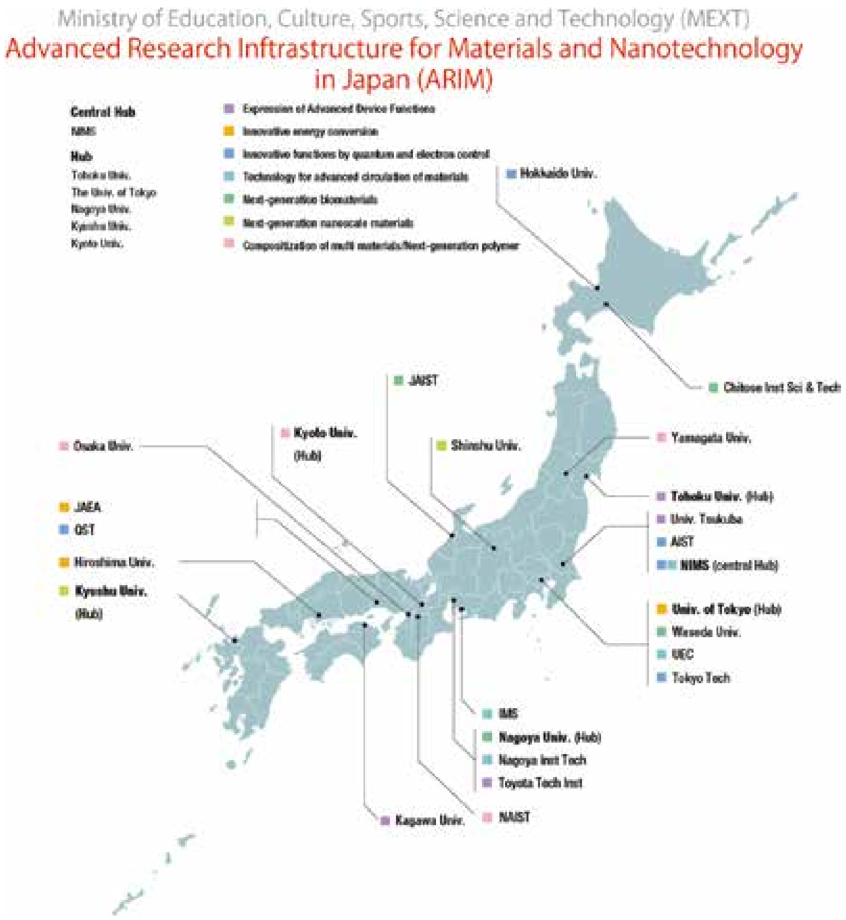
These five projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

(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 19,500 in 674 universities/institutions/companies (as of July, 2024). Network usage reaches more than 190,000 times a year, in which external usage amounts to 5,400 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 Infrastructure for Materials and Nanotechnology in Japan) program supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT) has been conducted, succeeding to MEXT Nanotechnology Platform program that was completed in March, 2022. In this new program, seven "key technology domains" are set. Each key technology domain team consist of one hub organization and several spoke organizations, with the center hub of National Institute of Materials Science (NIMS). The hub & spoke networks for collecting, accumulating, and structuring research data that are created from observation, measurement, synthesis and fabrication equipment and facilities, were launched in order to strengthen AI-driven materials & device R&D using informatics techniques. IMS belongs to one of the key technology domains of "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. Domestic and international equipment sharing is the most important purpose in this program, as in the Nanotechnology Platform program. Moreover, users and staffs are requested to provide experimentally obtained data to the Data Platform Center (DPC) that are being constructed in NIMS. Accumulated structured data will be shared through the NIMS DPC. In addition, we will contribute to strengthening material innovation force by building a "Material D Platform" in collaboration with the Data creation/utilization type material research and development project. In this program, three areas of shared methodology are set to promote cooperation across the seven key technology domains. IMS also acts as a representative organization for the cross-sectional technological area concerning the material synthesis process to promote technological cooperation among all the participating organizations. Human resource development is also an important aim in this program and IMS regularly conducts training sessions with "EQ-NET" to upskilling of the technical staffs engaged in this program. In IMS, the mission for the ARIM program is mainly organized by Instrument Center, supported by Research Center for Computational Science in data storage and transfer to NIMS DPC. Through this program, a new electron spin resonance (ESR) system and a new superconducting quantum interference device (SQUID) magnetometer were installed in IMS in 2021 and 2022, and a high-throughput low-temperature single-crystal x-ray diffractometer and an automatic organic synthesis system were introduced in FY2023. We hope that this program will successfully be performed and equipment sharing and data sharing will be accelerated.


Ministry of Education, Culture, Sports, Science and Technology (MEXT)
Advanced Research Inftrastructure for Materials and Nanotechnology in Japan (ARIM)

List of Equipment Supports in IMS Spoke (FY2023)

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
UVSOR Synchrotron Radiation	X-Ray Magnetic Circular Dichroism	T. Yokoyama	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		M. Fujiwara, M. Miyajima
	Small Angle X-Ray Scattering for Solutions	S. Akiyama	Y. Furuike
	Molecular Structure Analysis using Crystalline Sponge Method	M. Fujita	T. Mitsuhashi, T. Yokoyama
Electron Spectroscopy	X-Ray Photoelectron Spectroscopy	T. Yokoyama	S. Iki, 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	
	Magnetic Thin Films	T. Yokoyama	
	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 (MEXT) 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 by the committee. This 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.

The ongoing research project led by Prof. Kenji Ohmori at IMS and named “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, 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 Kyoto University, Okayama University, and Kindai University.

(d) "Large-Scale and High-Coherence Fault-Tolerant Quantum Computer with Dynamical Atom Arrays" Supported by the Cabinet Office / JST R&D 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 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.

The R&D project "Large-scale and high-coherence fault-tolerant quantum computer with dynamical atom arrays" led by Prof. Kenji Ohmori at IMS under Goal 6 develops dynamical qubit arrays in which each of the cold-atom qubits arranged in a large array of optical tweezers is freely and rapidly moved during computation including gate operations and error detection / correction. The goal is to realize a practical fault-tolerant quantum computer with high stability and usability through integration and packaging of the key components under the collaboration with industries.

(e) MEXT Promotion of Development of a Joint Usage/Research System Project: Coalition of Universities for Research Excellence Program (CURE): Frontier of Spin Life Sciences [Spin-L]

Spin-L

Frontier of Spin Life Sciences

In the MEXT CURE project, we form a new system for collaborating with research institutions and research communities that are different from conventional ones to advance research in interdisciplinary fields where research systems have not yet been established. The hub is based on the accumulation of joint usage/research systems that have been formed based on the centrality of specific fields.

The MEXT CURE project Frontier of Spin Life Sciences [Spin-L] started in September 2023. In order to develop a new field that combines molecular science, life science, and physiological science, we will establish "Frontier of Spin Life Sciences," which brings together the basic technology of magnetic resonance (MR) equipment and researchers across disciplines.

The three Okazaki institutions (NIPS, IMS, ExCELLS) form the core, and are working together to develop new molecular probes for MR and perform MR image measurements on model animals. We explore new principles and methods for MR measurements on living organisms. In order to strongly develop this cutting-edge research by bringing together researchers in related fields in Japan, we will promote industry–academia collaborative research using project research by specially appointed faculty and cross-appointments, human exchange, joint usage/research, and human resource development with companies at the Under One Roof on Okazaki Campus.

For technologies and compound synthesis that are not specialized in the three Okazaki institutions, Institute for Chemical Research (Kyoto University), Institute for Protein Research (Osaka University), Brain Research Institute (Niigata University), and Institute for Quantum Life Science (QST) collaborate as participating institutions to promote the project. This project not only promotes joint usage/research through collaboration with many universities, companies, and various equipment platforms and field communities, but also aims to train cross-disciplinary researchers and technical staff.

Main achievements in FY2023

(1) Establishment of management system:

Signed a memorandum of understanding regarding the operation of Spin-L Hub, *etc.* (core/node organization). Established operating rules. Established and held core meetings, hub meetings, and steering committees. Strengthened the management office. Assigned a full-time URA. Established the Spin-L logo mark. Held kickoff meeting.

(2) Promotion of joint usage/research:

Established "joint usage/joint research committee." Started spin-life joint utilization research (46 projects conducted).

(3) Human resource development:

Established the "interdisciplinary association of young researchers." Held 5 Co-sponsored seminars.

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) Establishing a Unified Picture of Multiscale Quantum Functions in Chiral Materials

KISHNE, Jun-ichiro (*Open Univ.*)
TOGAWA, Yoshihiko (*Osaka Metropolitan Univ.*)
SATO, Takuya (*Tokyo Inst. Tech.*)
KUSUNOSE, Hiroaki (*Meiji Univ.*)
KATO, Yusuke (*Univ. Tokyo*)
YAMAMOTO, Hiroshi (*IMS*)

The term "chirality" refers to forms that are mirror images of each other but cannot be superimposed, like right and left hands. As a term describing molecular shapes, it has become widely recognized across various branches of molecular science. A noteworthy point is the subtle connection between macroscopic hands and microscopic molecules, both referred to by the same term, "chirality." This connection raises an important question: How can the macroscopic classical world and the microscopic quantum world be linked? One of the key goals for material science researchers is to explore material functions on multiple scales and bridge these two realms. The analogy between "molecules and hands" illustrates the multiscale nature of chirality. Under this common keyword "chirality," vast research fields are expanding, spanning physics, chemistry, life sciences, and even space science. Chirality serves as a unifying concept across these disciplines.

The reason we focus on chirality is that while it may appear to be a geometric and static concept, chirality actually connects quantum degrees of freedom, such as charge, orbit, spin, and lattice vibrations, leading to a wealth of material functions. To use a familiar analogy, when ascending or descending a spiral staircase, one inevitably rotates around the helical axis. In other words, translation and rotation are coupled. Applying this perspective to materials reveals that electrical and magnetic degrees of freedom are similarly coupled.

Recently, the field of "chiral material science," which explores the structure and function of materials from this perspective, has emerged. Fields such as chiral magnetism, chiral plasmonics, chiral spintronics, chiral phononics, chiral optics, and chiral electronics are all emerging areas that are very active today. If you remove the prefix "chiral" from the names of these fields, you find they encompass nearly the entirety of physics and chemistry.

The goal of this research project was to bring together six researchers—three experimentalists and three theorists—who are fascinated by chirality, to investigate how microscopic quantum mechanical degrees of freedom, such as electron spin, orbit, and atomic vibrations, couple in chiral materials. Using techniques such as circularly polarized Raman spectroscopy and spin-polarized transport measurements, we have studied the chiral responses of a wide range of materials, including organic and inorganic compounds, conductors, semiconductors, dielectrics, bulk crystals, and thin films. These experimental investigations have been complemented by theoretical research.

Several significant achievements have emerged from this research. We successfully observed lattice vibrations (phonons) unique to chiral crystals using circularly polarized Raman scattering and identified the quantum numbers of phonons derived from chirality through Raman selection rules (Sato, Kishine, Togawa *et al.*, *Nat. Phys.* **19**, 35–39 (2023)). In addition, we discovered that applying a thermal gradient to quartz, a representative chiral inorganic crystal, induces a spin current, a previously unobserved phenomenon (Togawa *et al.*, *Phys. Rev. Lett.* **132**, 056302 (2024)). We also proposed a theoretical framework for defining chirality in quantum terms (Kusunose, Yamamoto, Kishine, *Israel J. Chem.* **62(11-12)**, e202200049 (2022); *Appl. Phys. Lett.* **124**, 260501 (2024)).

These studies, while seemingly diverse, all relate to elucidating the phenomenon where the spins of electrons passing through chiral molecules or crystals exhibit huge spin polarization. This phenomenon, known as Chirality-Induced Spin Selectivity (CISS), was first discovered by Naaman's group in Israel. CISS occurs on multiple scales, from DNA and peptides to inorganic crystals, and aligns electron spins without the need for a magnetic field, even at room temperature. This makes it a highly attractive phenomenon, and understanding its mechanism is a profoundly important scientific goal. All of the results from this project are critical steps towards unraveling the CISS mechanism.

To further advance this research, we have established the "Quantum Mechanical Research Initiative for Chiral Materials (QuaRC)" at the Institute for Molecular Science (IMS) (https://www.quarc-ims.com/). Leveraging IMS as a joint-use facility, we aim to develop this initiative into a consortium that promotes chirality research from both the physical and chemical perspectives.

Finally, we stress that brainstorming and refining ideas often become a lengthy process, much like an endurance race in front of the whiteboard, requiring in-depth, face-to-face interaction. A key achievement during this research period was the regular in-person meetings in Okazaki, where the six team members gathered multiple times for productive discussions.

(2) Research Symposia

(From Oct. 2023 to Sep. 2024)

Dates	Theme	Chair
Oct. 2–4, 2023	Frontier of Soft X-Ray Spectroscopy for Chemical Processes in Solutions	**NAGASAKA, Masanari** **KERA, Satoshi**
Aug. 19–23, 2024	The 63rd Summer School in Molecular Science	**TANAKA, Ryoichi** **SUGIMOTO, Toshiki**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2023–Mar. 2024		Apr. 2024–Sep. 2024		Total		
		Regular	ARIM	Regular	ARIM	Regular	ARIM	Sum
Special Projects		1		0		1		1
Research Symposia		1		0		1		1
Research Symposia for Young Researchers		0		1		1		1
Cooperative Research		16	28	18	26	34	54	88
Use of Facility	Instrument Center		98		73		171	171
	Equipment Development Center	0	5	0	6	0	11	11
	UVSOR	87	2	118	1	205	3	208
Use of Facility Program of the Computer Center						302*		302*

* from April 2023 to March 2024

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	7
Institute of Atomic and Molecular Sciences (IAMS) [Taiwan]	2005. 1–2026. 1	0	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2009.10–2029.10	7	1
Freie Universität Berlin (FUB) [Germany]	2013. 6–2025. 6	0	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. 5–2027. 5	0	0
National Yang Ming Chiao Tung University [Taiwan]	2018. 6–2028. 5	3	0
Peter Grünberg Institute, Forschungszentrum Jülich GmbH (FZJ) [Germany]	2018.10–2028. 9	0	1
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	0	0
Fritz-Haber-Institut der Max-Planck-Gesellschaft [Germany]	2021. 4–2026. 3	0	4
China Scholarship Council [China]	2023. 1–2028. 1	2	0

* No. of researchers during the period from Oct. 2023 to Sep. 2024

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

Institution	Period	Accept*	Send*
Kasetsart University, Faculty of Science [Thailand]	2011. 3–2026. 3	3	3
University of Malaya, Faculty of Science [Malaysia]	2014. 3–2024.11	4	2
Vidyasirimedhi Institute of Science and Technology [Thailand]	2018. 9–2028. 9	0	0
Friedrich Schiller University Jena [Germany]	2020. 7–2028. 7	1	0
Chulalongkon University [Thailand]	2010. 4–2027. 9	5	4

* No. of researchers during the period from Oct. 2023 to Sep. 2024

(2) IMS International Internship Program

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (IMS-IIP)	27*	–

* from Oct. 2023 to Sep. 2024

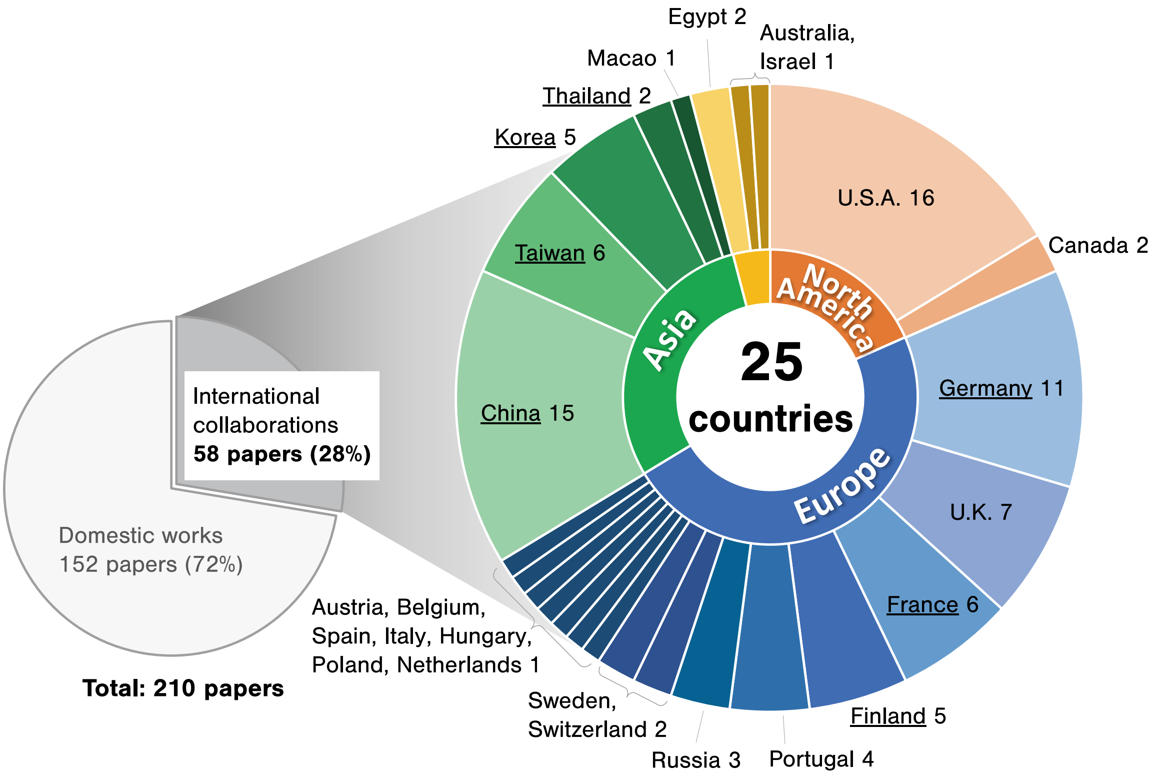
(3) IMS International Collaboration (Including online meetings)

Category	Number of People
International Joint Research Programs	97
International Use of Facilities Programs	40

from Oct. 2023 to Sep. 2024

Internationally Collaborated Publications

Articles and reviews published in 2023



Underlined countries include MOU Partnership Institutions
Scopus dataset, May 2024

KOBAYASHI, Hayao Professor Emeritus	The Order of the Sacred Treasure, Gold Rays with Neck Ribbon
SATO, Sota Life and Coordination-Complex Molecular Science	Japan Union of Chemical Science and Technology, Chemistry Communication Award 2023 "Dissemination of Cutting-Edge Molecular Science that Appeals to a Broad Audience" The University of Tokyo, 2023 Faculty of Engineering Best Teaching Award "Analytical Chemistry III & Structures Analysis Classrooms"
TANIMOTO, Shoichi ITOH, Satoru G. OKUMURA, Hisashi Theoretical and Computational Molecular Science	Best Author Award, Japan Society for Simulation Technology "Molecular Dynamics Simulations of the Ligand Recognition by SARS-CoV-2 RNA-dependent RNA Polymerase"
TAIRA, Yoshitaka UVSOR Synchrotron Facility	Young Scientist Award of the Japanese Positron Science Society "Positron Annihilation Spectroscopy Using Ultrashort Pulsed Gamma Rays in UVSOR"
OHNUKI, Jun Theoretical and Computational Molecular Science	Young Scientist Excellence Award of the Protein Science Society of Japan "Integration of AlphaFold with Molecular Dynamics for Uncovering Conformational States of Transporter Proteins"
HARASHIMA, Takanori Life and Coordination-Complex Molecular Science	Young Researcher Award at the 7th Annual Meeting of Molecular Robotics "Strategies for the Design of DNA Nanoparticle Motors with High-Speed and Long Run-Length"
KOSUGI, Takahiro Research Center of Integrative Molecular Systems	The 13th National Institutes of Natural Sciences Young Researcher Award "Control of Protein Complexes for Life Science Research"
YONEDA, Yusuke Research Center of Integrative Molecular Systems	PCCP Prize 2024 "Complex Electron-Nuclear Dynamics of Excited States in Condensed Phases Revealed by Ultrafast Nonlinear Spectroscopy"
SATO, Takuro Research Center of Integrative Molecular Systems	Young Scientist Award of the Physical Society of Japan, 2024 "Study of Novel Non-Equilibrium Electromagnetic Responses in Strongly Correlated Electron/Spin Systems"
NAGAO, Haruyo Instrument Center	ARIM Japan The Best Technical Support Contribution Award "Technical Support Using NMR and Thermal Analysis Equipment, *etc.*"

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 2023–September 2024) are listed below.

(1) IMS Councillor

Prof. LEIGH, David A.	Univ. of Manchester	U.K.	Dec. ’23
Prof. WEIDEMÜLLER, Matthias	Heidelberg Univ.	Germany	Feb. ’24
Prof. LISY, James	Univ. of Illinois Urbana-Champaign	U.S.A.	May ’24

(2) JSPS Invited Fellow

Prof. DASCHAKRABORTY, Snehasis	Indian Inst. of Tech., Patna	India	May ’24–Jul. ’24

(3) IMS Visiting Professor or Associate Professor from Abroad

Prof. PRIYAKUMAR, U. Deva	Int. Inst. of Information Tech., Hyderabad (IIIT-H)	India	Apr. ’24–May ’24

(4) IMS Visiting Scientist

Ms. SULONG, Nor Akmalyati	Univ. of Malaya	Malaysia	Oct. ’23–Mar. ’24
Ms. WONGKANYA, Ratchada	Kasetsart Univ.	Thailand	Oct. ’23–Mar. ’24
Ms. CHANYA, Archapraditkul	Kasetsart Univ.	Thailand	Oct. ’23–Mar. ’24
Mr. ZHU, Yupeng	Southern Univ. of Sci. Tech.	China	Oct. ’23
Mr. ZENG, Meng	Southern Univ. of Sci. Tech.	China	Oct. ’23 Jun. ’24
Ms. CHEN, Tien	Natl. Yang Ming Chiao Tung Univ.	Taiwan	Oct. ’23–Mar. ’24
Ms. DECHKRONG, Wassa	Khon Kaen Univ.	Thailand	Nov. ’23–Mar. ’24
Ms. KAMPAKAEW, Konchanok	Khon Kaen Univ.	Thailand	Nov. ’23–Mar. ’24
Ms. LEE, Jia Yen	Univ. of Malaya	Malaysia	Nov. ’23–Mar. ’24
Mr. KOCIK, Robin Rayane	Paris Saclay Univ.	France	Nov. ’23–Apr. ’24
Prof. PONG, Way-Faung	Tamkang Univ.	Taiwan	Dec. ’23
Prof. DONG, Chung-Li	Tamkang Univ.	Taiwan	Dec. ’23 Sep. ’24
Ms. TA, Thi Thuy Nga	Natl. Yang Ming Chiao Tung Univ.	Taiwan	Dec. ’23 Sep. ’24
Dr. KUMARAVELU, Thanigai Arul	Tamkang Univ.	Taiwan	Dec. ’23 Sep. ’24
Mr. YANG, Cheng-Chieh	Natl. Taiwan Univ. of Sci. Tech.	Taiwan	Dec. ’23 Sep. ’24
Mr. WANG, Pin-Cyuan	Natl. Taiwan Univ. of Sci. Tech.	Taiwan	Dec. ’23
Dr. KITTIKHUNNATHAM, Preecha	Chulalongkorn Univ.	Thailand	Dec. ’23–Jan. ’24 May ’24–Jul. ’24
Dr. NARUPAI, Benjaporn	Chulalongkorn Univ.	Thailand	Dec. ’23–Jan. ’24
Mr. KETAIAM, Kittisak	Chiang Mai Univ.	Thailand	Jan. ’24–May. ’24
Prof. ZHAO, Xiang	Xi’an Jiaotong Univ.	China	Jan. ’24–Feb. ’24 Jul. ’24–Aug. ’24
Dr. SAPCHAROENKUN, Chaweewan	Natl. Nanotechnology Cent.	Thailand	Feb. ’24–May. ’24
Ms. SIRIWORAKOONCHAI, Phatwarach	Chiang Mai Univ.	Thailand	Feb. ’24–Jul. ’24
Mr. BRAUN, Eduard	Heidelberg Univ.	Germany	Feb. ’24–May. ’24
Dr. KONG, Xiangrui	Univ. of Gothenburg	Sweden	Feb. ’24–Mar. ’24 Aug. ’24
Dr. THOMSON, Erik	Univ. of Gothenburg	Sweden	Feb. ’24–Mar. ’24
Mr. TRAUTMANN, Arno	Heidelberg Univ.	Germany	Mar. ’24
Mr. WEBER, Sebastian	Univ. Stuttgart	Germany	Mar. ’24
Prof. AVARVARI, Narcis	Univ. d’Angers	France	Apr. ’24
Mr. El Farouk KECIR, Omar	Paris Saclay Univ.	France	Apr. ’24–Aug. ’24
Ms. HASSANALY, Sapna	Paris Saclay Univ.	France	Apr. ’24–Aug. ’24
Mr. LERICHE, Axel-Ugo	Paris Saclay Univ.	France	Apr. ’24–Aug. ’24
Mr. ROUSSEL, Mathis	Chimie ParisTech	France	Apr. ’24–Aug. ’24
Ms. FARAH, Anne-Idil	Chimie ParisTech	France	Apr. ’24–Aug. ’24
Ms. DUREAU, Louise	Chimie ParisTech	France	Apr. ’24–Aug. ’24
Mr. PERY, Mattin	Chimie ParisTech	France	Apr. ’24–Aug. ’24

Ms. NACER, Lamia	Chimie ParisTech	France	Apr. ’24–Aug. ’24
Ms. LAHORE, Juliette	Chimie ParisTech	France	Apr. ’24–Jun. ’24
Mr. FAYAT, Milan	Chimie ParisTech	France	May. ’24–Aug. ’24
Mr. STELTER, Daniel	Friedrich Schiller Univ. Jena	Germany	Apr. ’24–Mar. ’25
Ms. DUPERON, Isaline	Inst. d’optique	France	May. ’24–Aug. ’24
Dr. SFORNA, Marie Catherine	Univ. of Orleans	France	May. ’24–Jun. ’24
Prof. MILOJEVIC, Tetyana	Univ. of Orleans	France	May. ’24–Jun. ’24
Prof. LIU, Chang	Southern Univ. of Sci. Tech.	China	Jun. ’24
Mr. LUO, Ronghao	Southern Univ. of Sci. Tech.	China	Jun. ’24
Mr. ISHIZAKA, Haru	Univ. of Oxford	U.K.	Jun. ’24–Aug. ’24
Mr. HWANG, Hansub	KAIST	Korea	Jul. ’24
Mr. BYUN, Andrew	KAIST	Korea	Jul. ’24
Ms. HWANG, Sunhwa	KAIST	Korea	Jul. ’24
Prof. WANG, Jian	City Univ. of Hong Kong	Hong Kong	Jul. ’24–Aug. ’24
Mr. ZHANG, Yunze	City Univ. of Hong Kong	Hong Kong	Jul. ’24–Aug. ’24
Mr. LEI, Jia	City Univ. of Hong Kong	Hong Kong	Jul. ’24–Aug. ’24
Mr. NOMURA, Gyohei	California Inst. of Tech.	U.S.A	Aug. ’24
Prof. CHUANG, Cheng-Hao	Tamkang Univ.	Taiwan	Aug. ’24
Mr. MARIANO, Carl Osby Marcelo	Tamkang Univ.	Taiwan	Aug. ’24
Mr. HSIEH, Zong-Jhe	Tamkang Univ.	Taiwan	Aug. ’24
Mr. LU, Hsin-Chan	Tamkang Univ.	Taiwan	Aug. ’24
Prof. HE, Ruihua	Westlake Univ.	China	Aug. ’24
Dr. HONG, Caiyun	Westlake Univ.	China	Aug. ’24
Dr. HUANG, Chaozhi	Westlake Univ.	China	Aug. ’24
Ms. JIANG, Congying	Westlake Univ.	China	Aug. ’24
Ms. ZHENG, Xiaonan	Westlake Univ.	China	Aug. ’24
Mr. ZHU, Mingyuan	Southern Univ. of Sci. Tech.	China	Sep. ’24
Assist Prof. MA, Xiaoming	Southern Univ. of Sci. Tech.	China	Sep. ’24
Prof. OOI, Chong Heng	Univ. of Malaya	Malaysia	Sep. ’24–Oct. ’24
Prof. KIM, Hongjoo	Kyungpook Natl. Univ.	Korea	Sep. ’24
Mr. CHO, Jaeyoung	Kyungpook Natl. Univ.	Korea	Sep. ’24
Mr. JEONG, Dongwoo	Kyungpook Natl. Univ.	Korea	Sep. ’24
Mr. LEE, Doohyeok	Kyungpook Natl. Univ.	Korea	Sep. ’24

(5) Visitor to IMS

Prof. PATE, Brooks H.	Univ. of Virginia	U.S.A.	Dec. ’23
Mr. SOMWANG, Poosin	Chulalongkorn Univ.	Thailand	Jan. ’24
Ms. KEARWAN, Natchapat	Chulalongkorn Univ.	Thailand	Jan. ’24
Ms. WONG, Xin Ai	Univ. of Malaya	Malaysia	Jan. ’24
Mr. HUANG, Hsu-Liang	Natl. Yang Ming Chiao Tung Univ.	Taiwan	Jan. ’24
Prof. ERNST, Karl-Heinz	Univ. of Zurich	Switzerland	Jan. ’24
Mr. CHOI, Seyong	Pusan Natl. Univ.	Korea	Feb. ’24
Ms. KIM, Dohee	Pusan Natl. Univ.	Korea	Feb. ’24
Prof. DOYLE, John M.	Harvard Univ.	U.S.A.	Feb. ’24
Prof. RUNGROTMONGKOL, Thanyada	Chulalongkorn Univ.	Thailand	Mar. ’24
Dr. KANE, Thomas	Kane OE	U.S.A.	Apr. ’24
Prof. ZHENG, Lihe	Yunnan Univ.	China	Apr. ’24
Prof. DE VIDO, Mariastefania	STFC Rutherford Appleton Laboratory	U.K.	Apr. ’24
Prof. BÖRJESSON, Karl	Univ. of Gothenburg	Sweden	Apr. ’24
Prof. PONGPRAYOON, Prapasiri	Kasetsart Univ.	Thailand	Jun. ’24
Prof. MUSAEV, Djamaladdin G.	Emory Univ.	U.S.A.	Jul. ’24
Prof. WHITLOCK, Shannon	Univ. Strasbourg	France	Jul. ’24
Mr. RAISSI, Slimane	Chimie ParisTech	France	Aug. ’24
Prof. WANG, Jun Joelle	Hong Kong Baptist Univ.	Hong Kong	Sep. ’24

Scientists who would like to visit IMS under program (2) and (3) are invited to make contact with IMS staff in their relevant field.

LIST OF PUBLICATIONS

Theoretical and Computational Molecular Science

J. ONO, Y. MATSUMURA, T. MORI and S. SAITO, “Conformational Dynamics in Proteins: Entangled Slow Fluctuations and Non-equilibrium Reaction Events,” *J. Phys. Chem. B (Perspective)* **128(1)**, 20–32 (2023). DOI: 10.1021/acs.jpcb.3c05307
S.-I. KODA and S. SAITO, “Locating Transition States by a Variational Minimum Energy Path Search with an Energy-Derivative-Free Objective Function,” *J. Chem. Theory Comput.* **20(7)**, 2798–2811 (2024). DOI: 10.1021/acs.jctc.3c01246
S. SAITO, “Unraveling the Dynamic Slowdown in Supercooled Water: The Role of Dynamic Disorder in Jump Motions,” *J. Chem. Phys.* **160(19)**, 194506 (2024). DOI: 10.1063/5.0209713
S.-I. KODA and S. SAITO, “Flat-Bottom Elastic Network Model for Generating Improved Plausible Reaction Paths,” *J. Chem. Theory Comput.* **20(16)**, 7176–7187 (2024). DOI: 10.1021/acs.jctc.4c00792
R. MALIK, S. SAITO and A. CHANDRA, “Effect of Counterions on the Structure and Dynamics of Water near a Negatively Charged Surfactant: A Theoretical Vibrational Sum Frequency Generation Study,” *Phys. Chem. Chem. Phys.* **26(24)**, 17065–17074 (2024). DOI: 10.1039/D4CP00537F

K. FUNO and A. ISHIZAKI, “Dynamics of a Quantum System Interacting with White Non-Gaussian Baths: Poisson Noise Master Equation,” *Phys. Rev. Lett.* **132(17)**, 170402 (2024). DOI: 10.1103/PhysRevLett.132.170402
Y. FUJIHASHI, A. ISHIZAKI and R. SHIMIZU, “Pathway Selectivity in Time-Resolved Spectroscopy Using Two-Photon Coincidence Counting with Quantum Entangled Photons,” *J. Chem. Phys.* **160(10)**, 104201 (2024). DOI: 10.1063/5.0189134
J. Y. DONG, Y. KITAHAMA, T. FUJITA, M. ADACHI, Y. SHIGETA, A. ISHIZAKI, S. TANAKA, T. H. XIAO and K. GODA, “Manipulation of Photosynthetic Energy Transfer by Vibrational Strong Coupling,” *J. Chem. Phys.* **160(4)**, 045101 (2024). DOI: 10.1063/5.0183383

W. W. WANG, T. TANAKA and M. EHARA, “Theoretical Study on the Mechanism of Alcohol Photooxidation on Nb_2O_5 Surface,” *J. Comput. Chem.* **45(25)**, 2128–2135 (2024). DOI: 10.1002/jcc.27435
Y. HORITA, S. HOSSAIN, M. ISHIMI, P. ZHAO, M. SERA, T. KAWAWAKI, S. TAKANO, Y. NIIHORI, T. NAKAMURA, T. TSUKUDA, M. EHARA and Y. NEGISHI, “Clarifying the Electronic Structure of Anion-Templated Silver Nanoclusters by Optical Absorption Spectroscopy and Theoretical Calculation,” *J. Am. Chem. Soc.* **145(43)**, 23533–23540 (2023). DOI: 10.1021/jacs.3c07194
S. A. IKBAL, P. ZHAO, M. EHARA and S. AKINE, “Acceleration and Deceleration of Chirality Inversion Speeds in a Dynamic Helical Metallocryptand by Alkali Metal Ion Binding,” *Sci. Adv.* **9(44)**, eadj5536 (2023). DOI: 10.1126/sciadv.adj5536
J. L. JIN, S. F. ZHANG, P. ZHAO, Y. L. SHEN, J. J. FANG, Z. LIU, M. EHARA, L. W. MI, Y. P. XIE and X. LU, “$Ag_6Cu_8(C{=}CAr)_{14}(DPPB)_2$: A Rigid Ligand Co-Protected Bimetallic Silver(I)-Copper(I) Cluster with Room-Temperature Luminescence,” *Chem. –Asian J.* **18(22)**, e202300844 (2023). DOI: 10.1002/asia.202300844
W. W. WANG, X. ZHAO and M. EHARA, “Mechanistic Studies of Regiocontrolled Bisaddition of Fullerenes Driven by Oriented External Electric Fields,” *J. Org. Chem.* **88(22)**, 15783–15789 (2023). DOI: 10.1021/acs.joc.3c01850
T. NAKAJIMA, S. TASHIRO, M. EHARA and M. SHIONOYA, “Selective Synthesis of Tightly- and Loosely-Twisted Metallomacrocycle Isomers Towards Precise Control of Helicity Inversion Motion,” *Nat. Commun.* **14(1)**, 7868 (2023). DOI: 10.1038/s41467-023-43658-5
Y. SHUI, D. LIU, P. ZHAO, X. ZHAO, M. EHARA, X. LU, T. AKASAKA and T. YANG, “Element Effects in Endohedral Metal−Metal-Bonding Fullerenes $M_2@C_{82}$ (M = Sc, Y, La, Lu),” *J. Chem. Phys.* **159(24)**, 244302 (2023). DOI: 10.1063/5.0180309
S. MURATSUGU, K. SAWAGUCHI, T. SHIRAOGAWA, S. CHIBA, Y. SAKATA, S. SHIRAI, H. BABA, M. EHARA, S. AKINE and M. TADA, “Induced Chirality at Surface: Fixation of a Dynamic M/P Invertible Helical Co_3 Complex on SiO_2,” *Chem. Commun.* **60(15)**, 2094–2097 (2024). DOI: 10.1039/D3CC05534E
B. BOEKFA, T. MAIHOM, M. EHARA and J. LIMTRAKUL, “Investigation of the Suzuki-Miyaura Cross-Coupling Reaction on Palladium H-Beta Zeolite with DFT Calculations,” *Sci. Rep.* **14(1)**, 611 (2024). DOI: 10.1038/s41598-023-51116-x
Z. LEI, P. ZHAO, Z. J. GUAN, Z. A. NAN, M. EHARA and Q. M. WANG, “‘Passivated Precursor’ Approach to All-Alkynyl-Protected Gold Nanoclusters and Total Structure Determination of Au_{130},” *Chem. –Eur. J.* **30(42)**, e202401094 (2024). DOI: 10.1002/chem.202401094
X. L. PEI, P. ZHAO, H. UBE, Z. LEI, M. EHARA and M. SHIONOYA, “Single-Gold Etching at the Hypercarbon Atom of C-Centred Hexagold(I) Clusters Protected by Chiral *N*-Heterocyclic Carbenes,” *Nat. Commun.* **15(1)**, 5024 (2024). DOI: 10.1038/s41467-024-49295-w
H. MIURA, K. IMOTO, H. NISHIO, A. JUNKAEW, Y. TSUNESADA, Y. FUKUTA, M. EHARA and T. SHISHIDO, “Optimization of Metal-Support Cooperation for Boosting the Performance of Supported Gold Catalysts for the Borylation of C–O and C–N Bonds,” *J. Am. Chem. Soc.* **146(40)**, 27528–27541 (2024). DOI: 10.1021/jacs.4c08340

D. FUKUHARA, S. G. ITOH and H. OKUMURA, “Inhibition of Amyloid-β(16–22) Aggregation by Polyphenols Using Replica Permutation with Solute Tempering Molecular Dynamics Simulation,” *Biophys. Physicobiol.* **20(4)**, e200045 (2023). DOI: 10.2142/biophysico.bppb-v20.0045
S. TANIMOTO and H. OKUMURA, “Theoretical Analysis of the Aggregation-Inhibition Effect of Arginine on Polyglutamine Protein by the Generalized-Ensemble Method,” *J. Comput. Chem., Jpn.* **22(2)**, 18–20 (2023). DOI: 10.2477/jccj.2023-0020
S. TANIMOTO and H. OKUMURA, “Why Is Arginine the Only Amino Acid That Inhibits Polyglutamine Monomers from Taking on Toxic Conformations?” *ACS Chem. Neurosci.* **15(15)**, 2925–2935 (2024). DOI: 10.1021/acschemneuro.4c00276
H. KOYAMA, H. OKUMURA, T. OTANI, A. M. ITO, K. NAKAMURA, K. KATO and T. FUJIMORI, “Effective Mechanical Potential of Cell–Cell Interaction in Tissues Harboring Liquid Cavity and in Cell Sheet toward Morphogenesis,” *Front. Cell Dev. Biol.* **12(12)**, 1414601 (2024). DOI: 10.3389/fcell.2024.1414601

J. OHNUKI, T. JAUNET-LAHARY, A. YAMASHITA and K. OKAZAKI, "Accelerated Molecular Dynamics and AlphaFold Uncover a Missing Conformational State of Transporter Protein OxlT," *J. Phys. Chem. Lett.* **15(3)**, 725–732 (2024). DOI: 10.1021/acs.jpclett.3c03052
J. OHNUKI and K. OKAZAKI, "Integration of AlphaFold with Molecular Dynamics for Efficient Conformational Sampling of Transporter Protein NarK," *J. Phys. Chem. B* **128(31)**, 7530–7537 (2024). DOI: 10.1021/acs.jpcb.4c02726
T. MATSUDA, S. SAKAI, K. OKAZAKI and T. NAGAI, "Improvement of the Green-Red Förster Resonance Energy Transfer-Based Ca^{2+} Indicator by Using the Green Fluorescent Protein, Gamillus, with a Trans Chromophore as the Donor," *ACS Sens.* **9(4)**, 1743–1748 (2024). DOI: 10.1021/acssensors.3c02398
K. OKADA, T. KIKUTSUJI, K. OKAZAKI, T. MORI, K. KIM and N. MATUBAYASI, "Unveiling Interatomic Distances Influencing the Reaction Coordinates in Alanine Dipeptide Isomerization: An Explainable Deep Learning Approach," *J. Chem. Phys.* **160(17)**, 174110 (2024). DOI: 10.1063/5.0203346

M. KOYAKKAT, T. ISHIDA, K. FUJITA and H. SHIROTA, "Low-Frequency Spectra of Hydrated Ionic Liquids with Kosmotropic and Chaotropic Anions," *J. Phys. Chem. B* **128(17)**, 4171–4182 (2024). DOI: 10.1021/acs.jpcb.4c01255

Photo-Molecular Science

T. TOMITA, T. MATSUBARA, S. DE LÉSÉLEUC and K. OHMORI, "Ultrafast Laser Control of Cold Rydberg-Atom Arrays: Application to Ultrafast Quantum Computing," *Ouyoubutsuri*, **93(2)**, 89–95 (2024). DOI: 10.11470/oubutsu.93.2_89 (in Japanese)
V. BHARTI, S. SUGAWA, M. KUNIMI, V. S. CHAUHAN, T. P. MAHESH, M. MIZOGUCHI, T. MATSUBARA, T. TOMITA, S. DE LÉSÉLEUC and K. OHMORI, "Strong Spin-Motion Coupling in the Ultrafast Quantum Many-Body Dynamics of Rydberg Atoms," *Phys. Rev. Lett.* **133**, 093405 (2024). DOI: 10.1103/PhysRevLett.133.093405

T. YAMADA, R. NEMOTO, F. NISHINO, T. HOSOKAI, C. H. WANG, M. HORIE, Y. HASEGAWA, S. KERA and P. KRÜGER, "On-Surface Growth of Transition-Metal Cobalt Nanoclusters Using a 2D Crown-Ether Array," *J. Mater. Chem. C* **12(3)**, 874–883 (2023). DOI: 10.1039/d3tc03339b
K. HAGIWARA, E. NAKAMURA, S. MAKITA, S. SUGA, S. TANAKA, S. KERA and F. MATSUI, "Development of Dual-Beamline Photoelectron Momentum Microscopy for Valence Orbital Analysis," *J. Synchrotron Radiat.* **31(Pt3)**, 540–546 (2024). DOI: 10.1107/s1600577524002406
J. P. ITHIKKAL, K. FUKUTANI, F. NISHINO, T. MINATO, H. ISHII, S. IZAWA, K. TANAKA, M. HIRAMOTO and S. KERA, "Direct Observation of the Electronic Structure and Many-Body Interactions of Low-Mobility Carriers in Perylene Diimide Derivative," *Appl. Phys. Lett.* **125(5)**, 052102 (2024). DOI: 10.1063/5.0221293
F. MATSUI, K. HAGIWARA, Y. SATO, E. NAKAMURA, R. SAGEHASHI, S. KERA and S. SUGA, "Dual-Beamline Photoelectron Momentum Microscopy for Valence Orbital Characterization," *Synchrotron Radiat. News* **37(4)**, 43–48 (2024). DOI: 10.1080/08940886.2024.2391256
T. YAMADA, S. KANAZAWA, K. FUKUTANI and S. KERA, "Growth of Transition-Metal Cobalt Nanoclusters on 2D Covalent Organic Frameworks," *J. Phys. Chem. C* **128(3)**, 1477–1486 (2024). DOI: 10.1021/acs.jpcc.3c07435

Y. HIKOSAKA, T. KANEYASU, S. WADA, H. KOHGUCHI, H. OTA, E. NAKAMURA, H. IWAYAMA, M. FUJIMOTO, M. HOSAKA and M. KATOH, "Frequency-Domain Interferometry for the Determination of Time Delay between Two Extreme-Ultraviolet Wave Packets Generated by a Tandem Undulator," *Sci. Rep.* **13(1)**, 10292 (2023). DOI: 10.1038/s41598-023-37449-7
T. KANEYASU, Y. HIKOSAKA, S. WADA, M. FUJIMOTO, H. OTA, H. IWAYAMA and M. KATOH, "Time Domain Double Slit Interference of Electron Produced by XUV Synchrotron Radiation," *Sci. Rep.* **13(1)**, 6142 (2023). DOI: 10.1038/s41598-023-33039-9
S. WADA, H. OHTA, A. MANO, Y. TAKASHIMA, M. FUJIMOTO and M. KATOH, "Young's Double-Slit Experiment with Undulator Vortex Radiation in the Photon-Counting Regime," *Sci. Rep.* **13(1)**, 22962 (2023). DOI: 10.1038/s41598-023-49825-4
M. KATOH, M. FUJIMOTO, E. SALEHI, M. HOSAKA and H. KAWAGUCHI, "Chirality in Electromagnetic Radiation from Relativistic Electrons," *Chirality* **36(5)**, e23677 (2024). DOI: 10.1002/chir.23677
E. SALEHI and M. KATOH, "Bayesian Optimization of the Dynamic Aperture in UVSOR-IV Design Study," *J. Phys.: Conf. Ser.* **2687(3)**, 032030 (2024). DOI: 10.1088/1742-6596/2687/3/032030
M. KATOH, H. OTA, J. YAMAZAKI, K. HAYASHI, Y. OKANO, E. SALEHI, Y. TAIRA, A. MANO, M. FUJIMOTO, Y. TAKASHIMA, M. HOSAKA, F. SAKAMOTO, T. KANEYASU and H. ZEN, "Light Source Developments at UVSOR BL1U," *J. Phys.: Conf. Ser.* **2687(3)**, 032005 (2024). DOI: 10.1088/1742-6596/2687/3/032005

S. ENDO, R. ABE, H. FUJIOKA, T. INO, O. IWAMOTO, N. IWAMOTO, S. KAWAMURA, A. KIMURA, M. KITAGUCHI, R. KOBAYASHI, S. NAKAMURA, T. OKU, T. OKUDAIRA, M. OKUIZUMI, M. OMER, G. ROVIRA, T. SHIMA, H. M. SHIMIZU, T. SHIZUMA, Y. TAIRA, S. TAKADA, S. TAKAHASHI, H. YOSHIKAWA, T. YOSHIOKA and H. ZEN, "Circular Polarization Measurement for Individual Gamma Rays in Capture Reactions with Intense Pulsed Neutrons," *Eur. Phys. J. A* **60(8)**, 166 (2024). DOI: 10.1140/epja/s10050-024-01392-6
M. KATOH, H. OTA, J. YAMAZAKI, K. HAYASHI, Y. OKANO, E. SALEHI, Y. TAIRA, A. MANO, M. FUJIMOTO, Y. TAKASHIMA, M. HOSAKA, F. SAKAMOTO, T. KANEYASU and H. ZEN, "Light Source Developments at UVSOR BL1U," *J. Phys.: Conf. Ser.* **2687(3)**, 032005 (2024). DOI: 10.1088/1742-6596/2687/3/032005

H. MATSUDA, K. OZAWA, Y. HASHIMOTO, T. MATSUSHITA and F. MATSUI, "Use of Planar Retarding Field to Improve Energy Resolution of Projection-Type Electron Spectroscopy Collimator Analyzer," *Jpn. J. Appl. Phys.* **63(4)**, 046503 (2024). DOI: 10.35848/1347-4065/ad3ab8

K. HAGIWARA, E. NAKAMURA, S. MAKITA, S. SUGA, S. TANAKA, S. KERA and F. MATSUI, "Development of Dual-Beamline Photoelectron Momentum Microscopy for Valence Orbital Analysis," *J. Synchrotron Radiat.* **31(Pt3)**, 540–546 (2024). DOI: 10.1107/s1600577524002406

T. UCHIYAMA, H. GOTO, E. UESUGI, A. TAKAI, L. ZHI, A. MIURA, S. HAMAO, R. EGUCHI, H. OTA, K. SUGIMOTO, A. FUJIWARA, F. MATSUI, K. KIMURA, K. HAYASHI, T. UENO, K. KOBAYASHI, J. AKIMITSU and Y. KUBOZONO, "Semiconductor–Metal Transition in Bi_2Se_3 Caused by Impurity Doping," *Sci. Rep.* **13(1)**, 537 (2023). DOI: 10.1038/s41598-023-27701-5

T. INOUE, T. INA, H. MASAI, N. KONDO, F. MATSUI, T. KINOSHITA and A. NAKAJIMA, "Extended X-Ray Absorption Fine Structure (EXAFS) Measurements on Alkali Metal Superatoms of Ta-Atom-Encapsulated Si_{16} Cage," *J. Phys. Chem. Lett.* **15(20)**, 5376–5381 (2024). DOI: 10.1021/acs.jpclett.4c00492

F. MATSUI, K. HAGIWARA, Y. SATO, E. NAKAMURA, R. SAGEHASHI, S. KERA and S. SUGA, "Dual-Beamline Photoelectron Momentum Microscopy for Valence Orbital Characterization," *Synchrotron Radiat. News* **37(4)**, 43–48 (2024). DOI: 10.1080/08940886.2024.2391256

H. TANAKA, A. V. TELEGIN, Y. P. SUKHORUKOV, V. A. GOLYASHOV, O. E. TERESHCHENKO, A. N. LAVROV, T. MATSUDA, R. MATSUNAGA, R. AKASHI, M. LIPPMAA, Y. ARAI, S. IDETA, K. TANAKA, T. KONDO and K. KURODA, "Semiconducting Electronic Structure of the Ferromagnetic Spinel $HgCr_2Se_4$ Revealed by Soft-X-Ray Angle-Resolved Photoemission Spectroscopy," *Phys. Rev. Lett.* **130(18)**, 186402 (2023). DOI: 10.1103/PhysRevLett.130.186402

M. HORIO, X. PEIAO, M. MIYAMOTO, T. WADA, K. ISOMURA, J. OSIECKI, B. THIAGARAJAN, C. M. POLLEY, K. TANAKA, M. KITAMURA, K. HORIBA, K. OZAWA, T. TANIGUCHI, M. FUJITA and I. MATSUDA, "Influence of Oxygen Coordination Number on the Electronic Structure of Single-Layer La-Based Cuprates," *Phys. Rev. B* **108(3)**, 035105 (2023). DOI: 10.1103/PhysRevB.108.035105

K. YANAGIZAWA, K. SUGAWARA, T. KAWAKAMI, R. ANDO, K. YAEGASHI, K. NAKAYAMA, S. SOUMA, K. TANAKA, M. KITAMURA, K. HORIBA, H. KUMIGASHIRA, T. TAKAHASHI and T. SATO, "Switching of Charge-Density Wave by Carrier Tuning In Monolayer $TiTe_2$," *Phys. Rev. Mater.* **7(10)**, 104002 (2023). DOI: 10.1103/PhysRevMaterials.7.104002

T. NAKAMURA, H. SUGIHARA, Y. CHEN, R. YUKAWA, Y. OHTSUBO, K. TANAKA, M. KITAMURA, H. KUMIGASHIRA and S. KIMURA, "Two-Dimensional Heavy Fermion in a Monoatomic-Layer Kondo Lattice $YbCu_2$," *Nat. Commun.* **14(1)**, 7850 (2023). DOI: 10.1038/s41467-023-43662-9

A. HONMA, D. TAKANE, S. SOUMA, K. YAMAUCHI, Y. WANG, K. NAKAYAMA, K. SUGAWARA, M. KITAMURA, K. HORIBA, H. KUMIGASHIRA, K. TANAKA, T. K. KIM, C. CACHO, T. OGUCHI, T. TAKAHASHI, Y. ANDO and T. SATO, "Antiferromagnetic Topological Insulator with Selectively Gapped Dirac Cones," *Nat. Commun.* **14(1)**, 7396 (2023). DOI: 10.1038/s41467-023-42782-6

T. ITO, T. OUISSE, M. MITA, K. TANAKA, L. JOUFFRET, H. PAZNIAK and S. QUESSADA, "Electronic Structure of the Surface States of the Zr_3SnC_2 MAX Phase," *Phys. Rev. B* **108(23)**, 235145 (2023). DOI: 10.1103/PhysRevB.108.235145

Y. P. ZHU, X. CHEN, X. R. LIU, Y. LIU, P. LIU, H. ZHA, G. QU, C. HONG, J. LI, Z. JIANG, X. M. MA, Y. J. HAO, M. Y. ZHU, W. LIU, M. ZENG, S. JAYARAM, M. LENGER, J. DING, S. MO, K. TANAKA, M. ARITA, Z. LIU, M. YE, D. SHEN, J. WRACHTRUP, Y. HUANG, R. H. HE, S. QIAO, Q. LIU and C. LIU, "Observation of Plaid-Like Spin Splitting in a Noncoplanar Antiferromagnet," *Nature* **626(7999)**, 523–528 (2024). DOI: 10.1038/s41586-024-07023-w

R. NAKAZAWA, A. MATSUZAKI, K. SHIMIZU, I. NAKAMURA, E. KAWASHIMA, S. MAKITA, K. TANAKA, S. YASUNO, H. SATO, H. YOSHIDA, M. ABDI-JALEBI, S. D. STRANKS, S. TADANO, P. KRÜGER, Y. TANAKA, H. TOKAIRIN and H. ISHII, "Reliable Measurement of the Density of States Including Occupied In-Gap States of an Amorphous In-Ga-Zn-O Thin Film via Photoemission Spectroscopies: Direct Observation of Light-Induced In-Gap States," *J. Appl. Phys.* **135(8)**, 085301 (2024). DOI: 10.1063/5.0185405

P. RAN, B. LIN, C. HONG, B. WANG, X. XIE, C. JIANG, K. TANAKA and R. H. HE, "Observation of Novel In-Gap States on Alkali Metal Dosed Ti_2O_3 Film," *J. Appl. Phys.* **135(9)**, 095303 (2024). DOI: 10.1063/5.0191245

S. ICHINOKURA, K. TOKUDA, M. TOYODA, K. TANAKA, S. SAITO and T. HIRAHARA, "Van Hove Singularity and Enhanced Superconductivity in Ca-Intercalated Bilayer Graphene Induced by Confinement Epitaxy," *ACS Nano* **18(21)**, 13738–13744 (2024). DOI: 10.1021/acsnano.4c01757

J. P. ITHIKKAL, K. FUKUTANI, F. NISHINO, T. MINATO, H. ISHII, S. IZAWA, K. TANAKA, M. HIRAMOTO and S. KERA, "Direct Observation of the Electronic Structure and Many-Body Interactions of Low-Mobility Carriers in Perylene Diimide Derivative," *Appl. Phys. Lett.* **125(5)**, 052102 (2024). DOI: 10.1063/5.0221293

T. KATO, K. NAKAYAMA, Y. LI, Z. WANG, K. SUGAWARA, K. TANAKA, T. TAKAHASHI, Y. YAO and T. SATO, "Quasi-Homoepitaxial Growth of Highly Strained Alkali-Metal Ultrathin Films on Kagome Superconductors," *Adv. Sci.* **11(29)**, 2309003 (2024). DOI: 10.1002/advs.202309003

C. VOLLMER, D. KEPAPTSOGLOU, J. LEITNER, A. B. MOSBERG, K. EL HAJRAOUI, A. J. KING, C. L. BAYS, P. F. SCHOFIELD, T. ARAKI and Q. M. RAMASSE, "High-Spatial Resolution Functional Chemistry of Nitrogen Compounds in the Observed UK Meteorite Fall Winchcombe," *Nat. Commun.* **15(1)**, 778 (2024). DOI: 10.1038/s41467-024-45064-x

E. HARDING, T. ARAKI, J. ASKEY, M. HUNT, A. VAN DEN BERG, D. RAFTREY, L. ABALLE, B. KAULICH, E. MACDONALD, P. FISCHER and S. LADAK, "Imaging the Magnetic Nanowire Cross Section and Magnetic Ordering within a Suspended 3D Artificial Spin-Ice," *APL Mater.* **12(2)**, 021116 (2024). DOI: 10.1063/5.0176907

Y. HIKOSAKA, T. KANEYASU, S. WADA, H. KOHGUCHI, H. OTA, E. NAKAMURA, H. IWAYAMA, M. FUJIMOTO, M. HOSAKA and M. KATOH, "Frequency-Domain Interferometry for the Determination of Time Delay between Two Extreme-Ultraviolet Wave Packets Generated by a Tandem Undulator," *Sci. Rep.* **13(1)**, 10292 (2023). DOI: 10.1038/s41598-023-37449-7

T. KANEYASU, Y. HIKOSAKA, S. WADA, M. FUJIMOTO, H. OTA, H. IWAYAMA and M. KATOH, "Time Domain Double Slit Interference of Electron Produced by XUV Synchrotron Radiation," *Sci. Rep.* **13(1)**, 6142 (2023). DOI: 10.1038/s41598-023-33039-9

F. ALLUM, Y. KUMAGAI, K. NAGAYA, J. HARRIES, H. IWAYAMA, M. BRITTON, P. H. BUCKSBAUM, M. BURT, M. BROUARD, B. DOWNES-WARD, T. DRIVER, D. HEATHCOTE, P. HOCKETT, A. J. HOWARD, J. W. L. LEE, Y. LIU, E. KUKK, J. W. MCMANUS, D. MILSESEVIC, A. NIOZU, J. NISKANEN, A. J. ORR-EWING, S. OWADA, P. A. ROBERTSON, A. RUDENKO, K. UEDA, J. UNWIN, C. VALLANCE, T. WALMSLEY, R. S. MINNS, D. ROLLES, M. N. R. ASHFOLD and R. FORBES, "Direct Momentum Imaging of Charge Transfer Following Site-Selective Ionization," *Phys. Rev. A* **108(4)**, 043113 (2023). DOI: 10.1103/PhysRevA.108.043113

H. ONO, Y. UMEDA, K. YOSHIDA, K. TSUTSUI, K. YAMAMOTO, O. ISHIYAMA, H. IWAYAMA, E. NAKAMURA, T. YOKOYAMA, M. MIZUGUCHI and T. MIYAMACHI, "Intermolecular Interaction Induced Magnetic Decoupling at an Organic–Inorganic Interface," *J. Phys. Chem. C* **127(49)**, 23935–23940 (2023). DOI: 10.1021/acs.jpcc.3c05966

Y. UMEDA, H. ONO, K. YAMAMOTO, O. ISHIYAMA, H. IWAYAMA, E. NAKAMURA, T. YOKOYAMA, M. MIZUGUCHI and T. MIYAMACHI, "Annealing Temperature Dependence of Magnetic Properties in FeCo Ordered Alloy Thin Films Fabricated Using the Nitrogen Surfactant Effect," *Jpn. J. Appl. Phys.* **63(4)**, 04SP80 (2024). DOI: 10.35848/1347-4065/ad396b

W. O. RAZMUS, F. ALLUM, J. HARRIES, Y. KUMAGAI, K. NAGAYA, S. BHATTACHARYYA, M. BRITTON, M. BROUARD, P. H. BUCKSBAUM, K. CHEUNG, S. W. CRANE, M. FUSHITANI, I. GABALSKI, T. GEJO, A. GHRIST, D. HEATHCOTE, Y. HIKOSAKA, A. HISHIKAWA, P. HOCKETT, E. JONES, E. KUKK, H. IWAYAMA, H. V. S. LAM, J. W. MCMANUS, D. MILESEVIC, J. MIKOSCH, S. MINEMOTO, A. NIOZU, A. J. ORR-EWING, S. OWADA, D. ROLLES, A. RUDENKO, D. TOWNSEND, K. UEDA, J. UNWIN, C. VALLANCE, A. VENKATACHALAM, S. WADA, T. WALMSLEY, E. M. WARNE, J. L. WOODHOUSE, M. BURT, M. N. R. ASHFOLD, R. S. MINNS and R. FORBES, "Exploring the Ultrafast and Isomer-Dependent Photodissociation of Iodothiophenes *via* Site-Selective Ionization," *Phys. Chem. Chem. Phys.* **26(16)**, 12725–12737 (2024). DOI: 10.1039/d3cp06079a

T. WALMSLEY, J. W. MCMANUS, Y. KUMAGAI, K. NAGAYA, J. HARRIES, H. IWAYAMA, M. N. R. ASHFOLD, M. BRITTON, P. H. BUCKSBAUM, B. DOWNES-WARD, T. DRIVER, D. HEATHCOTE, P. HOCKETT, A. J. HOWARD, J. W..L. LEE, Y. LIU, E. KUKK, D. MILESEVIC, R. S. MINNS, A. NIOZU, J. NISKANEN, A. J. ORR-EWING, S. OWADA, P. A. ROBERTSON, D. ROLLES, A. RUDENKO, K. UEDA, J. UNWIN, C. VALLANCE, M. BROUARD, M. BURT, F. ALLUM and R. FORBES, "The Role of Momentum Partitioning in Covariance Ion Imaging Analysis," *J. Phys. Chem. A* **128(22)**, 4548–4560 (2024). DOI: 10.1021/acs.jpca.4c00999

M. NAGASAKA, F. KUMAKI, Y. YAO, J. ADACHI and K. MOCHIZUKI, "Mechanism of Poly(*N*-isopropylacrylamide) Cononsolvency in Aqueous Methanol Solutions Explored *via* Oxygen K-Edge X-Ray Absorption Spectroscopy," *Phys. Chem. Chem. Phys.* **26(18)**, 13634–13638 (2024). DOI: 10.1039/D4CP00676C

M. NAGASAKA, "Probing Isolated Water Molecules in Aqueous Acetonitrile Solutions Using Oxygen K-Edge X-Ray Absorption Spectroscopy," *J. Phys. Chem. Lett.* **15(19)**, 5165–5170 (2024). DOI: 10.1021/acs.jpclett.4c01087

M. NAGASAKA, S. TSURU and Y. YAMADA, "Metal–Ligand Delocalization of Iron and Cobalt Porphyrin Complexes in Aqueous Solutions Probed by Soft X-Ray Absorption Spectroscopy," *Phys. Chem. Chem. Phys.* **26(36)**, 23636–23645 (2024). DOI: 10.1039/D4CP02140A

Y. KUDO, F. KUMAKI, M. NAGASAKA, J. ADACHI, Y. NOGUCHI, N. KOGA, H. ITABASHI and M. HIYAMA, "Experimental and Theoretical Study for Core Excitation of Firefly Luciferin in Carbon K-Edge Spectra," *J. Phys. Chem. A* **128(3)**, 611–617 (2024). DOI: 10.1021/acs.jpca.3c07504

Y. YAO, M. NAGASAKA and K. MOCHIZUKI, "Salt-Specific Effect on the Solubility and Aggregation of 1-Butanol in Water," *Phys. A* **647**, 129917 (2024). DOI: 10.1016/j.physa.2024.129917

Materials Molecular Science

T. YOKOYAMA, H. T. FUJII, S. MATSUMURA, N. SAKAGUCHI, N. KURAHASHI and N. MAEJIMA, "Local Thermal Expansion of Co-Containing Invar Alloys," *Phys. Rev. Mater.* **8**, 083603 (2024). DOI: 10.1103/PhysRevMaterials.8.083603

Y. UMEDA, H. ONO, K. YAMAMOTO, O. ISHIYAMA, H. IWAYAMA, E. NAKAMURA, T. YOKOYAMA, M. MIZUGUCHI and T. MIYAMACHI, "Annealing Temperature Dependence of Magnetic Properties in FeCo Ordered Alloy Thin Films Fabricated Using the Nitrogen Surfactant Effect," *Jpn. J. Appl. Phys.* **63**, 04SP80 (2024). DOI: 10.35848/1347-4065/ad396b

H. ONO, Y. UMEDA, K. YOSHIDA, K. TSUTSUI, K. YAMAMOTO, O. ISHIYAMA, H. IWAYAMA, E. NAKAMURA, T. YOKOYAMA, M. MIZUGUCHI and T. MIYAMACHI, "Intermolecular Interaction Induced Magnetic Decoupling at Organic–Inorganic Interface" *J. Phys. Chem. C* **127**, 23935–23940 (2023). DOI: 10.1021/acs.jpcc.3c05966

Z. LIN, H. SAITO, H. SATO and T. SUGIMOTO, "Positive and Negative Impacts of Interfacial Hydrogen Bonds on Photocatalytic Hydrogen Evolution," *J. Am. Chem. Soc.* **146(32)**, 22276–22283 (2024). DOI: 10.1021/jacs.4c04271

H. SATO and T. SUGIMOTO, "Direct *Operando* Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides," *J. Am. Chem. Soc.* **146(36)**, 24800–24807 (2024). DOI: 10.1021/jacs.3c14558

N. AIGA and T. SUGIMOTO, "Tuning the Thermodynamic Ordering of Strongly Correlated Protons in Ice by Angstrom-Scale Interface Modification," *Commun. Mater.* **5**, 204 (2024). DOI: 10.1038/s43246-024-00648-4

J. HARUYAMA, T. SUGIMOTO and O. SUGINO, "First-Principles Study of Water Adsorption Monolayer on Pt(111): Adsorption Energy and Second-Order Nonlinear Susceptibility," *Phys. Rev. Mater.* **7**, 115803 (2023). DOI: 10.1103/PhysRevMaterials.7.115803

S. TSUBOKURA, S. KAWANO, Y. IMAI, T. UEDA, K. NAKAMOTO, H. NOMA, H. HIOKI and T. MINATO, "Development of a Method for Analyzing the Positional Correlation of Local Structures in Scanning Probe Microscopy Images Using Template-Matching Image-Processing Method," *Appl. Phys. Express* **17(3)**, 035003 (2024). DOI: 10.35848/1882-0786/ad2784

Y. ARAKI, T. MINATO and T. ARAI, "Microscopic Behavior of Nano-Water Droplets on a Silica Glass Surface," *Sci. Rep.* **14(1)**, 10693 (2024). DOI: 10.1038/s41598-024-61212-1

R. YANAGISAWA, T. UEDA, K. NAKAMOTO, Z. LU, H. ONISHI and T. MINATO, "The Interface between Ice and Alcohols Analyzed by Atomic Force Microscopy," *J. Chem. Phys.* **161(2)**, 024702 (2024). DOI: 10.1063/5.0211501

H. AIZAWA, T. SATO, S. MAKI-YONEKURA, K. YONEKURA, K. TAKABA, T. HAMAGUCHI, T. MINATO and H. M. YAMAMOTO, "Enantioselectivity of Discretized Helical Supramolecule Consisting of Achiral Cobalt Phthalocyanines *via* Chiral-Induced Spin Selectivity Effect," *Nat. Commun.* **14(1)**, 4530 (2023). DOI: 10.1038/s41467-023-40133-z

J. NISHIDA, A. OTOMO, T. KOITAYA, A. SHIOTARI, T. MINATO, R. IINO and T. KUMAGAI, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24(3)**, 836–843 (2024). DOI: 10.1021/acs.nanolett.3c03479

J. P. ITHIKKAL, K. FUKUTANI, F. NISHINO, T. MINATO, H. ISHII, S. IZAWA, K. TANAKA, M. HIRAMOTO and S. KERA, "Direct Observation of the Electronic Structure and Many-Body Interactions of Low-Mobility Carriers in Perylene Diimide Derivative," *Appl. Phys. Lett.* **125(5)**, 052102 (2024). DOI: 10.1063/5.0221293

Y. HORITA, S. HOSSAIN, M. ISHIMI, P. ZHAO, M. SERA, T. KAWAWAKI, S. TAKANO, Y. NIIHORI, T. NAKAMURA, T. TSUKUDA, M. EHARA and Y. NEGISHI, "Clarifying the Electronic Structure of Anion-Templated Silver Nanoclusters by Optical Absorption Spectroscopy and Theoretical Calculation," *J. Am. Chem. Soc.* **145(43)**, 23533–23540 (2023). DOI: 10.1021/jacs.3c07194

K. ORIHASHI, A. YAMAUCHI, M. INOUE, B. PARMAR, S. FUJIWARA, N. KIMIZUKA, M. ASADA, T. NAKAMURA and N. YANAI, "Radical Qubits Photo-Generated in Acene-Based Metal-Organic Frameworks," *Dalton Trans.* **53(3)**, 872–876 (2023). DOI: 10.1039/d3dt03959e

K. ORIHASHI, A. YAMAUCHI, S. FUJIWARA, M. ASADA, T. NAKAMURA, J. K.-H. HUI, N. KIMIZUKA, K. TATEISHI, T. UESAKA and N. YANAI, "Spin-Polarized Radicals with Extremely Long Spin-Lattice Relaxation Time at Room Temperature in a Metal-Organic Framework," *J. Am. Chem. Soc.* **145(50)**, 27650–27656 (2023). DOI: 10.1021/jacs.3c09563

S. NAKAGAWA, A. YOKOYA, M. OHARA, N. USAMI, M. ASADA, M. FUJIWARA, T. NAKAMURA and K. ISHIKAWA, "High Linear Energy Transfer (LET) Nature of Alanine Radical Yield by Soft X-Ray Irradiations Studied by Electron Spin Resonance (ESR) Applications," *Radiat. Phys. Chem.* **214**, 111304 (2024). DOI: 10.1016/j.radphyschem.2023.111304

A. YAMAUCHI, S. FUJIWARA, N. KIMIZUKA, M. ASADA, M. FUJIWARA, T. NAKAMURA, J. PIRILLO, Y. HIJIKATA and N. YANAI, "Modulation of Triplet Quantum Coherence by Guest-Induced Structural Changes in a Flexible Metal-Organic Framework," *Nat. Commun.* **15(1)**, 7622 (2024). DOI: 10.1038/s41467-024-51715-w

M. INOUE, A. YAMAUCHI, B. PARMAR, K. ORIHASHI, M. SINGH, M. ASADA, T. NAKAMURA and N. YANAI, "Guest-Responsive Coherence Time of Radical Qubits in a Metal-Organic Framework," *Chem. Commun.* **60(48)**, 6130–6133 (2024). DOI: 10.1039/D4CC01564A

T. FUJINO, R. KAMEYAMA, K. ONOZUKA, K. MATSUO, S. DEKURA, T. MIYAMOTO, Z. GUO, H. OKAMOTO, T. NAKAMURA, K. YOSHIMI, S. KITOU, T. ARIMA, H. SATO, K. YAMAMOTO, A. TAKAHASHI, H. SAWA, Y. NAKAMURA and H. MORI, "Orbital Hybridization of Donor and Acceptor to Enhance the Conductivity of Mixed-Stack Complexes," *Nat. Commun.* **15(1)**, 3028 (2024). DOI: 10.1038/s41467-024-47298-1

N. OHTSUKA, H. OTA, S. SUGIURA, S. KAKINUMA, H. SUGIYAMA, T. SUZUKI and N. MOMIYAMA, "Perfluorohalogenated Naphthalenes: Synthesis, Crystal Structure, and Intermolecular Interaction," *CrystEngComm* **26**, 764–772 (2024). DOI: 10.1039/d3ce01124k

K. TAKEDA, N. OHTSUKA, T. SUZUKI and N. MOMIYAMA, "Prediction Method for Reaction Yield of Deuteration of Polyfluoroperylene Using Generative AI Techniques," *Comput.-Aided Chem. Eng.* **53**, 2689–2694 (2024). DOI: 10.1016/b978-0-443-28824-1.50449-x

Life and Coordination-Complex Molecular Science

S. YANAKA, H. WATANABE, R. YOGO, M. KONGSEMA, S. KONDO, H. YAGI, T. UCHIHASHI and K. KATO, "Quantitative Analysis of Therapeutic Antibody Interactions with Fcγ Receptors Using High-Speed Atomic Force Microscopy," *Biol. Pharm. Bull.* **47**, 334–338 (2024). DOI: 10.1248/bpb.b23-00751

H. YAGI, S. TATEO, T. SAITO, Y. OHTA, E. NISHI, S. OBITSU, T. SUZUKI, S. SEETAHA, C. HELLEC, A. NAKANO, T. TOJIMA and K. KATO, "Deciphering the Sub-Golgi Localization of Glycosyltransferases *via* 3D Super-Resolution Imaging," *Cell Struct. Funct.* **49(2)**, 47–55 (2024). DOI: 10.1247/csf.24008

S. NAKAGAWA, H. IMACHI, S. SHIMAMURA, S. YANAKA, H. YAGI, M. YAGI-UTSUMI, H. SAKAI, S. KATO, M. OHKUMA, K. KATO and K. TAKAI, "Characterization of Protein Glycosylation in an Asgard archaeon," *BBA Adv.* **6**, 100118 (2024). DOI: 10.1016/j.bbadva.2024.100118

M. FABIANO, N. OIKAWA, A. KERKSIEK, J. FURUKAWA, H. YAGI, K. KATO, U. SCHWEIZER, W. ANNAERT, J. KANG, J. SHEN, D. LÜTJOHANN and J. WALTER, "Presenilin Deficiency Results in Cellular Cholesterol Accumulation by Impairment of Protein Glycosylation and NPC1 Function," *Int. J. Mol. Sci.* **25(10)**, 5417 (2024). DOI: 10.3390/ijms25105417

T. SATOH, M. YAGI-UTSUMI, N. ISHII, T. MIZUSHIMA, H. YAGI, R. KATO, Y. TACHIDA, H. TATENO, I. MATSUO, K. KATO, T. SUZUKI and Y. YOSHIDA, "Structural Basis of Sugar Recognition by SCFFBS2 Ubiquitin Ligase Involved in NGLY1 Deficiency," *FEBS Lett.* **598**, 2259–2268 (2024). DOI: 10.1002/1873-3468.15003

S. NAKAGAWA, H. D. SAKAI, S. SHIMAMURA, Y. TAKAMATSU, S. KATO, H. YAGI, S. YANAKA, M. YAGI-UTSUMI, N. KUROSAWA, M. OHKUMA, K. KATO and K. TAKAI, "*N*-Linked Protein Glycosylation in *Nanobdellati* (formerly DPANN) archaea and Their Hosts," *J. Bacteriol.* **206**, e00205-24 (2024). DOI: 10.1128/jb.00205-24

J. NISHIDA, A. OTOMO, T. KOITAYA, A. SHIOTARI, T. MINATO, R. IINO and T. KUMAGAI, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24(3)**, 836–843 (2024). DOI: 10.1021/acs.nanolett.3c03479

Y. MATSUMOTO, S. YAMASAKI, K. HAYAMA, R. IINO, H. NOJI, A. YAMAGUCHI and K. NISHINO, "Changes in the Expression of *mexB*, *mexY*, and *oprD* in Clinical *Pseudomonas aeruginosa* Isolates," *Proc. Jpn. Acad. Ser. B* **100(1)**, 57–67 (2024). DOI: 10.2183/pjab.100.006

S. OKUMURA, T. TAKAHASHI, K. TORII and Y. UOZUMI, "Photocatalytic 1,4-Addition of Aromatic Aldehydes or Ketones *via* Umpoled Carbinol Anions," *Synlett* **35**, 303–306 (2024). DOI: 10.1055/a-2122-8631

K. ZHANG, S. OKUMURA and Y. UOZUMI, "Transfer Hydrogenolysis of O- and N-Benzyl Groups in Water with Tetrahydroxydiboron by Using an Amphiphilic Polymer-Supported Nano-Palladium Catalyst," *Eur. J. Org. Chem.* **27(26)**, e202400322 (2024). DOI: 10.1002/ejoc.202400322

S. OKUMURA, S. HATTORI, L. FANG and Y. UOZUMI, "Multielectron Reduction of Esters by a Diazabenzacenaphthenium Photoredox Catalyst," *J. Am. Chem. Soc.* **146(25)**, 16990–16995 (2024). DOI: 10.1021/jacs.4c05272

N. OHTSUKA, H. OTA, S. SUGIURA, S. KAKINUMA, H. SUGIYAMA, T. SUZUKI and N. MOMIYAMA, "Perfluorohalogenated Naphthalenes: Synthesis, Crystal Structure, and Intermolecular Interaction," *CrystEngComm* **26**, 764–772 (2024). DOI: 10.1039/d3ce01124k

K. TAKEDA, N. OHTSUKA, T. SUZUKI and N. MOMIYAMA, "Prediction Method for Reaction Yield of Deuteration of Polyfluoroperylene Using Generative AI Techniques," *Comput.-Aided Chem. Eng.* **53**, 2689–2694 (2024). DOI: 10.1016/b978-0-443-28824-1.50449-x

S. HIROTA, S. NAKANO, H. SUGIYAMA and Y. SEGAWA, "Synthesis of Polycyclic Arenes Composed of Four-, Five-, Six-, and Eight-Membered Rings via an Unexpected Four-Membered Ring Formation Reaction," *Org. Lett.* **25(45)**, 8062–8066 (2023). DOI: 10.1021/acs.orglett.3c03039

R. YOSHIDA, H. SUGIYAMA and Y. SEGAWA, "Synthesis, Structure, and Properties of a Bay-Fluorinated Triphenylene," *Chem. Lett.* **53(4)**, upae048 (2024). DOI: 10.1093/chemle/upae048

H. SHUDO, M. KUWAYAMA, Y. SEGAWA, A. YAGI and K. ITAMI, "Half-Substituted Fluorocycloparaphenylenes with High Symmetry: Synthesis, Properties and Derivatization to Densely Substituted Carbon Nanorings," *Chem. Commun.* **59(90)**, 13494–13497 (2023). DOI: 10.1039/d3cc04887j

K. OTA, K. NAGAO, D. HATA, H. SUGIYAMA, Y. SEGAWA, R. TOKUNOH, T. SEKI, N. MIYAMOTO, Y. SASAKI and H. OHMIYA, "Synthesis of Tertiary Alkylphosphonate Oligonucleotides through Light-Driven Radical-Polar Crossover Reactions," *Nat. Commun.* **14(1)**, 6856 (2023). DOI: 10.1038/s41467-023-42639-y

Research Center of Integrative Molecular Systems

Y. FURUIKE, E. YAMASHITA and S. AKIYAMA, "Structure-Function Relationship of KaiC around Dawn," *Biophys. Physicobiol.* **21**, e210001 (2023). DOI: 10.2142/biophysico.bppb-v21.0001

Y. FURUIKE, Y. ONOUE, S. SAITO, T. MORI and S. AKIYAMA, "The Priming Phosphorylation of KaiC Is Activated by the Release of Its Autokinase Autoinhibition," *bioRxiv* 2024.03.21.584037 (2024). DOI: 10.1101/2024.03.21.584037

T. INOBE, R. SAKAGUCHI, T. OBITA, A. MUKAIYAMA, S. KOIKE, T. YOKOYAMA, M. MIZUGUCHI and S. AKIYAMA, "Structural Insights into Rapamycin-Induced Oligomerization of a FRB–FKBP Fusion Protein," *FEBS Lett.* **598(18)**, 2292–2305 (2024). DOI: 10.1002/1873-3468.14986

H. KURAMOCHI, T. TSUTSUMI, K. SAITA, Z. WEI, M. OSAWA, P. KUMAR, L. LIU, S. TAKEUCHI, T. TAKETSUGU and T. TAHARA, "Ultrafast Raman Observation of the Perpendicular Intermediate Phantom State of Stilbene Photoisomerization," *Nat. Chem.* **16(1)**, 22–27 (2024). DOI: 10.1038/s41557-023-01397-6

Y. YONEDA and H. KURAMOCHI, "Room-Temperature Solution Fluorescence Excitation Correlation Spectroscopy," *J. Phys. Chem. Lett.* **15(33)**, 8533–8539 (2024). DOI: 10.1021/acs.jpclett.4c01798

H. AIZAWA, T. SATO, S. MAKI-YONEKURA, K. YONEKURA, K. TAKABA, T. HAMAGUCHI, T. MINATO and H. M. YAMAMOTO, "Enantioselectivity of Discretized Helical Supramolecule Consisting of Achiral Cobalt Phthalocyanines via Chiral-Induced Spin Selectivity Effect," *Nat. Commun.* **14(1)**, 4530 (2023). DOI: 10.1038/s41467-023-40133-z

H. KUSUNOSE, J. KISHINE and H. M. YAMAMOTO, "Emergence of Chirality from Electron Spins, Physical Fields, and Material-Field Composites," *Appl. Phys. Lett.* **124(26)**, 260501 (2024). DOI: 10.1063/5.0214919

T. UBE, I. SUKA, S. OGIKUBO, G. HASHIMOTO, M. SUDA, H. M. YAMAMOTO and T. IKEDA, "Inducing Motions of Polymers in Liquid Nitrogen with Light," *Adv. Mater.* **35(47)**, 2306402 (2023). DOI: 10.1002/adma.202306402

Y. OSHIMA, T. TAKENOBU, J. PU, K. ISHIGURO, R. KATO, H. M. YAMAMOTO and T. KUSAMOTO, "A Memristive Oscillator," *Adv. Phys. Res.* **3(4)**, 2300117 (2024). DOI: 10.1002/apxr.202300117

P. V. MÖLLERS, A. J. URBAN, S. DE FEYTER, H. M. YAMAMOTO and H. ZACHARIAS, "Probing the Roles of Temperature and Cooperative Effects in Chirality-Induced Spin Selectivity: Photoelectron Spin Polarization in Helical Tetrapyrroles," *J. Phys. Chem. Lett.* **15(38)**, 9620–9629 (2024). DOI: 10.1021/acs.jpclett.4c02209

A. INDA, R. OIWA, S. HAYAMI, H. M. YAMAMOTO and H. KUSUNOSE, "Quantification of Chirality Based on Electric Toroidal Monopole," *J. Chem. Phys.* **160(18)**, 184117 (2024). DOI: 10.1063/5.0204254

K. SAKUMA, N. KOBAYASHI, T. SUGIKI, T. NAGASHIMA, T. FUJIWARA, K. SUZUKI, N. KOBAYASHI, T. MURATA, T. KOSUGI, R. TATSUMI-KOGA and N. KOGA, "Design of Complicated All-α Protein Structures," *Nat. Struct. Mol. Biol.* **31(2)**, 275–282 (2024). DOI: 10.1038/s41594-023-01147-9

Y. KAMADA, C. UMEDA, Y. MUKAI, H. OHTSUKA, Y. OTSUBO, A. YAMASHITA and T. KOSUGI, "Structure-Based Engineering of Tor Complexes Reveals that Two Types of Yeast TORC1 Produce Distinct Phenotypes," *J. Cell Sci.* **137(4)**, jcs261625 (2024). DOI: 10.1242/jcs.261625

Center for Mesoscopic Sciences

J. YAMANISHI, H.-Y. AHN and H. OKAMOTO, "Nanoscopic Observation of Chiro-Optical Force," *Nano Lett.* **23(20)**, 9347–9352 (2023). DOI: 10.1021/acs.nanolett.3c02534

K. ENDO, S. HASHIYADA, T. NARUSHIMA, Y. TOGAWA and H. OKAMOTO, "Circular Dichroism of Pseudo-Two-Dimensional Metal Nanostructures: Rotational Symmetry and Reciprocity," *J. Chem. Phys.* **159(23)**, 234706 (2023). DOI: 10.1063/5.0178943

H.-Y. AHN, T. NARUSHIMA and H. OKAMOTO, "Creation of a Photopolymerized Double Spiral Structure by Interference of Plasmonic Scattering and Circularly Polarized Light," *J. Phys. Chem. C* **128(17)**, 7159–7168 (2024). DOI: 10.1021/acs.jpcc.3c08473

H.-Y. AHN, K. Q. LE, T. NARUSHIMA, J. YAMANISHI, R. M. KIM, K. T. NAM and H. OKAMOTO, "Highly Chiral Light Emission Using Plasmonic Helicoid Nanoparticles," *Adv. Opt. Mater.* **12(22)**, 2400699 (2024). DOI: 10.1002/adom.202400699

C. LIN, F. KRECINIC, H. YOSHINO, A. HAMMUD, A. PAN, M. WOLF, M. MÜLLER and T. KUMAGAI, "Continuous-Wave Multiphoton-Induced Electron Transfer in Tunnel Junctions Driven by Intense Plasmonic Fields," *ACS Photonics* **10(10)**, 3637–3646 (2023). DOI: 10.1021/acsphotonics.3c00714

J. NISHIDA, A. OTOMO, T. KOITAYA, A. SHIOTARI, T. MINATO, R. IINO and T. KUMAGAI, "Sub-Tip-Radius Near-Field Interactions in Nano-FTIR Vibrational Spectroscopy on Single Proteins," *Nano Lett.* **24(3)**, 836–843 (2024). DOI: 10.1021/acs.nanolett.3c03479

B. CIRERA, S. LIU, Y. PARK, I. HAMADA, M. WOLF, A. SHIOTARI and T. KUMAGAI, "Single-Molecule Tip-Enhanced Raman Spectroscopy of C_{60} on the Si(111)-(7×7) Surface," *Phys. Chem. Chem. Phys.* **26(32)**, 21325–21331 (2024). DOI: 10.1039/d4cp01803f

Y. PARK, I. HAMADA, A. HAMMUD, T. KUMAGAI, M. WOLF and A. SHIOTARI, "Atomic-Precision Control of Plasmon-Induced Single-Molecule Switching in a Metal–Semiconductor Nanojunction," *Nat. Commun.* **15(1)**, 6709 (2024). DOI: 10.1038/s41467-024-51000-w

Division of Advanced Molecular Science

K. IIZUKA, H. TAKEZAWA and M. FUJITA, "Chemical Site-Differentiation of Calix[4]arenes through Enforced Conformations by Confinement in a Cage," *J. Am. Chem. Soc.* **145(48)**, 25971–25975 (2023). DOI: 10.1021/jacs.3c10720

Y. JUNG, T. MITSUHASHI, S. SATO, M. SENDA, T. SENDA and M. FUJITA, "Function and Structure of a Terpene Synthase Encoded in a Giant Virus Genome," *J. Am. Chem. Soc.* **145(48)**, 25966–25970 (2023). DOI: 10.1021/jacs.3c10603

B. ZHOU, S. UTJAPIMUK, K. K. YAN, R. DUBEY, T. KIKUCHI, T. MITSUHASHI and M. FUJITA, "Rapid Analysis of Trace Amounts of Amino Acid Derivatives by a Formyl Group-Installed Crystalline Sponge," *Chem. –Asian J.* **19(3)**, e202300969 (2023). DOI: 10.1002/asia.202300969

H. TAKEZAWA, K. IIZUKA and M. FUJITA, "Selective Synthesis and Functionalization of an Acyclic Methylene-Bridged-Arene Trimer in a Cage," *Angew. Chem., Int. Ed.* **63(6)**, e202319140 (2023). DOI: 10.1002/anie.202319140

H. TAMURA, T. NAKAMA, A. ROSSEN, H. ISHIKITA and M. FUJITA, "Organic Solvent-Induced Structural Changes in a Protein Confined in a Giant Coordination Cage," *Chem. Lett.* **53(5)**, upae101 (2024). DOI: 10.1093/chemle/upae101

Y. JUNG, T. MITSUHASHI, T. KIKUCHI and M. FUJITA, "Functional Plasticity of a Viral Terpene Synthase, OILTS, that Shows Non–Specific Metal Cofactor Binding and Metal–Dependent Biosynthesis," *Chem. –Eur. J.* **30(31)**, e202304317 (2024). DOI: 10.1002/chem.202304317

Y. JUNG, T. MITSUHASHI, K. KAGEYAMA, T. KIKUCHI, S. SATO and M. FUJITA, "Conformational Analysis of (+)-Germacrene D-4-ol Using the Crystalline Sponge Method to Elucidate the Origin of its Instability," *Chem. –Eur. J.* **30(39)**, e202400512 (2024). DOI: 10.1002/chem.202400512

S. KIMURA, H. WATANABE, S. TATSUKAWA, T. NAKAMURA, K. IMURA, H. SUZUKI and N. K. SATO, "Current-Induced Metallization and Valence Transition in Black SmS," *J. Phys. Soc. Jpn.* **93(1)**, 013701 (2024). DOI: 10.7566/jpsj.93.0137013

R. IKEDA, H. WATANABE, M. J. HEON, M. H. JUNG, K. TAKASAN and S. KIMURA, "Light-Field-Driven Non-Ohmic Current Generation by an Intense THz Pulse in a Weyl Semimetal," *J. Phys. Soc. Jpn.* **93(5)**, 053701 (2024). DOI: 10.7566/JPSJ.93.053701

T. NAKAMURA, H. SUGIHARA, Y. CHEN, R. YUKAWA, Y. OHTSUBO, K. TANAKA, M. KITAMURA, H. KUMIGASHIRA and S. KIMURA, "Two-Dimensional Heavy Fermion in a Monoatomic-Layer Kondo Lattice $YbCu_2$," *Nat. Commun.* **14(1)**, 7850 (2023). DOI: 10.1038/s41467-023-43662-9

M. BUESSLER, S. MARUYAMA, M. ZELENKA, H. ONISHI and E. H. G. BACKUS, "Unravelling the Interfacial Water Structure at the Photocatalyst Strontium Titanate by Sum Frequency Generation Spectroscopy," *Phys. Chem. Chem. Phys.* **25(45)**, 31471–31480 (2023). DOI: 10.1039/D3CP03829G

Y. H. CHEW and H. ONISHI, "Infrared Absorption of $Zn_{0.5}Cd_{0.5}S$ Photocatalyst Bandgap-Excited Under an Aqueous Environment," *J. Phys. Chem. C* **128(11)**, 4535–4543 (2024). DOI: 10.1021/acs.jpcc.3c08343

T. OTAKE, R. KAJITA, I. OGASAWARA, M. IWAKI, H. ONISHI and K. AMANO, "Theoretical Investigation of Interaction Measurements in Liquid Systems with Viscosity Distributions," *Phys. A* **647**, 129918 (2024). DOI: 10.1016/j.physa.2024.129918

R. YANAGISAWA, T. UEDA, K. NAKAMOTO, Z. LU, H. ONISHI and T. MINATO, "The Interface between Ice and Alcohols Analyzed by Atomic Force Microscopy," *J. Chem. Phys.* **161(2)**, 024702 (2024). DOI: 10.1063/5.0211501

Y. TANAKA, T. UCHIHASHI and A. NAKAMURA, "Product Inhibition Slow Down the Moving Velocity of Processive Chitinase and Sliding-Intermediate State Blocks Re-Binding of Product," *Arch. Biochem. Biophys.* **752**, 109854 (2024). DOI: 10.1016/j.abb.2023.109854

Y. OGURA, Y. HASHINO and A. NAKAMURA, "Direct Screening of PET Hydrolase Activity in Culture Medium Based on Turbidity Reduction," *ACS Omega* **9(31)**, 34151–34160 (2024). DOI: 10.1021/acsomega.4c05488

T. MORI, S. SUGIMOTO, S. ISHII, J. WU, A. NAKAMURA, H. DOHRA, K. NAGAI, H. KAWAGISHI and H. HIRAI, "Biotransformation and Detoxification of Tetrabromobisphenol A by White-Rot Fungus Phanerochaete sordida YK-624," *J. Hazard. Mater.* **465**, 133469 (2024). DOI: 10.1016/j.jhazmat.2024.133469

Division of Research Innovation and Collaboration

V. YAHIA, A. KAUSAS, A. TSUJI, M. YOSHIDA and T. TAIRA, "Joule-Class Sub-Nanosecond Pulses Produced by End-Pumped Direct Bonded YAG/Sapphire Modular Amplifier," *Opt. Express* **32(8)**, 14377–14393 (2024). DOI: 10.1364/OE.518251

K. TAMURA, R. NAKANISHI, H. OHBA, T. KARINO, T. SHIBATA, T. TAIRA and I. WAKAIDA, "Development of a Radiation Tolerant Laser-Induced Breakdown Spectroscopy System Using a Single Crystal Micro-Chip Laser for Remote Elemental Analysis," *J. Nucl. Sci. Technol.* **61(8)**, 1109–1116 (2024). DOI: 10.1080/00223131.2023.2298485

R. MIYAGAWA, T. OHGAI, S. YOSHIKAWA, H. H. LIM, SA. REZVANI, T. TAIRA and O. ERYU, "Effects of Laser Pulse Duration on the Formation Dynamics of Laser-Induced Periodic Nanostructures," *Opt. Express* **32(7)**, 11863–11872 (2024). DOI: 10.1364/OE.520565

LIST OF REVIEW ARTICLES AND TEXTBOOKS

Theoretical and Computational Molecular Science

A. AKIYAMA, H. SAKIAT, Y. NIIHORI, T. KAWAWAKI, D. OGATA, P. ZHAO, J. YUASA, M. EHARA and Y. NEGISHI, "Commentary: Synthesis and Luminescence Characterization of Sulfonate-Protected Silver Nanoclusters," *The Bulletin of the Society of Nano Science and Technology*, **22**, 13–19 (2023). (in Japanese)
Y. MAEDA, P. ZHAO and M. EHARA, "Recent Progress in Controlling the Photoluminescence Properties of Single-Walled Carbon Nanotubes by Oxidation and Alkylation," *Chem. Commun.* **59(98)**, 14497–14508 (2023). DOI: 10.1039/D3CC05065C
Y. MAEDA and M. EHARA, "Commentary: Controlling the Near-Infrared Emission Properties of Carbon Nanotubes by Chemical Modification —Aiming to Use as a Light Source for Bioimaging and Photonics Devices," *Kagaku*, **79**, 37–40 (2024). (in Japanese)
B. SRIDHARAN, A. SINHA, J. BARDHAN, R. MODEE, M. EHARA and U. D. PRIYAKUMAR, "Deep Reinforcement Learning in Chemistry: A Review," *J. Comput. Chem.* **45(22)**, 1881–1885 (2024). DOI: 10.1002/jcc.27354

H. OKUMURA, "Perspective for Molecular Dynamics Simulation Studies of Amyloid-β Aggregates," *J. Phys. Chem. B* **127(51)**, 10931–10940 (2023). DOI: 10.1021/acs.jpcb.3c06051
H. OKUMURA, "Amyloid-Fibril Disruption by Ultrasonic Wave and Infrared Laser Observed by Molecular Dynamics Simulation," *The Review of High Pressure Science and Technology*, **33(2)**, 76–82 (2024). DOI: 10.4131/jshpreview.33.76 (in Japanese)

A. YAMASHITA and K. OKAZAKI, "Mechanism of Oxalate Transporter in an Oxalate-Degrading Bacterium in the Gut Microbiota," *Seibutsubutsuri*, **64(1)**, 25–27 (2024). DOI: 10.2142/biophys.64.25 (in Japanese)

Photo-Molecular Science

S. KERA, T. ARAKI, K. TANAKA, Y. TAIRA, M. KATOH and F. MATSUI, "UVSOR Synchrotron Facility 40th Anniversary," *Synchrotron Radiat. News* **37(2)**, 41–42 (2024). DOI: 10.1080/08940886.2024.2330876
T. YOKOYAMA, F. MATSUI, H. ABE and T. KINOSHITA, "60 Years of Synchrotron Radiation in Japan (JPSR60)," *Synchrotron Radiat. News* **37(2)**, 43–44 (2024). DOI: 10.1080/08940886.2024.2330877

Materials Molecular Science

Y. TAKAGI and T. YOKOYAMA, "Present Status and Prospects of Operando Measurement by Atmospheric Pressure Hard X-Ray Photoelectron Spectroscopy," *Vac. Surf. Sci.,* **67(3)** (Special Feature: Recent Progress of Near Ambient Pressure and Atmospheric X-Ray Photoelectron Spectroscopy), 123–128 (2024). DOI: 10.1380/vss67.123 (in Japanese)
T. KOITAYA, S. YAMAMOTO, I. MATSUDA, J. YOSHINOBU and T. YOKOYAMA, "*Operando* Observation of Hydrogenation of Carbon Dioxide by Near Ambient Pressure X-Ray Photoelectron Spectroscopy," *Vac. Surf. Sci.*, **67(3)** (Special Feature: Recent Progress of Near Ambient Pressure and Atmospheric X-Ray Photoelectron Spectroscopy), 117–122 (2024). DOI: 10.1380/vss.67.117 (in Japanese)
Y. TAKAGI, T. KOITAYA and T. YOKOYAMA, "Catalyst Structure Analysis by Near Ambient Pressure Hard X-Ray Photoelectron Spectroscopy," *Shokubai (Catalysis)*, **66(4)** (Special issue: Advanced analysis techniques of catalysts using synchrotron radiation and neutrons), 204–209 (2024). (in Japanese)
T. KOITAYA and T. YOKOYAMA, "*Operando* Characterization of Copper-Zinc-Alumina Catalyst for Methanol Synthesis by Ambient-Pressure Hard X-Ray Photoelectron Spectroscopy," *SPring-8 Research Frontiers 2023*, 78–79 (2024).

T. SUGIMOTO, "Pioneering Interfacial Molecular Science for Realistic Catalyst under Reaction Condition :Molecular-Level Insights into the Critical Impacts of Interfacial Water on C–H Activation in Photocatalytic Methane Conversion," *Vac. Surf. Sci.* **66(10)**, 580 (2023). DOI: 10.1380/vss.66.580 (in Japanese)

Life and Coordination-Complex Molecular Science

H. YAGI and K. KATO, “Methods for Glycostructuromics Analysis,” *The Cell*, **56**, 260–262 (2024). (in Japanese)

H. YAGI, K. TAKAGI and K. KATO, “Exploring Domain Architectures of Human Glycosyltransferases: Highlighting the Functional Diversity of Non-Catalytic Add-On Domains,” *Biochim. Biophys. Acta, Gen. Subj.* **1868**, 130687 (2024). DOI: 10.1016/j.bbagen.2024.130687

D. KOGA, S. KUSUMI, H. YAGI and K. KATO, “Three-Dimensional Analysis of the Intracellular Architecture by Scanning Electron Microscopy,” *Microscopy*, **73**, 215–225 (2024). DOI: 10.1093/jmicro/dfad050

N. YAZDANPANAH, C. SEDIKIDES, H. D. OCHS, C. A. CAMARGO JR., G. L. DARMSTADT, A. CERDA, V. CAUDA, G. J. PETERS, F. SELLKE, N. D. WONG, E. COMINI, A. R. JIMENO, V. GLOVER, N. HATZIARGYRIOU, C. E. VINCENOT, S. P. A. BORDAS, I. M. RAO, H. ABOLHASSANI, G. B. GHAREHPETIAN, R. WEISKIRCHEN, M. GUPTA, S. S. CHANDEL, B. O. OLUSANYA, B. CHESON, A. POMPONIO, M. TANZER, P. S. MYLES, W.-X. MA, F. BELLA, S. GHAVAMI, S. M. MOGHIMI, D. PRATICO, A. M. HERNANDEZ, M. MARTINEZ-URBISTONDO, D. M. URBISTONDO, S.-M. FERESHTEHNEJAD, I. ALI, S. KIMURA, A. W. HAYES, W. CAI, C. K. J. ERNEST, S. THOMAS, K. RAHIMI, A. SOROOSHIAN, M. SCHREIBER, K. KATO, J. H. T. LUONG, S. PLUCHINO, A. M. LOZANO, J. F. SEYMOUR, K. S. KOSIK, S. G. HOFMANN, R. S. MCINTYRE, M. PERC, A. LEEMANS, R. S. KLEIN, S. OGINO, C. WLEZIEN, G. PERRY, J. J. NIETO, L. LEVIN, D. J. KLIONSKY, B. MOBASHER, T. DORIGO, N. REZAEI and USERN ADVISORY BOARD, “Global Challenges After a Global Challenge: Lessons Learned from the COVID-19 Pandemic,” *Adv. Exp. Med. Biol.* (*The COVID-19 Aftermath. Advances in Experimental Medicine and Biology)*, N. Rezaei, Ed., **1457**, 1–31 (2024). DOI: 10.1007/978-3-031-61939-7_1

Y. SEGAWA, “The Transannular Scholl Reaction for the Introduction of Heptagons into Aromatic Hydrocarbons,” *Chem* **9**, 2725–2727 (2023). DOI: 10.1016/j.chempr.2023.09.014

Research Center of Integrative Molecular Systems

T. KOSUGI, “Method to Design Allosteric Sites by Restoring Lost Functions: A Demonstration for Rotary Molecular Motor V_1-ATPase,” *Protein Science Society of Japan (PSSJ) Archives*, **16**, eEssay13 (2023). (in Japanese)

T. KOSUGI, “Structural Analysis for Engineering Protein and Interpreting its Mechanism,” *Photon Factory News*, **42(1)**, 26 (2024). (in Japanese)

Center for Mesoscopic Sciences

H. OKAMOTO, “Chiro-Optical Effects of Plasmon Resonances,” *Japanese Journal of Optics*, **53(7)**, 285–291 (2024). (in Japanese)

Division of Advanced Molecular Science

T. NAKAMURA and S. KIMURA, “Realization of Monoatomic Layer Heavy-Fermion Systems—Kondo Effect on a Monoatomic Layered Material—,” *Solid State Physics*, **59(6)**, 331–339 (2024). (in Japanese)

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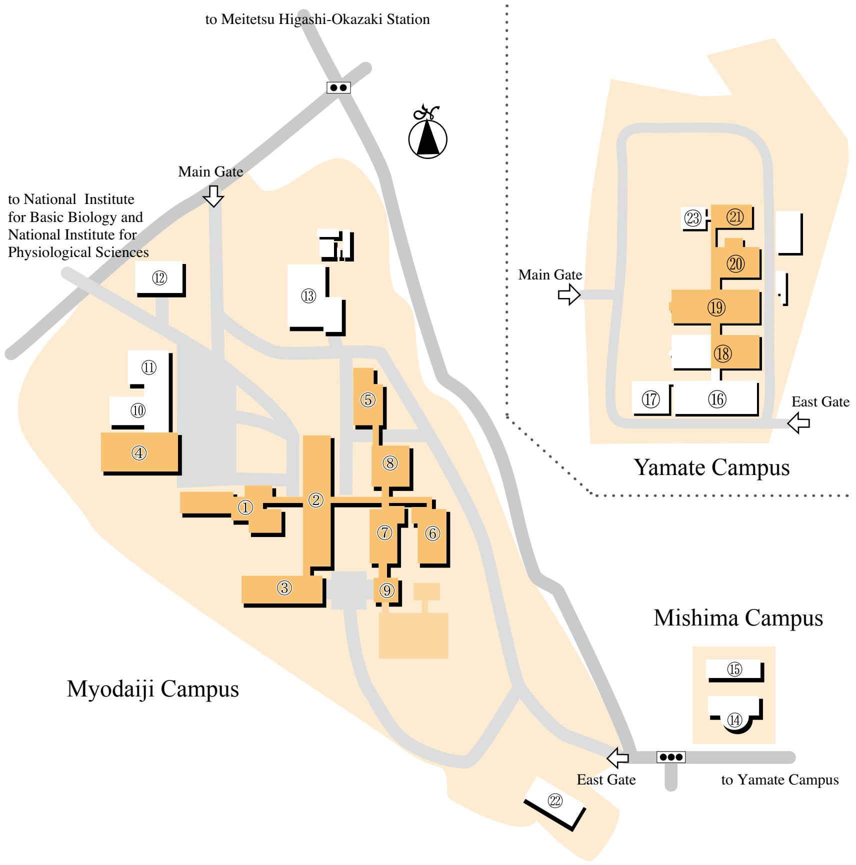
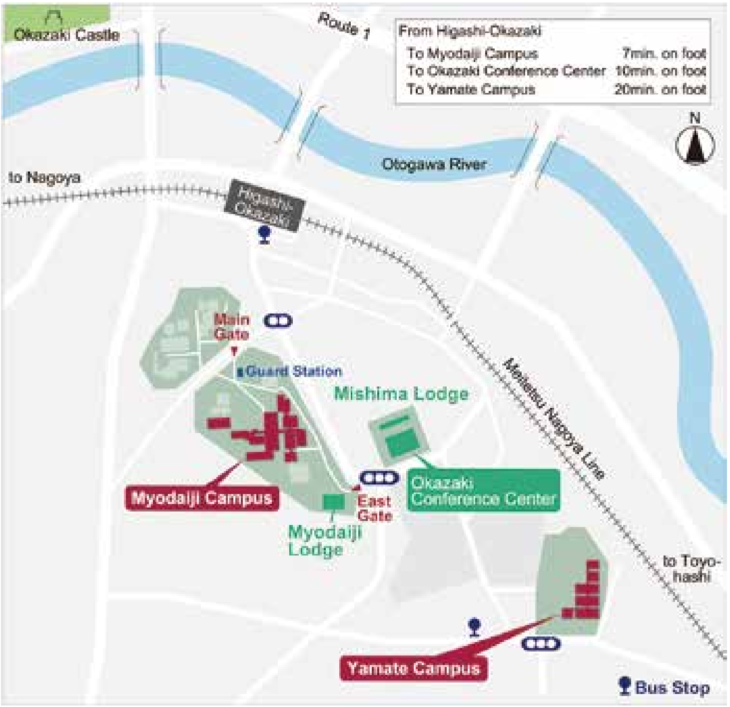


1. Main Office Bldg.
2. Main Laboratory Bldg.
3. South Laboratory Bldg.
4. Computer Center Bldg.
5. Joint Research Bldg. A
6. Joint Research Bldg. D
7. Joint Research Bldg. C
8. Joint Research Bldg. B
9. Joint Research Bldg. UVSOR
10. Administration Bureau
11. Library
12. Faculty Club & Coop
13. Electricity Control Station
14. Okazaki Conference Center
15. Mishima Lodge
16. Yamate No.1 Bldg. A
17. Yamate No.1 Bldg. B
18. Yamate No.2 Bldg.
19. Yamate No.3 Bldg.
20. Yamate No.4 Bldg.
21. Yamate No.5 Bldg.
22. Myodaiji Lodge
23. NIBB Center of Interuniversity Bio-Backup Project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To Okazaki Conference Center	10min. on foot
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